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"Estudio y síntesis de catalizadores heterogéneos a base de óxidos de metales de transición para la Desulfuración Oxidativa de compuestos organoazufrados del diesel"

T E S I S

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RESUMEN

Las nuevas regulaciones con respecto al contenido del azufre en el diesel han motivado la búsqueda de métodos alternativos para su desulfuración. Las tecnologías tradicionales como el proceso de hidrotratamiento (HDT), presentan serios problemas para cumplir con estas regulaciones debido a la presencia de compuestos poliaromáticos de azufre en grandes cantidades, tal como el dibenzotiofeno (DBT) y sus derivados, especialmente el 4,6-dimetil dibenzotiofeno.

El proceso de Desulfuración Oxidativa (ODS) es una ruta alternativa para la desulfuración del diesel que complementa al hidrotratamiento, ya que los compuestos más refractarios en hidrotratamiento son los más reactivos en ODS. Este tipo de desulfuración convierte las especies de azufre de los combustibles en sulfonas en presencia de una agente oxidante. Las sulfonas son compuestos con alta polaridad, lo que hace más fácil su separación, siendo la extracción uno de los métodos más utilizados. Los agentes oxidantes más utilizados actualmente para este proceso son el peróxido de hidrógeno o los hidroperóxidos de alquilo. Estos oxidantes necesitan de un catalizador para llevar a cabo la oxidación de los compuestos de azufre y son los catalizadores sólidos a base de metales de transición la principal opción para lograr un proceso rentable. Dada la complejidad de este sistema (fase polar, no polar y el catalizador sólido) y con el objeto de evaluar sólo el desempeño del catalizador, en este estudio se llevó a cabo la reacción de oxidación del dibenzotiofeno en presencia de catalizadores de vanadio soportados en alúmina preparados por diferentes métodos. Se observó que los catalizadores que presentan especies cristalinas de vanadio no son estables a la lixiviación del vanadio y presentan actividad parcialmente homogénea. También se analizó cómo activa el catalizador al agente oxidante (específicamente hidroperóxido de tert-butilo, TBHP) mediante espectroscopía de Infrarrojo (IR). Se propone la formación de especies alkylperoxy como especies oxidantes. Se observó que los soportes también adsorben fuertemente al hidroperóxido, pero la presencia de vanadio incrementa de forma considerable la activación. Se llevó a cabo la reacción en condiciones de vacío seguida por IR. El compuesto de azufre utilizado en este estudio fue el benzotiofeno por su mayor presión de vapor. Aunque este compuesto es más difícil de oxidar por su menor densidad electrónica en el átomo de S, a estas condiciones se confirmó su oxidación a sulfona y se dedujo que la formación del sulfóxido es el paso determinante.

ABSTRACT

New regulations regarding sulfur content in fuels have motivated a search of alternative methods for desulfurization. Traditional technologies, like hydrotreatment (HDT) process, have major problems to meet such regulations due to the presence, in high quantities, of poliaromatic sulfur compounds such as dibenzotiophene (DBT) and its derivatives, especially 4,6-dimethyl dibenzothiophene (4,6-DMDBT).

Oxidative desulfurization (ODS) process represents an alternative route to diesel desulfurization that complements HDT, since refractory compounds in hydrodesulfurization are the most reactive in ODS. This type of desulfurization converts the sulfur species in fuels to sulfones in presence of an oxidant agent. These compounds are increased in polarity, which makes their separation via solvent extraction more feasible. Currently the most commonly used oxidant agents are hydrogen peroxide and alkyl hydroperoxides. These oxidants need a catalyst to oxidize the sulfur compounds and transition based solid catalyst are a good choice for a profitable process.

Due to the complexity of the system (polar phase, apolar phase and solid catalyst) and aiming at evaluating only the performance of the catalyst, oxidation of dibenzothiophene in presence of vanadium pentoxide catalysts prepared by different methods was carried out. It was observed that the catalysts that present vanadium crystallites are not stable to leaching and present partially homogeneous activity. Also the way how catalyst activates the oxidant (specifically tert-butyl hydroperoxide) was analyzed by Infrared Spectroscopy (IR). The formation of alkyl- peroxy species as oxidant species is proposed. It was observed that TBHP is strongly adsorbed also by the supports, but the presence of vanadium oxide increase considerably activation. The reaction was also carried out in vacuo conditions and followed by IR. The sulfur compound used in these tests was benzothiophene (BT) due to its higher vapor pressure. Although this compound is more difficult to oxidize than DBT because of lower electron density in the sulfur atom, at these reaction conditions, the formation of BT sulfone was confirmed and it was observed that sulfoxide formation is the rate determining step.

1. Introduction

Environmental regulations regarding sulfur specifications in diesel have become more stringent worldwide. In the USA, the acceptable level of sulfur in the high way diesel was first reduced from 2000 ppm to 500 ppm by the Clean Air Act (CAA) amendments in the nineties, then to 350 ppm, 50 ppm and 15 ppm, respectively, in the years 2000, 2005, and 2006. In Europe, Germany introduced 10 ppm sulfur limit for diesel from January 2003. Other European Union countries and Japan introduced diesel fuel with 10 ppm to the market from the year 2008. Similar ultra low sulfur specifications are also targeted in many other countries, and will be predominant worldwide during the next decade [1].

These measures will require refineries producing ultra-low sulfur content (ULS) fuels. Even though conventional hydrodesulfurization (HDS) products meet some requirements such as oxygen content, vapor pressure, benzene and overall aromatics content, octane and cetane numbers, limits of ULS are very difficult to reach. Therefore, increasing the efficiency of desulfurization technologies has become a must.

In Mexico, some modifications to the law NOM-086-SEMARNAT-2006 have taken place and a minimum sulfur content of 30 ppm for Premium gasoline and 15 ppm for diesel have been proposed. As a consequence the National Refineries System has considered some improvements to the HDS process, for example: increasing the catalyst activity, feeding high purity hydrogen to the reactor, higher process conditions specifically temperature and pressure, improving flow distribution and thermal profiles in the reactor by using new technology, etc. However, process costs and the investment needed for such alternatives are thought to be very high. Additionally, there is some uncertainty on meeting the final product specifications such as aromatic content, cetane number, etc. This will emphasize the need for flexible solutions that reach future specifications of fuels with a minimum cost.

All this has motivated the research and development of alternative technologies that allow producing ULS diesel minimizing investment and process costs. Desulfurization (DS) processes can be classified according to [2] by the fate of the organosulfur compounds during desulfurization, the role of hydrogen, or the nature of the process used (chemical and/or physical). Based on the way in which the organosulfur compounds are transformed, the processes can be divided into three groups depending on whether the sulfur compounds

are decomposed, separated from refinery stream without decomposition, or both separated and then decomposed. HDS process is a typical example of a process where the molecule is decomposed, forming gaseous sulfur-products.

Other possibilities that nowadays are the basis of the new technologies, provide interesting alternatives for producing ULS fuels, for example separation of the organosulfur compounds by extraction or selective adsorption. These processes do not require oxygen.

Among the alternative processes outstands Oxidative Desulfurization (ODS). This process has been known since long ago but recently has gained importance as a solution to the need of producing sulfur-free fuels [2]. The ODS process consists essentially on converting the sulfur compounds by oxidation to their corresponding sulfoxides and subsequently to sulfones. The latter compounds are more polar and can be removed by extraction [3-5].

Compared with conventional HDS, ODS can be considered as an alternative for deep desulfurization, since it is carried out in mild conditions such as temperatures around 70°C and atmospheric pressure [6]. During oxidation of benzothiophenic or dibenzothiophenic compounds to their corresponding sulfones, the divalent sulfur is oxidized by the electrophilic addition of oxygen atoms to obtain the hexavalent sulfur characteristic of sulfones [7]. Physicochemical properties of sulfones are considerably different from their precursor hydrocarbons. As sulfones are soluble in polar solvents, they can be easily removed by extraction or adsorption. Since the process is carried out at mild temperatures, atmospheric pressure and without hydrogen consumption, it seems to have considerable economical and technical advantages over deep hydrotreating processes.

Some oxidants and catalysts have been used successfully in the ODS process, Aída et al. [8] report that the best oxidants for organosulfur compounds are: performic acid, perfluoroacetic acid and a mixture of formic or trifluoroacetic acid with hydrogen peroxide. These homogeneous systems with organic peracids generally increase their catalytic activity by means of a radical promoter such as ultraviolet light.

Pointing towards a more competitive process, ODS research has focused on the oxidation of model sulfur molecules using solid catalysts based on Ti-Zeolites and hydrogen peroxide [9, 10], although this type of catalysts has shown to have problems regarding internal mass transfer restrictions due to the size of the molecules to be oxidized and also poisoning of the active sites due to the presence of water in the system. In this line, other materials have

been evaluated so as to be employed as hydrophobic catalysts [11, 12]. These solids have shown better performance in liquid phase oxidation reactions in presence of hydrogen peroxide as oxidant.

Recent investigations of our group [13-18] have tested vanadium catalysts obtaining good results in the oxidation of benzothiophenic compounds present in diesel. Several variables of the ODS process have been studied such as process conditions, solvent and oxidant effects, nitrogen compounds and catalytic support. In the last study, vanadium catalysts supported on Al_2O_3, TiO_2, CeO_2, Nb_2O_5, SBA-15 y Al_2O_3-TiO_2 were tested in the ODS reaction using H_2O_2 or TBHP as oxidants. Even some pure supports were evaluated and it was observed that they presented low catalytic activity and it increased considerably by supporting vanadium oxide. Catalytic activity also changes with the support used, being Al_2O_3 and Nb_2O_3 the ones that present better activity. It is interesting to note that no correlations were found between the physicochemical properties of supports (acidity, isoelectric point and specific area) and catalytic activity. Only in some cases some correlation was found with reducibility of catalysts according to temperature programmed reduction (TPR) tests. These tests also show that the interaction between vanadium and the support changes in each case.

The best catalysts were tested in the ODS of a hydrotreated Mexican diesel with 300 ppm S, obtaining very interesting results:

- Quality of diesel remains practically unaltered (paraffinic hydrocarbon).

- Oxidation of dibenzothiophenic compounds was clearly observed, even detecting the sulfone of the most refractory compound, 4,6-DMDBT.

- Simple extraction of aromatic compounds, which is an advantage if aromatic content wants to be lowered. Otherwise these compounds can be easily recovered by distillation.

- Cromatograms detecting specifically sulfur-compounds (Pulsed Flame Photometric Detector) show a major decrease in DBT and C3DBT's. 4 and 4,6-DMDBT have also substantially decreased their concentration, but are still the most refractory compounds.

- Oxidative desulfurization of actual diesel after 30 minutes with V_2O_5/Al_2O_3 at 60 °C and acetonitrile as solvent reached 99% of total S-removal, obtaining diesel with 10 ppm S.

Our group [18] also evaluated the influence of the extraction step in the ODS process. In this study different tests were carried out: conventional ODS process, exhaustive extraction with phase separation (E y O) to carry out the reaction only in the solvent phase and long term extraction and oxidation (E4-O) in presence of both phases. Results show that sulfone yield with the E4-O process is higher than with ODS, although total S-removal is equal with both processes.

On the contrary, E y O process, where reaction takes place only in presence of the polar phase, presents lower sulfur yield. This result highlights the importance of the presence of both phases (diesel and solvent) to obtain better results, not only regarding oxidation yield but also total sulfur removal. The need of both phases during ODS process has also been reported by Campos-Martín et al. [19] recently. However, the process is very complex and analysis becomes very difficult because of the three phases present in the system: solid catalyst, apolar (diesel) and polar (solvent) phase.

Oxidative desulfurization of fuels is an effective and current alternative process with many variables still unstudied. With the purpose of knowing more in detail the aspects of oxidative desulfurization process, this work studies the stability of different preparations of vanadium catalysts supported on alumina, and the formation of oxidant species that participate in the oxidation of the sulfur compounds present in diesel.

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2. State-of-the-art

This chapter includes the literature review on the importance of studying the desulfurization processes, the conventional methods of desulfurization and the new alternatives, which includes the Oxidative Desulfurization, the process under study. Finally the objectives of this thesis are presented.

2.1 Introduction

Nowadays, the main source of energy is petroleum, since it covers around half the energetic requirements of the world. Petroleum is a complex hydrocarbon mixture with significant amounts of nitrogen (up to 6%), sulfur (up to 8%), oxygen (up to1.8%) and little amounts of vanadium and nickel among others. This mixture is subjected to a refining process in order to obtain products with specific characteristics such as fuels, lubricants, waxes, asphalt and solvents.

Distillation allows separating the different shares of crude oil. From the upper part liquefied petroleum gas, gasoline and naphtha are obtained. The medium products include jet fuels and diesel. Kerosene and other special solvents are obtained by distillation of these two fractions. The lower fractions can be used as fuel oil but are generally distilled in vacuum to obtain a better output of the distilled oil. Also these heavier fractions can be used to produce asphalt, tar, paraffin wax, etc.

Gasoline, diesel and other fuels account approximately for 75-80% of all refinery products. Currently, about 2.2 million barrels of diesel fuel is consumed everyday in the United States road transportation market. According to recent studies a considerably increasing demand is expected during the first part of this century, probably producing a fuel shortage in Europe and United States.

Increasing attention worldwide is being paid to chemistry of diesel fuel processing, especially everything that is related to thermal efficiency and environmental aspects, which includes pollutants and green house gas emissions [1]. Sulfur compounds are particularly undesirable in fuels since they cause corrosion in refining equipment. They also generate

SO_x during their combustion in the catalytic converters, which are atmospheric pollutants that cause acid rain, ozone and smog [2].

Consequently, due to the increasing uptake of gasoline and diesel fuels, the environmental regulations have become stricter regarding fuel quality. The European Community has reduced the sulfur limits in diesel to less than 50 ppm in 2005 and the United States to 15 ppm in 2006 [3]. In Mexico, some modifications to the law NOM-086-SEMARNAT-2006 have taken place and a minimum sulfur content of 30 ppm for Premium gasoline and 15 ppm for diesel have been proposed.

The heightened interests in ultra-clean fuels are also due to the need for using new emission control technologies for internal combustion engines (especially those for diesel fuels), and for using on-board or on-site reforming of hydrocarbon fuels for new fuel cell vehicles [1].

2.2. Desulfurization

There are different ways of classifying desulfurization processes; one of them is based on the nature of the key physico-chemical process used for sulfur removal, as it is shown in figure 2.1.
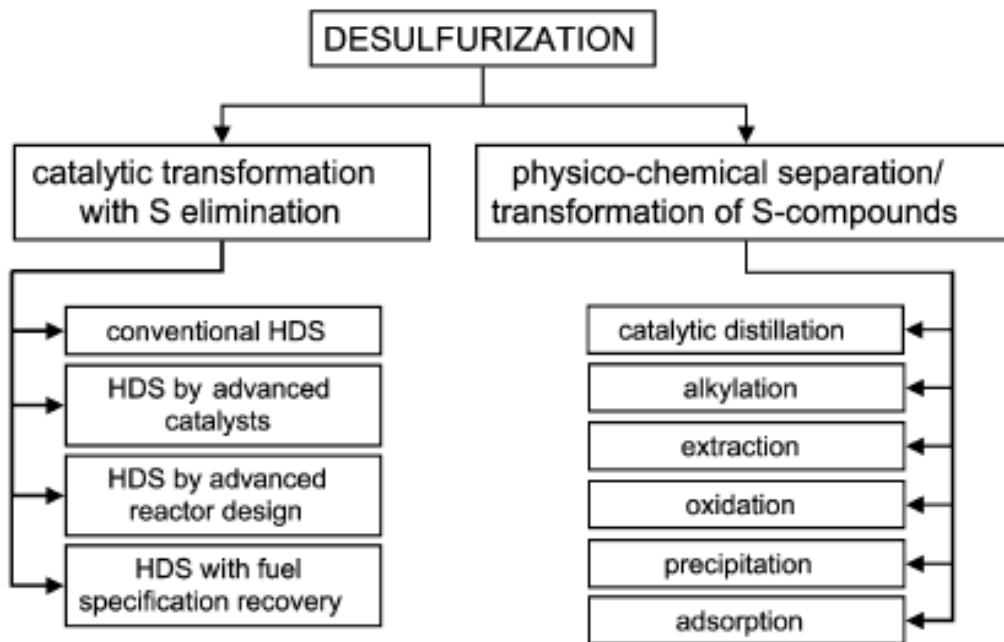
2.1. Desulfurization technologies classified by nature of the key process to remove sulfur [4].

The most developed and commercialized technologies are those that catalytically convert organosulfur compounds with sulfur elimination. Such catalytic conversion technologies include conventional hydrotreating, hydrotreating with advanced catalysts and/or reactor design, and a combination of hydrotreating with some additional chemical processes to maintain fuel specifications, which in diesel are cetane number, aromatics content, total nitrogen, total sulfur, etc.

The main feature of the technologies of the second type is the application of physico-chemical processes different in nature from catalytic HDS to separate and/or to transform organosulfur compounds from refinery streams. Such technologies include as a key step distillation, alkylation, oxidation, extraction, adsorption or combination of these processes.

2.2.1. Hydrodesulfurization technologies

Catalytic hydrodesulfurization (HDS) of crude oil and refinery streams carried out at elevated temperature and hydrogen partial pressure converts organosulfur compounds to hydrogen sulfide (H_2S) and hydrocarbons. Some typical catalysts used in conventional HDS are sulfided CoMo and NiMo supported on Al_2O_3. Their performance in terms of desulfurization level, activity and selectivity depends on the properties of the specific catalyst used, the reaction conditions, nature and concentration of the sulfur compounds present in the feed stream, and reactor and process design.

Organosulfur compounds are usually present in almost all fractions of crude oil and their reactivity varies depending on their structure and electronic density. Lower boiling point fractions mainly contain aliphatic organosulfur compounds; examples of these compounds are mercaptanes, sulfides and bisulfides. These compounds are very reactive in conventional hydrotreating (HDT) processes and they can be easily removed. Higher boiling point fractions contain relatively more sulfur and the sulfur compounds are of higher molecular weight. Characteristic compounds of these fractions are benzothiophene (BT), dibenzothiophene (DBT) and their alkyl derivatives which are more difficult to desulfurize via HDT.
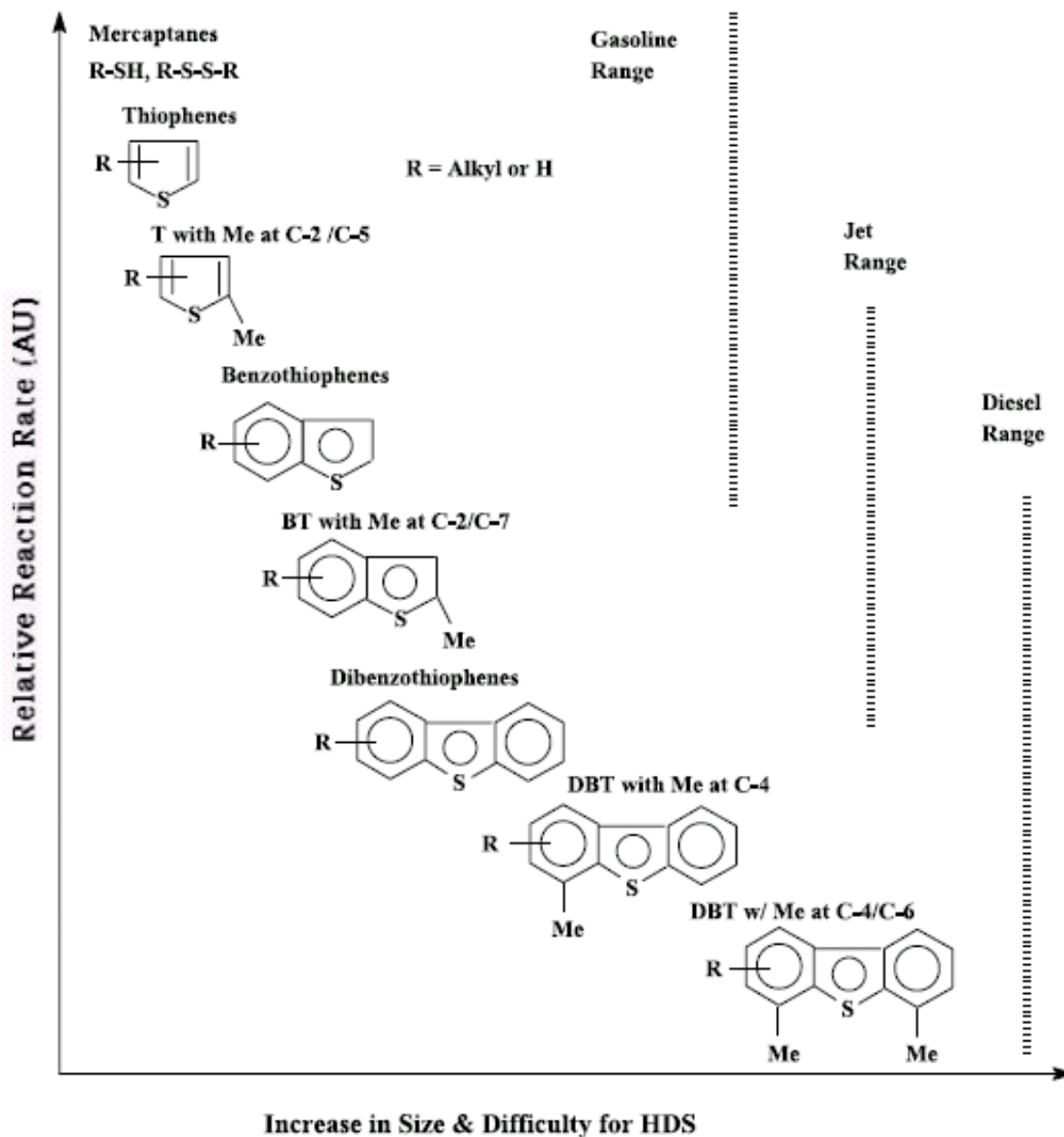
Figure 2.2. Reactivity of various organic sulfur compounds in HDS [Song 2003].

Figure 2.2 shows some of the organosulfur compounds characteristic of different types of fuels as well as their reactivity in HDS. It can be observed that reactivity of sulfur compounds diminishes in the following order: mercaptanes > thiophene > alkyl substituted thiophene > BT > alkyl substituted BT > DBT > alkyl substituted DBT. In agreement with these results, Song et al. [1] classify sulfur compounds in four groups according to their reactivity in HDS, these reactivities were described by their pseudo first order constants. The first group is dominantly alkyl BTs; the second, DBT and alkyl DBTs without alkyl

substituents at the 4- and 6-positions; the third, alkyl DBTs with only one alkyl substituent at either the 4- or 6-position; the fourth, alkyl substituents at the 4- and 6-positions. The relative rate constant of HDS for each of the four groups is 36, 8, 3, and 1, respectively [5,6].

Investigations [5,7,8] have demonstrated that when the total sulfur content in diesel is reduced to 500 ppmw, the sulfur compounds remaining in the hydrotreated oil are the third and fourth group sulfur compounds, these are alkyl substituted DBT's in the 4 and/or 6 positions. Therefore, to reduce sulfur content to 15 ppm, by conventional HDS it would be necessary to increase 3.2 times the actual volume of the catalyst in the process [1].

HDT of thiophenic compounds proceeds by two different mechanisms of reaction. The first one is called hydrogenolysis, which consists in the direct elimination of the sulfur atom by breaking the C-S bond. In the second mechanism the aromatic ring is hydrogenated and sulfur is subsequently removed (hydrogenation pathway). It has been demonstrated that refractory compounds such as 4,6-DMDBT are desulfurized predominantly by the latter mechanism [9,10].

For these reasons, the new catalytic formulations focus on removing 4,6-DMDBT more effectively, by modifying catalyst formulations to: (1) enhance hydrogenation of aromatic ring in 4,6-DMDBT by increasing the hydrogenating ability of the catalyst; (2) incorporate acidic feature in catalyst to induce isomerization of methyl groups away from the 4- and 6-positions; (3) remove inhibiting substances (such as H_2S) and tailoring the reaction conditions for specific catalytic functions. The catalytic materials may be improved for better activity by using different supports as TiO_2, TiO_2-Al_2O_3, HY, MCM-41, etc., increasing the loadings of the active metals. Also modifying preparation procedures, using additives and promoters, adding other base metals or incorporating noble metals as Pt, Pd, Ru, etc. [1].

