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Development of Catalysts for the Elimination of Volatile Organic Compounds

DEVELOPMENT OF CATALYSTS FOR THE ELIMINATION OF VOLATILE ORGANIC COMPOUNDS

DESENVOLVIMENTO DE CATALISADORES PARA ELIMINAÇÃO DE COMPOSTOS ORGÂNICOS VOLÁTEIS

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Ph.D. Thesis

Tese de Doutoramento

This work was carried out at the Laboratory of Catalysis and Materials of the Faculty of Engineering, University of Porto, and at the Laboratoire de Catalyse en Chimie Organique, Université de Poitiers.

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DEPARTAMENTO DE ENGENHARIA QUÍMICA
FACULDADE DE ENGENHARIA DA UNIVERSIDADE DO PORTO

2004

UNIVERSIDADE DO PORTO	
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BIBLIOTECA M	
N.º	79785
CDU	66(043)
Data	8 1 6 20 04

Agradecimentos

Em primeiro lugar quero agradecer aos meus orientadores, Professor Doutor José Luís Figueiredo e Doutor José Órfão, por todos os ensinamentos que me transmitiram, pelo encorajamento, constante disponibilidade e apoio no acompanhamento deste trabalho, bem como ao Professor Doutor Michel Guisnet pelo caloroso acolhimento e orientação que me dispensou em Poitiers.

Deixo um agradecimento muito especial ao Doutor Patrick Magnoux pelo acompanhamento do meu trabalho em Poitiers e pela sua permanente disponibilidade para a discussão de ideias no decurso de todo este trabalho.

Agradeço à Fundação para a Ciência e a Tecnologia a bolsa de doutoramento BD/21815/99 e ao Laboratório de Catálise e Materiais que disponibilizou as condições materiais para a execução do projecto.

No que diz respeito ao trabalho experimental, agradeço ao Philippe Ayrault pelas análises de FTIR, à Christine Canaff pelas análises de GC-MS, ao Doutor Carlos Sá pelas análises de XPS e ao Doutor Fernando Pereira a ajuda no arranque do reactor. Agradeço ainda todo o apoio prestado pelo Departamento de Engenharia Química, nomeadamente pela disponibilização de alguns meios de análise.

Agradeço a todos os meus colegas do LCM, em especial à Filomena, ao Helder, à Cláudia, à Patrícia e à Purnakala, pelo bom ambiente de trabalho que sempre proporcionaram. Agradeço também a todos os meus colegas de Poitiers, nomeadamente Sébastien, João Pedro, Ludovic, Michaela.

Aos meus pais, a toda a minha família e ao Yalçın obrigada por todo o apoio que sempre me deram.

Resumo

Este trabalho tem como objectivo o desenvolvimento de catalisadores de platina suportada em zeólitos para a eliminação de compostos orgânicos voláteis (COVs).

Foram escolhidos dois compostos representativos de duas famílias de COVs: um composto aromático (o-xileno) e um composto oxigenado (metil-isobutil-cetona: MIBK). A oxidação catalítica destes compostos foi estudada individualmente e em mistura.

Numa primeira fase, estudou-se a oxidação catalítica do o-xileno usando diferentes catalisadores de platina suportados em zeólitos. Analisou-se a influência de variáveis do processo, tais como a temperatura, quantidade de platina, o estado do metal (estado electrónico e dispersão), e finalmente a influência do suporte (acidez e estrutura porosa). Concluiu-se que os parâmetros mais importantes nesta reacção são a presença de platina reduzida e um suporte hidrofóbico (com uma razão Si/Al elevada).

No caso da oxidação da MIBK, estudou-se inicialmente a influência das variáveis do processo (temperatura, pressão parcial dos reagentes) bem como a natureza dos produtos secundários e do coque. Analisou-se também a influência das propriedades fisico-químicas dos catalisadores (dispersão metálica, acidez, estrutura porosa e catião de compensação). Os parâmetros mais importantes na oxidação deste COV são semelhantes aos mencionados na oxidação do o-xileno. Testes de estabilidade do catalisador foram também efectuados, bem como a influência de tratamento regenerativo. O catalisador apresentou apenas uma ligeira desactivação nos testes de longa duração, assim como após tratamento regenerativo. Analisou-se também o efeito da presença de vapor de água na alimentação, tendo-se verificado que praticamente não tem nenhuma influência na actividade do catalisador. Quanto à oxidação da mistura de o-xileno e MIBK, observou-se que a conversão de o-xileno não é afectada pela presença de MIBK, enquanto que o contrário não acontece.

No decorrer do estudo de oxidação da MIBK, verificou-se que os zeólitos permutados com metais alcalinos eram activos e selectivos em CO_2 e observou-se também que, para determinadas condições experimentais e com determinados catalisadores, ocorriam oscilações na conversão aparente em CO_2 . Estas duas observações abriram dois novos caminhos para este trabalho de investigação: o estudo da oxidação da MIBK em zeólitos básicos e o estudo das oscilações na oxidação de COVs.

Testaram-se dois zeólitos (Y e X) permutados com metais alcalinos (sódio e cério) na oxidação da MIBK. Verificou-se que estes catalisadores são activos e selectivos em CO_2 ,

produzindo, no entanto, para temperaturas de reacção baixas, produtos secundários e coque. Demonstrou-se também que a basicidade dos zeólitos é um parâmetro chave para a obtenção das altas conversões e selectividades, tendo-se obtido uma relação linear entre a basicidade dos zeólitos e a conversão em CO_2 .

Finalmente, o estudo das oscilações baseou-se em determinações da reactividade do coque formado durante a reacção de oxidação tanto do o-xileno como da MIBK. A reactividade foi determinada por oxidação a temperatura programada (TPO) do coque acumulado nos catalisadores. Verificou-se que existem oscilações na conversão aparente em CO_2 quando há acumulação de coque mais reactivo. Concluiu-se que as oscilações estão relacionadas com ciclos de acumulação de coque reactivo e respectiva oxidação. Verificou-se também que a acumulação de coque reactivo está relacionada com as propriedades de adsorção do suporte: um suporte que seja capaz de adsorver o COV a temperaturas superiores à temperatura de reacção pode originar oscilações na conversão aparente em CO_2 .

Estes dois últimos temas deixam várias portas abertas para futuras investigações.

Abstract

The main objective of this thesis is the development of platinum catalysts supported on zeolites for the elimination of volatile organic compounds (VOCs).

Two organic compounds were chosen, representative of different families of VOCs: an aromatic (o-xylene) and an oxygenated compound (methylisobutylketone, MIBK). The catalytic oxidation of these compounds was studied individually and in mixtures.

Initially, the catalytic oxidation of o-xylene was studied on different zeolite supported platinum catalysts. The influence of several parameters was investigated, such as the temperature, amount of metal, electronic state and dispersion of platinum, acidity and porous structure of the support. It was concluded that the most important parameters in this process are the presence of reduced platinum and a hydrophobic support (high Si/Al ratio).

In the case of MIBK, the effect of process conditions, such as temperature and partial pressures of the reactants, as well as the nature of side products and coke were studied. The influence of catalyst properties (such as metal dispersion, acidity, porous structure and compensation cation of the support), was also analysed in detail. The most important parameters for the oxidation of this VOC are the same that were found for o-xylene. Catalyst stability tests were carried out, as well as the effect of catalyst regeneration. The catalyst suffered only a very mild deactivation in long duration tests, as well as after regeneration. The presence of water vapour in the feed was found to have negligible influence in the catalyst activity. In the case of mixtures, it was observed that the conversion of o-xylene was not affected by the presence of MIBK, while the conversion of MIBK was impaired in the presence of o-xylene.

In the course of these studies, it was observed that zeolites exchanged with alkaline metals were active for MIBK oxidation, and selective towards CO₂. It was also found that, under certain circumstances, there were oscillations in the apparent conversion into CO₂. These findings suggested two additional topics of research, which were addressed in this thesis: The study of the oxidation of MIBK over basic zeolites, and the investigation of oscillations in the oxidation of VOCs.

Two zeolites (Y and X) exchanged with alkaline metals (Na and Cs) were tested in the oxidation of MIBK. It was found that these catalysts are active and selective to CO₂; however, at low temperatures, side products and coke are formed. It was demonstrated that the zeolite

basicity is a key parameter to reach high conversions and selectivities, a linear relationship between zeolite basicity and conversion into CO_2 being obtained.

Finally, the study of oscillations was based on the determination of the reactivity of the coke deposits formed during the oxidation of both o-xylene and MIBK. The reactivity was determined by temperature-programmed oxidation (TPO). The accumulation of the so-called reactive coke was found to be at the origin of oscillations in the apparent conversion into CO_2 . It was concluded that the oscillations result from cycles of accumulation and oxidation of this reactive coke. On the other hand, the accumulation of reactive coke was found to be related to the adsorption properties of the support. In particular, a support which is capable of retaining the VOC at temperatures higher than the reaction temperature may lead to oscillations in the apparent conversion into CO_2 .

These last two topics provide interesting suggestions for future work.

Résumé

L'objectif principal de cette thèse était de développer des catalyseurs au platine supporté sur zéolithes pour l'élimination de Composés Organiques Volatiles (COV). Deux composés organiques, représentatifs des différentes familles de COV, ont été choisis: un hydrocarbure aromatique (l'o-xylène) et un composé oxygéné (la méthylisobutylcétone, MIBK). L'oxydation catalytique de ces composés a été étudiée individuellement et en mélange.

Dans un premier temps, l'oxydation catalytique de l'o-xylène a été étudiée sur différents catalyseurs au platine supporté sur zéolithe. L'influence de différents paramètres tels que la température de réaction, la quantité, l'état électronique et la dispersion du platine, l'acidité et la structure poreuse du support a été évaluée. Il a ainsi été montré que la présence de platine à l'état réduit et d'un support hydrophobe (avec un support Si/Al élevé) étaient les paramètres les plus importants.

Dans le cas de l'oxydation catalytique de la MIBK, l'effet des conditions opératoires (température, pressions partielles des réactifs) ainsi que la nature des produits secondaires et du coke ont été déterminés. L'influence des propriétés du catalyseur (dispersion du métal, acidité, structure poreuse du support et nature du cation compensateur) a également été étudiée en détail. Les conclusions sont les mêmes que précédemment. Des tests de stabilité et de régénération du catalyseur ont été effectués. Le catalyseur ne subit qu'une légère désactivation durant les tests catalytiques de longue durée, ainsi qu'après régénération. De plus, la présence de vapeur d'eau dans le milieu réactionnel n'a qu'un effet négligeable sur l'activité catalytique. Enfin, l'étude de l'oxydation d'un mélange MIBK/o-xylène a montré que la conversion de l'o-xylène n'est pas affectée par la présence de MIBK, alors que la conversion de MIBK diminue fortement en présence d'o-xylène.

Au cours de cette étude, les zéolithes échangées par des cations alcalins (et donc basiques) se sont révélées particulièrement actives et sélectives en CO_2 . Par ailleurs, dans certaines circonstances, des oscillations dans la conversion apparente en CO_2 ont été observées. La suite de ce travail concerne l'étude de ces deux phénomènes.

Deux zéolithes (Y et X), échangées par des cations alcalins (Na et Cs) ont été testées en oxydation catalytique du MIBK et se sont montrées actives et sélectives en CO_2 . Néanmoins, à basse température, des produits secondaires et du coke sont formés. Une relation de proportionnalité entre la basicité de la zéolithe et la conversion en CO_2 a pu être

établie, ce qui démontre que la basicité du support est le paramètre clé pour l'obtention de hautes conversions et sélectivités.

Enfin, l'estimation par Oxydation en Température Programmée (TPO) de la réactivité des dépôts de coke formés lors de l'oxydation de l'o-xylène et de la MIBK montre qu'une accumulation de coke «réactif» est à l'origine des oscillations observées dans la conversion apparente en CO_2 . Ce phénomène résulte d'un procédé cyclique d'accumulation puis d'oxydation du coke, l'accumulation de coke «réactif» étant due aux propriétés d'adsorption du support. Ceci suggère qu'un support capable de retenir les COV à des températures supérieures à la température d'oxydation conduirait à des oscillations dans la conversion apparente en CO_2 . Ce dernier point constitue une perspective intéressante pour de futurs travaux.

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1. Introduction

1.1. The Volatile Organic Compounds

Volatile Organic Compounds (VOCs) are considered air pollutants as they can cause hazard to human health directly or indirectly [1-3]. Several definitions can be found to describe VOCs. They can be defined regarding the effects caused: all organic compounds arising from human activities, other than methane (NMVOCs), which are capable of producing photochemical oxidants by reactions with nitrogen oxides in the presence of sunlight [4]. However, other definitions are given, namely in the EU directive on limitations of organic solvents: VOCs is defined as any organic compound having a vapour pressure of 0.01 kPa or more at 293.15 K [5].

Individual components of VOCs are known for harmful effects on man, such as toxic effects (a number of organic compounds, such as carcinogens and mutagenic substances, are directly harmful to health). Some VOCs are regulated individually as hazardous substances [6]. However, the main environmental effect of VOCs is their role in the formation of smog. In the presence of nitrogen oxides, VOCs are precursors to the formation of ground level (tropospheric) ozone, the primary constituent of smog [1-3]. High concentrations of ozone cause respiratory damage as well as eye irritation to man and also damage to the vegetation. Moreover, some VOCs also contribute to the problem of global warming, as they are powerful infrared absorbers [2].

The main reaction responsible for ozone production does not depend directly on VOCs, as it is due to the presence of nitric oxides, oxygen and sunlight [2]. In the presence of light, NO_2 is decomposed to NO and the oxygen radical, which reacts with O_2 to form O_3 . On the other hand, ozone reacts also with NO to produce NO_2 and molecular oxygen. In the absence of VOCs, the concentration of ozone will depend on the intensity of solar radiation and will not depend strongly on the amount of nitrous oxides (as it is being produced by NO_2 but consumed by NO). The role of VOCs in this process is to convert NO to NO_2 without using up O_3 . In this case ozone will not be consumed by reacting with NO and it will accumulate in the atmosphere, because the concentration of NO_2 will increase and the concentration of NO will decrease. In this way, although VOCs do not take part in the main reaction of ozone formation, their presence will cause accumulation of ozone at ground level.

VOC sources can be of two types: natural sources (emitted from different species of vegetation) or anthropogenic (man-made) sources [3]. There are many anthropogenic activities that contribute for the emission of VOCs to the atmosphere, such as transports, use of solvents, industry, fugitive emissions, etc. The main sources of VOCs are the road transports and solvent use. In the countries of the European Union, the distribution of NMVOC by sector in 1999 is shown in Figure 1.

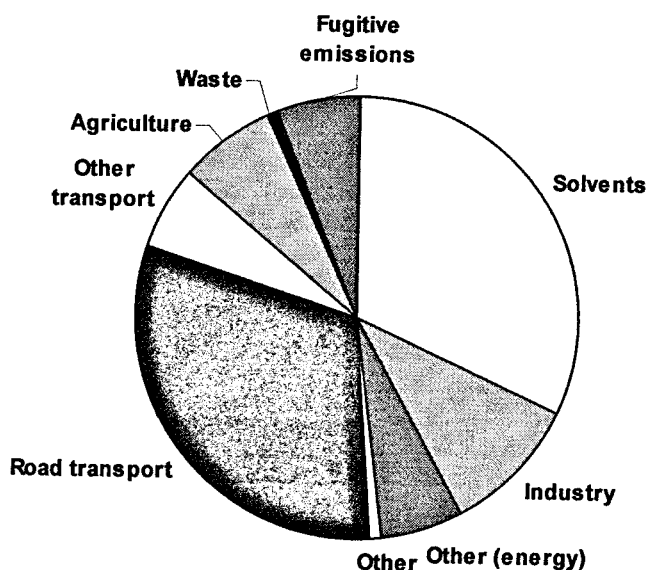


Fig. 1 – Sector split of EU-15 emissions of NMVOC in 1999 [7].

Road transport (combustion and petrol evaporation) and solvent use (paints, glues, printing, vehicle spraying, etc) are responsible for 31 and 32%, respectively, of the overall VOCs emissions in EU-15 countries [7]. The reduction of VOCs emissions by road transport will not be discussed in this work, but can be achieved by the use of exhaust catalysts. This work deals with the reduction of the emissions from stationary sources. The use of solvents is responsible for the higher emissions of VOCs in the EU-15 countries (Figure 1). These compounds can be divided into different families: hydrocarbons (alkanes, alkenes and aromatics), halogenated hydrocarbons, and oxygenated compounds (alcohols, aldehydes and ketones) [3]. The reduction in the emissions of VOCs due to the use of solvents is regulated by the EU directive 1999/13/EC [5].

The reduction of the emissions of air pollutants is a major concern nowadays, and many actions are taking place. EU-15 emissions of VOCs have been reduced by 28% from 1990 to 1999 [7], this reduction being mainly due to the transport sector (reduction of 42% between these years). Still substantial emissions reductions are needed in order to reach the 2010 targets of the national emissions ceilings directive [4]. This EU directive establishes ceilings for the emissions of certain atmospheric pollutants (SO_2 , NO_x , VOC and NH_3) for the different members, which should be reached by 2010. In the case of Portugal, studies were made in order to define strategies to reach the levels defined in the 2001/81/CE directive [8]. The following graphic (Figure 2) compares two reference scenarios (low and high) for 2010 and the ceilings established by the 2001 directive.

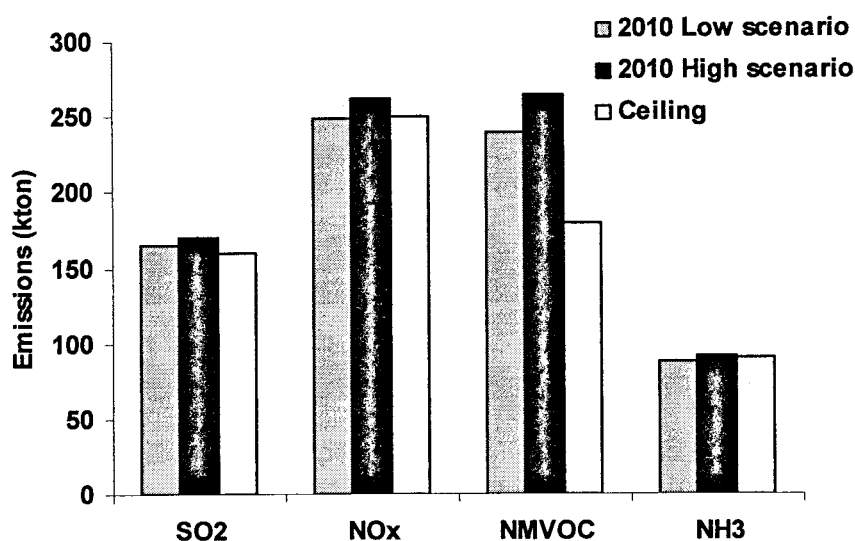


Fig. 2 – Comparison of the positions of the emissions of NMVOC in Portugal in the reference scenarios and the ceilings established in the EU directive 2001/81/CE [8]

The ceilings established for SO_2 , NO_x and NH_3 are close to the predicted, although not in the case of VOCs, the ceiling being much lower than the predicted emission values for 2010. Other additional measures should be taken into account in order to reduce VOCs emissions.

1.2. Techniques for reducing VOCs emissions

There are many different techniques for VOCs removal. The choice of the technique to use depends on the characteristics of the effluent to be treated, such as VOCs nature and concentration and waste gas flow rate. The reduction of VOCs emissions can be made at different levels [2,9-13]:

- by prevention, such as changing the industrial procedures so that less volatile compounds will be released (like using water-based paints instead of oil-based) or leakage control;
- by concentration and recovery, such as changing the units so that the volatile compounds can be recovered and re-used in the process (this is possible using techniques like condensation, adsorption, absorption and membrane technology);
- by destruction, when none of the other processes can be applied. In this case, VOCs are transformed into CO_2 and H_2O by combustion (incineration), catalytic oxidation or biological oxidation (biofiltration).

The choice of the best control strategy should be made in the following order: prevention, recovery and finally destruction. However, it is not always possible, or economically favoured, to use non-destructive techniques.

Among the recovery techniques, adsorption is a good solution for treating low concentration VOCs streams [2]. Adsorbents work at low temperatures, for the adsorption to be favoured. The most used adsorbents are activated carbon and zeolites. There are several studies on the adsorption on these two materials [14-17]. The main disadvantage of activated carbon is that humidity has a strong effect on the process, while hydrophobic zeolites are less sensitive to humidity. Moreover, although zeolites have a lower adsorption capacity, they are non-combustible which is important when treating streams that contain highly flammable VOCs. VOCs can be recovered by regeneration (by pressure or thermal treatments) of the adsorbent when it is saturated [11]. The stream can pass through a condenser so that VOCs can be recovered.

As a matter of fact, condensation is a good technique for treating low-flow concentrated VOCs streams. Condensation can be achieved using a refrigeration system. The main problem is when highly volatile compounds are to be recovered, as the cooling temperature should be very low.

Another non-destructive technique is absorption (scrubbing). This technique is used to separate and recover streams containing high concentrations of organics, specially water-soluble compounds [11]. Absorption has several limiting factors, namely the choice of a suitable solvent. The VOC must be soluble in the absorbing liquid. Moreover, this technique requires regeneration of the VOC containing solvent by stripping. The VOC is then recovered in a condenser.

Finally, some VOCs can also be recovered from waste streams by membrane separation. In this process, the organic compounds present in the waste stream permeate the membrane separating from the treated air. The VOCs in the permeate stream can be recovered afterwards. This technique is costly [12] and should only be considered for low flow rate streams, when condensation or adsorption cannot achieve the desired levels of recovery efficiency.

When the non-destructive techniques cannot be applied, waste streams containing VOCs should be treated using destructive processes. Thermal oxidation (incineration) is a process by which the VOCs are oxidised to carbon dioxide and water, by increasing the temperature, in the presence of oxygen. The operating temperatures range between 650 to 1100°C. However, incomplete combustion is a permanent problem, leading to the formation of undesirable by-products (that are even more harmful than the input gas) such as furans and dioxins [2]. Moreover, when the waste stream contains chlorinated VOCs, special care should be taken, as highly corrosive acid gases are formed. There are three types of systems: direct flame (thermal afterburner, with no heat recovery), recuperative (the waste gas is pre-heated with hot, clean gas leaving the combustion chamber) and regenerative (the heat is stored in a ceramic packed bed which will be used to pre-heat the incoming waste gas stream). This process is suitable to reduce emissions from almost all VOC sources with high efficiencies. However, the heat recovery systems are only suitable for high concentration VOC streams.

Another way of oxidising VOCs is by catalytic oxidation. The catalyst increases the reaction rate, allowing the reaction to occur at lower temperatures (between 320 and 430°C) than with thermal oxidation [11]. Catalysis is a versatile and efficient technique not only for destroying VOCs but also for the elimination of other air pollutants [18], being known in this context as Environmental Catalysis [19,20]. Catalytic oxidation offers high destructive efficiency, lower operating temperature than thermal combustion systems and smaller units [11]. The main disadvantage of this process is that the catalyst can be sensitive to poisoning by non-VOC materials present in the waste stream, such as sulphur [10]; in addition, the

catalyst efficiency can be affected by particulates present in the waste gas [11,18] which can block the catalyst pores. The type of catalyst used depends on the nature of the waste stream to be treated and will be discussed in more detail in the next section.

Finally, among the destructive techniques, there is also biofiltration. The key component of this system is a biofilter, which contains micro-organisms that can convert organic pollutants to carbon dioxide and water. This kind of process also requires an adequate moisture level to work efficiently. Moreover, this technique is suitable to treat streams containing low molecular weight compounds and compounds like aldehydes, ketones, alcohols and organic acids. When the waste stream contains halogenated and polyaromatic compounds, the biofiltration process is more difficult and not so efficient [11].

The most used control technologies are shown in Figure 3 [11]. This Figure shows the range of flow rates and VOC concentration in which the devices operate most efficiently and cost-effectively.

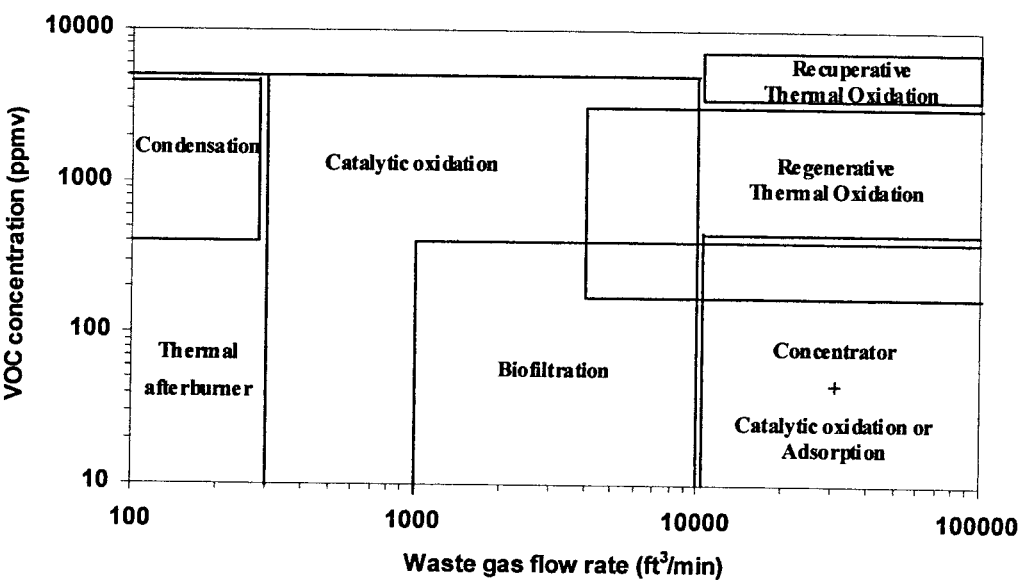


Fig. 3 –Selection map, based on lowest cost, to choose the appropriate VOC abatement technology [11].

Catalytic oxidation can be applied effectively and at lower cost in a wide range of VOCs concentration and waste gas flow rates, presenting then an interesting solution for VOCs elimination.

Other emerging technologies are currently being evaluated [11], such as ultraviolet (UV) oxidation technology and plasma technology. UV oxidation uses oxygen-based oxidants like ozone or peroxide to convert VOCs into carbon dioxide and water in the presence of UV light. This technique can also be used together with an adsorbent like activated carbon which removes the unreacted VOCs from the process [21]. The other technology uses plasma (a high temperature ionized gas that is very reactive), which can initiate dissociation reaction in VOC molecules. The decomposition reaction is initiated by free-radical mechanisms. This technique is highly selective for the decomposition of halogenated hydrocarbons.

1.3. Catalytic oxidation of VOCs over supported metal catalysts

Heterogeneous catalytic oxidation of industrial vapours and gases is a well studied subject that has been reviewed by several authors [22-26]. There are two different types of heterogeneous catalytic oxidation processes: partial oxidation (for production of commercial products) and complete oxidation of organic contaminants in air (like industrial emissions or automotive exhaust catalysts). The majority of the studies of catalytic oxidation were developed for industrial partial oxidation processes, which have quite different operation conditions and goals than complete oxidation. Catalytic oxidation of VOCs is carried out at atmospheric pressure, with low reactant concentration and with excess of oxygen, CO₂ and H₂O being the desired products (which are undesired in partial oxidation reactions). The catalyst sought should be highly active (so that the reaction can be carried out at lower temperatures) and non-selective (in the sense that only total oxidation products should be formed). If the oxidation is not complete there can be the formation of other compounds that are more toxic than those to be treated. Finally, these catalysts should be resistant to contaminants present in the air streams to be treated, such as sulphur-containing compounds. Moreover, the efficiency of the catalytic oxidation depends on the reactivity of the VOC to be treated and also on the mixture effect.

1.3.1. The reactants

Not all VOCs have the same reactivity, and the temperature for which a compound is totally oxidised depends on its nature. Moreover, some compounds, in particular oxygenated compounds, produce partial oxidation products, for instance ethyl acetate can produce

ethanol, acetic acid or diethyl ether when oxidised over a Pt/alumina catalyst [27]. It is then important to know if other products which are less reactive are formed.

The reactivity in oxidation depends on the adsorption strength of the VOC and on its structure. A sequence was found for the reactivity of different VOCs regarding their functional group [28]: alcohols>aldehydes>aromatics>ketones>alkanes. In the case of C1-C4 alkanes, the easiest to oxidise was butane and the hardest methane [29].

Several authors claim that C-H bond activation is a crucial first step in the oxidation of saturated hydrocarbons [30,31], where the substrate is activated on the metal surface through rupture of the weakest C-H bond. After that, the reactions that produce CO₂ and H₂O are relatively facile. In the case of oxygenated and aromatic compounds, the same conclusion was reached, and a correlation was found between the reactivity of the VOC and the strength of the weakest C-H bond in the structure over a platinum/zeolite catalyst [32]. A single weak bond on the VOC leads to a high reactivity.

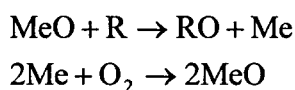
However, the behaviour of the compounds when present in mixtures can be different from the individual compound and this can affect the oxidation efficiency. It is then important to study the oxidation not only of individual compounds, but how they are affected when other VOCs are present. Only a few detailed studies on the catalytic combustion on mixtures are found in the literature [33-35]. For some VOCs there is an inhibition of the oxidation (for example n-hexane in the presence of benzene [33]). This inhibition can be related to the competition of the VOCs for adsorption on the active sites. In other cases, the oxidation of a compound is independent of the presence of the other compound (like benzene and toluene in the presence of n-hexane [34]). Finally, there are cases in which a positive synergistic effect occurs, there being an increase of the conversion when the compounds are mixed with respect to single compounds (for example, in mixtures of methyl-ethyl-ketone and toluene [35]). A more detailed overview of what has been done in this area will be given in section 3.3 of this work.

1.3.2. The catalysts

The mechanisms involved in catalytic complete oxidation depend on the catalyst used. There are two main types of conventional catalysts being used: metallic oxides or supported noble metals [24-26,36].

1.3.2.1. Metal oxides

Catalytic oxidation over base metal oxides have been extensively studied both in selective and complete oxidation, and it was nicely reviewed by Sokolovskii [30]. These catalysts are generally less active than the supported noble metal catalysts for complete oxidation, but they are more resistant to poisoning. The main advantage of metal oxide catalysts over noble metal catalysts is the lower cost. Furthermore, when the appropriate composition is chosen, high thermal stability can be achieved with metal oxides. Two possible states of activated oxygen can be recognised: highly reactive surface adsorbed oxygen and less active lattice oxygen species [25,36]. The so called p-type semiconductors, which can conduct electrons by means of positive “holes”, are the most active oxides for oxidation catalysis, as they can easily adsorb oxygen to form active species such as O^- [25]. When lattice oxygen species are involved in the oxidation, a redox mechanism (known as Mars-van Krevelen) is considered [26]:



where Me is a metal cation and R the hydrocarbon.

There are several studies published on the total oxidation of VOCs over metal oxides, the most used oxides being those of Cu [37,38], Mn [39,40], Fe [41], Cr [42], Co and Ni [25,36]. However, other types of metal oxide catalysts are being tested. For example, the use of uranium oxide based catalysts can achieve total oxidation of VOCs (aromatics, oxygenated and chlorinated) in the temperature range 300-450°C [43].

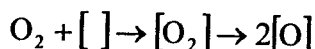
Mixed metal oxides have unique properties of activity and stability, comparing to the individual oxides [24]. Perovskites, which are mixed oxides of the type ABO_3 (where A represents a lanthanide and/or alkaline earth metal ion and B a transition metal ion) are also used with high efficiency in catalytic oxidation of VOCs. [44-46], specially for oxygenated compounds [45]. Other mixed oxides like CuMn_2O_4 were also studied [46], although the perovskite catalysts presented better results in the oxidation of oxygenated compounds. Side products were formed in both cases. Moreover, the use of $\text{V}_2\text{O}_5\text{-WO}_3\text{-TiO}_2$ SCR catalysts did not give good results in the total oxidation of VOC, as they were poorly active and originated significant amounts of partial oxidation products like CO [47].

Studies of total oxidation of ketones over metal oxides will be further discussed in Chapter 4, as we also studied the total oxidation of methyl-isobutyl-ketone over alkali-exchanged zeolites in this work.

1.3.2.2. Noble metals

According to Bond [48], only very few metals can be used as heterogeneous catalysts for oxidation reactions, as most of the metals are unstable in oxygen, originating thick oxide layers on the catalyst surface.

A general mechanism of oxidation over noble metals is thought to involve the dissociative adsorption of oxygen [25]:



where $[\]$ represents a surface adsorption site. The VOC can react with this adsorbed oxygen directly from the gas phase (Eley-Rideal mechanism) or can react after adsorption on the catalyst (Langmuir-Hinshelwood mechanism). Nevertheless, some authors consider the redox mechanism of the metal surface, similar to the mechanism over metal oxide catalysts, namely in the case of gold catalysts [49,50], palladium [51,52] or even platinum [53,54]. In this case the noble metal would be oxidised by oxygen and reduced by the hydrocarbon.

Among the noble metals, the most used for total oxidation of VOCs are Pt and Pd [25,36], being usually supported on an oxide such as Al_2O_3 or SiO_2 . However, some recent studies using highly dispersed gold particles supported on Fe_2O_3 [49,50] or on $\text{CeO}_2/\text{Al}_2\text{O}_3$ [55] show interesting results in the oxidation of VOCs.

In general, platinum presents a higher activity than palladium for the total oxidation of VOCs, namely for alkenes [56,57], alkanes (other than methane) [57,29], oxygenated VOCs [58,59] and aromatics [56,59,60]. The fact that platinum has a higher ionization potential than palladium favours its tendency to be in the metallic state [61]. Moreover, some studies show that the combination of both metals is more efficient than one metal alone [42,62,63], although there are exceptions. For instance, Skoglundh *et al.* [56] showed that, for the total oxidation of xylenes, the efficiency of palladium is improved for a molar ratio Pd/Pt of 80/20, considering the same total amount of metal. However, platinum alone is more active for these oxidations, the reaction being not promoted by the presence of palladium.

Moreover, the active phase can also be a mixture of a noble metal with other metals. For example, a 0.1%Pt,3%Ni/ $\gamma\text{-Al}_2\text{O}_3$ catalyst was tested in the oxidation of C_5 to C_9 hydrocarbon mixtures [64]. The oxidation of formaldehyde/methanol was also enhanced by the use of Pd-Mn/ Al_2O_3 catalysts [40].

The choice between using a metal oxide or noble metal to catalyse the VOC oxidation depends on several factors (nature of the stream to be treated, contaminants, etc), although it is generally accepted that noble metals are more active than metal oxides, the latter being

more resistant to poisoning [25]. A comparison between base metal oxide catalysts and noble metal catalysts was made by Vigneron and co-workers [42]. Noble metals catalysts were found to be more active than metal oxides, as expected, and also more resistant to poisoning in the oxidation of a mixture of organic solvents in the presence of contaminants such as metals or compounds containing silicon. On the other hand, other studies show that metal oxides, in particular MnO_2 , have a better performance than noble metals, like Pt/TiO_2 , in the oxidation of ethylacetate, benzene and n-hexane [39]. Moreover, when the compounds are in mixture, metal oxides are less sensitive than noble metals to the effect of interferences between the compounds. They are also less affected by the presence of water vapor than the platinum catalyst.

1.3.2.3. The supports

The choice of the support is also important. Usually the support used for these reactions is γ -alumina, although it is not necessarily the best one. For instance, Okumura et al. [65] found that palladium supported on ZrO_2 exhibits very high activity for the oxidation of toluene compared to palladium supported on other oxides, such as MgO , Al_2O_3 , SiO_2 , SnO_2 , Nb_2O_5 and WO_3 , which was due to the higher stabilisation of metallic Pd on ZrO_2 . Good performance of Pt supported on sulphated zirconia was also found in the oxidation of n-pentane [66]. Moreover, other supports like activated carbon presented better results than alumina in the oxidation of BTX [67], due to the fact that this support is able to concentrate the VOCs favouring the oxidation. Furthermore, the performance of Pt/TiO_2 catalysts for the oxidation of benzene and ethyl acetate was found to increase when the support was doped with W^{6+} cations [68,69]. This enhancement was explained by the ability of the doped acidic support for the formation of reactive intermediates with high mobility, which can be easily oxidised on the Pt surface.

An important property pointed out by several authors is the hydrophobicity of the support [53,54,62,70,71]. The advantage of using a hydrophobic support is that moisture from the atmosphere and released during the reaction will not remain adsorbed on the catalyst, specially at low reaction temperatures. Kinetic studies of the oxidation of formaldehyde over platinum supported on a hydrophobic support [54] showed that there was no water inhibition effect on the oxidation rate, resulting in a higher activity and selectivity to CO_2 .

Zeolites can also be used as supports or even as catalysts for oxidation reactions, as discussed below.

Zeolites, due to their remarkable properties, have an important role in catalysis or adsorption processes nowadays. This also applies to the development of cleaner and more efficient processes, as well as pollution abatement [72]. Zeolites can be used in oxidation reactions exchanged with transition metal ions or with supported noble metals. Some examples of oxidation over nonacidic zeolites are given by Maxwell [73]. However, there are not many studies on the use of zeolites in the oxidation of VOCs.

Since the pioneer work by Rabo et al. [74], noble metals supported on zeolites have been used in industrial catalysis, as bifunctional catalysts. Zeolites are excellent supports as they allow for the preparation of highly dispersed platinum or palladium catalysts with narrow particle size distribution [75]. The study of the preparation methods and location of the metallic particles was extensively studied by the group of Sachtler [76-78], being still a subject of research nowadays [79]. Moreover, the electronic properties of the metal also depend on the zeolite support [75,78,80].

The use of zeolites as support for noble metals can bring advantages in oxidation. For example, Li and Armor [81] showed that the oxidation of methane over a $\text{PdO}/\text{Al}_2\text{O}_3$ requires temperatures 70-80°C higher than $\text{Pd}/\text{ZSM-5}$ catalyst to achieve the same conversions. This was related to the higher reducibility of palladium when supported on the zeolite. Neyestanaki et al. [82] confirmed these results in the oxidation of propane over the same type of catalysts. In the oxidation of aromatics [60,83,84], the reduced catalysts were found to be more active in the oxidation [60,83]. Furthermore, platinum was found to be more active than palladium for o-xylene oxidation [60]. The acidity of the zeolite had a negative effect on the oxidation [83,84]; this effect was also observed in the presence of steam, the more acidic catalyst being more affected by the presence of water than the less acidic ones [60]. In the case of chlorinated VOCs, platinum supported on acidic zeolites showed higher activity compared to platinum supported on alumina in the oxidation of chlorobenzene [85]. Moreover, over a Pt/NaY bifunctional catalyst, Pinard et al. [86] found that dichloromethane oxidation occurs in two steps: hydrolysis on NaY with formation of formaldehyde and HCl, and then complete oxidation of formaldehyde in the Pt sites.

Not only noble metals are used in oxidation. Gentry *et al.* [87] found that the exchange of sodium by copper enhanced the catalytic activity of the X zeolite to propylene oxidation. Chatterjee and Greene [88] used Cr-Y catalyst to oxidise dichloromethane, and they found

feasible the dual site mechanism involving the adsorption of the VOC on the Bronsted acid sites and adsorption of oxygen on the cationic site. However, noble metals supported on zeolite catalysts have proven to be more active in VOCs oxidation. For instance, the oxidation of propane [82] and benzene [83] was enhanced in the presence of Pd/ZSM-5 catalyst and Pd/Y catalyst, respectively, in comparison with the corresponding copper exchanged catalysts.

1.3.2.4. Deactivation and presence of contaminants

One of the major problems in using catalytic oxidation for VOCs elimination is catalysts deactivation. Generally, the streams to be treated contain contaminants, such as particulates, heavy metals, sulphur, etc.). Noble metal catalysts can be poisoned by chlorinated compounds and sulphur-containing compounds [89]. Moreover, high operating temperatures can also provoke sintering of the metal. In the case of metal oxide catalysts, chlorinated compounds can also deactivate the catalyst, as chlorine atoms may lead to the loss of metal due to the formation of volatile species [90]. Sulphur also has a negative effect on the performance of metal oxides, as it can be incorporated into the support [89].

Catalyst deactivation can also be due to the accumulation of coke formed during the reaction. Some authors have studied the modes of coke formation in the catalytic oxidation of aromatics over copper supported on zeolites [91,92] or palladium supported on zeolites [93].

The presence of steam can also have a negative effect on catalyst performance [39,59,60,88,94]. This effect is generally reversible [60,89]. However, the inhibition effect of water can be diminished by using hydrophobic supports [54,60]. Moreover, Lahousse *et al.* [39] found that a manganese oxide catalyst was slightly more resistant to deactivation in the presence of water than platinum supported on titania. This was explained by a competition of VOCs and water for specific sites. On the platinum catalyst, the presence of water also affected the selectivity, and side products were formed.

However not all the contaminants have a negative effect. Oxidation of ethylacetate, propane and ethanol over a Pt/ γ -Al₂O₃ was enhanced in the presence of SO₂, but there was no effect when the reaction was carried out over a Pt/SiO₂ catalyst [94]. The authors proposed that the presence of sulphate groups enhance the oxidation of these VOCs by creating additional reaction pathways.

1.4. Objectives and layout of the work

The objective of the present work is the development of platinum catalysts supported on zeolites for the complete oxidation of volatile organic compounds.

Two different VOCs were chosen for this study, which are representative of two different families: one aromatic (o-xylene) and one oxygenated (methyl-isobutyl-ketone). These compounds were studied individually and in mixture.

The results obtained during this thesis are divided in four chapters. In the first part (Chapter 2), the deep oxidation of o-xylene is studied over several platinum catalysts supported on zeolites (HBEA and HFAU). The influence of several operating parameters was investigated, such as temperature and platinum content, the state of the metal (electronic state and dispersion), and finally the influence of the support, such as acidity and porous structure. This work was carried out at the *Laboratoire de Catalyse en Chimie Organique* at the University of Poitiers.

In Chapter 3, the total oxidation of methyl-isobutyl-ketone (MIBK) is studied over several platinum catalysts. The influence of the operation conditions is first investigated over one of the catalysts (temperature, reactants partial pressure) as well as the side products and soluble coke. Then the physico-chemical properties of the catalysts are discussed, namely metal dispersion, acidity, porous structure and effect of the compensation cation. Finally, the stability and regeneration of the catalyst is addressed as well as the performance of the catalyst in the presence of steam in the feed.

When performing the oxidation of MIBK on the supports alone (without platinum) it was found that the alkali-exchanged zeolites are selective to CO₂. This finding originated Chapter 4 of this thesis, where the oxidation of MIBK is studied over basic zeolites. A series of basic zeolites are tested, namely CsX and NaX, showing high activities and selectivity to CO₂.

In the course of our study on the oxidation of MIBK (Chapters 3 and 4), a peculiar phenomenon of oscillations in the apparent conversion into CO₂ was observed under certain conditions. This phenomenon is investigated in detail in Chapter 5, both in the case of MIBK and o-xylene oxidation.

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2. Catalytic oxidation of o-xylene over Pt/zeolites*

2.1. Introduction

Volatile Organic Compounds (VOCs) can be considered as a major source of air pollution, and in many cases, legislation has already been introduced to reduce their emissions. VOCs can be produced from a variety of industrial and commercial process, including printing, metal decorating, paint drying, metal degreasing, manufacturing of organic compounds and polymers, food processing...[1]. These Volatile Organic Compounds are thought to be implicated in the formation of photochemical smog and destruction of ozone layer. VOCs in exhaust gases can be removed by incineration, condensation, scrubbing, adsorption or catalytic oxidation. Incineration, the most often used method, destroys these compounds by burning them at temperatures higher than 1000°C. Such high temperatures generate the formation of undesirable by-products such as nitrogen oxides, dibenzofurans and dioxins. Catalytic oxidation offers high destructive efficiency, lower operating temperature, lower capital cost and smaller units than thermal combustion systems [1]. This process can be considered an effective way for reducing the emissions of VOCs from stationary sources [2-4]. Both noble metals and mixed metal oxides can be used as catalysts [2], the first ones being often preferred for the destruction of non-halogenated VOCs [3]. Noble metals are generally supported on alumina, however other supports and particularly zeolites can be also used. Various results show that platinum is more active in total combustion than palladium [5-11], thus the total oxidation of aromatic VOC (o-xylene) was investigated over Pt/zeolite catalysts. In a previous study [11] it was found that, in the case of HFAU zeolites, the hydrophobicity of the support was an important parameter in this context, and so it was decided to investigate if the same effect occurred with another zeolite such as HBEA.

The aim of this paper is to show how the physicochemical characteristics of various Pt/HBEA samples (platinum content, oxidation state of platinum, particle size of metal, acidity of the support...) influence the o-xylene oxidation. Two series of catalysts were used for such purpose. In the first one, the samples differed by their Pt content (from 0 to 0.3wt%), HBEA(50) zeolite being used as support. In the second series two zeolites differing by their framework Si/Al ratio (15 and 50) were chosen as support of Platinum. Finally, the performances of Pt/HBEA and Pt/HFAU catalysts for o-xylene oxidation were compared.

* Published in: Applied Catalysis B: Environmental 46 (2003) 371-379.

2.2. Experimental

2.2.1. Preparation and characterisation of the catalysts

Pt/HBEA catalysts with different Pt loadings were prepared by ion exchange of two HBEA samples (framework Si/Al ratio of 15 and 50). The exchange was made using an adequate diluted solution of $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ at $\text{pH}=7$, continuously stirred for 4 h at room temperature. Afterwards, the samples were filtered, washed and dried at 100°C overnight. Calcination was carried out at 300°C for 6h under dry air flow ($20 \text{ l h}^{-1} \text{ g}^{-1}$). The calcined samples were then tableted and crushed to 0.2-0.4 mm size. Before reaction, the catalysts were treated *in situ* in the reactor under air flow (90 ml min^{-1}) at 500°C for 6 h (pre-calcined samples). The percentage of Pt was measured by the “Centre d’Analyse du CNRS de Vernaison-France”.

The Pt catalysts were labelled as follows: xPtHBEA(y) with x for the percentage of platinum and (y) for the zeolite framework Si/Al ratio.

The dispersion of the catalysts (Table 1) was determined by the toluene hydrogenation reaction, after catalyst reduction. This reaction was carried out at 110°C in a flow reactor at atmospheric pressure. To minimise the thermal effects of the reaction a n-hexane/toluene (5:1) mixture was used as reactant. The molar ratio of hydrogen to the mixture n-hexane/toluene was equal to 45. The number of accessible atoms of platinum was determined by comparing the initial activity of these catalysts with the activities obtained for the Pt/HFAU catalysts [12].

The acidity of the samples (Table 1) was determined by pyridine adsorption followed by IR spectroscopy. Excess of pyridine was adsorbed at 150°C and physisorbed pyridine was desorbed by evacuation at the same temperature. The concentrations of Brönsted and Lewis acid sites were calculated from the integrated intensities of the PyH^+ and PyL bands (1545 and 1450 cm^{-1}) using the values of the molar extinction coefficients of these bands (1.13 and $1.28 \text{ cm} \mu\text{mol}^{-1}$, respectively) determined in a previous study [13] by sorption of measured amounts of pyridine on HMOR zeolite (containing only Brönsted sites) and on alumina (containing only Lewis sites).

The carbonaceous compounds retained on the catalyst (coke) were analysed by a technique developed to analyse the coke formed on zeolites [14]. The zeolite is dissolved in a solution of 40% hydrofluoric acid, and the coke compounds are recovered in an organic solvent (CH_2Cl_2). These soluble compounds are analysed by GC and by GC/MS.

Table 1 – Characteristics of Pt/HBEA(15, 50) and Pt/HFAU(47) catalysts: dispersion of platinum, number of accessible platinum sites (n_{Pt}), number of Brönsted (A_B) and Lewis (A_L) acid sites.

