Oxidative desulfurization of synthetic diesel using supported catalysts Part II. Effect of oxidant and nitrogen-compounds on extraction–oxidation process

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Abstract

Oxidative desulfurization (ODS) of a synthetic diesel was carried out at mild conditions (atmospheric pressure and 60 °C) in presence of V_2O_5/Al_2O_3 and V_2O_5/TiO_2 catalysts. Two main aspects were studied: the effect of the oxidant reagent and the presence of nitrogen compounds on ODS of benzothiophenic compounds prevailing in diesel, such as benzothiophene, dibenzothiophene and alkyl substituted in positions 4 and 6. Results show that activity is improved when using hydrogen peroxide, as oxidant reagent, and V_2O_5/Al_2O_3, as catalyst. This result was attributed to the high decomposition of peroxide due to the presence of catalyst. In presence of nitrogen compounds, the ODS activity decreases in the order: quinoline > indole > carbazole. In order to explain this effect, successive chemisorption of DBT and quinoline on V_2O_5/Al_2O_3 catalyst was evaluated by FT-IR, and the results show that DBT is displaced by quinoline, occupying the adsorption sites of catalyst. N-compound effect could be explained by strong adsorption of nitrogen compounds on catalytic sites.
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1. Introduction

Sulfur compounds removal from petroleum is necessary for both industrial and environmental reasons. Sulfur in petroleum products poisons catalytic converters, corrodes parts of internal combustion engines and refineries because the formation of oxyacids of sulfur and causes air pollution due to exhaust from diesel engines.

The conventional method for reducing sulfur is catalytic hydrodesulfurization (HDS). In the HDS process, hydrogen and organic sulfur compounds react together at high temperatures and pressures [1]. The effectiveness of HDS process depends on the type of sulfur compounds. The complete sulfur removal depends on reactivity of refractory HDS compounds, as dibenzothiophenes, mainly alkyl substituted in 4 and 6 positions. Other processes have been studied in order to remove these compounds [2]. Among these options, oxidesulfurization (ODS) is an attractive alternative to the HDS process [3–14].

ODS has a significant advantage over HDS, since the sulfur compounds that are the most difficult to eliminate by HDS are the most reactive on ODS [10]. Compared with traditional HDS, ODS has several advantages such as mild conditions (atmospheric pressure and temperature lower than 80 °C), high selectivity, absence of expensive hydrogen and potential for desulfurization of sterically hindered sulfides as alkyl benzothiophenes.

ODS, in presence of a solid catalyst, generally is defined in two steps: oxidation of S-compounds to sulfones and removal or extraction of oxidized S-compounds from the treated fuels [3,7]. Previous results [15] suggest that the first step is removal of sulfur compounds by extraction from the treated fuel, and the following step is their oxidation to the corresponding sulfones in the solvent phase, since having reactants in the polar phase facilitates their reaction. In these conditions, the solvent is very important in the process, the extraction of sulfur compounds took noticeable place without catalyst. By the contrast, in presence of catalyst and oxidant but without extraction solvent,

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there was no oxidation reaction of these compounds [16]. Then, total removal depends on the contribution of extraction and oxidation steps. Butyrolactone and acetonitrile were the most efficient dipolar aprotic solvents in ODS process, but oxidation to sulfone was higher with the latter. Total removal of DBT was close to 100%, but the oxidation to sulfone was only about 80%, using butyrolactone as solvent [15]. For this reason, it is important to evaluate the contribution of each step, in order to know the real activity of the catalyst.

Several oxidants have been used in ODS, such as hydrogen peroxide, tertbutyl hydroperoxide (TBHP), per-acids and ozone [17]. Among these reactants, peroxides are very attractive since generally the reaction proceeds rapidly and selectively under mild conditions. The oxidant selection depends on the hydrophobic character of the catalyst, given that hydrogen peroxide produces water and it inhibits the ODS activity [16]. However, in this case, the vanadium-based catalysts showed good ODS activity for sulfur compounds prevailing in diesel, with hydrogen peroxide. Unlike the group IV–VI metal oxide based catalyst, silicates are active in diluted aqueous solutions of hydrogen peroxide, whereas anhydrous organic hydroperoxides, such as TBHP, are the oxidants of choice for the former catalysts [18]. These catalysts favor the adsorption of the organic substrates over the more polar water molecules present in the aqueous H_2O_2 solutions [19]. In this sense, the aim of the study is to evaluate the oxidative reactivities of S-compounds in presence of vanadium oxide catalysts with hydrogen peroxide and TBHP, as oxidants. Firstly, oxidation of a model diesel was carried out, using V_2O_5 supported on alumina or titania as catalysts, to evaluate their oxidative activities. Secondly, oxidation of model sulfur compounds was studied with H_2O_2 or TBHP, to analyze the oxidant effect on the activities of these sulfur compounds.

