

Catalytic Valorization of Glycerol

(Valorização Catalítica do Glicerol)

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Abstract

Glycerol is currently obtained in large amounts, as an inevitable by-product, during the conventional production of biodiesel. Consumption of this extra glycerol is a necessary requisite for the commercial viability of the biodiesel industry. Liquid phase catalytic oxidation focuses on the synthesis of fine chemicals with very high added value and is a promising route to convert glycerol into useful compounds, provided that the catalyst used is sufficiently active and selective. The main purpose of this work is to investigate the catalytic partial oxidation of glycerol in a systematic way, mainly evaluating the influence of the metal phase, the support properties and the catalyst preparation method, focusing on the use of carbon materials as support.

Platinum group metals supported on activated carbon and prepared by the incipient wetness method lead to a high and constant selectivity (around 75%) to the product of commercial interest, i.e. glyceric acid. Nevertheless, these catalysts are very sensitive to the amount of oxygen dissolved in the reaction media, and suffer deactivation caused by over-oxidation on the metal surface.

Contrarily to the incipient wetness method, the sol immobilization technique appears to be suitable for generating small gold crystallites supported on activated carbon, originating highly effective catalysts for glycerol oxidation under basic conditions. One of the main advantages of using gold is related to its strong resistance to oxygen poisoning.

A series of activated carbons, differing in their surface chemistry were prepared and used as support for gold nanoparticles. Gold particles with similar average sizes resulted in different performances, being the surface oxygenated acid groups particularly prejudicial for the catalytic activity. Basic oxygen-free supports characterized by a high density of free π -electrons lead to more active catalysts, which can be due to their capability to promote electron mobility. Similarly to the results obtained with Pt, Rh and Pd catalysts supported on activated carbon, gold catalysts lead to a high selectivity to glyceric acid of about 75%.

The use of carbon nanotubes as support was investigated. This type of carbon material has a strictly mesoporous nature, differing largely from the activated carbon used before. Gold nanoparticles were supported on multi-walled carbon nanotubes by different methods. The sol immobilization technique was concluded to be the most suitable. Nevertheless, in spite of the similar average gold particle sizes obtained, gold catalysts supported on carbon nanotubes are less active and less

selective to glyceric acid than Au/activated carbon catalysts ($\approx 45\%$ vs. $\approx 75\%$). The former lead to high selectivities to formic acid ($\approx 20\%$).

Similarly to that was observed with activated carbons, the catalytic activity of gold supported on multi-walled carbon nanotubes was correlated with the amount of oxygen groups on the surface of the support. This means that performance of gold catalysts is not only ruled by gold crystallite sizes; the support chemical characteristics also play a key role.

Two mesoporous carbon xerogels having different average pore sizes were synthesized and used as support of gold catalysts prepared by the sol immobilization. It was observed that the selectivities can be tuned with the appropriate choice of the carbon support. In fact, materials with narrow pores lead to an enhancement of the selectivity to glyceric acid, whereas carbons with wide mesopores favor the formation of formic acid, probably via dihydroxyacetone as intermediate, since this compound is not stable under basic conditions. Therefore, performances are not only dependent on the chemical properties of the carbon supports, but also on their textural features.

Platinum catalysts supported on multi-walled carbon nanotubes are able to promote glycerol conversion in both acid and basic conditions. Nevertheless, the effective production of dihydroxyacetone, which is a very high-value compound, is only achieved under base-free conditions, since it is not stable in basic media, where apparently acts as an intermediate leading to the formation of other products, mainly formic acid. In spite of its lower performance, it is possible to enhance the selectivity to dihydroxyacetone under acid conditions (relatively to the Pt catalyst) by using a Pt-Au bimetallic catalyst.

Preliminary studies of glycerol oxidation over gold supported on ceria, zirconia and a Ce-Zr mixed oxide were also carried out under basic conditions. Although the activities obtained are lower than those reported for gold supported on carbon materials, all these catalysts promote the oxidation of glycerol to the main product (glyceric acid) with a high selectivity of about 70%. Moreover, successive experiments with Au/CeO₂ show that this catalyst does not lose efficiency, contrarily to carbon supported gold catalysts, which suffer progressive performance loss.

Sumário

O glicerol é atualmente obtido em elevadas quantidades, uma vez que corresponde a um subproduto inevitável do processo de fabrico do biodiesel. O consumo deste glicerol excedentário constitui um requisito necessário para a viabilidade económica da indústria do biodiesel. A oxidação catalítica em fase líquida permite obter produtos químicos com elevado valor acrescentado e é uma forma promissora de valorizar o glicerol, desde que o catalisador utilizado seja suficientemente ativo e, sobretudo, seletivo. O principal objetivo deste trabalho é estudar de uma forma sistemática a oxidação catalítica do glicerol, avaliando principalmente a influência da fase metálica, das propriedades do suporte e do método de preparação do catalisador, dando especial atenção à utilização de materiais de carbono como suporte.

Os metais do grupo da platina suportados em carvão ativado e preparados pelo método de impregnação incipiente permitem obter uma seletividade elevada e constante (cerca de 75%) no produto de interesse comercial, ácido glicérico. No entanto, estes catalisadores são muito sensíveis à quantidade de oxigénio dissolvida no meio reacional, e sofrem desativação por sobre-oxidação da superfície metálica.

Contrariamente ao método de impregnação incipiente, a técnica de imobilização coloidal permite obter partículas de ouro de pequenas dimensões suportadas em carvão ativado, originando catalisadores altamente eficientes para a oxidação do glicerol em condições básicas. A principal vantagem da utilização de ouro é a sua alta resistência ao envenenamento pelo oxigénio.

Preparou-se uma série de carvões ativados com químicas superficiais diferentes, que foram seguidamente usados como suportes de nanopartículas de ouro. Catalisadores com partículas de ouro de tamanhos médios semelhantes tiveram desempenhos diferentes; a presença de grupos oxigenados ácidos na superfície do suporte é particularmente prejudicial para a atividade catalítica. Suportes básicos com quantidades baixas de oxigénio, caracterizados por uma elevada densidade de eletrões π livres, conduzem a catalisadores mais ativos, provavelmente devido à capacidades para promoverem a mobilidade de eletrões. De modo semelhante aos resultados obtidos com os catalisadores de Pt, Rh e Pd suportados em carvão ativado, os catalisadores de ouro promovem uma elevada seletividade para o ácido glicérico (cerca de 75%).

Os nanotubos de carbono foram avaliados como suporte do ouro na reação. Este tipo de material de carbono é estritamente mesoporoso, diferindo assim do carvão ativado utilizado anteriormente. As nanopartículas de ouro foram suportadas neste material por diferentes métodos. Concluiu-se que o método de imobilização coloidal era o mais adequado. No entanto, apesar dos tamanhos médios das partículas serem semelhantes, os catalisadores de ouro suportados em nanotubos de carbono são menos ativos e seletivos para a formação de ácido glicérico do que os catalisadores Au/carvão ativado ($\approx 45\%$ vs. $\approx 75\%$). Os primeiros levaram a uma seletividade elevada em ácido fórmico ($\approx 20\%$).

Como se tinha observado para os carvões ativados, a atividade catalítica do ouro suportado nos nanotubos de carbono foi correlacionada com a quantidade de grupos oxigenados à superfície do suporte. Isto significa que o desempenho dos catalisadores de ouro não é só função do tamanho das cristalites; as características químicas do suporte também desempenham um papel decisivo.

Dois xerogéis de carbono com tamanhos de poros diferentes foram sintetizados e utilizados como suporte de catalisadores de ouro preparados por imobilização coloidal. Observou-se que as seletividades podem ser ajustadas através da escolha apropriada do suporte de carbono. De facto, os materiais com poros estreitos levam a um aumento da seletividade em ácido glicérico, enquanto aqueles que têm mesoporos largos favorecem a formação de ácido fórmico, provavelmente através da dihidroxiacetona que atua como intermediário, uma vez que não é estável em condições básicas. Assim, o desempenho dos catalisadores não é apenas dependente das propriedades químicas dos suportes de carbono mas também das suas características texturais.

Os catalisadores de platina suportados em nanotubos de carbono promovem a conversão de glicerol tanto em meios ácidos como básicos. No entanto, a produção efetiva de dihidroxiacetona, que é um composto de alto valor acrescentado, só é alcançada em condições ácidas, uma vez que não é estável em meios básicos, nos quais atua como intermediário levando à formação de outros produtos, nomeadamente o ácido fórmico. Apesar do seu pior desempenho, é possível aumentar a seletividade em dihidroxiacetona em condições ácidas (relativamente ao catalisador de Pt) usando um catalisador bimetálico Pt-Au.

Estudos preliminares com ouro suportado em óxido de cério, óxido de zircónio e num óxido misto Ce-Zr foram também efetuados sob condições básicas. Embora as atividades sejam inferiores às obtidas com o ouro suportado em materiais de

carbono, todos estes catalisadores conduzem a seletividades elevadas em ácido glicérico (cerca de 70%). Além disso, experiências sucessivas com o catalisador Au/CeO₂ mostram que este não perde eficiência, contrariamente aos catalisadores de ouro suportados em materiais de carbono, que sofrem uma progressiva perda de eficiência.

Résumé

Le glycérol est actuellement obtenu en grandes quantités, comme un sous-produit inévitable, lors de la production conventionnelle du biodiesel. La consommation de ce glycérol supplémentaire est une condition nécessaire à la viabilité commerciale de l'industrie du biodiesel. L'oxydation catalytique en phase liquide permet d'obtenir des produits chimiques à haute valeur ajoutée et est voie prometteuse pour valoriser le glycérol, à condition que le catalyseur utilisé soit suffisamment actif et particulièrement sélectif. L'objectif principal de ce travail est d'étudier l'oxydation partielle catalytique du glycérol d'une façon systématique, évaluant principalement de l'influence de la phase métallique, les propriétés du support et la méthode de préparation du catalyseur, en se concentrant sur l'utilisation de matériaux carbonés comme support.

Des métaux du groupe du platine supportés sur charbon actif et préparés par la méthode d'impregnation classique mènent à une sélectivité élevée et constante (environ 75%) en acide glyérique, produit d'intérêt commercial. Néanmoins, ces catalyseurs sont très sensibles à la quantité d'oxygène dissous dans le milieu réactionnel et souffrent de désactivation causée par la sur-oxydation de la surface du métal.

Contrairement à la méthode d'impregnation, la technique d'immobilisation colloïdal permet d'obtenir des cristallites d'or de petites dimensions sur charbon actif, étant à l'origine de catalyseurs très efficaces pour l'oxydation du glycérol en milieu basique. L'un des principaux avantages de l'utilisation de l'or est liée à sa forte résistance à l'empoisonnement par l'oxygène.

Une série de charbons actifs avec différentes propriétés chimiques superficielles ont été préparés et utilisés comme support de nanoparticules d'or. Les particules d'or avec des tailles moyennes similaires aboutissent à des performances différentes; la présence de groupes oxygénés acides à la surface du support est particulièrement préjudiciable à l'activité catalytique. Les supports basiques avec de faibles quantités d'oxygène et caractérisé par une forte densité d'électrons libres π conduisent à des catalyseurs plus actifs, ce qui peut être due à leur capacité à promouvoir la mobilité des électrons. De même que pour les résultats obtenus avec les catalyseurs de Pt, Rh et Pd supporté sur charbon actif, les catalyseurs d'or préparés conduisent à une sélectivité élevée en acide glyérique d'environ 75%.

L'utilisation de nanotubes de carbone comme support a été étudiée. Ce type de matériel carboné est strictement mésoporeux, étant ainsi largement différent du

charbon actif. Les nanoparticules d'or ont été supportées sur des nanotubes de carbone multiparois à travers différentes méthodes. Il a été conclu que la technique d'immobilisation colloïdal était la plus appropriée. Néanmoins, en dépit des tailles moyennes similaires des particules d'or obtenues, les catalyseurs d'or supportés sur les nanotubes de carbone sont moins actifs et moins sélectif en acide glycérique que les catalyseurs Au / charbon actif ($\approx 45\%$ vs. $\approx 75\%$). Le premier mène à des sélectivités élevées en acide formique ($\approx 20\%$).

Comme il a été observée avec le charbon actif, l'activité catalytique de l'or supporté sur nanotubes de carbone varie selon la quantité de groupes oxygénés à la surface du support. Cela signifie que les performances des catalyseurs d'or ne dépendent pas seulement de la taille des cristallites, les caractéristiques chimiques du support jouent également un rôle décisif.

Deux xérogels de carbone avec différentes tailles de pores ont été synthétisés et utilisés comme support de catalyseurs d'or préparés par la technique d'immobilisation colloïdal. Il a été observé que la sélectivité peut être ajusté par un choix approprié du support de carbone. En effet, les matériaux avec des pores étroits conduisent à une augmentation de la sélectivité en acide glycérique, tandis que ceux ayant des mésopores larges favorisent la formation de l'acide formique, probablement à travers la dihydroxyacétone, qui agit en tant qu'intermédiaire, puisque ce composé n'est pas stable dans des conditions basiques. Par conséquent, la performance des catalyseurs ne dépend pas seulement des propriétés chimiques du support de carbone, mais aussi de ses caractéristiques texturales.

Les catalyseurs de platine supportés sur nanotubes de carbone sont en mesure de promouvoir la conversion du glycérol en milieu acide et basique. Toutefois, la production effective de la dihydroxyacétone, qui est un composé à haute valeur ajoutée, n'est atteinte que dans des conditions acides, car elle n'est pas stable en milieu basique, où elle agit comme intermédiaire conduisant à la formation d'autres produits, notamment l'acide formique. Malgré sa faible performance (relativement au catalyseur Pt), il est possible d'augmenter la sélectivité de la dihydroxyacétone en utilisant un catalyseur bimétallique Au-Pt dans des conditions acides.

Des études préliminaires avec l'or supporté sur l'oxyde de cérium, l'oxyde de zirconium et un oxyde mixte Ce-Zr ont également été effectuées dans des conditions basiques. Bien que les activités soient inférieures à celles obtenues avec de l'or supporté sur les matériaux carbonés, l'ensemble de ces catalyseurs conduisent à la formation d'acide glycérique avec une sélectivité élevée (70%). En

outre, des expériences successives montrent que le catalyseur Au/CeO₂ ne perd pas son activité, à la différence des catalyseurs d'or supportés sur des matériaux carbonés, qui souffrent d'une perte progressive d'efficacité.

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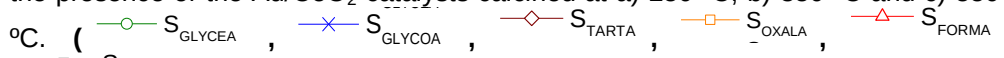
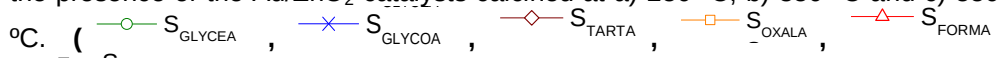
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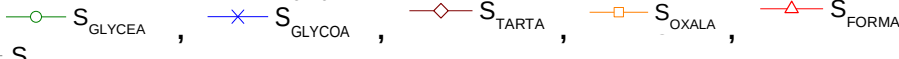
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Chapter 1

1 Introduction

This chapter of this thesis presents some general considerations about the economical and environmental relevance of the conversion of glycerol into high-value chemicals. A brief overview of the catalytic strategies that can be used for this purpose is also shown. The chemoselective oxidation of glycerol in the presence of noble metal supported catalysts is emphasized. A review of the results reported in the literature is provided, focusing on the parameters that have been identified as having an important impact on the catalytic performance, such as the nature and dispersion of metal, the reaction conditions and the nature of the support. A short description of the preparation of supported gold nanoparticles is presented next, since the major part of this thesis centers on this type of catalyst. Similarly, by the same reasons, special attention was given to carbon supports. Finally, the main objectives of this work and the thesis outline are presented.

1.1 Introduction

The growing concerns about global warming, emissions of green house gases, the increase in oil prices and the expected larger need for energy in the future lead to numerous discussions about sources of energy. The use of renewable feedstocks is essential for the sustainable development of society, since fossil energy resources are limited [1]. Therefore, the transition to a low carbon footprint society based on renewable resources is necessary. Most of the current renewable energy options, including solar, wind, hydroelectric and geothermal activity, can replace natural gas and coal in the production of heat and electricity. On the other hand, only biomass was pointed out as a sustainable source of carbon-based fuels and chemicals, i.e. as an equivalent to petroleum [2]. However, contrarily to petroleum, biomass is renewable and widely available. It includes agricultural food and feed crops and, principally, feedstocks such as agriculture and forestry residues, manure and waste oils and fats, which can be considered as residues [3-4]. Biomass resources can be converted to solid, liquid or gaseous fuels via a number of processes, including biological, thermal, and/or chemical conversion, in addition to mechanical treatments [5].

Biofuels are liquids or gases for transport purposes that are produced from biomass. Considering that the CO_2 emission is not larger than the quantity consumed by photosynthesis their production has net zero carbon emission (Figure 1.1) [6-7].

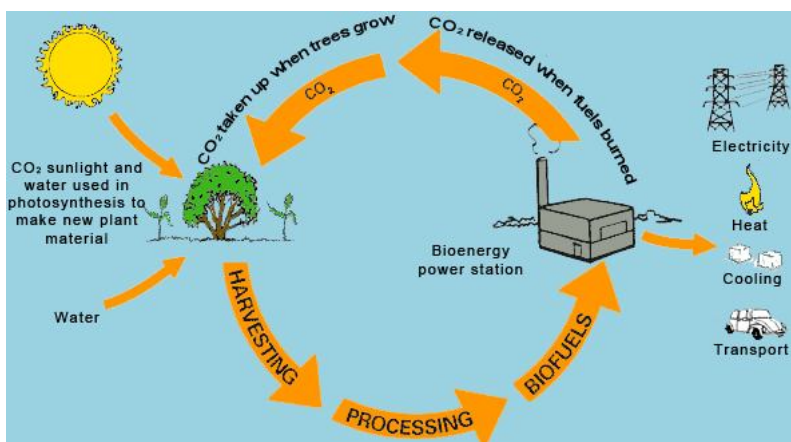


Figure 1.1 The carbon cycle (adapted from [7]).

The main first generation biofuels used commercially are bioethanol and biodiesel. They are currently being produced from starch, sucrose and vegetable oils as feedstocks and are characterized by their ability to be mixed with petroleum-based fuels or used in existing alternative vehicle technology [8]. In the last years, political decisions have pushed the production of biofuels in an attempt to reach the CO₂ reduction objectives fixed by the Kyoto climate protocol [9]. Accordingly, Biofuels Directive of the European Union Commission requests the use of at least 5.75% of renewable bio-component in traffic fuels by 2010 and 20% by 2020 [10].

At present, the production of first-generation bioethanol mainly utilizes plants rich in carbohydrates (i.e., sugar containing crops, starch containing crops), such as corn, sugar cane, wheat, barley, potato, wood, corn, or sugar beet [1, 8]. Its production by hydrolysis and fermentation is an energy-intensive and complex process. In practice 1000 kg of fermentable sugar would produce about 583 liter of pure ethanol [8]. In contrast, the first generation biodiesel production uses a very simple process, i.e. the transesterification of vegetable oils.

1.2 Glycerol: by-product of biodiesel production

The vegetable oil based fatty acid methyl esters, popularly known as biodiesel, has emerged as a viable clean fuel over the last decade. It is obtained by transesterification with methanol of triglycerides extracted from seed oils, leaving glycerol as an inevitable by-product (Figure 1.2). In this process, about 100 kg of glycerol are produced for every ton of biodiesel [11].

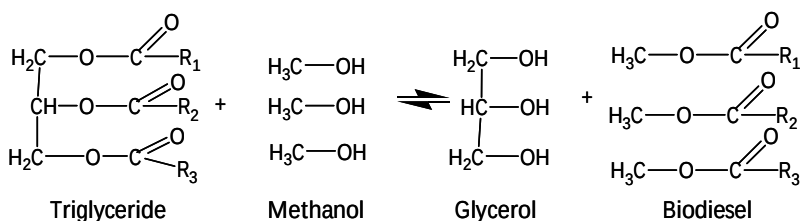


Figure 1.2 Overall reaction for the production of biodiesel by vegetable oil methanolysis yielding glycerol as by-product.

During the last years the market for biodiesel has been increasing continuously (Figure 1.3) [12]. The world production reached 16 billion L in 2009, and it is

expected that this trend remains, corresponding to an increase to 45 billion L by 2020 [13]. Due to this tremendous growth of the biodiesel industry, the glycerol market is experiencing a surplus [14]. About 1.54 millions tonnes of glycerol are expected to be generated worldwide in 2015 [15]. Markets have reacted strongly to this increased availability of glycerol, which resulted in a significant drop of prices for this compound from US\$ 0.55 per kg in 2004 to US\$ 0.055 per kg in 2006 [4]. This decrease in glycerol value affects directly both glycerol and biodiesel producers. In fact, consumption of the surplus of glycerol is a necessary requisite for the commercial viability of biodiesel production [16-17]. It has been shown that adding value to the glycerol by-product could reduce the net production cost of biodiesel from US\$ 0.55 per liter to US\$ 0.35 per liter [16]. In order to achieve a sustainable and an economically competitive business, when compared with fossil fuels, crude glycerol will have to be processed efficiently.

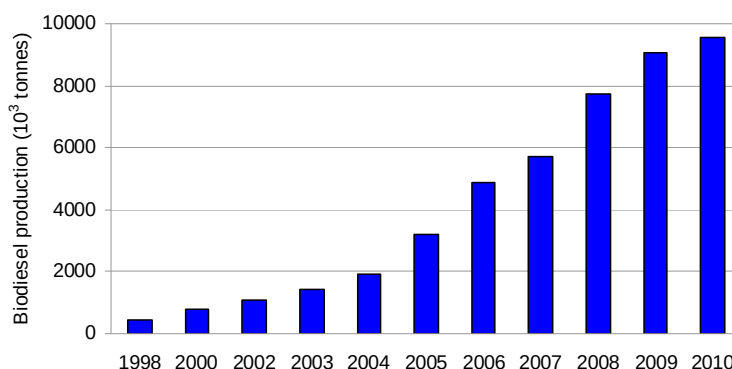


Figure 1.3 EU member states' biodiesel production [12].

1.3 Glycerol: traditional uses

Glycerol, also known as 1,2,3-propanetriol, is an organic molecule discovered for the first time in 1779 by the Swedish scientist Carl Wilhelm Scheele while investigating the saponification products of olive oil with lead oxide [18]. In 1823, the French chemist Michel Eugene Chevreul showed that this natural polyol was involved in the triglyceride structure, the main component of fats and oils [19]. Nevertheless, it was only in 1855 that the structure of glycerol was established by Charles-Adolphe Würtz [19].

The first chemical industrial application of glycerol, reported in 1866, was the production of nitroglycerin, which gave access later to dynamite [18]. Then, during the 20th century, glycerol became an industrial chemical with more than 1500 direct applications, especially in the pharmaceutical and cosmetic industries, where it is used for its emollient, demulcent and humectant properties. It is also commonly used as a moistening agent or solvent in food industry and in personal care products and as a softener in resins and plastics [15, 19-20]. The large versatility of glycerol use is based on both its chemical and physical properties. Figure 1.4 summarizes the current applications of glycerol by activity sectors and the corresponding distributions [20].

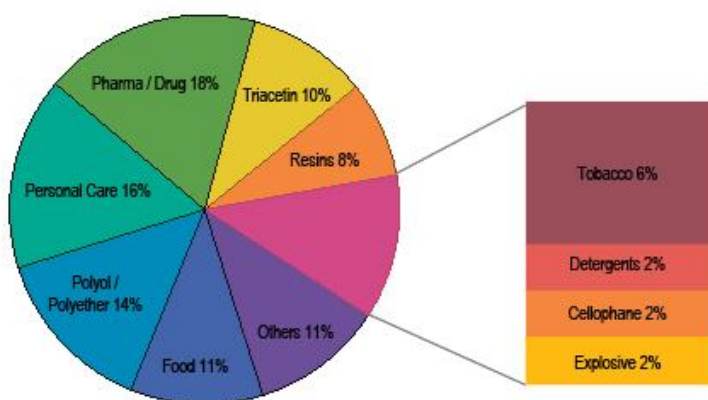


Figure 1.4 Distribution of the glycerol consumption [20].

Glycerol is a viscous sweet tasting clear hygroscopic liquid with no odor, non-toxic and easily biodegradable [19]. Due to the presence of three hydroxyl groups it is completely soluble in water and alcohol and insoluble in hydrocarbons. Table 1.1 shows some properties of this compound.

Table 1.1 Some properties of glycerol.

Structure	Molar Mass	Boiling Point	Density (20 °C)	Flash Point
$\text{HO}-\text{CH}_2-\underset{\text{OH}}{\text{CH}}-\text{CH}_2-\text{OH}$	92.09 g mol ⁻¹	290 °C	1.2375 g cm ⁻³	176 °C

1.3.1 The necessity of new applications

Crude glycerol cannot be used in food, personal care products or pharmaceuticals, which constitute almost 50% of today's glycerol applications, unless a previous purification step is carrying out. In fact, the crude glycerol obtained from most of the conventional biodiesel process contains approximately 80 wt% of glycerol, but also a mixture of water, inorganic salts, methanol, free fatty acids and inorganic and organic compounds [15-16]. The purification step consists in an expensive vacuum distillation or ion exchange processes, which is not a viable option due to the inexistence of a market able to consume the massive overproduction [16]. Indeed, the majority of the traditional markets of glycerol is relatively mature and does not allow to absorb the large excess of glycerol coming from the manufacture of biodiesel. On the other hand, as mentioned before, the production of crude glycerol largely exceeds the present commercial demand for purified glycerol. Therefore, nowadays, the non distilled glycerol by-product is discarded as waste and usually burned [15]. However, this readily available organic raw material can potentially be very useful taking into account its unique multifunctional structure and properties.

1.4 From glycerol to valued-added chemicals

In the past, glycerol was most commonly used without any changes or only with very simple structural modifications, since the production of more complex chemical compounds was too costly. However, the decrease in the crude glycerol price can be beneficial and may open new significant markets. Due to the large amount of cheap glycerol, the novel technologies have to allow a large-scale processing of this renewable resource in order to obtain high added value products. Driven by economical interests and as a result of glycerol's unique structure, properties, bioavailability and renewability, the conversion of glycerol into high-value chemicals is a research area that has received tremendous attention in recent years [16, 18, 20] (Figure 1.5). Research has to face new challenges, develop and/or improve catalytic processes and technologies in order to provide new opportunities to better utilize glycerol.

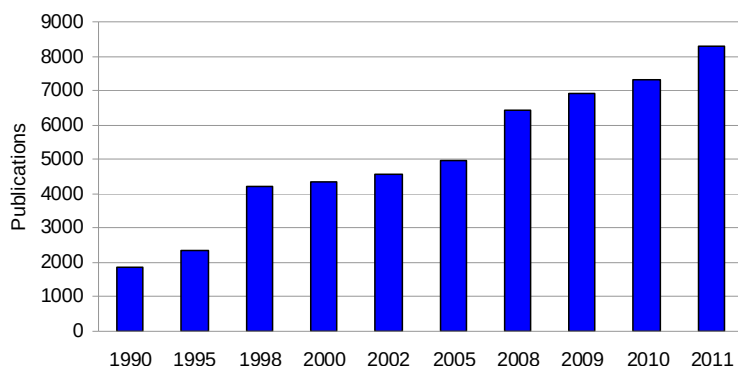
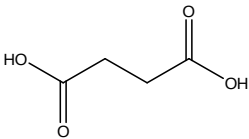
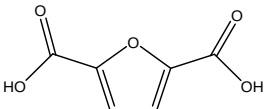
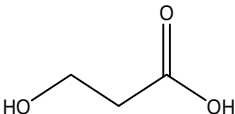
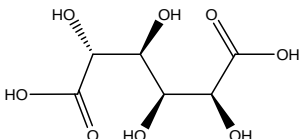
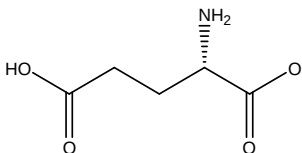
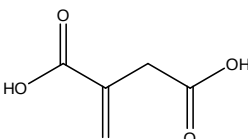
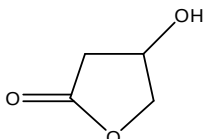
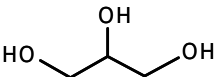
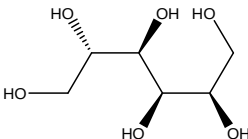
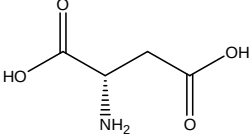
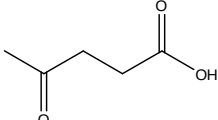
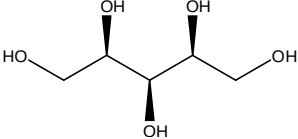


Figure 1.5 The increase in the number of scientific publications related to glycerol (collected from ISI Web of Knowledge database, in 05/2012).

1.4.1 Glycerol: a platform molecule

Glycerol exhibits a versatile and high chemical reactivity due to its three hydroxyl groups (two primary and one secondary hydroxyl group). Since glycerol is a highly functionalized molecule compared to hydrocarbons from petrochemistry, this makes it an attractive and advantageous potential starting material for the synthesis of valuable derivatives [16]. In 2004, the US Department of Energy (DOE) highlighted a group of twelve target compound, which could serve as platform molecules for the production of fuels, valuable chemicals and energy, and in the near future replace petroleum-based products (Table 1.2) [21]. These platform molecules derived from biomass show a high flexibility and can lead to a large variety of useful intermediates or specialty chemicals. As it can be seen in Table 1.2, glycerol has been identified as one of the building blocks for future biorefineries, since it can be converted in a large number of chemicals by several reaction pathways. A non-exhaustive selection of these possibilities is shown in Figure 1.6 [4, 16, 20, 22]. A multitude of routes based on chemical and biochemical oxidation, reduction, bond breaking, polymerization, etc. lead to the transformation of the glycerol molecule into chemicals of commercial interest. A multitude of chemicals can be derived from glycerol. However, each reaction can lead to a mixture of products. Therefore, the main challenge is to find highly active and selective catalysts for the target product as well as advantageous operating conditions (e.g. moderate temperatures and pressures).

Table 1.2 The DOE platform molecules [21].

Succinic acid 	2,5-Furan dicarboxylic acid 	3-Hydroxypropionic acid 
Glucaric acid 	Glutamic acid 	Itaconic acid 
3-Hydroxybutyrolactone 	Glycerol 	Sorbitol 
Aspartic acid 	Levulinic acid 	Xylitol / Arabitol 

For the moment, only a few applications use glycerol in a large scale for its conversion into higher value materials. One of them, commercialized since 2007 by Solvay, is the chlorination of glycerol to epichlorohydrin, which is used in the manufacture of epoxy resins. Currently, their patented Epicerol process produces 10 000 tonnes per year of epichlorohydrin [19, 23]. By using glycerol as the starting material, the Solvay process reduces chlorinated residues eight fold and water use by 90% relatively to conventional epichlorohydrin processes [22].

The reforming of glycerol over Pt-Rh catalysts to syngas is a technology commercialized since 2006 by the Dutch company BioMethanol Nederland Chimie with a production capacity of 800 000 tonnes per year [23]. Syngas can be used for methanol synthesis or in the exothermic Fischer-Tropsch process to produce alkanes [4].

Catalytic hydrogenolysis is another possible route to increase the profitability of biodiesel. This chemical reaction allows the conversion of glycerol into 1,2-propanediol and 1,3-propanediol. These valuable compounds are large-volume intermediates for the polymer industry [16, 19]. The current market for 1,2-propanediol is about 2 million tonnes per year and the 1,3-propanediol market is expected to reach 227 tonnes by 2020 [19]. In 2011, the company Archer Daniels Midland began to produce 1,2-propanediol using refined glycerol as feedstock. The plant has a capacity of 100 000 tonnes per year [22].

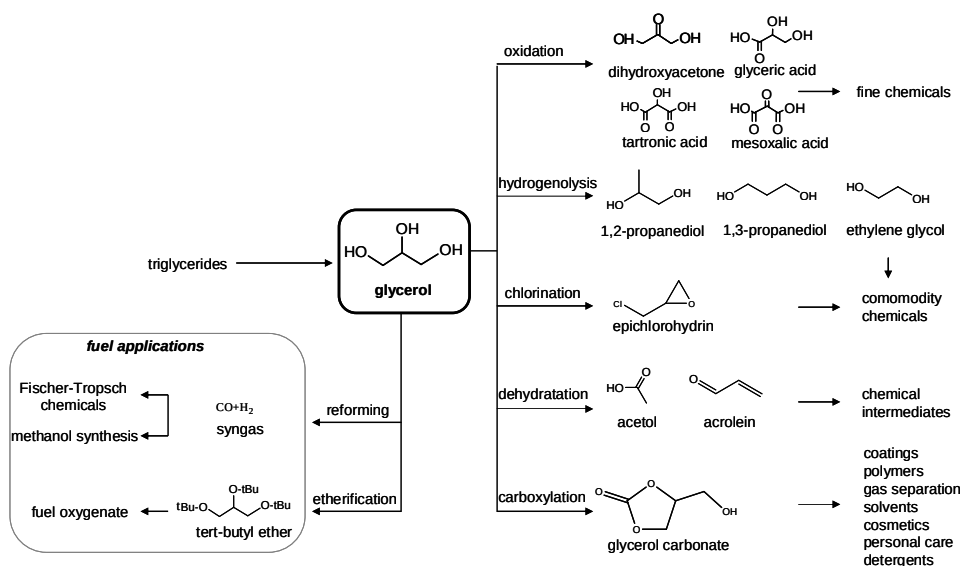


Figure 1.6 Glycerol as a primary biorefinery building block (adapted from [4, 16, 20, 22]).

A large diversity of potential routes for the valorization of glycerol has not yet reached the commercial stage, but intensive investigation is on going. Some of them are briefly described here.

Catalytic and thermal dehydration of glycerol can provide several derivatives depending on the conditions used [15-16, 22]. Acrolein, which is an important industrial intermediate for the chemical and the agro-industries, has received particular attention [15]. It was shown that a competitive production of acrolein could be reached if the price of glycerol became lower than 300 US\$ per tonne [24].

Glycerol cannot be added directly to fuel because it polymerizes at high temperature. However, its selective etherification allows the conversion to tert-butyl ether, used as a valuable additive for gasoline, due to its property of increasing the octane number [20].

Glycerol carbonate can be obtained from the carboxylation of glycerol. It is a promising material with multiple uses (component of gas separation membranes, polyurethane foams, a nonvolatile reactive solvent for several types of materials, a component in coating, paints and detergents, etc.) [16, 22]. At low glycerol costs, glycerol carbonate could replace dimethyl carbonate in the production of green polycarbonates and polyurethanes [20].

In contrast to these large-volume commodities, catalytic partial oxidation is a small-scale application that focuses on the synthesis of fine chemicals with very high value. From an economic point of view and considering the large fluctuation in glycerol price, this process can be more advantageous, since it involves a relatively low risk when compared with the use of glycerol for the production of lower value-added chemicals. The oxidation of glycerol leads to a complex reaction pathway in which a large number of products, many of them potentially valuable, can be obtained. The main challenge is to find catalysts highly selective to the target molecule. As this work focuses on the selective catalytic oxidation of glycerol a more detailed description of this process is presented in the next section.

1.4.2 Glycerol oxidation

Liquid phase catalytic oxidation is a promising route to convert glycerol into useful compounds, provided that the catalyst used is sufficiently active and predominantly selective for the formation of chemicals of commercial interests, potentially useful as chemical intermediates in the fine chemicals industry, particularly for the synthesis of pharmaceuticals and cosmetics [16, 25]. However, the extensive functionalization of this molecule, with three hydroxyl groups similarly reactive, renders its selective oxidation particularly difficult [26] and a large number of products can be obtained, by a complex reaction pathway [16, 23, 27] (Figure 1.7).

The oxidation of primary hydroxyl groups yields glyceric acid (GLYCEA) and tartronic acid (TARTA), whereas the oxidation of the secondary hydroxyl group yields dihydroxyacetone (DIHA). Finally, the oxidation of all three hydroxyl groups leads to the highly functionalized mesoxalic acid molecule (MESOA). It should be

noticed that simultaneously to the oxidation reaction, decarboxylation ($-\text{CO}_2$), decarbonylation ($-\text{CO}$), hydration, isomerization and polymerization reactions can occur. Accordingly, the partial oxidation of glycerol is difficult to control.

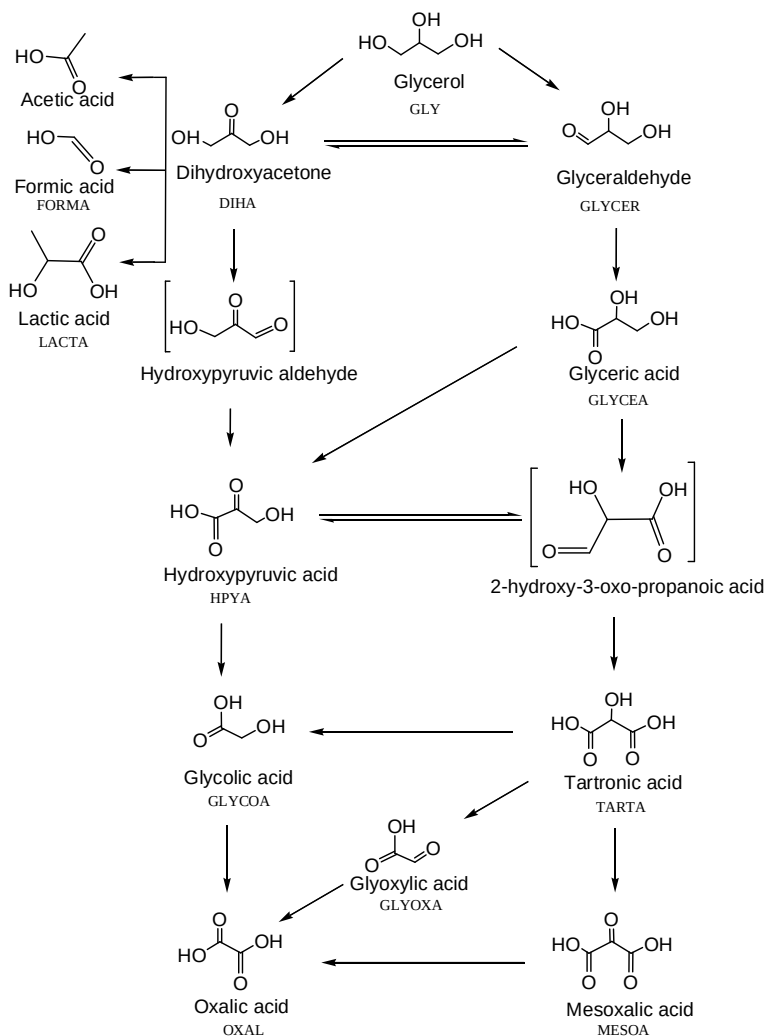


Figure 1.7 Possible reaction pathways to oxygenated derivatives of glycerol (adapted from [16, 23, 27]).

1.4.2.1 Products of interest

Among the various target compounds that can be obtained by the oxidation of glycerol, dihydroxyacetone is economically the most interesting. It is a versatile

compound extensively used as a cosmetic ingredient, mainly in sunless tanning formulations, as precursor of pharmaceuticals and as a chemical intermediate in organic synthesis [23]. The global market for this compound is of approximately 1800 tonnes per year [19]. DIHA is currently obtained in the industrial scale by a low-productivity incomplete microbial fermentation of glycerol by *Gluconobacter oxidans* [20, 28]. In this conventional cumbersome biotechnological process, DIHA is obtained with a 87-94% yield after ~ 32 h [28-29], and only low concentrations (typically ~ 60 kg m⁻³) can be reached during long term operation [30]. The productivity is fairly low, and even with genetically modified *Gluconobacter oxidans* no more than 2.9 g L⁻¹ h⁻¹ were obtained [31]. The very high value of DIHA (150 US\$/ kg) in comparison to the price of crude glycerol have lead to efforts in order to improve productivity and selectivity by the use of catalysts in which a careful design is required to control the chemoselective orientation of the process towards the oxidation of the secondary alcohol function, in order to obtain preferentially DIHA [16, 23]. However, oxidation of the secondary hydroxyl group of glycerol seems to be preferred only under acidic conditions [16, 32].

Although there is no commercial application for glyceric acid (GLYCEA) at the moment, there are several patents involving the application of this compound as a raw material for chemical products, pharmaceuticals and cosmetics, which suggest the huge potential of this molecule [33]. Glyceric acid and its derivates have excellent biological functions, such as liver stimulant, cholesterolytic activity, and an action to accelerate alcohol metabolism [33-34]. However, industrial methods have not been established for their production. If it can be produced at low cost, wide uses will be expected, including as raw material for chemical products such as bioplastics, pharmaceuticals for alcohol metabolism acceleration or disease treatment, and cosmetics [33, 35-39].

Tartronic and mesoxalic acids are valuable agents, which can be used as intermediate compounds for the synthesis of fine chemicals and novel polymers. Due to their current high price, applications are limited to high value added fields, such as for medicinal use [40]. Tartronic acid is already used in the treatment of osteoporosis and obesity [23]. This compound also has anti-corrosive properties and could be used as protective agent and oxygen absorber in the food industry [23]. Permanganate is used as oxidizing agent in its current synthesis, whereas mesoxalic acid can be obtained from the oxidation of glycerol diacetate with concentrated nitric acid [23].

Until now, these products of large commercial interest are being produced by expensive and non-environmentally safe oxidation processes or by low productivity microbial fermentation processes. The heterogeneously catalyzed glycerol oxidation using clean oxidizing agents, such as air or oxygen, would be an environmentally friendly and cost-efficient process to produce these valuable compounds. Accordingly, catalysis represents a critical approach to green chemical technology in the activation and utilization of glycerol. The reaction is usually carried out in the presence of supported noble metals.

1.4.2.2 Chemoselective catalytic oxidation of glycerol

As it can be observed in Figure 1.7, a mixture of C_3 , C_2 and C_1 products can be obtained from the oxidation of glycerol. Partial oxidations are difficult to control and various types of catalysts have been tested. The aerobic catalytic oxidation has been investigated mainly using supported noble metal nanoparticles such as platinum, palladium and more recently gold. Due to its high boiling point (290 °C at atmospheric pressure), the selective oxidation of glycerol is usually carried out in the liquid phase using water as solvent. Most of the reactors used are stirred-tank slurry reactors and autoclaves, which are used in batch or continuous mode.

Catalyst activity and selectivity seem to be influenced by the nature of the metal, nanoparticle sizes and nature of support, but also by the reaction conditions (pH, temperature, ratio of glycerol/NaOH, amount of catalyst and oxidants). Catalytic oxidation of glycerol has been investigated by several research groups under different reaction conditions with different metals and different supports, making comparisons difficult, since many parameters influence the catalyst performance. Table 1.3 lists some results of catalytic oxidation of glycerol reported by several groups.

Table 1.3 Some typical results of catalytic oxidation of glycerol.

Catalyst	Oxidant	pH	Other reaction conditions	Glycerol conversion and/or TOF ¹	Selectivities or yields to the main products	Other products mentioned	Ref.
Bi – Pt/C (Bi/Pt = 0.37 mol/mol)	Air (1 bar)	2	1 M GLY, 60 °C, 5 h	70%	55% (S _{DIHA})	HPYA, GLYCEA, GLYCER	[32]
3% Pt – 0.6% Bi/C	O ₂ (3 bar)	2	1 M GLY, 80 °C, 5 h	80% TOF = 370 h ⁻¹	60% (S _{DIHA})	GLYCEA, GLYCER, CO ₂	[28]
5% Pd/C	Air (1 bar)	11	1 M GLY, 60 °C, 4 h	90%	77% (S _{GLYCEA}), 8% (S _{DIHA})	TARTA, OXAL	[32]
5% Pt/C	Air (1 bar)	11	1 M GLY, 60 °C, 5 h	90%	55% (S _{GLYCEA}), 12% (S _{DIHA})	TARTA, OXAL	[32]
5% Pt/C	Air (1 bar)	neutral	1 M GLY, NaOH/GLY = 1 (mol/mol) , 60 °C, 3 h	63%	74% (S _{GLYCEA}), 21% (S _{GLYCER})	TARTA	[41]
5% Pt - Cu/C	O ₂ (1 bar)	natural	1 M GLY, 60 °C, 6 h	86%	70% (S _{GLYCEA}), 10% (S _{DIHA})	GLYCOA, GLYCER	[42]
1% Au/C	O ₂ (3 bar)	basic	12 mmol GLY, NaOH/GLY = 1 (mol/mol), 60 °C, 3 h	56%	100% (S _{GLYCEA})	-	[43]
1% Au/C	O ₂ (3 bar)	basic	0.3 M GLY, NaOH/GLY = 4 (mol/mol), 30 °C, 6 h	90%	92% (S _{GLYCEA})	TARTA, GLYCOA	[27]

Catalyst	Oxidant	pH	Other reaction conditions	Glycerol conversion and/or TOF ¹	Selectivities or yields to the main products	Other products mentioned	Ref.
1% Au/graphite	O ₂ (3 bar)	basic	0.3 M GLY, NaOH/GLY = 4 (mol/mol), 50 °C	63% TOF = 152 h ⁻¹	77% (S _{GLYCEA}), 12% (S _{TARTA}), 10% (S _{GLYCOA})	HPYA, OXAL	[44]
1% Pd/graphite	O ₂ (3 bar)	basic	0.3 M GLY, NaOH/GLY = 4 (mol/mol), 50 °C	90% TOF = 320 h ⁻¹	62% (S _{GLYCEA}), 20% (S _{TARTA}), 16% (S _{GLYCOA})	HPYA, OXAL	[44]
1% Au – 1% Pd/graphite	O ₂ (3 bar)	basic	0.3 M GLY, NaOH/GLY = 4 (mol/mol), 50 °C	90% TOF = 675 h ⁻¹	59% (S _{GLYCEA}), 19% (S _{TARTA}), 20% (S _{GLYCOA})	HPYA, OXAL	[44]
1% Au/carbon black	O ₂ (1 bar)	12	1.5 M GLY, 60 °C, 2.7 h	50%	33% (S _{GLYCEA}), 27% (S _{DIHA})	GLYCOA, HPYA, TARTA, OXAL	[45]
0.5% Au/C	O ₂ (10 bar)	basic	0.3 M GLY, NaOH/GLY = 2 (mol/mol), 60 °C	50%	65% (S _{GLYCEA})	GLYCOA, TARTA, LACTA, OXAL	[46]
2.2% Au – 2.8% Pd/C	O ₂ (10 bar)	basic	0.3 M GLY, NaOH/GLY = 2 (mol/mol), 60 °C	50%	80% (S _{GLYCEA})	GLYCOA, TARTA, LACTA, OXAL	[46]
1% Au/C	O ₂ (1 bar)	12	1.5 M GLY, 60 °C, 1.5 h	50%	26% (S _{DIHA}), 44% (S _{GLYCEA})	GLYCOA, HPYA, TARTA, OXAL	[45]
Au _{0.66} – Pt _{0.33} /C	O ₂ (1 bar)	12	1.5 M GLY, 60 °C, 1.5 h	50%	36% (S _{DIHA}), 31% (S _{GLYCEA})	GLYCOA, HPYA, TARTA, OXAL	[45]

Catalyst	Oxidant	pH	Other reaction conditions	Glycerol conversion and/or TOF ¹	Selectivities or yields to the main products	Other products mentioned	Ref.
Ti-Si co-gel	H ₂ O ₂ (30% w/v)	n.c.	10 g GLY, 80 °C, 24 h	22%	37% (S _{GLYCER}) 37% (S _{formate ester})	DIHA, GLYCEA	[26]
1% Au/C	O ₂ (3 bar)	basic	0.3 M GLY, NaOH/GLY = 4 (mol/mol), 50 °C, 0.25 h	21% TOF = 845 h ⁻¹	66% (S _{GLYCEA}), 24% (S _{GLYCOA})	TARTA, OXAL	[47]
1% Pd – 1% Au/C	O ₂ (3 bar)	basic	0.3 M GLY, NaOH/GLY = 4 (mol/mol), 50 °C, 0.25 h	79% TOF = 3260 h ⁻¹	71% (S _{GLYCEA}), 11% (S _{GLYCOA})	TARTA, HPYA, OXAL	[47]
1% Pt – 1% Au/C	O ₂ (3 bar)	basic	0.3 M GLY, NaOH/GLY = 4 (mol/mol), 50 °C, 0.25 h	88% TOF = 3455 h ⁻¹	61% (S _{GLYCEA}), 23% (S _{GLYCOA})	TARTA, OXAL	[47]
Au _{0.60} – Pd _{0.40} /C	O ₂ (3 bar)	basic	0.3 M GLY, NaOH/GLY = 4 (mol/mol), 50 °C	90% TOF = 3500 h ⁻¹	78% (S _{GLYCEA}), 18% (S _{GLYCOA})	n.c.	[48]
1% Au/C	O ₂ (3 bar)	natural	0.3 M GLY, 100 °C, 2 h	3%	51% (S _{FORMA} + S _{CO2}), 39% (S _{GLYCEA})	n.c.	[49]
1% Au/H- mordenite	O ₂ (3 bar)	natural	0.3 M GLY, 100 °C, 2 h	5%	70% (S _{GLYCEA}), 9% (S _{TARTA})	FORMA, CO ₂	[49]
3.7 nm 0.75% Au/carbon black	O ₂ (10 bar)	basic	1.5 M GLY, NaOH/GLY = 2, 60 °C, 3 h	100%	75% (S _{GLYCEA}), 15% (S _{GLYCOA})	n.c.	[50]

Catalyst	Oxidant	pH	Other reaction conditions	Glycerol conversion and/or TOF ¹	Selectivities or yields to the main products	Other products mentioned	Ref.
42 nm 0.72% Au/carbon black	O ₂ (10 bar)	basic	1.5 M GLY, NaOH/GLY = 2, 60 °C, 3 h	85%	49% (S _{GLYCEA}), 21% (S _{GLYCOA}), 20% (S _{DIHA})	n.c.	[50]
12 nm 1% Au/C	O ₂ (10 bar)	basic	0.3 M GLY, NaOH/GLY = 2 (mol/mol), 60 °C	50%	69% (S _{GLYCEA}), 22% (S _{GLYCOA})	TARTA, OXAL, LACTA	[51]
45 nm 1% Au/C	O ₂ (10 bar)	basic	0.3 M GLY, NaOH/GLY = 2 (mol/mol), 60 °C	50%	83% (S _{GLYCEA}), 11% (S _{GLYCOA})	TARTA, LACTA	[51]
1% Au/TiO ₂ (PVA)	O ₂ (3 bar)	basic	0.3 M GLY, NaOH/GLY = 4 (mol/mol), 50 °C	90% TOF = 178 h ⁻¹	69% (S _{GLYCEA}), 17% (S _{GLYCOA})	TARTA, OXAL, HPYA	[52]
1% Au/TiO ₂ (THPC)	O ₂ (3 bar)	basic	0.3 M GLY, NaOH/GLY = 4 (mol/mol), 50 °C	90% TOF = 367 h ⁻¹	52% (S _{GLYCEA}), 15% (S _{GLYCOA})	TARTA, OXAL, HPYA	[52]
1% Au/CeO ₂	O ₂ (1 bar)	12	1.5 M GLY, 60 °C, 5 h	38%	45% (S _{GLYCEA}), 25% (S _{DIHA})	GLYCOA, TARTA	[53]
3.1% Au/MgAl ₂ O ₄	O ₂ (3 bar)	basic	0.3 M GLY, NaOH/GLY = 4 (mol/mol), 50 °C	50%	61% (S _{GLYCEA}), 29% (S _{GLYCOA})	TARTA, OXAL, FORMA	[54]
1% Au/Nb ₂ O ₅	O ₂ (6 bar)	basic	0.12 M GLY, NaOH/GLY = 2 (mol/mol), 60 °C, 5 h	67%	47% (S _{GLYCEA})	TARTA, GLYCOA, FORMA	[55]

Catalyst	Oxidant	pH	Other reaction conditions	Glycerol conversion and/or TOF ¹	Selectivities or yields to the main products	Other products mentioned	Ref.
1% Au/CNF	O ₂ (5 bar)	basic	0.3 M GLY, NaOH/GLY = 2 (mol/mol), 50 °C, 5 h	30% TOF = 3.1 h ⁻¹	22.1% (S _{GLYCEA}), 64% (S _{GLYCOA})	HPYA, MESOA	[56]
5% Pt/C	O ₂ (1 bar)	natural	1.0 M GLY, 60 °C, 6 h	47% TOF = 35 h ⁻¹	60% (S _{GLYCEA}), 28% (S _{FORMA} + S _{CO2})	DIHA, GLYCER, HPYA, GLYCOA	[57]
5% Pt/MWCNT	O ₂ (1 bar)	natural	1.0 M GLY, 60 °C, 6 h	70% TOF = 52 h ⁻¹	70% (S _{GLYCEA}), 22% (S _{FORMA} + S _{CO2})	DIHA, GLYCER, HPYA, GLYCOA	[57]
5% Pt/S-MWCNT	O ₂ (1 bar)	natural	1.0 M GLY, 60 °C, 6 h	90% TOF = 336 h ⁻¹	68% (S _{GLYCEA}), 13% (S _{DIHA})	GLYCOA, GLYCER, OXAL, CO ₂ , CO	[58]
5% Pt/S-MWCNT	O ₂ (1 bar)	basic	1.0 M GLY, NaOH/GLY = 2 (mol/mol), 60 °C, 6 h	93% TOF = 932 h ⁻¹	24% (S _{GLYCEA}), 24% (S _{DIHA})	GLYCOA, OXAL, CO ₂ , CO	[58]

n.c.: not communicated.

¹ TOF – Turnover frequency.

1.4.2.2.1 Influence of noble metal

Mainly palladium, platinum and gold based catalysts have been tested in the selective oxidation of glycerol.

In the early 1990s, Kimura et al. reported for the first time the glycerol heterogeneous catalytic oxidation [59-60]. Their motivation was to show that glycerol can be oxidized to dihydroxyacetone not only by an enzymatic process but also using heterogeneous selective catalysts. They found that platinum supported on charcoal (Pt/C) show low activity in an acidic media, which was confirmed later on (in 1995) by Garcia et al. [32], and the yield in DIHA did not exceed 4%. In an attempt to optimize the Pt/C catalysts, they added promoters (Bi, Te, Pb, Sb and Se) to platinum, and the best catalytic performance was observed with bismuth.

This greatly improved the selectivity towards DIHA; the optimum 1% Bi- 5% Pt/C catalyst allowed to reach a yield of 20% at 25% conversion [60]. More recently, the optimum catalyst composition was determined to be 3 wt% Pt-0.6 wt% Bi supported on activated carbon and working at 80 °C, 3 bar and at an initial pH of 2, leading to a maximum selectivity to DIHA of 60% at 80% glycerol conversion, but still with a fairly low glycerol oxidation rate ($\text{TOF} = 370 \text{ h}^{-1}$) [28]. However, a deactivation of the bismuth-promoted platinum catalysts was observed at acidic pH as reaction time progressed [32]. This was attributed to the increase in the amount of strongly adsorbed acids (such as glyceric acid and hydroxypyruvic acid, formed concurrently) on the surface [32]. Nevertheless, the improvement in both activity and selectivity towards the oxidation of the secondary alcohol function by associating platinum with p-electron metals is meaningful.

When using acid reaction conditions, the oxidation of the secondary primary alcohol function is promoted, whereas basic conditions favor the oxidation of the primary alcohol group. Accordingly, the main product of glycerol oxidation using platinum supported on activated carbon in a basic media is GLYCEA (selectivity of 55% at 90% conversion) with a small amount of DIHA (selectivity of 12%) [32].

In general, palladium based catalysts are found to be more selective for the formation of glyceric acid than platinum [32, 61-63]. Pd catalysts supported on activated carbon under basic conditions have a high selectivity towards GLYCEA (77% at 90 % conversion), whereas the selectivities to the other reaction products (including DIHA) are lower than 10% [32]. No interpretation was given for the different selectivities observed over Pt and Pd.

The main disadvantage of catalysts that are based on the Pt-group is their deactivation at increasing reaction time due to oxygen poisoning, which depends directly on the oxygen partial pressure used [27, 61, 64]. On the other hand, gold has a better resistance to oxygen poisoning, allowing for the use of high oxygen partial pressures [65]. It was found that gold is highly active in the oxidation of glycerol. Nevertheless, contrarily to palladium and platinum catalysts, its activity is almost exclusively limited to basic media.

It was reported that the use of bimetallic systems Au-Pd/C and Au-Pt/C significantly improved the activity with respect to the monometallic systems and selectivity could be tuned by using different preparation methods [44, 47-48, 66]. The addition of Au to Pd or Pt metals also enhanced the resistance to oxygen or by-product poisoning with respect to monometallic catalysts [48]. On the other hand, Ketchie et al. tested

bimetallic Au-Pd/C catalysts and observed that, although the activity of bimetallic catalysts was dependent on the amount of gold present, none of them had a larger TOF than that obtained with monometallic Au. However, the bimetallic catalysts lead to a higher selectivity to GLYCEA when compared with monometallic gold. Therefore, they suggest that Pd could catalyze the decomposition of the side product H_2O_2 , which is also formed over Au, but is detrimental to the selectivity toward glyceric acid [46].

Demirel et al. showed that the presence of Pt on Au/C catalysts increases not only the activity but also the selectivity towards DIHA in basic media [45].

In addition to noble metal supported catalysts, a range of transition metal containing silicates and aluminophosphate catalysts have been tested in the presence of hydrogen peroxide as oxidant [26]. However, due to the reaction conditions and / or catalysts, mono-formate ester of glycerol was observed as the main product.

In summary, catalysts that are based on noble metals of the platinum group promote glycerol conversion in both acid and basic conditions, but suffer severely from oxygen poisoning. Gold is considered as the catalyst of preferential choice in glycerol oxidation, since it is highly active and selective for the formation of glyceric acid, besides allowing the use of higher oxygen partial pressures. Nevertheless, its activity is restricted to basic media.

