

Novel Catalytic Systems for the Selective Hydrogenation of α,β -Unsaturated Aldehydes

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***What we do in life
echoes through eternity...***

(unknown)

ABSTRACT

Hydrogenation of α,β -unsaturated aldehydes generates two primary reaction products: the saturated aldehyde and the unsaturated alcohol. Because the C=C bond is more easily hydrogenated than the C=O, low yield of the desired unsaturated alcohol is usually observed. Thus, the hydrogenation of the unfavored carbonyl group is an interesting challenge, both from the academic and the industrial point of view. A typical model reaction that can be used to assess the performance of a given catalyst is the selective hydrogenation of cinnamaldehyde to cinnamyl alcohol. The yield towards the latter is found to be significantly improved by addressing key aspects of catalyst design, like the control of support nature and its chemical surface and criterious choice of the active metal phase.

Two different types of supports are explored in this thesis: carbon materials and metal oxides. The carbon materials tested are multi-walled carbon nanotubes and two types of polymeric carbon forms: xerogels and aerogels. Regarding the metal oxides, three different types of supports are used: TiO₂, CeO₂ and Ce-Ti-O, and ZnO materials.

The preparation of Pt, Ir or Ru monometallic catalysts supported on different carbon materials is described. The functionalization of the support is found to play an important role on metal dispersion, with liquid-phase nitric acid activation producing the more thermally stable catalysts. In this case, Pt deposition is successfully correlated to the amount of oxygenated groups at the surface. Pt and Ru catalysts initially reveal a very low selectivity towards cinnamyl alcohol, in opposition to Ir catalysts. A high temperature thermal treatment at 700°C is found to remove most groups from the support surface while simultaneously increasing the metal particle size. This combined effect causes a remarkable increase in the selectivity for Pt catalysts supported over nanotubes and xerogels. With Ir and Ru catalysts the performance is not so marked, but a small increase in selectivity to cinnamyl alcohol is observed. An opposite trend is observed for carbon aerogels as catalytic supports, i.e., lower selectivities to cinnamyl alcohol are observed after the thermal treatment. The general improvement in selectivity is interpreted in terms of mobility and variance of electron density of the metal phase. Selectivities of thermally treated catalysts (700°C) can be ordered according to the nature of the support: xerogels $\approx$ nanotubes > aerogels.

In what concerns metal oxides, TiO_2 is prepared according to a sol-gel method ($\text{TiO}_{2\text{sg}}$), CeO_2 -based materials are synthesized using a solvothermal approach and ZnO is produced according to a chemical vapor deposition process (ZnO_{CVD}). In the case of TiO_2 and ZnO , several commercially available samples are tested for comparison purposes ($\text{TiO}_{2\text{c}}$ and ZnOc). Platinum metal is photochemically deposited over the surface of the different metal oxides. A thermal treatment at 500°C with H_2 is performed to Pt supported over the reducible metal oxides. This treatment promotes the occurrence of the strong metal support interaction effect in the catalysts, associated to high selectivities towards cinnamyl alcohol. In this effect, TiO_x sites in the vicinity of the Pt surface coordinate the oxygen atom of the $\text{C}=\text{O}$ bond via interaction with a lone pair of electrons, increasing its reactivity towards the preferential hydrogenation. In the case of ZnO supported catalysts, characterization results indicate the existence of a PtZn alloy. The high selectivities observed are attributed to this alloy formation. Selectivities towards cinnamyl alcohol are found to vary, according to the metal oxide support, in the following way: $\text{TiO}_{2\text{sg}} > \text{TiO}_{2\text{c}} \approx \text{ZnOc} > \text{Ce-Ti-O} > \text{CeO}_2 > \text{ZnO}_{\text{CVD}}$.

Finally a global comparison of all supported catalysts is made and a few conclusions on their adequacy to the process are drawn. The conditions used are much milder than the usually reported and nevertheless selectivities as high as 83% are obtained, for 50% conversion of cinnamaldehyde.

RESUMO

A hidrogenação selectiva de aldeídos α,β -insaturados gera dois produtos de reacção principais: o aldeído saturado e o álcool insaturado. A hidrogenação da ligação C=C é mais fácil que a hidrogenação da ligação C=O, pelo que é normalmente obtido um rendimento baixo para a formação do álcool insaturado desejado. Desta forma, a hidrogenação preferencial do grupo carbonilo representa um desafio interessante, quer do ponto de vista académico, quer do ponto de vista industrial. Uma reacção modelo típica que pode ser utilizada para estudar o desempenho de um dado catalisador é a hidrogenação selectiva do cinamaldeído a álcool cinâmico. A produção deste álcool insaturado pode ser significativamente melhorada através do controlo de aspectos fundamentais no projecto e preparação do catalisador, como a natureza do suporte e a sua química superficial e uma escolha cuidada da fase metálica activa.

Nesta tese são explorados dois tipos de suportes diferentes: materiais de carbono e óxidos metálicos. Os materiais de carbono estudados são nanotubos de carbono de parede múltipla e duas formas de carbono polimérico: xerogéis e aerogéis. Em relação aos óxidos metálicos, são utilizados três tipos de suporte diferentes: TiO_2 , CeO_2 e Ce-Ti-O, e ZnO.

Utilizando os diferentes materiais de carbono como suporte, é descrita a preparação de catalisadores monometálicos de platina, irídio ou ruténio. A funcionalização do suporte desempenha um papel importante na dispersão do metal. Quando o suporte é activado com ácido nítrico em fase líquida são produzidos catalisadores termicamente mais estáveis, estando a deposição da platina correlacionada com a quantidade de grupos oxigenados presentes na superfície do suporte. Os catalisadores que contêm platina e ruténio revelam inicialmente uma selectividade bastante baixa para a formação de álcool cinâmico, por oposição aos catalisadores de irídio. Um tratamento térmico a alta temperatura (700°C) remove a maior parte dos grupos superficiais do suporte, contribuindo simultaneamente para o aumento da dimensão das partículas metálicas. Esta combinação de efeitos provoca um aumento notável da selectividade dos catalisadores de platina suportados em nanotubos e em xerogéis de carbono. No caso dos catalisadores de irídio e ruténio, o desempenho não é tão acentuado, observado-se apenas um pequeno aumento na selectividade para o álcool cinâmico. Uma tendência oposta é observada quando se utilizam aerogéis de carbono como suporte catalítico, ou seja, existe uma diminuição da selectividade para o álcool cinâmico após o tratamento

térmico. A melhoria geral na selectividade após o tratamento térmico pode ser interpretada em termos de mobilidade e variação da densidade electrónica da fase metálica. A selectividade dos catalisadores tratados termicamente (700°C) pode ser ordenada segundo a natureza do suporte: xerogéis $\approx$ nanotubos > aerogéis.

No que diz respeito aos óxidos metálicos, o TiO_2 é preparado de acordo com um método sol-gel (TiO_2sg), os materiais baseados em CeO_2 são sintetizados utilizando uma abordagem solvotérmica, enquanto que o ZnO é produzido de acordo com um processo de deposição química em fase de vapor (ZnO_{CVD}). Nos casos do TiO_2 e do ZnO , são testadas várias amostras comercialmente disponíveis para fins de comparação (TiO_2c e ZnOc). A platina foi dispersa sobre a superfície dos diferentes óxidos metálicos por fotodeposição, sendo posteriormente tratada a 500°C, em H_2 . Este tratamento favorece a ocorrência de uma interacção forte entre o metal e o suporte nos catalisadores, associada a selectividades elevadas para o álcool cinamílico. Nesta interacção, os centros activos TiO_x localizados na vizinhança da superfície da platina coordenam o átomo de oxigénio da ligação $\text{C}=\text{O}$ através da sua interacção com um par de electrões, aumentando a sua reactividade para a hidrogenação preferencial do grupo carbonilo. No caso dos catalisadores suportados em ZnO , os resultados da caracterização indicam a existência de uma liga PtZn . As elevadas selectividades observadas, utilizando este suporte, são atribuídas à formação desta liga. A selectividade em relação ao álcool cinamílico varia de acordo com o óxido metálico usado como suporte da seguinte forma: $\text{TiO}_2\text{sg} > \text{TiO}_2\text{c} \approx \text{ZnOc} > \text{Ce-Ti-O} > \text{CeO}_2 > \text{ZnO}_{\text{CVD}}$.

Para finalizar, é efectuada uma comparação global de todos os catalisadores suportados, sendo retiradas algumas conclusões sobre a sua adequação à reacção estudada. As condições operatórias são bastante mais amenas que aquelas utilizadas vulgarmente, tendo sido obtidas selectividades máximas de 83%, para uma conversão de 50% de cinamaldeído.

RÉSUMÉ

L'hydrogénation des aldéhydes α,β -insaturés génère deux principaux produits de réaction: l'aldéhyde saturé et l'alcool insaturé. Comme le lien C=C est plus facilement hydrogéné que le C=O, un faible rendement de l'alcool insaturé désiré est généralement observé. Ainsi, l'hydrogénation du groupe carbonyle défavorisé est un défi intéressant à relever, autant du point de vue académique qu'industriel. Un modèle type de réaction qui peut être utilisé pour évaluer le rendement du catalyseur est l'hydrogénation sélective de cinnamaldéhyde à l'alcool cinnamique. Le rendement de celui-ci est considérablement amélioré par les principaux aspects de la préparation du catalyseur, comme le contrôle de la nature de support, sa chimie superficielle et des critères de choix de phase active métallique.

Deux types de supports sont explorés dans cette thèse: les matériaux de carbone et d'oxydes de métaux. Les matériaux de carbone qui ont été testés sont des nanotubes de carbone multi-parois et deux types de carbone polymérique: xérogels et aérogels. En ce qui concerne les oxydes de métaux, trois types de supports différents ont été utilisés: TiO_2 , CeO_2 et Ce-Ti-O, et ZnO.

La préparation de catalyseurs monométalliques de platine, iridium ou ruthénium supportés sur différents matériaux de carbone est décrite. Il a été observé que la fonctionnalisation du support joue un rôle important sur la dispersion des métaux, étant l'activation avec l'acide nitrique en phase liquide celle qui mène à la production des catalyseurs les plus stables thermiquement. Dans ce cas, le dépôt de platine est corrélé avec succès avec la quantité de groupes oxygénés à la surface. Les catalyseurs de platine et ruthénium révèlent initialement un très faible taux de sélectivité envers l'alcool cinnamique, contrairement aux catalyseurs d'iridium. Il a été observé qu'un traitement thermique à haute température (700°C) élimine la plupart des groupes de la surface du support tout en augmentant la taille des particules de métal. Cet effet combiné provoque une remarquable augmentation de la sélectivité dans le cas du catalyseur de platine supporté en nanotubes et xérogels de carbone. Avec les catalyseurs d'iridium et ruthénium, la performance n'est pas si marquée, mais une petite augmentation de la sélectivité envers l'alcool cinnamique est observée. Une tendance inverse a été observée pour l'aérogel de carbone, c'est-à-dire, une réduction des sélectivités envers l'alcool cinnamique est observée après le traitement thermique. L'amélioration générale de la sélectivité est interprétée en termes de mobilité et de variation de densité électronique de

la phase métallique. Les sélectivités des catalyseurs avec traitement thermique (700°C) peuvent être classés en fonction de la nature du support: xérogels $\approx$ nanotubes $>$ aérogels.

En ce qui concerne les oxydes de métaux, le TiO_2 est préparé en fonction d'une méthode sol-gel ($\text{TiO}_{2\text{sg}}$), des matériaux à base de CeO_2 ont été synthétisés à travers une approche solvothermal et le ZnO a été élaborée en vertu d'un processus de dépôt chimique en phase vapeur (ZnO_{CVD}). Dans le cas de TiO_2 et du ZnO , plusieurs échantillons disponibles commercialement ont été testés à fins de comparaison ($\text{TiO}_{2\text{c}}$ et ZnOc). Le métal platine a été photochimiquement déposé sur la surface de différents oxydes métalliques et traité thermiquement à 500°C avec H_2 . Ce traitement favorise l'apparition d'une forte interaction entre le support et le métal, associées aux catalyseurs ayants une haute sélectivité envers l'alcool cinnamique. Dans ce cas, les sites TiO_x à proximité de la surface de la Pt coordonnent l'atome d'oxygène du lien $\text{C}=\text{O}$ à travers l'interaction avec une paire d'électrons, augmentant sa réactivité à l'hydrogénation préférentiel du groupe carbonyle. Dans le cas des catalyseurs supportés sur le ZnO , les résultats de la caractérisation indiquent l'existence d'un alliage PtZn . Les hautes sélectivités observées ont été attribuées à la formation de cet alliage. Il a été observé que les sélectivités envers l'alcool cinnamique varient en fonction de l'oxyde métallique supporté de la manière suivante: $\text{TiO}_{2\text{sg}} > \text{TiO}_{2\text{c}} \approx \text{ZnOc} > \text{Ce-Ti-O} > \text{CeO}_2 > \text{ZnO}_{\text{CVD}}$.

Finalement, une comparaison globale de tous les catalyseurs supportés a été faite et quelques conclusions sur leur adéquation au processus ont été tirées. Les conditions opératoires utilisées sont beaucoup plus douces que celles habituellement rapportées et néanmoins les sélectivités atteignent 83%, pour une conversion de 50% de cinnamaldéhyde.

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PART I:

INTRODUCTION

Selective hydrogenation of unsaturated aldehydes has been targeted as a crucial reaction for agrochemical, cosmetic and pharmaceutical applications. Being a catalyzed reaction, several approaches have been taken to maximize the selectivity of the catalyst towards the production of the unsaturated alcohol. In this first chapter, an extensive review of the work performed in this area is presented. The influence of a set of parameters on catalyst design and production, such as the nature of the support, the active metal and the type of promoter are reviewed. The influence of reaction operating conditions, such as the type of solvent, hydrogen pressure and reaction temperature are among the many important factors thoroughly discussed in this introductory chapter.

1. General Background & State of the Art

1.1 Fine chemicals

One of the greatest challenges currently faced by the chemical industry is the need for cleaner, safer and environmentally friendly technologies. Processes should be efficient in both energy and raw materials consumption and produce minimal waste. Chemicals are broadly classified as commodities (bulk), fine and specialty chemicals [1, 2]. Bulk chemicals, are those produced on a large scale with a low unit price, and rather simple molecules (plastics, methanol, and ammonia, among many others). Specialties are on the opposite side of this spectrum and represent small scale products with a high unit price. These products show a high degree of complexity and representative examples are food additives, pesticides, pharmaceuticals, photographic chemicals or specialty polymers. The intermediate group belongs to the so-called fine chemicals, produced from bulk chemicals and used as starting materials for specialties. Fine chemicals are produced in moderate quantities for a moderate price and show average complexity (bulk drugs and pesticides, active ingredients, bulk vitamins and flavor and fragrance chemicals).

The amount of by-products/wastes generally increases substantially as we go from bulk to fine chemicals, to specialties [2]. This is partly due to the fact that the production of fine chemicals and specialties generally involves multi-step syntheses that result in accumulation of by-products that need to be removed. Hence, the key to waste minimization is selectivity.

1.2 Selective hydrogenation

Hydrogenation reactions have been intensively studied ever since Paul Sabatier discovered heterogeneous catalysts for the addition of hydrogen to unsaturated bonds [3]. Today, catalysts are commonly used for the hydrogenation of alkenes, alkynes, aromatics, aldehydes, ketones, esters, carboxylic acids, nitro groups, nitriles and imines.

One typical heterogeneous catalytic hydrogenation process is the production of margarine and shortenings from vegetable oils. The hydrogenation of the unsaturated bonds in fats and oils provides products with the desired melting profile and texture. Usually, as the degree of hydrogenation increases so does the consistency of the oil, allowing a more stable and less sensitive to oxidation product. Hydrogenation of carbohydrates, namely glucose to sorbitol, is also a common application. Sorbitol is often used as sweetener in all kinds of food products as well as a starting material for vitamin C synthesis. These hydrogenation processes are usually carried out over very active Ni catalysts [4].

Homogeneous catalysts are flexible regarding the choice of active metal, ligands and reaction conditions and can lead to highly selective hydrogenations. The stoichiometric reduction with metal hydrides has been the preferred synthetic route due to the difficulty in preparing a heterogeneous catalyst able to perform the hydrogenation reaction with high selectivity. Unfortunately, that route generates large quantities of inorganic wastes, most of them harmful to the environment. The heterogeneous catalytic process is easier to handle and leads to a lower amount of waste products. Hence, research focused on chemo- and regio-selective heterogeneous catalytic hydrogenation of unsaturated compounds to produce fine chemicals is growing and, in the past few years, considerable effort has been dedicated to the development of a suitable catalytic system.

Selective catalytic hydrogenation of organic substrates containing unsaturated functional groups is an important step in the industrial preparation of fine chemicals. This area of research is especially attractive if there are two or more unsaturated bonds present. As an example, allylic alcohols are obtained from the chemo-selective hydrogenation of the carbonyl group in α,β -unsaturated aldehydes and are valuable intermediates for the production of perfumes, flavoring additives, pharmaceuticals and agrochemicals [5-9]. Frequently, the hydrogenation of the C=O bond competes with the hydrogenation of one or more C=C bonds. The challenge is to specifically hydrogenate one of them and stop the reaction, in order to obtain the desired product, leaving the other double bond intact. Unfortunately, the selectivity towards unsaturated alcohols (the commonly desired products) is difficult to achieve since thermodynamics favors the

hydrogenation of the C=C over the C=O bond by about 35 kJ mol^{-1} [10] and due to kinetic reasons, as the reactivity of the olefinic bond is higher than that of the carbonyl. In spite of these difficulties the selectivity towards unsaturated alcohols, using heterogeneous catalysts, has been significantly improved. It requires specific reaction conditions and carefully designed catalysts.

Several reviews deal with the hydrogenation of α,β -unsaturated aldehydes involving either experimental results [11-18] or theoretical calculations [19-21]. Some industrially important α,β -unsaturated aldehydes are represented in Figure 1.1.

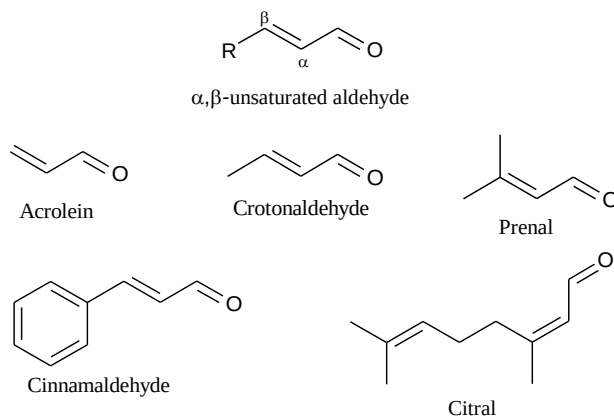


Figure 1.1 General structure formula and several industrial and scientifically important α,β -unsaturated aldehydes.

An indication of the importance that hydrogenation reactions have received in the last few years can be obtained by analyzing the number of papers published per year. Figure 1.2 shows the result of a search performed on ISI Web of KnowledgeSM for the terms “Selective hydrogenation” and “citral or cinnamaldehyde or crotonaldehyde or prenal or acrolein”. Since the year 2000 the number of papers has been increasing year after year. In 2008 alone (up to November), 68 papers have been published in this area.

In this thesis, the liquid-phase selective hydrogenation of cinnamaldehyde to cinnamyl alcohol was chosen as test reaction in the evaluation of the activity/selectivity properties of the synthesized catalysts. Therefore, the introduction will focus mainly on cinnamaldehyde and its hydrogenation products.

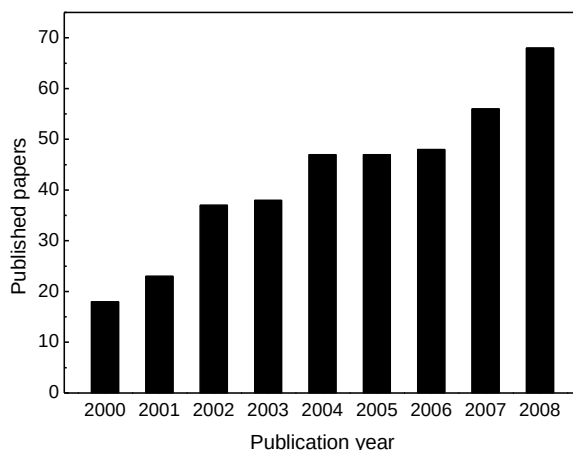


Figure 1.2 Number of papers published per year on the selective hydrogenation of α,β -unsaturated aldehydes.

1.2.1 Synthesis and applications

Cinnamaldehyde is a yellowish liquid with a characteristic cinnamon-like spicy odor. On an industrial scale, this aldehyde is produced almost exclusively by alkaline condensation of benzaldehyde and acetaldehyde. Cinnamaldehyde is used in compositions to create spicy and oriental notes (e.g. soap perfumes) and is the main component of artificial cinnamon oil. In addition, it is an important intermediate in the synthesis of cinnamyl alcohol and hydrocinnamyl alcohol [8].

Cinnamyl alcohol is a valuable chemical in the cosmetic industry for its odor and fixative properties. It can be found in many flower compositions like lilac and hyacinth and is a starting material for cinnamyl esters, often used as fragrance compounds. The alcohol is used for cinnamon notes and for rounding off fruit aromas. It is also applied as an intermediate in the synthesis of antibiotic Chloromycetin. Cinnamyl alcohol is industrially produced by reduction of cinnamaldehyde with isopropyl or benzyl alcohol in the presence of the corresponding aluminum alcoholate (yield *ca.* 85%), by reduction of cinnamaldehyde using an Os/C catalyst (yield 95%), or by reduction of cinnamaldehyde with alkali borohydrides [8].

Hydrocinnamaldehyde is a colorless liquid with a strong, flowery, slightly balsamic, heavy hyacinth-like odor. It can be obtained with high degree of purity by selective hydrogenation of cinnamaldehyde. It is used in perfumery for hyacinth and lilac

compositions [8] and as an intermediate reagent of anti-viral pharmaceuticals, particularly human immunodeficiency virus (HIV) protease inhibitors [22, 23].

Hydrocinnamyl alcohol is a slightly viscous, colorless liquid with a blossomy-balsamic odor, slightly reminiscent of hyacinths. It has been identified in fruit and cinnamon. Esterification with aliphatic carboxylic acids is important because it leads to additional fragrance and flavor compounds. Hydrocinnamyl alcohol can be prepared by hydrogenation of cinnamaldehyde or by a modified oxo synthesis of styrene. It is used in blossom compositions for balsamic and oriental notes [8].

1.2.2 Reaction network

The reaction of unsaturated aldehydes is described as a parallel consecutive network in which one or both of the unsaturated functionalities may be hydrogenated. In addition to the carbonyl and olefinic double bonds, cinnamaldehyde also contains an aromatic ring. All these groups can be affected by different chemical transformations besides the hydrogenation, such as decarbonylations, isomerizations and hydrogenolysis leading to rather intricate networks. These reactions are not very common and require some specific conditions in order to occur. A detailed pathway of the hydrogenation of cinnamaldehyde is presented in Figure 1.3. The hydrogenolysis of cinnamyl alcohol results in the formation of highly reactive β -methylstyrene that is readily hydrogenated to 1-propylbenzene. This reaction has been observed by Neri *et al.* [24], Lashdaf *et al.* [25] and Vergunst *et al.* [16].

Decarbonylation of cinnamaldehyde yields styrene that is subsequently hydrogenated to ethylbenzene. This reaction has been observed by Neri *et al.* [24]. The formation of CO due to this decarbonylation can, however, poison the active sites of the catalyst. Isomerization reactions have been previously reported to occur during the hydrogenation of α,β -unsaturated aldehydes [26, 27]. However, little or no information has been given about the isomerization of cinnamyl alcohol into hydrocinnamaldehyde using heterogeneous catalysts. The aromatic ring is perhaps the most stable element of the cinnamaldehyde molecule. Further hydrogenation of hydrocinnamyl alcohol produces the saturation of aromatic ring and the formation of 3-cyclohexyl-1-propanol [16].

Acid-site reactions may occur as a result of reaction of an alcoholic solvent with either cinnamaldehyde or hydrocinnamaldehyde to form acetals; solvent may react with cinnamyl alcohol or hydrocinnamyl alcohol to form ethers and dehydration reactions may occur with formation of β -methylstyrene.

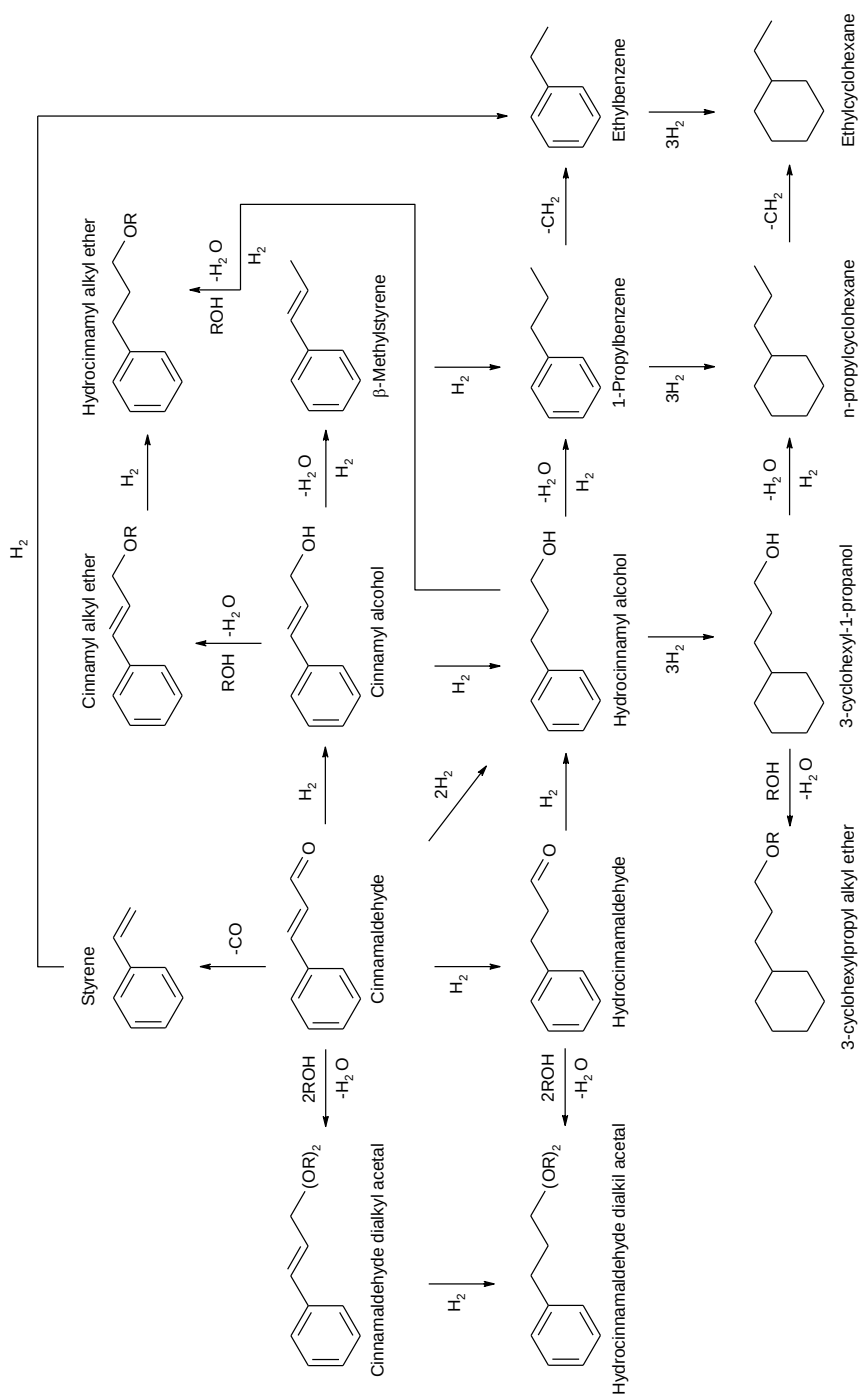


Figure 1.3 Complete pathway for the hydrogenation of cinnamaldehyde.

1.3 Reaction mechanism

A heterogeneously catalyzed hydrogenation over metal supported surfaces includes several reactions steps [28]: (i) external diffusion, (ii) internal diffusion and (iii) adsorption of the reactants; (iv) chemical reaction on the surface; (v) desorption, (vi) internal diffusion and (vii) external diffusion of products. Each of the mentioned steps could influence reaction rates, but there are systems where it can be simplified (in non-porous catalysts, for example, there is no need to consider internal diffusion steps).

Kinetics of hydrogenation have been reviewed by Singh and Vannice [14]. A more recent report by Loffreda *et al.* [19] provides for a theoretical approach to the competitive hydrogenation of C=O and C=C bonds.

Two main reaction mechanisms are usually considered: Langmuir-Hinshelwood (LH) or Eley-Rideal (ER). In the LH mechanism the reaction occurs between species that are adsorbed on the surface, whilst on ER the reaction occurs between a reactant molecule in the gas or liquid-phase and one that is adsorbed on the surface. LH mechanism is a good approximation for the cinnamaldehyde hydrogenation kinetics [16, 24, 29-33]. In order to be able to differentiate between different possible surface reactions the complete kinetic curve should be taken as a basis for kinetic analysis. The models can include either competitive or non-competitive adsorption steps as well as dissociative or non-dissociative adsorption of H₂. Furthermore, the kinetic model may consider either one or two different types of adsorptions sites. The model can grow in complexity including the formation of by-products.

A high selectivity towards the desired unsaturated alcohol is not always easy to achieve and requires specific reaction conditions and efficient catalyst design. Over the next few sections the influence of the substrate structure, size and nature of the active metal, type of support, presence of promoters and operating conditions will be discussed.

1.4 Structure of the substrate

The structure of the substrate plays an important role concerning the selectivity towards the unsaturated alcohols. Steric hindrance around the C=C bond enables a selective hydrogenation of the carbonyl group, whereas the absence of large substituents on the same bond directs the reaction toward the formation of the saturated aldehyde (SAL) [34]. Among the several α,β -unsaturated aldehydes discussed in section 1.2, acrolein is considered the most difficult to selectively hydrogenate to the corresponding

unsaturated alcohol (UOL). Crotonaldehyde possesses an extra methyl group regarding acrolein and so the hydrogenation of the carbonyl bond takes place more easily. Further addition of a methyl group to the C=C bond of crotonaldehyde yields prenal, and enhances even more the probability to selectively reduce the carbonyl function. For cinnamaldehyde and citral this effect is even more pronounced. Hence, as the size of the substituent grows so does the steric hindrance around the C=C bond, thus favoring the formation of UOL.

1.5 Metal phase

1.5.1 Metal nature

Many of the group VIIIB transition metals (Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt) have been reported in hydrogenation reactions [12, 35]. These metals, whose catalytic properties are well established, have a marked ability to activate the hydrogen molecule by dissociative chemisorption. Activities and selectivities observed in the hydrogenation of cinnamaldehyde differ remarkably among the different metals. Supported Pt catalysts remain the most commonly used [36-41], but other metals like Ir [42], Os [43], Ru [44-48], Co [49-52] and Cu [53, 54] are also gaining importance due to their selective behavior.

In addition, other metals like Au [55-58] and metal borides [59-61] have also been found to selectively produce higher amounts of UOL. The use of Au catalysts is based on weaker interactions with reactants, intermediates and products comparing to other transition metals [55]. Silver catalysts have been tested for the preferential hydrogenation of the carbonyl bond in acrolein and crotonaldehyde showing excellent UOL selectivities [18, 62-64].

Other metals like Pd [65-70], Ni [71] and Rh [65, 72] display a rather poor selectivity towards cinnamyl alcohol and are associated with higher SAL yields.

Summarizing, it can be said that the selectivity towards cinnamyl alcohol increases in the following order: $0 \approx \text{Pd} < \text{Rh} < \text{Ru} < \text{Pt} < \text{Au} < \text{Ir} < \text{Os} \approx 1$. This sequence was explained in terms of radial expansion of the *d*-band, since a larger *d*-band lowers the probability of the C=C bond adsorption. Indeed, *d*-band width follows the same order as the selectivity towards cinnamyl alcohol ($\text{Pd} < \text{Pt} < \text{Ir} \approx \text{Os}$) [12].

1.5.2 Metal surface and particle size

Metal particle size is known to determine the relative proportion of atoms on the corners, edges and planes of the crystallites. Atoms in different crystallographic positions can have different catalytic properties as a result of a different electronic and/or geometric structure. Theoretical calculations performed by Delbecq and Sautet [20] showed that the adsorption mode, which determines the selectivity, depends on the crystal plane exposed. Figure 1.4 shows commonly distinguished adsorption modes of α,β -unsaturated aldehydes. The η^1 on top, the η^2 , μ , di- σ_{CO} and the η^2 π_{CO} yield the desired UOL, whereas the other adsorption modes yield SAL. According to Delbecq and Sautet, the Pt(111) plane, unlike the Pt(111) steps, does not favor the coordination with the C=C bond and a higher selectivity to the UOL is observed for cinnamaldehyde hydrogenation. With increasing particle size, the fraction of steps and corners decreases and the crystal plane distribution shifts towards the Pt(111) plane [73]. Hence, higher selectivities to cinnamyl alcohol are observed for larger particles.

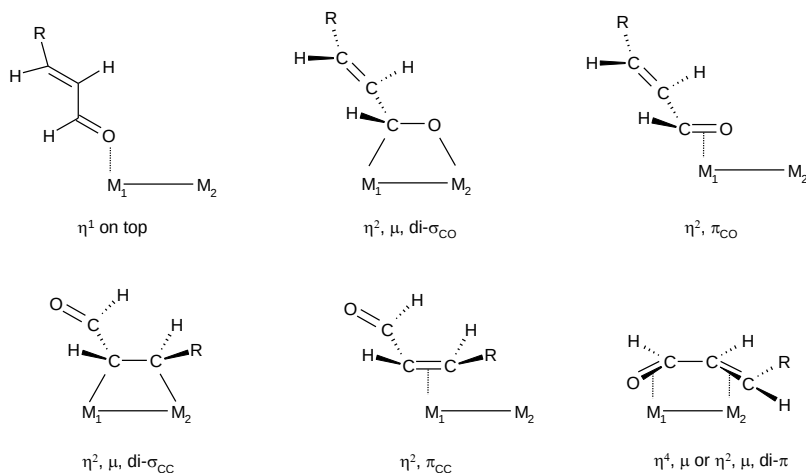


Figure 1.4 Adsorption modes of α,β -unsaturated aldehydes on metal surfaces (adapted from [20]).

Calculations involving the Pt(100) and Pt(110) planes indicate a favored adsorption through both double bonds and through the C=C bond, respectively. In both cases the final result is higher yields of the SAL [20], regardless of the substrate. Other Pt crystallographic planes have also been reported in hydrogenation reactions. Bircherm *et al.* [74] studied the effect of Pt(553) plane, made of (111) terraces and steps, in the gas-phase hydrogenation of prenal. In spite of the higher activities, they observed that this plane induced lower selectivities to UOL when compared to Pt(111) [75].

Changes in the metal particle size and morphology have been studied and discussed by several authors [11, 12, 18, 44, 76]. A strong dependence of selectivity on the metal particle size in the liquid phase hydrogenation of cinnamaldehyde over monometallic Pt catalysts was found by Gallezot *et al.* [12, 76]. Large Pt particles ($d \approx 5$ nm) gave a selectivity of 98% to COL (at 50% conversion) compared to 83% with small Pt particles (1.3 nm). Similar effects were observed with Rh [76], Ru [77] and Co [49] catalysts. The hindered adsorption of the olefinic bond of the α,β -unsaturated aldehyde by a steric repulsion between the flat metal surface in large metal particles and the aromatic ring (Figure 1.5a) was concluded to be responsible for the high selectivity toward C=O group hydrogenation. Cinnamaldehyde can be tilted far from the surface due to repulsive interaction between the aromatic rings and the large ($d > 3$ nm) metal particles [12, 76]. This repulsion is supported by theoretical calculations showing that the aromatic ring cannot get closer than 0.3 nm without having to overcome an energy barrier (Figure 1.5b) [78]. Because of this barrier, the C=C bond cannot approach the surface as closely as the C=O bond, yielding higher amounts of UOL.

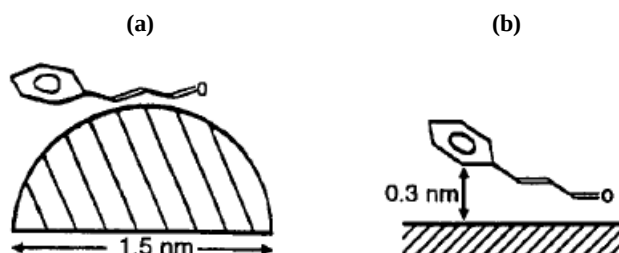


Figure 1.5 Cinnamaldehyde adsorption on (a) a small metal particle and (b) a flat surface [12].

On the other hand, the unhindered acrolein molecule can adsorb as a flat species independently of the morphology of the metal particle, and does not show any changes in allyl alcohol selectivity [26, 79].

The metal particle size is a major factor to be taken into consideration when interpreting selectivity results. There is a general idea that in order to achieve high UOL yields big metal particles are needed. This is true in most cases, but there is also a strong dependence on the metal nature and the type of crystals exposed, as mentioned above. In addition, the support is also known to influence the selectivity to different extents.

1.6 Support

Supports are typically porous materials with high surface areas, which possess high thermostability and stabilize the dispersion of the active component. For industrial process applications they must also have a sufficient mechanical strength. Although supports are often considered to be inert, this is not generally the case. Supports often actively interfere with the catalytic process. In the case of hydrogenation of unsaturated aldehydes, such as those shown in Figure 1.1, some benefits can be withdrawn from using supports with the appropriate properties and characteristics. The specificity of this reaction allowed numerous materials with different properties to be tested as supports. They can go from metal oxides (Al_2O_3 [29, 44, 55, 80-82], TiO_2 [50, 56, 83], SiO_2 [84-90] and MgO [91, 92]), clays [93-96], carbon materials (nanofibers [30, 40, 48, 65, 68], graphite [38, 42, 97], nanotubes [36, 39, 69, 98], xerogels [37, 99], activated carbon [67, 70], fullerenes [100] and carbon black [101]), zeolites [46, 102-105], mesoporous molecular sieves (MCM-41 [45, 91, 106, 107] and MCM-48 [108, 109]) to nylon [110-112].

Metal oxides like CeO_2 [113-116] and ZnO [117-119] have been tested mainly in the selective hydrogenation of crotonaldehyde showing high selectivities towards crotyl alcohol. Application of ZnO as support in the hydrogenation of cinnamaldehyde was not performed until very recently with a Pt catalyst [120], evidencing excellent selectivities. CeO_2 supported metal catalysts have not been reported in the hydrogenation of cinnamaldehyde.

There are three effects, generally attributed to the support, which can affect the selectivity towards cinnamyl alcohol: metal-support interactions, and steric and electronic effects [12, 18].

1.6.1 Metal-support interactions

1.6.1.1 Metal-support interactions with metal oxides

Metal oxides make up a large and important class of catalytically active materials, their surface properties and chemistry being determined by their composition and structure. After reduction at high temperatures (*ca.* 500°C), group VIII metals supported on reducible oxides (TiO_2 , CeO_2 , ZnO and Nb_2O_5) may undergo a change in the metal-support interface due to a strong metal-support interaction (SMSI) effect [121, 122]. The later was first reported by Tauster and is attributed to both electronic and geometric effects [121, 123]. Titania suboxide (TiO_x) particles decorate the surface of the metal

phase by means of coordinatively unsaturated Ti cations that may interact with electron pair donor sites. The strongest electron pair donor in α,β -unsaturated aldehydes is the oxygen of the carbonyl group. Thus, the carbonyl function is suggested to strongly interact with the Lewis acid sites contained in the suboxide species [124]. These sites coordinate the oxygen atom of the C=O bond via a lone pair of electrons and, thus, increase its reactivity for the hydrogenation. Catalysts evidencing the SMSI effect show an increase in both activity and selectivity in hydrogenation reactions involving α,β -unsaturated aldehydes [125-127].

The presence of the SMSI effect is characterized by the suppression of H₂ or CO chemisorption properties of the supported metal, but some reports indicate that metal decoration can also be visualized using high resolution electron microscopy [123, 128]. In spite of their positive effect, excessive decoration of metal surface with TiO_x particles can lead to deactivation of the catalyst by full encapsulation of the metal phase [129]. Fortunately, an important characteristic of the SMSI effect is its reversibility [129, 130], i.e., upon re-oxidation followed by a mild reduction treatment, the conventional behavior of the supported metal may be recovered.