	Dispersion ^a (%)	n_{Pt} (10^{18} atoms.g ⁻¹)	A_B^b (10^{18} H ⁺ .g ⁻¹)	A_L^b (10^{18} H ⁺ .g ⁻¹)
HBEA(15)			278	143
0.23PtHBEA(15)	62	4.4		
HBEA(50)			90	9
0.10PtHBEA(50)	81	2.5	75	16
0.21PtHBEA(50)	69	4.5	86	16
0.25PtHBEA(50)	84	6.5		
0.30PtHBEA(50)	86	8.0		
HFAU				
0.09PtHFAU(47)	35	1.0	49	7

^a determined by the model reaction of toluene hydrogenation

^b determined by pyridine adsorption followed by IR

2.2.2. Catalytic study

The reactions were carried out in a fixed bed reactor at atmospheric pressure in the temperature range of 180 to 240°C. The catalyst (140mg) was supported in a small plug of glass wool in a vertical Pyrex reactor (5 mm i.d. and 0.72 m of total length). The reactor was inserted in an oven and the temperature controlled by a regulator (Minicor Coreci). The temperature of the reactor was measured by a thermocouple placed along the outside wall of the glass reactor. At the beginning of the experiment the temperature was found to rise 1 or 2°C but then remained constant. The reactant mixture, consisting of a pre-mixed gas (20 % O₂ in nitrogen) with a concentration of ca. 1,700 ppmv of o-xylene, was introduced in the reactor with a total flow rate of 86 ml min⁻¹ controlled by a mass flow regulator (Brooks 5850). The concentration of o-xylene in the reactant mixture was obtained by passing the pre-mixed gas through a saturator which was kept at 0°C by means of a cryostatic bath (Huber). The space velocity was kept constant in all the experiments (18,000 h⁻¹, calculated at ambient temperature and pressure).

The analytical system consists of a gas chromatograph (Varian 3400) equipped with a thermal conductivity detector (TCD) and a flame ionisation detector (FID). A capillary column (CPSil 5, 50 m, 0.32 mm and 1.2 µm thickness) was connected to the FID for the separation and analysis of the organic compounds. Connected to the TCD was a Porapak R

column for carbon dioxide and carbon monoxide analysis. Both columns were maintained at 70°C.

The total amount of coke in the catalysts after reaction was measured by total calcination of the sample at 1020°C in an elemental analyser THERMOQUEST NA2100.

2.3. Results and discussion

Two main reactions can be observed on all catalysts: total oxidation into CO₂ (and H₂O) and formation of heavy non-desorbed products (coke). For each experiment, a carbon mass balance close to 100% is obtained when the desorbed products and coke are considered.

2.3.1. Influence of the temperature and time-on-stream (TOS)

The results obtained over pre-calcined 0.30PtHBEA(50) are compared in Figure 1 at four temperatures: 200, 215, 220 and 225°C.

At 225°C (and at higher temperatures), whatever the TOS, there is no o-xylene at the reactor exit and the conversion into CO₂ is complete. In the range from 200°C to 220°C, the o-xylene conversion initially close to 100% decreases progressively as a function of TOS (Fig. 1 a) and the conversion into CO₂ increases with TOS till a quasi-constant value (Fig. 1 b).

At those temperatures, a mixture of m-, p- xylene, toluene and trimethylbenzene appears in very low amount (<3%) at the reactor exit for TOS>10 min. These compounds result most likely from o-xylene transformation (isomerization and disproportionation) over the acid sites of the catalyst. It can be noticed that whatever the reaction temperature no traces of CO were detected. The conversion of xylene into coke, taken as the difference between the total conversion of o-xylene and its conversion into CO₂ and secondary products, depends also both on the temperature and TOS (Fig. 1c). Adsorbed products are retained in the zeolite pores at 200°C, 215°C and 220°C. The conversion of o-xylene into coke is initially complete at 200°C, then decreases with TOS. After 1 hour of reaction, the percentage of carbon deposited on the catalyst decreases from 5.5wt% to 4.5wt%, respectively at 200 and 220°C. This result can be attributed to the greater oxidation rate of o-xylene at 220°C. It can be underlined that, whatever the reaction temperature, coke formation deactivates the transformation of o-xylene (Fig 1a) but has no effect on its oxidation (Fig 1b). This is

certainly the result of coke molecules being preferentially adsorbed on the acid sites which do not participate in the oxidation reaction.

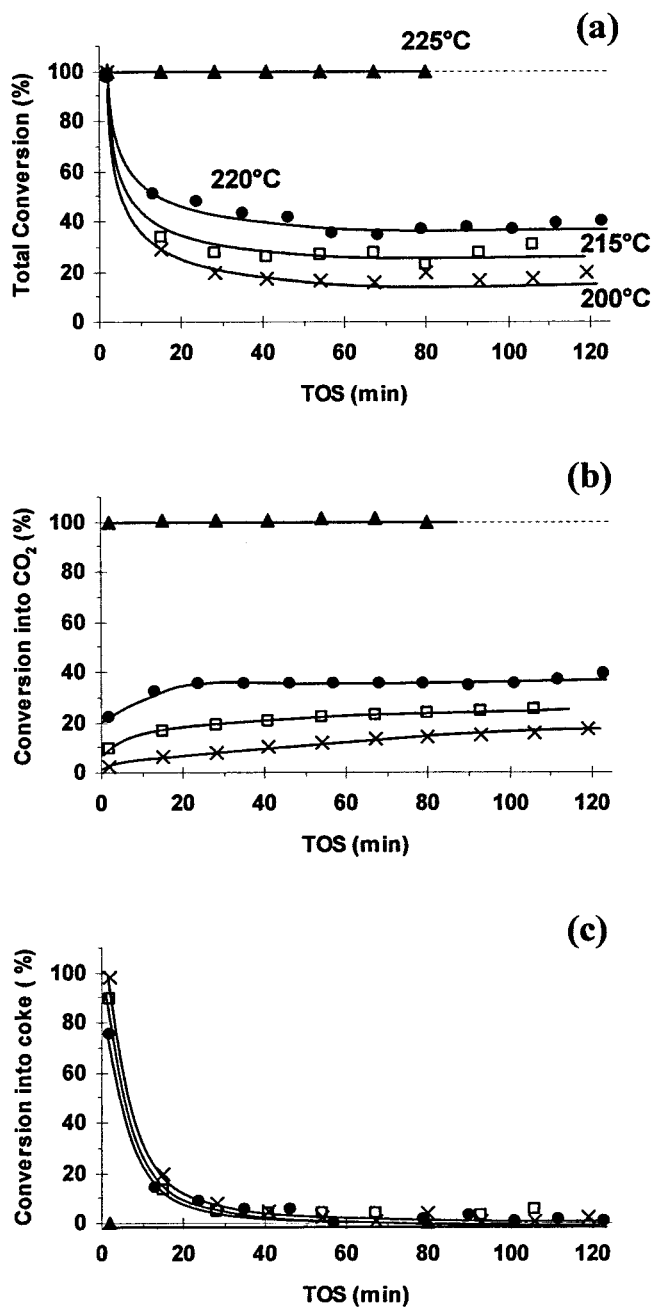
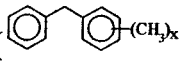
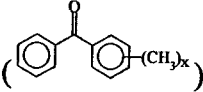
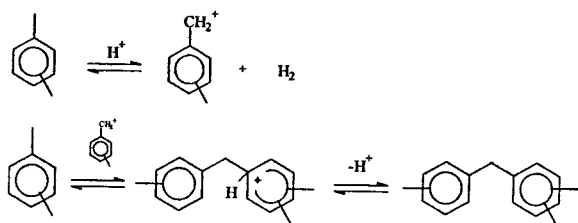


Fig. 1. Influence of time-on-stream (TOS) on the total conversion of o-xylene (a), conversion into CO₂ (b) and conversion into coke (c) over the 0.30PtHBEA(50) catalyst at (▲) 225, (●) 220, (□) 215 and (×) 200°C.

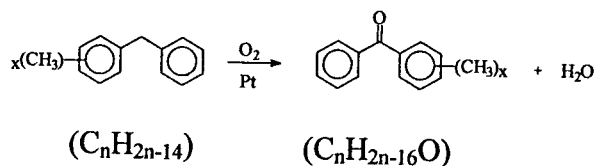
Coke analysis was carried out after 1 h reaction at 200°C by the method developed for the characterisation of coke formed on zeolites [14]. All the carbonaceous compounds formed on 0.30PtHBEA(50) at 200°C can be recovered in methylene chloride after dissolution of the zeolite in a HF solution. The coke molecules soluble in methylene chloride were characterised by GC and GC/MS. Two main families were found: aromatic hydrocarbons with C_nH_{2n-14} formula () and aromatic oxygenated compounds with $C_nH_{2n-16}O$ formula

() $(C_nH_{2n-16}O)$. Aromatic hydrocarbons and aromatic oxygenated compounds represent respectively 35% and 65% of the total extract. These products were already detected in the zeolite pores during oxidation of benzene [15], toluene [16] and o-xylene [17] over doped zeolites.

Methyl diphenyl compounds are the intermediates of xylene disproportionation which is a well known acid transformation [18]. Their formation involves the electrophilic substitution of a xylene molecule by a benzylic cation formed from another molecule of xylene:



The oxygenated compounds of coke can be formed on the acid sites of the zeolite [17] although oxidation of C_nH_{2n-14} molecules into $C_nH_{2n-16}O$ will be certainly promoted by the presence of the Platinum sites:



2.3.2. Influence of the platinum content

The influence of platinum content was studied for o-xylene transformation at various temperatures between 200 and 300°C by using a series of pre-calcined Pt/HBEA(50) catalysts with platinum contents from 0 to 0.30wt%, with similar Pt dispersion (Table 1). The results were presented as a function of reaction temperature for the steady state catalyst, hence after 1 h of reaction (Fig. 2).

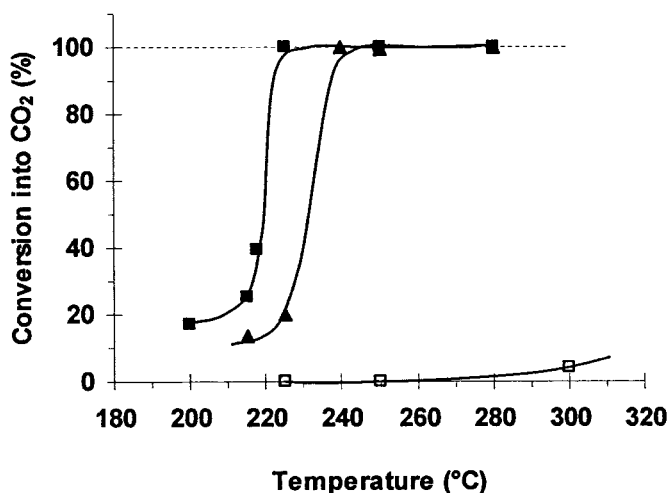


Fig. 2. Conversion of o-xylene into CO₂, after 1 h, as a function of the temperature on (□) HBEA(50), (▲) 0.10PtHBEA(50) and (■) 0.30PtHBEA(50).

The higher the platinum content, the faster the transformation of o-xylene and its oxidation. Thus, complete conversion of o-xylene into CO₂ is obtained at 225°C over the 0.30PtHBEA(50) catalyst and at 240°C for 0.10PtHBEA(50). Moreover, the presence of Pt is indispensable to transform o-xylene into CO₂. Indeed, over HBEA(50), the oxidation of o-xylene is very slow, even at 300°C (Fig. 2). However, whatever the temperature, o-xylene is initially totally transformed into coke over this protonic zeolite. The percentage of carbon deposited on HBEA(50) after 1 h of reaction depends on the temperature (4wt% to 6wt% between 225 and 300°C). Whereas the coke content increases with the reaction temperature over HBEA, it decreases over PtHBEA. Furthermore, for a given temperature, the higher the degree of platinum exchange, the lower the coke content (4wt% over 0.10PtHBEA(50) against no coke over 0.30PtHBEA(50) at 225°C). This phenomenon can be directly related to the larger extent of oxidation of o-xylene over the more exchanged Pt catalysts.

2.3.3. Effect of the pre-treatment

2.3.3.1. Pre-reduction of the catalyst under hydrogen flow

It was previously suggested that metallic species (Pd^0 and Pt^0) are very active for o-xylene oxidation over Pd/HFAU and Pt/HFAU catalysts [11, 19]. In order to check that Pt^0 was also an active species over PtHBEA samples, the catalysts were reduced before reaction at 300°C under hydrogen flow for 6 h (pre-reduced catalyst).

Pre-reduced and pre-calcined 0.30PtHBEA(50) catalysts were characterised by CO adsorption followed by IR spectroscopy (Figure 3).

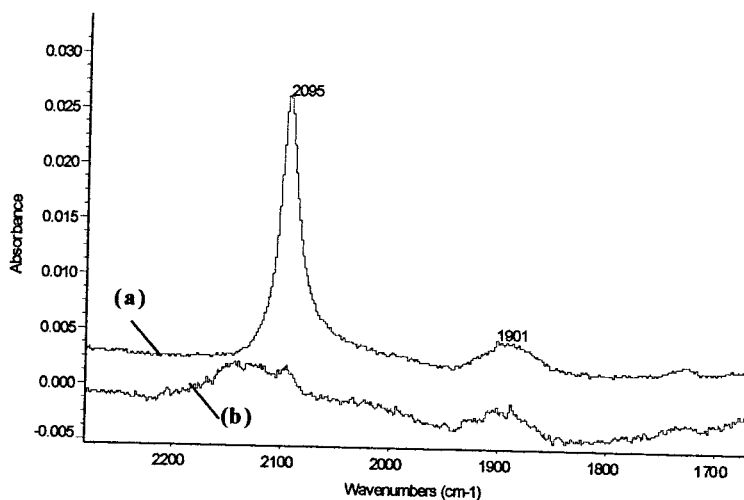


Fig. 3. IR spectra of CO adsorption over the 0.30PtHBEA(50) pre-reduced catalyst (a) and the pre-calcined catalyst (b).

The stretching of the CO bond depends on the platinum species in which CO is adsorbed. The pre-reduced catalyst presents a peak at 2095 cm^{-1} , which can be attributed to CO linearly bonded to metallic Pt atoms [20,21]. However, it was mentioned that over Pt/Ceria, the band at $2091\text{--}2096\text{ cm}^{-1}$ can be attributed to CO adsorbed on Pt with oxidized Pt as neighbour, and the CO linearly adsorbed on step-site Pt should be assigned to $2080\text{--}2086\text{ cm}^{-1}$ [22]. On the pre-calcined catalysts, the band at 2095 cm^{-1} was not found and a broad band at about $2100\text{--}2150\text{ cm}^{-1}$ appears. This can be related to the presence of oxidised platinum species [21,22].

The pre-reduced catalyst is more active in the oxidation of o-xylene than the catalyst pre-calcined under air (Fig. 4).

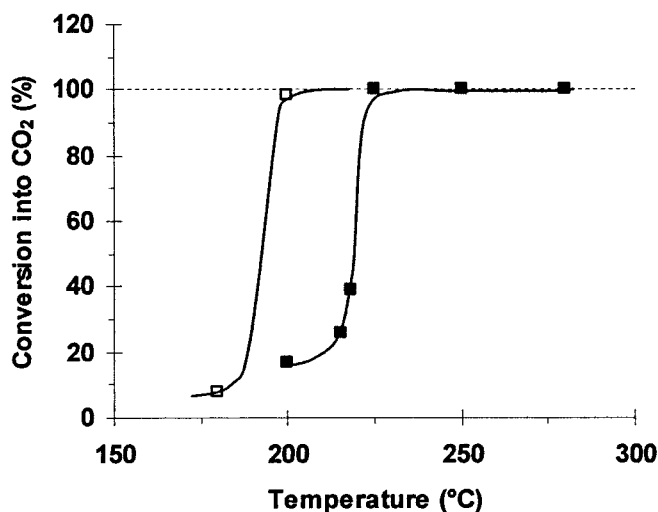


Fig. 4. Conversion of o-xylene into CO₂, after 1h, as a function of temperature for the 0.30PtHBEA(50) catalyst pre-calcined at 500°C (■) and pre-reduced at 300°C (□).

At 200°C after 1 h of reaction all the o-xylene was converted into CO₂ over the pre-reduced 0.3PtHBEA(50) catalyst, while only 13% of CO₂ can be detected in the reactor exit for the catalyst activated under air. This latter catalyst can only oxidise all the xylene into CO₂ at temperatures higher than 225°C, so there is at least a difference of 25°C in the temperatures for which the conversion of o-xylene into CO₂ is complete.

This result confirms, as in the case of PtHFAU catalysts [19], that the most active species for o-xylene oxidation are the metallic platinum species (Pt⁰). Furthermore, with a pre-reduced catalyst, no increase in the CO₂ conversion with TOS was observed as in the case of pre-calcined catalysts. This phenomenon observed in the pre-calcined samples can be explained by the partial reduction of platinum species by o-xylene during the reaction.

2.3.3.2. Pre-treatment under water

The influence of the metallic particle size can also be an important parameter in oxidation reactions. During the total oxidation of n-heptane, J. Völter et al. [23] concluded that the activity of Pt/Al₂O₃ was not diminished by higher calcination temperature, although the Pt dispersion was drastically decreased. This phenomenon was also observed by T.F. Garetto and C.R. Apesteguía for the total oxidation of benzene over Pt/Al₂O₃ [24]. On the other hand, P. Briot and M. Primet [25] showed that the sintered metal catalyst was more active than the more dispersed Pd/Al₂O₃ catalysts in the catalytic oxidation of methane over Pd/Al₂O₃.

In the present study, the influence of the metallic particle size was examined over pre-calcined 0.10PtHBEA(50) catalysts. In order to obtain catalysts with a low metal dispersion, the calcined Pt catalyst was treated at 500°C under an air/water mixture with 20% H₂O by volume for one hour. After such treatment, the metal dispersion was found to decrease from 81% to 10% (Table 2).

Table 2 – Characteristics of the steamed and not-steamed catalysts: Dispersion of the platinum, number of accessible platinum sites (n_{Pt}), Brönsted (A_B) and Lewis (A_L) acidity.

	Dispersion (%)	n_{Pt} (10 ¹⁸ atoms.g ⁻¹)	A_B (10 ¹⁸ H ⁺ .g ⁻¹)	A_L (10 ¹⁸ H ⁺ .g ⁻¹)
0.10%Pt/HBEA(50)	81	2.5	75	16
0.10%Pt/HBEA(50) steamed	10	0.3	49	16

IR spectroscopy showed that no extensive dealumination of the zeolite occurred after water treatment (steaming). Indeed the band around of 1090 cm⁻¹ which corresponds to an asymmetric stretch vibration [26] was shifted to 1096 cm⁻¹, which corresponds to a framework Si/Al ratio of 60 [27] and the other band around 575 cm⁻¹ (576 cm⁻¹), which can be assigned to the ring breathing vibration, was not displaced (framework Si/Al = 50). However a decrease in the number of Brönsted acid sites was measured by pyridine adsorption over 0.10PtHBEA(50) (Table 2).

TEM analysis of the steamed catalyst showed a bimodal distribution of particle size: large particles of about 50 nm and agglomerates of small particles (5 nm).

The results obtained over the steamed and pre-calcined 0.10PtHBEA(50) catalysts show that the platinum dispersion does not influence significantly the oxidation of o-xylene into CO₂.

Similar activities were found over both catalysts (Fig. 5) while n_{Pt} , the number of accessible platinum atoms, decreases from 2.5×10^{18} atoms g⁻¹ to 0.3×10^{18} atoms g⁻¹. This result points out that n_{Pt} is not the main factor defining the oxidation rate of o-xylene, the platinum content becomes the most important parameter. However, the specific oxidative activity of platinum atoms (turnover) is strongly enhanced over the low dispersed catalysts. This enhancement of the specific activity of the larger particles can be explained by a faster oxygen adsorption on those particles. Indeed, over Pt/Al₂O₃ catalysts the reaction of ¹⁶O/¹⁸O equilibration was faster over large platinum particles, hence with the less dispersed catalyst [28].

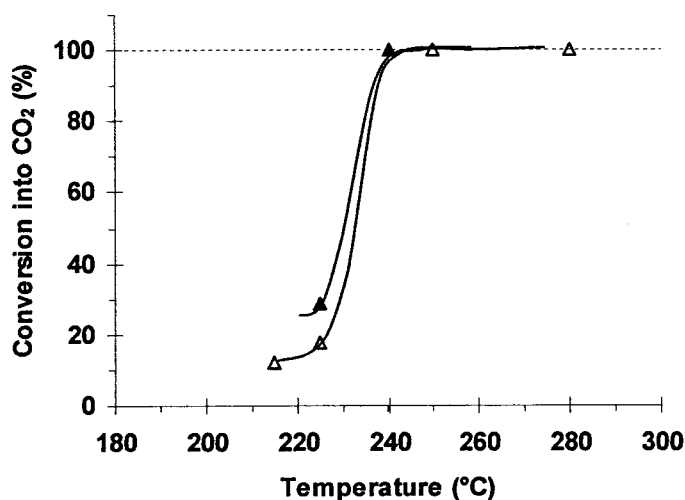


Fig. 5. Conversion of o-xylene into CO₂, after 1h, as a function of temperature for pre-calcined (Δ) and steamed (▲) 0.10PtHBEA(50) catalyst.

Similar light off curves were also obtained over pre-reduced and steamed pre-reduced catalysts. Consequently, it was possible to conclude that whatever the oxidation state of platinum, the platinum dispersion does not influence the oxidation of o-xylene into CO₂.

In conclusion, whatever the catalyst, the higher the platinum content the greater the o-xylene oxidation (Fig.6).

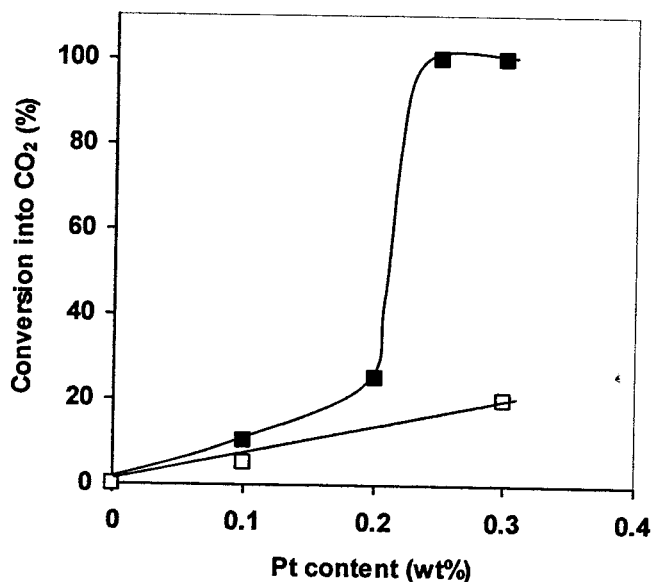


Fig. 6. Conversion of o-xylene into CO₂ as a function of platinum content for T = 200°C and TOS=1h. (□) pre-calcined catalysts, (■) pre-reduced catalysts.

In the case of the pre-calcined samples the conversion into CO₂ increases in direct relation to the platinum content, while a significant increase in oxidation was observed between 0.20-0.25 pre-reduced PtHBEA catalysts. For similar platinum content, it was highlighted that the performance of Pt catalysts was enhanced by pre-treatment under hydrogen flow. For T=200°C, this improvement was more significant from Pt ≥ 0.20wt%.

2.3.4. Effect of the support

The oxidation of o-xylene was studied over two catalysts which differ by their framework Si/Al ratio: 0.23PtHBEA(15) and 0.25PtHBEA(50). These catalysts were pre-reduced *in situ* at 300°C for 6 h before use. As for Pd/HFAU and Pt/HFAU catalysts [11,18], the framework Si/Al ratio of zeolites has a significant effect on the xylene oxidation over PtHBEA catalysts. For similar Pt content, the higher the Si/Al ratio, the lower the temperature required for total xylene oxidation into CO₂ (Fig.7).

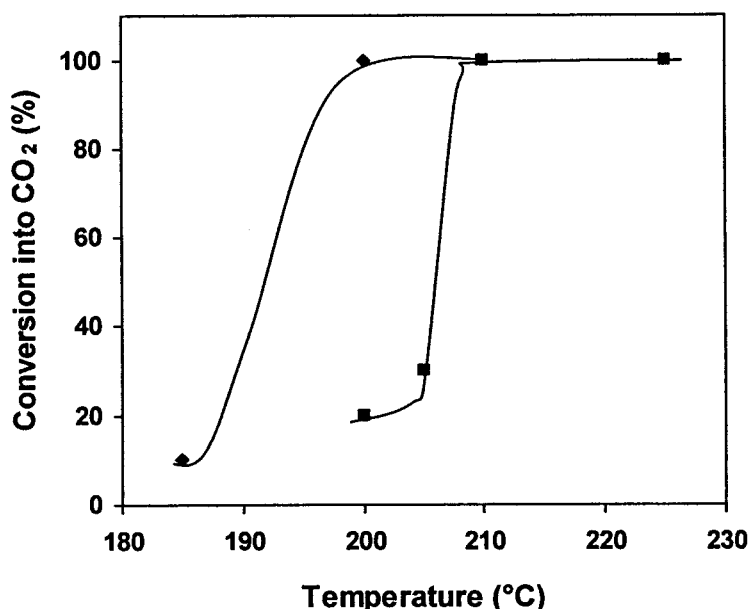


Fig. 7. Conversion of o-xylene into CO₂, after 1h, as a function of temperature for 0.25PtHBEA (50) (◆) and 0.23PtHBEA(15) (■) catalysts.

This can be explained by the hydrophobic character of the more dealuminated zeolite (high Si/Al ratio) [29,30] and by the adsorption competition between water liberated during oxidation and the reactant on the acidic sites of zeolites. This points out that the zeolite support plays an active role in aromatic hydrocarbon VOCs oxidation.

To investigate the influence of the zeolite pore structure, experiments were made over pre-reduced 0.09PtHFAU(47) and 0.10PtHBEA(50) catalysts. Whatever the framework Si/Al ratio of the zeolite, PtHBEA catalysts were slightly more active than the corresponding PtHFAU samples (Fig.8).

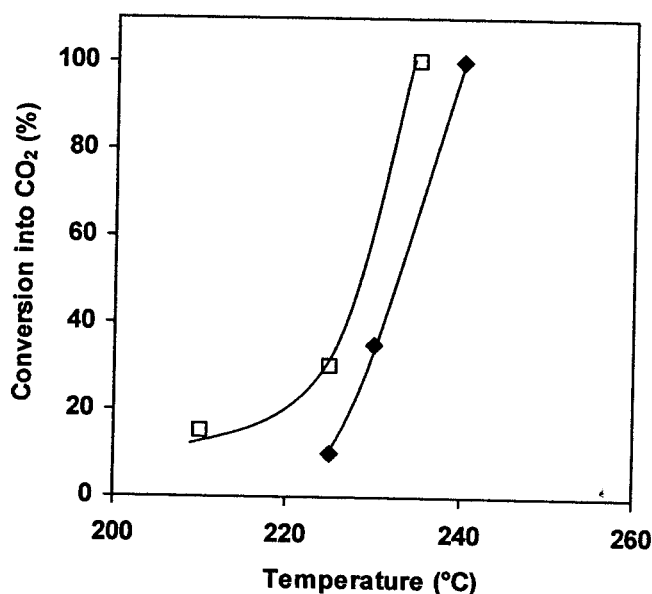


Fig. 8. Conversion of o-xylene into CO₂, after 1h, as a function of temperature for pre-reduced 0.10PtHBEA(50) (□) and 0.09PtHFAU(47) (◆) catalysts

Nevertheless, the difference in oxidation rate between both catalysts was not really significant: total oxidation was obtained at 235 and 240°C for 0.10PtHBEA(50) and 0.09PtHFAU(47), respectively.

2.4. Conclusions

With all the PtHBEA catalysts, o-xylene undergoes two parallel reactions: total oxidation (CO₂ and H₂O) and transformation into non desorbed compounds (“coke”). The rate of o-xylene oxidation increases with the reaction temperature to the detriment of “coke” formation. These compounds, trapped in the zeolite pores, are mainly constituted by aromatic hydrocarbons and oxygenated aromatic compounds. It can be underlined that coke formation has no deactivating effect on xylene oxidation into CO₂. For a given zeolite carrier, the rate of o-xylene oxidation increases with the platinum content whereas the platinum dispersion has practically no effect on the oxidation reaction.

Finally, it was shown that the presence of metallic species (Pt⁰) deposited over an hydrophobic zeolite (high Si/Al ratio) enhanced the reactivity of the catalyst in total oxidation of xylene.

2.5. References

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3. Catalytic oxidation of methyl-isobutyl-ketone over Pt/zeolite catalysts

3.1. Introduction

Ketones are included in the group of aldehydes and ketones, which are characterised by the carbonyl group. They are generally used in industry as solvents for gums, resins, paints, varnishes, etc. Little work has been done on the study of the catalytic combustion of carbonyl VOCs, and ketones in particular. These compounds are certainly easier to oxidise than compounds belonging to the aromatic family (previously studied in chapter 2).

Acetone and methyl-ethyl-ketone (MEK) are the most studied VOCs of this family [1-6]. There is a study about the combustion of acetone in air over Pt-Pd/fluorinated carbon catalysts, which shows that these catalysts are able to convert only 80% of acetone at 400°C [1]. The total amount of noble metal was 0.1% and the space velocity ranged between 3,000 and 15,000 h⁻¹. O'Malley and Hodnett [2] found that the complete combustion of acetone over a 0.5%Pt/BEA catalyst was achieved at 220°C. In this work, they compared the catalytic performance with deuterated acetone and found that this one is more difficult to oxidise. They also compared the behaviour of several other VOCs with different functional groups, and found that the reactivity of the VOC is related to the bond dissociation enthalpy of the weakest C-H bond in the molecule.

The group of Gandía [3,4] found that, over catalysts of 2.3wt%Pt/Al pillared clays, the complete conversion of was reached at 352°C with acetone and at 317°C with MEK [3]. MEK resulted easier to oxidise than acetone, this fact being related to the strength of the weakest C-H bond in these ketones. Using manganese oxide supported on alumina- and zirconia-pillared clays, the same group found that the temperature required for total oxidation of acetone ranged between 337 and 387°C. In both cases, the authors found that not all acetone was being transformed into CO₂ when performing isothermally reactions, as the conversion into CO₂ was lower than the conversion of acetone. No other products were released other than CO₂ and H₂O. The authors believe that the difference in the conversions is related to the competition between acetone combustion and aldol condensation of acetone, which results in polymerisation products that can stay strongly held on the catalyst surface. Other possible explanation is the retention of acetone itself on the catalyst.

Acetone and MEK were found to oxidise completely at 340 and 270°C respectively, over a catalyst of platinum supported on Al₂O₃/Al monoliths [5]. By performing oxidation of binary mixtures of toluene, MEK and 2-propanol, the authors found that complete oxidation

of toluene and MEK were not affected by the presence of other VOCs, and suggested that these two VOCs are oxidised directly from the gas phase with the oxygen atoms adsorbed on the platinum. On the other hand, 2-propanol oxidation is inhibited by the other two VOCs, as the oxidative dehydrogenation of 2-propanol to acetone is inhibited by the presence of the other VOC. The authors concluded that the main competition was not for the adsorption sites of the Al_2O_3 , but for the oxygen atoms adsorbed on Pt.

Moreover, Pina *et al* [6] found total conversion of MEK in air at around 180°C over a $0.17\text{wt\%Pt}/\gamma\text{-Al}_2\text{O}_3$ catalytic membrane. This was achieved with concentrations of MEK of 1750 and 3100 ppmv. While performing the oxidation of mixtures of MEK and toluene, the authors found that MEK has a very low inhibiting effect on toluene oxidation, while the inhibiting effect of toluene in MEK oxidation is much higher. This was explained by competition of toluene and MEK for adsorption sites, for which the toluene adsorption would be favoured.

The adsorption of methyl-isobutyl-ketone (MIBK) on granular activated carbon was reported [7], the carbon being regenerated by exposure to UV/O_3 . Several products were identified by GC-MS after desorption and/or destruction of MIBK, the smaller ones were acetone and acetic acid and several other oxygenated molecules such as 3-methyl-butanoic acid, 2-methyl-propanoic acid, valeric acid, 4-methyl-3-pentene-2-one and 2,4-dimethyl-3-pentanol. This shows that MIBK was broken down into smaller molecules which became more oxygenated.

The aim of the work described in this chapter is to study the complete oxidation of MIBK over Pt/zeolite catalysts. The chapter is divided in four parts. In the first part the oxidation over Pt/HFAU(47) catalysts is studied, and the influence of process variables (temperature and reactants partial pressures) are reported, as well as the effect of the electronic state and content of platinum. The side products of the reaction are also analysed. In the second part, the influence of the physico-chemical properties of the catalysts (metal dispersion, acidity, texture and presence of alkali cations, such as sodium and cesium) is investigated. In the third part the stability and regeneration of the catalyst is considered, as well as the effect of the presence of steam in the reactant feed. Finally, in the fourth part, the oxidation of MIBK in the presence of o-xylene over a Pt/HFAU catalyst is studied.

3.2. Experimental

3.2.1. Preparation and characterisation

HFAU zeolite (framework Si/Al ratio of 5 and 47) and HBEA zeolite (framework Si/Al ratio of 15) were supplied by PQ zeolites, NaFAU zeolite (framework Si/Al ratio of 2.4) was supplied by Linde, γ -Al₂O₃ was supplied by Condea and SiO₂ was supplied by Saint-Gobain. HBEA(50) zeolite was prepared at the *Laboratoire de Catalyse en Chimie Organique* (Poitiers) by dealumination with a solution of HCl 1.0 N at 100°C for 3h. The CsFAU support was prepared from the NaFAU zeolite as explained in more detail in chapter 4.

The acidity of the zeolites was determined by pyridine adsorption followed by IR spectroscopy. This technique was already explained in chapter 2.

The texture of the supports was determined from the nitrogen equilibrium adsorption isotherms, performed at 77K with a gas adsorption system (Coulter Omnisorp 100CX). Prior to adsorption, the samples were outgassed at 350°C to a vacuum of less than 10⁻⁵ torr. Micropore volumes and mesopore surface areas were determined by the *t*-plot method.

The Pt/zeolite catalysts were prepared by ion exchange of the zeolite supports using an adequate dilute solution of Pt(NH₃)₄Cl₂ (Alfa), continuously stirred for 4 h at room temperature. In the case of the protonic zeolites, a competing ion (NH₄⁺) was added in order to achieve an homogeneous macroscopic distribution of the metal [8]. Afterwards, the samples were filtered, washed and dried overnight at 100°C. Calcination was carried out at 300°C for 6h under dry air flow. The Pt/ γ -Al₂O₃ and Pt/SiO₂ samples were prepared by incipient wetness impregnation using an appropriate solution of H₂PtCl₆ (Alfa). The stirring time was 24h, and then the catalyst was dried at 100°C overnight. The sample is then calcined at 500°C for 2h under dry air flow. The calcined samples were then tableted and crushed to 0.2-0.4 mm size. Before reaction, the catalysts were reduced *in situ* under hydrogen flow at 300°C for 2 h. This treatment is the most suitable to achieve high platinum dispersion [9].

The dispersion of the catalysts was determined by different methods. One of them is based on activity measurements in the toluene hydrogenation reaction [10]. This reaction was carried out at 110°C in a flow reactor at atmospheric pressure. To minimise the thermal effects of the reaction, a n-hexane/toluene (5:1) mixture was used as feed. The liquid mixture was injected by a Kd Scientific syringe into the reactor. The molar ratio of hydrogen to the mixture n-hexane/toluene was equal to 45. The effluents were analysed by GC (Varian 3400) equipped with FID and a 100 m PPG capillary column. The number of accessible atoms of platinum was determined by comparing the initial activity of the catalyst with the activities

obtained with standard Pt/HFAU catalysts of known dispersion [10]. For the Pt/ γ -Al₂O₃ and Pt/SiO₂, a calibration curve corresponding to the hydrogenation over a Pt/ γ -Al₂O₃ catalyst of known dispersion was used.

The dispersion of some catalysts was also determined by hydrogen chemisorption at 25°C, performed in a typical U-shaped cell in the equipment Coulter 100CX. The samples were pre-reduced *in situ* under hydrogen. Then vacuum was made in the cell before starting hydrogen adsorption. After the first isotherm, vacuum was again made in the cell in order to remove the physisorbed hydrogen and another isotherm was started. The total amount of chemisorbed hydrogen is obtained by subtraction of the two isotherms.

The metal dispersion can also be calculated by CO adsorption followed by IR. The catalyst, in pellet form, is pre-reduced under hydrogen. After cooling to 200°C, the secondary vacuum is made for 1 h. The reference spectrum is taken and different amounts of CO are injected in the cell for 2 min. The difference between these spectra and the reference, give the characteristic spectra of CO adsorbed in the catalyst. The areas of the peaks of adsorbed CO increase with the increase in the CO pressure, and remain steady at saturation.

3.2.2. Reaction study

Kinetic experiments were carried out in a fixed bed reactor (BTRS Jr Autoclave Engineers) at atmospheric pressure. The catalyst sample (0.140 g) was supported in a small plug of glass wool in a vertical stainless steel tubular reactor. The reactor was inserted into an oven, and the temperature controlled by a Eurothem 847 controller with PID action. The temperature was measured by a K-type thermocouple that was inserted into the catalyst bed. The reactant mixture, consisting of a pre-mixed gas (20% O₂ in nitrogen (Air Liquide)) with a concentration of MIBK of 1,340 ppmv, was introduced in the reactor with a total flow rate of 4.16 mmol min⁻¹, which was controlled by mass flow controllers (Bronkhorst). The desired concentration of MIBK in the reactant mixture was obtained by passing the pre-mixed gas through a saturator which was kept at the appropriate temperatures by means of a cryostatic bath (Techne) and by mixing this stream with the same pre-mixed gas so that the required concentration was achieved. The space velocity was kept constant in all the experiments (20,000 h⁻¹, calculated at ambient temperature and pressure).

The products distribution (also called selectivity) is reported in terms of the relative yields defined as:

$$s_i = \frac{\text{product i}}{\text{converted reactant}}$$

where both terms are expressed as molar flow rates.

The analytical system consisted of a gas chromatograph (Tremetrics 9001) equipped with a flame ionisation detector (FID) for the analysis of the hydrocarbons, and two non-dispersive infrared (NDIR) analysers for the analysis of CO (Analytical Development Company) and CO₂ (NOVA Analytical Systems Inc.). The GC was fitted with a CP Wax 52 capillary column, with 30 m of length and 0.32 mm of internal diameter, kept at 70°C. The conversion into CO₂ is defined as the molar flow rate of CO₂ at the reactor outlet, divided by six times the molar flow rate of MIBK in the feed.

For the oxidation of the mixture of MIBK and o-xylene, another saturator containing o-xylene was used which was also kept in the cryostatic bath. The reactants were then mixed with the appropriate flow rates in order to obtain the desired concentrations (1340 ppmv of MIBK and 1500 ppmv of o-xylene).

The amount of coke in the catalysts after reaction was measured by temperature programmed oxidation in air (TPO). After reaction, the catalyst was cooled in nitrogen till 80°C. Then a stream of air was passed and the temperature increased at 10°C min⁻¹ till 520°C and was maintained until there was no further change in the gas concentration. The CO and CO₂ released were determined by the NDIR analysers. The amount of coke was calculated by integration of the CO and CO₂ curves obtained. Elemental analysis was also made after some experiments, in order to determine the total amount of coke deposited in the catalysts. The CHNS-O elemental analyser used was a Carlo Erba Instruments, model EA 1108.

The analysis of side products was made by collecting gas samples on a trap at the reactor outlet. These samples were then analysed by GC-MS (Varian – CP-3800 with a ITD detector Saturn 2000) by means of a gas syringe (Hamilton) of 0.5 mL. The separation was made by a chromatograph column CP-Sil 8 CB lowbleed/MS kept at 50°C for 5 min and increasing the temperature till 200°C at a rate of 20°Cmin⁻¹, keeping this temperature for 10min.

The carbonaceous compounds retained on the catalyst (“coke”) were analysed by a technique developed for that purpose [11]. This technique was explained in chapter 2.

Temperature programmed desorption of MIBK and o-xylene (individually or in mixtures) was also studied after pre-adsorption of the reactants at 40°C over the Pt/HFAU(47) catalyst. The reactants were adsorbed on the catalysts at 40°C from a nitrogen stream, using the same concentration as in the reaction study. After saturation (when the concentration of reactant in the gas phase did not change), the system was purged with a nitrogen stream and the TPD started. The temperature was increased at 5°C min⁻¹ till 520°C and was maintained at this value until there was no more reactant at the exit. The reactants were analysed by GC/FID.

3.3. Results and discussion

The properties of the supports used in this work (acidity and texture) are shown in Table 1. The dispersion of platinum, determined in some cases by different methods, is shown in Table 2.

Table 1 – Properties of HBEA (15 and 50), HFAU (47 and 5), NaY, CsY, SiO₂ and γ-Al₂O₃ supports: concentration of Brönsted (*A_B*) and Lewis (*A_L*) acid sites, mesoporous surface area (*S_{meso}*) and micropore volume (*V_{micro}*).

	<i>A_B</i> (10 ¹⁸ atoms.g ⁻¹)	<i>A_L</i> (10 ¹⁸ atoms.g ⁻¹)	<i>S_{meso}</i> (m ² g ⁻¹)	<i>V_{micro}</i> (cm ³ g ⁻¹)
γ-Al ₂ O ₃	-	240	196	-
SiO ₂	-	-	164	-
HBEA(50)	90	9	268	0.143
HBEA(15)	278	143	206	0.152
HFAU(47)	49	7	134	0.284
HFAU(5)	403	149	38	0.264
NaFAU	-	n.d.	6	0.304
CsFAU	-	n.d.	1	0.188

* determined by the *t*-method.

When platinum is introduced in the zeolites there can be some changes in their textural and chemical properties. The textural properties of the zeolite HFAU(47) were checked after ion exchange with platinum (0.16%) and calcination. The micropore volume was

0.283 cm³ g⁻¹ and the mesoporous surface area was 131 m² g⁻¹. So, there was practically no difference between the support alone and impregnated with platinum.

Table 2 – Platinum dispersion of Pt/HBEA (15 and 50), Pt/HFAU (47 and 5), Pt/NaFAU, Pt/CsFAU, Pt/SiO₂ and Pt/Al₂O₃ catalysts.

	Dispersion (%)
0.32Pt/ γ -Al ₂ O ₃	59 ^a /56 ^b /62 ^c
0.09Pt/SiO ₂	43 ^a /36 ^b
0.21Pt/HBEA(50)	69 ^b
0.23Pt/HBEA(15)	62 ^b
0.09Pt/HFAU(47)	35 ^b
0.16Pt/HFAU(47)	34 ^b
0.52Pt/HFAU(5)	50 ^b
0.21Pt/NaFAU	39 ^b
0.23Pt/CsFAU	21 ^b
(a) determined by H ₂ chemisorption	
(b) determined by toluene hydrogenation reaction	
(c) determined by CO adsorption followed by IR	

Concerning the acidity of the zeolite after ion exchange with platinum, there was a decrease in the Brönsted acidity and an increase in the Lewis acidity. In fact, the Brönsted acidity of HBEA(50) decreased to 86x10¹⁸ atoms g⁻¹ and the Lewis acidity increased to 16x10¹⁸ atoms g⁻¹ after impregnation with 0.21% of platinum. This can be related to the preparation method of the catalyst and/or to the incertitude of the measurements.

In the case of Pt/NaFAU and Pt/CsFAU, it would be expected that some Brönsted acid sites would appear, due to the process of ion exchange. Although with these supports no compensation cation was used (to prevent the formation of acid sites), there can be always some degree of exchange of the cations with NH₄⁺ ions of the precursor [9]. The acidity of these catalysts was measured by pyridine adsorption followed by IR, and very low Brönsted acidities were found (2x10¹⁸ atoms g⁻¹ for Pt/NaFAU and no acidity for Pt/CsFAU). There was no Lewis acidity (at least associated with the band at 1455 cm⁻¹), although there are always Lewis acid sites associated with the cation (like in the supports NaFAU and CsFAU), but these sites were not quantified.

The dispersion of platinum was measured by three different methods over Pt/ γ -Al₂O₃. The results obtained are similar, showing that all three methods can determine the dispersion of the metal. Hydrogen chemisorption was also used over some Pt/zeolite catalysts, but not successfully. This technique does not seem suitable to determine the platinum dispersion on zeolite supported catalysts with such low amounts of metal. The problem is that when performing the adsorption isotherms of hydrogen, there is hydrogen that chemisorbs on the platinum but there is also physisorbed hydrogen (this is why two isotherms are made: total adsorption and physisorption only). If the amount physisorbed is much higher than the chemisorbed amount, the equipment is not sensible enough, and the isotherms will overlap. So, what happened was that there was no significant difference between these two isotherms when Pt/zeolite catalysts were used, and therefore it was preferred to use toluene hydrogenation to determine the metal dispersions.

3.3.1. Catalytic oxidation over Pt/HFAU(47) catalysts

3.3.1.1. Influence of the temperature and time-on-stream (TOS)

Two main reactions were observed in the oxidation of MIBK over the 0.09Pt/HFAU(47) catalyst: total oxidation into CO₂ (and H₂O), and formation of heavy non-desorbed products (“coke”). Some other side products were detected at the lower reaction temperatures, particularly below 200°C. The results obtained over this catalyst are compared in Figure 1 at different temperatures (from 175 to 220°C).

At 220°C, whatever the TOS, there was no MIBK at the reactor exit, nor any side products or coke, and the conversion into CO₂ was complete. At 200°C, the MIBK conversion was also complete whatever the TOS and the conversion into CO₂ increased till 98%. Side products and coke were formed in very small amounts.

At the temperatures of 195 and 190°C there were oscillations in the observed conversion into CO₂. At 190°C the molar flow rate of CO₂ increased initially, and then started to oscillate. These oscillations would correspond to apparent conversions into CO₂ ranging between 125% and 75%. The total conversion of MIBK was more difficult to follow, but taking experimental points at a maximum and a minimum of the CO₂ oscillations, we found that the total conversion varied from 92 to 100%. At 195°C the amplitude of the oscillations was smaller (apparent conversions into CO₂ between 97 and 103%) and the frequency was higher. No MIBK was found at the reactor exit. This phenomenon will be discussed in more

detail in chapter 5. In figure 1, only the values at the minima of the oscillations are represented, as explained in chapter 5.