1.4.2.2.2 Influence of pH

The decisive influence of the pH on the reaction course was first reported by Gallezot et al. [32]. They examined the aerobic Pt/C and Pd/C catalyzed reaction at constant pH (value in the range 2 to 11) and showed that the reaction rate increases with the pH. Therefore, the low activity of the Pd/C and Pt/C catalysts reported by Kimura et al. [60] was due to a pH effect. In fact, when using palladium catalysts and a pH of 11, complete conversion of glycerol was reached after no longer than 4 h of reaction, whereas lower pH values resulted in incomplete conversion, even after 8 h. Glyceric acid, resulting from the activation of the primary hydroxyl group of glycerol, was always the main product obtained. The selectivity is enhanced by the increase of pH. For instance, selectivity to glyceric acid increases from 30% at pH 7 to 77% at pH 11. At this latter pH, the selectivities to the other reaction products (DIHA, TARTA and OXALA) were always smaller than 10%. Therefore, not only the activities but also the selectivities of the catalysts change drastically with the pH of the reaction medium.

Villa et al. reported the formation of mainly C₁ products (formic acid and CO₂) when using carbon-supported palladium at pH 5 [49]. Carretin et al. investigated the effect of the NaOH/glycerol molar ratio using a 5% Pt/C catalyst [41]. After 3 h of reaction at 60 °C and 3 bar of oxygen, the glycerol conversion increased from 27% to 63% by increasing the NaOH/glycerol ratio from 0 to 1. At the same time, the selectivities to glyceric acid and glyceraldehyde increased from 28% to 74% and from 0% to 21% respectively. Moreover, the presence of base drastically decreased the selectivity to oxalic acid (selectivity of 57% without base addition to 0% at NaOH/glycerol = 1). This indicates that under basic conditions, the oxidative cleavage to C₁ products is essentially eliminated. Moreover, they concluded that different metal hydroxides dramatically changed the catalytic activity. In fact, for the same reaction conditions, the glycerol conversion after 3 h decreased in the sequence: NaOH (63.1%) > CsOH (52.0%) > LiOH (48.9%) > RbOH (37.0%) > NaNO₃ (36.0%) > KOH (35.4%). On the other hand, a correlation with the change in selectivities was not so obvious, as the highest (87.0%) and the lowest (13.7%) selectivities to GLYCEA were obtained for KOH and RbOH, respectively. Nevertheless, it is worth to notice that TARTA was only obtained in the presence of NaOH (selectivity of 3.1%).

Recently, there have been many studies dealing with the oxidation of glycerol to chemical intermediates using supported gold nanoparticles as catalysts [45, 54, 67]. As already mentioned, when using gold catalysts, a basic medium is necessary in order to observe significant glycerol conversions [50, 68-69]. Sodium hydroxide is generally chosen for that purpose.

Demirel et al. studied the influence of the pH on the catalytic oxidation of glycerol using carbon-supported gold catalysts and reported the highest initial reaction rate for a NaOH/glycerol ratio of 4 [50]. However, in opposition to the experiments with NaOH/glycerol molar ratio up to 2, the selectivities obtained with a ratio of 4 do not remain constant, and the oxidation of glyceric acid to tartronic acid is strongly favoured. Under the basic conditions used, the sodium salt of GLYCEA is generally found with a yield up to 90% [27]. However, a wide range of products have already been detected, mainly GLYCER, DIHA, TARTA, OXALA, HPYA, MESOA and LACTA, as it can be seen in Table 1.3.

The role of the base is still under discussion. It appears to be involved in the first step of alcohol oxidation, which consists in the dehydrogenation of the alcohol function followed by the oxidation of the formed intermediate. The basic pH could also favors the desorption of the acid from the metal [32]. Recent labeling

experiments have shown that the presence of surface bound hydroxide intermediates facilitate the activation of both C-H and O-H bonds of glycerol, as it lowers considerably the activation barrier [68] (see Figure 1.8). In particular, the activation of the O-H bond is unlikely for gold alone, since in this metal, contrarily to platinum, this step has a very high activation barrier [68]. This can explain the activity (although lower) observed with the platinum-based catalysts in acid conditions. One of the main advantages for working in acidic media is the prevention of salt formation, since the corresponding elimination costs are always a problem in the design of industrial processes.

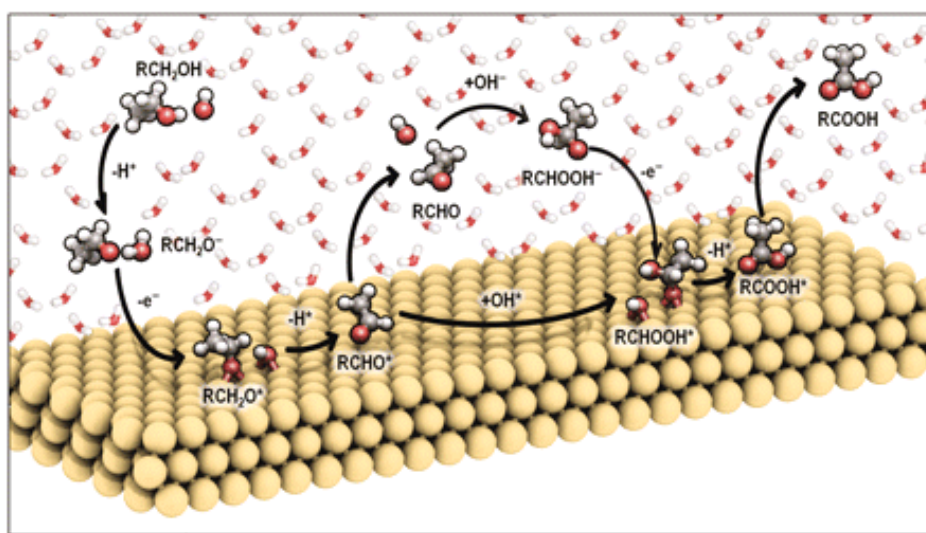


Figure 1.8 Reaction scheme for alcohols to acids over a Au surface in water at high pH. Hydroxide facilitates elementary steps in alcohol oxidation in both the solution phase and at the metal/solution interface [68].

Prati et al. try to push the reaction under neutral/acidic conditions by increasing the temperature to 80 °C [48-49, 70]. They obtained only a low conversion of 10% even after 6 h of reaction using a 1% Au/C catalyst. Moreover, the main products were formic acid and carbon dioxide, which is a result completely different from those obtained in basic media (the main product is generally glyceric acid). C – C bond cleavage is probably due to the formation of hydrogen peroxide, a well-known by-product under these reaction conditions [51]. In fact, the addition of MnO_2

(promotes the decomposition of peroxide) to the reaction mixture increases the selectivity to glyceric acid from 64% to 78% at 40% glycerol conversion [51].

Recent experiments in glycerol oxidation catalyzed by gold supported on carbon showed that oxygen atoms incorporated into the reaction products were originated from hydroxide ions, which play a decisive role during the reaction, and not from molecular oxygen, which is only necessary for the regeneration of hydroxide ions [68]. Glycerol oxidation is aided by high-pH conditions, since the hydroxide species adsorbed over gold have the ability to facilitate the activation of both the C-H and O-H bonds of glycerol (also adsorbed on the catalyst surface), leading to the addition of electrons to the metal surface [68]. In this way, the oxidation mechanism does not involve the dissociation of molecular oxygen to atomic oxygen. The production of peroxide during oxidation reactions over Au indicates that O₂ is reduced before dissociation; activation of O₂ occurs by the formation and subsequent dissociation of peroxide and hydrogen peroxide intermediates on the metal surface, according to the following mechanism [68]:



where * represents a site on the metal surface. The last step allows for the removal of electrons added to the surface during the adsorption of hydroxide ions and the regeneration of these species. Accordingly, the presence of a base is a key factor in the selective glycerol oxidation over gold catalysts.

As it was highlighted in this section, the pH of the reaction medium has a great impact on the catalytic performance, since it influences largely both the activity and the selectivities. Whereas palladium and platinum catalysts can be used in acid or basic conditions, the activity of gold is limited to basic media. One of the main advantages of working in acid media is the prevention of salt formation. Nevertheless, the activities obtained under these conditions are far lower than those reached in the presence of a base.

1.4.2.2.3 Influence of the particle size

Catalyst activity and selectivity are affected by the dispersion of the active phase, especially with gold-based catalysts, which are said to be structure sensitive [50].

Liang et al. prepared a series of carbon-supported platinum catalysts with average particle sizes ranging from 3.2 nm to 26.5 nm [71]. It was found that the conversion of glycerol is similar when the particle size of Pt is smaller than 6 nm, but decreases dramatically for larger particles. This was ascribed to the lower metallic surface area of the larger sized Pt crystallites. On the other hand, they observed that the selectivity to GLYCEA gradually increases with the growing of Pt particles (from 47% to 55%).

Dimitratos et al. used a colloidal method to tune the average particle size of palladium catalysts from 2 to 16 nm. They observed that the increase of particle size led to a decrease of the turnover frequency (TOF), but on the other hand an enhancement of the selectivity towards GLYCEA was observed [72]. Moreover, both glycolic and tartronic acids were reduced by increasing particle size (from 15% to 5% for GLYCOA and from 21% to 11% for TARTA).

The first systematic approach for studying the influence of the gold content and nanoparticle sizes was performed by Carretin et al. [41, 43, 73]. They showed that the selectivity to GLYCEA and the conversion of glycerol increase with the gold loading of the catalyst. Then, they observed that when changing the average particle size from 25 to 50 nm, at the same amount of gold (1% Au/graphite), the conversion decreased to zero. These results indicate that there may be an optimum particle size for the desired selective catalysts. Furthermore, characterization of active Au/graphite catalysts by cyclic voltammetry, carried out in the presence of NaOH, revealed the existence of oxide species, which were proposed as the active sites for this kind of catalysts.

Porta and Prati also investigated the influence of gold nanoparticle sizes in the range of 6 to 20 nm [27]. They also found that smaller particles showed higher catalytic activities. These authors suggest that the higher surface exposition of the metal in small size particles was responsible for the higher performance. They also observed that whereas the selectivity to GLYCEA was maintained constant during the reaction for larger gold particles (> 15 nm), it decreased during reaction in the case of small particles. This was tentatively explained by a competition between the increase in the particle size during the reaction and the density of the (111) planes, since they stated that gold particle edges can be the active centers for oxygen activation. Demirel et al. studied Au/C catalysts with gold particle size in the range from 2 to 45 nm and confirmed that higher activities were obtained with smaller gold particles [50]. Moreover, the selectivity to GLYCEA was increased with decreasing gold particle size, but only until a maximum value of 75% (with an average size of

3.7 nm). With smaller particles, the selectivity drops to 40%. As postulated by Porta et al. [27], they obtained more oxidized products, such as glycolic acid, with smaller particles. On the other hand, catalysts with larger gold nanoparticles showed increased selectivity to DIHA (selectivity of 20% with a gold average particle size of 42 nm).

Ketchie et al. also confirmed these results, but they noticed that the particle size could not be the only factor responsible for the difference in selectivities [51]. They attributed the lower selectivity of small Au particles to a higher formation rate of H_2O_2 during glycerol oxidation, which eventually promotes C – C cleavage, as discussed before.

One can see that results are sometimes inconsistent and differ from one group to the other. Furthermore, under similar reaction conditions and using gold catalysts with comparable particle sizes, the catalytic performance can be very different depending on the support used [45]. Nevertheless, it is well established that the average particle size influences both activity and selectivity. Generally, smaller gold particles lead to higher catalytic performances, but there is no direct clear correlation with the selectivities observed. Even though various studies have demonstrated the influence of the gold particle size on the catalytic performance, it seems that there is no general consensus about the corresponding interpretation. Other features of the catalysts can play a decisive role in reaction.

1.4.2.2.4 Influence of the support

In addition to the particle size, the activity of gold catalysts seems to be affected by the nature of support. Nano-sized gold particles supported on different carbon materials (e.g. carbon black, activated carbon and graphite) and oxides (TiO_2 , MgO and Al_2O_3) are active for the oxidation of glycerol, but show very different performances, carbon supported gold catalysts being more active than most oxides supported catalysts [45, 53, 65].

Demirel et al. investigated the influence of the specific surface area of ceria-supported gold catalysts on the performance. They could not find any significant correlation, and in the studied range of 4 to $170 \text{ m}^2 \text{ g}^{-1}$ the optimum catalytic activity was achieved over ceria with a specific surface area of no more than $60 \text{ m}^2 \text{ g}^{-1}$. They also compared their results with titania and activated carbon supported catalysts. Although carbon-supported gold catalysts lead to higher activities, they

concluded that the selectivities obtained were independent of the nature of the support and remained in any case around 45% for GLYCEA and 25% for DIHA [53].

In another study, Demirel et al. [45] reported that the selectivity to DIHA can be increased from 15%, when using gold supported on the activated carbon NORIT NSX1G, to 27% using the carbon black “Black Pearls 2000”; therefore, it seems that the textural properties of the carbon support can influence the product distribution. Moreover, by analyzing the preparation of gold catalysts on various activated carbon supports, they found that carbon support also influenced the catalytic performance; a low fraction of micropores led to the highest activity in the glycerol oxidation (Figure 1.9).

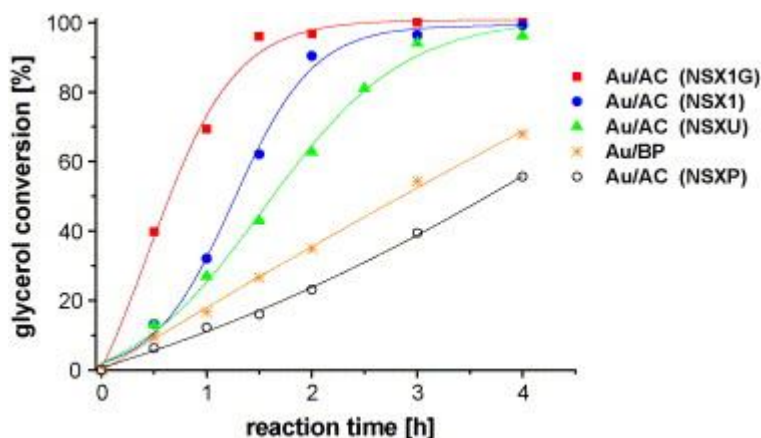


Figure 1.9 Glycerol conversion with 1% Au/AC depending on the carbon support.

Reaction conditions: 150 mL of 1.5 M aqueous glycerol solution, glycerol/Au = 2460 mol/mol, pH = 12, P_{O_2} = 1 bar, T = 60 °C, rpm = 500 [45].

An increasing number of studies suggest that textural and chemical properties of the support influence directly the selectivity of the process [54, 58, 74].

Villa et al. used several $MgAl_2O_4$ -spinel as support for gold catalysts and found that the catalytic performance was not only mediated by particle sizes [54]. Instead, a correlation between the Ag/Mg ratio (thus, the basicity of the support) and the selectivity towards GLYCEA and TARTA was proposed.

Sobczak et al. used V_2O_5 , Nb_2O_5 , Ta_2O_5 and Al_2O_3 as support for gold [55]. Among group V metal oxides the highest activity was obtained with Nb_2O_5 (conversion of

67% after 5 h of reaction and 47% selectivity towards GLYCEA). Although all catalysts were active for the reaction, mainly promoting the production of glyceric acid, other products such as glycolic, tartronic, oxalic and formic acids were also formed. The authors stated that the acid – base properties of the supports can be an important feature for the catalytic activity. They suggested that the large acid character of some supports was responsible for their high selectivity to C – C bond cracking products, leading to the formation of glycolic acid, formaldehyde and formic acid.

More recently, platinum supported on multi-walled carbon nanotubes (MWCNTs) was tested in glycerol oxidation [57]. The reaction was carried out in a base free aqueous solution and it was found that the MWCNT-supported platinum catalyst was more active than the activated carbon-supported one. This was explained by an easier accessibility of the reactants (glycerol and oxygen) to the metal active sites, located on the external walls of MWCNT. However, both catalysts exhibited a similar selectivity to GLYCEA (60 - 70%) under the conditions tested.

In conclusion, in spite of its well known influence on the catalyst activity, the role of the support in the mechanism of glycerol oxidation is still not clear, and probably depends on the type of support considered (e.g. carbon materials, oxides, etc.).

1.5 Gold in catalysis

The history of gold in catalysis started in the mid-nineteenth century when Michael Faraday prepared gold colloids by reducing a solution of HAuCl_4 with elemental phosphorus, resulting in the formation of ruby-red gold sols. However, the significant turning point in its history occurs only in the 1990s with the works of Haruta et al. [75-77]. They investigated the ability of gold nanoparticles to catalyze CO oxidation and disclosed the peculiarities of the activity of this metal on catalysis. This was followed by an impressive increase of the number of publications related with catalysis by gold (Figure 1.10).

Today, gold is considered as the catalyst of preferential choice in a large number of reactions [78-79]. Although gold was known as being the most inert of all the noble metals, it presents peculiar properties as a catalytic material at a nanoscale level. However, since the beginning, the use of gold catalysts in a large number of industrial and environmentally relevant reactions was affected by a high variation of the catalytic results depending on the preparation method employed and on the

support used. In fact, these two factors generally have a dramatic effect on the catalytic performance, since they determine the morphology of the gold particles. Therefore, several methods have been developed for the preparation of supported gold catalysts. For gold to be an active catalyst, the use of a careful preparation procedure is crucial, since it is necessary to obtain nanoparticles well dispersed on the support.

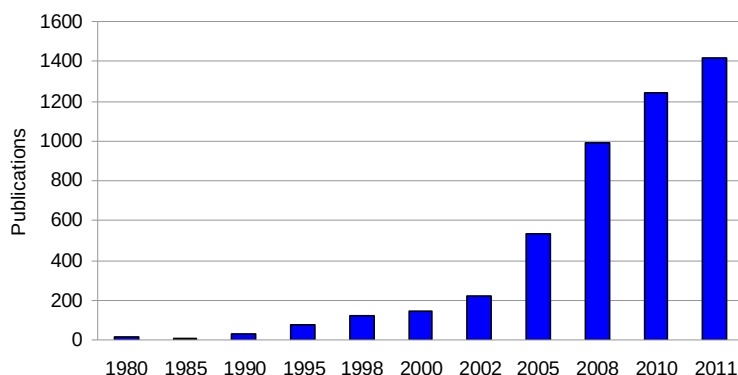


Figure 1.10 The increase in the number of scientific publications related to gold catalysts (collected from the ISI Web of Knowledge database, in 05/2012).

Impregnation is the classical method used to prepare supported noble metal catalysts. The support contacts with a solution of the metal precursor; the subsequent steps consist in aging, drying, calcination and reduction. In the so-called incipient wetness impregnation, the volume of the solution does not exceed the pore volume of the support, in opposition to the “wet” impregnation method. The simplicity of the methodology makes impregnation attractive for industrial scale-up purposes. Chloroauric acid (HAuCl_4) or auric chloride (AuCl_3 or Au_2Cl_6) are usually used but complex salts, such as potassium aurocyanide ($\text{KAu}(\text{CN})_2$) and the ethylenediamine complex $[\text{Au}(\text{en})_2]\text{Cl}_3$, are alternatives [79]. However, these conventional techniques result in fairly large gold particles and consequently poorly active catalysts. On one hand, gold has a low melting point (for instance when compared with Pt and Pd), and therefore, sintering can occur during the calcination and/or reduction steps. The extension of the agglomeration will also depend on the level of interaction of gold with the support. On the other hand, it has been found that residual chloride can act as a catalyst poison (it is important to notice that

supported Au catalysts are generally prepared from chloride-containing Au precursors, as mentioned before). Although the effect of residual chloride in the catalytic performance is not yet completely understood, it seems that it can cause poisoning, excessive sintering of the Au particles during thermal treatments and inhibition of gold reduction [79]. This is due to the fact that gold and chloride ions can combine easily to form bridges, favoring the growth of particles upon heating [80]. However, heating steps are necessary in impregnation techniques in order to decompose the gold precursor and reduce the metal, as already mentioned. Therefore, chloride removal is a very important step in the preparation of well-dispersed gold catalysts.

Chloride can be displaced by other ions. For instance, Bowker et al. [81] described an alternative called the double impregnation method, in which a double impregnation of chlorauric acid and a base are used to precipitate out gold hydroxide within the pores of the catalyst, followed by washing. The main reason for the enhanced activity of such catalysts is that the double impregnation results in the deposition of Au as $\text{Au}(\text{OH})_3$. As a result, Cl is not associated with Au and is removed from the catalysts by washing.

The immobilization of pre-formed metallic sol is widely used to prepare gold catalysts [79, 82]. The method is based on the preparation of Au nanoparticles and their subsequent immobilization on a support. The advantage of this method lies in the possible control of the particle size. In fact, depending on the preparative conditions used, the sol obtained can have different colors, due to the interaction of visible light with surface electrons of the gold nanoparticles. It was noticed that colloidal gold is red when particles are smaller than 20 nm, and blue when larger (Figure 1.11) [83]. The preparation of colloidal gold is generally accomplished by reduction of chlorauric acid (HAuCl_4) with a reducing agent, such as sodium citrate or borohydride. In order to stabilize the nanostructured colloidal gold and prevent their agglomeration, a protective agent is usually added (for instance, surfactants or rigid hydrophilic macromolecules)[82].

During the immobilization step, the kinetic of adsorption of the sol on the support depends on the sol stabilizer used, as well as on the surface area and the surface charge of the support [82]. In this technique, chloride remains in the liquid phase, and its negative effect is avoided.



Figure 1.11 Colours corresponding to different sizes of colloidal gold particles (from [83]).

Precursor, methodology and support are only a few parameters important in the preparation of gold catalysts. The reasons of the catalytic activity of gold are not yet completely established; however, it is generally established that the presence of gold as well-dispersed nanoparticles is a necessary requisite to obtain active catalysts. On the other hand, the presence of small gold nanoparticles alone cannot explain completely the catalytic performance of gold. In fact, similar sized gold particles on different supports show differences in catalytic activity [79, 84]. Therefore, the support, particularly its morphology and surface area [85], seems to have also an effect on the activity. It has also been shown that the nature of the support, particularly its redox properties, plays a decisive role in the activity [86].

1.6 Carbon supports

Carbon materials are largely used in heterogeneous catalysis, specially for liquid phase reactions, because they can satisfy most of the desirable properties required for a suitable support, such as inertness, stability under reaction and regeneration conditions, resistance to acidic and basic environments, easy accessibility, good recycling characteristics, low density, adequate mechanical properties, diverse porous structures, possibility to control the surface chemistry, easy recovery of precious metals by support burning and amenability to synthesize variants or

introduce post-synthetically engineer traits, using a wide range of manufacturing, activation and carbonization methods [87].

A wide diversity of structural forms of solid carbon exists. Although they are all composed of carbon, they can differ on the physical structures. Two variants are amorphous and crystalline carbons [88].

Among the amorphous carbons, activated carbon is the most common in catalysis, and is an effective catalyst by itself in a large number of reactions. Activated carbons are produced from natural sources and their pore texture is not easily controlled [89]. It can be modified to some extent by chemical and thermal treatments, but the control of texture is still limited. Recently, carbon xerogels have emerged as a type of amorphous carbon with well controlled pore size. In fact, these polymer based porous carbons with tailored textural properties can be prepared by simple sol-gel condensation of resorcinol and formaldehyde and subsequent carbonization of the organic aerogel, provided that the correct synthesis conditions are chosen [90]. Indeed, mesoporous and macroporous textures combined with large pore volume, which is more adequate for liquid phase applications, can be obtained by this method. The key variable is the pH of the precursor solution (see Figure 1.12) [91]. Comparatively to activated carbon, the advantages of carbon xerogels are their high purity and flexibility in what concerns the textural properties.

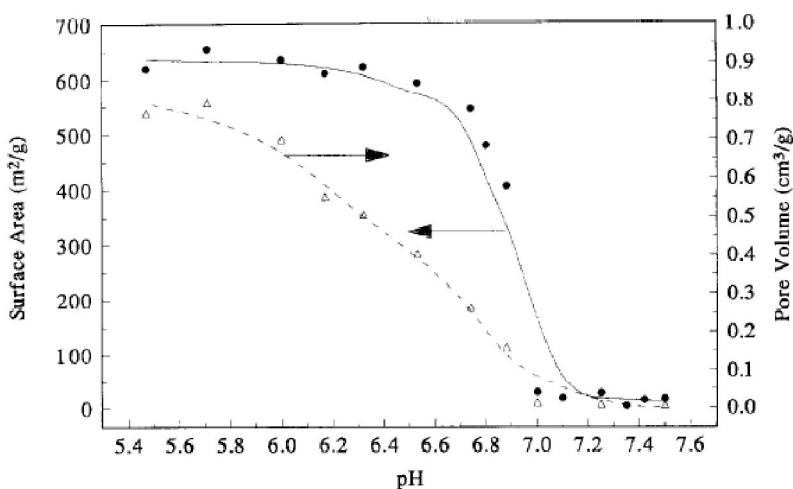


Figure 1.12 Effect of the initial pH of the resorcinol and formaldehyde solution on the surface area and pore volume of carbon xerogels [91].

Amorphous carbons are primarily made of cross-linked aromatic sheets and imperfect strips with no regular order and variable gaps of molecular dimension between them, corresponding to the pores of the material (Figure 1.13) [92-93].

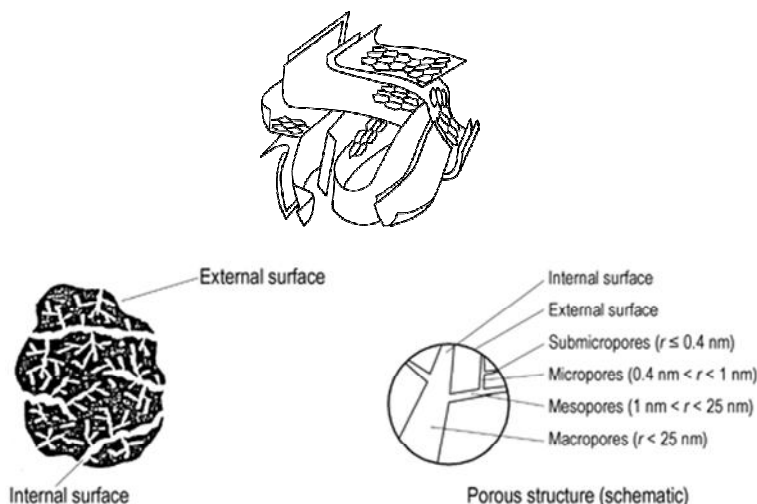


Figure 1.13 Schematic model of the structure of activated carbon [92], and respective pore structure [93].

The formal discovery of multi-walled carbon nanotubes by Iijima in 1991 [94] stimulated research on the application of these crystalline, nanostructured carbon materials in a wide range of areas, including electronics, materials, catalysis and gas storage, due to their excellent properties, which include high specific area, high electronic conductivity, outstanding chemical and electrochemical stability [95]. Carbon nanotubes can be divided into two categories: single-walled carbon nanotubes (SWCNT) and multi-walled carbon nanotubes (MWCNT). Ideally, SWCNT are made of a perfect graphene sheet, whereas MWCNT can be considered as concentric SWCNT with increasing diameter and coaxially disposed [96] (Figure 1.14). The number of walls present can vary from two to several tens, so that the external diameter can reach 100 nm. The concentric walls are regularly spaced by 0.34-0.36 nm [95]. These materials also have a porous nature. Pores in MWCNT can be divided into inner hollow cavities of small diameter (narrowly distributed) and, mainly, aggregated pores (widely distributed) formed by interaction of isolated MWCNT [95]. Therefore, due to their peculiar morphology, carbon

nanotubes can facilitate the interaction with their environment and present specific adsorption properties when compared with graphite or activated carbon [95].

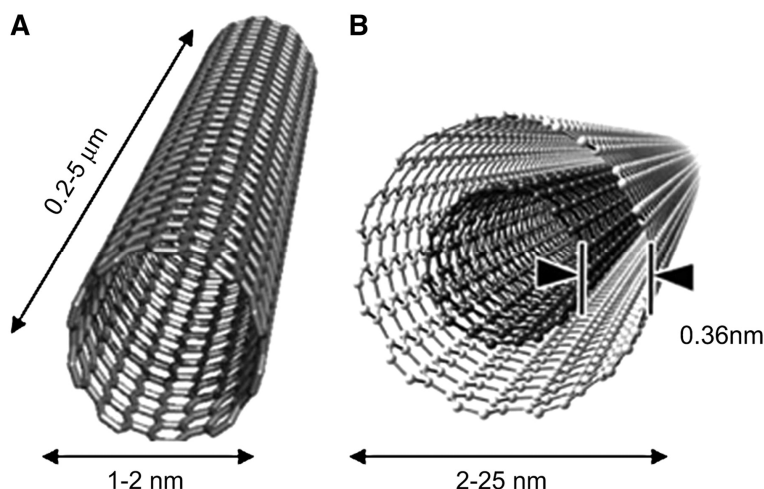


Figure 1.14 Conceptual diagram of (A) single-walled carbon nanotube and (B) multi-walled carbon nanotube showing typical dimensions of length, width, and separation distance between graphene layers in MWCNTs [96].

The catalytic performance can be influenced not only by the porous structure of carbon supports, but also by their surface chemical properties. In fact, most applications of carbon materials involve interfacial interactions where substances in gas or liquid phases access the carbon surface. Moreover, the surface chemical features of the carbon material used as support can influence the interaction with the catalyst precursor.

Usually, appreciable amounts of oxygen and hydrogen, in addition to other heteroatoms, such as chlorine, sulphur and nitrogen, are present in activated carbons and other carbon materials [93]. Such elements may be present in the starting material and become chemically bonded to the structure, in the form of functional groups, during calcination and activation steps. Among them, oxygenated groups, such as carboxyl, phenol, carbonyl, quinone, and lactone groups, are the most important in the definition of the surface chemical properties of carbons [92, 97]. Figure 1.15 [98] summarizes the different oxygen and nitrogen functional groups (the most important in catalysis) that can be formed on carbon surfaces.

Although the as-produced carbon nanotubes and xerogels do not have a high amount of functional groups on their surface, these may be introduced after preparation, via adequate post-treatments [90, 95, 99-102]. In fact, carbon-oxygen surface groups can result from the contact of the material with many oxidizing gases (oxygen, ozone, nitrous oxide, nitric oxide, carbon dioxide, etc.) and with oxidizing solutions (nitric acid, sodium hypochlorite, hydrogen peroxide, etc.). On the other hand, heat treatments under inert atmosphere may be used to selectively remove some of those groups, leading to an increase in the basicity of carbons [92].

The main contribution to the surface basicity is attributed to the electron rich oxygen-free sites located on the carbon basal planes, i.e. within the graphene layers that constitute the carbon crystallites [103]. Accordingly, carbon basicity is mainly related to the absence of functional groups, predominantly of acidic nature (electron-withdrawing groups), and subsequent availability of delocalized π -electrons on the carbon surface [104].

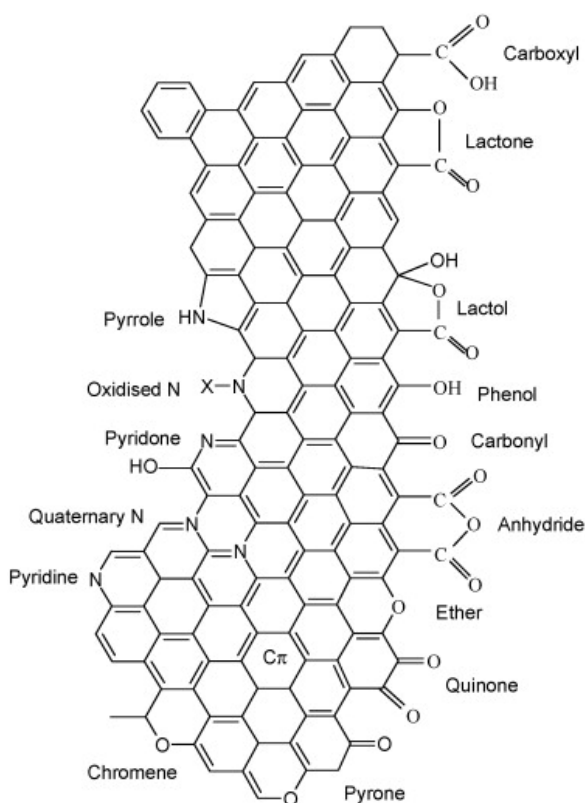


Figure 1.15 Nitrogen and oxygen surface groups on carbon [98].

In summary, both the textural and chemical surface properties of carbon materials can influence the performance of supported catalysts. In fact, porous carbon can also contain chemically active centres eventually responsible for specific interactions, and therefore special attention should be given to these characteristics.

1.7 Objectives and thesis outline

The transformation of glycerol into high-value fine chemicals obtained by selective oxidation is an important and developing area of research due to the recent incentives for the production of biodiesel. Nevertheless, this catalytic process has not been commercially applied yet, since the main problem remains: the selective activation of the hydroxyl groups of the molecule, which have very similar reactivity, is somewhat difficult. Therefore, the main objective of this work is the development of active and, especially, selective catalysts for the liquid phase catalytic oxidation of glycerol.

The center of the work started with the assessment of several noble metal catalysts, being activated carbon used as the reference support. Subsequently, activated carbon, carbon nanotubes, carbon xerogels and oxides were evaluated as supports. The influence of the surface chemistry and textural properties of these materials on the catalytic performance was analyzed. In order to discuss the different efficiencies observed, support and catalysts were fully characterized. Moreover, due to the scarce information in literature, special attention was given to gold supported on carbon nanotubes. Several preparation methods were evaluated.

The oxidation reactions were carried out in a 350 mL stainless steel reactor (see Appendix A).

This work is organized in nine chapters. This introductory chapter is Chapter 1. The main core of the thesis is composed of Chapters 2 to 8.

Chapter 2 is dedicated to the assessment of noble metal catalysts supported on a commercial activated carbon.

Chapter 3 describes the influence of the surface chemical characteristics of activated carbons on the performance of gold catalysts. A possible role of the support surface chemistry in the reaction mechanism is proposed in this chapter.

In Chapter 4, gold nanoparticles are supported on multi-walled carbon nanotubes by several methods, and the effect of the preparation technique on the catalytic performance is evaluated.

A study similar to that reported in Chapter 3 but using carbon nanotubes as support is described in Chapter 5.

In Chapter 6, carbon xerogels with different pore size distributions are explored as gold support. The influence of the textural properties of carbon materials on the selectivity of the process is discussed.

Chapter 7 focuses on the performance of platinum group metals supported on carbon nanotubes, under basic and acid conditions. The influence of the pH on the distribution of products is evaluated.

Chapter 8 reports preliminary results of the performance of gold nanoparticles supported on ceria, zirconia and ceria-zirconia mixed oxides.

Finally, Chapter 9 summarizes and integrates the main conclusions of this work. Some suggestions for further work are also presented.

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Chapter 2

2 Selective oxidation of glycerol catalyzed by Rh/activated carbon: importance of support surface chemistry

Noble metal catalysts (Pt, Ir, Pd, Rh, Au) supported on activated carbon were assessed for glycerol oxidation. Rhodium is a highly efficient catalyst when the support has neutral or basic properties. The surface chemistry of activated carbon plays a key role in the performance.

2.1 Introduction

The growing concern about global warming leads to numerous discussions about sources of energy. The use of renewable feedstocks is essential for the sustainable development of society, since fossil energy resources are limited. Over the last decade, biodiesel has emerged as a viable clean fuel. It is obtained by transesterification with methanol of triglycerides extracted from seed oils, leaving glycerol as the main by-product. In this process, about 100 kg of glycerol are produced for every ton of biodiesel [1]. During the last years the market for biodiesel was continuously increasing, and it is expected that this trend remains [2]. Consumption of the surplus of glycerol is a necessary requisite for the commercial viability of biodiesel production [3]. The conversion of glycerol into high-value chemicals is a research area that has received tremendous attention in recent years, as a result of glycerol's unique structure, properties, bioavailability and renewability [2, 4-5]. Liquid phase catalytic oxidation is a promising route to convert glycerol into useful compounds, provided that the catalyst used is sufficiently active and selective for the formation of chemicals such as glyceric acid (GLYCEA) and/or dihydroxyacetone (DIHA), potentially useful as chemical intermediates in the fine chemicals industry, particularly in pharmaceuticals [2, 6]. Until now, these products are being produced by expensive and non-environmentally safe oxidation processes, or by low productivity microbial fermentation processes [7]. However, the extensive functionalization of this molecule, with similar reactive hydroxyl groups, renders its selective oxidation particularly difficult [8].

In recent years, there have been many studies dealing with the oxidation of glycerol to chemical intermediates using supported catalysts with noble metal nanoparticles, such as Pd, Pt and mainly Au on diverse supports [9-15]. The main product of glycerol oxidation using platinum supported on activated carbon is GLYCEA (selectivity 55% at 90% conversion) with a small amount of DIHA (selectivity 12%) [11]. Pd catalysts supported on activated carbon under basic conditions have a high selectivity towards GLYCEA (77% at 90 % conversion), whereas the selectivities to the other reaction products (including DIHA) are always lower than 10% [11]. The main disadvantage of catalysts that are based on these metals is their deactivation at increasing reaction time due to oxygen poisoning [12, 16]. On the other hand, gold has a better resistance to oxygen poisoning compared to platinum, allowing for the use of high oxygen partial pressures [17]. However, the catalytic activity of gold depends mainly on nanoparticle sizes, which in turn depend on the preparation method used [12, 18].

Under alkaline conditions, catalyst activity and selectivity seem to be influenced by the nature of the metal, nanoparticle sizes and support. However, catalytic oxidation of glycerol has been investigated by several research groups under different reaction conditions (pH, temperature, oxidants, etc.) with different metals and different supports, leading to a difficult catalyst evaluation and comparison, since many parameters influence catalyst performance. Therefore, this work begins with a comparative study among catalysts under the same reaction conditions and preparation method. Additionally to metals already studied in the literature (platinum, palladium and gold), two other metals (iridium and rhodium) were tested in the glycerol oxidation reaction. Moreover, the influence of the activated carbon surface chemical groups on the rhodium catalyst performance was evaluated. For this purpose, the support surface was modified by appropriate chemical and thermal treatments. The possible role of the surface functional groups of the support in the reaction mechanism was also considered.

2.2 Experimental

2.2.1 Catalysts preparation

2.2.1.1 Materials

The metal precursors H_2PtCl_6 (99.9 % ACS, Pt min 37.5%), PdCl_2 (99.9% ACS, Pd min 59.5%), RhCl_3 (99.9% ACS, Rh 38.5-45.5%), $(\text{NH}_4)_3\text{IrCl}_6$ (99.9% ACS, Ir 38-42%) and $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (99.99% ACS, Au min 49.5%) were supplied by Alfa Aesar.

NaBH_4 of purity > 95% from Riedel-de Haën, NaOH (> 97%) and polyvinylalcohol (PVA) (purity > 99%) from Aldrich were also used. The commercial activated carbon NORIT ROX 0.8 was selected as starting material for the preparation of supports with different surface chemistries.

2.2.1.2 Preparation procedures

Gold, iridium, palladium, platinum and rhodium catalysts were prepared by incipient wetness impregnation on the commercial activated carbon. In addition, a gold catalyst was also prepared via the sol immobilization method [19].

The NORIT ROX 0.8 activated carbon has a small amount of surface oxygenated groups. In order to evaluate if the activity of the catalysts correlates with the concentration of oxygenated surface functional groups, the original support was

modified by chemical and thermal treatments to obtain supports with different surface chemical properties. Rhodium was supported on these modified activated carbon materials.

2.2.1.2.1 Preparation of supports

A NORIT ROX 0.8 activated carbon (pellets of 0.8 mm diameter and 5 mm length) was used as starting material for this study (sample AC₀). This material was submitted to different chemical and thermal treatments. Both liquid phase oxidations and thermal treatments have been reported not to significantly change the textural properties of activated carbons [20-21].

An adequate amount of sample AC₀ was introduced in a Soxhlet extraction apparatus connected to a boiling flask, with a nitric acid 6 M solution, and to a condenser. The reflux was stopped after 3 h. The oxidized material was subsequently washed with distilled water until neutral pH, and then dried at 110 °C for 24 h (sample AC₁). The purpose of this liquid phase oxidation is to increase the amount of oxygen-containing surface groups on the support.

All the thermal treatments were performed on sample AC₁, since it is important that the starting material presents a large amount of surface groups in order to produce activated carbons with a high basic character by heat treatment at high temperatures [22]. Support AC₁ was treated under nitrogen flow for 30 min at different temperatures (400, 600 or 900 °C) followed by treatment under dry air flow at room temperature for 1 h. These thermal treatments selectively remove the oxygen-containing surface groups previously introduced [20-21]. The final treatment in air is intended to stabilize the surface chemistry of the samples. The following samples were obtained: AC_{1tt400} – AC₁ thermally treated under nitrogen flow at 400 °C for 30 min plus 1 h under dry air flow at room temperature; AC_{1tt600} – similar to AC_{1tt400} but with treatment at 600 °C; AC_{1tt900} – similar to the others but treated at 900 °C. These treatments were carried out in order to remove selectively the oxygen-containing groups on the surface, while maintaining the original textural properties as far as possible.

Before use, all samples were ground to a particle diameter between 0.1 and 0.3 mm in order to minimize mass transfer resistance effects.

2.2.1.2.2 Preparation of catalysts

Au, Pt, Pd, Rh and Ir catalysts were prepared by incipient wetness impregnation of activated carbon with aqueous solutions of the corresponding metallic precursors (HAuCl_4 , H_2PtCl_6 , PdCl_2 , RhCl_3 , $(\text{NH}_4)_3\text{IrCl}_6$). The amount of noble metal was calculated to obtain a nominal metal loading of 1 wt%. In a complementary study, Au catalyst was also prepared by the sol immobilization method with NaBH_4 as reducing agent (Auc). Briefly, $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (35.1 mg) was dissolved in 690 ml of H_2O , and polyvinyl alcohol was added (1.6 ml, 0.2 wt%) under stirring. NaBH_4 (4 ml, 0.1 M) was added to the yellow solution under vigorous magnetic stirring. The resulting sol was ruby-red in color. Within a few minutes of sol generation, the colloid was immobilized by adding the support under vigorous stirring. The amount of support was calculated to reach a final metal loading of 1 wt%. After 3-4 days, the colorless solution was filtered, the catalyst washed thoroughly with distilled water until the filtrate was free of chloride (AgNO_3 test) and dried at 110 °C for 24 h [19].

After heat treatment under nitrogen flow for 3 h, the catalysts were activated by reduction under hydrogen flow for 3 h. The appropriate reduction temperature for each catalyst was determined by Temperature Programmed Reduction (TPR), namely 250 °C for the Pd catalyst, 350 °C for Ir, Pt and Au catalysts and 200 °C for Rh catalysts (see section 2.2.2). The treatment under nitrogen flow was carried out at the same temperature used for the reduction.

A supplementary catalyst, called Rh/PTAC_{1tt600}, was also prepared. It was obtained similarly to Rh/AC₁ as follows: while Rh/AC₁ was heat-treated under nitrogen at 200 °C, Rh/PTAC_{1tt600} was heat-treated at 600 °C before reduction at 200 °C.

An additional catalyst (Au/C), provided by the World Gold Council, was used as reference. Data sheets accompanying this sample indicate that it was prepared by the sol method and has a metal load of 0.8 wt%; the support is a carbon black. This catalyst was used without any additional treatment.

2.2.2 Characterization of supports and catalysts

The supports were characterized by N_2 adsorption at -196 °C, temperature programmed desorption (TPD) and by determination of the pH at the point of zero charge (pH_{pzc}). The catalysts were also characterized by temperature programmed reduction (TPR). Samples that showed the most interesting catalytic performances

were further characterized by microscopy and inductively coupled plasma (ICP) analysis.

2.2.2.1 N₂ adsorption

Textural characterization of the samples was based on the analysis of nitrogen adsorption isotherms, measured at -196 °C in a NOVA 4200e Quantachrome Instruments apparatus. BET surface areas (S_{BET}) were calculated, as well as micropore volumes (V_{micro}) and mesopore surface areas (S_{meso}) according to the t-method.

2.2.2.2 Temperature programmed reduction (TPR)

Temperature programmed reduction allows to find the most adequate reduction temperature for each metal. TPR profiles were obtained with a fully automated AMI-200 (Altamira Instruments). The catalyst (150 mg) was placed in a U-shaped quartz tube inside an electrical furnace and submitted to a 5 °C min⁻¹ linear temperature increase up to 600 °C under 5% (v/v) hydrogen flow diluted in helium (total flow rate = 30 Ncm³ min⁻¹). A thermal conductivity detector and a quadrupole mass spectrometer (Dymaxion 200, Ametek) were used to monitor the change in composition of the reactor effluent. H₂ consumption peaks indicate directly the temperature ranges where reduction occurs. The selected reduction temperatures are indicated in section 2.1.2.2.

2.2.2.3 Surface chemistry characterization

The qualitative and quantitative determination of oxygenated surface functional groups was performed by temperature programmed desorption - mass spectrometry (TPD-MS) [20-21]. CO and CO₂ TPD spectra were obtained with the fully automated AMI-200 (Altamira Instruments) already mentioned. The samples (150 mg) were placed in a U-shaped quartz tube inside an electrical furnace and subjected to a 5 °C min⁻¹ linear temperature increase up to 1100 °C under helium flow (25 Ncm³ min⁻¹). A quadrupole mass spectrometer (Dymaxion 200, Ametek) was used to monitor CO and CO₂ signals. For quantification of the CO and CO₂ released, calibration of these gases was carried out at the end of each analysis.

The determination of the pH at the point of zero charge (pH_{pzc}) of the samples was carried out as follows [23]. 50 ml of NaCl 0.01M solution was introduced in closed Erlenmeyer flasks. The pH was adjusted to a value between 2 and 12 by adding HCl 0.1M or NaOH 0.1M solutions. Then, 0.15 g of the carbon sample was added and the final pH measured after 48 h under agitation at room temperature. Blank experiments (without addition of support) were also prepared for each pH, and the values measured after 48h correspond to $\text{pH}_{\text{initial}}$. The pH_{pzc} is the point where the curve pH_{final} vs. $\text{pH}_{\text{initial}}$ crosses the line $\text{pH}_{\text{final}} = \text{pH}_{\text{initial}}$.

2.2.2.4 Microscopy

Transmission electron microscopy (TEM) measurements were performed for the most promising catalysts in a JEOL2010F instrument, with 0.19 nm spatial resolution at Scherzer defocus conditions. High Angle Annular Dark Field – Scanning Transmission Electron Microscopy (HAADF-STEM) images were obtained with the same microscope. An electron probe with diameter of 0.5 nm at a diffraction camera length of 10 cm was used for the HAADF mode. The samples were deposited on the Cu grids coated holey-carbon for TEM analysis.

2.2.2.5 Inductively coupled plasma (ICP)

The metal loadings of the prepared catalysts were determined in duplicate by ICP, using an Iris Intrepid Spectrometer (Thermo Elemental). An Ethos 1600 microwave labstation (Milestone) was used to prepare the acid solution of all the samples for ICP analysis.

2.2.3 Catalysts evaluation

The reaction tests were performed in a 350 mL stainless steel reactor equipped with manometer, temperature sensor, magnetic stirrer and sample outlet. The oxidation reactions were carried out with oxygen under pressure up to 10 bar and at temperatures from 40 to 100 °C. NaOH solution (NaOH/glycerol molar ratio = 2) and catalyst (700 mg) were added to a 0.3 M aqueous solution of glycerol ($V = 150$ mL) under stirring at 1000 rpm. Preliminary experiments show that external mass transfer limitations were overcome at this stirring speed. After heating under nitrogen to the desired temperature, the reaction was initiated by switching from

inert gas to oxygen. The reaction was monitored by taking samples (0.5 ml) for analysis at regular time intervals.

The quantitative analysis of the reaction mixtures was carried out by high performance liquid chromatography (HPLC). The chromatograph (Elite LaChrom HITACHI) was equipped with a refractive index and an ultraviolet (210 nm) detector. Reactant and products were separated in an ion exclusion column (Alltech OA 1000). The eluent was a solution of H_2SO_4 (0.01 M). An injection volume of 20 μL , a measuring time of 15 min and a flow rate of 0.5 mL min^{-1} were selected. Products were identified by comparison with standard samples. Glycerol (> 99.5%) was purchased from Fluka and all reaction products from Sigma-Aldrich. The selectivities (S_i) (also named relative yields by other authors) into the different products i at time t were calculated as:

$$S_i = \frac{C_i / \nu \cdot C_0}{X} \times 100 \quad (2.1)$$

where C_i is the concentration of product i (mol L^{-1}), C_0 is the initial concentration of glycerol (mol L^{-1}), X is the glycerol conversion and ν corresponds to the moles of i produced per mol of glycerol consumed, according to the stoichiometry.

2.3 Results and discussion

2.3.1 Characterization of supports and catalysts

2.3.1.1 Textural properties

The textural characterization of the different supports and of the Pd/AC_0 catalyst is presented in Table 2.1. As expected, no major differences in the textural properties of the materials were observed. The slight decrease in AC_1 surface area may be due to the abundant presence of oxygen-containing groups introduced on the surface of the activated carbon by treatment with HNO_3 , which possibly block the entry of N_2 inside the small pores. After treatment at 900 $^\circ\text{C}$ (sample $\text{AC}_{1\text{tt}900}$), the mentioned functional groups were removed by thermal decomposition and the area of the corresponding support increased slightly comparatively to the original carbon [24-25].

The textural parameters of the Pd/AC_0 catalyst decreased only slightly compared to the unloaded carbon. Therefore, it was assumed that the textural properties of the

modified supports and of the supported metal catalysts are not significantly different from those of the original activated carbon.

Table 2.1 Textural properties and pH_{pzc} of original and modified activated carbons.

Sample	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	S_{meso} ($\text{m}^2 \text{g}^{-1}$)	V_{micro} ($\text{cm}^3 \text{g}^{-1}$)	pH_{pzc}
AC_0	1025	180	0.361	7.9
AC_1	965	156	0.369	3.2
$\text{AC}_{1\text{tt}400}$	952	200	0.350	n.d.
$\text{AC}_{1\text{tt}600}$	1042	150	0.391	n.d.
$\text{AC}_{1\text{tt}900}$	1106	184	0.399	8.2
Pd/AC_0	887	140	0.366	n.d.

2.3.1.2 Surface chemistry characterization

The total amounts of the various surface groups (acidic carboxylic acids, carboxylic anhydrides, lactones, phenols, and carbonyls or quinones) on carbon materials can be determined from TPD spectra, since these groups are decomposed upon heating by releasing CO and/or CO_2 in different temperature ranges. Accordingly, it is possible to identify the oxygenated groups on the surface of a given material by TPD experiments. It was reported that CO_2 results from the decomposition of carboxylic acids at low temperatures (150 - 450 °C) and from lactones at high temperatures (600 - 800 °C); carboxylic anhydrides originate both CO and CO_2 (400 – 650 °C); groups such as phenols (600 – 800 °C), carbonyls and quinones (750 – 1000 °C) originate CO [20-21].

Figures 2.1 a) and 2.1 b) show, respectively, the CO and CO_2 TPD spectra of the commercial activated carbon as received (AC_0) and the modified samples. An increase in the amount of surface oxygenated groups is evidenced by the increase of CO and CO_2 released. Analyzing the results, it is clear that the liquid phase oxidation with HNO_3 significantly increased the amount of CO_2 evolved at low temperatures (carboxylic acid groups) and introduced a large amount of surface oxygen, which decomposes at high temperatures by releasing CO (phenol and

carbonyl/quinone groups), originating a support with acidic and hydrophilic characteristics (sample AC₁) [26].

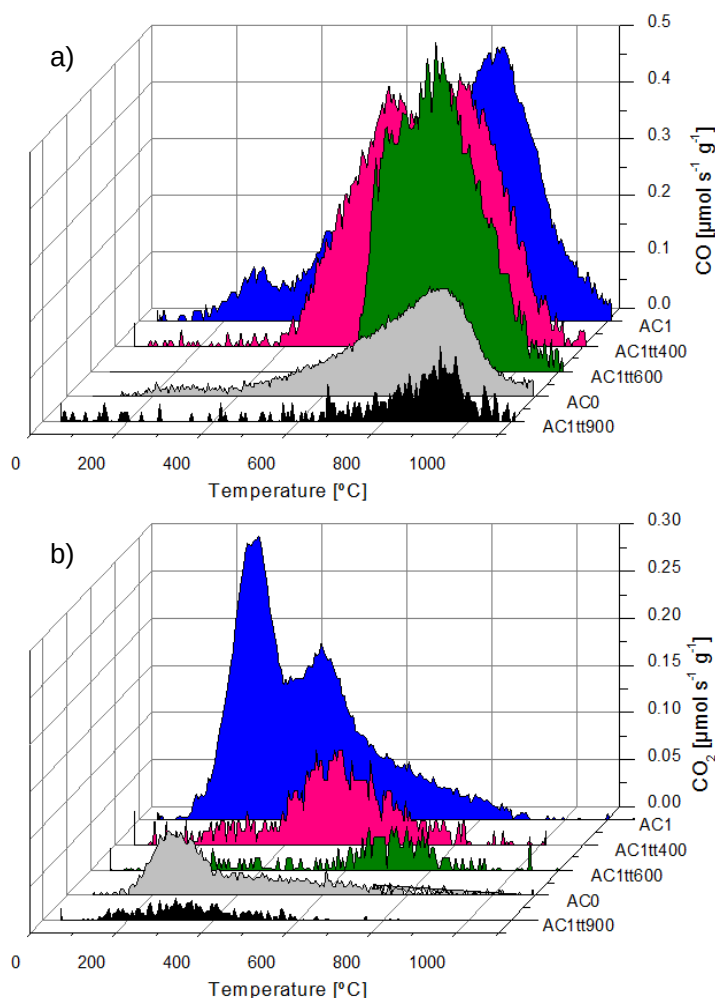


Figure 2.1 TPD spectra of the different activated carbons: a) CO; b) CO₂.

As expected, the oxidized sample AC₁ has a low pH_{pzc} (see Table 2.1), due to the introduction of the mentioned oxygen-containing functional groups with acidic properties, namely carboxylic acids. Thermal treatments selectively remove those surface groups, originating materials with progressively lower oxygen content. Practically all groups were removed from sample AC_{1tt900}, which has basic

properties [27]. According to Leon y Leon et al. [28], this basic character is mainly due to the electron rich oxygen-free sites located on the carbon basal planes.

2.3.1.3 Microscopy and ICP analyses

TEM micrographs were collected in order to get information about the metal particle size distributions (Figure 2.2). The average crystallite sizes of the studied catalysts are presented in Table 2.2. It should be noticed that the value corresponding to Ir/AC₀ was obtained by hydrogen chemisorption; details of the experimental technique used can be found elsewhere [29]. When using the incipient wetness method it was possible to obtain relatively small metal crystallite sizes for the catalysts prepared. The only exception was the gold catalyst, which required a different method for promoting a high dispersion. It is well-known [12] that sizes of gold nanoparticles mainly depend on the synthesis method used. For instance, the conventional impregnation technique (incipient wetness) results in much larger gold particles than the sol immobilization method (50 nm vs. 6.8 nm). This is in part due to the negative effect of the chloride involved in the preparation, which results in poisoning and excessive sintering of the Au particles [30]. This does not occur in the case of the other noble metals, for which the incipient wetness method allows to produce well-dispersed nanoparticles.

A large amount of oxygen-containing groups on the activated carbon surface can influence the metal dispersion. The surface oxygen groups were considered to act as anchoring sites that interact with metallic precursors [31]. However, the functional groups present on activated carbon are easily decomposed upon heating even at low temperatures. This occurs with some carboxylic acid groups, which already decompose at temperatures below 200 °C, as it can be seen in the TPD spectra (Figure 2.1, sample AC₁). When the catalysts are submitted to heat treatment and reduction processes, these oxygenated groups are thermally decomposed and the rhodium particles that were anchored to them may have low stability and could be prone to sintering. This can possibly explain why Rh/AC₁ and Rh/PTAC_{1tt600} catalysts have larger metallic particles than Rh/AC₀, Rh/AC_{1tt600} and Rh/AC_{1tt900}, because on this latter group of samples, contrarily to the former, there was no oxygenated groups that decompose at low temperatures during the preparation step.

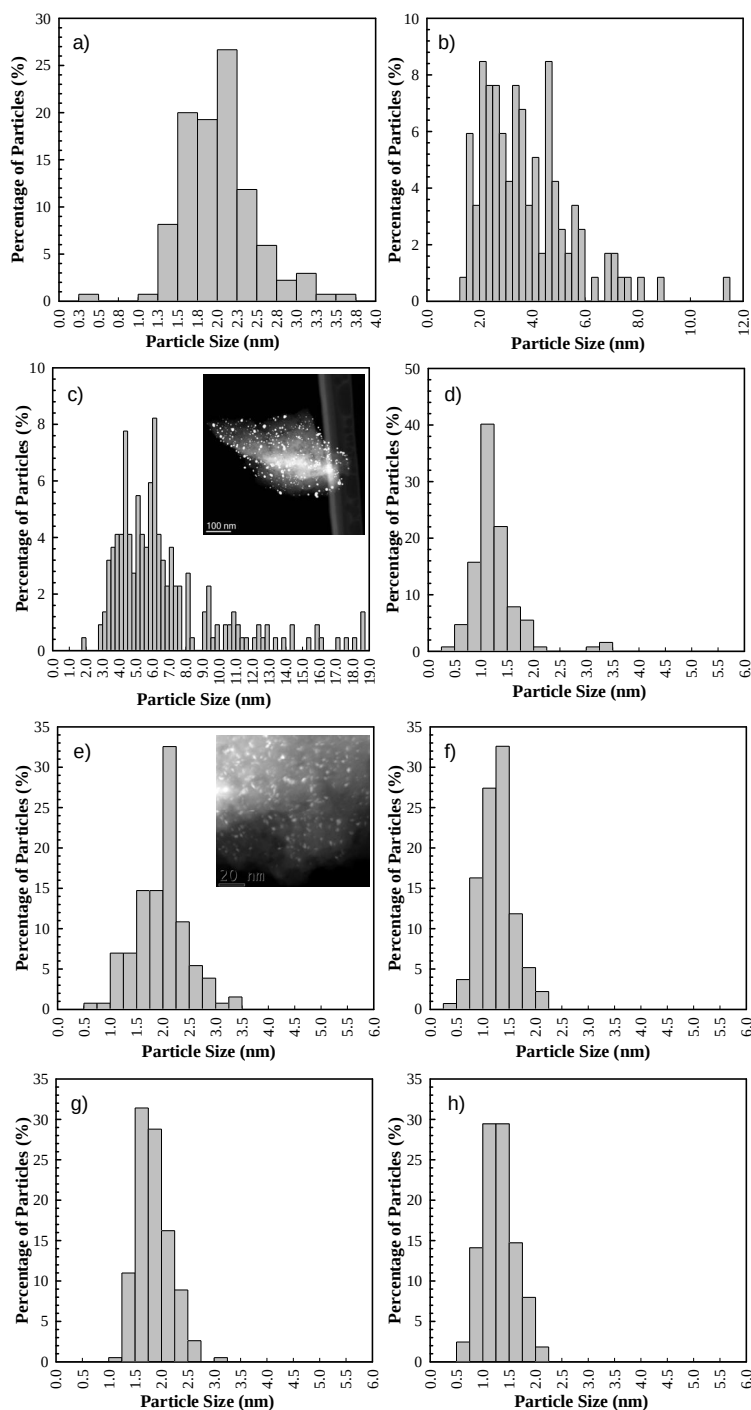


Figure 2.2 Particle sizes distribution of a) Pd/AC₀, b) Pt/AC₀, c) Au/AC₀, d) Rh/AC₀, e) Rh/AC₁, f) Rh/AC_{1tt600}, g) Rh/PTAC_{1tt600} and h) Rh/AC_{1tt900}. In some cases the HAADF-STEM images are inserted.