Thus, the selective hydrogenation of α,β -unsaturated aldehydes to the corresponding unsaturated alcohols using noble metals supported on titania or other reducible oxides, is a very promising field in catalysis.

1.6.1.2 Metal-support interactions in carbon materials

As mentioned previously, several carbonaceous supports can be used in the selective hydrogenation of cinnamaldehyde. Functionalization of these materials (gas- or liquid-phase) results in the creation of various oxygen carrying functionalities on the otherwise inert carbon surface [131, 132]. The degree of surface functionalization depends on the strength of the activation treatment. Nitric acid is commonly used to functionalize different carbon materials such as nanotubes [133, 134], nanofibers [40, 135] or activated carbons [132, 136]. Applications such as enhanced adhesion in composite materials [137], improved dispersibility in solvents [138, 139] or effective dispersion of metals particles over the surface of the support [140] are reported for the treated materials. Regarding the last application, there are indications that oxygen surface groups act as anchoring sites for the metal precursor [140]. This allows for a much stronger interaction between the metal and the surface, resulting in improved catalytic properties at the metal-support interface.

Coloma *et al.* [141] emphasized the importance of oxygen-containing surface groups on carbon supports. In their study, on the gas-phase hydrogenation of crotonaldehyde

over Pt on activated carbon catalysts, they found an increased selectivity to the alcohol with a larger amount of oxygen-containing groups present on the carbon surface. Recently, the influence of surface groups in supports like single- and multi-walled carbon nanotubes (SWCNT, MWCNT) and carbon nanofibers (CNF) has been studied in the hydrogenation of cinnamaldehyde [36, 40]. In all cases a strong activity uptake was achieved after removal of the surface groups. However, depending on the type of support selectivities were different. CNFs produced high yields of saturated aldehyde whereas carbon nanotubes (CNT) were more selective towards the unsaturated alcohol after group removal. The mobility of the delocalized π -electrons in these materials could help explain the differences in selectivity observed. For CNF this effect will probably be less pronounced than for CNT because of the orientation of the graphitic planes.

1.6.2 Steric effect

Steric effects are commonly observed when zeolites or microporous carbons are used as catalytic supports [36, 103, 105]. Excellent selectivities of up to 97% to cinnamyl alcohol at high conversion were obtained by Gallezot *et al.* [105] using Y-type and beta zeolites with perfect encapsulated Pt particles in the micropores of the zeolite. This end-on adsorption results in high yields towards cinnamyl alcohol, also for metals that are intrinsically non-selective [103]. However, due to diffusion constraints induced by the small pore size of zeolites, lower reaction rates are observed when microporous materials are used as catalyst support [36, 103].

1.6.3 Electronic effect

An important electronic effect is observed when graphite is used as support in the selective hydrogenation of cinnamaldehyde. Gallezot *et al.* [12] reported that selectivity to COL was higher using graphite rather than activated carbon as catalytic support, under comparable experimental conditions. The higher selectivity was explained by the incorporation of the metal sites in the electronic structure of the graphite planes. Because metal particles are preferentially located on steps and edges of graphitic planes, the π -electrons of the graphitic planes can be easily extended to the metal particles, thus increasing the charge density of the metal. The increased charge density decreases the probability of adsorption via C=C bond, so that the selectivity towards the UOL increases.

1.7 Metal promoters

In the last decade, much research effort has been dedicated to the improvement of the selectivity of heterogeneous supported metal catalysts. Consequently, high yields of unsaturated alcohols have been obtained on Group VIII metal catalysts by addition of promoters [44]. The role and the effects of these metals have been reviewed for the hydrogenation of α,β -unsaturated aldehydes [11, 15]. As a general rule, the turn-over frequency (TOF) and the selectivity to the unsaturated alcohol are improved by adding a more electropositive metal (Sn, Fe, Ge, Zn, Ga) to the active transition metal (Me). Among the different combinations, Pt-Sn catalysts supported on different materials have been widely studied [37, 89, 111, 142, 143]. The effectiveness of the promoter (P) is determined by both its charge and amount on the catalyst. Normally, there is an increase in the activity up to an optimum Me/P ratio after which the activity decreases. The increase in selectivity might follow this same pattern but, most times, the Me/P ratio does not coincide with that of the maximum activity.

Two models based on electronic effects have been proposed to explain the improvement in selectivity. The first model is based on an increased electron density on the base metal induced by the formation of metal alloys. The probability for C=C bond adsorption is decreased and, at the same time, the interaction with a C=O bond is enhanced. The second model is based on the presence of surface Lewis acid sites ($P^{\delta+}$) at or near the metal particles that may interact with the lone electron pairs of the oxygen from the carbonyl group (Figure 1.6). This effect is very similar to that described in section 1.6.1.1 for the SMSI effect.

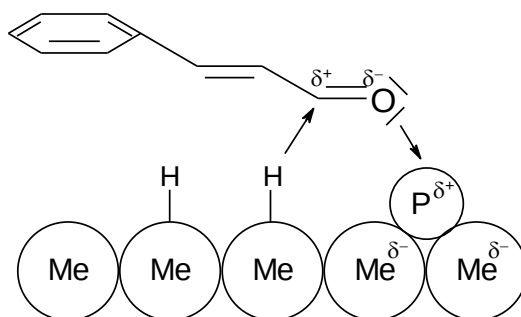


Figure 1.6 Adsorption of a cinnamaldehyde molecule over a promoted catalyst.

A series of various metal chloride promoters were tested by Gallezot *et al.* [144] in the selective hydrogenation of cinnamaldehyde to cinnamyl alcohol over Pt/nylon catalysts. Their effectiveness was ranked as: $\text{GeCl}_4 > \text{SnCl}_4 > \text{FeCl}_3 > \text{CoCl}_2 > \text{no promoter}$.

Yu *et al.* [145] used metal chlorides and nitrates as promoters in the hydrogenation of cinnamaldehyde over colloidal Pt catalysts. In the absence of metal salts 12% selectivity to cinnamyl alcohol was observed. Addition of Zn^{2+} cations to the reaction mixture increased the selectivity to cinnamyl alcohol up to 99.8% (conversion of only 13%). Replacement of Zn^{2+} by Fe^{3+} resulted in higher conversions of cinnamaldehyde and selectivities to cinnamyl alcohol up to 98.5%. These results were attributed to the interaction of metal cations with the C=O groups in the reactants.

Richard *et al.* [146] also observed the positive effect of the promoter up to an optimal Pt/Fe ratio of 5. This was interpreted by a dual-site mechanism where electron acceptor $\text{Fe}^{\delta+}$ species at the surface of Pt act as adsorption sites for the cinnamaldehyde molecule via the oxygen atom. The thus activated C=O bond is hydrogenated by dissociated hydrogen on nearby Pt atoms, which also maintain the iron in a low oxidation state.

1.8 Operating conditions

Hydrogenation selectivity can be influenced not only by the choice of the catalyst, as described so far, but also by the conditions under which the reaction is performed. Hence, the catalyst performance can be optimized by choosing a suitable reaction system and the proper reaction conditions. Important parameters like the hydrogen pressure, reaction temperature, type of solvent, and concentration of the substrate are reviewed over the next few sections.

1.8.1 Hydrogen pressure

The effect of hydrogen pressure on the activity and selectivity of cinnamaldehyde hydrogenation has hardly been studied and only a few reports address this parameter [30, 38, 41, 42].

Most studies indicate a relatively constant selectivity with increasing H_2 pressure. This was observed by Koo-Amornpattana *et al.* [38] over a Pt/graphite catalyst and by Breen *et al.* [42] using an Ir catalyst also supported in graphite. The later tested a range of pressures from 10 to 40 bar, with results showing an increase in the rate of conversion of cinnamaldehyde with increasing hydrogen pressure. Pressures as high as 70 bar were used by Toebes *et al.* [30], with a Pt/CNF catalyst, and corroborated the previous results, i.e., no influence of the hydrogen pressure on the selectivities was observed.

Shirai *et al.* [41], on the other hand, used a Pt/ SiO_2 catalyst to observe that an increase of the hydrogen pressure, up to 120 bar, decreased the selectivity of cinnamyl

alcohol but increased that of hydrocinnamaldehyde. The reason given for this decrease was claimed to be related to the nature of the solvent. According to the same authors, the solvent is likely to change with hydrogen pressure which would affect the properties of Pt particles and/or cinnamaldehyde molecules adsorbed.

A possible explanation for these results could be related to the H₂ solubility in the solvent. A high solubility, coupled with a H₂ adsorption significantly faster than the reaction step, should provide good H₂ coverage over the catalyst surface, therefore, increasing pressure should not influence the activity or the selectivity. On the other hand, if H₂ mass transfer from the gas-phase to the solid surface is considered the rate determining step, together with a low solubility solvent, then higher pressures should be helpful, because they can increase the surface coverage of H₂ on the catalyst.

1.8.2 Reaction temperature

Hydrogenation is a strong exothermic reaction and hence, control of the reaction temperature is an important factor to be taken into account. The selective hydrogenation of cinnamaldehyde is usually performed at low temperatures, varying from room temperature [147, 148] to temperatures as high as 160°C [149]. The reaction temperature also affects the activity and the selectivity to cinnamyl alcohol, with its effect being visible in the reaction rate constants and adsorption coefficients.

The effect of the reaction temperature on the activity and selectivity of cinnamaldehyde hydrogenation can have various outputs. Breen *et al.* [42] used an Ir/graphite catalyst, to carry out the reactions in the range between 85 and 130°C. Selectivities over 90%, and approaching 100%, were observed with higher temperatures. An opposite trend was observed by Koo-Amornpattana *et al.* [38]. Selectivities higher than 95% were observed at room temperature, decreasing significantly with temperature increase. The reaction was performed using a Pt/graphite catalyst and toluene/water (1:1) mixture as solvent. Neri *et al.* [24], on the other hand, studied the effect of reaction temperature using a Ru/Al₂O₃ catalyst. A modest increase of the selectivity to cinnamyl alcohol with decreasing temperature was observed.

It is clear, from these results, that the choice of the reaction temperature should be subject of special attention in order to optimize the selectivity to the unsaturated alcohol.

1.8.3 Solvent effect

Most of the hydrogenation reactions in the pharmaceutical and fine chemical sectors are conducted in the liquid phase where the solvent used can serve different functions.

The most important are the solvent polarity, hydrogen solubility, interactions between the catalyst and the solvent, as well as solvation of reactants and products in the bulk liquid-phase [14]. The adsorption/desorption of reactants and products at the catalyst surface is commonly affected by competitive adsorption of the solvent. It has been found that a polar solvent enhances adsorption of the non-polar reactant while a non-polar solvent enhances the adsorption of a polar reactant [150]. Moreover, the solubility of the reactants in the solvent can change the availability of reactants and products for consecutive reaction on the catalyst surface.

In the selective hydrogenation of cinnamaldehyde, the use of both polar and non-polar solvents has been reported [41, 45, 46]. Hájek *et al.* [45] found that selectivity and activity were considerably influenced by the solvent: the hydrogenation activity increased with the solvent polarity, whereas the selectivity decreased [45, 46]. The highest selectivities were achieved over Ru/Y in non-polar solvents (cyclohexane, hexane) whereas the acidity of the Ru/Y and Ru/MCM-41 yielded *ca.* 60-80% of side-products (acetals) in 2-propanol. Moreover, they observed that hydrogenations in 2-propanol did not exhibit any deactivation, while reactions carried out in non-polar solvents were prone to this effect.

Besides the common two- and three-phase systems, a four-phase system (gas, organic and aqueous liquid phases and solid catalyst) was also studied in the hydrogenation of cinnamaldehyde. Yamada *et al.* [151] tested this reaction over Pt/C catalyst in the presence of water and KOH in the organic phase. Selectivity to cinnamyl alcohol was close to 80%. The presence of water was shown to be essential for the formation of unsaturated alcohol since, in its absence, no cinnamyl alcohol was observed.

Synthetic organic reactions performed under non-traditional conditions are gaining popularity due to environmental considerations. The emerging area of green chemistry envisages the use of minimum hazardous chemicals as far as possible and the use of efficient and catalytic processes with less waste. One of the approaches for achieving this target is to look for alternative reaction conditions and reaction media to accomplish the desired chemical transformations with minimal by-product and waste.

In addition to conventional solvents, supercritical carbon dioxide (scCO₂) has been used in the hydrogenation of cinnamaldehyde [108, 109, 152]. Reactions performed in scCO₂ show enormous potential due to the replacement of the conventional solvents. In addition, supercritical mixtures allow for much higher H₂ solubilities than other commonly used solvents, with positive aspects regarding the reaction rate [153]. Chatterjee *et al.* [152] observed an optimum scCO₂ pressure, which lead to the highest selectivity to cinnamyl alcohol.

Ionic liquids, which along with scCO₂ are considered as green solvents, have also been investigated in cinnamaldehyde hydrogenation [154-156]. The specific advantage of ionic liquids is associated with their lower vapor pressure, in spite of their usually low H₂ solubility.

1.8.4 Aldehyde concentration

An interesting effect that has a relative impact on the selectivity during the hydrogenation of α,β -unsaturated aldehydes is the reactant amount [12, 75]. A higher substrate concentration leads to an increased selectivity towards the α,β -unsaturated alcohol compared to a lower reactant concentration that yields both saturated aldehyde and alcohol [41]. At low reactant concentration the surface coverage is low enabling the adsorption in the η^4 mode, while at higher reactant concentrations the η^1 on top mode is preferred because it requires less space and more molecules can be dispersed. The adsorption mode of the molecules has a large impact on the product selectivity, as already mentioned in section 1.5.2.

1.9 Scope and thesis outline

The hydrogenation of α,β -unsaturated aldehydes yields predominantly saturated aldehydes, although unsaturated alcohols are desired as intermediates for fine chemicals and flavoring compounds. The use of a proper catalyst together with optimal reaction conditions can shift the selectivity towards the production of unsaturated alcohols. The hydrogenation of cinnamaldehyde is a complex reaction in which cinnamyl alcohol, the α,β -unsaturated alcohol obtained from cinnamaldehyde, is often the desired reaction product. The selectivity towards cinnamyl alcohol is induced by the adsorption mode of cinnamaldehyde to a catalytic site. The adsorption mode can be affected by the metal, support, and type of promoter used. Additionally, the process conditions applied also have a great influence in the pathway of the reaction.

The aim of the work described in this thesis was to investigate the potential of different materials as catalytic supports. Metals like Pt, Ir and Ru are commonly reported to be selective towards the hydrogenation of the carbonyl group and were tested in the selective hydrogenation of cinnamaldehyde.

This work is based on the material published or in the process of publication. A detailed list of publications can be found at the end of the dissertation.

The present manuscript is organized in eight chapters, divided into three parts. Part I consists of this introductory chapter. Part II includes Chapters 2 to 5 and reports the use of carbon materials as supports, whereas, in Part III (Chapters 6 to 8), application of metal oxide supported catalyst is described. All the catalysts discussed in this work were tested in the liquid-phase selective hydrogenation of cinnamaldehyde to cinnamyl alcohol.

More precisely, **Chapter 1** offers some background information concerning the key issues present in the selective hydrogenation of cinnamaldehyde.

Chapters 2 and 3 are dedicated to the same support, i.e. multi-walled carbon nanotubes. In **Chapter 2** the functionalization of these materials using three distinct methods (nitric acid oxidation, air oxidation and ball milling) is described along with its effect in terms of size and amount of Pt deposited over the MWCNTs.

Chapter 3 describes the same MWCNTs treated in nitric acid and its use as support for Pt and Ir monometallic catalysts. The metal loads were lower than those tested in Chapter 2, in order to minimize possible sintering effects. Characterization data seeking to establish appropriate structure/activity relationships is also discussed in this chapter.

An analysis similar to that performed in Chapter 3, but using carbon xerogels as catalytic supports is discussed in **Chapter 4**. The xerogel was functionalized with nitric acid and used to disperse monometallic catalysts containing Pt, Ir and Ru.

In **Chapter 5**, carbon aerogels with different textural properties are explored as catalytic supports. Different functionalization treatments, other than those performed in the previous chapters, were tested. Hydrogen peroxide and ammonium peroxydisulfate were used to change the surface chemistry of carbon aerogels prior to Pt deposition.

In **Chapter 6**, a sol-gel approach is reported to prepare a fully anatase-containing TiO_2 . Other commercially available TiO_2 , with different anatase/rutile proportions, were tested for comparison purposes. All these materials were used as catalytic supports for the photodeposition of Pt.

Chapter 7 reports the synthesis, characterization and use of nanostructured CeO_2 -based materials prepared by a solvothermal approach. Mixed-oxides, Ce-Ti-O, with different Ce/Ti molar ratios were synthesized and tested.

Finally, the CVD synthesis of ZnO is described in **Chapter 8**. Commercially available ZnO from Evonik and Strem Chemicals were also used for comparison purposes.

The last part of this thesis gathers the main conclusions and discusses the prospects for further investigations.

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PART II:

SELECTIVE HYDROGENATION WITH CARBON MATERIALS

Carbon materials often present enhanced electronic and adsorptive properties, making them attractive for a wide range of applications. In this chapter these properties are used, and the application of structurally different materials as supports is discussed. Depending on the type of support, several activation treatments are used to improve the dispersion of metals such as platinum, iridium or ruthenium. The prepared catalysts are tested in the liquid-phase selective hydrogenation of cinnamaldehyde under mild temperature and pressure conditions. A thermal post-treatment at 700°C increases the catalyst selectivity towards the preferential reduction of the carbonyl group. Platinum and iridium catalysts reveal excellent selectivity towards the desired cinnamyl alcohol whilst ruthenium is found to hydrogenate preferentially the olefinic bond.

2. Platinum catalysts supported on multi-walled carbon nanotubes: effect of support activation in selective hydrogenation reactions

Multi-walled carbon nanotubes are subjected to three different activation procedures: nitric acid oxidation, air oxidation and ball-milling. The influence of these treatments on the nanotubes surface chemistry and morphology is evaluated by photoemission and vibrational spectroscopies, temperature programmed adsorption/desorption techniques, and electron microscopy. The activated materials are used to prepare Pt supported catalysts from the organometallic precursor $[\text{Pt}(\text{CH}_3)_2(\text{COD})]$. The influence of the activation treatments, together with that of a post-reduction thermal treatment, on the performance of the catalytic systems in the selective hydrogenation of cinnamaldehyde is investigated. It is shown that the best compromise between catalyst activity and selectivity requires a low amount of oxygenated groups on the support surface of the final catalyst (typically less than $700 \mu\text{mol g}^{-1}$ CO + CO₂ evolving during temperature-programmed desorption experiments), together with an optimized Pt particle size ranging between 10 and 20 nm.

2.1 Introduction

Carbon nanotubes (CNTs) present remarkable intrinsic properties. Promising applications of CNTs include field emission, mechanical strengthening, sensors or hydrogen storage [1-7]. For applications in which they have to interact with, or be integrated in a given system, it is necessary to functionalize their surfaces in order to obtain higher performances. Among the main processes for CNT surface functionalization, fluorination or the introduction of oxygenated groups are the most frequently used, due to the simplicity of the relevant reactions involved and the possibility of further reactions after these treatments [8]. The first studies on CNT activation were largely inspired on the methods used for activated carbons or carbon fibers oxidation. The most widespread method is based on liquid-phase oxidation with concentrated boiling nitric acid or $\text{H}_2\text{SO}_4/\text{HNO}_3$ mixtures. These activation processes were studied on carbon nanofibers [9-13], single-walled (SWCNT) [14-16] and multi-walled carbon nanotubes (MWCNTs) [17-21]. The oxidation procedure generally leads to the opening of CNT tips while producing carboxylic acid, hydroxyl and carbonyl groups, that can be identified by infrared (IR) spectroscopy [18, 19, 21], X-ray photoelectron spectroscopy (XPS) [14, 18, 20] or temperature-programmed desorption (TPD) [22, 23]. Other liquid phase oxidations using, for example, potassium permanganate [24] or persulfate [25] solutions have also been successfully employed. Alternatively, gas phase oxidation under air can be used but, contrarily to liquid-phase oxidation, which often introduces significant amounts of carboxylic acid groups, this method is employed to generate phenolic or carbonyl groups [20, 26]. A hydrothermal method [27] has also been reported. Additionally, the ball-milling of CNTs under reactive atmosphere was shown to produce short and functionalized nanotubes [28-31].

The purpose of these oxidative treatments is: (i) to improve CNTs interaction with solvents and dispersion, (ii) to allow the grafting of nanoparticles, (iii) to modify CNT adsorption properties or (iv) to perform chemical treatments on nanotubes [8, 32, 33]. It has been shown that the introduction of oxygenated groups enables a better interaction with the solvents [34, 35] in which the oxidized nanotubes are well dispersed. Moreover, several authors [19, 36] have reported that oxidized-CNTs suspensions in water or ethanol are stable. Even though no specific study has yet appeared on the subject, it has also been shown that functionalized CNTs produce well dispersed supported catalysts [37]. CNT functionalization can also affect some properties of these materials, which may be important in catalysis. Bulk electrical measurements on oxidized CNTs have shown that covalent functionalization significantly reduces conductivity of the tubes.

The electric resistance was observed to increase proportionally to the amount of covalently bonded moieties [38]. Similarly, the chemical functionalization of CNTs also has a direct impact of their adsorption properties [39, 40].

In this chapter, a comprehensive study is described dealing with the various processes of MWCNTs activation. The functionalizations were performed by (i) nitric acid treatment; (ii) air oxidation and (iii) ball-milling under air. The so-activated MWCNTs were fully characterized and used to prepare supported catalysts using the organometallic Pt precursor $[\text{Pt}(\text{CH}_3)_2(\text{C}_8\text{H}_{12})]$. The catalysts were tested in the selective hydrogenation of cinnamaldehyde to cinnamyl alcohol.

2.2 Experimental

2.2.1 Support preparation and functionalization

The MWCNTs (purity > 90%) were supplied by the group of Prof. Philippe Serp (Laboratory of Coordination Chemistry, Toulouse, France) and were grown by chemical vapor deposition from ethylene on $\text{Fe}/\text{Al}_2\text{O}_3$ catalysts at 650°C . Details of the preparation procedure are given elsewhere [41]. For purification purposes (removal of catalyst), 500 mL of H_2SO_4 (95 vol. %) were slowly dropped under constant stirring into a suspension of raw MWCNTs (20 g) in 500 mL of distilled water. The suspension was refluxed at 140°C for 3 hr. Subsequently, the nanotubes were filtered on a fritted glass funnel and washed with distilled water until a stable pH value was reached (*ca.* 6). The MWCNTs were then dried at 120°C for 2 days before the functionalization step.

Three independent treatments were performed to the nanotubes in order to introduce different oxygenated groups on their surface: (i) liquid- and (ii) gas-phase activation and (iii) ball-milling. A detailed description of each treatment can be found below.

- i. Pure (*ca.* 14 M) HNO_3 : 1 g of purified nanotubes was reacted with 50 mL of nitric acid (65 vol. %) at 120°C , for 1 to 8 hr, under stirring. The MWCNTs were then filtered on a hot fritted glass funnel (size of the pores: 16-40 μm) and washed with distilled water until a stable pH value was obtained. The nanotubes were dried at 120°C , for 2 days, and grinded to a thin powder. Samples treated with pure nitric acid were named MWCNT-na.
- ii. For gas-phase activation, 1 g of purified MWCNTs was placed in a furnace and calcined under air for a given time (1 to 120 min) at a certain temperature (425 to 550°C). The burn-off was then calculated. Samples oxidized under air were named MWCNT-air.

- iii. Mechanical cutting of purified carbon nanotubes was performed by ball-milling. 1 g of MWCNT powder was introduced into the mortar of the ball milling apparatus (Pulveriser “Pulverisette”) containing an agate ball (5 cm diameter); grinding was carried out for 60 hr in order to obtain carbon nanotubes of 200-300 nm average length. The ball-milled samples were named MWCNT-bm.

2.2.2 Catalyst preparation and characterization

The synthesis of the Pt precursor involved the preparation of the intermediate $[\text{PtI}_2(\text{COD})]$, by addition of 1,5-cyclooctadiene (commonly designated as COD, C_8H_{12} , Aldrich 99%) to platinum(II) iodide (PtI_2 , Strem Chemicals 99%). Further addition of diethyl ether ($\text{C}_4\text{H}_{10}\text{O}$), methyllithium solution (CH_3Li , Fluka 5%) and sodium sulphate (Na_2SO_4 , Acros Organics 99%) was necessary to prepare the final complex $[\text{Pt}(\text{CH}_3)_2(\text{COD})]$. Additional details regarding this synthesis can be found elsewhere [42].

MWCNT supported catalysts were prepared by wet impregnation. The desired amounts of precursor, support and n-hexane (solvent) were placed in a Schlenk tube under argon atmosphere. After being stirred for 2 days at 45°C the catalysts were filtered and dried at 120°C in an oven overnight. Prior to reaction, the Pt catalysts were calcined in N_2 at 400°C (4 hr, 100 mL min^{-1}) and reduced in H_2 at 350°C (2 hr, 20 mL min^{-1}). A post-reduction treatment (PRT) under nitrogen at 700°C (2 hr, 100 mL min^{-1}) was used in indicated cases to remove the excess of oxygenated surface groups from the support.

The transmission electron microscopy (TEM) micrographs were obtained using a Philips CM12 microscope operating at 120 kV. The samples were dispersed in ethanol, sonicated and collected on a copper carbon-coated TEM grid.

Nitrogen adsorption-desorption analysis at -196°C were performed using either a Micrometrics Asap 2010 equipment or a Coulter Omnisorp 100CX to measure the BET specific surface area and to get information concerning the porosity of the powders.

Thermogravimetric analysis (TGA) were conducted under air in a Setaram apparatus, using a $10^\circ\text{C min}^{-1}$ ramp between 25 and 1000°C , followed by an isothermal period of 30 min at the final temperature.

TPD spectra were obtained with a fully automated AMI-200 Catalyst Characterization Instrument (Altamira Instruments), equipped with a quadrupole mass spectrometer (Dymaxion 200 amu, Ametek). The catalyst sample (0.10 g) was placed in a U-shaped quartz tube located inside an electrical furnace and heated at 5°C min^{-1} to 1100°C using a constant flow rate of helium (25 mL min^{-1} , STP). The amounts of CO

and CO₂ released during the thermal analysis were calibrated at the end of each analysis. This allowed the identification and quantification of the oxygen functional groups of the corresponding TPD spectra using the peak assignment and deconvolution procedures described by Figueiredo *et al.* [22, 23].

The distribution of grain diameters was measured with a Mastersizer Sirocco 2000 laser granulometer.

Raman spectra were recorded on a Labram HR800 of Jobin et Yvon (632.82 cm⁻¹).

XPS analyses were performed on a VG Escalab model MK2 spectrophotometer with pass energy of 20 eV and with Al K α (1486.6 eV, 300 W) photons as an excitation source.

2.2.3 Selective hydrogenation procedure

A cinnamaldehyde solution (C₉H₈O, Fluka 98%) with a concentration of *ca.* 14 mmol L⁻¹ was prepared in a 100 mL volumetric glass flask; heptane (C₇H₁₆, Aldrich 99%) was used as solvent and 60 μ L of decane (C₁₀H₂₂, Fluka 98%) were used as internal standard for gas chromatography. Hydrogenation of cinnamaldehyde was carried out with 80 mL of the as prepared solution and 0.2 g of catalyst in a 160 mL well-stirred stainless steel reactor (Figure 2.1). Possible traces of dissolved oxygen were removed by bubbling nitrogen several times through the solution. The reactor was then pressurized with hydrogen (3 bar) several times, in order to purge the nitrogen. Finally, the temperature was set to 90°C and the reactor pressurized with hydrogen to the desired 10 bar, immediately before the reaction start.

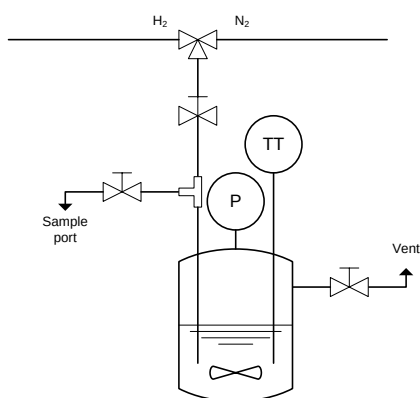


Figure 2.1 Schematic representation and photograph of the batch reactor used for the hydrogenation reactions.

As the reaction proceeded, samples were withdrawn to monitor product distribution. The analysis was performed in a DANI GC-1000 gas chromatograph, equipped with a split/splitless injector, a capillary column (Chrompack CP5865, WCOT Fused Silica 30 m, 0.32 mm i.d., coated with CP-Sil 8 CB low bleed/MS 1 μm film) and a flame ionization detector. For a complete separation of the peaks, the oven temperature was maintained for 2 minutes at 100°C, followed by a ramp of 10°C min⁻¹ up to 140°C; this temperature was then kept for 9 minutes, as the analysis time added up to a total of 15 minutes. A ChromStar v4.06 software running on a 486 DX2-50 PC was used to record the peak data. The results of the reaction runs were analyzed in terms of reactant conversion:

$$X_{\text{CAL},t} = \frac{C_{\text{CAL},0} - C_{\text{CAL},t}}{C_{\text{CAL},0}} \times 100 \quad (\%) \quad (\text{Eq. 2.1})$$

and product selectivity:

$$S_{i,t} = \frac{C_{i,t}}{C_{\text{CAL},0} - C_{\text{CAL},t}} \times 100 \quad (\%) \quad (\text{Eq. 2.2})$$

where $C_{i,t}$ represents the concentration of the main identifiable hydrogenation products of cinnamaldehyde (CAL), namely cinnamyl alcohol (COL), hydrocinnamaldehyde (HCAL) and hydrocinnamyl alcohol (HCOL), at a given time, t .

To compare the activity exhibited by the catalysts, the turn-over frequency (TOF) was calculated based on cinnamaldehyde consumption:

$$\text{TOF} = \frac{\text{mol}_{\text{CAL converted}}}{\text{time} \frac{m_{\text{cat}} y_{\text{Me}}}{M_{\text{Me}}} D_{\text{Me}}} \quad (\text{s}^{-1}) \quad (\text{Eq. 2.3})$$

where m_{cat} , y_{Me} , M_{Me} represent the catalyst mass, metal load and molar mass, respectively. D_{Me} stands for the metal dispersion and was determined by either H₂ chemisorption measurements or based on the particle size observed by TEM.

2.3 Results and discussion

2.3.1 *Effect of the activation treatment*

2.3.1.1 Liquid-phase activation with nitric acid

A simple, effective and widely used treatment to functionalize nanotubes consists in their activation with nitric acid solutions. These solutions are usually composed of just concentrated HNO_3 or binary mixtures of $\text{HNO}_3/\text{H}_2\text{SO}_4$ with different proportions. Although there are a few reports on the nature of the functional groups that are created on the CNT surface [43], no systematic research in this topic has yet been carried out. It has been shown that the HNO_3 treatment leads mainly to carboxylic acid functions, lactones, phenols, carbonyls, anhydrides, ethers and quinones [43]. The oxidation occurs first on the MWCNT defects, and initially gives $-\text{OH}$, then $\text{C}=\text{O}$ and finally COOH groups [9, 44].

To study the kinetics of nitric acid oxidation and the influence of this treatment on MWCNT morphology and surface composition, six treatments were carried out consisting of different reaction times (1, 2, 4, 5, 6 and 8 hr). The amount of atomic oxygen present on the MWCNTs surface was evaluated by XPS, whereas the amount of acidic functions was measured according to the method developed by Pittman [45]. The results obtained are presented in Figure 2.2. Other materials like graphite nanofibers (GNF) often present higher amounts of atomic oxygen at the surface when compared to CNTs, assuming identical oxidation conditions [9, 10]. This is related to the number of graphene edges exposed at their surface when compared to the concentric arrangement observed in CNTs.

The kinetic curves reveal two regimes for MWCNTs oxidation with HNO_3 . For activations below 1 hr (Zone A), a fast formation of acidic functions (carboxylic acid and phenolic groups) is observed, while after 1 hr (Zone B) it becomes much slower. Thus, it seems reasonable to assume that two different phenomena occur during the oxidation treatment.

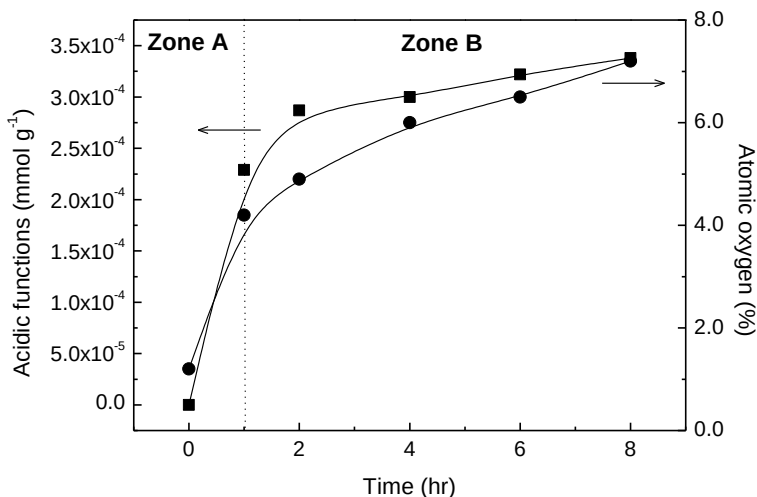


Figure 2.2 Evolution of the percentage of atomic oxygen and acid functions with nitric acid oxidation time (trend lines with no mechanistic expression were added for the sake of clarity).

In order to better understand the kinetic features involved, TGA, Raman spectroscopy and high-resolution transmission electron microscopy (HRTEM) analysis were performed. TGA allowed us to follow the temperature at which MWCNTs present the maximum oxidation rate and the weight loss as a function of the treatment time (Figure 2.3a). The weight loss decreases monotonously with increasing treatment time. Indeed, the nitric acid treatment consumes carbon, which in turn increases the proportion of ferrous residues in the sample. This also means that a small amount of iron can be removed during this treatment. As the catalyst contains iron, which in turn catalyzes carbon oxidation [46], one might expect a decrease in the temperature of carbon gasification while increasing the HNO_3 treatment duration. A different trend was, however, observed after 5 hr.

In Raman spectroscopy, CNTs are characterized by three distinct zones: a zone known as “breathing mode” between 100 and 300 cm^{-1} , the D band zone (diamond-like) associated with disorder and defects in MWCNTs (sp^3 , *ca.* 1330 cm^{-1}) and the G band zone (graphite-like) that characterizes the graphitic structure of MWCNTs (sp^2 , *ca.* 1600 cm^{-1}) [47]. By measuring the ratio of the areas of the D and G bands, an idea of the MWCNTs disorder can be attained. The evolution of the I_D/I_G ratio, according to reaction time, is described in Figure 2.3b.

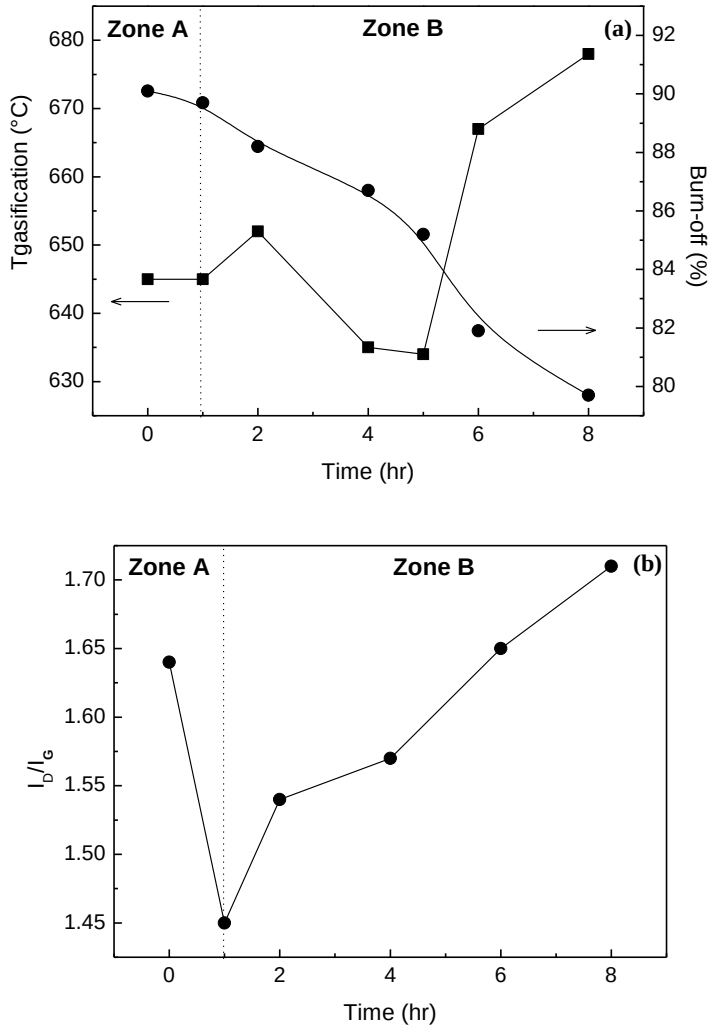


Figure 2.3 (a) Variation of the mass loss (burn-off) and of the temperature of maximum gasification rate as a function of the reaction time, and (b) evolution of the I_D/I_G ratio during the nitric acid treatment.

Analysis of these results can lead to some valuable conclusions. First, in zone A the rate of functionalities formation is high. The oxidation reaction would seemingly start (as for carbon nanofibers [9]) on the “native” and reactive amorphous carbon present on the MWCNT surface (Figure 2.4a). This is confirmed by both the decrease of the I_D/I_G ratio during the first hour and HRTEM observations (Figure 2.4b). The consumption of amorphous carbon at the beginning of the oxidation process has already been reported

and correlated to a decrease in the I_D/I_G ratio by Gotovac *et al.* [40]. TGA results also suggest a low amount of amorphous carbon on pristine MWCNTs. The large increase in the amount of carboxylic acid groups on the MWCNT surface measured during the first hour of reaction could be then associated with the functionalization at the MWCNT defects (Figure 2.4b) rather than to a direct attack on the graphene layers.

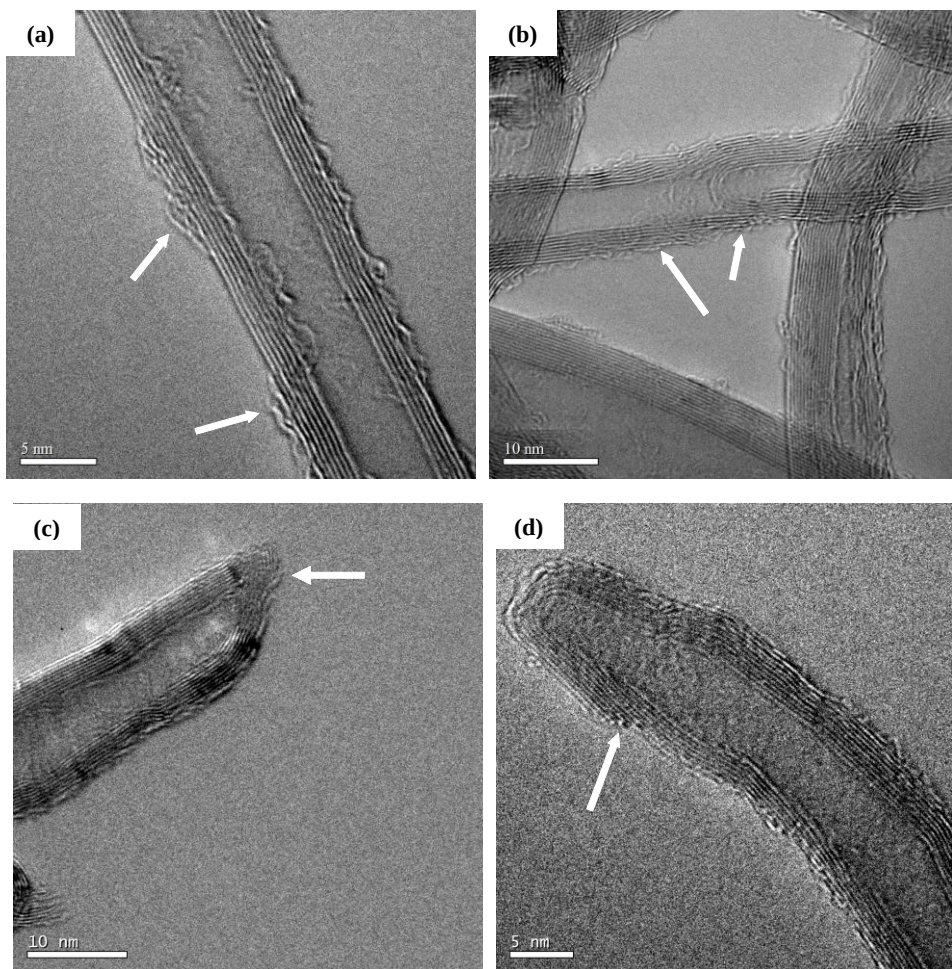


Figure 2.4 HRTEM micrographs of (a) purified MWCNTs; (b) slightly oxidized MWCNTs; (c) damaged tip of MWCNTs; (d) highly oxidized MWCNTs.