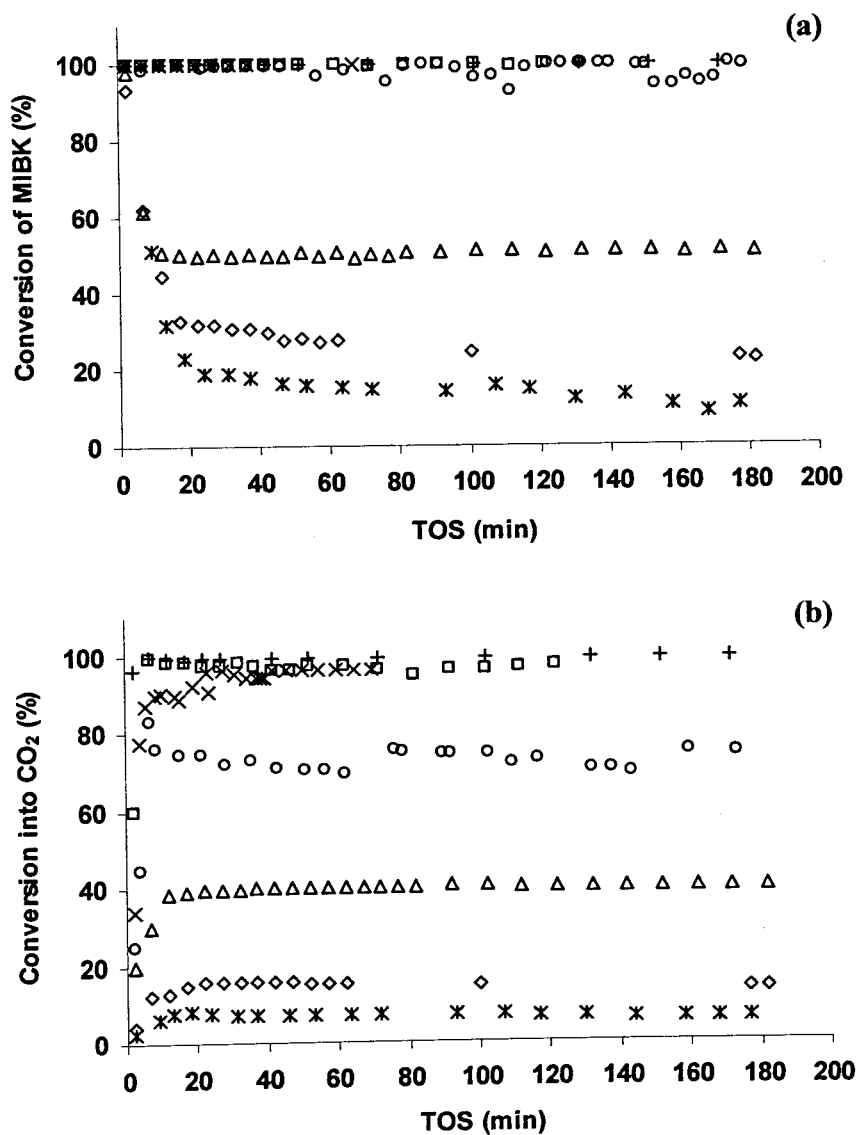


Fig. 1 – Influence of time-on-stream on the total conversion of MIBK (a) and conversion into CO₂ (b) over the 0.09Pt/HFAU(47) catalyst at (+) 220, (□) 200, (x) 195, (○) 190, (Δ) 185, (◇) 180 and (*) 175°C.

At temperatures of 185, 180 and 175°C, the conversion of MIBK decreased progressively as TOS increased (Fig. 1a), reaching a constant value for the reaction temperature of 185°C after approximately 10min. The conversion into CO₂ increased to constant values for all these three temperatures (Fig. 1b). Side products were formed, as well

as coke. It should be noted that no traces of CO were detected at the reactor exit, whatever the reaction temperature.

The exothermicity of the reactions could be measured by the thermocouple placed into the catalyst bed. Outside the range 190-195°C, the temperature was found to increase after starting the reaction, reaching a higher level which remained constant for the duration of the run. The temperature increases ranged from 1°C (run at 180°C) to 8°C (run at 220°C). However, in the experiments where cyclic behaviour was observed there were also temperature oscillations: increases between 2 and 9°C at 195°C and between 3 and 25°C at 190°C. These temperature oscillations were synchronized with the oscillations in the apparent conversion into CO₂. All the reaction temperatures considered in this work are the temperatures of the oven and not of the catalyst during the reaction.

At the lower temperatures, there was formation of side products that could be detected by GC. In figure 2 the selectivity in CO₂ is represented for each temperature versus TOS.

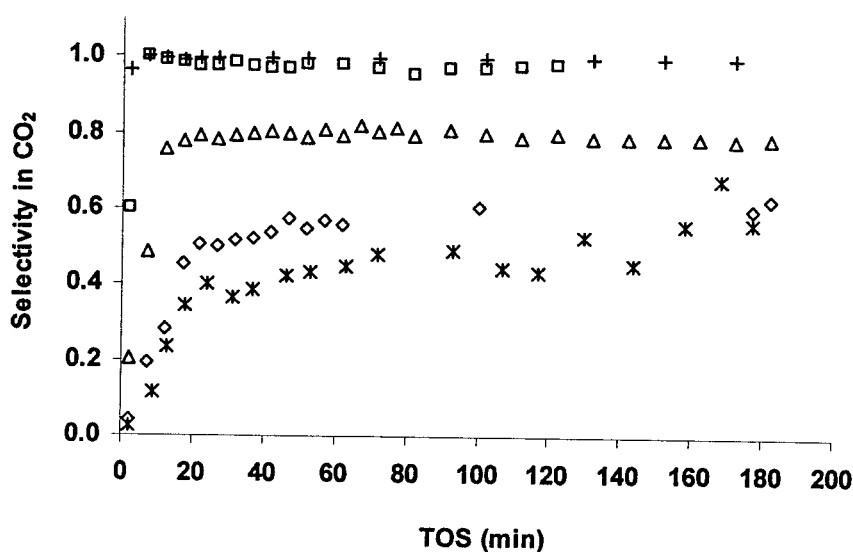


Fig. 2 – Influence of time-on-stream on the selectivity in CO₂ over the 0.09Pt/HFAU(47) catalyst at (+) 220, (□) 200, (Δ) 185, (◇) 180 and (*) 175°C.

The selectivity in CO₂ increases with the reaction temperature, being 1.0 at temperatures higher than 200°C. At lower temperatures the selectivity in CO₂ decreases due to the formation of coke and side products. The nature of these compounds will be discussed later in this chapter.

As stated before, at almost all reaction temperatures studied there was the formation of heavy non-desorbed products that remained in the zeolite pores. The conversion of MIBK into

coke depends also on the temperature. The TPO of coke after reaction at different temperatures is represented in Figure 3. TPO for the experiments at 190 and 195°C will be discussed in chapter 5.

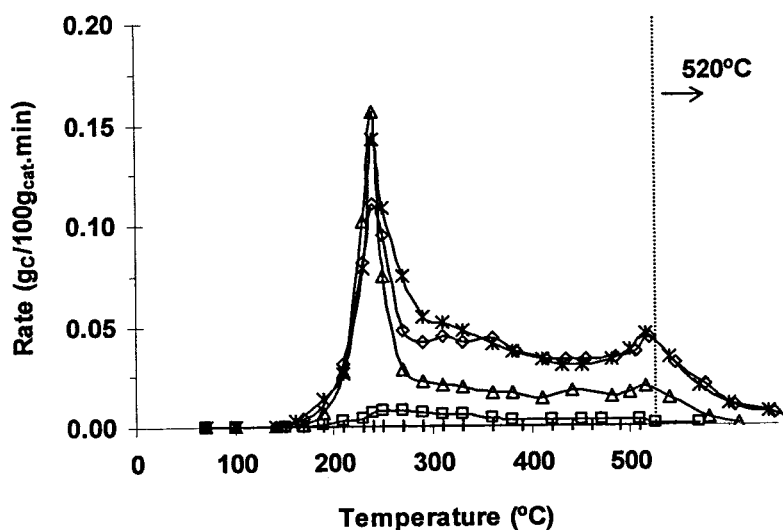


Fig. 3 – Temperature programmed oxidation of the coke after reaction at (+) 220, (□)200, (Δ)185, (◇)180 and (*) 175°C over the 0.09Pt/HFAU(47) catalyst.

In a TPO experiment it is possible to determine the reactivity of the coke compounds as well as the amount in terms of carbon. Some studies of coke oxidation on zeolites show that the zeolite structure plays a dominant role in coke oxidation [12]. It was also shown [13,14] that the coke content (nature and location) has a limiting effect on its oxidation, while the nature of the zeolite had a very pronounced effect, the more acid zeolites being more active for coke oxidation. This was also concluded in oxidation of pyrene, where the effect of the oxidative treatment was the same as over coked samples [15]. In the case of the catalytic oxidation of o-xylene over Pd/HFAU catalysts [16] it was also shown that the TPO curves are the same at different reaction temperatures, which is in agreement with other authors. Moreover, the oxidation of the carbonaceous compounds depends on the metal load. The higher the metal load, the lower the onset temperature for coke oxidation [16].

For the coke formed during MIBK oxidation over Pt/HFAU catalysts, whatever the reaction temperature, no CO is produced in TPO. There are mainly two coke components with different reactivities (Figure 3): one that oxidises at low temperatures (peak maximum 240°C) and another which oxidises at high temperatures (peak maximum 510°C). Most of these carbonaceous deposits start to oxidise at approximately 170°C, the reaction being exothermic.

It should be noted that it is also possible that transformations of the coke occurred during the TPO experiments, and that in fact what we call “less reactive coke” consists of compounds formed as a consequence of the transformation of other coke compounds, which therefore would not be formed directly from the oxidation of MIBK. The nature of the coke will be discussed later in this chapter, as well as in chapter 5 when discussing the oscillations in the apparent conversion into CO_2 . This shape of the TPO curves was also observed by Dégé [16] in o-xylene oxidation studies, but only when the reaction was carried out over Pd/NaFAU catalysts. When the reaction was carried out over Pd/HFAU catalysts, there was no peak at low temperatures as in the case of the present work, only one peak at temperatures higher than 400°C being observed.

DTG analysis of one coked sample was also made in air stream, but till 800°C . This was done in order to see if more coke was present in the catalyst, which did not oxidise till 520°C . The derivative weight loss curve had the same shape as the TPO curves and with two maxima: at 240°C and 500°C . So there was no need to increase the temperature over 520°C . This fact will also be important when considering the regeneration of the catalyst, as the catalyst should be regenerated at the lower possible temperature, to avoid sintering of the metal.

The amounts of coke retained in the zeolite pores (expressed as carbon released in the form of CO_2), obtained by integration of the TPO curves, are presented in Figure 4 as a function of the temperature. Average values (between a maximum and a minimum) were taken for the temperatures of 190 and 195°C .

The amount of carbonaceous compounds retained on the zeolite pores diminishes with the reaction temperature. This fact is naturally due to the progressive conversion of MIBK into CO_2 as the temperature increases.

Elemental analysis was made in order to verify if the amount of coke was the same as obtained by integration of the TPO curves. There were only some small differences, not exceeding $0.1 \text{ gC}/100\text{g}_{\text{cat}}$. The values are close enough to validate the method of coke determination by integration of the TPO curves.

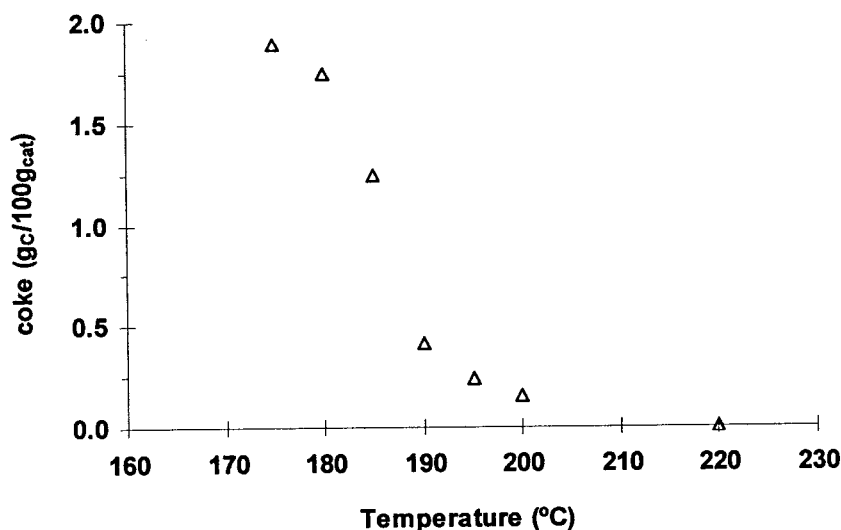


Fig. 4 – Amounts of coke after 3h reaction over the 0.09Pt/HFAU(47) catalyst at different temperatures.

3.3.1.2. Influence of the electronic state of the platinum

The effect of the electronic state of the platinum was studied in this reaction by comparing the activities of the 0.09Pt/HFAU(47) catalyst pre-reduced under hydrogen at 300°C and pre-calcined under air at 500°C. This treatment under air was performed because after calcination of the catalyst at 300°C (section 3.2.1.) part of platinum is already in the reduced state [17,18]. Thus, the treatment at 500°C under air was made so that platinum will be oxidised [19].

The behaviour of both catalysts (pre-calcined and pre-reduced) was compared for MIBK oxidation into CO₂ (Figure 5).

The pre-reduced catalyst is more active in the oxidation than the calcined one, as for the same reaction temperature it can oxidise more MIBK into CO₂. At 200°C the pre-reduced catalyst is capable of oxidising all the MIBK in CO₂, while the pre-calcined one can only achieve this at 240°C.

This result is in agreement with previous observations in the oxidation of o-xylene (chapter 2), where metallic platinum was also found to be the most active species. Studies by other authors also show the same behaviour, namely in the catalytic oxidation of n-heptane over Pt/Al₂O₃ [20].

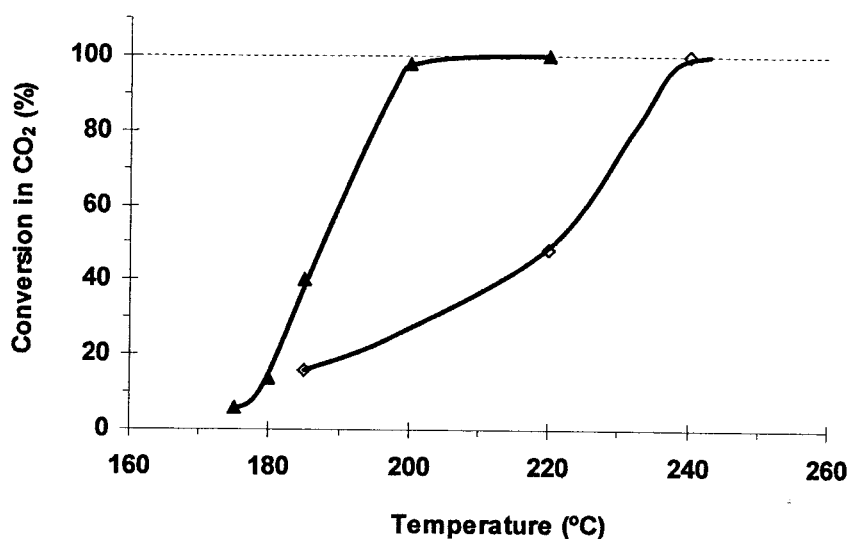


Fig. 5 – Conversion into CO₂ after 3h of reaction as a function of temperature for the 0.09Pt/HFAU(47) catalyst (◊) pre-calcined at 500°C and (▲) pre-reduced at 300°C.

The TPO of the samples after reaction at 220° is shown in Figure 6.

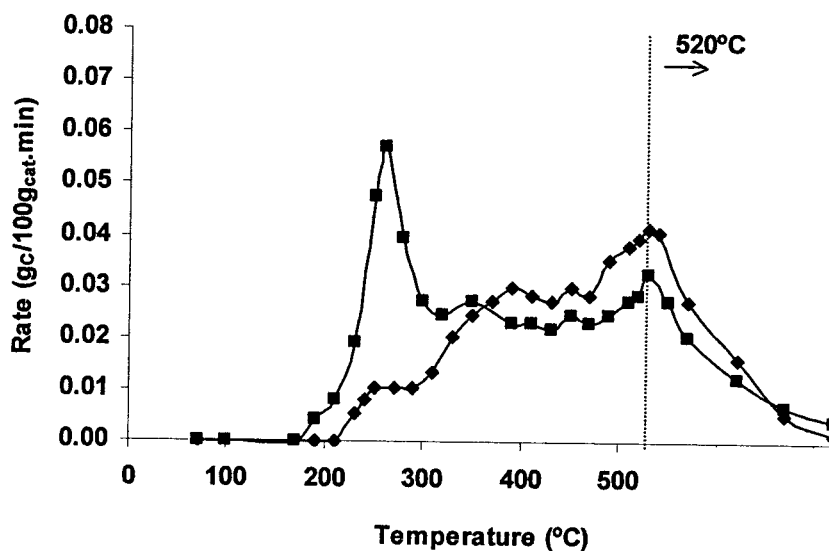


Fig. 6 – Oxidation of the coke after 3h of reaction at (■) 185 and (◆) 220°C on the 0.09Pt/HFAU(47) pre-calcined catalyst.

The TPO curve after reaction at 185°C has the same shape as when the catalyst is pre-reduced. The only difference is that the peak maximum occurs at higher temperatures (260°C). Oxidised platinum is also less active for coke combustion, which is in agreement with the results of the oxidation of MIBK. The fact that the TPO curve after reaction at 220°C

is different from those after reaction at 185°C and with the pre-reduced catalysts, may be due to the fact that the nature of the coke is different. At this temperature there is relatively less highly reactive coke and relatively more coke that oxidises at higher temperatures. This observation suggests that at this temperature there is a faster conversion of more reactive coke into less reactive coke. Nevertheless, an analysis of the soluble coke after reaction over the pre-calcined catalyst would be required in order to assess more precisely its nature.

3.3.1.3. Effect of the platinum load

The influence of the platinum content was studied in the oxidation of MIBK at temperatures between 160 and 220°C on the catalysts 0.16Pt/HFAU(47) and 0.09Pt/HFAU(47) and also on the support HFAU(47) alone. The results are presented as the conversion into CO₂ as a function of reaction temperature after 3h of reaction (Figure 7).

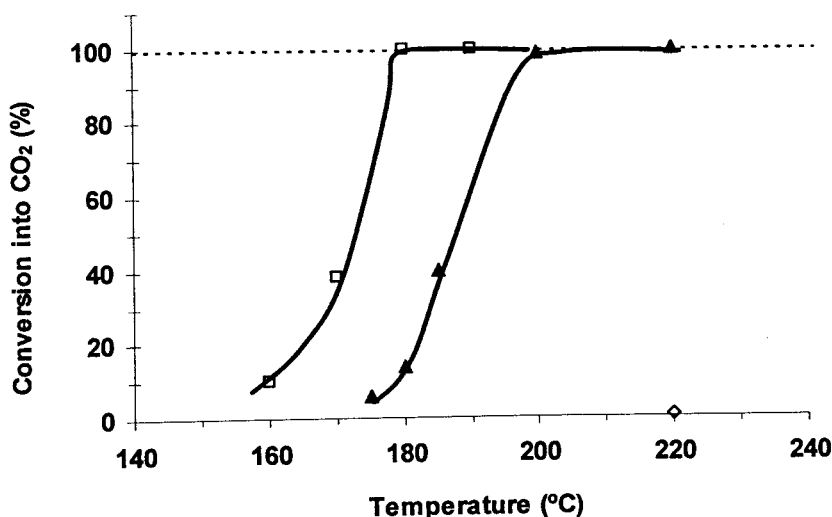


Fig. 7 – Conversion into CO₂ after 3h of reaction as a function of temperature on the (□) 0.16Pt/HFAU(47), (▲) 0.09Pt/HFAU(47) and (◇) HFAU(47) catalysts.

The higher the platinum content the higher the conversion of MIBK into CO₂. The complete conversion of MIBK into CO₂ is obtained at 180°C for a Pt content of 0.16wt% and at 200°C for 0.09wt%. Moreover, the presence of Pt is indispensable to transform MIBK into CO₂ in the temperature range studied. Indeed, over the HFAU(47) zeolite, at 220°C, the total transformation of MIBK is low (13%) and the formation of CO₂ and CO is almost non-existent (1%). The formation of side products is relatively high when the support is alone.

The results of the amount of coke oxidized at 520°C after reaction at different temperatures over the Pt/HFAU(47) catalysts and the HFAU(47) zeolite are represented in Figure 8.

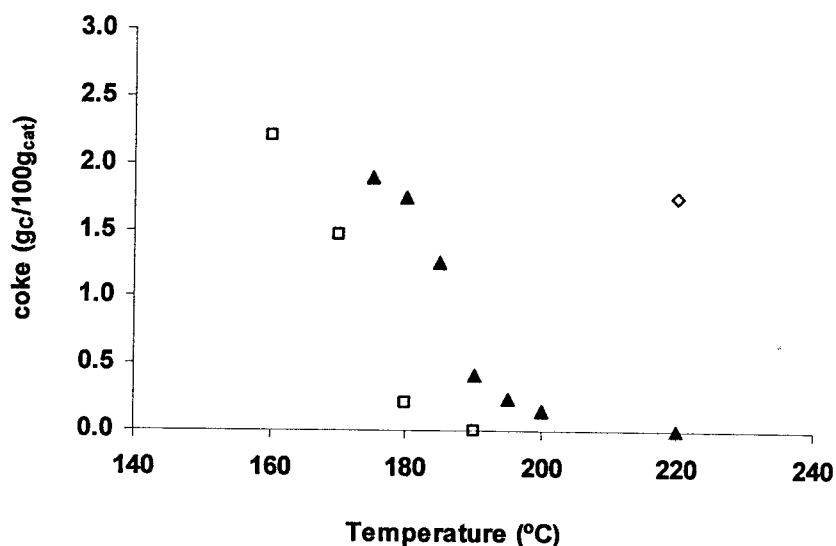


Fig. 8 – Coke amount in the catalysts after 3h of reaction as a function of temperature of reaction on the (□) 0.16Pt/HFAU(47), (▲) 0.09Pt/HFAU(47) and (◇) HFAU(47) catalysts.

The total amount of coke present in the catalyst after reaction depends not only on the temperature of the reaction, but also on the amount of platinum. There is a displacement of the amount of coke towards lower temperatures as the amount of platinum increases. This fact is certainly due to the higher oxidation activity of the catalyst with more platinum. For example, at 180°C the conversion over 0.16Pt/HFAU(47) is complete and therefore the amount of coke is very low. For the same reaction temperature, over the 0.09Pt/HFAU(47) the conversion of MIBK is not complete and so coke is accumulating. In the case of the zeolite alone, coke is also being formed. The amount of coke increases with the temperature (not shown in the figure), as after reaction at 300°C the amount of coke is of 2.8 gc/100g_{cat} (this result is shown in chapter 4). Moreover, CO was produced only during TPO of the coke deposited on the support.

For comparison of the differences in the coke, TPO curves after reaction at 170°C over 0.16Pt/HFAU(47), 185°C over 0.09Pt/HFAU(47) and 220°C over the HFAU(47) zeolite are shown in Figure 9.

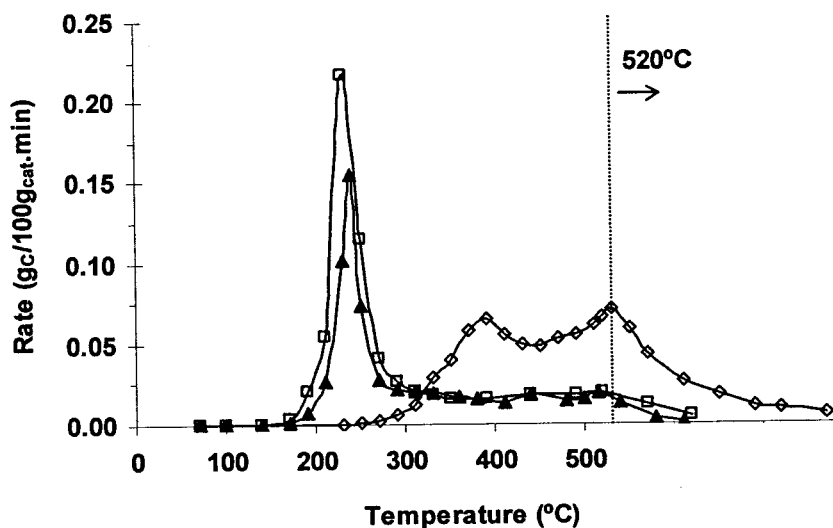


Fig. 9 – Oxidation of the coke after reaction over the (□) 0.16Pt/HFAU(47) catalyst at 170°C, (▲) 0.09Pt/HFAU(47) catalyst at 185°C and (◇)HFAU(47) zeolite at 220°C.

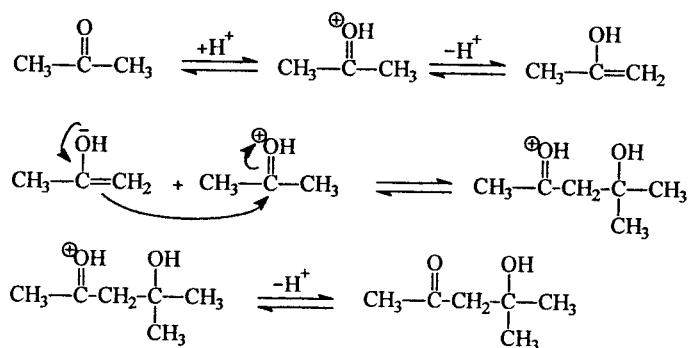
With the 0.16Pt/HFAU(47) catalyst, the oxidation of coke starts at slightly lower temperatures than with the catalyst with less platinum: peak maximum at 230°C against 240°C. This fact can be due to the higher oxidation activity of the catalyst with more platinum, which also presented a higher activity in the oxidation of MIBK. On the other hand, over the support alone coke combustion is different from the catalysts with platinum. The support alone has a lower oxidation power, hence the coke combustion starts at higher temperatures. Moreover, the nature of the coke is certainly different from the Pt/HFAU catalysts (as discussed in next section), and this fact also can have an influence on the shape and position of the TPO curves.

3.3.1.4. Analysis of the side products and soluble coke

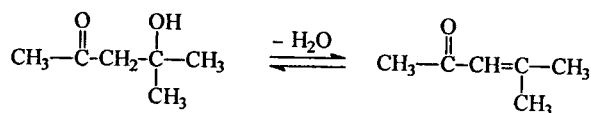
During the reactions in the presence of Pt/HFAU(47) and HFAU(47), MIBK was not only oxidised into CO (in the case of the zeolite) and CO₂ but also other products were formed. The products that were released during the reaction were collected in a gas trap and analysed by GC/MS and those that remained adsorbed on the catalyst were analysed by a technique developed for the analysis of the soluble coke [11]. These two techniques were performed over the 0.09Pt/HFAU(47) catalyst and HFAU(47) zeolite after reaction at 180°C and 220°C, respectively.

In the experiment over the 0.09Pt/HFAU(47) catalyst, acetone and branched heptenes were the main side products found in the gas phase. Other compounds like acids and aromatics were also identified. Compounds like acetone and acids were also identified in the regeneration of activated carbon saturated with MIBK, after oxidative treatment with UV/O₃ [7]. In the case of HFAU(47), the side products found by GC/MS were branched heptenes (major products), acetone (traces), methyl-butanoic and acetic acids and aromatics.

These products are most likely formed via aldol condensation, followed by cracking and cyclisation reactions. Aldol condensation of acetone can occur in acid medium as follows:

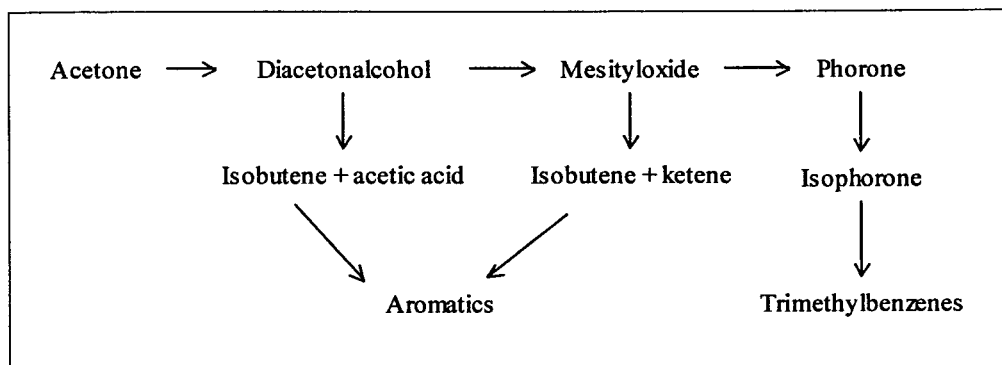


Dehydration leads to mesityloxide:



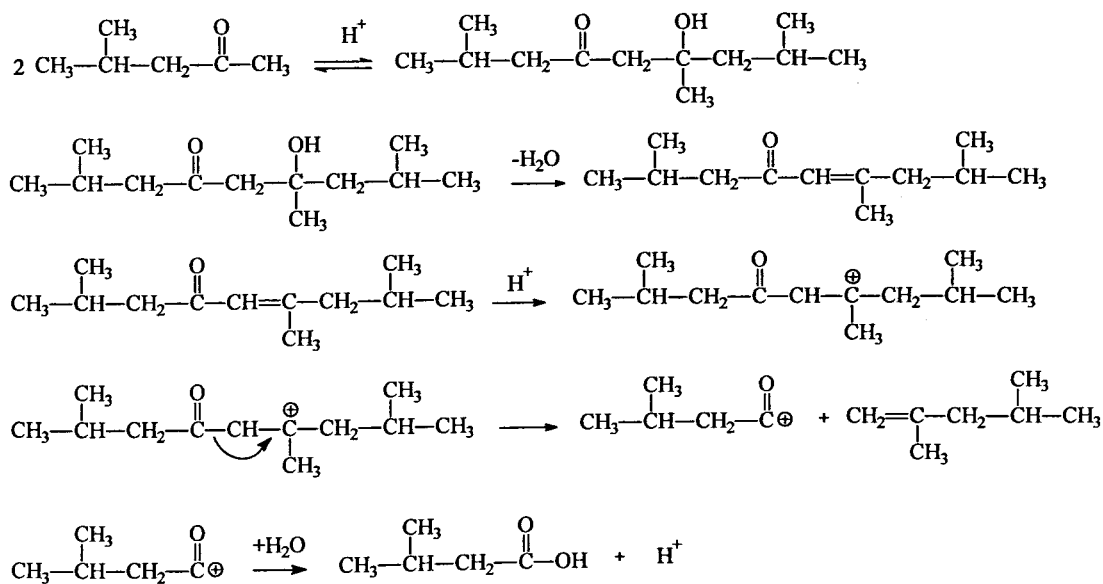
Kubelková and co-workers [21], when studying acetone conversion over HZSM-5 and HY zeolites, found a fast deactivation of the zeolites due to coke formation. This coke has a very complex nature, presenting aromatic rings, alkane and alkene groups and unsaturated ketonic species on the surface of the catalyst. These compounds were identified by IR and

NMR. The reaction path starts with aldolisation, and proceeds via cracking, cyclisation and aromatisation. The following scheme was proposed [21]:

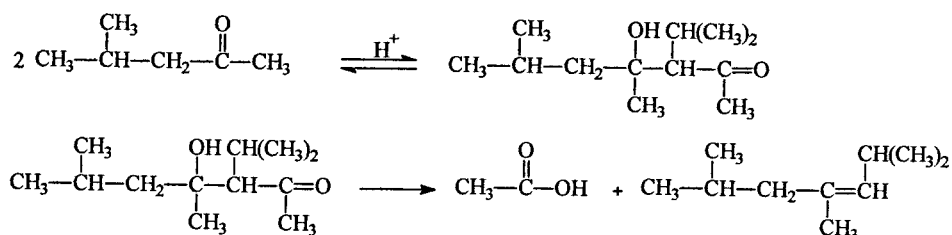


Similar compounds were obtained by Melo *et al.* [22,23] when studying the transformation of acetone towards MIBK as well as Flego and Perego [24] in their work of the aldol condensation of acetone. Coke analysis after reaction showed mainly isophorone and polyalkylbenzenes.

Aldol condensation of MIBK followed by cracking can lead to the formation of alkenes and acids considering the following reactions:

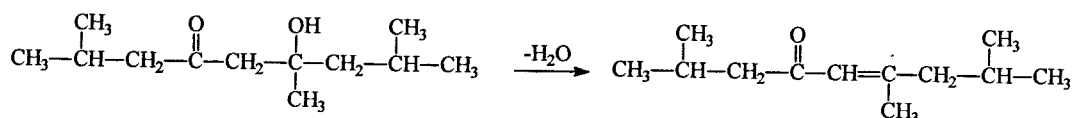


There are other possible ways of condensation:



The alkene with 10 carbon atoms was not identified. Most probably it would crack, forming heptenes and propene. This last molecule can easily oxidise into acetone.

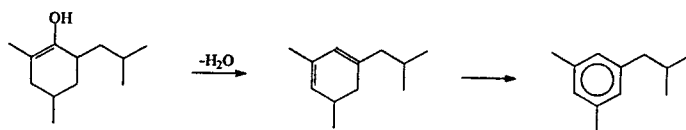
Dehydration of the condensation products leads to compounds of the type:



Isomers of this compound can be formed, depending on how the condensation reaction and dehydration take place. Cyclisation can lead to compounds of the following type (and corresponding enol form):



Aromatic compounds can be formed by dehydration followed by hydrogen transfer. This transfer can occur from alkenes that were formed.



Another possibility of obtaining this last compound is by aldol condensation of MIBK with two molecules of acetone. In this case, the aromatic would be obtained directly from dehydration after cyclisation.

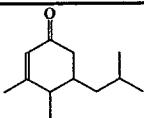
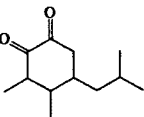
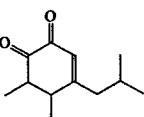
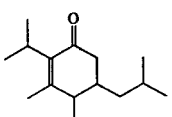
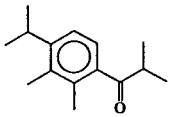
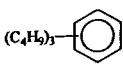
It should be noted that all these products (except the C_{10}) were identified by GC/MS, although there was the presence of isomers (specially with the C_7).

Acetone can be formed in two ways: by oxidation of propene, or by oxidation of MIBK. In fact, when no platinum is present, only traces of acetone are present in the

chromatograms, which means that the oxidation function is important for the formation of acetone. On the contrary, the formation of alkenes is enhanced when no platinum is present. This suggests that these compounds are formed in the acid sites of the zeolite.

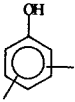
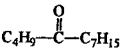
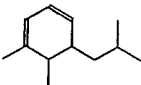
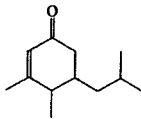
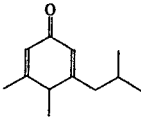
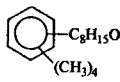
The main compounds that were present in the soluble coke after 3h of reaction over the 0.09Pt/HFAU(47) catalyst at 180°C are shown in Table 3 (total amount of coke: 1.7%; amount of coke recovered: 0.7%). There is a great difference between these two values of coke content, and this cannot be due only to the incertitude in the quantification of the amount of soluble coke recovered. As will be shown in chapter 5, a large part of the coke (which we call reactive coke) is composed of reactant and other volatile compounds that remain adsorbed in the catalyst. These compounds will not remain in the soluble coke, as it was concentrated by means of evaporation at 50°C under vacuum. This explains the large difference between the two values.

Table 3 –Soluble coke after reaction at 180°C over the 0.09Pt/HFAU(47) catalyst.

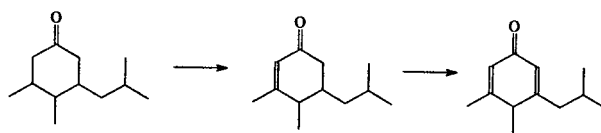
Molar mass (g.mol ⁻¹)	Formula	Amount (%)	Compound
180	C ₁₂ H ₂₀ O	25	
196	C ₁₂ H ₂₀ O ₂	52	
194	C ₁₂ H ₁₈ O ₂	8	
222	C ₁₅ H ₂₆ O	2	
218	C ₁₅ H ₂₂ O	3	
246	C ₁₈ H ₃₀	10	

The main compounds that were present in the soluble coke after 3h of reaction over the HFAU(47) zeolite at 220°C are shown in Table 4.

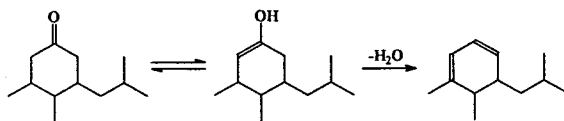
Table 4 – Soluble coke after reaction at 220°C over the HFAU(47) zeolite.

Molar mass (g.mol ⁻¹)	Formula	Amount (%)	Compound
122	C ₈ H ₁₀ O	11	
184	C ₁₂ H ₂₄ O	21	
164	C ₁₂ H ₂₀	33	
180	C ₁₂ H ₂₀ O	5	
178	C ₁₂ H ₁₈ O	18	
260	C ₁₈ H ₂₈ O	12	

Condensation of two molecules of MIBK followed by cyclisation and dehydrogenation (or hydrogen transfer) can lead to molecules of the type:

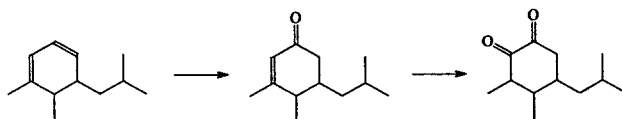


Condensation of two molecules of MIBK followed by cyclisation and dehydration can lead to molecules of the type:



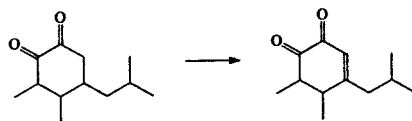
This last compound was detected on the support after reaction.

Oxidation of the unsaturated bonds can lead to:

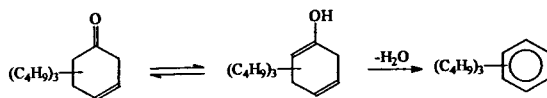
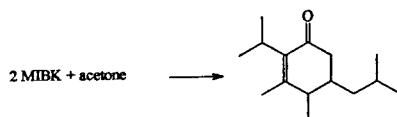


These molecules were detected in the Pt/HFAU(47) catalyst, and also some traces in the zeolite alone. This makes sense, because platinum would promote oxidation reactions.

The molecule with molar mass 194 g mol⁻¹ is certainly formed from this last one, by dehydrogenation, or hydrogen transfer:



The other molecules with higher molar mass are probably formed from the condensation of more ketone molecules:



Analysis of the catalyst after reaction shows that the coke is composed mainly by condensation products, which are formed in the acid site of the zeolite. Therefore, the acid sites are responsible for coke formation during the reaction.

3.3.1.5. Effect of the MIBK partial pressure

The total conversions of MIBK and the conversions into CO_2 obtained over 0.09Pt/HFAU(47) at 183°C with different concentrations of MIBK are compared in Figure 10. These concentrations, 1340, 960 and 630 ppmv, were achieved by keeping the reactant in a thermostatic bath at -5 , -10 and -15°C , respectively, and keeping the oxygen partial pressure constant (20%).

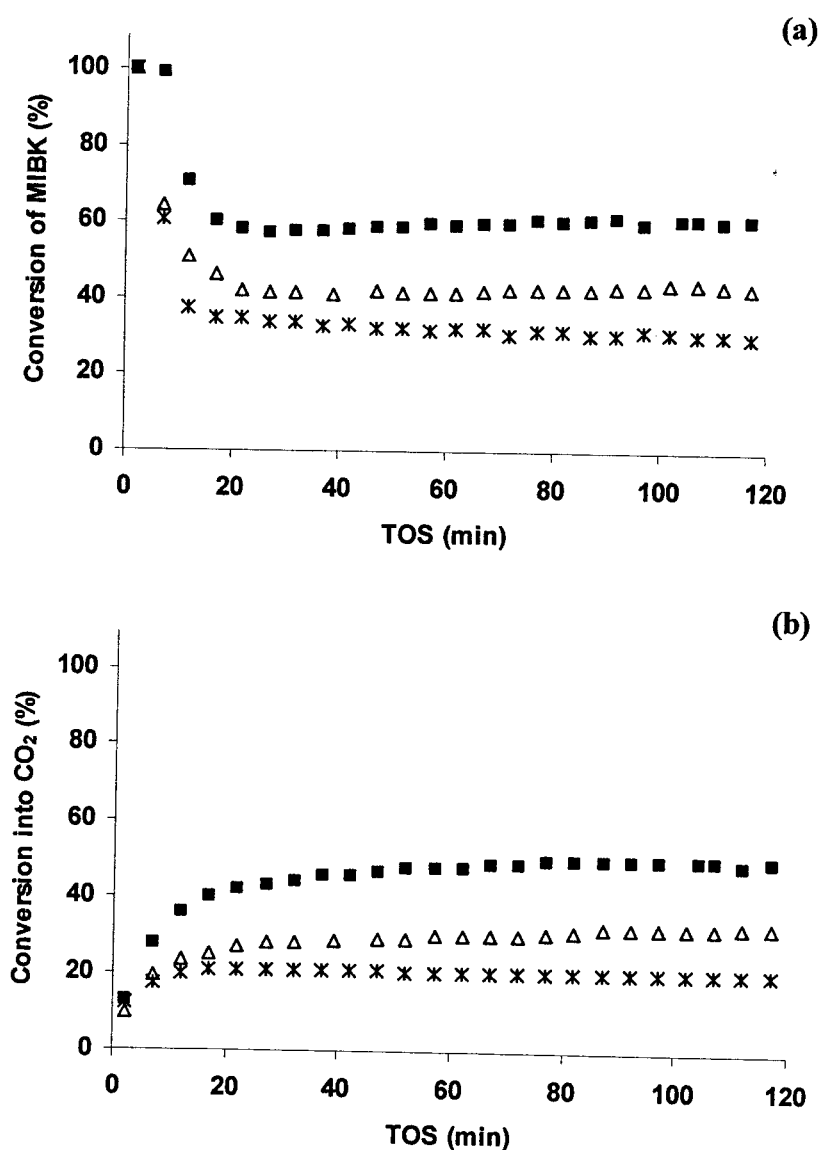


Fig. 10 – Influence of time-on-stream on the total conversion of MIBK (a) and conversion into CO_2 (b) over the 0.09Pt/HFAU(47) catalyst at 183°C with concentration of MIBK of (*) 1340, (Δ) 960 and (■) 630 ppmv.

When the reaction is performed with lower concentration of the reactant, both the conversion of MIBK and the conversion into CO_2 are higher. Whatever the inlet MIBK concentration, the conversion of MIBK is complete at low TOS. This conversion decreases progressively with TOS till constant values. The conversion into CO_2 increases with TOS till constant values.

The selectivity in CO_2 also increases with the decrease of the concentration of MIBK, as can be seen in Figure 11.

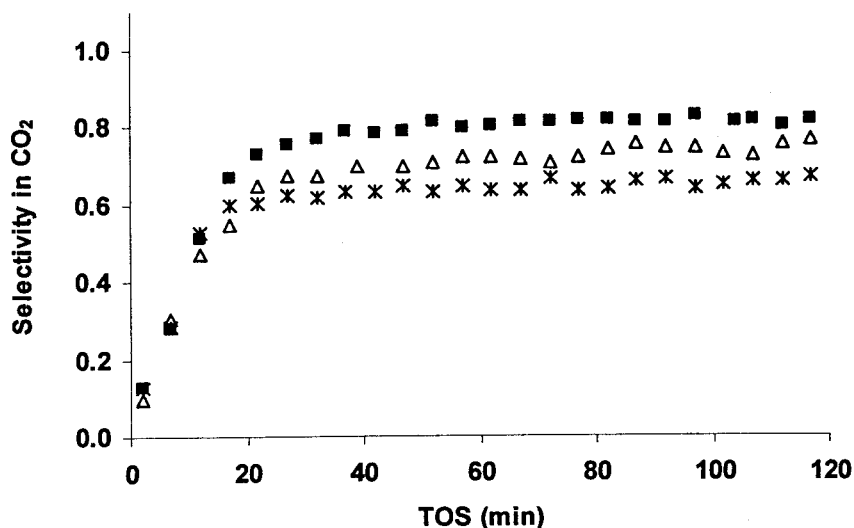


Fig. 11 – Influence of time-on-stream on the selectivity into CO_2 over the 0.09Pt/HFAU(47) catalyst at 183°C with concentration of MIBK of (*) 1340, (Δ) 960 and (■) 630 ppmv.

For lower concentrations of MIBK, the catalyst is more selective in CO_2 and therefore lower amounts of side products are formed.

It is evident that there is a dependency of the conversion on the concentration of MIBK. Similar results were found in the literature, namely in the oxidation of acetone [1] and formaldehyde [25]. In the case of aromatic hydrocarbons, the reaction was found to be of zero order with respect to the VOC concentration [26,27]. It was also shown that the reaction order and apparent activation energy did not change with the metal dispersion [27].

3.3.1.6. Effect of the oxygen partial pressure

The effect of oxygen in the process was studied by comparing the total conversion of MIBK and the conversion into CO_2 obtained over 0.09Pt/HFAU(47) at 183°C with different concentrations of oxygen in the feed: 1.2 (stoichiometric amount for complete conversion), 5, 8, 14, 20 and 40% (Figure 12). These concentrations were achieved by mixing a stream of nitrogen with a stream of oxygen (or a mixture of 20% oxygen diluted in nitrogen), maintaining the total flow rate. The concentration of VOC was maintained constant (1340 ppmv).

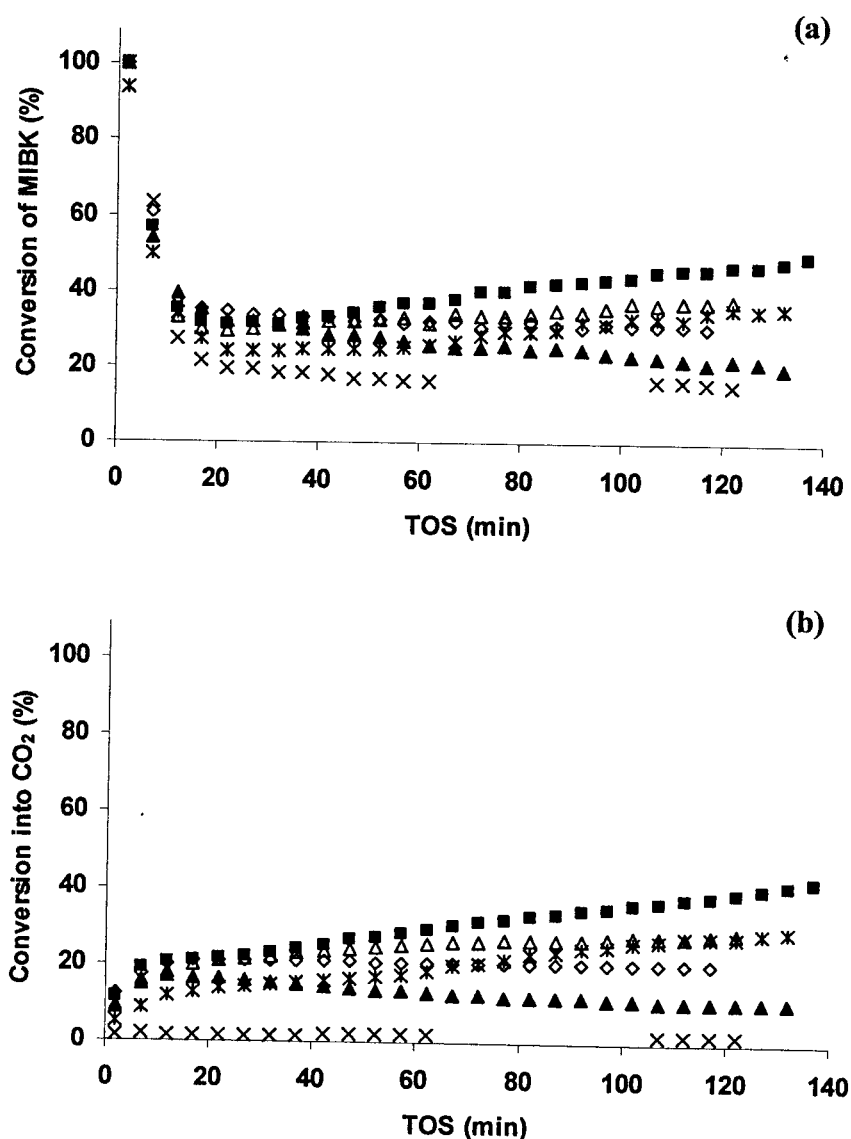


Fig. 12 – Influence of time-on-stream on the total conversion of MIBK (a) and conversion into CO_2 (b) over the 0.09Pt/HFAU(47) catalyst at 183°C with different concentration of oxygen: (x) 1.2%, (*) 5%, (■) 8%, (Δ) 14%, (◇) 20%, (▲) 40%.