Another important factor in ODS process is to evaluate the effect of other compounds present in the oil fractions. Otsuki et al. [20] studied the effect of nitrogen-model compounds, olefins, aliphatic and aromatic hydrocarbons, found in light gas oil, on oxidation of DBT. This study shows that the conversion of DBT was not influenced by the addition of *n*-pentadecane or by addition of xylene, indicating that aliphatic and aromatic compounds did not affect the oxidation of DBT. In contrast, the addition of diisobutylene and indole retarded the oxidation reaction. These results were attributed to a higher reactivity of these compounds compared to that of DBT, in conditions of the oxidation reaction. Ishihara et al. [21] reported that denitrogenation performance of N-containing compounds in oxidation process is possible. Denitrogenation activity order of model compounds was: indole > quinoline > acridine > carbazole. However, while the oxidation products of N-compounds were not fully identified, they suggested the presence of polymeric compounds. Since sulfur compounds are removed quantitatively from fuels by physical extraction without oxidation reaction [15], then the N-compounds could be removed only by extraction. In order to analyze the effect of nitrogen compounds on ODS reactions, in this work we also study the

ODS of synthetic diesel in presence of several N-compounds, such as indole, carbazole or quinoline.

2. Experimental

2.1. Materials

All compounds were purchased from Sigma–Aldrich and used without further treatment. Benzothiophenes, which represent sulfur species in diesel, were selected to evaluate the reactivity in ODS reaction. Hexadecane (99.8%) was used as solvent of model compounds: benzothiophene (BT, 98%), dibenzothiophene (DBT, 98%), 4-methyl dibenzothiophene (4-MDBT, 96%) and 4,6-dimethyl dibenzothiophene (4,6-DMDBT, 97%). This synthetic diesel was prepared with 936 S ppmw: 308 of BT, 224 of DBT, 209 of 4-MDBT and 195 of 4,6-DMDBT. Acetonitrile (99.9%) was used as extraction solvent. Indole (99%), carbazole (96%) and quinoline (98%) were used as the model N-compounds.

2.2. Catalysts and characterization

V_2O_5/Al_2O_3 and V_2O_5/TiO_2 catalysts were obtained by thermal spreading at 500 °C during 5 h in air [22,23]. Catalyst represents a physical mixture of the support (alumina with 175 m^2/g or TiO_2 with 120 m^2/g) and V_2O_5 (99.6%, Aldrich) obtained through intensive manual milling. Each catalyst was prepared with a V_2O_5 loading equivalent to a monolayer coverage [24,25], 17 wt.% for V_2O_5/Al_2O_3 (V/Al) and 11 wt.% for V_2O_5/TiO_2 (V/Ti).

Catalysts were characterized by: X-ray diffraction (XRD) using a Siemens D500 powder diffractometer with Cu Kα radiation. Textural properties were obtained by N_2 adsorption–desorption isotherms of the samples, with a Tristar Micromeritics apparatus. Nitrogen physisorption isotherms were analyzed using the BJH 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. The FT-Raman spectra of catalysts were performed in a Nicolet FT-Raman 950 spectrometer with a resolution of 4 cm^{-1} and 500 scans. Before the analysis, the samples were pretreated at 100 °C during 12 h in static air. A conventional temperature programmed reduction (TPR) apparatus was used for the study of 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. The IR spectra were performed on a Nicolet Magna 760 Fourier Transform Spectrometer with a resolution of 2 cm^{-1} and 100 scans. For IR experiments, wafers of the pure catalyst were made (∼20 mg) and outgassed under vacuum in a special IR cell at 250 °C during 1 h to physically remove adsorbed impurities from the catalyst sample. After that, a pulse of the probe molecules was introduced and a spectrum was taken. Finally, the cell was outgassed at room temperature and a

spectrum was collected. The probe molecules, dibenzothio-phene and quinoline, were products from Aldrich.