During the initial stages of the reaction, no significant burn-off is measured and most of the MWCNTs keep their intrinsic morphology (same number of walls and closed tips). A different regime is however observed in zone B, associated with a slower functionalization rate and with a significant consumption of the carbon matrix. During

this step, MWCNT tips are first damaged and then attacked at their walls (Figure 2.4c and d). The oxidation of the tips would start at reactive sites such as pentagons [48], and the oxidation of the walls would progress via CO_2 elimination from the previously oxidized sites and further oxidation of these sites. This regime, in which the nanotube walls are damaged, contributes to an increase in the burn-off but not to a significant increase in the concentration of oxygenated groups; indeed, a low increase in the atomic oxygen percentage (XPS results) and in the D-band (Raman results) is observed. Further oxidation results in an attack to the outer walls of CNTs, as already reported by Osswald *et al.* [49].

As already mentioned, the second regime is also associated with an increase in the temperature of MWCNT decomposition under air, with the temperature at the maximum gasification rate rising from 635 to 680°C (Figure 2.3a). Such data are quite surprising, since the amount of residual iron increases with burn-off increase and this should enhance the air oxidation rate of MWCNTs. A first attempt to explain this result could come from a poorer contact between the iron particles and carbon in highly oxidized MWCNTs [50]. A second explanation could arise from a different oxidation state of iron in oxidized MWCNTs, but it is known that both iron and iron oxide are active catalysts for the oxidation reaction. Finally, a third hypothesis could be a passivation of the surface after prolonged nitric acid treatment.

TPD is a method of characterization of adsorbed surface species by heating the sample and, simultaneously, detecting the residual gas by means of mass spectrometry. As the temperature rises, certain adsorbed species will have enough energy to escape from the surface. The temperature at which the species are released provides information about their binding energy to the surface. TPD experiments performed on CNT-na (Figure 2.5) show the presence of lactone (CO_2 evolution at 600°C), anhydride (CO and CO_2 at 500°C) phenol and carbonyl or quinone groups (CO at 750°C) in addition to carboxylic acids (CO_2 at 300°C) [23]. GNFs activated with a $\text{HNO}_3/\text{H}_2\text{SO}_4$ solution also present similar oxygenated groups at the surface [9].

The observed results may be rationalized on the basis of two combined effects. Firstly, HNO_3 oxidation contributes to the removal of the iron particles located at MWCNT tips (Figure 2.6a) - these iron particles catalyze MWCNT gasification, while other nanoparticles remain inaccessible inside the tube cavity (Figure 2.6b); secondly, the oxygenated groups created on the MWCNT surface contribute to passivate the tube surface towards air oxidation since their thermal desorption is needed for further reaction with oxygen.

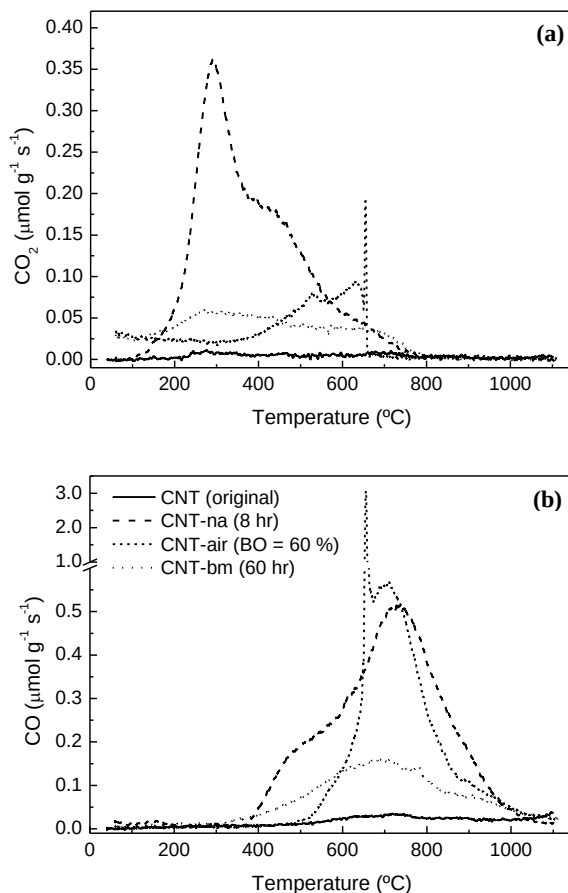


Figure 2.5 TPD spectra for original MWCNTs, MWCNT-na, MWCNT-air and MWCNT-bm: (a) CO_2 and (b) CO evolution.

Finally, it is worth noting that, although nitric acid oxidation opens MWCNT tips, this treatment has no significant effect on the specific surface area of the material, as determined by the BET method, from N_2 isotherms at -196°C , since it increases only from 177 to $188 \text{ m}^2 \text{ g}^{-1}$, after 8 hr of reaction. This is due to the existence of closed compartments in the inner cavity of MWCNTs (Figure 2.4b and Figure 2.6b), which prevent the nitrogen access. The observed limited increase of specific surface area upon nitric acid oxidation, confirms the results already reported by Chen *et al.* for CNTs [51].

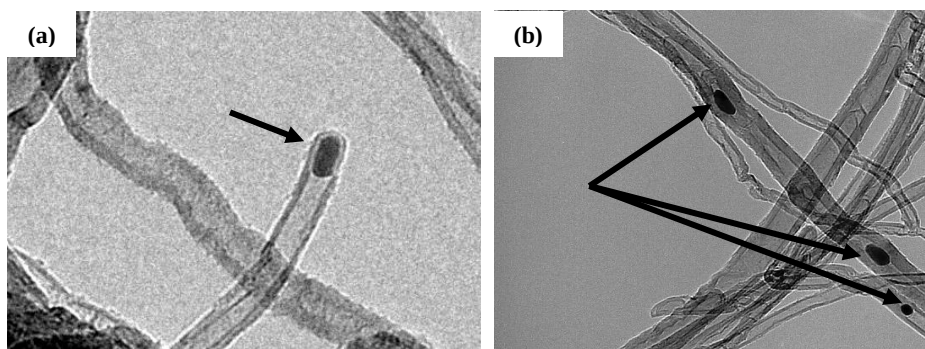


Figure 2.6 Iron nanoparticles located (a) on a tip of MWCNT and (b) inside the MWCNT inner cavity.

Figure 2.7 shows a schematic representation of the oxidation process by nitric acid and is based on the previously described information.

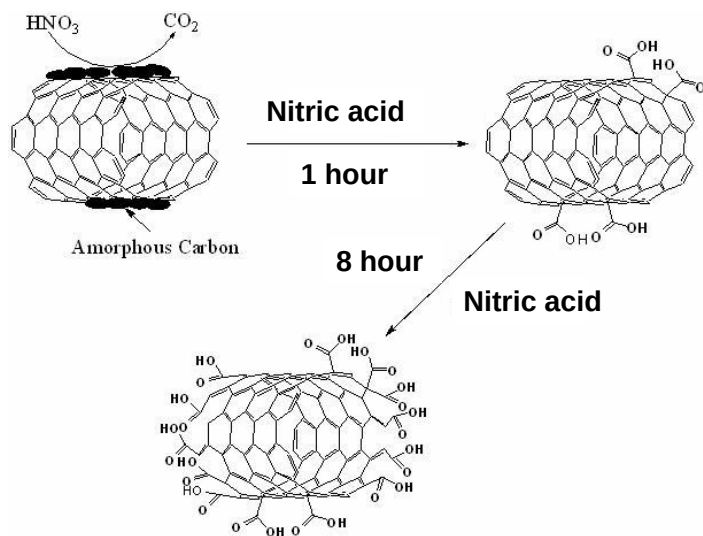


Figure 2.7 Schematic representation of the different steps involved in the nitric acid oxidation of MWCNTs.

2.3.1.2 Gas-phase activation with air

Air or CO_2 oxidation has become a frequently used method for the removal of disordered carbon species from carbon nanotubes [26, 52-55]. In the first set of experiments the influence of the oxidation temperature between 450 and 550°C for 10 min reaction was examined, with a linear increase of the burn-off from 10% at 450°C

to 92% at 550°C being observed. A second set of experiments was performed at 500°C under air at various time intervals. Figure 2.8 shows the effect of oxidation time on the burn-off and I_D/I_G ratio. Two different slopes crossing at around 60% burn-off can be distinguished, a similar behavior having already been reported [53]. In this study, the MWCNTs were contaminated with significant amounts of amorphous carbon and the authors suggested that these two different slopes could correspond first to the oxidation of amorphous carbon and then of MWCNTs. In our case, the amount of amorphous carbon on the CNTs surface is extremely low and such an explanation is not plausible. Instead, an explanation similar to that suggested for the nitric acid treatment is proposed. A poor contact between the catalyst and carbon for highly oxidized MWCNTs [49] or the passivation of their surface after prolonged oxidative treatment, may cause this change of reactivity. The TPD profile of air-oxidized MWCNTs (Figure 2.5) shows that this treatment affects significantly the CO/CO₂ ratio in comparison with all the other samples, which ranges from 3 (other samples) to 7 for MWCNT-air. The CO evolution at high temperatures can be associated to the presence of phenol and carbonyl or quinone groups [23]. Moreover, a peculiar reproducible phenomenon occurs at 660°C, the temperature at which CO₂ evolution stops abruptly at the same time that CO evolution starts to increase markedly. This could be due to the Boudouard reaction catalyzed by some accessible iron. The presence of the latter at high temperatures, in these TPD experiments, could be explained in terms of some opened MWCNT tips by CO₂ [52, 56]. Hence, it is proposed that a part of the CO₂ evolving during the TPD experiments reacts with the MWCNT surface, thus opening their tips and exposing some iron.

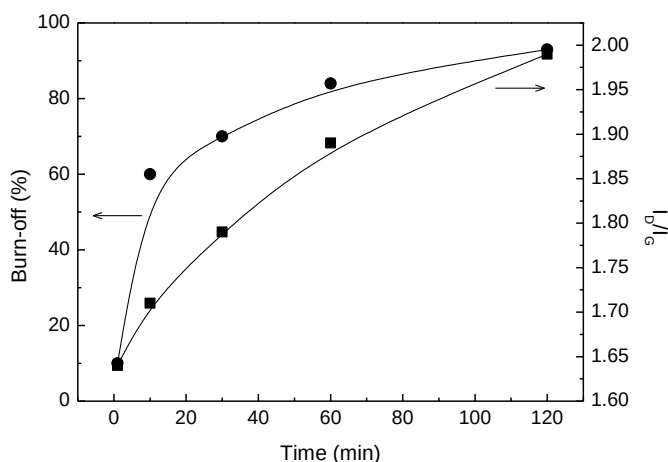


Figure 2.8 Effect of oxidation time (air, 500°C) on the burn-off of MWCNTs and I_D/I_G ratio.

The I_D/I_G ratio increases with the burn-off (Figure 2.8) and reaches 1.99 for 93% burn-off. This result is in agreement with a recent study on the effect of thermal treatment on the structure of MWCNTs [26]. TEM observations on a sample with 60% burn-off show that the tubes are opened and their surface is seriously compromised (Figure 2.9); the specific surface area of the nanotubes increases 30%, from 177 to 230 m² g⁻¹. Thus, air oxidation introduces significant amounts of functionalities, at the cost of MWCNTs quantity (TGA results) and quality, as evidenced by Raman and TEM observations. Both nitric-acid and air activations were found not to significantly affect the MWCNT length, contrarily to ball-milling treatment discussed in the next section.

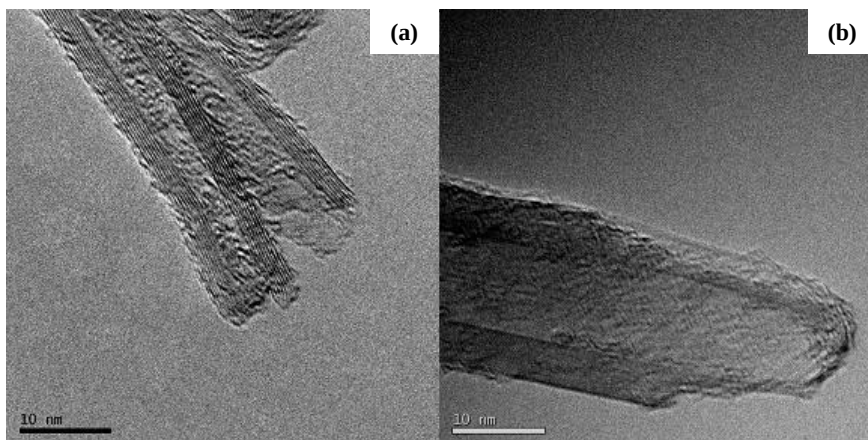


Figure 2.9 TEM micrographs of MWCNT-air at 60% burn-off showing: (a) opened tips and (b) damaged walls.

2.3.1.3 Mechanical activation with ball-milling

Amongst the different methods proposed to cut nanotubes [28-30, 57-59], ball-milling is the most popular. This method has also been used to produce nanoparticles from graphite [60] or nanoporous carbon from MWCNTs [61]. The effect of ball-milling on purified MWCNTs was analyzed, focusing on (i) the diameter of MWCNTs aggregates, (ii) MWCNTs specific surface area and length and (iii) MWCNTs surface chemistry. The evolution of the grain diameter formed by MWCNTs agglomeration was studied as a function of milling time (Figure 2.10). The average diameter decreases as a function of time, from 37 to 4.7 μm (60 hr), remaining constant afterwards. Thus, ball-milling has potentially a negative effect whenever filtration in liquid phase catalysis is required.

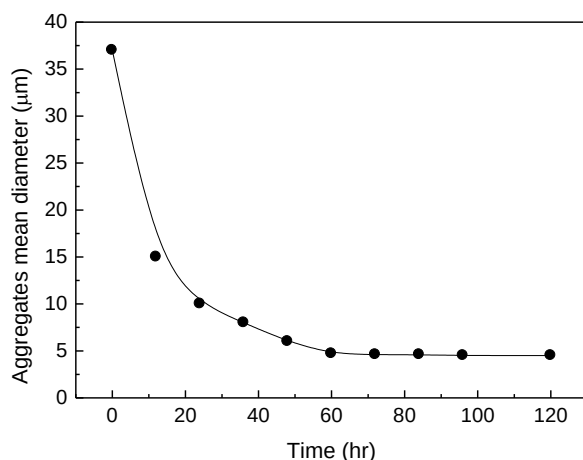


Figure 2.10 Effect of the ball-milling time on the MWCNT grain diameter.

The reason for this decrease is mainly due to MWCNT shortening and agglomeration; their length decreases from up to 50 μm for purified MWCNTs to 0.1-1 μm for ball-milled MWCNTs (MWCNT-bm) after 60 hr. Such length distribution is in agreement with literature reports [29, 30, 60]. This shortening contributes to the formation of MWCNTs agglomerates with a densely-packed structure (Figure 2.11).

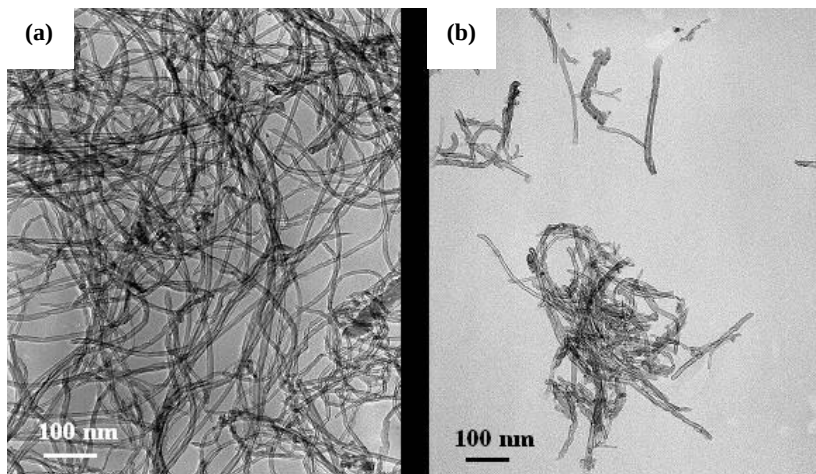


Figure 2.11 TEM micrographs of (a) purified MWCNTs, (b) MWCNTs after 60 hr ball-milling.

The specific surface area of the material increases from 177 to a maximum of 260 $\text{m}^2 \text{g}^{-1}$ after 60 hr of treatment followed by a slight decrease with longer milling times. The variation in the surface area, corresponding to the first 60 hr of milling, can

be attributed to the increase in MWCNT entanglement, as shown by the decrease in the diameter of the agglomerates. The slight decrease in MWCNT surface area after 60 hr may be associated to the fact that MWCNTs present partially or completely collapsed openings upon prolonged milling [58]. The ball-milling treatment does not allow the opening of all the nanotubes and this is due to the presence of compartments that constitute weak points at which the mechanical cutting easily takes place [62]. The number of opened and closed tips was calculated for a sample of 106 tubes, found in various zones of the grid: 22 were found open and 84 closed.

The effect of ball-milling on the proportion of G and D bands was investigated by Raman spectroscopy (Table 2.1). An increase in the defect density (I_D/I_G ratio) when increasing the milling time was observed. This result is in agreement with literature reports [63] and indicates that the sp^2 structure of carbon is disrupted by ball milling. XPS data (Table 2.1) and TPD profiles (Figure 2.5) are in agreement with a low degree of functionalization of MWCNTs surface by this technique. The TPD profiles of MWCNT-bm indicate the existence of some surface groups regarding those obtained with purified MWCNTs. Additionally, the CO/CO₂ ratio is similar to that measured for MWCNT-na (3.0 and 2.9, respectively).

Table 2.1 Influence of the ball-milling time on MWCNTs structural features.

Time (hr)	0	12	24	60	120
Length (μm)	~ 50	-	-	0.1-1	-
S_{BET} ($\text{m}^2 \text{g}^{-1}$)	177	180	201	260	240
I_D/I_G (Raman)	1.6	-	1.8	2.2	2.3
At. Ox. % (XPS)	1.1	-	1.4	2.1	3.1

A noticeable macroscopic evidence of the MWCNTs with different activation treatments was the variation in their apparent density. Visually, air activation provided for the “fluffiest” material, while nitric acid and ball-milled samples possessed similar densities.

2.3.2 Metal-phase characterization

The characterization results obtained for naked and Pt containing MWCNTs, namely BET specific surface areas (determined by N₂ adsorption desorption at -196°C), Pt load (determined by inductively coupled plasma, ICP), Pt particle size (determined by TEM) and CO and CO₂ amounts (determined by integration of TPD curves), are collected in Table 2.2.

Table 2.2 BET specific surface areas (S_{BET}), Pt load (y_{Pt}) and particle size (d_{Pt}), and amounts of CO and CO₂ released for MWCNT supported catalysts.

Catalyst	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	y_{Pt} (wt. %)	d_{Pt} (nm)	CO	CO ₂
				(μmol g ⁻¹)	
MWCNT-na [*]	241	-	-	1960	952
Pt/MWCNT-na	241	4.8±0.1	5.2	1448	468
Pt/MWCNT-na700	262	4.8±0.1	8.5	393	120
MWCNT-air [*]	311	-	-	1584	312
Pt/MWCNT-air	297	2.1±0.1	9.7	1144	244
Pt/MWCNT-air700	289	2.1±0.1	17.2	405	240
MWCNT-bm [†]	201	-	-	792	336
Pt/MWCNT-bm	226	2.7±0.1	13.5	788	260
Pt/MWCNT-bm700	233	2.7±0.1	18.5	366	87

^{*}initial surface area of 225 m² g⁻¹; [†]initial surface area of 177 m² g⁻¹.

The Pt particle size distribution undergoes a shift towards larger particles for MWCNT-air (Figure 2.12b) and MWCNT-bm (Figure 2.12c) supported catalysts when compared to Pt/MWCNT-na (Figure 2.12a). For Pt/MWCNT-na, the population of particles with diameters lower than 6 nm is the most represented amongst all, in spite of the higher Pt load. A clear correlation between the amount of potential anchoring groups for Pt, which can be quantified by the CO + CO₂ (released during TPD experiments) and the mean Pt particle size was observed. Figure 2.13 shows that the mean particle diameter of Pt decreases as the amount of anchoring sites of the support increases. Thus, reactive oxygen-containing functional groups formed during the oxidative treatments assist the metal deposition step. The density of these surface sites can be estimated using the TPD and S_{BET} results. A value of 8.8 sites nm⁻² is obtained for the nitric acid treated samples, 5.7 sites nm⁻² for air and 3.4 sites nm⁻² for the ball-milled ones. Accordingly, the adsorption of the Pt precursor and the deposition of nanoparticles should only occur at those available sites. The deposition of nanoparticles is controlled by the density of these sites, as a low value (MWCNT-bm) gives rise to the formation of large Pt nanoparticles (mean diameter 13.5 nm), whereas smaller Pt particles (mean diameter 5.2 nm) are obtained on a support with a large amount of sites (such as MWCNT-na). A similar phenomenon has already been reported for Pd [64] and Co [65] catalysts supported on CNFs.

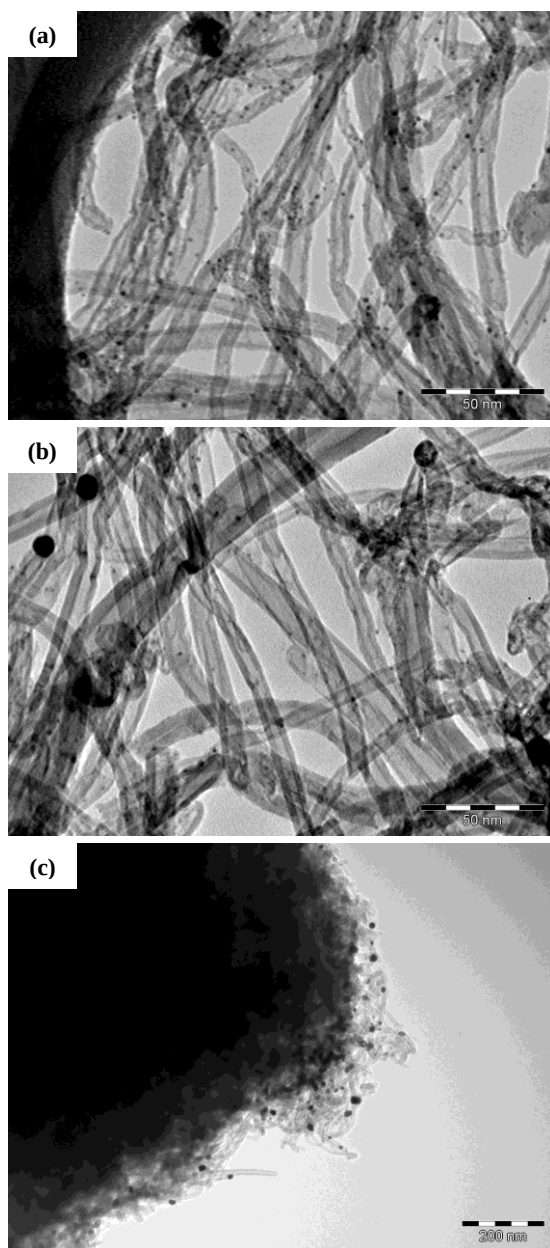


Figure 2.12 TEM micrographs of (a) Pt/MWCNT-na, (b) Pt/MWCNT-air and (c) Pt/MWCNT-bm catalysts.

Analyzing the amounts of CO and CO₂ released during the TPD experiments (Table 2.2) it can be observed that part of the surface groups are removed during the catalyst

preparation. Thus, the amount of CO_2 evolved during the TPD experiments changes from $952 \mu\text{mol g}^{-1}$ (for MWCNT-na) to $468 \mu\text{mol g}^{-1}$ (for Pt/MWCNT-na), corresponding to a decrease of 50% in the concentration of these sites. This can be attributed to the disappearance of carboxylic acid groups. These groups are actively involved in the anchoring of the organometallic Pt(II) precursor, allowing higher dispersions and loadings. It has been recently evidenced that finely dispersed Pt clusters bind to the MWCNT surface via bonding with the ionic form of carboxylate $-\text{COO}(\text{Pt})$ [66].

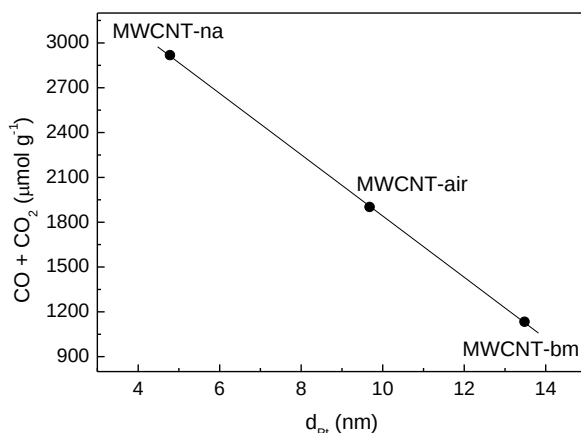


Figure 2.13 Influence of the concentration of oxygenated groups at MWCNTs surface on the Pt mean particle size.

A post-reduction thermal treatment (PRT) performed at 700°C in N_2 was able to remove additional surface groups and provide materials, in some cases, with 80% less surface groups regarding the initial amount. Since Pt catalyses the gasification of the support in the presence of oxygen, it is not reliable to assign the surface groups by deconvolution, as performed for the naked supports. Hence, only the total amounts of CO and CO_2 are given as means of global characterization.

The PRT also contributes to the sintering of Pt particles. The increase of the mean particle size is less pronounced for the MWCNT-bm (37%) when compared to MWCNT-na (63%) and MWCNT-air (77%) supports. One possible explanation for the observed sintering effect lies on the high metal load of Pt/MWCNT-na (4.8 wt. %), which is not the case for Pt/MWCNT-air where the metal load is similar to that of Pt/MWCNT-bm (2.1% wt. %). If one considers the length of the MWCNTs, which differs significantly from MWCNT-bm ($0.1 < L (\mu\text{m}) < 1$) to MWCNT-air ($10 < L (\mu\text{m}) < 50$), a reason for the observed differences in sintering can be found. Indeed, for similar metal loadings, Pt nanoparticles will be more abundant on a single

nanotube of MWCNT-air than on MWCNT-bm. Hence, surface diffusion of Pt over MWCNT-air will give rise to an increase in the metal particle size. In addition, Pt transfer from one crystallite to another, with consequent decrease in the Pt crystallite density and an increase in particle size, is subject to the activation barrier of the Pt atoms diffusion over the CNTs surface, which may vary with the concentration of oxygenated sites on the surface.

2.3.3 Selective hydrogenation of cinnamaldehyde

The main reaction scheme for the selective hydrogenation of cinnamaldehyde in heptane is shown in Figure 2.14. The desired (but thermodynamically unfavored) pathway leads to the preferential hydrogenation of the carbonyl group, and thus to the production of the unsaturated alcohol (COL). An alternative route involves the reduction of the olefinic C=C bond, leading to the saturated aldehyde (HCAL). Additionally, both COL and HCAL can be further hydrogenated to produce the saturated alcohol (HCOL). In some experiments, towards the end of the reaction, significant amounts of 1-propylbenzene (PB) were also detected. PB can be obtained either by hydrogenation of β -methylstyrene (MS) or by a loss of the OH group in HCOL. In some cases, mainly in the presence of the MWCNT-na samples, the hydrogenation of aromatic ring was observed to yield 3-cyclohexyl-1-propanol (CHP) and n-propylcyclohexane (PCH).

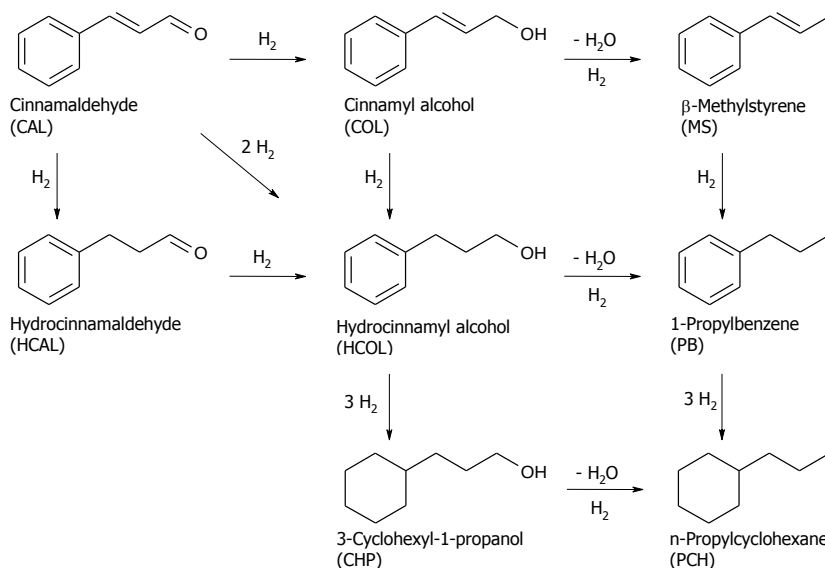


Figure 2.14 Reaction scheme for the selective hydrogenation of cinnamaldehyde using MWCNT supported Pt catalysts.

The reaction results, obtained at 90°C and 10 bar total pressure are gathered in Table 2.3. Looking at the catalysts activity, and independently of the PRT, it can be observed that the TOF decreases when the amount of oxygenated groups on the support surface increases, for a Pt mean particle size between 5 and 13 nm (Figure 2.15). The PRT induces severe sintering to catalysts Pt/MWCNT-air700 and Pt/MWCNT-bm700 even, when low amounts of oxygenated groups are present on the surface. Pt mean particle sizes higher than 13 nm were obtained. As a consequence their TOF decreases when compared with the catalysts without PRT.

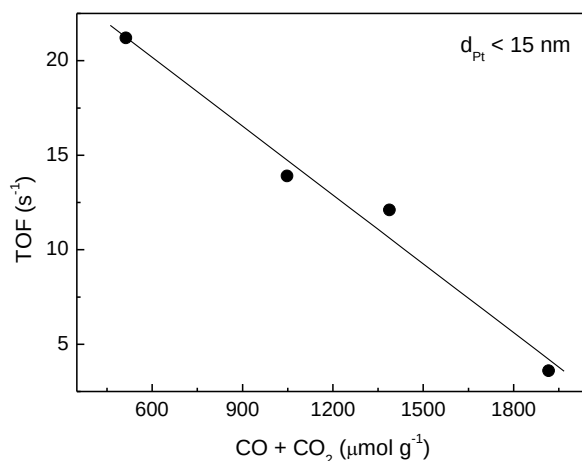


Figure 2.15 Influence of the concentration of oxygenated groups on the TOF of the catalysts.

The highest TOF is obtained with Pt/MWCNT-na700, which presents a low amount of oxygenated groups and small Pt particles. The catalysts without any PRT were relatively non-selective towards COL, whereas after the PRT a very strong increase in the selectivity to COL was observed. In all cases a clear shift in HCAL to COL selectivity was detected after the PRT. This effect was more pronounced in the case of MWCNT-air, where a selectivity increase from 4 to 69%, at 50% conversion, was observed (Figure 2.16 and Table 2.3).

The influence of surface groups in carbon supported catalysts has received increasing attention [67-70]. Recently, it has been reported that the hydrogenation of α,β -unsaturated aldehydes, with CNF supported catalysts, provides more active materials and increases selectivity towards the saturated aldehyde, upon surface group removal [67-69]. Comparing these results with the findings for Pt/MWCNT-na, an increase in activity is confirmed, but they contradict the selectivity towards hydrocinnamaldehyde, since higher amounts of cinnamyl alcohol were obtained. A possible explanation could

be related to an electronic effect produced by the different orientation of the graphitic planes in CNFs and MWCNTs, originating a shift in the cinnamaldehyde adsorption mode on the support surface. It seems also reasonable to suggest a faster diffusion of CAL on the surface of MWCNTs free of oxygenated groups.

Table 2.3 Catalytic results obtained for the hydrogenation of cinnamaldehyde using MWCNT supported Pt catalysts (selectivities measured at 50% conversion).

Catalyst	TOF (s^{-1})	Selectivity (%)		
		COL	HCOL	HCOL
Pt/MWCNT-na	3.6	15	36	18
Pt/MWCNT-na700	21.2	43	24	25
Pt/MWCNT-air	12.1	4	47	12
Pt/MWCNT-air700	7.2	69	14	14
Pt/MWCNT-bm	13.9	20	44	21
Pt/MWCNT-bm700	10.4	65	18	17

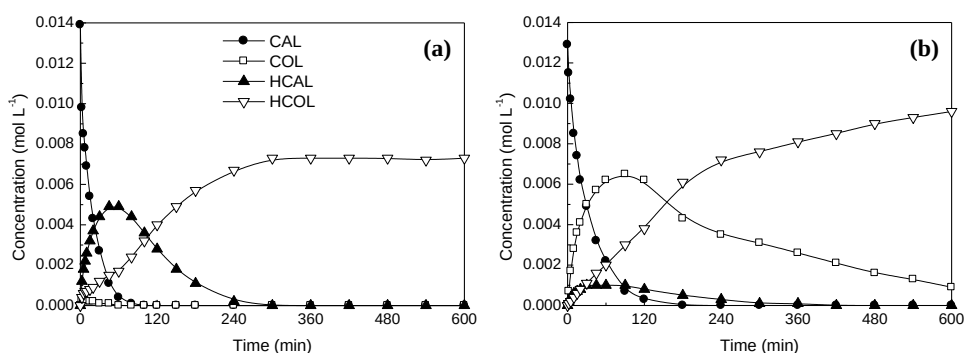


Figure 2.16 Product distribution for the selective hydrogenation of cinnamaldehyde using (a) Pt/MWCNT-air and (b) Pt/MWCNT-air700 catalysts.

Another explanation could be linked to the electronic conductivity of the supports. Indeed CNTs should be more conductive than CNFs due to the arrangement of the graphene layers. It is therefore possible that the interaction of Pt with the support enhances the electron availability of the metal centre, which tends to favor the back-bonding interactions with π^*_{CO} to a larger extent than with π^*_{CC} , promoting C=O coordination and hydrogenation [71].

Finally, the better selectivity obtained after PRT on MWCNT-air and MWCNT-bm, compared with MWCNT-na is not directly linked to the amount of oxygenated groups but rather to the Pt particles size increase. Thus, it has been proposed that for

α,β -unsaturated aldehydes hydrogenation, an increase of the mean particle size may result in an increase of the selectivity towards the unsaturated alcohol [72]. This is mainly due to the fact that the dense Pt(111) plane, present on large faceted particles, is not very favorable for the C=C coordination [71].

2.4 Conclusions

Three different approaches for MWCNT activation were used in order to modify its surface chemistry and morphology.

Activation with pure nitric acid treatment created a large amount of carboxylic groups without significant damage of the MWCNT surface structure. The oxidation occurred first on surface defects and prolonged reflux induced the opening of the MWCNT tips, thus starting to damage the walls and slightly increasing the BET surface area.

Air oxidation was a destructive treatment that introduced moderate amounts of oxygen functionalities, mainly phenol and carbonyl or quinone groups.

Ball-milling in air was able to open some MWCNTs while introducing very little amounts of oxygenated groups; this treatment affected mainly the MWCNT length.

The Pt particle size of Pt/MWCNT catalysts prepared from $[\text{Pt}(\text{CH}_3)_2(\text{COD})]$ was correlated with the concentration of oxygenated functionalities present on MWCNT surface. Carboxylic groups were observed to be particularly efficient in the anchoring of the organometallic precursor.

A post-reduction high temperature treatment of the catalysts at 700°C led to various degrees of sintering, mainly dependant on the length of the MWCNT.

The presence of oxygenated functionalities in the final catalyst was detrimental to the selective hydrogenation of cinnamaldehyde to the unsaturated alcohol. The high temperature treatment, which removed most of these functionalities, and Pt particle diameters larger than 15 nm, allowed a higher selectivity towards the unsaturated alcohol.

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3. Liquid-phase hydrogenation of unsaturated aldehydes: enhancing catalyst selectivity by thermal activation

Platinum and iridium organometallic precursors are used to prepare nanosized thermally stable multi-walled carbon nanotube supported catalysts. These materials are characterized by N₂ adsorption at -196°C, temperature programmed desorption coupled with mass spectroscopy, H₂ chemisorption, transmission electron microscopy and thermogravimetric analysis. Then they are tested in the selective hydrogenation of cinnamaldehyde to cinnamyl alcohol under mild conditions (90°C and 10 bar). In Chapter 2, a thermal activation at 700°C was found to have a very positive effect over both activity and selectivity. In this chapter, a similar treatment leads to selectivities of *ca.* 70%, at 50% conversion, regardless of the active metal phase (Pt or Ir). Since no noticeable differences in the metal particle sizes are detected, the results are interpreted in light of an enhanced metal-support interaction. This effect, induced by the removal of oxygenated surface groups, is thought to change the adsorption mechanism of the cinnamaldehyde molecule.

3.1 Introduction

Carbon nanotubes (CNTs) were discovered soon after the successful laboratory synthesis of fullerenes [1]. Since their discovery in 1991 by Iijima [2], CNTs have been the focus of materials research as a result of their unique electronic and mechanical properties, in combination with their chemical stability [3, 4]. Promising applications of CNTs include electronic devices, field emitters and mechanical strengthening, hydrogen storage and sensing, energy storage and catalysts [5-8].

Carbon materials are nowadays one of the most commonly used materials in catalysis and can be used either as a support for different heterogeneous catalysts or as a catalyst themselves. Structures like activated carbons, xerogels, fullerenes, nanofibers and nanotubes are important among the carbon family in the hydrogenation of unsaturated aldehydes such as crotonaldehyde [9, 10], cinnamaldehyde [11-13] and citral [14, 15]. In fact multi-walled carbon nanotubes (MWCNTs) containing metals like Pt or Pd and promoters like Ni, Ru or Co have been successfully used to selectively reduce either the unwanted C=C [16, 17] or the desired C=O [18, 19] bond in cinnamaldehyde molecule. It has been found that selectivity towards the allylic alcohol is highly dependent on the nature of the precious metal used. Metals such as Pt, Os, Ir, Pd, Rh and Ru, among others, have been studied, leading to differences in activity and selectivity. Gallezot and Richard [20] reported that unpromoted Ir and Os catalysts are considered to be rather selective for unsaturated alcohol formation while Pt, Ru and Co are moderately selective, and Pd, Rh and Ni are nonselective.

A key factor that has been many times overlooked, especially in carbonaceous materials, is the influence of oxygenated surface groups and how these interact with the adsorption mechanism of the molecule [18, 21].

In Chapter 2, a study regarding the effect of different activation procedures on Pt/MWCNT was reported. It was found that the thermal stability of the catalyst is greatly enhanced when the support is treated with nitric acid, comparing to air activation and ball-milling. In the present chapter, MWCNTs are treated in nitric acid. The support is then used to disperse Pt (1 and 3 wt. %) and Ir (1 and 2 wt. %) metals from organometallic precursors. The selective hydrogenation of cinnamaldehyde to cinnamyl alcohol was chosen as a test reaction to assess the catalytic performance.