Table 2.2 summarizes the metal loading of some of the catalysts. Regarding to the sol immobilization method, the electrostatic interaction between the stabilized Au particles and the support play an important role during the preparation [32]. The pH of the gold sols was about 6. At this pH the zeta potential of gold sols is negative [32] while the surface charge of activated carbon is only slightly positive, considering that their pH_{pzc} is 7.9. Thus, the interaction between the support and the gold sol was relatively weak, which can explain the low loading of the Auc/AC₀ catalyst.

Chemical and heat-treatments of activated carbon did not influence substantially the metal content of rhodium catalysts.

Table 2.2 Average crystallite size and metal content of the studied catalysts.

Catalyst	Metal loading (%)	d_M (nm)
Pd/AC ₀	0.65 ± 0.03	2.0
Pt/AC ₀	0.50 ± 0.02	3.8
Ir/AC ₀	n.d.	1.7 ^a
Au/AC ₀	n.d.	50
Auc/AC ₀	0.32 ± 0.05	6.8
Rh/AC ₀	0.74 ± 0.05	1.3
Rh/AC ₁	0.74 ± 0.01	2.0
Rh/AC _{1tt600}	0.74 ± 0.01	1.3
Rh/AC _{1tt900}	0.78 ± 0.01	1.3
Rh/PTAC _{1tt600}	0.70 ± 0.03	1.8
Au/C	0.8	11

^a Obtained by hydrogen chemisorption.

2.3.2 Oxidation experiments

2.3.2.1 Catalyst evaluation

Many parameters play a role in determining the activity of catalysts in the liquid phase oxidation of glycerol. It is not easy to compare the performances of catalysts that are tested under widely different conditions, as reported in the literature. Therefore, in the first part of this work, several metals were supported on activated carbon AC₀, using the same preparation method (incipient wetness), and the same operational conditions were maintained in all catalytic tests.

The conversion of glycerol on AC₀ supported catalysts was studied as a function of time for different metals. Using typical conditions (60 °C, 3 bar, 150 mL of glycerol 0.3 M, NaOH/glycerol = 2 mol/mol, catalyst amount = 700 mg), the performances presented in Figure 2.3 were obtained, which decrease in the order: Pd > Rh >> Pt. Under the conditions tested, Ir and Au prepared by incipient wetness are not active.

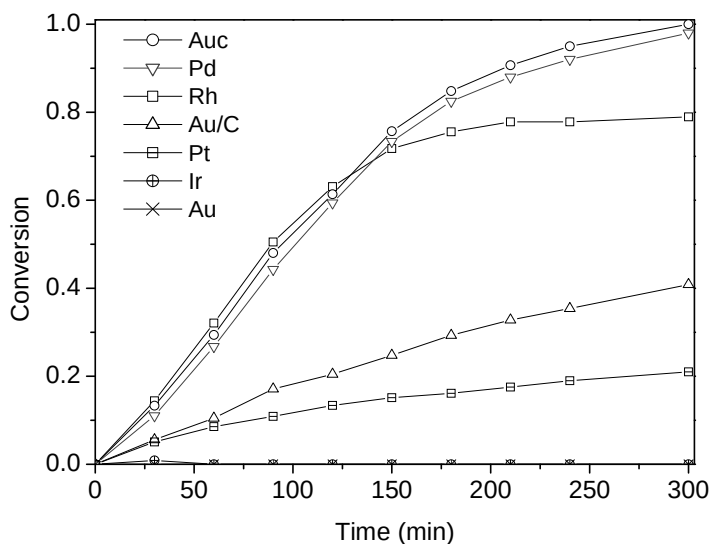


Figure 2.3 Oxidation of glycerol over noble metal catalysts supported on activated carbon AC₀. Reaction conditions: 60 °C, p_{O_2} = 3 bar, 150 mL of glycerol 0.3 M, NaOH/glycerol = 2 mol/mol, catalyst amount = 700 mg.

Even though platinum has a dispersion slightly lower than palladium and rhodium, the low performance observed is probably due to oxygen poisoning, which is directly related to the oxygen partial pressure, as mentioned in the literature [11].

This can also explain the inactivity of the iridium catalyst. However, according to Van Dam et al. [33], metals with a higher oxidation potential are less prone to oxidation. Thus, among the metals tested, platinum would be the less easily poisoned by over-oxidation, followed by iridium, palladium and rhodium, which was not verified. Actually, incipient wetness allows obtaining very active Pd and Rh catalysts in a simple, easy and quick way; these catalysts promote a high glycerol conversion even at a working pressure of 3 bar. The absence of deactivation by oxygen on various platinum-group metals due to strong metal-substrate interactions has already been reported [34]. So, the high activity obtained can possibly be attributed to the high affinity of glycerol for rhodium and palladium, which limits oxygen adsorption. This is particularly interesting, since no study concerning rhodium catalysts for glycerol oxidation has been published previously.

Contrarily to the other catalysts prepared by the incipient wetness method, the gold catalyst was the only that presented low particle dispersion. This can explain its inactivity once, as already mentioned, well-dispersed gold nanoparticles are required in order to obtain an active catalyst. Therefore, to study the influence of the preparation method on the gold catalyst performance, a sol immobilization method was applied. From TEM analysis (Table 2.2), it was concluded that this method appears to be suitable for generating small crystallite sizes supported on active carbon, originating an active catalyst as it can be observed in Figure 2.3. When comparing with the reference Au/C catalyst, Auc/AC₀ exhibits a much higher activity. In fact, after 3 h, this gold catalyst supported on activated carbon is able to reach 85% glycerol conversion, whereas only 29% is achieved with Au/C. This can be explained by the larger gold particles of the latter catalyst (11 nm vs 6.8 nm), but a support effect can also influence its performance, since these gold particles are supported on carbon black. It should be noted that the prepared Auc/AC₀ has a remarkable catalytic activity, particularly considering its low metal loading (0.32%).

The selectivities to products obtained in the presence of the different catalysts are compared in Table 2.3 at constant reaction time (3 h), since the selectivities to the main products changed only slightly during the reaction. However, for comparison purposes, Table 2.3 also shows the selectivities at the same glycerol conversion (20%). The evolution of selectivities of the main products (glyceric acid and glycolic acid) as a function of time in the presence of Rh/AC₀ can be seen in Figure 2.4.

Table 2.3 Product selectivities at $t = 3\text{ h}$ and $X = 20\%$ for glycerol oxidation over noble metal catalysts supported on activated carbon AC_0 and over the Au/C reference catalyst. Reaction conditions: $60\text{ }^\circ\text{C}$, $p_{\text{O}_2} = 3\text{ bar}$, 150 mL of glycerol 0.3 M , $\text{NaOH/glycerol} = 2\text{ mol/mol}$, catalyst amount = 700 mg .

	$t = 180\text{ min}$					$X_{\text{GLY}} = 20\%$			
	X_{GLY}	S_{GLYCEA}	S_{GLYCOA}	S_{TARTA}	S_{FORMA}	S_{GLYCEA}	S_{GLYCOA}	S_{TARTA}	S_{FORMA}
Pd	0.82	0.75	0.10	0.12	0.03	0.76	0.10	0.12	0.02
Rh	0.76	0.74	0.13	0.10	0.03	0.75	0.14	0.09	0.02
Pt	0.16	0.77	0.15	0.06	0.02	0.77	0.15	0.06	0.02
Auc	0.85	0.75	0.14	0.08	0.03	0.76	0.15	0.07	0.02
Au/C	0.29	0.64	0.25	0.02	0.09	0.66	0.26	0.01	0.07

A very similar distribution of the products was observed independently of the nature of the metal. Besides the desired product of commercial interest GLYCEA, glycolic acid (GLYCOA), tartronic acid (TARTA) and formic acid (FORMA) were also measured; oxalic acid was detected in some cases, but always with very low concentrations. The selectivity to GLYCEA is high for all the catalysts prepared (around 75% after 3h). The selectivities to GLYCOA and to TARTA are fairly similar (between 6% and 15%). The performance of the reference Au/C catalyst differs, as it seems to promote the over-oxidation of GLYCEA to GLYCOA. Accordingly, the observed selectivities to these products after 3 h are 64% and 25%, respectively.

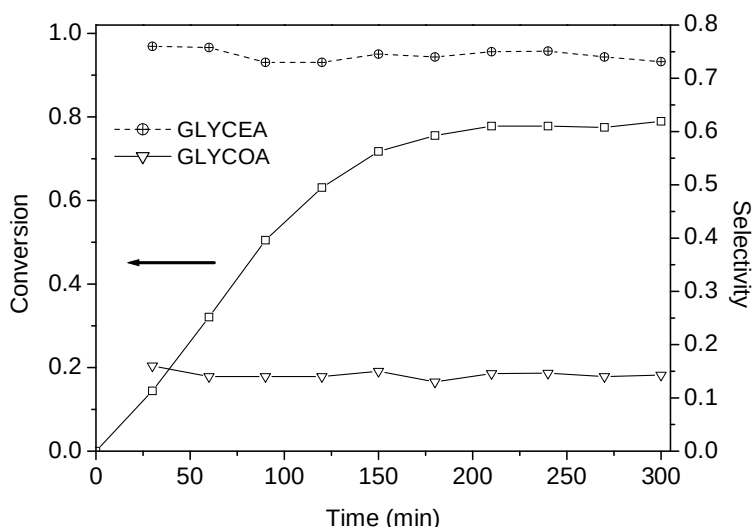


Figure 2.4 Evolution of GLYCEA and GLYCOA selectivities and glycerol conversion during the reaction in the presence of the Rh/AC₀ catalyst.

2.3.2.2 Influence of pressure and temperature

A more detailed study was carried out with the rhodium catalyst, which as far as we are aware is reported here for the first time as active in glycerol oxidation. The influence of oxygen pressure and temperature on the reaction kinetics was examined. The aim of this investigation was to establish the dependency of the reaction rate and catalyst selectivity on the oxygen pressure and reaction temperature for the Rh/AC₀ catalyst.

Experiments were carried out with 150 mL of glycerol (0.3 M), NaOH/glycerol ratio = 2 mol/mol and 700 mg of catalysts. The oxygen pressure was varied between 3 and 10 bar and the temperature between 40 and 100 °C.

Under the tested conditions, it was found that the oxygen pressure influences significantly the reaction rates of glycerol oxidation (Figure 2.5 a)). The initial reaction rate increases with the oxygen pressure but the catalyst deactivates more readily. Increasing the oxygen pressure seems to lead to a higher oxygen coverage of the surface, and thus to a premature deactivation of the rhodium catalyst due to oxygen poisoning of the surface. This metal appears to be very sensitive to the amount of oxygen dissolved in the reaction medium. This situation is similar to that described by Garcia et al. [11] for Pt catalysts.

Selectivity to FORMA is slightly increased with the increase of oxygen pressure while selectivity to GLYCOA decreases (Table 2.4).

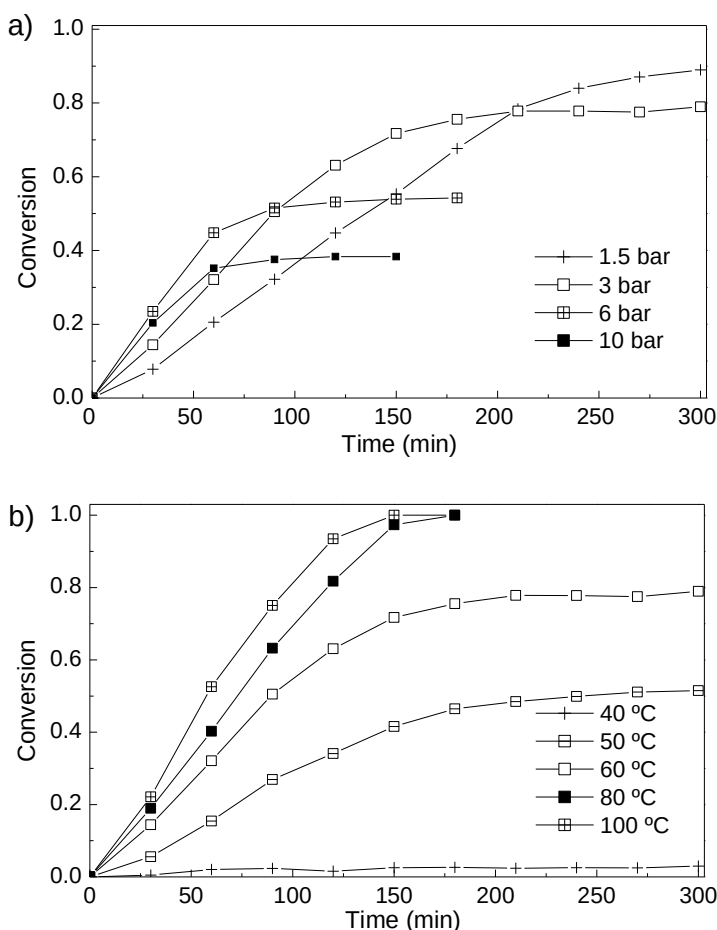


Figure 2.5 Dependency of glycerol conversion on the oxygen pressure at 60 °C (a) and on reaction temperature at $p_{O_2} = 3$ bar (b) with Rh/AC₀. Other reaction conditions: 150 mL of glycerol 0.3 M, NaOH/glycerol = 2 mol/mol, catalyst amount = 700 mg.

The temperature increase leads to an increase of catalytic activity in the system studied (Figures 2.5 b)), but seems to be very detrimental to the selectivity of the interesting product, glyceric acid, which oxidizes very easily to glycolic acid and further to oxalic acid at high temperatures (Table 2.4). Once again, the results obtained at 40 °C and 50 °C show that rhodium suffers deactivation resulting from

the high level of oxygen present in the reaction medium at these temperatures. It is a common assumption that the mechanism of glycerol oxidation involves an oxidative dehydrogenation step. The last step is the elimination of hydrogen by reaction with dissociatively adsorbed oxygen [35]. Therefore, an increase of the oxygen coverage on the metal surface progressively eliminates glycerol adsorption. Over-oxidation leads to a loss of activity due to the transformation of metal M to M^{n+} , the conversion reaching a plateau (Figures 2.5 a) and 2.5 b)). However, this deactivation can be eliminated by decreasing the rate of oxygen supply (e.g. by working at higher temperatures [16], as can be seen in Figure 2.5 b)).

Table 2.4 GLYCEA, GLYCOA, TARTA and FORMA selectivities (S_{GLYCEA} , S_{GLYCOA} , S_{TARTA} , S_{FORMA}) at different oxygen pressures and temperatures, for 50% glycerol conversions (X_{GLY}) and after 2 h of reaction in the presence of the Rh/AC₀ catalyst.

	t = 120 min					$X_{\text{GLY}} = 50\%$			
	X_{GLY}	S_{GLYCEA}	S_{GLYCOA}	S_{TARTA}	S_{FORMA}	S_{GLYCEA}	S_{GLYCOA}	S_{TARTA}	S_{FORMA}
Rh/AC₀									
1.5 bar ^a	0.45	0.70	0.19	0.09	0.02	0.70	0.19	0.09	0.02
3 bar ^a	0.63	0.73	0.14	0.10	0.03	0.73	0.14	0.10	0.03
6 bar ^a	0.53	0.74	0.11	0.11	0.04	0.74	0.11	0.11	0.04
10 bar ^a	0.38	0.71	0.13	0.11	0.04	-	-	-	-
50 °C ^b	0.34	0.70	0.16	0.10	0.04	0.72	0.13	0.11	0.04
60 °C ^b	0.63	0.73	0.14	0.10	0.03	0.73	0.14	0.10	0.03
80 °C ^b	0.82	0.55	0.22	0.12	0.06	0.58	0.25	0.11	0.06
100 °C ^b	0.93	0.41	0.29	0.10	0.06	0.41	0.31	0.07	0.07

^a Reaction conditions: 60 °C, 150 mL of glycerol 0.3 M, NaOH/glycerol = 2 mol/mol, catalyst amount = 700 mg.

^b Reaction conditions: $p_{\text{O}_2} = 3$ bar, 150 mL of glycerol 0.3 M, NaOH/glycerol = 2 mol/mol, catalyst amount = 700 mg.

In some cases, the sum of the calculated selectivities in Table 2.4 is lower than 1, since some oxalic acid was also detected. It is important to notice that in the experiment with the Rh/AC₀ catalyst at 100 °C, even after accounting for the oxalic acid formed (selectivity = 0.05), the sum of selectivities is still lower than 1. As no additional product was detected by HPLC, we supposed that, in this particular case, some complete oxidation of the partial oxidation products to CO₂ occurs. The formation of CO₂ as a by-product in the glycerol oxidation was also observed by Carrettin et al.[9].

It can be concluded that, for rhodium catalyst, a compromise between activity and selectivity has to be achieved using suitable temperature and oxygen pressure in order to avoid problems of over-oxidation.

2.3.2.3 Investigation of the support effects in the glycerol oxidation

The surface oxygenated functional groups of activated carbon can be controlled by chemical and heat treatments, and can change the catalytic properties. Figure 2.6 reveals a strong influence of the surface chemical properties of the support on the catalytic performance in glycerol oxidation. It was observed by ICP analysis that the metal loading did not change significantly from support to support. As the textural properties of the support also do not differ substantially, the metal particle sizes were analyzed by TEM to establish differences in metal dispersion (Figure 2.2 and Table 2.2). Rh/AC₀, Rh/AC_{1tt600} and Rh/AC_{1tt900} catalysts have similar crystallite sizes, which are on average smaller than those of Rh/AC₁ and Rh/PTAC_{1tt600}. The differences of metal dispersions in these activated carbon supported rhodium catalysts are mainly related to the oxygen-containing groups anchored on the surface of the support, as already mentioned (see section 2.3.1.3). However, even though Rh/AC₀, Rh/AC_{1tt600} and Rh/AC_{1tt900} catalysts have similar particles sizes, rhodium particles supported on AC₀ exhibit a much higher activity.

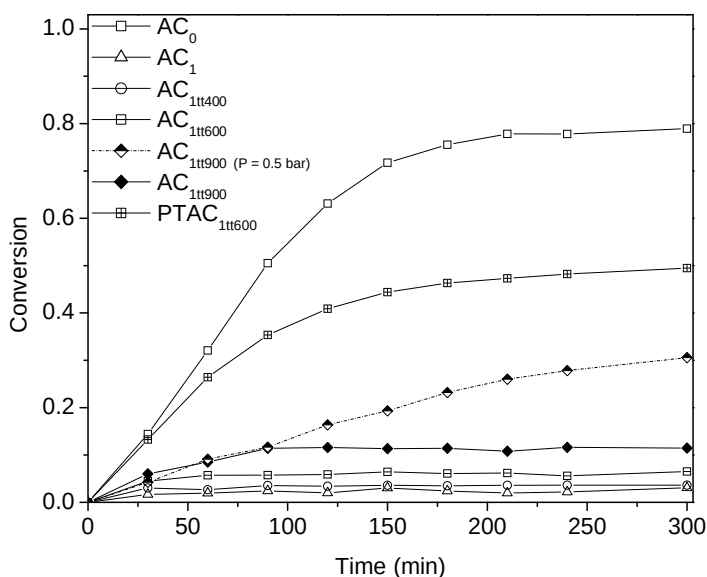


Figure 2.6 Influence of modified activated carbon supports on the activity of rhodium catalysts. Reaction conditions: 60 °C, $p_{O_2} = 3$ bar, 150 mL of glycerol 0.3 M, NaOH/glycerol = 2 mol/mol, catalyst amount = 700 mg.

The histograms of the rhodium particle size distribution for AC_0 , AC_{1tt600} and AC_{1tt900} supported catalysts are shown in Figure 2.2 d), f) and h), respectively. It can be seen that the distribution of rhodium particle diameters in the Rh/AC_0 catalyst is less homogeneous than those of Rh/AC_{1tt600} or Rh/AC_{1tt900} . Although most particles have about 1.0 - 1.5 nm, there are a few particles larger than 2.25 nm that are not present in the other two catalysts. Then, it seems that the deactivation of the Rh/AC_{1tt600} and Rh/AC_{1tt900} catalyst can be explained by over-oxidation, since small metal nanoparticles (< 2 nm) deactivate more readily because of their stronger affinity to oxygen [35]. In fact, in section 2.3.2.2., it was already observed that rhodium is very sensitive to oxygen. Moreover, an experiment carried out with Rh/AC_{1tt900} shows that over-oxidation can be delayed when working at an oxygen pressure of 0.5 bar (see Figure 2.6), which confirms that the deactivation observed is due to oxygen poisoning; however, as expected, the initial reaction rate is much lower. In conclusion, the obtained results suggest that rhodium supported on activated carbon seems to be a suitable catalyst for glycerol oxidation provided that its particles are large enough to avoid over-oxidation. Nevertheless, when considering the Rh/AC_1 catalyst, which has a significant fraction of particles larger than 2 nm, only a residual activity is observed. This indicates that surface acid

groups are prejudicial for rhodium catalyst activity. Indeed, when a similar catalyst is prepared and post-heat-treated at 600 °C (instead of 200 °C) before reduction, the more acidic groups are eliminated, and activity increases dramatically, although the average particle size remains approximately the same. This catalyst (Rh/PTAC_{1tt600}) does not have carboxylic acid or carboxylic anhydride groups. Additionally, a Rh/PTAC_{1tt400} catalyst (heat-treated at 400 °C) was prepared in order to remove only carboxylic acids from the surface, but no enhancement of the activity was observed when compared with Rh/AC₁ (data not shown). So, not only carboxylic acid groups (released by thermal treatment up to 400 °C) but also the carboxylic anhydrides (released between 400 and 600 °C) appear to lead to almost inactive catalysts.

Two different deactivation procedures were distinguished: over-oxidation (oxygen poisoning) and the presence of a large amount of surface oxygenated acidic groups. Therefore, rhodium catalysts appear to be suitable for glycerol oxidation, provided that their crystallites are not too small and the support has neutral or basic properties. These two parameters can easily be controlled by thermal treatments.

In terms of selectivity, the presence of oxygenated surface groups on Rh/PTAC_{1tt600} leads to similar selectivities to GLYCOA and GLYCEA when compared with the Rh/AC₀ catalyst (0.15 vs. 0.14 at X = 50% and 0.70 vs. 0.73 at X = 50%, respectively).

The presence of surface groups may cause differences in adsorption performance [36], i.e. the functional groups located near the metal particles can influence glycerol adsorption. The AC₁ support has the largest amount of surface groups, so the Rh/AC₁ catalyst has the most hydrophilic character, and consequently the highest affinity for the aqueous phase. This functionalized carbon surface facilitates adsorption of glycerol from water. So, glycerol may adsorb preferentially on the support and/or functional groups can impede the access of the glycerol molecule to the metal. However, the Rh/PTAC_{1tt600} catalyst shows an increase of activity, in spite of the relatively high content of oxygenated groups on the surface (despite its less acidic nature). Moreover, a study carried out on AC₀, without any additional treatment, allowed to conclude that glycerol also adsorbs on this support, and its adsorption is well-represented by the Langmuir isotherm [37]. Then, the adsorption of glycerol on the support does not seem to explain, at least completely, the largely different activities.

Basic carbons are characterized by a high content of electron rich sites on their basal planes and a low concentration of electron withdrawing groups; the presence of oxygen-containing functional groups with electron-withdrawing properties has a negative effect on the adsorption of anionic species [28]. So, assuming that the glycerol oxidation mechanism on rhodium involves the spillover of activated oxygen from the metal to the support, Rh/AC₁ is the catalyst with the lower capacity to accept these species. Therefore, Rh/AC₁ cannot store oxygen, as the support is already oxygenated, and the reaction will stop; on the contrary, Rh/PTAC_{1tt600} has some oxygen-free carbon sites, which could provide for an enhancement of activity.

Although it is assumed that alcohol oxidations on metal surfaces proceed via a dehydrogenation mechanism, the precise reaction pathway is still not clear, which further complicates the interpretation of these results. Nevertheless, these experiments clearly demonstrate that the support surface chemistry is a key-factor in the catalytic oxidation of glycerol, at least when using rhodium catalysts.

2.4 Conclusions

Under the same reactions conditions and for the same support (activated carbon) and preparation method (incipient wetness), the catalytic performance in the selective oxidation of glycerol decreases in the order: Pd > Rh >> Pt; on the other hand, Ir and Au are not active. Contrarily to the other catalysts prepared by the conventional method, the gold catalyst presented low particle dispersion. This can explain its inactivity once well-dispersed gold nanoparticles are required in order to obtain an active catalyst. This can be achieved by using a sol immobilisation method of preparation. Palladium and rhodium showed high activities, whereas platinum was rapidly deactivated due to oxygen poisoning. The rhodium catalyst, as far as we know reported for the first time in the present work as active for the reaction, was found to be very promising, namely taking into account its simple preparation method. Additionally, the influence of the surface chemical properties of the support on the activity of this catalyst was clearly demonstrated, being concluded that the presence of acid groups are prejudicial. Particularly, carboxylic acids and anhydrides appear to be the most detrimental groups. The prepared catalysts lead to a high total selectivity to glyceric acid (about 75%).

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Chapter 3

3 Influence of activated carbon surface chemistry on the activity of Au/AC catalysts in glycerol oxidation

The main goal of this work is the study of the relationship between the surface chemical characteristics of activated carbon and the performance of the respective gold supported catalysts in the oxidation of glycerol. For that purpose, a set of modified activated carbons with different levels of oxygenated functional groups on the surface, but with no major differences in their textural parameters, was prepared. A strong effect of the activated carbon surface chemistry on the catalytic activity was observed. Gold particles with similar average sizes resulted in different performances, being the surface oxygenated acid groups particularly prejudicial for the catalytic activity. Basic oxygen-free supports characterized by a high density of free π -electrons lead to more active catalysts, which was tentatively explained on the basis of a recent proposed mechanism by considering the capability to promote electron mobility. However, the presence of oxygenated groups on the support does not influence significantly the selectivities.

3.1 Introduction

Over the last decades, biodiesel has emerged as a viable clean fuel. During its production via transesterification of oils from plants, about 100 kg of glycerol is produced for every ton of biodiesel [1]. During the last years this market has been continuously increasing, and it is expected that this trend remains [1]. The rapid expansion of the global production of biodiesel has created a major surplus of glycerol, leading to a decline in glycerine pricing. Consumption of this extra glycerol is a necessary requisite for the commercial viability of biodiesel production. Liquid phase catalytic oxidation is a promising route to the valorisation of glycerol by its conversion into useful compounds, provided that catalysts used are sufficiently active and selective for the formation of compounds such as glyceric acid (GLYCEA) and/or dihydroxyacetone (DIHA), potentially useful as chemical intermediates in the fine chemicals industry, particularly in pharmaceuticals [1-2]. However, the extensive functionalization of the glycerol molecule, with similar reactive hydroxyl groups, renders its selective oxidation particularly difficult [3-4].

Recently, there have been many studies dealing with the oxidation of glycerol to chemical intermediates using supported gold nanoparticles as catalysts [5-7]. One of the advantages of using this metal is related with its strong resistance to oxygen poisoning, compared to platinum-based catalysts, allowing for the use of high oxygen partial pressures [8]. However, under alkaline conditions, catalyst performance and selectivity seem to mainly depend on the nanoparticles size, which in turn can be controlled by the preparation method [9-10]. Generally, small nanoparticles (5 nm) were found to be more active than larger particles (20 nm) [11]. Apparently, the gold-sol immobilisation method is the most appropriate technique in order to obtain these well dispersed nanoparticles on carbons [9, 12]. In addition to the particles size, the activity of gold catalysts seems to be affected by the nature of support. Nano-sized gold particles supported on different carbon materials (e.g. carbon black, activated carbon and graphite) and oxides (TiO_2 , MgO and Al_2O_3) are active for the oxidation of glycerol but show very different performances, being carbon supported gold catalysts more active than most oxides supported catalysts [5, 8, 13]. However, even when different carbon materials are compared, textural and chemical properties could largely differ, which make the role of the support complex to understand. Moreover, in spite of its well known influence on the catalyst activity, the role of the support in the mechanism of glycerol oxidation is still not clear.

In this study, a NORIT ROX 0.8 activated carbon was modified by chemical and thermal treatments in order to obtain supports with different surface chemical properties, but with no major differences in their textural parameters. The sol immobilisation method was used for preparing gold catalysts supported on the different activated carbon samples. Then, the performance of the prepared catalysts was investigated and the possible role of the support surface chemistry in the reaction mechanism was discussed.

3.2 Experimental

3.2.1 Materials and methods

3.2.1.1 Materials

The gold precursor, $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (99.99% ACS, Au 49.5% min), was supplied by Alfa Aesar. NaBH_4 of purity > 95% from Riedel-deHaël, NaOH (> 97%) and polyvinylalcohol (PVA) (purity > 99%) from Aldrich were used. The commercial activated carbon NORIT ROX 0.8 was selected as starting material for the preparation of supports.

3.2.1.2 Preparation procedures

The NORIT ROX 0.8 activated carbon has a small amount of surface oxygenated groups. In order to evaluate how catalyst activity correlates with the concentration of those groups, the original support was modified by chemical and thermal treatments in order to obtain supports with different surface chemical properties. Gold was supported on these modified activated carbon materials by the sol immobilisation method.

3.2.1.2.1 Preparation of modified activated carbons

A NORIT ROX 0.8 activated carbon (pellets of 0.8 mm diameter and 5 mm length) was used as starting material for this study (sample AC_0). This sample was submitted to different chemical and thermal treatments in order to obtain materials with different surface chemistries, while maintaining the original textural properties as far as possible.

Oxidation treatment: Initially, HNO_3 6 M was introduced into a round-bottom flask. A Soxhlet extraction apparatus with activated carbon AC_0 was connected to the flask and to a condenser. The acid solution was heated to boiling temperature and the reflux was stopped after 3 h. The oxidized material was subsequently washed with distilled water until neutral pH, and then dried at 110 °C for 24 h (sample AC_1). The purpose of this liquid phase oxidation is to increase the amount of oxygen-containing surface groups on the support.

Thermal treatments: Sample AC_1 was used as the starting material for the thermal treatments since it is important that the starting material presents a large amount of surface groups in order to produce activated carbons with a highly basic character [14]. Support AC_1 was treated under nitrogen flow for 30 min at different temperatures (400, 600 or 900 °C) followed by a treatment under dry air flow at room temperature for 1 h. Therefore, the following samples are respectively prepared: $\text{AC}_{1\text{tt}400}$, $\text{AC}_{1\text{tt}600}$, $\text{AC}_{1\text{tt}900}$. The same procedure was repeated but under a flow of hydrogen at 900 °C (sample $\text{AC}_{1\text{tt}900-\text{H}_2}$).

These thermal treatments selectively remove the oxygen-containing surface groups, previously introduced in the treatment with HNO_3 , by thermal degradation [15-16]. The final treatment under air is intended to stabilize the surface chemistry of the samples. Besides, thermal treatments under H_2 flow are expected to generate higher basicity on the surface of the carbon than thermal treatments under N_2 flow [17].

After these treatments, all samples were ground to a particle diameter between 0.1 and 0.3 mm before use.

3.2.1.2.2 Preparation of catalysts

Gold on carbon catalysts were prepared by the sol immobilisation method with NaBH_4 as reducing agent [18]. Briefly, $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (35.1 mg) was dissolved in 690 ml of H_2O and polyvinyl alcohol was added (1.6 ml, 0.2 %wt) under stirring. The gold colloid was subsequently reduced by the addition of NaBH_4 (4 ml, 0.1 M) under vigorous magnetic stirring. The resulting ruby-red sol was formed immediately. Within a few minutes of sol generation, the colloid was immobilised by adding the support under vigorous stirring. The amount of support was calculated to reach a final nominal metal loading of 1 wt%. After 3-4 days, the colourless solution was filtered, the catalyst washed thoroughly with distilled water until the filtrate was free of chloride (AgNO_3 test) and dried at 110 °C for 24 h. After heat treatment under N_2

flow for 3 h at 350 °C, in order to remove any possible organic waste, the catalysts were activated by reduction in a stream of H₂ flow for 3 h at 350 °C.

3.2.2 Characterization

The supports were characterized by N₂ adsorption at -196 °C in a NOVA Quantachrome Instruments apparatus.

The qualitative and quantitative determination of oxygenated surface functional groups was performed by temperature programmed desorption - mass spectrometry (TPD-MS) [15-16]. CO and CO₂ TPD spectra were obtained with a fully automated AMI-200 equipment (Altamira Instruments). The samples (150 mg) were placed in a U-shaped quartz tube inside an electrical furnace and subjected to a 5 °C min⁻¹ linear temperature increase up to 1100 °C under helium flow (25 Ncm³ min⁻¹). A quadrupole mass spectrometer (Dymaxion 200, Ametek) was used to monitor CO and CO₂ signals. For quantification of the CO and CO₂ released, calibration of these gases was carried out at the end of each analysis.

In some cases the determination of the pH at the point of zero charge (pH_{pzc}) was also carried out.

The average metal particles size was determined by high-resolution transmission electron microscopy (HRTEM) using a JEOL2010F instrument, with 0.19 nm spatial resolution at Scherzer defocus conditions. High Angel Annular Dark Field – Scanning Transmission Electron Microscopy (HAADF-STEM) images were obtained with the same microscope. The average diameter was calculated by the measurement of at least 200 particles.

The noble metal loading of the samples was determined by inductively coupled plasma (ICP) analysis using an Iris Intrepid Spectrometer (Thermo Elemental). An Ethos 1600 microwave labstation (Milestone) was used to prepare the acid solution of all the samples for ICP analysis.

Details of these characterization methods are described elsewhere [19] (see Chapter 2).

3.2.3 Catalysts evaluation

The standard oxidation experiments were carried out with oxygen under 3 bar, at 60 °C. NaOH solution (NaOH/glycerol molar ratio = 2) and catalyst (700 mg) were

added to a 0.3 M aqueous solution of glycerol ($V = 150$ mL) under stirring at 1000 rpm. Additionally, a limited number of runs were carried out at different oxygen pressures (6, 10 bar) or temperatures (40, 80 °C). After heating under nitrogen to the selected temperature, the reaction was initiated by switching from inert gas to oxygen.

The reaction was monitored by taking samples (0.5 mL) for analysis at regular time intervals. The quantitative analysis of mixtures was carried out by high performance liquid chromatography (HPLC). The chromatograph (Elite LaChrom HITACHI) was equipped with a refractive index and an ultraviolet (210 nm) detector. Reactant and products were separated in an ion exclusion column (Alltech OA 1000). Products were identified by comparison with standard samples. Glycerol (> 99.5%) was purchased from Fluka, glyceric acid (GLYCEA), and the by-products glycolic acid (GLYCOA), glyceraldehyde (GLYCER), tartronic acid (TARTA), oxalic acid (OXALA) and formic acid (FORMA) were obtained from Sigma-Aldrich. Further details can be found elsewhere [19] (see Chapter 2). The selectivities (S_i) into the different products i at time t were calculated as:

$$S_i = \frac{C_i}{\nu_i \cdot C_0 \cdot X} \quad (3.1)$$

where C_i is the concentration of product i (mol L^{-1}), C_0 is the initial concentration of glycerol (mol L^{-1}), X is the glycerol conversion and ν_i corresponds to the moles of i produced per mol of glycerol consumed, according to the stoichiometry.

3.3 Results and discussion

3.3.1 Characterization of supports and catalysts

The main goal of the present work is to study the relationship between the surface chemical characteristics of activated carbons and the catalytic performance of gold supported on these materials for glycerol oxidation. For that purpose, a set of modified activated carbons with different levels of acidity/basicity was prepared. Both liquid phase oxidations and thermal treatments have been reported not to significantly change the textural properties of activated carbons [15-16].

3.3.1.1 Textural properties

The textural characterization of the different supports and the Au/AC₀ catalyst is presented in Table 3.1. As expected, no drastic changes in the textural properties of the materials were observed. The slight decrease in AC₁ surface area may be due to the abundant presence of oxygen-containing groups introduced on the surface of the activated carbon by the treatment with HNO₃, which possibly block the entry of N₂ inside the small pores, as reported by Yin et al. [20]. After treatment at 900 °C, the mentioned functional groups were removed by thermal decomposition and the area of the corresponding support slightly increased comparatively to the original carbon [21].

The BET surface area of the Au/AC₀ catalyst decreased only slightly compared to the unloaded carbon. Therefore, it was assumed that the textural properties of modified supports and supported gold catalysts are not significantly different from those of the original activated carbon.

Table 3.1 Textural properties and pH_{Hzc} of activated carbons and the Au/AC₀ catalyst.

Sample	S _{BET} (m ² /g)	S _{meso} (m ² /g)	V _{micro} (cm ³ /g)	pH _{Hzc}
AC ₀	1025	180	0.361	7.9
AC ₁	965	156	0.369	3.2
AC _{1tt400}	952	200	0.350	-
AC _{1tt600}	1042	150	0.391	-
AC _{1tt900}	1106	184	0.399	8.2
AC _{1tt900-H2}	1062	193	0.359	9.0
Au/AC ₀	958	195	0.343	-

3.3.1.2 Surface chemistry characterization

TPD is a thermal analysis method that is becoming popular for the characterization of the oxygen-containing groups on the surface of carbon materials. In this technique, the total amount of the various oxygenated surface groups (carboxylic acids, carboxylic anhydrides, lactones, phenols, and carbonyls or quinones) on

carbon materials can be determined, since these groups are decomposed upon heating by releasing CO and/or CO₂ at different temperature ranges. Accordingly, it is possible to identify and estimate the amount of the oxygenated groups on a given material by TPD experiments. The nature of the groups can be assessed by the decomposition temperature and the type of gas released, and their respective amounts determined by the areas of the component peaks, obtained by deconvolution techniques [15-16]. It was reported that CO₂ results from the decomposition of carboxylic acids at low temperatures (150 - 450 °C) or from lactones at high temperatures (600 - 800 °C); carboxylic anhydrides originate both CO and CO₂ (400 – 650 °C); groups such as phenols (600 – 800 °C), and carbonyls and quinones (750 – 1000 °C) originate CO [15-16]. Consequently, an increase in the amount of surface oxygen is evidenced by the increase of CO and CO₂ released.

Figures 3.1 a) and 3.1 b) show, respectively, the CO and CO₂ TPD spectra of the commercial activated carbon as received (AC₀) and the modified samples. The deconvolution of these CO and CO₂ spectra was carried out in order to determine the amount of each surface group. A multiple Gaussian function was used for fitting each spectrum. The numerical calculations were based on a non-linear routine, which minimized the sum of squared deviations, using the Levenberg-Marquardt method to perform the iterations and some assumptions according to [15-16] (details can be seen in Appendix C). Table 3.2 shows the results obtained.

Analysing the results, it is clear that the sample AC₁, which was oxidised with HNO₃, has the highest amount of oxygen-containing surface groups. The liquid phase oxidation significantly increased the amount of CO₂ evolved at low temperatures (carboxylic acid groups) and CO at high temperatures (phenol and carbonyl/quinone groups). As a result, the oxidised sample AC₁ has a low pH_{pzc} (see Table 3.1) due to the introduction of the mentioned oxygen-containing functional groups with acidic properties, namely carboxylic acids (see Table 3.2), originating a support with acidic and hydrophilic characteristics [22].

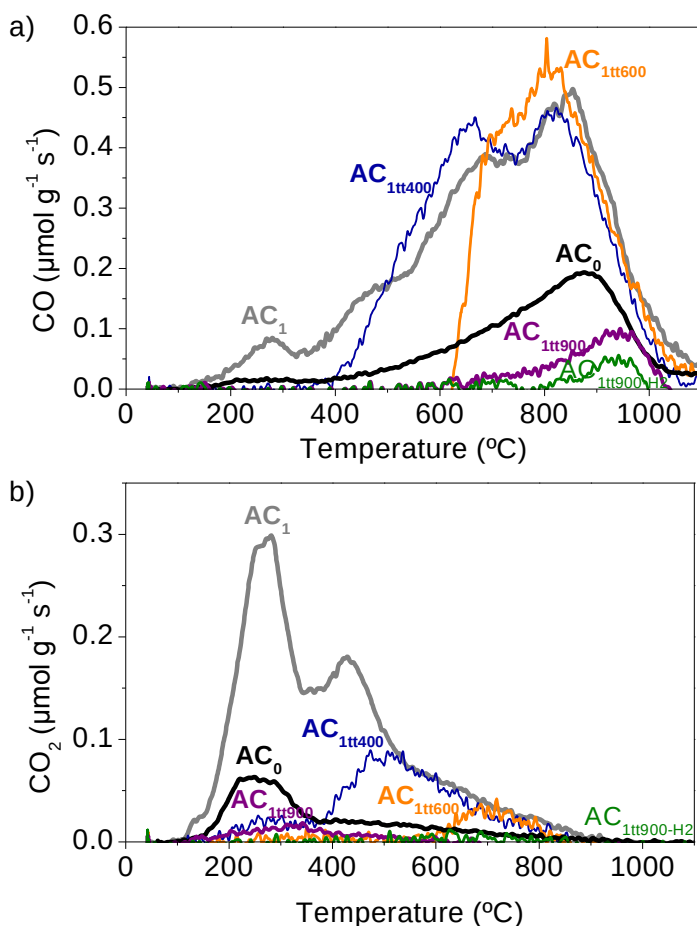


Figure 3.1 TPD spectra of the different activated carbons: a) CO; b) CO_2 .

Thermal treatments selectively remove the oxygen-containing surface groups, originating materials with progressively lower oxygen contents (see Figure 3.1 and Table 3.2). It can also be observed in Table 3.2 that the amount of carboxylic acids and anhydrides considerably decreases for thermal treatments above 400 $^{\circ}\text{C}$; on the other hand, phenols and carbonyl/quinones only decrease significantly after heat-treatment above 600 $^{\circ}\text{C}$. As can be seen in the TPD spectra of samples $\text{AC}_{1\text{tt}900}$ and $\text{AC}_{1\text{tt}900-\text{H}_2}$, the CO_2 and CO releasing groups have almost completely been removed; these samples have basic properties [17]. According to Leon y Leon et al. [23], this basic character is mainly due to the electron rich oxygen-free sites located on the carbon basal planes. It was also reported that heat treatments under hydrogen flow at high temperatures are more effective in removing oxygen than

under inert atmosphere, once they originate stable basic surfaces by forming stable C-H bonds, whereas the activated carbon heat-treated under nitrogen has a surface with reactive sites capable of readsorbing oxygen, leading to the formation of some of the previously removed groups, as it can be observed in Table 3.2 [17]. This is in agreement with our TPD data, since sample AC_{1tt900} shows a higher content of CO₂ releasing groups than sample AC_{1tt900-H2} (see Figure 3.1 and Table 3.2). As expected, sample AC_{1tt900-H2} has the highest pH_{pzc} value (see Table 3.1) and corresponds to the most basic material.

Table 3.2 Amounts of the different oxygenated surface groups present on activated carbon supports (obtained by deconvolution of CO₂ and CO spectra) and total amounts of CO, CO₂ and oxygen released.

Sample	Carboxylic acids ($\mu\text{mol g}^{-1}$)	Carboxylic anhydrides ($\mu\text{mol g}^{-1}$)	Lactones ($\mu\text{mol g}^{-1}$)	Phenols ($\mu\text{mol g}^{-1}$)	Carbonyl / Quinones ($\mu\text{mol g}^{-1}$)	CO ($\mu\text{mol g}^{-1}$)	CO ₂ ($\mu\text{mol g}^{-1}$)	O ($\mu\text{mol g}^{-1}$)
AC ₀	134	37	18	191	500	776 ^a	189	1154
AC ₁	608	239	82	788	1209	2414 ^a	929	4272
AC _{1It400}	48	233	75	895	1082	2210	356	2922
AC _{1It600}	44	27	101	658	1080	1765	172	2109
AC _{1It900}	84	31	12	71	170	272	127	526
AC _{1It900-H2}	0	0	0	26	70	96	0	96

^a The total amount of CO is slightly higher than the sum of the groups that decompose releasing CO. The justification can be found elsewhere [16].

3.3.1.3 Microscopy and ICP analyses

HAADF-STEM images were collected in order to get information about metal particle size distributions (Figure 3.2). The average crystallite sizes of the studied catalysts are presented in Table 3.3. For oxidation catalysis by gold, it has been shown that the average particle size influences both activities and selectivities [9, 24]. Although small gold particle sizes (< 5 nm) have a higher activity, catalysts with gold crystallites as large as 42 nm have already shown a relevant activity in glycerol oxidation [24]. Carrettin et al. [25] reported that active catalytic sites have a broad size distribution between 15 and 30 nm diameter for gold nanoparticles supported on carbon, the 15 nm size being predominant.

Nevertheless, in the present work, gold catalysts prepared by the sol immobilisation method have particles with sizes lower than 15 nm, and therefore these catalysts are expected to be highly active. The same impregnation procedure was used in order to obtain gold catalysts with similar particle sizes, independently of the support used. This was effectively achieved for Au/AC₀, Au/AC_{1tt400}, Au/AC_{1tt600}, Au/AC_{1tt900} and Au/AC_{1tt900-H2}, which have fairly low and similar average gold particle sizes, suggesting that the difference in the performance of these catalysts will be mainly due to the different chemical surface properties of the supports.

Table 3.3 Average crystallite size and metal content of the studied catalysts.

Catalyst	Loading (%wt) ^a	d_M (nm)
Au/AC ₀	0.59	6.8
Au/AC ₁	0.62	12.5
Au/AC _{1tt400}	0.60	4.4
Au/AC _{1tt600}	0.56	5.8
Au/AC _{1tt900}	0.57	6.4
Au/AC _{1tt900-H2}	0.66	5.0
Au/AC ₀ (after 2 run)	0.62	8.3
Au/AC ₀ (after 4 run)	0.56	11.4

^a Obtained by ICP analysis after combustion of activated carbon.

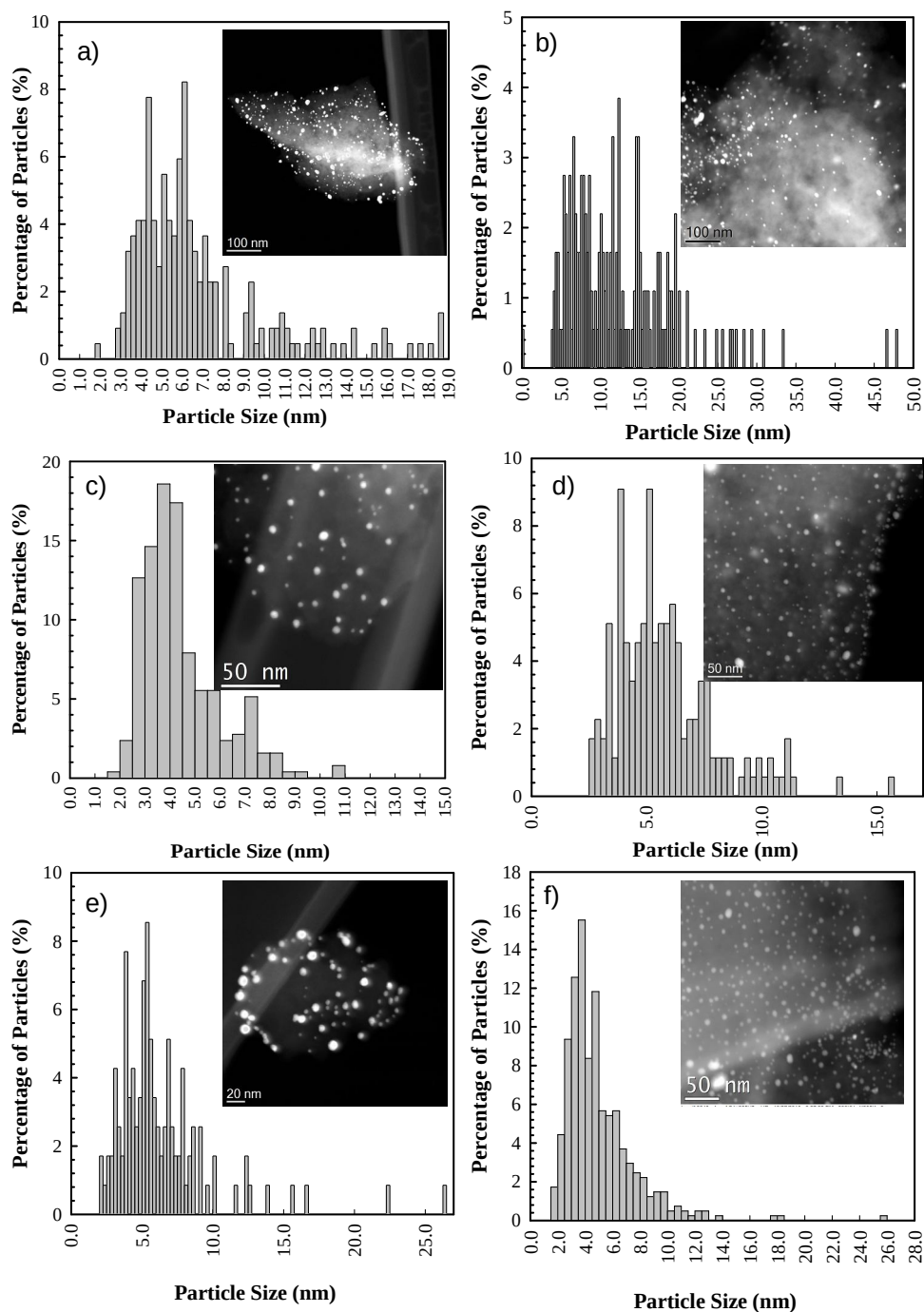


Figure 3.2 Particle size distributions and HAADF-STEM images of the Au catalysts supported on a) AC₀, b) AC₁, c) AC_{1tt400}, d) AC_{1tt600}, e) AC_{1tt900} and f) AC_{1tt900-H2}.

The Au/AC₁ sample has a higher average particle size. This can be due to the large amount of oxygen-containing groups on support AC₁, which could influence the metal dispersion. On one hand, the surface oxygenated groups are considered to act as anchoring sites that interact with metallic precursors, improving the metal dispersion [26]. However, some of these functional groups present on activated carbon are easily decomposed upon heating even at low temperatures. This occurs with some carboxylic acid groups, which already decompose at temperatures below 350 °C, as it can be seen in the TPD spectra (Figure 3.1). The sample AC₁ is the unique support that has a significant amount of oxygenated groups able to decompose at temperatures below 350 °C (Figure 3.1). Therefore, during the heat-treatment and reducing steps, used in the preparation of the Au/AC₁ catalyst, some groups are thermally decomposed and the gold particles that are anchored to them may have a low stability and could be prone to sintering. This can possibly explain why the Au/AC₁ catalyst has larger metallic particles than Au/AC₀, Au/AC_{1tt400}, Au/AC_{1tt600}, Au/AC_{1tt900} and Au/AC_{1tt900-H2}, because on this latter group of samples, contrarily to the former, there was no oxygenated groups that decompose at low temperatures during the preparation step. The supports AC_{1tt400}, AC_{1tt600}, AC_{1tt900} and AC_{1tt900-H2} were already heat-treated at temperatures above 350 °C before gold impregnation; therefore, as it can be seen in TPD spectra (Figure 3.1), they do not release CO and/or CO₂ below 350 °C.

Table 3.3 summarises the metal loadings of the catalysts. The gold content obtained by ICP analysis is slightly lower than the nominal. However, chemical and heat-treatments of activated carbon did not influence substantially the gold content of catalysts and all the samples present a similar value of approximately 0.6%.

3.3.2 Kinetic experiments

3.3.2.1 Influence of pressure and temperature

The influence of oxygen pressure and temperature on the reaction was examined for the Au/AC₀ catalyst. Experiments were carried out with 150 mL of glycerol (0.3 M), NaOH/glycerol = 2 mol/mol and 700 mg of catalyst. The oxygen pressure was varied between 3 and 10 bar and the temperature between 40 and 80 °C.

Under the tested conditions, it was found that the reaction rate increases with the oxygen pressure as depicted in Figure 3.3 a). For instance, when this value is 10

bar, total glycerol conversion is achieved after about 2.5 h. Moreover, selectivity to GLYCOA (Table 3.4) slightly decreases with the increase of oxygen pressure.

The temperature increase also leads to an increase of the catalytic activity as seen in Figure 3.3 b), but appears to be very unfavorable for the selectivity of glyceric acid, which seems to oxidize very easily to glycolic acid at high temperatures (Table 3.4). This result was described before by Porta and Prati [9] under similar conditions.

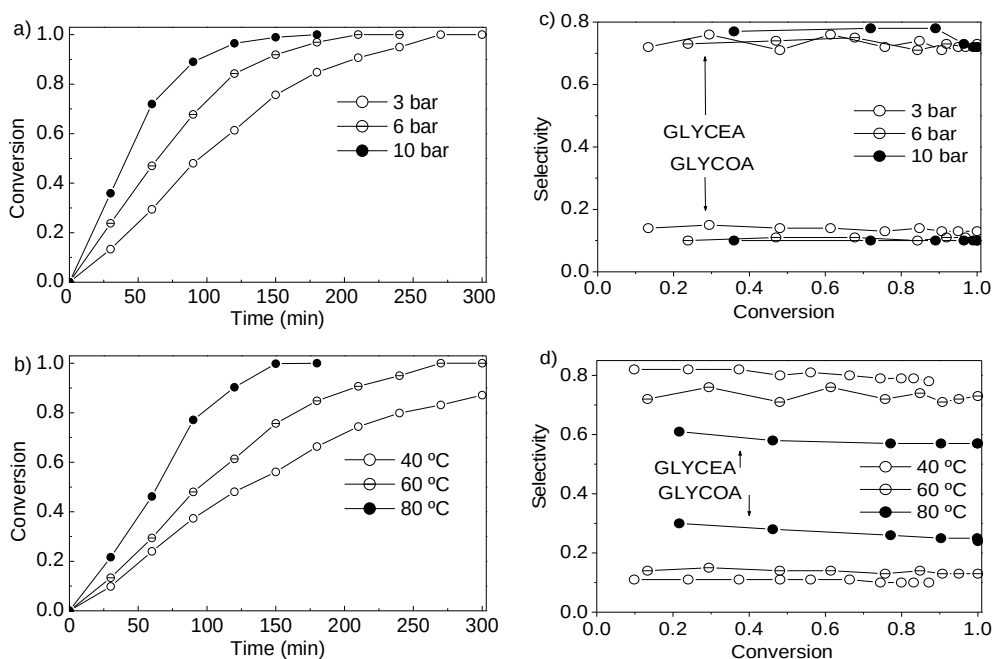


Figure 3.3 Glycerol conversion over Au/AC₀ varying a) the oxygen pressure or b) the temperature, and evolution of GLYCEA and GLYCOA selectivities as a function of glycerol conversion at different c) oxygen pressures and d) reaction temperatures. Reaction conditions: 150 mL of glycerol 0.3 M, catalyst amount = 700 mg, NaOH/glycerol = 2 mol/mol.

For comparative purposes, selectivities to the different products are presented at constant reaction time (3 h) and also at the same glycerol conversion (90%) in Table 3.4. The selectivities obtained are practically independent of time and glycerol conversion, varying only slightly during the reaction for all the conditions and catalysts tested in this work. As an illustrative example, the evolution of GLYCEA

and GLYCOA selectivities (main reaction products) as a function of glycerol conversion in the presence of Au/AC₀ at different oxygen pressures and reaction temperatures can be seen in Figure 3.3 c) and Figure 3.3 d), respectively. In some cases, the sum of the calculated selectivities is lower than 1 (see Table 3.4), since some oxalic acid was also detected but always with low concentrations. Nevertheless, in the experiment with the Au/AC₀ catalyst at 80 °C, even after accounting for the oxalic acid formed (selectivity = 0.05), the sum of selectivities is still lower than 1. As no additional product was detected by HPLC, we supposed that, in this particular case, some complete oxidation of the partial oxidation products to CO₂ occurs.

Table 3.4 GLYCEA, GLYCOA, TARTA and FORMA selectivities (S_{GLYCEA} , S_{GLYCOA} , S_{TARTA} , S_{FORMA}) at different oxygen pressures and temperatures for 90% glycerol conversion (X_{GLY}) and after 3 h of reaction with the Au/AC₀ catalyst.

t = 180 min						$X_{\text{GLY}} = 90\%$			
Catalyst	X_{GLY}	S_{GLYCEA}	S_{GLYCOA}	S_{TARTA}	S_{FORMA}	S_{GLYCEA}	S_{GLYCOA}	S_{TARTA}	S_{FORMA}
Au/AC₀									
3 bar ^a	0.85	0.74	0.14	0.08	0.03	0.71	0.13	0.10	0.04
6 bar ^a	0.97	0.72	0.11	0.09	0.04	0.73	0.11	0.10	0.04
10 bar ^a	1	0.72	0.10	0.10	0.04	0.78	0.10	0.08	0.04
40 °C ^b	0.66	0.80	0.11	0.06	0.03	-	-	-	-
60 °C ^b	0.85	0.74	0.14	0.08	0.03	0.71	0.13	0.10	0.04
80 °C ^b	1	0.57	0.25	0.08	0.03	0.57	0.25	0.08	0.03

^a Reaction conditions: 60 °C, 150 mL of glycerol 0.3 M, NaOH/glycerol = 2 mol/mol, catalyst amount = 700 mg.