2.3. Catalytic experiments

A batch reactor, fitted with condenser, mechanical stirrer and a thermocouple, was used to carry out the oxidation reaction. The reactor was immersed in a thermostatically controlled water bath to carry out the reactions at 60 °C. In a typical run, the water bath was first heated up and stabilized to the desired reaction temperature, and the mixture of synthetic diesel-solvent (1:1, v/v) was added to the reactor. After that, oxidant reagent and catalyst were added to the reactor and stirred at ~500 rpm. Reaction samples, from diesel and solvent phases, at 3, 10, 20, 30 and 60 min were withdrawn and injected (auto sampler) to the GC-FID after cooling to room temperature. GC-FID analyses were performed with an HP5890 Series II Gas Chromatograph with a PONA capillary column (Methyl silicone Gum, 50 m × 0.2 mm × 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). Tertbutyl hydroperoxide (70 wt.% TBHP) or hydrogen peroxide (30 wt.% H_2O_2) was used as oxidant (O/S = 8 initial ratio, mol/mol). TBHP was measured during reaction by standard permanganometric titration and GC-FID. H_2O_2 content was measured by standard iodometric titration. H_2O_2 was added in small doses to reduce thermal decomposition, according to previous results [16].

3. Results and discussion

The reactive system on study is very complex due to the presence of two liquid phases (diesel and solvent) and a solid catalyst. The goal of this work is to evaluate the effect of the catalyst, oxidant reagent and N-compounds on ODS activity of S-compounds in diesel. In this line, first we will present the characterization results of the catalysts: V_2O_5/Al_2O_3 (V/Al) and V_2O_5/TiO_2 (V/Ti). Second, we will analyze the ODS activity of S-compounds, using hydrogen peroxide or tertbutyl hydroperoxide (TBHP), in order to select the best oxidant. Finally, the effect of N-compounds will be discussed.

3.1. Characterization of catalysts

BET surface areas of the catalysts were found to be 168 and 37 m^2/g for V/Al and V/Ti, respectively. These decrements in surface area of the catalysts respect to supports are due to penetration of V_2O_5 into the pores of the support during preparation step, covering the surface of supports. For V/Al this effect is not important because the area decreases only 4%, but for V/Ti catalyst it diminishes significantly. This result is attributed to the obstruction of micropores since the pore average diameter increased from 130 to 232 Å, for V/Ti. According to SEM-EDX results, a good surface distribution of V_2O_5 was obtained on both supports. XRD results clearly show
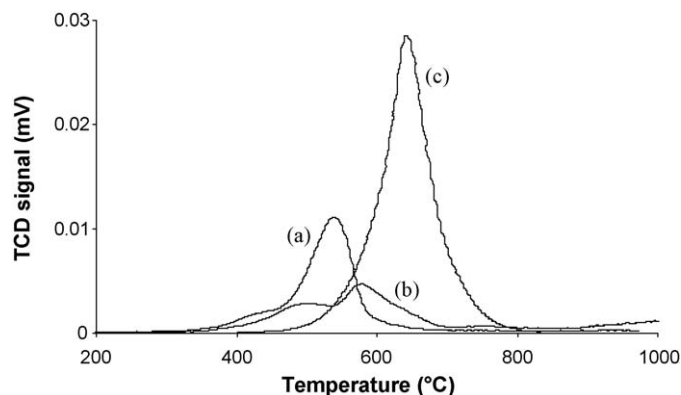

Fig. 1. TPR patterns of: (a) V_2O_5/Al_2O_3, (b) V_2O_5/TiO_2 and (c) V_2O_5.

reflections attributable to crystalline V_2O_5, titania (anatase) and alumina (gamma) phases.