3.2 Experimental

3.2.1 Support preparation and functionalization

The MWCNTs used in this study were obtained and purified in an identical way to that described in Chapter 2, section 2.2.1 (MWCNT-orig.). However, the functionalization conditions of the nanotubes were milder than those described. Accordingly, 200 mL of a *ca.* 7 M solution of HNO_3 were used to treat 5 g of purified nanotubes at 120°C for 3 hr under vigorous stirring. This treatment is often performed to introduce carboxylic acid groups ($-\text{COOH}$) [22], which will act as anchoring sites for the metal complexes and thus to increase metal dispersion. The MWCNTs were then filtered on a hot fritted glass funnel and washed with distilled water until a stable pH value was obtained. The nanotubes were dried at 120°C for 2 days and grinded to a thin powder (MWCNT- HNO_3).

3.2.2 Catalyst preparation and characterization

Two different organometallic precursors were prepared according to the metal. The Pt precursor used was $[\text{Pt}(\text{CH}_3)_2(\text{C}_8\text{H}_{12})]$ (Figure 3.1a) and the Ir precursor was $[\text{Ir}(\mu\text{-SC}(\text{CH}_3)_3)(\text{CO})_2]_2$ (Figure 3.1b). Details regarding the synthesis of Pt precursor can be found in Chapter 2, section 2.2.2. The synthesis of the Ir precursor involved addition of calculated amounts of iridium (III/IV) iodide ($\text{IrI}_{3,4}$, Johnson Matthey, 31.8%), *N,N*-dimethylformamide ($\text{C}_3\text{H}_7\text{NO}$, Acros Organics, 99%), distilled water and 2-methyl-2-propanethiol ($(\text{CH}_3)_3\text{CSH}$, Acros Organics, 99%). Further details for the preparation of $[\text{Ir}(\mu\text{-SC}(\text{CH}_3)_3)(\text{CO})_2]_2$ can be found elsewhere [23].

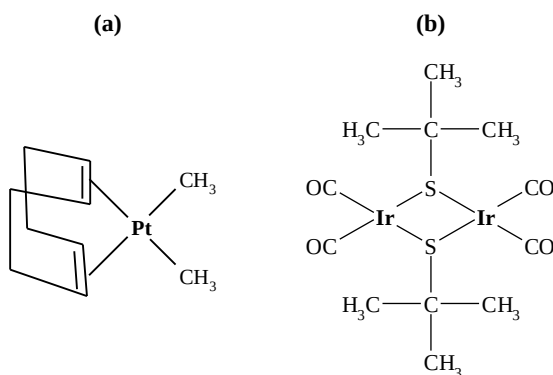


Figure 3.1 Structural formula of synthesized (a) Pt and (b) Ir organometallic precursors.

The preparation of the MWCNT-HNO₃ supported catalysts (1 or 3 wt. % Pt; 1 or 2 wt. % Ir) was identical to that described in Chapter 2, section 2.2.2. The catalysts were calcined in nitrogen, reduced in hydrogen and flushed with nitrogen at the desired reduction temperature (xPt/MWCNT at 350°C and xIr/MWCNT at 500°C, x being the metal load present) in order to remove physisorbed hydrogen. In the case of the Ir catalysts, it was necessary to remove the sulfur contained in the precursor [23] and thus a higher temperature than that used for Pt was required. A post-reduction treatment (PRT) under nitrogen at 700°C was used in indicated cases to purge the excess of oxygenated surface groups (xPt/MWCNT700 and xIr/MWCNT700).

The textural characterization (BET surface areas, S_{BET}) of the materials was based on the N₂ adsorption isotherms determined at -196°C, using a Coulter Omnisorp 100CX apparatus.

The metal dispersion was determined by H₂ chemisorption at room temperature in a U-shaped tubular quartz reactor after a thermal treatment to remove contaminant species from the catalyst surface. Pulses of H₂ were injected through a calibrated loop into the sample at regular time intervals until the area of the peaks became constant. The amounts of H₂ chemisorbed were calculated from the areas of the resultant H₂ peaks. The H₂ was monitored with a SPECTRAMASS Dataquad quadrupole mass spectrometer. Assuming an adsorption stoichiometry H/M (M = Pt, Ir) of 1 and the formation of spherical particles, it was possible to estimate the mean particle diameter based on the chemisorption results. Hence, based on a surface metal distribution of 1.12×10^{19} at m⁻² for Pt and 1.30×10^{19} at m⁻² for Ir [24], the metal particle size can be calculated from equations 3.1 and 3.2.

$$d_{\text{Pt}} = \frac{1.015}{D_{\text{Pt}}} \quad (\text{nm}) \quad (\text{Eq. 3.1})$$

$$d_{\text{Ir}} = \frac{1.099}{D_{\text{Ir}}} \quad (\text{nm}) \quad (\text{Eq. 3.2})$$

where D_{Pt} and D_{Ir} is the metal dispersion of Pt (H/Pt) and Ir (H/Ir), respectively.

TPD and TEM analysis were performed in an identical way to that described in Chapter 2, section 2.2.2.

Quantification of the metal load was performed by thermogravimetric analysis (TGA) analysis and inductively coupled plasma (ICP).

TGA was performed using a Mettler M3 balance equipped with a TC 11 thermal analysis processing unit. In the TGA experiments, the sample was first heated in N₂ from

30 to 900°C at 25°C min⁻¹, allowing the quantification (mass loss) of the volatiles present at the materials surface, which decompose upon heating. After 7 min at 900°C in N₂, the gas feed was changed to air in order to burn the carbon samples and determine their fixed carbon and ash contents. The decrease in sample weight due to gasification was monitored as a function of temperature. Knowing the ash content of the naked support, the metal load could be easily calculated. The accuracy of this procedure is very good for higher metal loads but requires high amounts of sample for low metal contents. In tests under oxidative atmosphere the sample was heated from 50 to 900°C at 20°C min⁻¹.

3.2.3 Selective hydrogenation procedure

The hydrogenation procedure was identical to that already described in Chapter 2, section 2.2.3.

3.3 Results and discussion

3.3.1 Support characterization

The production process of MWCNTs gives essentially a non-porous material (the inner cavity of the nanotube being inaccessible) with all the observed surface area due to adsorption at the external surface of the tubes. The shape of the adsorption isotherms (Figure 3.2) can be associated to type IV, with H1 hysteresis loop, characteristic of mesoporous materials [25].

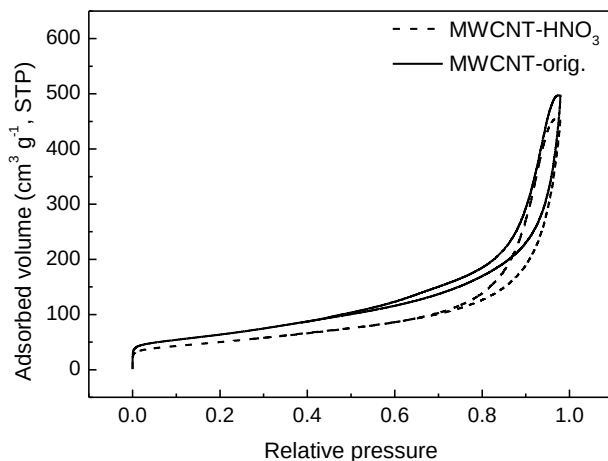


Figure 3.2 Nitrogen adsorption-desorption isotherms at -196°C for MWCNT-orig and MWCNT-HNO₃.

Since MWCNT are non-porous, the nature of the isotherms can be explained in terms of particle aggregation to form very small inter-particle mesopores. The slight microporous behavior evidenced in the low pressure region ($p/p_0 < 0.01$) could be attributed to a reduced number of opened MWCNT tips with very small diameter.

Following nitric acid oxidation, carbon materials often develop large amounts of surface groups, namely carboxylic acid (strong and weak, I and II in Figure 3.3, respectively), anhydrides (III), lactones (IV), phenols (V), ethers, and carbonyl/quinone (VI) [26]. TPD experiments performed on the MWCNTs, before and after nitric acid activation (Figure 3.4), clearly show the difference in the amount of surface groups between both samples.

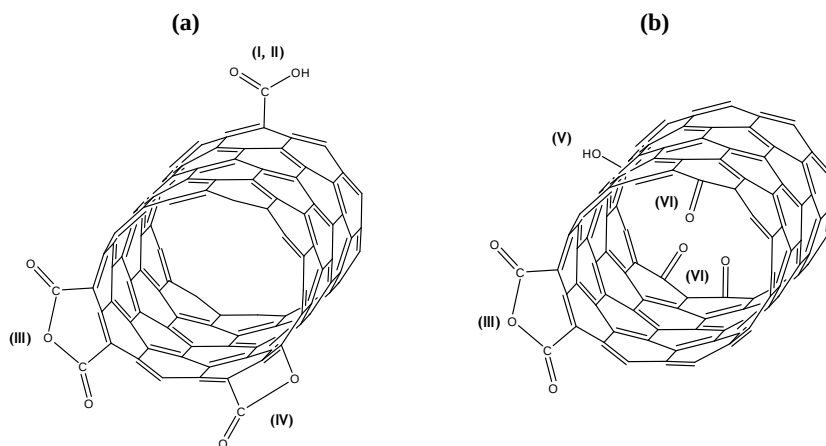


Figure 3.3 Oxygenated surface groups commonly found after nitric acid oxidation: (a) releasing as CO_2 and (b) as CO by TPD.

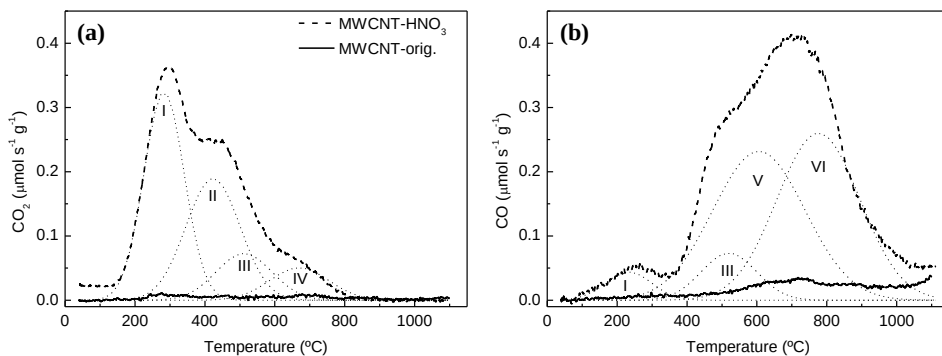


Figure 3.4 TPD spectra for MWCNT-orig and MWCNT- HNO_3 and deconvolution for MWCNT- HNO_3 : (a) CO_2 and (b) CO evolution.

The effect of nitric acid oxidation on the textural and surface properties of the MWCNTs can be extracted from the data in Table 3.1.

Table 3.1 BET specific surface areas (S_{BET}) and amounts of CO and CO₂ released for MWCNT-orig. and MWCNT-HNO₃ (TPD deconvolution results using a multiple Gaussian function).

Support	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	CO ($\mu\text{mol g}^{-1}$)	CO ₂ ($\mu\text{mol g}^{-1}$)
MWCNT-orig.	220	211	62
MWCNT-HNO ₃	179	2132	1296
I. Carboxylic strong acidic, 290°C		120	577
II. Carboxylic weak acidic, 430°C		-	440
IV. Lactones, 665°C		-	108
III. Anhydrides, 520°C		163	163
V. Phenols, 610°C		917	-
VI. Carbonyl/Quinones, 780°C		920	-

Untreated MWCNT present a surface area of $220 \text{ m}^2 \text{g}^{-1}$ and a rather inert surface, with a scarce amount of oxygen-containing functionalities released as CO and CO₂. Following nitric acid activation, the MWCNTs surface area decreased *ca.* 20%; at the same time the amount of oxygen groups released as CO increased by a factor of 10 while those released as CO₂ increased over 20 times.

TPD deconvolution for surface group identification is a common technique within the LCM group and details regarding curve fitting can be found elsewhere [26, 27]. Following the described procedures it was possible to identify high amounts of carboxylic acid groups (I and II in Figure 3.4), phenols (V) and carbonyl/quinones (VI), and lower amounts of anhydrides (III) and lactones (IV). No deconvolution was carried out for untreated MWCNT sample due to the very low amounts of CO and CO₂ desorbed. An indication of the MWCNT surface acidity can be provided by the CO/CO₂ ratio, since most acidic groups are released as CO₂, while the weak acidic and basic groups release as CO. A strong increase in acidity was observed as CO/CO₂ lowered from 3.4 to 1.6.

3.3.2 Catalyst characterization

From the textural point of view, metal deposition does not change significantly the surface area of the support, as only small oscillations around $200 \text{ m}^2 \text{g}^{-1}$ were observed.

The oxygenated surface groups, mainly carboxylic acids, act as anchoring sites and bond covalently to the metal precursor [22]. The strength of this connection allows the catalysts containing 1 wt. % metal to be treated at 700°C, thus removing most surface groups, without any indication of sintering by the metal-phase. Besides their high thermal stability, these catalysts also evidenced a narrow metal size distribution for Pt and Ir with particles in the range of 2 and 1 nm, respectively (Table 3.2).

Table 3.2 BET specific surface areas (S_{BET}), metal load (y_{Me}) and particle size (d_{Me}), determined by H_2 chemisorption and TEM analysis for MWCNT supported Pt and Ir catalysts.

Catalyst	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	y_{Me} (wt. %)	d_{Me} (nm)	
			H_2 Chem.	TEM
1Pt/MWCNT	208	1.0	1.2	2.1
1Pt/MWCNT700	205	0.9	2.0	1.9
3Pt/MWCNT	214	3.1	2.4	2.6
3Pt/MWCNT700	226	3.1	4.2	6.2
1Ir/MWCNT	200	0.9	2.0	1.2
1Ir/MWCNT700	224	0.8	2.6	1.6
2Ir/MWCNT	166	1.7	2.0	1.1
2Ir/MWCNT700	176	1.7	2.7	1.5

In catalysts with higher loads, metal particles are more likely to be close to each other and, thus tend to sinterize, forming larger clusters, when thermally heated to high temperatures. This effect was observed for the catalyst containing 3 wt. % of Pt, where particles aggregated to form clusters with *ca.* 6 nm. In the case of Ir catalysts, with a lower metal load than the Pt ones, particles remained practically unchanged after the PRT.

Comparing the metal particle size obtained by H_2 chemisorption with that observed by TEM, some significant differences can be noticed. Pt particle size, in spite of some variation, is in good agreement between both techniques. On the other hand, the particle size for the Ir catalysts determined by H_2 chemisorption is always higher than that observed by TEM. A possible explanation can be attributed to a spill-over phenomenon, where some hydrogen atoms remain attached to the metal whilst others diffuse to the support, leading to an overestimate of the particle size.

Figure 3.5 shows TEM micrographs of MWCNT- HNO_3 supported 2 wt. % Ir catalysts before and after the post-reduction treatment. From these micrographs it is evident that no sintering effect occurred, as the particles look approximately the same size.

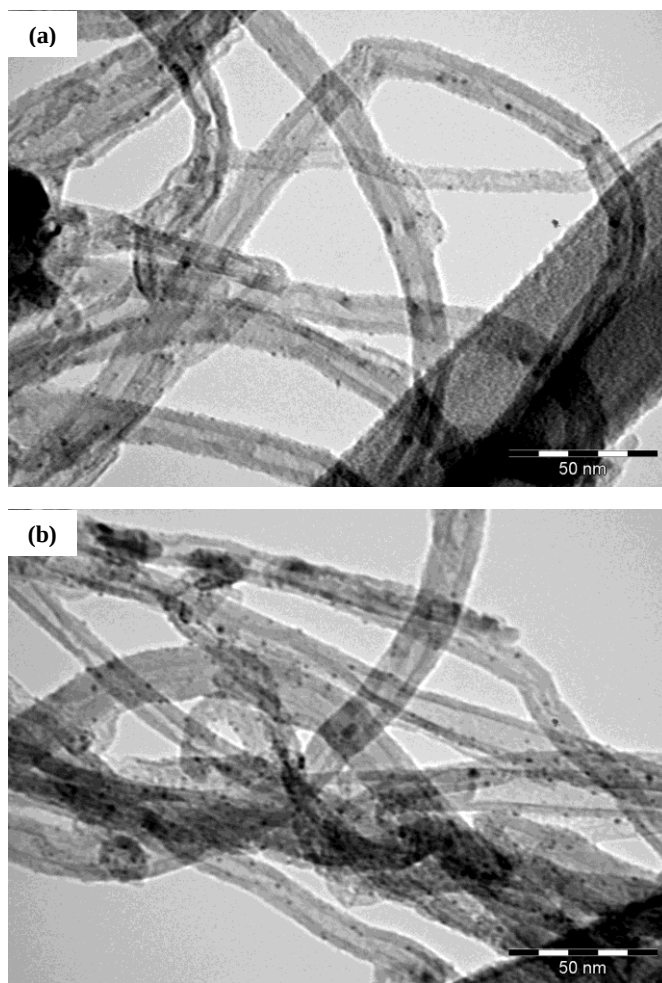


Figure 3.5 TEM micrographs of (a) 2Ir/MWCNT and (b) 2Ir/MWCNT700 catalysts.

The development of surface groups, in spite of very useful for the metal deposition as mentioned above, damages the carbon surface structure by introducing high amounts of defects. These defects are usually analyzed by Raman spectroscopy, following the intensities of D (diamond-like sp^3 , 1330 cm^{-1}) and G (graphite-like sp^2 , 1600 cm^{-1}) bands [28] as seen in Chapter 2, but TGA under oxidative atmosphere (reconstituted air) can also provide some qualitative results. Using the latter technique, MWCNT- HNO_3 revealed only a slight decrease in gasification temperature (600°C) when compared with the original material (630°C). This behavior could be explained by an increased local reactivity in nanotube walls at the defects, leading to a lower oxidation and gasification temperature of the carbon, visible in the TGA weight loss profile. In the original

material, the gasification process is carried out at higher temperatures by a low amount of defects whereas, in the nitric acid treated nanotubes, the high amount of defects introduced in the oxidation step allows the graphite sheets to be consumed at lower temperatures (Figure 3.6). This gasification process is also enhanced by the presence of traces of metal catalyst not totally removed in the purification step (also mentioned in Chapter 2).

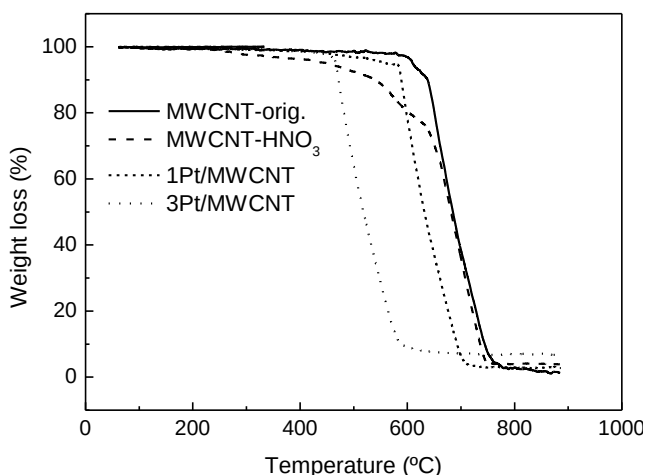


Figure 3.6 Weight-loss as a function of temperature for MWCNT-orig, MWCNT-HNO₃, 1Pt/MWCNT and 3Pt/MWCNT.

The thermal behavior of the MWCNT supported catalysts was also studied and lower gasification temperatures were observed when compared to the naked supports. The difference regarding the original MWCNTs (630°C) is due to the enhanced gasification process catalyzed by Pt and Ir. This enhancement is dependent on the amount of metal present at the support surface and, as the load increases, the temperature needed to burn the carbon matrix is lower (e.g. for Pt: 585°C for 1 wt. % and 465°C for 3 wt. %). These results are in agreement with those published by Stevens and Dahn [29] where the effect of the Pt load over the gasification temperature of a carbon black support was studied. Comparing both Pt and Ir catalysts with 1 wt. % metal content, no significant differences were observed as they exhibited similar behaviors.

3.3.3 Selective hydrogenation of cinnamaldehyde

Among all the reported operating conditions for selective hydrogenation reactions the ones used in this work were amongst the mildest ever reported and thus easier to apply

from an industrial point of view. The use of heptane as solvent deals with the high H_2 solubility, compared to other commonly used solvents [30] and to the fact that it lowers the probability of acetal formation during the reaction [31, 32], reported when using alcohol-based solvents. The used pressure, 10 bar total, was much lower than that reported on other works, where pressures up to 50 bar are normally common. The temperature chosen (90°C) is agreement with most published works.

In Figure 3.7 is depicted the proposed reaction scheme for the liquid-phase selective hydrogenation of cinnamaldehyde. The desired pathway for the preferential hydrogenation of the carbonyl group and thus the production of cinnamyl alcohol (COL) is highlighted. One parallel route involves the reduction of the olefinic $\text{C}=\text{C}$ bond providing hydrocinnamaldehyde (HCAL); both COL and HCAL can be further hydrogenated to produce the fully saturated hydrocinnamyl alcohol (HCOL).

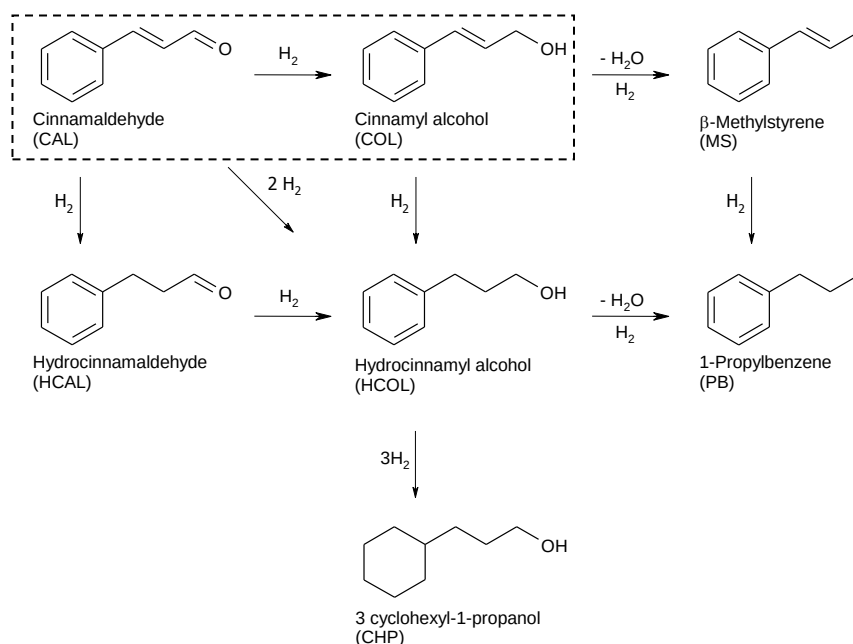


Figure 3.7 Reaction scheme for the selective hydrogenation of cinnamaldehyde using MWCNT supported Pt and Ir catalysts.

A number of side-products involving the loss of the hydroxyl group was detected regardless the type of metal. The presence of β -methylstyrene and 1-propylbenzene could indicate a strong adsorption of the hydroxyl groups over the metal sites and a possible poisoning effect. Catalysts with 3 wt. % Pt allowed the reaction to proceed via hydrogenation of the aromatic ring, to yield 3-cyclohexyl-1-propanol in small amounts.

The catalytic results obtained for Pt and Ir catalysts are reported in Table 3.3. Pt catalysts without PRT were non selective towards COL, whereas after the PRT an increase in activity (TOF) and selectivity to COL was observed. Among the catalysts not subjected to PRT, Ir catalysts evidenced higher selectivities towards COL. The reason can be explained in terms of a higher processing temperature during calcination step (necessary to remove the sulfur from the Ir precursor), allowing for a partial removal of the surface groups. Accordingly, the enhancement observed after PRT was not as pronounced as that observed for Pt catalysts.

Table 3.3 Catalytic results obtained for the hydrogenation of cinnamaldehyde using MWCNT supported Pt and Ir catalysts (selectivities measured at 50% conversion).

Catalyst	TOF (s ⁻¹)	Selectivity (%)			
		COL	HCOL	HCOL	Others
1Pt/MWCNT	0.9	8	51	13	28
1Pt/MWCNT700	1.1	68	10	9	13
3Pt/MWCNT	1.5	20	33	21	26
3Pt/MWCNT700 [†]	6.6	45	18	24	13
1Ir/MWCNT	1.5	57	18	13	12
1Ir/MWCNT700	1.1	54	19	14	13
2Ir/MWCNT	0.8	56	18	10	16
2Ir/MWCNT700	1.4	68	17	11	4

[†]obtained at 74.4% conversion of cinnamaldehyde.

In all cases, with Pt/MWCNT, a clear shift from HCOL to COL selectivity was detected after the PRT. This effect was more pronounced in the case of 1Pt/MWCNT where an increase from 8 to 68%, at 50% CAL conversion, was observed (Table 3.3 and Figure 3.8) without any visible particle agglomeration. The selectivity to COL using the 3 wt. % Pt catalyst evidenced a value lower than what would be expected. This is due to the fact that the selectivity was measured at *ca.* 75% conversion. According to a typical COL selectivity profile, there is a strong initial increase followed by a rapid decay as it is consumed to yield the saturated alcohol. Hence, it would be expected a similar selectivity, at 50% conversion, to that observed with the 1 wt. % catalyst. An interesting observation of the last column in Table 3.3, mainly for Pt/MWCNT catalysts, is that after the activation treatment selectivity towards others (β -methylstyrene and 1-propylbenzene) decreases significantly. This might indicate that the oxygen-containing groups present at the support surface, besides hindering selectivity towards cinnamyl alcohol, may somehow favor the formation of these by-products.

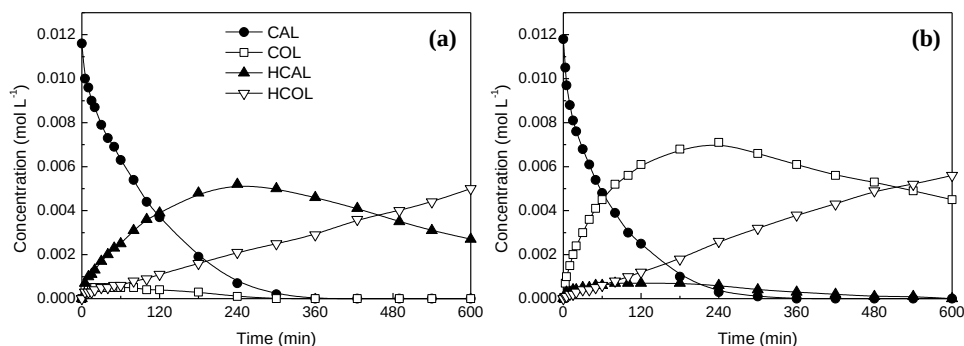


Figure 3.8 Product distribution for the selective hydrogenation of cinnamaldehyde using (a) 1Pt/MWCNT and (b) 1Pt/MWCNT700 catalysts.

Taking into account the characterization and catalytic results, a comparison can be made between the two studied metals. In terms of selectivity to COL it can be observed that both metals provided excellent results with values *ca.* 70%, at 50% conversion. According to Gallezot and Richard there is correspondence between the nature of active metals, their size and selectivity [20]. According to these authors, Ir catalysts are more selective than Pt ones, considering similar particle sizes; for each metal, selectivities were also observed to increase with increasing particle size. In this work, the similar selectivities exhibited by Pt and Ir catalysts can thus be related to the metal particle size. The less selective character of the Pt catalyst is somewhat surpassed by the increased metal particle size, regarding that observed for Ir particles.

Since metal particle size, on 1 wt. % catalysts, remained relatively unchanged by the high temperature thermal treatment, and the textural properties of the materials remained approximately the same, the shift in selectivity can be attributed to the removal of the oxygenated surface groups. Hence, a possible explanation could be related to a metal-support interaction, facilitated by π -electron transfer from the outer graphite sheets in MWCNT and the metal. This charge density displacement towards the metal, similar to that observed when promoters are used, would in turn enhance π^*_{CO} backbonding and favor the preferential adsorption and hydrogenation of the carbonyl group in the CAL molecule. Hence, with these materials, the selectivity towards hydrogenation of the carbonyl bond seems to be more affected by the surface chemistry of the support, rather than the metal particle size.

3.4 Conclusions

Activation with nitric acid created large amounts of oxygen-containing surface groups, namely carboxylic acids, phenols and carbonyl/quinones, without any significant damage to the multi-walled carbon nanotubes surface structure.

Catalysts prepared with Pt and Ir organometallic precursors by wet impregnation presented excellent thermal stability and small metal particles. Higher metal loads increased the sintering effect, after a thermal treatment of the catalysts at 700°C.

The stability of the multi-walled carbon nanotubes under oxidative atmosphere was decreased upon nitric acid activation. This effect was enhanced by the presence of supported metals; the gasification temperature depended on the load, but not on the nature of the metal.

The liquid-phase hydrogenation of cinnamaldehyde was very much influenced by the thermal treatment performed to the catalysts at 700°C. Untreated catalysts evidenced high selectivities towards the production of hydrocinnamaldehyde. After the thermal treatment, supported Pt particles with 2 nm were quite selective towards the production of cinnamyl alcohol; catalysts containing Ir particles with 1 nm were also extremely selective to the same product.

Unlike many results in the literature, it was here proved that high selectivities towards the unsaturated alcohol can also be obtained with very small metal particles.

The preferential reduction of the carbonyl group seemed to be more affected by the surface chemistry of the support rather than by the metal particle size. This could be attributed to a strong interaction between the metal and the graphite sheets, after the surface group removal.

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4. Carbon xerogel supported platinum, iridium and ruthenium metal catalysts

Carbon xerogel, a mesoporous material, is produced by polycondensation of resorcinol and formaldehyde. Oxygenated groups are introduced at the surface in high amounts through a treatment with concentrated nitric acid solution. The carbon xerogel is used as a support for preparing 1 wt. % Pt, Ir and Ru monometallic catalysts using organometallic precursors. The catalysts are tested in the liquid-phase selective hydrogenation of cinnamaldehyde to cinnamyl alcohol. The introduction of surface groups is important to increase metal dispersion but proves to limit selectivity towards the unsaturated alcohol. After a thermal treatment at 700°C, the catalysts show good thermal stability and small metal particles. Regarding the catalytic results measured at 50% conversion, Pt catalysts exhibit the highest selectivity to cinnamyl alcohol, 73 %, followed by Ir with 65 % and finally Ru with only 32 %.

4.1 Introduction

Since the 1990s, resorcinol-formaldehyde organic gels have received considerable attention as carbon precursors due to their unique properties, such as high surface areas and controlled porous structures [1-3]. Since the first report by Pekala *et al.* [4], research has been focused on achieving and controlling the degree of mesoporosity of these carbon materials and on modifying the synthesis procedures. From the reaction engineering point of view, when working in the liquid-phase, the use of mesoporous materials is considered highly desirable in order to avoid possible internal mass-transfer limitations [5].

Three different types of carbon gels can be obtained depending on the solvent drying method [5, 6]: aerogels (supercritical CO₂), xerogels (ambient temperature and pressure conditions) and cryogels (freeze-drying). Depending on the initial pH of the mixture and catalyst proportion, these materials can present very different textures [3, 7-10].

Current applications of carbon xerogels (CXs) involve mainly energy generation by means of fuel cells [1, 11, 12], using metals like Pt and Ru, but also advanced oxidation processes (AOPs) such as wet air oxidation [13, 14], and fine chemical applications [15, 16].

Efficiency and environmental impact are pushing the interest in the use of heterogeneous catalysts for the synthesis of fine chemicals. Indeed, heterogeneous catalytic processes are always easier to handle than the homogeneous ones and lead to lower amounts of waste products, thus lowering environmental risks [17]. Research focused on chemo- and regio-selective catalytic hydrogenation of unsaturated compounds to produce fine chemicals is rapidly growing. In the past few years, considerable efforts have been devoted to the development of catalytic systems able to perform selective hydrogenation of the carbonyl function in α,β -unsaturated aldehydes [18-21]. Formation of the corresponding unsaturated alcohols, in high yields, avoiding the use of toxic reducing agents such as metal hydrides, commonly applied in preparative organic chemistry, is thus highly desirable [17, 21, 22]. It has been found that selectivity towards the allylic alcohol is highly dependent on the nature of the metal used. Metals such as Pt, Os, Ir, Pd, Rh and Ru, among others, have been studied, leading to significant differences in activity and selectivity. Gallezot and Richard [21] reported that unpromoted Ir and Os catalysts are considered to be rather selective for unsaturated alcohol formation, while Pt, Ru and Co are moderately selective and Pd, Rh and Ni are non-selective.

In this chapter, the effect of a high temperature activation treatment over Pt, Ir and Ru monometallic catalysts supported on CX is described. The catalytic performance of the catalysts was evaluated in the liquid-phase selective hydrogenation of cinnamaldehyde.

4.2 Experimental

4.2.1 Support preparation and functionalization

A carbon xerogel was prepared by polycondensation of resorcinol (R) with formaldehyde (F) (1:2), adapting the procedure described elsewhere [10]. Accordingly, 56.6 g of resorcinol [$\text{C}_6\text{H}_4(\text{OH})_2$, Aldrich 99%] were added to 113 mL of deionised water in a glass flask. After complete dissolution, 82 mL of formaldehyde solution (CH_2O , Sigma 37 wt. % in water, stabilized with 15 wt. % methanol) were added. In order to achieve the desired initial pH of the precursor solution (6.0), a concentrated sodium hydroxide solution (5 and 10 M) was added dropwise, under continuous stirring and pH monitoring. The precise control of this parameter was found to be determinant in the development of the mesoporous character of CX materials [10]. The gelation step was allowed to proceed at 85°C, during 3 days, in a paraffin oil bath. After this period, the gel was dark red and the consistency of the material allowed the sample to be shaped as desired (ground to small particles *ca.* 0.1 mm). The gel was further dried in an oven from 60 to 150°C during several days, defining a heating ramp of 20°C per day. After drying, the gel was pyrolyzed at 800°C under a nitrogen flow (100 mL min⁻¹) in a tubular vertical oven (CX-orig).

In order to introduce oxygen-containing functional groups on the surface of the previously prepared CX material, a liquid-phase activation with diluted (*ca.* 7 M) HNO_3 , identical to that described in Chapter 3, section 3.2.1 was used (CX- HNO_3).

4.2.2 Catalyst preparation and characterization

Preparation of Pt and Ir organometallic precursors was identical to that described in Chapter 3, section 3.2.2. $\text{Ru}(\text{COD})(\text{COT})$ (NanoMePS) was used as received, as a precursor for Ru catalysts.

The preparation of the CX- HNO_3 supported catalysts (1 wt. % Pt, Ir or Ru) was identical to that described in Chapter 2, section 2.2.2. The catalysts were calcined in N_2 (4 hr, 400°C), reduced in H_2 (2 hr, 350°C for Pt/CX and Ru/CX, and 500°C for Ir/CX)

and flushed with N₂ at reduction temperature in order to remove physisorbed hydrogen. The difference between reduction temperatures was already explained in Chapter 3, section 3.2.2 and is due to the sulfur removal from the catalyst. A post-reduction treatment (PRT) at 700°C (2 hr, N₂) was used in indicated cases to purge the excess of oxygenated surface groups (Pt/CX700, Ir/CX700 and Ru/CX700).

Textural characterization was based on the analysis of the N₂ adsorption-desorption isotherms, determined at -196°C with a Coulter Omnisorp 100CX apparatus. Specific BET surface areas (S_{BET}) were calculated, as well as the micropore volumes (V_{MIC}) and the non-microporous surface areas (mainly mesoporous, S_{MES}) determined by the t-method, using the standard isotherm for carbon materials proposed by Rodriguez-Reinoso *et al.* [23].

Surface analysis for topographical characterization was carried out by scanning electron microscopy (SEM), using a JEOL JSM-6301F (15 keV) electron microscope. The sample powders were mounted on a double-sided adhesive tape and observed at different magnifications under two different detection modes, secondary and back-scattered electrons.

TGA and H₂ chemisorption measurements for Pt and Ir were carried out in an identical way to that described in Chapter 3, section 3.2.2. In addition, the Ru particle size can be estimated from H₂ chemisorption measurements using equation 4.1.

$$d_{\text{Ru}} = \frac{1.318}{D_{\text{Ru}}} \quad (\text{nm}) \quad (\text{Eq. 4.1})$$

where D_{Ru} is the metal dispersion of Ru (H/Ru).

Details regarding the TPD experiments can be found in Chapter 2, section 2.2.2. The identification and quantification of the oxygen functional groups in the corresponding TPD spectra was carried out using the peak assignment and deconvolution procedures described by Figueiredo *et al.* [24, 25].

4.2.3 Selective hydrogenation procedure

The hydrogenation procedure was identical to that already described in Chapter 2, section 2.2.3.

4.3 Results and discussion

4.3.1 Carbon xerogel activation results

A TPD analysis of the CX after nitric acid activation allowed the identification of the oxygenated groups present at the materials surface. A glance to the obtained spectra (Figure 4.1) provided a comparison with the MWCNTs discussed in Chapter 3, since the activation treatment was identical. The general shape of the curves is very similar, indicating the existence of the same type of groups. Hence, carboxylic acid groups (I and II, in Figure 4.1), anhydrides (III), lactones (IV), phenols (V) and carbonyl/quinones (VI) were also detected on the CX surface [24, 25]. A closer look, however, reveals a much higher concentration of surface groups over the CX-HNO₃. While in MWCNTs the available area for functionalization is somewhat limited to the outer surface of the tube (*ca.* 200 m² g⁻¹), in CXs this limitation is attenuated by the initial high surface areas observed (> 600 m² g⁻¹) and thus, much higher concentrations can be attained. For this reason, the amount of groups released as CO and CO₂ increases *ca.* 2.5 and 4.8 times, respectively, when compared to nanotubes. An indication of the material surface acidity can be provided by the CO/CO₂ ratio, since most acidic groups are released as CO₂, while the less acidic and basic ones release CO. A strong increase in acidity was observed upon nitric acid activation since CO/CO₂ decreased from 1.9 to 0.9, although the concentration of CO increases from 391 to 5468 $\mu\text{mol g}^{-1}$, and that of CO₂ from 205 to 6281 $\mu\text{mol g}^{-1}$.

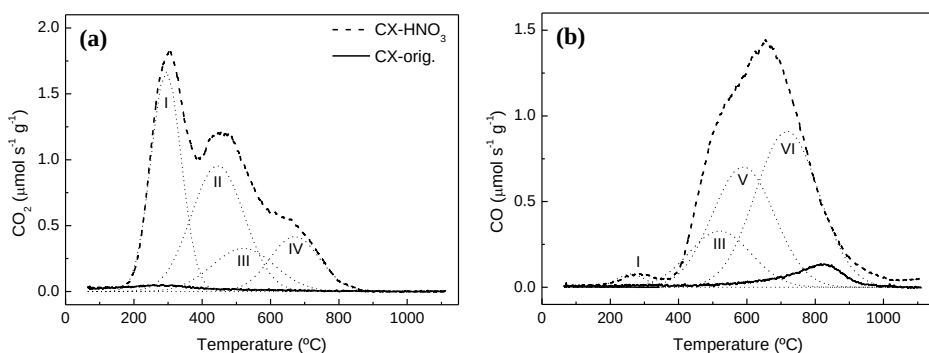


Figure 4.1 TPD spectra for CX-orig and CX-HNO₃ and deconvolution for MWCNT-HNO₃: (a) CO₂ and (b) CO evolution.

The type and amount of surface groups introduced depends on the concentration of the treatment (gas- or liquid phase). Usually, as the strength of the treatment increases, it

is more likely that the structure suffers some form of degradation. To study the effect of the liquid-phase activation over the texture of the material, N_2 adsorption-desorption isotherms at -196°C were performed. Both samples produced type IV adsorption isotherms (Figure 4.2) with H1 hysteresis loops characteristic of mesoporous materials [26]. The amounts of adsorbed nitrogen were, however, very different as a drastic decrease was observed for CX- HNO_3 (Table 4.1). The reason why this material underwent such a strong surface area reduction has to do with the severity of the acid treatment, which caused the porous structure to practically disappear, as shown by the calculated specific surface area. Recently, this limitation was in part solved in the LCM group [27] using a Soxhlet extractor to treat the xerogels. A surface area decrease was observed in a minor extent (4-6 %), but the degree of functionalization was much lower, at the level of the MWCNTs discussed in Chapter 3.