At the beginning of the runs, there is no MIBK at the reactor exit for almost all the oxygen concentrations, but the conversion of MIBK decreases progressively till constant values, in some cases. In other cases there is an increase of the conversion of MIBK after some time of reaction. The conversion into CO_2 increases initially till constant values, for some oxygen concentrations. For high concentrations (40%) the conversion into CO_2 presents a maximum. For concentrations of 5, 8 and 14% the conversion into CO_2 increases with TOS during the run.

The selectivity in CO_2 also depends on the oxygen concentration (Figure 13).

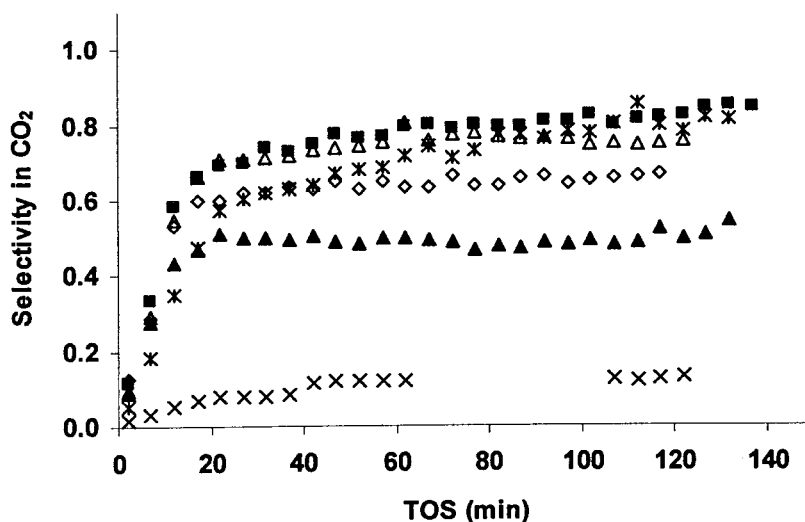


Fig. 13 – Influence of time-on-stream on the selectivity in CO_2 over the 0.09Pt/HFAU(47) catalyst at 183°C with different concentration of oxygen: (x) 1.2%, (*) 5%, (■) 8%, (Δ) 14%, (◇) 20%, (▲) 40%.

At low oxygen concentrations (1.2%), the selectivity in CO_2 is very low. Similar selectivities were found for oxygen concentrations of 5, 8 and 14%, which correspond to the maximum value of all the runs. At higher oxygen concentration, the selectivity diminishes.

The conversion into CO_2 after 2h of reaction at 183°C is plotted as a function of the inlet concentration of oxygen in Figure 14. This conversion increases with the oxygen concentration for low concentrations, decreasing for higher concentrations. The maximum of conversion into CO_2 was achieved with 8% oxygen in the feed.

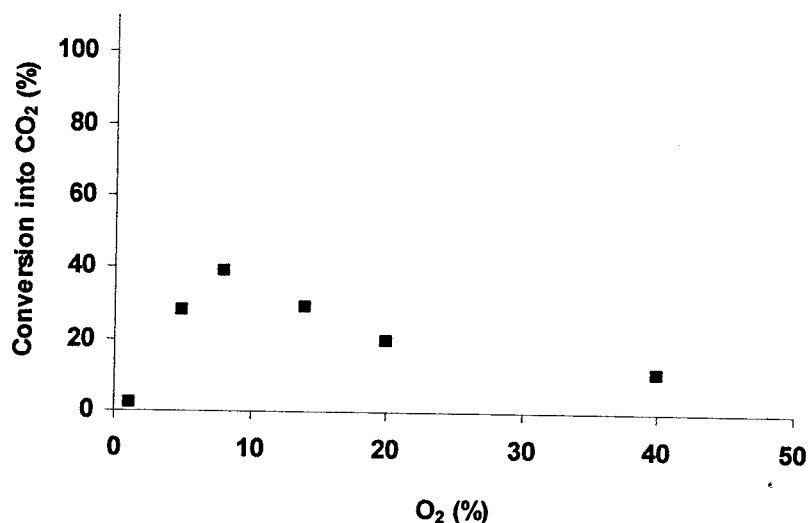


Fig. 14 – Conversion into CO₂ after 2h of reaction as a function of the inlet concentration of oxygen in the presence of the 0.09Pt/HFAU(47) catalyst at 183°C.

The amount of coke that remained in the zeolite pores after 2h of reaction is shown in Figure 15.

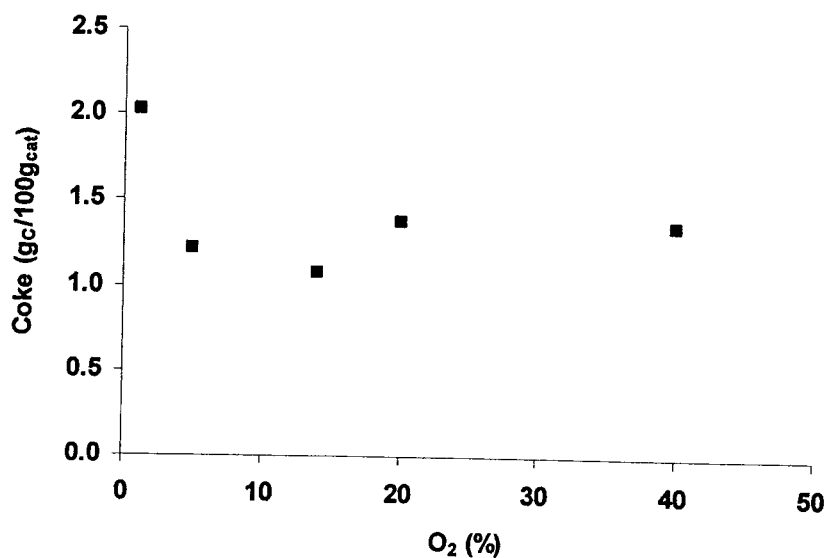


Fig. 15 – Amount of coke after 2h of reaction as a function of the inlet concentration of oxygen in the presence of the 0.09Pt/HFAU(47) catalyst at 183°C.

The total amount of coke after reaction is approximately the same in all cases, except for the inlet oxygen concentration corresponding to the stoichiometric amount for total

oxidation (1.2%),. This observation can be related to the fact that some adsorbed intermediate compounds of the coke are more difficult to oxidise, because of the lack of oxygen present.

It is clear that there is a negative effect on the conversion when the concentration of oxygen is very high. This phenomenon was also reported in the oxidation of heptane with a Pt/ γ -Al₂O₃ catalyst [20] and in the oxidation of ethyl acetate and butanol also with a Pt/ γ -Al₂O₃ catalyst [28]. In this last work, it was found that the reaction order was negative with respect to oxygen. With n-heptane [20], the activity decreased when the reaction was carried out in pure oxygen, due to the fact that in pure oxygen the atmosphere is more oxidising, hence the platinum will exist as Pt^{IV} which is less active for the oxidation of n-heptane.

On the other hand, if the amount of oxygen is very low, the activity of the catalyst is also low. When oxygen and MIBK are in the stoichiometric amounts, the conversion into CO₂ is very low, increasing when the oxygen concentration also increases.

This result shows that there is an optimum percentage of oxygen in the inlet for which the conversion will be maximum. For low oxygen concentrations (<8%), the activity increases with the oxygen concentration; for high oxygen concentrations (>8%), the activity decreases with the oxygen concentration.

The effect of oxygen concentration will be further discussed in the section of catalyst stability.

3.3.2. Influence of the physico-chemical properties of the catalysts

The influence of the physico-chemical properties of the catalysts was studied in as follows: first, the effect of the metal dispersion was studied over one of the catalysts; then supports with the same structure and different ratio Si/Al were used; afterwards, platinum catalysts in different supports (HFAU, HBEA, Al₂O₃ and SiO₂) were compared; and finally, the effect of the compensation cation was investigated.

3.3.2.1. Metal dispersion

Several authors have investigated the influence of the metal dispersion in the oxidation of VOCs. In most cases, the dispersion does not play a significant role in the activity of the catalysts. Papaefthimious *et al.* [28] found that the turnover frequency (TOF) in the oxidation of benzene and ethyl acetate over Pt/ γ -Al₂O₃ increased with a decrease in dispersion. They found that the catalyst sample with dispersion lower than 10% was approximately 40 times

more active than the highly dispersed catalyst for benzene oxidation, and 25 times more active in the case of ethyl acetate. The observed effects were ascribed to the structure-sensitive character of the reaction.

In the case of *n*-heptane oxidation, Völter *et al.* [20] found that the activity of Pt/Al₂O₃ is not diminished by high temperature calcination, although the dispersion is drastically decreased. A dual site model explained this phenomenon: the platinum state alternates between a less active oxidized platinum (Pt^{IV}) and high active metallic platinum. The calcination at high temperatures causes the decomposition of the complex into poorly dispersed metallic platinum, which is more active.

Garetto and Apesteguía [27] reported that in the oxidation of benzene over Pt/Al₂O₃, the catalysts with lower dispersion were more active in the oxidation. The temperature required for 50% conversion of benzene with a 65% dispersed catalyst was 566K, while with an 8% dispersed catalyst it was only 508K. This enhancement of activity in large particles was explained by the increase of the density of reactive Pt-O species with the increase of Pt particle size.

It was also concluded by Yazawa *et al.* [29] that the turnover frequency in the combustion of propane decreased with the increase of Pt dispersion, independently of the acid strength of the supports, this being due to the higher oxidation-resistance of platinum with small dispersion.

However, in the case of propane and propene oxidation over platinum supported on alumina, an optimum metal particle size was found, which maximises the catalytic activity [30]. This behaviour was explained by a competitive adsorption of hydrocarbons and oxygen on the same type of metal sites and different reactivities of oxygen adsorbed on the metal surface.

Studies of catalytic oxidation of methane over platinum supported catalysts showed that there is an effect of the platinum particle size on the reaction [31,32]. It was found that the turnover number (as activity per surface platinum site) was much higher on large platinum particles, which was due to the fact that the reactivity of chemisorbed oxygen increased with the increase of the size of platinum particles [31]. The differences in the reactivity of the adsorbed oxygen was explained by the formation of a chemisorbed layer when the platinum particles are in the form of large crystallites, but not a surface oxide [32]. When platinum is well dispersed, it oxidises to PtO₂ which is less reactive.

The enhancement of the activity of the larger particles can be explained by faster oxygen adsorption on the particles [33]. Indeed, these authors concluded that the rate of O₂ adsorption on the metal over a Pt/Al₂O₃ catalyst was higher for the less dispersed catalyst.

In the present work, the influence of metal dispersion was studied in the oxidation of MIBK by testing a catalyst with the same composition (support and Pt load) with different Pt particle sizes. The catalyst used for this purpose was the 0.32Pt/γ-Al₂O₃, and the differences in the metal dispersion were achieved by calcination at different temperatures in air stream with a heating rate of 10°Cmin⁻¹ and a hold of 2 h. The resulting metal dispersions are presented in Table 5.

Table 5 – Calcination temperatures and dispersion of the 0.32Pt/γ-Al₂O₃ catalysts.

	T _{calcination} (°C)	Dispersion ^(a) (%)
0.32Pt/Al ₂ O ₃	500	59
0.32Pt/Al ₂ O ₃ 700	700	34
0.32Pt/Al ₂ O ₃ 750	750	14

(a) determined by hydrogen chemisorption

These catalysts were tested in the oxidation of MIBK at 200°C. The conversion of MIBK and conversion into CO₂ obtained are shown in Figure 16.

In agreement with the observations of the cited authors, there seems to be no significant influence of the platinum dispersion on the oxidation of MIBK. However, the larger particles are indeed more active than the smaller particles, because for the same Pt load larger particles (lower dispersion) mean less accessible platinum sites. Because all the catalysts were reduced prior the beginning of the reaction, the dual site model does not apply here. So, a possible explanation can be that the adsorption of oxygen is faster on larger platinum particles. The fact that there are less platinum sites when the dispersion decreases, is compensated by faster adsorption of oxygen on larger particles.

Another possible explanation is that larger platinum particles are more resistant to oxidation [32]. If this hypothesis is considered, it also explains the effect of the oxygen concentration discussed in section 3.3.1.6. When the platinum particle size increases, the fact that there are less active sites can be compensated by the fact that these particles are more resistant to oxidation. When the reaction is carried out with higher concentrations of oxygen, there will be a more platinum oxidised, and consequently the activity of the catalyst will decrease.

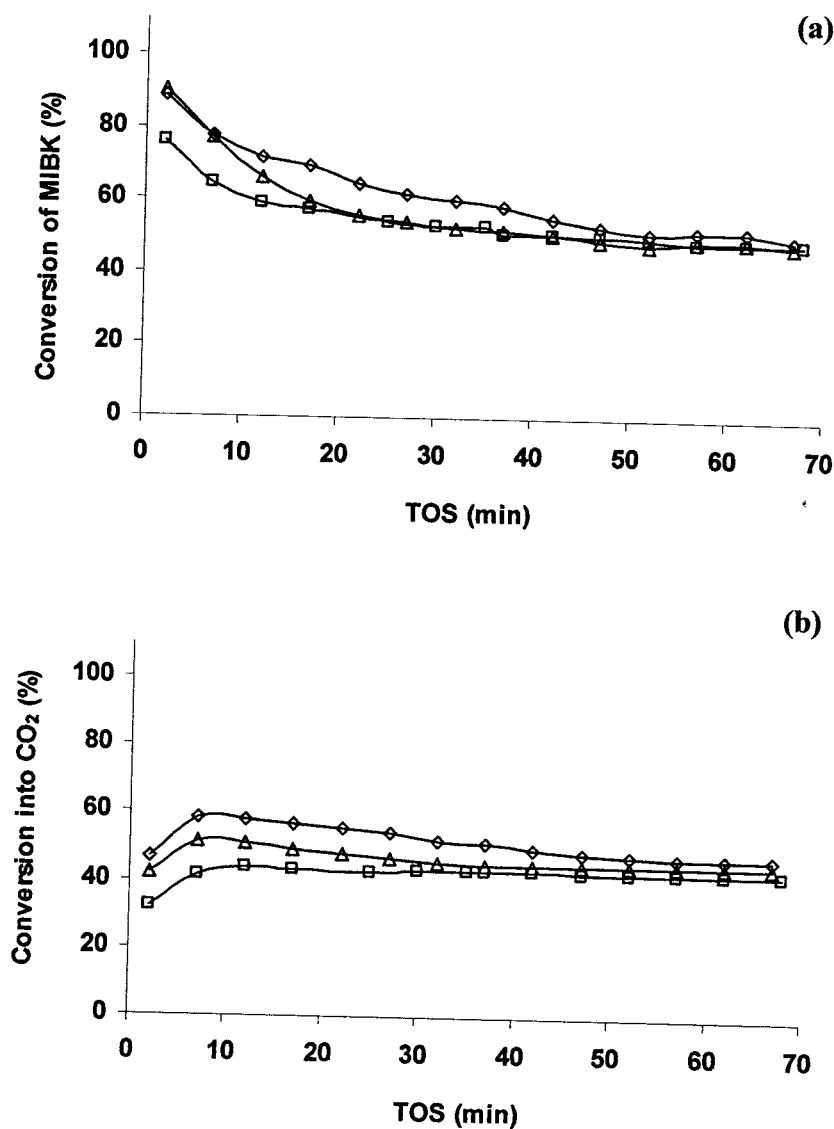


Fig. 16 – Influence of time-on-stream on the total conversion of MIBK (a) and conversion into CO₂ (b) over 0.32Pt/Al₂O₃ catalysts at 200°C with dispersions of (◇) 59, (Δ) 34 and (□) 14%.

3.3.2.2. Acidity

The oxidation of MIBK was studied over two catalysts with different Si/Al ratio: 0.09Pt/HFAU(47) and 0.52Pt/HFAU(5). These two catalysts have the same structure, but very different acidity, HFAU(5) having almost ten times more acid sites than HFAU(47) (Table 1). The conversion into CO₂ as a function of the temperature after 3h of reaction over these two catalysts is compared in Figure 17.

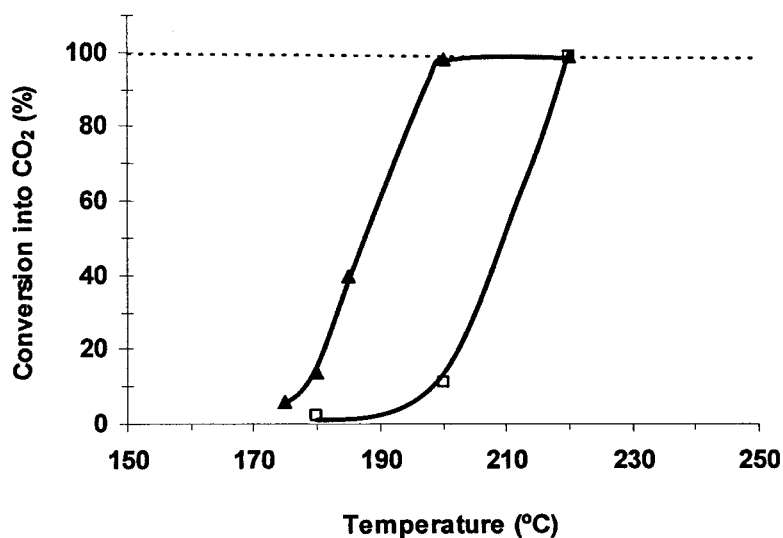


Fig. 17 – Conversion of MIBK into CO₂ after 3h of reaction as a function of temperature on the (▲) 0.09Pt/HFAU(47) catalyst and the (□) 0.52Pt/HFAU(5) catalyst.

These results show that the acidity of the support is not favourable to the oxidation reaction: the catalyst with a more acidic support, even with more platinum, presents a lower conversion into CO₂. The amounts of coke retained on the catalysts after 3 h of reaction are compared in Figure 18.

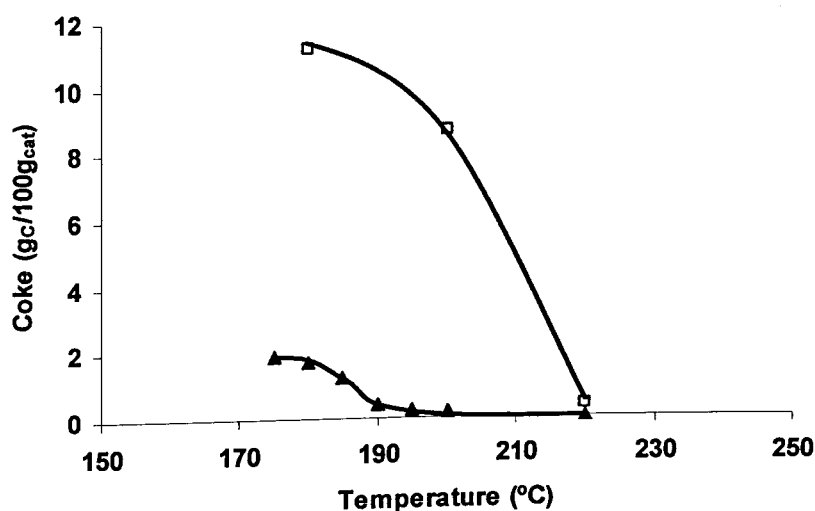


Fig. 18 – Amount of coke after 3h of reaction as a function of the temperature on the (▲) 0.09Pt/HFAU(47) catalyst and the (□) 0.52Pt/HFAU(5) catalyst.

Whatever the reaction temperature, the amount of coke after reaction is higher in the 0.52Pt/HFAU(5) catalyst than in the 0.09Pt/HFAU(47) catalyst.

Enhanced formation of side products, including coke, was observed on the more acidic support: after 3h of reaction at 180°C the percentage of coke on the 0.09Pt/HFAU(47) catalyst was 1.7%, while in the same conditions the percentage of coke was 11.2% on the 0.52Pt/HFAU(5) catalyst.

TPO after 3h of reaction at 180°C over these two catalysts is presented in Figure 19.

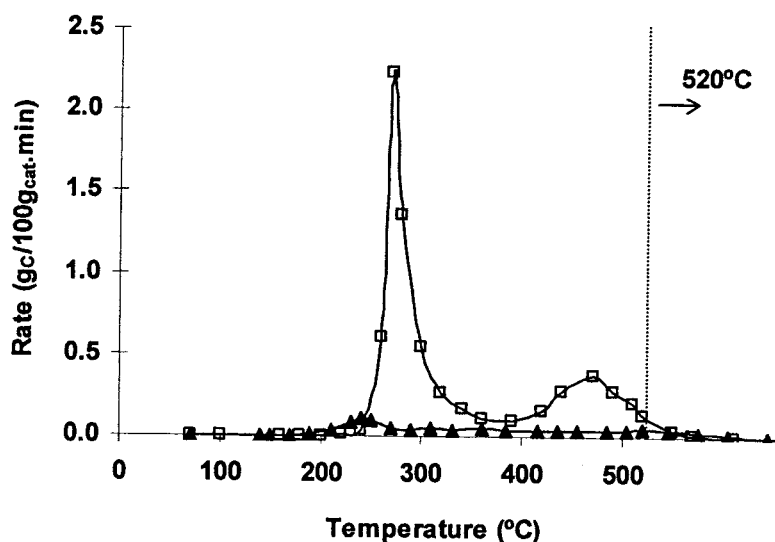


Fig. 19 – Oxidation of coke after 3h of reaction at 180°C on the (▲) 0.09Pt/HFAU(47) catalyst and the (□) 0.52Pt/HFAU(5) catalyst.

There is a higher accumulation of the two types of compounds present in the coke after reaction in the more acidic catalyst. Both peaks of the (previously defined) more and less reactive coke increase as the acidity of the support increases. It should also be noted that the position of the peak maxima are different: 270°C on the more acidic catalysts against 240°C on the less acidic for the more reactive coke, and 470°C against 510°C for the less reactive coke. The fact that the peak corresponding to the more reactive coke shifted to higher temperatures in the more acidic catalyst can be related to the fact that this catalyst is less active for oxidation than the less acidic one. On the other hand, the peak corresponding to the less reactive coke shifted to lower temperatures. This is in agreement with the observations of Moljord *et al* [13,14], who reported that the lower the Si/Al ratio the lower the temperatures of the TPO peak. This was also observed by Dégé [16] in the oxidation of o-xylene.

The same study was also made over two Pt/HBEA catalysts with similar amounts of platinum. The results obtained over the 0.21Pt/HBEA(50) catalyst and 0.23Pt/HBEA(15) catalyst are shown in Figure 20.

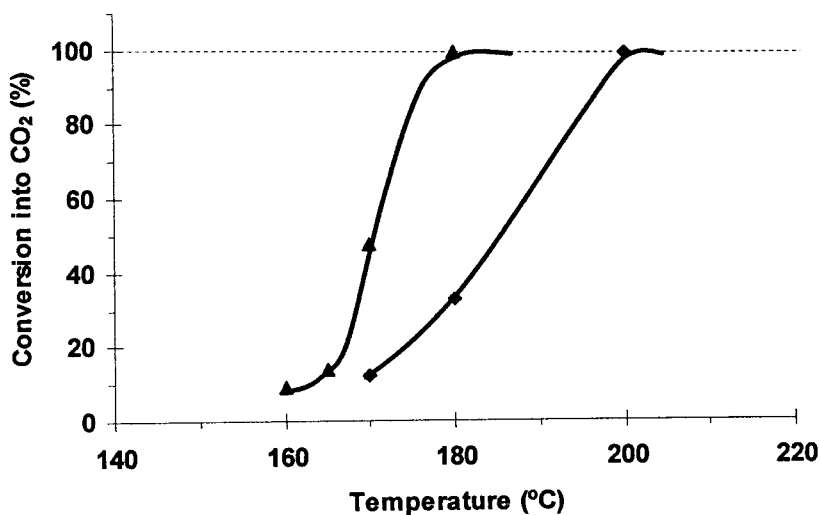


Fig. 20 - Conversion of MIBK into CO₂ after 3h of reaction as a function of temperature on the (♦) 0.23Pt/HBEA(15) catalyst and (▲) 0.21Pt/HBEA(50) catalyst.

The results are similar to those observed with the Pt/HFAU catalysts. In this case, it is also the less acidic catalyst that gives the best results in the oxidation reaction. The amount of coke after 3h of reaction is shown in Figure 21.

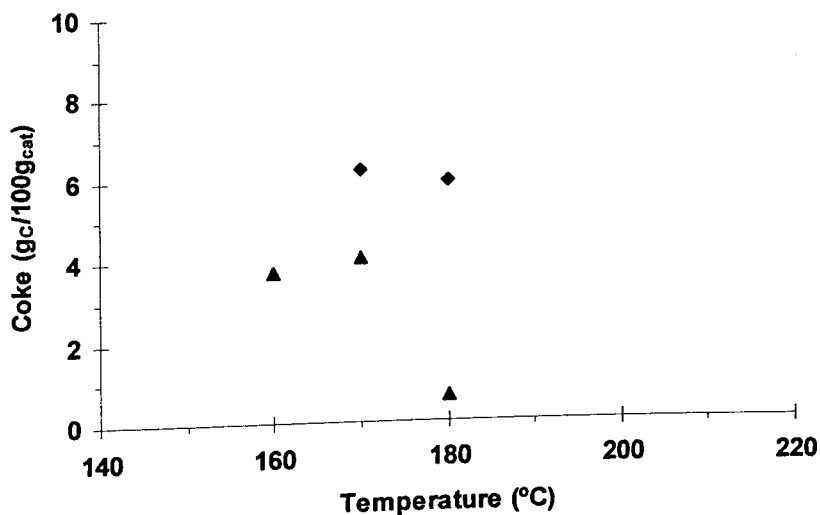


Fig. 21 -Amount of coke after 3h reaction as a function of the temperature on the (♦) 0.23Pt/HBEA(15) catalyst and (▲) 0.21Pt/HBEA(50) catalyst.

Again, the most acidic catalyst transforms more MIBK into compounds that remain in the zeolite pores. However, it should be noted that this difference is not as large as in the case of the Pt/HFAU catalysts.

We can conclude that the acidity of the support is an important factor in the oxidation of MIBK, the less acidic supports being preferred because they not only require lower temperature for total conversion into CO₂ but also because they produce less coke and other side products.

3.3.2.3. Porous structure

The influence of the porous structure was investigated by comparing catalysts with four different supports: two zeolites of large pores (HFAU(47) and HBEA(50)), SiO₂ and γ -Al₂O₃.

The properties of these supports can be compared in Table 1. The HFAU(47) and HBEA(50) supports have similar acidity and different texture: HBEA(50) presents a larger mesoporous surface area and a lower volume of micropores than HFAU(47). This larger mesoporous surface area is certainly due to the intercrystalline volume, which creates mesopores, and is a consequence of the agglomeration of very small crystallites (this was checked by SEM analysis). Alumina was used in this comparison because it is the most common support used in catalysts for the oxidation of VOCs. This support does not present any Brönsted acidity or micropores. However it has Lewis acid sites. SiO₂ is a more neutral support, as it does not have any acidity or micropores.

The conversion into CO₂ is represented in Figure 22 as a function of the reaction temperature for catalysts supported on these four materials. The amount of coke accumulated after 3h of reaction is represented in Figure 23.

The 0.16Pt/HFAU(47) and the 0.21Pt/HBEA(50) catalysts require a reaction temperature of 180°C to transform all MIBK into CO₂. Although it is difficult to evaluate the influence of the structure in the oxidation, because the Pt load is not the same, there does not seem to be a major difference between these two zeolites. Since the HBEA zeolite has a lower micropore volume and a higher mesoporous surface area, it might be thought that the diffusion of the reactants inside the pores would be easier; however, even with a higher platinum content, this zeolite presents approximately the same activity as PtHFAU. So, apparently the porous structure of the zeolite is not a major factor for the catalyst performance

in the oxidation of MIBK. The total amount of coke after reaction is higher in the PtHBEA catalyst, but this is probably due to the fact that this zeolite has a higher acidity (Table 1).

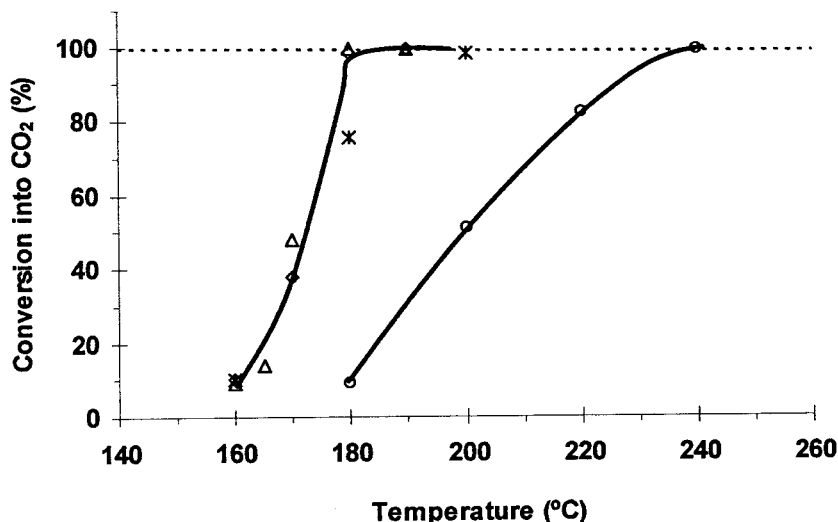


Fig. 22 - Conversion of MIBK into CO₂ after 3h of reaction as a function of temperature on the (◇) 0.16Pt/HFAU(47), (Δ) 0.21Pt/HBEA(50), (*) 0.09Pt/SiO₂ and (○) 0.32Pt/Al₂O₃ catalysts.

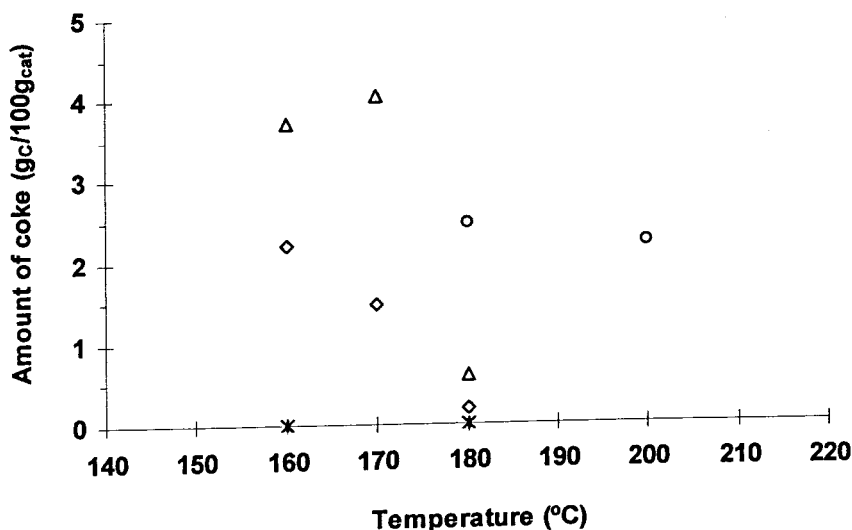


Fig. 23 – Amount of coke after 3h reaction as a function of temperature on the (◇) 0.16Pt/HFAU(47), (Δ) 0.21Pt/HBEA(50), (*) 0.09Pt/SiO₂ and (○) 0.32Pt/Al₂O₃ catalysts.

On the other hand, the 0.32Pt/Al₂O₃ catalyst is less active than any of the others. Only at 220°C the conversion into CO₂ is higher than 80%. There is also the formation of heavy products inside the pores, probably due to the acidity of the alumina. On the contrary, Pt/SiO₂

does not form any coke, because it does not have any acidity. So we can also conclude that coke is only formed in the acid sites and not on platinum, because Pt/SiO₂ does not present any coke. Moreover, this catalyst is not as active as those supported on zeolites: at 180°C the conversion into CO₂ on Pt/SiO₂ was 75% against 100% on the Pt/zeolite. However, the platinum content is lower on this catalyst. A comparison can be made between this catalyst and 0.09Pt/HFAU(47) (Figure 1). At 200°C the conversion of MIBK into CO₂ is 99% over 0.09Pt/SiO₂ and 100% over 0.09Pt/HFAU(47). However at 180°C the conversion into CO₂ is 75% over 0.09Pt/SiO₂ and only 14% over 0.09Pt/HFAU(47). This high activity of Pt/SiO₂ catalyst is certainly due to the fact that no coke is formed on the catalyst, which is not the case with any other catalyst studied in this chapter, there being coke accumulation even in 0.32Pt/Al₂O₃.

It is then clear that the key factor for the oxidation of MIBK is the acidity of the catalyst, the less acidic requiring lower temperatures for oxidising completely the VOC.

3.3.2.4. Effect of the cation

As previously discussed, the acidity of the support is not favourable for the oxidation reaction. Therefore, supports with basic properties were tested. For that purpose, Pt/NaFAU and Pt/CsFAU catalysts were prepared and compared with the Pt/HFAU catalyst.

The conversion of MIBK is plotted in Figure 24 as a function of the reaction temperature after 3 h of reaction over the catalysts 0.16Pt/HFAU(47), 0.21Pt/NaFAU and 0.23Pt/CsFAU. The amount of coke after 3h of reaction over these three catalysts is presented in Figure 25.

The conversion of MIBK is shown instead of the conversion into CO₂ (the usual choice in this work) due to the fact that on both the Pt/NaFAU and Pt/CsFAU catalysts, an oscillatory behaviour was observed in the CO₂ measured at the reactor exit at 180 and 200°C. These oscillations depended on the reaction temperature, being of higher amplitude and lower frequency for lower temperatures. These results will be discussed in chapter 5.

There is no great difference between the conversions of MIBK in these three catalysts. All of them require a temperature of 180°C to completely remove MIBK from the gas phase.

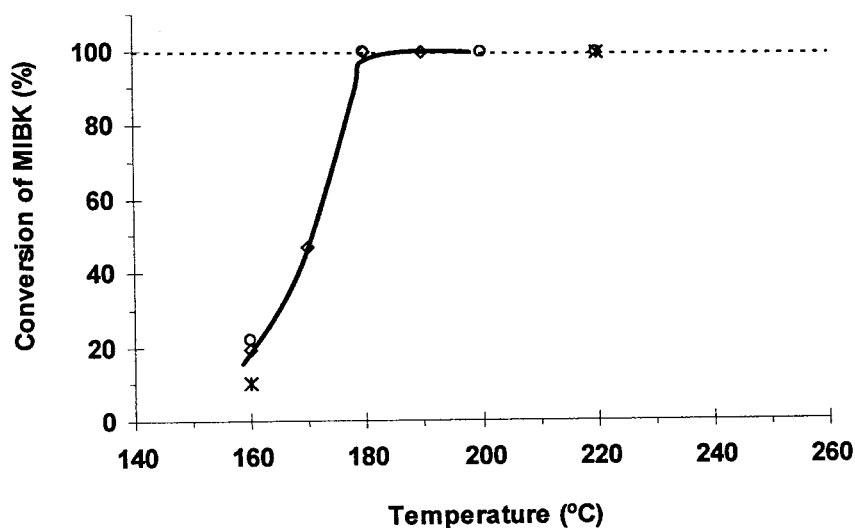


Fig. 24 - Conversion of MIBK after 3h of reaction as a function of temperature on (◇) 0.16Pt/HFAU(47), (○) 0.21Pt/NaFAU and (*) 0.23Pt/CsFAU.

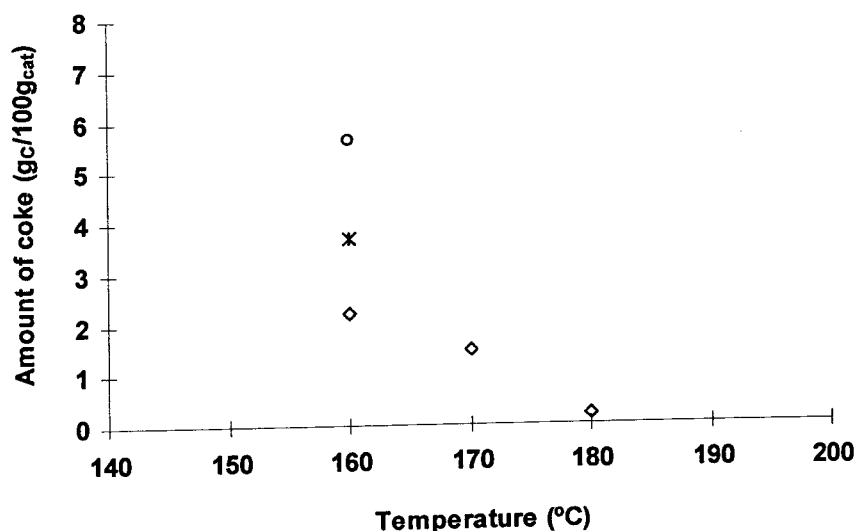


Fig. 25 – Total amount of coke after 3h of reaction as a function of temperature on the (◇) 0.16Pt/HFAU(47), (○) 0.21Pt/NaFAU and (*) 0.23Pt/CsFAU catalysts.

There is a larger amount of coke formed with the Pt/NaFAU and Pt/CsFAU than in the catalyst supported on the protonic zeolite. This means that the formation of coke is higher in the cations than in the protonic sites. The differences in coke oxidation behaviour after reaction at 160°C over these catalysts are shown in Figure 26.

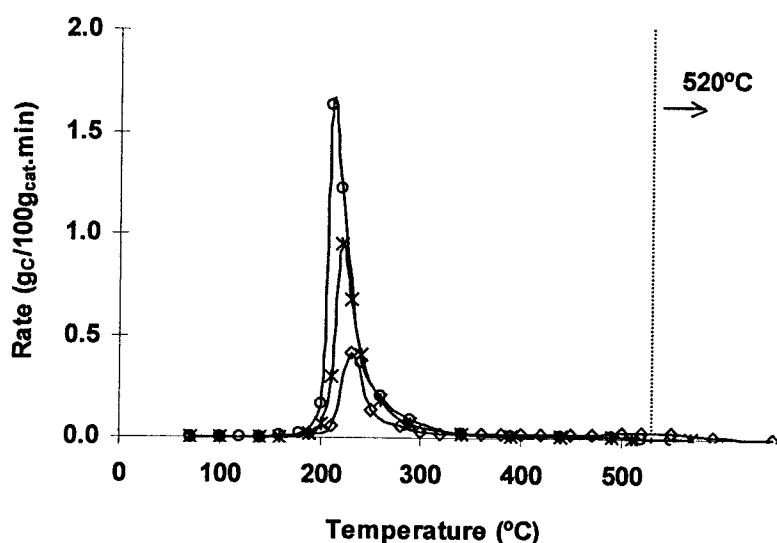


Fig. 26 – Oxidation of the coke after reaction at 160°C on the ($\diamond$) 0.16Pt/HFAU(47), ($\circ$) 0.21Pt/NaFAU and ($*$) 0.23Pt/CsFAU catalysts.

The differences in the TPOs of the coke formed on these three catalysts occur mainly in the more reactive coke. The acidic catalyst presents the peak with lower intensity (lower amount), followed by the Pt/CsFAU catalyst. The Pt/NaFAU catalyst presents the highest peak. As will be shown in chapter 5, a large part of this reactive coke is reactant that remains adsorbed on the catalyst. The fact that the alkali exchanged catalysts present more intense peaks in the TPO after reaction can be related to their higher adsorption strength. Moreover, the differences in the intensities of the TPO peaks between the Pt/NaFAU and the Pt/CsFAU catalysts can be due to the differences in their micropore volume (Table 1), NaFAU possessing a higher micropore volume than CsFAU.

3.3.3. Stability and regeneration of the catalysts

3.3.3.1. Long duration experiments

In order to analyse the stability of the catalyst in the presence of different amounts of oxygen, long duration experiments were made. The conversions into CO_2 obtained over 0.09Pt/HFAU(47) at 185°C with different concentrations of oxygen are compared in Figure 27. The conversion into CO_2 obtained over the pre-calcined catalyst at the same temperature and with a percentage of oxygen of 20% is also shown.

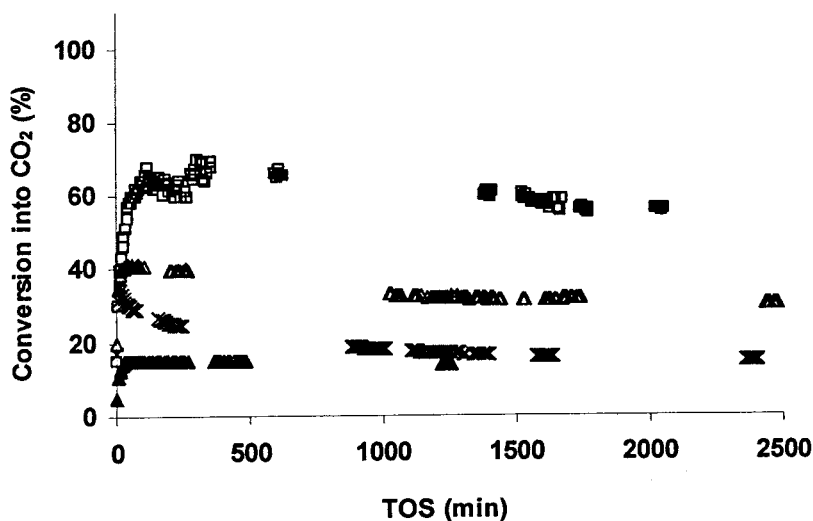


Fig. 27 – Influence of time-on-stream on the conversion into CO_2 over the 0.09Pt/HFAU(47) pre-reduced catalyst at 185°C with concentrations of oxygen of ($\times$) 40, (Δ) 20 and ($\square$) 8% and the ($\blacktriangle$) pre-calcined catalyst with 20% oxygen.

For the pre-reduced catalysts, the conversion into CO_2 is initially similar, but afterwards it follows different paths with time-on-stream: with 8% O_2 the conversion into CO_2 increases till a constant value, its deactivation being very low; with 20% O_2 the catalyst deactivates slowly in the first 20h, reaching a constant value afterwards; finally, with 40% O_2 deactivation is faster at the beginning of the reaction, the conversion reaching a constant value after 25h of time-on-stream. On the other hand, with the pre-calcined catalyst, no deactivation occurs when the reaction is carried out with 20% oxygen.

The conversions into CO_2 corresponding to all these experiments are compared in Figure 28.

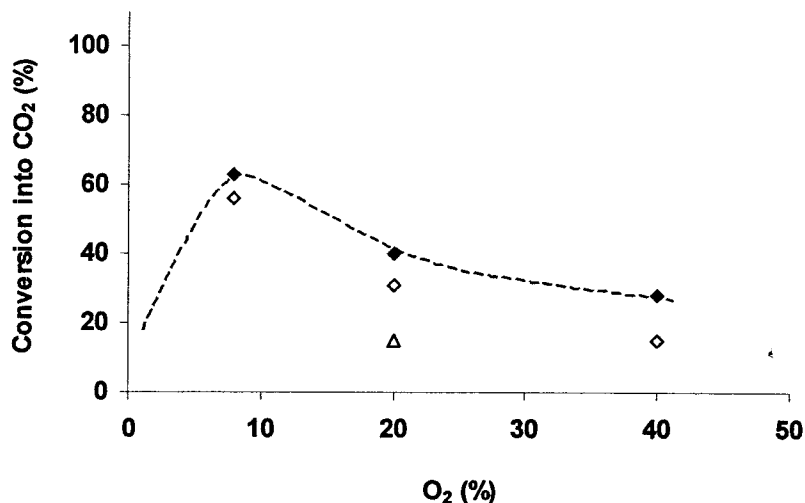


Fig. 28 – Conversion into CO_2 after 2 h of reaction (filled symbols) and 40 h reaction (open symbols) at 185°C as a function of the concentration of oxygen on the $0.09\text{Pt}/\text{HFAU}(47)$ pre-reduced (◇) and pre-calcined (Δ) catalysts.

The conversion into CO_2 after 2h and after 40 h is not the same for any percentage of oxygen at 185°C . The difference between the conversion into CO_2 after 2h and 40h is higher when working with a higher percentage of oxygen in the feed. Moreover, if we compare the conversion into CO_2 after 40h and 40% O_2 with that on the pre-calcined catalyst with 20% O_2 , we can observe that it is almost the same, which may indicate that when more oxygen is present the platinum can oxidise, or that the formation of an oxide layer that causes a higher deactivation of the catalyst can occur.

In order to check for the electronic state of platinum after reaction with different amounts of oxygen, adsorption of CO followed by IR was done. Unfortunately, it was impossible to see any bands of adsorbed CO in the IR spectrum due to the fact that the amount of platinum was very low.

There are also textural changes in the catalysts after long duration experiments. The micropore volumes and mesoporous surface areas of the fresh catalyst, and after 3 h and 40 h of reaction at 185°C with 20% of oxygen, are shown in Table 6.

Table 6 – Textural properties (micropore volumes and mesoporous surface areas) of the 0.09Pt/HFAU(47) catalyst fresh and after 3 h and 40 h of reaction at 185°C.

	$V_{\text{micro}} \text{ (cm}^3 \text{ g}^{-1}\text{)}$	$S_{\text{meso}} \text{ (m}^2 \text{ g}^{-1}\text{)}$
Pt/HFAU(47) fresh	0.283	131
Pt/HFAU(47) 3h reaction	0.245	114
Pt/HFAU(47) 40h reaction	0.172	97

There is a decrease in the micropore volume and mesoporous surface area after reaction. However this decrease is much higher after 40 h of reaction (39%) than after 3 h of reaction (13%). It should be noted that the samples after reaction were outgassed only at 150°C during 24 h (against 350°C on the fresh sample) so that the transformation of coke compounds would be avoided. It may be concluded that catalyst deactivation can also be due to coke accumulated on the catalyst.

In order to check if the mentioned differences in the textural properties with time-on-stream are due to a higher accumulation of coke or to the formation of coke of different nature, TPOs after stopping the reaction at 185°C at different TOS were made (Figure 29).

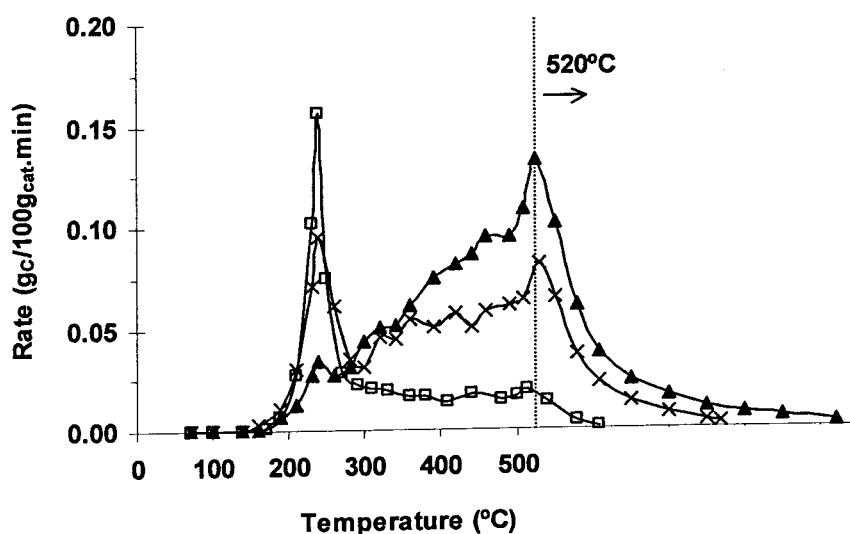


Fig. 29 – Oxidation of coke after (□) 3h, (×) 10h and (▲) 20h of reaction at 185°C on the 0.09Pt/HFAU(47) catalyst.