Besides new catalysts formulations, another option to improve hydrotreating is to focus on reaction equipments. A new equipment design consists on adding a second reactor to increase the degree of desulfurization. If H_2S and NH_3 are removed from the first reactor outlet, the performance of this reactor can be improved. Also new reactors have been designed with two or three catalytic beds operating co-currently or counter-currently [11,12]. The co-current design presents a disadvantage regarding the concentration profiles

of H_2 and H_2S, since the concentration of H_2S at the reactor outlet is very high and this inhibits desulfurization of the most refractory sulfur compounds. To overcome this problem a solution is the counter-current design. A disadvantage of this design in the case of distillate HDT, is the difficulty of vapor-liquid contact and the prevention of hot points in the reactor.

Another option to produce ultra low sulfur diesel is increasing the severity of the hydrotreating process, but at the same time this generates undesired reactions that end up in the reduction of the cetane number. On the other hand, nowadays heavier crude oils are being processed also with a higher quantity of aromatics and polyaromatics [13]. Particularly in Mexico Maya crude oil is being processed (22 °API with 3.6% of S) and it has been planned to process other Mexican crude oils such as Ku-Maloob-Zaap which is even heavier with 12 °API and 5% of S. This not only means processing a higher amount of pollutants but also processing the most refractory sulfur compounds such as DBT, 4-MDBT and 4,6-DMDBT and other alkyl substituted DBT.

In this context, since the year 2006, PEMEX-Refinación has placed on the market of Mexico City, Monterrey and Guadalajara gasoline Premium UBA (ultra low S content) with less than 30 ppm S. This gasoline is obtained from the mixture of 65% imported gasoline and only 35% of Mexican gasoline, since refineries in Mexico are not currently able to reach the actual standards or those of the immediate future (S < 15 ppm).

In conclusion, conventional hydrodesulfurization process hardly allows to reach such low sulfur levels in fuels to meet the new environmental regulations. This has led to the search of new catalyst formulations, different reactor designs and more severe process conditions, which increase the cost of the process.

2.2.2. Alternative Technologies for desulfurization

There are other alternatives for desulfurization of fuels that have become more important as environmental regulations change, taking into account the difficulties that HDT is facing. One of the main characteristics of the alternative processes is the lack of hydrogen consumption. It is interesting to note that many of these alternative processes have not been implemented, it is they have not gotten through the pilot plant. Among the most

outstanding alternatives are the change in boiling point of the organosulfur compounds, extraction, adsorption and decomposition by selective oxidation.

2.2.2.1. Change in boiling point by alkylation

This method is used mainly to treat gasoline. It consists on increasing the boiling temperature of organsulfur compounds in order to be removed from lighter fractions by distillation, and subsequently be concentrated in the heavier fractions of the refineries. Alkylation of thiophenic compounds is obtained by making them react with the olefin present in the stream [4].

2.2.2.2. Adsorptive Desulfurization

This process is based on the ability of some solids to adsorb organosulfur compounds. Based on the interaction mechanisms of S-compounds with the solid adsorbent, this type of desulfurization can be divided in two groups: Adsorptive Desulfurization and desulfurization by reactive adsorption. The first one is based on the physical adsorption of organosulfur compounds on the adsorbant surface. A great variety of adsorbants is based on transition metal complexes supported in porous materials, zeolites, metallic oxides, activated carbon, etc. Regeneration of the adsorbants is carried out by washing with a solvent, which results in a stream with high concentration of organosulfur compounds. Reactive adsorption takes advantage of the selective chemical interaction of the organosulfur compounds and the adsorbant.

Sulfur is fixed commonly as sulfide, the hydrocarbon free of sulfur is released into the purified fuel stream. Regeneration of used adsorbant results in sulfur elimination in the form of H_2S, S or SO_x, depending on the process applied [4].

ConocoPhilips [14] published about a desulfurization process by reactive adsorption for diesel called S-Zorb. In this process the diesel stream and the adsorbant are put in contact in a fluidized bed reactor at a temperature between 340-410°C and pressure ranging from 2 – 20 bar in presence of H_2. In this process, the sulfur atom is removed from the molecule and retained by the adsorbant. The hydrocarbon returns to the final product without structural changes. The wasted adsorbant is withdrawn from the reactor continuously and sent to regeneration, where sulfur is separated and the resulting SO_2 is sent to the sulfur plant.

ConocoPhilips reports that this process can treat distillates with sulfur content of 500 ppm or less.

Song [13] and his group propose a process that combines selective adsorption for separating organosulfur compounds coupled to hydrodesulfurization of the sulfur concentrated stream. It is considered that reactor utilization is more efficient with this arrangement due to the high concentration of sulfur in the stream and the higher rate of reaction caused by the absence of aromatic compounds.

2.2.2.3. Desulfurization by extraction

This alternative is based on the fact that sulfur compounds are more soluble than hydrocarbons in a suited solvent. The process consists on the transfer of the organosulfur compounds from diesel to the solvent [15]. Subsequently, the mixture of fuel and solvent are fed to a separator where hydrocarbon is separated from the solvent. Sulfur compounds in the solvent are separated by distillation and the solvent is recycled [Babich et al., 2003].

This process is carried out at mild conditions (nearly ambient temperature and pressure), which is its most attractive characteristic. The chemical structure of the fuel does not change, the equipment used is conventional and can be easily added to the refinery.

2.2.2.4. Biodesulfurization

This process removes sulfur from fuels by a series of enzyme catalyzed reactions [16]. Some bacteria (biocatalysts) are capable of biotransforming sulfur compounds and even remove the sulfur atom from heterocyclic molecules like DBT [17].

Energy biosystems developed a biodesulfurization process for sulfur removal of naphtha and other distillantes using bacteria [16]. This process consists on mixing the bacteria stream in aqueous media, caustic soda and bacteria nutrients. The enzymes in bacteria first oxidize sulfur atoms and subsequently break the C-S bonds. Sulfur leaves the process as hydroxyl phenyl benzene sulfonate, which can be used commercially to produce surfactants.

Gallagher et al. [18] report a biodesulfurization mechanism of DBT with Rhodococcus IGTS8 at growing conditions. The intermediates are DBT sulfoxide, DBT sulfone, 2-hydroxy biphenyl- 2-sulfonate and 2,2-dihydroxy biphenyl.

Kobayashi et al. [19] studied the mechanisms of reaction using complete cells of Rhodococcus erythropolis KA2-5-1 and report that desulfurization activity of alkyl DBT's decreases when being mixed. This phenomenon is caused by apparent competitive inhibition of substrates.

There are still a lot of disadvantages related to biocatalysis and in order to consider biodesulfurization a feasible alternative it is necessary to improve the activity of biocatalysts, reach faster reaction kinetics, overcome mass transfer limitations, render bacteria more tolerant to temperature and solvents and extend specificity of the substrate to attack a wider range of heterocyclic compounds.

2.2.2.5. Desulfurization by Selective Oxidation

This method, also called Oxidative Desulfurization (ODS), has gained importance in the last years as an alternative to produce fuels with ultra low sulfur content. The most interesting advantages of this method are lack of hydrogen consumption as well as mild process conditions, this is atmospheric pressure and temperatures lower than 100 °C. In general, ODS consists of two processes: the oxidation of sulfur compounds and the subsequent separation of the oxidized sulfur compounds. During the process, divalent sulfur of thiophenic compounds reacts by electrophilic addition of oxygen atoms to form the respective sulfoxide and further oxidation will produce the hexavalent sulfur characteristic of sulfones [20]. Since oxidized sulfur compounds have higher polarity, they can be easily separated by distillation, adsorption and extraction or even be decomposed. The separation methods of choice are commonly adsorption or extraction.

The history of Oxidative Desulfurization began since 1920 [21,22]. The initial attempts involved nitric oxides/acids type oxidants like HNO_3 or NO/NO_2 gases, later several reports were made on other oxidants like t-butyl hypochlorite, very toxic RuO_4, persulphate based oxidant (i.e., $2KHSO_5.KHSO_4.K_2SO_4$) or on H_2O_2–H_2SO_4 system. The purpose of the attempts in the initial period was two-fold; one was to oxidize sulfur for desulfurization, and another aimed at nitration of aromatic molecules with use of NO_x oxidants. Since nitrated aromatics are thought to have a high cetane number.

Later on, around 1990 when sulfur specifications in diesel became more stringent, this process re-gained interest among the scientific community.

Funakoshi and Aida [23] report a method to desulfurize fuels using oxidant agents, followed by distillation, extraction or adsorption. Sulfur compounds are recovered as sulfoxides or sulfones.

According to Zannikos et al. [24], with an oxidation/extraction scheme, it is possible to reach even 90% of desulfurization of gas oil, using hydrogen peroxide as oxidant agent and acetic acid as catalyst. Fuels treated by this scheme did not report any negative effects in their properties.

Another advantage of oxidative desulfurization is the high reactivity of dibenzothiophenic compounds, considered refractory in HDS. Otsuki et al [25] calculated the electronic density on the sulfur atom of different organosulfur compounds using formic acid and hydrogen peroxide as oxidant. They reported that refractory compounds in HDS, as alkyl dibenzothiophenes in the 4 and 6 positions, are highly reactive in oxidation due to their high electronic density in the sulfur atom. The apparent reaction rate constants observed in this study decreased in the following order: methyl phenyl sulfide > thiophenol > diphenyl sulfide > 4, 6-DMDBT > 4-MDBT > DBT > BT.

Shiraishi et al. [26], with a formic acid – hydrogen peroxide system, observed that sulfur polyaromatic compounds with at least a naphthenic ring adjacent to the thiophenic ring, have even higher electron density than DBT's and are more easily removed. This authors report a desulfurization of 89% in a VGO (vacuum gas oil) with a 1.9899% weight of sulfur.

The catalytic system used in ODS plays a very important role in reactivity tendencies of organosulfur compounds in diesel. In a reactivity study of DBT's using H_2O_2 and polyoxometalates as catalysts, Te et al. [3] observed a reactivity trend similar to HDS. To explain these results, the authors suggested that molecular size of catalysts can hinder contact between oxygen reactive species and the sulfur atom of alkyl dibenzothiophenic compounds. Phosphotungstic acid hydrate used in this study in presence of hydrogen peroxide forms $PO_4[WO(\mu\text{-}O_2)(O_2)]_4^{3-}$. Tungsten atom in this polyoxometalate is a very rigid structure with 7 coordinations. If DBT interacts with this species by the sulfur atom to form a transition state (direct oxidation or catalytic oxygenation), it is possible that alkyl groups of 4,6-DMDBT do not allow the interaction because of steric hindrance. However, it

is considered that these compounds can be effectively removed from diesel by ODS with either longer reaction times or higher temperatures.

In an attempt to use molecular oxygen as oxidant, Murata et al. [27] used an aldehyde (n-octanal) in presence of a transition metal salt (cobalt acetate II) to react with molecular oxygen to produce a peroxyacid which would in turn oxidize organosulfur compounds. In this system, reactivity order of DBT's is equal than in HDS.

As it has been observed, oxidation of organosulfur compounds is usually carried out in presence of a catalyst. Without it, the reaction proceeds very slowly by nucleophilic attack of the sulfur atom to the O-O bond of the peroxide used [28].

Another way of catalyzing ODS is with a phase transfer catalyst and ultrasound. Phase transfer agents diminish superficial tension and allow the formation of microbubbles by ultrasound. This way, liquid-liquid interphase area is enhanced by emulsification. It is also considered that this method can produce a microenvironment of high temperature and pressure, which could create active intermediates that react instantaneously. Mei et al. [29] obtained excellent results in diesel desulfurization by using ultrasound, hydrogen peroxide, tetraoctil ammonium bromide and phosphotungstic acid as oxidant, phase transfer agent and catalyst, respectively.

Pointing towards a more competitive process, ODS research has focused on the oxidation of model sulfur molecules using solid catalysts based on Ti-Zeolites and hydrogen peroxide [2,30]. It was reported that TS-1 has problems oxidizing big molecules like BT due to internal mass transfer restrictions, consequently to oxidize these higher sized molecules mesoporous Ti-beta and Ti-HMS were used [2]. In this study sulfur compounds reactivity was ascribed to the nucleophilic character of the sulfur atom as well as to its size.

Palomeque et al. [31] studied DBT oxidation in hidrotalcitas (HT) MgLa with H_2O_2 as oxidant. These authors suggest that oxidation of DBT to its corresponding sulfone with HT takes place by a base catalyzed mechanism where the active sites are probably hydroxyls.

In an attempt to simplify the process to a single liquid phase with a solid catalyst in a continuous reactor, Wang et al. [32] studied oxidative desulfurization of kerosene in presence of Mo/Al_2O_3 with tert-butyl hydroperoxide (TBHP) as oxidant agent, since it can form a single phase with the fuel.

Different ODS patents to obtain ultra low sulfur diesel have been tested. Some of them are Lyondell [33], PetroStar [34], UniPure [35], etc.

The process patented by Lyondell consists on the oxidation of sulfur compounds with TBHP as oxidant in presence of a heterogeneous catalyst. Reaction takes place in a fixed bed reactor at temperatures lower than 93°C and a pressure of 7 atmospheres to maintain the fuel/TBHP mixture in liquid phase and the hydraulic pressure to pass the fuel stream through the catalyst bed. The reaction time to oxidize sulfur compounds to their corresponding sulfones is less than 10 minutes. The process also includes decomposition of remaining TBHP, since hydroperoxides diminish the storage stability of fuels. Sulfur removal is carried out by extraction with a polar solvent, which is separated by distillation for its reuse [33].

The UniPure process is also based on oxidizing aromatic sulfur compounds before extracting them. During the process an aqueous H_2O_2 phase is applied along with a dissolved oxidation catalyst (organic acid). Organosulfur compounds are claimed to be converted to sulfones at nearly atmospheric pressure and mild temperature (up to 120 °C) within short residence times (about 5 min). After separation of the aqueous and oil streams, the aqueous phase that contains wasted catalyst and some sulfones is sent to a recovering section for sulfone separation and catalyst regeneration. The oil stream is treated with an adsorbant to separate sulfones. This catalyst is subsequently regenerated with methanol [35]. The sulfur level is reported to be reduced from 270 to 2 ppm sulfur.

Conversion/extraction desulfurization (CED) technology began in 1996 when Petro Star Inc. combined conversion and extraction to remove sulfur from diesel fuel. Before liquid/liquid extraction, the fuel is mixed with an oxidant (peroxoacetic acid). The oxidation requires a stoichiometric amount of the oxidant and proceeds at temperatures below 100 °C at atmospheric pressure. In laboratory-scale experiments straight-run diesel fuel with 4200 ppm S was treated to below 10 ppm S. Other fuel specifications like cetane number, API gravity and aromatics content were also improved. Reaction products are extracted with a solvent to produce low sulfur fuel and a high sulfur extract. Again, a solvent cocktail should be more suitable than an individual solvent with similar polarity to sulfones produced and minimum affinity to apolar components in fuel. After extraction, polishing is required to eliminate little amounts of oxidized sulfur compounds remaining in

fuel. This is carried out with a solid phase that adsorbs little amounts of sulfones. Possible ways to treat the suldur rich extract are oxidation to sulfate, sulfite or sulfonate or biochemical treatment.

2.3. Deeper in Oxidative Desulfurization (ODS).

In catalytic oxidation processes, air is the ideal oxidant since it is the cheapest, greenest and most available but it is not always possible to use. Thus, hydrogen peroxide or alkyl hydroperoxides have demonstrated to be good options. Since 1990, most of ODS research have used these oxidants. H_2O_2 presents a high amount of active oxygen by mass unit (47%). It is a commercial product often used at industrial level, and gives only water as a by-product. Alkyl hydroperoxides are also more environmentally friendly than other inorganic oxidants and allow simpler reactor design such as a fixed bed reactor due to their miscibility with the fuel, which is a considerable advantage. Tert-butyl hydroperoxide (TBHP) is the most used hydroperoxide [36], although it has a higher cost and generates tert-butanol as by-product. These oxidants need a catalyst to carry out sulfur compounds oxidation. Heterogeneous transition metal based catalysts are the best choice to achieve good oxidation yields. These catalysts activate peroxides by three possible routes. Based on the active intermediate, metal ions catalyze oxygen transfer reactions with H_2O_2 or RO_2H forming a peroxometal or an oxometal complex which oxidize the sulfur atom. Peroxometal pathways usually involve early transition elements with d^0 configuration, e.g. Mo(VI), W(VI), V(V), Ti(IV). Late or first row transition elements, e.g. Cr(VI), V(V), Mn(V), Ru(VI), Ru(VIII), Os(VIII), generally employ oxometal pathways. One-electron oxidants, e.g. Co(III), Mn(III), Ce(IV), Fe(III), Cu(II), etc. catalyze free radical autoxidation processes by promoting the decomposition of alkyl hydroperoxides into chain initiating alkoxy and alkyl peroxy radicals in one-electron transfer processes. Strictly speaking the metal ion acts as an initiator of free radical autoxidation [37].

The major advantage of heterogeneous catalysts is the ease of separation of the catalyst for successive reuse. Thus, catalysts must be stable towards leaching of the active metal into the liquid phase under operating conditions. This is true for all types of catalytic reactions but leaching is particularly a problem in oxidation catalysis owing to the strong complexing

and solvolytic properties of oxidants (H_2O_2, RO_2H) and/or products (H_2O, ROH, RCO_2H, etc.). Leaching is generally a result of solvolysis of metal–oxygen bonds, through which the catalyst is attached to the support (e.g. SiO_2), by such polar molecules.

In a solid catalyst, the active phase is anchored to the support by metal – oxygen bonds. These bonds can be broken by polar molecules (solvolysis), which results in leaching of the active phase. According to Besson et al. [38], leaching of metal atoms depends upon the reaction medium (pH, oxidation potential, chelating properties of molecules) and upon bulk and surface metal properties.

Stability of heterogeneous catalysts is an essential characteristic for industrial use. Therefore analyzing heterogeneity is a must, taking into account that catalyst recycling, in batch experiments without apparent loss of activity cannot be construed as proof of heterogeneity. Three different scenarios can be found for heterogeneous catalysts in the liquid phase [39]

1. The metal does not leach and the observed catalysis is truly heterogeneous.
2. The metal does leach but is not an active catalyst; the observed catalysis is (predominantly) heterogeneous.
3. The metal leaches to form a (highly active) homogeneous catalyst; the observed catalysis is homogeneous in nature.

Therefore, the definitive test for leaching is to filter the catalyst, at the reaction temperature, during the course of the reaction and allow the filtrate to react further. If no further reaction is observed this is strong evidence in support of heterogeneous catalysis. If the reaction mixture is allowed to cool to ambient temperature before filtration, readsorption of leached metal ions onto the solid support can occur or different oxidation states of the metal can be formed in solution.

2.4. Significance of this study

Heterogeneous catalysts during the ODS process are prone to leaching of the active metal, given that oxidation is carried out in presence of polar solvents and strong oxidant agents like hydrogen peroxide or tert-butyl hydroperoxide. Although this is a current problem little attention has been paid to testing heterogeneity in ODS research.

2.5. Objectives and hypothesis

The objectives of the present thesis are:

- To study the stability of heterogeneous catalysts towards leaching in liquid phase oxidation.

- To study the activation of the peroxide in the oxidative desulfurization of organosulfur compounds present in diesel.

The hypothesis of this study states that if active phases with a proper interaction metal-support are generated, it is possible to avoid leaching and allow the interaction of the active phase with the peroxide to form a peroxocomplex, which can be considered the oxidant species.

2.6. Methodology

Based on previous results of our group mentioned before, the following activities are proposed to accomplish the objectives of this thesis:

- Preparation of vanadium catalysts supported on alumina by different methods (since alumina presented the best results as support) varying also vanadium loading:

  - Thermal spreading (Precursor: V_2O_5)

  - Incipient Wet Impregnation (Precursor: NH_4VO_3)

  - Sol-gel (Precursors: $V(acac)_3$, $Al(O\text{-}sBu)_3$ of vanadium and alumina, repectively).

- Characterization of catalysts by the following techniques:

  - Textural properties of the catalysts by N_2 physisorption

  - Scaning Electron Microscopy (SEM-EDX), to evaluate distribution of the active metal on the catalyst.

  - X- Ray Diffraction (XRD), to detect crystalline species.

  - Temperature Programed Reduction (TPR), to evaluate reducibility of vanadium species.

  - Raman Spectroscopy, to detect the type of vanadium species supported.

- UV-Vis Diffuse Reflectance Spectroscopy, to evaluate the coordination of vanadium in the catalysts, especially those prepared by sol-gel.
- Probe molecules adsorption followed by FT-IR, to evaluate Lewis acidity.
- Oxidant species detection
- Heterogeneity tests.

2.7. Outline of the thesis

The three following chapters of this thesis are papers published by Elsevier. Chapter 3 presents results on liquid phase oxidation of dibenzothiophene with alumina-supported vanadium oxide catalysts. As oxidative desulfurization with solid catalysts is a complex process that consists of a three-phase system (L-L-S): two liquid phases, which are diesel (apolar phase) and solvent (polar phase) and the solid catalyst. In order to simplify the process, liquid phase oxidation of dibenzothiophene (DBT) was studied as a model molecule for organosulfur compounds present in hydrotreated diesel. In this case, the reaction takes place only in the polar phase (solvent) where DBT has been previously dissolved, so the complexity of the system has been reduced to two phases (L-S). This way, it is possible to evaluate only the intrinsic activity of the catalyst.

Chapter 4 focuses on the oxidant agent – catalyst interaction. This can be studied with NMR using V^{51}, which has already been able to characterize a vanadium-H_2O_2 peroxocomplex. Another possible choice is to study the oxidant – catalyst interaction by a more accessible technique like IR spectroscopy. It is known that when using this technique, water has to be eliminated from the system, since it displays strong absorption bands that cover the spectrum of interest. That is why it is necessary to use another oxidant that practically does not contain water. Thus, the objective of this chapter is to study the interaction of tert-butyl hydroperoxide (TBHP) and V_2O_5 catalysts supported on alumina and zirconia using Infrared spectroscopy (IR). Catalysts were prepared by incipient wetness impregnation, since better dispersion of vanadium was observed along with good oxidation results.

In an attempt to obtain more information on the sulfoxidation mechanism, chapter 5 focuses on the coadsorption of TBHP and benzothiophene (BT) on vanadium catalysts supported on alumina followed by IR spectroscopy. Benzothiophene was used since it has higher vapor pressure than dibenzothiophene, which facilitates vapor adsorption on the catalyst. Finally a general discussion of all the results is made and conclusions are presented.

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Chapter 3.

Liquid phase oxidation of dibenzothiophene with alumina-supported vanadium oxide catalysts: An alternative to deep desulfurization of diesel.

Liquid phase oxidation of dibenzothiophene with alumina-supported vanadium oxide catalysts: An alternative to deep desulfurization of diesel.

1. Introduction

Refiners worldwide are substantially reducing sulfur levels in transportation fuels in order to meet current and upcoming regulations imposed in various countries. Depending on locality, some gasoline and on-road diesel sulfur concentrations will need to be less than 30 ppm, versus levels that may exceed 500 ppm today. As with past fuel specification changes, refiners and technology providers are finding resourceful solutions to comply with new, more stringent fuel specifications [1-2]. Dibenzothiophene derivatives are the predominant sulfur species remaining after hydrodesulfurization [2]. Oxidative desulfurization (ODS) wherein the dibenzothiophene derivative is converted to its corresponding sulfone is an approach that is being actively pursued using a variety of different methodologies [3]. ODS is a current process and has been discussed recently in previous publications [4-12], where the oxidized sulfur compounds can be removed from the hydrocarbon phase by extraction or precipitation. The sulfones are highly polar compounds and are easily separated, during ODS process, from the fuel product by extraction [10]. In that study, the sulfones were obtained predominantly in the solvent phase, and activity profiles describe a consecutive process scheme, being the dibenzothiophenes (DBTs) extracted the intermediate "product":

$$\text{DBTs}_{\text{(diesel)}} \rightarrow \text{DBTs}_{\text{(solvent)}} \rightarrow \text{Sulfone}_{\text{(solvent)}}.$$
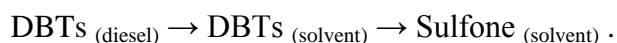
Hence, liquid phase oxidation of sulfur compounds is the basis of the ODS process, since extraction step occurs in a few minutes and oxidation is the rate determining step.

Vanadium oxide has demonstrated to improve S-compounds oxidation, thus it has been used as active phase in our recent studies [10-12]. In these studies we evaluate vanadium-based catalysts with different supports [12], which show high activity for sulfur removal of actual Mexican diesel, and for a model diesel with N-compounds [11]. In order to improve the activity of these catalysts, this work evaluates different preparation methods of V_2O_5/Al_2O_3, concerning their catalytic performance in the liquid phase oxidation of dibenzothiophene, which is the basis of the ODS process.