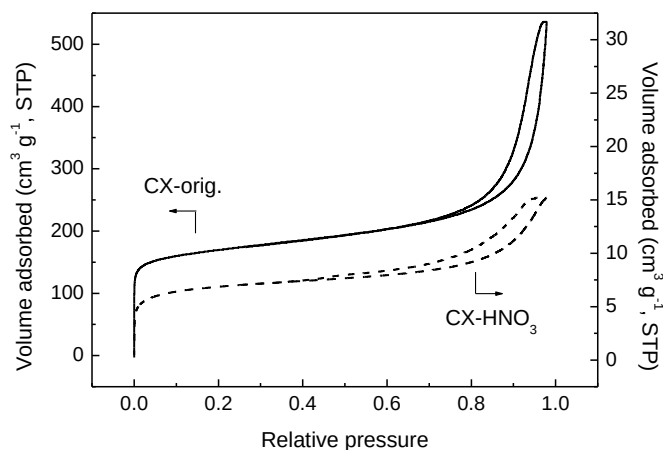
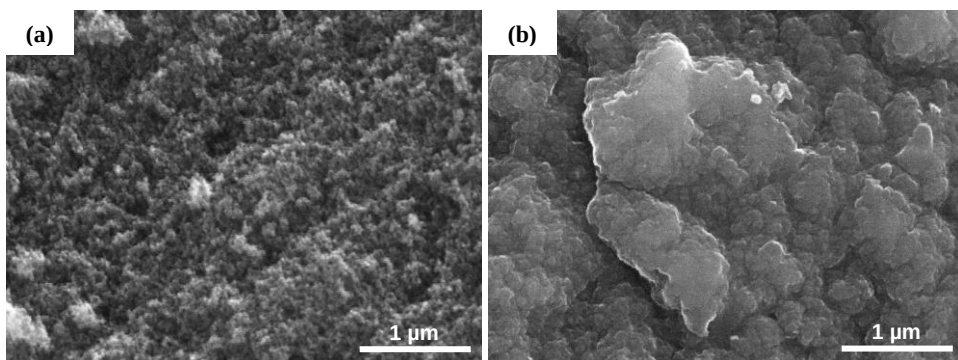


Figure 4.2 Nitrogen adsorption-desorption isotherms at -196°C for the CX samples.

SEM analysis was performed in order to check a possible reason for the observed decrease in the surface area. A typically high porous structure can be observed in Figure 4.3a, whilst a much smoother arrangement of the surface is present in Figure 4.3b, confirming the collapse of the structure. Comparing CXs with other carbon materials, namely single- and multi-walled nanotubes or nanofibers, it was observed that the xerogel structure is not as stable under strong liquid-phase oxidative conditions as the latter. The degree of functionalization is nonetheless much higher for CX, with greater amounts of surface groups produced during the activation treatment. Hence, a compromise regarding the strength of the treatment has to be taken into account in order to preserve the carbon xerogel pore structure.

Table 4.1 Textural properties for carbon xerogels.

Sample	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	S_{MES} ($\text{m}^2 \text{g}^{-1}$)	V_{MIC} ($\text{cm}^3 \text{g}^{-1}$)
CX-orig.	627	180	0.18
CX-HNO ₃	20	6	0.01

Figure 4.3 SEM micrographs of (a) CX-orig and (b) CX-HNO₃.

4.3.2 Metal-phase characterization

The mean metal particle size was determined by H₂ chemisorption measurements and TEM analysis. The results are presented in Table 4.2.

Table 4.2 Metal dispersion (D_{Me}) and mean particle size (d_{Me}) determined by H₂ chemisorption and TEM analysis for CX supported Pt, Ir and Ru catalysts.

Catalyst	D_{Me} (%)	d_{Me} (nm)	$d_{\text{Me}}^{\dagger}$ (nm)
Pt/CX	35	2.9	3.3
Pt/CX700	24	4.2	6.8
Ir/CX	61	1.8	2.2
Ir/CX700	41	2.7	3.2
Ru/CX	94	1.4	1.8
Ru/CX700	53	2.5	2.3

[†]determined by TEM analysis.

The results obtained by TEM for Pt catalysts are quite reliable due to the elevated number of particles measured. The number of Ir and Ru particles present in the micrographs was rather small and thus, the particle sizes presented may not be entirely representative of the catalysts. Pt particles with *ca.* 3 nm, and Ir and Ru particles with

approximately 2 nm were observed. After the PRT at 700°C, an increase in the metal particle size due to a sintering phenomenon was observed. The Pt catalyst displayed the highest increase (noticeable in Figure 4.4) to yield particles with *ca.* 7 nm. The extent of the sintering effect for the other catalysts was somewhat lower. The larger extent of the sintering, when compared to MWCNT supported catalysts, can be explained in terms of reduced surface area, since the nitric acid-treated CX possesses only 20 m² g⁻¹.

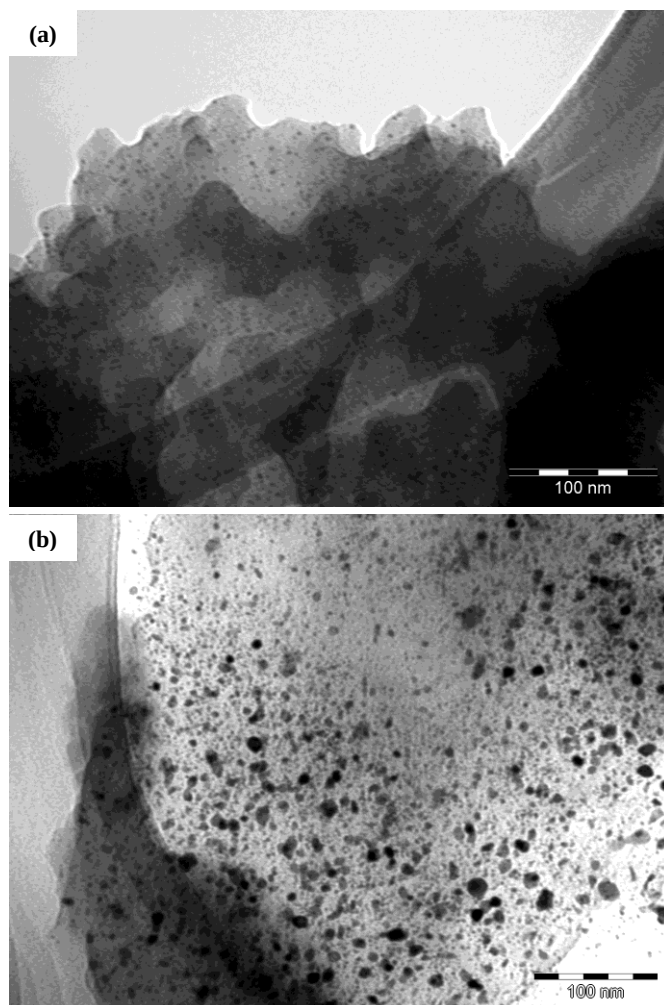


Figure 4.4 TEM micrographs of (a) Pt/CX and (b) Pt/CX700 catalysts.

In spite of the low surface area of the activated CX, a high metal dispersion was initially observed regardless of the metal nature. There are two main factors that can help explaining the obtained dispersion values: low metal load present (perhaps the most

important) and the oxygenated groups at the surface. The importance of the surface groups as anchoring sites was already discussed in the previous chapters for MWCNTs. In this case, the catalysts are not as thermally stable as in the case of MWCNTs, with some sintering, especially in the case of Pt catalysts. Nevertheless, it is still possible to prepare highly dispersed and thermally stable catalysts by treating the surface of the support accordingly.

4.3.3 Selective hydrogenation of cinnamaldehyde

The reaction pathway observed for the selective hydrogenation of cinnamaldehyde (CAL) with CX supported catalysts is shown in Figure 4.5. The hydrogenation of CAL involves the parallel and consecutive reduction of different functional groups i.e., C=C and C=O bonds. Typically, a mixture of the desired unsaturated alcohol (COL), the undesired saturated aldehyde (HCAL) and the saturated alcohol (HCOL) is obtained.

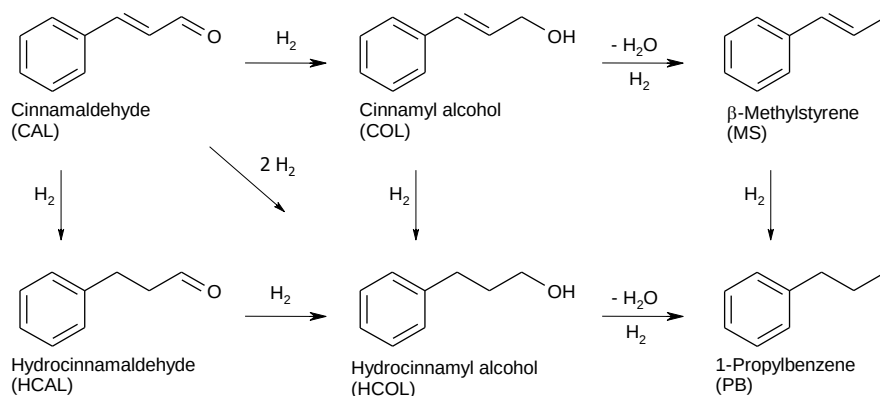


Figure 4.5 Reaction scheme for the selective hydrogenation of cinnamaldehyde using CX supported Pt, Ir and Ru catalysts.

Similarly to what was observed in Chapter 3, a number of side-products that involved the loss of the hydroxyl group were also detected when using the CX supported catalysts in the reaction. The catalytic results are gathered in Table 4.3.

Initially, all catalysts, with the exception of Ir, evidenced a preference towards the selective hydrogenation of the C=C bond. The reason for the high selectivity of the Ir catalyst towards COL is described in Chapter 3, and has to do with the high processing temperature (500°C) used during the calcination step.

Table 4.3 Catalytic results obtained for the hydrogenation of cinnamaldehyde using CX supported Pt, Ir and Ru catalysts (selectivities measured at 50% conversion).

Catalyst	TOF (s ⁻¹)	Selectivity (%)		
		COL	HCAL	HCOL
Pt/CX	1.4	20	39	18
Pt/CX700	3.8	73	7	6
Ir/CX	2.1	57	20	9
Ir/CX700	2.4	65	20	8
Ru/CX	0.7	5	65	8
Ru/CX700	0.9	32	42	14

To confirm the positive effects of a high temperature post-reduction treatment, observed in Chapters 2 and 3, an identical procedure was attempted for CX supported catalysts. The results confirmed the beneficial effect over both activity (TOF) and selectivity after a PRT at 700°C. In all cases, a significant improvement could be observed in the production of COL. The most outstanding result was obtained when using Pt, where a shift in HCAL to COL selectivity was noticed (Figure 4.6). Ru catalysts were very active, but also very selective towards the normally undesired HCAL (selectivity of 65 % at 50 % conversion). The influence of the Ru particle size supported on activated carbon was studied by Galvagno *et al.* [28] with this same reaction. They observed that selectivity to cinnamyl alcohol increased with Ru particle size to values as high as 61%, when particles *ca.* 17 nm were used. In this case, the increase in selectivity from 5 to 32% could also be attributed to the increase in particle size, although not to the extent evidenced in the work of Galvagno *et al.*, due to much smaller Ru particles.

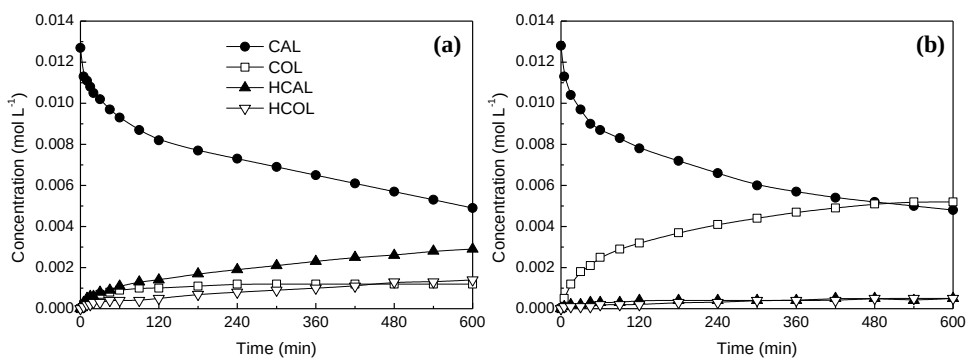


Figure 4.6 Product distribution for the selective hydrogenation of cinnamaldehyde using (a) Pt/CX and (b) Pt/CX700 catalysts.

The results obtained with CX supported catalysts are in perfect agreement with those obtained using MWCNTs for Pt and Ir metals, and reveal that in the studied conditions the hydrogenation of cinnamaldehyde does not depend much on the structure of the support. Nevertheless, CX supported catalysts showed slightly higher selectivity values with similar activities. This increase is thought to be related to the somewhat larger metal particles present over the CX surface.

For MWCNT supported catalysts, the enhanced selectivity observed with Pt, compared to Ir, was attributed to the larger Pt particles. In CX supported catalysts the difference in selectivities between Pt and Ir catalysts is more evident and the same explanation is also valid.

4.4 Conclusions

Activation with nitric acid created large amounts of surface groups. The development of oxygenated functionalities in the CX surface compromised the initial porous structure to yield a practically non-porous material, with a low surface area.

The amount of surface groups introduced in the CX surface was much higher than that obtained for MWCNTs.

Catalysts prepared from Pt, Ir and Ru organometallic precursors by wet impregnation presented small metal particles over the activated CX: 3 nm for Pt and around 2 nm for Ir and Ru.

A post-reduction thermal treatment of the catalysts at 700°C led to various degrees of sintering, mainly dependant on the nature of the active metal-phase.

The same thermal treatment also influenced the catalyst performance in the liquid-phase hydrogenation of cinnamaldehyde, pushing the selectivity towards cinnamyl alcohol, regardless of the metal nature.

Pt catalysts were found to be more selective towards the preferential hydrogenation of the carbonyl group, followed by Ir and finally Ru ones.

The hydrogenation of cinnamaldehyde, under the studied conditions, did not depend on the structure of the support, since both MWCNT and CX presented a similar catalytic behavior.

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5. Carbon aerogel supported platinum catalysts

Taking into consideration the results obtained with Pt in Chapter 4, this metal is selected to evaluate the properties of aerogels as catalytic support. The present Chapter describes the preparation and characterization of 1 wt. % Pt catalysts supported in carbon aerogels for the application in the liquid-phase selective hydrogenation of cinnamaldehyde. Carbon aerogels with different textures are activated with hydrogen peroxide and ammonium peroxydisulfate leading to large amounts of surface groups but keeping unchanged their textural properties. After Pt deposition, the surface chemistry and morphology of the catalysts is characterized by analytical techniques like scanning and transmission electron microscopy, temperature-programmed desorption, N₂ adsorption isotherms, mercury porosimetry and H₂ chemisorption. Catalysts prepared with activated aerogels exhibit good selectivity towards the desired product, the cinnamyl alcohol.

5.1 Introduction

The synthesis of carbon aerogels was first reported by Pekala [1]. Depending on the solvent removal step, carbon gels are referred to as: (i) aerogels, if supercritical CO₂ is used; (ii) xerogels, when the removal takes place under ambient temperature and pressure conditions and (iii) cryogels, if a freeze-drying method is used. Carbon aerogels usually have surface areas between 400-1000 m² g⁻¹ and are promising for applications such as adsorbents, catalysts or capacitors [2-6]. Their potential is based on their unique properties: purity, homogeneity and above all, controllable porosity. Different precursors and methods have been developed over the years to produce highly porous carbon aerogels. The sol-gel polymerization of resorcinol and formaldehyde [7] is still the most common, but the use of other precursors like phenol-formaldehyde [8] phenol-furfural [9, 10] or resorcinol-furfural [11] have also been successfully tested. The porous texture of carbon aerogels, and consequently their applications, strongly depends on several experimental conditions. The most important is the polymerization step, since it defines the structure and consequently the porous texture of the organic aerogels.

Because the support plays an important role in catalyst design, in order to optimize the dichotomy between metal and support, the use of a material whose properties can be finely tuned is highly desirable. Polymer-based [4, 12] and other carbon materials like nanofibers, nanotubes or fullerenes [13] are important classes of materials to produce noble metal supported catalysts. This type of catalyst is extremely useful in heterogeneously catalyzed selective hydrogenation of unsaturated aldehydes to the corresponding unsaturated alcohols. This is a key process for the production of important intermediates in the preparation of fine chemicals for fragrance, pharmaceutical and agrochemical industries. Unfortunately, as discussed in previous chapters, there are some thermodynamic and kinetic constrictions that limit the selectivity towards the unsaturated alcohol formation. In spite of these drawbacks, the selectivity to unsaturated aldehydes using heterogeneous catalysts can be improved by careful design of the catalysts, control of the type and surface chemistry of the support, the nature of the active metal, by addition of a promoter, among others.

In this chapter, several carbon aerogel supported Pt catalysts were prepared, using materials with different textures and surface chemistries, seeking to establish appropriate structure/activity relationships, which are useful for smart catalyst design.

5.2 Experimental

Carbon aerogels supports and supported Pt catalysts were supplied, prepared and characterized by S. Morales-Torres *et al.*, from the Carbon Materials Research Group of University of Granada (Spain).

5.2.1 Support preparation and functionalization

Organic aerogels were synthesized by polymerization of resorcinol (R) with formaldehyde (F) in aqueous solution (W) according to the methodology developed originally by Pekala *et al.* [14] using alkali carbonates (M_2CO_3 ; $M = Li$ or Cs) as polymerization catalysts (C). The molar ratios used were $R/F = 0.5$, $R/C = 300$ and $R/W = 0.07$. The initial solution pH was set to 5.5. After curing, the samples were washed with acetone for 2 days and dried under supercritical CO_2 . Carbon aerogels were prepared from these organic precursors by carbonization in a 100 mL min^{-1} N_2 flow at 900°C . Carbon aerogel samples will be here referred as Li900 and Cs900 indicating the metal alkali and the carbonization temperature used in their synthesis.

Samples of Li900 were further oxidized (1 g carbon/10 mL of solution) with concentrated hydrogen peroxide (H_2O_2 , 9.8 M) and with a saturated solution of ammonium peroxydisulfate $[(NH_4)_2S_2O_8]$ in sulfuric acid (H_2SO_4 , 1 M) for 48 hr at ambient temperature [15]. After oxidation, the samples were washed with distilled water and dried at 120°C in an oven during 24 hr. The samples oxidized with H_2O_2 and $(NH_4)_2S_2O_8$ will be referred as Li900H and Li900S, respectively.

5.2.2 Catalyst preparation and characterization

The materials described in the previous section were used as supports to prepare 1 wt. % Pt catalysts. Incipient wetness impregnation was used to deposit the Pt precursor, $Pt(NH_3)_4(NO_3)_2$, over the different aerogels. Prior to reaction, the resulting catalysts (Li900Pt, Li900HPt, Li900SPt and Cs900Pt) were treated in N_2 during 4 hr and reduced in H_2 for 2 hr. A post-reduction treatment (2 hr, N_2) was performed at 700°C to remove part of the surface groups (Li900Pt700, Li900HPt700, Li900SPt700 and Cs900Pt700).

The surface morphology of the aerogels was studied by scanning electron microscopy (SEM) with a LEO, model Gemini-1530, equipped with energy-dispersive X-ray spectroscopy (EDX) microanalysis apparatus.

Textural characterization was carried out using mercury porosimetry (Quantachrome Autoscan 60) and N₂ adsorption at -196°C (Quantachrome autosorb-1). Mercury porosimetry allowed the determination of pore volume (V_{MES} : 3.5 nm < dpore < 50 nm and V_{MAC} : dpore > 50 nm) and the external surface area (S_{EXT} : dpore > 3.7 nm). The BET equation [16] and Dubinin-Raduskevich and Stoeckli *et al.* [17] relations were used for analysis of N₂ adsorption isotherms.

The surface chemistry of the carbon aerogels was characterized by temperature programmed-desorption (TPD). These experiments were carried out by heating the samples up to 1000°C, in He flow (60 cm³ min⁻¹) at a heating rate of 50°C min⁻¹. The amount of evolved gases was recorded as a function of temperature using a quadrupole mass spectrometer (Balzers, model Thermocube), as described elsewhere [18]. The oxygen content was calculated from the amounts of CO and CO₂ released during the TPD experiments.

Pt dispersion (D_{Pt}) and average particle size (d_{Pt}) were obtained by H₂ chemisorption measurements performed at 40°C. Assuming the formation of spherical particles and a H:Pt = 1:1 stoichiometry, it was possible to determine the Pt particle size (Eq. 3.1). H₂ chemisorption isotherms were measured in conventional volumetric equipment made of Pyrex glass, free from mercury and grease, which reached a dynamic vacuum better than 10⁻⁶ mbar at the sample location. Equilibrium pressure was measured with a Baratron transducer from MKS.

5.2.3 Selective hydrogenation procedure

The hydrogenation procedure was identical to that already described in Chapter 2, section 2.2.3.

5.3 Results and discussion

5.3.1 Carbon aerogel characterization

5.3.1.1 Effect of the polymerization catalyst

According to IUPAC [19], the limits to define the pore dimensions are: micropores ($d < 2$ nm), mesopores ($d = 2$ -50 nm) and macropores ($d > 50$ nm). Within this classification, two types of materials with different textures were produced: one with small mesopores, carrying an average pore diameter of 12 nm, and another with very

large mesopores, almost in the macropore range, with 48 nm. The difference between the above described materials reflects the selection of the polymerization catalyst used in the synthesis step. Obviously this choice had a great influence on the porous texture of the aerogel. Smaller cations like Li were found to produce materials with significant mesoporous volume, whereas larger Cs cations led to materials with larger agglomerates (Figure 5.1). The higher BET surface area of the Li900 materials (with an increase of *ca.* 150 m² g⁻¹), relatively to the macroporous material, is explained in terms of smaller particle size. The textural properties of the carbon aerogels obtained by nitrogen adsorption and mercury porosimetry are gathered in Table 5.1.

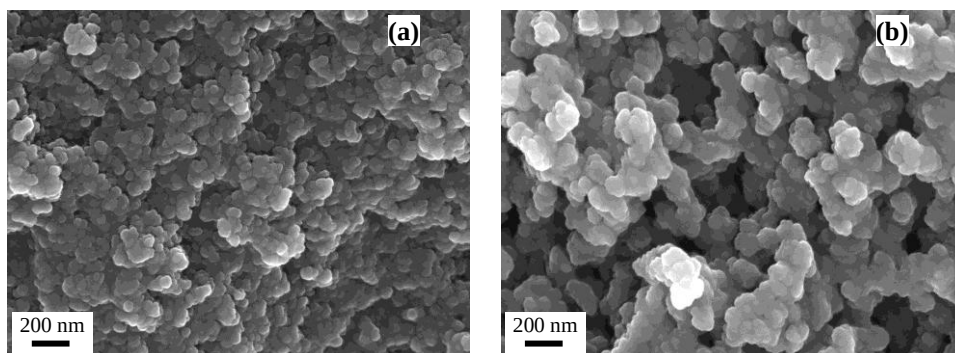


Figure 5.1 SEM micrographs of (a) Li900 and (b) Cs900 aerogels.

Table 5.1 Textural properties for carbon aerogels.

Support	S_{BET} (m ² g ⁻¹)	$V_{\text{MIC}}^{\dagger}$ (cm ³ g ⁻¹)	$L_0^{\dagger}$ (nm)	S_{EXT}^* (m ² g ⁻¹)	V_{MES}^* (cm ³ g ⁻¹)	V_{MAC}^* (cm ³ g ⁻¹)
Li900	902	0.37	1.0	191	1.06	0.00
Li900H	863	0.35	1.1	-	-	-
Li900S	861	0.35	1.1	-	-	-
Cs900	758	0.30	0.7	59	0.07	1.20

[†]Dubinin-Radushkevich and Stoecki equations applied to N₂ adsorption data.

*determined by mercury porosimetry.

5.3.1.2 Effect of the activation treatment

The surface chemistry of carbon materials is basically determined by the acidic and basic character of their surface and can be changed by treating the surface with oxidizing agents either in the gas- or liquid-phase [15, 20, 21]. There is a general agreement in the type of surface groups that contribute to the acidic character of a carbon material (i.e., carboxylic acids, lactones, phenols and lactol groups) [22]. Regarding basic groups some reservations arise on the strength and extent of their contribution to the overall carbon

basicity, yet several models have been suggested: chromene structures, quinone and pyrone-like groups [22].

The aerogel surface oxidation treatments with H_2O_2 and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ were followed by TPD, and resulted in the formation of different oxygen-containing surface groups. Carboxylic acids, ketones, quinones (conjugated ketones), ethers, lactones, anhydrides and phenol groups were introduced with both treatments, although higher amounts of more acidic groups were obtained with the $(\text{NH}_4)_2\text{S}_2\text{O}_8$ treatment. Similar results were reported with identical oxidation procedures using an activated carbon [15, 20], and the enhanced acidity using $(\text{NH}_4)_2\text{S}_2\text{O}_8$ is attributed to carboxyl groups close to other groups, such as carbonyl and hydroxyl.

The introduction of these groups was achieved without any significant changes to the initial textural properties of the aerogels (a decrease of only *ca.* 4% was observed in the S_{BET} values, Table 5.1). On the other hand, the surface acidity of the material was seriously affected by the oxidation procedure. The acidic character of the samples, determined by pH_{PZC} measurements, was found to vary in the following order: Li900S (3) > Li900H (5) > Li900 $\approx$ Cs900 (10). In addition, the amount of O_2 present at the surface was found to increase with decreasing pH_{PZC} , i.e.: Li900S (10 wt. %) > Li900H (3 wt. %) > Li900 $\approx$ Cs900 (1 wt. %).

5.3.2 Metal-phase characterization

Platinum dispersions and particle sizes of the carbon aerogel supported catalysts are given in Table 5.2. Excellent Pt dispersions over the untreated aerogels (Li900Pt and Cs900Pt) were observed, but somewhat lower values were detected when using the oxidized supports (Li900HPt and Li900SPt).

There are two main factors that can affect the metal dispersion over a support: (i) the available surface area and (ii) the interaction between the surface and the precursor solution. The textural properties of the supports were not significantly changed by the oxidation treatments, as already showed, but the presence of oxygenated surface groups increased the hydrophilic character of the surface. Taking into consideration that the surface is negatively charged ($\text{pH}_{\text{PZC}} < 10.5$, pH of precursor solution) and the cationic nature of the precursor ($[\text{Pt}(\text{NH}_3)_4]^{+2}$), an improved metal dispersion was expected when using the oxidized supports, in comparison with the catalysts prepared using the untreated supports. However this is not the case. The explanation relies on the surface containing oxygen groups, which act as anchoring sites, retaining the Pt-precursor molecules at the entrance of the pores and preventing the Pt diffusion through the porous

structure. On the other hand, during the reduction treatment, the less stable oxygen surface complexes may be removed, promoting the mobility of the Pt particles, thus favoring their agglomeration [23].

Table 5.2 Pt dispersion (D_{Pt}) and mean particle size (d_{Pt}) determined by H_2 chemisorption and TEM analysis for CA supported Pt catalysts.

Catalyst	D_{Pt} (%)	d_{Pt} (nm)	$d_{Pt}^{\dagger}$ (nm)
Li900Pt	74.1	1.5	1.4
Li900Pt700	31.3	3.4	2.8
Li900HPt	46.1	2.3	2.5
Li900HPt700	30.5	3.5	2.6
Li900SPt	44.4	2.4	2.1
Li900SPt700	28.7	3.8	2.2
Cs900Pt	87.3	1.2	1.5
Cs900Pt700	40.3	2.7	2.4

[†]determined by TEM analysis.

When a post-reduction treatment is carried out in N_2 at 700°C, the experimental conditions are severe enough to induce some sintering of the Pt particles. This effect was particularly more intense in the catalysts with higher dispersion. After the thermal treatment, all materials (independently of their surface chemistry) show Pt particles with sizes around 2.2-2.8 nm, as determined by TEM. A possible explanation could be related to the surface chemistry of the materials, as the Pt particles supported in untreated aerogels increased *ca.* 2 times while, for the activated supports no sintering effect was observed (Figure 5.2). As seen in the previous chapters, some surface groups can act as anchoring sites and increase the thermal stability of the catalysts. Activated carbon aerogels could, thus, present a similar behavior.

Comparing the Pt particle size obtained by H_2 chemisorption and TEM it can be seen that there is a general agreement between these two techniques. The only significant discrepancies were observed for activated aerogel supported catalysts after a thermal treatment. This could be due to either a spill-over phenomenon or a change in the H:Pt stoichiometry. The latter is more likely because, in the presence of oxygen (in this case in the form of surface groups), the amount of chemisorbed H_2 increases and thus, tends to overestimate the real particle size.

Besides a sintering effect, the treatment at 700°C is able to purge most of the CO_2 -releasing groups, but only a part of the oxygenated surface groups desorbing as CO are removed. Hence, groups like ethers, ketones or quinones, which are only released at

higher temperatures due to their stability [24], should remain to some extent on the surface.

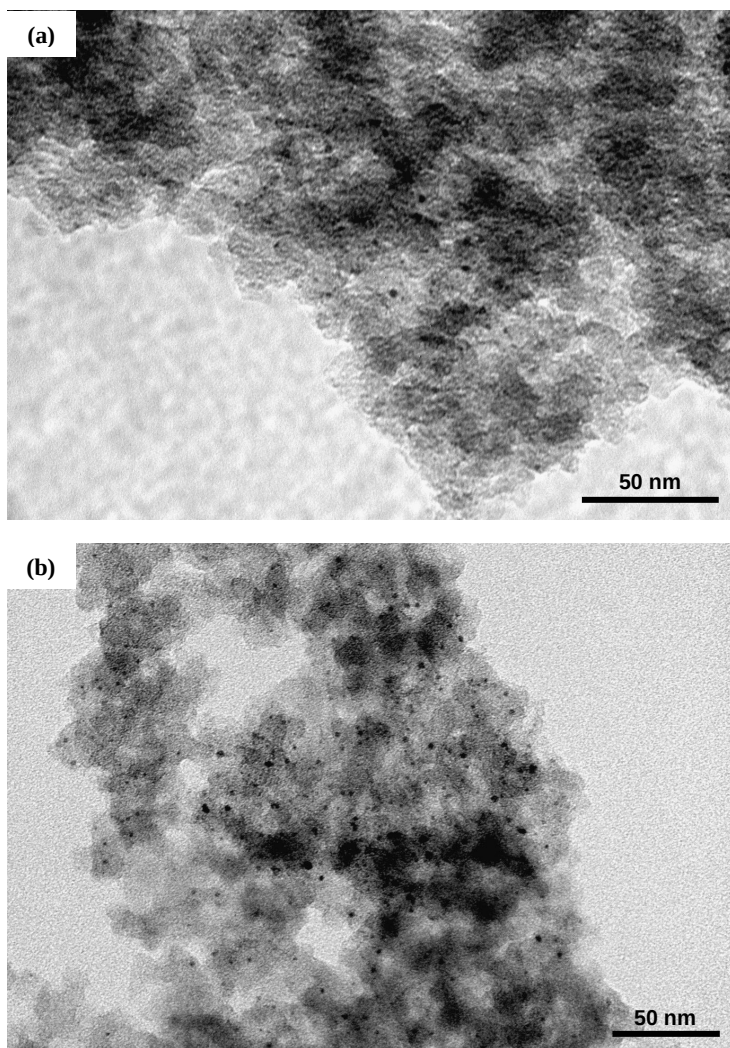


Figure 5.2 HRTEM micrographs of (a) Li900HPt and (b) Li900HPt700 catalysts.

5.3.3 Selective hydrogenation of cinnamaldehyde

All of the observed pathways for the selective hydrogenation of cinnamaldehyde in heptane are shown in Figure 5.3. The thermodynamically preferred path goes through the hydrogenation of the C=C bond yielding the saturated aldehyde (hydrocinnamaldehyde, HCAL). Selective hydrogenation of the C=O bond gives the unsaturated alcohol

(cinnamyl alcohol, COL). Both COL and HCAL can be further hydrogenated to produce the fully saturated alcohol (hydrocinnamyl alcohol, HCOL). In some experiments, a number of side-products involving the loss of the hydroxyl group, β -methylstyrene (MS) and 1-propylbenzene (PB), were also detected in different amounts, indicating a strong adsorption over the metal sites and a possible poisoning effect.

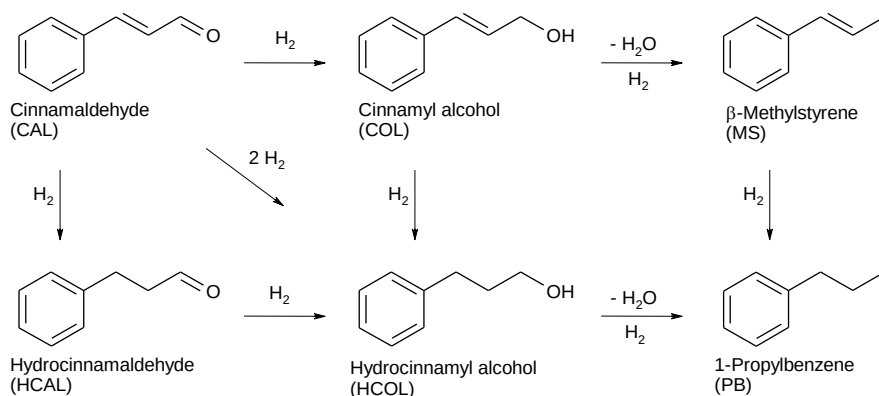


Figure 5.3 Reaction scheme for the selective hydrogenation of cinnamaldehyde using CA supported Pt catalysts.

The reaction results obtained at 90°C and 10 bar (total pressure) are gathered in Table 5.3. In this table it is indicated the TOF based on the conversion of cinnamaldehyde and the selectivities towards cinnamyl alcohol, hydrocinnamaldehyde and hydrocinnamyl alcohol, at 50% conversion of cinnamaldehyde.

Table 5.3 Catalytic results obtained for the hydrogenation of cinnamaldehyde using CA supported Pt catalysts (selectivities measured at 50% conversion).

Catalyst	TOF (s ⁻¹)	Selectivity (%)		
		COL	HCAL	HCOL
Li900Pt	1.6	11	54	20
Li900Pt700	3.4	12	54	25
Li900HPt	1.6	53	18	20
Li900HPt700	3.5	21	41	28
Li900SPt	2.3	36	23	25
Li900SPt700	4.4	21	44	27
Cs900Pt	0.9	24	34	35
Cs900Pt700	2.8	12	54	19

Taking into account the average pore size diameter in both aerogels (12 and 48 nm) and the cinnamaldehyde molecule size (< 1 nm), the absence of internal mass transfer limitations during the reaction could be expected. This assumption was confirmed by the higher activity (TOF) exhibited by Li900Pt regarding the macroporous Cs900Pt catalyst.

Oxidation of the carbon materials had a marked effect over the selectivity towards cinnamyl alcohol (Figure 5.4). Selectivity increased by a factor of 4.8 for Li900HPt (53% at 50% conversion of cinnamaldehyde) and 3.3 for Li900SPt (36%), compared with the catalyst prepared using the untreated support (11%). This result is in agreement with the work published by Coloma *et al.* [25] on the gas-phase hydrogenation of crotonaldehyde over carbon black supported Pt catalysts. They reported that the selectivity towards the desired unsaturated alcohol increased when the support had been previously oxidized with hydrogen peroxide. This behavior, which was not related to the metal particle size, was said to be associated to the decomposition of the oxygen surface groups upon the thermal treatments in hydrogen.

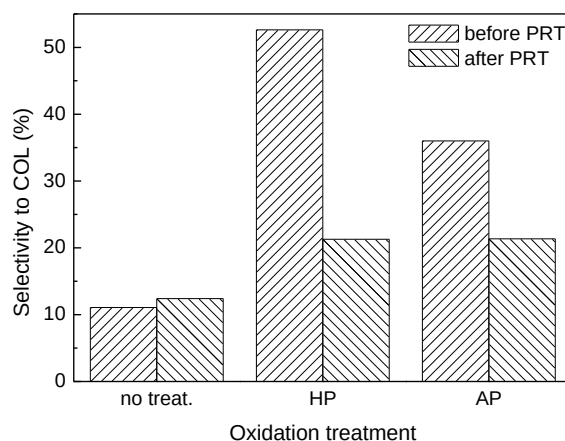


Figure 5.4 Effect of the oxidation treatment of Li900 and of the post-reduction treatment on the selectivity towards cinnamyl alcohol.

In chapters 2, 3 and 4, a high temperature treatment at 700°C in N₂ (PRT) was used to enhance both the activity and the selectivity of the catalysts. In the present work, the same thermal treatment was found to increase the TOF for all tested materials by a factor up to 3, but shifted selectivity to the C=C bond. Selectivity towards the hydrogenation of the carbonyl function appears to be enhanced by the presence of oxygenated groups on the material surface. Similarly to the supports previously described, the initial materials also had a strong acidic surface after which a decrease in acidity due to PRT was observed. In this case, and due to the type of treatment performed, the amount of

remaining surface groups is higher. Moreover, the groups present are thought to have a more basic character. Hence, for carbon aerogels, a more acidic surface favors the interaction with the carbonyl group whilst a more basic surface favors the reduction of the olefinic bond.

Another interpretation could be associated with the polarity of the surface. Toebes *et al.* [26, 27] related an increased activity and selectivity towards the olefinic bond, in the non-polar surface of Pt/CNF catalysts, upon surface group removal. They suggested that the hydrogenation of the C=C bond was assisted by adsorption of the cinnamaldehyde aromatic ring on the non-polar CNF support surface, thus increasing the selectivity towards hydrocinnamaldehyde.

5.4 Conclusions

Macro or mesoporous carbon aerogels were obtained depending on the type of polymerization catalyst used.

Oxidation treatment with H_2O_2 and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ allowed the porous structure to remain relatively unchanged while introducing significant amounts of oxygenated groups. The acidic character of most groups led to a strong decrease of the pH_{PZC} of the support surface.

The Pt dispersion over the aerogels was strongly influenced by the chemical modifications, decreasing in all cases after oxidation treatments.

The increased acidity of the oxidized supports led to a higher selectivity towards cinnamyl alcohol. A thermal treatment of the catalysts at 700°C favored the hydrogenation of the C=C bond.

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PART III:

SELECTIVE HYDROGENATION

WITH METAL OXIDES

Since it was first reported by Tauster in 1978, the strong metal support interaction effect is an important attribute in reducible semi-conducting metal oxides that helps to achieve high selectivities towards unsaturated alcohols in the hydrogenation of α,β -unsaturated aldehydes. Different approaches are followed to synthesize different types of reducible metal oxides. Therefore, TiO_2 is prepared according to a sol-gel method, while CeO_2 -based materials are synthesized using a solvothermal approach and ZnO is produced according to a chemical vapor deposition process. Several commercially available samples are also tested for comparison purposes. Photochemical deposition is used to prepare well dispersed platinum catalysts. The catalytic performance of the prepared materials is assessed using cinnamaldehyde hydrogenation as model reaction for α,β -unsaturated aldehydes. All metal oxide supported catalysts evidence good carbonyl bond activation, and thus high selectivities to cinnamyl alcohol are typically observed. The behavior of the catalysts is explained in terms of the high support reducibility and advantageous metal-support interactions.

6. Nanostructured TiO₂ supported platinum catalysts by photochemical deposition

Titanium dioxide, with 100% anatase, is prepared through a sol-gel route and compared with other commercially available samples. These materials are used as supports to prepare 5 wt. % Pt catalysts, using photochemical deposition as preparation method. The catalysts are thermally treated in N₂ and H₂ at high temperatures (500°C) and tested in the liquid-phase hydrogenation of cinnamaldehyde, at 90°C and 10 bar of total pressure. Characterization techniques, such as N₂ adsorption-desorption isotherms at -196°C, X-ray diffraction, H₂ chemisorption and transmission electron microscopy, are used to assess possible relations between catalyst design and its performance. The sol-gel based TiO₂ catalyst is extremely efficient in the selective reduction of the carbonyl group, when compared with other commercial samples. The results might be explained by a stronger metal-support interaction effect over the synthesized material.

6.1 Introduction

Nowadays there is an enormous research interest in the field of nanosized semiconductors, due to their unusual catalytic, electronic and optical properties. Among these materials, nanocrystalline titanium dioxide is one of the most versatile, due to its excellent properties. As a result, TiO_2 has found applications in areas that can range from environmental remediation to solar energy [1-6].