^b Reaction conditions: $p_{\text{O}_2} = 3$ bar, 150 mL of glycerol 0.3 M, NaOH/glycerol = 2 mol/mol, catalyst amount = 700 mg.

It should be noticed that the comparison between the results obtained in this work and those reported in literature is particularly difficult since the reaction conditions

changed from author to author. Moreover, the results are often presented as conversion obtained after a certain reaction time. For example, under conditions identical to the present research, Carretin et al. [27] obtained 56% glycerol conversion after 3 h of reaction at 60 °C and 3 bar using 1 wt% Au/graphite. In the present work, 85% conversion was achieved at this same reaction time with Au/AC₀. Additionally, the turnover frequencies (TOFs) calculated after 1 h of reaction for the Au/AC₀ catalyst tested at different temperatures and oxygen pressures are shown in Table 3.5 and compared with some typical results from the literature [28-30]. It can be concluded that the activities obtained in this work are similar or even higher than those reported by different groups.

Table 3.5 Comparison between turnover frequencies (TOFs) obtained after 1h of reaction for the Au/AC₀ catalyst tested at different temperatures and oxygen pressures and some typical results from the literature.

Reaction Conditions			TOF (h ⁻¹)	Ref.
T (°C)	<i>P</i> _{O₂} (bar)	NaOH/GLY (mol/mol)		
40	3	2	3300	This work
60	3	2	3640	This work
60	3	2	1430 ^a	This work
60	6	2	5820	This work
60	10	2	8810	This work
80	3	2	6350	This work
60	10	2	8640	[28]
50	3	4	900	[29]
50	3	4	830	[30]
70	3	4	960	[30]

^a Au/AC₀ catalyst used without prior heat-treatments at 350 °C.

It is important to mention that about 80% selectivity to glyceric acid was achieved at 40 °C and 3 bar. Then, it may be concluded that gold prepared by the sol

immobilisation method is highly effective and the selectivity can be slightly altered by changing the reaction conditions. Furthermore, gold allows high levels of oxygen in the reaction medium without suffering any significant deactivation.

3.3.2.2 Investigation of the support effects in the glycerol oxidation

Figure 3.4 shows the evolution of glycerol conversion in the presence of the gold catalysts prepared on different activated carbons.

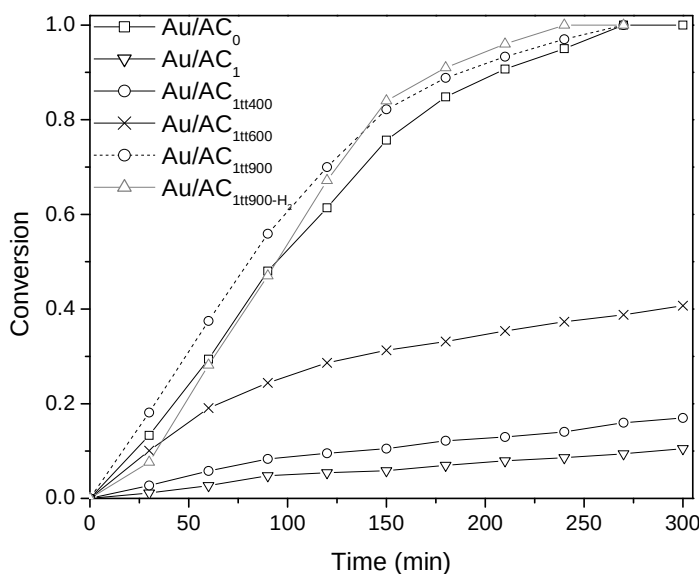


Figure 3.4 Influence of the modified activated carbon supports on the performance of gold catalysts. Reaction conditions: 60 °C, $p_{O_2} = 3$ bar, 150 mL of glycerol 0.3 M, catalyst amount = 700 mg, NaOH/glycerol = 2 mol/mol.

The surface chemical functional groups of activated carbon can be controlled by chemical and heat treatments. Since no drastic changes were observed in the textural properties of the supports (cf. Table 3.1), in gold average particle sizes and in metal loadings of the catalysts (cf. Table 3.3), the disparities in performances observed in Figure 3.4 must be related almost exclusively to the differences in support chemical properties. In fact, whether the activity was only dependent on the gold particles size, the following order of performances would be expected: $Au/AC_{1tt400} > Au/AC_{1tt900-H_2} > Au/AC_{1tt600} > Au/AC_{1tt900} > Au/AC_0 > Au/AC_1$ (see Table

3.3). However, sample Au/AC_{1tt400}, which has the smallest gold particles size (average diameter = 4.4 nm), only shows a weak efficiency in glycerol oxidation, mainly when compared with Au/AC_{1tt900-H₂}, which has a similar average particle size (5.0 nm), but also with Au/AC₀ (6.8 nm) and Au/AC_{1tt900} (6.4 nm). These catalysts, all with similar distributions of gold particle sizes, clearly resulted in different performances depending on the amount of oxygenated groups on the carbon surface. In general, as the oxygenated groups of the support are removed, the catalytic performance gradually increases.

We also tested the Au/AC₀ catalyst in successive experiments. Each run was carried out under the standard conditions described previously. The catalyst was recovered by filtering off the solution of the previous run after 5 h of reaction and reused. Due to some losses during the filtration procedure, a limited amount of fresh catalyst (< 5% of the total weight) was also added to the reaction medium. It can be observed in Figure 3.5 that the first two runs correspond to similar results, but in the third and mainly in the fourth the catalyst performance significantly decreased (conversion after 3 h is about 45 % lower in run 4).

ICP analyses (see Table 3.3) show that the gold content remains unchanged after the four runs; then, metal leaching is not the cause of the observed deactivation. However, a growing size of Au particles was observed by microscopy analysis of the recovered catalyst after successive experiments (see Table 3.3), which probably explains the poor performance. On the other hand, this may affect positively the selectivity to GLYCEA, which slightly increased from 0.74 in the first run to 0.78 in the fourth (Figure 3.5). The effect of the particle size on the GLYCEA selectivity is in agreement with the results of Porta and Prati [9]. Although these authors [9] prepared gold catalysts by a similar PVA-protected sol preparation, they used them directly as obtained after the synthesis (i.e. without any previous heat-treatments in N₂ and H₂, as described in section 3.2.1.2.2).

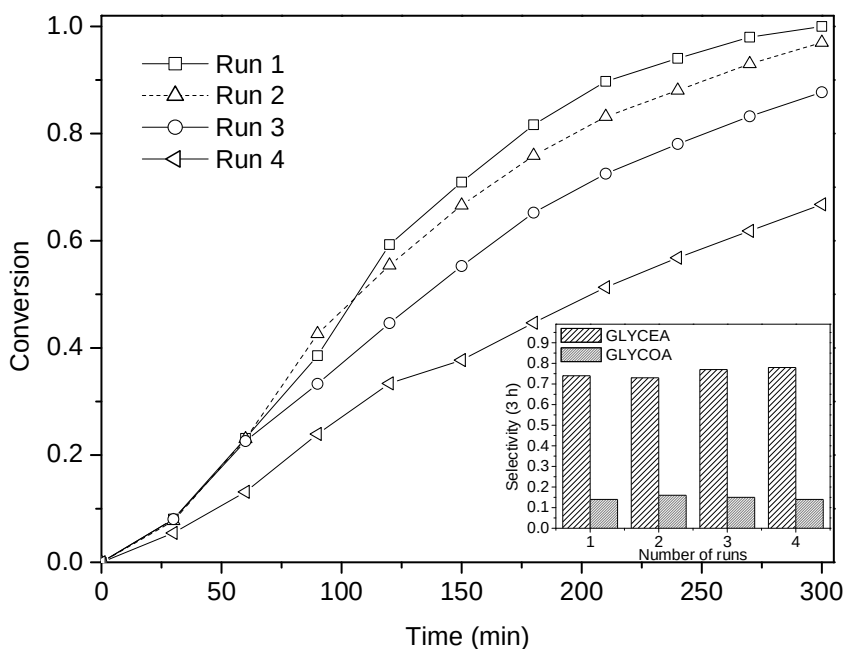


Figure 3.5 Successive experiments with the Au/AC₀ catalyst. Selectivities to GLYCEA and GLYCOA at $t = 3$ h in each cycle are also presented inside. Reaction conditions: 60 °C, $p_{O_2} = 3$ bar, 150 mL of glycerol 0.3 M, catalyst amount = 700 mg, NaOH/glycerol = 2 mol/mol.

In order to study the influence of the mentioned activation in the catalyst performance, we tested the Au/AC₀ catalyst as obtained and heat-treated at 350 °C. A better performance was achieved with the catalyst prepared by the standard procedure (section 3.2.1.2.2), as it can be seen in Table 3.5 (TOF reduces by more than 50% in the catalyst prepared without heat-treatments). Moreover, successive runs carried out under the standard experimental conditions with the Au/AC₀ catalyst, with or without heat-treatments at 350 °C, allow to conclude that deactivation of the catalyst used without heat-treatments is much more significant than that of the sample heat-treated at 350 °C. For example, the glycerol conversion after 3 h in the third run is about 20% lower in the presence of the catalyst prepared by the standard procedure (Figure 3.5), while the sample used without PVA removal leads to a relative conversion decrease of 59%. Moreover, it was observed by microscopy analysis of the recovered catalyst after successive experiments that the average size of gold particles in the sample Au/AC₀ heat-treated at 350 °C increases from 6.8 nm (fresh catalyst) to 11.4 nm after four runs

(see Table 3.3), while the average crystallite size of the sample used in the reaction without heat-treatments increases from 4.6 nm (fresh catalyst) to 25 nm after only three runs. Therefore, it seems that the standard procedure for the preparation of catalysts leads to stronger metal/support interactions, slowing down the sinterization rate of Au particles. As the catalyst heat-treated at 350 °C presents higher performance and stability, the procedure adopted seems to be the most adequate to prepare the gold catalysts.

The successive experiments carried out with the Au/AC₀ catalyst heat-treated at 350 °C confirm the influence of the gold dispersion on the catalytic performance, but also allow concluding that even with a metal average size of 11.4 nm (see Table 3.3) the Au/AC₀ catalyst shows a fairly high activity (Figure 3.5). Therefore, the poor efficiency of the Au/AC₁ catalyst, which has a similar average particle size, cannot be explained only by the gold dispersion.

The Au/AC₁ catalyst has a high content of oxygenated functional groups and only a residual performance (see Table 3.2 and Figure 3.4). When carboxylic acid groups were removed from the surface (sample Au/AC_{1tt400}) no significant enhancement was observed. However, after removing carboxylic acid and carboxylic anhydride groups (sample Au/AC_{1tt600}), the catalytic performance improves. Finally, catalysts with a low content of oxygenated surface groups, such as Au/AC₀, Au/AC_{1tt900} and Au/AC_{1tt900-H₂}, show a similar high activity. Therefore, Figure 3.4 reveals a strong influence of the surface chemical properties of the support on the catalytic performance in glycerol oxidation, indicating that surface oxygenated groups, mainly those with acid nature, are prejudicial.

As the temperature used in the preparation of supports is increased, oxygenated groups are decomposed sequentially, releasing CO and/or CO₂, and therefore the resulting supports have a gradual lower amount of oxygen, as it can be seen in Table 3.2. As a result, the oxygen content of the surface seems to be a factor of large influence in the reaction, since a trend can be observed in Figure 3.6. Additionally, TOFs obtained after 3 h of reaction for the different catalysts are also presented in Figure 3.6 as a function of the oxygen content.

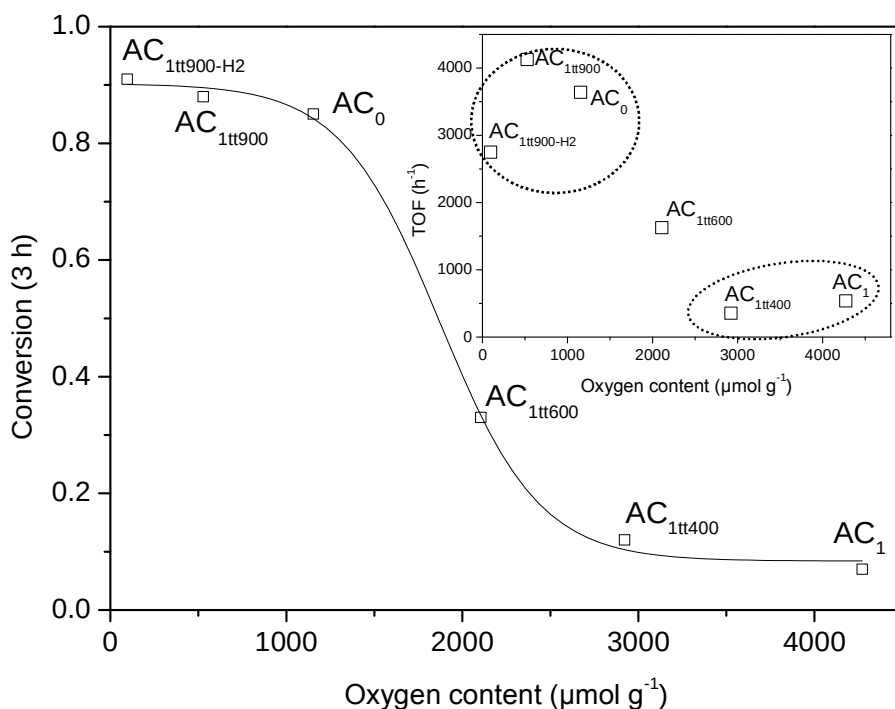


Figure 3.6. Influence of the oxygen content of activated carbons on the catalytic performance. Insert: TOF after 3 h of reaction for the different catalysts vs. the oxygen content.

It seems that the catalysts tested can be assorted in three distinct groups:

- Au/AC₁ and Au/AC_{1tt400}: catalysts with a high amount of oxygen-containing functional groups (mainly acid groups) and low activity.
- Au/AC_{1tt600}: catalyst with an intermediate amount of oxygen-containing functional groups (lower concentration of acid groups) and intermediate activity.
- Au/AC₀, Au/AC_{1tt900} and Au/AC_{1tt900-H2}: catalysts corresponding to basic supports (only with a limited concentration of oxygenated surface groups, particularly those of acid nature) and high activity.

Summarising, supports with basic characteristics lead to more active gold catalysts.

Yang et al. [31] tested a series of metal carbonate supported gold nanoparticles for the liquid-phase oxidation of benzyl alcohol and observed that the catalytic performance depends strongly on the basicity of the support material. They suggest

that the initial O-H bond cleavage can occur on the support basic sites. On the contrary, also in a study of benzyl alcohol oxidation, but using activated carbon supports, Zhu et al. [32] concluded that the activity of Au/AC catalysts was improved by the presence of oxygen-containing species on the surface, which were proposed as responsible for oxygen activation.

In Table 3.6, the selectivities obtained in the presence of the most active catalysts are compared at constant reaction time and at the same glycerol conversion ($X = 40\%$). Contrary to what was observed with the conversions, the presence of oxygenated groups on the support did not influence significantly the selectivities. The prepared catalysts lead to a high selectivity to glyceric acid of about 75%, and a very similar distribution of the products was observed, independently of the amount of oxygenated surface groups present.

Table 3.6 Influence of the support on the selectivities of GLYCEA, GLYCOA, TARTA and FORMA for Au catalysts prepared on activated carbons with different surface chemistries.

Catalyst	t = 180 min					$X_{\text{GLY}} = 40\%$			
	X_{GLY}	S_{GLYCEA}	S_{GLYCOA}	S_{TARTA}	S_{FORMA}	S_{GLYCEA}	S_{GLYCOA}	S_{TARTA}	S_{FORMA}
Au/AC ₀	0.85	0.74	0.14	0.08	0.03	0.76	0.14	0.07	0.03
Au/AC _{1tt600}	0.33	0.72	0.09	0.08	0.01	0.72	0.09	0.07	0.02
Au/AC _{1tt900}	0.89	0.72	0.16	0.09	0.02	0.69	0.21	0.08	0.02
Au/AC _{1tt900-H2}	0.91	0.75	0.15	0.07	0.03	0.76	0.16	0.06	0.02

3.3.2.3 Discussion on the influence of support surface chemistry

The role of the support in the catalytic reaction studied is still under discussion. The mechanism for oxygen adsorption and activation on supported gold catalysts is not yet completely established. For the discussion of our observations, it could be assumed that oxygen adsorption proceeds directly on the metal particles [33]. However, in this mechanism, the support would have only a secondary role in the catalytic activity, limited to the dispersion and stabilization of metal particles, and therefore could not explain the results obtained. Additionally, this is not compatible with the well known low capacity of gold for adsorbing molecular oxygen.

Nevertheless, recent experiments in glycerol oxidation catalyzed by gold supported on carbon showed that oxygen atoms incorporated into the reaction products were originated from hydroxide ions, which play a decisive role during the reaction, and not from molecular oxygen, which is necessary for the regeneration of hydroxide ions [34]. In fact, very poor or no activity is observed when using gold catalysts without a relatively high concentration of added base [24]. Glycerol oxidation is aided by high-pH conditions, since the hydroxide species adsorbed over gold have the ability to facilitate the activation of both the C-H and O-H bonds of glycerol (also adsorbed on the catalyst surface), leading to the addition of electrons to the metal surface [34] (see Figure 3.7; step I). In this way, the oxidation mechanism does not involve the dissociation of molecular oxygen to atomic oxygen.

Instead, activation of O_2 occurs by the formation and dissociation of peroxide and hydrogen peroxide intermediates on the metal surface, according to the following mechanism [34]:



where * represents a site on the metal surface. The last step allows for the removal of electrons added to the surface during the adsorption of hydroxide ions and regenerates these species. In that study [34], the support was not considered to be involved in the mechanism. However, the presence of delocalized π -electrons in basic carbon supports leads to a high electronic mobility, whereas oxygen-containing functional groups (electron-withdrawing groups) decrease the electron density and the electrical conductivity [35-36]. The mobility of electrons to the basic support could potentially reduce the excess of negative charge on gold and enhance the possibility of further hydroxide bonding (Figure 3.7, step II), whereas the transition of this electrons from the support to the metal enhance the regeneration of the hydroxide ions (equations (3.2-3.4) and Figure 3.7, step III and IV). Therefore, the mobility of the electrons from and to the gold surface could potentially promote both adsorption and regeneration of hydroxide ions and thus the catalytic performance.

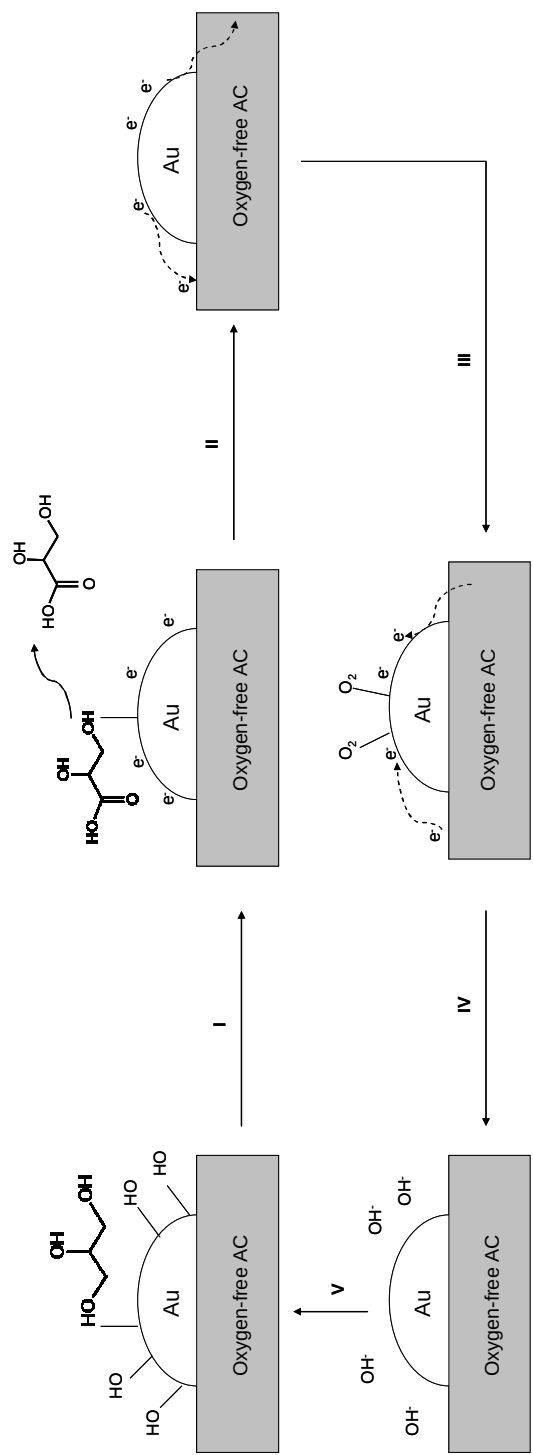


Figure 3.7 Role of the basic supports on the mechanism of glycerol oxidation.

3.4 Conclusions

A strong effect of the activated carbon surface chemistry on the activity of Au/AC catalysts for glycerol oxidation was observed. Gold particles with similar average sizes resulted in different performances, depending on the amount of oxygenated groups on the surface of the support used. As a result, the oxygen content on the surface is a factor of large influence in the reaction. Basic oxygen-free supports, characterized by a high density of free π -electrons, lead to an enhancement of the gold catalyst activity. These characteristics can easily be achieved by thermal treatments at high temperatures, which remove the oxygen-containing surface groups. The role of the activated carbon surface chemistry was explained on the basis of a recent published mechanism, by considering the capability of oxygen-free supports to promote electron mobility. The prepared catalysts lead to a high selectivity to glyceric acid of about 75%.

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Chapter 4

4 Gold supported on carbon nanotubes for the selective oxidation of glycerol

Gold nanoparticles were supported on multi-walled carbon nanotubes (MWCNTs) by different methods and tested in the selective oxidation of glycerol under basic conditions, with the main purpose of evaluating the effect of the preparation technique on the activity and selectivity. The catalytic performances largely depended on the gold crystallite size. The sol immobilization method was the most suitable technique to prepare gold supported on carbon nanotubes.

4.1 Introduction

Glycerol is a highly functionalized molecule widely available from bio-sustainable sources. Therefore, its conversion into high-value chemicals is of large industrial importance. Recently, the oxidation of glycerol for the production of valuable oxygenated derivatives has received remarkable attention [1-6]. However, the extensive functionalization of this molecule, with three hydroxyl groups, renders its selective oxidation particularly difficult since, in general, a large number of products can be obtained [5, 7-10] (Figure 4.1).

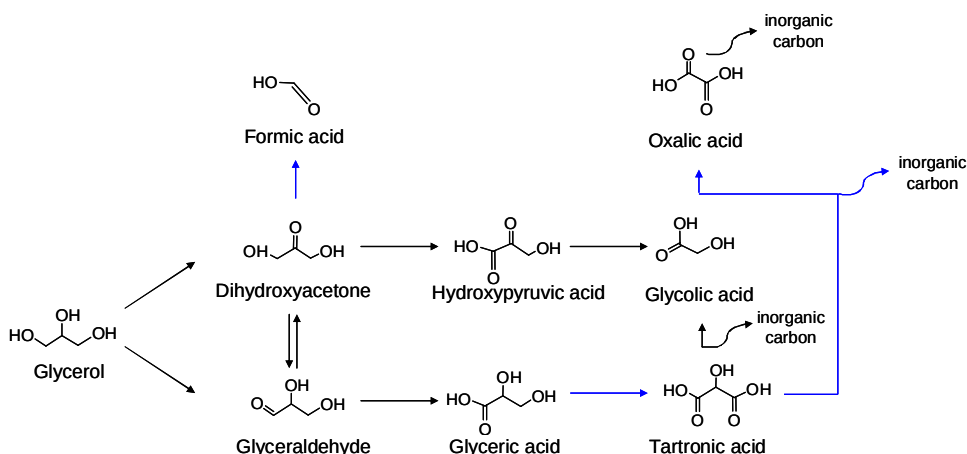


Figure 4.1 Possible reaction pathways.

In order to control the selectivity, a careful design of the catalyst is required. Gold catalysts are well known for their high activity in glycerol oxidation. Their better resistance to oxygen poisoning compared with catalysts based on metals of the platinum group allows the use of high oxygen partial pressures in the reactor [11]. However, when using gold containing catalysts, a basic medium is necessary in order to obtain significant glycerol conversions [12-13]. Gold nanoparticles supported on different carbon materials or oxides are active for the oxidation of glycerol, but show very different performances, being carbon-supported catalysts more active than most oxide-supported catalysts [2, 11, 14]. Accordingly, in the majority of the reported studies the supports used are activated carbon, carbon black or graphite [1, 15]. On the other hand, except from a very recent publication from Prati *et al.* [16], multi-walled carbon nanotubes (MWCNTs) have not been investigated as supports for gold nanoparticles in the scope of the liquid phase

oxidation of glycerol. Recently, this type of material have been drawing increasing attention for catalytic applications because of its unique features, such as high graphitization, high specific surface area, good physical and chemical stability and excellent electronic properties [17], which were recently reported as being important in the performance of gold catalysts [18] (see Chapter 3). Furthermore, an increasing amount of studies suggest that the textural and chemical properties of the support influence directly the selectivity of the glycerol oxidation reaction [4, 12, 16]. As a result, the use of MWCNT as support is appealing due to its strictly mesoporous nature, differing largely from the widely used activated carbon supports.

Nevertheless, both the performance of catalysts and the selectivities attained are also sensitive to gold nanoparticle sizes, which in turn depend on the preparation method and type of supporting material used [19-20]. In particular, the presence of chloride is very detrimental for the catalytic performance, since it is known to cause agglomeration of gold particles [21-22]. Apparently, the gold-sol immobilization method is the most appropriate technique in order to obtain well-dispersed nanoparticles on activated carbons [19, 23]. However, there is no information about the most suitable method to support gold on MWCNTs for the oxidation of glycerol. Therefore, in the present work, gold nanoparticles were supported on MWCNTs by different methods and tested for the selective oxidation of glycerol. Besides the well-known incipient wetness impregnation (IW) and immobilization techniques, some less usual methods were also considered for the preparation of the samples, namely liquid phase reductive deposition (LPRD), double impregnation (DIM) and reduction with citric acid (citric). As far as we know, these methods had not been used for the preparation of Au/MWCNT catalysts.

The influence of the preparation method on the catalytic performance in glycerol oxidation and on the selectivity was analysed.

4.2 Experimental

4.2.1 Catalyst preparation

A commercial Nanocyl 3100 MWCNT sample was used as support for this study. According to the supplier, these nanotubes have an average diameter of 9.5 nm, an average length of 1.5 μm and carbon purity higher than 95%. In a recent work, it

was shown that this material presents average inner and outer diameters of 4 and 10 nm, respectively [24].

In this work, gold catalysts with a nominal metal loading of 1 wt% were prepared on the original MWCNT using $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ as precursor and different techniques: incipient wetness impregnation (IW), double impregnation (DIM), liquid phase reductive deposition (LPRD), reduction with citric acid (citric) and sol immobilization (c).

4.2.1.1 Incipient wetness impregnation

An appropriate volume of an aqueous solution of the gold precursor was added dropwise via a peristaltic pump to the support until incipient wetness ($6 \text{ cm}^3 \text{ g}^{-1}$). During the impregnation, the sample was placed in an ultrasonic bath. After 1.5 hours, the resultant wet sample material was dried at 110°C overnight. Finally, the catalyst was heat treated under nitrogen flow for 3 h at 350°C , and subsequently activated by reduction under hydrogen flow for 3 h at 350°C .

4.2.1.2 Double impregnation

This method consists in impregnating the support with an aqueous solution of the gold precursor and then with a solution of Na_2CO_3 , in order to precipitate gold hydroxide within the pores [25]. Firstly, $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ was dissolved in a small amount of water and impregnated on the support using a peristaltic pump, as described above. During impregnation, the sample was placed in an ultrasonic bath. It should be noticed that the amount used is insufficient to wet completely the support. Then, an additional aqueous solution of Na_2CO_3 1 M was added to the support. The amount of this solution was just sufficient to reach the incipient wetness point. A constant ultrasonic stirring of the sample was maintained during 1.5 hours. The mixture was washed five times with 14 mL of the sodium carbonate solution in 100 mL of water, followed by five washings with 100 mL of water for chloride removal from the sample. The resultant material was dried at 110°C overnight.

4.2.1.3 Liquid phase reductive deposition

In this method, gold (III) ions from the precursor are hydroxylated by reaction with NaOH and a washing procedure is carried out in order to eliminate residual chloride [26]. Therefore, an aqueous solution of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ was mixed with a solution of NaOH (ratio of 1:4 in weight) while stirring at room temperature. The resulting yellow solution was aged for 24 h in the dark at room temperature to complete the hydroxylation of Au^{3+} ions. At this point, the solution was colorless. Then, the appropriate amount of support was added to the solution and, after ultrasonic dispersion for 30 min, the suspension was aged in the oven at 110 °C overnight. The resulting solid was washed repeatedly with distilled water in order to remove impurities such as chloride ions, and finally dried at 110 °C overnight.

4.2.1.4 Reduction with citric acid

In this procedure, the gold nanoparticles were prepared by the reaction of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ with citric acid (used as reducing agent) [27]. The colloidal gold forms because the citrate ions can act as reducing and capping agent. Typically, after ultrasonic dispersion of the sample in 2-propanol for 15 min, the same weights of HAuCl_4 and citric acid, both dissolved separately in 2-propanol, were simultaneously added dropwise to the suspension. The ultrasonication was then interrupted and the resulting dispersion was vigorously stirred at room temperature for 2 h. The mixture was subsequently washed several times with 2-propanol in order to remove impurities and dried at 110 °C overnight.

4.2.1.5 Sol immobilization

A catalyst sample was synthesized via the sol immobilization technique using polyvinyl alcohol (PVA) as protective agent and NaBH_4 as reducing agent [28]. Briefly, $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (35.1 mg) was dissolved in 690 mL of H_2O , and PVA was added (1.6 mL, 0.2 wt %) under stirring. PVA is necessary to stabilize the nanostructured colloidal gold and to prevent agglomeration. NaBH_4 (4 mL, 0.1 M) was added to the yellow solution under vigorous magnetic stirring. The resulting sol was ruby-red in color. Within a few minutes of sol generation, the colloid was immobilized by adding the support under fast stirring. After 3-4 days, the solution becomes colorless and the suspension was filtered. The catalyst was washed thoroughly with distilled water until the filtrate was free of chloride (checked by the AgNO_3 test) and dried at 110 °C for 24 h. The organic scaffold was removed from

the support by a heat treatment under nitrogen flow for 3 h at 350 °C and then the catalyst was activated by reduction under hydrogen flow for 3 h also at 350 °C. A TG-DSC experiment was carried out under N₂ atmosphere in a Netzsch STA 409 PC Luxx® System. About 15 mg of PVA were loaded into a ceramic crucible and the temperature was raised to 350 °C at 10 °C/min. It was verified that PVA decomposition occurs in the range 240 – 320 °C (see Appendix D).

4.2.2 Catalyst characterization

Catalysts and supports were characterized by N₂ adsorption at -196 °C in a NOVA Quantachrome Instruments apparatus. Pore size distributions were obtained by using the non-local density functional theory (NLDFT), applying the kernel file provided by Quantachrome's data reduction software, where a cylindrical-pore model is assumed.

The determination of oxygenated surface functional groups was performed by temperature programmed desorption – mass spectrometry (TPD-MS) [29-30]. CO and CO₂ TPD spectra were obtained with a fully automated AMI-200 equipment (Altamira Instruments). Briefly, the sample (150 mg) was placed in a U-shaped quartz tube inside an electrical furnace and subjected to a 5 °C min⁻¹ linear temperature increase up to 1100 °C under helium flow (25 cm³ (STP) min⁻¹). A quadrupole mass spectrometer (Dymaxion 200, Ametek) was used to monitor CO and CO₂ signals. For quantification of the CO and CO₂ released, calibration of these gases was carried out at the end of the analysis.

The gold loading of the prepared catalysts was determined in duplicate by inductively coupled plasma-optical emission spectroscopy (ICP/OES) in an external laboratory, using a PerkinElmer Optima 4300 DV spectrometer.

Electron micrographs of samples were obtained using a JEOL2010F instrument (equipped with an energy dispersive X-ray spectroscopy detector), with 0.19 nm spatial resolution at Scherzer defocus conditions. High Angel Annular Dark Field – Scanning Transmission Electron Microscopy (HAADF-STEM) images were acquired with the same equipment. Particle size distributions were obtained by the measurement of at least 200 particles and the average diameter was calculated by $d_M = \sum d_i n_i / \sum n_i$, where n_i is the number of particles of diameter d_i .

In order to determine Au oxidation states, X-ray photoelectron spectroscopy (XPS) analyses were carried out with a VG Scientific ESCALAB 200A spectrometer using

Al K α radiation (1486.6 eV). The accuracy of the resulting data was checked by performing at least five repetitions for each sample.

Further details of the experimental setup and analytical techniques used can be found elsewhere [31] (see Chapter 2).

4.2.3 Catalytic experiments

Typically, a NaOH solution and the gold catalyst (700 mg) were added to a 0.3 M aqueous solution of glycerol (total volume 195 mL; NaOH/glycerol molar ratio = 2) under stirring at 1000 rpm. The reactor was pressurized with nitrogen at 3 bar. After heating under this atmosphere to 60 °C, the reaction was initiated by switching from inert gas to oxygen (3 bar). Additionally, a limited number of runs were carried out at different NaOH/glycerol molar ratios.

The reaction was monitored by taking samples (0.5 mL) for analysis at regular time intervals. The quantitative analysis of these samples was carried out by high performance liquid chromatography (HPLC). The chromatograph (Elite LaChrom HITACHI) was equipped with an ultraviolet (210 nm) and a refractive index detector in series. Products were identified by comparison with standard samples.

In order to investigate the reproducibility of the catalytic tests and the errors associated to the glycerol conversion, four experiments with the same batch of the Auc/MWCNT catalyst were carried out. The maximum relative error observed was $\pm 7\%$.

The selectivities (S_i) into the different products i at time t were calculated as:

$$S_i = \frac{C_i}{\nu_i \cdot C_0 \cdot X} \quad (4.1)$$

where C_i is the concentration of product i (mol L⁻¹), C_0 is the initial concentration of glycerol (mol L⁻¹), X is the glycerol conversion and ν_i corresponds to the moles of i produced per mol of glycerol consumed, according to the stoichiometry.

4.3 Results and discussion

4.3.1 Characterization of supports and catalysts

4.3.1.1 Textural properties

The carbon nanotubes sample shows a N_2 adsorption isotherm typical of non-porous materials. The BET surface areas (S_{BET}) of the support and catalysts are presented in Table 4.1. It can be observed that the surface areas of catalyst samples are quite similar to the respective unloaded support. The pore size distribution (Figure 4.2) confirms that most of the porosity observed in the MWCNT support corresponds to large mesopores (widths as large as 40 nm are present), which result from the free space between carbon nanotubes in the respective bundles [17]. In fact, carbon nanotubes are not used individually but as aggregates, leading to the formation of pores. So, the NLDFT method shows the MWCNT mesoporous nature. Therefore, it can be concluded that pores in MWCNT are widely distributed and are formed by interaction of isolated nanotubes.

Table 4.1 Surface areas of support and gold catalysts.

Sample	S_{BET} (m^2/g)
MWCNT	285
Au IW/MWCNT	296
Au DIM/MWCNT	298
Au LPRD/MWCNT	266
Au citric/MWCNT	283
Auc/MWCNT	288

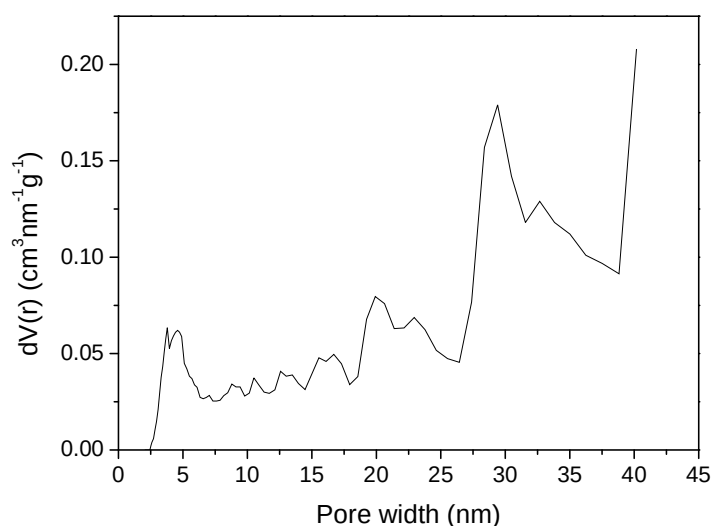


Figure 4.2 Pore size distribution obtained by Non-Local Density Functional Theory (NLDFT).

4.3.1.2 Surface chemistry characterization

TPD is a thermal analysis method that is becoming popular for the characterization of the oxygen-containing groups on the surface of carbon materials. In this technique, the total amount of the various oxygenated surface groups (carboxylic acids, carboxylic anhydrides, lactones, phenols, and carbonyls or quinones) on carbon materials can be determined, since these groups are decomposed upon heating by releasing CO and/or CO₂ at different temperature ranges. Accordingly, it is possible to identify and estimate the amount of the oxygenated groups on a given carbon material by TPD experiments. The nature of the groups can be assessed by the decomposition temperature and the type of gas released, and their respective amounts determined by the areas of the component peaks, obtained by deconvolution techniques [29-30]. Actually, the oxygen content obtained from the CO and CO₂ TPD spectra of the support tested in this work is very low. In fact, the MWCNT sample only have a limited content of oxygenated functional groups on its surface corresponding to an oxygen content of 532 $\mu\text{mol g}^{-1}$. For comparison, results obtained with moderately and highly oxidized carbon materials can be found elsewhere [18, 29-30, 32-33]. Therefore, it can be concluded that the support used in this work have a very small amount of oxygenated groups on the surface, which is important since this may influence the performance of catalysts. In fact, in a recent work, we demonstrated that the presence of surface oxygenated acid groups

lowers significantly the activity of gold supported on activated carbon [18] (see Chapter 3).

4.3.1.3 ICP analyses

It is important to mention that the oxidation of the support has been carried out by some authors before anchoring the metal-containing species, in order to improve the interaction between support and the catalyst precursor [17, 27]. However, despite the chemical inertness and very regular structure of carbon nanotubes, gold was successfully anchored without any pretreatment of the surface, as it can be seen in Table 4.2, which summarizes the metal loadings achieved with the different techniques. The gold content obtained by ICP analysis is lower than the nominal. Most of the preparation methods does not influence substantially the gold content of catalysts, and the corresponding prepared samples present a similar value of approximately 0.7%. The unique exception is the Au LPRD/MWCNT catalyst, which has a significantly lower loading (0.40%). This latter result indicates that a large fraction of gold present in the aqueous solution was not deposited on the support.

The LPRD technique is based on the adsorption of metal-containing ions on the surface followed by reduction, being that initial adsorption of metal the key point of the method [26]. In the citric acid method, contrarily to the LPRD method, MWCNT and the gold precursor were immersed in a large amount of 2-propanol, which improve the support dispersibility, leading to a better contact between support and metal when compared to water, once carbon nanotubes are hydrophobic. Regarding the sol immobilization method, the electrostatic interactions between the stabilized Au particles and the support play an important role during the preparation [34]. The pH of the gold sol is about 6 and its zeta potential is negative [34], while the surface charge of MWCNT is slightly positive, considering that their pH_{pzc} is 7.0 [33]. Thus, there is an attractive interaction between the support surface and the gold sol, although the attraction forces between them seem to be relatively low since the solution only becomes colorless after 3-4 days, as mentioned in Section 4.2.1.5. Accordingly, apart from the LPRD method, the other techniques used in this work were able to originate catalysts with gold contents reasonably close to the expected loading.

Table 4.2 Characterization of the gold catalysts prepared by different methods on MWCNT and activities (TOFs) after 2 h of reaction.

Catalyst	Metal loading (%)	d_M (nm)	Au 4f _{7/2} BE (eV) ^a	Surface Au species	TOFx10 ⁻³
	[ICP]	[TEM]	[XPS]	[XPS]	(h ⁻¹)
Au IW/MWCNT	0.75 ± 0.05	23	83.9 (1.50)	Au ⁰	0
Au DIM/MWCNT	0.74 ± 0.03	6.5	84.0 (1.41)	Au ⁰	0.7
Au LPRD/MWCNT	0.40 ± 0.01	5.5	-	-	3.3
Au citric/MWCNT	0.76 ± 0.01	3.2	84.1 (1.69)	Au ⁰	n.d.
Auc/MWCNT	0.66 ± 0.02	5.0	84.2 (1.70)	Au ⁰	2.2

^a Half-width of XPS peaks inside round brackets.

4.3.1.4 Microscopy analyses

The gold average size (d_M) of the different catalysts is presented in Table 4.2. Figure 4.3 shows representative HAADF-STEM micrographs of the gold catalysts prepared by the different methods and their respective particle size distributions. It can be seen that small spherical metal particles are found for all the methods used. N₂ adsorption and microscopy results reveal that gold particles are deposited on the external walls of individual nanotubes and therefore they can contact easily with reactants. Additionally, it is worth to notice that the tips of carbon nanotubes are closed and thus their inner hollow cavities are not accessible. LPRD, citric and immobilization methods produced smaller particle sizes (from 0.5 to 11 nm) than DIM (1.5 – 50 nm, although in this case most of the particles have sizes between 1.5 and 17 nm), and especially than IW (0.5 – 65 nm). This latter technique does not remove chloride, which is known to cause poisoning and excessive sintering of the Au particles during thermal treatments. This is due to the ease with which gold and chloride ions combine to form bridges, favoring the growth of particles during heating [22]. However, heating steps are necessary to decompose the gold precursor and reduce the metal, and consequently activating the catalyst (in the case of the IW method). In the sol immobilization technique they are also required in order to achieve a strong metal/support interaction [18] (see Chapter 3). Therefore, chloride removal is a very important step in the preparation of well-dispersed gold catalysts.

In the DIM method, gold is deposited on the surface of MWCNT as $\text{Au}(\text{OH})_3$, i. e. without involving chloride as in the IW method. As a result, Cl is not associated with Au and is removed from the catalyst by washing. This explains the more homogeneous particle distribution when compared to the Au IW catalyst. However, as it can be seen in Figure 4.3, this catalyst still has a limited percentage of large gold crystallites. On the contrary, catalysts prepared by LPRD, citric or immobilization methods exhibit a relatively narrow distribution of gold nanoparticles, which have small average sizes (5.5 nm, 3.2 nm and 5.0 nm, respectively). In all these techniques, Cl largely remains in solution and is eliminated by extensive washing.

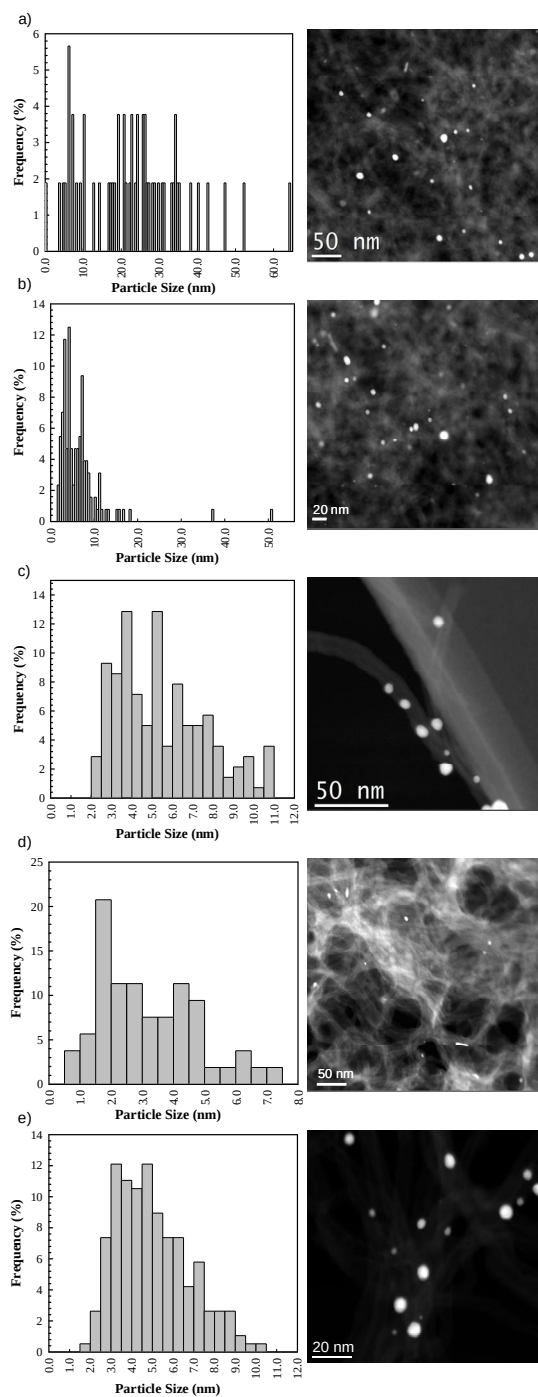


Figure 4.3 Particle size distributions and HAADF-STEM images of the Au catalysts prepared on MWCNT by the following methods: a) IW, b) DIM, c) LPRD, d) reduction with citric acid and e) sol immobilization.

4.3.1.5 XPS analyses

XPS analysis of the Au 4f region was carried out and the gold oxidation states obtained with the different preparation methods can be seen in Table 4.2, where the values of binding energies (BE) are referred to the Au 4f_{7/2} peak and the half-widths of the XPS peaks are given inside round brackets. XPS data confirmed the presence of Au in the metallic state in the case of Au IW/MWCNT, Au DIM/MWCNT, Au citric/MWCNT and Auc/MWCNT catalysts. Whereas Au IW/MWCNT, Au citric/MWCNT and Auc/MWCNT catalysts were directly reduced, respectively with hydrogen, citric acid and both NaBH₄ and hydrogen, in the DIM method the Na₂CO₃ added can dissociate and its reaction with water leads to the generation of hydroxyl ions, which can hydroxylate the Au³⁺ species of the gold precursor. Subsequently, Au³⁺ can be reduced to metallic gold by electron transfer from coordinated OH⁻ ions on the surface of the support [26]. This can explain the presence of only Au⁰ in the Au DIM/MWCNT catalyst. In the case of the Au LPRD/MWCNT catalyst, gold was not detected by this technique, most likely due to the low loading and the small particle sizes. However, it can not be excluded that gold could be located in the pores of the aggregates formed by interaction of isolated MWCNT and not in their surface.

4.3.2 Catalytic studies

4.3.2.1 Influence of the preparation method

In this part of the work, the effect of the preparation method on the activity and selectivity of gold catalysts was evaluated. For this purpose, gold was supported on MWCNT by several techniques as described before.

4.3.2.1.1 On the catalytic activity

Firstly, a glycerol oxidation blank experiment was carried out with the MWCNT support, and no glycerol conversion was detected.

Figure 4.4 shows the evolution of glycerol conversion in the presence of the gold catalysts prepared by different methods. Since the support is the same for all catalysts (MWCNT), the differences observed must be related to the metal phase. In fact, it is well known that the preparation method is crucial to obtain catalysts with small particle sizes. However, for gold, a high dispersion of the active phase on the support is not so easily achieved as with other metals [35-36]. Therefore, the

inactivity observed with Au IW/MWCNT is due to the low metal dispersion. As it was observed with activated carbons [31] (see Chapter 2), this method is not suitable to obtain active catalysts. Indeed, as already mentioned in Section 4.3.1, this classical method lead to a broad particle size distribution (Figure 4.3) mainly caused by the presence of chloride. The average gold particle size obtained with this catalyst (23 nm) appears to be too high for being active in glycerol oxidation, contrarily to what was observed for gold nanoparticles supported on carbon black. In this latter support, although small gold particle sizes (< 5 nm) have a higher activity, catalysts with gold crystallites as large as 42 nm have already shown a relevant activity in glycerol oxidation [9].

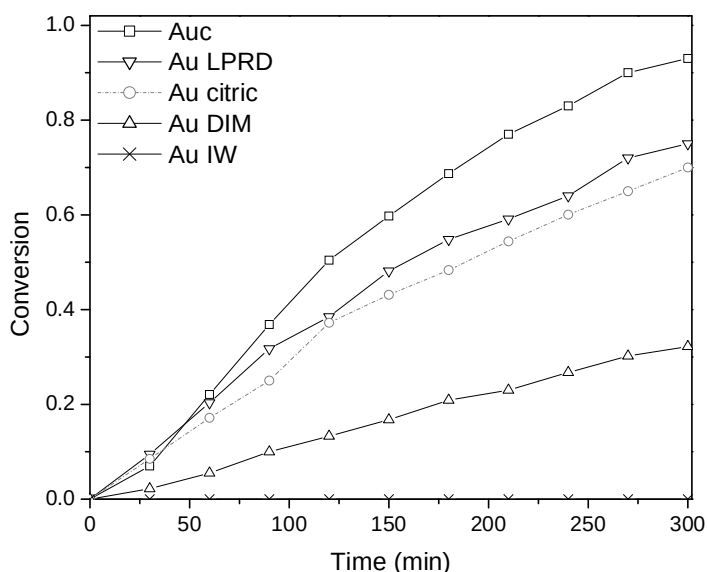


Figure 4.4 Influence of the preparation method on the performance of gold catalysts supported on MWCNT. Reaction conditions: 60 °C, $p_{O_2} = 3$ bar, 150 mL of glycerol 0.3 M, catalyst amount = 700 mg, NaOH/glycerol = 2 mol/mol.

DIM is a less usual method for gold impregnation, although the procedure is very similar to the incipient wetness technique. The main reason for the enhanced performance observed in the corresponding catalyst is related to the lower gold particle sizes obtained, when compared to the Au IW/MWCNT catalyst, once most of the gold crystallites are smaller than 17 nm (Figure 4.3). Thus, the mere fact of

depositing gold as gold hydroxide instead of gold chloride is sufficient to obtain an active catalyst.

Considering that the average crystallite size is an important parameter in reactions catalyzed by gold, other preparation methods were tested. It can be observed that Auc/MWCNT, Au LPRD/MWCNT and Au citric/MWCNT catalysts stand out relatively to the other two, due to the high performance achieved. In fact, all these samples have small average particle sizes and exhibit fairly homogeneous distributions of gold particles when compared with Au IW/MWCNT and Au DIM/MWCNT (Table 4.2 and Figure 4.3). As a result, it could be concluded that the catalytic performance can be dramatically increased by appropriate choice of the preparation method of carbon nanotubes supported gold catalysts.

The correct choice of the solvent to disperse carbon nanotubes is also very important. In the citric method, the use of 2-propanol is intended to enhance carbon nanotubes dispersibility and, according to Zanella et al. [27], avoid considerable agglomeration of gold over the nanotube bundles, which may occur when this method is carried out in the presence of water. Multi-walled carbon nanotubes nicely decorated with well-dispersed gold nanoparticles were successfully obtained (Figure 4.3 d). In fact, the smaller average gold particle size was obtained with this specific method (3.2 nm). However, although this method seems to be the most advantageous in terms of both gold particle size and gold loading (see Table 4.2), the Au citric/MWCNT catalyst does not exhibit the highest performance (Figure 4.4). In fact, a closer inspection of the multi-walled carbon nanotubes reveals that gold entered and filled some of them, as it can be in Figure 4.5. The presence of gold inside the nanotubes was confirmed by energy dispersive X-ray spectroscopy (EDS) and was observed with a high frequency. It should be noticed that these agglomerates of gold are not active and therefore correspond to a percentage of metal that does not contribute to the catalytic reaction, which means that the loading of active, available gold nanoparticles is actually lower than 0.76%. This phenomenon can explain the lower performance of this catalyst despite the presence of very well-dispersed gold nanoparticles. Ultrasonic cavitation has already been reported as an efficient way of breaking the regularity of the structure of carbon nanotubes [37]. In this particular case, an intense sonication may have led to the opening of some nanotubes. The possible importance of 2-propanol in this context should not be ignored too. It is important to note that this phenomenon was only observed with the Au citric/MWCNT catalyst.

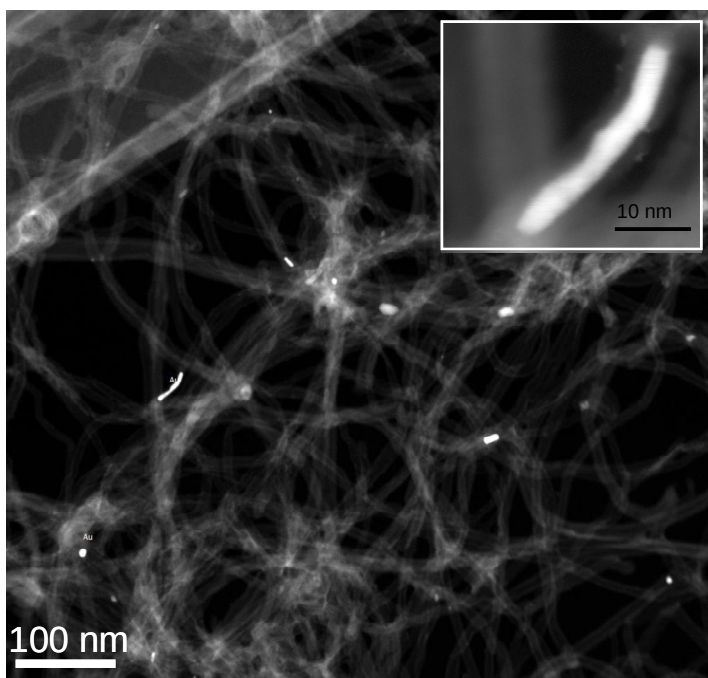


Figure 4.5 Image of the Au citric/MWCNT catalyst showing some gold inside carbon nanotubes.

The Au LPRD/ MWCNT catalyst shows a good performance; however, this method does not seem appropriate to prepare gold supported on MWCNT, since it leads to a significant loss of metal as described in Section 4.3.1. Nevertheless, considering the value of the relative error on the conversions measured (see Section 4.2.3), it may be concluded that performances of Au LPRD/MWCNT and Au citric/MWCNT are not too different.

The highest performance was obtained with the Auc catalyst (Figure 4.4). In the sol immobilization technique, gold particles are formed in the solution, and then transferred to the support. The protective agent (PVA) prevents efficiently the agglomeration in solution and during the supporting step by steric and polar stabilization of gold particles, leading to a narrow distribution of particle dimensions and to a low average size (5.0 nm). This catalyst presents a high turnover frequency (TOF) of $2.2 \times 10^3 \text{ h}^{-1}$ after 2 h of reaction, as shown in Table 4.2. This method was also described as being the most appropriate technique in order to obtain well-dispersed nanoparticles on activated carbon [19, 23]. Gil *et al.* also

confirmed recently that this preparation method is very efficient to prepare gold catalysts supported on carbon nanofibers [38].

It is important to note that the TOF value was not calculated for the Au citric/MWCNT catalyst, since this sample has a significant percentage of inactive gold and thus an overestimated content of active metal, as mentioned before.

4.3.2.1.2 On the selectivity

The effect of the preparation method on the distribution of products was also evaluated. The selectivities obtained in the presence of the different catalysts are compared at the same glycerol conversion ($X = 30\%$) and at constant reaction time (4 h) in Table 4.3.

Glyceric acid is the main reaction product for all catalysts tested in this work. However, besides the desired GLYCEA, glycolic acid (GLYCOA), tartronic acid (TARTA), formic acid (FORMA) and oxalic acid (OXALA) were also detected in the reaction medium. It should be noticed that the sum of the calculated selectivities is lower than 1 (see Table 4.3). Therefore, except for the Au DIM/MWCNT catalyst, complete oxidation to inorganic carbon, in the form CO_3^{2-} due to the high pH used, occurs in a fairly large extension (final selectivities of 15 - 20%). In fact, when comparing the selectivities obtained at the same conversion, it can be observed that only the catalyst with larger gold nanoparticles (Au DIM) does not promote complete oxidation. Nevertheless, no direct correlation between selectivity to GLYCEA and particle sizes was observed, and the higher selectivity to this compound was obtained with the Auc/MWCNT catalyst.

The selectivities towards C_3 compounds (GLYCEA and TARTA) but also C_2 (GLYCOA) decrease slightly at increasing conversion, whereas the amount of inorganic carbon increases. Therefore, the mineralization observed could be due to the oxidation of both TARTA to GLYCOA and TARTA to OXALA; in addition, the complete oxidation of OXALA can also occur (Figure 4.1). In fact, Dimitratos et al. [39] stated that tartronic acid would be expected to undergo relatively facile decarboxylation to give glycolic acid. The same would be feasible for oxalic acid, which is also a dicarboxylic acid. However, no oxidation of oxalic acid 0.01 M was observed even after 24 h using the Auc/MWCNT catalyst (experimental conditions: 2 M NaOH, 60°C, $p_{\text{O}_2} = 3$ bar, catalyst amount = 700 mg). Therefore, it seems that this product is fairly stable under the conditions tested, and it is not easily

mineralized. Moreover, under similar reaction conditions, a solution of tartronic acid 0.005 M was decarboxylated to form directly oxalic acid and CO_3^{2-} . The oxidation of a solution containing 0.05 M glycolic acid with the Auc/MWCNT catalyst (experimental conditions: 2 M NaOH, $T = 60^\circ\text{C}$, $p_{\text{O}_2} = 3$ bar, catalyst amount = 700 mg) confirmed that GLYCOA is converted into OXALA. However, the conversion rate observed was fairly low. In fact, only 6% of conversion was achieved after 24 h of reaction. Under similar conditions, Ketchie et al. [10] were unable to observe any GLYCOA conversion (after 3 h of reaction). These authors suggested that the higher acidity of the carboxylic group, when compared with the alcohol group, disfavors $-\text{OH}$ deprotonation. The verified pathways are highlighted in the general reaction scheme with blue arrows (see Figure 4.1). Therefore, it may be concluded that the main pathway for the formation of inorganic carbon is associated to the conversion of TARTA into oxalic acid. Nevertheless, it should be noticed that the mentioned experiments may not reproduce exactly the phenomena taking place during the glycerol oxidation process (e.g. different forms of activation of the molecules).