2. Experimental

2.1 Catalyst preparation

VO_x/Al_2O_3 catalysts with various vanadium loadings were prepared by thermal spreading (TS), incipient wetness impregnation (IWI) and sol-gel (SG). Preparations by TS consisted in intensive mixing and manual milling of vanadium pentoxide (J.T. Baker) and γ-Al_2O_3 (Gilder). The solid mixtures were subsequently calcined at 500°C during 8 h.

Other catalysts were prepared by IWI of Al_2O_3 with solutions of ammonium metavanadate (Sigma-Aldrich, 99%) dissolved in aqueous oxalic acid 2M (Aldrich, 97%). After 12 h of aging, catalysts were dried at 100°C during 24 h and calcined at 500°C during 8 h.

Sol-gel catalysts were prepared by mixing, at 60°C, vanadium (III) acetyl-acetonate ($V(acac)_3$. Aldrich, 97%) with 1M solutions of aluminum tri-sec-butoxide (Aldrich, 97%) dissolved in 2-butanol (Fluka, 99.5%). After complete dissolution of $V(acac)_3$ was achieved, the mixture was cooled to room temperature and a stoichiometric amount of water (H_2O: $Al[OCH(CH_3)C_2H_5]_3$, 3:1) was added to perform hydrolysis. The obtained gels were dried at 120°C during 24 h and consequently calcined at 500°C during 5 h.

Catalysts labels are composed by a number that stands for the nominal percentage of V_2O_5 on alumina (VA), and the last two or three letters for the preparation method, i. e. 10VATS.

2.2 Catalyst characterization

Textural properties of the catalysts were obtained by N_2 adsorption–desorption isotherms of the samples, with a Tristar Micromeritics apparatus. Nitrogen physisorption isotherms were analyzed using the BJH and BET method. Prior to the textural analysis, the samples were outgassed for 8 h in vacuum at 350 °C. Elemental composition was determined by SEM-EDX in a Jeol JSM-5900 LV microscope equipped with an energy dispersive X-ray (EDX) elemental analysis system. Catalysts were further characterized by: X-ray diffraction (XRD) using a Siemens D500 powder diffractometer with Cu Kα radiation. The FT-Raman spectra of catalysts were taken at ambient conditions in a Thermo- Nicolet Almega Dispersive Raman spectrometer with a resolution of 4 cm^{-1} and 500 scans per spectrum. A conventional temperature programmed reduction (TPR) apparatus was used to study the reducibility of the catalysts. TPR of the catalysts was performed using a flow of H_2/Ar mixture (30% H_2, v/v, 25 cm^3/min) at atmospheric pressure, 0.25 g of sample and a heating rate of 10 °C/min from room temperature to 1000 °C. Diffuse reflectance spectra were

collected with a Cary 500 Scan UV-Vis-NIR Spectrophotometer at room temperature with a Halon white reflectance standard as baseline. Before the analysis, the samples were pretreated at 100 °C during 5 days in static air, except NH_4VO_3 due to its known decomposition into V_2O_5 and NH_3 at this or higher temperatures. This compound was only dried at room temperature with desiccant. IR spectra were performed on a Nicolet Magna 760 Fourier Transform Spectrometer with a resolution of 2 cm^{-1} and 300 scans. For IR experiments, wafers of pure catalyst were made and outgassed under vacuum in a special IR cell at 450 °C during 1 h to physically remove adsorbed impurities from the catalyst sample. After that, the sample was cooled up to room temperature and then 12 Torr of pivalonitrile (PN. Aldrich, 98%) were introduced and the corresponding spectrum was taken. The cell was outgassed from room temperature up to 200 °C and spectra were collected after each evacuation. All spectra were normalized to wafers weighing 15 mg.

2.3 Catalytic Experiments

A glass batch reactor jacketed in a thermostatically controlled water bath, fitted with a condenser, mechanical stirrer and a thermocouple, were used to carry out the oxidation reaction. In a typical run, the mixture containing 2196 S-ppm of dibenzothiophene (Aldrich, 98%) dissolved in acetonitrile (J.T.Baker, 99.99 %) was added. When the desired temperature was reached and stabilized the solid catalyst and H_2O_2 (PQF, 30% wt.), with an initial O/S molar ratio of 4.5, were introduced into the reactor with vigorous stirring. ODS reactions were carried out at 60°C and atmospheric pressure. Reaction products were analyzed with an HP5890 Series II Gas Chromatograph with a PONA capillary column (Methyl silicone Gum, 50 m x 0.2 mm x 0.5 μm film thickness). Reactant and product identifications were achieved by comparing retention times in GC-FID and, from results obtained with a GC-PFPD (Varian CP-3800) and GC–MS (HP5890 Series II with MS detector). H_2O_2 profiles were measured by standard iodometric titration.

3. Results and Discussion

3.1 Catalyst characterization

Elemental analysis by SEM-EDX shows that the composition is similar to nominal contents presented in Table 1. Textural properties of the prepared catalysts by TS and IWI present a normal behavior as V is incorporated on the support (see Table 1), wherein surface area and

pore volume decrease according to V loading increase, while average pore is practically constant. But with SG method, V precursor was incorporated during preparation of the support, which permits to obtain a mixed oxide with small pores and higher surface area.

Table 1. Textural properties of support and catalysts.

	BET Area (m²/g)	Pore Vol. (cm³/g)	Average Pore Size (Å)	Surface density (V/ nm^2)
Al_2O_3	206	0.39	76	---
5VATS	181	0.37	82	1.67
10VATS	171	0.35	81	3.28
15VATS	158	0.33	82	4.89
20VATS	147	0.3	82	6.50
5VAIWI	198	0.37	75	1.61
10VAIWI	180	0.33	74	3.21
15VAIWI	164	0.31	75	4.82
20VAIWI	150	0.28	76	6.43
8VASG	479	1.22	32	1.24 *
15VASG	512	0.49	31	2.33 *
26VASG	388	0.22	< 26	4.03 *

* Calculated from the V/Al molar ratio of the mixed oxide and the BET area of the alumina prepared by SG

XRD results (Figure 1) show that all catalysts prepared by thermal spreading present the main diffraction peaks attributable to crystalline V_2O_5, in $2\theta = 15, 20, 22, 26, 31, 32$ and $34°$ [13]. While catalysts prepared by incipient wetness impregnation do not show any diffraction peak characteristic of V_2O_5 up to 15%, where the diffraction peak in $2\theta = 20$ and $26°$ slightly appear. Catalysts prepared by sol-gel (not shown) did not show any crystalline phases. Raman spectroscopy under ambient conditions further confirmed this result by showing well-defined peaks of V_2O_5 localized at 993, 695, 515, 477, 403, 281 and 141 cm^{-1} in catalysts prepared by TS and 20VAIWI. 15VAIWI displays two broad peaks at 993 and 141 cm^{-1}. These peaks are indicative of microcrystalline V_2O_5 particles [14]. As observed by XRD, raman spectra of sol-gel catalysts (not shown) do not display any characteristic

peak of crystalline V_2O_5. Only a broad peak around 925 cm^{-1} is observed, which increases intensity with vanadium loading.
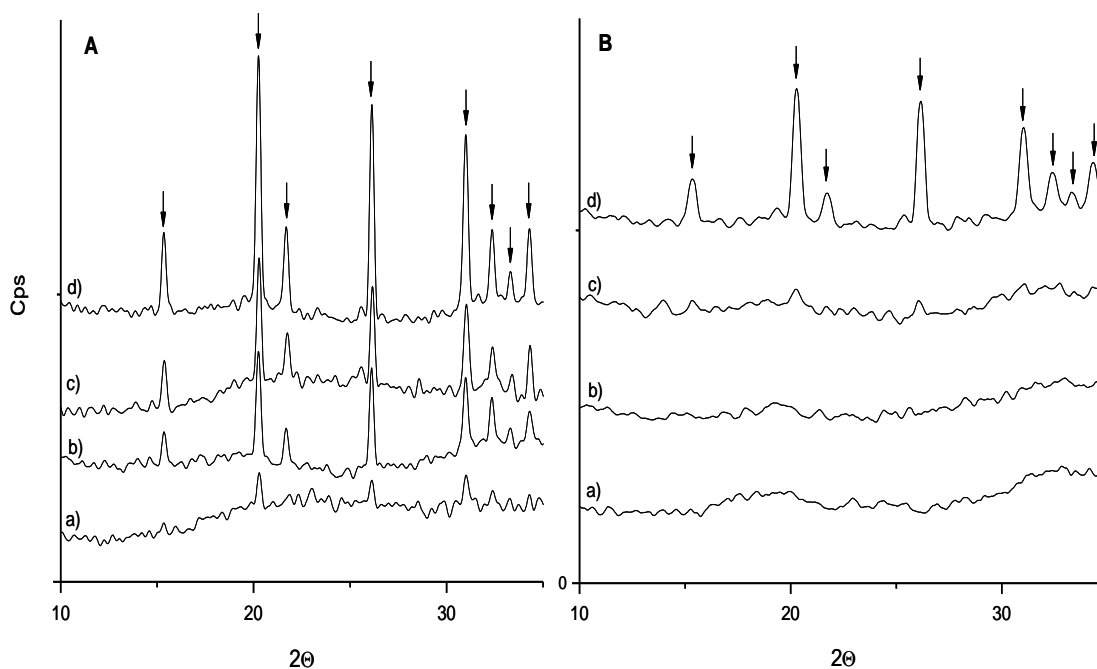

Figure 1. XRD patterns of VO_x/Al_2O_3 catalysts prepared by (A) TS and (B) IWI, with (a) 5%, (b) 10%, (c) 15% and (d) 20% of V_2O_5.

The broadness of this peak increases and a slight shoulder at 993 cm^{-1} is observed in 26VASG. This frequency matches with the main peak of V_2O_5 suggesting the presence of microcrystallites. A peak at ~940 cm^{-1} in VO_x/Al_2O_3 catalysts has been previously assigned [14] to surface metavanadate species (($VO_3)_n$). In order to clarify this assignment, the Raman spectrum of pure crystalline ammonium metavanadate was taken as reference and it displayed a sharp peak at ~920 cm^{-1} (Fig. 2) as well as other peaks at 896, 647, 495, 387, 321, 262 and 217 cm^{-1}. Thus, the band at 920 cm^{-1} suggests the presence of polymeric metavanadate species. The spectrum of V_2O_5 is also shown in order to simplify the assignment.
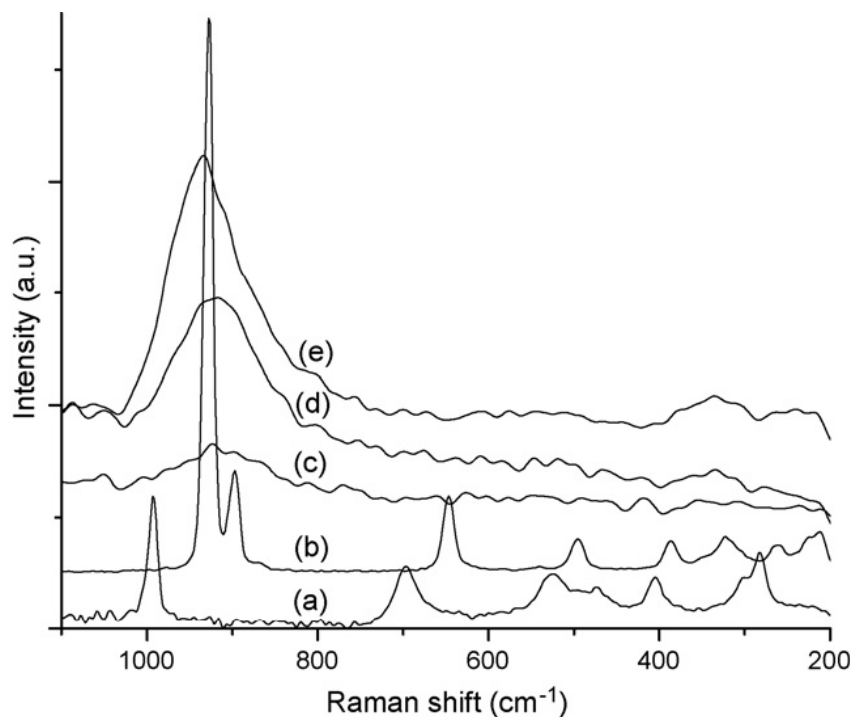
Figure 2. Raman spectra under ambient conditions of: (a) crystalline V_2O_5, (b) crystalline NH_4VO_3, (c) 8VASG, (d) 15VASG and (e) 26VASG. (a) and (b) spectra were divided by a factor of 10.

Temperature-programmed reduction (TPR) has provided very useful information on the nature and the strength of the interaction between supported species and support, and it has shown to be a sensitive technique for studying reducibility of V species [15]. Figure 3 shows the TPR profiles of the catalysts. Thermal conductivity detector (TCD) signal of TPR experiments is calibrated by reduction of a high purity V_2O_5 sample, which is precisely the active phase of these catalysts and it was taken as reference. Bulk V_2O_5 exhibits a well-defined reduction peak from 450 to 850°C, with temperature of reduction rate maximum (Tmax) at 645°C [11]. This peak is associated to the reduction of V(+5) to V(+3) species [15]. Supported vanadium oxide catalysts present similar reduction profiles at lower temperatures [12]. In this work, reduction peaks of alumina-supported vanadium oxide prepared by different methods start between 300 and 400°C. These temperature shifts can be attributed to the presence of more easily reducible highly dispersed V species on surface. TPR quantitative results show that the reduction degree is very high in the catalysts prepared by TS and IWI (more than 80 %) and it depends on the V loading. In general, if V

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loading increases Tmax increases and two reducible species are observed. At low surface coverage ($\upsilon<15\%$) a shoulder or small peak at $T<600°C$ was obtained, which could be attributed to monomeric and polymeric VO_4 units on the surface. At higher V content, the monolayer surface coverage was exceeded and V species were segregated showing a reduction peak at higher temperature.
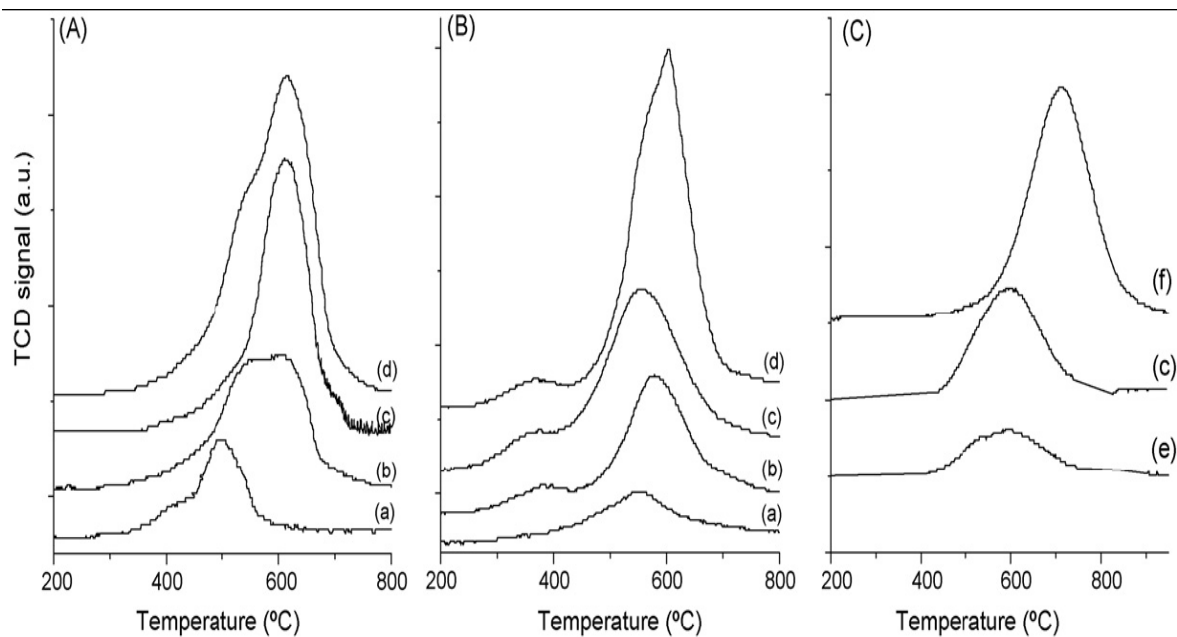

Figure 3. TPR profiles of VO_x/Al_2O_3 prepared by (A) TS, (B) IWI and (C) SG, with (a) 5%, (b) 10%, (c) 15%, (d) 20%, (e) 8% and (f) 26% of V_2O_5.

The reduction degree and Tmax of catalysts with the same V loading, prepared by TS or IWI method, were similar. But catalysts prepared by SG method present higher Tmax and lower reduction degree going from 41% for 8VASG to 73% for 26VASG. This result suggests a strong V species-support interaction, which is expected with this kind of preparation. Reducibility trend obtained for the catalysts with similar vanadium content was: 15VAIWI (88.5% and Tmax=558°C) > 15VATS (79.7% and 614°C) > 15VASG (51.8% and 608°C).
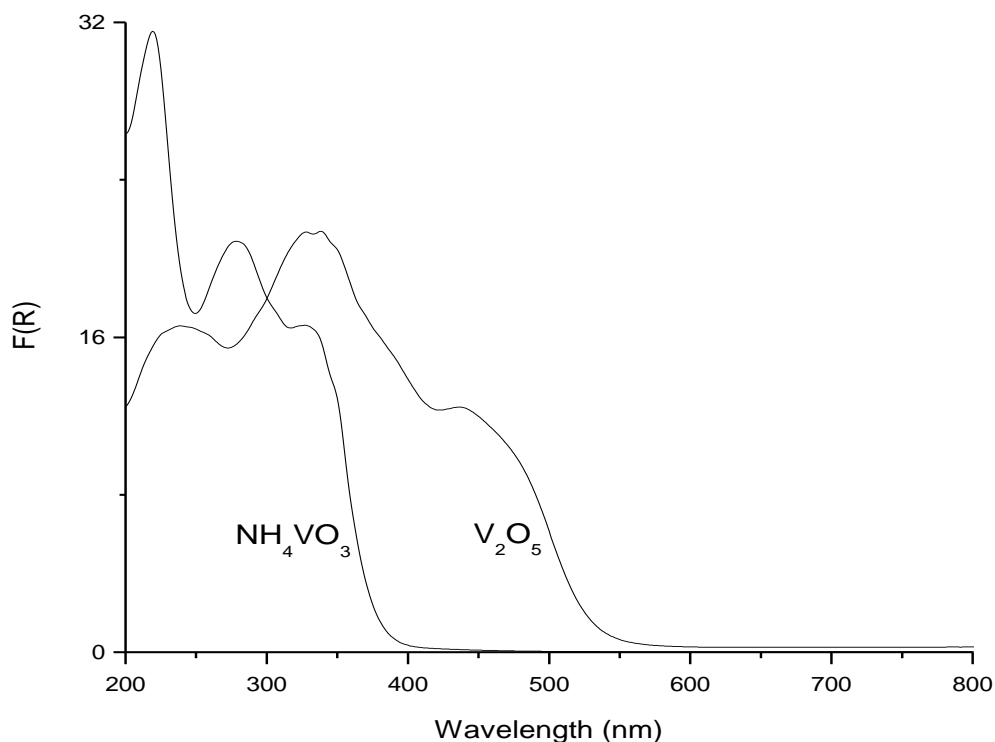
Figure 4. UV-Vis spectra of reference V^{5+} compounds.

In order to obtain information about V species coordination UV-vis DRS was performed. Electronic spectra of reference V^{5+} compounds are shown in Fig. 4. V_2O_5 is known to have a distorted octahedral coordination while chains of corner shared tetrahedral vanadate units compose ammonium metavanadate. From this figure, differences in band maxima and edge energy of these two compounds are clearly observed. Electronic spectra of catalysts prepared by TS and IWI are presented in Figure 5. These catalysts show a ligand to metal charge transfer (LMCT) band at 250 - 260 nm due to electronic transitions of $O^{2-} \rightarrow V^{5+}$ which can be assigned to tetrahedral V^{5+} species [16-18]. These bands are not all quite symmetrical and the region at higher wavelength becomes broader as V loading increases up to a point where two bands are clearly observed. The first band maxima shift to lower wavelength and the second band is centered at ~303 nm on catalysts with the highest loading. It has been reported [19] that the band maximum of the CT transitions of V^{5+} shifts to higher energy (lower wavelength) with decreasing coordination number and that the

polymerization of tetrahedral V^{5+} is only evidenced by a broadening of the absorption bands and/or a small shift of the absorption maxima to lower energy (higher wavelength).
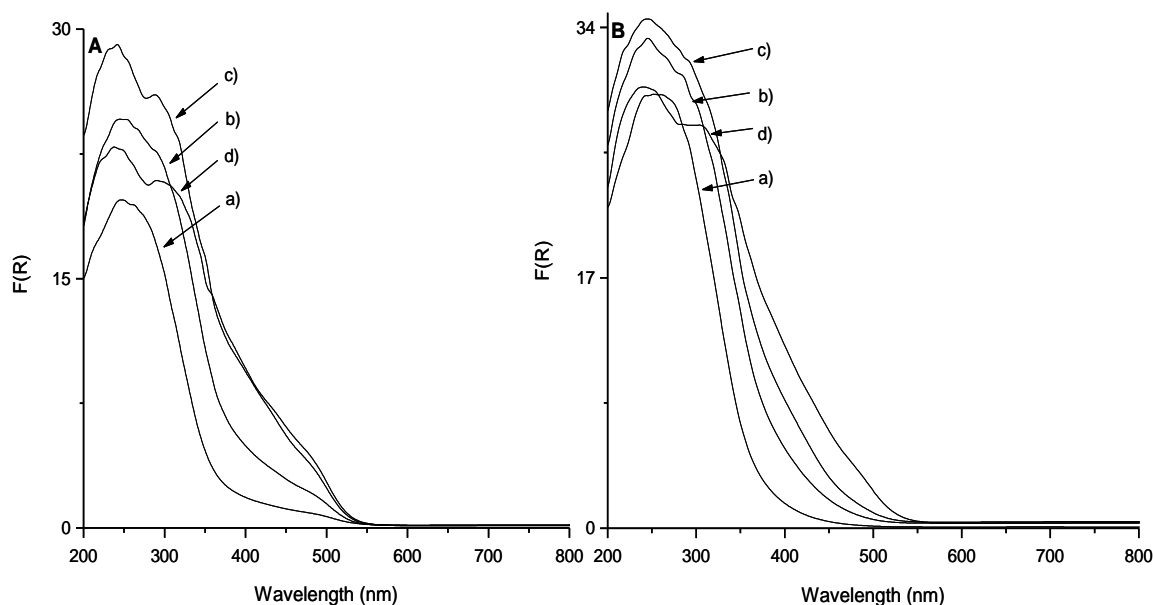

Figure 5. UV-Vis spectra of VO_x/Al_2O_3 prepared by (A) TS and (B) IWI, with (a) 5%, (b) 10%, (c) 15% and (d) 20% of V_2O_5.

These results indicate that these catalysts present a highly heterogeneous surface composed of tetrahedral vanadate species and possibly segregated octahedral V_2O_5–like species. It is also observed that all catalysts prepared by TS display a slight tail extending beyond 540 nm, which increases intensity with vanadium loading. This absorption can also be assigned to V_2O_5 crystallites, as observed by XRD, with higher coordination (VO_5, VO_6).

Figure 6 shows DRS spectra of sol-gel catalysts, which display two absorption bands at 218 and 268 nm. These bands change intensity with increasing vanadium loading and move towards higher wavelengths as it is observed with the first band of 26VASG, which reaches 238 nm.
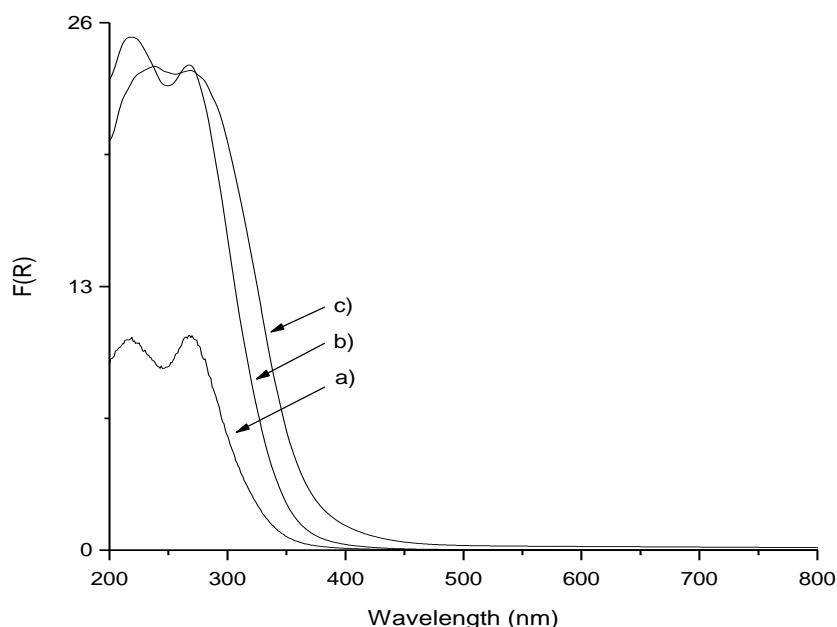
Figure 6. UV-Vis spectra of VO_x/Al_2O_3 prepared by SG, with (a) 8%, (b) 15% and (c) 26% of V_2O_5.