TiO_2 exists in three main crystallographic forms: anatase, rutile and brookite. Rutile (Figure 6.1b) is the stable form, whereas anatase (Figure 6.1a) and brookite (Figure 6.1c) are metastable and are readily transformed to rutile upon heating. The synthesis of TiO_2 is commonly achieved using either a sol-gel [7, 8] or a solvothermal approach [9]. Within the sol-gel route, the hydrolysis of titanium chlorides [10] or alkoxides [8] is still the most commonly used technique. During this process, the sol (liquid suspension of solid particles smaller than $1\ \mu\text{m}$) is obtained by the hydrolysis and partial condensation of the metal alkoxide. Further condensation of sol particles into a three-dimensional network results in the formation of the gel. The phases normally formed in the sol-gel synthesis of TiO_2 are anatase and rutile (and also some amorphous titanate), depending on the temperature.

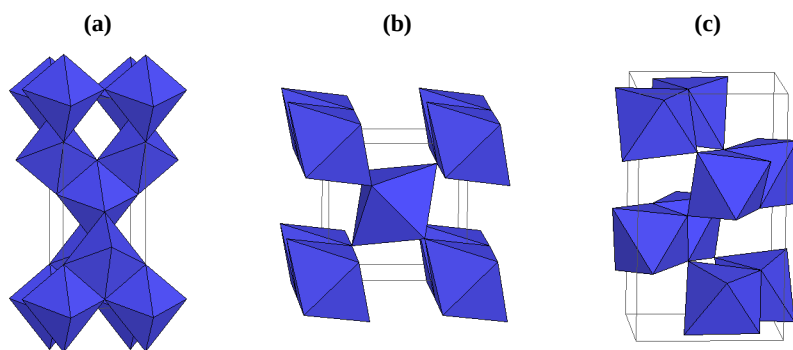


Figure 6.1 TiO_2 allotropic forms: (a) anatase, (b) rutile and (c) brookite [3].

When metals are supported on an oxide material, there is an intimate metal-oxide interaction that can have a significant impact on the properties of the metal component. In such a nanosized structure, the oxide is not merely a support. Group VIII metals (Ru, Rh, Pd, Os, Ir, Pt) dispersed over reducible supports (TiO_2 , ZrO_2 , CeO_2 , V_2O_5 , Nb_2O_5) exhibit a strong metal support interaction (SMSI), making them extremely attractive for several applications such as selective hydrogenation of unsaturated aldehydes. Platinum

supported on TiO_2 has been an intensively studied classic catalytic system for this reaction. It is widely reported in the literature [11-13] that, after high temperature treatment under hydrogen, the metal surface of these catalytic materials becomes covered with sub-stoichiometric (TiO_x) species originated from the support. These sites interact with the oxygen atom in the carbonyl group, by activating and weakening the $\text{C}=\text{O}$ bond, enabling its preferential hydrogenation. The SMSI phenomenon was first introduced by Tauster [14] in 1978. It is characterized by an almost complete suppression of the metal capacity to chemisorb both H_2 and CO due to physical blockage of sub-oxide species. The use of these systems combines both the improved catalytic activity and elevated carbonyl bond activation and enhances unsaturated alcohol selectivity, in comparison with other catalysts where no SMSI effect is detected [15, 16].

Many studies have been dealing with the selective hydrogenation of α,β -unsaturated aldehydes, using mainly acrolein [17, 18], crotonaldehyde [15, 19, 20], cinnamaldehyde [21-23] and citral [24-26]. The development and characterization of catalysts for, these reactions, with special emphasis on cinnamaldehyde, has been reviewed by Gallezot and Richard [27]. Selectivity towards unsaturated alcohols, the desired products, is hindered due to thermodynamic and kinetic constraints. There are many factors that can affect the catalyst activity and selectivity. Hence, choosing the proper solvent [28], support [16, 29], active metal [30], metal promoter [31], reduction temperature [32], or catalyst preparation and activation methods, is essential to obtain high unsaturated alcohol yields. These and other important aspects of selective carbonyl reduction are reported in several review articles [27, 33, 34].

The technique used to deposit the metal over the support is also very important and should be both straightforward and efficient. Common techniques, like incipient wetness or wet impregnation, provide high metal dispersions among carbonaceous supports, for example. This is mainly due to the ability of the surface to be specifically tailored (liquid or gas-phase activation) in order to improve the anchoring rate of the metal complex. However, such techniques are not efficient when using nanosized metal oxides as supports, due to the irregularity of the dispersed metal particles.

Photochemical deposition of noble metals is nowadays gaining importance as an alternative method, due to its simplicity and advantages. The ability of this technique to control the particle size and oxidation state of the deposited metal is notorious [35]. In order to improve the rate of the photodeposition, sacrificial electron donors like formaldehyde, methanol or 2-propanol are generally added. An additional advantage of this method is that deposition occurs at or near the photoexcited sites, promoting an enhanced dispersion [36].

In this chapter, it is described the preparation of several titanium dioxide supported Pt catalysts by photochemical deposition and their application in the selective hydrogenation of cinnamaldehyde to cinnamyl alcohol. The preparation method used yielded very active and selective catalysts. SMSI effect was used to rationalize the catalysts selectivity.

6.2 Experimental

6.2.1 Support preparation

Titanium dioxide was prepared from alkoxide precursors, according to an acid-catalyzed sol-gel method [37, 38]. The preparation was performed at room temperature through the addition of 0.1 mol (19.2 mL) of titanium isopropoxide [$\text{Ti}(\text{OC}_3\text{H}_7)_4$, Aldrich 97%] to 125 mL of ethanol ($\text{C}_2\text{H}_5\text{OH}$, Panreac p.a. 99%). The solution was stirred for 30 min before 1 mL of nitric acid (HNO_3 , Panreac 65%) was added. The mixture was kept under constant stirring until a homogeneous gel was formed. The latter was allowed to age in air for 1 week before being grinded into a fine powder ($d < 0.1$ mm). This powder was calcined at 400°C , in a vertical tubular furnace, under a constant nitrogen flow (2 hr, 75 mL min^{-1}), in order to obtain anatase TiO_2 (SG400). Five other commercially available TiO_2 samples were tested for comparison purposes. Two of them were composed only by anatase: Hombikat UV100 (H-UV100) and Tronox A-K-1 (TA-K-1), two others had a mixture of anatase and rutile: Aldrich (ALD) and P-25 from Evonik (P-25), and finally one made of rutile, Tronox TR-HP-2 (TR-HP-2). Quantification of each phase will be calculated and discussed in section 6.3.1.

6.2.2 Catalyst preparation and characterization

Different TiO_2 supported Pt catalysts, containing 5 wt. % metal loading, were prepared by the photochemical deposition method. Aqueous solutions containing the desired amounts of the sacrificial electron donor, methanol (CH_3OH , Riedel-de Haën, 99.8), dihydrogen hexachloroplatinate (IV) ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, Alfa Aesar, 99.9%) and titanium dioxide were sonicated for 30 minutes in order to improve dispersion [39]. The suspension was then transferred to a glass reactor, where it was irradiated by a low-pressure mercury-vapor UV lamp (*Heraeus* TNN 15/32), with an emission line at 253.7 nm (*ca.* 3 W of radiant flux), during 4 hr. The Pt loaded to the support was indirectly controlled by monitoring the 261 nm band (Figure 6.2) using an UV-Vis spectrophotometer (Jasco V560). The initial sample had a strong orange color and had to

be diluted 10 times before analysis, due to the high Pt concentration. The catalysts were then recovered by filtration and a sample of filtrate was analyzed by UV-Vis in order to determine the remaining amount of Pt. After the photodeposition process the solution had already turned colorless, while the support acquired a grayish coloration, indicative that Pt reduction had occurred at the TiO_2 surface.

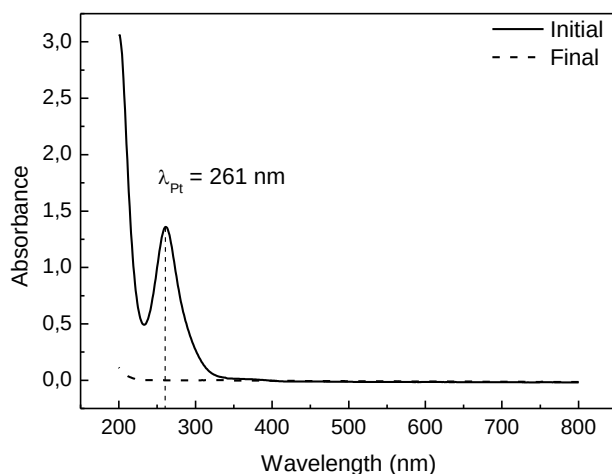


Figure 6.2 UV-Vis pattern of a Pt containing solution before and after the photodeposition process.

The catalysts were dried in an oven at 90°C for 2 days. The Pt present in the supported catalysts was treated in nitrogen (4 hr , 100 mL min^{-1}), hydrogen (2 hr , 20 mL min^{-1}) and flushed again with nitrogen for 30 min at 500°C in order to remove physisorbed hydrogen.

H_2 chemisorption measurements were carried out on either a custom built set-up using a SPECTRAMASS Dataquad quadrupole mass spectrometer or with a fully automated AMI-200 Catalyst Characterization Instrument (Altamira Instruments), equipped with a Dymaxion Dycor quadrupole mass spectrometer from Ametek. The chemisorption was performed at room temperature in a U-shaped tubular quartz reactor after a thermal treatment ($2 \text{ mL min}^{-1} \text{ H}_2$ and $28 \text{ mL min}^{-1} \text{ He}$ for 2 hr , and $30 \text{ mL min}^{-1} \text{ He}$ for another 2 hr at 300 or 500°C) to remove possible contaminant species from the catalyst surface. Pulses of H_2 were injected through a calibrated loop into the sample at regular time intervals until the area of the recorded peaks became constant. The amounts of H_2 chemisorbed were calculated from the areas of the resultant H_2 peaks. Metal dispersion was calculated according to Eq. 3.1 of Chapter 3, section 3.2.2.

The BET specific surface area (S_{BET}) was calculated from the nitrogen adsorption-desorption isotherms, obtained at -196°C using either a Coulter Omnisorp 100CX or a Quantachrome NOVA 4200e multi-station apparatus.

Surface analysis for topographical characterization was carried out by scanning electron microscopy (SEM) using a Jeol JSM-6301F (15 keV) electron microscope equipped with an OXFORD INCA ENERGY 350 energy dispersive X-ray spectroscopy (EDS) system. The sample powders were mounted on a double-sided adhesive tape and observed at different magnifications under two different detection modes, secondary and back-scattered electrons.

Transmission electron microscopy (TEM) observations were made using a LEO 906 E from LEICA (120 keV). The samples were dispersed in ethanol and collected on a copper carbon-coated TEM grid.

Powder X-ray diffraction (XRD) patterns were recorded in the 2θ range of $20-80^{\circ}$ in steps of 0.05° on a Philips X'Pert MPD rotatory target diffractometer. A $\text{CuK}\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$) was used as X-ray source, operated with an accelerating voltage of 40 kV and 50 mA applied current. Crystallite size of rutile, anatase and Pt were determined from the line broadening using Scherrer's equation:

$$d = \frac{k \lambda}{\beta \cos(\theta)} \quad (\text{nm}) \quad (\text{Eq. 6.1})$$

where d is the crystal size of the particle, λ is the X-ray wavelength, β is the broadening of diffraction line measured at half of maximum intensity (FWHM) of the peak, k is a constant (0.9 assuming spherical particles) and θ is the diffraction angle. The proportion of anatase and rutile in the samples can be estimated from the respective XRD peak intensities using the following equations:

$$f_A = \left(1 + 1.265 \frac{I_R}{I_A} \right)^{-1} \quad (\text{wt. \%}) \quad (\text{Eq. 6.2})$$

$$f_R = 1 - f_A \quad (\text{wt. \%}) \quad (\text{Eq. 6.3})$$

I_A , I_R , f_A and f_R represent the intensities and the weight fractions for the anatase (A) and rutile (R) peaks.

6.2.3 Selective hydrogenation procedure

The hydrogenation procedure was identical to that already described in Chapter 2, section 2.2.3, but using a catalyst mass of 0.1 g.

6.3 Results and discussion

6.3.1 TiO_2 characterization

An acid catalyzed sol-gel process was used to obtain a nanocrystalline TiO_2 , by thermally treating the gel at 400°C under nitrogen flow. It has been showed that if lower temperatures are used, the TiO_2 obtained is not fully crystalline, whereas, using higher temperatures, an anatase to rutile transformation is induced [40]. Therefore, at the temperature of 400°C, a TiO_2 material consisting of anatase with small crystallite sizes is obtained.

Figure 6.3 shows the XRD patterns of the TiO_2 samples. The position of the characteristic peaks of anatase and rutile was confirmed by the JCPDS files No. 73-1764 and 76-0649, respectively. The X-ray diffraction measurements confirm that the material consists of crystalline anatase for SG400, H-UV100 and TA-K-1. In addition to anatase, a very small amount of rutile is found in the ALD sample. P-25 has a higher amount of rutile, when compared to ALD, whereas TR-HP-2 is exclusively composed of rutile phase.

Table 6.1 includes the specific surface areas, anatase and rutile particle sizes and corresponding weight fractions for all TiO_2 samples. Calculations were based on the Scherrer equation (eq. 6.1), described in the experimental section, for $2\theta = 25.2^\circ$ to anatase (101) and 27.3° to rutile (110).

Table 6.1 BET specific surface areas (S_{BET}), crystallite sizes of anatase (d_{A}) and rutile (d_{R}) with corresponding weight fraction (f_{A} , f_{R}) for the TiO_2 .

Support	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	d_{A} (nm)	f_{A} (wt. %)	d_{R} (nm)	f_{R} (wt. %)
SG400	100	9.7	100	-	0
H-UV100	248	9.3	100	-	0
TA-K-1	80	17	100	-	0
ALD	11	45.2	98	35.6	2
P-25	47	20.9	81	28.2	19
TR-HP-2	7	-	0	42.9	100

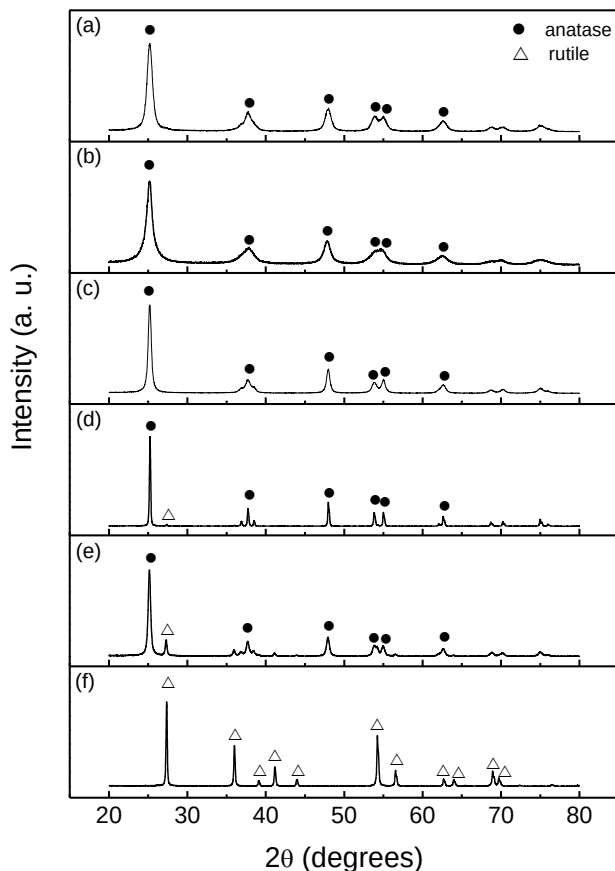


Figure 6.3 X-ray diffraction patterns of TiO_2 : (a) SG400, (b) H-UV100, (c) TA-K-1, (d) ALD, (e) P-25 and (f) TR-HP-2.

XRD calculations performed on SG400 confirm the formation of a nanosized crystalline anatase, with particles in the range of 10 nm. A similar pattern was obtained for H-UV100 with a similar particle size. The specific surface area was, however, much higher for the later ($248 \text{ m}^2 \text{ g}^{-1}$). The difference can be explained in terms of the material porosity, much higher for H-UV100 than for SG400. TA-K-1 sample revealed a particle size somewhat bigger than the previous samples which originated a smaller surface area. The particle size around 45 nm is also responsible for the low surface area observed ($11 \text{ m}^2 \text{ g}^{-1}$) for ALD. The P-25 TiO_2 contains an anatase fraction of 81% and particles around 21 nm, corresponding to a surface area of $47 \text{ m}^2 \text{ g}^{-1}$. Finally, the lowest surface

area of all tested samples ($7 \text{ m}^2 \text{ g}^{-1}$) and a particle size of 43 nm were observed for rutile TR-HP-2.

Due to the production mechanism of TiO_2 samples, these materials are essentially non-porous, the exception being H-UV100, with all the reported surface area due to adsorption on the external surface. The calculated particle sizes, surface areas and anatase/rutile fractions are in good agreement with those reported by the manufacturers.

6.3.2 *Pt/TiO₂ catalysts*

XRD patterns for the TiO_2 supported Pt catalysts, after a thermal treatment at 500°C , are shown in Figure 6.4. The reflections for Pt were observed at $2\theta = 39.7^\circ$ (111), 46.3° (200) and 67.5° (220) and were confirmed by the JCPDS file No. 87-0646, indicating the metallic nature of the Pt [41, 42]. Apart from the expected appearance of the Pt related peaks, no major differences were found between the Pt/TiO_2 thermally treated catalysts and the naked TiO_2 supports. Only SG400 supported Pt catalyst revealed the presence of rutile traces.

The gel calcination temperature is known to affect the proportion between the two TiO_2 main polymorphic forms [40]. As the temperature increases above 450°C , an anatase to rutile phase transition is observed. For this reason, the Pt/SG400 catalyst treated at 500°C developed a small amount of rutile (*ca.* 9%). The thermal treatment performed to SG400 at 500°C allowed the study of the Pt effect on the phase transition. Without Pt on the surface, a transition of 30% between anatase and rutile was observed, which can be due to a possible stabilization effect of Pt over the crystal structure.

A similar effect was reported by Wenbin *et al.* [43] and by Maeda and Watanabe [44]. The explanation given by these authors was based on the fact that Pt doping might lead to an increased potential energy of atomic diffusion barrier, hindering the crystal rearrangement and, thus, the anatase to rutile transformation. On the other hand, some authors report an enhanced transformation of anatase to rutile in the presence of Pt [45, 46]. In these cases, the metal is said to promote the transformation by diffusing into the lattice and increasing the defect concentrations, leading to bond rupture and atomic rearrangements.

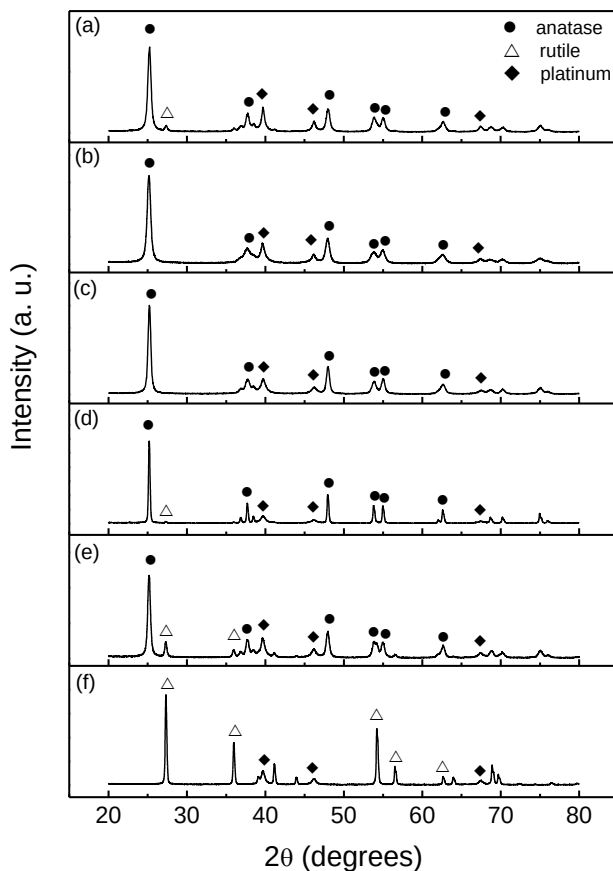


Figure 6.4 X-ray diffraction patterns of TiO_2 supported Pt catalysts: (a) 5Pt/SG400, (b) 5Pt/H-UV100, (c) 5Pt/TA-K-1, (d) 5Pt/ALD, (e) 5Pt/P-25 and (f) 5Pt/TR-HP-2.

The crystallite size of the Pt clusters was estimated from the line broadening of the (111) reflection, using the Scherrer equation. The results are presented in Table 6.2 along with the crystallite sizes for anatase and rutile.

The particle size obtained for anatase varies from 15 to 34 nm whereas rutile varies from 15 to 36 nm. Regarding the naked support, the anatase crystallite size increased in most cases (for ALD and P-25 supports, a decrease was detected) while the one of rutile decreased regardless of the TiO_2 sample.

Table 6.2 Pt load (y_{Pt}), crystallite sizes of anatase (d_A) and rutile (d_R) after calcination at 500°C and Pt particle size (d_{Pt}) determined by XRD and TEM analysis for TiO₂ supported catalysts.

Support	y_{Pt} (wt. %)	d_A (nm)	d_R (nm)	d_{Pt} (nm)	d_{Pt}^* (nm)
Pt/SG400	4.1	16.0	14.9	17.2	4.4
Pt/H-UV100	4.2	14.8	-	11.4	4.1
Pt/TA-K-1	4.4	18.9	-	10.3	3.8
Pt/ALD	3.7	33.9	20.4	10.4	4.2
Pt/P-25	4.4	19.9	22.1	13.0	4.1
Pt/TR-HP-2	4.4	-	35.6	14.1	4.3

*determined by TEM analysis.

Pt particle size determined by XRD and TEM is also presented in Table 6.2. In all cases, much higher values were obtained with XRD. This can be explained by the limitations of this technique regarding the particle size. Since XRD is rather insensitive to small dimensions, when larger particles are present, an overestimation of size occurs. For this reason, TEM analysis seems to be a more reliable technique than XRD. A particle size of *ca.* 4 nm was observed for all the TiO₂ samples. Hence, photodeposition of Pt over the TiO₂ support appears to be independent of the crystallite size and nature of the polymorphic phase composition.

The results obtained by H₂ chemisorption, for samples treated at 300°C (not shown), are in good agreement with those obtained by TEM analysis. Strong discrepancies were, however, observed for the samples thermally treated at 500°C, well beyond the sintering effect. In this case, an almost complete absence of H₂ chemisorption was observed. This effect is characteristic of the SMSI state and is not related to a significant increase (sinterization) of the Pt particle size. The reduced chemisorption capacity is often explained in terms of a partial coverage of Pt surface by partially reduced TiO_x species (oxygen vacancies). Since the SMSI effect can be reduced or even eliminated when exposed to oxygen under ambient conditions [47, 48], special care was taken in order to minimize air contact with the catalyst before the reactions. After exposing the catalysts to air for several days, H₂ chemisorption measurements were repeated. The results indicated an almost total absence of the SMSI effect (chemisorption capability restored), as particle size was in good agreement to that obtained by chemisorption, for the catalysts treated at 300°C.

TEM micrographs for the several TiO₂ supported catalysts are presented in Figure 6.5. A TEM image of the Pt/SG400 nanoparticles is shown in Figure 6.5a, evidencing an almost spherical shape for both Pt and anatase/rutile crystallites. In the remaining micrographs, Pt retains a circular form but the support structure varies in shape.

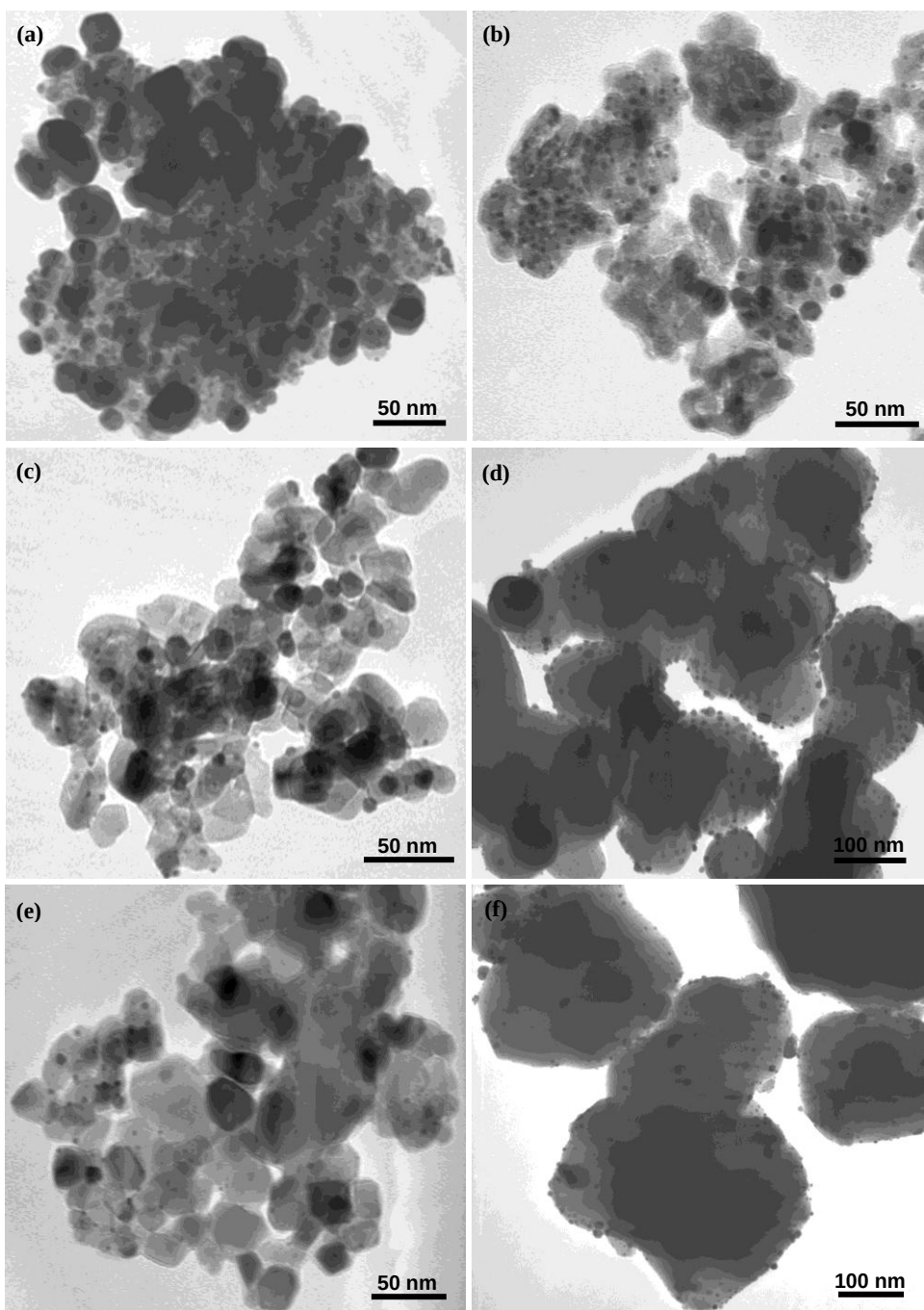


Figure 6.5 TEM micrographs of TiO₂ supported Pt catalysts: (a) Pt/SG400, (b) Pt/H-UV100, (c) Pt/TA-K-1, (d) Pt/ALD, (e) Pt/P-25 and (f) Pt/TR-HP-2.

6.3.3 Selective hydrogenation of cinnamaldehyde

TiO₂ supported Pt catalysts are a classical system that develops the SMSI effect, when treated at high temperatures (500°C) in H₂. Significant improvements in both activity and selectivity in the hydrogenation of cinnamaldehyde have been correlated with its appearance, and were proven to be beneficial for the preferential reduction of the carbonyl group. In order to optimize the selectivity towards cinnamyl alcohol, prior to the reaction, all the catalysts were thermally treated in H₂ to develop this effect.

Several tests were performed in order to optimize the hydrogenation reaction conditions. The effect of the catalyst mass was studied using 0.05, 0.1 and 0.2 g of catalyst, while keeping other experimental conditions constant. As expected, a linear increase in the conversion with catalyst weight increase was observed. Hence, given the high metal load present, a catalyst mass of 0.1 g was chosen.

The effect of hydrogen pressure on the hydrogenation activity was also studied, by varying the total pressure (5, 10 and 15 bar), while keeping the temperature and catalyst mass constant. In this case, there was no difference in the conversion level between 10 and 15 bar. At 5 bar, conversion was, however, considerably lower than the obtained at 10 and 15 bar. Based on the observed results, a total pressure of 10 bar was chosen to perform the reactions.

Finally, an important enhancement in the catalytic activity with reaction temperature increase was observed. Temperatures from 70 up to 100°C were tested and no significant changes in the selectivity were detected. For lower temperatures, the reaction was slower, meaning that the selectivity to cinnamyl alcohol was kept at high levels for longer periods of time, at the cost of the conversion level that decreased substantially. Hence, as a compromise, a temperature of 90°C was preferred for the reactions.

In order to avoid possible external mass transfer limitations, the stirring speed was maintained at the highest level possible in the agitation plate (*ca.* 750 rpm) and a catalyst particle size lower than 0.1 mm was used.

Figure 6.6 shows the reaction pathways observed in the selective hydrogenation of cinnamaldehyde (CAL) using Pt/TiO₂ catalysts: the C=O bond can be hydrogenated to give the cinnamyl alcohol (COL); C=C bond can be reduced to form the hydrocinnamaldehyde (HCAL) and finally both COL and HCAL can be further hydrogenated to produce the fully saturated hydrocinnamyl alcohol (HCOL). Similarly to the results reported in Chapter 2, hydrogenation over Pt/TiO₂ was allowed to proceed via the formation of β -methylstyrene (MS), 1-propylbenzene (PB), n-propylcyclohexane (PCH) and 3-cyclohexyl-1-propanol (CHP).

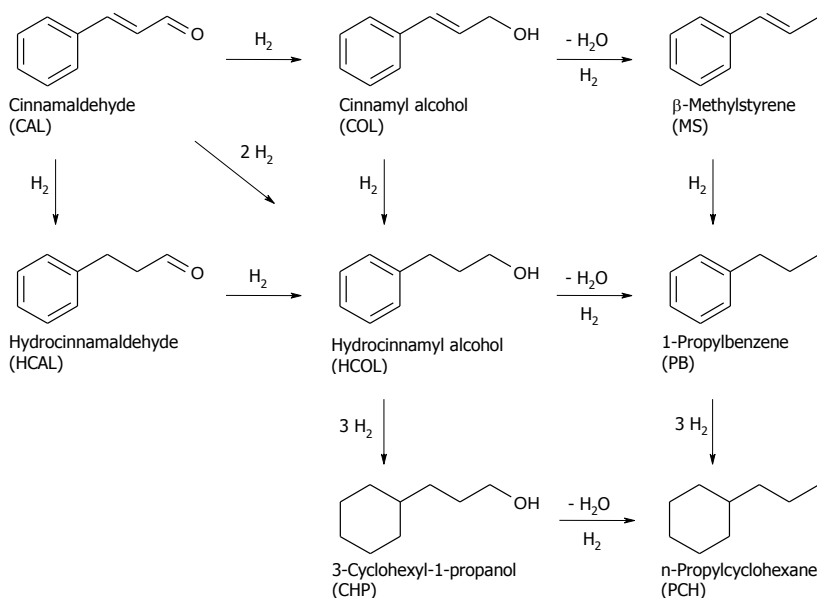


Figure 6.6 Reaction scheme for the selective hydrogenation of cinnamaldehyde using TiO_2 supported Pt catalysts.

The reaction results obtained at 90°C and 10 bar of total pressure are gathered in Table 6.3. In order to evaluate the possible influence of the naked support in the reaction, a catalytic run with this material was also performed under the same reaction conditions. The results indicated no significant activity and after over 30 hr only *ca.* 15% of cinnamaldehyde was converted without any favored products.

Table 6.3 Catalytic results obtained for the hydrogenation of cinnamaldehyde using TiO_2 supported Pt catalysts (selectivities measured at 50% conversion).

Support	TOF (s^{-1})	Selectivity (%)			
		COL	HCOL	Others	
Pt/SG400	3.9	83	5	10	2
Pt/H-UV100	5.8	50	11	14	25
Pt/TA-K-1	3.1	64	6	10	20
Pt/ALD	5.1	66	8	15	11
Pt/P-25	8.3	75	5	12	8
Pt/TR-HP-2	4.4	64	7	14	15

The last column in Table 6.3 indicates the relative amount of by-products like MS, PB, CHP and PCH. The concentration of these products cannot be quantified due to the

absence of their calibration curves. Hence, the calculation of the selectivities towards these by-products (S_{others}) is given by difference to 100%.

The selectivity to cinnamyl alcohol is much higher over the sol-gel derived Pt catalyst (83%) than on any other commercial support. P-25 supported catalyst also evidence excellent C=O bond activation, to yield 75% of COL. Pt/H-UV100 catalyst presented the lowest selectivity among the studied materials, with still an interesting 50% being obtained. The remaining materials presented very similar selectivities. The lower values exhibited by these materials are in part explained by the higher amounts of unwanted by-products (Figure 6.6).

Comparing a material composed by 100% anatase (TA-K-1) with a 100% rutile (TR-HP-2) one, it can be concluded that the preferential hydrogenation of the carbonyl group is independent of the polymorphic phase present. This may suggest an important solution effect, since these findings are at variance with gas-phase results. In the work performed by Claus *et al.* [49] the influence of the phase composition of TiO_2 in the gas-phase hydrogenation of crotonaldehyde is relevant. They observed that the selectivity towards crotyl alcohol was strongly dependent on the anatase-to-rutile ratio.

Looking at the activities of the catalysts (TOF) it can be seen that they vary considerably. Pt/SG400 reveals a TOF of about half of that observed for P-25. In spite of having one of the slowest conversion rates, the extremely high selectivity attained can justify further studies using this material. Figure 6.7 shows the evolution of the concentration along the time of reaction when using the Pt/SG400 catalyst.

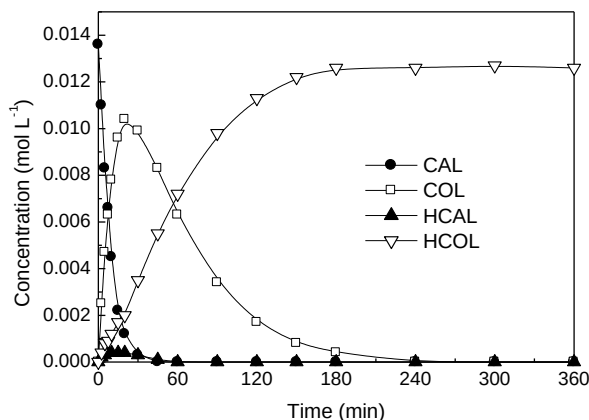


Figure 6.7 Product distribution for the selective hydrogenation of cinnamaldehyde using the Pt/SG400 catalyst.

These variations in selectivity should not be directly related to the Pt particle size, as the samples have roughly the same diameter. A possible explanation for the high selectivity observed for Pt/SG400 could, thus, be associated with a much more intense interaction between the SG400 support and the metal. This shows that the preparative technique could be the decisive factor for controlling the formation of interfacial sites. Sol-gel method can, therefore, have an important impact on the preparation of new hydrogenation catalysts.

Atoms in different crystallographic positions can have different catalytic properties as a result of a different electronic and/or geometric structure, as already mentioned in Chapter 1. Theoretical calculations performed by Delbecq and Sautet [50] showed that the adsorption mode, which determines the selectivity, depends on the metal crystal surface exposed. According to these authors the Pt (111) plane does not favor the coordination with the C=C bond and a higher selectivity to the unsaturated alcohol should be observed. Also the Pt(111) plane is preferentially exposed in larger Pt clusters and thus higher selectivities to COL are observed [27]. Among the Pt peaks present in the XRD spectra of Pt/TiO₂ (Figure 6.4) there is a strong peak at $2\theta = 39.6^\circ$ that is assigned to the Pt(111) plane. The intensity of this peak, in comparison with others, means that the later plane is predominant over the Pt crystal, which can help explain the higher selectivities observed for the Pt/TiO₂ catalysts. In addition, according to Gallezot and Richard [27] particle size also plays an important role in the hydrogenation of cinnamaldehyde over Pt catalysts. Adsorption of the C=C bond is hindered due to a steric repulsion between the flat metal surface in large Pt particles and the aromatic ring, leading to an increase in the carbonyl group reduction. Other published works show that the selectivity towards the formation of cinnamyl alcohol increases with the increase of the particle size, in particular for particles larger than 3 nm [51]. Hence, Pt particles of *ca.* 4 nm, with a Pt(111) preferential orientation, in combination with the SMSI effect, reflected very positively on cinnamyl alcohol selectivity.

6.4 Conclusions

The sol-gel method produced a TiO₂ anatase with an average particle size of 9.7 nm. This material was non-porous with a specific surface area of 100 m² g⁻¹. The photochemical deposition method produced Pt nanoparticles in the range of 4 nm regardless of the TiO₂ surface area and type of crystalline phase present. The method proved to be very simple and effective.

A thermal treatment of Pt/TiO₂ catalysts at 500°C induced an anatase-to-rutile transformation of the support. However it did not induce a significant sintering of the Pt particles.

The determination of Pt particle size by different techniques was not straightforward due to the interface of the support. Especially indirect measurements such as H₂ chemisorption need to be regarded with caution.

There was no relation between activity and selectivity for the average Pt particle size of 4 nm. Activity/selectivity performances were more related to the nature of the support. Thus, commercial TiO₂ P-25 produced the most active catalyst with a reasonable selectivity. The sol-gel TiO₂ calcined at 400°C produced the most selective catalysts with a reasonable activity. The maximum production of cinnamyl alcohol for this catalyst was achieved at 91% conversion of the initial substrate in less than 30 min of reaction.

A sol-gel based TiO₂ proved to be extremely efficient in the selective reduction of the carbonyl group, when compared with several other commercially available samples. The results were thought to be associated with an enhanced SMSI effect over the synthesized material. Hence, the sol-gel approach combined with the photodeposition of Pt particles has an important impact on the preparation of new highly selective hydrogenation catalysts.

The reaction operating conditions used were milder than those reported in the literature, especially the pressure, since values up to 50 bar are quite common.

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7. Platinum nanoparticles supported over Ce-Ti-O: the solvothermal and photochemical approaches

Ce-Ti-O supports with different Ce/Ti molar ratios are synthesized by the solvothermal method using hexadecyltrimethylammonium bromide. Pt nanoparticles are supported by photochemical deposition. The shape, size and structure of the prepared materials are analyzed by high-resolution transmission electron microscopy. The single CeO₂ support is also prepared and consists of agglomerated cubic particles ranging from *ca.* 3 to 8 nm. When titania is combined with ceria, a nanostructured architecture is produced, evidencing the strong influence of Ti in the support structure. Photodeposition of Pt nanoparticles is more efficient on Ce-Ti-O supports than on CeO₂, revealing crystalline Pt nanoparticles (mainly *ca.* 2-4 nm). The catalytic properties of the materials are tested in the selective hydrogenation of cinnamaldehyde to cinnamyl alcohol. It is observed that Pt supported on Ce-Ti-O is more active and selective than Pt on CeO₂. The catalyst with 40 mol % Ce originates total conversion of cinnamaldehyde in a few minutes; however, higher selectivities towards the desired product (cinnamyl alcohol) are obtained with higher amounts of Ce (50 mol %).

7.1 Introduction

Synthesis of nanostructured catalysts has gained importance with the understanding of the relationships between size-derived properties in nanoparticles at molecular-level and catalytic performance [1, 2]. The advantage of using small particles in heterogeneous catalysis is obvious and arises from the larger fraction of atoms which are available to participate in the catalytic process. Especially in the liquid phase, the surface-to-volume ratio increases significantly when particle size "goes nano" [3]. Moreover, surface atoms at the corners and edges of these nanoparticles tend to be chemically more active.

Ceria (CeO_2) is a rare-earth oxide extensively used in catalysis, mainly as support or dopant [4-8]. Hydrothermal oxidation of metals is a useful preparation method for ceria nanoparticles with different shapes [9, 10]. When a solvent (other than water) is used, the process is usually known as solvothermolysis [11-13]. This lanthanide oxide, considered as the most abundant in the earth crust, has attracted special attention due to its ability to be easily and reversibly reduced from CeO_2 to non-stoichiometric oxides CeO_{2-x} . The reducibility of the support plays an important role in the properties of Pt catalysts, especially those used for selective hydrogenation of α,β -unsaturated aldehydes [14, 15]. It is well known that a high temperature treatment in H_2 improves the selectivity of the catalysts to the unsaturated alcohol [16, 17], and sometimes also the activity. This effect is mostly attributed to strong metal support interaction (SMSI) [18-20] when reducible supports are used.