It is well known that more oxidized products, such as GLYCOA, are favoured by smaller gold particles [9, 19]. However, in the present work, a large amount of C_1 organic products are formed. In fact, a relatively high, constant and similar selectivity towards FORMA ($\approx 20\%$) was obtained, independently of the catalyst tested and thus of the gold particle size. A similar selectivity to this compound was reported by Prati et al. [16] when testing gold supported on carbon nanofibers. The selectivities achieved under alkaline conditions could be due to the combination of the nature of the catalysts, such as gold particle dimensions and type of support, and to the experimental conditions, specially the OH^- concentration. However, the active catalysts prepared have variable average particle sizes (from 3.2 nm for Au citric/MWCNT to 6.5 nm for Au DIM/MWCNT), and this does not lead to significant differences in the selectivity to FORMA (see Table 4.3), which makes to believe that the particular characteristics of the support used play an important role in the distribution of products. In fact, when testing gold supported on activated carbon, under the same reaction conditions, only a very limited amount of formic acid was detected (selectivity lower than 5%; see Chapter 3).

Table 4.3 Influence of the preparation method of Au catalysts supported on multi-walled carbon nanotubes on conversion and selectivities to glyceric acid (GLYCEA), glycolic acid (GLYCOA), tartronic acid (TARTA), formic acid (FORMA) and oxalic acid (OXALA).

X _{GLY} = 30%											
t = 240 min											
Catalyst	S _{GLYCEA}	S _{GLYCOA}	S _{TARTA}	S _{FORMA}	S _{OXALA}	X _{GLY}	S _{GLYCEA}	S _{GLYCOA}	S _{TARTA}	S _{FORMA}	S _{OXALA}
Au DIM/MWCNT	0.38	0.32	0.07	0.19	0.04	0.27	0.39	0.32	0.08	0.18	0.03
Au citric/MWCNT	0.29	0.25	0.17	0.20	0.04	0.60	0.23	0.21	0.14	0.20	0.04
Au LPRD/MWCNT	0.35	0.24	0.10	0.18	0.03	0.64	0.31	0.21	0.08	0.20	0.03
AuC/MWCNT	0.47	0.25	0.03	0.17	0.01	0.83	0.44	0.18	0.04	0.18	0.01

The origin of formic acid is still under discussion. It was suggested that formic acid could be obtained from GLYCEA [39]. According to these authors, GLYCEA could suffer a retro-aldol reaction to give directly glycolic acid as well as formaldehyde, which would then be easily oxidized to formic acid. In order to determine if FORMA is originated from glyceric acid, the oxidation of a 0.15 M solution of this compound was carried out with the Auc/MWCNT catalyst (experimental conditions: NaOH/GLYCEA = 2, 60 °C, p_{O_2} = 3 bar, catalyst amount = 700 mg). After 7 h of reaction, a conversion of 20% was obtained. GLYCEA was converted into tartronic and oxalic acids and inorganic carbon, but no formic acid was observed during the experiment. Therefore, the presence of FORMA is apparently not related to glyceric acid.

Another possible explanation corresponds to the formation of formic acid via the base catalyzed degradation of dihydroxyacetone or glyceraldehyde [1, 10, 40]. In this way, the high selectivity towards FORMA may support the presence of these intermediates, which are rapidly degraded due to the highly basic medium. This degradation was confirmed by adding 45 mL of NaOH 2 M to 150 mL of DIHA 0.3 M, even in the absence of catalyst. All dihydroxyacetone was almost instantly converted into a mixture of glyceric, glycolic, tartronic, oxalic and formic acids and other unidentified products. When Prati et al. [16] tested gold nanoparticles supported on carbon nanofibers in a base free medium, they were able to observe the formation of hydroxypyruvic acid, which can be obtained from the oxidation of dihydroxyacetone (see Figure 4.1). In fact, the oxidation of the secondary hydroxyl group of glycerol seems to be preferred under acidic conditions [1, 41]. Prati et al. [16] carried out the reaction at 100 °C without addition of base (at 60°C no conversion was detected), and no formation of dihydroxyacetone was observed, probably because high temperatures are also unfavorable to its stability [40]. In conclusion, the high FORMA selectivity observed in this work may be explained by the peculiar porous characteristic of MWCNTs, including the presence of large mesopores, which may favor the binding of glycerol over the gold surface in an adequate configuration for the initial formation of dihydroxyacetone by the direct oxidation of the secondary hydroxyl group. Accordingly, we suggest that glycerol can be initially oxidized to dihydroxyacetone; a fraction could be readily converted into formic acid due to the highly basic medium, and the remaining is further oxidized, via glyceraldehyde, to glyceric, tartronic, glycolic and oxalic acids and inorganic carbon (Figure 4.1).

Summarizing, among the various methods tested in this work, it can be concluded that the sol immobilization method is the most suitable technique to prepare gold supported on carbon nanotubes, since it allows a better use of gold, leading to a high activity and to the highest selectivity to the product of commercial interest (GLYCEA $\approx$ 45 %).

4.3.2.2 Influence of base concentration

As already mentioned, the distribution of products can be influenced by the pH of the reaction medium. Therefore, in an attempt to observe changes in that distribution, the base concentration was decreased. For this purpose, the evolution of the glycerol conversion was examined using different NaOH/glycerol ratios (0, 0.5, 1 and 2) in the presence of the Auc/MWCNT catalyst. The results of glycerol conversion are shown in Figure 4.6.

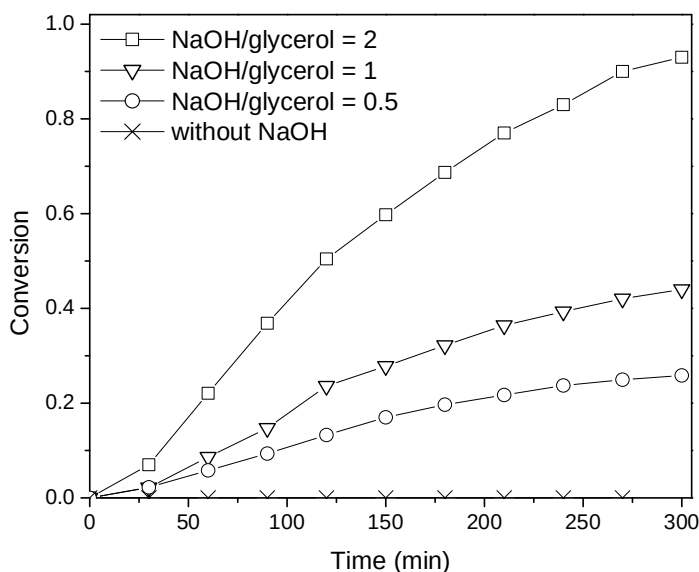


Figure 4.6 Influence of the NaOH/glycerol molar ratio on the glycerol conversion over the Auc/MWCNT catalyst. Reaction conditions: 60 °C, p_{O_2} = 3 bar, 150 mL of glycerol 0.3 M, catalyst amount = 700 mg.

It can be easily observed that the base concentration has a large influence on the reaction rate. In fact, as expected, no activity is observed when using gold catalysts

without addition of base. Moreover, the decrease of the base concentration leads to lower oxidation rates. In fact, Zope et al. [12] showed that glycerol oxidation is favored by high-pH conditions, since the hydroxide species adsorbed on gold are necessary to activate both C – H and O – H bonds of glycerol (also adsorbed on the surface). Moreover, it has been demonstrated that oxygen atoms incorporated into the reaction products were originated from hydroxide ions and not from molecular oxygen [12]. From our results (Figure 4.6), a first-order reaction relatively to the hydroxide concentration was determined in the range studied, which effectively suggests its direct participation in the reaction mechanism.

On the other hand, the decrease of the NaOH/glycerol ratio only influences (negatively) the reaction rate, and no significant effect was observed in the distribution of products. Nevertheless, it should be noticed that even when working with a NaOH/glycerol ratio of 0.5 the pH of the medium remains very high, far away from conditions that were reported as favoring the formation of dihydroxyacetone (acid medium) [40-41].

4.3.2.3 Reutilization experiments

We tested the Auc/MWCNT catalyst in four successive experiments. Each run was carried out under the standard conditions. The catalyst was recovered by filtering off the solution of each run after 5 h of reaction and reused in the subsequent experiment. Due to some losses during the filtration procedure, a limited amount of fresh catalyst (< 5% of the total weight) was also added to the reaction medium. The amount of gold eventually leached during reaction was measured in an atomic absorption spectrometer using the remaining solution after each run. Gold was not detected, and so the gold particles seem to interact strongly with the support, preventing leaching. However, the glycerol conversion after 4 h decreased from 83% to 80% in the second run and finally to 62% in the fourth run (Figure 4.7 a), as it was previously observed in a recent study with Au/AC catalysts [18] (see Chapter 3). Moreover, at the same glycerol conversion (50%), the selectivity to FORMA decreased slightly from 18% to 15% in the second run and was fairly stable in the subsequent runs, whereas the selectivity to GLYCEA was enhanced from 43% to 47% in the second run and finally to 52% in the last one (Figure 4.7 b). This may be due to the increase of the average Au particle size of the recovered catalyst after successive experiments, which not only favors the selectivity to GLYCEA, as mentioned in the literature [19], but also diminishes the catalytic performance. In

fact, it was observed by microscopy that the average size of metal particles in Auc/MWCNT increases from 5.0 nm (fresh catalyst) to 6.4 nm after two runs and to 9.4 nm after four successive experiments.

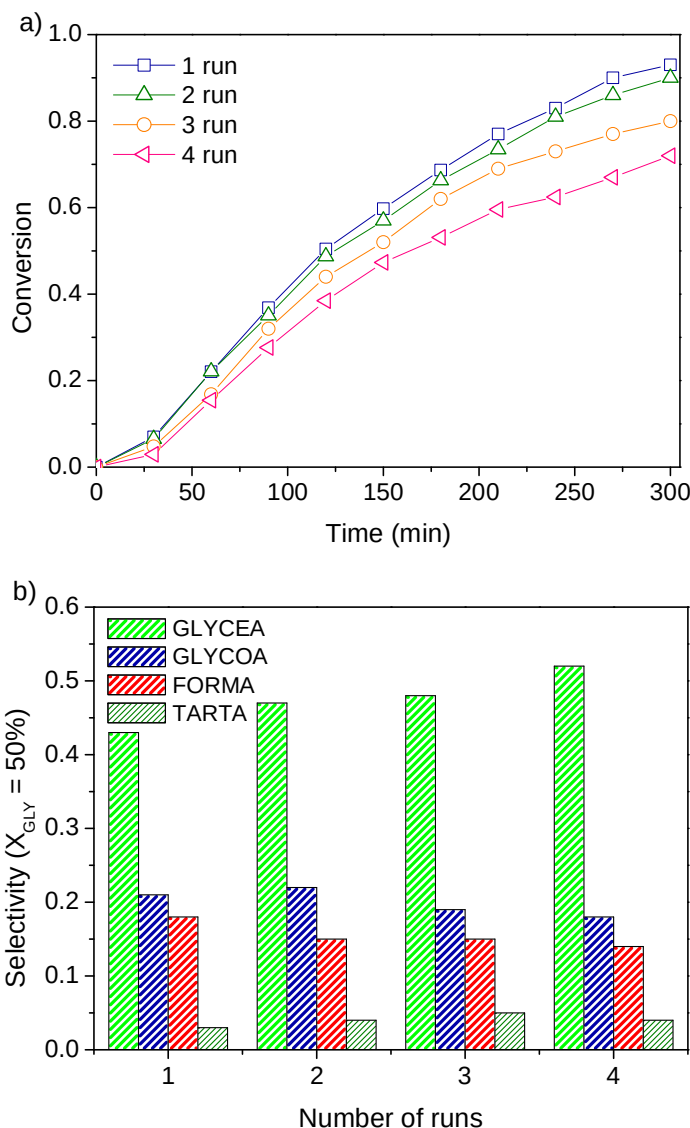


Figure 4.7 Successive experiments with the Auc/MWCNT catalyst: a) conversion of glycerol as function of time; b) selectivities to GLYCEA, GLYCOA, FORMA and TARTA obtained at $X_{GLY} = 50\%$ in each cycle. Reaction conditions: 60 °C, $p_{O_2} = 3$ bar, 150 mL of glycerol 0.3 M, catalyst amount = 700 mg, NaOH/glycerol = 2 mol/mol.

4.4 Conclusions

Gold was successfully supported on the surface of multi-walled carbon nanotubes by several methods. The performance of gold catalysts in glycerol oxidation greatly depends on the preparation technique used, which in some cases influences the distribution of particle sizes. The sol immobilization method was concluded to be the most suitable to prepare gold supported on carbon nanotubes, since it allows a better use of gold, leading to a high activity and to the highest selectivity to glyceric acid.

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Chapter 5

5 Selective oxidation of glycerol catalyzed by gold supported on multi-walled carbon nanotubes with different surface chemistries

Multi-walled carbon nanotubes with different levels of oxygenated groups on the surface were prepared and used as support for gold nanoparticles. These catalysts were tested in glycerol oxidation. It was concluded that the support plays an active and direct role in the catalytic performance. Gold catalysts are highly active and selective only when the support has a limited amount of oxygenated groups on the surface. These groups, mainly those with acid character, are prejudicial for the catalytic activity and favor the formation of over-oxidation products, such as glycolic acid. Accordingly, TOF values vary between 30 h^{-1} and 1870 h^{-1} depending on the support used. Catalysts supported on oxygen-free carbon nanotubes lead to selectivities towards glyceric acid in the range 50-60%, whereas only 40% was obtained with an oxygen-rich support.

5.1 Introduction

During the last decade, biodiesel has emerged as a viable renewable clean substitute for petroleum diesel and its production has been encouraged all over the world. Its conventional production is mainly based on the transesterification of vegetable oils and leads to a large amount of glycerol as an inevitable by-product. Adding value to this by-product is a necessary requisite for the commercial viability of biodiesel production [1-2]. Selective oxidation of glycerol leads to various valuable oxygenates (glyceric acid, tartronic acid and dihydroxyacetone) [2]. Nevertheless, the large number of functional groups of glycerol (three reactive hydroxyl groups) renders its catalytic selective oxidation particularly difficult. In fact, the selectivities obtained depend strongly on the reaction conditions and the nature of catalysts (type of metal, metal particle size and support).

Nano-sized gold particles supported on different carbon materials (e.g. carbon black, activated carbon and graphite) and oxides (TiO_2 , MgO and Al_2O_3) are active for the oxidation of glycerol but show very different performances, carbon supported gold catalysts being more active than most oxides supported catalysts [3-5]. However, even gold particles with comparable sizes show different activities depending on the nature of the carbon support [6]. Therefore, the activity is not only ruled by gold particle dimensions. In fact, an increasing number of studies suggest that textural and chemical properties of the support influence directly the performance of the process [7-9]. For instance, a strong effect of the activated carbon surface chemistry on the catalytic activity was observed previously, and it was reported that the surface oxygenated acid groups are particularly prejudicial [9] (see Chapter 3).

Recently, multi-walled carbon nanotubes (MWCNTs) have been drawing increasing attention for catalytic applications because of its unique features, such as high graphitization, high specific surface area, good physical and chemical stability and excellent electronic properties [10], which were reported as being important in the performance of gold catalysts [9] (see Chapter 3). In order to optimize the catalyst design, it is important to understand which factors can have an active role in the activity and/or selectivity of the catalysts. Among these factors, the influence of the surface chemical properties of the support, which can be easily modified by chemical and thermal treatments, is worthy of investigation.

Therefore, MWCNTs differing mainly in their surface chemistries were prepared and used as support for gold nanoparticles. Subsequently, the prepared catalysts were

evaluated in the liquid phase glycerol oxidation, in order to investigate the possible role of the mentioned properties on the catalytic performance.

5.2 Experimental

5.2.1 Preparation of modified MWCNT samples

A commercial Nanocyl 3100 MWCNT sample was used as the starting material for this study. According to the supplier, these nanotubes have an average diameter of 9.5 nm, an average length of 1.5 μm and a carbon purity higher than 95%. In a recent work, it was shown that this material presents average inner and outer diameters of 4 and 10 nm, respectively [11]. Moreover, these multi-walled carbon nanotubes contain impurities, mainly residual metallic particles coming from the production process, namely Fe and Co (0.19% of Fe and 0.07% of Co), but also sulfur (0.14%) and traces of Al (0.03%) [11]. The material has a very limited amount of surface oxygenated groups [12] (see Chapter 4). Therefore, in order to evaluate how catalyst performance correlates with the concentration of those groups, the original support was submitted to different chemical and thermal treatments in order to obtain materials with different surface chemistries. It is worth to notice that, since the main goal of this work is to study the role of the surface chemistry, it is important to maintain the original textural properties as far as possible.

5.2.1.1 Oxidation treatment

In order to produce carbon nanotubes with a large amount of oxygen-containing surface groups, the original sample (MWCNT_0) was oxidized with concentrated nitric acid in the liquid phase [9-10]. For that purpose, 300 mL of HNO_3 6 M and 4 g of MWCNT_0 were introduced into a Pyrex round-bottom flask connected to a condenser. The acid solution was heated to boiling temperature during 3 h. The oxidized material was subsequently washed with distilled water until neutral pH and dried in an oven at 110 $^\circ\text{C}$ for 24 h (sample MWCNT_1). In order to evaluate the level of structural modifications of the carbon nanotubes, which can occur due to the drastic oxidative treatment performed under very acidic conditions [10], the same procedure was repeated using HNO_3 7 M (sample MWCNT_2).

5.2.1.2 Thermal treatments

It is important that the starting material used for the thermal treatments presents a large amount of surface groups, in order to produce different carbon nanotubes with a successively lower acid character, by selectively removing those groups at increasing temperatures [13-15]. Then, sample MWCNT₁ was used as the starting material for these treatments. The selection of this sample, instead of MWCNT₂, is explained later in Section 5.3.1.1.

About 4 g of support MWCNT₁ was placed in a fused-silica tubular reactor, heated to 400 °C at 10 °C/min under nitrogen flow (50 cm³ (STP) min⁻¹), and kept at this temperature for 30 min. The sample was cooled to room temperature under the same atmosphere and then treated under dry air flow (50 cm³ (STP) min⁻¹) at room temperature for 1 h, originating the sample MWCNT_{1tt400}. The final treatment in air is intended to stabilize the surface chemistry of the materials [13]. Sample MWCNT₁ was also submitted to a similar thermal treatment at 900 °C (sample MWCNT_{1tt900}).

5.2.2 Catalysts preparation

Gold catalysts with a nominal metal loading of 1 wt% were prepared on the original and modified MWCNTs using HAuCl₄·3H₂O as precursor. Gold on carbon nanotubes were synthesized via the sol immobilization technique using polyvinyl alcohol (PVA) as protective agent and NaBH₄ as reducing agent [16]. This preparation technique was recently reported as being the most efficient in order to prepared Au/MWCNT catalysts for glycerol oxidation [12] (see Chapter 4). Briefly, HAuCl₄·3H₂O (35.1 mg) was dissolved in 690 ml of H₂O, and PVA was added (1.6 ml, 0.2 wt %) under stirring. PVA is necessary to stabilize the nanostructured colloidal gold and to prevent agglomeration. NaBH₄ (4 ml, 0.1 M) was added to the yellow solution under vigorous magnetic stirring. The resulting sol was ruby-red in color. Within a few minutes of sol generation, the colloid was immobilized by adding the support under fast stirring. After some days, the solution becomes colorless and the suspension was filtered. The catalyst was washed thoroughly with distilled water until the filtrate was free of chloride (checked by the AgNO₃ test) and dried at 110 °C for 24 h. The organic scaffold was removed from the support by heat treatment under nitrogen flow for 3 h at 350 °C and then the catalyst was activated by reduction under hydrogen flow for 3 h also at 350 °C.

5.2.3 Characterization techniques

Supports were characterized by N₂ adsorption at -196 °C in a NOVA Quantachrome Instruments apparatus. Pore size distributions were obtained by using the non-local density functional theory (NLDFT), applying the kernel file provided by Quantachrome's data reduction software, where a cylindrical-pore model is assumed.

The determination of oxygenated surface functional groups of multi-walled carbon nanotube samples was performed by temperature programmed desorption – mass spectrometry (TPD-MS) [14-15]. CO and CO₂ TPD spectra were obtained with a fully automated AMI-200 equipment (Altamira Instruments). Briefly, the sample (150 mg) was placed in a U-shaped quartz tube inside an electrical furnace and subjected to a 5 °C min⁻¹ linear temperature increase up to 1100 °C under helium flow (25 cm³ (STP) min⁻¹). A quadrupole mass spectrometer (Dymaxion 200, Ametek) was used to monitor CO and CO₂ signals. For quantification of the CO and CO₂ released, calibration of these gases was carried out at the end of the analysis.

The gold loading of the prepared catalysts was determined in duplicate by inductively coupled plasma-optical emission spectroscopy (ICP-OES) in an external laboratory, using a PerkinElmer Optima 4300 DV spectrometer.

Electron micrographs of samples were obtained using a JEOL2010F instrument (equipped with an energy dispersive X-ray spectroscopy detector), with 0.19 nm spatial resolution at Scherzer defocus conditions. High Angel Annular Dark Field – Scanning Transmission Electron Microscopy (HAADF-STEM) images were acquired with the same equipment, and were used for the determination of gold nanoparticles size distributions.

5.2.4 Catalytic experiments

Typically, a NaOH solution (2 M) and the gold catalyst (700 mg) were added to a 0.3 M aqueous solution of glycerol (total volume 195 mL; NaOH/glycerol molar ratio = 2) under stirring at 1000 rpm. The reactor was pressurized with nitrogen at 3 bar. After heating under this atmosphere to 60 °C, the reaction was initiated by switching from inert gas to oxygen (3 bar).

The reaction was monitored by taking samples (0.5 mL) for analysis at regular time intervals. The quantitative analysis of these samples was carried out by high performance liquid chromatography (HPLC). The chromatograph (Elite LaChrom

HITACHI) was equipped with an ultraviolet (210 nm) and a refractive index detector in series. Products were identified by comparison with standard samples.

Activities were evaluated by calculation of turnover frequencies (TOF), which values were obtained from the amount of glycerol converted at time t divided by the reaction time and the total amount of gold active sites on the surface, obtained from ICP and microscopy analyses, i.e.:

$$TOF = \frac{\text{mole of glycerol converted at } t}{t \times \text{mole of gold active sites}} \quad (5.1)$$

The amount of gold active sites was calculated from:

$$\frac{6 y n_s W_{cat}}{d_M \rho N} \quad (5.2)$$

where y and d_M are the gold weight fraction (from ICP) and the average particle diameter (from microscopy), respectively; ρ and n_s are the density of gold (19.30 g cm^{-3}) and the number of gold atoms per unit of area ($1.15 \times 10^{19} \text{ m}^{-2}$), respectively; W_{cat} is the catalyst mass used in the experiments (0.7 g); and N is the Avogadro number.

The selectivities (S_i) into the different products i at time t were calculated as:

$$S_i = \frac{C_i}{\nu_i C_0 X} \quad (5.3)$$

where C_i is the concentration of product i (mol L^{-1}), C_0 is the initial concentration of glycerol (mol L^{-1}), X is the glycerol conversion and ν_i corresponds to the moles of i produced per mole of glycerol consumed, according to the stoichiometry.

5.3 Results and discussion

5.3.1 Characterization of supports and catalysts

5.3.1.1 Textural properties

The samples show N_2 adsorption isotherms of type II, typical of non-porous materials. The BET surface areas (S_{BET}) of the different supports and of catalyst Au/MWCNT₀ are presented in Table 5.1.

Table 5.1 BET surface areas of supports and a gold catalyst.

Sample	S_{BET} ($\text{m}^2 \text{g}^{-1}$)
MWCNT ₀	285
MWCNT ₁	360
MWCNT ₂	396
MWCNT _{1tt400}	342
MWCNT _{1tt900}	362
Au/MWCNT ₀	288

It can be observed that the oxidative treatment with nitric acid leads to an increase of the surface area. This occurs because this oxidative process opens up the endcaps of carbon nanotubes and create sidewall openings [10]. Moreover, as expected, the increase of the BET surface area is more significant in the case of MWCNT₂ than MWCNT₁ due to the higher HNO₃ concentration used. The pore size distributions confirm the previous observations (Figure 5.1). In fact, it is clearly observed that a new contribution corresponding to small mesopore widths appears in the pore size distributions of the samples subject to oxidation (MWCNT₁, MWCNT₂, MWCNT_{1tt400} and MWCNT_{1tt900}), which may be explained by the opening of the nanotube tips. In addition, sample MWCNT₂ presents a higher fraction of this smaller mesopores when compared with MWCNT₁. Accordingly, it seems that the oxidative treatment with HNO₃ 7 M (sample MWCNT₂) leads to a higher level of modification in textural properties. Therefore, the oxidative treatment with nitric acid 6 M was chosen in order to still introduce a significant amount of oxygenated groups on MWCNT₀, but avoiding considerable structural modifications. This was also observed by TEM analyses (Figure 5.2). In fact, whereas nanotube tips were opened and internal caps removed in most of the carbon nanotubes of sample MWCNT₂ (Figure 5.2 c), only slight damages on the tube caps were observed for some of the nanotubes in sample MWCNT₁ (Figure 5.2 b). A residual metallic particle coming from the production process can be observed in the inner cavity of the original carbon nanotube presented in Figure 5.2 a.

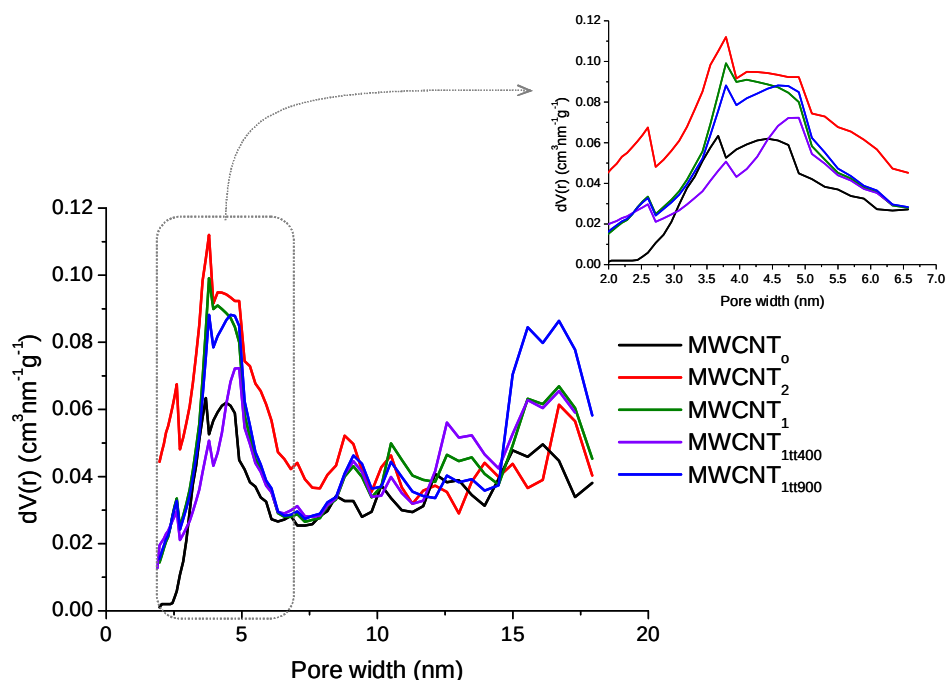


Figure 5.1 Pore size distributions of original and modified MWCNTs (obtained by NLDFT).

The pore size distributions show that most of the porosity observed in the different supports corresponds to large mesopores, which result from the free space between individual carbon nanotubes in the respective bundles. Additionally, it can be observed that the surface area of the Au/MWCNT_0 catalyst is quite similar to the respective unloaded support (Table 5.1). Therefore, it was assumed that the textural properties of modified supports and the corresponding supported gold catalysts are not also significantly different.

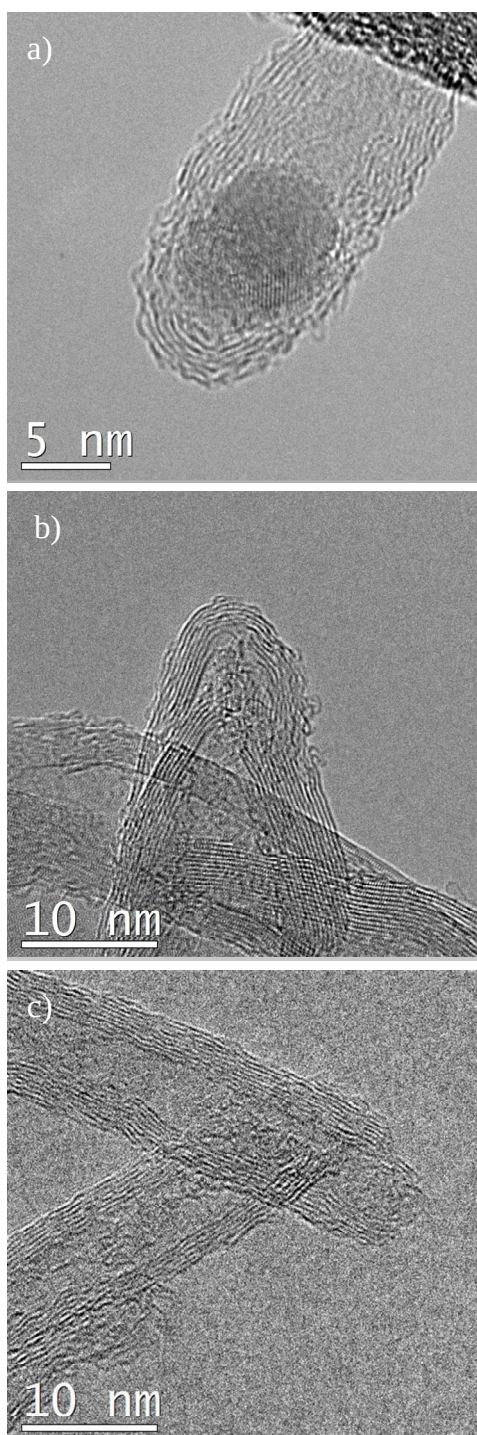


Figure 5.2 TEM micrographs at high magnification of a) MWCNT₀, b) MWCNT₁, c) MWCNT₂.

5.3.1.2 Surface chemistry characterization

TPD-MS was used in this study to evaluate the surface chemistry of the different multi-walled carbon nanotubes. The decomposition under heating of the oxygen containing groups on the surface of carbon materials into CO and CO₂ at different temperatures is well established in the literature [14-15]. Accordingly, it is possible to identify and estimate the amounts of the oxygenated groups on a given material by TPD experiments. In fact, it was reported that CO₂ results from the decomposition of carboxylic acids at low temperatures (150 - 450 °C) and from lactones at high temperatures (600 - 800 °C); carboxylic anhydrides originate both CO and CO₂ (400 – 650 °C); groups such as phenols (600 – 800 °C), and carbonyls/quinones (750 – 1000 °C) originate CO [14-15]. Consequently, an increase in the amount of surface oxygen is evidenced by the increase of CO and CO₂ amounts released. Treatments with HNO₃ are known to originate materials with large amounts of surface acidic groups, mainly carboxylic acids and, to a smaller extent, lactones, anhydrides and phenol groups [14].

The ultimate goal of the present work is the study of the relationship between the surface chemical characteristics of MWCNTs and the performance of Au/MWCNT catalysts in glycerol oxidation. For that purpose, a set of modified MWCNTs with different levels of acidity/basicity was prepared as shown before. Figures 5.3 a) and 5.3 b) show, respectively, the CO and CO₂ TPD spectra of the commercial multi-walled carbon nanotubes as received (MWCNT₀) and the modified samples. In order to quantify the oxygen-containing groups, the deconvolution method proposed in the literature was applied [14-15] (Figure 5.4). A multiple Gaussian function was used for fitting each spectrum. CO₂ spectra were decomposed into three component peaks, the first corresponding to carboxylic acid groups, the second to anhydrides and the third to lactones. Similarly, the CO profiles of the samples were decomposed into three component peaks corresponding to anhydrides, phenols and carbonyl-quinones groups. This deconvolution procedure proved to fit the data quite well. It should be noticed that deconvolution of the CO₂ spectrum of the MWCNT_{1tt900} support was not done, since the corresponding groups are absent in this sample.

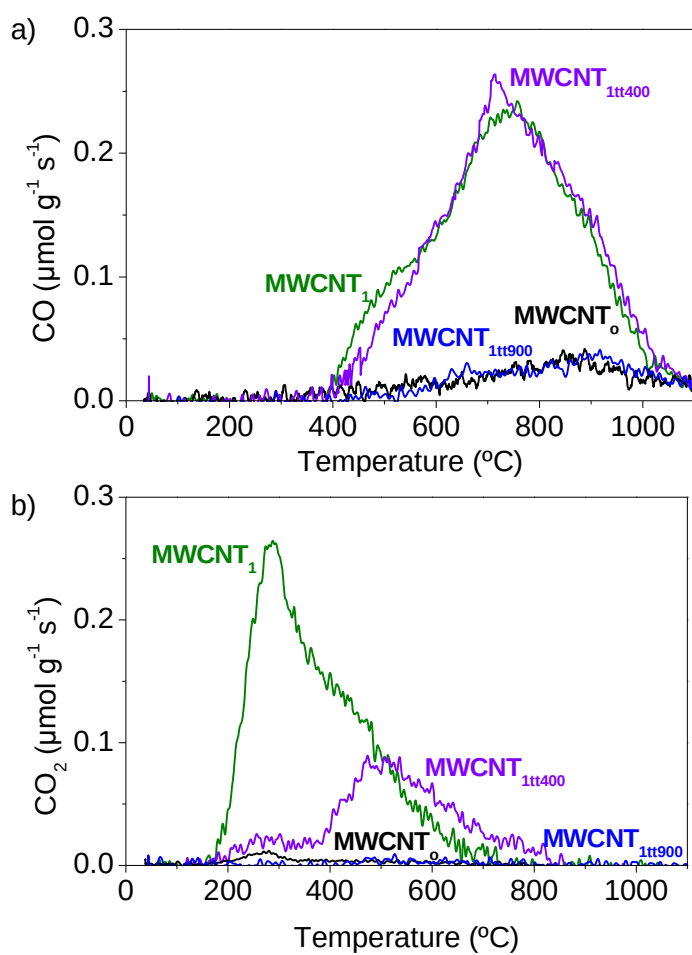


Figure 5.3 TPD spectra of the different supports: a) CO; b) CO₂.

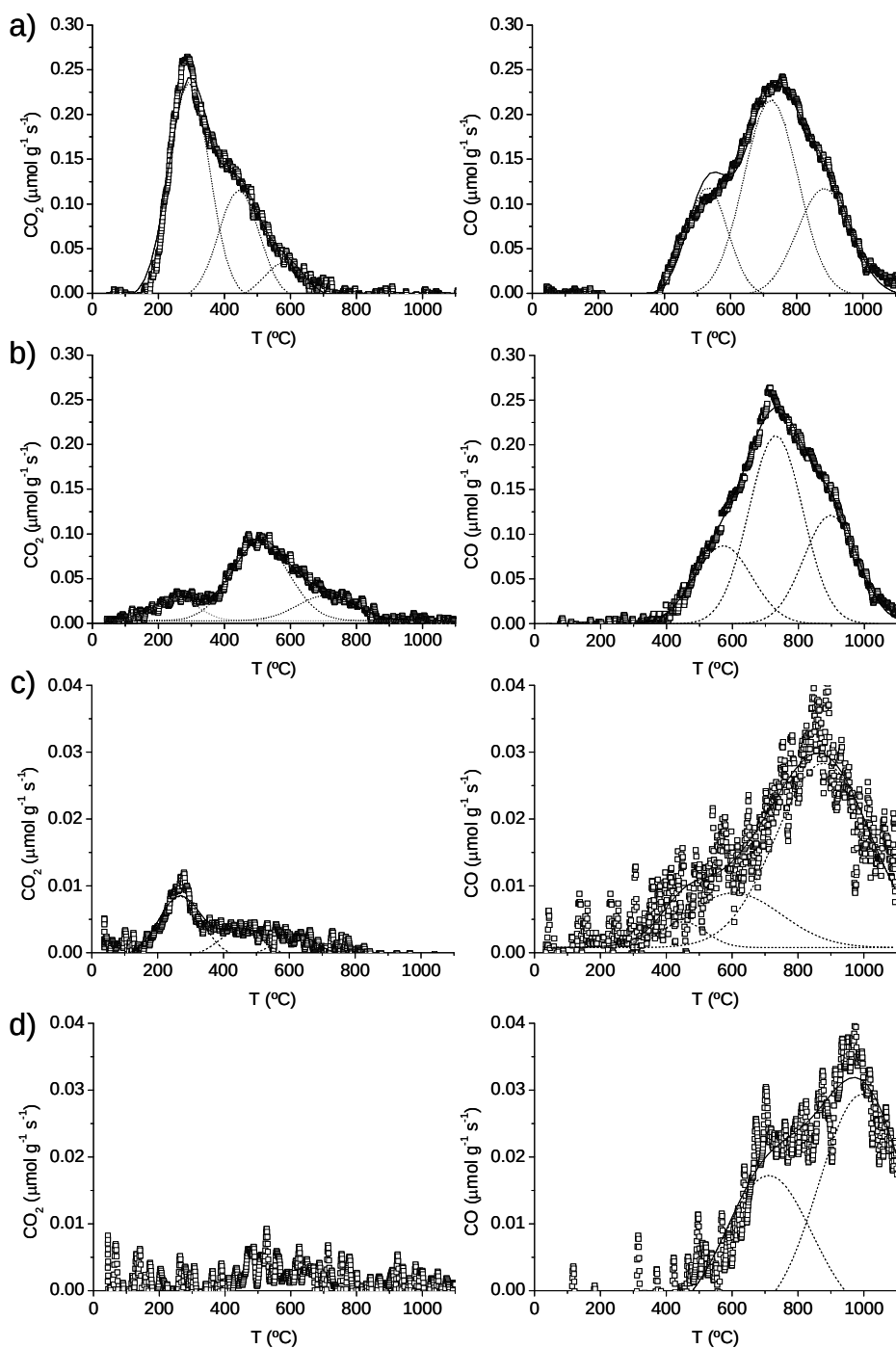


Figure 5.4 Deconvolutions of TPD spectra using a multiple Gaussian function: a) MWCNT₁; b) MWCNT_{1tt400}; c) MWCNT₀; d) MWCNT_{1tt900} (□ experimental data; --- individual peaks; – sum of individual peaks).

The amounts of surface groups calculated from the areas of the deconvoluted peaks are presented in Table 5.2. The total amounts of CO and CO₂ released were calculated from the corresponding TPD spectra and are also presented in Table 5.2. The results indicate that sample MWCNT₀ contains a very limited amount of surface oxygen groups, especially of CO₂ releasing groups. On the other hand, it can be observed that HNO₃ oxidation of the original support led to drastic increases in both CO and CO₂ releasing groups. In particular, the very high total CO₂ obtained for MWCNT₁ results from the dominant contribution of carboxylic acids and, in less extent, anhydrides and lactones. The liquid phase oxidation also increased the amount of CO evolved at high temperatures (phenol and carbonyl/quinone groups). In summary, this sample has the highest amount of oxygen-containing surface groups. Due to the introduction of the mentioned oxygen-containing groups with acidic properties, namely carboxylic acids (see Table 5.2), the MWCNT₁ support has acidic and hydrophilic characteristics [17]. The thermal treatment at 400 °C (sample MWCNT_{1tt400}) does not change significantly the CO profile when compared to MWCNT₁ (see Figure 5.3). In fact, similar amounts of carboxylic anhydrides, lactones, phenols and carbonyls/quinones are present on these supports (Table 5.2). The major difference between MWCNT₁ and MWCNT_{1tt400} is the almost complete removal of the carboxylic acid groups from the support (see Table 5.2), which leads to a decrease of the acidity. Finally, as it can be seen in the TPD spectra of MWCNT_{1tt900}, the CO₂ and CO releasing groups were almost completely removed in this sample. Accordingly, no carboxylic acids and anhydrides or lactones were detected (Table 5.2). It should be noticed that samples MWCNT_{1tt900} and MWCNT₀ have very low and similar amounts of oxygen-containing groups, especially acidic groups (Table 5.2). Therefore, thermal treatments selectively remove the oxygenated surface groups, originating materials with progressively lower oxygen contents.

Table 5.2 Amounts of the different oxygenated surface groups present on MWCNT supports (obtained by deconvolution of CO₂ and CO spectra) and total amounts of CO, CO₂ and oxygen released.

Sample	CO spectra										Surface oxygen (wt%)
	Carboxylic acids ($\mu\text{mol g}^{-1}$)	Carboxylic anhydrides ($\mu\text{mol g}^{-1}$)	Lactones ($\mu\text{mol g}^{-1}$)	Phenols ($\mu\text{mol g}^{-1}$)	Carbonyls / Quinones ($\mu\text{mol g}^{-1}$)	CO ($\mu\text{mol g}^{-1}$)	CO ₂ ($\mu\text{mol g}^{-1}$)	CO ₂ /CO	O ($\mu\text{mol g}^{-1}$)		
MWCNT ₀	18	8	6	119	35	162	32	0.20	226		0.36
MWCNT ₁	446	223	75	537	294	1054	744	0.71	2542		4.07
MWCNT _{1tt400}	48	228	74	517	298	1043	350	0.34	1743		2.79
MWCNT _{1tt900}	0	0	0	86	134	220	0	0	220		0.35

Moreover, considering the acidic nature of the CO₂ releasing groups, the ratio CO₂/CO can be taken as a measure of the surface acidity (high values) or basicity (low values). The sample oxidized with nitric acid has the highest amount of surface oxygen (Table 5.2). As expected, this sample also presents the highest ratio CO₂/CO, indicating that this is the most acidic sample. The acid character of the samples decreases by increasing the thermal treatment temperature, because the acid groups are removed at lower temperatures than neutral and basic groups. Therefore, sample MWCNT_{1tt900} has basic properties, whereas MWCNT₀ is neutral [18]. According to Leon y Leon et al. [19], this basic character is mainly due to the electron rich oxygen-free sites located on the carbon basal planes.

The results in this section show that carbon nanotubes with very different surface chemistries were successfully prepared; they were used as support for gold catalysts.

5.3.1.3 ICP analyses

Table 5.3 summarizes the metal loadings of the catalysts. The gold content obtained by ICP analysis is lower than the nominal, which indicates that a fraction of gold present in the aqueous solution was not deposited on the supports. With the exception of one of the samples, the prepared catalysts present a similar gold content of approximately 0.7%. Despite the chemical inertness and very regular structure of carbon nanotubes, gold was successfully anchored without any pretreatment of the surface (Au/MWCNT₀). Nevertheless, it should be noticed that the creation of oxygen-containing surface groups, which can act as anchoring sites, possibly enhances the interaction between the gold sols and the support (Au/MWCNT₁), in accordance with some authors [10, 20]. On the other hand, a slight decrease of the metal content can be observed in the case of Au/MWCNT_{1tt400}. Moreover, it was not possible to support gold on sample MWCNT₁ previously subjected to thermal treatment at 600 °C (this support only has lactone, phenol and carbonyl/quinone groups [18]). In fact, the liquid phase remained red even after several weeks of contacting with that sample during the immobilization procedure, which indicates that the deposition of gold on this support was not achieved. Therefore, it seems that acid groups like carboxylic acids, which are present in MWCNT₁ but not in MWCNT_{1tt400}, and carboxylic anhydrides (present in the surface of both materials) favor the interaction between gold sols and the support, whereas neutral and/or basic groups like lactones, phenols and

carbonyls/quinones are inadequate for that purpose. In fact, carboxylic anhydrides are still present in MWCNT_{1tt400} and the immobilization of gold on this support was possible. However, when these groups were removed but neutral and basic oxygenated groups remained on the surface (MWCNT₁ thermally treated at 600 °C), the deposition of gold was not achieved. It was only when lactones, phenols and carbonyls/quinones were almost completely removed that immobilization was efficient again (support MWCNT_{1tt900}). It should be noticed that MWCNT₀ and MWCNT_{1tt900} have a low concentration of surface functional groups, and in these cases mainly surface defects can be considered as anchoring sites [10].

Table 5.3 Metal content, average crystallite size and activities (TOFs) after 2 h of reaction for the studied catalysts.

Catalyst	Loading (%wt)	d_M (nm)	TOF (h ⁻¹)
Au/MWCNT ₀	0.66 ± 0.02	5.2 ± 1.8	1740
Au/MWCNT ₁	0.75 ± 0.10	9.1 ± 4.3	30
Au/MWCNT _{1tt400}	0.52 ± 0.08	8.8 ± 4.7	780
Au/MWCNT _{1tt900}	0.71 ± 0.03	5.5 ± 3.6	1870

5.3.1.4 Microscopy analyses

The average gold crystallite sizes of the studied catalysts are presented in Table 5.3. The same impregnation procedure was used in an attempt to obtain gold catalysts with similar particle sizes, independently of the support used. This was effectively achieved for Au/MWCNT₀ and Au/MWCNT_{1tt900}, which have fairly low and similar average gold nanoparticle sizes. On the other hand, Au/MWCNT₁ and Au/MWCNT_{1tt400} catalysts have a comparable but higher average particle size. As preformed gold nanoparticles are identically generated in all cases, the differences observed between catalysts should be related to the nature and/or concentration of the surface functional groups present; in fact, the presence of oxygen-containing surface groups leads to poorer metal dispersion. According to the literature, the surface oxygenated groups are considered to act as anchoring sites that interact with precursors, improving the metal dispersion [10, 20]. However, some of these functional groups present on the surface of multi-walled carbon nanotubes are

easily decomposed by heating even at low temperatures. This occurs with most carboxylic acid groups, which already decompose at temperatures below 350 °C, as it can be seen in the pertinent TPD spectra (Figure 5.3). These groups are present not only in MWCNT₁ but also (in much lower amounts) in MWCNT_{1tt400}. Therefore, during the heat-treatment and reducing steps used in the preparation of catalysts Au/MWCNT₁ and Au/MWCNT_{1tt400}, some groups are thermally decomposed and the gold particles that are anchored to them may have a low stability and could be prone to sintering. This can possibly explain why Au/MWCNT₁ and Au/MWCNT_{1tt400} catalysts have larger metallic particles than Au/MWCNT₀ and Au/MWCNT_{1tt900}, since these samples, contrarily to the former, do not contain oxygenated groups able to decompose at low temperatures during the preparation step, as it can be seen in the corresponding TPD spectra (Figure 5.3). This is in accordance with that was reported by Prati et al. [8]; these authors observed that the acidic groups, introduced by an oxidative treatment, were less efficient than the basic groups in stabilizing gold particle sizes.

In addition, it should be also noticed that gold particles supported on MWCNT₁ and MWCNT_{1tt400} have dimensions relatively widely distributed (see standard deviation indicated in Table 5.3) and, particularly in Au/MWCNT_{1tt400}, several nanotubes were found without metallic nanoparticles, whereas they concentrate in some areas.

5.3.2 Catalytic studies

The main goal of this work is the study of the relationship between the surface chemical characteristics of multi-walled carbon nanotubes and the performance in the oxidation of glycerol of the respective gold supported catalysts. In this section the influence on the activity and selectivity are discussed separately.

5.3.2.1 Influence of the surface chemistry of the support on the catalytic activity

Figure 5.5 shows the evolution of glycerol conversion in the presence of the gold catalysts prepared on different supports. Large differences are observed between catalysts. Au/MWCNT₀ and Au/MWCNT_{1tt900} show a good and similar performance, allowing about 75% glycerol conversion after 4 h. On the contrary, Au/MWCNT_{1tt400} and mainly Au/MWCNT₁ have a low efficiency. In fact, even after 5 h of reaction, a

very limited conversion of approximately only 6% is achieved in the presence of the latter catalyst.

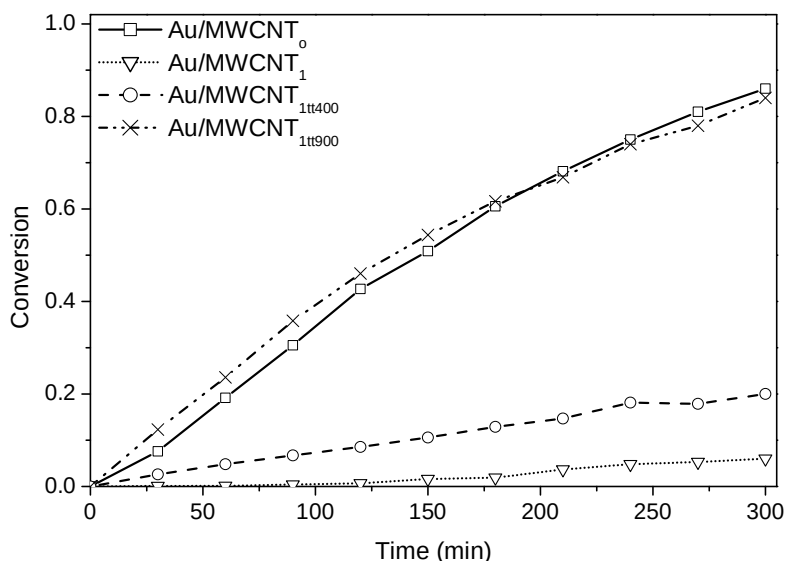


Figure 5.5 Conversion of glycerol vs. time for the different catalysts. Reaction conditions: 60 °C, $p_{O_2} = 3$ bar, 150 mL 0.3 M of glycerol solution, catalyst amount = 700 mg, NaOH/glycerol = 2 mol/mol.

It is well known that the performance of catalysts is sensitive to gold nanoparticle sizes, smaller particles being more active than bigger ones [2, 21]. Therefore, the order of performances obtained was expected: $Au/MWCNT_0 \approx Au/MWCNT_{1tt900} > Au/MWCNT_{1tt400} > Au/MWCNT_1$, as it is in agreement with the microscopy analyses. Nevertheless, the differences observed between catalysts seem to be too important to be exclusively related to nanoparticle dimensions. For instance, $Au/MWCNT_1$ and $Au/MWCNT_{1tt400}$ have fairly similar particle sizes (see Table 5.3) and the former shows a much lower performance, implying that the surface chemistry plays a significant role on these results.

In addition, a gold catalyst supported on $MWCNT_0$ was tested in four successive experiments under the same reaction conditions (60 °C, $p_{O_2} = 3$ bar, 150 mL of glycerol 0.3 M, catalyst amount = 700 mg, NaOH/glycerol = 2 mol/mol). It was observed that the glycerol conversion decreased from 83% after 4 h in the first run to 62% in the fourth run due to the increase of the average Au particle size from 5.0

nm (this fresh sample had a slightly lower particle size than the Au/MWCNT₀ catalyst reported in the present work) to 9.4 nm after four successive experiments (see Chapter 4). These experiments confirm the influence of the gold dispersion on the catalytic performance, but also allow concluding that even with a metal average size of 9.4 nm the catalyst shows a fairly high performance. Therefore, the poor efficiency of the Au/MWCNT₁ catalyst, in which gold nanoparticles have a similar average particle size (9.1 nm), cannot be explained only by the relatively low gold dispersion. Since no important differences were observed in gold average particle sizes, the disparities in performances between the gold catalyst supported on MWCNT₀ after four experiments and Au/MWCNT₁ must be mainly related to the differences in support chemical properties. The same can be concluded for the Au/MWCNT_{1tt400}, which has an even lower average particle size (8.8 nm), but only allows 18% glycerol conversion after 4 h of reaction.

In order to take into consideration the variation of particle size among the samples, as well as the different metal loadings, TOF values obtained after 2 h of reaction were calculated for each catalyst (see Table 5.3). The Au/MWCNT₁ catalyst has a high content of oxygenated functional groups and only a residual activity. When carboxylic acid groups were removed from the surface (sample Au/MWCNT_{1tt400}) a significant enhancement was observed. In fact, TOF increases from 30 h⁻¹ (sample Au/MWCNT₁) to 780 h⁻¹. Finally, catalysts with a low content of oxygenated surface groups, such as Au/MWCNT₀ and Au/MWCNT_{1tt900} present high activities (1740 h⁻¹ and 1870 h⁻¹, respectively). Summarizing, as the amount of oxygenated groups on the support surface gradually decreases, the catalytic activity increases. More particularly, the improvement observed for the Au/MWCNT_{1tt400} catalyst (when compared with Au/MWCNT₁) seems to be almost exclusively related to the removal of carboxylic acid groups from the surface (see Table 5.2). This suggests that surface oxygenated groups, mainly those with acid nature, are prejudicial for the activity of catalysts in glycerol oxidation.

These results are in agreement with those obtained before with gold supported on activated carbon [9] (see Chapter 3). According to a recent proposed mechanism, the hydroxide species adsorbed over gold facilitate the activation of glycerol but lead to the addition of electrons to the metal surface [22]. It was suggested that basic oxygen-free carbon supports, which promote the mobility of electrons, lead to more active catalysts by the enhancement of the regeneration of hydroxide ions involved in the glycerol oxidation mechanism [9] (see Chapter 3). In fact, the presence of delocalized π -electrons on the surface of non-oxygenated carbon

supports, such as MWCNT_0 and $\text{MWCNT}_{1\text{t}900}$, leads to a high electronic mobility, while oxygen-containing groups (electron-withdrawing groups) decrease the electron density and the electrical conductivity (MWCNT_1 and $\text{MWCNT}_{1\text{t}400}$) [23-24]. Therefore, in order to obtain highly active gold catalysts, oxygen-free carbon supports should be preferred.

5.3.2.2 Influence of the surface chemistry of the support on the selectivities

The effect of the support surface chemistry on the distribution of products was also evaluated. The selectivities vary slightly during the reaction for all the catalysts tested. Therefore, the selectivities obtained in the presence of the more active catalysts are compared at the same glycerol conversion ($X = 20\%$) and at constant reaction time (4 h) in Table 5.4. The products detected were glyceric acid (GLYCEA), glycolic acid (GLYCOA), formic acid (FORMA), tartaric acid (TARTA) and oxalic acid (OXALA), the latter in a very limited amount. It should be noticed that at increasing conversions, the sum of the selectivities becomes lower than 1, since complete oxidation to inorganic carbon (in the form CO_3^{2-} due to the high pH used) occurs. As an illustrative example, the evolution of the selectivities in the presence of the $\text{Au/MWCNT}_{1\text{t}900}$ catalyst is depicted in Figure 5.6. For this catalyst, as well as for Au/MWCNT_0 , the selectivity toward CO_3^{2-} reaches 10% at approximately 60% glycerol conversion and remains fairly constant afterwards.

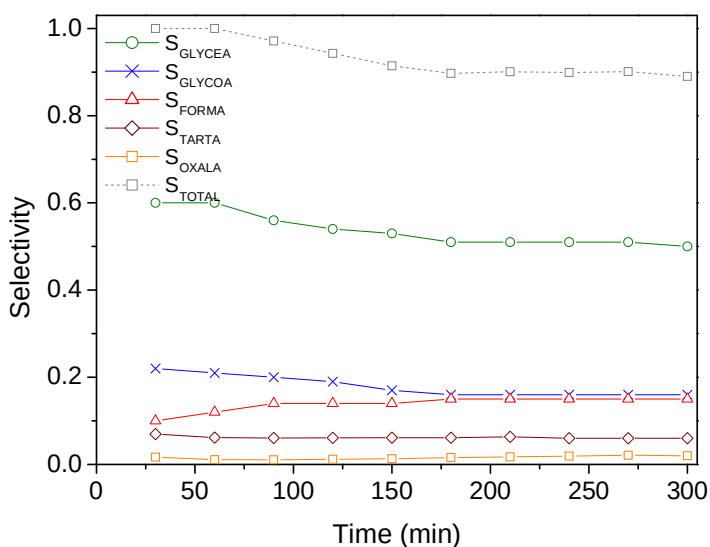


Figure 5.6 Selectivities towards the products of reaction and their sum (S_{TOTAL}) in the presence of the $\text{Au/MWCNT}_{1\text{tt}900}$ catalyst. Reaction conditions: 60 °C, $p_{\text{O}_2} = 3$ bar, 150 mL of 0.3 M glycerol solution, catalyst amount = 700 mg, $\text{NaOH/glycerol} = 2$ mol/mol.

Some differences in selectivities can be observed in Table 5.4. Whereas glyceric acid is the major product obtained with catalysts Au/MWCNT_0 and $\text{Au/MWCNT}_{1\text{tt}900}$ (52% and 60%, respectively, at $X_{\text{GLY}} = 20\%$), $\text{Au/MWCNT}_{1\text{tt}400}$ promote the formation of glyceric acid and glycolic acid almost in the same way (40% and 38%, respectively). It is noticeable that the highest selectivity to the product of commercial interest is obtained with the most basic catalyst ($\text{Au/MWCNT}_{1\text{tt}900}$). As already seen, Au/MWCNT_0 and $\text{Au/MWCNT}_{1\text{tt}900}$ catalysts have similar and smaller particle sizes than $\text{Au/MWCNT}_{1\text{tt}400}$. Some studies [6, 25] show that smaller particles led to more oxidized products, such as glycolic acid, which is the trend opposite to that observed here. In fact, the factors ruling selectivities are not yet completely established; the selectivities are not directly correlated to the size of the nanoparticles. Instead, it seems that the explanation for the distributions of products obtained could be due to the combination of several factors, including gold nanoparticle dimensions and support properties [7-8, 26]. Therefore, the differences observed between catalysts could be explained by the different surface chemistries of the supports.

Table 5.4 Selectivities of GLYCEA, GLYCOA, TARTA, FORMA and OXALA (S_{GLYCEA} , S_{GLYCOA} , S_{TARTA} , S_{FORMA} , S_{OXALA}) for Au catalysts supported on multi-walled carbon nanotubes with different surface chemistries.