Fig. 1 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 the temperature of reduction rate maximum (T_{max}) at 645 °C. This peak is associated to the reduction of V(+5) to V(+3) species [26]. V/Al catalyst exhibits a similar reduction peak, but at lower temperatures, its reduction starts at 350 up to 700 °C and the T_{max} is about 540 °C, which agrees with results obtained by Chen et al. [27]. This temperature shift can be attributed to presence of the most easily reducible highly dispersed V species, on alumina surface. V/Ti catalyst exhibits two peaks that can be assigned to low-temperature species present in V/Al catalyst and bulk V_2O_5. The TPR quantitative results show that the reduction degree is very high in both catalysts (about 99%) and V(+5) species present in the catalysts were reduced totally to V(+3). However, for V/Ti catalyst there are different reducible species, which could be attributed to monomeric and polymeric VO_4 units on the surface. The quantity of V_2O_5 needed to cover the support surface with a monolayer can be estimated by different methods [22]. This monolayer surface coverage is defined as the maximum amount of amorphous or two-dimensional vanadia in contact with the oxide support, and it depends not only on the support surface area but also on the concentration of reactive surface hydroxyl groups, among other preparative variables [25]. Therefore, the catalysts prepared in this study could not have a monolayer, resulting in different superficial distribution of V species.

To analyze surface V species on the catalysts, FT-Raman characterization was performed. The spectra of the catalysts and bulk V_2O_5 (not shown) exhibit similar well-defined bands localized at 993, 699, 515, 477, 404, 303, 283, 195 and 143 cm^{-1}. Another additional band at 638 cm^{-1} is present only in V/Ti catalyst and titania support, it is assigned to stretching vibration of Ti–O bond [23]. The sharp peak at 993 cm^{-1} is assigned to the terminal V=O vibration of characteristic crystalline V_2O_5. In view of the fact that Raman signal for crystalline V_2O_5 is more intense than that of surface vanadium
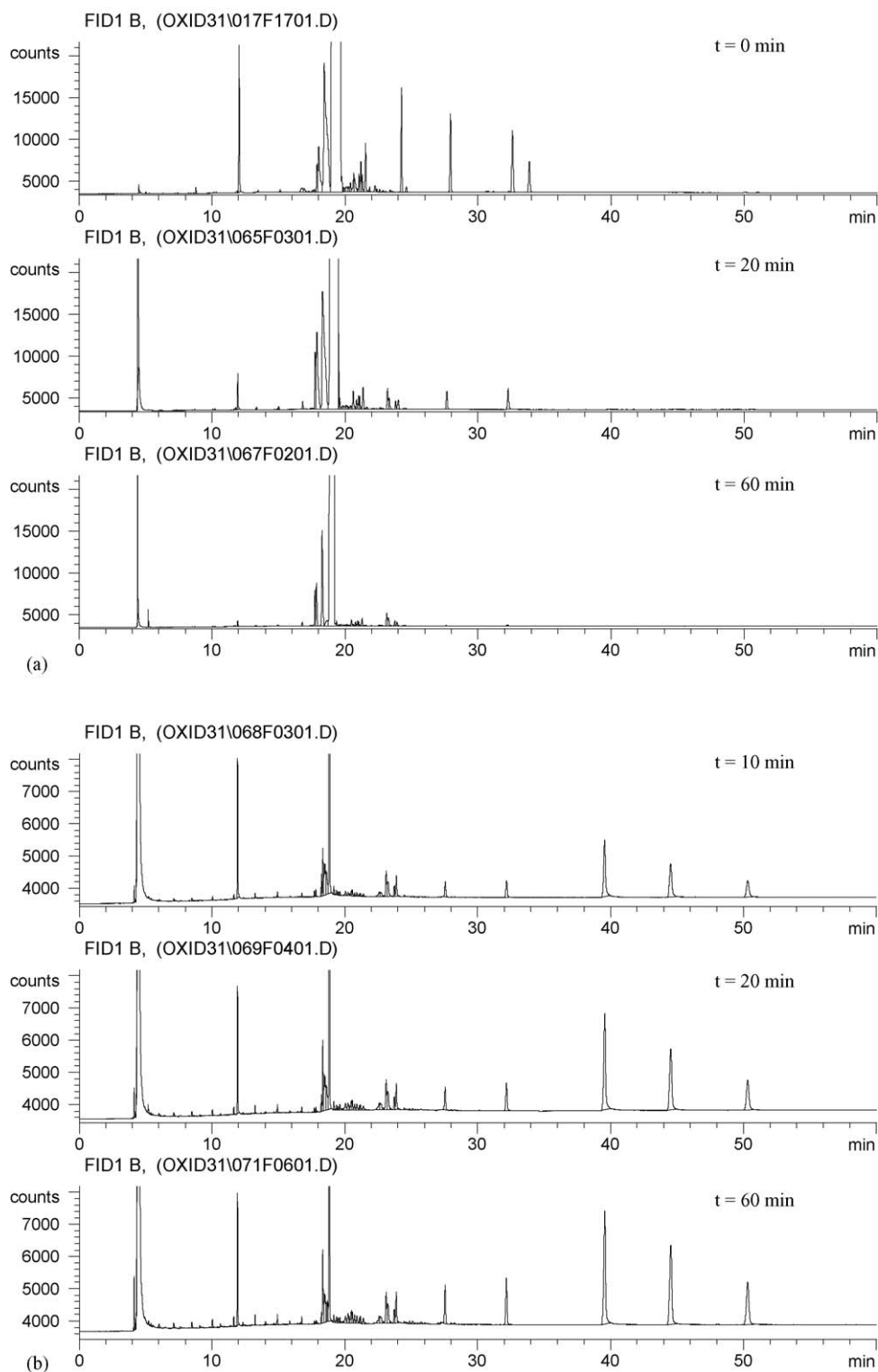
Fig. 2. Time-sequence of the GC-FID chromatograms for the ODS of S-compounds: (a) diesel phase and (b) solvent phase. Retention times (min): acetonitrile, 4.4; BT, 12.1; BT sulfone, 18.4; hexadecane, 19.0; DBT, 24.1; 4-MDBT, 27.5; 4,6-DMDBT, 32.2; DBT sulfone, 39.6; 4-MDBT sulfone, 44.5; 4,6-DMDBT sulfone, 50.3.