The formation of high amounts of unsaturated alcohol is commonly attributed on Pt/ TiO_2 catalysts, to the reactivity of the interfacial Pt- TiO_x sites [21]. However, in Pt/ CeO_2 catalysts, the origin of the specific catalytic behavior of Pt in the SMSI state is still a matter of debate. Some possible explanations have been suggested in literature, such as: (i) formation of a Pt-Ce alloy [22], (ii) electronic effect on Pt particles due to the partial reduction of ceria [23] or (iii) decoration of Pt particles by patches of partially reduced ceria [24].

Mixing different oxides offers an opportunity not only to improve the performance of the involved metal oxide, but also to form new stable compounds that might lead to completely different physical and chemical properties from the single components [25]. The preparation of Ce-Ti-O mixed oxides is usually carried out to achieve either a TiO_2 photocatalyst responding to visible light, or to improve the thermostability of CeO_2 at

high temperatures [26-28], but other possible applications involving its use as a support, have also been envisaged [25, 29, 30].

In the present chapter, the synthesis of CeO₂ and Ce-Ti-O (with different Ce/Ti molar ratios) by the solvothermal method is described, as well as their application on catalytic hydrogenation. In addition it is described how Pt nanoparticles are supported by photochemical deposition on the prepared materials. When Ti is combined with Ce, nanostructured architectures are produced, evidencing the strong influence of Ti in the support. The catalytic properties of the prepared materials are assessed in the selective hydrogenation of cinnamaldehyde to cinnamyl alcohol. It is observed that Pt supported on Ce-Ti-O is more active and selective than Pt on CeO₂ separately.

7.2 Experimental

7.2.1 Support preparation

The solvothermal synthesis of cerium and titanium colloids was performed in a 160 mL 316-SS high-pressure autoclave (Parr Instruments, USA Mod. 4564) equipped with a temperature controller (Mod. 4842). Cerium(III) nitrate hexahydrate [Ce(NO₃)₃·6H₂O, Fluka 99%] and tetraisopropyl orthotitanate [Ti(OCH(CH₃)₂)₄, Aldrich 97%] were used as Ce and Ti precursors, respectively. Calculated amounts of Ce and Ti were slowly dissolved in 75 mL of methanol (CH₃OH, Chromanorm > 99.8%) containing 0.1 M of cetyltrimethylammonium bromide, commonly designated as CTAB [CH₃(CH₂)₁₅N(Br)(CH₃)₃, Sigma ≥ 99%]. The pH of the Ce-Ti colloid solution was set to 11, using a 3 M solution of potassium hydroxide (KOH, Fluka > 86%). Maintaining the total molar concentration equal to 0.1 M, different Ce:Ti molar percentages: 30:70, 40:60 and 50:50 (56:44, 66:34 and 75:25 in wt. %, respectively) were prepared. The as obtained solution was transferred to a teflon vessel, inserted in the autoclave and heated to the desired temperature (150°C) under autogenous pressure. The solution was maintained at that temperature for 150 min, under a continuous stirring speed of 500 rpm. The autoclave was then cooled to room temperature and the colloids were continuously washed in up-flow mode with deionized water (*ca.* 3 mL min⁻¹), during several hours, with the aid of a peristaltic pump.

7.2.2 Catalyst preparation and characterization

A solution was prepared by dissolving the adequate amount of H₂PtCl₆·6H₂O in methanol. Since hydroxylated ceria is a basic precipitate which dissolves in acidic

solutions [9], KOH (3 M) was added to the Pt solution. The cerium (or the cerium-titanium) colloids were then transferred to a photocatalytic reactor and mixed with the Pt precursor solution (5 wt. % Pt). The remaining photochemical deposition procedure was identical to that described in Chapter 6, section 6.2.2.

A JEOL 2010F analytical electron microscope, equipped with a field-emission gun, was used for transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) investigations. The microscope was operated at 200 kV and an energy-dispersive X-ray spectrometer (EDXS) LINK ISIS-300 from Oxford Instruments, with an UTW Si-Li detector, was employed for the chemical analysis. The samples for TEM were prepared from the diluted suspension of nanoparticles in ethanol. A drop of suspension was placed on lacey carbon coated Ni grid and allowed to dry in air.

Z-contrast images were collected by using high-angle annular dark-field detector (HAADF) in scanning transmission mode (STEM).

Scanning electron microscopy (SEM) analysis were performed in a high performance FEI Quanta 200 FEG SEM microscope equipped with a Schottky field emission gun (FEG), for optimal spatial resolution, and an Oxford Inca Energy Dispersive X-ray (EDX) system for chemical analysis. The samples were mounted on a double sided adhesive tape made of carbon.

X-ray diffraction (XRD) analysis was carried out in the same apparatus previously described in Chapter 6, section 6.2.2 in order to identify the crystallographic phases present and calculate the crystallite size through the XRD diffraction peaks by the use of the modified Scherrer equation (Eq. 6.1).

Thermogravimetric analysis (TGA) was performed in air with a Mettler TA 4000 system, from 30 to 900°C, at the rate of 10°C min⁻¹.

The particle size distribution was monitored by light scattering in a Coulter LS230 instrument.

7.2.3 Selective hydrogenation procedure

The hydrogenation procedure was identical to that already described in Chapter 2, section 2.2.3.

7.3 Results and discussion

7.3.1 CeO_2 and Ce-Ti-O

Preliminary experiments were performed in order to analyze the effect of the main parameters involved in the solvothermal synthesis of ceria. The presence of a base in the initial solution and the temperature used in the solvothermal process had a strong effect in the colloids. For the synthesis carried out at 150°C, a dark purple color was observed for solutions with excess of KOH while a white color was characteristic of the materials synthesized in the presence of low KOH concentration (0.2 M). It was also observed that the color of the material is dependent on the temperature used. For instance, the particles are white for temperatures lower than 150°C, while a mixture of purple and white colloids is obtained at 220°C. It has been previously reported that the purple color is characteristic of cerium(III) hydroxide $[\text{Ce}(\text{OH})_3]$ species, while the white color is related to cerium(IV) hydroxide $[\text{Ce}(\text{OH})_4]$ [31]. Since cerium(III) is very unstable under air atmosphere, the temperature was set to 150°C.

A representative HRTEM micrograph of the nanosized colloids (Figure 7.1a) shows the as-obtained Ce particles after solvothermal synthesis (suspended in methanol), identified by EDXS. These colloids appear to be ultrafine agglomerated crystallites, mostly in the form of cubes, with a length of *ca.* 3-8 nm. These ceria nanoparticles are assembled with different orientations and, in some cases, rounded edges are observed. Similar HRTEM micrographs were observed for nanosized ceria, obtained by the hydrothermal method using higher temperatures (250°C) and longer synthesis times (between 6 and 24 hr) [9], by the microemulsion method with toluene [32] and by applying the solvothermal method at 150°C with ethanol [13].

The particle size distribution of the agglomerates composed of ceria nano-particles, measured in volume percentage, was monitored using light scattering. The solution containing the nano-particles was allowed to settle down for several days, with deposition of the agglomerates being observed at the bottom of the flask. Figure 7.1b shows that the agglomerates size distribution have a maximum at 30.1 μm (t_1). When ultrasonic irradiation was applied to the colloidal solution, a shift in the maximum of the size distribution towards lower particle sizes was observed, which can be explained by particle deagglomeration.

The colloids were slowly dried at *ca.* 80°C and pale yellow particles were obtained. TGA analysis of these precipitates resulted in a weight loss of 11.5%, between 30 and 900°C, indicating dehydration of the hydrous oxide form of CeO_2 ($\text{CeO}_2 \cdot x\text{H}_2\text{O}$) [9].

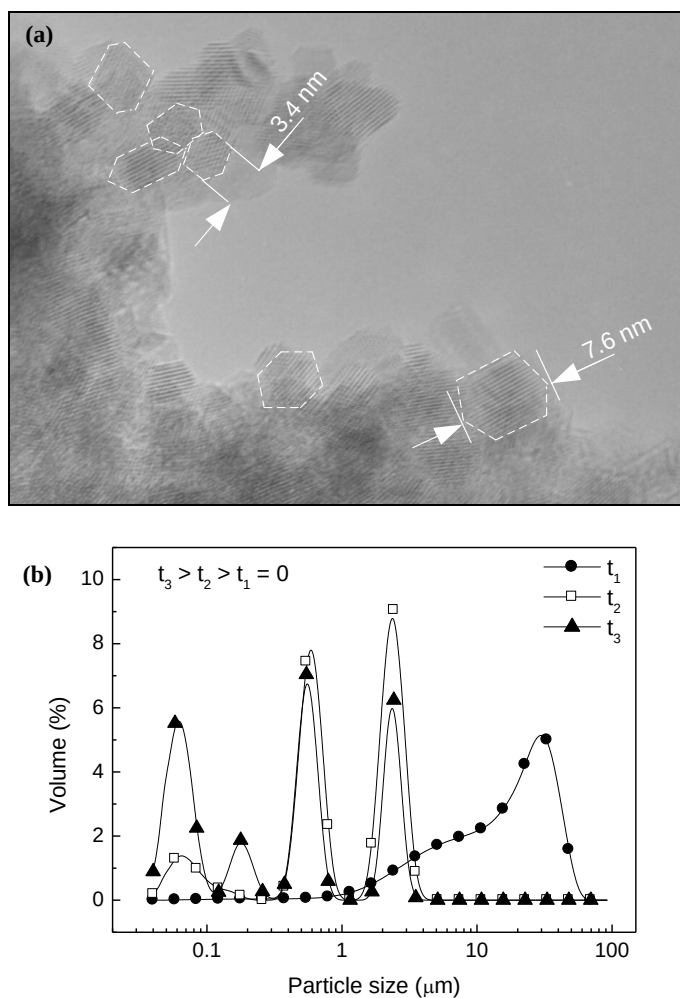


Figure 7.1 (a) HRTEM micrograph of CeO_2 ; (b) Particle size distribution before (t_1) and after ($t_2 < t_3$) different time periods of ultrasound irradiation.

The interaction between Ce and Ti, when prepared together, was also investigated. Figure 7.2 shows the HRTEM micrograph of $\text{Ce}_{0.5}\text{-Ti}_{0.5}\text{-O}$. In contrast with CeO_2 , Ce-Ti-O particles are practically amorphous, with some crystalline nuclei (identified as cubic CeO_2 , with a few nm in size) being observed.

In summary, while CeO_2 is essentially crystalline, Ce-Ti-O supports are mostly amorphous, with some CeO_2 crystalline nanoparticles dispersed over the materials.

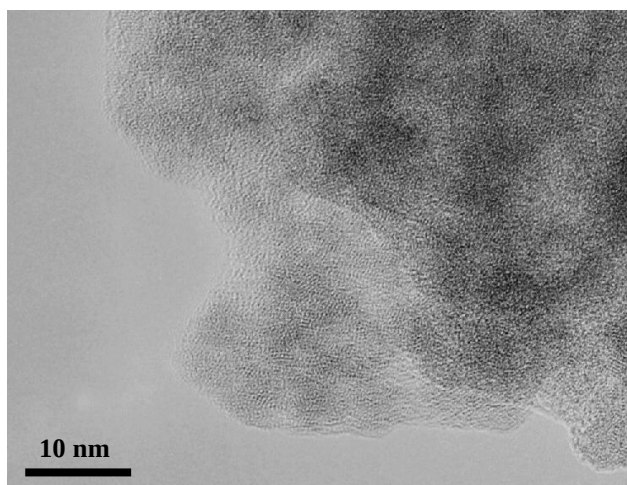


Figure 7.2 HRTEM micrograph of $\text{Ce}_{0.5}\text{-Ti}_{0.5}\text{-O}$.

7.3.2 Pt/CeO_2 and Pt/Ce-Ti-O

The suitability of the photodeposition method to support Pt on the nanostructured CeO_2 was first evaluated. Figure 7.3 shows HRTEM micrographs of a Pt/CeO_2 sample obtained by this technique. It is possible to identify small dark spots (some of them marked by arrows) which represent the deposited Pt nanoparticles (5 wt. % as confirmed by EDXS).

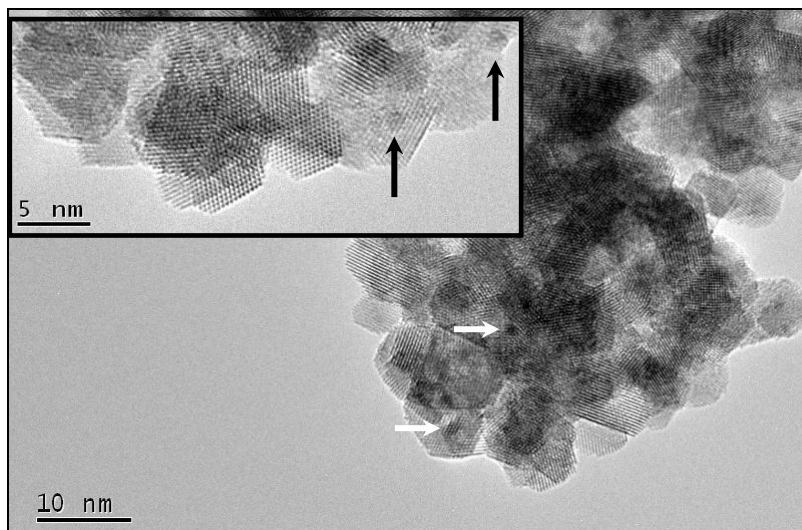


Figure 7.3 HRTEM micrographs of Pt/CeO_2 catalyst with cubic CeO_2 particles (arrows indicate Pt nanoparticles).

Figure 7.4 shows a typical HRTEM micrograph of Pt photodeposited on the Ce-Ti-O amorphous support.

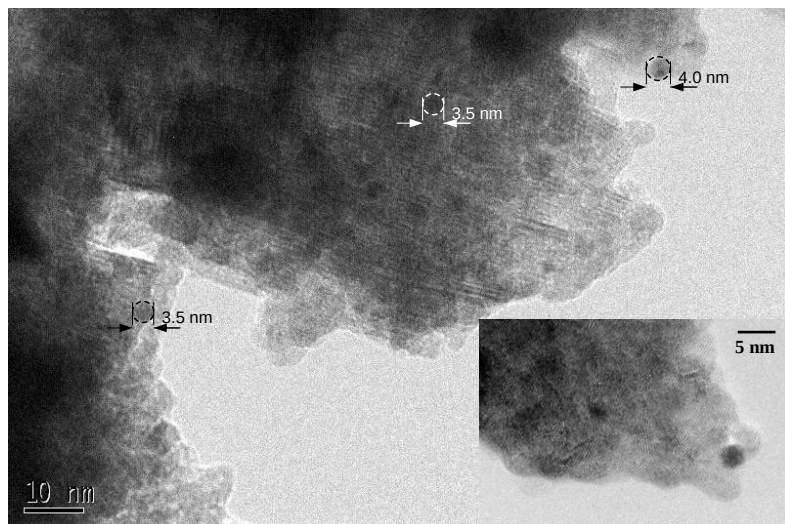


Figure 7.4 HRTEM micrograph of Pt/Ce_{0.5}-Ti_{0.5}-O catalyst; (inset) HRTEM micrograph at higher magnification showing a Pt particle.

Pt particles, ranging from 2.5 to 4 nm in size, are clearly identified. A spherical Pt particle (identified by means of EDXS) is visible at higher magnification in the inset of Figure 7.4. The composition of the support (Ce-Ti) was also estimated by EDXS spectra. The average mass percentages predicted for this sample by EDXS in terms of Ce and Ti were 75 and 25 wt. %, respectively, which fully agree with the nominal value of the Pt/Ce_{0.5}-Ti_{0.5}-O catalyst. Moreover, a 5 wt. % Pt with respect to Ce-Ti (95%) was estimated.

SEM analysis was also performed for this Pt/Ce_{0.5}-Ti_{0.5}-O sample (Figure 7.5). The Pt particles were clearly identified with the Back Scattered Electron Detector (BSED), seen as small bright points distributed on the surface of Ce-Ti-O.

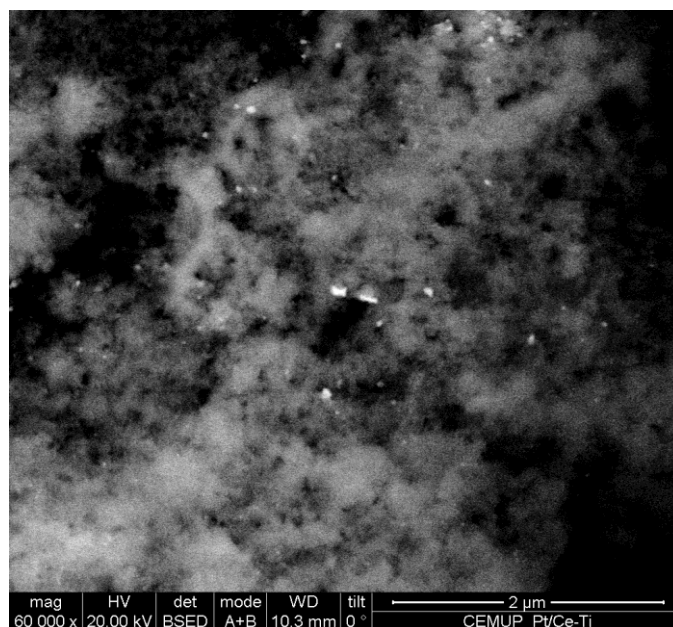


Figure 7.5 SEM micrograph of Pt/Ce_{0.5}-Ti_{0.5}-O catalyst with BSE detector.

Figure 7.6 shows the XRD diffraction patterns of the prepared Pt catalysts (the XRD patterns of pure CeO₂ before and after calcination are also shown for comparison). The diffraction peaks of pure CeO₂ are indexed as 100% CeO₂ with cubic structure. From the XRD spectra, it can be seen that the particles have a lower degree of crystallinity before calcination. These diffraction peaks are slightly broader and less intense, when compared with the diffraction peaks obtained for the calcined CeO₂. Using the modified Scherrer equation, the calculated values of particle size are 3.6 and 6.5 nm, respectively before and after calcination, which are within the range observed in the TEM images (Figure 7.1a and Figure 7.3). The XRD diffraction peaks identified as Pt are normally attributed to $2\theta = 39.7, 46.3$ and 67.6° . They were clearly identified in the Pt/Ce-Ti-O samples and evidence of Pt was also found by XRD in the Pt/CeO₂ catalyst, in agreement with the previous HRTEM analyses. The characteristic diffraction peaks of TiO₂ anatase ($2\theta = 25.3, 48.0$ and 54.7°) or TiO₂ rutile ($2\theta = 27.4$ and 41.3°) were not observed by XRD. Moreover, as the amount of Ti increases, the diffraction peaks of CeO₂ disappear from the XRD spectra.

In fact, Fang *et al.* [25], who studied interfacial structures of Ce-Ti-O oxides prepared by the sol-gel technique found that, by increasing the amount of titanium on ceria, the diffraction peaks in the XRD patterns became broader and weaker than those

observed for pure cubic CeO_2 . This means that the crystalline structure of the cubic CeO_2 is affected and its crystalline size decreases. One possible explanation is that Ti^{4+} substitutes Ce^{4+} in the lattice of cubic CeO_2 . Furthermore, Nakagawa *et al.* [33] studied various CeO_2 - TiO_2 composite nanostructures. When cerium was present in higher amounts than titanium, TiO_2 peaks were not observed by XRD. These authors concluded that the materials are not a simple mixture of pure CeO_2 and TiO_2 ; instead, composite materials were formed due to the good mixture of the precursors at the molecular scale. Therefore, it can be concluded that, in the 40 mol % Ce support, Ce and Ti are very well dispersed in small particles, originating a nanostructured architecture.

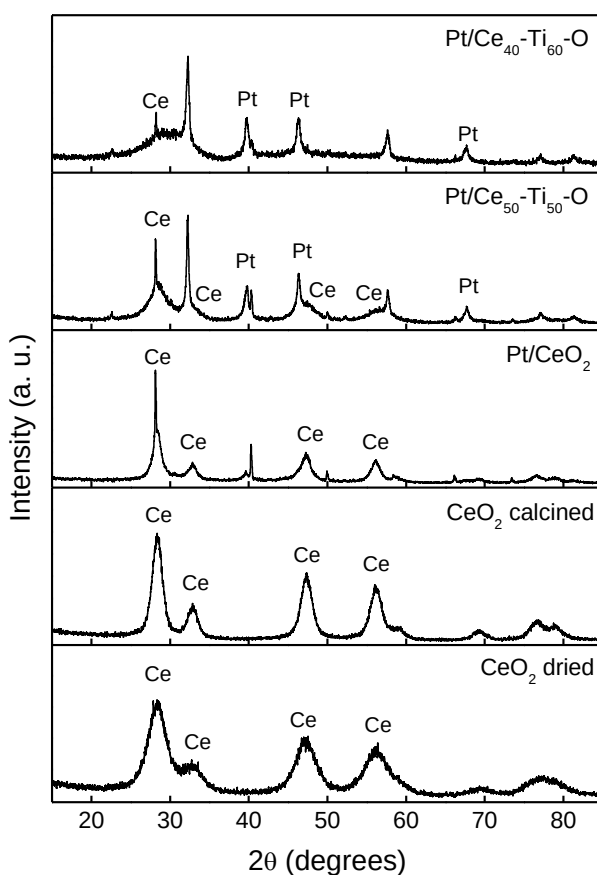


Figure 7.6 X-ray diffraction patterns of the CeO_2 -based supports and Pt catalysts.

The size of the Pt particles, in most of the samples, is in the nanometer range (*ca.* 3 nm). Nevertheless, Pt was detected in the Ti-based materials by XRD analysis,

suggesting that larger Pt particles are present. The HAADF/STEM image (Z-contrast) of the Pt/Ce_{0.4}-Ti_{0.6}-O material, in Figure 7.7a, shows a *ca.* 30 nm Pt particle (white contrast). The small Pt particles (*ca.* 3 nm) are labeled with arrows. Therefore, apart from small Pt particles, there are also some larger ones over the Ce-Ti-O support. The HRTEM image is shown in Figure 7.7b, together with a detailed HRTEM image of a 3 nm sized crystalline Pt particle on the amorphous Ce-Ti-O matrix.

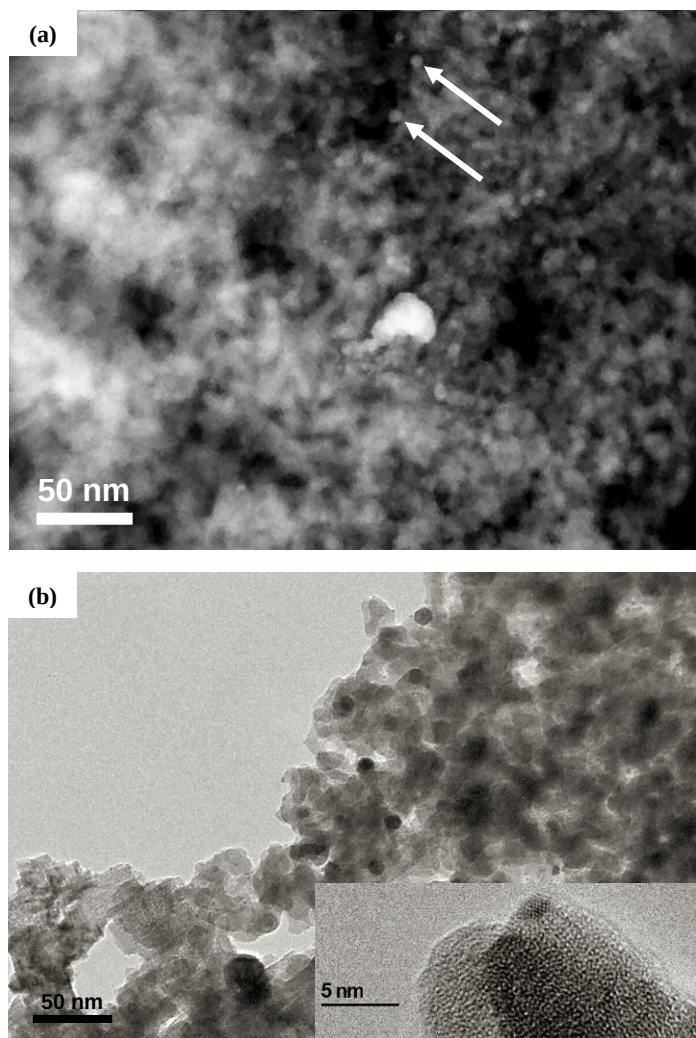


Figure 7.7 (a) HAADF/STEM micrograph (Z-contrast image) and (b) HRTEM micrograph of Pt/Ti_{0.4}-Ce_{0.6}-O catalyst, (inset) HRTEM micrograph of a 3 nm sized crystalline Pt particle.

7.3.3 Selective hydrogenation of cinnamaldehyde

The liquid-phase selective hydrogenation of cinnamaldehyde (CAL) was studied with the synthesized nanostructured catalysts. Cinnamyl alcohol (COL) is obtained by the hydrogenation of the carbonyl group of the CAL. When the reaction follows the thermodynamically favored hydrogenation of the C=C bond, hydrocinnamaldehyde (HCAL) is produced. Hydrogenation of both double bonds leads to the formation of the saturated alcohol (hydrocinnamyl alcohol - HCOL). In addition, traces of β -methylstyrene (MS) and 1-propylbenzene (PB), resulting from a dehydration reaction, were also detected. The general reaction scheme for the hydrogenation of cinnamaldehyde is presented in Figure 7.8. Since the reaction is carried out in heptane, the production of acetals and/or ethers was not expected to occur and, in fact, they were not detected (therefore not included in the scheme).

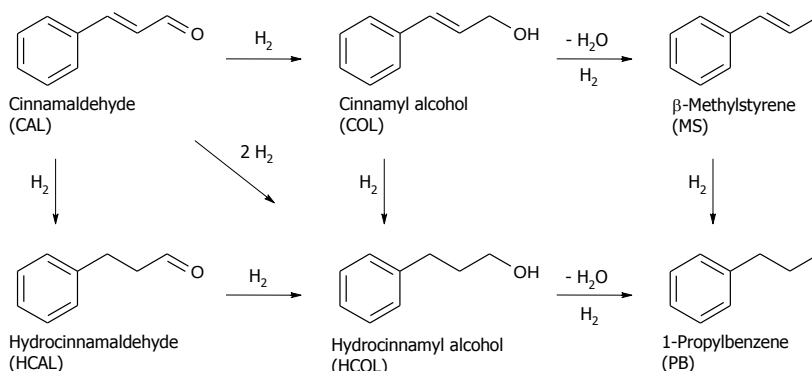


Figure 7.8 Reaction scheme for the selective hydrogenation of cinnamaldehyde using CeO_2 -based Pt catalysts.

The results obtained during the hydrogenation experiments are shown in Figure 7.9, in terms of cinnamaldehyde conversion, at different reaction times, namely 10, 300 and 600 min (Figure 7.9a), and in terms of selectivity to the reaction products at constant conversion of 50% (Figure 7.9b). The conversion level achieved with Pt/ CeO_2 catalyst was low when compared to the mixed-oxide supports. Combination of Ce with Ti had a positive effect on the conversion level, which increased significantly. The maximum activity was obtained with Pt/ $\text{Ce}_{0.4}\text{-Ti}_{0.6}\text{-O}$, with 80% of cinnamaldehyde being converted in less than 10 minutes. The behavior regarding the selectivity results was similar to that observed for the conversion.

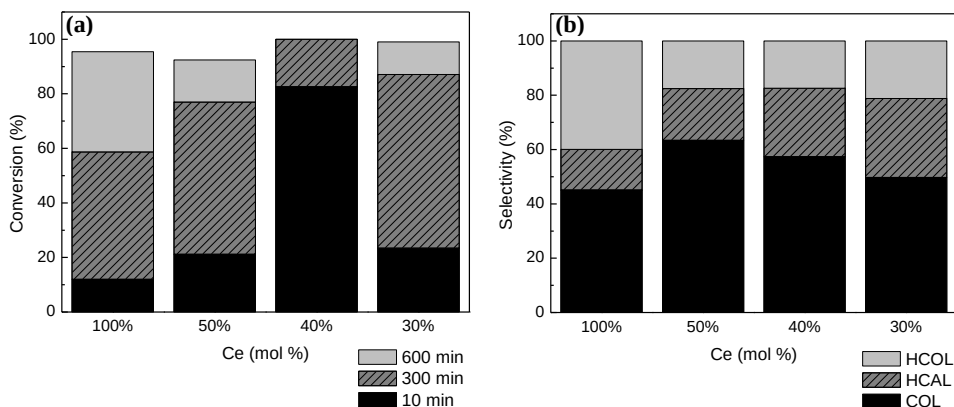


Figure 7.9 Hydrogenation of cinnamaldehyde at 90°C and 10 bar: (a) conversion and (b) selectivity results obtained with Pt/Ce-Ti-O catalysts at different Ce mol %.

The use of CeO_2 supported catalyst resulted in low amounts of the desired COL, which increased upon combination of Ce with Ti. For Pt/ CeO_2 a lower amount of HCAL was produced (15% selectivity, at 50 % conversion) in comparison with the amounts of COL and HCOL, which were equivalent (around 43%). Regarding the mixed-oxide supported catalysts, Pt/ $\text{Ce}_{0.5}\text{-Ti}_{0.5}\text{-O}$ provided the best results: a selectivity of 63% was observed with respect to COL and a low selectivity value with respect to HCAL. The values for HCOL were lower than those obtained with Pt/ CeO_2 . Hence, an interesting fact can be evidenced: when used separately, the CeO_2 supported catalyst provides high amounts of HCOL, but when mixed with Ti, the selectivity towards this product decreases significantly, increasing the selectivity to the desired COL. This may be explained by the occurrence of two effects: (i) the structure created between Ce and Ti when prepared together enhances the strong metal-support interaction (SMSI) effect resulting from the migration of reduced CeO_x and TiO_x species onto the Pt particles. The occurrence of the SMSI effect is well known in Pt/ CeO_2 and Pt/ TiO_2 catalysts reduced at high temperatures [24] and affects the interaction between the metal and the oxygen atom in the carbonyl group of unsaturated aldehydes, activating and weakening the C=O bond, enabling its preferential hydrogenation [21, 23]; (ii) the higher Pt particle size in Pt/Ce-Ti-O catalysts, which promotes the preferential hydrogenation of the C=O bond [14]. Therefore, it can be concluded that the combination of Ce with Ti increases the conversion of CAL and the selectivity towards COL, being possible to enhance the catalytic performance of the catalyst.

7.4 Conclusions

The solvothermal method affected the crystalline structure of the CeO_2 . While CeO_2 was essentially crystalline (particles with sizes *ca.* 3-8 nm), Ce-Ti-O supports were mostly amorphous, with some CeO_2 crystalline nanoparticles dispersed over the materials. This was probably due to the replacement of some Ce^{4+} by Ti^{4+} .

The photochemical deposition led to the dispersion of Pt particles with 2.5 to 6.5 nm sizes in a 5 wt. % Pt catalyst. The size was corroborated by diffraction analysis within the error of experimentation.

An enhancement of the catalytic activity in the cinnamaldehyde hydrogenation and higher selectivities towards cinnamyl alcohol were observed for Ce-Ti-O supported catalysts, in comparison with the single CeO_2 .

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8. Nanostructured ZnO supported platinum catalysts by chemical vapor deposition

The performance of ZnO prepared by chemical vapor deposition as support for Pt catalysts is compared with other commercially available ZnO samples. The catalysts are thermally treated in N₂ and H₂ at 500°C and tested in the hydrogenation of cinnamaldehyde, at 90°C and 10 bar. The treatments performed to the Pt/ZnO catalysts, combined with the high reducibility of the support, results in a PtZn alloy formation, confirmed by X-ray diffraction measurements. The high selectivities towards cinnamyl alcohol are ascribed to the alloy formation and specific metal-support interactions.

8.1 Introduction

In recent years, synthesis of nanoscaled inorganic semiconductors with specific size and morphology has attracted a lot of interest due to the potential applications in various fields. Zinc oxide (ZnO), a semiconductor with a band gap of 3.37 eV at room-temperature, is one of the most promising materials for applications in electronics, photoelectronics and sensors [1-4]. The production of nanostructured materials emphasizes not only the extremely small size, geometry and chemical homogeneity, but also the simplicity and practicability of the synthesis technique. Various nanostructures of ZnO including nanowires, nanotubes, nanobelts, nanorings and star-shaped nanostructures have been synthesized and investigated by a variety of techniques [3, 5-10].

The selective hydrogenation of the carbonyl bond in α,β -unsaturated aldehydes with supported metal catalysts is still a challenge with heterogeneous catalysts. The support can affect the catalytic behavior of the noble metal through several mechanisms. It is widely reported that some oxide supports can provide the desired promotion of Pt [11]. The possible interaction of Pt with the partially reduced oxide [12-16], or even with the metal formed upon a reduction treatment [17, 18], has been proposed to be responsible for the improved selectivity, when compared with other Pt catalysts. In fact, when a Pt/ZnO catalyst is reduced in hydrogen flow above 400°C a significant reduction of ZnO is observed, along with the formation of PtZn intermetallic alloys generated by the interaction of reduced Zn with metallic Pt [19-21]. The electronic effects are due to free electrons produced upon the partial reduction of ZnO to Zn, these free electrons being donated to Pt [22]. If the Pt atom is electron-rich, it repels the electrons of the C=C bond while it is attracted by the electropositive carbon of the C=O bond and the electronegative oxygen atom is bonded to the electropositive Zn atom.

In this final chapter, some preliminary results using ZnO supported Pt catalysts are reported. A ZnO prepared by CVD is compared with two other commercially available samples as supports for Pt-containing catalysts in the selective hydrogenation of cinnamaldehyde.

8.2 Experimental

8.2.1 Support preparation

The Zn metal powder (325 mesh size) was placed in an alumina sample holder inside a horizontal quartz reactor at 900°C (Figure 8.1). The metal was then allowed to melt under argon atmosphere. During this period of time the furnace temperature decreased *ca.* 20°C. After the temperature was re-stabilized at 900°C, air was introduced in counter-current (temperature measured at this point was 410°C) in the furnace and the argon flow was increased. The oxidized zinc vapor gave rise to thick white fumes that coalesce to form small white flakes. The as obtained material was collected using a trap cooled with liquid nitrogen. It was seen that a value around 50-70% of the total ZnO could be collected at these traps (ZnO_{CVD}). The remaining material was accumulated at the reactor walls. During the ZnO formation a bright green thermo luminescence was seen in the mixing zone. The material was used as collected without any further treatment. Additional details regarding the preparation of ZnO can be found elsewhere [23].

Two commercial ZnO samples were used for comparison purposes: one purchased from Strem Chemicals (ZnO_{SC}; 85-95% ZnO, 3-7% Al₂O₃, 0.5-3% CaO) and another from Evonik (ZnO_{EV}; AdNano VP 20, aggregated nanoparticles of hydrophilic ZnO).

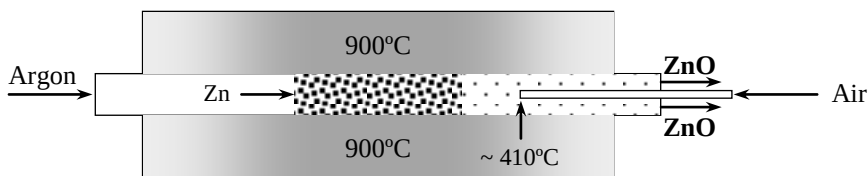


Figure 8.1 Scheme of the reactor used for the ZnO synthesis by CVD (adapted from [23]).

8.2.2 Catalyst preparation and characterization

The photochemical deposition procedure used to introduce 5 wt. % Pt was identical to that described in Chapter 6, section 6.2.2. The as-obtained catalysts are referred to as 5Pt/ZnO*. The catalysts were thermally treated in H₂ at 500°C (5Pt/ZnO) according to the method also described in section 6.2.2.

The textural properties of the prepared materials were determined from the nitrogen adsorption-desorption isotherms, measured at -196°C using a Quantachrome NOVA 4200e multi-station system. Their surface areas were calculated by the BET method in the relative pressure range from 0.05 to 0.20. XRD and TEM analysis were carried out in

the same apparatus and conditions previously described in Chapter 6 section 6.2.2 and Chapter 2, section 2.2.2, respectively.

Scanning electron microscopy (SEM) was performed in a Jeol JSM6700F with a field emission gun (SEM-FEG) and an accelerating voltage of 5 kV.

8.2.3 Selective hydrogenation procedure

The hydrogenation procedure was identical to that already described in Chapter 2, section 2.2.3.

8.3 Results and discussion

8.3.1 ZnO

Figure 8.2 shows the nitrogen adsorption-desorption isotherms measured at -196°C , for the synthesized and commercial ZnO supports.

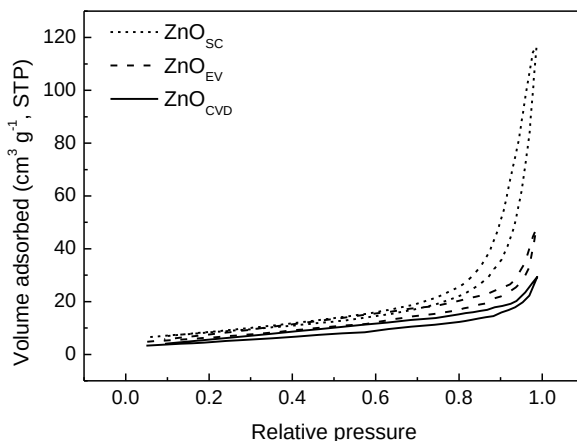


Figure 8.2 Nitrogen adsorption-desorption isotherms at -196°C for ZnO.

Commonly to most ZnO samples reported in the literature, the materials tested in this study also revealed a rather low specific surface area. The highest area of $30\text{ m}^2\text{ g}^{-1}$ was measured for sample ZnO_{SC} , whereas sample ZnO_{CVD} showed the lowest value ($17\text{ m}^2\text{ g}^{-1}$). An intermediate result was obtained for ZnO_{EV} with $22\text{ m}^2\text{ g}^{-1}$. The surface area and morphology of the ZnO prepared by CVD was previously found to depend on the oxidation temperature [23]. Accordingly, at low temperatures ($200\text{--}300^{\circ}\text{C}$) small

spherical particles with decreased surface areas are produced, while at high temperatures ($> 400^{\circ}\text{C}$) a change in the growth mechanism was reported and rods with higher surface areas were obtained.

X-ray powder diffractograms of ZnO supports are shown in Figure 8.3.

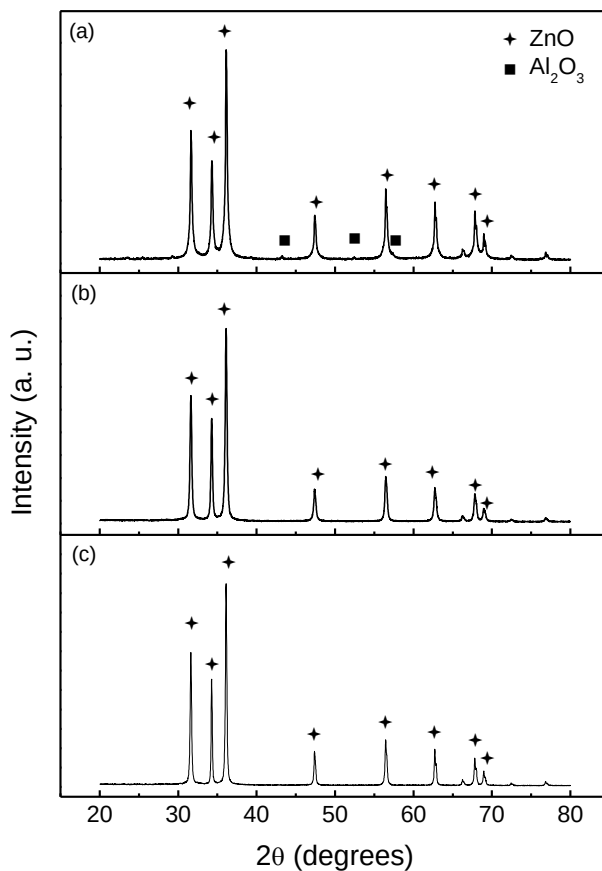


Figure 8.3 X-ray diffraction patterns of ZnO: (a) ZnO_{SC} , (b) ZnO_{EV} and (c) ZnO_{CVD} .