The intensity of the peak corresponding to the so-called more reactive coke (coke which starts to oxidise at lower temperatures) decreases with TOS. On the other hand, the less

reactive coke (coke which starts to oxidise at higher temperatures) increases with TOS. The total amounts of coke are compared in Table 7.

Table 7 – Amount of coke that remains in the 0.09Pt/HFAU(47) catalyst after 3 h, 10 h and 20 h of reaction.

TOS (h)	Coke (g _C /100g _{cat})
3	1.1
10	2.4
20	3.2

The amount of coke accumulated in the catalyst increases with TOS. This is mainly due to the formation of less reactive coke. The fact that the amount of reactive coke decreases with TOS can be due to its transformation into less reactive coke, which is formed in the acid sites of the zeolite (section 3.3.1.4.). This transformation will be slow, as after 3 h of reaction the amount of less reactive coke is very low compared with that obtained after 20 h. On the other hand, the more reactive coke is mainly formed by low molecular weight compounds (including reactant) as it will be discussed in chapter 5. These compounds will certainly stay adsorbed in the support. So the formation of the less reactive coke will probably occupy the acid sites of the zeolite, provoking a decrease in the amount of the more reactive coke.

TPO curves of coke formed on the pre-calcined catalysts show a different behaviour. TPOs after stopping the reaction at 185°C at different TOS are shown in Figure 30.

As in the case of the pre-reduced catalyst, the amount of less reactive coke over the pre-calcined catalyst increases with TOS. However, the amount of highly reactive coke does not decrease in the same way as over the pre-reduced catalyst.

In the case of the pre-calcined catalyst there was no deactivation in the conversion into CO₂, even though coke accumulation increases with TOS. This fact suggests that deactivation over the pre-reduced catalyst is mainly due to the changes in the electronic state of platinum rather than to coke accumulation on the catalyst.

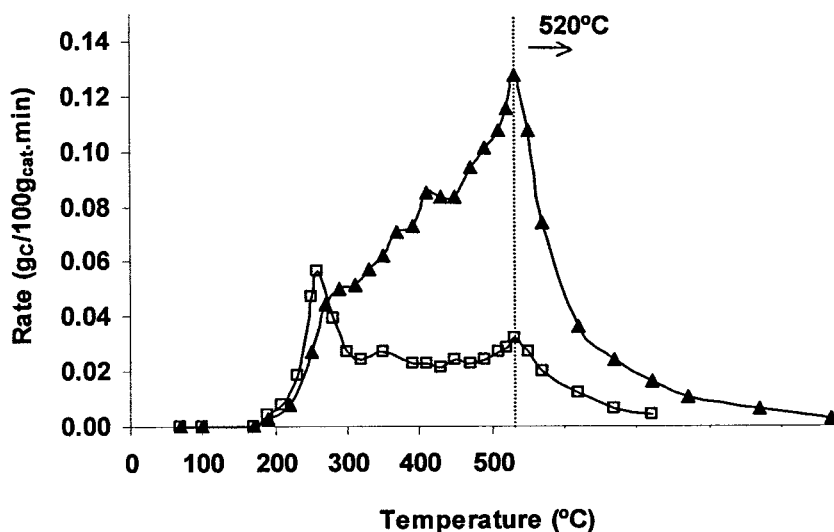


Fig. 30 – Oxidation of coke after (□) 3h and (▲) 20h of reaction at 185°C on the pre-calcined 0.09Pt/HFAU(47) catalyst.

3.3.3.2. Regeneration of the catalyst

Some tests were made in order to evaluate the performance of the catalysts after being used in the reaction and treated in air at 520°C for coke removal. These tests were made with the 0.09Pt/HFAU(47) and 0.52Pt/HFAU(5) catalysts.

The results of the conversion into CO_2 with time-on-stream for the 0.52Pt/HFAU(5) catalyst at 180°C after being regenerated twice are presented in Figure 31. Surprisingly there was an activation of the catalyst upon regeneration. This result can however be explained by the fact that during the regeneration treatment at 520°C dealumination of the catalyst can occur due to the water adsorbed (which is also a reaction product) and the high temperature, with a consequent decrease in acidity. To confirm this hypothesis, the IR spectra of the zeolite before and after reaction were taken, in order to see if there was a shift in the T-O-T bands [34]. Indeed, there was a shift in the T-O-T bands of the zeolite of about 7 cm^{-1} . This confirms that the enhancement of the activity was really due to dealumination of the zeolite during the regeneration treatments.

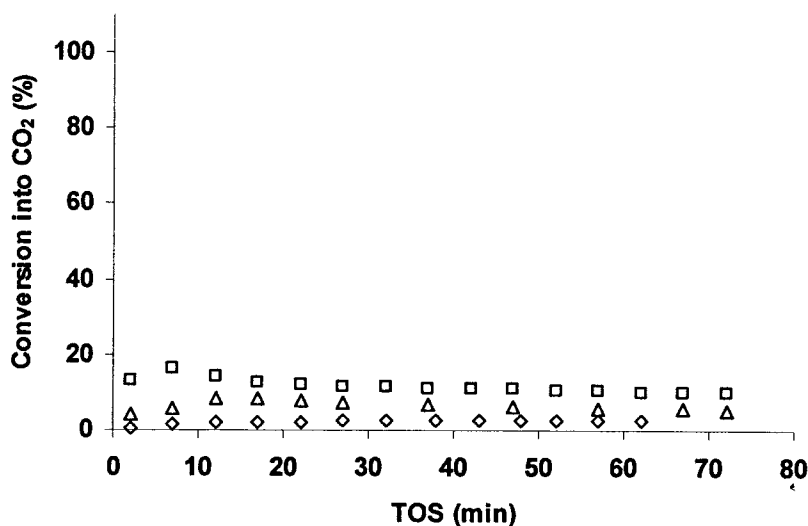


Fig. 31 – Influence of time-on-stream on the conversion into CO_2 over the 0.52Pt/HFAU(5) catalyst at 180°C : fresh ($\diamond$), after one regeneration (Δ) and after two regenerations ($\square$).

The TPOs after reaction with the fresh catalyst and the catalyst after reaction and one regeneration are shown in Figure 32.

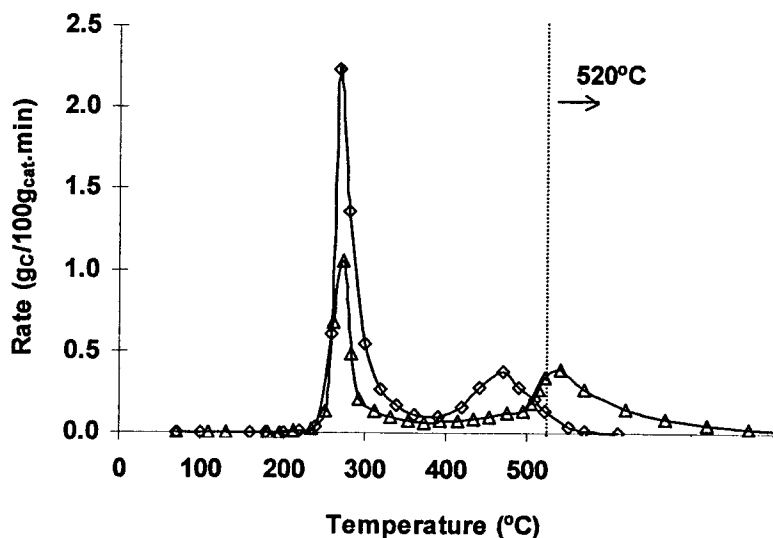


Fig. 32 – Oxidation of the coke after reaction at 180°C on the 0.52Pt/HFAU(47) catalyst: ($\diamond$) fresh and (Δ) after regeneration.

The TPO curves present some differences, namely the intensity of the first peak (it is smaller in the regenerated catalyst) and the temperature range of the less reactive coke (peak maximum shifted to higher temperatures).

In the case of the 0.09Pt/HFAU(47) catalyst, the regeneration treatments originated the following results (Figure 33).

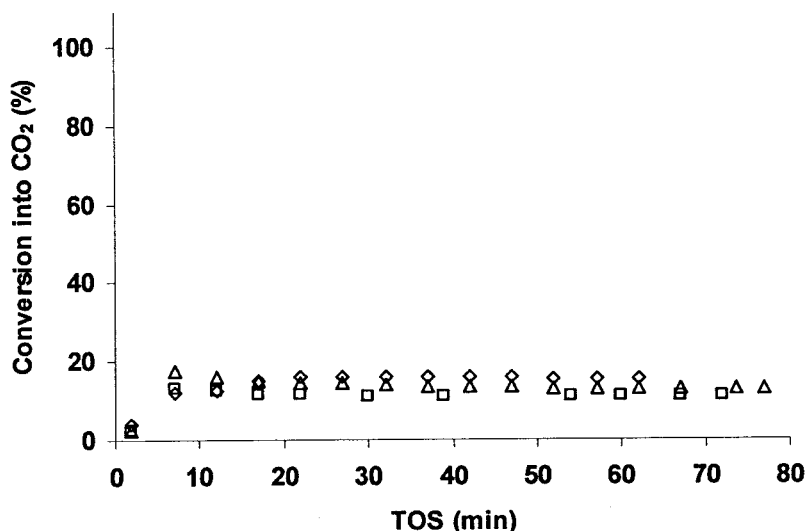


Fig. 33 – Influence of time-on-stream on the conversion into CO₂ over the 0.09Pt/HFAU(47) catalyst at 180°C: fresh (◇), after one regeneration (Δ) and after two regenerations (□).

In this case, as it would be expected, the activity diminished with the number of regenerations. In this case there was no significant shift in the T-O-T bands. The fact that there was less (or none) dealumination of the catalyst with the regeneration treatments is due to the fact that this zeolite HFAU(47) already has a lower Si/Al ratio.

The TPOs after reaction with the fresh catalyst and the catalyst after reaction and one regeneration are shown in Figure 34. A decrease in the intensity of the first peak of the TPO is observed as in the case of the more acidic catalyst. On the other hand, the oxidation temperature ranges of the less reactive coke are approximately the same.

Similar results were obtained in the oxidation of o-xylene over Pd/HFAU catalysts [35]. No deactivation occurred after regeneration of the catalysts by oxidative treatment under air up to 520°C. Moreover, it was found that over a Pd/HZSM-5 catalyst there was a shift towards high temperatures on the oxidation of coke with the number of regenerations of the catalyst [16]. It was suggested that this shift was due to metal sintering during regeneration, and therefore to the decrease in the metal dispersion.

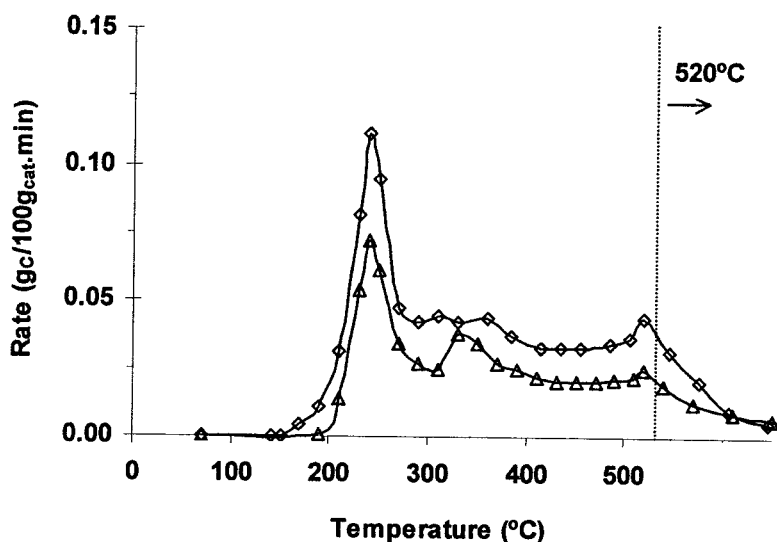


Fig. 34 – Oxidation of the coke after reaction at 180°C on the 0.09Pt/HFAU(47) catalyst ($\diamond$) fresh and (Δ) after regeneration.

This study shows that the 0.09Pt/HFAU(47) catalyst presents only a small decrease in the activity upon regeneration. In this way, this catalyst is very resistant to thermal treatments, and consequently is very stable.

3.3.3.3. Reaction in the presence of steam

Industrially, the conditions for the oxidation of VOCs will not be as the standard conditions used in this work. For example, humidity will be present in the air. The amount of water in the air will certainly affect catalyst performance in the oxidation of VOCs.

In order to study the effect of humidity in the air, reactions were carried out over the 0.16Pt/HFAU(47) catalyst in the standard conditions, but with 5% of steam added to the feed. For that purpose, the reactant passed through a saturator containing water kept at constant temperature.

The results after 3 h of reaction at different temperatures in the presence and absence of steam are compared in Figure 35. Above 180°C, there is no major difference between the conversion into CO_2 in the presence or absence of steam, although slightly lower conversions were observed at 160 and 170°C in the presence of steam. At 170°C the conversion into CO_2 in the absence of steam is 38% while in the presence of steam it is 28%. Nevertheless, this catalyst in the presence of steam is still able to oxidise totally MIBK into CO_2 at 180°C. In the

case of o-xylene oxidation over a Pd/HFAU catalyst [16], no effect was observed when water was present, as long as the catalyst was pre-reduced. Nevertheless, when the catalyst was pre-calcined there was some deactivation in the presence of steam.

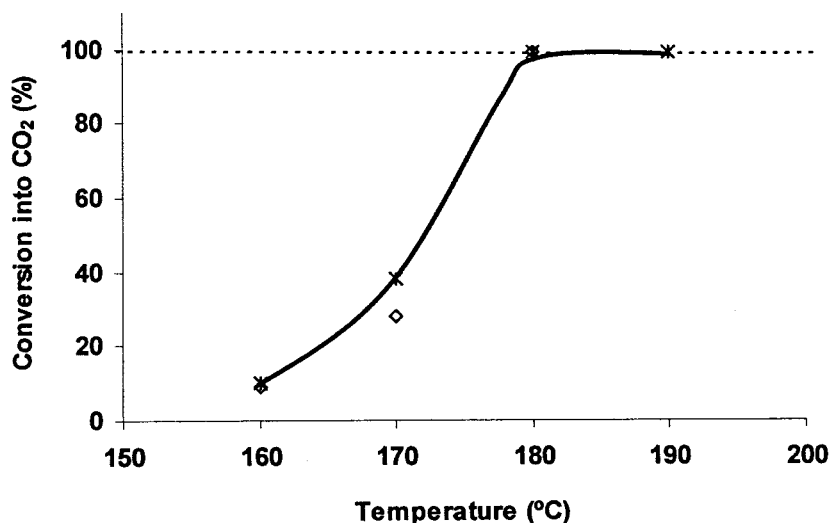


Fig. 35 - Conversion of MIBK into CO₂ after 3h of reaction as a function of temperature on 0.16Pt/HFAU(47) with (*) no steam and (◇) 5% steam.

The amount of coke that remained in the catalyst after reaction is shown in Figure 36.

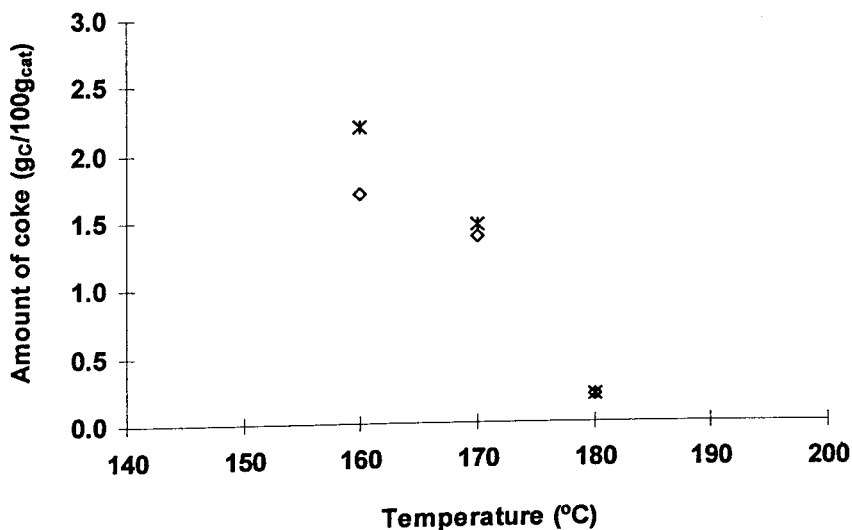


Fig. 36 -Amount of coke after 3h reaction as a function of temperature on 0.16Pt/HFAU(47) with (*) no steam and (◇) 5% steam.

Coke formation during reaction at 160 and 170°C is lower in the presence of steam. This difference is more pronounced for the reaction at 160°C. At 180°C the conversion of MIBK is complete and therefore the accumulation of coke is very low and similar in both cases (with and without steam). The differences in the amounts of coke can be due to adsorption of water on the support, which will compete with the reactant (as we will see, the more reactive coke partially consists of reactant), preventing the formation of coke on the acid sites of the zeolite.

It may be concluded that Pt/HFAU(47) catalysts present a good resistance to the presence of steam in the reactant mixture, since only a small loss of activity occurs. This catalyst can oxidise all the MIBK into CO₂ at the same temperature as when no steam is present in the feed. The presence of steam will lead to a decrease in coke formation at low reaction temperatures.

3.3.4. Catalytic oxidation of the mixture of o-xylene and MIBK

Catalytic oxidation of VOC mixtures can be very complex, as a VOC in mixtures can react differently from the individual compound, and therefore it is difficult to predict its behaviour. Only a few detailed studies on the catalytic combustion of mixtures are found in the literature [5,6,26,36-40].

Certain authors found out that the mixing effect results in an inhibition of the oxidation for some reactants, so that higher temperatures are required to achieve the same conversion. This increase in the temperature required for total oxidation will be different for each compound. This effect can be due to competition for adsorption in the active sites [26,40]. For example, benzene oxidation over platinum based catalysts is very much affected by ethyl acetate [36] and also by other aromatics which adsorb strongly on the catalyst [38]. The oxidation of 2-propanol over platinum supported on a monolith is negatively affected by the presence of either toluene or MEK [5]. It has been proposed that this inhibition effect is due to the competition for the oxygen atoms chemisorbed on Pt, and not due to competition for the adsorption sites on the support.

On the other hand, the oxidation of certain compounds is independent of the presence of other VOCs. For example, the presence of benzene does not affect the oxidation of ethylacetate over a Pt/TiO₂ doped with W⁶⁺ [36] neither of other aromatics [38]. The oxidations of methylacetate and butanal are not affected by the presence of each other as well as toluene in the presence of n-hexane [39] over a Pt/Pd honeycomb monolith converter. It

was concluded by Barresi and Baldi [26] that the addition of a compound that is adsorbed on the catalyst more weakly than the main one does not affect the conversion rate significantly.

Finally, there is a third possible effect: the temperature required for total oxidation decreases when certain compounds are in a mixture [37,39,40]. This effect is certainly a consequence of the higher exothermicity of the process when a mixture is considered, as the total concentration of VOCs is higher than when the compound is being oxidised alone. For example, n-hexane oxidation is enhanced by the presence of toluene [39]. In the case of the oxidation of benzene over PdY [40], it was found that the conversion of benzene increases when toluene is added. The oxidation of chlorobenzene over a Pt/ γ -Al₂O₃ catalyst [37] was found to be enhanced by the addition of aliphatic hydrocarbons, such as pentane, heptane or decane, while the conversion of these hydrocarbons is retarded. Although the authors did not completely discharge the possibility that this enhancement is due to heat generation during the reaction, they suggest that the main factor that explains this behaviour is the ability of the alkanes to remove Cl from the Pt surface (at the same time reducing the Pt), which otherwise would only be removed at higher temperatures. Adsorbed Cl on the platinum would prevent adsorption of the reactants.

In the present work, o-xylene and MIBK were studied separately over several catalysts, so it would be interesting to determine the effect on the oxidation of these compounds when mixed. Thus, reactions were carried out over the 0.09Pt/HFAU(47) catalyst at different temperatures in the standard conditions, but with the mixture of MIBK and o-xylene, first in the same concentrations as studied previously, and then with a lower concentration of o-xylene. Both conversions (conversion of MIBK and conversion of o-xylene) were followed by GC/FID. The overall conversion into CO₂ will not be shown here, as it would not be possible to distinguish which part corresponds to o-xylene or to MIBK.

The conversion of o-xylene alone (1500 ppm) and in the presence of 1340 ppm of MIBK over the 0.09Pt/HFAU(47) catalyst after 3 h of reaction as a function of the reaction temperature is shown in Figure 37. The conversion of MIBK alone (1340 ppm) and in the presence of 600 ppm and 1500 ppm of o-xylene over the 0.09Pt/HFAU(47) catalyst after 3 h of reaction as a function of the reaction temperature is shown in Figure 38.

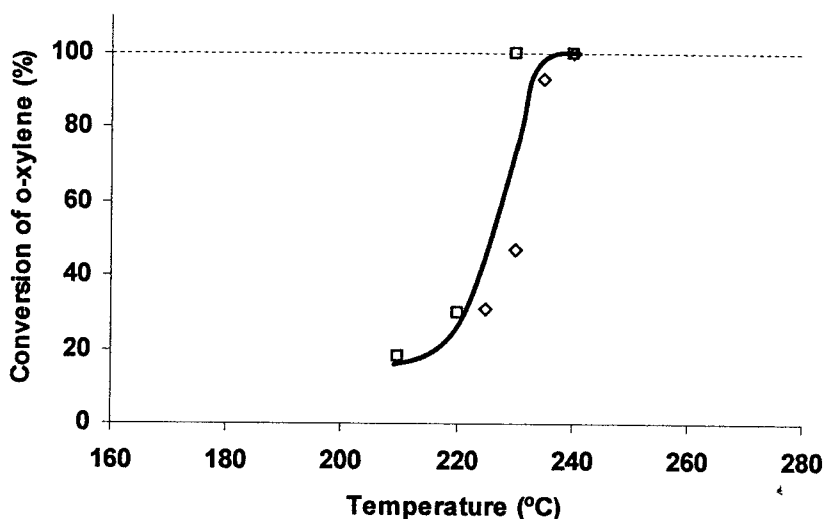


Fig. 37 - Conversion of o-xylene after 3h of reaction as a function of temperature on 0.09Pt/HFAU(47): o-xylene alone ($\diamond$) and with 1340 ppm ($\square$) of MIBK.

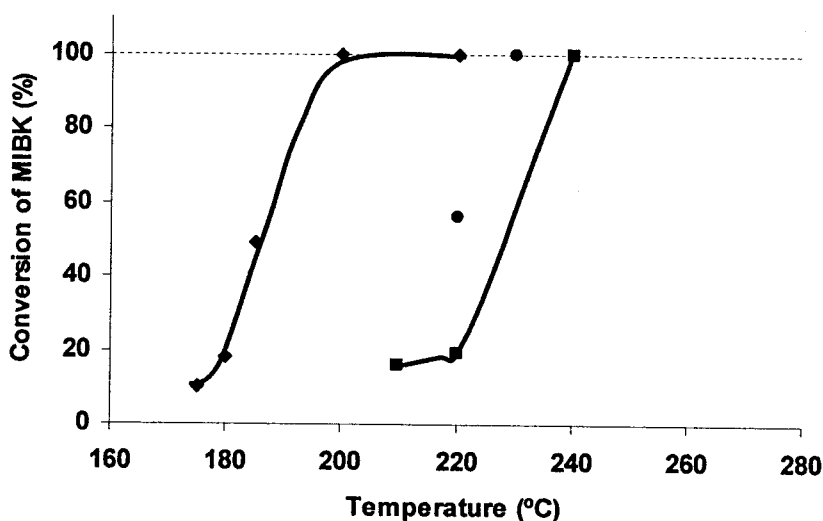


Fig. 38 - Conversion of MIBK after 3h of reaction as a function of temperature on 0.09Pt/HFAU(47): MIBK alone ($\diamond$) and with 600 ppm ($\bullet$) and 1500 ppm ($\blacksquare$) of o-xylene.

The conversion of o-xylene was not significantly affected by the presence of MIBK, although the temperature required for total conversion slightly decreased, the catalyst being able to oxidise all o-xylene in the presence of MIBK at 230°C. This effect is certainly related to the high temperature increase in the catalyst bed when the two VOCs are oxidised together. The exothermicity of the reaction could raise the temperature by up to 14°C, which is

considerably more than when the reactants are oxidised alone. This self heating of the catalyst can be the main factor that provokes this enhancement on the conversion of o-xylene.

In the case of MIBK, there is a decrease in the conversion when o-xylene is present. At 220°C the conversion is complete when this VOC is alone, decreasing with the addition of o-xylene. This inhibiting effect of o-xylene on MIBK can be due to the competition between these two compounds to the active sites. It should also be noted that side products were present at the reactor exit in all the experiments, except at reaction temperatures for which complete conversion of the VOCs was reached.

Similar results were obtained by Pina *et al.* [6] in the oxidation of toluene and MEK over Pt/ γ -Al₂O₃ catalytic membranes. They found that there is an inhibition effect of toluene in the oxidation of MEK, while only a little difference was found in the conversion of toluene when MEK was added. With the help of *in situ* DRIFT technique, they concluded that, under reaction conditions, toluene successfully competes with MEK for adsorption sites.

On the other hand, other authors [5] did not find any difference in the conversions of toluene and MEK individually and in mixture over Pt/Al₂O₃/Al monolith. The oxidation of these compounds was also not affected by the presence of 2-propanol. The explanation given was related to the fact that the adsorption of toluene and MEK was inhibited by 2-propanol, without affecting their oxidation rate. It was concluded that the reactants (toluene and MEK) react from the gas phase [5].

TPOs after reaction over the 0.09Pt/HFAU(47) catalyst with the compounds alone and in mixture are shown in Figure 39. TPO after the oxidation of the mixture of MIBK and o-xylene shows that the respective coke is a mixture of the coke components obtained when the reaction is carried out with the individual compounds. There is a part of the coke that oxidises at low temperatures (more reactive coke) with a peak maximum at 240°C, as when MIBK is oxidised alone. Moreover, there is a larger amount of less reactive coke, which requires higher temperatures for oxidation, that is also present when o-xylene is oxidised alone.

Temperature programmed desorption was made after adsorption of the compounds alone and in mixture at 40°C (1340 ppmv of MIBK and 1500 ppmv of o-xylene). These results are shown in Figure 40. For both reactants, there is a first peak on the TPD at low temperatures (peak maxima at around 140°C). The catalyst is not able to retain o-xylene at temperatures higher than 210°C. On the other hand, on the same catalyst, MIBK remains adsorbed till 300°C (second small peak with maximum at around 260°C). Moreover, over both

catalysts there was a decrease in the intensity of the first peak of the TPD in the case of mixtures. In the case of MIBK, the second peak did not change with the presence of o-xylene.

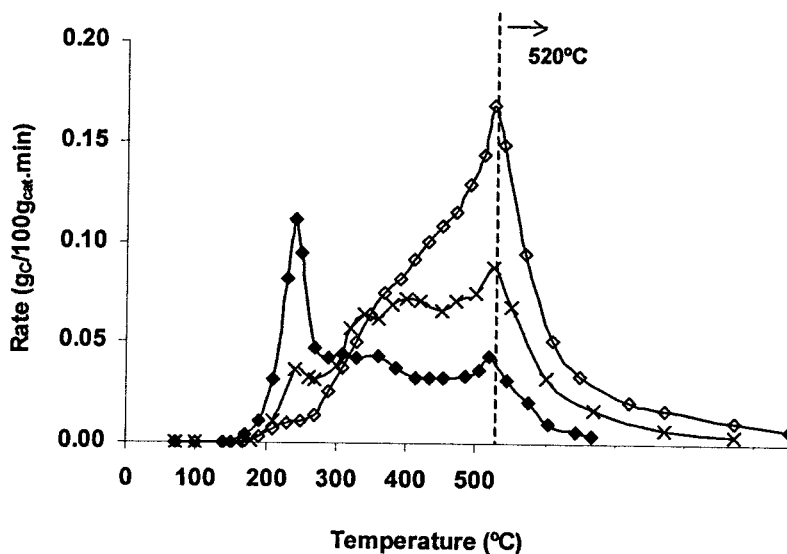


Fig. 39 – Oxidation of coke after reaction on 0.09Pt/HFAU(47) with (♦) MIBK at 180°C, (◇) o-xylene at 225°C and (x) with the mixture MIBK/o-xylene at 210°C.

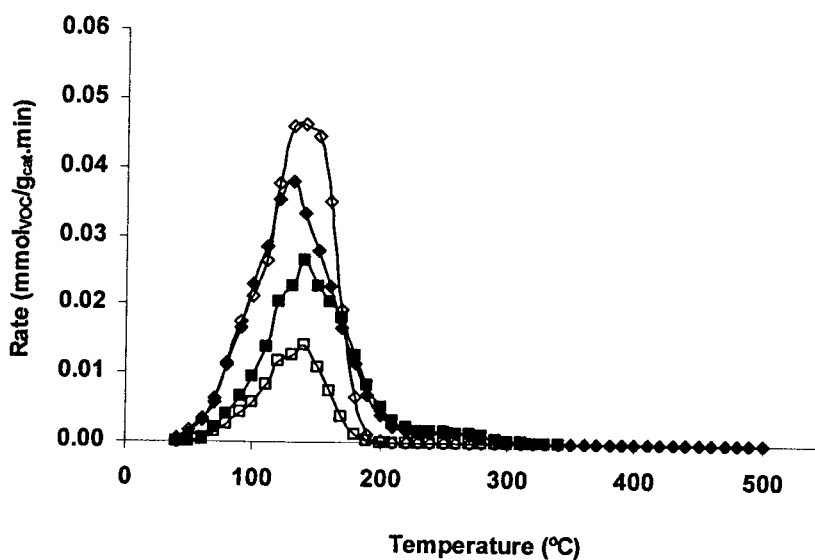


Fig. 40 - TPD after pre-adsorption at 40°C of MIBK (♦) and o-xylene alone (◇) and the mixture of them (■-MIBK; □-o-xylene) over 0.09Pt/HFAU(47).

The amounts of VOCs released (obtained by integration of the TPD curves) when the compounds were adsorbed individually and in mixture are shown in Table 8.

Table 8 – Amounts of VOCs desorbed after TPD in the 0.09Pt/HFAU(47) catalyst after adsorption at 40°C of the VOCs alone and in mixture.

	Amount (mmol _{VOC} /g _{cat})		
	o-xylene	MIBK	mixture
o-xylene	0.65	-	0.17
MIBK	-	0.60	0.42

The presence of the second compound affects more the adsorption of o-xylene than the adsorption of MIBK, because the amount of MIBK adsorbed decreased less than the amount of o-xylene. This result means that the adsorption of MIBK is favoured over the Pt/HFAU(47) catalyst. This does not help to explain the results obtained in the oxidation of the mixture, because if MIBK adsorption is favoured, then its conversion should not decrease relatively to the oxidation of the compound alone.

The fact that o-xylene oxidation is not significantly affected by the presence of MIBK (Fig. 37), even though its adsorption is affected (Fig. 40 and Table 8), suggests that this aromatic reacts independently of what is adsorbed on the support. It should also be noted that at the reaction conditions (temperatures higher than 210°C) the TPD shows that no o-xylene is adsorbed. Moreover, TPD of MIBK over the support alone was carried out (result shown in chapter 5), and no changes were observed between this one and TPD with platinum. In fact, in these TPDs only what is adsorbed on the support is seen.

The only conclusion that can be taken from TPD analysis is that the mixture effect on the conversions of these two VOCs is not related to their adsorption on the support. The fact that the adsorption of a compound is affected by the presence of the other is not a sufficient condition to say that this compound reacts from the gas phase, as suggested in [5]. Other experiments would have to be carried out in order to see what happens to the reactants in the active sites (platinum) at reaction conditions.

3.4. Conclusions

The following conclusions can be taken from this chapter:

- With Pt/HFAU catalysts, MIBK undergoes two simultaneous processes: total oxidation (into CO_2 and H_2O) and transformation into side products (including coke).
- The rate of MIBK oxidation increases with the reaction temperature, while the formation of coke and other side products decreases.
- The higher the platinum content, the lower the temperature necessary to convert all the MIBK. Moreover, platinum should be reduced for a better catalyst performance.
- There is an optimal concentration of oxygen (about 8%) in the feed for which the conversion of MIBK is maximum over a Pt/HFAU(47) catalyst.
- The oxidation of MIBK over Pt/ γ - Al_2O_3 is structure-sensitive, because the larger the platinum particles, the faster the oxidation will be.
- The acidity of the support is a key factor that determines catalyst activity in MIBK oxidation, the less acidic supports being preferred, as coke formation is lower on them. The zeolite structure (BEA or FAU) does not have any influence in the performance of the catalysts.
- Long duration experiments show that there is some deactivation of the pre-reduced catalyst in the first 20 h of reaction, the conversion being constant afterwards. This deactivation can be due to coke accumulation or to changes in the platinum surface caused by excess of oxygen in the feed.
- Regeneration of the catalyst by oxidative treatment up to 520°C and the presence of 5% of steam in the feed do not have a major influence on the performance of the Pt/HFAU(47) catalyst for MIBK conversion.
- Oxidation of the mixture of o-xylene and MIBK over a Pt/HFAU(47) catalyst does not have any negative effect on the oxidation of o-xylene (on the contrary it is slightly enhanced), and has a negative effect on the oxidation of MIBK. This fact is not associated with the adsorption of the reactants on the support.

3.5. References

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4. Catalytic oxidation of MIBK over basic zeolites*

4.1. Introduction

Zeolites are used in catalysis mainly because of their acid properties. However, both acid and basic sites exist simultaneously in zeolites, and, in some catalytic reactions, the basic character of the zeolite is required. The basic sites on a zeolite come from the framework oxygen which is bearing the negative charge. The zeolite chemical composition and type of structure have an effect on the oxygen basicity. The different locations of oxygen atoms on faujasite are shown in Figure 1.

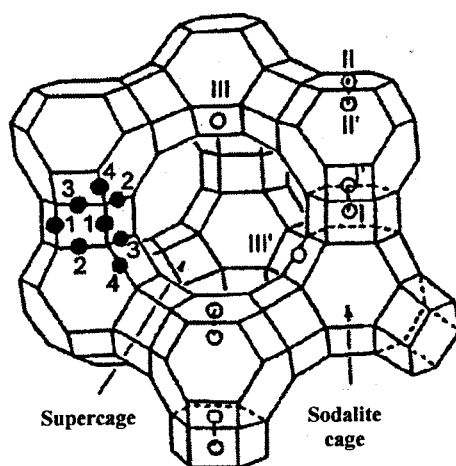


Fig. 1 – Scheme of the faujasite structure with oxygen (●) types and cation (○) location.

Oxygen atoms that bear a higher negative charge are those belonging to the Si-O-Al species, while those connected to silicon (Si-O-Si) do not have basic properties. When the framework negative charge is compensated by a cation with low electronegativity, the charge of the oxygen can be high enough to create basic sites. The cation acts like a Lewis acid site, while the oxygen acts like a basic site. The strength of these sites depends on the zeolite chemical composition (Al content) and on the nature of the cation. With alkali metal cations, the bigger the cation (the less electronegative) the more basic properties will the zeolite have. CsY zeolites are already considered to be of medium basicity [1], while the NaY zeolites are considered neutral. The basic strength increases as: $\text{HY} < \text{NaY} < \text{CsY}$. In addition, considering the same compensation cation, the higher the Al content, the higher the basicity. For instance, zeolite NaX is more basic than NaY.

* These results were accepted for publication in Applied Catalysis B.

The basic strength of a zeolite can be calculated theoretically using the Sanderson principle of equalization of electronegativities in a compound [1]. This approach was first used in the field of zeolites by Mortier [2]. For a compound $P_pQ_qR_r$ the intermediate electronegativity (S_{int}) is given as:

$$S_{\text{int}} = \left(S_P^p S_Q^q S_R^r \right)^{\frac{1}{p+q+r}} \quad (1)$$

where S_j is the electronegativity of the atom j .

This allows us to determine the electronegativity of a compound from its chemical composition. In the case of zeolites, the intermediate electronegativity will depend on the Si and Al content and on the cation identity and content.

The use of basic zeolites as catalysts and as catalyst supports is gaining importance nowadays [3]. The significant negative framework charge leads to electron donor properties, especially when a heavy alkali metal cation, like Cs^+ , is present for electroneutrality. This makes these zeolites suitable for base-catalysed reactions. One of the most studied reactions using these catalysts is the alkylation of toluene with methanol [3-5]. The combination of Lewis acid sites and base sites is very important in this reaction.

Other reactions, like dehydrogenation (in particular, 2-propanol decomposition into acetone), were also studied using basic zeolites as catalysts [6-8]. In these studies, the basic strength of the zeolite was enhanced by occlusion of alkali metal cations. The increase in the rate of dehydrogenation of 2-propanol to acetone was attributed to the enhanced basicity of the zeolite [8].

The acid/base properties of catalysts for elimination reactions (dehydrogenation and dehydration) of 2-propanol were highlighted by Díez *et al.* [9]. They studied this reaction over MgO and alkali-modified MgO catalysts. The addition of alkaline promoters increased the basic site density and strength and improved the MgO activity for 2-propanol elimination reactions. Both Lewis acid sites and basic sites play a role in these elimination reactions, the dehydration being favoured by strong basic sites, while dehydrogenation is favoured by medium strength basic sites.

The importance of acid-base properties of an oxidation catalyst was put into evidence by Viedrine *et al* [10]. Examples of partial oxidation reactions were given in order to show the important characteristics of metal oxides catalysts. Such reactions need both acid and basic sites: the acid sites being of Lewis type (cations) and the basic sites being the framework oxygens.

The catalytic combustion of VOCs can be performed over metal oxides [11,12]. Gandia and co-workers [11] studied the catalytic oxidation of acetone and methyl-ethyl-ketone (MEK) over Mn_2O_3 catalysts. They found that when this oxide is modified by alkali additives like Na and Cs the conversion of the ketones is shifted to lower temperatures. For example, in the oxidation of MEK, T_{50} (the temperature for which the conversion of VOC is 50%) was 558K with Mn_2O_3 catalysts, against 526 and 509K when this oxide was modified with Na and Cs, respectively. It was pointed out that when alkali or acid additives are added to oxides, there is the formation of strongly bound enolic species that can also undergo aldol condensation, producing compounds that remain adsorbed in the catalyst [11]. The presence of alkali additives on the manganese oxide can favour the oxidation of these adsorbed species on the catalyst surface, thus reducing the combustion temperatures.

Catalytic combustion of C_3 hydrocarbons and oxygenates was studied by Baldi *et al.* [12] over Mn_3O_4 . Complete oxidation of these compounds into CO_2 occurs at temperatures below 673K. Partially oxidised compounds were observed only at temperatures where the VOC conversion was incomplete. In the case of acetone, the conversion into CO_2 is complete at temperatures around 550K.

Recent results also show that PtNaY should be a promising catalyst for total oxidation of dichloromethane [13].

In the course of our study on the catalytic oxidation of methyl-isobutyl-ketone (MIBK) over Pt/zeolite catalysts, it was found that NaFAU and CsFAU zeolites were active catalysts, being able to oxidise MIBK into CO and CO_2 . These results led us to start an investigation into the influence of the alkali cations Na and Cs on this oxidation reaction. The aim of the present report is to correlate the activity and selectivity of these zeolites with their basic properties. For that purpose, reactions were carried out at different temperatures over HFAU zeolite and also over NaY (NaFAU, in chapter 3), CsY (CsFAU, in chapter 3), NaX and CsX.

4.2. Experimental

4.2.1. Preparation and characterisation

CsY and CsX zeolites were prepared from NaY (Linde) and NaX (Grace Davidson) zeolites, respectively, by double exchange with a 0.5 M solution of CsNO₃ (Aldrich), at 80°C with a ratio volume of solution (mL) / zeolite weight (g) of 70 [14]. Afterwards the samples were filtered, washed and dried overnight at 110°C. Calcination was performed under air flow (3 L h⁻¹ g⁻¹) with a heating rate of 2°C min⁻¹ from ambient temperature till 500°C with a hold of 2 h.

The micropore volume of the supports was determined from the nitrogen adsorption isotherms, performed at 77K with a gas adsorption system (Coulter Omnisorp 100CX). Prior to adsorption, the samples were outgased at 350°C, up to a pressure lower than 10⁻⁵ mbar.

XPS analyses were performed on the alkali-exchanged zeolites with a VG Scientific ESCALAB 200A spectrometer using a non-monochromatised Mg K_α radiation (1253.6 eV). The pressure in the analysis chamber was always <1×10⁻⁷ Pa. The binding energies were referred to the C1s level at 285.0 eV.

4.2.2. Reaction study

The reaction apparatus was already described on chapter 3.

The products distribution is reported in terms of the relative yields defined as:

$$s_i = \frac{\text{product i}}{\text{converted reactant}} \quad (2)$$

where both terms are expressed as molar flow rates.

The analysis of side products was made by collecting gas samples in a trap at the reactor outlet. These samples were then analysed by GC-MS (Varian – CP-3800 with a ITD detector Saturn 2000). The separation was made by a chromatograph column CP-Sil 8 CB lowbleed/MS. The carbonaceous compounds retained on the catalyst (“coke”) were analysed by a technique developed for that purpose. This procedure was described in chapter 2. The soluble compounds present in the coke were analysed by GC/FID and by GC/MS.

Temperature programmed desorption was studied after pre-adsorption of MIBK (1340 ppmv) at 40°C. MIBK was adsorbed on the catalysts at 40°C from a nitrogen stream. This procedure was also described in more detail in chapter 3.

4.3. Results and discussion

The results of this chapter are divided in two parts. First MIBK oxidation was carried out over NaY zeolite and a more complete study was made, such as the effect of temperature, concentration of oxygen, analysis of the secondary products and analysis of the soluble coke. Then the oxidation of MIBK was studied over other basic zeolites at different temperatures (NaX, CsX and CsY). Finally, a relationship between the oxidation of MIBK into CO₂ and the basicity of these zeolites was put into evidence.

The characteristics of the zeolites used are shown in Table 1.

Table 1 – Properties of the zeolites: framework formula, cesium exchange percentage, microporous volume and intermediate electronegativity.

	formula	Cs exchange (%)	V_{micro} (cm ³ g ⁻¹)	S_{int}^*
HFAU47	H ₄ Al ₄ Si ₁₈₈ O ₃₈₄	-	0.284	4.24
NaY	Na ₅₆ Al ₅₆ Si ₁₃₆ O ₃₈₄	-	0.304	3.55
CsY	Cs ₄₀ Na ₁₆ Al ₅₆ Si ₁₃₆ O ₃₈₄	71	0.188	3.35
NaX	Na ₈₆ Al ₈₆ Si ₁₀₆ O ₃₈₄	-	0.301	3.26
CsX	Cs ₃₈ Na ₄₈ Al ₈₆ Si ₁₀₆ O ₃₈₄	44	0.179	3.09

* Calculated from equation 1, using the values of S of the different atoms in [2].

The exchange of the Na cations by Cs cations was not complete in both cases, the maximum being 71% exchange in the case of Y zeolite. This may be related to the fact that the exchange of Na cations in the sites I (hexagonal prism) is rather difficult. The exchange by Cs cations also provoked a decrease in the microporous volume, which was expected as the Cs cation is bigger than Na. The intermediate electronegativity values are also making sense. The HFAU zeolite an acidic zeolite as it does not have any alkali cation exchanged, hence its S_{int} is the highest, i.e., it will have more power to attract electrons. Comparing now Na and Cs zeolites (both X and Y), it also makes sense that Cs zeolites present a lower S_{int} , as the Cs cation is bigger and therefore they have lower electronegativities. So they will have higher basic strength than the corresponding Na zeolites. The difference in the intermediate electronegativities of Y and X zeolites is due to the fact that the Si/Al ratio is lower in the X zeolite, allowing it to have a higher amount of compensating cation, hence a lower electronegativity.

XPS is a powerful tool for the characterisation of zeolites and related materials [15] and is considered as a suitable method for direct investigation of the basic oxygens in zeolites [1,16]. XPS studies using probe molecules (like pyrrole [17] and chloroform [18]) also showed good results in the characterisation of the basic strength on zeolites. The intermediate electronegativities (S_{int}) of the alkali-exchanged zeolites as a function of the O 1s binding energy determined by XPS are shown in Figure 2.

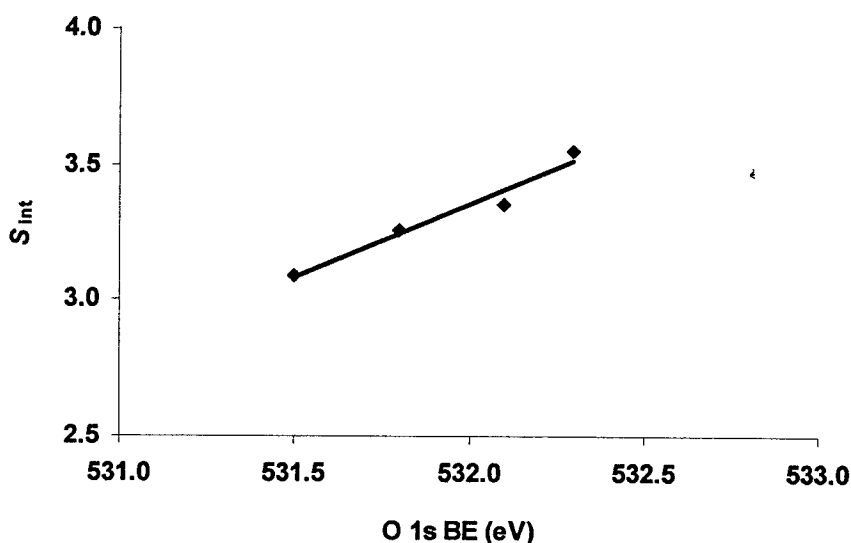


Fig. 2 – Intermediate electronegativity (S_{int}) of the zeolites as a function of the O 1s binding energy determined by XPS.

The lower the O 1s BE the lower the S_{int} (and the higher the basic strength). These results are in agreement with the findings of Okamoto *et al.* [19], who suggested that the basic strength of the framework oxygen increases with the increase of the Al content, regardless of the crystal structure, and with the increase of the Cs content.

4.3.1. Oxidation of MIBK over NaY zeolite

4.3.1.1. Influence of the temperature and time-on-stream (TOS)

The conversion of MIBK, the conversion into CO_2 and the conversion into CO obtained over the NaY zeolite at different temperatures are compared in Figure 3.

MIBK undergoes oxidation into CO and CO_2 and also formation of compounds that remain adsorbed in the zeolite ("coke"). At 270°C (and at higher temperatures), whatever the TOS, there was no MIBK at the reactor exit (Fig. 3a). At these temperatures, the conversion into CO and CO_2 increased at the beginning of reaction, till approximately constant values (Fig. 3b and c). At 200°C , MIBK conversion, initially of 100%, decreased progressively as a function of TOS (Fig. 3a) and the conversion into CO and CO_2 increased first with TOS decreasing again to a constant value (Fig. 3b and c). It was also observed that the catalyst temperature (read by the thermocouple that was placed in the catalyst bed) increased at the beginning of the experiments, reaching a constant value, which was maintained till the end of the reaction. At 220°C the conversion of MIBK did not always decrease with TOS, but there was an increase at about 25 min of reaction. Also the CO_2 and CO presented a peak at the same time. Afterwards the conversion of MIBK decreased progressively as well as the conversion into CO and CO_2 . The catalyst temperature also increased 3°C when the CO_2 peak appeared, decreasing progressively till $+1^\circ\text{C}$ at the end of the run.

At 250°C oscillations were observed in the apparent conversion into CO and CO_2 . This phenomenon will be explained in chapter 5. The conversions shown in Figure 3 correspond to the minima of these oscillations, as it is also explained in chapter 5.