The bands resemble those of NH_4VO_3 that consists of chains of tetrahedral vanadate units, such a similarity was also observed by Raman spectroscopy. It is interesting to note that their edge energies are the highest of all catalysts prepared in this study, going from ~4 eV for 8VASG to 3.62 eV for 26VASG. No bands are observed due to d-d transitions of V^{4+}/V^{3+} metal cations (not shown), which occur as weak broad bands in the visible region $(10000 - 30000 \text{ cm}^{-1})$ [19-20].

IR spectra of adsorbed pivalonitrile (PN) on selected VO_x/Al_2O_3 catalysts were taken in order to evaluate Lewis acidity. PN is a weak base, and its IR spectrum is characterized by a strong band observed in the liquid at 2235 cm^{-1}, due to the stretching vibration mode of the C≡N triple bond. This band shifts to higher frequency when PN interacts with electron withdrawing centers through its nitrogen lone pair [21]. Figure 7 shows the IR subtraction spectra of adsorbed PN on VO_x/Al_2O_3. Two well defined bands with maxima at ~2294 and ~2245 cm^{-1} are observed. According to the literature [22] these bands have been assigned to PN coordinated (high frequency, HF) and hydrogen bonded to OH's groups (low frequency, LF). When outgassing temperature is increased, the IR band intensity decreases,

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being this effect more pronounced for VASG catalysts. After evacuation at 100°C, shoulders at ~2273 and at ~2240 cm^{-1} are observed, their assignment will be discussed later. It is also evident that the ratio between HF and LF band intensities changes with the catalysts preparation method and with V loading, especially for VATS and VASG catalysts. This behavior could be attributed to a higher amount of hydroxyl groups on the surface coming either from alumina support due to vanadium segregation or by polymerization of surface VOx species when V loading is increased from 5 to 15%.
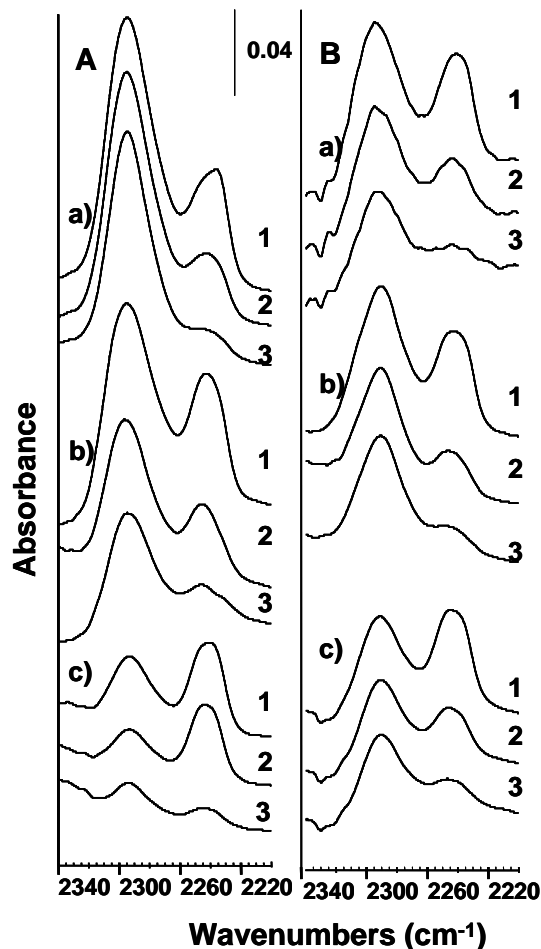

Figure 7. IR subtraction spectra of evacuated PN at: (1) room temperature, (2) 50°C and (3) 100°C on VO$_x$/Al$_2$O$_3$. (A) Low loadings: (a) 5VATS, (b) 5VAIWI and (c) 8VASG. (B) High loadings: (a) 15VATS, (b) 15VAIWI and (c) 15VASG.

The fundamental region in the subtraction spectra after PN adsorption (not shown) shows a negative band at ~1030 cm^{-1}, characteristic of stretching vibration mode of terminal V=O groups whose intensity decreases (as the band assigned to coordinated PN) and shifts to

higher wavenumbers with outgassing temperature. This means that the intensity of the band assigned to Lewis acidic sites must have the contribution of V^{5+} and Al^{3+} CUS.
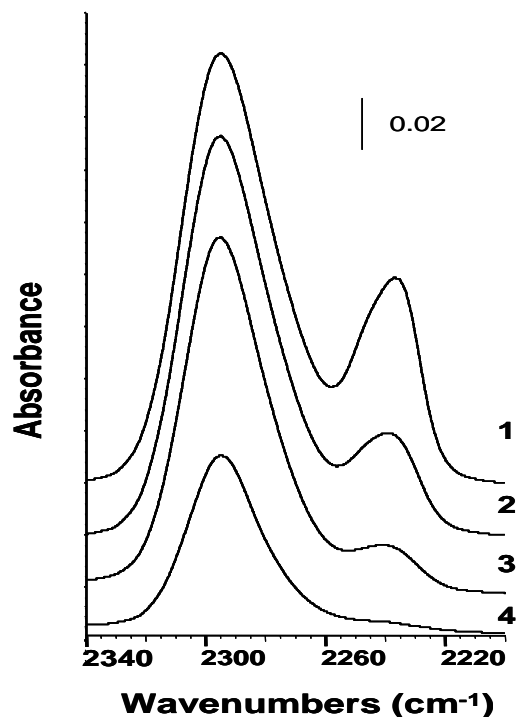

Figure 8. IR subtraction spectra of evacuated PN on Al_2O_3 at: (1) room temperature, (2) 50°C, (3) 100°C and (4) 200°C.

Table 2. H_2O_2 remaining after 30 min of reaction and Lewis acidity ratio.

	TS catalyst		IWI catalyst		SG catalyst	
V_2O_5 (wt.%)	H_2O_2 (%)	LAl/LV [a]	H_2O_2 (%)	LAl/LV	H_2O_2 (%)	LAl/LV
5	36.6	5.2	69.5	2.9	-----	-----
10	1.0	n.d.	3.7	n.d.	91.5 [b]	1.9 [b]
15	1.0	3.1	1.2	2.5	85.4	3.4
20	1.0	n.d.	1.2	n.d.	82.9 [c]	n.d.

(a) LAl/LV ratios calculated from the area under the curve of each IR band.

(b) 8 % and (c) 26 % of V_2O_5. (n.d.) Not determined.

Al_2O_3 and V_2O_5 are known to possess Lewis acid sites and their corresponding vibration frequencies with adsorbed PN are 2295 and 2280 cm^{-1}, respectively [22]. Subtraction IR Al_2O_3 spectra obtained after PN adsorption (Fig. 8) show indeed a broad peak at 2295 cm^{-1}

also composed by a shoulder at 2274 cm^{-1}. This can be assigned to the presence of two types of Al^{3+} coordinative unsaturated sites. In an attempt to distinguish between Lewis acid sites corresponding to vanadium and those of support, deconvolution of IR bands was made. The ratio of Lewis acid sites corresponding to Al (LAl) and V (LV) are presented in Table 2. It can be observed that LAl/LV ratio of TS and IWI catalysts decreases with increasing vanadium loading, which might be due to a higher amount of vanadium species that chemisorbs PN at coordinative unsaturated sites or defect sites. It is also observed that LAl/LV ratio of not well dispersed 5VATS is higher than well dispersed 5VAIWI. This indicates that for the later, a higher amount of LV sites is "available". Sol-gel catalysts do not show the trend observed with TS and IWI. The IR bands for these mixed oxides presented the lowest IR intensity indicating poor accessibility for PN adsorption. IR spectrum of adsorbed PN on 26VASG (not shown) displayed practically no Lewis acidity.

In summary, these catalysts characterizations show that the preparation method does affect V dispersion. Surface V^{5+} species are known to be independent on preparation method, when calcined during long time at higher temperatures than Tamman [23]. However, as stated above, the amount of each type of vanadium species con be varied with the preparation method.

3.2 Oxidative desulfurization (ODS)

Liquid phase oxidation of dibenzothiophene with H$_2$O$_2$ was carried out in presence of VO$_x$/Al$_2$O$_3$ as catalysts and acetonitrile as solvent. Full oxidation of dibenzothiophene was often reached, which results in high yield to dibenzothiophene sulfone (DBTDO) and practically no DBT sulfoxide. Activity results after 30 minutes of reaction with all catalysts, expressed as V/nm^2, are shown in Fig. 9. It can be observed that catalysts prepared by TS present higher activity at lower loadings than the ones prepared by IWI. The latter catalysts show a clearer increase in activity as V loading increases up to the monolayer, where the V$_2$O$_5$ phase begins to appear. Sol-gel catalysts have low oxidation activity and it decreases with increasing vanadium loading. It was stated in the previous section that all TS preparations presented V$_2$O$_5$ crystallites, while IWI catalysts presented better dispersed V-species and V$_2$O$_5$ crystallites begin to appear with 15% of V2O5. This fact suggests that V$_2$O$_5$ crystallites increase activity at low V loadings up to a point where

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bigger V clusters are formed and V "accessibility" is lowered. Sol-gel catalysts did not display crystalline phases, and correlations between V-species and performance are not straightforward in this case. IR spectra of adsorbed PN on these catalysts exhibit low Lewis acidity and it seems to decrease with increasing vanadium loading, although 15VASG does not follow this trend. H_2O_2 profiles were monitored in every reaction test and no clear changes in the percentage of H_2O_2 remaining after reaction were observed with TS and IWI (Table 2). Reducibility of these catalysts is over 80%, as observed by TPR, and it follows no trend either, which explains the low amounts of H_2O_2 after reaction in these cases. H_2O_2 titrations with sol-gel catalysts demonstrate that peroxide is not decomposed, since more than 80% of the oxidant remains in the system after reaction time (Table 2). Reducibility of these catalysts was rather low and it increases with vanadium loading, this is in agreement with the percentages of H_2O_2 shown in Table 2.
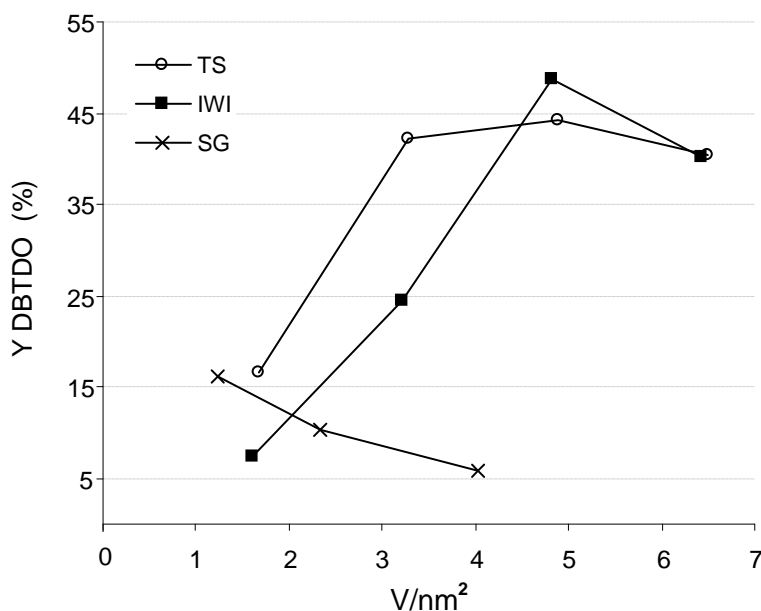

Figure 9. DBT sulfone yield (after 30 min. of reaction) in function of V surface density, for TS, IWI and SG catalysts.

As liquid phase reactions catalyzed by solids are known to involve leaching of the active phase [24-25], heterogeneity tests of some IWI catalysts were performed. These tests consisted in filtering the catalyst after 10 min of reaction at the same reaction temperature, then the filtrate is introduced into the reactor, and the homogeneous reaction is carried out.

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It was observed that partially homogenous reaction was taking place with 15VAIWI (4.8 V/nm^2) while 5VAIWI (1.6 V/nm^2) presented heterogeneous activity without leaching, as it can be observed in Figure 10. This might be due to the presence of "three legged" monovanadate species at such low vanadium loading [26], which agrees with the result obtained by TPR that shows only one reduction peak. Also, the final solution of the liquid phase oxidation of DBT when using 5VAIWI did not show any color indicative of leached V, as most of the solutions of the other catalysts did, except 8VASG and 15VASG. All catalysts prepared by TS undergo leaching of vanadium due to poor stability of V$_2$O$_5$ crystallites and surface polyvanadates in presence of polar molecules. Thus, it is believed that such higher activities obtained with low V loadings are due to homogenous activity of leached vanadium.
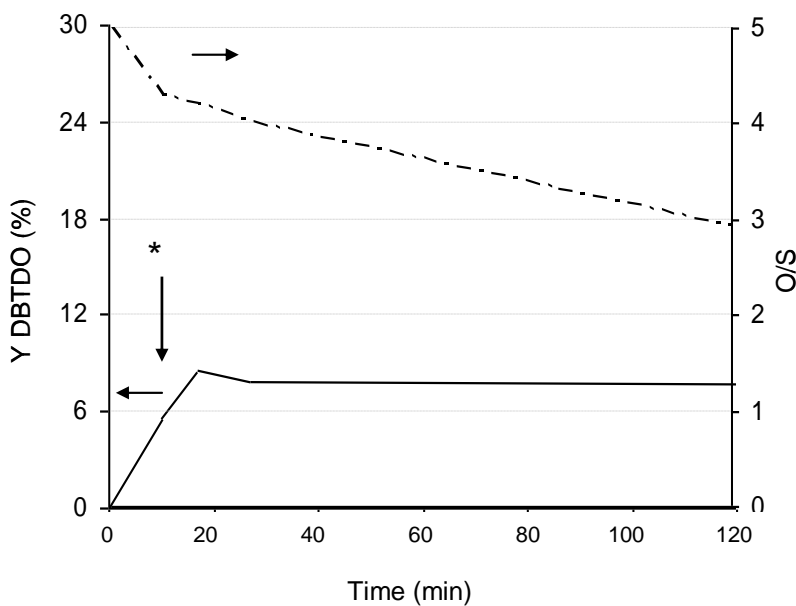

Figure 10. Heterogeneity test of 5VAIWI. Straight line corresponds to sulfone profile and dashed line to H$_2$O$_2$ profile. (*) Catalyst withdrawal at 10 min.

As it was described elsewhere [12, 25], these catalysts "activate" H$_2$O$_2$ by homolytic or heterolytic routes. In homolytic routes transition metals catalyze the free radical autoxidation process and undergo a change in oxidation state. Heterolytic routes involve complex formation of oxometal and peroxometal kind, where only the former involves a redox process. V^{5+} should typically follow the peroxometal route when catalyzing

heteroatom oxidations, acting as a Lewis acid to render the peroxidic bond more reactive. There lies the importance of discriminating between Lewis acid sites corresponding to alumina (LAl) and vanadium (LV), given that coordinative unsaturated vanadium species will most likely be able to form the oxidant peroxocomplex. It has been reported by Martinez-Huerta et al [27] that monomeric vanadium species possess stronger Lewis acidity than polymerized species, but with our catalytic tests no comparisons can yet be made regarding this topic because more polymerized species presented leaching of the active phase and catalytic activity in those cases could have involved homogeneous and heterogeneous contributions.

Vanadium species in sol-gel catalysts have shown to have a strong interaction with alumina as observed by their low reducibility in TPR. With these catalysts the amount of H_2O_2 in the system after reaction decreased with increasing reducibility (see Fig. 2 and Table 2), which suggests that OH^* radicals formed after H_2O_2 homolytic decomposition are not responsible of dibenzothiophene oxidation, since more reducible 26VASG presented the lowest activity. Hence, according to these results the vanadium peroxocomplex is the oxidant species responsible of dibenzothiophene oxidation. It was also observed that 8VASG seems to activate H_2O_2 more selectively as a high percentage of peroxide remains in the system after reaction and its activity is higher than that of 5VAIWI.

Conclusions

High liquid phase DBT oxidation activities were obtained with VO_x/Al_2O_3 prepared by TS and IWI methods. Catalysts prepared by IWI resulted in better dispersed V species than TS. SG catalysts have a strong interaction with alumina, and ODS activity decrease with increasing V loading while their reducibility exhibits a reverse trend.

IWI method produced a higher amount of vanadium Lewis acidic sites comparing with TS and SG methods according to PN adsorption results. Apparently the V Lewis acidic sites could be related to ODS activity.

Partially homogenous reaction was observed beyond 1.6 V/nm^2 with IWI and TS, which can be attributed to lower V-O-Al interaction of polymerized V species and V_2O_5 crystallites, while monovanadates have higher interaction with the support due to their three

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V-O-Al bonds. The proposed reaction pathway is the peroxocomplex formation as oxidant species since it does not involve a change in oxidation state of the metal.

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Chapter 4.

An FT-IR study of the adsorption and reactivity of tert-butyl hydroperoxide over oxide catalysts

An FT-IR Study of the Adsorption and Reactivity of Tert-Butyl Hydroperoxide over Oxide Catalysts

1. Introduction

Catalytic partial oxidation is largely applied in classical organic chemistry [1] as well as at industrial scale [2] for the conversion of organic reactants into more valuable and more oxidized products. Air is, quite obviously, the cheapest and greenest oxidant, being thus preferred, when possible [3]. However, in many cases the use of air or of pure oxygen is not possible, giving rise (even in the presence of catalysts) to total oxidation of the substrate or to unwanted products. Chemical oxidants can be used, alternatively. Hydrogen peroxide is considered to be a good alternative as an oxidant [4,5], in terms of low environmental impact as well as of selectivity in several cases. Another possible choice is the use of organic peroxides, among which tert-butylperoxide is one of the most usual. The behaviour of oxidants, including hydrogen peroxide and organic peroxides, is determined, in terms of selectivity to the desired product, by using appropriate catalysts.

When air or oxygen are used in oxidations over oxide catalysts, the surface oxide anions on the oxidized catalyst surface are most frequently considered to act as the active species [6-8]. In the case of oxidations performed with hydrogen peroxide in the presence of Ti-silicalite catalyst, the active species has been characterized as a side-on adsorbed peroxide species on Ti [9]. Much less is known, to our knowledge, on the adsorption and activation of organic hydroperoxides on solid catalysts.

In our recent studies [10-12], supported vanadium oxides have been used as catalysts of the oxidation of benzothiophenes and dibenzothiophenes to the corresponding sulphones, using hydrogen peroxide and tert-butyl hydroperoxide as oxidants.

$$\tag{1}$$
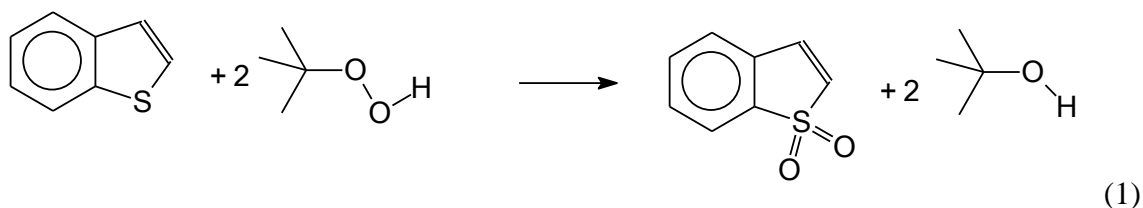
This reaction represents the first step of the so-called Oxidative Desulfurization (ODS) of fuels [13] which has been shown to be a promising alternative (due to its moderate process conditions and lack of hydrogen consumption) to conventional desulphurization processes

currently carried out in refineries [14,15], in view of a further decrease of the maximum allowed sulphur content in commercial fuels.

This reaction parallels the well established sulphoxidation catalytic activity typical of vanadium- containing enzymes [16], cyclodextrin inclusion compounds [17] and complexes [18], which is the object of much interest today. On the other hand, several other oxidation reactions, such as the hydroxylation of aromatic hydrocarbons to phenols [19], the epoxidation of olefins [20] as well as the oxidation of methylaromatics to the corresponding aldehydes [21], can be performed quite efficiently using V-containing catalysts and peroxide reactants. In all these cases, efforts have been undertaken to develop vanadium-containing solids as heterogeneous catalysts instead of homogeneous complexes, to obtain more efficient processes.

According to the literature [22,23], V^{5+} typically forms peroxometal complexes acting as a Lewis acid, thus activating peroxide species. A number of side-on bonded monoperoxo-, diperoxo- and even triperoxo- vanadium complexes have been prepared by reaction with hydrogen peroxide, and characterized. The complexation of vanadium ion with tert-butyl-hydroperoxide is reported to be far weaker than with H_2O_2 [24]. However, also tert-butyl-peroxo vanadium complex exists. The structure of VO(OOtBu)(dipic)(H_2O) (dipic = pyridine-2,6-dicarboxylate dianion, implies an asymmetric side-on coordination of tert-butyl hydroperoxide species, and pentagonal bipyramidal geometry around vanadium [25,26]. This complex is reported to be active in the oxidation of organic sulphides [27].

Similar complexes are expected to form on the surface of vanadium containing solid catalysts. However, to our knowledge, the experimental data concerning the interaction of alkyl-hydroperoxides with solid surfaces are very scarce if at all. To have more information on the mechanism of heterogeneously catalyzed oxidations with alkyl hydroperoxides, the details of the interaction of the oxidant with the catalyst should be investigated, e.g. with spectroscopic method. Infrared spectroscopy is a widely used technique for the surface characterization of metal oxide catalysts [28] as well as for the study of vapour-solid interactions and catalytic reaction mechanisms.

In this paper we present the results of the adsorption, from the vapor phase, of tert-butyl hydroperoxide (TBHP) over alumina and zirconia supported vanadia catalysts, which were found to be active for dibenzothiophene oxidation to the corresponding sulfone. To allow

the band assignment, we also investigated the adsorption of tert-butyl alcohol (TBOH) over the same catalysts. For completeness, the adsorption of both TBHP and TBOH over the pure supports has also been investigated.

2. Experimental

Tert-butyl hydroperoxide (TBHP, 5-6 M solution in nonane) and tert-butyl alcohol (TBOH, 99%) were purchased from Aldrich. γ-Alumina was obtained from Gilder with a surface BET area of 206 m^2/g while zirconia was obtained from Degussa with 50 m^2/g (81 % tetragonal, 19 % monoclinic from XRD analysis).

Vanadia supported catalysts were prepared by impregnation with solutions of ammonium metavanadate (Sigma-Aldrich, 99%) dissolved in aqueous oxalic acid 2M (Aldrich, 97%). After 12 h of maturation, catalysts were dried at 100°C during 24 h and calcined at 500°C during 8 h. Vanadia zirconia contains 2 %wt V while vanadia-alumina contains 5 %wt V both average loadings correspond to less than 1.9 V atoms/nm^2.

IR spectra were recorded on a Nicolet Nexus Fourier transform instrument, using pressed disks of pure catalyst powders (20 mg average wt., 1 in diameter), activated by outgassing at 673 K into the IR cell for 30 minutes. A conventional gas manipulation / outgassing ramp connected to the IR cell was used. The adsorption procedure involves contact of the activated sample disk with TBHP and TBOH vapors and outgassing in steps from r.t. up to 423 K.

3. Results and discussion

3.1. IR spectra of TBHP and TBOH.

In Fig. 1 the spectra of liquid and gaseous TBHP/nonane mixture are reported and compared with those of liquid and gaseous TBOH. The positions of the observed peaks are summarized in Table 1 where data arising from the literature are also reported. To our knowledge, a complete description, discussion and assignment of the IR spectrum of TBHP does not exist. The spectrum has been reported by Shreeve et al. [29] and by Zyat'kov et al. [30], The bands associated to the hydroperoxide group have been discussed by William and

Mosher [31] and by Vacque et al. [32]. The comparison with the spectrum of tert-butyl alcohol, widely described by Korppi Tommola [33] will also help.