oxide species, results difficult to assess the presence of surface vanadium oxide species on the catalysts. According to literature reports, the band at 980–1030 cm^{-1} is also assigned to the terminal V=O vibration of the surface metal oxide species [24], corresponding to the presence of metal oxide microcrystals in polymeric species [23]. Moreover, SEM-EDX shows that the

catalyst does not present segregation of V_2O_5, but according to the XRD results we can identify crystalline V_2O_5. Then, polymeric species are well dispersed on supports, and the interaction of V species-support delineates the V reduction. Therefore, the two TPR peaks of V/Ti can be attributed to successive reduction of V(+5) to V(+4) and V(+3) species,

because titania is able to stabilize V(+4) oxidation state, probably due to the removal of an oxygen bridge from a V–O–V linkage in microcrystals of polymeric surface vanadium species [25].

3.2. Oxidesulfurization (ODS) activity and selection of oxidant reagent

As it was stated above, the reactive system consists of two phases and a solid catalyst. For this reason, we will present the results obtained from the analysis of the diesel phase to evaluate total removal of S-compounds, and the solvent phase will be analyzed in order to estimate the physical extraction and the reactivities of benzothiophenes to sulfones. Experiments were carried out at 60 °C in presence of V/Al or V/Ti catalysts, using acetonitrile as extraction solvent, and hydrogen peroxide or tertbutyl hydroperoxide (TBHP), in order to select the best oxidant.

In these conditions, the results show that oxidation of thiophenic compounds, as thiophene, 2 methylthiophene and 2,5 dimethylthiophene, did not take place. These compounds are the most reactive in HDS reaction, but they are the most refractory in ODS reactions [10]. However, after hydrotreating, these compounds are removed totally and mainly benzothiophenic compounds are present in higher proportion. Since ODS is proposed as a post-treatment for conventional HDS, the study of thiophenic compounds removal is not necessary. Therefore, we selected only benzothiophenic compounds as model compounds of synthetic diesel.