At all the temperatures studied there was the formation of side products which were released during the reaction or that remained adsorbed/trapped in the zeolite pores ("coke"). After 3 h of reaction at 220°C the micropore volume was $0.117 \text{ cm}^3 \text{ g}^{-1}$. There was a decrease of 62 % relative to the initial value, due to the presence of coke. It should be noted that prior to nitrogen adsorption, the sample was outgased only at 150°C during 24 h against 350°C (section 4.2.1.) so that the coke would not decompose.

Temperature programmed oxidation was made after reaction at different temperatures (Figure 4).

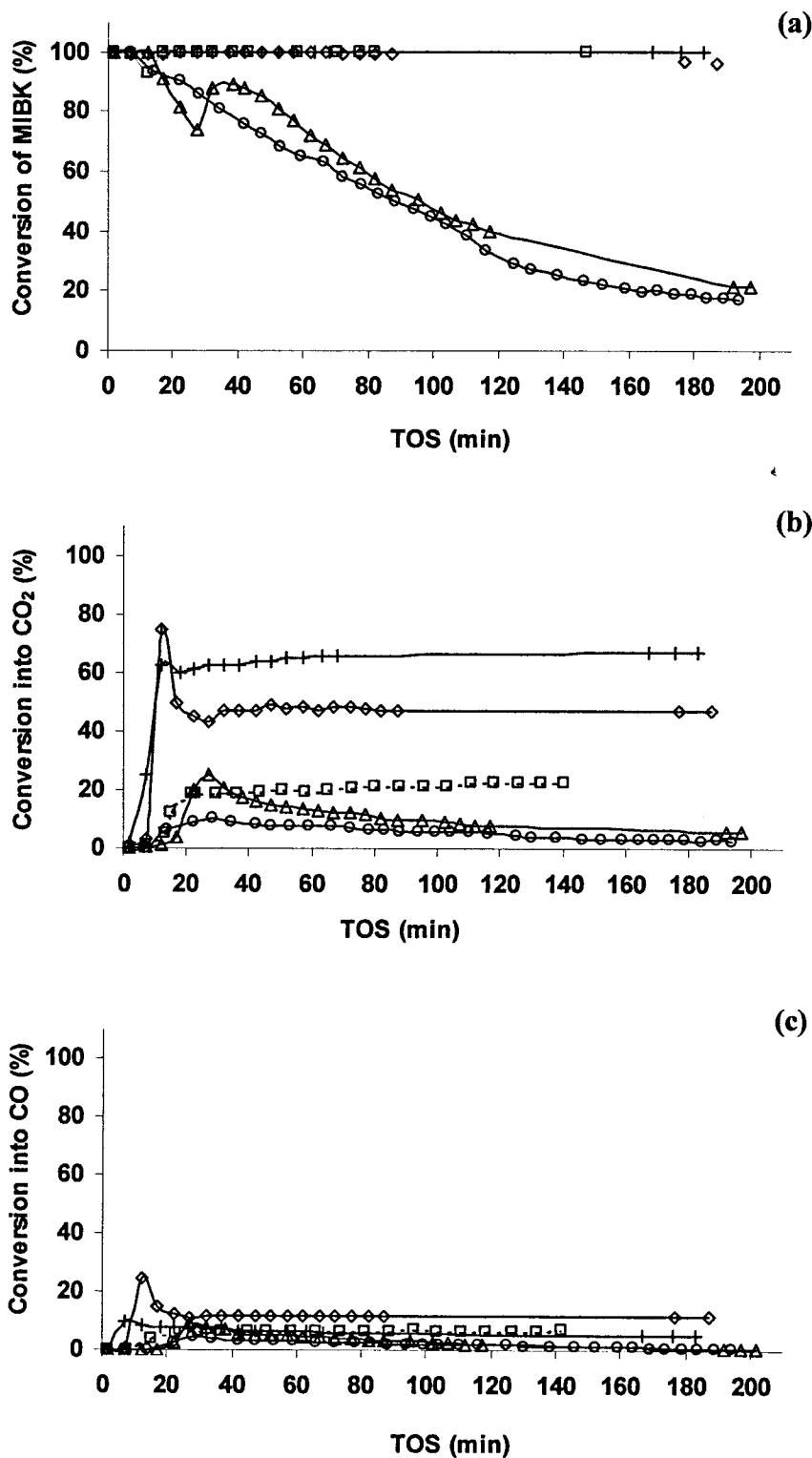


Fig. 3 – Influence of time-on-stream on the: (a) total conversion of MIBK, (b) conversion into CO₂ and (c) conversion into CO over the NaY zeolite at 200 (○), 220 (Δ), 250 (□), 270 (◇) and 300°C (+).

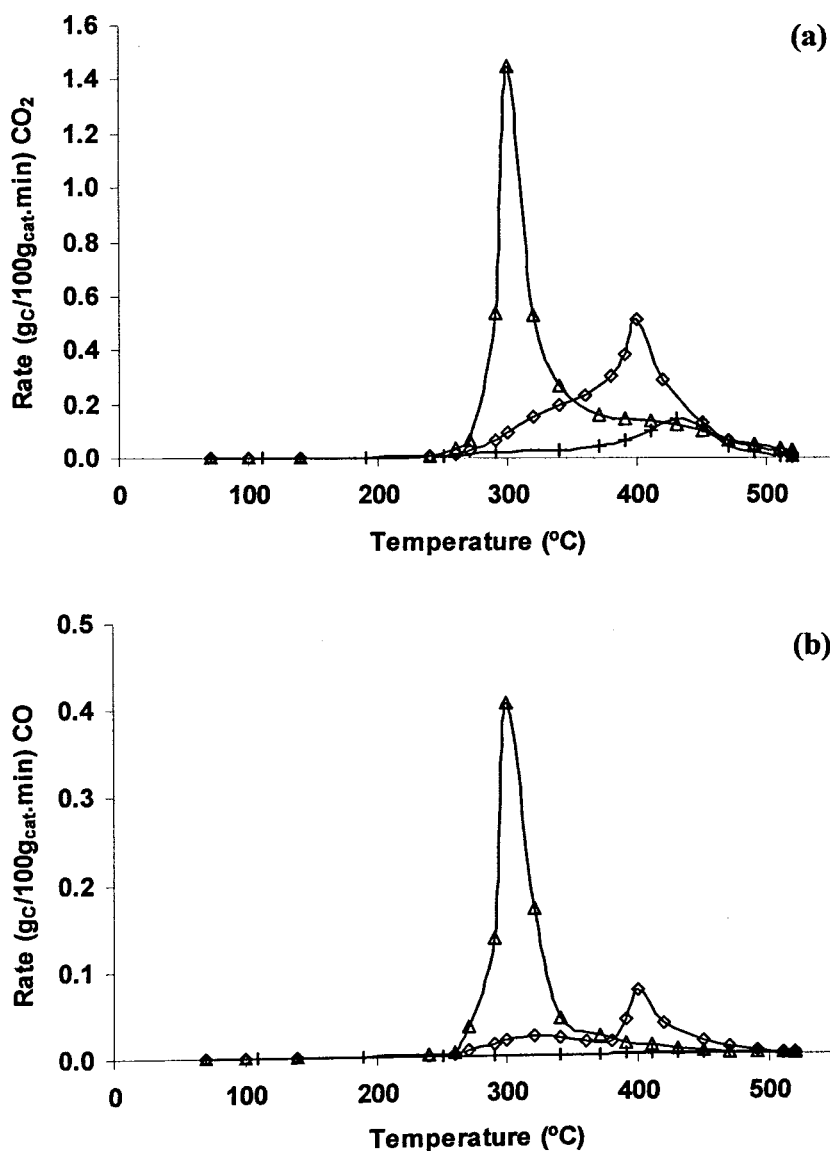


Fig. 4 – TPO after reaction over the NaY zeolite at 220 (Δ), 270 ($\diamond$) and 300°C (+) in terms of (a) CO_2 and (b) CO released.

After reaction at 220°C there are two types of coke present in the catalyst: a more reactive component that oxidises at low temperature and a less reactive one that only oxidises at high temperatures. As it will be shown in chapter 5, the reactive coke is composed partially by the reactant that remains adsorbed on the catalyst and other low molecular weight compounds. At 270 and 300°C there is much less reactive coke present, but there is a higher formation of less reactive coke at 270°C, which decreases with the reaction temperature. It should be noted that at 220°C the initial values of the conversions (Fig. 3) are certainly due to the fact that coke formation is faster than its oxidation, as the conversion of MIBK is

complete and the conversions into CO and CO₂ are practically zero. After approximately 10 min, the temperature of the catalyst increases, because of the exothermic character of the oxidation, and the oxidation rate into CO_x increases, originating the peaks in the conversions of Figure 3. Nevertheless, the catalyst deactivates afterwards with TOS, probably due to coke accumulation.

The influence of the reaction temperature on the products distribution is shown in Table 2.

Table 2 – Conversion of MIBK (X_{MIBK}), products distribution: CO₂ (s_{CO_2}), CO (s_{CO}) and other side products (s_{sp}) and amount of coke after 3 h reaction at different temperatures over the NaY zeolite.

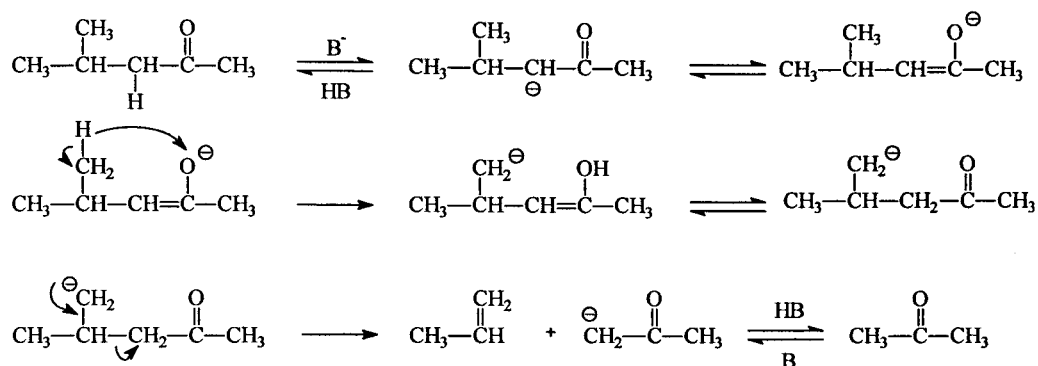
Temperature (°C)	X_{MIBK} (%)	s_{CO_2} (%)	s_{CO} (%)	s_{sp} (%)	Coke (g _C /100g _{cat})
200	17	15	3	82	n.d.
220	20	28	4	68	8.3
270	99	49	12	39	5.0
300	100	67	5	28	1.4

The higher the reaction temperature, the higher the conversion of MIBK and the selectivity in CO₂. On the contrary, side products and coke formation decreased at higher temperatures. The selectivity in CO first increased with the temperature, decreasing again for higher temperatures.

4.3.1.2. Analysis of the side products and soluble coke

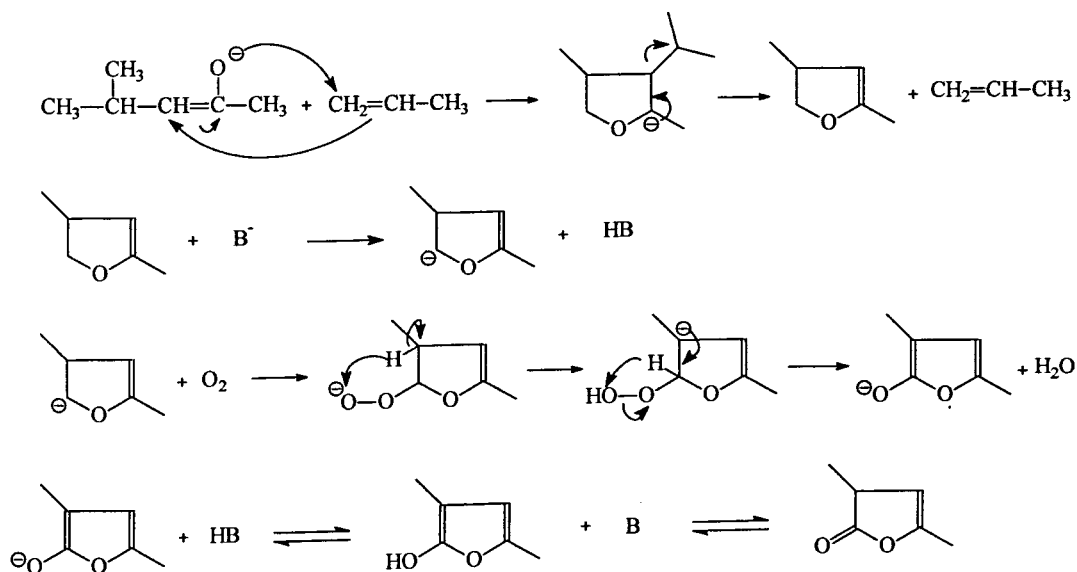
During the reactions over NaY zeolite, MIBK not only is oxidised into CO and CO₂ but also some other products were formed. Those that were released during the reaction were collected in a gas trap and analysed by GC/MS and those that remained adsorbed inside the zeolite were analysed by the technique developed for the analysis of the soluble coke. These two techniques were performed in a run at a reaction temperature of 220°C.

The main secondary product collected at the reactor exit at this reaction temperature was acetone. Light hydrocarbons were also detected at low retention times. Acetone and propene can be formed in the following way:



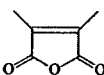
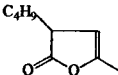
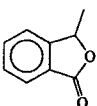
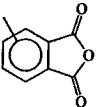
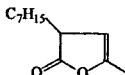
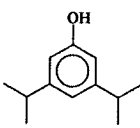
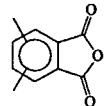
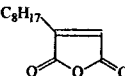
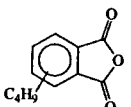
The compounds that were present in the soluble coke after reaction at 220°C for 3h are shown in Table 3 (amount of coke after reaction: 8.3%; amount of soluble coke recovered: 2%). The difference between these values is very high, and cannot be due only to the uncertainty in the quantification of the amount of soluble coke recovered. What happened is that, as it will be shown in chapter 5, a large part of the coke (which we call reactive coke) is composed of reactant that remained adsorbed in the zeolite and other volatile compounds. These compounds will not remain in the soluble coke, as it was concentrated by means of evaporation at 50°C under vacuum. This explains the large difference between these two values.

The analysis of soluble coke shows mainly the formation of oxygenated compounds, namely anhydrides and aromatics. The formation of the lighter compounds can proceed as follows:



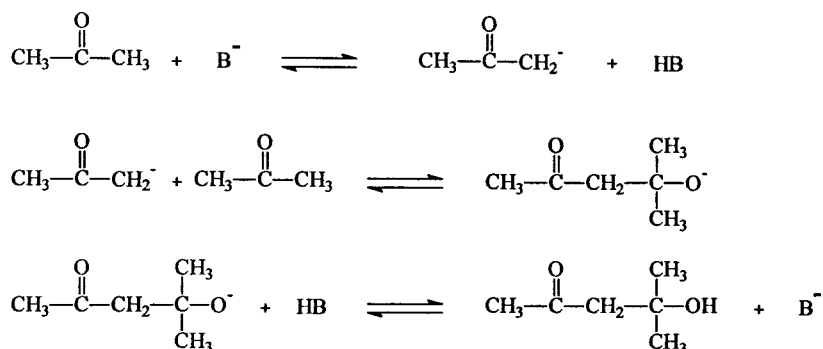
Further oxidation can occur, leading to other more oxidised compounds.

Table 3 – Nature of the soluble coke after reaction at 220°C over the NaY zeolite.

Molar mass (g.mol ⁻¹)	formula	Amount (%)	Compound
112	C ₆ H ₈ O ₂	31	
126	C ₆ H ₆ O ₃	17	
154	C ₉ H ₁₄ O ₂	7	
148	C ₉ H ₈ O ₂	2	
162	C ₉ H ₆ O ₃	7	
196	C ₁₂ H ₂₀ O ₂	10	
178	C ₁₂ H ₁₈ O	3	
176	C ₁₀ H ₈ O ₃	3	
210	C ₁₂ H ₁₈ O ₃	16	
204	C ₁₂ H ₁₂ O ₃	2	
256		2	Acid

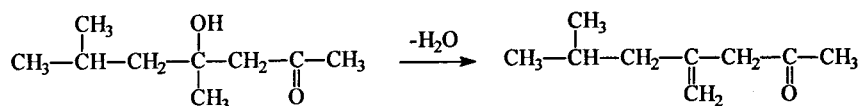
The formation of compounds with higher number of carbon atoms can be due to the condensation reaction of MIBK, or acetone (side product of the reaction). Catalysts for aldol

condensation may be either acidic or basic [20]. In basic medium, aldol condensation of acetone (in homogeneous systems) proceeds as follows:

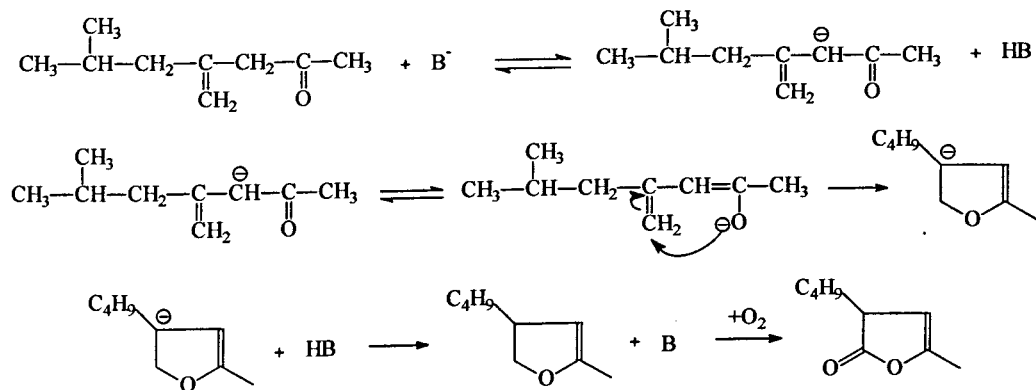


Condensation of acetone over basic catalysts was extensively studied by the group of Hattori [21]. They used magnesium oxide as catalyst, and found that the increase in basicity attained by addition of metal cations (like Na, for example) had a positive effect on the condensation reaction.

If the condensation would occur between an acetone molecule (formed as secondary product) and a MIBK molecule, compounds of the following type would be obtained, which can be dehydrated:



Cyclisation of such compounds can occur as follows:



This last oxidation would occur in the same way as described previously.

If the condensation would occur between two molecules of MIBK, then the same type of compounds would appear, but this time with twelve carbon atoms instead of nine. These compounds can be further oxidised, originating compounds as shown in Table 3.

Further dehydrogenation reactions might be the reason for the appearance of aromatics. As it was discussed in the introduction, these reactions can occur over metal oxides.

The high oxygenation degree of the compounds suggests that they are intermediates for the oxidation into CO and CO₂. In fact, such type of intermediates was referred to by Andersson [22] in the catalytic oxidation of toluene and xylene over metal oxides. Phthalic anhydride was identified, its oxidation resulting in maleic anhydride, which can be oxidised into CO and CO₂.

4.3.1.3. Influence of the oxygen partial pressure

An experiment with a higher oxygen partial pressure was performed in order to determine its influence in the oxidation of MIBK over NaY zeolite (Figure 5).

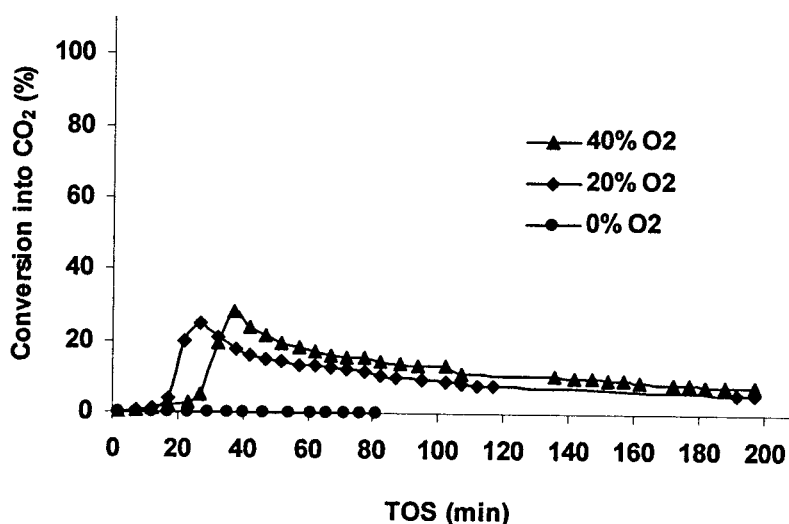


Fig. 5 – Influence of time-on-stream on the conversion into CO₂ over the NaY zeolite at 220°C with 0% O₂ (●), 20% O₂ (◆) and 40% O₂ (▲).

When no oxygen is present there is no conversion into CO₂, as expected. When the reaction is carried out with 40% of oxygen, the conversion into CO₂ has the same behaviour as with 20% O₂. The conversion into CO₂ increases slowly at the beginning of the reaction,

followed by a CO_2 peak, which is accompanied by an increase of the catalyst temperature of 3°C . Afterwards, the conversion into CO_2 decreases progressively till 8% after approximately 3h of reaction, against 6% when the reaction is carried out with 20% O_2 . There is no major difference in the conversion into CO_2 considering these two cases. This result is not surprising, because oxygen is already in excess in comparison to the ketone under the standard experimental conditions, so it would be expected that a higher oxygen pressure would not have a major effect on the oxidation reaction.

4.3.2. Oxidation of MIBK over other basic zeolites. Comparison of results.

Catalytic oxidation of MIBK was also performed over the other zeolites: CsY, NaX and CsX. The influence of the basic strength of the zeolite in the reaction was investigated.

4.3.2.1. Influence of the temperature and time-on-stream (TOS)

Total conversion of MIBK, conversion into CO_2 and conversion into CO obtained over the CsY zeolite at different temperatures are compared in Figure 6.

The behaviour of the conversions with TOS is similar to the curves obtained with the NaY zeolite. In this case, the conversions into CO_2 are higher than with the NaY at the same reaction temperature. There were also oscillations in the apparent conversion into CO_2 when the reaction was carried out at 220°C . The minima of the oscillations are presented in the figure. The same small peaks in the conversion of MIBK and conversion into CO_2 were observed at 200°C after approximately half hour of reaction. Moreover, the stability of these catalysts should be emphasized. At temperatures higher than 250°C , there is no deactivation in the conversion into CO_2 (at least during 3 h). Therefore, these zeolites present a very good stability in this reaction.

TPOs after 3 h of reaction at 200, 250 and 300°C are shown in Figure 7. As in the case of the NaY zeolite, reactive coke is detected in the TPO experiments after reaction at lower temperatures. In the case of this zeolite, there is also unreactive coke, but in smaller amount compared to NaY.

Similar curves of conversion versus TOS were obtained over NaX and CsX zeolites, as well as similar TPO curves (Figures 8, 9, 10 and 11)

The results of the conversions into CO_2 and CO after 3 h of reaction at different temperatures over the different zeolites are shown in Figure 12.

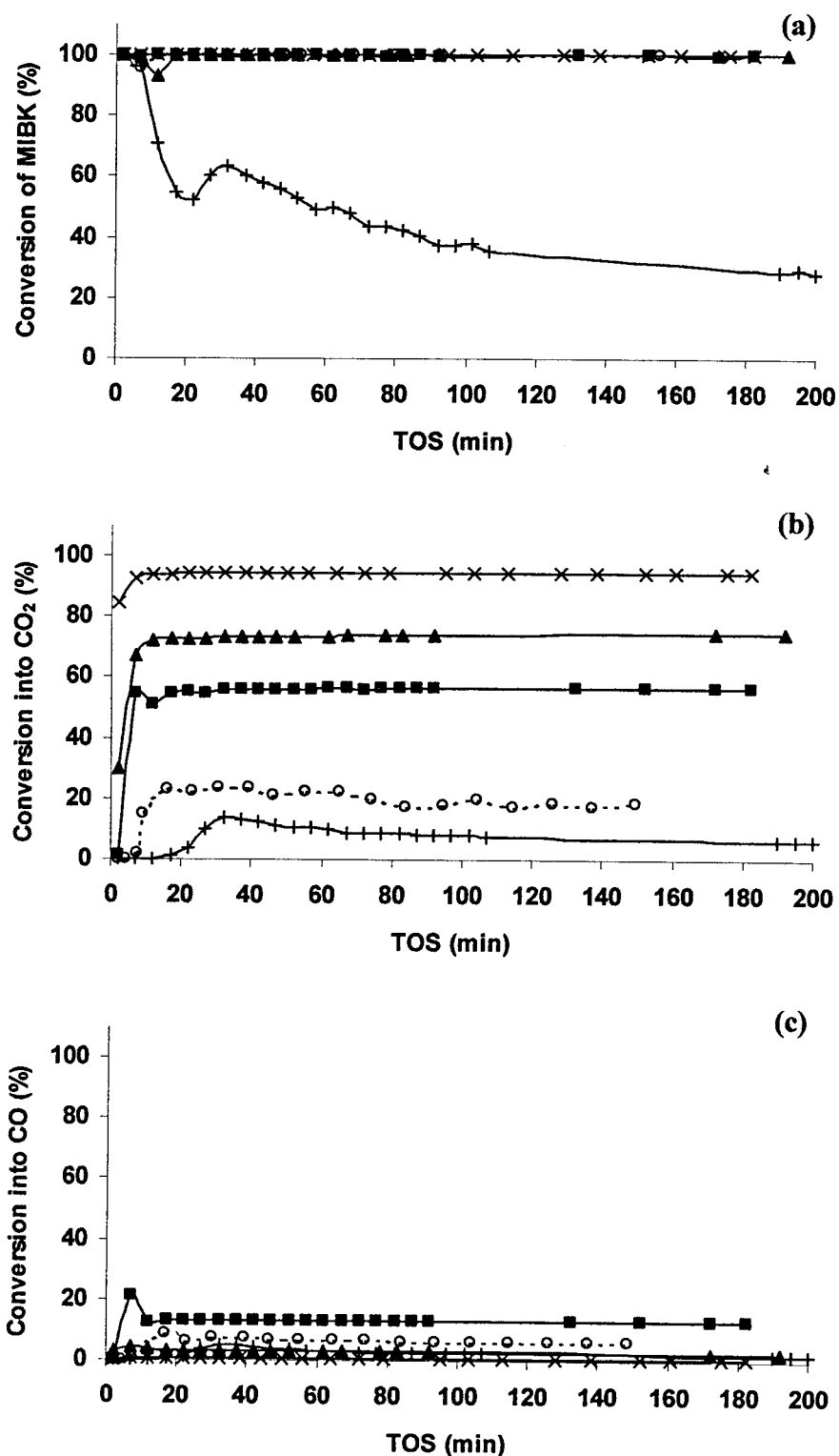


Fig. 6 – Influence of time-on-stream on the: (a) total conversion of MIBK, (b) conversion into CO₂ and (c) conversion into CO over the CsY zeolite at 200 (+), 220 (○) 250 (■), 300 (▲) and 350°C (X).

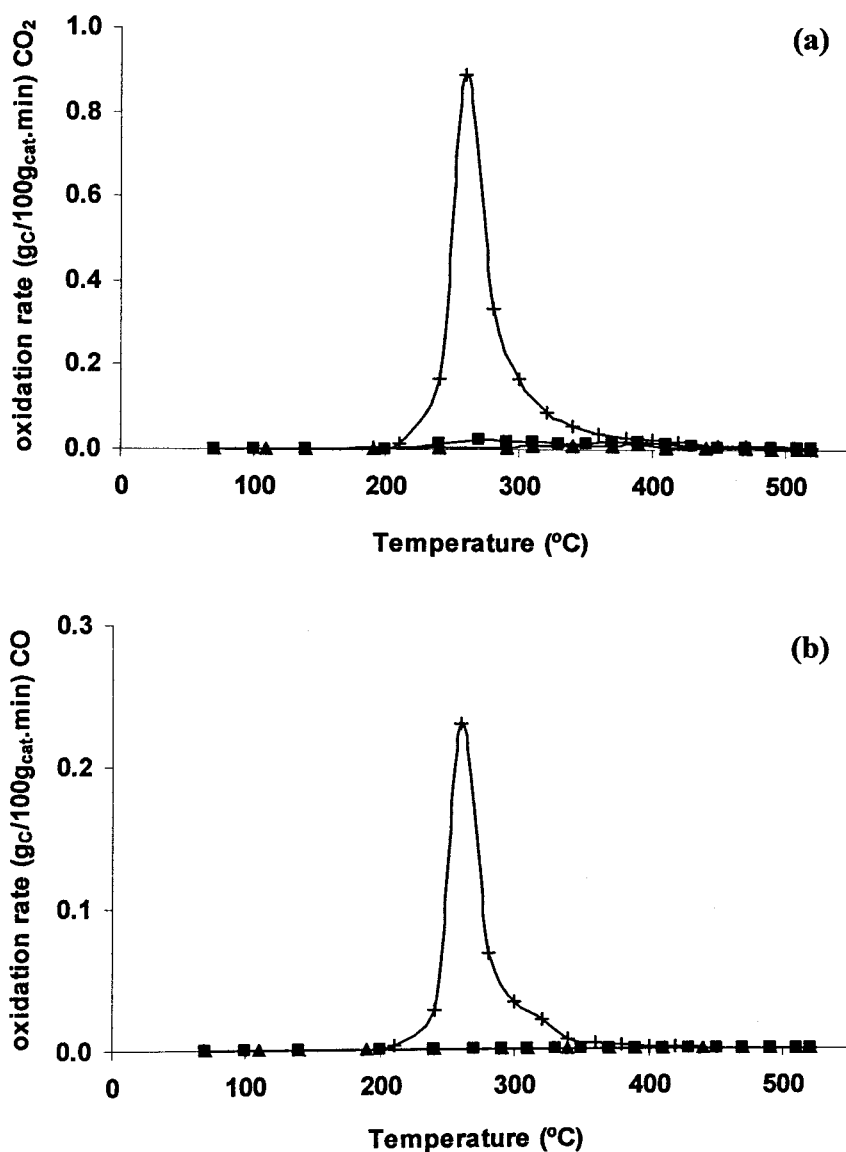


Fig. 7 – TPO after reaction over the CsY zeolite at 200 (+), 250 (■) and 300°C (▲) in terms of (a) CO_2 and (b) CO released.

At 300°C, the conversion of MIBK was 100% over all the zeolites with the exception of HFAU (conversion of 25%), the basic zeolites presenting also a high conversion into CO_2 (Figure 12). In fact, the CsX zeolite is even able to oxidise all the MIBK into CO_2 at this temperature. With the other zeolites, side products (like CO, acetone and light alkenes) and coke are formed (Table 4).

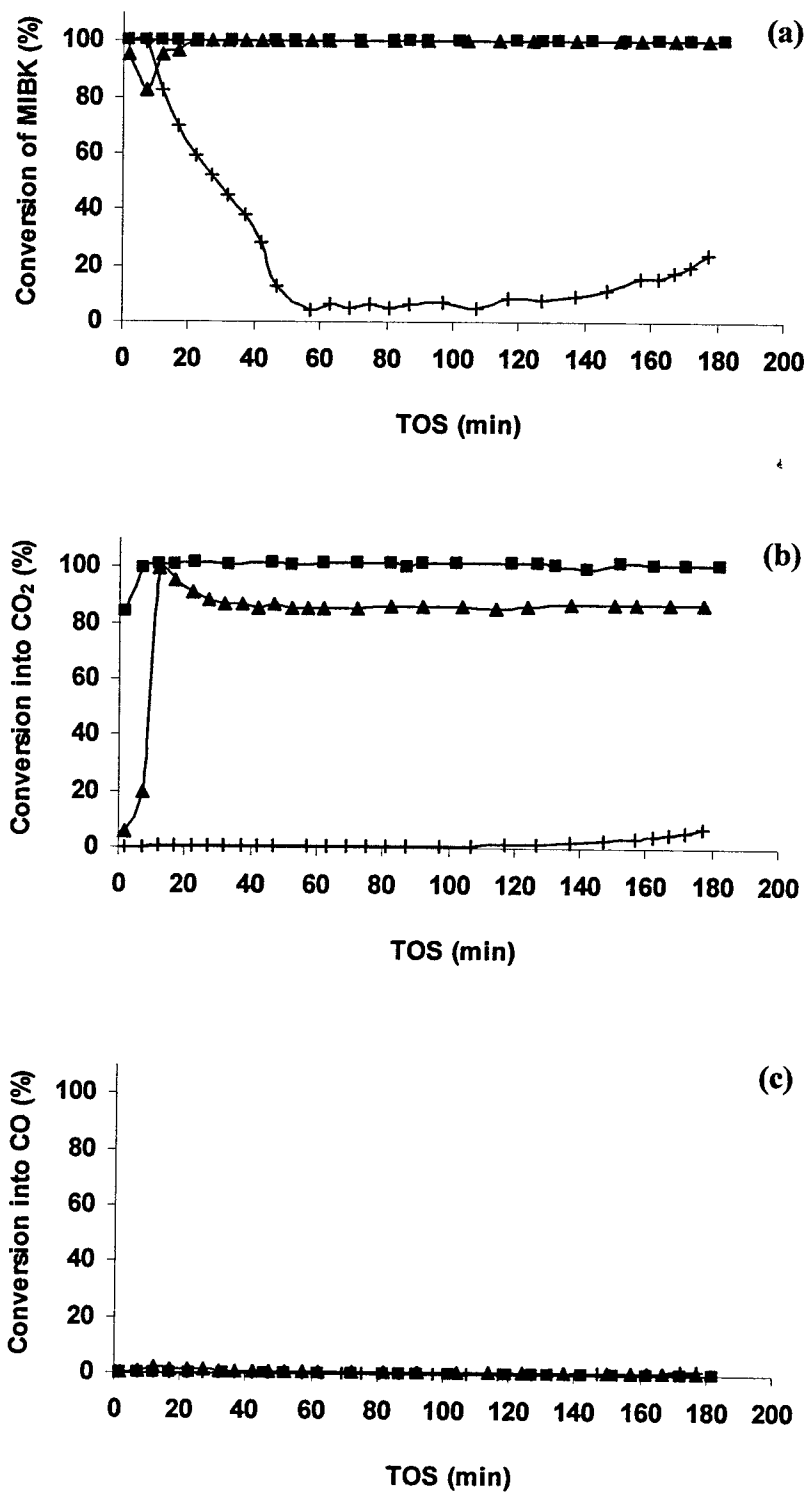


Fig. 8 – Influence of time-on-stream on the: (a) total conversion of MIBK, (b) conversion into CO₂ and (c) conversion into CO over the NaX zeolite at 200 (+), 300 (▲) and 350°C (■).

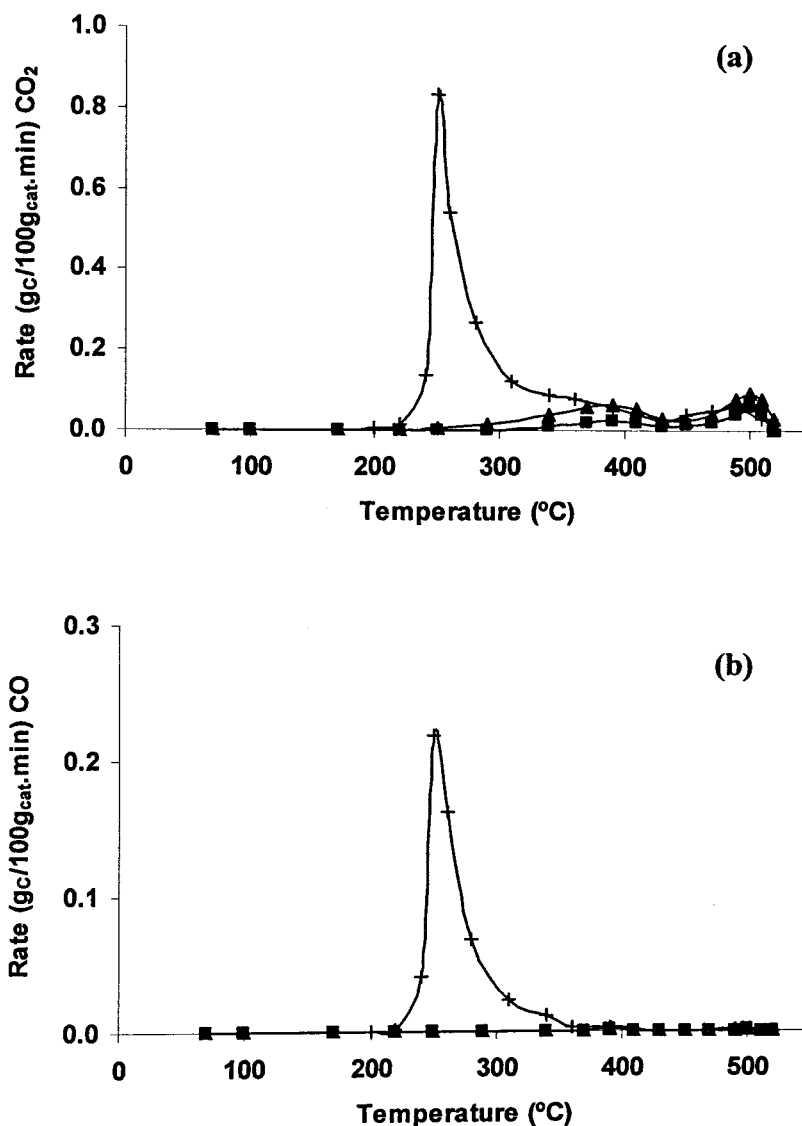


Fig. 9 – TPO after reaction over the NaX zeolite at 200 (+), 300 (▲) and 350°C (■) in terms of (a) CO₂ and (b) CO released.

Table 4 – Reaction products distribution: CO₂ (s_{CO_2}), CO (s_{CO}) and other side products (s_{sp}) and amount of coke after 3 h reaction at 300°C over the different zeolites.

	s_{CO_2} (%)	s_{CO} (%)	s_{sp} (%)	Coke (gc/100g _{cat})
CsX	100	0	0	0.2
NaX	87	1	12	1.2
CsY	75	2	23	0.2
NaY	67	5	28	1.4
HFAU	20	4	76	2.8

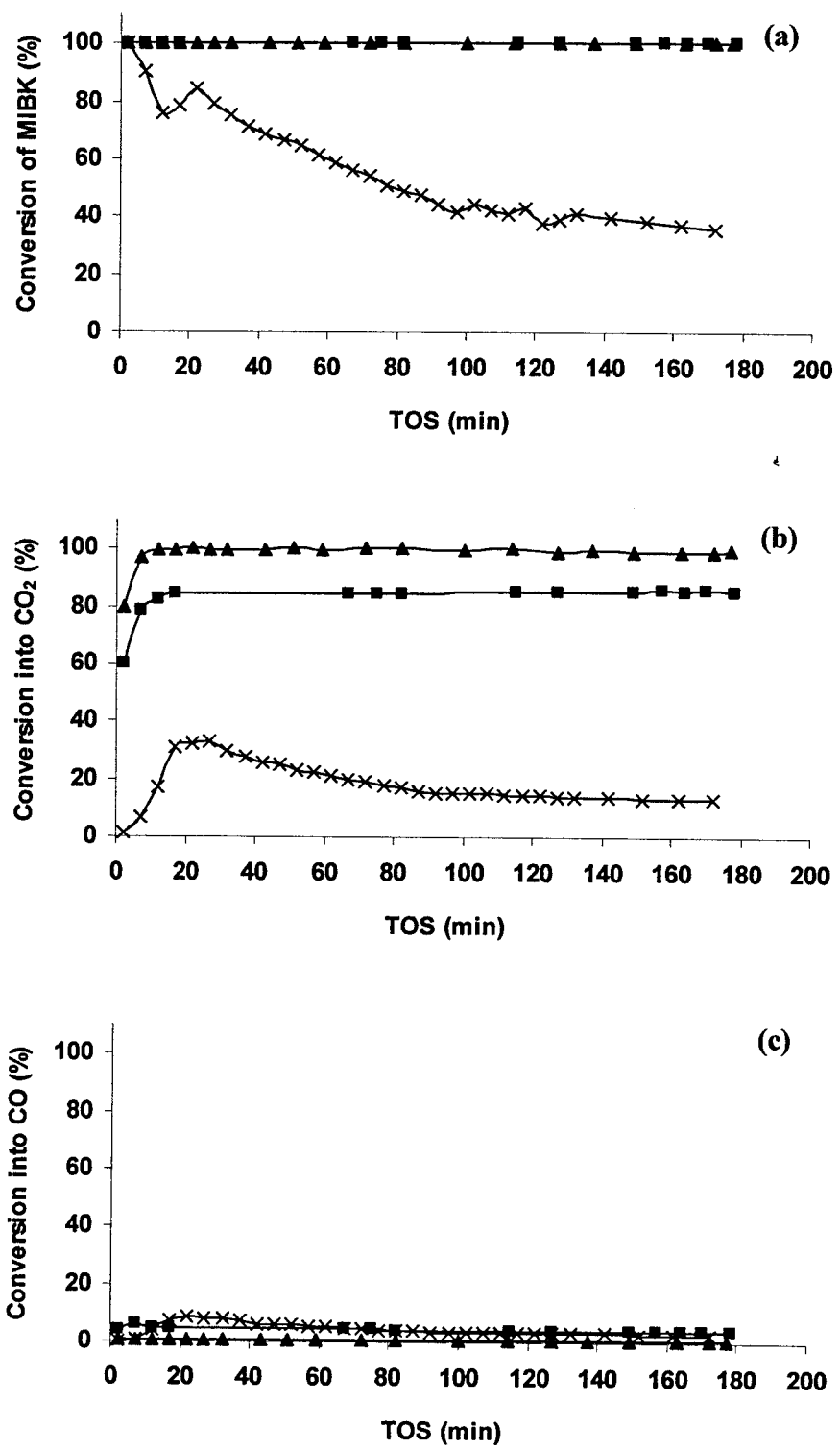


Fig. 10 – Influence of time-on-stream on the: (a) total conversion of MIBK, (b) conversion into CO₂ and (c) conversion into CO over the CsX zeolite at 200 (X), 270 (■) and 300°C (▲).

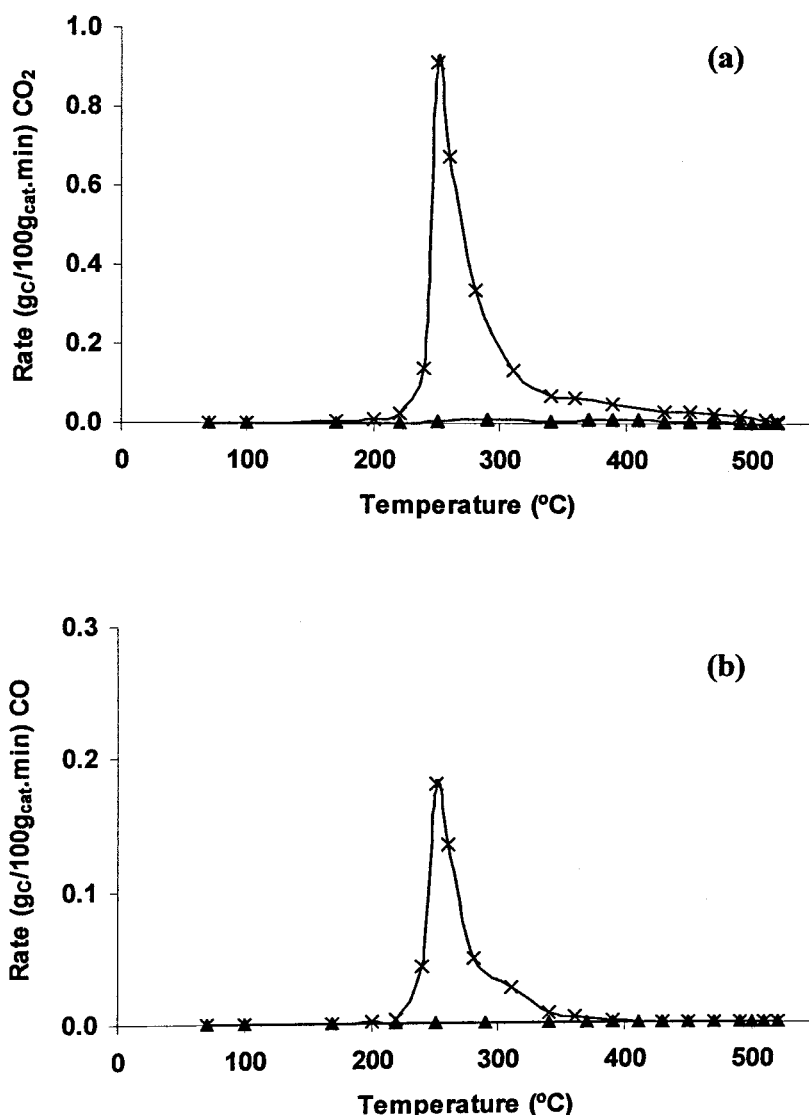


Fig. 11 – TPO after reaction over the CsX zeolite at 200 (X) and 300°C (▲) in terms of (a) CO₂ and (b) CO released.

An acidic zeolite such as HFAU(47) was the less active in MIBK oxidation, as it presents a conversion into CO₂ lower than 5% even at 300°C. On the other hand, basic zeolites were able to transform directly MIBK into CO₂. Moreover, CsX and NaX zeolites are more active and selective than the corresponding Y zeolites, as they can reach higher conversion into CO₂ at the same temperature. Thus, MIBK was totally oxidized into CO₂ at 300°C on CsX against 350°C on CsY. This is not surprising, because CsX and NaX also contain larger amounts of cation than CsY and NaY, due to their lower Si/Al ratios (Table 1).

Furthermore CsX, the more basic catalyst, was also more active and selective than NaX zeolite.

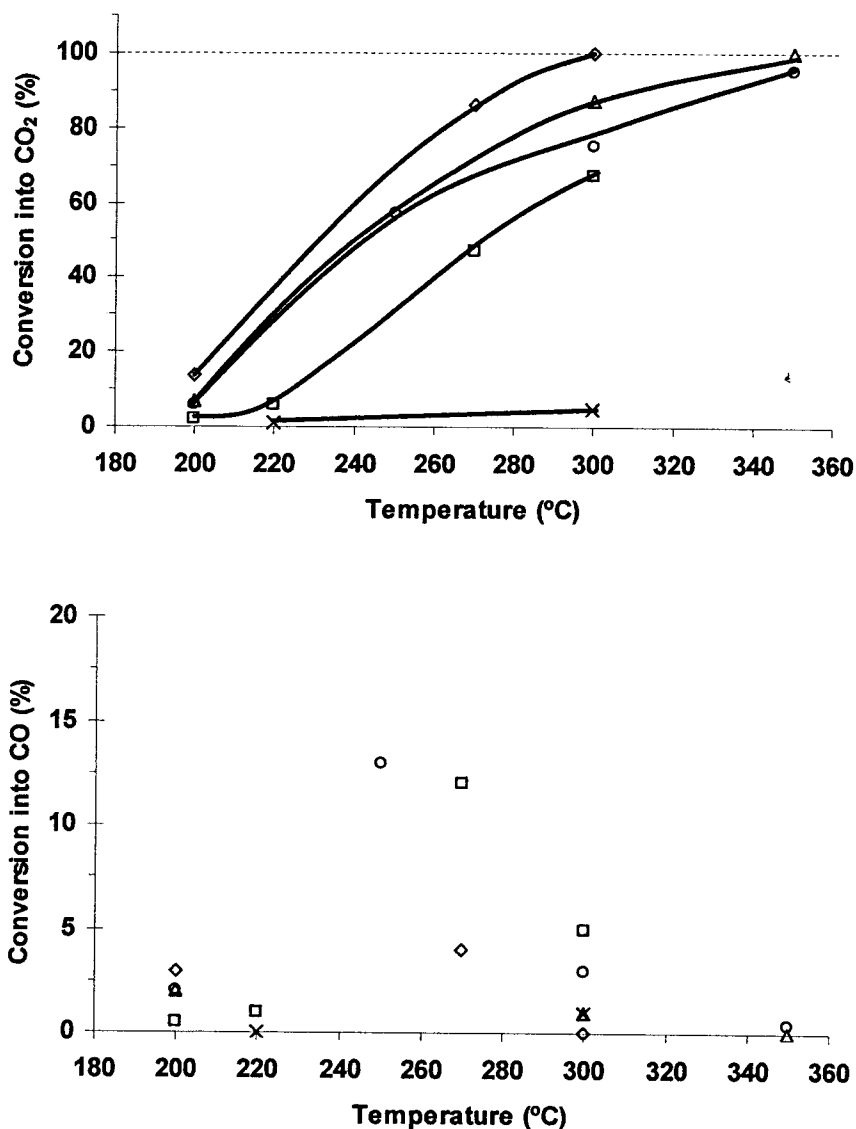


Fig. 12 - Conversion of MIBK into CO₂ and CO after 3h of reaction as a function of the temperature for the HFAU (x), NaY (□), CsY (○), NaX (Δ) and CsX (◇) zeolites.