Table 1. Fundamental vibrations of TBHP and TBOH.

Korppi Tommola [25]		Ramis et al [33]					Experimental results, Assigments made using Colthup			
TBOH (Ar matrix)	Assignment	TBOH (Monomer	Assignment	TBOH (liq)	TBHP (liq)	Assignment	TBOH (liq)	Assignment	TBHP (liq)	Assignment
3626.5 w	ν (OH)	3671		3472	3521	ν (OH)	3680			
3622.3 vw	ν25, end group						3613			
							3373	H bonded	3376	H bonded
2988 s		2974		3003	3049	ν (C-H)				
2973.1 s	νa (CH3)	2933	νa (CH3)	2597			2971	νa (CH3)	2977	νa (CH3)
2942.7 m							2934		2957	
2907.6 w	νs (CH3)	2904	νs (CH3)				2913	νs (CH3)		
									2925	CH2 νa (nonane)
2888.5 vw	νs (CH3)	2870	νs (CH3)				2873	νs (CH3)	2872	νs (CH3)
2875.5 vw									2855	CH2 νs (nonane)
				1647						
1490 vw	combination mode									
1476.6 w							1472	δa (CH3)	1463	δa (CH3), CH2 δ sci (nonane)
1469.3 w	δa (CH3)	1468	δa (CH3)	1466	1468	δ (C-H)				
1464.4 w		1456								
1450 vw	combination mode									
1391.6 w	δs (CH3)									
1372.5 s	δs (CH3)	1389	δs (CH3)	1368	1381	δs (CH3)	1381	δs (CH3)	1383	δs (CH3) (including nonane)
1367.1 s		1368			1366		1364		1364	
1328.2 s	δ (OH)	1330	δ (OH)							
1241.5	combination mode	1236	νa (CCC)	1238	1252	vibrations of tert-butyl structure	1239	ν (CC)	1245	ν (CC)
1213.5 vs	νa (CCC)	1208	νa (CCC)	1199	1193		1201	CCO ν oop	1194	CCO ν oop
1183 w	ν5, assoc. (CO)			1174						
1145.1 sh	ν (CO)	1142	ν (CO)							
1139.5 vs										
1027.1 vw	combination mode			1022	1031	uncertain origin	1022	n. a.	1029	n. a.
1019 vw	ν20, assoc. (CH3)									
1013.4 m	ρa (CH3)	1016	ρa (CH3)							
921.2 s										
914.6 vs	ρs (CH3)			916		uncertain origin	912	CCO ν ip	908	CCO ν ip
					889				888	n. a.
					846	related to OO			845	OO ν
				801		n. a.				
747.8 vw	νs (CCC)			750	747	uncertain origin	749	n. a.	747	n. a.
745.9 w										
									721	rocking (CH2) (nonane)
									526	COO δ
461 vw	combination mode									
456 w	δa (CCO)						466	δ (CC)	466	δ (CC)
418.3 vw	δs (CCC)						425		411	
344 w	δa (CCC)									
275.7 w	τ (CH3)									
226.9 m	τ (OH)									
222.5 s										

[a] Ref. [33], [b] Ref. [41], [c] Ref. [29], [d] This work.

3.2. IR spectra of the activated catalyst disks.

The spectra of the different catalytic materials used in this study, all recorded after activation by outgassing at 673 K, are reported in Fig. 2. The spectra of alumina and zirconia correspond to those reported in the literature. In particular, the OH stretching modes of the surface hydroxy groups are observed at 3768 and 3663 cm^{-1} for zirconia, their relative intensities being in agreement with the predominance of tetragonal zirconia [28] and at 3765 (shoulder), 3730, 3672 and 3580 cm^{-1} for alumina, quite typical of γ-Al$_2$O$_3$. In

both cases traces of impurities (carbonates, carboxylates) are found in the region 1700-1000 cm^{-1}.
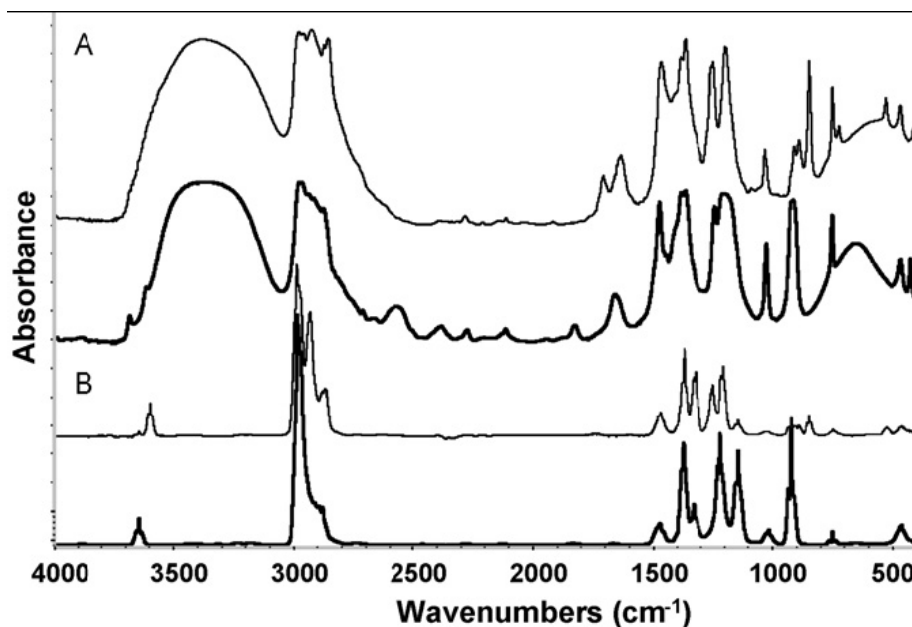

Fig. 1. FT-IR spectra of TBHP (thin lines) and TBOH (bold lines) on (A) liquid and (B) vapor phases.

The addition of vanadium causes mostly the appearance of sharp bands due to V=O bonds of vanadyl groups [34]. The fundamental V=O stretchings are observed at 1028 cm^{-1} for vanadia-alumina and at 1024 cm^{-1} for vanadia zirconia. In the latter case, where the bulk cut-off limit is at lower frequency, a broad band is also observed centered near 850 cm^{-1} which is likely due to V-O…Zr asymmetric stretching modes. At higher frequencies the first overtones of V=O stretchings [35] are also evident at 2040 and 2033 cm^{-1} for alumina and zirconia, respectively. These data, which agree with literature data, indicate that vanadium is in the form of pyramidal mono-oxo complexes in such low loading catalysts. The position of the V=O stretching modes at lower frequency on zirconia with respect to alumina point to the stronger basicity of the surface oxide species acting as ligands for the vanadyl complexes [36,37], on zirconia with respect to alumina [38].

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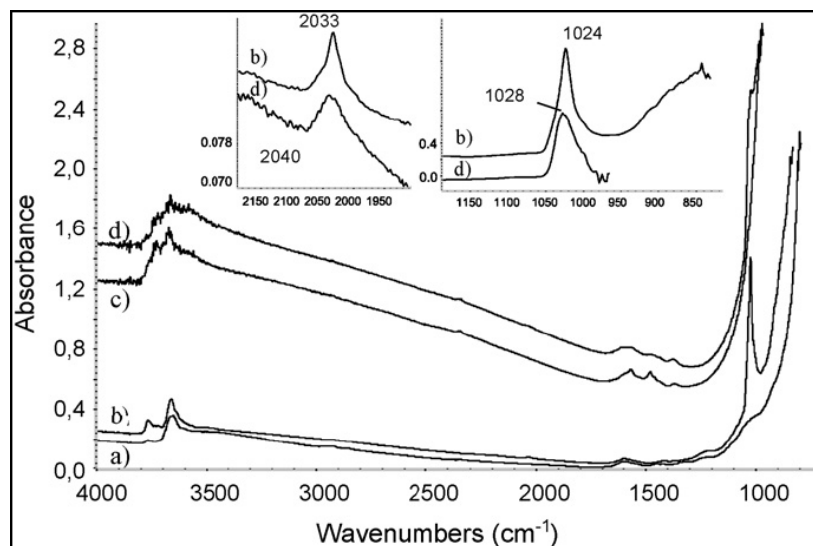
Fig. 2. FT-IR spectra of (a) ZrO$_2$, (b) VZ, (c) Al$_2$O$_3$ and (d) VA after activation. On top, inserts of the region of VO stretchings of vanadyl groups: first overtones (left) and fundamental (right, after subtraction of the spectrum of the pure supports).

3.3. IR study of the adsorption of TBHP and TBOH over zirconia.

In Fig. 3 the spectra relative to the adsorption of TBHP over zirconia are reported. Assignment of the relevant bands is summarized in Table 2. The spectrum obtained after contact of the vapour mixture with zirconia at r.t. (Fig. 3,a) shows a broad absorption in the region 3600 – 3000 cm^{-1}, due to the formation of hydrogen bonds between the molecule(s) and the surface. At lower frequencies, bands due to C-H stretchings (3000-2800 cm^{-1}), CH$_3$ asymmetric deformations (a split band at 1475 and 1466 cm^{-1}), CH$_3$ symmetric deformations (1387, weaker; 1366 cm^{-1}, stronger), C-C stretchings (1257 and 1245 cm^{-1}), C-O stretching (1193 cm^{-1}) and OO stretching (844 cm^{-1}) show that the spectrum is dominated by the features of adsorbed TBHP. All these features in fact resist short outgassing at r.t. (Fig. 3,b-d). A feature centered at 1325 cm^{-1} is likely due to the in plane OOH deformation of vapour TBHP, and disappears by brief outgassing. The spectrum of nonane (not shown) displays three sharp bands at 1460 (CH$_3$, CH$_2$ deformations), 1380 (CH$_3$, symmetric deformations) and 720 cm^{-1} (CH$_2$ rocking) besides the bands corresponding to C-H stretchings in the high frequency region. These bands are not evident.
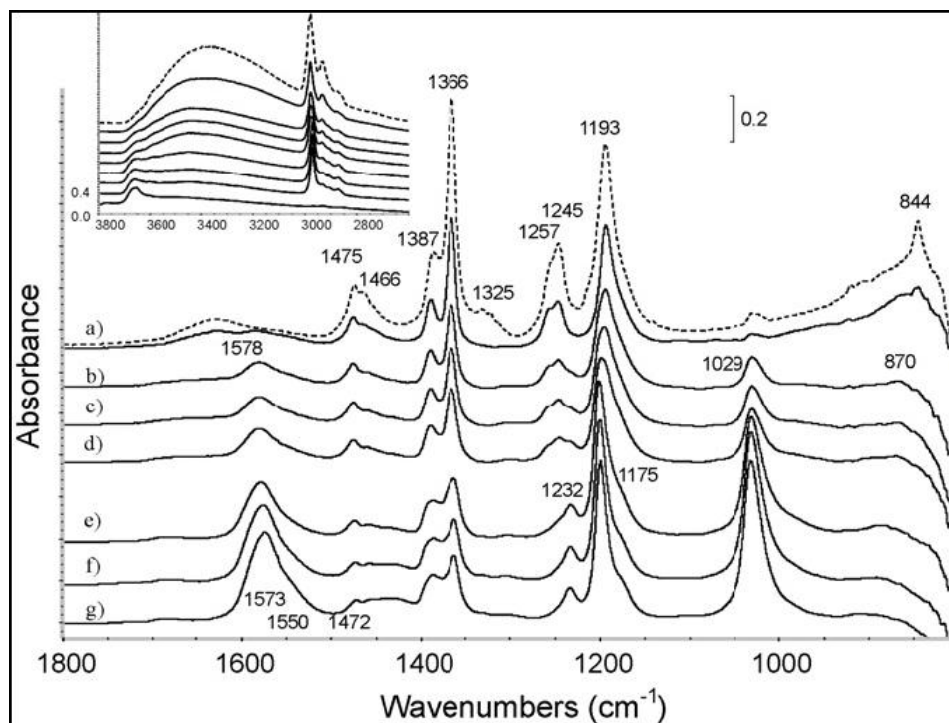
Fig. 3. FT-IR spectra of adsorbed TBHP over ZrO_2: non-evacuated (dashed line) (a) ev rt; (b) ev diff; (c) ev 15 min; (d) ev 30 min; (e) ev 330 K; (f) ev 373 K; (g) ev 423 K. The spectrum of the activated catalyst has been subtracted. In the insert: nonsubtracted spectra in the high frequency region. The spectrum on the bottom is the activated catalyst, the others are in the same order (a to g, from top down).

Table 2. Assignments of IR bands (cm^{-1}) of surface species on zirconia.

Assignment	Tert-butoxides	Adsorbed tert-butanol	Tert-butyl peroxides	Adsorbed tert-butyl peroxide
$\delta_{asym}CH_3$	1473		1475	
$\delta_{asym}CH_3$	1462		1466	
$\delta_{sym}CH_3$	1386		1387	
δCOH	-	1369	-	
$\delta_{sym}CH_3$	1361		1366	
δOOH	-	-	-	1325
$\nu CC/\nu CO/\rho CH_3$			1257	
	1233	1245	1245	
	1204		1193	1175
	1028	995		
νOO			870	845

51

On the other hand, this molecule has a much lower vapour pressure than TBHP (3.22 and 174 torr, respectively at 293 K [39,40]), which suggests that only a small amount of nonane is weakly adsorbed on the solid, if at all. By outgassing the sample from room temperature up to 423 K (Fig. 3,b-g) an evident reactivity of the adsorbed TBHP was observed. In the first spectrum recorded under evacuation (Fig. 3,b) the feature of OO stretching (845 cm^{-1}) of TBHP is still observed, although weaker, while an additional shoulder at 870 cm^{-1} is found. New bands at 1029 and 1578 cm^{-1} are observed which do not belong to TBHP species and increase intensity with outgassing time and temperature. After outgassing for 30 minutes (Fig. 3,d), the spectrum of the adsorbed species displays a new band at 1232 cm^{-1}. This band becomes more evident after outgassing at 330 K, since the doublet at 1257 and 1245 cm^{-1} disappears. Also the bands at 1387 and 1366 cm^{-1} change their shape and the C-O stretching at 1193 cm^{-1} sharpens clearly, losing its low frequency tail now reduced to a shoulder near 1175 cm^{-1}, which suggests that the TBHP molecule has been decomposed. The spectrum after treatment at 423 K (Fig. 3,g) shows a complete change. In the high frequency region, bands due to adsorbed C-H remain, but the broad absorption at 3600 – 3000 cm^{-1} is certainly decreased in intensity and the surface hydroxyl groups of zirconia have been partly restored. The low frequency region displays a broad band at 1573 with a shoulder at 1550 cm^{-1}, a weak absorption at 1472 cm^{-1}, a medium doublet at 1387 and 1363 cm^{-1}. The band at 1232 cm^{-1} is still observed and the shoulder at 1175 cm^{-1} becomes clearer. It is also observed that the strong band at 1029 cm^{-1} has continued to grow.

To have more information, we investigated the adsorption of tert-butyl alcohol over the same zirconia sample. The spectra obtained after adsorption of TBOH over zirconia (Fig. 4) are similar to those previously discussed for TBOH adsorption on titania [41]. A broad absorption due to the formation of hydrogen bonds between the molecule(s) and the surface is observed again in the range 3600-3000 cm^{-1} (Fig. 4,insert). In the range 3000-2800 cm^{-1} the bands corresponding to C-H stretchings are observed. In the lower frequency region, after outgassing at r.t. for 30 min (Fig. 4,d) we observe bands due to CH_3 asymmetric deformations (split at 1473 and 1462 cm^{-1}), CH_3 symmetric deformations (1386, weaker; ~1361 cm^{-1}, stronger), C-C / C-O coupled stretchings (weak band at 1233 cm^{-1}, a strong one at 1204 cm^{-1} with a weak component at its lower frequency side, and a strong band at 1028 cm^{-1}).

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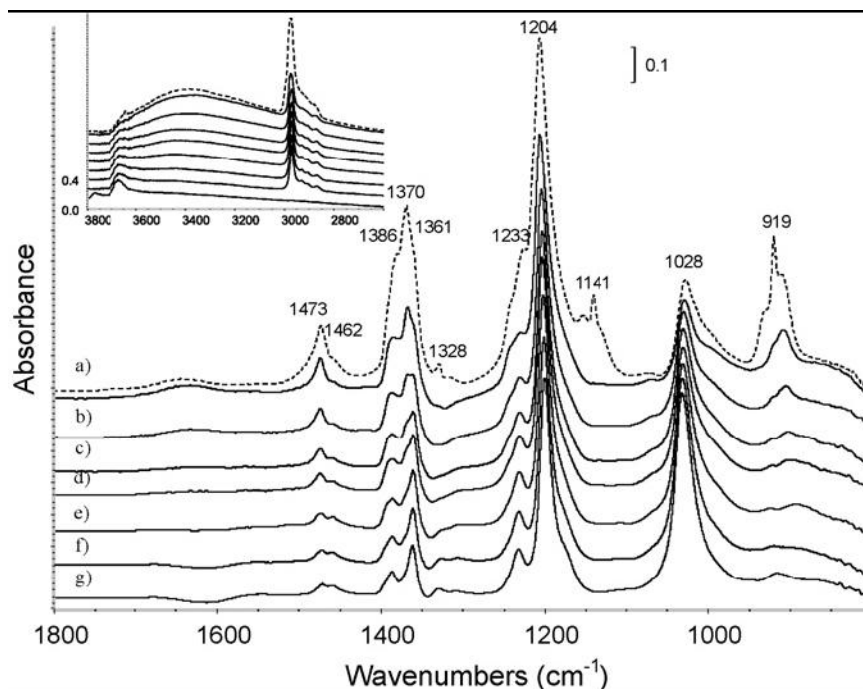Gomez-Bernal et al. Appl. Catal. A:Gen 369 (2009) 27

Fig. 4. FT-IR spectra of adsorbed TBOH over ZrO2: non-evacuated (dashed line) (a) ev rt; (b) ev diff; (c) ev 15 min; (d) ev 30 min; (e) ev 330 K; (f) ev 373 K; (g) ev 423 K. The spectrum of the activated catalyst has been subtracted. In the insert: nonsubtracted spectra in the high frequency region. The spectrum on the bottom is the activated catalyst, the others are in the same order (a to g, from top down).

Additional sharp bands at 1370, 1328, 1141 and 919 cm^{-1} disappear after the first evacuation, (Fig. 4,b) showing that they belong to vapour or very weakly adsorbed TBOH. Other features, like shoulders at 1245 and 995 cm^{-1} and independent bands at 1369 cm^{-1} and 900 cm^{-1} disappear slowly upon outgassing at r.t. (Fig. 4,b-d), showing that they are due to an adsorbed species that desorbs slowly at r.t. Upon outgassing, also the OH stretching mode (3600-3000 cm^{-1}) almost disappears. Moreover we remark that the band at 1369 cm^{-1} may be assigned to the COH in plane deformation mode of adsorbed undissociated TBOH previously reported at 1378 cm^{-1} for the corresponding species adsorbed on titania [41]. This suggests that adsorbed undissociated TBOH either desorbs or dissociates upon outgassing. In parallel the characteristic absorptions of the surface OH groups of zirconia are partially restored.

Outgassing at higher temperature (300-423 K, Fig. 4,e-g) only causes slight changes in the shape of the absorption bands, the more evident one involving the band at 1028 cm^{-1} which

increases in intensity and slightly shifts to higher wavenumbers (1032 cm^{-1}). The spectrum observed after outgassing at 423 K may be assigned entirely to adsorbed tert-butoxy-species.

We may now remark that the spectrum obtained after adsorption of TBOH and outgassing at 423 K (Fig. 4,g) is, in the regions 4000-3000 cm^{-1} and 1500-950 cm^{-1}, almost perfectly coincident with that observed after contact with TBHP and outgassing at the same temperature (Fig. 3,g). In particular, the unsplit weak component at 1232 cm^{-1} and the strong band at ~ 1030 cm^{-1} belong to tert-butoxy species and provide the proof that TBHP converted upon adsorption and mild heating under outgassing, into surface tert-butoxy species.

$$(2)$$
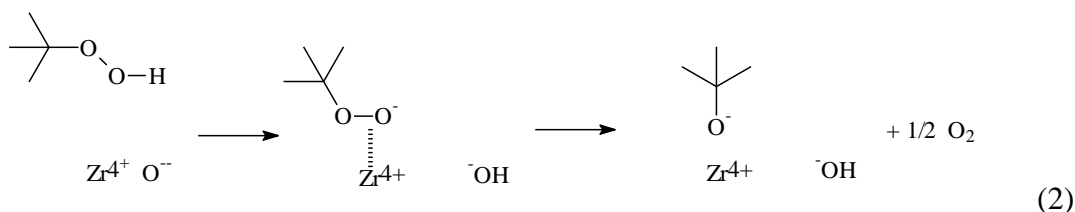
Additionally, after TBHP adsorption and mild heating an evident strong band is observed at 1578 cm^{-1} together a broad weak absorption in the region 1450-1400 cm^{-1}, which do not form after TBOH adsorption. The position of these absorptions suggest they are due to surface carboxylate anions (asymmetric and symmetric COO stretchings), like acetate species. The chemistry of the system is consequently, at least in part, a redox disproportionation reaction: tert-butylperoxide species (dissociated TBHP) convert into tert-butoxy species, oxidizing part of tert-butyl peroxide species. According to previous studies [42], the species resulting from deep oxidation of tert-butyl species are likely one acetate and two formate species. A possible stoichiometry for this reaction is the following,

$$(3)$$
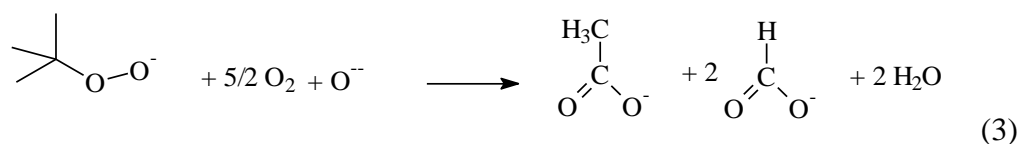
that implies five peroxo species needed to deeply oxidize a sixth one. More in detail, the IR spectra show that TBHP adsorbs at least in two forms. In Fig. 5,a the spectrum of species which are desorbed by very short outgassing at r.t. is reported. This spectrum is predominantly due to adsorbed undissociated TBHP. The O-O stretching is observed at 845 cm^{-1}, which is almost the same position found for the vapour but without the rotovibrational

components, as expected for an adsorbed species. In Fig. 5,d the spectrum of adsorbed tert-butoxide species, obtained by adsorption of TBOH and outgassing at 373 K is reported. In Fig. 5,b the spectrum of species present on the catalyst after TBHP adsorption and outgassing is shown, after subtraction of the spectrum of tert-butoxides. The subtraction is not perfect. In spite of this, we can say this spectrum is predominantly due to tert-butylperoxide adsorbed species. We note that the spectrum of this species shows a broad feature centered near 867 cm^{-1}. It is possible that this absorption is due to O-O stretching. In fact this feature is not present after adsorption of TBOH and disappears upon heating after adsorption of TBHP. In agreement with this assignment, the O-O stretching in vanadium tert-butylperoxo- compounds is reported to be shifted at higher frequency with respect to the position in TBHP, i.e. in the range 890-925 cm^{-1} [26].
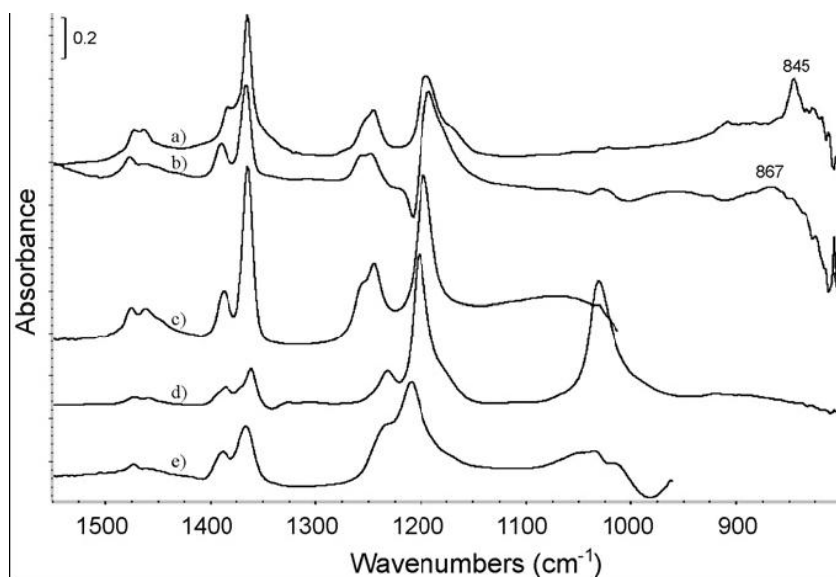
Fig. 5. FT-IR spectra of adsorbed species: (a) species after TBHP adsorption on ZrO2, desorbed upon short outgassing at r.t., corresponding to adsorbed molecular TBHP. (b) Species after TBHP adsorption on ZrO2, disappeared upon 30 min outgassing at r.t., corresponding mainly to adsorbed tert-butylperoxide species. (c) Species after TBHP adsorption on Al2O3, stable upon 30 min outgassing at r.t., corresponding mainly to adsorbed tert-butylperoxide species. (d) Species after TBOH adsorption on ZrO2, after 30 min outgassing at r.t., corresponding to adsorbed tert-butoxide species. (e) Species after TBOH adsorption on Al2O3, after 30 min outgassing at r.t., corresponding to adsorbed tert-butoxide species.