For the typical ODS reaction, Fig. 2 reports the time-sequence of the GC-FID chromatograms of the two phases. The model mixture of synthetic diesel presents peaks of S-compounds ($t = 0$ min), but after 20 and 60 min we can observe that these compounds were removed considerably (Fig. 2a). In the solvent phase (Fig. 2b), we can appreciate small amounts of S-compounds, which were only extracted, and the progressive formation of sulfones during the reaction. The peaks of benzothiophenic compounds were identified by GC–MS, comparing their retention times with reference compounds, while the peaks of their corresponding sulfones were identified using a GC-PFPD and GC–MS. During reaction, the peaks of
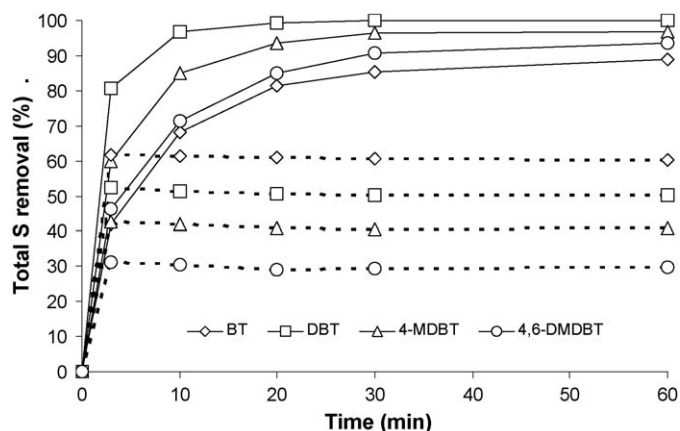
benzothiophenic compounds in diesel phase disappeared almost completely, while in solvent phase, the sulfone peaks appeared, confirming that the oxidation of benzothiophenes led to the formation of their sulfones. Besides, peaks of benzothiophenes in solvent phase appear due to extraction of these compounds, and they remain there when oxidation is not complete.

Fig. 3 shows total sulfur removal, of benzothiophenic compounds, obtained with V/Al catalyst and different oxidants, for equal O/S ratio. Total S removal is the fraction of benzothiophenic compounds eliminated from diesel phase respect to the initial concentration. These results show that it is possible to obtain the highest removal of benzothiophenes using H_2O_2 as oxidant. BT compounds, which contribute mainly to S-compounds in diesel, are removed around 90–100% with H_2O_2. Using TBHP as oxidant, the total S removal achieved is only 30, 40 and 50% of 4,6-DMDBT, 4-MDBT and DBT, respectively. Since oxidation to sulfones was insignificant, these results can be attributed only to extraction process. In this case, BT shows the highest total S removal because it is more easily extracted than all the other BT compounds as it is reported in Refs. [15,16].

For V/Ti catalyst, when using H_2O_2 as oxidant, total S removal was slightly lower than on V/Al. In contrast, with TBHP, S removal was higher with V/Ti catalyst. Total removal, in presence of this catalyst and TBHP, was 54, 62 and 77% of 4,6-DMDBT, 4-MDBT and DBT, respectively.

As it was mentioned before, the extraction–oxidation desulfurization process is carried out in two steps; first the sulfur compounds are extracted and subsequently oxidized to their corresponding sulfones in a consecutive reaction scheme [15]. In general, removal of sulfur compounds is attained in a few minutes (<10 min at 60 °C, see Fig. 3) but oxidation reaction takes place afterward. Then, total removal depends on physical extraction of S-compounds without reaction, and sulfone production. Table 1 shows the results of total removal and yield to sulfone obtained with H_2O_2 as oxidant for both catalysts. The results obtained using V/Al as catalyst were better than those with V/Ti. It is important to observe that the difference in total S removal is not so noticeable, but the yield to sulfones is considerably higher with V/Al catalyst.

These differences in activity can be ascribed to the catalyst capacity to decompose the oxidant [15,16]. To corroborate this, we followed the oxidant decomposition in absence of reactants; results are shown in Fig. 4. These results show that TBHP decomposition is lower than that of H_2O_2 for both catalysts, but

Fig. 3. Total removal of S-compounds with V_2O_5/Al_2O_3 catalyst at 60 °C, using TBHP (dotted lines) or H_2O_2 (full lines) as oxidant.

Table 1
Total S removal and yield to sulfone (mol%) of the model compounds at 60 min

S-compound	V_2O_5/TiO_2		V_2O_5/Al_2O_3	
	Total S removal	Yield to sulfone	Total S removal	Yield to sulfone
BT	84.0	24.6	88.9	43.9
DBT	99.9	89.9	99.9	99.9
4-MDBT	91.7	63.8	96.8	83.6
4,6-DMDBT	82.2	44.7	93.5	66.1