Catalyst	$X_{\text{GLY}} = 20\%$					$t = 240 \text{ min}$					
	S_{GLYCEA}	S_{GLYCOA}	S_{TARTA}	S_{FORMA}	S_{OXALA}	X_{GLY}	S_{GLYCEA}	S_{GLYCOA}	S_{TARTA}	S_{FORMA}	S_{OXALA}
Au/MWCNT ₀	0.52	0.28	0.02	0.17	0.01	0.75	0.49	0.20	0.04	0.16	0.01
Au/MWCNT ₁₁₄₀₀	0.40	0.38	0.01	0.20	0.01	0.18	0.40	0.38	0.01	0.20	0.01
Au/MWCNT ₁₁₈₉₀₀	0.60	0.21	0.06	0.12	0.01	0.74	0.51	0.16	0.06	0.15	0.02

Oxygen-free and hydrophobic supports (MWCNT₀ and MWCNT_{1tt900}) lead to a higher selectivity to GLYCEA than the support containing a high concentration of oxygenated groups (MWCNT_{1tt400}). This is in agreement with the results reported recently by Prati et al. [8], when using gold supported on commercial carbon nanofibers treated at different temperatures with NH₃, in order to produce N-containing groups on the surface. These authors concluded that catalysts with hydrophobic surfaces enhanced the selectivity towards primary oxidation products, probably due to a lower H₂O₂ formation during the reaction, which is believed to be responsible for the C-C cleavage of glyceric acid [21]. In fact, according to Zope et al. [22], the formation of hydrogen peroxide on the metal surface is achieved by the following mechanism:



where * represents a site on the catalyst surface. Accordingly, MWCNT₀ and MWCNT_{1tt900}, which are more hydrophobic, have less tendency to interact with water and therefore lead to a lower amount of H₂O₂ than MWCNT_{1tt400}. This can explain the higher selectivities toward glyceric acid obtained in the present study with the basic supports. In conclusion, besides catalytic activity, the presence of oxygenated groups also influences the distribution of products.

5.4 Conclusions

The role of the support on the catalytic performance of gold catalysts supported on multi-walled carbon nanotubes was investigated. A set of modified MWCNTs with different levels of oxygenated functional groups on the surface, was prepared and characterized. It was concluded that the support has an active role in the catalytic activity and selectivity. Oxygen-free carbon nanotubes lead to highly active gold catalysts, whereas supports with significant amounts of surface oxygenated groups, mainly those with acid nature, are unfavorable. In addition to the negative influence on the catalytic activity, oxygen-rich supports also promote the formation of glycolic acid, which is a normally unwanted over-oxidized by-product, in detriment of glyceric acid. Therefore, in the design of gold catalysts for glycerol oxidation, special attention should be given to the nature and amount of oxygenated groups present on the carbon support surface and, more generally, to its surface chemistry.

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Chapter 6

6 Glycerol oxidation with gold supported on carbon xerogels: tuning selectivities by varying mesopore sizes

Two carbon xerogels (CX) with different pore size distributions were prepared by the conventional approach (condensation of resorcinol and formaldehyde). The key variable to control those sizes is the pH of the aqueous solution. Gold nanoparticles were supported on the prepared CXs by the sol immobilization method and tested in the selective oxidation of glycerol, with the main purpose of evaluating the influence of the textural properties on the activity and selectivity. Mesopore sizes of the support have a strong effect on the distribution of products: narrow mesopores favor the oxidation towards glyceric acid, whereas wide pores enhance the formation of formic acid possibly via dihydroxyacetone. Additionally, the selectivity results obtained with carbon xerogels were compared with those achieved with other carbon supports (activated carbon and multi-walled carbon nanotubes) and a general trend was observed. Therefore, it seems that the distribution of products can be controlled by the adequate choice of the support. For this purpose, carbon xerogel is a promising material since its pore size can be easily modified in a controllable way during the preparation stage.

6.1 Introduction

Over the last decade, biodiesel has emerged as a viable clean fuel. Nevertheless, its increasing global demand has created a major surplus of glycerol [1]. The valorization of this highly versatile molecule is a research area that has received tremendous attention in recent years, as glycerol is nontoxic, easily available, biodegradable and a potential starting material for numerous value-added chemicals [1-2].

Liquid phase catalytic oxidation is a promising route to convert glycerol into useful compounds, due to the significant industrial importance of some products, which are valuable intermediates in the synthesis of fine chemicals [1-2]. However, due to the high functionality of glycerol, a complex reaction pathway exists [2-4].

Platinum, palladium and rhodium catalysts have been described as highly active for the oxidation of glycerol in the liquid phase [5-8] (see Chapter 2). However, catalysts that are based on these metals deactivated at increasing reaction time due to oxygen poisoning [9-10]. On the other hand, gold has a better resistance, allowing for the use of higher oxygen partial pressures [11-12] (see Chapter 3). Nano-sized gold particles supported on different carbon materials (e.g. carbon black, activated carbon and graphite) and oxides (TiO_2 , MgO and Al_2O_3) are active for the oxidation of glycerol but show very different performances, carbon supported gold catalysts being more active than most oxides supported catalysts [11, 13-14]. Moreover, an increasing number of studies suggest that textural and chemical properties of the support influence directly the selectivity of the process [15-17]. In Chapter 4, it was reported that the use of multi-walled carbon nanotubes as support for Au nanoparticles lead to a relatively high selectivity to formic acid, which can be originated from the formation of dihydroxyacetone; on the other hand, an activated carbon supported gold catalyst, with similar metal content and average particle size, promotes the formation of glyceric acid. It was suggested that the peculiar porous characteristics of MWCNTs, including the presence of large mesopores, may favor the oxidation towards dihydroxyacetone due to a different adsorption mode; dihydroxyacetone is able to be rapidly degraded because of the highly basic medium. The same explanation was proposed by Prati *et al.* [17] when testing gold supported on carbon nanofibers for the oxidation of glycerol under base-free conditions. Therefore, it seems that the support textural properties, namely mesopore sizes, can be a key factor in order to tune the selectivity of catalysts. For the purpose of studying this subject, carbon xerogel (CX) is a promising material since its pore size distribution can be easily modified in a controllable way [18]. Until

now, this material has not been investigated as support for gold nanoparticles in the scope of the liquid phase oxidation of glycerol. However, these polymer derived mesoporous carbon materials have been drawing increasing attention for catalytic applications since they possess high surface area, high porosity, high stability in acid and basic media, open pore network and controllable pore size [18]. A suitable support material is crucial for good catalytic activity and stability. Carbon materials are widely used since they present advantages as high stability in acidic and basic media. This feature is primordial in gold catalyzed glycerol oxidation, since reactions are performed in a high pH medium [16, 19-20]. Moreover, carbon supports offer the possibility of recovering precious metals by burning off spent catalysts. Therefore, CXs possess excellent characteristics as catalyst support.

In the present work, two mesoporous carbon xerogels having different pore sizes were prepared and used as support in the preparation of gold catalysts. Then, the prepared catalysts were evaluated in the liquid phase glycerol oxidation, in order to investigate the possible role of the mentioned property on the catalytic performance.

6.2 Experimental

6.2.1 Preparation procedures

Two carbon xerogels differing in their textural properties were synthesized. Subsequently, gold was supported on these materials by the sol immobilization method [21].

6.2.1.1 Preparation of carbon xerogels

Two carbon xerogels were prepared by the sol-gel condensation of resorcinol and formaldehyde at two different pHs (5.5 and 6.0), and subsequent carbonization of the dried gels, according to Job et al. [18].

In this procedure, 30 g of resorcinol were dissolved in 57 mL of distilled water under magnetic stirring. After dissolution the pH was about 3; then it was adjusted to a value close to the chosen one by the addition of 2 M NaOH aqueous solution. Subsequently, 40 mL of formaldehyde solution (37 wt%, containing 10-15 wt% MeOH) were added to the resorcinol solution under continuous stirring. The final pH value was then adjusted by addition of diluted sodium hydroxide solution (0.5 M). Stirring continued for 90 min, and then it was stopped, the magnetic bar was

removed, and the content was left for 3 days in a shaker at 85 °C to perform the gelation. The hard gel formed was then ground and water was removed by drying in an air oven for a period of 7 days. The temperature was increased stepwise from 60 to 150 °C as following: 1st day at 60 °C, 2nd day at 80 °C, 3rd day at 100 °C, 4th day at 120 °C, and from 5th to 7th day at 150 °C. Mesoporous carbon samples were obtained by pyrolysis of the dried gels under nitrogen flow (100 cm³ min⁻¹, STP) at 800 °C in a tubular furnace. The heating program included the following sequential steps: 1) ramp at 2 °C min⁻¹ to 150 °C and hold for 60 min; (2) ramp at 2 °C min⁻¹ to 400 °C and hold for 60 min; (3) ramp at 2 °C min⁻¹ to 600 °C and hold for 60 min; (4) ramp at 2 °C min⁻¹ to 800 °C and hold for 360 min; (5) slow cooling to room temperature. A shrinkage corresponding to approximately 50 wt% was observed after carbonization.

The carbon xerogels obtained were designated as 5CX (sol-gel processing at pH 6.0) and 20CX (sol-gel processing at pH 5.5). The numbers 5 and 20 correspond to the most frequent mesopore diameters of the samples (in nm), as it can be seen in Section 3.1.1. These materials were ground to a particle diameter between 0.1 and 0.3 mm before use, in order to avoid mass transfer resistance effects and facilitate the accessibility of reactants to gold active sites.

6.2.1.2 Preparation of catalysts

Catalyst samples were prepared via the sol immobilization technique, using polyvinyl alcohol (PVA) as protective agent and NaBH₄ as reducing agent [21]. Briefly, HAuCl₄·3H₂O (35.1 mg) was dissolved in 690 mL of H₂O, and PVA was added (1.6 mL, 0.2 wt %) under stirring. Then, NaBH₄ (4 mL, 0.1 M) was introduced in the yellow solution under vigorous magnetic stirring, leading to the generation of a ruby-red metallic sol. After a few minutes, the carbon xerogel was added under fast stirring. The amount of support was calculated in order to have a final gold loading of 1 wt% in the catalyst. When the solution became colorless, the suspension was filtered. The catalyst was washed thoroughly with distilled water until the filtrate was free of chloride (checked by the AgNO₃ test) and dried at 110 °C for 24 h.

The organic scaffold was removed by heat treatment under nitrogen flow for 3 h at 350 °C, and then the catalyst was activated by reduction under hydrogen flow for 3 h also at 350 °C.

This method typically provides nanoparticle sizes around 5 - 6 nm both in activated carbon and carbon nanotubes [12, 21-22] (see also Chapter 3 and Chapter 4).

6.2.2 Characterization

Catalysts and supports were characterized by N₂ adsorption at -196 °C in a NOVA Quantachrome Instruments apparatus. BET surface area (S_{BET}), mesopore surface area (S_{meso}) and micropore volume (V_{micro}) were calculated using the BET equation and the t-method, respectively. Pore size distributions were obtained from the desorption branch of the isotherm using the Barrett, Joyner and Halenda (BJH) method.

The determination of oxygenated surface functional groups was performed by temperature programmed desorption – mass spectrometry (TPD-MS) [23-24]. CO and CO₂ TPD spectra were obtained with a fully automated AMI-200 equipment (Altamira Instruments). In a typical experiment, the sample (150 mg) was placed in a U-shaped quartz tube inside an electrical furnace and subjected to a 5 °C min⁻¹ linear temperature increase up to 1100 °C under helium flow (25 cm³ (STP) min⁻¹). A quadrupole mass spectrometer (Dymaxion 200, Ametek) was used to monitor CO and CO₂ signals. For quantification of the CO and CO₂ released, calibration of these gases was carried out at the end of the analysis.

The gold loading of the prepared catalysts was determined in duplicate by inductively coupled plasma-optical emission spectroscopy (ICP-OES) in an external laboratory (CACTI Vigo, University of Vigo), using a PerkinElmer Optima 4300 DV spectrometer.

Electron micrographs of samples were obtained at CACTI Vigo, University of Vigo, using a JEOL 2010F instrument. Size distributions were determined by the measurement of more than 200 nanoparticles and the average diameter was calculated by $d_M = \sum d_i n_i / \sum n_i$, where n_i is the number of particles with diameter d_i .

6.2.3 Catalytic experiments

In standard tests, a NaOH solution and the gold catalyst (700 mg) were added to a 0.3 M aqueous solution of glycerol (total volume 195 mL; NaOH/glycerol molar ratio = 2) under stirring at 1000 rpm. The reactor was pressurized with nitrogen at 3 bar.

After heating to 60 °C under this atmosphere, the reaction was initiated by switching from inert gas to oxygen (3 bar). The stirring speed of 1000 rpm was selected on the basis of preliminary experiments, which showed that external mass transfer limitations were overcome in these conditions.

The reaction was monitored by taking samples (0.5 mL) for analysis at regular time intervals. The quantitative analysis of the mixtures was carried out by high performance liquid chromatography (HPLC). The chromatograph (Elite LaChrom HITACHI) is equipped with an ultraviolet (210 nm) and a refractive index detector in series. Compounds were identified by comparison with standard samples and concentrations were calculated using calibration curves previously determined.

The selectivities (S_i) into the different products i at time t were calculated as:

$$S_i = \frac{C_i}{\nu_i \cdot C_0 \cdot X} \quad (6.1)$$

where C_i is the concentration of product i (mol L^{-1}), C_0 is the initial concentration of glycerol (mol L^{-1}), X is the glycerol conversion and ν_i corresponds to the moles of i produced per mol of glycerol consumed, according to the stoichiometry.

6.3 Results and discussion

6.3.1 Characterization of supports and catalysts

The main goal of the present work is to study the relationship between the textural properties of the carbon xerogels, namely the respective mesopore sizes, and the catalytic performance of gold supported on these materials for glycerol oxidation. The key variable that controls those properties is the pH of the resorcinol-formaldehyde aqueous solution [18].

6.3.1.1 Textural properties

The textural characterization of the supports and the Au/20CX catalyst is presented in Table 6.1; pore size distributions profiles are depicted in Figure 6.1. The BET surface area of the Au/20CX catalyst decreased only slightly compared to the unloaded carbon xerogel. Therefore, it was assumed that the textural properties of the supported gold catalysts are not significantly different from the corresponding supports.

Table 6.1 Textural properties of supports and catalyst Au/20CX.

Sample	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	S_{meso} ($\text{m}^2 \text{g}^{-1}$)	V_{micro} ($\text{cm}^3 \text{g}^{-1}$)	d_{BJH} (nm) ^a	V_{BJH} (cm^3/g) ^b
5CX	663	217	0.215	5	0.31
20CX	683	272	0.195	20	0.62
Au/20CX	632	220	0.171	19	0.62
AC	1025	180	0.361	4	0.24
MWCNT	285	285	0	32	1.6

^a d_{BJH} : most frequent mesopore diameter (obtained from the desorption branch of the isotherm using the Barrett, Joyner and Halenda (BJH) method).

^b V_{BJH} : pore volume calculated from the BJH method (corresponds to pore widths between about 4 and 90 nm).

It is evident from Table 6.1 and Figure 6.1 that the two pHs used in sol-gel processing resulted in carbon samples with significantly different textural properties. Although the BET area is fairly similar for both samples, the 20CX support has a higher mesoporous area than 5CX, as well as a much higher average pore diameter. This difference was attributed to the lower pH used during the sol-gel processing of the parent gel (5.5 compared to 6.0 in the case of 5CX). This trend between pH and average pore size is in agreement with the observation of Job et al. [18], who reported that the average pore diameter of the final carbon material rapidly decreased with the increase of the pH used in the preparation of the parent gel. Moreover, according to literature data [25], the increase of the concentration of base in the sol-gel processing leads to carbon samples with lower mesopore volume, which also matches our results. Therefore, two carbon xerogels differing mainly in the average pore size were successfully prepared by controlling the initial pH. Additionally, it should be noticed that the use of supports with large mesopores may be favorable, particularly for liquid phase reactions, as they decrease mass transfer limitations, principally compared to the traditional microporous activated carbons.

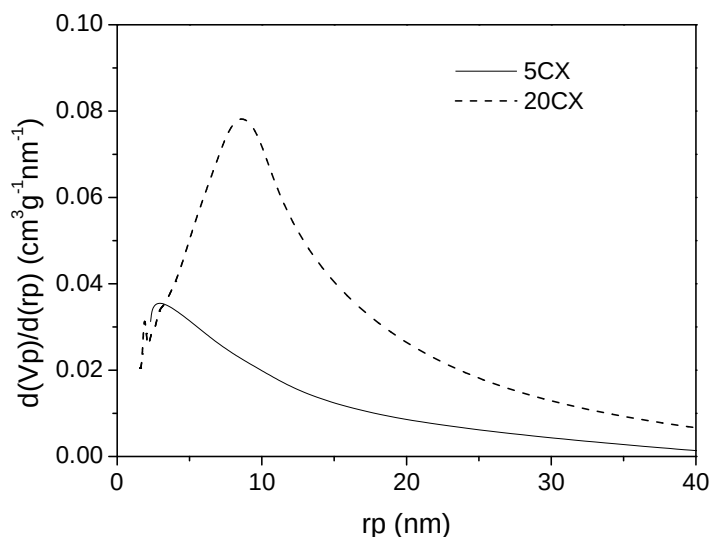


Figure 6.1 Pore size distribution obtained by the BJH method.

6.3.1.2 Surface chemistry characterization

The surface oxygen groups present on the carbon xerogels were characterized by TPD. In this technique, the total amount of the various oxygenated surface groups on carbon materials can be determined, since these groups are decomposed upon heating by releasing CO and/or CO₂ at different temperature ranges. Consequently, a high amount of surface oxygen is evidenced by a large release of CO and CO₂. Therefore, it is possible to identify and estimate the amount of the oxygenated groups on a given material by TPD experiments [23-24].

Both samples show similar surface chemistries, containing only a limited concentration of oxygenated functional groups on their surface corresponding to oxygen contents of 268 $\mu\text{mol g}^{-1}$ (5CX) and 435 $\mu\text{mol g}^{-1}$ (20CX). For comparison, results obtained with moderately and highly oxidized carbon materials can be found elsewhere [12, 23-24, 26]. Therefore, it can be concluded that both supports used in this work have a very small amount of oxygenated groups on their surface, which is important since this may influence the performance of catalysts. In fact, in a recent work, it was demonstrated that the presence of surface oxygenated acid groups significantly lowers the activity of gold supported on activated carbon [12] (see Chapter 3 and also Chapter 5). The surface chemistry results obtained are in agreement with those reported by Job et al. [18], who did not find any detectable

absorption peak corresponding to oxygenated groups in carbon xerogels prepared in the same way as our samples, using infra-red spectroscopy.

6.3.1.3 Microscopy and ICP analyses

Gold nanoparticles were successfully supported on the two carbon xerogels by the sol immobilisation method. Representative HRTEM images were collected in order to get information about metal particle size distributions (Figure 6.2). It can be seen that small spherical metal particles are found for both catalysts prepared. The gold average particle size (d_M) and standard deviation of the studied catalysts are presented in Table 6.2. The protective PVA prevents efficiently the agglomeration in solution and during the supporting step by steric and polar stabilization of gold particles, leading to narrow distributions of particle sizes and to low average diameters (< 5.0 nm) [27]. In fact, the gold-sol method has the advantage of predetermining the size of the gold particle, which is maintained during the immobilization step. Accordingly, similar average particle sizes were obtained for both catalysts prepared, independently of the different textural properties of the supports.

Table 6.2 Average crystallite size and metal content of the studied catalysts.

Catalyst	Metal loading (wt%)	d_M (nm)	Standard deviation
	[ICP]	[TEM]	(nm)
Au/5CX	0.62 ± 0.02	4.6	1.5
Au/20CX	0.59 ± 0.02	4.7	1.7

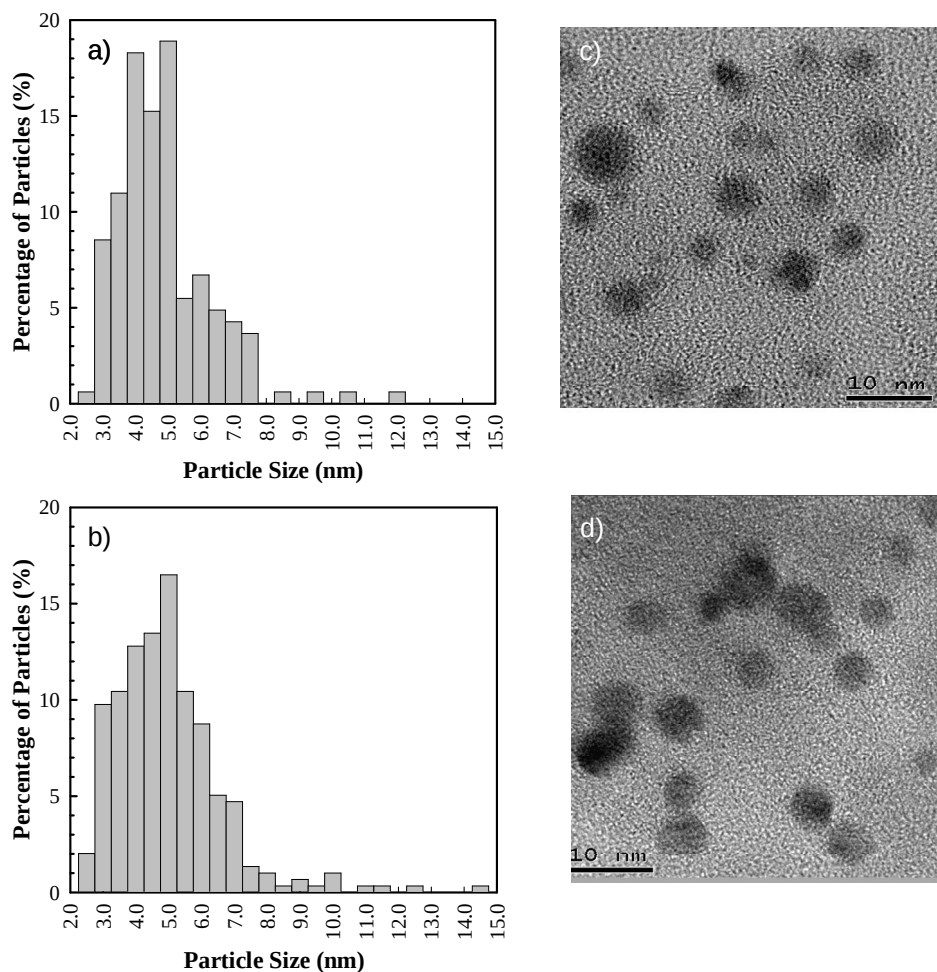


Figure 6.2 Gold particle size distributions on a) 5CX, b) 20CX and HRTEM images of c) Au/5CX and d) Au/20CX.

Table 6.2 also shows the metal loadings of the catalysts. The gold content obtained by ICP analysis is lower than the nominal, which indicates that a fraction of gold present in the aqueous solution was not deposited on the supports. In fact, it should be noticed that the adsorption of gold sols on the carbon xerogels was difficult, particularly when concentrations of gold in solution become low, resulting in fairly high immobilization times (approximately 3 weeks). A similar situation was observed by Porta et al. [27] when using the same method of gold immobilization (i.e. based on PVA sols) on oxides. This behavior can be due to the absence of significant concentrations of functional groups on the surface of carbon xerogels [28], as

mentioned in Section 6.3.1.2. As a result, the hydrophobic surface of carbon xerogels has a very limited affinity to the gold hydrosol. In spite of the low efficiency, it was possible to obtain a gold loading of approximately 0.6 wt% for both samples.

It should be noticed that the acidification of the sol to pH 2 (using H_2SO_4) was also considered in an attempt to improve the efficiency of the preparation method and enhance the interaction between the gold sol and the support. Although the solution become colorless after a few hours, a much lower activity of the resulting catalyst was observed (about 3 times inferior), and therefore no further catalyst preparations were carried out at low pH.

6.3.2 Evaluation of carbon xerogels supported gold catalysts

The principal aim of this study is to evaluate possible correlations between activity and/or selectivity of the Au/CX catalysts and the textural properties of the support.

Figure 6.3 shows the evolution of glycerol conversion in the presence of the gold catalysts prepared on the two carbon xerogels. It can be observed that gold supported on CXs are efficient catalysts for glycerol oxidation. The amount of gold eventually leached during reactions was measured in a UNICAM 939/959 atomic absorption spectrometer using the remaining solution after 5 h of reaction. In these determinations, no gold was detected, and so gold particles seem to have a strong interaction with both xerogel supports, which prevents leaching. Au/5CX shows a better performance than Au/20CX. However, the turnover frequencies (TOFs) calculated after 2 h of reaction are fairly high for both catalysts, as reported in Table 6.3. A higher TOF for Au/5CX can be noticed, but the errors involved do not allow definitive conclusions. It is well known that the catalytic activity is largely influenced by the gold particle size, the catalysts with smaller gold particles being more active [9, 19, 29-30]. However, Au/5CX and Au/20CX have almost identical average particle sizes (4.6 nm and 4.7 nm, respectively), and therefore similar activities were expected from this point of view.

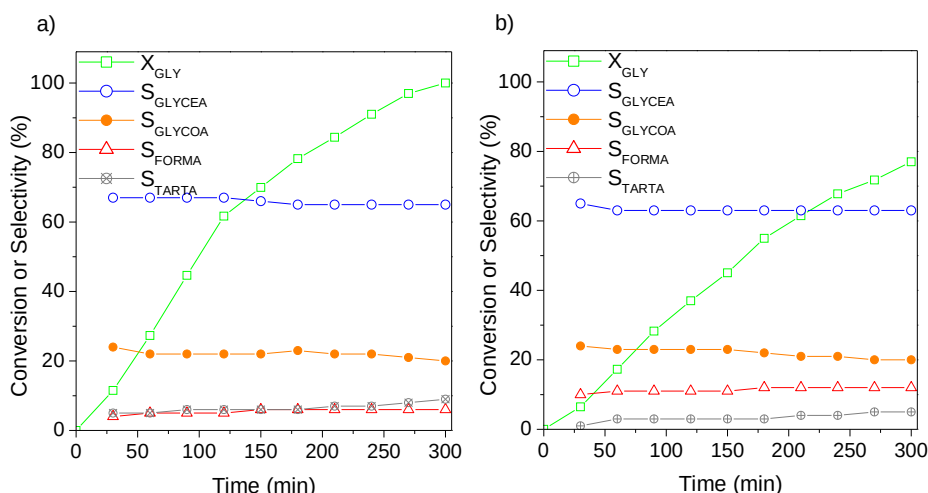


Figure 6.3 Conversion of glycerol (X_{GLY}) and selectivities to different products of reaction (S_{GLYCEA} , S_{GLYCOA} , S_{TARTA} and S_{FORMA}) as a function of time using a) Au/5CX and b) Au/20CX in glycerol oxidation. Reaction conditions: $T = 60\text{ }^{\circ}\text{C}$, $p_{O_2} = 3\text{ bar}$, 150 mL of glycerol 0.3 M, catalyst amount = 700 mg, NaOH/glycerol = 2 mol/mol.

Mass transfer resistances inside the porous network of the support can be limiting, and then influence strongly the performance of the catalysts. As the catalysts tested in this work show different pore sizes, the influence of intraparticle diffusion was assessed on the basis of the Weisz-Prater criterion [31]. The calculations of the Weisz modulus Φ indicated that the process is not significantly influenced by intraparticle diffusion, under the conditions used (see Appendix E).

The putative difference in the activities of the two catalysts can be due to the electrical resistivity of the materials. In fact, it was suggested that supports that allow a high electronic mobility, and therefore have a low electrical resistivity, promote the catalytic performance by the enhancement of the regeneration of hydroxide ions [12] (see Chapter 3 and also Chapter 5). Job et al. [18] showed that the electrical resistivity of carbon xerogels strongly depends on the textural properties and decreases with the decrease of the average pore diameter. Accordingly, the support of Au/5CX ($d_{BJH} = 5\text{ nm}$) has a lower electrical resistivity than that of sample Au/20CX ($d_{BJH} = 20\text{ nm}$), and consequently the former catalyst enhances the mobility of electrons, which is in agreement with the results observed.

Table 6.3 Influence of the textural properties of the support on the activities and selectivities to glyceric acid (GLYCEA), glycolic acid (GLYCOA), tartronic acid (TARTA) and formic acid (FORMA) for the Au/CX catalysts.

Catalyst	t = 120 min		X _{GLY} = 50%			
	X _{GLY} (%)	TOF × 10 ⁻³ (h ⁻¹) ^a	S _{GLYCEA} (%)	S _{GLYCOA} (%)	S _{TARTA} (%)	S _{FORMA} (%)
Au/5CX	62	2.4 ± 0.9	67	22	6	5
Au/20CX	37	1.7 ± 0.9	63	23	3	11

^a $TOF (h^{-1}) = \frac{\text{mol of glycerol converted after 2 h}}{\text{reaction time (= 2 h)} \times \text{mol of gold active sites}}$; the amount of gold active sites were

calculated from $\frac{6 \times y \times n_s \times W_{cat}}{d_M \times \rho \times N}$, where y and d_M are the gold weight fraction (from ICP) and the

average particle diameter (from HRTEM), respectively; ρ and n_s are the density of gold (19.30 g cm⁻³) and the number of gold atoms per unit of area (1.15 × 10¹⁹ m⁻²), respectively; W_{cat} is the catalyst mass used in the experiments (0.7 g); and N is the Avogadro number; errors of TOF were calculated on the basis of errors related to the measurements of gold loadings and standard deviations of particle size distributions.

While various studies have demonstrated the influence of gold particle size on the catalytic activity, the selectivities do not seem to correlate directly with the size of nanoparticles [2, 7, 19, 29]. Indeed, Villa et al. concluded that during glycerol oxidation in the presence of gold on MgAl₂O₄ the selectivity of the reaction was only partially determined by the gold particle size [15]. On the other hand, an increasing number of recent studies suggest that the textural and chemical properties of the support influence directly the selectivities attained in the glycerol oxidation reaction [12, 15, 17]. Then, the effect of the porous texture of the CX supports on the distribution of products was also evaluated.

The selectivities obtained in the presence of the two catalysts are compared at constant glycerol conversion (X_{GLY} = 50%) in Table 6.3. It is important to mention that the selectivities are practically independent of time or glycerol conversion, varying only slightly during the reaction, as can be seen in Figure 6.3, where the selectivities to the reaction products are also plotted as a function of time. For both catalysts tested the main reaction product is glyceric acid (GLYCEA) (selectivities of 67% for Au/5CX and 63% for Au/20CX), which corresponds to a valuable

oxygenated compound. Besides glyceric acid, also glycolic acid (GLYCOA), tartronic acid (TARTA), formic acid (FORMA) and oxalic acid (OXALA) were detected. It should be noticed that the amounts of this latter compound were very limited and did not lead to selectivities higher than 1%. The selectivity towards GLYCOA is similar for both catalysts. A slightly larger amount of TARTA was obtained in the case of Au/5CX (see Table 6.3). This can be explained by the presence of narrow pores in this support, which can lead to an easier over-oxidation of the primary products [4]. On the other hand, it can be observed that there is an important variation in the selectivity towards FORMA. In fact, whereas a low selectivity of 5% is obtained with the Au/5CX catalyst, Au/20CX leads to the formation of significant amounts of this compound (selectivity of 11%).

In this study, catalysts with similar gold average particle sizes, metal loadings and support chemical properties were successfully prepared. Therefore, the disparities in the selectivities observed in Figure 6.3 and Table 6.3 seem to be related almost exclusively to the differences in the textural properties. Indeed, an increase of the most frequent pore diameter from 5 to 20 nm leads to an enhancement of the selectivity to FORMA from 5% to 11% and to a slight decrease of the selectivity to GLYCEA from 67% to 63%.

6.3.3 Comparison between different carbon materials used as support for gold nanoparticles

In order to investigate more deeply the relationship between pore size and selectivity, a comparison with other carbon materials previously studied as supports, namely multi-walled carbon nanotubes (MWCNT) and activated carbon (AC), was also carried out (see Chapter 3 and 4).

The selectivities obtained with the different supports were compared at the same glycerol conversion ($X = 50\%$). It was reported that gold supported on MWCNT lead to a selectivity of 18% to FORMA and only 44% to GLYCEA (see Chapter 4). This catalyst has mesopore sizes largely distributed with a mode of 32 nm. On the contrary, when gold is supported on activated carbon (AC), which corresponds to a support with micropores and small mesopores (Figure 6.4), a high selectivity of 75% of GLYCEA was obtained and only a very limited amount of FORMA was detected ($S_{\text{FORMA}} = 3\%$). This is in accordance with the trend observed for the Au/CX catalysts, which make to believe that the textural properties of the supports can be responsible for the different distributions of products observed. For comparison,

some textural properties of MWCNT and AC are shown in Table 6.1. It is also important to mention that all the carbon supports of this work have a similar (very limited) amount of oxygenated groups on their surface; only in this way the comparison between catalysts is possible [12] (see Chapter 3 and also Chapter 5). Additionally, for all the materials, the sol immobilization technique was used to support gold nanoparticles and the average particle size varies only slightly (from 4.6 nm for Au/5CX to 6.8 nm for the Au/AC catalyst). No relationship between this parameter and the product distribution was observed. Demirel et al. [13] also reported that carbon supported gold catalysts have significantly different selectivity performances depending on the textural properties of the support. All these results suggest that the pore sizes of the support play an important role on the distribution of the products. Wide pores apparently favor the formation of formic acid, whereas narrow pore lead to an enhancement of the selectivity towards glyceric acid.

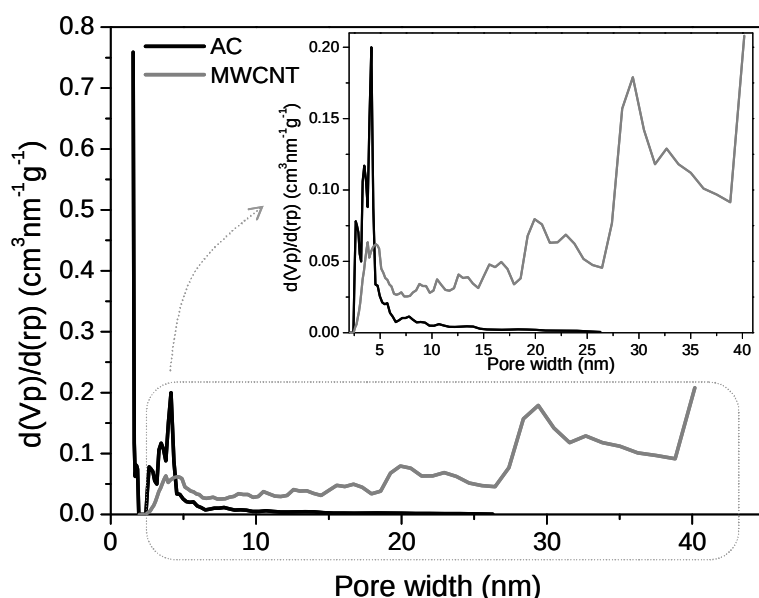


Figure 6.4 Pore size distributions of activated carbon (AC) and multi-walled carbon nanotubes (MWCNT) obtained by Non-Local Density Functional Theory (NLDFE).

In Figure 6.5, the selectivities to FORMA and GLYCEA obtained in the presence of gold supported on different carbon materials (AC, CXs and MWCNT) were plotted as a function of the most frequent mesopore diameter. Significant correlations are

noticed, particularly in the case of FORMA. Accordingly, an increase in the mesopore sizes of the support leads to an increase in the selectivity to FORMA and a decrease to GLYCEA.

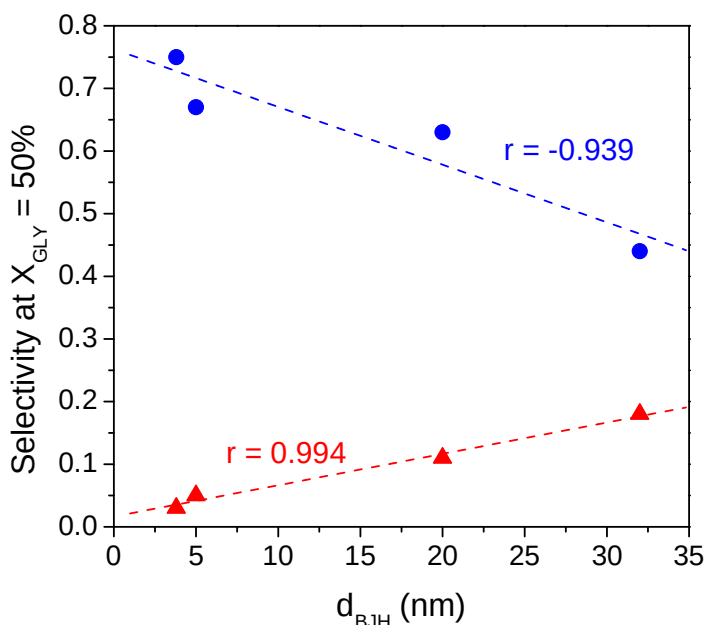


Figure 6.5 Correlations between selectivities to FORMA (▲) and GLYCEA (●) and the most frequent mesopore size of carbon supports (calculated by the BJH method). Reaction conditions: $T = 60\text{ }^{\circ}\text{C}$, $p_{O_2} = 3\text{ bar}$, 150 mL of glycerol 0.3 M, catalyst amount = 700 mg, NaOH/glycerol = 2 mol/mol.

Several mechanisms of the glycerol oxidation process are presented in the literature and the reaction pathways are not completely well established [17, 32-34]. Particularly, the origin of formic acid is still matter of discussion. It was suggested that formic acid could be obtained via the base catalyzed degradation of dihydroxyacetone [1, 32, 35]. Therefore, the formation of FORMA may support the presence as intermediate of that compound, which is rapidly degraded due to the highly basic medium (see Chapter 4). In fact, the oxidation of the secondary hydroxyl group of glycerol seems to be preferred under acidic conditions [1, 5]. Therefore, supports leading to a higher selectivity to FORMA are probably those that lead initially to higher amounts of dihydroxyacetone. Taking into account the

results obtained in this work, it can be suggested that the formation of dihydroxyacetone can require the binding of the glycerol molecule in a conformation that needs more space, and therefore is favored by supports with large pores (Figure 6.6).

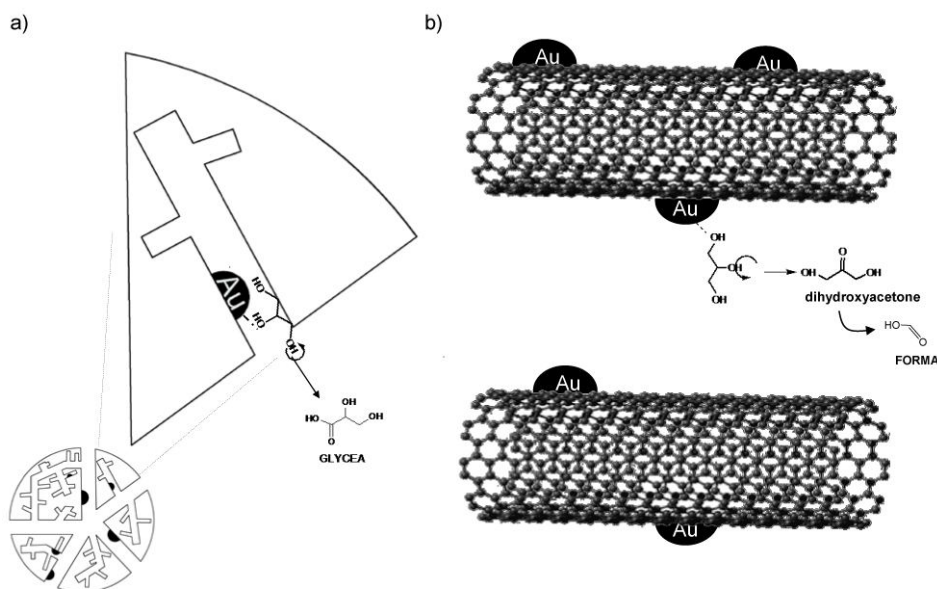


Figure 6.6 Possible differences in orientations of glycerol molecules in a) Au/AC and b) Au/MWCNT.

As a result, it seems that the distribution of products can be tuned within certain limits by the adequate choice of the support. Therefore, carbon xerogel appears to be a useful material since their porous textural features can be easily tailored to meet specific requirements.

6.4 Conclusions

The mesopore size distribution of carbon xerogels used as support of gold catalysts in glycerol oxidation influences the selectivity. Narrow pores lead to an enhancement of the selectivity to glyceric acid, whereas wide mesopores favor the formation of formic acid, probably via dihydroxyacetone. The same trend was observed with gold supported on activated carbon and multi-walled carbon nanotubes. Therefore, the type of carbon support plays an important role in the

distribution of the products and it seems possible to tune selectivities. In this way, carbon xerogel is an advantageous material since its average pore size can be easily adjusted in a controllable way during the preparation process.

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Chapter 7

7 Selective oxidation of glycerol catalyzed by platinum-group metals supported on multi-walled carbon nanotubes

Noble metals (Pt, Pd and Rh) were supported on multi-walled carbon nanotubes by the traditional incipient wetness impregnation and tested in the selective oxidation of glycerol. Under strongly basic conditions, the performances decrease in the order Pd > Pt > Rh. Nevertheless, these catalysts are prone to deactivation by oxygen poisoning. A platinum catalyst prepared by the sol immobilization technique is less susceptible to over-oxidation, probably due to the higher average size of the particles obtained; in addition a high and stable selectivity towards glyceric acid was observed throughout the reaction (67%). Tests with a Pt-Au alloy catalyst under high pH conditions show that oxygen poisoning is suppressed. Moreover, this catalyst is able to enhance the selectivity towards dihydroxyacetone (DIHA) in acid medium, when compared to a monometallic platinum catalyst with the same total metal loading (21% vs. 13%), although a poorer performance had been obtained.

7.1 Introduction

Vegetable oil based fatty acid methyl esters, popularly known as biodiesel, has emerged as a viable clean fuel over the last decade. It is obtained by transesterification with methanol of triglycerides extracted from seed oils, leaving glycerol as an inevitable by-product. Nowadays, the production of crude glycerol exceeds the present commercial demand for purified glycerol, and therefore this compound is often discarded as waste and usually burned [1]. However, this readily available organic raw material can potentially be very useful, since it exhibits a versatile and high chemical reactivity due to its unique multifunctional structure and properties. This makes it an attractive and advantageous potential starting material for the synthesis of valuable derivatives [2]. Catalytic partial oxidation is a small-scale application of commercial interest, which focuses on the synthesis of fine chemicals (e.g. glyceric acid and dihydroxyacetone) with very high value.

In order to control the reaction selectivity, a careful design of the catalyst is required. Supported noble metal catalysts are well known for their high activity in glycerol oxidation. However, catalysts that are based on platinum group metals suffer oxygen poisoning, which is directly dependant on the oxygen partial pressure, as mentioned in the literature [3], and leads to a premature and progressive deactivation of the catalyst at increasing reaction time [4-5]. So, when this type of catalyst is applied, a low oxygen partial pressure is normally used to limit oxygen dissolution [3, 6]. Moreover, it has already been reported that small metal nanoparticles (< 2 nm) deactivate more readily because of their stronger affinity to oxygen [7]. On the other hand, gold has a better resistance to oxygen poisoning [8], but its catalytic activity depends on nanoparticle sizes [5]. As a result, the catalytic activity and/or the selectivity of noble metals are strongly influenced by the crystallite size, which in turn depends on the preparation method used [5, 9-10]. For instance, the conventional incipient wetness impregnation technique results in much larger gold particles than the sol immobilization method [5, 10]. Unfortunately, gold-based catalysts are only active under strong basic conditions. In fact, Zope et al. [11] concluded that glycerol oxidation is promoted by high-pH conditions, since the hydroxide species adsorbed over gold have the ability to facilitate the activation of both the C-H and O-H bonds of glycerol. Similarly, the activities of Pd and Pt also depend on the basicity of the reaction medium [3, 11]. Additionally, even for Pt and Pd, which have the ability to dissociate molecular oxygen, it was proposed that O₂ participates in the catalytic cycle not by dissociation to atomic oxygen but by

regenerating hydroxide ions via the catalytic decomposition of a peroxide intermediate [11]. Contrarily to gold catalysts, reasonably high activities in base-free conditions have already been reported for Pt and Pd catalysts [3, 12-14]. However, higher activities and selectivities were obtained for platinum based catalysts [3, 14]. In fact, the energy barrier for the activation of C-H bond is fairly low for Pt [11]. It was reported that the addition of bismuth to platinum catalysts leads to better catalytic performance and improved the selectivity towards dihydroxyacetone under acidic conditions [3]. The addition of Au to Pt also seems to enhance the resistance to oxygen or by-product poisoning relatively to monometallic catalysts in basic medium [15]. In later developments, the concepts behind the utilization of bismuth-platinum and gold based catalysts were combined. In fact, Yanli et al. [16] showed that a gold-doped bismuth-platinum catalyst supported on activated carbon led to a high selectivity to dihydroxyacetone in acid medium (up to 64%), whereas the conversion did not surpass 40%. Liang et al. [17] studied the formation of a Pt-Cu alloy catalyst on carbon, which allowed to reach a selectivity of 70% towards glyceric acid in a base-free aqueous solution. The use of multi-walled carbon nanotubes as support can have advantages in terms of reactant accessibility [18]. Until now, the promoter effect of gold on platinum supported multi-walled carbon nanotube catalysts under acid conditions has not been investigated.

In the present work, noble metals (Pt, Pd and Rh) were supported on multi-walled carbon nanotubes by incipient wetness impregnation, and tested for the selective oxidation of glycerol. Additionally, monometallic platinum and bimetallic platinum-gold catalysts were prepared by the sol immobilization method. The influence of the preparation technique and the possible promoter effect of gold on the catalytic performance and distribution of products were evaluated at different pH of the reaction medium.

7.2 Experimental

7.2.1 Materials

The metal precursors H_2PtCl_6 (99.9 % ACS, Pt min 37.5%), PdCl_2 (99.9% ACS, Pd min 59.5%), RhCl_3 (99.9% ACS, Rh 38.5-45.5%) and $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (99.99% ACS, Au min 49.5%) were supplied by Alfa Aesar.

NaBH_4 of purity > 95% from Riedel-de Haën, NaOH (> 97%) and polyvinylalcohol (PVA) (purity > 99%) from Aldrich were also used. The commercial sample of multi-

walled carbon nanotubes Nanocyl 3100 (MWCNT) was used as received for supporting active phases in this study. Further details of the characteristics of this material can be found elsewhere [10] (see Chapter 4).

7.2.2 Preparation of catalysts

Palladium, platinum and rhodium catalysts were prepared by incipient wetness impregnation on the commercial multi-walled carbon nanotubes (MWCNT). In addition, gold, platinum and bimetallic platinum-gold catalysts were also prepared via the sol immobilization method [15, 19].

7.2.2.1 Incipient wetness impregnation

Pt, Pd and Rh catalysts were prepared by incipient wetness impregnation of multi-walled carbon nanotubes with aqueous solutions of the corresponding metallic precursors (H_2PtCl_6 , PdCl_2 , RhCl_3). The resultant wet samples were dried at 110 °C overnight. The amounts of noble metals were calculated in order to obtain nominal metal loadings of 1 wt%.

After heat treatment under nitrogen flow for 3 h, the catalysts were activated by reduction under hydrogen flow for 3 h. The temperatures used were the following: 250 °C for the Pd catalyst, 350 °C for the Pt catalyst and 200 °C for the Rh catalyst [20] (see Chapter 2). The treatment under nitrogen flow was carried out at the same temperature used for the reduction.

These catalysts were labeled M/MWCNT (M = Pt, Pd or Rh).

7.2.2.2 Sol immobilization

Au, Pt and Pt-Au catalysts supported on multi-walled carbon nanotubes were prepared using a sol immobilization method with NaBH_4 as reducing agent and PVA as stabilizer. NaBH_4 and PVA solutions were prepared just before use.

7.2.2.2.1 Monometallic sol

Au sol: $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (35.1 mg) was dissolved in 690 mL of H_2O , and polyvinyl alcohol was added (1.6 mL, 0.2 wt%) under stirring. NaBH_4 (4 mL, 0.1 M) was

added to the yellow solution under vigorous magnetic stirring. The resulting Au(0) sol was ruby-red in color.

Pt sol: H_2PtCl_6 (38.8 mg) was dissolved in 690 mL of H_2O , and polyvinyl alcohol was added (2 mL, 0.2 wt%) under stirring. NaBH_4 (3 mL, 0.1 M) was added to the yellow solution under vigorous magnetic stirring. The resulting Pt(0) sol was light-brown in color.

7.2.2.2.2 Bimetallic sol

H_2PtCl_6 (19.4 mg) was dissolved in 690 mL of H_2O , and polyvinyl alcohol was added (2 mL, 0.2 wt%). The solution was stirred for 3 min and 0.1 M NaBH_4 (1.5 mL) was added under vigorous magnetic stirring. The light-brown Pt(0) sol was immediately formed. After 5 min, $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (17.5 mg dissolved in 2 mL of H_2O) and NaBH_4 solutions (2 mL, 0.1 M) were added. A dark brown sol was formed.

It should be noticed that in this preparation method, the platinum precursor was firstly reduced and only after that the gold precursor was added and reduced. This sequence of addition of metals was selected since it was reported that it leads to more active and selective bimetallic Au-Pt catalysts [15].

7.2.2.2.3 Immobilization

Within a few minutes of sol generation, colloids were immobilized by adding the support under vigorous stirring. The amount of support required was calculated in order to reach a final metal loading of 1 wt% when monometallic catalysts were prepared and 0.5 wt% Pt – 0.5 wt% Au when the bimetallic catalyst was prepared. After 3-4 days, the colorless solutions were filtered, the catalysts were washed thoroughly with distilled water until the filtrate was free of chloride (AgNO_3 test) and dried at 110 °C for 24 h [19]. The organic scaffold was by heat-treatment under nitrogen flow for 3 h at 350 °C, and then the catalysts were activated by reduction under hydrogen flow for 3 h at 350 °C.

Monometallic catalysts containing gold or platinum, prepared by the sol immobilization methodology, were denoted Auc/MWCNT and Ptc/MWCNT, respectively, and the bimetallic catalyst was named Ptc-Auc/MWCNT.

7.2.3 Characterization of catalysts

The metal dispersion was determined by hydrogen chemisorption at 35 °C and atmospheric pressure, in an Altamira AMI-200 apparatus. The samples were pre-reduced in situ in a stream of hydrogen for 2 h. The temperatures used in this procedure correspond to the temperatures used to reduce the catalysts during its preparation (see sections 7.2.2.1 and 7.2.2.2.3). Then, samples were cooled to 35 °C in He flow, in order to proceed with the pulse chemisorption of hydrogen. A stoichiometric ratio of $H_2/M = 0.5$ was assumed (dissociative chemisorption); 58 μL doses of H_2 were successively injected, via a calibrated loop, in the carrier gas (25 $\text{cm}^3 \text{min}^{-1}$ of He, STP), until the catalyst surface saturation was achieved. The H_2 adsorption was followed on-line, by means of a thermal conductivity detector placed at the outlet of the catalyst bed (0.1 g). The amounts of H_2 adsorbed were calculated from the areas of the resultant H_2 peaks. Blank tests showed that H_2 adsorption on the MWCNT support was negligible.

Some of the samples were further characterized by transmission electron microscopy (TEM). Measurements were performed in a JEOL2010F instrument, with 0.19 nm spatial resolution at Scherzer defocus conditions. High Angel Annular Dark Field – Scanning Transmission Electron Microscopy (HAADF-STEM) images were obtained with the same microscope. An electron probe with diameter of 0.5 nm at a diffraction camera length of 10 cm was used for the HAADF mode. Energy-dispersive X-ray spectroscopy (EDX) data were acquired with the same equipment. Samples for examination were ultrasonically dispersed in high purity ethanol. Subsequently, a drop of the suspension was deposited on holey carbon-coated copper grids for TEM analysis. The average particle size of each catalyst was obtained by measuring at least 100 nanoparticles over multiple areas.

After selected reaction tests, the amounts of metal eventually leached during reaction were measured in a UNICAM 939/959 atomic absorption spectrometer, using the remaining solution.

7.2.4 Catalyst evaluation

The reaction tests were performed in a 350 mL stainless steel reactor equipped with manometer, temperature sensor, magnetic stirrer and sampling port. The oxidation reactions were carried out with oxygen at 3 bar and 60 °C. In a typical reaction, NaOH solution (NaOH/glycerol molar ratio = 2) and catalyst (700 mg) were added to a 0.3 M aqueous solution of glycerol ($V = 150 \text{ mL}$) under stirring at 1000 rpm.

Additional experiments were carried out in a base free glycerol aqueous solution or under acid conditions (in this case, pH was adjusted with HCl 0.1 M).

After heating under nitrogen to the desired temperature, the reaction was initiated by switching from inert gas to oxygen. The reaction was monitored by taking samples (0.5 ml) for analysis at regular time intervals.

The quantitative analysis of the reaction mixtures was carried out by high performance liquid chromatography (HPLC). The chromatograph (Elite LaChrom HITACHI) was equipped with a refractive index and an ultraviolet (adjusted to 210 nm) detector. Reactant and products were separated in an ion exclusion column (Alltech OA 1000). The eluent was a solution of H₂SO₄ 0.01 M. An injection volume of 20 µL, a measuring time of 15 min and a flow rate of 0.5 mL min⁻¹ were selected. Products were identified by comparison with standard samples. Glycerol (> 99.5%) was purchased from Fluka and all reaction products from Sigma-Aldrich. The selectivities (S_i) (also named relative yields by other authors) into the different products i at time t were calculated as:

$$S_i = \frac{C_i / \nu \cdot C_0}{X} \times 100 \quad (7.1)$$

where C_i is the concentration of product i (mol L⁻¹), C_0 is the initial concentration of glycerol (mol L⁻¹), X is the glycerol conversion and ν corresponds to the moles of i produced per mol of glycerol consumed, according to the stoichiometry.

7.3 Results and discussion

7.3.1 Catalysts characterization

The characteristics of the different catalysts prepared are summarized in Table 7.1. From the hydrogen chemisorption experiments and the TEM analyses it was possible to obtain the average particle size for monometallic and bimetallic catalysts. Low size metal crystallites were obtained for all catalysts prepared (from 1.7 nm for the Pt/MWCNT catalyst to 5.0 nm for the gold catalyst prepared by the sol immobilization method).

Table 7.1 Average crystallite sizes of the catalysts prepared and metal leaching after reaction.

Catalyst	d_M (nm) ^a	d_M (nm) ^b	Metal leaching (%) ^c
Pd/MWCNT	3.0	n.d.	8.8
Pt/MWCNT	2.1	1.7	3.6
Rh/MWCNT	n.d.	2.7	n.d.
Ptc/MWWCNT	n.d.	3.0	3.0
Auc/MWCNT	-	5.0	0.0
Ptc-Auc/MWCNT	n.d. ^c	4.1	4.9 (Pt) -1.4 (Au)

^a Obtained by hydrogen chemisorption.^b Obtained by TEM analysis.^c Reaction conditions: 60 °C, p_{O_2} = 3 bar, 150 mL of glycerol 0.3 M, NaOH/glycerol = 2 mol/mol, catalyst amount = 700 mg.

In the case of Pt/MWCNT the average particle diameter was determined by hydrogen chemisorption and TEM analysis. The results are slightly different, the average particle size determined by hydrogen chemisorption being slightly higher than that obtained by TEM analysis. Nevertheless, the experimental limitations of the chemisorption method, imposed by the low metal loading of 1 wt%, should be considered. Moreover, this technique becomes increasingly sensitive as particle sizes decrease, and the uncertainty concerning the stoichiometry of chemisorption, especially for very small particles, is a limitation.

The particle size distribution of the Pt/MWCNT catalyst can be seen in Figure 7.1.

Regarding platinum catalysts, it should be noticed that the incipient wetness method allows to obtain smaller particles than the sol immobilization method (average diameters around 2 and 3 nm, respectively).

To determine the dispersion of Pt and the equivalent average particle size in the bimetallic catalyst, it was assumed that H₂ chemisorption on gold was negligible under the conditions used. Nevertheless, for this catalyst, results obtained were not completely conclusive because hydrogen chemisorption was strongly limited, which

may be an indication that some interaction exists between platinum and gold (for instance, corresponding to the formation of an alloy).

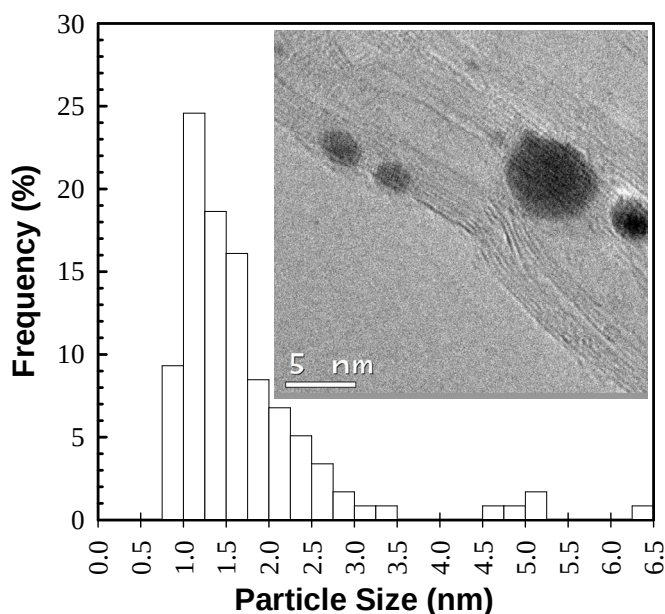


Figure 7.1 Particle size distribution of Pt/MWCNT. A TEM micrograph at high magnification is inserted.

The particle size distributions of the platinum catalyst prepared by the immobilization method as well as the bimetallic Ptc-Auc catalyst are shown in Figure 7.2. All measured particles are smaller than 10 nm. Inserted micrographs (Figure 7.2) show that the metallic nanoparticles are uniformly distributed on the external surface of MWCNT.