Adsorbed tert-butylperoxo species would later evolve by decomposition (to tert-butoxide species + O_2) and/or disproportionation into tert-butoxide and carboxylate species.

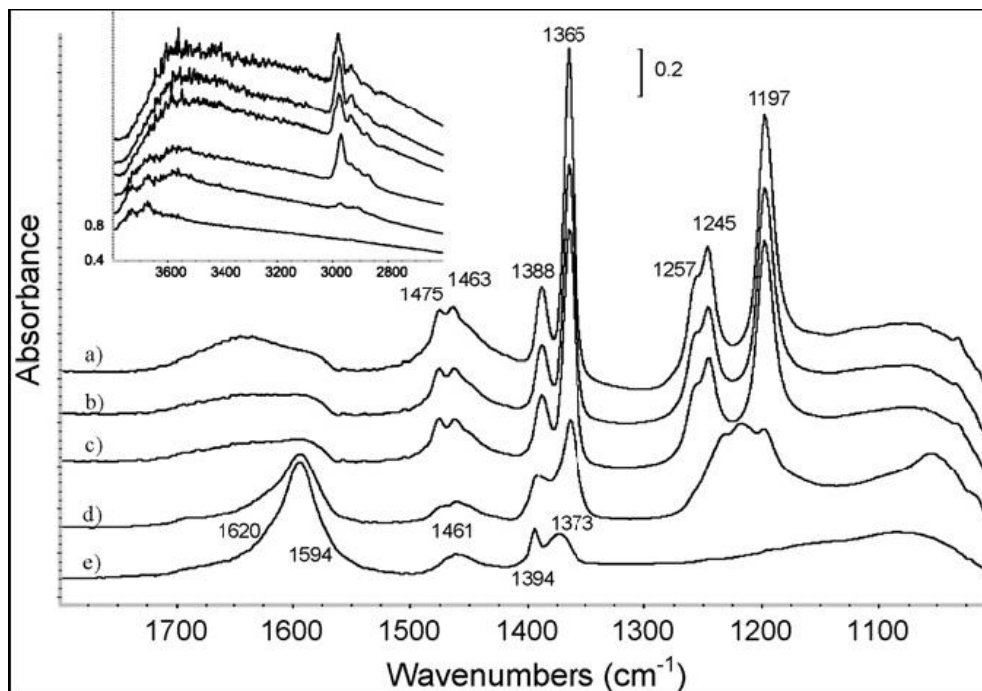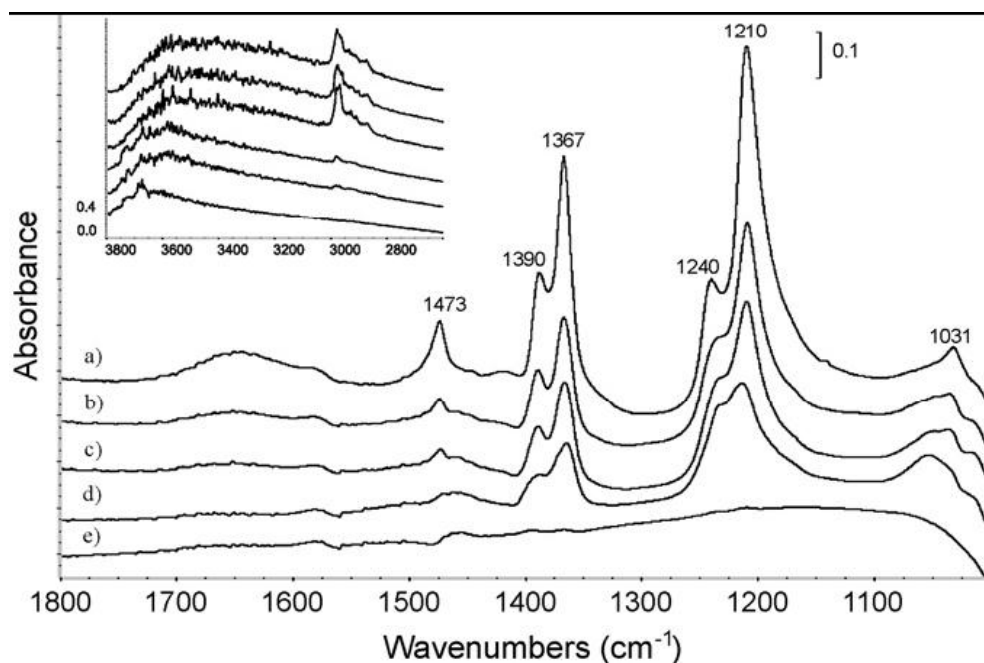### 3.4. IR study of the adsorption of TBHP and TBOH over alumina.

Fig. 6. FT-IR spectra of adsorbed TBHP over Al_2O_3: (a) ev rt; (b) ev 30 min; (c) ev 330 K; (d) ev 373 K; (e) ev 423 K. The spectrum of the activated catalyst has been subtracted. In the insert: non-subtracted spectra in the high frequency region. The spectrum on the bottom is the activated catalyst, the others are in the same order (a to e, from top down).

The spectra of adsorbed TBHP over alumina are shown in figure 6. Due to the spectra cut-off limit near 1000 cm^{-1}, alumina, does not allow the inspection of the region below this limit. The spectrum observed after contact at r.t. is closely similar to that observed on zirconia (Figs. 3 and 5,b, Table 2), showing again the formation of tert-butylperoxide species. However, the evolution with time presents remarkable differences. In fact, the spectrum does not modify significantly upon outgassing at r.t. and 323 K (Fig. 6,a-c) but transforms rapidly and deeply by outgassing at 373 and 423 K (Fig. 6, d and e). After this treatment, the features of adsorbed TBHP are fully disappeared while bands at 1594 cm^{-1} (strong and quite broad, with a shoulder at 1620 cm^{-1}), 1461, 1394 and 1373 cm^{-1} are

observed. The evident bands at 1594, 1394 and 1373 cm^{-1} closely correspond to those of formate ions (COO asymmetric stretching, CH bending, COO symmetric stretching [43]), while the broad feature at 1460 cm^{-1} and the weak component at 1620 cm^{-1} can be confidently assigned to acetate ions (COO asymmetric and symmetric stretchings). This agrees with the tentative stoichiometry reported in eq. (3), and with previous studies [42].

Also in this case, to have further information we studied the adsorption of TBOH on alumina. The spectra (Fig. 7) agree with those reported and discussed previously [44], and may be assigned to adsorbed tert-butoxy- species. Besides the CH$_3$ stretchings, in the region 3000-2800 cm^{-1}, we find the CH$_3$ asymmetric and symmetric deformations, C-C / C-O stretchings at 1473, 1390, 1367, 1240, 1210 and 1031 cm^{-1}, respectively. We can remark here that the positions of the C-C / C-O stretching modes are slightly higher on alumina than on zirconia (Table 2), and that some differences in the relative intensity also exist.
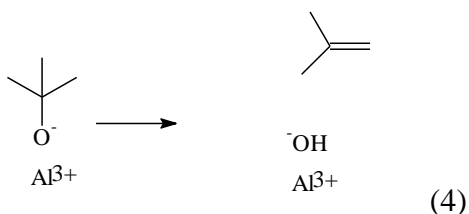

Fig. 7. FT-IR spectra of adsorbed TBOH over Al$_2$O$_3$: (a) ev rt; (b) ev 30 min; (c) ev 330 K; (d) ev 373 K; (e) ev 423 K. The spectrum of the activated catalyst has been subtracted. In the insert: non-subtracted spectra in the high frequency region. The spectrum on the bottom is the activated catalyst, the others are in the same order (a to e, from top down).

However, the spectrum fully disappears at 423 K, due to the decomposition of tert-butoxide species into isobutene and a surface OH group [44].

$$(4)$$

The data show that TBHP on alumina adsorbs dissociatively like on zirconia. However, it is still stable as tert-butyl peroxide species (Fig. 5,c) until 330 K and converts only above this temperature, giving rise again to oxidized species (formate and acetate ions) and, possibly, also to tert-butoxide species. Tert-butoxides, however, decompose completely on alumina already at 423 K giving rise to gas phase isobutene.
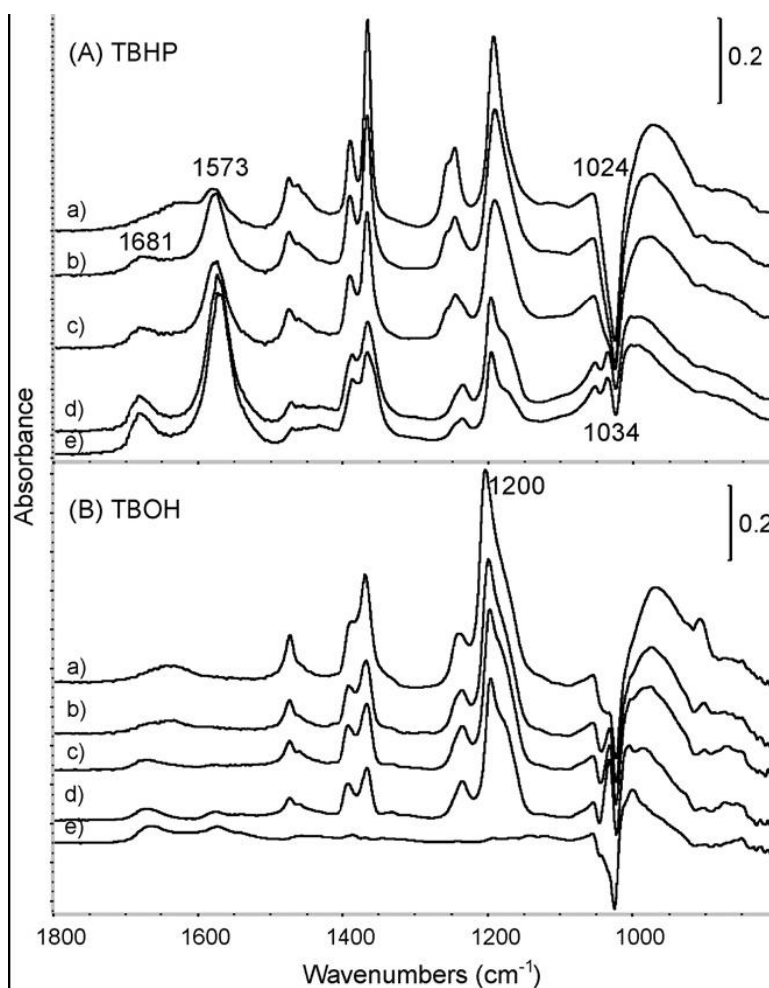

Fig. 8. FT-IR spectra of adsorbed TBHP (A) and TBOH (B) over VZ: (a) ev rt; (b) ev 30 min; (c) ev 330 K; (d) ev 373 K; (e) ev 423 K. The spectrum of the activated catalyst has been subtracted.

3.5. Adsorption of TBHP and TBOH over vanadia-zirconia catalysts.

The spectra of adsorbed TBHP on vanadia-zirconia catalyst on figure 8 (A) present all the features described on -zirconia (Table 2), along with relevant differences. The negative band centered at 1024 cm^{-1} in these subtracted spectra corresponds to V=O stretching of vanadyl species.
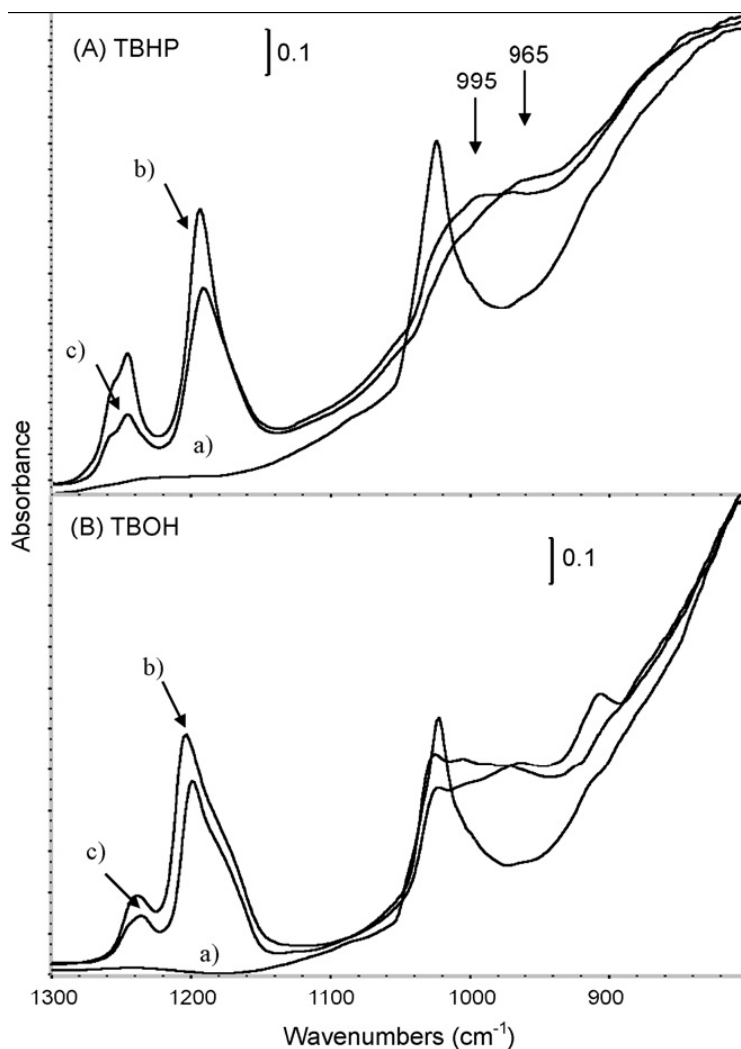

Fig. 9. FT-IR spectra of VZ catalyst after activation (a) and in contact with TBHP (Ab) and TBOH (Bb) and after outgassing at r.t. (Ac and Bc).

In Fig. 9 the region of fundamental V=O stretching mode is seen using unsubtracted spectra. It is evident that V=O stretching band is perturbed upon adsorption of TBHP and shifted to lower frequencies, giving rise to two unresolved components centered near 995 and 965 cm^{-1}. Also a faster reactivity of the peroxide is obtained as observed by formation

of the band at 1573 cm^{-1} already upon outgassing at room temperature (Fig. 8 (A),b). This band continues to grow with outgassing time and temperature, while simultaneously a weaker band at 1681 cm^{-1} is also formed, likely due to the formation of an adsorbed carbonyl species, most probably acetone.

$$\text{(structure with O—O}^-\text{)} \longrightarrow \text{(acetone, C=O)} \quad + \quad H_3CO^-$$

$$(5)$$
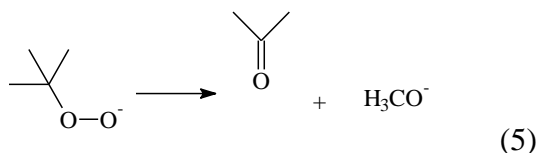
This is likely an intermediate step with respect to the reaction (3), methoxy groups being intermediates in formate ions formation.
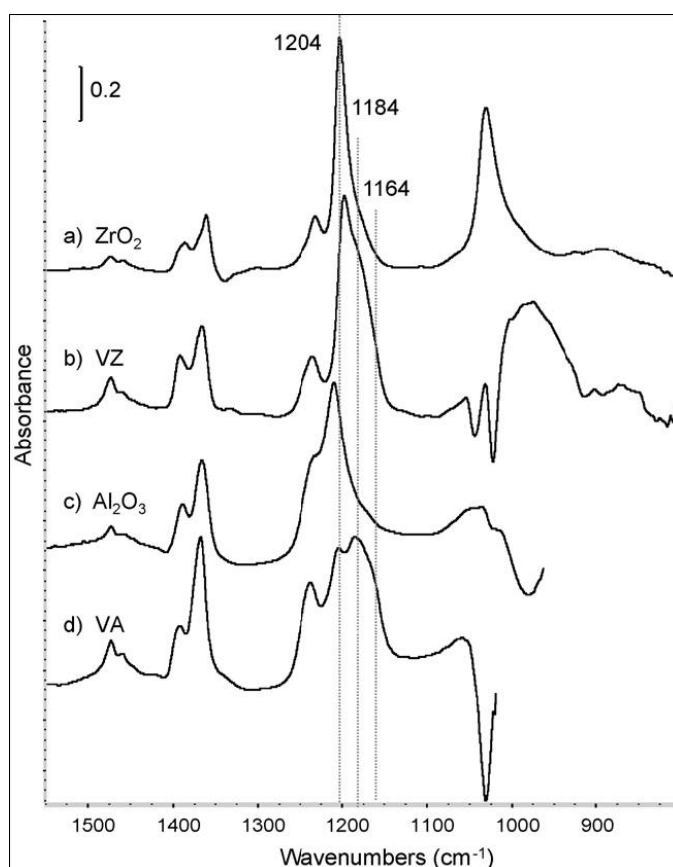

Fig. 10. Comparison of the FT-IR spectra of tert-butoxide species (after adsorption of TBOH) outgassed at 57 8C on ZrO$_2$, VZ, Al$_2$O$_3$ and VA.

By outgassing at 330 K, a shoulder at 1034 cm^{-1} comes out and increases intensity with thermal treatment (Fig. 8 (A), c-e). This absorption, superimposed to the negative vanadyl band, is ascribed to terbutoxy- species. In fact the spectrum in the region 1500-900 cm^{-1}

becomes very similar to that obtained with the adsorption of TBOH on the same surface (Fig. 8 (B)). The overall spectra obtained after adsorption of TBOH over vanadia-zirconia, with the characteristic shape of the absorption near 1200 cm^{-1}, is similar to that observed after adsorption of TBOH on vanadia titania [45], attributed to tert-butoxy groups. In Fig. 10 the spectra of tert-butoxy- groups observed on the four catalytic materials are shown. It is evident that the spectra of tert-butoxy- groups on V-containing solids are characterized by components in the 1200-1150 cm^{-1} range which are not present or much less intense in the spectra of tert-butoxy- groups on zirconia and alumina. This is also true for tert-butoxy groups on titania [41] and vanadia-titania respectively [45]. This is likely due to the fact that, on vanadium sites, quite covalent terminal alkoxy groups are formed, while on typically ionic oxides bridging and triply bridging species predominate, as discussed previously for methanol adsorption [7]. Ionic tert-butoxides may stand perpendicular to the surface with the C-O bond, thus the three methyl groups almost equivalent, in a highly symmetrical arrangement. Instead, for covalent alkoxides the C-O bond must bend with respect to the V-O bond, thus with a lower symmetry. This shows that vanadium sites participate to the adsorption of TBOH on these catalysts, as also confirmed by the shift of the V=O stretching band (Fig. 9), which is shifted again, down to near 995 and 965 cm^{-1}.

These data show that TBHP transforms even faster on vanadia-.zirconia than on zirconia (already at r.t.) with the formation of a carbonyl compound and carboxylate species, and producing also tert-butoxide species. It also seems that vanadyl complexes participate to the adsorption.

3.6. Adsorption of TBHP and TBOH over vanadia-alumina catalysts.

The spectra of TBHP (Fig. 11 (A)) and TBOH (Fig. 11 (B)) adsorbed on vanadia-alumina catalyst show that tert-butyl peroxide species are formed after TBHP adsorption, while tert-butoxide species are formed after TBOH adsorption. As discussed above and shown in Fig. 10, tert-butoxide species on VA show the features of vanadium tertbutoxides. In the case of both TBHP and TBOH adsorption, the perturbation of the vanadyl stretching band is shown, just above the transmittance cut-off limit. The negative band observed in the subtraction spectra is due to the shift to lower frequencies (i.e. below the cut-off) of this stretching mode, as observed above for vanadyl groups on zirconia. This is confirmed by

the analysis of the overtone band. Tert-butyl peroxide species react at 373 K converting into a carbonyl compound (band at 1689 cm^{-1}) and carboxylate species (band at 1594 cm^{-1} with a component near 1630 cm^{-1}). On the contrary, tert-butoxide species simply disappear by heating at 373 K, by decomposing into isobutene gas and a hydroxy group.
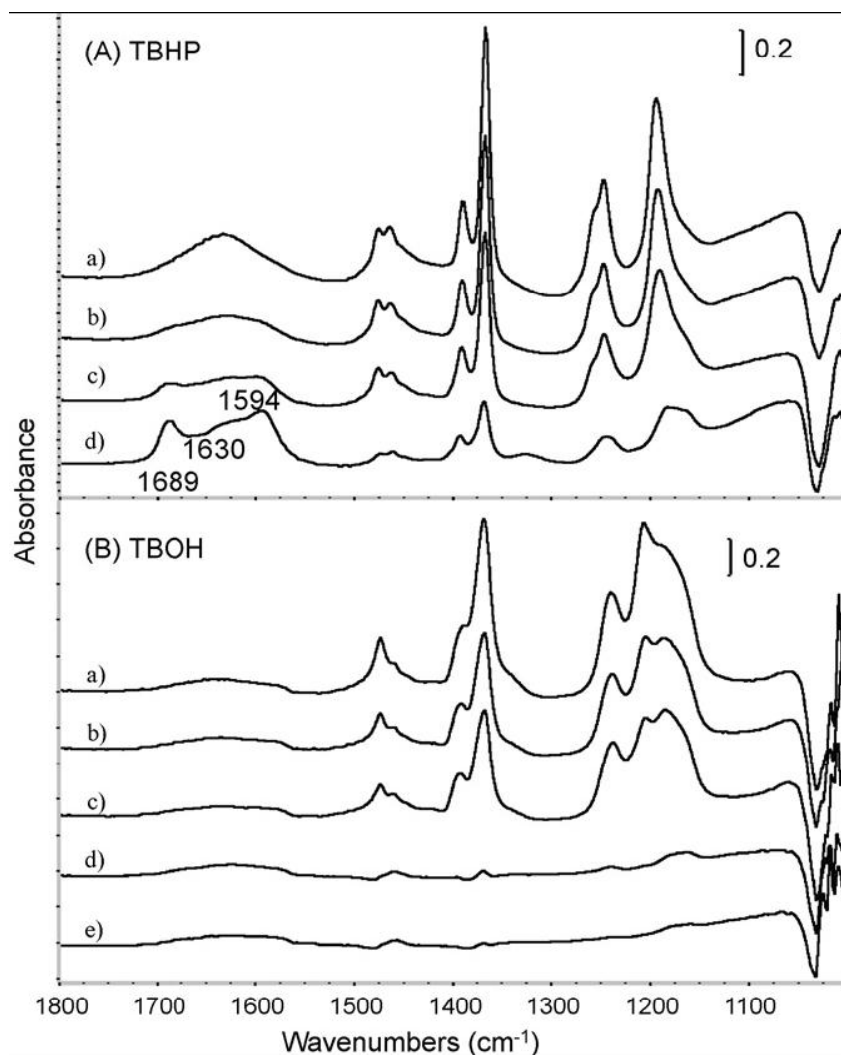

Fig. 11. FT-IR spectra of adsorbed TBHP (A) and TBOH (B) over VA: (a) ev rt; (b) ev 30 min; (c) ev 330 K; (d) ev 373 K; (e) ev 423 K. The spectrum of the activated catalyst has been subtracted.