The amount of coke that remains in the zeolite pores after 3h reaction, which is released as CO and CO₂ in the TPO, is presented in Figure 13. Coke formation is higher on the NaY (or NaX) than on the CsY (or CsX). After reaction at 300°C there is almost no coke in the pores of the CsY and CsX zeolites. From Table 1 it can be seen that the NaY zeolite lost part of its micropores after cation exchange. So, it is possible that there is also less formation of coke in CsY zeolite because the micropore volume is lower than in NaY.

Another possible reason is that CsX/Y have higher activity and selectivity and this can lead to the oxidation of the products that otherwise would form coke.

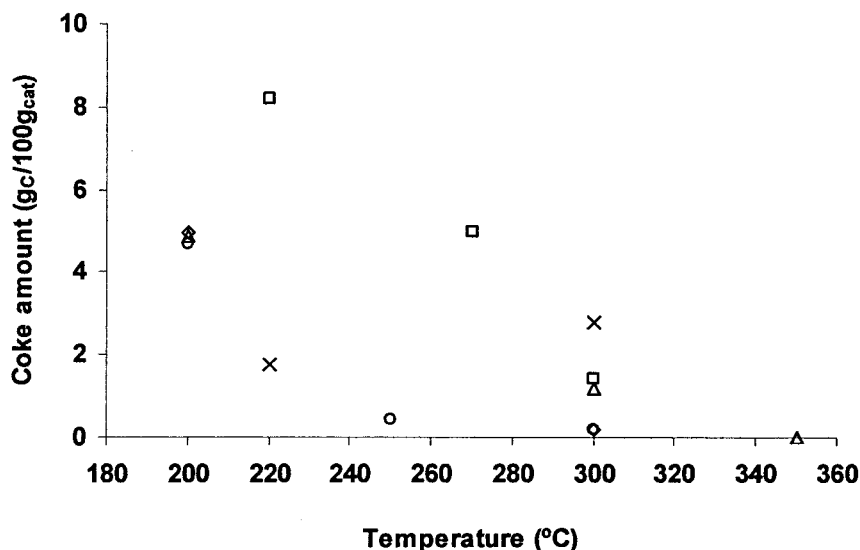


Fig. 13 – Amount of coke after 3h reaction as a function of the temperature on the HFAU (x), NaY (□), CsY (○), NaX (Δ) and CsX (◇) zeolites.

In the case of the basic zeolites the amount of coke diminished with the temperature (and total conversion), while with the protonic catalyst it increases. In fact, with the protonic zeolite the conversion is always low, so the transformation of MIBK into coke increases with the temperature. With the basic zeolites, the conversion of MIBK into CO₂ increases with the temperature and consequently the conversion into coke diminishes.

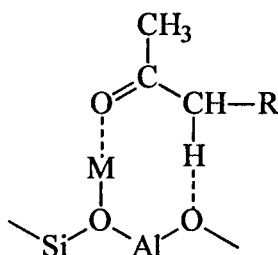
Another important factor is that these catalysts do not deactivate. In Figures 3, 6, 8 and 10 at the higher reaction temperatures, we can see that the conversion into CO₂ does not decrease with TOS.

Thus, the basic zeolites are very promising catalysts for the oxidation of ketone-type VOCs, since 100% conversion and selectivity towards CO₂ is achieved at 300°C even without platinum.

4.3.2.2. Adsorption strength of the alkali exchanged zeolites

The interaction of ketones, in particular acetone, on acidic zeolites was extensively studied by several authors [23-26], with the aim of understanding Brönsted acidic properties and the aldol condensation of acetone. With acidic zeolites, acetone adsorbs via the bridging hydroxyls [23]. At room temperature, the C=O bond in ketones is more perturbed by these bridging hydroxyls (of H-ZSM-5) than by the electron-accepting sites (NaZSM-5 and dehydroxylated HZSM-5) [23]. The bridging hydroxyls on the HZSM-5 stimulate the aldolization of acetone, while this does not happen in the NaZSM-5. Acetone was also used as probe molecule for characterisation of the acidity of several zeolites [24]. The ability of the acid site to form a hydrogen bond with the carbonyl oxygen can be measured by ^{13}C NMR spectroscopy, by the chemical shift in the acetone carbonyl at 125K. Lewis acid sites can also adsorb acetone [25], but the adsorption is less energetic than in Brönsted acid sites. Nevertheless, these sites can activate the acetone molecule towards condensation reactions. More recently, Hunger and co-workers [26] studied the chemical state of acetone adsorbed on the acidic zeolite by means of multi-nuclear MAS NMR spectroscopy. This was made in order to clarify the mechanism for the formation of acetone enol in acidic zeolites. They used acetone- D_6 and ^{13}C -2-acetone compounds as adsorbates and H- and D-ZSM-5 zeolites. The H/D exchange between Brönsted acid sites and adsorbate molecules indicated that the enol formation was due to the action of not only the bridging hydroxyl protons, but also of the neighbouring framework oxygen atoms. These results point out to the importance of the neighbouring framework oxygen atoms in the formation of the enol species. The hydrogen bond induces a partial charge transfer from the framework to the carbonyl group, making the framework oxygen more basic. The basicity of these framework oxygens is then important for determining the adsorption strength of acetone in zeolites.

For the adsorption of MIBK over an alkali exchanged zeolite, the following scheme can be proposed (where M is the compensation cation: Na or Cs) as in the case of adsorption of chloroform [27] and dichloromethane [28] over NaY and NaX zeolites:



scheme 1

MIBK is a molecule of the ketone group, and is considered as a weak base, because of the carbonyl group. Moreover, the hydrogen in α position is considered acidic, as it is adjacent to the carbonyl group. When MIBK is adsorbed on a zeolite with alkali cations, it is probable that the carbonyl group will adsorb on the cation (acting as a Lewis acid site), and that the H_α will absorb on the basic framework oxygen (scheme 1). The more basic this oxygen is, the stronger the adsorption will be.

Adsorption over alkali exchanged zeolites is highly favoured, specially to avoid catalytic transformation in the acid sites [1]. In these cases, the alkali cations will act as Lewis acid sites and the framework oxygen atoms as basic sites. The acid/basic character of the zeolite is then very important concerning the adsorption strength. The location and interaction of the molecules in the cages of the zeolites can also be an important factor [1].

With the purpose of determining whether the catalytic activity of the alkali zeolites in the oxidation of MIBK was related to their adsorption strength, temperature programmed desorption of the MIBK was made after adsorption at 40°C (Figure 14).

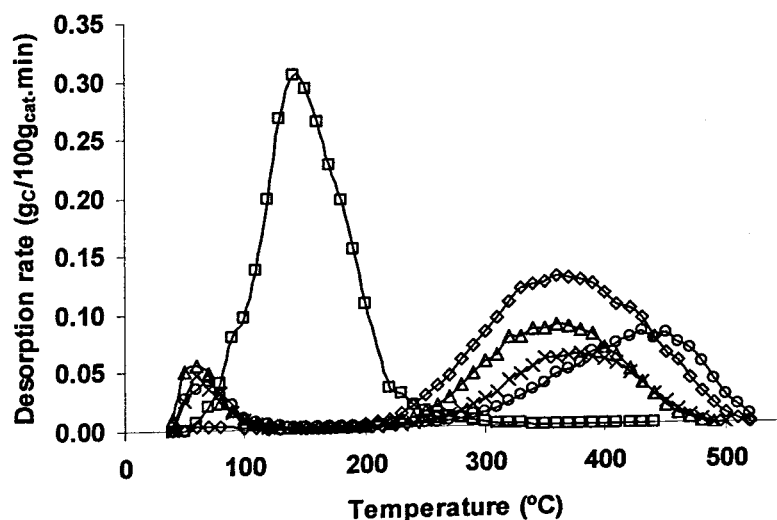


Fig. 14 - TPD after pre-adsorption at 40°C of MIBK over HFAU ($\square$), NaY ($\diamond$), NaX ($\circ$), CsX ($\times$) and CsY (Δ) zeolites.

While performing the TPDs, there was not only MIBK being released but also other products, at higher temperatures, so there was desorption and reaction at the same time. Also some non-desorbed products remained in the zeolites. This was detected visually, as the zeolites became coloured. Because of this, it is difficult to evaluate the adsorption strength in this case. Nevertheless, from Figure 14 we can say that the adsorption on the acidic zeolite is

always weaker than on the alkali metal exchanged zeolites. Comparison of the later is impossible for the reasons already mentioned.

In order to confirm that MIBK does not stay adsorbed at higher temperatures on the HFAU zeolite, TPD of MIBK was made after adsorption at 220°C over HFAU and NaY (Figure 15). In this way we can determine if MIBK did not appear in the TPDs at higher temperature because it reacted or because it did not stay adsorbed.

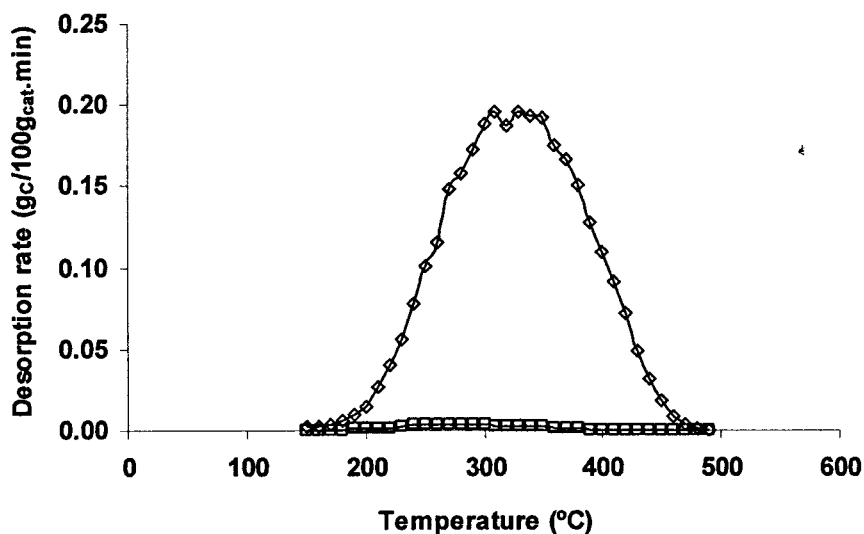


Fig. 15 - TPD after pre-adsorption of MIBK at 220°C over HFAU (□) and NaY (◇) zeolites.

After adsorption of MIBK at 220°C, only traces of MIBK appear on the TPD of the HFAU zeolite. On the contrary, a large amount was adsorbed on NaY, confirming that the alkali metal zeolites have higher adsorption strength than the acidic ones.

From the TPDs of MIBK it is not possible to reach conclusions concerning the adsorption strength of the Na or Cs zeolites.

4.3.2.3. Role of the basicity of the support

The conversion of MIBK into CO₂ over the zeolites studied can be directly related to their basic strength. Using the values of the intermediate electronegativities (S_{int}) calculated (Table 1), a linear relationship between the conversion of MIBK into CO₂ at 300°C and the basic strength of the supports was found (Figure 16).

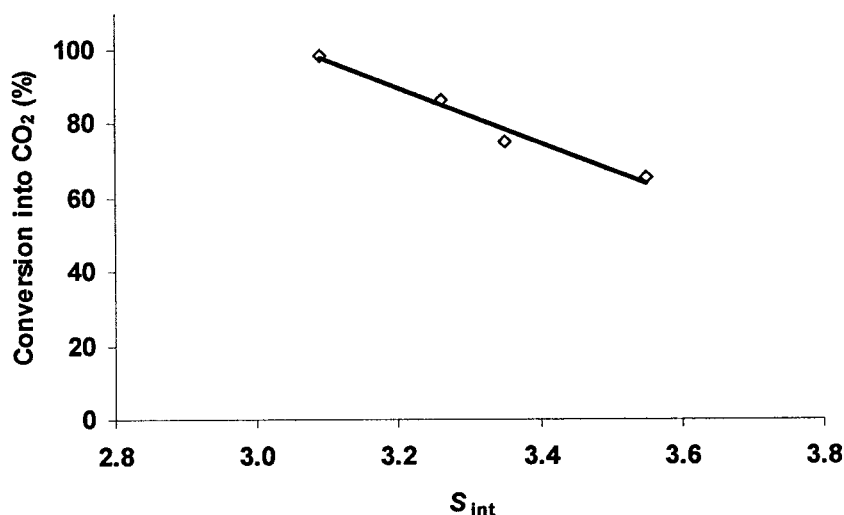


Fig. 16 - Conversion of MIBK into CO_2 after 3h of reaction at $300^\circ C$ as a function of the intermediate electronegativity of the zeolites.

The lower the intermediate electronegativity, the higher the conversion into CO_2 . So, the more basic the zeolite is, the more it can convert MIBK into CO_2 . These results suggest that the activity of these zeolites towards CO_2 is associated with their basic strength. This fact can be related to the adsorption properties of basic zeolites.

It was shown in several works [29-33] that an important factor that determines the reactivity over oxidation catalysts is the activation of the weakest C-H bond in the hydrocarbon. This was shown not only for alkanes [30], but also for other substrates containing different functional groups [29]. A correlation was found between the reactivity of the VOC and the bond dissociation enthalpy of the weakest C-H bond in the different structures on platinum supported catalysts [29]. It was also shown that the activation of methane on oxides requires highly basic sites [30], and that an important additional factor is the adsorption strength of the hydrocarbon on the surface of the catalyst. IR studies [31-33] of oxidation of hydrocarbons over metal oxide catalysts show that the activation occurs by abstraction of a hydrogen from the weakest C-H bond, seen by the formation of a surface alkoxy-group.

According to these results, the fact that the acidic hydrogen of the ketone is strongly adsorbed on the zeolite will make the $C-H_\alpha$ bond weaker and consequently its dissociation will be easier. This can explain why the total oxidation of MIBK is promoted on the basic zeolites and the relation observed between basic strength and conversion into CO_2 .

The acid-basic character of these alkali exchanged zeolites makes them very interesting catalysts for the study of oxidation reactions. In fact, there are several studies of VOCs oxidation over oxide-based catalysts but very few on zeolites. Nowadays, the applications of basic zeolites in catalysis are increasing, making this subject very interesting for future work.

4.4. Conclusions

- Cation exchanged zeolites are active catalysts for the oxidation of MIBK into CO_2 and H_2O . Side products are also formed, but their total amount decreases as the temperature increases.
- The basic strength of the zeolites is a key parameter for the conversion of MIBK into CO_2 , the more basic zeolites presenting a higher oxidation activity. A linear relationship between the intermediate electronegativity of the zeolites and the conversion into CO_2 was found.

4.5. References

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5. Oscillations in the oxidation of VOCs*

5.1. Introduction

Oscillatory behaviour in oxidation reactions is a well known phenomenon which has been reported several times in the case of CO oxidation by noble metal catalysts. There are two main models that describe this phenomenon: the oxidation-reduction and the carbon model. Both explain the oscillatory behaviour as a consequence of activation-deactivation of the surface. In fact, they only differ from each other in the particular mechanism responsible for the deactivation.

The oxidation-reduction model, first described by Sales *et al.* [1], is related with the noble metal and its oxidation state. The metal is oxidised by oxygen and reduced by CO, cyclically, so that it becomes successively less and more active, originating the oscillatory behaviour.

The carbon model was proposed by Collins *et al.* [2]. In this model the deactivation is due to carbon impurities present in the system that block the adsorption sites on the surface. These carbon atoms can be removed from the surface by reacting with adsorbed oxygen. So, the oscillations result from the cyclic adsorption and reaction of these carbon impurities on the surface of the catalyst.

More recently Lund *et al.* [3] published a very interesting paper where they compare these two models in the oxidation of CO over a platinum thin-film catalyst at atmospheric pressure. They found that the oscillation phenomenon is better described by the oxidation-reduction model.

Other authors [4] also studied the oxidation of CO at intermediate pressures (1-10 Torr) over Pt/SiO₂ catalysts followed by FTIR. They proposed a mechanism in which there is the formation of packed CO islands that block a portion of active sites during the reaction. The size of these islands was found to be related with the amplitude of the oscillations. The mechanism for island formation was not well determined, but the authors think that it is related to surface-phase transitions of the platinum, chlorine impurities or particle reshaping during the reaction.

* Part of this chapter is published in: *Catalysis Communications* 4 (2003) 651-656, and other part was submitted for publication.

Slinko *et al.* studied the oxidation of CO over Pd supported on NaX at atmospheric pressure [5]. The kinetic parameters for this reaction were determined using the oxidation-reduction model. It was found that there is a strong influence of the Pd particle size as well as the initial oxidation state of the palladium on the shape of the oscillations. Chaotic behaviour was also observed, which was favoured by the increase in the concentration of CO in the feed, the increase in the temperature of the catalyst and the increase of activity due to the reduction of the catalyst. The size of the metal particles and the size of the zeolite crystallites are also important factors. In fact, the authors assume that the chaotic behaviour is originated at the level of the zeolite crystallite: there is an increase of the concentration gradient of CO within the crystallites, and it is this gradient that causes a breakdown of the oscillation on the level of the metal particles, that are situated inside the crystallites.

Oscillations were also observed in other oxidation reactions. Völter *et al.* [6] reported periodic oscillations in the catalytic combustion of heptane over a Pt/Al₂O₃ catalyst at some specific reaction conditions. This was included in a work where they studied the role of metallic and oxidic platinum in this oxidation reaction. The oscillations were explained again by the oxidation-reduction model. In this case platinum is oxidised by oxygen (transforming the reduced platinum into a less active oxidic Pt) and reduced by the heptane (transforming the platinum back again to the reduced state). This reaction is also accompanied by temperature oscillations. During the period of increasing conversion, the exothermicity of this reaction causes the self-heating of the sample. The temperature decreases again in the decreasing period of the conversion.

Oscillations in the oxidation of methane over a Pd/Al₂O₃ catalyst were observed by Deng and Nevell [7]. In this case, the authors propose that the oxidised surface of palladium is the more active state, the reduced state being less active for the methane oxidation. Again the oxidation-reduction model is applied here. In oxidising conditions, no oscillations occurred and the palladium maintained its oxidised state. But in oxygen deficient conditions, a change in the electronic state of palladium can occur, and part of the more active oxidised state of Pd can be cyclically transformed into the reduced state, originating oscillations in the conversion.

In the present work, oscillations were frequently observed in the apparent conversion into CO_2 . These oscillations presented maxima which were generally higher than 100% conversion. In this context it is interesting to refer the work of Paulis *et al.* [8]. These authors studied the influence of the adsorption-desorption processes on the ignition curves of VOCs oxidation, in particular in the oxidation of toluene and acetone over $\text{Pd}/\text{Al}_2\text{O}_3$, $\text{Mn}_2\text{O}_3/\text{Al}_2\text{O}_3$ and $\text{Mn}_2\text{O}_3/\text{SiO}_2$ catalysts. Disagreements were found between the conversion of the VOC and the CO_2 released when performing temperature programmed oxidation of the VOCs. At low temperatures, it was observed that the conversion of the VOC was higher than the conversion into CO_2 . This difference was explained by the adsorption-desorption processes on the catalyst. At the beginning of the experiments, at low temperatures, the catalyst is able to adsorb the VOC. When the temperature increases, CO_2 starts to be produced and part of it can also stay adsorbed in the catalyst. As the oxidation reaction is exothermic, it will lead to the desorption of the VOC and of the products. The desorbed VOC can be oxidised into CO_2 leading to further increase in the temperature. These combined processes lead to the appearance of a CO_2 peak in the ignition curve corresponding to conversions into CO_2 higher than 100%. It was concluded that these CO_2 peaks appear in the ignition curves whenever the activity of the catalyst is high enough to start the oxidation of the VOCs at low temperatures, which are close to the temperatures for which the adsorption-desorption of the VOCs and products take place.

The aim of this chapter is to get a deeper understanding of the oscillatory behaviour observed in the oxidation of VOCs. For that purpose, the oxidation of MIBK and o-xylene was studied over two Pt/zeolite catalysts (Pt/HFAU and Pt/NaFAU) as well as NaFAU and $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$. TPO and TPD of the reactants after reaction were also analysed in order to get better insight into the nature of the compounds that remain adsorbed in the support. In the case of MIBK, the oscillatory behaviour was observed with all the zeolite catalysts but not on $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$. With o-xylene, oscillations were observed with the Pt/NaFAU catalyst and not with Pt/HFAU catalyst. These oscillations are a consequence of the oxidation of compounds that remain adsorbed inside the zeolite pores, including the reactant; therefore, the strength of adsorption of the VOC on the support seems to be the major parameter which determines the oscillation phenomenon.

5.2. Experimental

5.2.1. Preparation and characterisation of the catalyst

HFAU zeolite (framework Si/Al ratio of 47) was supplied by PQ zeolites, NaFAU zeolite (framework Si/Al ratio of 2.4) was supplied by Linde and γ -Al₂O₃ was supplied by Condea. The characterisation of the HFAU and NaFAU zeolites and γ -Al₂O₃ is presented in Table 1.

Table 1 – Properties of HFAU and NaFAU zeolites and γ -Al₂O₃: concentration of Brönsted (A_B) and Lewis (A_L) acid sites able to retain pyridine at 150°C, mesoporous surface area, micropore volume and BET surface area (S_{meso} , V_{micro} and S_{BET}).

	A_B (10 ¹⁸ H ⁺ .g ⁻¹)	A_L (10 ¹⁸ H ⁺ .g ⁻¹)	S_{meso} (m ² g ⁻¹)	V_{micro} (cm ³ g ⁻¹)	S_{BET} (m ² g ⁻¹)
HFAU	49	7	134	0.284	795
NaFAU	-	n.d.	6	0.304	765
γ -Al ₂ O ₃	-	240	196	-	196

* Determined by the *t*-method

The acidity of the zeolites was determined by pyridine adsorption followed by IR spectroscopy. The concentration of acidic sites was estimated from the number of pyridinium ions which remain adsorbed at 150°C.

The texture of the supports (micropore volume and mesoporous surface area) was determined from the nitrogen adsorption isotherms, performed at 77K with a gas adsorption system (Coulter Omnisorp 100CX).

The Pt/zeolite catalysts were prepared by ion exchange of the HFAU and NaFAU zeolites using an adequate dilute solution of Pt(NH₃)₄Cl₂, continuously stirred for 4 h at room temperature. Afterwards, the samples were filtered, washed and dried overnight at 100°C. Calcination was carried out at 300°C for 6h under dry air flow. The Pt/ γ -Al₂O₃ sample was prepared by incipient wetness impregnation using an appropriate solution of H₂PtCl₆. The sample is then calcined at 500°C for 2h under dry air flow. The calcined samples were then tableted and crushed to 0.2-0.4 mm size. Before reaction the catalysts were reduced *in situ* under hydrogen flow at 300°C for 2 h.

The dispersion of the catalysts (Table 2) was determined by the toluene hydrogenation reaction [9]. This reaction was carried out at 110°C in a flow reactor at atmospheric pressure.

To minimise the thermal effects of the reaction a n-hexane/toluene (5:1) mixture was used as feed. The molar ratio of hydrogen to the mixture n-hexane/toluene was equal to 45. The number of accessible atoms of platinum was determined by comparing the initial activity of the catalyst with the activities obtained with standard Pt/HFAU catalysts of known dispersion [9]

Table 2 – Dispersion of Pt/HFAU, Pt/NaFAU and Pt/ γ -Al₂O₃.

	% Pt	Dispersion (%)
Pt/HFAU	0.1	35
Pt/NaFAU	0.2	39
Pt/ γ -Al ₂ O ₃	0.3	56

5.2.2. Reaction study

The reactions were carried out in a fixed bed reactor (BTRS Jr Autoclave Engineers) at atmospheric pressure. The catalyst sample (0.140 g) was supported in a small plug of glass wool in a vertical stainless steel tubular reactor. The reactor was inserted into an oven, and the temperature controlled by a Eurothem 847 controller with PID action. The temperature was measured by a K-type thermocouple that was inserted into the catalyst bed. The reactant mixture, consisting of a pre-mixed gas (20% O₂ in nitrogen (Air Liquide)) with a concentration of MIBK of 1,340 ppmv or a concentration of o-xylene of 1,500 ppmv, was introduced in the reactor with a total flow rate of 4.16 mmol min⁻¹, which was controlled by mass flow controllers (Bronkhorst). The desired concentration of MIBK or o-xylene in the reactant mixture was obtained by passing the pre-mixed gas through a saturator which was kept at the appropriate temperatures by means of a cryostatic bath (Techne) and by mixing this stream with the pre-mixed gas so that the required concentration was achieved. The space velocity was kept constant in all the experiments (20,000 h⁻¹, calculated at ambient temperature and pressure).

The analytical system consisted of a gas chromatograph (Tremetrics 9001) equipped with a flame ionisation detector (FID) for the analysis of the hydrocarbons, and two non-dispersive infrared (NDIR) analysers for the analysis of CO (Analytical Development Company) and CO₂ (NOVA Analytical Systems Inc.). The GC was fitted with a CP Wax 52 capillary column, with 30 m and 0.32 mm of internal diameter, kept at 70°C. The conversion

into CO₂ is defined as the molar flow rate of CO₂ at the reactor outlet, divided by six (or eight) times the molar flow rate of MIBK (or o-xylene) in the feed.

The total amount of coke in the catalysts after reaction was measured by temperature programmed oxidation in air (TPO). After reaction, the catalyst was cooled in nitrogen till 80°C. Then a stream of air was passed and the temperature increased at 10°C min⁻¹ till 520°C and was maintained until there was no further change in the gas concentration. The CO and CO₂ released were determined by the NDIR analysers. The total amount of coke was calculated by integration of the CO and CO₂ curves obtained.

Temperature programmed desorption of the reactant was also studied after certain runs. After reaction, the catalysts were cooled in nitrogen till 100°C and then the temperature was increased at 5°C min⁻¹ till 520°C and was maintained until there was no more reactant at the exit. The reactant was analysed by GC/FID. Temperature programmed desorption was also studied after pre-adsorption of the reactants at 40°C. The TPD conditions were the same as above, except that desorption started at 40°C. The reactants were adsorbed on the catalysts at 40°C from a nitrogen stream, using the same concentration as in the reaction study. After saturation (when the concentration of reactant did not change), the catalyst was purged in a nitrogen stream and the TPD started.

The products of reaction that remained adsorbed in the catalysts were identified by GC/MS (Varian CP-3800 with a ITD Saturn 2000, column: CP-Sil 8 CB lowbleed/MS). After reaction, the catalysts were placed in a closed glass vessel filled with nitrogen. This vessel was then heated up to the temperature corresponding to the maximum of the reactive coke peak in the TPOs. A sample of the desorbed products was collected and analysed by GC/MS.

5.3. Results

The results of this chapter are divided in two sections: oxidation of MIBK and oxidation of o-xylene. Because oscillations are a more general phenomenon that occurred in the oxidation reactions of both reactants, it will be discussed together in the discussion section.

5.3.1. Oxidation of MIBK

The results obtained over the Pt/HFAU catalyst are compared in Figure 1 at reaction temperatures of 190 and 195°C.

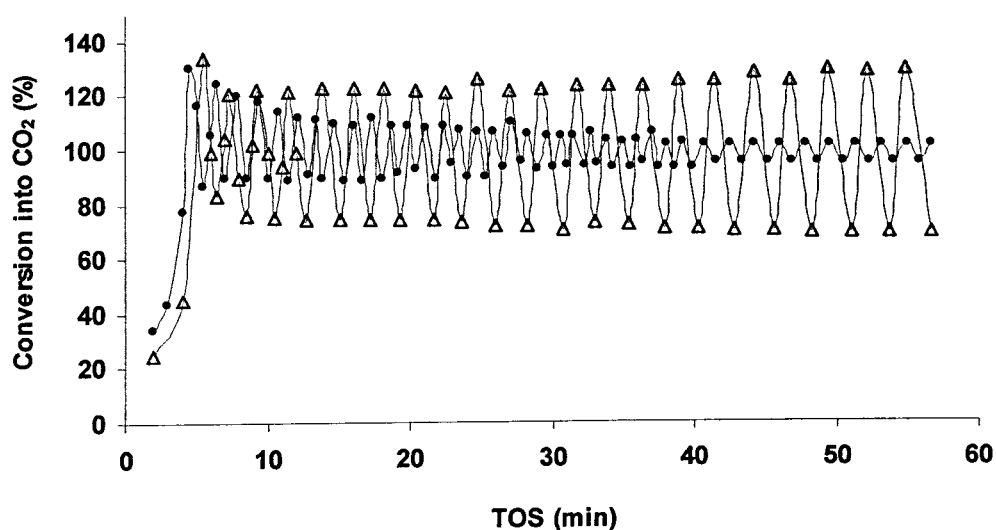


Fig. 1 - Influence of time-on-stream on the apparent conversion into CO₂ over the Pt/HFAU catalyst at 195°C (●) and 190°C (Δ).

At these temperatures there were oscillations in the observed conversion into CO₂. At 190°C the conversion into CO₂ increased initially, and then started to oscillate between approximately 125% and 75%. The total conversion of MIBK was more difficult to follow, but taking experimental points at a maximum and a minimum of the CO₂ oscillations, we found that the total conversion varied from 92 to 100%. At 195°C the amplitude of the oscillations was smaller (conversion into CO₂ between 97 and 103%) and the frequency was higher. No MIBK was found at the reactor exit.

The exothermicity of the reactions could be measured by the thermocouple placed into the catalyst bed. Outside the range 190-195°C, the temperature was found to increase after starting the reaction, reaching a higher level which remained constant for the duration of the

run. The temperature increases ranged from 1°C (run at 180°C) to 8°C (run at 220°C). However, in the case of cyclic behaviour there were also temperature oscillations: increases from 2 to 9°C at 195°C and from 3 to 25°C at 190°C. These temperature oscillations were synchronized with the oscillations in the apparent conversion into CO₂.

Temperature programmed oxidation was performed on the catalyst samples after each run. This technique allows the identification and quantification of coke components of different reactivity [10]. The TPOs of the samples after reaction at 185 and 200°C are presented in Figure 2.

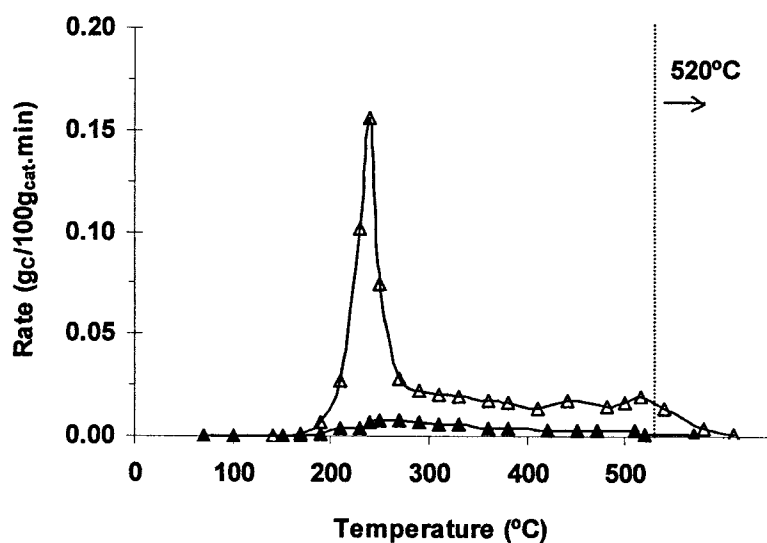


Fig. 2 - TPO curves after MIBK oxidation at (▲) 200°C and (Δ) 185°C over the Pt/HFAU catalyst.

There are two coke components with different reactivities: one that oxidises at low temperatures (peak maximum 240°C) and another which oxidises at high temperatures (peak maximum 510°C). These results are not surprising, previous studies having shown that the “coke” formed on zeolite catalysts includes a large range of compounds [11] with quite different reactivities [10].

For the reaction temperature of 190°C, three TPOs were made after stopping the reaction at different times (fresh catalyst was used for each experiment): after 4 min (point A in Fig. 3), at a minimum (point B in Fig. 3) and at a maximum (point C in Fig. 3) of the apparent conversion into CO₂. These TPOs are shown in Figure 4.

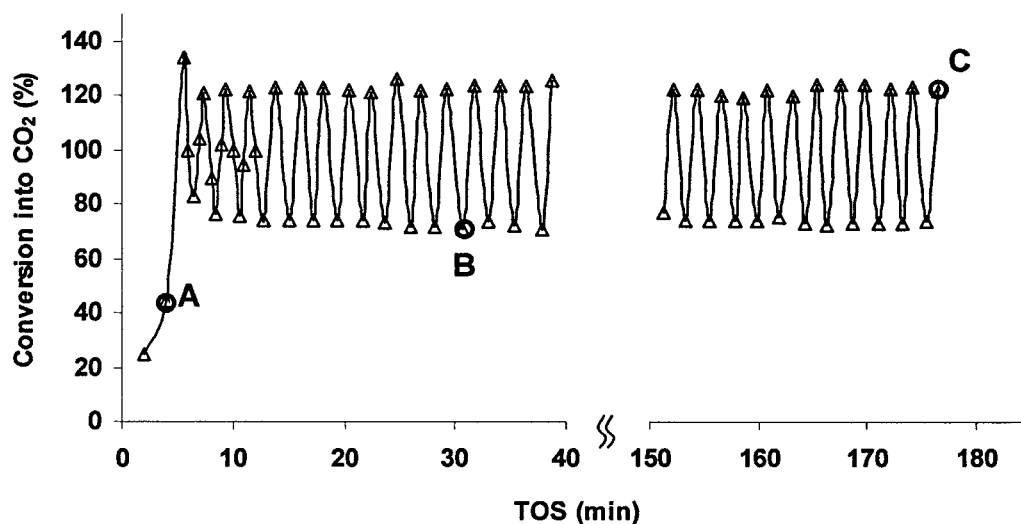


Fig. 3 – Influence of time-on-stream on the apparent conversion into CO_2 over the Pt/HFAU catalyst at 190°C .

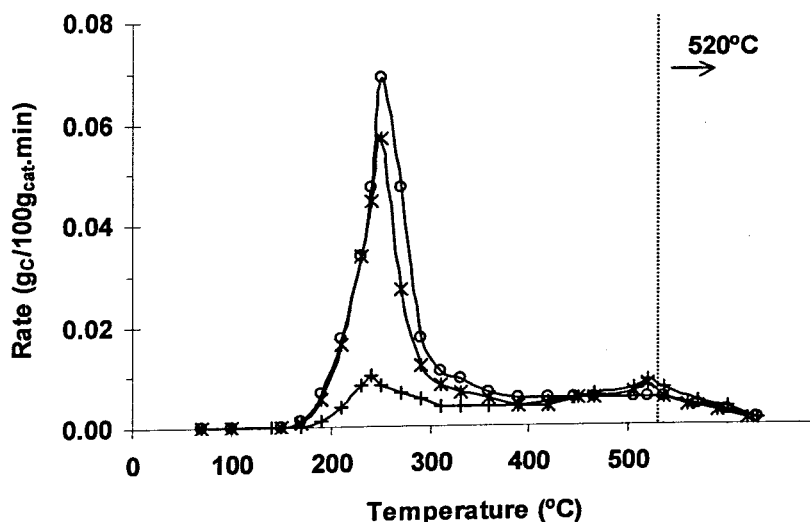


Fig. 4 - TPO curves for samples corresponding to points (○) A, (*) B and (+) C in Fig. 3.

After 4 min of reaction the total amount of coke present in the zeolite pores was 0.56wt%, most of it being oxidised at low temperature. At point B the total amount of coke was 0.47wt%. There was already some coke that can be oxidised only at higher temperatures. Finally, at point C the total amount of coke was 0.24wt%, two peaks of approximately the

same height being present in the TPO. Similar behaviour was observed with the corresponding samples recovered after reaction at 195°C.

In order to investigate the nature of these compounds, TPD analysis of the reactant was performed after reaction at 180°C. The TPD and TPO analyses are shown in Figure 5.

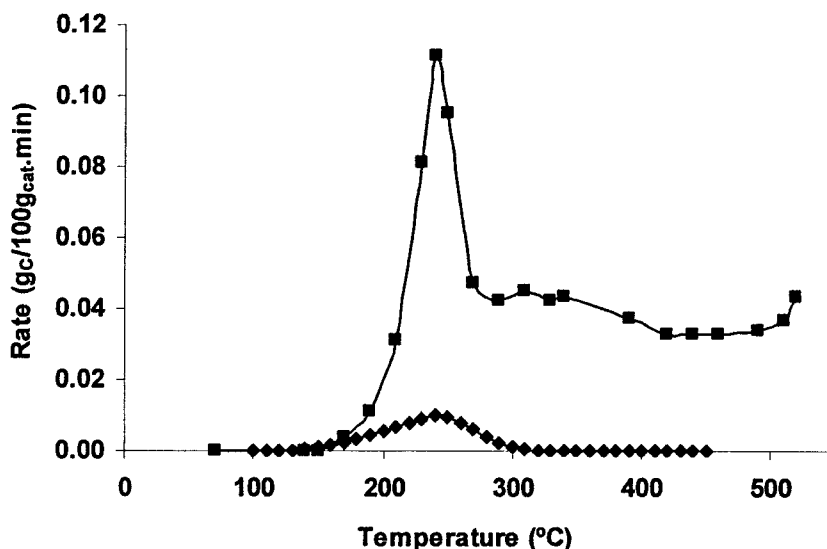


Fig. 5 - TPO (■) and TPD of MIBK (◆) after reaction of MIBK on the Pt/HFAU catalyst at 180°C.

The TPD of MIBK after reaction shows a broad peak with a maximum at 240°C. This means that some MIBK remains adsorbed on the catalyst after reaction at 180°C. The presence of MIBK adsorbed on the catalyst after reaction was also confirmed by GC/MS. The non-desorbed products of reaction were desorbed in a glass closed vessel in nitrogen till 240°C (maximum of the TPO peak). Along with MIBK, several other low molecular weight compounds were detected in small amounts, like i-butene, branched heptenes, acetone and propionic acid.

The same phenomenon was also observed with the Pt/NaFAU, namely oscillations in the apparent conversion into CO₂ occurred between 180 and 200°C (Figure 6).

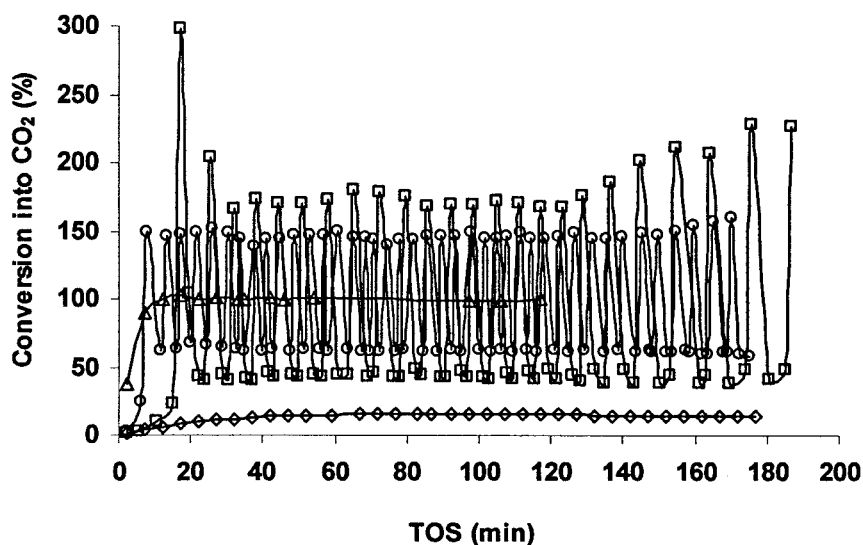


Fig. 6 - Influence of time-on-stream (TOS) on the apparent conversion of MIBK into CO_2 on the Pt/NaFAU catalyst at 160 ($\diamond$), 180 ($\square$), 200 ($\circ$) and 220°C(Δ).

With this catalyst, the oscillations occurred in a wider range of reaction temperatures than with the acidic catalyst. As in the case of the acidic catalyst, a more reactive type of coke was also present in the TPO after reaction at 160°C (peak maximum at 220°C). TPOs were performed after reaction at 180°C stopping the reaction in a maximum and at 200°C stopping the reaction in a minimum (Figure 7).

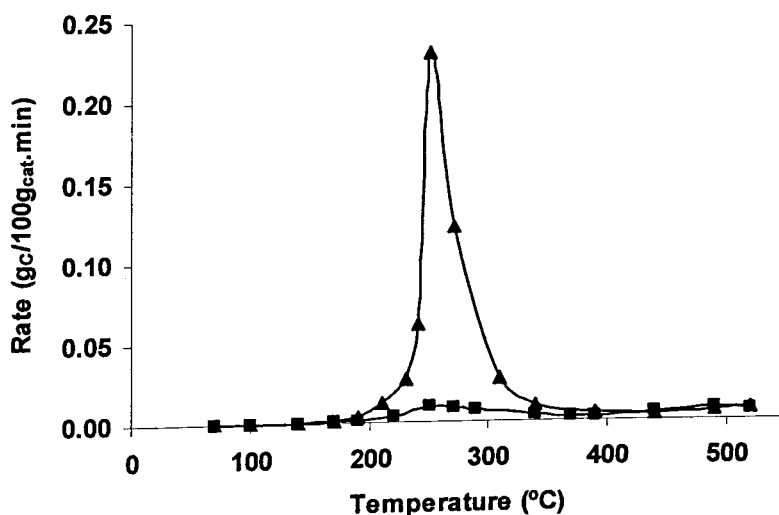


Fig. 7 - TPO curve after reaction at 180 ($\blacksquare$) and 200°C ($\blacktriangle$) on the Pt/NaFAU catalyst.

At 200°C there is more coke in the zeolite than at 180°C, which might be apparently surprising. But this is just because the reaction at 180°C was stopped at a maximum, and therefore the reactive coke was consumed. In the other TPO, the reaction was stopped on a minimum, and therefore there is still coke accumulated.

Surprisingly, the oscillation behaviour was also observed on the NaFAU zeolite at 250°C. In this case, while the total conversion of MIBK was always close to 100%, not only the apparent conversion into CO₂ oscillated, but also the apparent conversion into CO (Figure 8).

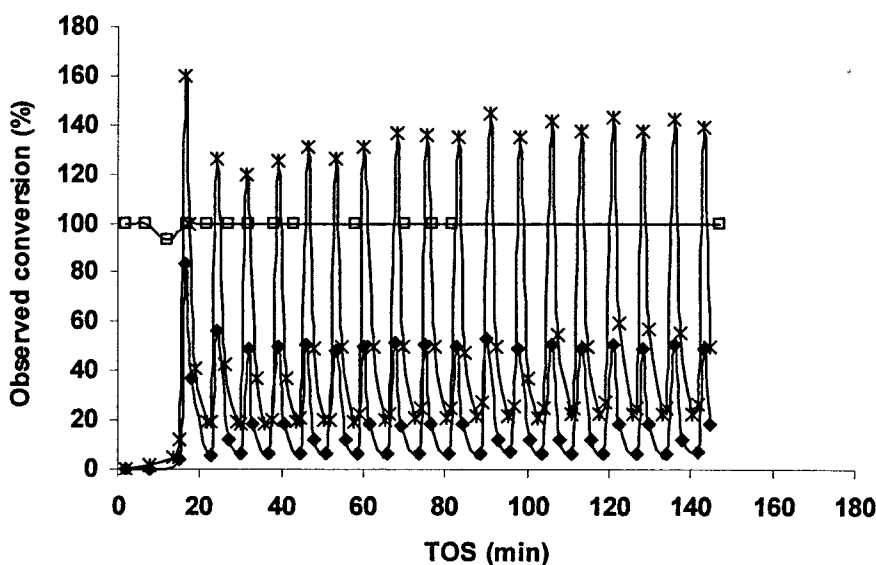


Fig. 8 - Total conversion of MIBK ($\square$), apparent conversion into CO ($\blacklozenge$) and apparent conversion into CO₂ (*) on NaFAU zeolite at 250°C.

In fact, this zeolite alone (without platinum) exhibited a high oxidation activity for the main reaction (MIBK oxidation) and a reasonable CO₂ selectivity (conversion into CO₂ higher than 60% at 300°C). The TPO and the TPD after reaction at 220°C are represented in Figure 9.

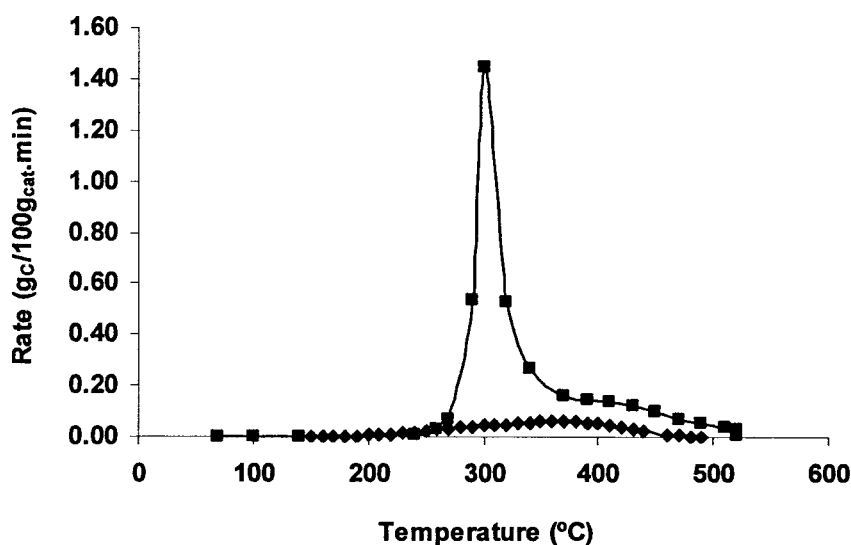


Fig. 9 - TPO (■) and TPD (◆) curves after reaction at 220°C on the NaFAU catalyst.

In the TPO after reaction at 220°C, the onset temperature was 240°C and the first peak maximum was at 300°C, so the reactive coke was again present. The TPD of MIBK after reaction at the same temperature showed also a large amount of this compound.

In the case of the oxidation over Pt/ γ -Al₂O₃, no oscillations were observed, whatever the reaction temperature (Figure 10).