Using H_2O_2, with V_2O_5/Al_2O_3 or V_2O_5/TiO_2 catalyst.
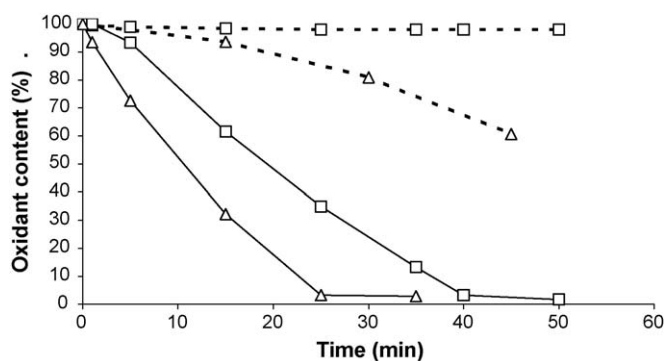
Fig. 4. Oxidant decomposition at 60 °C in absence of reactants, with V_2O_5/Al_2O_3 ($\square$) or V_2O_5/TiO_2 ($\triangle$) catalyst. Using TBHP (dotted lines) or H_2O_2 (full lines) as oxidant.

Fig. 5. FT-IR spectra of V_2O_5/Al_2O_3: (a) after adsorption of DBT, (b) followed by adsorption of quinoline and (c) subsequent evacuation at room temperature.

it is higher with V/Ti, in disagreement with ODS reactivity results. When H_2O_2 was used as oxidant, a higher decomposition was obtained with V/Ti, but V/Al presents the highest activity. The activity differences obtained with these catalysts are more significant on oxidation than on total S removal. This effect can be attributed to presence of water. In this sense, Arends and Sheldon [28] report that Ti(IV) species are ineffective catalysts for epoxidation with aqueous hydrogen peroxide, due to their marked sensitivity towards deactivation by strongly coordinating ligands, especially water. This effect was observed in similar conditions [15] with vanadium supported on alumina, but it is more significant on V/Ti catalyst due to the hydrophilic character of support.

3.3. Effect of N-compounds on ODS activity

Under experimental conditions above described, the oxidation reaction of benzothiophenic compounds led directly to the corresponding sulfone, and the oxidation of carbazole and quinoline did not take place. In this case, only physical extraction of these N-compounds was observed, and they were mainly extracted to solvent phase. Except for indole, where oxidized products (possibly indole-2,3-dione or indigo) were detected by GC–MS.

Results of total S removal and yield to sulfone, obtained in presence of 900 ppm of N-compounds (quinoline, carbazole or indole), with the best catalyst (V/Al) and oxidant (H_2O_2), are shown in Table 2. By comparing with results in absence of N-compounds (Table 1), it is observed that N-compounds (carbazole and indole) affect ODS activity of S-compounds: total S removal slightly decreases and the yield to sulfones is
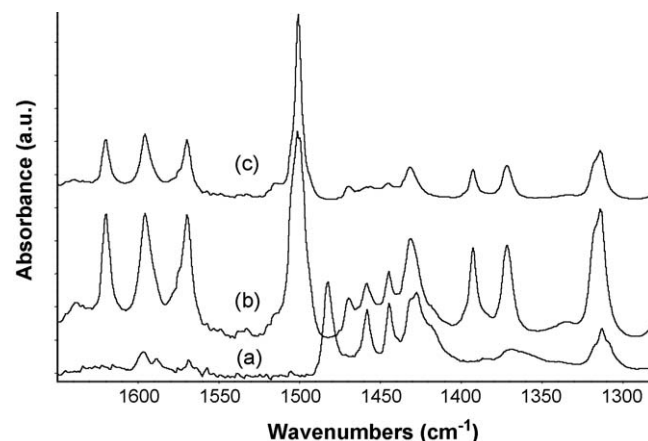
considerably diminished. In presence of quinoline, this effect is more significant. Then, the effect of N-compounds is higher on the yield to sulfones and ODS activity is inhibited in the next order: quinoline > indole > carbazole. Since total S removal depends on two contributions: extraction and oxidation, in this case the latter is inhibited, thus the difference in total removal can be attributed to the loss of activity.