The XRD results show the existence of a hexagonal structure (JCPDS 70-8072) for all the ZnO samples. Additionally, in agreement with the manufacturer information, the presence of an Al_2O_3 phase was also detected for ZnO_{SC} (JCPDS 88-0826). No crystalline impurities were observed with the other ZnO samples.

The structural differences between ZnO_{EV} and ZnO_{CVD} are evidenced in the scanning electron micrographs depicted in Figure 8.4.

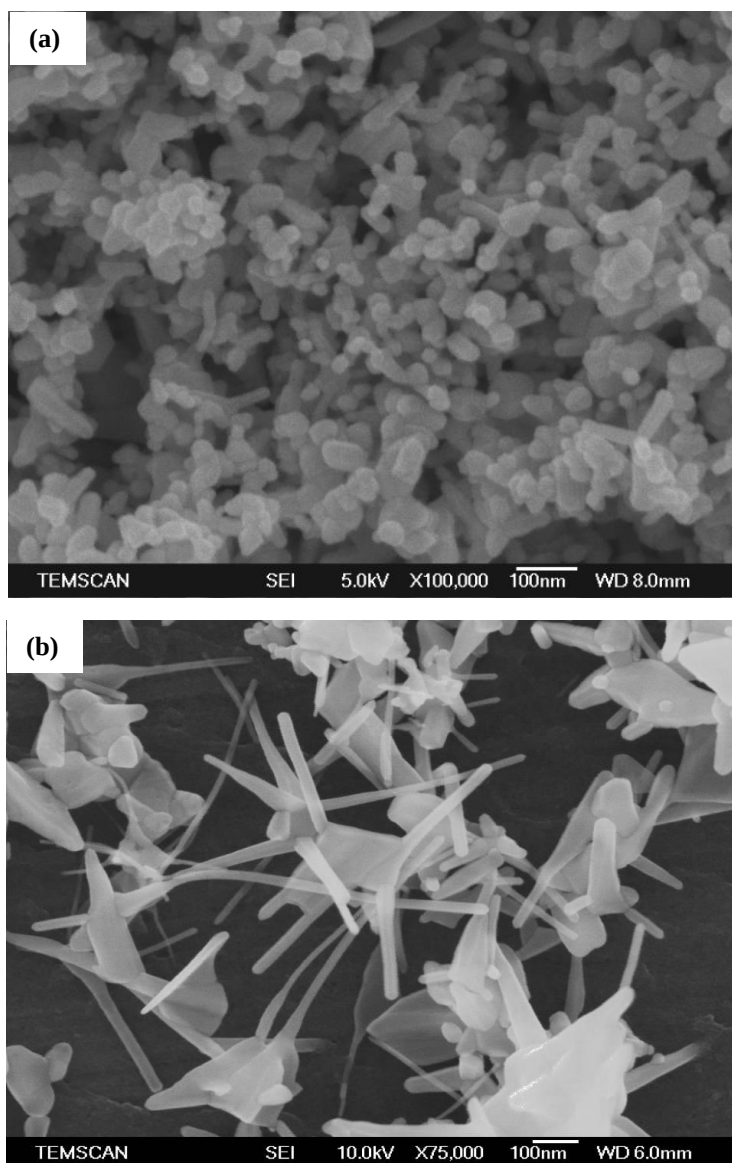


Figure 8.4 SEM micrographs of ZnO: (a) ZnO_{EV} and (b) ZnO_{CVD}.

The commercial ZnO sample from Evonik (ZnO_{EV}) consists mainly of small cylindrical-shaped particles (Figure 8.4a), whilst the ZnO_{CVD} sample is composed of tetrapod-like structures, where needles grow from a faceted seed particle [23]. The nanorods have diameters varying up to tens of nanometers and growing over 1 μm in length (Figure 8.4b).

8.3.2 Pt/ZnO

Figure 8.5 shows XRD patterns of ZnO supported Pt catalysts before (Figure 8.5a to c) and after (Figure 8.5d to f) thermal treatment in H_2 at 500°C in the 2θ range of 20 – 80° .

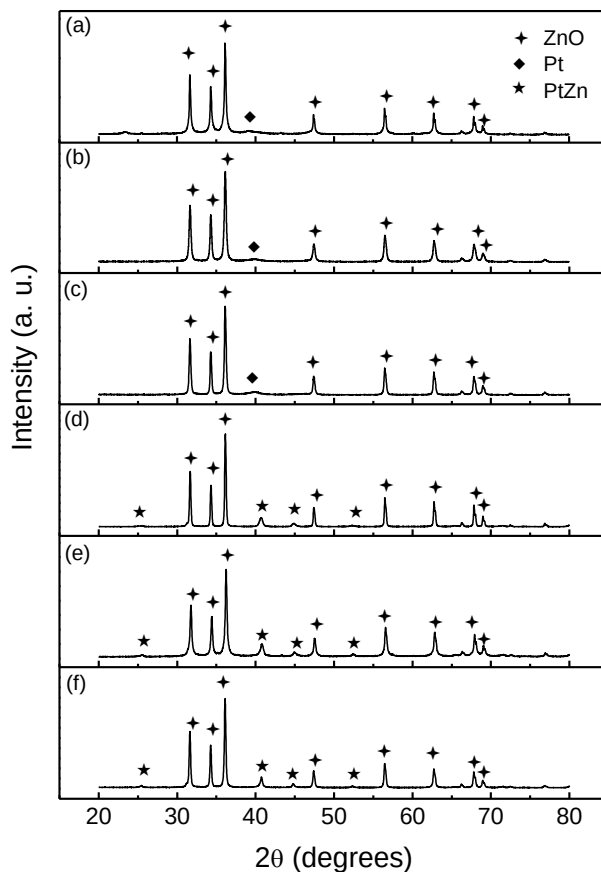


Figure 8.5 X-ray diffraction patterns of ZnO supported Pt catalysts: (a) 5Pt/ZnO_{SC}*, (b) 5Pt/ZnO_{EV}*, (c) 5Pt/ZnO_{CVD}*, (d) 5Pt/ZnO_{SC}, (e) 5Pt/ZnO_{EV} and (f) 5Pt/ZnO_{CVD}.

XRD patterns of 5Pt/ZnO catalysts show the presence of hexagonal ZnO (JCPDS 70-8072). The reflections for Pt were only observed at $2\theta = 39.7^\circ$ (111) for thermally untreated catalysts (5Pt/ZnO*), with no other characteristic peak being detected (JCPDS 87-0646). Noteworthy, is the fact that no Pt peaks are visible in the 5Pt/ZnO catalysts thermally treated at 500°C . In this case, only the presence of a tetragonal PtZn alloy (JCPDS 6-0604) was detected. This result is in agreement with that reported by Consonni *et al.* [21]. They observed that when a Pt/ZnO catalyst was treated in H_2 at

temperatures higher than 400°C, the Pt peaks disappeared, giving rise to those attributed to a PtZn alloy. A characteristic peak of this phase can be seen in the region $2\theta = 40.7^\circ$ corresponding to the PtZn(111) plane. The particle size calculated using the Scherrer equation (Eq. 6.1) based on this reflection is shown in Table 8.1. The same table also shows the Pt load determined by ICP and the PtZn particle size determined by TEM.

Table 8.1 Pt load (y_{Pt}) and PtZn particle size (d_{PtZn}) for ZnO supported catalysts.

Catalyst	y_{Pt} (wt. %)	$d_{\text{PtZn}}^{\dagger}$ (nm)	d_{PtZn}^* (nm)
Pt/ZnO _{SC}	4.7	13.1	1.8
Pt/ZnO _{EV}	4.5	22.9	3.7
Pt/ZnO _{CVD}	3.4	14.4	3.4 and 25

[†]calculated using XRD; *determined by TEM analysis.

TEM micrographs of the catalysts were acquired after reduction at 500°C and are shown in Figure 8.6. Darker zones in the micrographs represent PtZn particles, whereas lighter areas correspond to the ZnO support. Particles over ZnO_{SC} were very homogeneously disperse and uniform in size (Figure 8.6a). For Pt/ZnO_{EV} the particle sizes are slightly bigger than that observed for Pt/ZnO_{SC} (Figure 8.6b). The ZnO_{CVD} supported catalyst showed two types of particles: some smaller ones (Figure 8.6c) with sizes similar to those observed in Pt/ZnO_{EV}, together with much larger ones, in the range of 25 nm (Figure 8.6d). Comparing the metal particle size determined by TEM with that obtained by XRD, it can be seen that the latter presents larger values. Similarly to what was described in Chapter 6, section 6.3.2, the particle size obtained using XRD measurements seems to be greatly overestimated due to the small particle size of the active phase. Another fact that could be playing a role on the difference of Pt particle sizes between both techniques could be the existence of an alloyed phase.

A comparison between the ZnO surface area and the Pt particle size determined by TEM reveals a direct relation between increasing surface area and higher metal dispersions. Given the low surface area of ZnO samples and the relative high metal loading (5 wt. %) it could be expected somewhat bigger Pt particles. The fact that high metal dispersions are obtained validates the photochemical deposition as an efficient impregnation technique to achieve high Pt dispersions over ZnO supports.

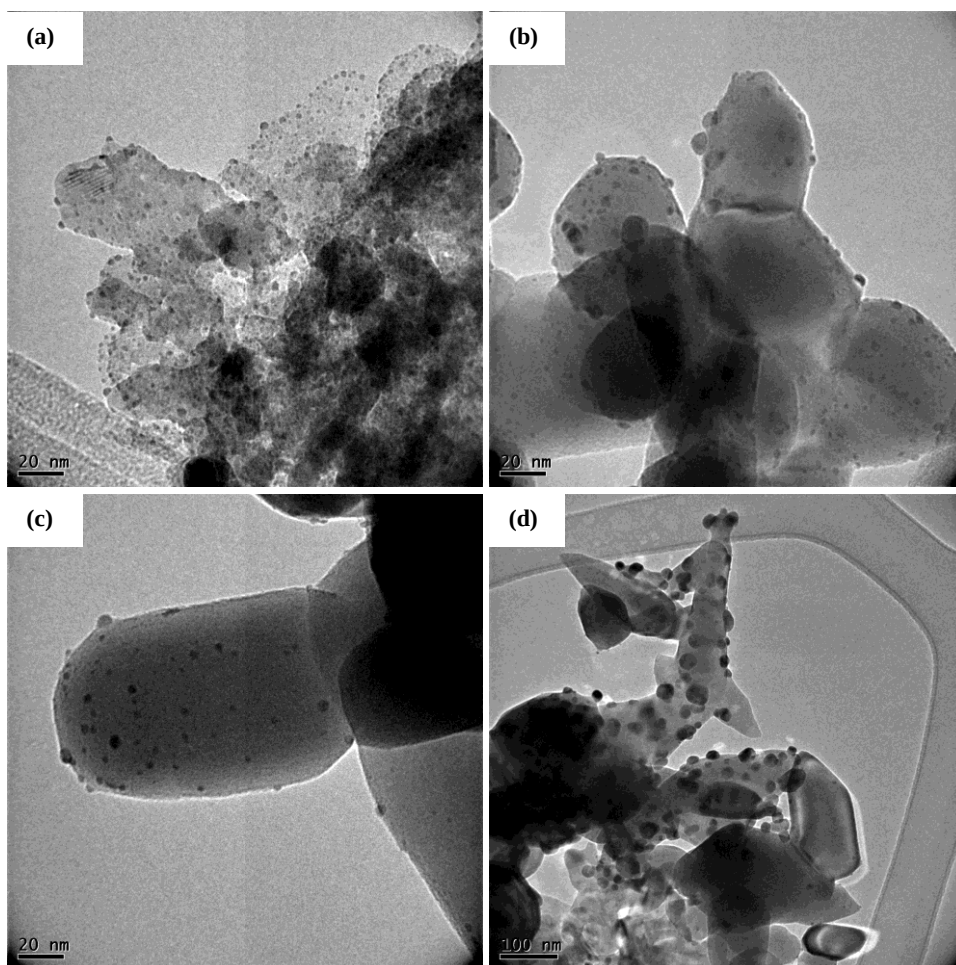


Figure 8.6 HRTEM micrographs of Pt catalysts supported in: (a) ZnO_{SC}, (b) ZnO_{EV}, (c) ZnO_{CVD} with small Pt particles and (d) ZnO_{CVD} with large Pt particles.

Also visible in the TEM micrographs, is the structure modification of the supports regarding the initial materials. In this case, the original shape of the ZnO samples is somehow compromised, with some structure degradation being visible (round particles). A possible explanation for this could be due to the PtZn alloy formation. During the thermal treatment in H₂ at 500°C, the ZnO lattice loses oxygen in the vicinities of Pt atoms; the Zn binds to Pt to form an alloy and possibly alters the support structure.

In the previous chapters, no changes in the structure of the support were detected. This could mean that ZnO is more easily reducible (by H₂) than the TiO₂ and CeO₂ supports.

8.3.3 Selective hydrogenation of cinnamaldehyde

The cinnamaldehyde hydrogenation reaction scheme observed when using ZnO supported Pt catalysts is simpler when compared to those observed in the previous chapters. In this case, only the three main reaction products were detected (Figure 8.7). A possible explanation could be the lower catalytic activity observed with Pt/ZnO catalysts.

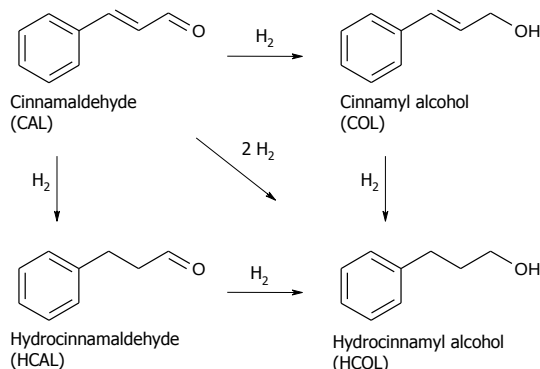


Figure 8.7 Reaction scheme for the selective hydrogenation of cinnamaldehyde using ZnO supported Pt catalysts.

The reaction results obtained at 90°C and 10 bar are gathered in Table 8.2.

Table 8.2 Catalytic results obtained in the liquid-phase hydrogenation of cinnamaldehyde with ZnO supported Pt catalysts (at 50% conversion).

Catalyst	TOF ($\times 10^2 \text{ s}^{-1}$)	Selectivity (%)		
		COL	HCAL	HCOL
Pt/ZnO _{SC}	5.2	69	17	14
Pt/ZnO _{EV}	2.1	83	8	9
Pt/ZnO _{CVD} *	0.8	71	17	12

*obtained at 20% conversion of cinnamaldehyde, after 600 min.

A full conversion of cinnamaldehyde was never observed for any of the tested catalysts. The Pt/ZnO_{SC} evidenced the highest conversion level, 98%, after 10 hr, whereas Pt/ZnO_{EV} converted *ca.* 55% during the same period of time. The conversion observed with the ZnO_{CVD} supported catalyst was only *ca.* 20%. These low activities are explained in terms of low catalyst dispersibility within the reaction solvent (heptane). Even after an ultrasonic treatment, the catalyst would almost immediately deposit in the bottom of the flask. This was especially visible for Pt/ZnO_{CVD} catalyst and to a lower extent for Pt/ZnO_{EV}. For the Pt/ZnO_{SC} catalyst this effect was hardly noticeable. During

the reaction, the catalyst was found to remain at the bottom and attached to the flask walls. Hence, significant mass transfer limitations might be responsible for the low activities detected. In addition, the catalyst is also subjected to a mechanical grinding effect by the magnetic stirrer, which could also result in a degradation of the catalytic properties of the material. Given the long rods present in ZnO_{CVD} , the attrition could easily result in the destruction of the structure. Reactions performed in an alcohol-based solvent could partially overcome this limitation, since the ZnO dispersions are found to be quite stable under these conditions [23]. However, this was not attempted in this preliminary study.

Regardless of the low activities observed, all the materials selectively catalyzed the formation of cinnamyl alcohol and thus, good selectivities were achieved. A value as high as 83%, at 50% conversion, was observed for $\text{Pt}/\text{ZnO}_{\text{EV}}$. The other two catalysts exhibited very similar behaviors with *ca.* 70% selectivity towards cinnamyl alcohol.

Figure 8.8 shows the concentration evolution with time for the $\text{Pt}/\text{ZnO}_{\text{EV}}$ catalyst. It can be seen that cinnamaldehyde is readily converted to cinnamyl alcohol, while the other hydrogenation products are hardly detected.

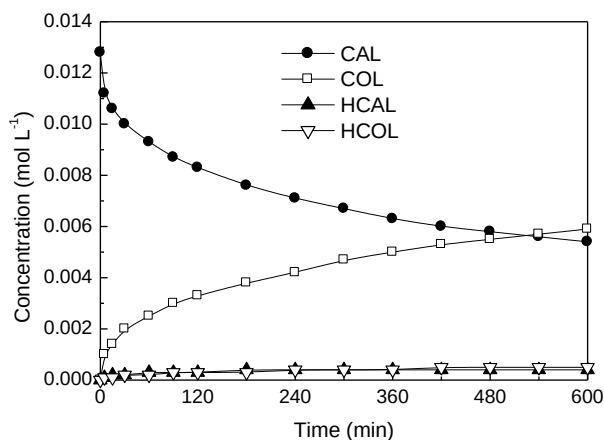


Figure 8.8 Product distribution for the selective hydrogenation of cinnamaldehyde using the $\text{Pt}/\text{ZnO}_{\text{EV}}$ catalyst.

The high selectivities exhibited by Pt/ZnO catalysts are generally attributed to either the strong interaction between the metal and the support or to the electronic donating interaction of the metallic Zn to the Pt (PtZn alloy). Both of these effects result in a lower interaction of the olefinic double bond of the aldehyde with the catalyst [19-22] and thus, favor the adsorption and respective hydrogenation through the carbonyl group.

Consonni *et al.* [21], studying crotonaldehyde hydrogenation, reported that the Pt sites, when alloyed to Zn, form $\text{Pt}^{\delta-}\text{-Zn}^{\delta+}$ entities, enabling an identical reaction mechanism to that described when a promoter is used. These entities would not adsorb the crotonaldehyde molecule through binding to the olefinic bond but rather through binding to the carbonyl bond. If the Pt atoms are electron-rich, they repel the electrons of the C=C bond while attracting the electropositive carbon of the C=O bond and the electronegative oxygen atom is bonded to the electropositive Zn atom. In this case, the formation of a PtZn alloy was clearly observed in XRD spectra, and thus is thought to play a key role in the high selectivities detected.

8.4 Conclusions

The CVD method led to materials with lower surface area when compared to other commercial ZnO samples. The surface area depended on the oxidation temperature and reflected the difference in the particle shape – there was a shape transition between 300 and 400°C.

The crystal phase was similar in all the studied materials suggesting that the basic units of the crystal matrix are common to the three samples. On a different level, it is possible to recognize variable geometries on particle size and shape.

After photodeposition of Pt, the commercial supports were found to distribute much more effectively the active metal than the one prepared by CVD, providing materials with smaller particle sizes.

A thermal treatment of the Pt/ZnO catalysts at 500°C induced a support modification. The absence of isolated Pt signals and the presence of PtZn in XRD patterns suggested a strong interaction within the two metals to form an alloy. The existence of this alloy was attributed to a high ZnO reducibility.

The low conversion levels observed during cinnamaldehyde hydrogenation were thought to be related with strong external mass transfer limitations, since these materials exhibited low dispersibility in the reaction solvent.

In spite of the low activity, catalysts were still able to selectively produce higher amounts of the unsaturated alcohol. The high selectivities towards cinnamyl alcohol were ascribed to an enhanced metal-support interaction favored by the PtZn alloy formation.

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CONCLUSIONS AND FUTURE WORK

In this section a brief summary of the main results is shown and some conclusions are drawn. Additionally, some guidelines for future work are suggested.

Different supports were used to prepare monometallic catalysts that were characterized throughout each chapter of this dissertation. Platinum was, in most cases, the preferred metal, but other active metals like Ir or Ru were also studied. The selective hydrogenation of cinnamaldehyde to cinnamyl alcohol was chosen as model reaction to assess the performance of the prepared catalytic systems.

Carbon materials. Three different approaches were attempted for MWCNT activation, which modify its surface chemistry and morphology: liquid-phase activation with nitric acid, gas-phase activation with air and mechanical activation with ball milling. Activation with pure nitric acid created large amounts of carboxylic acid groups without any significant damage of MWCNT surface structure. Air oxidation, on the other hand, was found to affect MWCNT structure and introduced moderate amounts of oxygen functionalities, mainly phenol and carbonyl/quinone groups. Finally, ball-milling in air was able to open some MWCNTs while introducing very little amounts of oxygenated groups. The latter affected mainly the MWCNT length.

The amount of Pt loaded, and the corresponding metal dispersion over each activated support were successfully correlated with the amount of oxygenated groups present at the surface of the MWCNTs. Carboxylic acid groups were particularly efficient in anchoring the organometallic Pt precursor. A thermal treatment at 700°C yielded to catalysts with various degrees of sintering, which were dependant on the length of the MWCNT.

The presence of oxygenated functionalities in the final catalyst was found to have a negative influence on the selectivity for the hydrogenation of cinnamaldehyde to cinnamyl alcohol. The high temperature thermal treatment at 700°C was found to remove most surface groups while increasing the Pt particle size. Pt supported on MWCNTs treated with nitric acid evidenced the best thermal stability, with the lowest sintering effect being observed.

Selectivity towards cinnamyl alcohol was found to increase significantly after the thermal treatment, regardless of the type of functionalization of the MWCNT. Both the Pt particle size increase and the surface group removal were thought to be responsible for the improved selectivity results, favoring a preferential adsorption through the carbonyl group.

MWCNT supported catalysts prepared with Pt and Ir organometallic precursors by wet impregnation presented excellent thermal stability and small metal particles. Higher metal loads increased the sintering effect, after a thermal treatment of the catalysts at 700°C.

The stability of the MWCNT under oxidative atmosphere was decreased upon nitric acid activation. This effect was enhanced by the presence of supported metals; the gasification temperature depended on the load, but not on the nature of the metal.

The liquid-phase hydrogenation of cinnamaldehyde was very much influenced by the thermal treatment performed to the catalysts at 700°C. Untreated catalysts evidenced high selectivities towards the production of hydrocinnamaldehyde. After the thermal treatment, MWCNT supported Pt particles with 2 nm were quite selective towards the production of cinnamyl alcohol; catalysts containing Ir particles with 1 nm were also extremely selective to the same product. Unlike many results in the literature, it was here proved that high selectivities towards the unsaturated alcohol can also be obtained with very small metal particles supported in MWCNTs.

The preferential reduction of the carbonyl group seemed to be more affected by the surface chemistry of the support rather than the metal particle size. This behavior was attributed to a strong interaction between the metal and the graphite sheets, after surface group removal.

Contrarily to MWCNTs, the development of oxygenated functionalities in the CX surface compromised the initial porous structure to yield a practically non-porous material, with a low surface area. However, the amount of surface groups introduced in the CX was much higher than that obtained for MWCNT.

Wet impregnation of Pt, Ir and Ru organometallic precursors over the activated CX produced catalysts with small metal particles: 3 nm for Pt and around 2 nm for Ir and Ru. A post-reduction thermal treatment at 700°C of the catalysts led to various degrees of sintering, mainly dependant on the nature of the active metal-phase.

The same thermal treatment also influenced the catalyst performance in the liquid-phase hydrogenation of cinnamaldehyde, pushing the selectivity towards cinnamyl alcohol, regardless of the metal nature. CX supported Pt catalysts were found to be more selective towards the preferential hydrogenation of the carbonyl group, followed by Ir and finally Ru ones.

The hydrogenation of cinnamaldehyde, under the studied conditions, did not depend on the structure of the support, since both MWCNT and CX presented a similar catalytic behavior.

Macro or mesoporous carbon aerogels were obtained depending on the type of polymerization catalyst used. Oxidation treatments with hydrogen peroxide and ammonium peroxydisulfate allowed the porous structure to remain relatively unchanged

while introducing significant amounts of oxygenated groups. The acidic character of most groups led to a strong decrease of the pH_{PZC} of the support surface.

The Pt dispersion over the aerogels was strongly influenced by the chemical modifications, decreasing in all cases after oxidation treatments. The surface acidity of the support was determinant for a higher selectivity towards cinnamyl alcohol. In all cases, a thermal treatment at 700°C favored the hydrogenation of the C=C bond.

Metal oxides. TiO_2 anatase was produced through the sol-gel method resulting in particles with an average size of 9.7 nm. This non-porous material had a specific surface area of $100 \text{ m}^2 \text{ g}^{-1}$. The photochemical deposition method resulted in Pt nanoparticles in the range of 4 nm, regardless of the TiO_2 surface area and type of crystalline phase present. The method proved to be very simple and effective.

A thermal treatment of Pt/ TiO_2 catalysts at 500°C induced an anatase to rutile transformation of the support. However, it did not induce a significant sintering of the Pt particles.

In metal oxides, the determination of Pt particle size by different techniques was not straightforward due to the interface of the support. Especially indirect measurements such as H_2 chemisorption need to be regarded with caution.

There was no relation between activity and selectivity for the average Pt particle size of 4 nm. Activity/selectivity performances were more related to the nature of the support. Thus, commercial TiO_2 P-25 produced the most active catalyst with a reasonable selectivity. The sol-gel TiO_2 calcined at 400°C produced the most selective catalysts with a reasonable activity. The maximum production of cinnamyl alcohol for this catalyst was achieved at 91% conversion of the initial substrate in less than 30 min of reaction.

The sol-gel based TiO_2 proved to be extremely efficient in the selective reduction of the carbonyl group, when compared with several other commercially available samples. The results were thought to be associated with an enhanced SMSI effect over the synthesized material. The sol gel approach demonstrated to have an important impact on the preparation of new highly selective hydrogenation catalysts.

The reaction operating conditions used in this work (especially the pressure of 10 bar) were milder than those reported in the literature (pressures up to 50 bar or sometimes above).

CeO₂ with different crystalline structures were produced by the solvothermal method. While CeO₂ was essentially crystalline (particles with sizes *ca.* 3-8 nm), Ce-Ti-O supports were mostly amorphous, with some CeO₂ crystalline nanoparticles dispersed over the materials. This was probably due to the replacement of some Ce⁴⁺ by Ti⁴⁺.

The photochemical deposition led to the dispersion of Pt particles with 2.5 to 6.5 nm sizes in a 5 wt. % Pt catalyst. The size was confirmed by diffraction analysis within the error of experimentation.

The enhancement of the catalytic activity in the cinnamaldehyde hydrogenation and higher selectivities towards cinnamyl alcohol were observed for Ce-Ti-O supported catalysts, in comparison with the single CeO₂.

The CVD method produced ZnO materials with lower surface area when compared with other commercial samples. The surface area depended on the oxidation temperature and reflected the difference in shape of the particles – there was a shape transition between 300 and 400°C.

The crystal phase was similar in all the studied materials suggesting that the basic units of the crystal matrix were common to the three samples. On a different level, it was possible to recognize variable geometries on particle size and shape.

After photodeposition of Pt, the commercial ZnO supports were found to disperse much more effectively the active metal than that prepared by CVD, providing materials with smaller particle sizes.

A thermal treatment at 500°C to the Pt/ZnO catalysts induced a support modification. The absence of isolated Pt signals and the presence of PtZn in XRD patterns suggested a strong interaction within the two metals to form an alloy. The existence of this alloy was attributed to a high ZnO reducibility.

The low conversion levels observed during cinnamaldehyde hydrogenation using Pt/ZnO were thought to be related with strong mass transfer limitations, since these materials exhibited low dispersibility in the reaction solvent.

In spite of the low activity, catalysts were still able to selectively produce higher amounts of the unsaturated alcohol. The high selectivities towards cinnamyl alcohol were ascribed to an enhanced metal-support interaction favored by the PtZn alloy formation.

Concluding remarks. In summary, most of the prepared catalysts have been successfully tested in the hydrogenation of cinnamaldehyde to cinnamyl alcohol. The complexity of the mechanisms involved to selectively produce high amounts of the unsaturated alcohol varies with the nature of the support. However, a common point can be identified: a closer interaction between the active metal phase and the support, especially from an electronic point of view, can bring enormous benefits; in carbon materials this is often achieved by proper functionalization treatments, whereas for reducible metal oxides a thermal treatment in H_2 is usually sufficient to shift the selectivity towards the desired, and economically more interesting, unsaturated alcohol.

Future work. Some suggestions for future work are presented over the next paragraphs. Some are based in successful exploratory experiments not described in this thesis, others may be a little speculative.

The use of composites often allows the development of new materials with improved properties regarding the original ones. In order to take advantage of the unique properties of reducible metal oxides and high surface area and electron density from carbon materials, a new composite material able to support different metals should provide some interesting results. Exploratory screening tests were performed with Pt supported in a TiO_2 -C composite material.

The support was prepared using the sol-gel approach described in Chapter 6. As carbon-phase, xerogels and multi-walled carbon nanotubes with different surface chemistries (gas- and liquid-phase activation) were used and added in different proportions.

Some promising results were observed with the addition of small amounts of carbon-phase (ca. 1 wt. %), improving the selectivity results regarding the naked TiO_2 material. Further addition of carbon to the TiO_2 matrix, had a negative impact on both the activity and the selectivity. As the amount of carbon in the composite increased, so did the probability that, during the photodeposition process, Pt was supported on the carbon phase instead of on the TiO_2 . Since the metal interaction was stronger with the TiO_2 phase, this could decrease the extent of the SMSI effect and, consequently, produce lower yields of unsaturated alcohol.

Solvent free reactions are highly desirable, especially from the environmental point of view. Hence, a system capable of performing selective hydrogenations in the absence of a solvent should be studied. Since most aldehydes exist in the liquid-phase, they could be used simultaneously as a reactant and as a solvent. This would require the reaction volume to be somewhat lower than that studied for this work (80 mL). The current

experimental setup could be adapted to these conditions by building a glass or Teflon liner that would reduce the internal diameter of the reactor, and hence its volume.

The use of different organic substrates like citral (whose literature is not as extensive as cinnamaldehyde or crotonaldehyde) should provide a comparison for the prepared catalytic materials. The current setup is only limited by the chromatographic column: although adequate to the separation of the cinnamaldehyde hydrogenation products, is not suitable to separate all the products obtained in the hydrogenation of citral (minimum of 7 different products can be obtained simultaneously).

LIST OF PUBLICATIONS & COMMUNICATIONS

During this Ph.D. a great part of the work was successfully published, resulting in some papers and many communications submitted to national and international conferences. In the following pages a complete list of these publications can be found.

Papers Published in International Journals with Referees

A. Solhy, **B.F. Machado**, J. Beausoleil, Y. Kihn, F. Gonçalves, M.F.R. Pereira, J.J.M. Órfão, J.L. Figueiredo, J.L. Faria, P. Serp, MWCNT activation and its influence on the catalytic performance of Pt/MWCNT catalysts for selective hydrogenation, *Carbon* 46 (2008) pp. 1194-1207.

Papers in Preparation or Submitted

B.F. Machado, H.T. Gomes, P. Serp, P. Kalck, J.L. Faria, Liquid phase hydrogenation of unsaturated aldehydes: Enhancing selectivity of MWCNT catalysts by thermal activation (in preparation).

B.F. Machado, H.T. Gomes, P. Serp, P. Kalck, J.L. Figueiredo, J.L. Faria, Carbon xerogel supported noble metal catalysts for fine chemical applications, *Catalysis Today* (in preparation).

B.F. Machado, H.T. Gomes, P.B. Tavares, J.L. Faria, Preparation on nanostructured TiO₂ supported platinum catalysts by photochemical deposition (in preparation).

A.M.T. Silva, **B.F. Machado**, H.T. Gomes, J.L. Figueiredo, G. Dražić, J.L. Faria, Pt nanoparticles supported over Ce-Ti-O: The solvothermal and photochemical approaches on the preparation of catalytic materials, *Journal of Nanoparticle Research* (submitted).

Papers in Conference Proceedings

B.F. Machado, S. Morales-Torres, H.T. Gomes, A.F. Pérez-Cadenas, F.J. Maldonado-Hódar, F. Carrasco-Marín, J.L. Figueiredo, J.L. Faria, Carbon aerogel supported platinum catalysts for selective hydrogenation of cinnamaldehyde, ChemPor 2008 - X International Chemical and Biological Engineering Conference, Braga (Portugal), Ed. CD-ROM (2008) pp. 901-906.

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Abstracts in National and International Conferences

B.F. Machado, A. Solhy, J. Beausoleil, Y. Kihn, F. Gonçalves, M.F.R. Pereira, J.J.M. Órfão, J.L. Figueiredo, J.L. Faria, P. Serp, Pt/MWCNT catalysts for the selective hydrogenation of cinnamaldehyde: Influence of surface modifications of the support, II European Chemistry Congress, Torino (Italy), 16-20 September 2008 (poster).

Abstracts in National and International Conferences (cont.)

B.F. Machado, S. Morales-Torres, H.T. Gomes, A.F. Pérez-Cadenas, F.J. Maldonado-Hódar, F. Carrasco-Marín, J.L. Figueiredo, J.L. Faria, Carbon aerogel supported platinum catalysts for selective hydrogenation of cinnamaldehyde, ChemPor 2008 - X International Chemical and Biological Engineering Conference, Braga (Portugal), 4-6 September 2008, pp. 372-373 (poster).

B.F. Machado, H.T. Gomes, P. Serp, P. Kalck, J.L. Figueiredo, J.L. Faria, Carbon xerogel supported noble metal catalysts for fine chemical applications, XXI Ibero-American Symposium of Catalysis, Malaga (Spain), 22-27 June 2008, p. 129 (oral).

B.F. Machado, H.T. Gomes, J.L. Faria, Titanium dioxide supported Pt catalysts for cinnamaldehyde hydrogenation, XXI National Meeting of Portuguese Chemical Society, Porto (Portugal), 11-13 June 2008, p. 89 (poster).

A.M.T. Silva, **B.F. Machado**, H.T. Gomes, J.L. Figueiredo, G. Dražić, J.L. Faria, Photodeposition of Pt nanoparticles on Ce-Ti-O, XXI National Meeting of Portuguese Chemical Society, Porto (Portugal), 11-13 June 2008, p. 90 (poster).

B.F. Machado, H.T. Gomes, P. Serp, P. Kalck, J.L. Faria, Liquid-phase hydrogenation of unsaturated aldehydes: Enhancing selectivity of MWCNT catalysts by thermal activation, NanoSpain2008, Braga (Portugal), 14-18 April 2008 (poster).

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B.F. Machado, H.T. Gomes, P. Serp, P. Kalck, J.L. Figueiredo, J.L. Faria, High temperature activation of noble metal catalysts supported on carbon multi-walled nanotubes for selective hydrogenation of unsaturated aldehydes, EuropaCat VIII, Turku (Finland), 26-31 August 2007, O5-10 (oral).

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Abstracts in National and International Conferences (cont.)

B.F. Machado, H.T. Gomes, J.L. Faria, Preparation on nanostructured TiO₂ supported platinum catalysts by photochemical deposition, I International School on Applied Catalysis and IX Italian Seminar on Catalysis 2007, Bari (Italy), 3-9 June 2007, p. 58 (poster).

B.F. Machado, H.T. Gomes, P. Serp, P. Kalck, J.L. Faria, Carbon nanotubes supported catalysts for selective hydrogenation of unsaturated aldehydes, XX National Meeting of Portuguese Chemical Society, Lisbon (Portugal), 14-16 December 2006, p. 242 (poster).

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J.L. Faria, **B.F. Machado**, H.T. Gomes, P. Serp, P. Kalck, Carbon supported noble metal catalysis prepared by photochemical deposition, CarboCat-II - II International Symposium on Carbon for Catalysis, St. Petersburg (Russia), 11-13 July 2006, pp. 50-51 (oral).

J.L. Faria, **B.F. Machado**, H.T. Gomes, Size-dependent effects in supported metal catalysts for liquid phase hydrogenation reactions, SizeMat - Workshop on Size-Dependent Effects in Materials for Environmental Protection and Energy Application, Varna (Bulgaria), 25-27 May 2006, p. 83 (oral).

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Other publications

The following works although not directly related to the thesis, used the materials here described and characterized.

A.C. Apolinário, A.M.T. Silva, **B.F. Machado**, H.T. Gomes, P.P. Araújo, J.L. Figueiredo, J.L. Faria, Wet air oxidation of nitro-aromatic compounds: Reactivity on single- and multi-component systems and surface chemistry studies with a carbon xerogel, *Applied Catalysis B: Environmental* 84 (2008) pp. 75-86 (full paper)

Other publications (cont.)

H.T. Gomes, **B.F. Machado**, A. Ribeiro, I. Moreira, M. Rosário, A.M.T. Silva, J.L. Figueiredo, J.L. Faria, Catalytic properties of carbon materials for wet oxidation of aniline, *Journal of Hazardous Materials* 159 (2008) pp. 420-426 (full paper)

R.M.D. Nunes, **B.F. Machado**, A.F. Peixoto, M.M. Pereira, M.J. Moreno, J.L. Faria, Platinum encapsulated in TiO₂ as a new selective catalyst on heterogeneous hydrogenation of α,β -unsaturated oxosteroids (full paper in preparation).

S. Morales-Torres, **B.F. Machado**, A.F. Pérez-Cadenas, A.M.T. Silva, F.J. Maldonado-Hódar, J.L. Faria, J.L. Figueiredo, F. Carrasco-Marín, Oxidación catalítica en fase acuosa (CWAO) de anilina con catalizadores de Pt soportados sobre carbón activado, XXI Ibero-American Symposium of Catalysis, Ed. USB Flash Drive (2008) pp. VI183-VI190 (paper in conference proceedings)

B.F. Machado, A. Ribeiro, I. Moreira, M. Rosário, H.T. Gomes, J.L. Figueiredo, J.L. Faria, Catalytic properties of carbon xerogels for wet oxidation of aniline, Environmental Applications of Advanced Oxidation Processes (EAAOP) - I European Conference, Ed. CD-ROM (2006) (paper in conference proceedings)

H.T. Gomes, A.C. Barbosa, C.A. Amaro, C.M. Oliveira, R.G. Sousa, J.L. Faria, **B.F. Machado**, Fe containing silica gel catalysts for catalytic wet peroxide oxidation processes, V International Conference on Environmental Catalysis (ICEC), Belfast (Northern Ireland), August 31-3 September 2008, p. 320 (abstract in international conference, poster)

S. Morales-Torres, **B.F. Machado**, A.F. Pérez-Cadenas, A.M.T. Silva, F.J. Maldonado-Hódar, J.L. Faria, J.L. Figueiredo, F. Carrasco-Marín, Oxidación catalítica en fase acuosa (CWAO) de anilina con catalizadores de Pt soportados sobre carbón activado, XXI Ibero-American Symposium of Catalysis, Malaga (Spain), 22-27 June 2008, p. 179 (abstract in international conference, oral).

B.F. Machado, A. Ribeiro, I. Moreira, M. Rosário, A.M. Silva, H.T. Gomes, J.L. Figueiredo, J.L. Faria, Effect of textural and chemical properties of carbon xerogels for the catalytic wet air oxidation of aniline, IX Meeting of the Spanish Group of Carbon, Teruel (Spain), 22-24 October 2007, pp. 237-238 (abstract in international conference, poster).

B.F. Machado, A. Ribeiro, I. Moreira, M. Rosário, H.T. Gomes, J.L. Figueiredo, J.L. Faria, Catalytic properties of carbon xerogels for wet oxidation of aniline, Environmental Applications of Advanced Oxidation Processes - I European Conference, Chania (Greece), 7-9 September 2006, p. 195 (abstract in international conference, oral).

R.M.D. Nunes, **B.F. Machado**, A. Peixoto, M.J. Moreno, M.M. Pereira, J.L. Faria, High diastereoselective hydrogenation of unsaturated oxo-steroids with new titanium dioxide supported platinum heterogeneous catalysts, I European Chemistry Congress, Budapest (Hungary), 27-31 August 2006, p. 55 (abstract in international conference, poster).