3.7. An IR study of the conversion of TBHP vapor over VA catalyst.

To have more information on the chemistry of this system, we followed by IR the gas-phase species upon contact of TBHP on vanadia alumina.
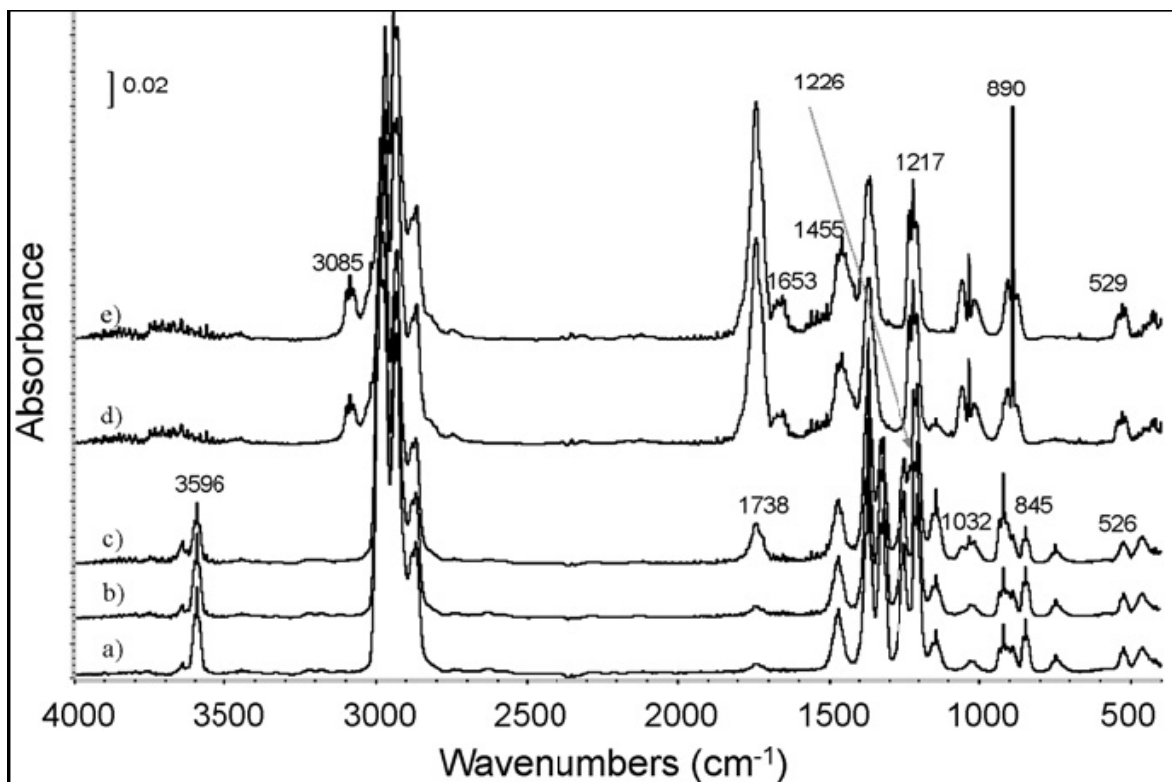
Fig. 12. Vapor FT-IR spectra of TBHP upon contact with VA at increasing temperatures: (a) rt; (b) 333 K; (c) 363 K; (d) 433 K; (e) 473 K.

Figure 12 shows the TBHP vapor spectra upon contact with VA from room temperature up to 333 K. TBHP spectra display the characteristic spectral features of the OOH group (i.e. νOH at 3596 cm^{-1}, νOO at 845 cm^{-1}, and δCOO(H) at 526 cm^{-1}) although a weak band corresponding to a carbonyl species is observed at 1738 cm^{-1}. Thermal treatment at 363 K (Fig. 12,c) results in an increase of the intensities of the bands at 1738, 1226 and 1032 cm^{-1}. The bands at 1738 and 1226 cm^{-1} correspond to vibrations of acetone (C=O stretching and CCC deformation modes, respectively) while the band at 1032 cm^{-1}, with its typical rotovibrational contour, belong to methanol (C-O stretching mode). This shows that TBHP decomposition reaction occurred in these conditions over the catalyst.

$$(H_3C)_3COOH \rightarrow H_3COH + (H_3C)_2C=O \qquad (6)$$
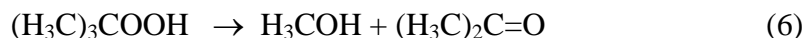
Which is the gas-phase reaction corresponding to the surface reaction (5). Further thermal treatment up to 473 K (Fig. 12,e), results in the total disappearance of the spectrum of TBHP vapor, while new bands at 3085, ~1653, 1455, 1217, 890 and 529 cm^{-1} appear,

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whose shape and frequency correspond to gaseous isobutene. In parallel, the spectrum of gaseous water is also observed. This provides evidence of the following reaction

$$(H_3C)_3COOH \rightarrow H_2O + (H_3C)_2C=CH_2 + 1/2\ O_2 \qquad (7)$$
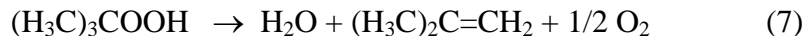
gaseous O_2 being undetectable by IR. Acetone and methanol vibrations are still observed at 473 K. We performed the same experiment without the presence of the catalyst: in this case features of tert-butyl alcohol, acetone, methanol and some characteristic bands of isobutene begin to appear at 573 K. This result is in partial agreement with literature data [46]. Our results show that VA catalyzes the decomposition of TBHP.
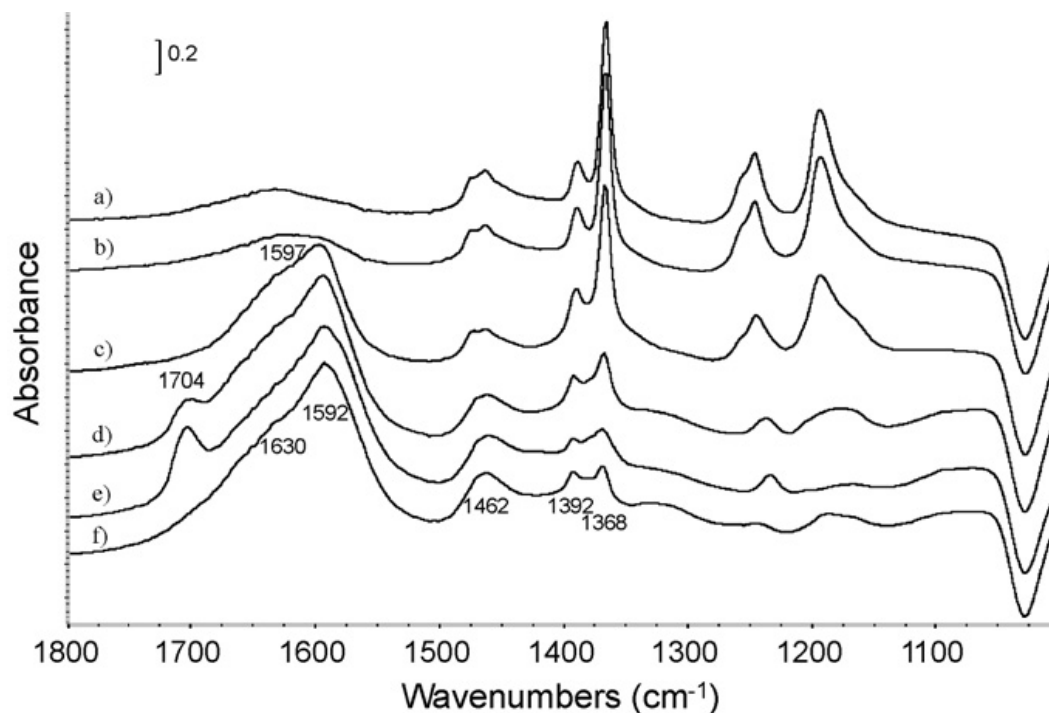

Fig. 13. FT-IR spectra of adsorbed TBHP on VA at increasing temperatures*: (a) rt; (b) 333 K; (c) 363 K; (d) 433 K; (e) 473 K; (f) outgassed. *All vapor spectra have been subtracted.

The spectra of the species adsorbed over the VA catalyst during this experiment are shown on figure 13. The spectral features are similar to those reported in Fig. 11 (A) but the intensities are quite different. The spectra are dominated by the features of tert-butylperoxide species until 333 K (Fig. 13, b), while carboxylate species (probably mostly formates, band at 1597 cm^{-1}) are additionally formed at 363 K (Fig. 13,c). In the temperature range 363-473 K (Fig. 13,c-e) the spectrum of adsorbed acetone (band at 1704 cm^{-1}) is additionally growing while the spectrum of tert-butylperoxide species progressively

disappears. Upon outgassing at 473 K (Fig. 13,f) adsorbed acetone disappears, the spectrum being now dominated by features of adsorbed formate ions at 1592, 1392, 1368 cm^{-1} and of other carboxylates (most likely acetates, shoulder near 1630 cm^{-1} and band at 1462 cm^{-1}). The parallel analysis of the spectra of the gaseous and surface species show that TBHP adsorbs dissociatively producing tert-butylperoxide species that react by disproportionation giving rise to the gas phase reaction (1) corresponding, at the surface, to the formation of adsorbed formates and acetone. It seems likely that surface methoxy groups are also formed, their spectrum being masked by the features of surface tert-butylperoxide species. However, surface methoxide species are at least in part converted into surface formate ions at very low temperature, as shown after adsorption of methanol over other V-containing catalysts [47].

Conclusions

The experiments described above allowed us to obtain the following conclusions;

a) The adsorption of tert-butyl hydroperoxide over zirconia, alumina, vanadia-zirconia and vanadia-alumina from gas phase produces small amounts of adsorbed undissociated species and predominant amounts of tert-butylperoxide species, by dissociative adsorption.

b) On the surface of zirconia tert-butylperoxide species convert, already starting from room temperature, into stable tert-butoxide species together with some carboxylate species.

c) The same reactivity is found over alumina but occurs at higher temperature (373 K). Additionally, on alumina tert-butoxide species are not stable, producing isobutene gas and leaving on the surface a mixture of formate and acetate species, as shown in Fig.6.

d) On vanadia-zirconia, the formation of acetone and carboxylates occurs at r.t., while tert-butoxide species form at 373 K. These species decompose at 423 K.

e) On vanadia alumina the formation of acetone and carboxylates (formates + acetates) is also observed, but occurs at higher temperature (373 K), when tert-butoxides already decompose.

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f) Vanadia - alumina catalyzes the gas-phase decomposition of TBHP through two ways, the decomposition into acetone and methanol (occurring already at 363 K) and that to isobutene, water and oxygen (starting above 400 K).

g) On both vanadia-alumina and vanadia-zirconia, vanadyl centers are involved in the formation of the adsorbed species. The presence of vanadium increases the rate of reactivity of tert-butylperoxide species.

h) Vanadia-alumina catalyzes the decomposition of gaseous TBHP through the same surface intermediates.

i) As discussed elsewhere [12] for the selective sulphoxidation of benzothiophenes, oxidations by tert-butyl-hydroperoxide catalyzed by supported vanadium oxides likely involve the previous formation of surface tert-butylperoxide species we have characterized here, which are active at room or slightly higher temperatures, i.e. below their decomposition temperature which is observed in the range 323-373 K.

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Chapter 5.

Oxidation of benzothiophene by tert-butyl hydroperoxide over vanadia–alumina catalyst: An FT-IR study at the vapor–solid interface

Oxidation of Benzothiophene by Tert-Butyl Hydroperoxide over Vanadia-Alumina Catalyst. An Ft-IR Study at the Vapor-Solid Interface.

Introduction

Most of sulphur compounds in automotive fuels arise from benzothiophenes and dibenzothiophenes which are contained in the heavier oil fractions, and are only partially converted, today, upon hydrodesulphurisation (HDS) and hydrocracking (HCR) processes in refineries [1,2]. The development of more efficient technologies to decrease sulphur concentration in commercial automotive fuels is a stringent target for the refinery industry. Oxidative Desulfurization (ODS) [3] has shown to be a promising alternative due to its moderate process conditions and lack of hydrogen consumption. In this process, organosulfur compounds in fuels are oxidized to form sulfoxides and subsequently sulfones. In our recent studies [4,5], alumina-supported vanadium oxide catalysts have been used along with hydrogen peroxide or tert-butyl hydroperoxide obtaining excellent desulfurization results of commercial diesel.
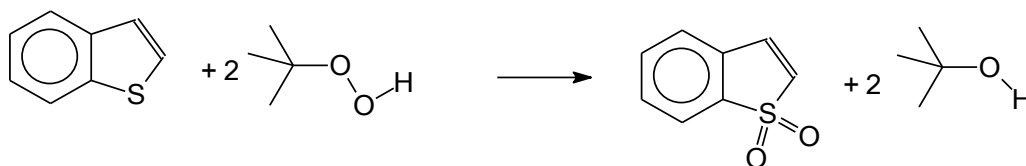
This reaction parallels the well established sulphoxidation catalytic activity of vanadium-containing materials. As for example, the well characterized complex $VO(OOtBu)(dipic)(H_2O)$ (dipic = pyridine-2,6-dicarboxylate dianion), whose structure implies an asymmetric side-on coordination of tert-butyl hydroperoxide species, and pentagonal bipyramidal geometry around vanadium [6,7] is reported to be active in the oxidation of organic sulphides [8].

Similar complexes are expected to form on the surface of vanadium containing solid catalysts. To have more information on the mechanism of reaction, the details of the interaction of the reactants with the catalyst should be investigated, e.g. with spectroscopic method. Infrared spectroscopy is a widely used technique for the surface characterization of metal oxide catalysts [9] and has been applied to study the interaction of benzothiophenes with catalysts and adsorbants [10, 11]. In this paper we present the results of an IR study on

the adsorption, from the vapor phase, and the coadsorption of tert-butyl hydroperoxide (TBHP) and benzothiophene (BT) over the active catalyst alumina-supported vanadia.

Experimental

Tert-butyl hydroperoxide (TBHP, 5-6 M solution in nonane), tert-butyl alcohol (TBOH, 99%) and benzothiophene (BT, 98%) were purchased from Aldrich. γ-Alumina was obtained from Gilder with a surface BET area of 206 m^2/g. 5 % wt alumina-supported vanadia catalyst was prepared by impregnation with a solution of ammonium metavanadate (Sigma-Aldrich, 99%) dissolved in aqueous oxalic acid 2M (Aldrich, 97%). After aging 12 h, catalysts were dried at 100°C during 24 h and calcined at 500°C during 8 h.

IR spectra were recorded on a Nicolet Nexus Fourier transform instrument, using pressed disks of pure catalyst powders (20 mg average wt.), activated by outgassing at 673 K into the IR cell for 30 minutes. A conventional gas manipulation / outgassing ramp connected to the IR cell was used. The adsorption procedure involves contact of the activated sample disk with TBHP, TBOH and BT vapors and outgassing in steps from r.t. up to 423 K.

Results and discussion

The spectrum of the vanadia-alumina catalyst is compared with that of the pure alumina support, both after activation by outgassing, in Fig. 1. The addition of vanadium causes mostly the appearance of sharp bands due to V=O bonds of vanadyl groups [12]. The fundamental V=O stretching mode is observed at 1028 cm^{-1} while its first overtone mode [13] is evident at 2040 cm^{-1}.

The OH stretching modes of the surface hydroxy groups are observed at 3765 (shoulder), 3730, 3672 and 3580 cm^{-1} for alumina, quite typical of γ-Al$_2$O$_3$ [9], and are slightly broadened and decreased in intensity in the case of vanadia-alumina, without any evident formation of new OH groups. These data, which agree with literature data, indicate that vanadium is in the form of pyramidal mono-oxo complexes in such low loading catalysts. In both cases traces of impurities (likely carboxylates) are found in the region 1700-1000 cm^{-1}.
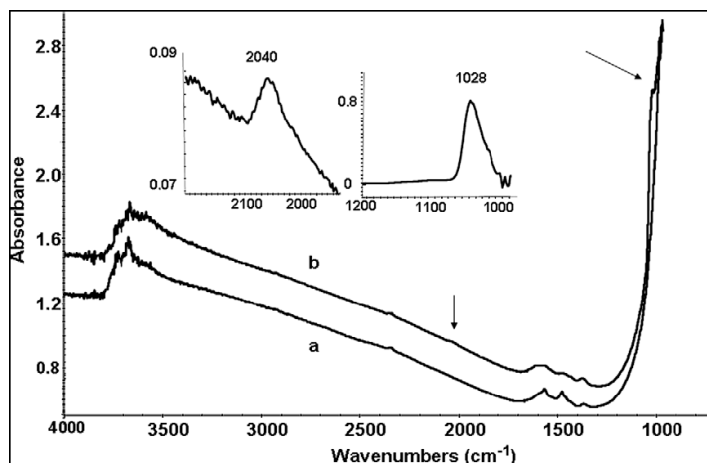
Fig. 1. IR spectra of: (a) alumina support and (b) vanadia–alumina catalyst, both after activation. Inserts show V=O stretching fundamental band (right) and first overtone (left).
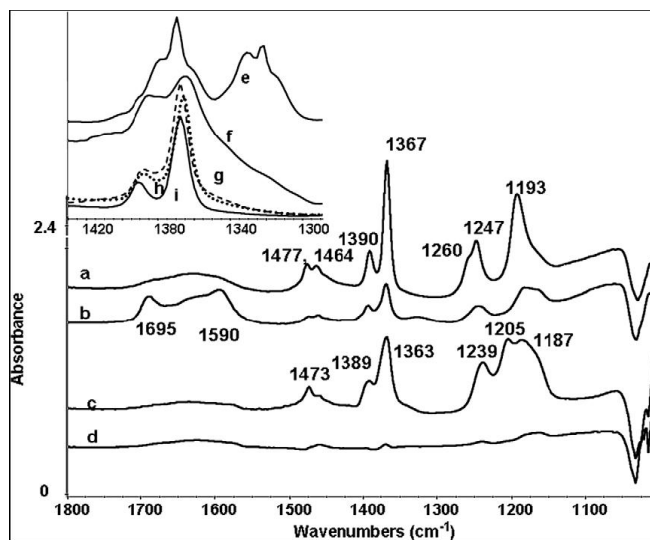

Fig. 2. IR spectra of TBHP (a, b) and TBOH (c, d) adsorbed on vanadia–alumina catalyst: (a, c) after contact and outgassing at r.t.; (b, d) outgassed at 373 K. In the insert: (e) TBPH gas; (f) TBPH–nonane mixture; (g) TBPH adsorbed on silica; (h and i) TBPH adsorbed on vanadia–alumina in contact with the vapour 10 Torr (h) and after outgassing (i).

The spectra of TBHP adsorbed on vanadia-alumina catalyst are reported in Fig. 2. In the same figure the spectrum of TBOH adsorbed on the same catalyst is also shown (Fig. 2c). The last one can be assigned to adsorbed tert-butoxide species, as discussed previously after TBOH adsorption on titania [14], alumina [15] and on vanadia–titania [16].The spectrum obtained after contact of the TBHP-nonane vapour mixture (Fig. 2,a) with the catalyst

shows a broad absorption in the region $3600 – 3000$ cm^{-1}, due to the formation of hydrogen bonds between the molecule(s) and the surface (not shown). At lower frequencies, bands due to C-H stretchings (3000-2800 cm^{-1}), CH$_3$ asymmetric deformations (a split band at 1475 and 1464 cm^{-1}), CH$_3$ symmetric deformations (1390, weaker; 1367 cm^{-1}, stronger), C-C stretchings (1260 and 1247 cm^{-1}), C-O stretching (1193 cm^{-1}) can be compared with that of liquid TBHP (reported by Shreeve et al. [17] and by Zyat'kov et al. [18]). The spectrum observed after adsorption of TBHP shows the features of the tert-butyl group, but it is clearly not due to tert-butoxy-species. On the contrary, the spectrum closely resembles that of liquid TBHP. In the insert in Fig. 2 the spectra of gaseous TBHP (Fig. 2e), that of the liquid TBHP–nonane mixture (Fig. 2f) and the spectrum of TBHP adsorbed on silica (Fig. 2g) are compared with those recorded after adsorption on the catalyst still in contact with the gas (Fig. 2h) and after outgassing (Fig. 2i). In the gas-phase spectrum a strong band feature centered at 1321 cm^{-1} is due to the in plane OOH deformation mode of TBHP. This adsorption is evident as a broad absorption in the liquid, extending in the range 1360–1300 cm^{-1}, due to hydrogen bonding. An absorption tail in the range 1370–1300 cm^{-1} is also observed in the spectrum of TBHP adsorbed on silica, where adsorption is, like in the case of the adsorption of alcohols, undissociative. A tail here is also evident after adsorption on vanadia–alumina before outgassing; showing that also in this case part of TBHP is adsorbed undissociatively. This feature disappears by outgassing at r.t., showing that in these conditions the spectrum is due to adsorbed tert-butyl-peroxides. In fact, also alcohols (which are less acidic than hydroperoxides) adsorb dissociatively on this catalyst.

To further confirm this assignment we studied the thermal evolution of these adsorbed species. Heating the surface after TBHP adsorption gives rise to the formation of a band at 1695 cm^{-1}, assigned to adsorbed acetone (C=O stretching) and a band at 1590 cm^{-1}, assigned to surface formate ions (COO asymmetric stretching). These assignments are supported by their position as well as by the detection, in the gas phase, of acetone, formaldehyde and methanol. This shows the decomposition of tert-butoxy species. In the same conditions, tert-butoxy groups simply disappear, while isobutene only is observed in the gas. These data allow us to conclude that TBHP adsorbs dissociatively on vanadia-alumina, giving rise to tert-butylperoxy groups, which are thermally stable at r.t. and 323 K.

The negative feature at 1028 cm^{-1} (Fig. 2,a and b) shows that these species at least in part interact with vanadyl species.

In Fig. 3,a the spectrum of the adsorbed species arising from contact of the catalyst with benzothiophene vapour (0.2 Torr) is shown. The spectrum is well consistent with that of pure BT [19, 20] as well as of adsorbed BT which, on metal oxides [10], bonds through the sulphur atom on Lewis acid sites. Adsorption of BT causes again the perturbation of surface vanadyl species, as evidenced by the negative band at 1030 cm^{-1} in the subtracted spectrum.
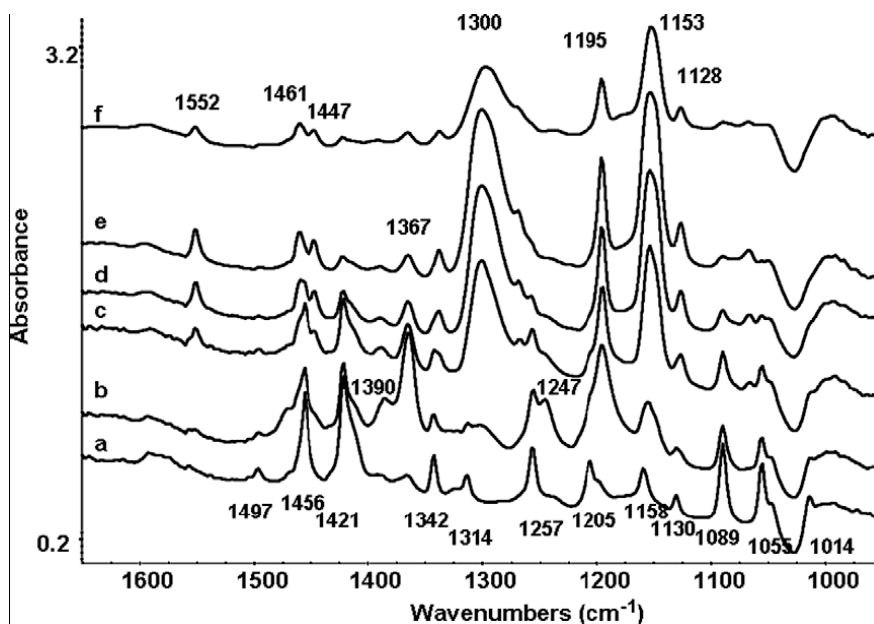

Fig. 3. IR spectra of the adsorbed species arising from BT and TBHP coadsorption on vanadia–alumina: (a) after contact with BT vapour (0.2 Torr, 15 min) and outgassing at r.t., (b) after further contact with TBHP vapour (5 Torr, 5 min, gas-phase spectrum subtracted), (c) successive outgassing at r.t. 15 min, (d) and 30 min, (e) at 323 K 15 min, (f) at 373 K 15 min.