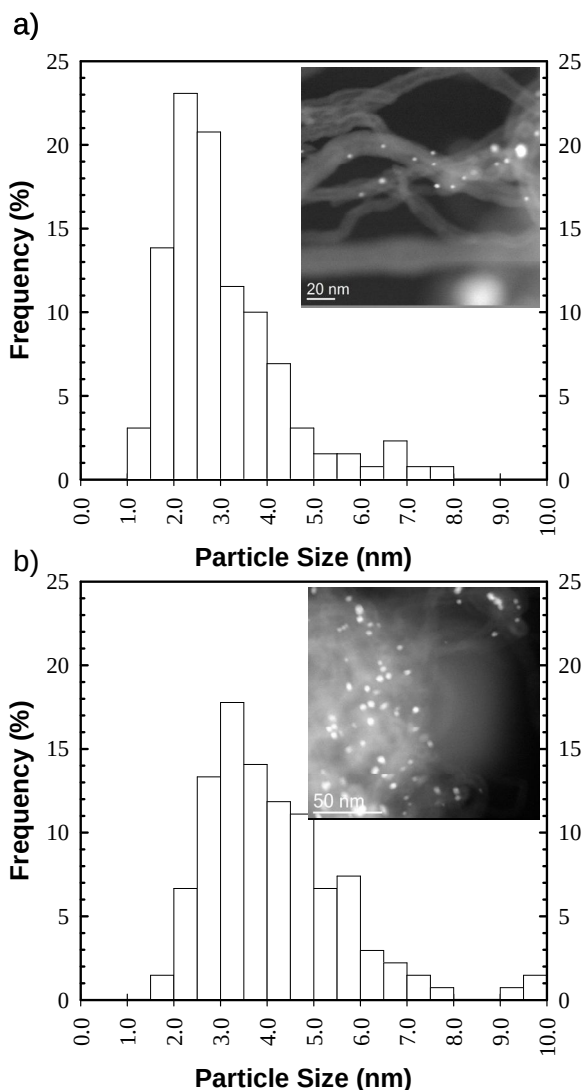


Figure 7.2 Particle size distributions of a) Ptc/MWCNT and b) Ptc-Auc/MWCNT. HAADF-STEM images are inserted.

More than 70 particles of different sizes in the bimetallic catalyst were analyzed in detail. Figure 7.3 shows a micrograph along with a representative EDX spectrum of an individual particle, which indicates the presence of both platinum and gold. Linescan of individual particles of the bimetallic Ptc-Auc/MWCNT catalyst revealed particles containing both Pt and Au (an example can be seen in Figure 7.3 b). EDX results indicate that most particles correspond to a bimetallic alloy (Figure 7.3 d). The average Pt content is 52%, confirming the nominal 1:1 Pt/Au weight ratio used

in the preparation of the bimetallic catalyst. The average diameter of gold nanoparticles in Auc/MWCNT is 5.0 nm, while for Ptc/MWCNT the average size is 3.0 nm. On the other hand, the average size for Au-Pt alloy particles is 4.1 nm.

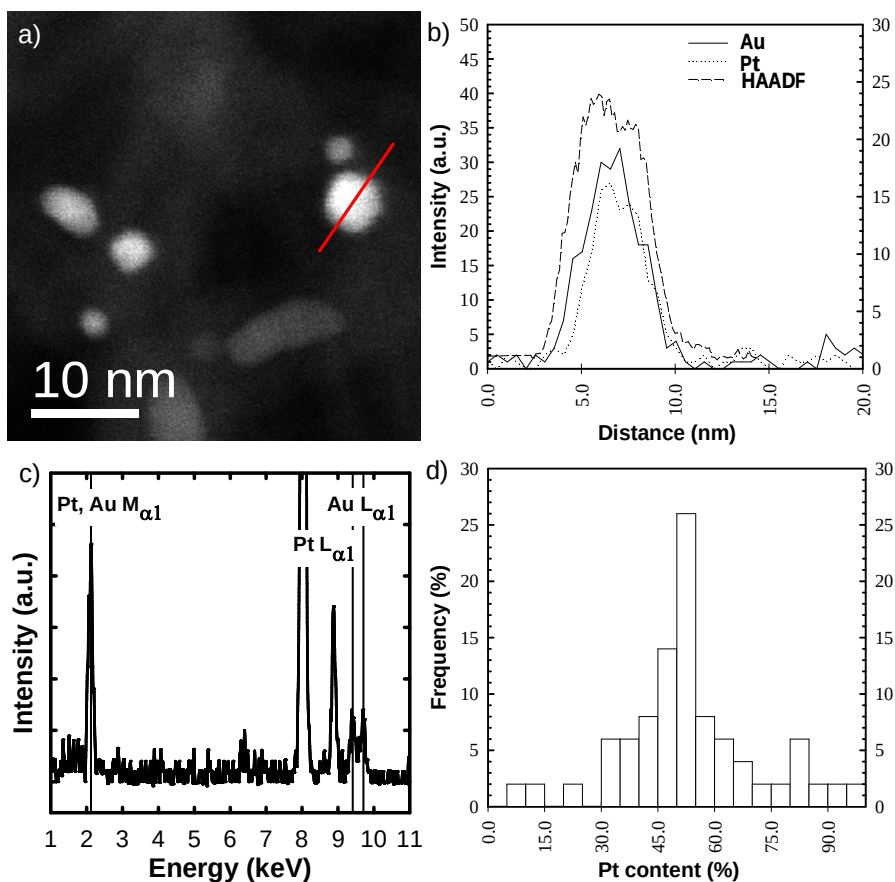


Figure 7.3 STEM-HAADF image of the Ptc-Auc/MWCNT catalyst (a), with the corresponding linescan from a single nanoparticle (b), a representative EDX spectrum for a single nanoparticle (c) and the frequency plot of particles composition (d).

7.3.2 Oxidation experiments

7.3.2.1 Evaluation of catalysts prepared by incipient wetness

Noble metals (Pd, Pt, Rh) were supported on multi-walled carbon nanotubes using the incipient wetness method. This impregnation method is largely used for the preparation of supported metal catalysts, since it is very simple and can be easily scaled up to industrial dimensions [21]. Moreover, this preparation technique does not produce wastewater, which is a great advantage in an industrial process, since wastewater treatment is generally costly.

The performance of MWCNT supported catalysts was studied as a function of time in basic medium. Using typical conditions (60 °C, $P_{O_2} = 3$ bar, 150 mL of glycerol 0.3 M, NaOH/glycerol = 2 mol/mol, catalyst amount = 700 mg), the conversion evolutions presented in Figure 7.4 were obtained.

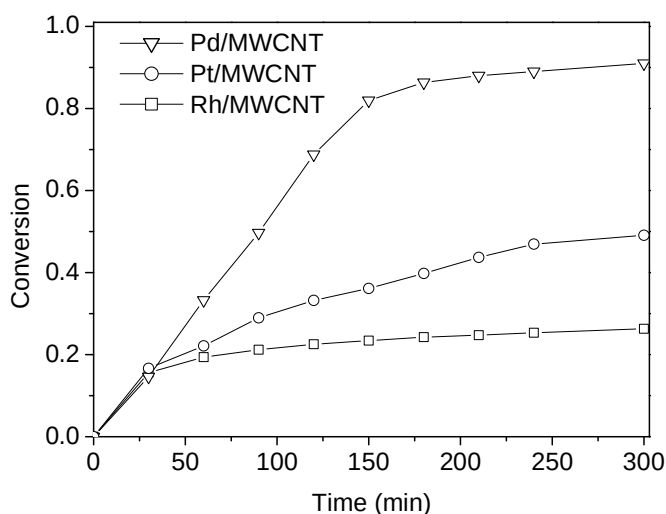


Figure 7.4 Oxidation of glycerol over noble metal catalysts supported on MWCNT. Reaction conditions: 60 °C, $p_{O_2} = 3$ bar, 150 mL of glycerol 0.3 M, NaOH/glycerol = 2 mol/mol, catalyst amount = 700 mg.

For all the catalysts tested, the conversion seems to reach a plateau. For instance, after only 1 h of reaction, the conversion obtained with the Rh/MWCNT catalyst remains practically constant (at $\approx 20\%$). This catalyst is rapidly deactivated.

As already mentioned in the literature, the main disadvantage of Pt-group catalysts is their deactivation at increasing reaction time due to oxygen poisoning, which depends on the oxygen partial pressure [3, 15]. Indeed, it is well-known that the rate of alcohol oxidation is much higher on a reduced metal surface than on an oxidized surface [22]. For this reason, catalysts are pre-reduced with hydrogen before reaction.

According to Van Dam et al. [23], metals with a lower oxidation potential are more prone to oxidation. Thus, among the metals tested, rhodium would be more sensitive to poisoning by over-oxidation, followed by palladium and platinum. Although it was observed that rhodium was indeed the metal more sensitive to the oxygen dissolved in the reaction medium, palladium was able to reach 80% conversion after 2.5 h without any sign of deactivation, whereas this was already visible after 1 h of reaction for the Pt/MWCNT catalyst. TOF values were calculated after 0.5 h of reaction (Table 7.2), before observation of any significant deactivation, and it was concluded that the platinum catalyst shows the highest activity ($\text{TOF} = 770 \text{ h}^{-1}$). This value is higher than those reported in the literature when testing Pt supported on activated carbon under similar reaction conditions (TOF values after 0.5 h of reaction vary between 30 h^{-1} and 472 h^{-1} depending on the preparation method used) [15]. However, besides the nature of the metal, the crystallite size should also be considered, since small metal nanoparticles ($< 2 \text{ nm}$) deactivate more readily because of their stronger affinity to oxygen [7]. This can explain the late poisoning of the palladium catalyst when compared with the platinum one. In fact, chemisorption results show that Pd/MWCNT has a higher metal particle average size than Pt/MWCNT (3.0 vs. 2.1 nm). In addition, the platinum size distribution (Figure 7.1) shows that most particles are smaller than 2 nm. In conclusion, the increase of the particle sizes of platinum catalysts can be an approach to delay oxygen poisoning when working at high oxygen pressures, which is favorable since it leads to higher catalytic performances.

Taking into account their practical application, the catalysts have to be active but also stable, i.e. metal leaching should be avoided. As it can be observed in Table 7.1, a leaching of almost 9% of the total metal loading was observed after 5 h of reaction with the Pd/MWCNT catalyst, whereas only 3.6% was measured after using the platinum catalyst. Accordingly, this latter metal seems to have a stronger interaction with the support. It should be noticed that metal dissolution is facilitated by the strongly basic medium used and by the high oxygen coverage of the metal [22].

The selectivities to products obtained in the presence of the different catalysts are compared in Table 7.2 at constant reaction time (3 h) and at the same glycerol conversion (25%). The prepared catalysts lead to a high total selectivity to glyceric acid (GLYCEA) of about 70%. Besides the desired GLYCEA, glycolic acid (GLYCOA), tartronic acid (TARTA), formic acid (FORMA) and oxalic acid (OXALA) were also measured. However, whereas palladium catalyst seems to promote the oxidation to tartronic acid during the reaction, when using platinum catalysts the formation of glycolic acid seems to be preferred (increase of the selectivity to GLYCOA associated to a decrease of GLYCEA during the reaction). It should also be noticed that this latter catalyst leads to a significant amount of FORMA ($S_{\text{FORMA}} = 11\%$) when compared with Rh and Pd catalysts (selectivities of 2% and 5% after 3 h, respectively). It was already suggested that the formation of this latter compound may support the initial formation of dihydroxyacetone, which is readily degraded due to the highly basic medium (see Chapter 4). Therefore, the use of platinum in acid media can lead to a higher amount of DIHA, which is an economically interesting target compound. Moreover, platinum catalysts are much more active at neutral and acid conditions than palladium catalysts, and therefore, when working without the addition of base, platinum is usually preferred [3]. Villa et al. [14] reported the formation of mainly C_1 products (at very low rates) when using carbon-supported palladium at pH 5, and higher yields of DIHA are obtained with platinum catalyst [3]. Platinum is particularly able to activate C – H bonds without the addition of a base, since this step has a low energy barrier over this metal [11]. Accordingly, special attention was given to this catalyst in the following parts of the work, where in an attempt to reduce or hinder over-oxidation, different approaches were considered.

Table 7.2 Product selectivities at X = 25% and t = 3 h for glycerol oxidation over noble metal catalysts supported on multi-walled carbon nanotubes. Reaction conditions: 60 °C, P_{O_2} = 3 bar, 150 mL of glycerol 0.3 M, NaOH/glycerol = 2 mol/mol, catalyst amount = 700 mg.

X _{GLY} = 25%							t = 180 min					
	TOF (h ⁻¹)	S _{GLYCEA}	S _{GLYCOA}	S _{TARTA}	S _{FORMA}	S _{OXALA}	X _{GLY}	S _{GLYCEA}	S _{GLYCOA}	S _{TARTA}	S _{FORMA}	S _{OXALA}
Pd	570 ^a	0.67	0.13	0.13	0.04	0.03	0.86	0.65	0.11	0.15	0.05	0.04
Pt	770 ^a	0.65	0.19	0.04	0.11	0.01	0.40	0.62	0.22	0.04	0.11	0.01
Rh	530 ^a	0.74	0.15	0.08	0.02	0.01	0.24	0.74	0.15	0.08	0.02	0.01
Ptc	1660 ^b	0.68	0.19	0.07	0.05	0.01	0.80	0.67	0.19	0.08	0.05	0.01
Auc	2240 ^c	0.47	0.25	0.03	0.17	0.01	0.69	0.44	0.18	0.04	0.18	0.01
Ptc-Auc	1760 ^{b,d}	0.62	0.20	0.07	0.10	0.01	0.98	0.47	0.20	0.07	0.13	0.01

^a TOF calculated after 30 min of reaction.

^b TOF calculated after 1 h of reaction.

^c TOF calculated after 2 h of reaction (from Chapter 4).

^d TOF calculated on the basis of the total metal loading.

7.3.2.2 Influence of the preparation method of platinum supported catalysts

It is known that the catalyst preparation method strongly influences the noble metal cluster size and its dispersion on the support surface [13]. Therefore, besides the well-known incipient wetness impregnation, a platinum catalyst sample was prepared by the sol immobilization technique. This method is based on the adsorption of a platinum colloid on the surface of the carbon support. The advantage of this method lies in the possible control of the particle sizes [24]. In fact, the average particle size can be tuned by varying the preparation conditions used.

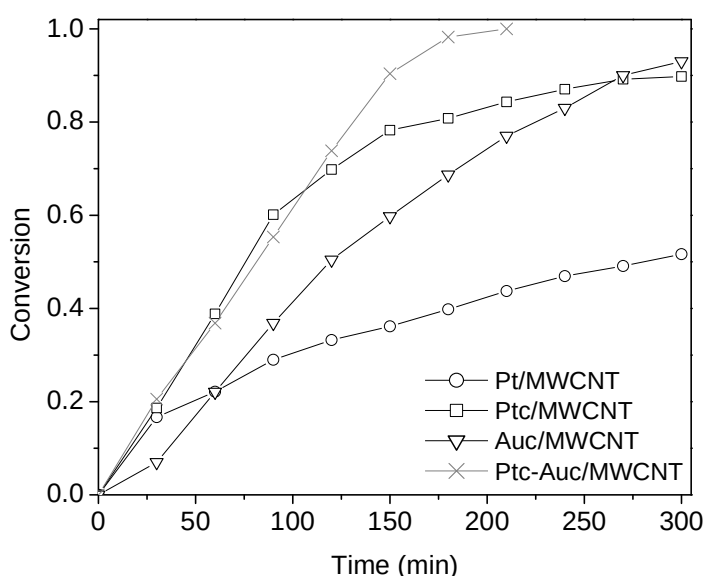


Figure 7.5 Oxidation of glycerol using monometallic Pt and Au and bimetallic Pt-Au catalysts supported on multi-walled carbon nanotubes. Reaction conditions: 60 °C, $p_{O_2} = 3$ bar, 150 mL of glycerol 0.3 M, NaOH/glycerol = 2 mol/mol, catalyst amount = 700 mg.

A dramatic increase of the performance of this catalyst (Ptc/MWCNT) was observed, when compared with the platinum catalyst prepared by the classical incipient wetness impregnation method (Figure 7.5 and Table 7.2). In fact, a conversion of 90% was achieved after 5 h of reaction. Therefore, the pre-formation of platinum particles in solution, which are then transferred to the support, allows to overcome premature oxygen-poisoning of the catalyst. Accordingly, no deactivation

was noticed during the first 90 min of reaction, period when the glycerol conversion reached a value near 60%. This can be explained by the higher crystallite sizes obtained with this method than with the classical incipient wetness technique (see Table 7.1). Moreover, the Ptc/MWCNT catalyst leads to a slight enhancement of the selectivity towards C_3 products (Table 7.2). Accordingly, a 67% selectivity to GLYCEA is obtained, whereas the formation of the C_1 product is much more limited ($S_{\text{FORMA}} = 5\%$). In addition, it is worth to mention that this catalyst exhibits stable selectivities throughout the reaction.

The simple increase of the average particle size allows to delay oxygen poisoning. This can be easily accomplished by the choice of an adequate preparation method. In conclusion, a possible great advantage of the immobilization technique is the control and replication of particle size distributions.

7.3.2.3 Promoter effect of gold on platinum catalysts

Bimetallic catalysts are presently the subject of considerable interest in heterogeneous catalysis due to the fact that their catalytic properties can be superior to monometallic catalysts. It was reported that the use of bimetallic systems Au-Pt/C and Au-Pd/C significantly improved the activity with respect to the monometallic systems, and additionally selectivity could be tuned by using different preparation methods [25-28]. The addition of Au to Pt-group metals also enhances the resistance to oxygen or by-product poisoning with respect to monometallic catalysts [28]. However, conflicting results are often obtained; in fact, different supports or other liquid phase oxidations of alcohols may produce different conclusions [27]. Moreover, bimetallic catalysts can be relatively non-uniform and have variations in morphology and particle composition. Therefore, efficient preparation methods and accurate characterization procedures are necessary.

Pt-Au catalysts supported on multi-walled carbon nanotubes have not been investigated yet. A catalyst containing a total metal loading of 1 wt% (0.5% Au + 0.5% Pt) was prepared and evaluated in glycerol oxidation. The results obtained under basic conditions are depicted in Figure 7.5. The Ptc/MWCNT shows a higher performance than the Auc/MWCNT catalyst. This same trend was observed under similar reaction conditions by Prati et al. [27] when using an activated carbon support. However, as already mentioned, contrarily to the Ptc/MWCNT catalyst, gold does not show any sign of significant deactivation. In addition, it is worth to notice that calculations of TOF, which take into account the surface metal area,

show that the gold catalyst is more active than Ptc/MWCNT (Table 7.2). The modification of the Ptc catalyst by adding gold leads to a general enhancement of the activity (see Table 7.2). More particularly, deactivation by oxygen poisoning is avoided by using the bimetallic 0.5 wt% Ptc - 0.5 wt% Auc catalyst, and total glycerol conversion is achieved after only 3.5 h of reaction, under the conditions tested. Accordingly, the modification of platinum catalyst by adding gold leads to a highly active and poisoning-resistant catalyst. Gold probably acts as a promoter, isolating Pt metallic sites, and thus limiting oxygen coverage, as it has already been mentioned in relation to Pd-Au systems [27]. Nevertheless, similarly to what was described by Ketchie et al. [29] when testing Au-Pd bimetallic catalysts, no activity enhancement was observed for the bimetallic Ptc-Auc catalyst in comparison with the monometallic gold catalyst (it should be remembered that activities are properly normalized by the amount of surface metallic sites; see Table 7.2). In fact, those authors tested bimetallic Au-Pd/C catalysts and, although the activity of bimetallic catalysts depends on the amount of gold present, none of them had a higher TOF than the monometallic Au catalyst.

As it was already reported (see Chapter 4), gold supported on MWCNT leads to a significant amount of FORMA and some complete oxidation to inorganic carbon also occurs. Moreover, the mineralization observed increases at increasing conversion (see Table 7.2). Unfortunately, these characteristics of the Auc/MWCNT catalyst are also found in the bimetallic catalyst. When comparing selectivities at iso-conversion ($X_{\text{GLY}} = 25\%$), the Auc catalyst leads to the lowest selectivity to GLYCEA (47%), whereas the Ptc catalyst tends to give more GLYCEA and TARTA ($S_{\text{GLYCEA}} = 68\%$ and $S_{\text{TARTA}} = 7\%$). For the multi-walled carbon nanotube supported bimetallic catalyst an intermediate but still fairly high selectivity to GLYCEA is obtained ($S_{\text{GLYCEA}} = 62\%$). This selectivity at low conversion is fairly close to that obtained with the monometallic Ptc/MWCNT catalyst. However, at increasing conversions, the selectivity to this compound steadily decreases and conversion to inorganic carbon increases as reported for Auc/MWCNT (Chapter 4), whereas the selectivities towards the other reaction products remain practically unchanged. This implies that glyceric acid is not stable in the presence of the Ptc-Auc/MWCNT catalyst. Accordingly, after 3 h of reaction, the selectivity to glyceric acid obtained with the bimetallic catalyst was decreased up to 20% with respect to Ptc/MWCNT, whereas a 2.6 fold increase in the selectivity of FORMA was observed. This is in agreement with the poor selectivities towards GLYCEA (between 34% and 58%)

reported by Dimitratos et al. [15] when using bimetallic Pt-Au catalysts supported on activated carbon for glycerol oxidation in a basic medium.

In the following section, the influence of the pH of the reaction medium in the performance of the catalysts containing platinum was investigated. Particularly, the bimetallic catalyst, which leads to higher selectivities to FORMA and inorganic carbon in basic media, was compared with the monometallic Ptc/MWCNT catalyst, in order to evaluate differences in the distribution of products, mainly related to the formation of DIHA.

7.3.2.4 Reaction over Pt-containing catalysts at neutral and acid conditions

One of the main disadvantages of working in basic media is the formation of the main product as glycerate, which requires additional acidification of the reaction mixture in order to get free glyceric acid. The corresponding costs are important in the design of industrial processes. Moreover, the intrinsic catalytic reaction pathway can be masked by the NaOH added, since the stability of some reaction intermediates is affected by the concentration of base [2].

A recent study showed that the presence of surface bound hydroxide intermediates facilitate the activation of both C-H and O-H bonds of glycerol, as they lower considerably the energy barrier [11]. In particular, the activation of the O-H bond is unlikely for gold alone since in this metal, contrarily to platinum, this step has a very high activation energy [11]. In the previous section it was concluded that the bimetallic Ptc-Auc catalyst leads to an enhancement of the selectivity towards FORMA when compared with monometallic Ptc/MWCNT. Therefore, the former catalyst can lead to higher amounts of dihydroxyacetone (DIHA), provided that the right reaction conditions for its stability are used.

The influence of the pH of the reaction medium on the rate can be seen in Figure 7.6. As expected, the initial rates of glycerol oxidation are pH dependent, and a higher activity was obtained with the monometallic Ptc catalyst when used under neutral conditions (see Table 7.3). However, the difference on performance becomes less significant as the glycerol conversion increases. This can be due to the reduction of pH caused by the formation of acid products. In fact, in both experiments (i.e. at initial pH values of 7 or 4) the pHs measured after reaction were similar (around 3).

Contrarily to that was observed in basic medium, the bimetallic catalyst shows a considerably poorer performance than the monometallic Ptc catalyst at pH 4. The low catalytic conversion obtained is probably due to the acid reaction conditions, which are unfavorable for gold catalysts [11]. Accordingly, no advantage in terms of activity was observed with the utilization of the Ptc-Auc catalyst. In fact, considering that only platinum (0.5 wt%) is active in this catalyst, the calculated TOF would be 65 h^{-1} , which is very similar to the value obtained with the monometallic catalyst at pH 4 (see Table 7.3).

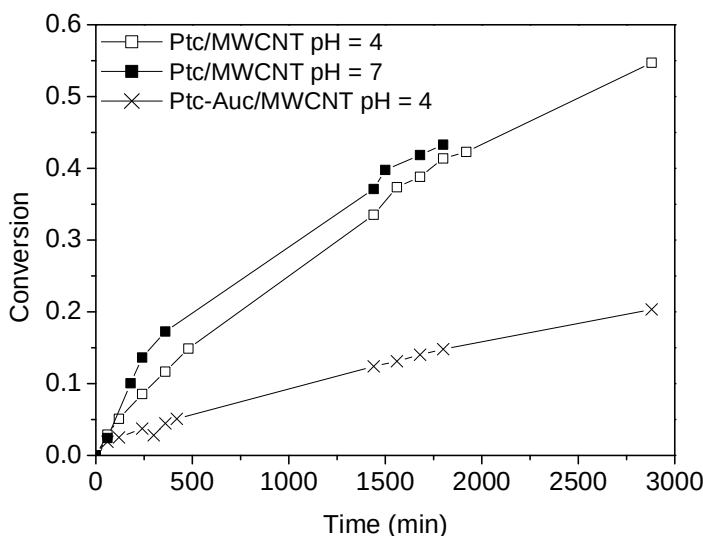


Figure 7.6 Influence of the pH medium on the oxidation of glycerol using multi-walled carbon nanotubes supported monometallic Pt and bimetallic Pt-Au catalysts prepared by the sol immobilization technique. Reaction conditions: 60°C , $p_{\text{O}_2} = 3$ bar, 150 mL of glycerol 0.3 M, catalyst amount = 700 mg.

Under neutral or acid conditions, a different distribution of products was observed (see Table 7.3). In fact, the main products are glyceric acid, glyceraldehyde (GLYCER) and dihydroxyacetone (DIHA). These last two products were not detected in basic media. Effectively, in base-free media, the direct catalytic oxidation of the secondary hydroxyl group of glycerol to form stable DIHA is observed. Apart from these compounds, GLYCOA and TARTA were also obtained, but in fairly limited amounts (selectivities not higher than 2%). In addition, contrarily

to the observed under highly basic conditions (Table 7.1), platinum leaching is significantly lower ($\approx 0.8\%$ at both pH = 7 and pH = 4).

DIHA is a versatile compound of high commercial interest extensively used as a cosmetic ingredient mainly in sunless tanning formulations, as precursor of pharmaceuticals and as a chemical intermediate in organic synthesis [30]. This compound is particularly stable between pH 3 and 4 [31]. Accordingly, a slight increase of its selectivity was observed when the initial pH was decreased from 7 to 4 (see Table 7.3), although the pH effect is not strongly marked since it tends to similar values (around 3) during reaction, as already mentioned.

As acid media favor the formation of DIHA, the bimetallic catalysts were tested under these conditions. Although the formation of an alloy does not lead to an increase of the catalytic activity under acid conditions, the use of the bimetallic Ptc-Auc/MWCNT catalyst leads to a significant enhancement in the selectivity to dihydroxyacetone. In fact, this selectivity increases from 13% to 21% at 20% glycerol conversion. Therefore, it seems that a cooperative effect between the two metals exists, which favors the formation of this highly added value compound under low pH conditions.

Table 7.3 Activities (TOF) after 6 h of reaction and product selectivities at $X_{\text{GLY}} = 20\%$ and 40% for glycerol oxidation over monometallic Pt and bimetallic Pt-Au catalysts at different pH of the reaction medium. Reaction conditions: $60\text{ }^{\circ}\text{C}$, $p_{\text{O}_2} = 3\text{ bar}$, 150 mL of glycerol 0.3 M , catalyst amount = 700 mg .

		$X_{\text{GLY}} = 20\%$						$X_{\text{GLY}} = 40\%$					
	TOF (h^{-1})	S_{GLYCEA}	S_{GLYCOA}	S_{STARTA}	S_{DIHA}	S_{GLYCER}	S_{GLYCEA}	S_{GLYCOA}	S_{STARTA}	S_{DIHA}	S_{GLYCER}	Others ^b	
Ptc	120	0.43	0.01	0.02	0.12	0.42	0.34	0.02	0.01	0.11	0.42	0.10	
pH = 7													
Ptc	70	0.44	0.01	0.02	0.13	0.40	0.37	0.02	0.01	0.13	0.42	0.05	
pH = 4													
Ptc-Auc	65 ^a	0.42	0.02	0.01	0.21	0.34	-	-	-	-	-	-	
pH = 4													

^a Value calculated considering only the contribution of platinum (gold is not active in acid media).

^b Others include total mineralization products.

7.4 Conclusions

Catalysts that are based on metals of the platinum group suffer oxygen poisoning. Different approaches were considered in order to minimize deactivation by over-oxidation of platinum catalysts. The sol immobilization method leads to higher platinum particle sizes, when compared to the classical incipient wetness method, and consequently a delay of the oxygen poisoning was observed. Therefore, the resulting catalyst shows improved performance and stable selectivities during the reaction in basic media.

Deactivation by oxygen poisoning is avoided by the formation of a Pt-Au alloy catalyst, but a decrease on the selectivity towards GLYCEA is observed, particularly at high reaction times.

The preferential chemoselective orientation of glycerol oxidation towards the reaction of the primary or the secondary alcohol functions can be controlled by the adequate choice of the reaction conditions. Whereas highly basic media promote the formation of glyceric acid, dihydroxyacetone is only stable under neutral or acid media. Under these conditions, although a poorer performance has been observed when using the Pt-Au bimetallic catalyst, its presence enhances the selectivity to dihydroxyacetone, when compared to a monometallic platinum catalyst with the same total metal loading.

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Chapter 8

8 Ceria and zirconia supported gold catalysts for the liquid phase oxidation of glycerol

Preliminary results on the performance of gold nanoparticles supported on ceria, zirconia and Ce-Zr mixed oxide are reported in this chapter. Catalysts having initially nanoparticle sizes were successfully obtained by calcination at different temperatures. Nevertheless, all the catalysts lead to similar performances in the oxidation of glycerol. In fact, it was observed that small particles are particularly prone to sintering during reaction, and therefore all samples tend to behave similarly. All the catalysts tested allow to obtain a high selectivity of about 70% towards the compound of commercial interest, i.e. glyceric acid.

8.1 Introduction

Glycerol is generated in large amounts during biodiesel production. Due to the tremendous growth of the biodiesel industry during the last years, the glycerol market is experiencing a surplus [1]. Adding value to this by-product is a necessary requisite for the commercial viability of biodiesel production [2-3]. In addition, glycerol has been identified as one of the twelve building blocks for future biorefineries [4]. Accordingly, the conversion of glycerol into high-value chemicals has received great attention in recent years [2, 5-6].

Since glycerol is a highly functionalized molecule compared to hydrocarbons from petrochemistry, this makes it an attractive and advantageous starting material for the synthesis of valuable oxygenated derivatives [2, 7]. Nevertheless, glycerol has three reactive hydroxyl groups, which render its catalytic selective oxidation particularly difficult [8], and a large number of products can be obtained [2].

Carbon black, activated carbon, and graphite have been extensively tested as gold supports in glycerol oxidation [2]. More recently, other carbon materials (nanotubes, nanofibers, xerogels) were also evaluated as supports in the same reaction [9-11]. Nano-sized gold particles supported on different oxides (TiO_2 , MgO , Al_2O_3 , CeO_2 , Nb_2O_5 , V_2O_5 and Ta_2O_5) are also active for the catalytic liquid-phase oxidation of glycerol [12-13]. Under alkaline conditions, the distribution of products can differ depending on the type of support used, but generally carbon supported catalysts show the highest activities [12, 14-15].

Small gold crystallites (2 - 5 nm) supported on nanocrystalline ceria were reported as active, selective and recyclable catalysts for the oxidation of primary and secondary alcohols [16]. This was attributed to a cooperative effect between gold and ceria [16]. Demirel et al. [12] investigated the performance of ceria supported gold catalysts in the glycerol oxidation. Nevertheless, although the gold nanoparticles also have an average diameter between 2 and 5 nm, only a poor glycerol conversion was achieved. Moreover, these authors concluded that the performances depend on the preparation method used and on the activation conditions of catalysts. They also observed that gold on ceria deactivates remarkably just after one reaction cycle, as a consequence of significant metal leaching [12]. Sobcazk et al. [13] studied the activity of gold catalysts supported on group five metal oxides in glycerol oxidation. They pointed out the importance of the acid-base properties and the crystallinity of the support, which influence the interaction of gold with the support and the catalytic performance.

Only a few results using oxides as gold supports in glycerol oxidation are reported in the literature [12-13, 17-18]. Several parameters seem to have a direct influence on the catalytic activity and selectivity, and the role of the oxide support is still not clear.

In this work, a preliminary study using ceria as support was carried out. As zirconia has not been investigated in glycerol oxidation, this support was tested as well. Additionally, a Ce-Zr mixed oxide was also used as support for gold. Special attention was given to gold nanoparticle sizes.

8.2 Experimental

8.2.1 Catalyst preparation

Both the CeO₂ nanopowder ($S_{\text{BET}} = 98 \text{ m}^2 \text{ g}^{-1}$) and the mixed oxide Ce_{0.68}Zr_{0.32}O₂ ($S_{\text{BET}} = 100 \text{ m}^2 \text{ g}^{-1}$) were kindly donated by Rhodia. The ZrO₂ nanopowder was purchased from TECNAN S.L. ($S_{\text{BET}} = 85 \text{ m}^2 \text{ g}^{-1}$). All samples were calcined at 550 °C before use.

Gold catalysts with a 3 wt% nominal metal loading were prepared on the three materials by a deposition-precipitation method, using sodium carbonate as the precipitating agent. The preparation method can be described as follow. First, 15 g of support was suspended in 800 mL of distilled water in a flask. The mixture was stirred and heated to 60 °C. Then, the precursor (HAuCl₄) solution, with a concentration of approximately 3.2 mM, was added slowly to the flask (3 mL min⁻¹). The pH of the liquid was adjusted with an aqueous solution of Na₂CO₃ 0.05 M, using a TIM 856 instrument in order to keep the pH value at 8.0 during the preparation. The titration time of HAuCl₄ with Na₂CO₃ is approximately 4 h. After ageing for 1 h at 60 °C, heating was turned off and the stirring was kept on for 1 h and 50 min, in order to cool down to room temperature. The synthesis was carried out in darkness.

The mixture was filtered and the catalyst washed with distilled water until there was no chloride anion in the filtered solution. Finally, the sample was dried at 110 °C for 12 h.

The dried sample was calcined in air at 250, 350 and 550 °C for 1 h. The calcined samples were kept in the freezer. The catalysts were labeled as following:

Au/CeO₂-T, Au/ZnO₂-T and Au/CeZr-T (where T corresponds to the calcination temperature in °C).

8.2.2 Catalyst characterization

The gold content was checked by ICP analysis of the filtrate.

High Angel Annular Dark Field – Scanning Transmission Electron Microscopy (HAADF-STEM) analyses were collected in order to get information about metal particle size distributions. Measurements were performed in a JEOL2010F instrument. An electron probe with diameter of 0.5 nm at a diffraction camera length of 10 cm was used. Samples for examination were prepared by dispersing the catalysts in high purity ethanol. Subsequently, a drop of the suspension was deposited on holey-carbon coated Cu grids for analysis. At least 200 particles were measured in each catalyst.

The amounts of gold eventually leached during reaction were measured in a UNICAM 939/959 atomic absorption spectrometer, using the remaining solution.

8.2.3 Catalytic experiments

The catalysts were tested in the liquid phase oxidation of glycerol under the following conditions: a NaOH solution and the gold catalyst (700 mg) were added to a 0.3 M aqueous solution of glycerol (total volume 195 mL; NaOH/glycerol molar ratio = 2) under stirring at 1000 rpm; the reactor was pressurized with nitrogen at 3 bar; finally, after heating under nitrogen to 60 °C, the reaction was initiated by switching from inert gas to oxygen (3 bar).

The reaction was monitored by taking samples (0.5 mL) for analysis at regular time intervals. The quantitative analysis of these samples was carried out by high performance liquid chromatography (HPLC). The chromatograph (Elite LaChrom HITACHI) was equipped with an ultraviolet (210 nm) and a refractive index detector in series. Products were identified by comparison with standard samples. More details about HPLC analyses can be found in Chapter 2 and Appendix B.

8.3 Results and discussion

8.3.1 Characterization of catalysts

The gold content, obtained by ICP analysis, is lower than the nominal (Table 8.1), which indicates that a fraction of gold present in the aqueous solution was not deposited on the supports during the preparation stage. Moreover, it should be noticed that the metal loading obtained is significantly different depending on the support used. Whereas most of the gold was successfully supported on CeO_2 and on the mixed oxide, only 1.66% was obtained with ZrO_2 , indicating that the gold precursor has a lower affinity to this support. This can be due to the different acid-base properties of the supports. In fact, $\text{AuCl}(\text{OH})_3^-$ ions (formed from AuCl_4^- at pH 6-8) may have more difficulty to anchor on the surface of ZrO_2 , which is more basic than the CeO_2 surface [19]. A similar explanation was presented by Sobczak et al. [13] when reporting the low anchoring efficiency of gold on alumina.

Gold nanoparticles were successfully prepared on the different supports. As an illustrative example, a STEM-HAADF image of the Au/ZrO_2 -350 catalyst is shown in Figure 8.1. In this technique, regions in which the average atomic number (Z) of the elements is high will appear in the image as very bright points, whereas those in which the average Z is small are imaged as lower intensity areas [20]. Considering the atomic numbers of the elements involved, it becomes clear that brighter areas in the image presented in Figure 8.1 correspond to gold.

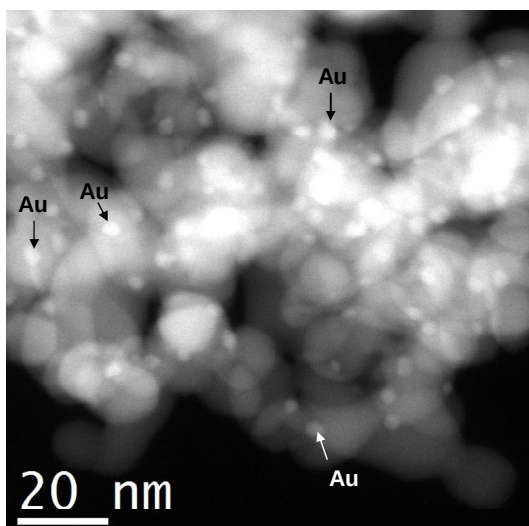


Figure 8.1 STEM-HAADF image of Au/ZrO_2 -350 (some gold particles are indicated as example).

The average diameters of gold particles were estimated by measuring the sizes of a high number of them (above 200) on different STEM-HAADF images. They vary between 1.2 and 5.1 nm, depending on the support and on the calcination temperature used (Table 8.1).

Table 8.1 Average crystallite size, metal content and gold leaching of fresh catalysts.

Sample	Metal Loading (%)	Average diameter (nm)	Au leached (%) ^a
Au/CeO ₂ -250	2.89	1.3	0.57
Au/CeO ₂ -350	2.89	2.7	0.86
Au/CeO ₂ -550	2.89	4.4	0.46
Au/ZrO ₂ -250	1.66	1.2	7.45
Au/ZrO ₂ -350	1.66	3.1	7.75
Au/ZrO ₂ -550	1.66	5.1	5.36
Au/CeZr-250	2.67	1.3	0.42
Au/CeZr -350	2.67	2.4	1.15
Au/CeZr -550	2.67	4.4	1.13

^a Obtained after 7 h (end of catalytic tests).

The results clearly indicate the effect of the temperature of calcination on the size and dispersion of gold, i.e. the average size of gold crystallites on the surface of samples increases with the calcination temperature.

The Hüttig and Tammann temperatures (T_H and T_T , respectively) give indication about the temperature range at which sintering of the metal starts to occur and are directly related to the absolute melting temperature of the metal, T_f , as follows:

$$T_H \approx 1/3T_f \quad (8.1)$$

$$T_T \approx 1/2T_f \quad (8.2)$$

For gold, T_f is equal to 1337 K (1064 °C). Therefore, sintering is expected to start occurring at temperatures between 173 and 396 °C. The two lower values used for the thermal treatment are in this range. Nevertheless, it is worth to mention that even with the higher temperature used (550 °C), the average gold sizes do not exceed about 5 nm; this can indicate that gold particles have a good interaction with the supports, which prevents significant sintering. In fact, no particles higher than 9 nm were found (see Figure 8.2). Moreover, when considering the same calcination temperature, comparable average gold particle sizes were effectively obtained, independently of the support used. For instance, when considering the calcination at 250 °C, gold particles supported on ceria and on the Ce-Zr mixed oxide have an average size of 1.3 nm, while 1.2 nm was obtained for gold supported on zirconia (see Table 8.1).

As it can be seen in Figure 8.2, narrow size distributions were observed in all catalysts, particularly in those calcined at 250 °C.

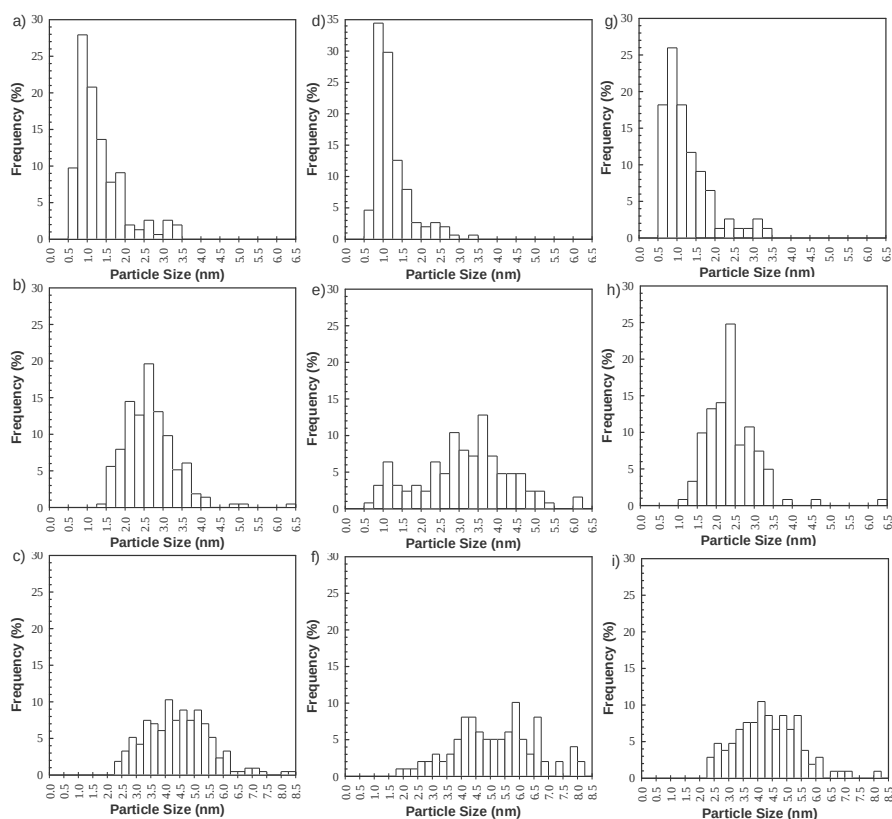


Figure 8.2 Particle size distributions in a) Au/CeO₂-250, b) Au/CeO₂-350, c) Au/CeO₂-550, d) Au/ZrO₂-250, e) Au/ZrO₂-350, f) Au/ZrO₂-550, g) Au/CeZr-250, h) Au/CeZr-350 and i) Au/CeZr-550.

8.3.2 Catalytic studies

8.3.2.1 CeO₂ and ZrO₂ supported gold catalysts

Figure 8.3 shows the evolution of glycerol conversion in the presence of the gold catalysts prepared on CeO₂ and ZrO₂. It can be observed that gold supported on these oxides are efficient catalysts for glycerol oxidation. All the CeO₂ supported gold catalysts present a higher performance than the ZrO₂ supported ones, a complete glycerol conversion being obtained after 3 - 3.5 h for the former, and only after 4.5 - 5 h for the latter catalysts. Nevertheless, as already mentioned in Section 8.3.1, gold loadings are not the same for both oxides. Accordingly, in order to take into account these differences, reaction rates after 2 h of reaction were calculated and normalized by the amount of gold present in each catalyst. For instance, comparing Au/CeO₂-250 and Au/ZrO₂-250, the following rates were obtained: $1.30 \times 10^{-2} \text{ mol h}^{-1} \text{ g}_{\text{Au}}^{-1}$ and $1.39 \times 10^{-2} \text{ mol h}^{-1} \text{ g}_{\text{Au}}^{-1}$, respectively. In fact, very similar values were obtained for all sample, even if prepared at different calcination temperatures. This indicates that there are no important differences, i.e. neither the nature of these supports nor the initial gold particle sizes seem to influence significantly the performance.

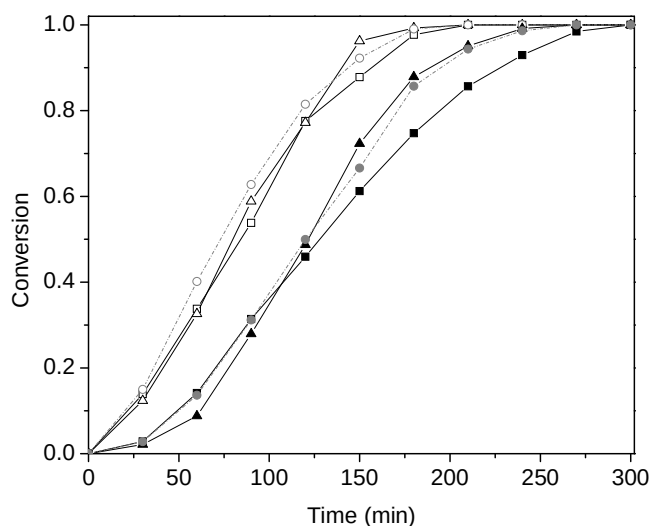


Figure 8.3 Influence of the calcination temperature on the performance of Au/CeO₂ (open symbols) and Au/ZrO₂ (filled symbols) catalysts; □: 250 °C, Δ: 350 °C, ○: 550 °C. Reaction conditions: 60 °C, p_{O_2} = 3 bar, 150 mL of glycerol 0.3 M, catalyst amount = 700 mg, NaOH/glycerol = 2 mol/mol.

The variation in the calcination temperature does not lead to importantly different performances, although it is generally accepted that these are largely influenced by particle sizes, the catalysts with smaller gold particles being more active [18, 21-22]. According to Figure 8.3, it seems that the samples heat-treated at 250 °C (average particle sizes in fresh samples of 1.2 - 1.3 nm) deactivate slightly. This phenomenon is more visible in the case of the Au/ZrO₂-250 catalyst. This can be due to the increase of gold particle sizes during the reaction. In fact, smaller particles are generally more prone to sintering [23]. It is possible that the average size of gold particles may increase during the oxidation reaction, and therefore all the catalysts have comparable average crystallite sizes, which would justify the similar performances observed. In order to confirm this assumption, TEM analyses of some catalysts after the corresponding reaction tests were carried out. The results are presented in Table 8.2.

Table 8.2 Average crystallite sizes of some catalysts after 7 hours in the reaction medium.

Sample	Average diameter (nm)
Au/CeO ₂ -550	4.8
Au/ZrO ₂ -250	5.3
Au/ZrO ₂ -550	5.8
Au/CeZr-250	4.3
Au/CeZr-550	4.8

The growing size of gold particles is confirmed (cf. Table 8.1 and Table 8.2). In fact, at the end of the experiments, the catalysts have fairly similar average crystallite sizes of about 5 nm. The higher difference between fresh and used catalysts is observed with those calcined at 250 °C. Accordingly, the average gold particle size of Au/ZrO₂-250 increases from 1.2 to 5.3 nm and particles as large as 9.5 nm are observed in this case (see Figure 8.4). In contrast, the Au/CeO₂-550 catalyst only suffers a slight increase of average size from 4.4 nm to 4.8 nm. Therefore, the use

of higher calcination temperatures in the preparation of catalysts, and thus higher initial nanoparticle sizes, could be beneficial since the resulting samples seem more stable and less prone to metal sintering. Comparing the Au/CeO₂ and Au/ZrO₂ catalysts calcined at the same temperature of 550 °C, it can be concluded that ceria seems to be more efficient to stabilize gold nanoparticles, as a lower increase is observed in this case (from 4.4 to 4.8 nm vs. 5.1 to 5.8 nm).

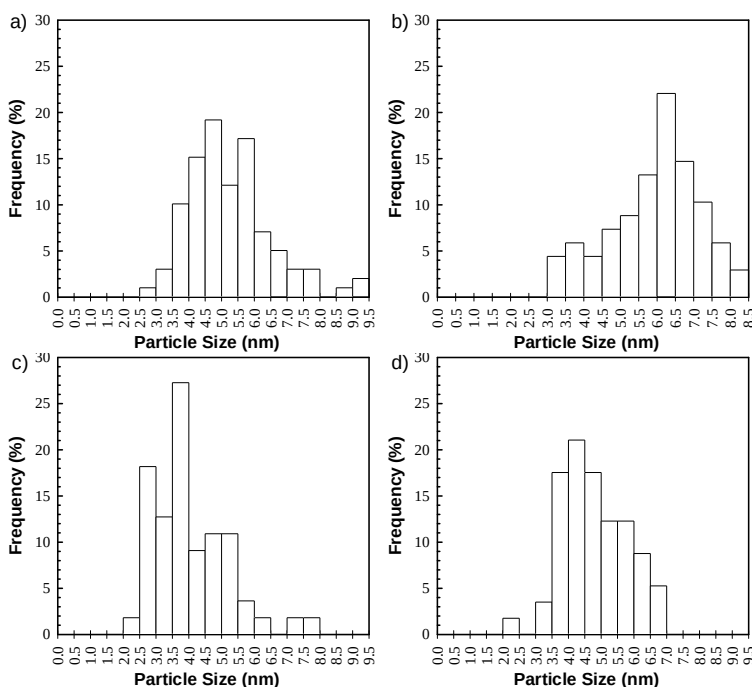


Figure 8.4 Particle size distributions of the catalysts after use: a) Au/ZrO₂-250, b) Au/ZrO₂-550, c) Au/CeZr-250 and d) Au/CeZr-550.

In view of their practical application, the catalysts have to be stable, i.e. metal leaching should also be avoided. Unfortunately, some leaching occurs (Table 8.1). Although this does not particularly affect the cerium oxide supported catalysts, it can be observed that leaching of almost 8% of the total gold loading was observed with the Au/ZrO₂ catalysts after 7 h in the reaction medium. Similarly to the results of TEM analyses after reaction, this also indicates a poorer interaction of the metal with the ZrO₂ support.

In summary, it can be more advantageous using ceria as support for gold nanoparticles and high calcination temperatures, which enhance the interaction between metal and support, preventing sintering more efficiently.

All catalysts oxidize glycerol to the main product, glyceric acid (GLYCEA), with a high selectivity of about 70%, as shown in Figure 8.5 and Figure 8.6. The other products detected are glycolic acid (GLYCOA), tartronic acid (TARTA), oxalic acid (OXALA) and formic acid (FORMA).

The selectivity to GLYCEA is fairly stable during the reaction for all catalysts supported on CeO_2 (Figure 8.5). Similar selectivities to this compound were obtained (average values of 69% with Au/CeO_2 -550, and 66% for Au/CeO_2 -250 and Au/CeO_2 -350).

In the case of ZrO_2 based catalysts (see Figure 8.6), it is worth to notice that, although the initial selectivity to glyceric acid is similar for all catalysts tested ($S_{\text{GLYCEA}} \approx 70\%$), the corresponding variation during the reaction differs. In fact, catalysts with initial smaller gold particles (Au/ZrO_2 -350 and mainly Au/ZrO_2 -250) show a decrease in the selectivity to the target compound (from 68% to 51% at 100% conversion in the case of Au/ZrO_2 -250 and from 71% to 60% for Au/ZrO_2 -350). On the other hand, the selectivity remains practically constant when using the Au/ZrO_2 -550 catalyst (S_{GLYCEA} decreases only from 70% to 65%). This is in accordance with the reported in the literature, i.e. small particles lead to decreasing selectivities during the reaction, whereas bigger gold particles are able to promote fairly constant selectivities from the beginning until complete glycerol conversion [21]. This can also be influenced by the lower stability of small gold particles in the samples calcined at lower temperatures, particularly in the case of this oxide, as discussed before.

Prolonging catalytic tests after reaching complete glycerol conversion resulted in the over oxidation of glyceric acid to tartronic acid and further to inorganic carbon. In fact, it should be noticed that the sum of the measured selectivities is always lower than 1 (see Figure 8.5 and Figure 8.6). Therefore, complete oxidation to inorganic carbon, probably in the form CO_3^{2-} , occurs (selectivities of 7 to 23%). Only limited amounts of oxalic acid were obtained (selectivities do not exceed 6%).

In the case of Au/ZrO_2 -550, glyceric acid over oxidation was substantially much slower. This can be explained by the higher average particle size of this catalyst, obtained after 7 hours (Table 8.2), since it is known that bigger particles are less active [18, 21-22].

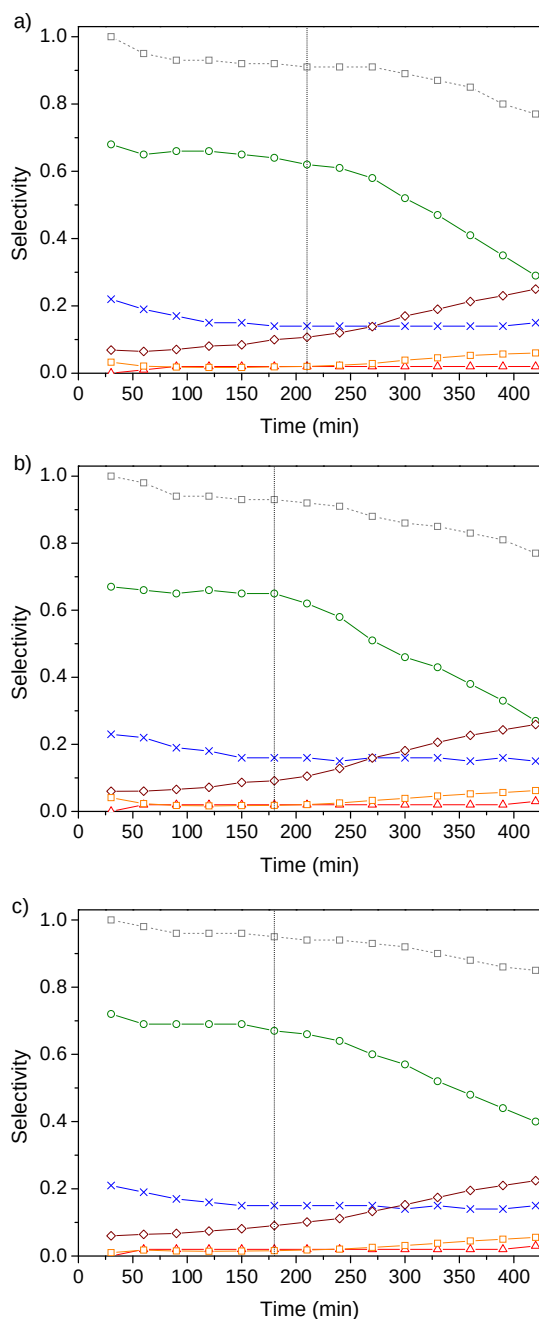


Figure 8.5 Selectivities towards the products of reaction and their sum (S_{TOTAL}) in the presence of the Au/CeO₂ catalysts calcined at a) 250 °C; b) 350 °C and c) 550 °C. ($\text{---}\circ\text{---}$ S_{GLYCEA} , $\text{---}\times\text{---}$ S_{GLYCOA} , $\text{---}\diamond\text{---}$ S_{TARTA} , $\text{---}\square\text{---}$ S_{OXALA} , $\text{---}\triangle\text{---}$ S_{FORMA} , $\text{---}\square\text{---}$ S_{TOTAL}). Vertical lines indicate the time corresponding to total glycerol conversion. Reaction conditions: 60 °C, p_{O_2} = 3 bar, 150 mL of 0.3 M glycerol solution, catalyst amount = 700 mg, NaOH/glycerol = 2 mol/mol.

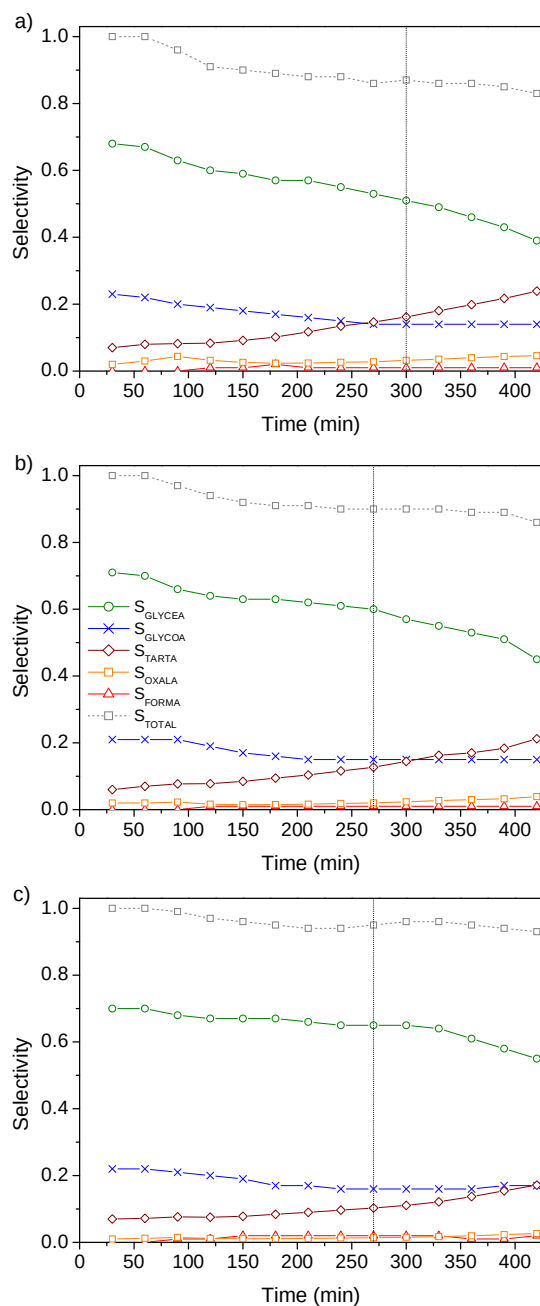


Figure 8.6 Selectivities towards the products of reaction and their sum (S_{TOTAL}) in the presence of the Au/ZnO₂ catalysts calcined at a) 250 °C; b) 350 °C and c) 550 °C. ($\text{---}\circ\text{---}$ S_{GLYCEA} , $\text{---}\times\text{---}$ S_{GLYCOA} , $\text{---}\diamond\text{---}$ S_{TARTA} , $\text{---}\square\text{---}$ S_{OXALA} , $\text{---}\triangle\text{---}$ S_{FORMA} , $\text{---}\square\text{---}$ S_{TOTAL}). Vertical lines indicate the time corresponding to total glycerol conversion. Reaction conditions: 60 °C, p_{O_2} = 3 bar, 150 mL of 0.3 M glycerol solution, catalyst amount = 700 mg, NaOH/glycerol = 2 mol/mol.

8.3.2.1.1 Effect of the pre-reaction period on the size of gold particles

Gold nanoparticles do not seem very stable, particularly when the support used is ZnO_2 and the calcination temperature is low. Despite the different average gold particle sizes, very similar results were obtained with the different Au/ZrO_2 catalysts, even at the very beginning of the reaction (see Figure 8.3). This suggests that growing of the gold nanoparticles could also occur during the initial preparation stage of the reactor, i.e. during heating until 60 °C, when the catalyst is already in contact with NaOH and glycerol under an inert atmosphere (see Section 8.2.3). Therefore, when the reaction is initiated by switching from inert gas to oxygen, the particles of the Au/ZrO_2 -250 catalyst could already have fairly large crystallites.