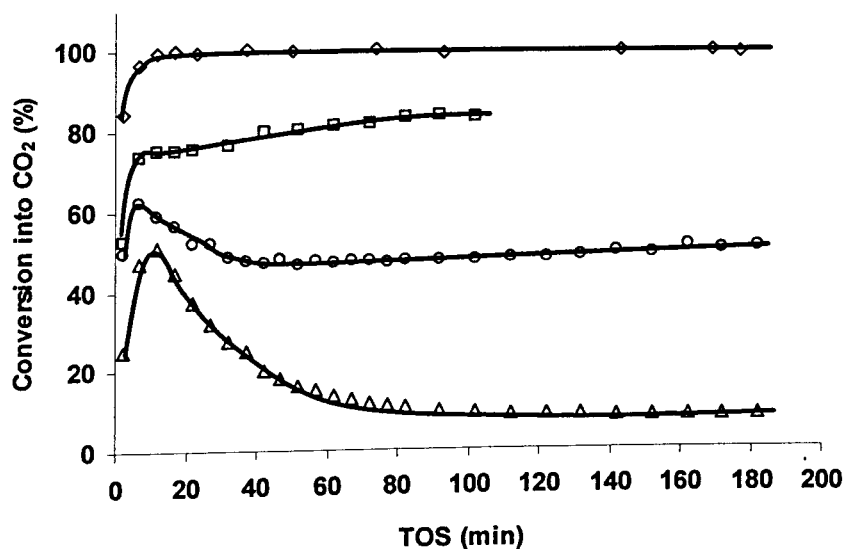


Fig. 10 - Influence of time-on-stream (TOS) on the conversion of MIBK into CO₂ on the Pt/ γ -Al₂O₃ catalyst at 240 (◇), 220 (□), 200 (○) and 180°C(Δ).

At 220°C the catalyst reached a steady state conversion into CO₂ of 85%, while on the other catalysts the oscillations occurred at temperatures just before the temperature for which the conversion of MIBK was complete. The TPO after reaction at 180°C is shown in Figure 11 together with the TPD of MIBK.

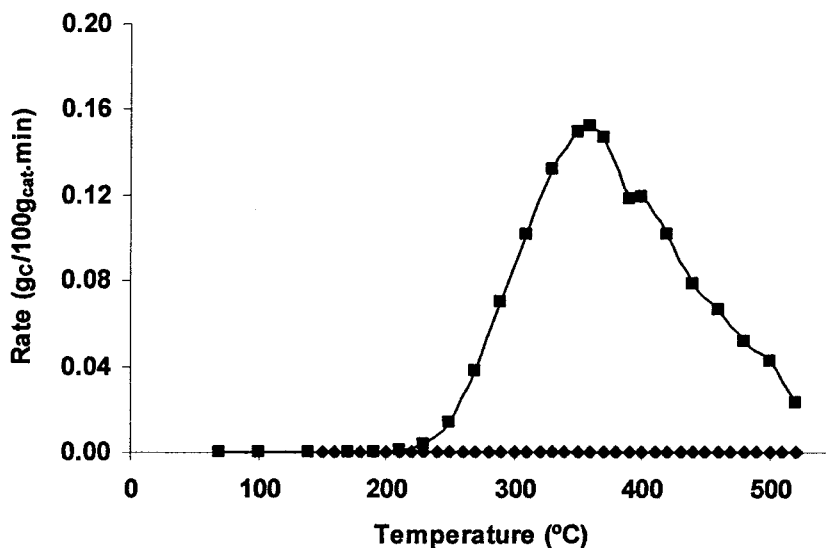


Fig. 11 - TPO (■) and TPD (♦) curves after reaction at 180°C on the Pt/ γ -Al₂O₃ catalyst.

In this case, the TPO presents only one peak (maximum at 360°C), the onset temperature being 210°C. Furthermore, the TPD of MIBK after reaction (Figure 12) shows only traces of MIBK still adsorbed on the catalyst.

It should be noted that the exothermic character of the oxidation reactions led to increases in the catalyst temperature. With all the catalysts, when no oscillations were observed, the temperature increased after starting the reaction, reaching a constant value which remained constant till the end of the run. However, in the case of cyclic behaviour there were also temperature oscillations. These temperature oscillations were synchronized with the oscillations in the apparent conversion into CO₂.

5.3.2. Oxidation of o-xylene

The results of the conversion of o-xylene into CO₂ obtained over the Pt/HFAU and Pt/NaFAU catalysts are compared in Figures 12 and 13, respectively, at different temperatures.

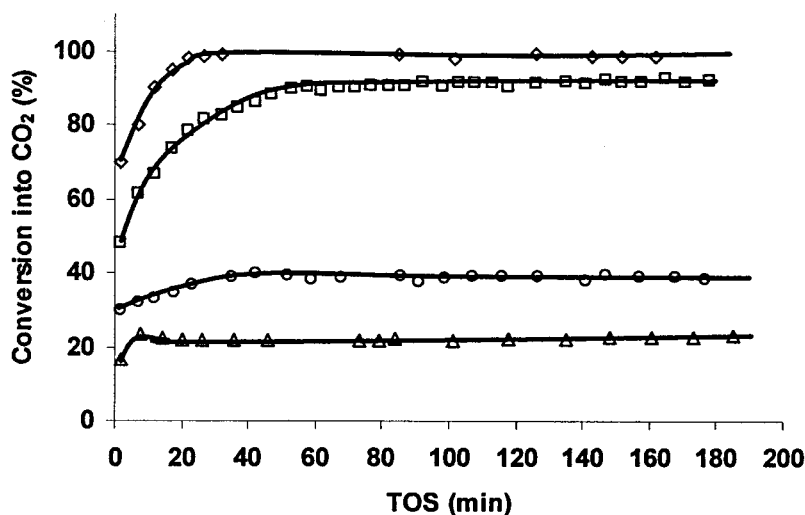


Fig. 12 - Influence of time-on-stream (TOS) on the conversion of o-xylene into CO₂ on the Pt/HFAU catalyst at 240 (◇), 235 (□), 230 (○) and 225°C(Δ).

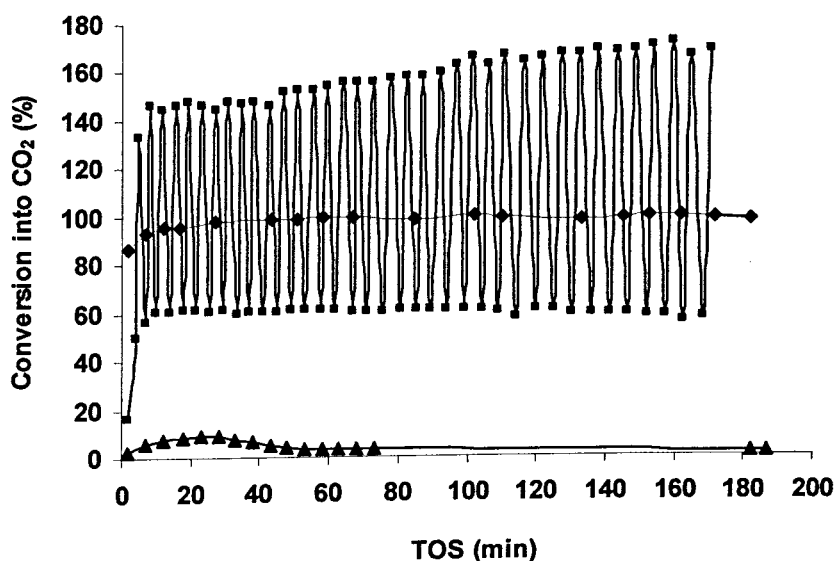


Fig. 13 - Influence of time-on-stream (TOS) on the conversion of o-xylene into CO₂ on the Pt/NaFAU catalyst at 240 (◇), 220 (■) and 200°C (▲).

In the temperature range studied, no oscillations occurred when the oxidation of o-xylene was tested with the Pt/HFAU catalyst (Figure 12). However, with the Pt/NaFAU catalyst this phenomenon occurred again at 220°C (Figure 13). At 240°C the conversion into CO₂ is complete and no MIBK is present at the reactor exit. At 200°C the conversion into CO₂ increases initially, decreasing afterwards till a constant plateau at 3%. At 220°C the apparent

conversion into CO_2 oscillates between 60% and a value between 160 and 170%. Oscillations in the temperature of the catalyst bed ranging from + 3 to +40°C were also observed, which were synchronized with the oscillations in the conversion into CO_2 .

The TPO/TPD of the samples after reaction at different temperatures with these two catalysts are shown in Figures 14 and 15, respectively.

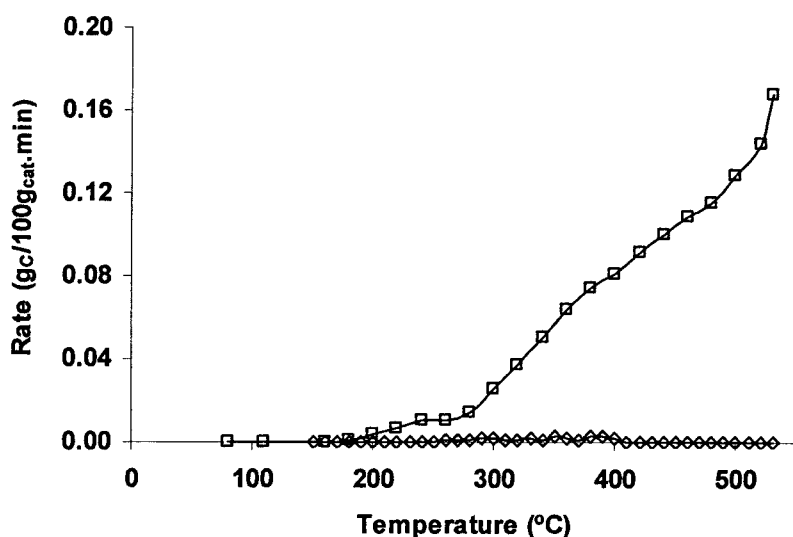


Fig. 14 – TPO ($\square$) and TPD ($\diamond$) curves after reaction of o-xylene on Pt/HFAU catalyst at 225°C.

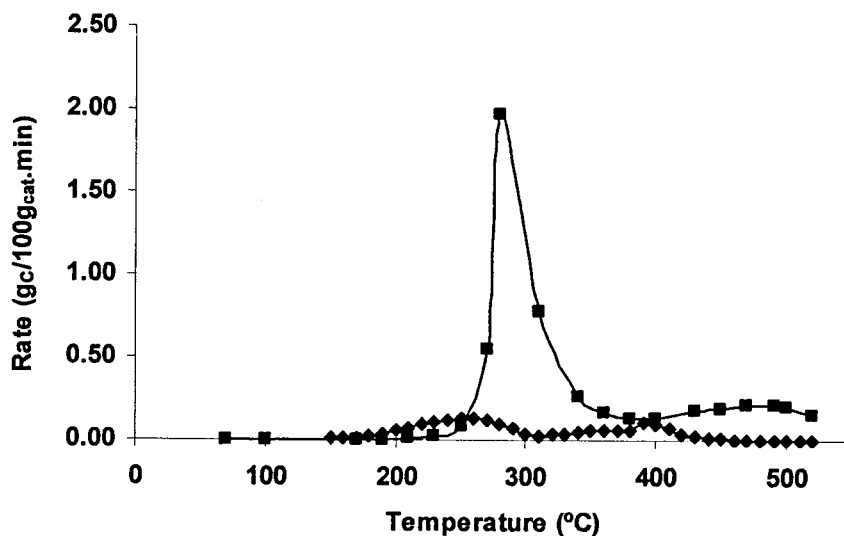


Fig. 15 – TPO ($\blacksquare$) and TPD ($\blacklozenge$) curves after reaction of o-xylene on the Pt/NaFAU catalyst at 200°C.

In the case of the reaction with the Pt/HFAU catalyst, the amount of the more reactive coke is not significant. The coke starts to oxidise at 170°C and the rate increases till the end of the analysis. Moreover, there are only traces of o-xylene present in the TPD experiments, confirming that o-xylene did not stay adsorbed in the catalyst after reaction.

On the other hand, with the Pt/NaFAU catalyst there is a first peak in the TPO, corresponding to the more reactive compounds which start to oxidise at 180°C, presenting a maximum at 280°C. There is also some o-xylene adsorbed after reaction, as can be seen in the TPD analysis (Figure 15).

The presence of xylene adsorbed on the catalyst after reaction was also confirmed by GC/MS. The non-desorbed products of reaction were desorbed in a closed glass vessel in nitrogen till 280°C. Along with o-xylene, there was also some toluene and trimethylbenzene. The same technique was also tested in the Pt/HFAU catalyst after reaction at 225°C, but in this experiment, the temperature of desorption was 300°C because there was no first peak in the TPO. Only traces of xylene were observed.

In order to confirm that the oscillations are a consequence of the oxidation of reactive coke in the case of the oxidation of o-xylene, TPOs after stopping the reaction at a maximum (after 3h reaction) and minimum (after 1h reaction) were made (Figure 16).

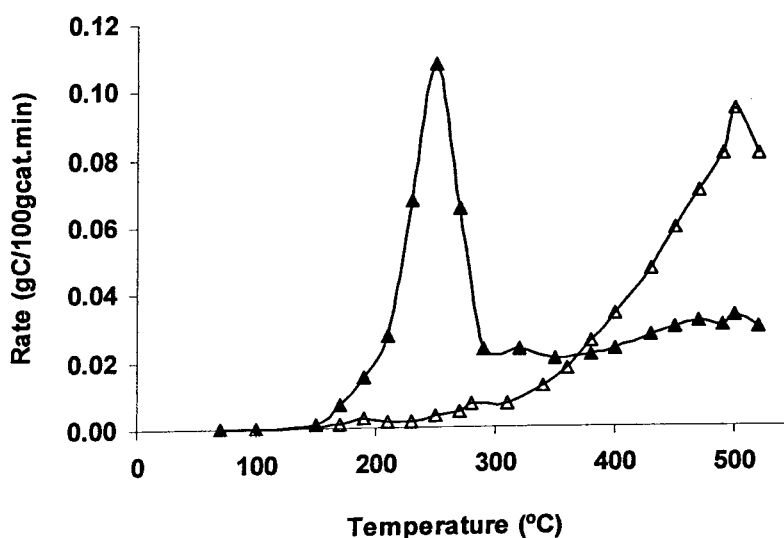


Fig. 16 – TPO after 3 h reaction in a maximum (Δ) and after 1 h reaction in a minimum (▲) on the Pt/NaFAU catalyst.

The reactive coke was almost all consumed at a maximum, while at a minimum it is still present in the TPO. It should be noted that the unreactive coke increased with the reaction

time: there is more unreactive coke present after 3h than after 1h of reaction. So this unreactive coke certainly does not influence the oscillatory behaviour.

5.4. Discussion

5.4.1. Relation between oscillations and adsorbed compounds

The main results of the VOCs oxidation over all the catalysts are collected in Table 3.

Table 3 – Summary of the results obtained

	Reaction		TPO		TPD*	
	xylene	MIBK	xylene	MIBK	xylene	MIBK
Pt/HFAU47	$T_{100\%} = 240^{\circ}\text{C}$ No oscillations	$T_{100\%} = 195^{\circ}\text{C}$ $T_{<} = 185^{\circ}\text{C}$ $T_{>} = 200^{\circ}\text{C}$	$T_{\text{onset}} = 170^{\circ}\text{C}$ $T_{\text{M}} = 520^{\circ}\text{C}$	$T_{\text{onset}} = 170^{\circ}\text{C}$ $T_{\text{M1}} = 240^{\circ}\text{C}$ $T_{\text{M2}} = 510^{\circ}\text{C}$	no	yes
Pt/NaFAU	$T_{100\%} = 240^{\circ}\text{C}$ $T_{<} = 200^{\circ}\text{C}$ $T_{>} = 240^{\circ}\text{C}$	$T_{100\%} = 200^{\circ}\text{C}$ $T_{<} = 160^{\circ}\text{C}$ $T_{>} = 220^{\circ}\text{C}$	$T_{\text{onset}} = 180^{\circ}\text{C}$ $T_{\text{M1}} = 280^{\circ}\text{C}$ $T_{\text{M2}} = 470^{\circ}\text{C}$	$T_{\text{onset}} = 160^{\circ}\text{C}$ $T_{\text{M1}} = 220^{\circ}\text{C}$ $T_{\text{M2}} = 450^{\circ}\text{C}$	yes	n.d.
Pt/ Al_2O_3		$T_{100\%} = 240^{\circ}\text{C}$ No oscillations		$T_{\text{onset}} = 210^{\circ}\text{C}$ $T_{\text{M}} = 360^{\circ}\text{C}$		no
NaFAU		$T_{100\%} = 250^{\circ}\text{C}$ $T_{<} = 220^{\circ}\text{C}$ $T_{>} = 270^{\circ}\text{C}$		$T_{\text{onset}} = 240^{\circ}\text{C}$ $T_{\text{M1}} = 300^{\circ}\text{C}$ $T_{\text{M2}} = 400^{\circ}\text{C}$		yes

$T_{100\%}$: temperature above which the conversion of MIBK is complete.

$[T_{<}, T_{>}]$: temperature range where oscillations were observed (experiments carried out at 5°C intervals on Pt/HFAU and 20°C intervals otherwise).

T_{onset} : temperature above which the oxidation rate is higher than 10^{-5} gC/gcat.min.

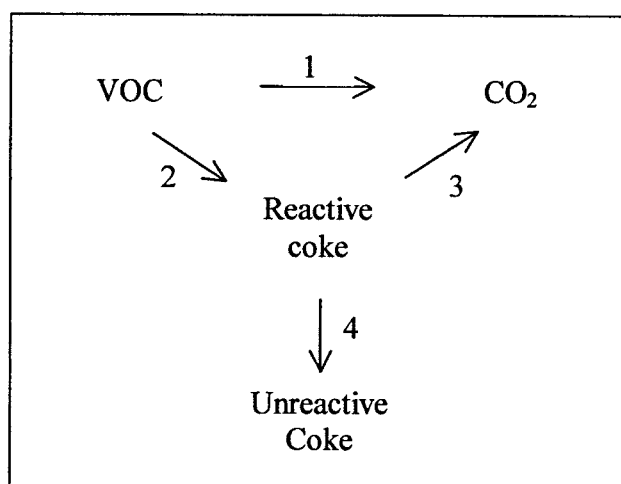
T_{M} : temperature of the maxima of the TPO peaks.

* Presence of reactant adsorbed on the catalyst after reaction.

It is evident that, for both VOC compounds, oscillations in the apparent conversion into CO_2 are associated to the presence of the more reactive coke in the TPO. Let us consider the run at 190°C (Fig. 3) of the oxidation of MIBK over the Pt/HFAU catalyst. At the beginning of the reaction, MIBK is being converted into CO_2 and into coke. Most of the coke formed initially is very reactive, because after 4 min of reaction the TPO shows essentially a single peak which is oxidised at low temperatures (Fig. 4). This reactive coke starts to oxidise, originating the first oscillation of the CO_2 apparent conversion (Fig. 3). The temperature also increases, as the oxidation is highly exothermic, leading to an increase in the coke gasification rate. When most of the coke present in the catalyst pores is consumed, the temperature decreases again to the initial value, and the amount of CO_2 at the reactor exit decreases accordingly. At this stage, the pores are again free of reactive coke and a new cycle starts. At

a minimum such as point B (Fig. 3), the amount of coke is nearly the same as after 4 min of reaction (Fig. 4), because at this point coke is being formed. At a maximum such as point C (Fig. 3) there is less coke, because it was partially oxidised into CO_2 . It should be noted that the less reactive coke is always present at any reaction time and is not oxidised during the reaction. Therefore, the oscillatory behaviour is due to the oxidation of the more reactive coke compounds that are formed during the reaction.

The experimental findings can be rationalized with the aid of the following simplified reaction scheme:



In the presence of the catalyst, the VOC can follow two reaction paths in parallel: total oxidation into CO_2 (and H_2O), and formation of reactive coke. The reactive coke can be further converted into unreactive coke (ie, which cannot be oxidised at the temperatures used in the present study), or oxidised into CO_2 (and H_2O). In general, the coke formation reactions should occur on the acid or basic sites, while the conversion into CO_2 (and H_2O) should occur on the oxidation sites.

Table 3 shows that there are oscillations whenever there is reactive coke in the TPO, as well as adsorbed VOC on the catalyst (as shown by TPD). These oscillations occur in a very narrow temperature range $[T<, T>]$ (Table 3). In these systems, at high temperatures (above $T>$), r_1 and r_3 will be much higher than r_2 ; therefore, there is no accumulation of coke (reactive or unreactive), and the conversion into CO_2 will be complete. At low temperatures (below $T<$), r_3 is negligible (as shown in the TPOs) and both types of coke will be present in the catalyst. In these two cases there are no oscillations, either in the temperature or in the apparent conversion into CO_2 .

At intermediate temperatures, r_2 will be higher than r_3 initially, but r_3 is not negligible; reactive coke is formed faster than it is oxidised, and starts to accumulate, together with

unreactive coke. However, as a result of the exothermic oxidation reaction 3, there will be a local temperature rise of the catalytic bed which leads to the self-heating of the catalyst. As the temperature increases, r_3 increases faster than r_2 . A situation will be reached where r_3 will be higher than r_2 , and most of the accumulated reactive coke will be consumed. Then, there will be no extra heat released, the temperature will drop to the baseline, and a new cycle starts. This mechanism explains the observed behaviour of the oscillation in the apparent conversion into CO_2 and in the temperature, provided that the activation energy for reactive coke combustion is higher than the activation energy for reactive coke formation ($E_3 > E_2$).

In the systems where no oscillations were observed, neither reactive coke in the TPO nor adsorbed VOC in the TPD were present (Table 3). In these cases, the rate of reaction 2 will never be higher than the rate of reactions 3 and/or 4 at any temperature, because no reactive coke is present after reaction. At high temperatures r_1 will be higher than r_2 and all the VOC will be converted into CO_2 . At low and intermediate temperatures, r_2 cannot be neglected and there will be coke formation. However, r_3 is negligible and there will be only unreactive coke. In these cases, it can be concluded that the phenomenon does not occur because there is no accumulation of oxidisable compounds that can lead to the oscillations.

We can now discuss the nature of the reactive coke and why it is formed only in some catalysts from the VOC molecules studied.

5.4.2. Nature of the reactive coke

From the TPD experiments after reaction, it is clear that the presence of the reactive coke in the TPO is associated with the presence of reactant which remains adsorbed on the catalyst after reaction. In the case of the oxidation of MIBK, adsorbed reactant was detected in the Pt/HFAU catalyst and in the NaFAU zeolite after reaction, while only traces were detected in the Pt/ γ - Al_2O_3 catalyst. With o-xylene, a large amount of reactant was detected after reaction on Pt/NaFAU, while only traces were found on Pt/HFAU. So, the systems where adsorbed reactant was detected after reaction are precisely those where a reactive coke is found in TPO (Cf. Table 3). Therefore, part of the first TPO peak is certainly due to the oxidation of adsorbed reactant. The amount of reactant present in the catalysts after reaction is shown in Table 4, together with the amount of reactive coke after reaction.

Table 4 – Amount of reactive coke and adsorbed VOC present in the catalyst after reaction at specific temperatures.

VOC	Catalyst	Reaction Temperature (°C)	Reactive coke ^{a)} (g _C /100g _{cat})	Adsorbed VOC ^{b)} (g _C /100g _{cat})
MIBK	Pt/HFAU	180	0.5	0.2
	NaFAU	220	3.0	2.0
o-xylene	Pt/NaFAU	200	8.1	3.8

a) determined by integration of the first peak of the TPOs, after deconvolution.

b) determined by integration of the TPDs after reaction, expressed as carbon.

It is clear that an important fraction of the reactive coke is in fact adsorbed reactant. The GC/MS analysis shows that other compounds formed during the reaction are also desorbed at the temperature of the maximum of the TPOs, suggesting that these compounds are also part of what we call “reactive coke”.

In order to determine the adsorption strength of the catalysts, temperature programmed desorption experiments were made with both VOCs, pre-adsorbed at 40°C (Figures 17 and 18).

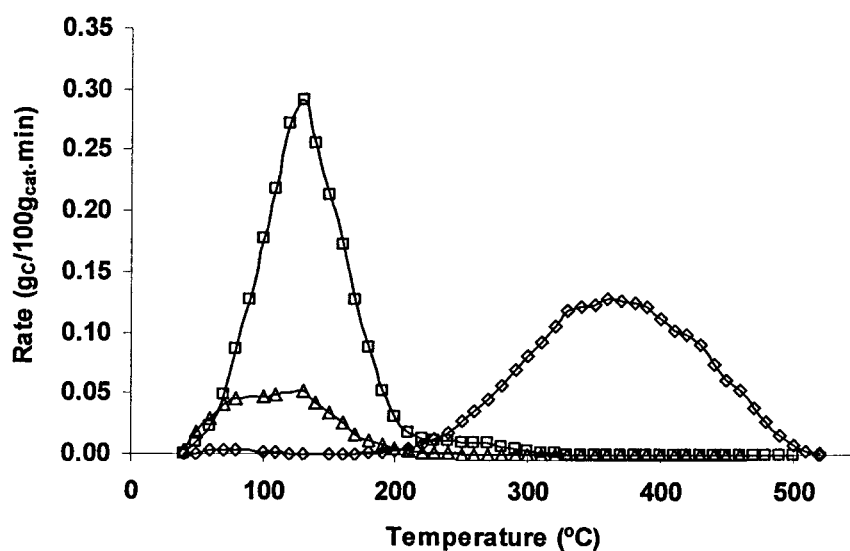


Fig. 17 - TPD after pre-adsorption at 40°C of MIBK over Pt/HFAU (□), Pt/γ-Al₂O₃ (Δ) and NaFAU (◇) catalysts.

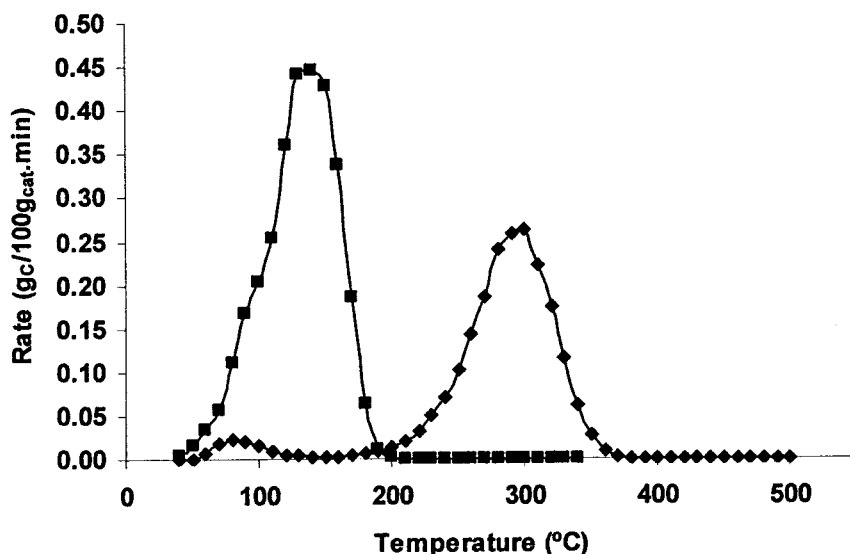


Fig. 18 - TPD after pre-adsorption at 40°C of o-xylene over Pt/HFAU (■) and Pt/NaFAU (◆) catalysts.

In the case of MIBK (Fig. 17), there is a large difference in the adsorption strength when sodium cations are present. In this case, the desorption of MIBK starts at 200°C and presents a broad peak with a maximum at around 360°C. With the Pt/ γ -Al₂O₃ catalyst, MIBK desorbs at much lower temperatures, with a peak maximum at 130°C. It should be noted that at 190°C the desorption rate is very low ($8 \times 10^{-5} \text{ gC} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{min}^{-1}$) and only traces of MIBK are found at higher temperatures. With the Pt/HFAU catalyst, MIBK also desorbs at low temperatures (peak maximum at 130°C), but at 190°C there is still some MIBK adsorbed, the desorption rate of MIBK being close to zero only at 320°C.

The interaction of acetone with ZSM-5 zeolites at ambient temperature was studied by FTIR spectroscopy by Kubelková *et al.* [12]. They found that acetone adsorbs on the acidic zeolite (HZSM-5) via the bridging hydroxyls and that the C=O bond in ketones is more perturbed by these bridging hydroxyls than by the electron-accepting sites (NaZSM-5 and dehydroxylated HZSM-5); so, there is a higher shift in the C=O IR band in the acidic zeolite. Panov and Fripiat [13] also describe Lewis acid sites binding acetone less energetically than Bronsted acid sites, when studying the acetone condensation reaction with several zeolites and alumina.

In the present work, it was shown (Fig. 17) that MIBK is less adsorbed in the Pt/ γ -Al₂O₃ catalyst (with only Lewis acid sites) than in the Pt/HFAU catalyst (with Bronsted and Lewis acid sites), which is in agreement with the cited references. Therefore, adsorption on

the Lewis acid sites of the γ - Al_2O_3 is not as strong as in the HFAU zeolite. On the other hand, MIBK adsorbed on the NaFAU zeolite desorbs at higher temperatures when compared to the acidic catalysts. This means that, in this case, MIBK is more strongly adsorbed on the cation sites of the zeolite than on the acidic sites. Nevertheless, it is clear that some MIBK remains adsorbed at temperatures higher than the reaction temperatures on both catalysts (Pt/HFAU and NaFAU) and that this does not happen with Pt/ γ - Al_2O_3 .

In the case of o-xylene (Fig. 18), it is also clear that the basic catalyst is able to keep the reactant adsorbed up to higher temperatures. O-xylene starts to desorb at 170°C and presents a peak maximum at 300°C. On the contrary, desorption takes place at much lower temperatures with the Pt/HFAU catalyst: the reactant starts to desorb near 50°C and the peak maximum is at 140°C. It should be noted that no o-xylene remains adsorbed in the catalyst at 210°C and higher temperatures.

It is well known that cations in zeolites are adsorption sites for molecules with π electrons [14]. Benzene, for example, is used to characterise the location of cations in zeolites [15]. In faujasite, benzene can adsorb on the cation or on the oxygen atoms of the 12R window. In the case of C8 aromatics the interactions are only with the cations [16], and are governed by a balance between the aromatic basicity and the Lewis acid character of the cation on the zeolite [16].

From the TPD experiments, we can conclude that the adsorption of xylene and MIBK on the cations of the faujasite is much stronger than in the acidic zeolite. The adsorption strength of the support is directly related to the oscillatory behaviour in the apparent conversion into CO_2 . When the catalyst is not able to retain the VOC molecule adsorbed up to temperatures higher than the reaction temperature (like Pt/ γ - Al_2O_3 with MIBK and Pt/HFAU with o-xylene), oscillations cannot occur because there are no oxidisable compounds accumulated in the catalyst. In the other cases, oscillations occur as a consequence of the accumulation of adsorbed compounds (reactant and other molecules that are produced from it and that do not desorb, which are the “reactive coke”) that can oxidise at a sufficiently high rate to cause a significant increase in the catalyst temperature, leading to cyclic oscillations in the apparent conversion into CO_2 .

It is then clear that the oscillatory phenomenon is mainly determined by the adsorption properties of the support. In particular, a support that is capable of adsorbing the reactant (and other easily oxidisable compounds) at temperatures higher than the reaction temperature, can

originate oscillations in the conversion into CO_2 when the reaction temperature is close to the temperature corresponding to complete conversion.

When oscillations occur, we can consider that the conversions into CO_2 in the minima would be the conversions that would be obtained if there were no oscillations (Figure 19). This assumption is followed in chapters 3 and 4.

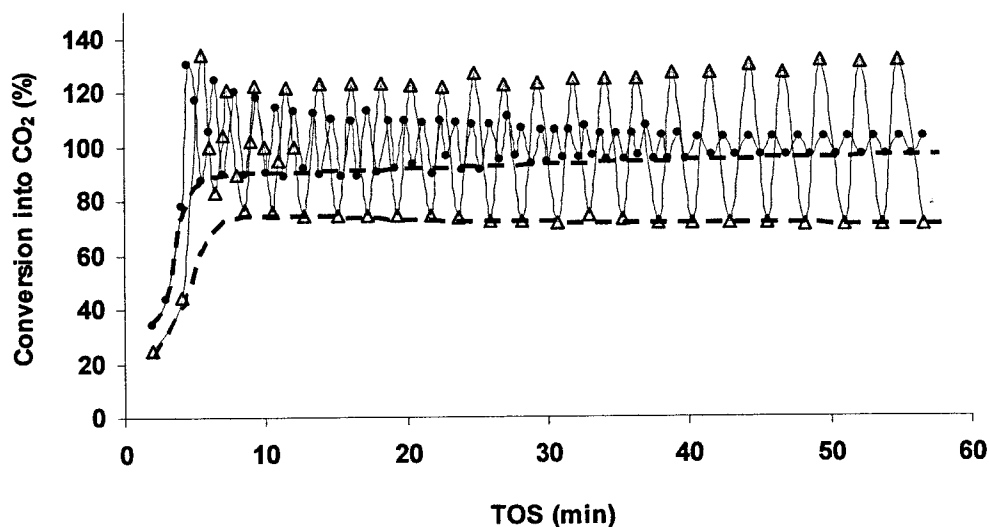


Fig. 19 - Influence of time-on-stream on the apparent conversion into CO_2 over the Pt/HFAU(47) catalyst at (●) 195°C and (Δ) 190°C (solid lines) and conversion into CO_2 if no oscillations would occur (dashed lines).

5.5. Conclusions

- Oscillations in the apparent conversion into CO_2 occur in the catalytic oxidation of MIBK and o-xylene whenever there is the presence of reactive coke in the TPOs. In these systems, at intermediate temperatures, reactive coke is formed faster than it is oxidised, and starts to accumulate. The oxidation of these compounds into CO_2 occurs at sufficiently high rate to lead to the self-heating of the catalyst and to oscillations in the apparent conversion into CO_2 .
- TPD of the reactant and GC/MS analysis after reaction show that the reactive coke is composed of reactant and other low molecular weight compounds that remain adsorbed in the catalyst.
- The occurrence of oscillations is determined by the adsorption properties of the support; in particular, a support that is capable of retaining the reactant at temperatures higher than the reaction temperature can originate oscillations in the apparent conversion into CO_2 .

5.6. References

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6. Conclusions and Perspectives

The following conclusions were taken from this work:

1. With all the PtHBEA catalysts, o-xylene undergoes two parallel reactions: total oxidation (CO_2 and H_2O) and transformation into non desorbed compounds ("coke"). The rate of o-xylene oxidation increases with the reaction temperature to the detriment of "coke" formation.
2. These compounds, trapped in the zeolite pores, are mainly constituted by aromatic hydrocarbons and oxygenated aromatic compounds. It can be underlined that coke formation has no deactivating effect on xylene oxidation into CO_2 . For a given zeolite carrier, the rate of o-xylene oxidation increases with the platinum content whereas the platinum dispersion has practically no effect on the oxidation reaction.
3. Finally, it was shown that the presence of metallic species (Pt^0) deposited over an hydrophobic zeolite (high Si/Al ratio) enhanced the reactivity of the catalyst in total oxidation of xylene.
4. With Pt/HFAU catalysts, MIBK undergoes two simultaneous processes: total oxidation (into CO_2 and H_2O) and transformation into side products (including coke).
5. The rate of MIBK oxidation increases with the reaction temperature, while the formation of coke and other secondary products decreases.
6. The higher the platinum content, the lower the temperature necessary to convert all the MIBK. Moreover, platinum should be reduced for a better catalyst performance.
7. There is an optimal concentration of oxygen (about 8%) in the feed for which the conversion of MIBK is maximum, over a Pt/HFAU(47) catalyst, in the conditions of this work
8. The oxidation of MIBK over $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$ is structure-sensitive, because the larger the platinum particles, the faster the oxidation will be.
9. The acidity of the support is a key factor that determines the catalyst activity in MIBK oxidation, the less acidic supports being preferred, as coke formation is lower on these supports. The zeolite structure (BEA or FAU) does not have any influence in the performance of the catalysts.

10. Long duration experiments show that there is some deactivation of the pre-reduced catalyst in the first 20 h of reaction, the conversion being constant afterwards. This deactivation can be due to coke accumulation or to changes in the platinum surface caused by excess of oxygen in the reactant.
11. Regeneration of the catalyst by oxidative treatment up to 520°C and the presence of 5% of steam in the reactant do not have a major influence on the performance of the Pt/HFAU(47) catalyst for the conversion of MIBK.
12. The oxidation of the mixture of o-xylene and MIBK over a Pt/HFAU(47) catalyst does not have any negative effect on the oxidation of o-xylene (on the contrary it is slightly enhanced), and has a negative effect on the oxidation of MIBK. This fact is not associated with the adsorption of the reactants on the support.
13. Cation exchanged zeolites are active catalysts for the oxidation of MIBK into CO₂ and H₂O. Side products are also formed, but their total amount decreases as the temperature increases.
14. The basic strength of the zeolites is a key parameter for the conversion of MIBK into CO₂, the more basic zeolites presenting a higher oxidation activity. A linear relationship between the intermediate electronegativity of the zeolites and the conversion into CO₂ was found.
15. Oscillations in the apparent conversion into CO₂ occur in the catalytic oxidation of MIBK and o-xylene whenever there is the presence of reactive coke in the TPOs. In these systems, at intermediate temperatures, reactive coke is formed faster than it is oxidised, and starts to accumulate. The oxidation of these compounds into CO₂ occurs at sufficiently high rate to lead to the self-heating of the catalyst and to oscillations in the apparent conversion into CO₂.
16. TPD of the reactant and GC/MS analysis after reaction show that the reactive coke is composed of reactant and other low molecular weight compounds that remain adsorbed in the catalyst.
17. The occurrence of oscillations is determined by the adsorption properties of the support; in particular, a support that is capable of retaining the reactant at temperatures higher than the reaction temperature can originate oscillations in the apparent conversion into CO₂.

The work carried out in this thesis opened up some new frontiers which may deserve further research.

Additional effort could be invested in the study of the oxidation of mixtures of VOCs. A “real” effluent to be treated always contains several compounds, and it was observed in this work that, even when the catalyst is very efficient in the oxidation of an individual VOC, this is not necessarily so in the case of a mixture.

The research carried out on the oxidation of MIBK with basic zeolites presented very interesting and novel results, showing that it is possible to achieve high conversions and selectivity to CO_2 using these catalysts. This finding deserves further investigation. I think that it would be interesting to increase even more the basic strength of the zeolite, for instance by preparing alkali-exchanged zeolites with occluded alkali metals (like Cs/CsX). The characterisation of basic zeolites is a subject which needs further inputs, as the existing methods are not completely satisfactory, namely in what concerns the determination of the amount of basic sites. Furthermore, oxidation of different classes of volatile compounds, both oxygenated (like acetone or i-propanol) and non-oxygenated (like heptane or xylene), should be carried out on these zeolites.

It might also be interesting to investigate in greater depth the oscillatory behaviour which was reported for the first time in this work.

Annex A. Reaction Set-up

A.1 Reactor Scheme

The reaction set-up used in this work in the experimental part is represented in a simplified scheme in Figure 1.

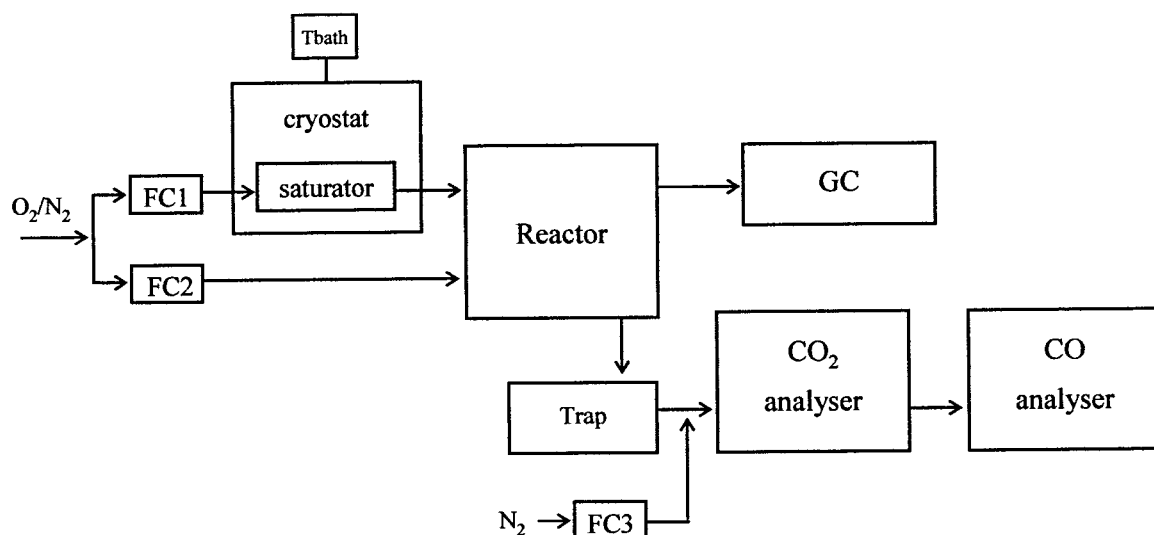


Figure 1 – Reaction set-up.

The reaction set-up can be divided in three parts: preparation of the reactants (mass flow controllers and saturator kept under a controlled temperature), reaction (reactor) and analysis system (GC and CO and CO₂ analysers).

The reactor system, a BTRS Jr (Autoclave Engineers), was design so that all the components (valves and tubes) are kept at uniform temperature. The reactor scheme is shown in Figure 2.

The reactants are mixed at the entrance of the oven. This oven is kept at 160°C throughout all the experiments. The stainless steel reactor (6mm of internal diameter and 15.2 cm of length) is kept inside a furnace. There are two multiport valves (Valco) with 2 positions that are activated by solenoid valves. The reactor valve has the following positions: purging the reactor with nitrogen or feeding the reactants. The sampling valve has a 0.25 mL calibrated loop, that allows the injection of the reactant sample in the GC. There is also a GC transfer line, kept at 220°C, that connects the reactor to the GC injector.

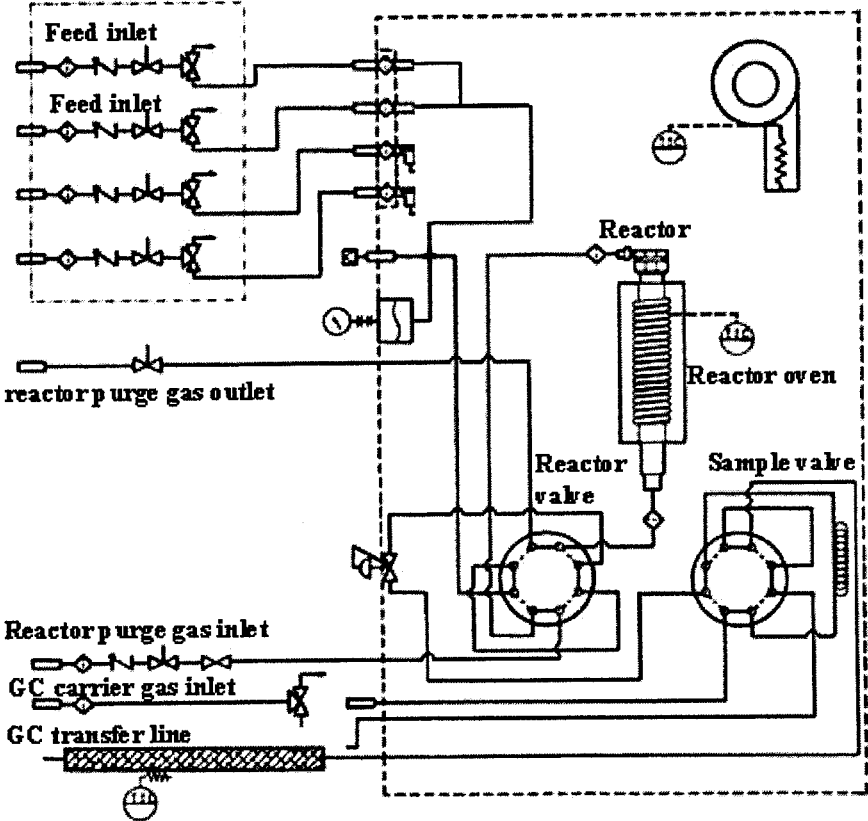


Figure 2 – Reactor scheme.

A.2 Absence of diffusional limitations

External mass transfer limitations were checked by experimental determination of the conversion of MIBK as a function of the mass flow rate (G), keeping the same contact time ($W/G = 1.08$ min). This was made over the reference catalyst ($0.32\text{Pt}/\gamma\text{-Al}_2\text{O}_3$) at 200°C , and the conversions obtained after 3h of reaction are shown in Figure 3.

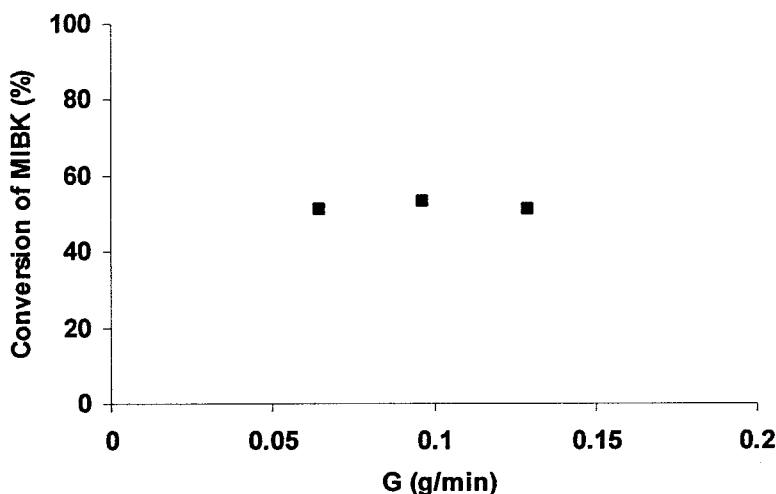


Figure 3 – Absence of external mass transfer limitations over the $0.32\text{Pt}/\gamma\text{-Al}_2\text{O}_3$ catalyst at 200°C with contact time of 1.08 min.

The conversion of MIBK is practically the same in all the experiments, ruling out any external mass transfer limitations.

Internal mass transfer limitations were checked by performing the reaction with a smaller particle size. This was made over the NaX zeolite at 300°C , comparing the conversion into CO_2 on the catalyst with a particle size between 0.2 and 0.4 mm and on the catalyst with particle size between 0.1 and 0.2 mm. The results of the conversion into CO_2 as a function of time-on-stream are shown in Figure 4.

The results are similar in both cases, which means that internal mass transfer limitations can be neglected.



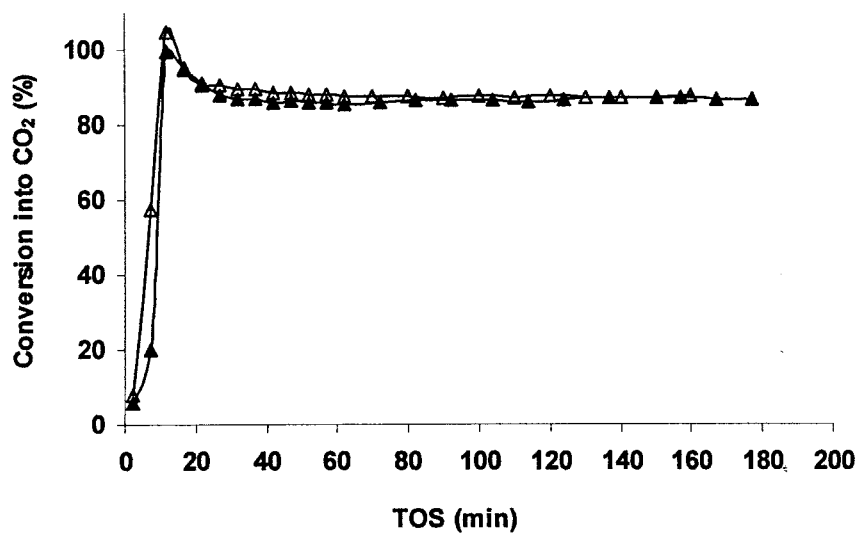


Figure 4 – Conversion into CO₂ over the NaX zeolite at 300°C with particles of 0.4-0.2 mm (▲) and 0.2-0.1 mm (Δ).





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