The successive coadsorption of TBHP causes first the formation of bands due to tertbutyl-peroxides (bands at 1390, 1367, 1247 and 1195 cm^{-1}, Fig. 3,b). However, even under outgassing, strong bands at 1300 and 1153 cm^{-1}, together with weaker bands, grow slowly at room or slightly higher temperatures. At 373 K under outgassing the spectrum can be assigned to the sulphone of benzothiophene, the strongest bands at 1300 and 1153 cm^{-1} being typical of asymmetric and symmetric O=S=O stretchings of sulphone species [21]

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including benzothiophene sulphone [22], slightly lowered in frequency due to adsorption on the surface. These data show that adsorbed BT is easily oxidized, at room temperature, by TBHP to the corresponding sulphone. The inspection of the region 1100-1000 cm-1 does not seem to show any intermediate formation of strong bands in this region, where the S=O stretching modes of sulphoxides typically fall [21]. This is likely ascribed to a faster oxidation rate of sulphoxide to sulphone, which does not allow the detection of such an intermediate. In fact the direct oxidation of BT to sulphone without the intermediate formation of its corresponding sulphoxide seems unlikely.
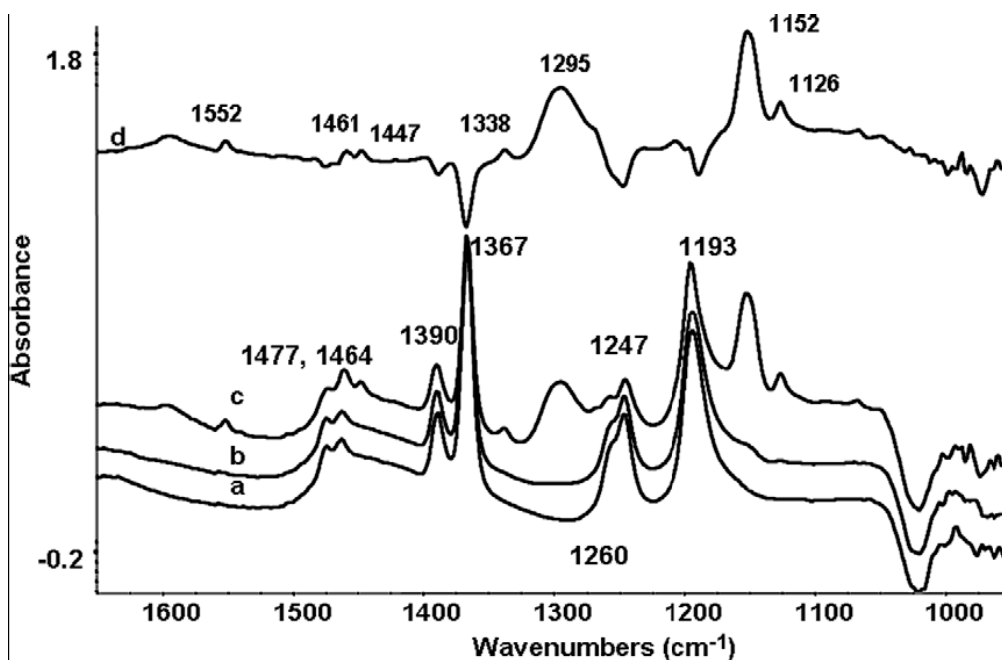

Fig. 4. IR spectra of the adsorbed species arising from TBHP and BT coadsorption on vanadia–alumina: (a) after contact with TBHP vapour (5 Torr, 15 min) and outgassing at r.t., (b) after further contact with BT vapour (0.2 Torr, gas-phase spectrum subtracted) 5 min and (c) 15 min. Spectrum d = subtraction c–a.

In Fig. 4 the spectra relative to the reverse experiment are reported. In Fig. 4,a the spectrum obtained after adsorption of TBHP and outgassing is reported. This spectrum has already been assigned to tert-butylperoxy species. Upon further coadsorption of BT strong bands at 1295 and 1152 cm^{-1} form. The overall spectrum formed (see the subtraction in Fig. 4, d) is closely similar to that reported in Fig. 3,f, with small shifts, and is clearly due to the

sulphone of benzothiophene. In the same subtraction, the spectrum of tert-butyl-peroxides is observed as negative features.

These data show that adsorbed tert-butylperoxide species react at r.t. with BT, producing the adsorbed sulphone. Again, no trace for an intermediate role of sulphoxide species is observed. Sulphone species we observe here are clearly adsorbed on the catalyst surface, in our conditions. This is mostly due to the very low volatility of these heavy molecules, near r.t. However, in the real reaction conditions at the catalyst–solution interface the sulphone is expected to desorb and dissolve on the hydrocarbon mixture. The competition with the more polar molecule TBHP, which would displace the sulphone from the surface, should also favour the dissolution of the sulphone.

Conclusions

The experiments described above allowed us to obtain the following conclusion;

a) The adsorption of tert-butyl hydroperoxide over vanadia-alumina from gas phase produces predominant amounts of tert-butylperoxide species produced by dissociative adsorption. Vanadyl centers are involved in the formation of such adsorbed species.

b) BT adsorbs on vanadia alumina in a molecular form, very likely through the sulphur atom on Lewis sites as found previously on different oxide solids.

c) Adsorbed tert-butylperoxide species react with adsorbed BT at room temperature, producing the corresponding sulphones. No trace of the corresponding sulphoxides is observed.

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6. Final Discussion

Vanadium oxide catalysts supported on alumina were prepared by different methods such as thermal spreading (TS), incipient wetness impregnation (IWI) and sol-gel (SG) with different vanadium loadings. Catalysts were characterized by N_2 physisorption, scanning electron microscopy (SEM), X-ray diffraction (XRD), temperature programmed reduction (TPR), Raman Spectroscopy, Diffuse Reflectance Spectroscopy (DRS) as well as Infrared Spectroscopy (IR) with pivalonitrile (PN) adsorption.

N_2 physisorption results show that catalysts prepared by TS and IWI have similar BET areas (~150 m^3/g) and pore diameters (~75 A), while the ones prepared by SG have higher areas (>300 m^3/g) and smaller pores (~ 30 A or less). SEM showed that all the catalysts have good vanadium distribution on the support and XRD detected V_2O_5 crystalline species in all the catalysts prepared by TS and also in 15 and 20 VAIWI. These results were confirmed by Raman spectroscopy, which further found a band at ~925 cm^{-1} in the catalysts prepared by SG. This band can be attributed to polymeric methavanadate species. It is interesting to note that the catalyst with 26% V_2O_5 seems to present little V_2O_5 crystals, as detected by a shoulder at 993 cm^{-1}, which were not detected by XRD. These characterizations were also confirmed by DRS, which shows completely different spectra for the catalysts prepared by SG. These catalysts present two absorption bands at 218 y 268 nm, their spectra resemble the one of NH_4VO_3. This technique did not detect the characteristic bands due to V^{4+} o V^{3+} in the visible region.

Reducibility of all these materials was measured by TPR. Catalysts prepared by TS and IWI show high reducibility (> 80%) without any clear tendency, while catalysts prepared by SG have low reducibility ($\leq$ 70%) and it clearly increases with vanadium loading.

Acidity of catalysts was also measured by PN adsorption followed by IR spectroscopy, which allows distinguishing Lewis acid sites from Brönsted acid sites. It was observed that the preparation method and the vanadium loading cause differences in the proportion of Lewis and Brönsted acid sites. In general, the catalysts prepared by TS have higher Lewis acidity and those prepared by SG the lowest. Deconvolution of the band at ~2295 cm^{-1}

allows to distinguish between Lewis acid sites from alumina (LAl) and Lewis acid sites from vanadium (LV) and this can be represented in a (LAl/LV) ratio. It was observed that LV increases with vanadium loading, however SG catalyst did not display this behavior. These results help us infer that IWI catalysts show better vanadium dispersion than TS catalysts since LAl/LV ratio is much higher in the latter catalysts. Vanadium species are probably agglomerated in this case and thus less available, which makes LV lower.

Once catalysts were characterized, their activity was evaluated in DBT oxidation with acetonitrile as solvent and H_2O_2 as oxidant. It was observed that catalysts prepared by TS show higher activity at lower vanadium loadings than catalysts prepared by IWI and that activity decreases in both cases beyond vanadium monolayer. Probably the presence of V_2O_5 crystals in catalysts prepared by TS even with low vanadium loadings produces a clear increase in activity. In the case of the catalysts prepared by SG, a decrease in activity with increasing vanadium loading was observed.

According to the characterizations, the amount of each type of vanadium species changes with the preparation method: catalysts prepared by TS result in microcrystals of V_2O_5. Catalysts prepared by IWI presented better dispersion of vanadium pentoxide with monomeric species on the catalyst with 5% of V_2O_5 and initial appearance of V_2O_5 crystals on the monolayer catalyst (15% V_2O_5). Catalysts prepared by SG present metavanadate type species and high interaction vanadium – support with the lowest reducibility according to TPR experiments.

As expected, these differences influence catalytic activity, which diminishes regarding the preparation method as follows: TS > IWI > SG. This seems to indicate that the presence of microcrystals of V_2O_5 increases $DBTO_2$ yields.

Another important factor during activity tests is H_2O_2 decomposition. Concentration profiles of this reagent were monitored by iodometric titrations and the final remaining percentage of each reaction test is reported. No differences regarding this percentage were observed with the catalysts prepared by TS and IWI except with the catalysts with 5% V_2O_5. In agreement with these results, TPR tests of these catalysts did not show clear differences in reducibility. On the other hand, catalysts prepared by SG display low

peroxide decomposition and it increases with increasing vanadium loading (as well as their reducibility) nevertheless their activity decrease.

In an attempt to observe differences in oxidant activation with the preparation method, hydrogen peroxide decomposition (without substrate) at reaction conditions with TS and IWI catalysts was performed. Results show that TS catalysts decompose H_2O_2 more rapidly than IWI catalysts.
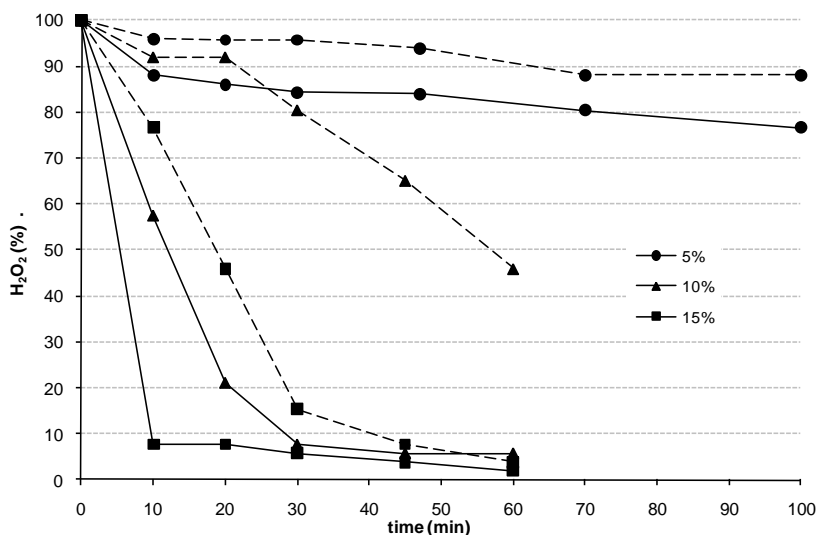

Figure 6.1. H_2O_2 decomposition without substrate at 60°C with acetonitrile as solvent in presence of TS (full lines) and IWI (dashed lines).

However, it is observed that H_2O_2 decomposition is not always selective and in some cases it does not lead to DBT oxidation. For example, when decomposition is excessively fast, $DBTO_2$ yields decrease as it is observed in figure 6.1 and figure 9 from chapter 3 with the results obtained with 15% of V_2O_5 (comparing TS and IWI) and also 20% (not shown). This in turn, agrees with the results obtained with SG catalysts, where a higher decomposition of the oxidant is obtained with higher V_2O_5 loadings but sulfone yields decrease. These data make us infer that *OH radicals produced by hydrogen peroxide decomposition are not responsible of DBT oxidation and that the active oxidant species is a peroxocomplex that is not related with catalyst reducibility.

Finally, since reaction is carried out in liquid phase, stability of catalysts towards leaching was tested with heterogeinity tests. Catalysts prepared by TS leach the active phase and display homogeneous activity. The final reaction solution in these cases is yellow, which

clearly indicates the presence of dissolved vanadium. Also 15VAIWI catalyst presented homogeneous reaction as can be seen in figure 6.2. The filtrate continues to react and sulfone yield increases around 20%. Also H_2O_2 concentration profile displays high oxidant decomposition even after catalyst removal.
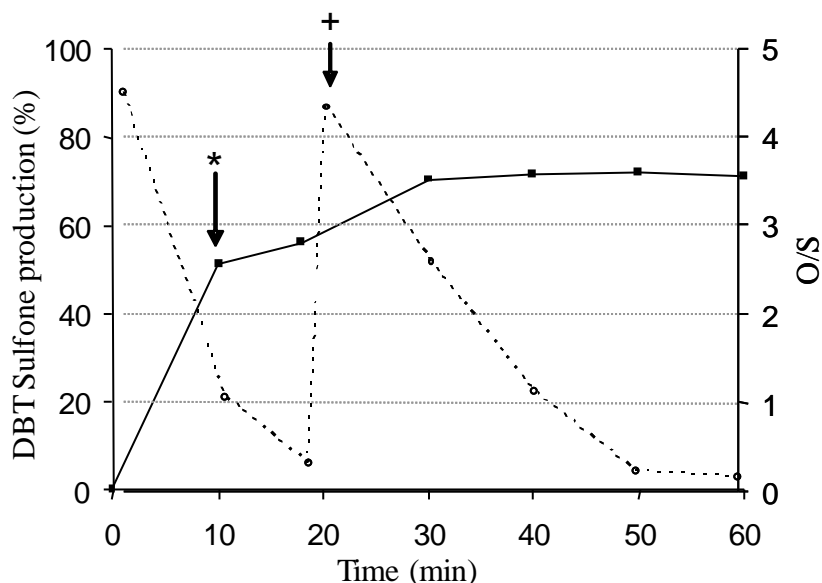

Figure 6.2. Heterogeneity test in presence of 15VAIWI and acetonitrile as solvent at 60°C. Full line corresponds to the sulfone profile and the dashed line to H_2O_2 profile. * Catalyst withdrawal, + H_2O_2 addition.

Heterogeneity test with 5VAIWI showed heterogeneous activity, although it is very low. This catalyst was stable at least during reaction time, probably due to the presence of monomeric vanadium species better anchored to the support.

Stability of 8 and 15VASG was not tested but it is possible that leaching of these catalysts does not take place, since also in this case the reaction solution remained colorless.

Therefore, it is considered that catalysts with monomeric vanadium species are more stable to leaching at these reaction conditions and activate the oxidant forming a peroxocomplex anchored to the catalyst. On the contrary, catalysts with polymeric species and especially microcrystals of V_2O_5, present leaching of vanadium caused by H_2O_2 and water that produce dissolved decavanadate with its characteristic orange-yellow color. These are probably the dissolved species that form the oxidant complex in these cases.

To corroborate the oxidant interaction with the supported catalysts, adsorption of TBHP over VO_x/Al_2O_3, VO_x/ZrO_2 and both pure supports was performed and followed by FT-IR spectroscopy. TBHP was chosen over H_2O_2 in order to exclude water from the system, since it produces prominent absorptions that cover the spectrum. The reason why zirconia was included in this study is its low IR cut-off limit that allows inspection of the O-O vibration frequency characteristic of peroxides.

The IR spectrum of TBHP has not been extensively studied so it was compared with tert-butyl alcohol (TBOH), whose spectrum has been more studied, in order to make a correct band assignment.

Supports and catalysts spectra were also analyzed before TBHP adsorption.

The catalysts clearly present the fundamental V=O vibration at 1028 cm^{-1} in the case of VO_x/Al_2O_3 y 1024 cm^{-1} for VO_x/ZrO_2, with their respective overtones at 2040 y 2033 cm^{-1}. Vibration at lower frequency of ZrO_2 is due to a higher basicity in the superficial oxides that act as ligands of the vanadyl complex. Another important characteristic of this material is the lower frequency cut-off limit, which allows observing the interactions at the low frequency region where the peroxide O-O bond typically falls.

TBHP adsorption on ZrO_2 shows the characteristic vibrations of this molecule. At 845 cm^{-1} the O-O stretching band is observed and it remains visible even after the first outgassing. Later on, an additional shoulder is observed at ~870 cm^{-1} which could be a displacement of the O-O stretching band due to a stronger dissociative adsorption. With increasing outgassing temperature, several interesting changes are observed in the adsorbed spectra.

After the adsorption of TBOH on the same support and comparing with TBHP, it was observed that the latter decomposes on the surface to form adsorbed TBOH. It is also interesting to note that only with TBHP adsorption acetate species are formed by the following reaction:
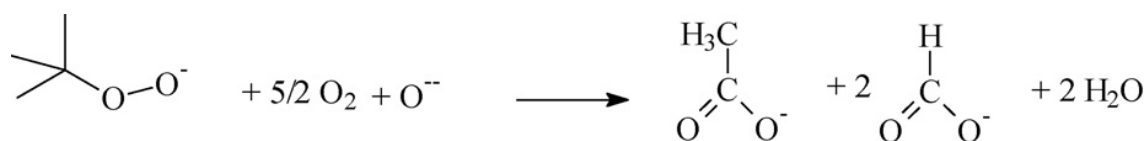
TBHP and TBOH adsorption on alumina also resulted in the formation of tert-butil peroxy and tert-butoxy species respectively, only their evolution with temperature was quite different. For example, TBOH under outgassing at 423 K is totally decomposed in

isobutene and superficial OH groups. In general the chemistry of the system seems to be the same than on zirconia: TBHP adsorbs dissociatively and subsequently, by increasing temperature, oxidized species appear (acetate and formate ions) as well as tert butoxy species that are totally decomposed to isobutene due to the acid sites of alumina.

TBHP adsorption spectra on VO_x/ZrO_2 catalyst show as major difference the negative band at 1024 cm^{-1} due to V=O stretching. Besides, a high increase in reactivity of peroxide is reached and new bands in the spectrum already at room temperature are observed corresponding probably to the following reaction:
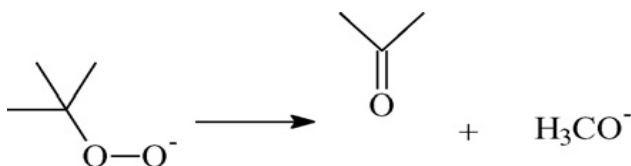
Also in this case, tert-butyl peroxy species convert to tert-butoxy species by outgassing already at 330 K. TBOH adsorption on this catalyst clearly shows the contribution of vanadium, not only with the negative V=O band, but also in the 1200 - 1150 cm^{-1} region with a less symmetrical C-O bond due to covalent alcoxides formed with vanadium.

TBHP y TBOH adsorption on VO_x/Al_2O_3 also resulted in the formation of tertbutil peroxy y tertbutoxy species, respectively and an increase in reactivity.

To better understand the chemistry of the system, TBHP was adsorbed on VO_x/Al_2O_3 and thermally treated without outgassing. The products of reaction were also followed spectroscopically. It was observed that TBHP vapors immediately after contact with the vanadium catalyst display a slight band at 1738 cm^{-1} due to acetone formation. It is interesting to note that this band is only visible when TBHP vapors are in contact with vanadium catalysts. The characteristic bands of the peroxidic group are still quite clear at 3596, 845 y 526 cm^{-1}. Thermal treatmet at 363 K shows an increase in intensity of the characteristic bands of acetone and methanol. Later on, at 473 K TBHP spectrum disappears completely resulting in isobutene and water as well as acetone and methanol.

In conclusion, with this study it was possible to see that TBHP adsorbs dissociatively in the four materials used. This is, it coordinates itself losing the proton to form an "alkyl peroxy" species. Adsorption on pure zirconia allowed observing the characteristic vibration of physisorbed O-O stretching (at the same frequency of liquid TBHP, 845 cm^{-1}), as well as a new vibration at higher frequency (867 cm^{-1}) attributed to chemisorption of TBHP to form

the "alkyl peroxy" complex. It is important to note that these species disappear rapidly due to its instability. The presence of vanadium oxide on the supports catalyzes TBHP activation and decomposition products of TBHP are observed at room temperature immediately after TBHP contact with the catalyst. The main products of TBHP decomposition are acetone and methanol.

Finally to study the oxidation reaction even on these conditions with a 5% VO_x/Al_2O_3 catalyst, coadsorption of TBHP and a S-compound characteristic of diesel such as benzothiophene (BT) was carried out. This compound was used because of its higher vapor pressure compared to DBT which simplifies adsorption.

Initially, vanadium catalyst over alumina was analyzed after outgassing. Subsequently TBHP adsorption was performed. As it was mentioned before, TBHP adsorbs dissociatively. In this case, the vibration at 1321 cm^{-1} ascribed to OOH deformation in the vapor TBHP spectrum was analyzed in detail and compared to the liquid TBHP spectrum as well as the one adsorbed on silica and on the VO_x/Al_2O_3 catalyst. It was observed that on VO_x/Al_2O_3 catalyst this vibration disappears by evacuating excess TBHP vapors, which indicates dissociative adsorption. Also the negative band at 1028 cm^{-1} characteristic of perturbed vanadyl groups shows that TBHP interacts with vanadium species. Evolution of the spectra with outgassing time and temperature confirm the formation of tert-butyl peroxy species on the catalyst after TBHP adsorption.

Then, BT adsorption on the outgassed catalyst was performed, which generated clear spectra of adsorbed BT, causing again perturbation of surface vanadyl groups as shown by the negative band at 1030 cm^{-1}. Subsequent TBHP coadsorption initially leads to the formation of tert-butyl peroxy species. Then, even under outgassing, strong growing bands at 1300 and 1153 cm^{-1} are observed. These bands are characteristic of asymmetric and symmetric O=S=O stretching of sulfones. Finally the obtained spectrum can be assigned to BT sulfone. It is interesting to note that sulfoxide formation was not detected as a result of a detailed analysis of the 1100 – 1000 cm^{-1} region characteristic of sulfoxide S=O stretching. This can be attributed to a higher oxidation rate from sulfoxide to sulfone, which does not allow detection of the characteristic bands of BT sulfoxide. Thus, sulfoxide formation must be the determining step in this reaction.

In the second type of experiments, adsorption of TBHP was carried out as a first step, outgassing excess vapor to have only adsorbed peroxy species, then BT was coadsorbed. This experiment also led to the formation of BT sulfone. In this case its main bands are observed at 1295 y 1152 cm^{-1}.

In these experiments the sulfone remains adsorbed on the catalysts, most likely due to low volatility of these species. It is expected that at reaction conditions the molecule desorbs more easily. Competition with more polar TBHP should favor its desorption to dissolve in acetonitrile, the reaction solvent.

Also, these two types of experiments show that the order of adsorption of reagents on the catalyst may not be important for sulfone production.

In conclusion, this study supports again the formation of "alkyl peroxy" species after adsorbing TBHP which in turn oxidize BT to form its respective sulfone as shown by vibrations at 1300 and 1153 cm^{-1}, characteristic of asymmetric and symmetric stretching O=S=O. The characteristic vibration of the sulfoxide found in the region from 1100-1000 was not observed, which indicates that the determining step of this reaction is sulfoxide formation and its oxidation to sulfone is very fast, which does not allow detection by IR.

CONCLUSIONS

- Vanadium catalysts supported on alumina were prepared by three methods:

- Thermal spreading, incipient wet impregnation and sol-gel. The preparation method influenced the superficial vanadium species obtained

- Catalyst activity in DBT oxidation with acetonitrile at 60°C with hydrogen peroxide decrease with the preparation method as follows: TS > IWI > SG.

- Stability of catalysts towards leaching of active phase was tested and it was observed that catalyst prepared by TS present leaching of vanadium and homogeneous activity.

- From catalysts prepared by IWI, only the one with lowest loading (5VAIWI) presents heterogeneous activity without leaching at these reaction conditions. This result could be ascribed to the presence of just monomeric species better anchored to the support.

- No heterogeneity tests were carried out with the catalysts prepared by SG, but the colorless solution obtained after reaction with 8 and 15 VASG might indicate heterogeneous activity.

- Formation of "alkyl peroxy" species after adsorption of TBHP over 5VAIWI was observed by Infrared spectroscopy. These species are considered the oxidant complex.

- Adsorption of TBHP on pure alumina also leads to the formation of "alkyl peroxy" species, but their reactivity is not as high as alkyl peroxy species formed with vanadium catalysts.

- Coadsorption of TBHP and BT over 5VAIWI shows rapid oxidation of BT to form its corresponding sulfone.

- Sulfoxide formation was not observed, which indicates that the rate of reaction from sulfoxide to sulfone is higher.