In order to investigate the influence of this pre-reaction time, Au/ZrO_2 -250 was mixed with NaOH and glycerol solutions (the conditions used were the same as during a typical reaction experiment). Then, the reactor was pressurized with nitrogen at 3 bar and heated to 60 °C. After a stabilization time of 5 min at this temperature, the reactor was purged and the heating was switch off. Finally the catalyst was recovered by filtration and TEM analysis was carried out. The results are presented in Table 8.3. As expected, after this preparation time, an approximately 3 fold increase of the average particle size is observed (from 1.2 to 3.2 nm). This implies that at the beginning of the reaction, this sample already has gold particles with diameters comparable to the fresh Au/ZrO_2 -350 catalyst (cf. Table 8.1). In order to evaluate the influence of the different species present in the reaction medium, additional pre-reaction treatments were performed (see Table 8.3). The presence of water during heating under pressure, already leads to a significant sintering of gold (from 1.2 to 2.8 nm). The addition of NaOH amplifies even more this effect, whereas glycerol does not seem to contribute significantly.

Table 8.3 Average crystallite sizes of gold particles after different pre-reaction treatments.

Sample	Diameter (nm)
Au/ZrO_2 -250 (water)	2.8
Au/ZrO_2 -250 (water + NaOH)	3.1
Au/ZrO_2 -250 (water + NaOH + glycerol)	3.2

Given these results, the tendency to sintering displayed by small gold nanoparticles may be difficult to overcome. The gold dispersion is not constant during the reaction; the average gold particle size of the fresh catalysts is not even maintained during the preparation stage of the laboratorial reactor. Accordingly, using catalysts with larger particles can in fact be beneficial, since they allow similar performances associated to constant selectivities in the course of reaction.

8.3.2.1.2 Successive experiments

Due to the good stability in terms of metal leaching and sintering observed with the Au/CeO₂-550 catalyst, successive experiments were carried out using this sample (Figure 8.7).

Each run was carried out under the standard conditions described previously. The catalyst was recovered by filtering off the solution of the previous run after 3.5 h of reaction and reused. Since the catalyst corresponds to a very thin powder, some losses occurred during the filtration procedure, and thus a limited amount of fresh catalyst ($\approx 10\%$ of the total weight) was also added to the reaction medium.

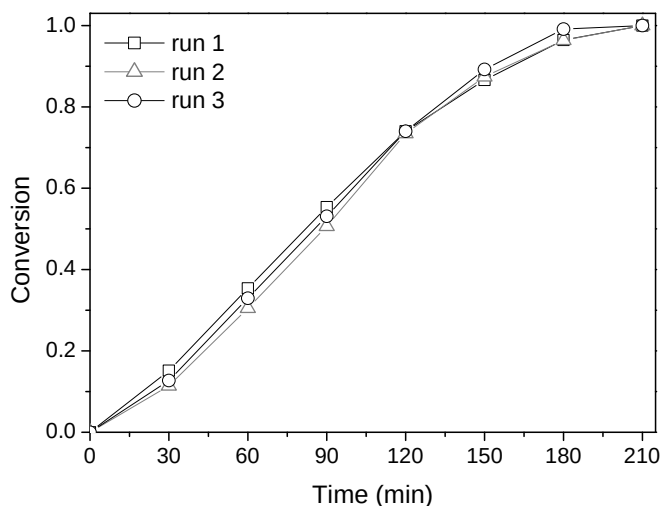


Figure 8.7 Successive experiments with the Au/CeO₂-550 catalyst. Reaction conditions: 60 °C, $p_{O_2} = 3$ bar, 150 mL of glycerol 0.3 M, catalyst amount = 700 mg, NaOH/glycerol = 2 mol/mol.

These experiments show that the Au/CeO₂-550 catalyst is stable, contrarily to what occurs with carbon supported gold catalysts, where a significant loss of performance is observed from run to run (see Chapter 3 and Chapter 4). Moreover, no differences in selectivities were noticed between the different runs. In spite of the much lower performances obtained with gold supported on oxides, when compared with carbon supports, the results of the successive experiments show an important advantage, since these catalysts can be used several times without loss of efficiency and selectivity.

8.3.2.2 Ce-Zr mixed oxide supported gold catalysts

It is worth to notice that, although Au/ZrO₂-250 and Au/CeZr-250 fresh catalysts have similar average gold crystallite sizes (Table 8.1), the increase observed after reaction with Au/ZrO₂-250 is more significant (Table 8.2). Then, the use of the mixed oxide as support can lead to a higher stability of the particles, and therefore be advantageous. Moreover, gold leaching is also very limited, as it occurs in ceria supported gold (Table 8.1). Therefore, this support was investigated as carrier of gold nanoparticles for the selective oxidation of glycerol.

Figure 8.8 shows the evolution of glycerol conversion in the presence of the gold catalysts supported on Ce_{0.68}Zr_{0.32}O₂. Although the initial rate of glycerol conversion is practically equal for all catalysts, the performances differ slightly during the reaction, increasing as the calcination temperature decreases, which eventually could be explained by the lower gold average sizes (Table 8.1). Nevertheless, the average sizes of the different catalysts recovered after use tend to similar values (see Table 8.2). In this way, it is difficult to elaborate definitive conclusions about the real influence of the particle size on the performance and further investigations should be carried out. In spite of this commentary, it is important to notice that the performances obtained are only marginally different (see Figure 8.8), and therefore variations can be related to experimental errors, at least partially.

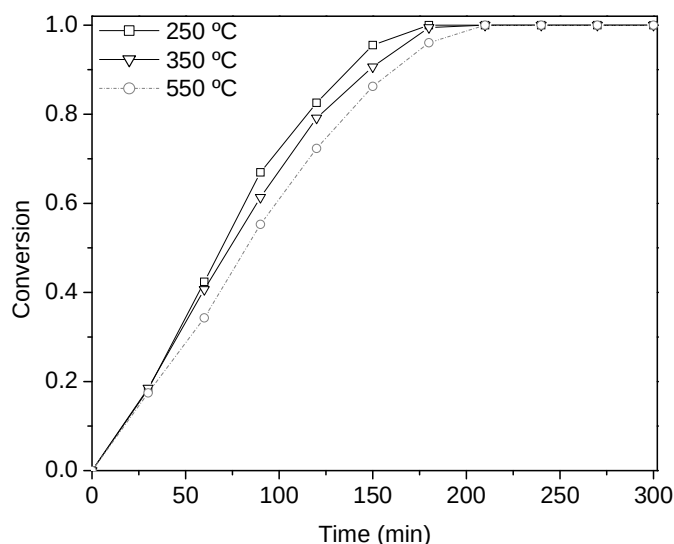


Figure 8.8 Influence of the calcination temperature on the performance of Au/CeZr catalysts. Reaction conditions: 60 °C, $p_{O_2} = 3$ bar, 150 mL of glycerol 0.3 M, catalyst amount = 700 mg, NaOH/glycerol = 2 mol/mol.

Figure 8.9 shows the selectivities towards the different products during the reaction and after complete glycerol conversion was reached.

The use of the mixed oxide as support leads to selectivities towards glyceric acid comparable to those obtained when testing CeO_2 or ZrO_2 supported catalysts ($\approx 70\%$). The main advantage is that the selectivity towards this compound is reasonably constant during all the reaction period, particularly in the cases of Au/CeZr-350 and Au/CeZr-550, which can indicate that the gold particles are particularly stable on this support. In fact, particles on the Au/CeZr-550 catalyst only grew from 4.4 to 4.8 nm after 7 h (cf. Tables 8.1 and 8.2). As observed before, after 100% glycerol conversion is reached, GLYCEA is mainly oxidized to TARTA and inorganic carbon.

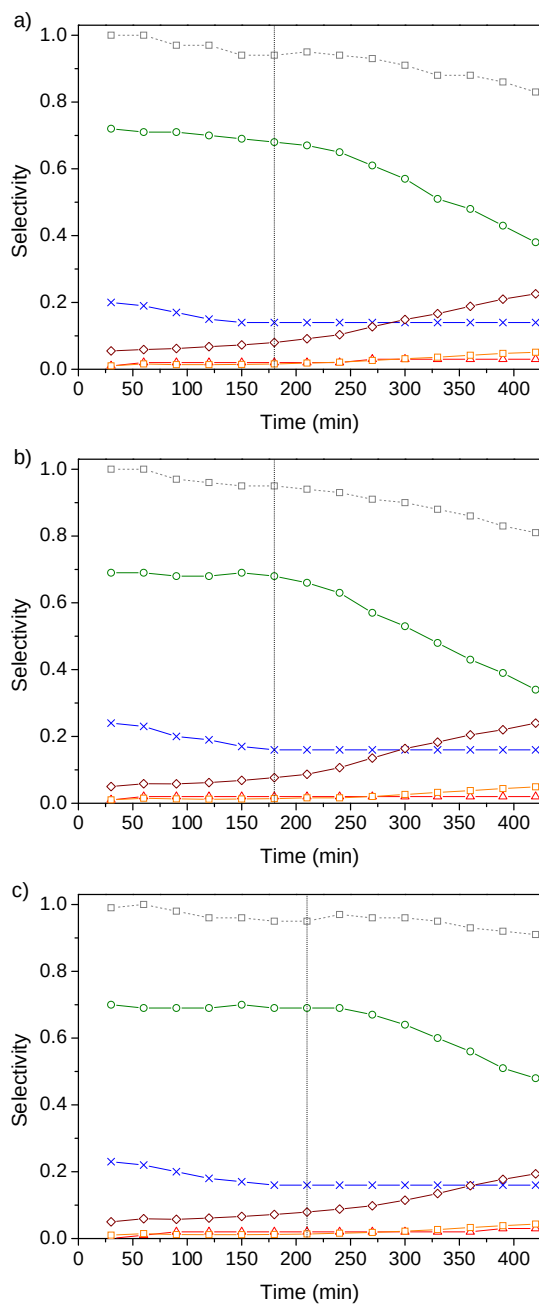


Figure 8.9 Selectivities towards the products of reaction and their sum (S_{TOTAL}) in the presence of the Au/CeZr catalysts calcined at a) 250 °C; b) 350 °C and c) 550 °C. (—○— S_{GLYCEA} , —×— S_{GLYCOA} , —◇— S_{TARTA} , —□— S_{OXALA} , —△— S_{FORMA} , - - -□- - - S_{TOTAL}). Vertical lines indicate the time corresponding to total glycerol conversion. Reaction conditions: 60 °C, $p_{\text{O}_2} = 3$ bar, 150 mL of 0.3 M glycerol solution, catalyst amount = 700 mg, NaOH/glycerol = 2 mol/mol.

8.4 Conclusions

Gold nanoparticles supported on cerium oxide, zirconium oxide and Ce-Zr mixed oxide are efficient for converting glycerol into glyceric acid, product of commercial interest. Accordingly, a high selectivity of about 70% was obtained with all the catalysts tested in this work. Different supports do not lead to important performance variations, provided that gold contents are similar. Moreover, fresh catalysts with different average gold particle sizes also lead to similar performances. This can be explained by the observed metal sintering during the reaction, smaller particles being more prone to this phenomenon. More particularly, gold seems to have a lower interaction with ZrO_2 , since significant leaching and higher sintering of particles were observed when compared with the other supports.

The main advantage of using the mixed oxide studied is the very constant selectivity to glyceric acid that is obtained throughout the reaction. Moreover, successive experiments with Au/CeO₂-550 show no loss of performance.

A relationship between average gold particle size and catalyst performance was difficult to establish. In fact, it was clearly observed that gold dispersion is a dynamic parameter. Moreover, the support itself can have an influence on the performance. Further studies are necessary in order to explain these aspects.

Gold particles with comparable average sizes lead to very different performances when supported on oxides or on carbon materials. Once again, this indicates that the catalytic activity is not merely dependent on the properties of the active phase. The support may have also a large influence, and generally it does not act only as carrier. Further studies taking into account specific redox and acid-base properties of oxide supports should be carried out.

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Chapter 9

9 Conclusions and future work

In this final chapter of the thesis, a general overview of the main results is presented, along with the most relevant conclusions. Finally, some ideas for future work are suggested.

9.1 Motivation

Biodiesel has emerged as a viable clean fuel over the last decade. Its conventional production is a chemical process based on transesterification, leaving glycerol as an inevitable by-product. Due to the tremendous growth of the biodiesel industry, the glycerol market is experiencing a surplus. In fact, nowadays, the production of crude glycerol largely exceeds the commercial demand for purified glycerol, and thus the non distilled glycerol by-product is discarded as waste and usually burned. Nevertheless, adding value to the glycerol by-product would reduce the net production cost of biodiesel. Accordingly, in order to achieve a sustainable and economically competitive biodiesel business, when compared with fossil fuels, crude glycerol must be processed efficiently.

Glycerol is a highly functionalized molecule when compared to hydrocarbons from petrochemistry; this makes it an attractive and advantageous potential starting material for the synthesis of valuable derivatives. In fact, this readily available organic raw material exhibits a versatile and high chemical reactivity due to its three hydroxyl groups. As a result, glycerol has been identified as a building block for future biorefineries, since it can be converted to a large number of chemicals by several reaction pathways.

Selective hydrogenolysis, selective dehydration, selective etherification, reforming and conversion of glycerol into glycerol carbonate are only a few examples that allow the catalytic conversion of glycerol into commodity chemicals. In contrast to these large-volume commodities, catalytic partial oxidation is a small-scale application that focuses on the synthesis of fine chemicals with very high added value.

Liquid phase catalytic oxidation is a promising route to convert glycerol into useful compounds, provided that the catalyst used is sufficiently active and (predominantly) selective for the production of chemicals of commercial interest, potentially useful as chemical intermediates in fine chemical industries, particularly for the synthesis of pharmaceuticals and cosmetics. However, the extensive functionalization of the molecule, with three hydroxyl groups similarly reactive, renders its selective oxidation particularly difficult and a large number of products can be obtained by a complex reaction pathway. The main challenge is to find catalysts highly selective to target molecules. It has been shown that the activity and selectivity of catalysts are strongly influenced by several factors, such as the

nature and dispersion of metal, the catalyst preparation procedure, the reaction conditions and also the nature of the support.

Gold presents peculiar properties as a catalytic material at a nanoscale level and is considered as the catalyst of preferential choice in glycerol oxidation. However, the catalytic results largely depend on the preparation method employed and on the support used. For gold to be an active catalyst, the use of a careful preparation procedure is crucial, since it is necessary to obtain nanoparticles well dispersed on the support.

Carbon supported gold catalysts are generally reported as more active than most oxide supported catalysts. Carbon materials have been used for a long time in heterogeneous catalysis, since they can satisfy most of the properties required for a suitable support: inertness, stability under reaction and regeneration conditions, adequate mechanical properties and high surface area. Nevertheless, the role of the support may not be merely that of a carrier; the interaction between the active phase and the support can also affect the catalytic performance.

At the time the present research began, information in the literature on activated carbon supported metal catalysts was already relatively abundant. However, no data about the role of the support surface chemistry were available. In addition, other carbon supports, such as carbon nanotubes and carbon xerogels had not been tested. The study of these subjects was the principal motivation for the research work that led to the presentation of this dissertation.

9.2 Main conclusions

The main purpose of this work was to investigate the liquid phase catalytic oxidation of glycerol in a systematic way, focusing on the use of carbon materials as support. The typical reaction conditions used in most of the present studies were the following: 60 °C, $P_{O_2} = 3$ bar, 150 mL of glycerol 0.3 M, NaOH/glycerol = 2 mol/mol, catalyst amount = 700 mg. Different metal catalysts, preparation techniques and supports were evaluated. Activated carbons and carbon nanotubes (including chemically and thermally modified samples), carbon xerogels and oxides were assessed as supports. Several metal catalysts were prepared, characterized and tested in the process.

The first goal of this thesis was to study several metals supported on a commercial activated carbon under the same reaction conditions and preparation method

(incipient wetness), in order to accurately compare the catalytic performances. Additionally to metals already studied in the literature (platinum, palladium and gold), two other metals (iridium and rhodium) were tested in the glycerol oxidation reaction in highly basic aqueous solutions. Using the typical conditions mentioned above, the performances decrease in the order: Pd > Rh >> Pt. The platinum catalyst deactivates promptly due to oxygen poisoning, whereas iridium does not even show any activity. On the other hand, incipient wetness allows obtaining very active Pd and Rh catalysts in a simple, easy and quick way; these catalysts promote a high glycerol conversion. Contrarily to the other catalysts prepared by the incipient wetness method, the gold catalyst presented low particle dispersion. It was concluded that the incipient wetness method is not suitable to obtain well-dispersed active gold nanoparticles. A very similar distribution of the products was observed, independently of the nature of the metal. In fact, Pd, Rh and Pt supported on activated carbon lead to a high and constant selectivity (around 75%) to the product of commercial interest, i.e. glyceric acid.

A more detailed study was carried out with the rhodium catalyst, since no previous reports about its activity in glycerol oxidation was found in literature. Two different deactivation causes were distinguished: over-oxidation (oxygen poisoning) and loss of activity by the eventual presence of large amounts of surface oxygenated groups on the activated carbon surface, namely those of acid nature. Therefore, rhodium catalysts appear to be suitable for glycerol oxidation, provided that their crystallites are not too small, since small metal nanoparticles deactivate more readily because of their stronger affinity to oxygen, and the support has neutral or basic properties. These two parameters can be easily controlled by thermal treatments.

Contrarily to the incipient wetness method of impregnation, the sol immobilization technique appears to be suitable for generating small gold crystallite sizes supported on activated carbon, originating highly effective catalysts for glycerol oxidation under basic conditions. The main advantage of using gold is related to its strong resistance to oxygen poisoning, compared to catalysts of the platinum group, allowing high levels of oxygen in the reaction medium without significant deactivation. TOF values as high as 8810 h^{-1} were obtained using an oxygen partial pressure of 10 bar. Au/AC catalysts were chosen in order to understand more deeply the relationship between the surface chemical characteristics of activated carbon and the catalytic performances. A strong effect of the activated carbon surface chemistry on the catalytic activity was observed. Gold particles with similar average sizes resulted in different performances, being the surface oxygenated acid

groups particularly prejudicial for the catalytic activity. As a result, the oxygen content on the surface of the support is a factor of large influence in the reaction. Basic oxygen-free supports characterized by a high density of free π -electrons lead to more active catalysts, which can be due to their capability to promote electron mobility. In fact, according to a proposed mechanism, the mobility of the electrons from and to the gold surface could potentially promote both adsorption and regeneration of hydroxide ions, and thus the catalytic performance.

Nevertheless, contrary to what was observed with the activities, the presence of oxygenated groups on the support surface did not influence significantly the selectivities. Similarly to the results obtained with Pt, Rh and Pd catalysts supported on activated carbon, the prepared gold catalysts lead to a high selectivity to glyceric acid of about 75%. Moreover, identical distributions of products were observed, independently of the amount of oxygenated surface groups present on the activated carbon surface.

The use of carbon nanotubes as support was investigated. This type of carbon material has a strictly mesoporous nature, differing largely from the activated carbon used before. Gold nanoparticles were supported on multi-walled carbon nanotubes by different methods with the main purpose of evaluating the effect of the preparation techniques on the activity and selectivity, and therefore select the best of them.

The sol immobilization method was concluded to be the most suitable to prepare gold supported on carbon nanotubes, since it allows a better use of gold, leading to a high active catalyst and to the highest selectivity to glyceric acid. Nevertheless, in spite of the similar average gold particle sizes obtained, gold supported on carbon nanotubes is less active and less selective to glyceric acid than Au/activated carbon ($\approx 45\%$ vs. $\approx 75\%$).

Although, glyceric acid still was the main reaction product for all catalysts tested, gold nanoparticles, with variable average particle sizes, supported on multi-walled carbon nanotubes lead to high and similar selectivities to formic acid ($\approx 20\%$), which seems to indicate that the particular characteristics of the support used play an important role in the distribution of products. In fact, when testing gold supported on activated carbon, under the same reaction conditions and with a similar average particle size, only a very limited amount of formic acid was detected (selectivity lower than 5%). The high selectivity towards formic acid in Au/MWCNT catalysts may support the presence as intermediate of dihydroxyacetone, which is rapidly

degraded due to the highly basic medium. Unfortunately, no activity is observed when using gold catalysts without addition of base.

An increase of the average Au particle size of the recovered catalyst after successive experiments is generally observed, independently of the support used; this favors the selectivity to glyceric acid, but diminishes significantly the catalytic performance.

Multi-walled carbon nanotubes with different levels of oxygenated groups on the surface were prepared, and the sol immobilization method was chosen to support gold nanoparticles. Regarding activities, the results obtained with these catalysts were similar to those established for activated carbon supported gold catalysts. Accordingly, Au/MWCNT catalysts are highly active only when the support has a limited amount of oxygenated groups on the surface. However, in this case, the surface chemistry of carbon nanotubes also influences the distribution of products. In fact, oxygen-rich supports promote the formation of glycolic acid, which is normally an unwanted over-oxidized by-product, in detriment of glyceric acid. The highest selectivity to the product of commercial interest (glyceric acid) was obtained with the most basic support, which only contains a very low amount of oxygenated groups on the surface.

In conclusion, in the design of gold catalysts for glycerol oxidation, special attention should be given to the nature and amount of oxygenated groups present on the carbon support surface and, more generally, to its surface chemistry. The performance of gold catalysts is not only ruled by the crystallite size, since the support also plays a key role.

The large differences in selectivities observed when gold with a similar content and average particle size is supported on activated carbon or multi-walled carbon nanotubes seem to indicate that the support textural properties, namely mesopore sizes, can be a key factor in order to tune the distribution of products. For the purpose of studying this subject, two mesoporous carbon xerogels having different pore sizes were prepared and used as support in the preparation of gold catalysts. The sol immobilization method has the advantage of predetermining the size of the gold particles, which is maintained during the immobilization step. Therefore, comparable crystallite sizes were obtained for the different carbon supports tested throughout this work. Moreover, due to the importance of surface chemistry, only carbon supports having a similar (very limited) amount of oxygenated groups are compared. It was observed that the mesopore size distribution of carbon xerogels

used as support of gold influences the selectivity in glycerol oxidation. In fact, an increase of the most frequent pore diameter from 5 to 20 nm leads to an enhancement of the selectivity to formic acid from 5% to 11% and to a slight decrease of the selectivity to glyceric acid from 67% to 63%. Moreover, the gold catalyst supported on the carbon xerogel with narrow mesopores shows a higher activity. This support has a lower electrical resistivity (i.e. higher electron mobility), which is in agreement with the results obtained with activated carbons and carbon nanotubes chemically and thermally modified (Chapters 3 and 5, respectively).

Carbon materials predominantly with narrow pores lead to an enhancement of the selectivity to glyceric acid, whereas those having wide mesopores favor the formation of formic acid, probably via dihydroxyacetone. The same trend was observed with gold supported on activated carbon and multi-walled carbon nanotubes. In fact, significant correlations between the selectivities to glyceric acid and to formic acid, calculated at iso-conversion, and the most frequent mesopore diameters of carbon supports were noticed. In addition, the type of carbon support plays an important role in the distribution of products, and therefore it is possible to tune selectivities by changing it. A 75% selectivity towards glyceric acid can be reached with gold supported on activated carbon, whereas a selectivity of about 20% to formic acid is obtained when carbon nanotubes are used as support.

Supports leading to high selectivities to formic acid are probably those that lead initially to higher amounts of dihydroxyacetone, which is an economically interesting target compound. Taking into account the results obtained in this work, it was suggested that the formation of dihydroxyacetone can require the binding of the glycerol molecule in a conformation that needs more space, and therefore is favored by supports with wide pores. Accordingly, the use of multi-walled carbon nanotubes can be advantageous in acid media, which are favorable to the stability of dihydroxyacetone.

Platinum catalysts supported on multi-walled carbon nanotubes promote glycerol conversion in both acid and basic conditions, but, as also observed with activated carbon as support, suffer severely from oxygen poisoning. Platinum impregnated on carbon nanotubes by incipient wetness disfavors the formation of glyceric acid and enhances the formation of formic acid in basic media, when compared with platinum supported on activated carbon by the same method (the selectivity towards glyceric acid decreases from $\approx 75\%$ to $\approx 60\%$). It was found that oxygen poisoning can be greatly delayed simply by increasing the average particle size. This can be achieved by using the sol immobilization method. Moreover, deactivation by oxygen

poisoning is completely overcome by using a bimetallic Pt-Au catalyst, but a decrease on the selectivity to glyceric acid is observed, particularly at prolonged reaction times (i.e. high glycerol conversions).

Nevertheless, whereas a highly basic pH promotes the formation of glyceric acid, dihydroxyacetone is only observed under neutral or acid conditions. Although a poorer performance in terms of glycerol conversion was observed under acid conditions with the bimetallic Pt-Au catalyst, this enhances the formation of dihydroxyacetone when compared with the monometallic platinum catalyst.

Finally, some preliminary studies of glycerol oxidation over gold supported on ceria, zirconia and a Ce-Zr mixed oxide were also carried out under basic conditions. Although the activities obtained are lower than those reported for gold supported on carbon materials, all these catalysts oxidize glycerol to the main product (glyceric acid) with a high selectivity of about 70%. Moreover, successive experiments with Au/CeO₂ show that this catalyst does not deactivate (i.e. similar conversion results were obtained), contrarily to carbon supported gold catalysts, which results in progressive performance loss.

In summary, it was demonstrated that the catalytic oxidation of glycerol is an effective method of producing added-value compounds being largely influenced by the metal phase, the pH of the reaction medium, the catalyst preparation method and the support. High glycerol conversions can be obtained under basic conditions with gold prepared by the sol immobilization method and supported on oxygen-free (basic) carbon materials. In addition to the high activity, selectivities of 75% towards glyceric acid were obtained using noble metals supported on activated carbon, under basic conditions. The selectivities can be tuned with the appropriate choice of the carbon support. In fact, materials with narrow pores lead to an enhancement of the selectivity to glyceric acid, whereas carbons with wide mesopores favor the formation of formic acid, probably via dihydroxyacetone as intermediate, since this compound is not stable under basic conditions. Platinum catalysts supported on multi-walled carbon nanotubes are able to promote glycerol conversion in both acid and basic conditions. Nevertheless, the effective production of dihydroxyacetone, which is a very high-value compound, is only achieved under acid conditions, since it is not stable in basic media, where apparently acts as an intermediate leading to the formation of formic acid. In spite of its lower performance, it is possible to enhance the selectivity to dihydroxyacetone under acid conditions (relatively to the Pt catalyst) by using a Pt-Au bimetallic catalyst.

9.3 Suggestions for future work

Liquid phase catalytic oxidation is a promising route to convert glycerol into useful compounds, but achieving adequate selectivities remains a challenge and more fundamental work should be carried out for further insights.

In order to increase the electronic mobility, the use of nitrogen-doped carbons as support could be interesting and can lead to an enhancement of the catalytic activity.

The good redox properties of some oxide supports can eventually play a role in the reaction. Taking into account the preliminary results obtained with cerium oxide, further research is necessary in order to understand the interaction between this type of support and the metal and/or its influence in the reaction mechanism. Moreover, other supports, such as manganese oxides, particularly cryptomelane, should also be investigated.

Due to possible promoter effects obtained when adding some metals to gold, other bimetallic catalysts such as Au-Rh, Au-Pd and Au-Ru could be tested under basic conditions.

It should be considered that, even if the activity obtained in basic media is higher, the corresponding valuable product (i.e. glyceric acid) is obtained as glycerate, and then a supplementary process step (acidification) is necessary. On the other hand, the catalytic oxidation of glycerol to dihydroxyacetone in acid media should be more deeply investigated, using platinum supported on multi-walled carbon nanotubes and carbon xerogels. The addition of other metals, such as bismuth, antimony or copper, which can have a promoter effect in Pt-based catalysts, should be studied and the catalyst formulations optimized. Effectively, some interesting results with Pt-Bi and Pt-Cu catalysts supported on activated carbon are mentioned in the literature.

Knowledge about the reaction mechanism is scarce. Then, it is important to obtain more information about intermediate species on the catalyst surface. For that purpose, in situ spectroscopic methods (FTIR) could be useful.

It would be interesting to test in the oxidation of crude glycerol the most promising catalysts prepared in the scope of the present work, in order to evaluate the feasibility of industrial application.

Appendices

Appendix A. Schematic representation of the experimental set-up

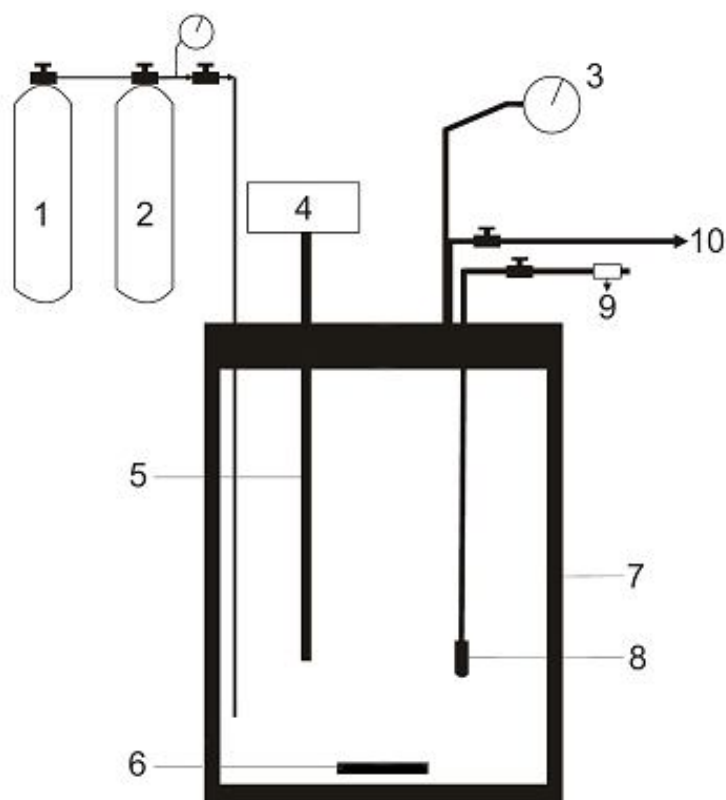


Figure A.1 Scheme of the experimental set-up used for the oxidation of glycerol. 1- Oxidant (O₂); 2- Inert gas (N₂); 3- Manometer; 4- Temperature controller; 5- thermocouple; 6- Magnetic stirrer; 7- Reactor; 8- Sampling tube; 9- Sampling valve; 10- Gas outlet.

Appendix B. Calibration lines and evaluation of reactant and products

During the reaction, the reaction mixture was analyzed by taking samples of 500 μl at regular time intervals. The qualitative and quantitative analyses of mixtures were carried out by high performance liquid chromatography (Elite Lachrom HITACHI). The conditions used are presented in Table B.1.

Table B.1 Measurement conditions of HPLC analyses.

Column	Alltech OA 1000
Eluent	H_2SO_4 0.01 M
Flow rate	0.5 mL min^{-1}
Detectors	Ultraviolet (210 nm) Refractive index (40 °C)
Measuring time	20 min

The individual components were identified by comparison with standard samples. The retention times are presented in Table B.2. The corresponding calibration lines are shown in Figure B.1 and Figure B.2.

Table B.2 Measured retention times of glycerol and its oxidation products.

Compound	Abbreviation	Retention time UV (min)	Retention time RI (min)
Oxalic acid	OXALA	5.8	6.5
Tartronic acid	TARTA	7.9	8.6
Glyceric acid	GLYCEA	11.2	11.9
Glyceraldehyde	GLYCER	10.9	11.6
Glycolic acid	GLYCOA	12.5	13.2
Formic acid	FORMA	13.4	14.1
Dihydroxyacetone	DIHA	13.4	14.1
Glycerol	GLY	n.d.	13.2

n.d. – not detectable.

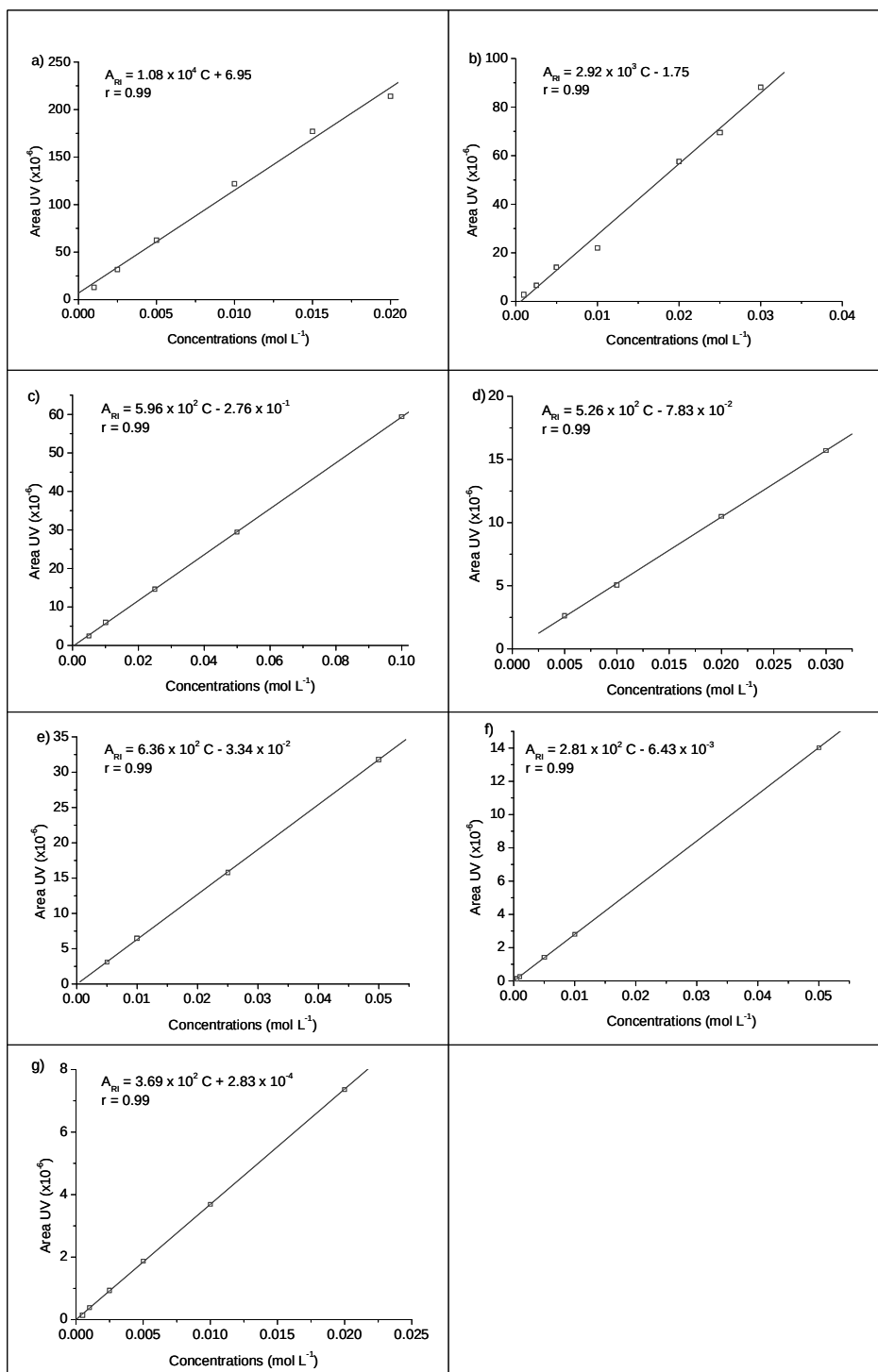


Figure B.1 UV calibration lines of a) OXALA, b) TARTA, c) GLYCEA, d) GLYCOA, e) FORMA, f) GLYCER and g) DIHA.

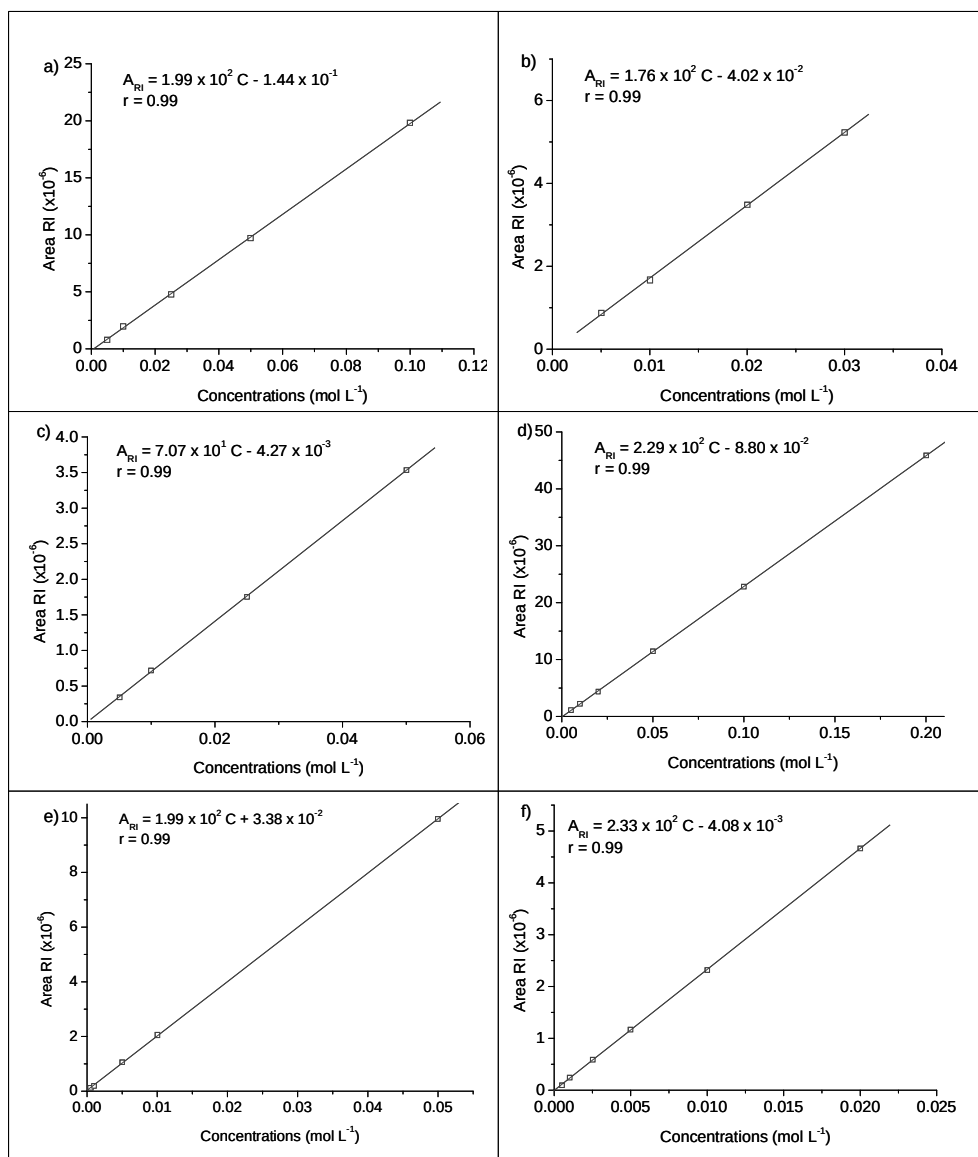


Figure B.2 RI calibration lines of a) GLYCEA, b) GLYCOA, c) FORMA, d) GLY, e) GLYCER and f) DIHA.

The calibration lines have been used to determine the composition of the reaction mixture. An example of the chromatograms obtained during the glycerol oxidation under highly basic conditions can be seen in Figure B.3.

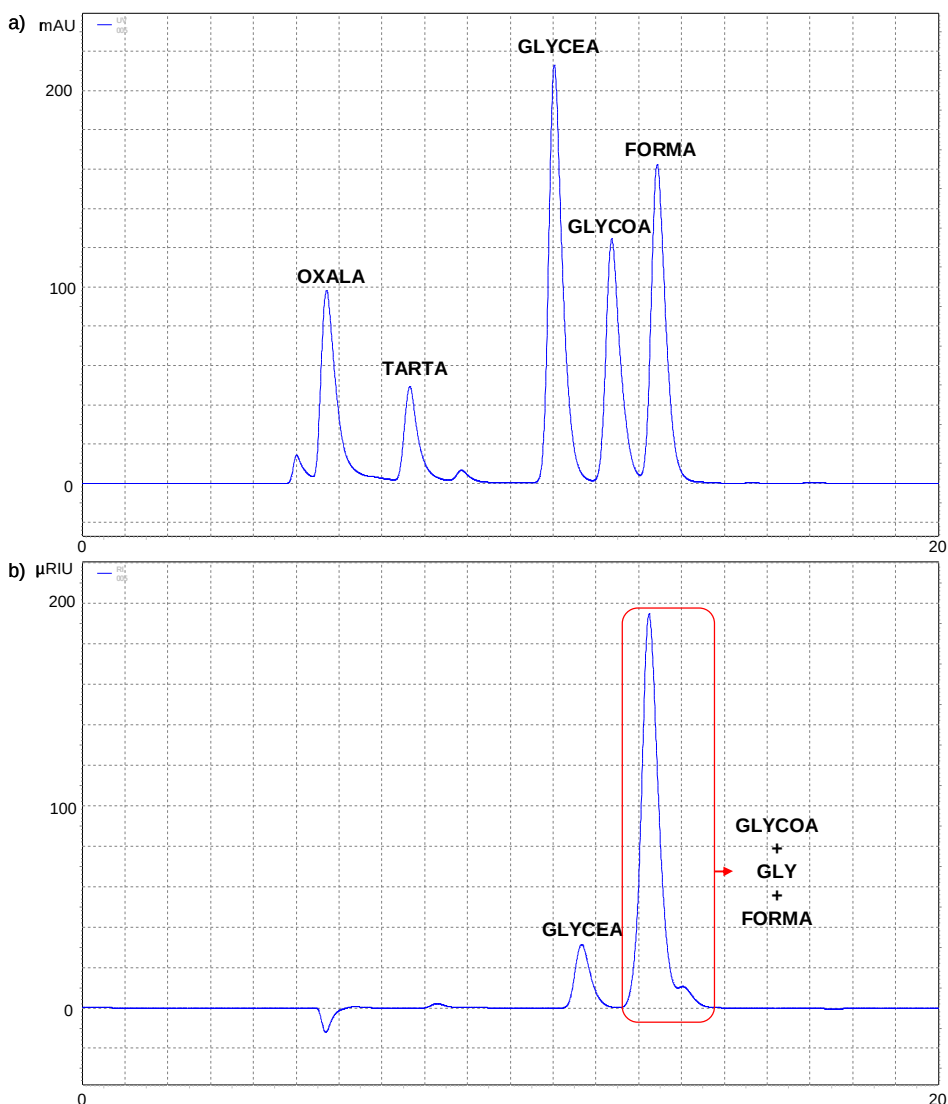


Figure B.3 Chromatograms of a reaction mixture during glycerol oxidation in the presence of a gold catalyst in basic medium: a) UV detector and b) RI detector.

A particular challenge in the development of the quantification method was to separate glycolic acid, glycerol and formic acid from each other since these components appear as a single peak in the RI detector (see Figure B.3). However, the accurate quantification of glycerol is important for further calculations and interpretation of results (e.g. conversion, selectivities).

Since glycerol is not detectable with the UV detector, glycolic acid and formic acid can be quantified accurately with the UV signal and respective calibration lines (see Figure B.1 and Figure B.3), as following:

$$C_{GLYCOA} = \frac{A_{GLYCOA_UV} + 7.83 \times 10^4}{5.26 \times 10^8} \quad (B.1)$$

$$C_{FORMA} = \frac{A_{FORMA_UV} + 3.34 \times 10^4}{6.36 \times 10^8} \quad (B.2)$$

where C_x is the concentration of the compound x (mol L⁻¹) and A_{x_UV} is the area obtained with the UV detector.

In this way, the concentrations of GLYCOA and FORMA in the sample are known from the UV chromatogram. Using the calibration curves obtained for these compounds in the RI detector (Figure B.2), it is possible to calculate the corresponding areas in the RI chromatogram:

$$A_{GLYCOA_RI} = 1.76 \times 10^8 C_{GLYCOA} - 4.02 \times 10^4 \quad (B.3)$$

$$A_{FORMA_RI} = 7.07 \times 10^7 C_{FORMA} - 4.27 \times 10^3 \quad (B.4)$$

These areas are subtracted to the total area A_{SUM_RI} (corresponding to the sum of glycerol, glycolic and formic acid areas; see Figure B.3) obtained in the RI chromatogram. In this way, the glycerol concentration can be determined:

$$C_{GLY} = \frac{(A_{SUM_RI} - A_{GLYCOA_RI} - A_{FORMA_RI}) + 8.80 \times 10^4}{2.29 \times 10^8} \quad (B.5)$$

The concentrations of other reaction products are determined using directly the information from the UV chromatogram.

Appendix C. Deconvolution of TPD spectra of activated carbons

To determine the amount of each oxygenated surface group, the deconvolution of the CO and CO₂ TPD spectra was carried out. A multiple Gaussian function was used for fitting each spectrum. The numerical calculations were based on a non-linear routine, which minimizes the sum of squared deviations, using the Levenberg-Marquardt method to perform the iterations. The use of Gaussian functions is justified by the shape of the TPD peaks, which are a result of continuous random distributions of binding energies of the surface groups. Some assumptions, justified in previous works (J.L. Figueiredo, M.F.R. Pereira, M.M.A. Freitas, J.J.M. Órfão, *Modification of the surface chemistry of activated carbons*. Carbon **37** (1999) 1379-1389; J.L. Figueiredo, M.F.R. Pereira, M.M.A. Freitas, J.J.M. Órfão, *Characterization of active sites on carbon catalysts*. Ind. Eng. Chem. Res. **46** (2007) 4110-4115), were followed:

- The CO₂ spectra are decomposed into three contributions, corresponding to carboxylic acids (CO₂ peak #1 and #2), carboxylic anhydrides (CO₂ peak #3) and lactones (CO₂ peak #4). The samples heat treated above 400 °C do not present CO₂ evolution at low temperatures, because they were processed at a temperature higher than those corresponding to the decomposition of carboxylic acids.
- There are two types of carboxylic groups, which can be assigned to strongly acidic (CO₂ peak #1) and less acidic (CO₂ peak #2) carboxylic groups.
- Each carboxylic anhydride group decomposes by releasing one CO and one CO₂ molecule. The first component in the CO spectrum corresponds to the carboxylic anhydrides, and the corresponding peak (CO peak #3) has the same shape and equal magnitude to the CO₂ peak #3. This peak is pre-defined from the deconvolution of the CO₂ spectrum.

- In addition to carboxylic anhydrides (CO peak #3), the CO spectrum includes contributions from phenols (CO peak #4) and carbonyl/quinones (CO peak #5). This sequence of decomposition temperatures (first phenols, then carbonyl/quinones) is justified by the higher stability of the later groups.

- The same width at half-height was imposed for CO₂ peaks #3 and #4.

- The same width at half-height was considered for phenol and carbonyl/quinone groups. This was necessary mainly in the case of samples where there were no peak shoulders.

- It was assumed that there are two CO peaks at low temperature (CO peaks #1 and #2) with the same center and width at half-height of those obtained for the carboxylic groups in the CO₂ TPD spectrum. This hypothesis is deeply discussed in J.L. Figueiredo, M.F.R. Pereira, M.M.A. Freitas, J.J.M. Órfão, *Characterization of active sites on carbon catalysts*. Ind. Eng. Chem. Res. **46** (2007) 4110-4115.

This deconvolution procedure proved to fit data quite well for TPD spectra. As an illustrative example, the deconvolution of sample AC₁ (see Chapter 2 and Chapter 3) is shown in Figure C.1.

Tables C.1 and C.2 show the results obtained for the activated carbons mentioned in Chapter 2 and Chapter 3, where T_m is the temperature of the component peak maximum, W is the corresponding width at half-height and A is the specific amount of each component.

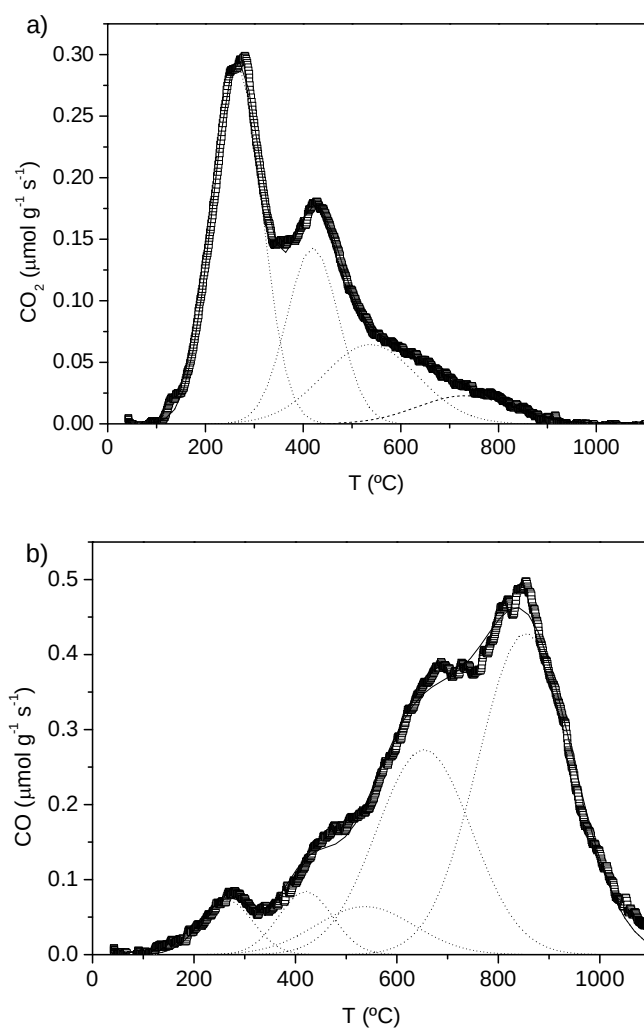


Figure C.1 Results of the deconvolution of the TPD spectra of sample AC₁ using a multiple Gaussian function: a) CO₂ spectrum and b) CO spectrum (□, TPD experimental data.; ---, individual peaks; —, sum of individual peaks).

Table C.1 Results of the deconvolution of CO₂ spectra using a multiple Gaussian function.

Sample	Peak #1			Peak #2			Peak #3			Peak #4		
	T _M	W	A	T _M	W	A	T _M	W	A	T _M	W	A
	(°C)	(°C)	(μmol g ⁻¹)	(°C)	(°C)	(μmol g ⁻¹)	(°C)	(°C)	(μmol g ⁻¹)	(°C)	(°C)	(μmol g ⁻¹)
AC ₀	249	104	95	376	175	39	537	213	37	734	203	18
AC ₁	265	101	433	420	99	175	496	221	239	709	221	82
AC _{1tt400}	254	122	48	-	-	-	507	176	233	710	176	75
AC _{1tt600}	316	198	44	-	-	-	539	185	27	721	185	101
AC _{1tt900}	294	251	84	-	-	-	564	227	31	848	227	12
AC _{1tt900-H2}	-	-	-	-	-	-	-	-	-	-	-	-

Table C.2 Results of the deconvolution of CO spectra using a multiple Gaussian function.

Sample	Peak #1			Peak #2			Peak #3			Peak #4			Peak #5		
	T _M	W	A	T _M	W	A	T _M	W	A	T _M	W	A	T _M	W	A
	(°C)	(°C)	(μmol g ⁻¹)	(°C)	(°C)	(μmol g ⁻¹)	(°C)	(°C)	(μmol g ⁻¹)	(°C)	(°C)	(μmol g ⁻¹)	(°C)	(°C)	(μmol g ⁻¹)
AC ₀	249	104	18	376	175	30	537	213	37	665	183	191	869	183	500
AC ₁	265	101	100	420	99	85	496	221	239	654	186	788	854	186	1209
AC _{1tt400}	-	-	0	-	-	0	507	176	232	644	169	895	840	169	1082
AC _{1tt600}	-	-	0	-	-	0	688	168	27	741	199	658	836	199	1080
AC _{1tt900}	-	-	0	-	-	0	564	227	31	784	114	71	932	114	170
AC _{1tt900-H2}	-	-	0	-	-	0	-	-	0	832	77	26	933	77	70

The same procedure was used for the characterization of the surface chemistry of MWCNT sample (see Chapter 5).

Appendix D. Investigation of the degradation temperature of PVA

A TG-DSC experiment was carried out under N_2 atmosphere in a Netzsch STA 409 PC Luxx[®] System. About 15 mg of sample were loaded into a ceramic crucible and the temperature was raised to 350 °C at 10 °C/min. This technique was used to determine the optimum degradation temperature of PVA. Results are presented in Figure D.1, which shows that 350 °C is sufficient to remove PVA in the preparation of gold supported catalysts by the immobilization method.

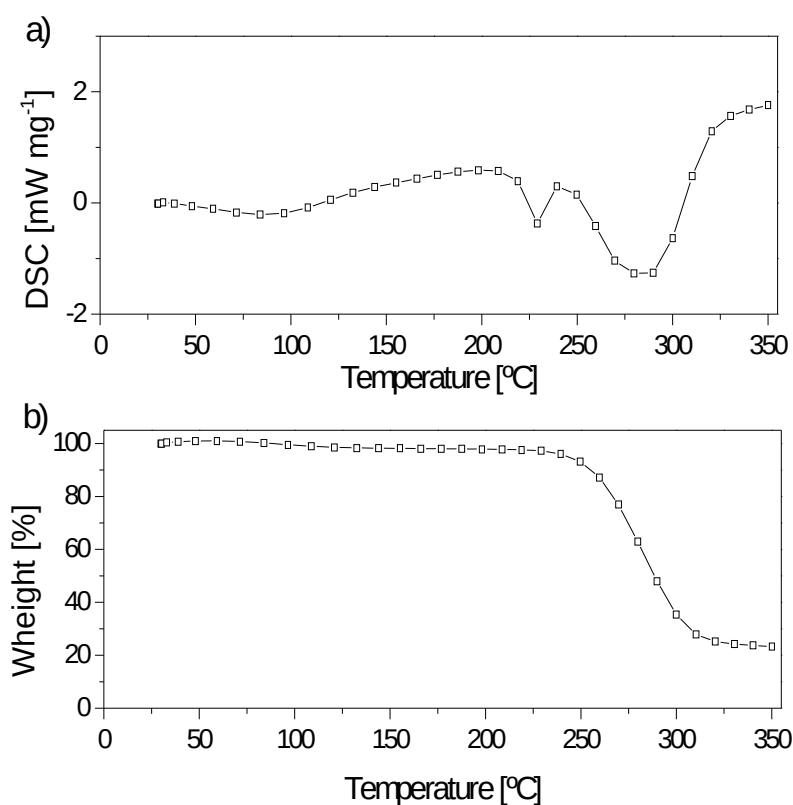


Figure D.1 TG-DSC curves of PVA in N_2 under linear temperature programming (10 °C/min): a) DSC curve; b) TG curve.

Appendix E. Evidence for the absence of the internal diffusion limitations in carbon xerogel supported catalysts

Since particle sizes are very low, the experimental investigation of internal diffusion limitations is difficult. Therefore, a theoretical approach was applied. The absence of diffusional limitations can be highlighted by the Weisz-Prater criterion, based on the calculation of the Weisz modulus Φ (G.F. Froment, K.B. Bischoff, Chemical Reactor Analysis and Design, second ed., Wiley, New York, 1990). This parameter is defined as:

$$\Phi = \frac{r_a \rho_{bulk} L^2}{w D_e C_s}$$

where r_a is the observed reaction rate, ρ_{bulk} is the bulk density of the catalyst, L is the ratio between the volume and the external surface area of the porous catalyst particle, w is the catalyst mass per unit volume of fluid in the reactor, D_e is the effective diffusion coefficient and C_s is the concentration at the catalyst surface. In the case of spherical catalyst particles, $L = \frac{d_p}{6}$, where d_p is the particle diameter.

On the other hand, $D_e = D_m \frac{\varepsilon}{\tau}$, where D_m corresponds to the molecular diffusion coefficient, ε to the particle porosity and τ to the tortuosity. Taking into account the reasonable approximation of the random pore model (G.F. Froment, K.B. Bischoff, Chemical Reactor Analysis and Design, second ed., Wiley, New York, 1990), it can be assumed that $\tau = \frac{1}{\varepsilon}$.

The Weisz modulus compares the observed reaction rate with the diffusion rate. When $\Phi < 1$ the diffusion phenomenon has no significant effect, and r_a is equal to the intrinsic reaction rate. When $\Phi > 1$ diffusional limitations modify the kinetics, and r_a can be very different from the intrinsic reaction rate.

For each parameter, the following values were considered:

$$\blacksquare d_p = 2 \times 10^{-4} \text{ [m]}$$

- $530 < \rho_{bulk} < 980$ [kg m⁻³] (from N. Job, R. Pirard, J. Marien, J.-P. Pirard, *Porous carbon xerogels with texture tailored by pH control during sol-gel process*. Carbon **42** (2004) 619-628)

- $1.75 \times 10^{-5} < r_a < 2.53 \times 10^{-5}$ [kmol m⁻³ s⁻¹]

- $w = \frac{7 \times 10^{-4} \text{ kg}}{1.95 \times 10^{-4} \text{ m}^3} = 3.59$ [kg m⁻³]

- $2 \times 10^{-10} < D_m < 5 \times 10^{-10}$ [m³_{fluid} m⁻¹_{catalyst} s⁻¹] (as typical values for molecular diffusion of liquids, from G.F. Froment, K.B. Bischoff, Chemical Reactor Analysis and Design, second ed., Wiley, New York, 1990)

- $0.55 < \varepsilon < 0.76$ (from N. Job, R. Pirard, J. Marien, J.-P. Pirard, *Porous carbon xerogels with texture tailored by pH control during sol-gel process*. Carbon **42** (2004) 619-628)

- $C_s = 0.23 \text{ kmol m}^{-3}$

The calculations led to Φ values varying between 0.04 and 0.55. Therefore, under the conditions used, it can be concluded that the process is not significantly influenced by intraparticle diffusion.