ODS activity trend of S-compounds prevails in presence or absence of N-compounds: DBT > 4-MDBT > 4,6-DMDBT > BT, according to results obtained on solid catalysts: i.e. MoO_3/Al_2O_3 with TBHP [13] and V_2O_5/TiO_2 with H_2O_2 [16]. So, the presence of N-compounds does not influence ODS reaction mechanism. Also, since only indole is oxidized, and all these N-compounds inhibited ODS reaction of S-compounds, this effect cannot be ascribed to competitive reactivity between sulfur and nitrogen compounds for reactive oxygen species. Given that these species are obtained on the catalyst surface [19,28] and the fact that oxidant decomposition slightly diminishes in presence of N-compounds, the inhibition effect could be attributed to adsorption of reactants (N and S-compounds) on the catalyst, poisoning the adsorption sites where reactive oxygen species are formed.

In general, the yield to sulfone and total S removal are markedly diminished in presence of a N-compound and this effect is clearer when quinoline is present. In an attempt to explain this behavior, two successive adsorptions of DBT and quinoline, and then quinoline and DBT on V/Al catalyst were performed and analyzed by FT-IR spectroscopy. FT-IR results for the two tests were very similar, so Fig. 5 only shows IR

Table 2
Total S removal and yield to sulfone (mol%) of the model compounds at 60 min

S-compound	With quinoline		With carbazole		With indole	
	Total S removal	Yield to sulfone	Total S removal	Yield to sulfone	Total S removal	Yield to sulfone
BT	73.8	16.5	87.2	42.9	87.8	31.3
DBT	97.0	68.9	99.0	92.0	98.2	73.0
4-MDBT	77.0	35.0	97.0	80.0	96.0	60.0
4,6-DMDBT	59.0	15.0	90.0	62.0	89.0	41.3

Using V_2O_5/Al_2O_3 catalyst and H_2O_2, in presence of 900 ppm of N-compound (quinoline, carbazole or indole).

Table 3
IR bands for quinoline and dibenzothiophene compounds

Compound	IR absorption band (cm^{-1})
Quinoline	1620(s), 1596(s), 1570(s), 1501(vs), 1469(w), 1431(s), 1392(s), 1371(s), 1314(s)
Dibenzothiophene	1596(vw), 1568(vw), 1482[a], 1457(s), 1444(s), 1427(s), 1415(sh), 1368(w), 1312(w), 1308(sh)

[a] Biphenyl in DBT. (vs) very strong; (s) strong; (w) weak and (vw) very weak absorption; (sh) shoulder.

results obtained for DBT and quinoline sequence. In this figure, we observe the presence of characteristic bands due to adsorbed DBT and quinoline compounds (see Table 3). It is also evident that after quinoline adsorption, the IR bands of DBT localized at 1457, 1444 and 1427 cm^{-1} decrease in intensity and the shoulders at 1415 and 1308 cm^{-1} almost disappeared. Sample evacuation at room temperature, gives as result an IR spectrum only with bands of adsorbed quinoline. The fact that quinoline bands remain after evacuation suggests that DBT is being displaced, occupying therefore the adsorption sites of catalyst.

In view of the IR results and from the obtained activity differences in yield to sulfones (Table 2), the poisoning effect could be influenced not only by a competitive adsorption between nitrogen and sulfur compounds on the adsorption sites of catalyst but also by the basic character of N-compounds. It is generally accepted that five-membered N-ring compounds are less basic (less aromatic character) than 6-membered ring compounds, therefore it would be expected that quinoline, with a six-membered heteroatom ring, preferentially exhibited a stronger poisoning effect than carbazole, containing a five-membered ring, as in hydrotreating [29,30]. Thus, N-compounds poison the adsorption sites of the catalysts and according to the activity results; quinoline is a stronger poison than indole and carbazole.

4. Conclusions

The reactivity towards oxidesulfurization (ODS) by extraction–oxidation of sulfur compounds generally present in diesel was investigated, using V$_2$O$_5$ supported on alumina or titania as catalysts. Two main effects were analyzed: the oxidant reagent, H$_2$O$_2$ or tertbutyl hydroperoxide, and the presence of nitrogen compounds, such as quinoline, carbazole and indole. The results of this study show that V$_2$O$_5$/Al$_2$O$_3$ catalyst and H$_2$O$_2$ is the best combination in order to improve the ODS reactivity of S-compounds. This result is attributed to the catalytic decomposition of the oxidant and lower inhibition of water with V$_2$O$_5$/Al$_2$O$_3$ compared with V$_2$O$_5$/TiO$_2$.

N-compounds present in oil fractions, which are poisons of typical hydrodesulfurization catalysts, inhibited ODS activity of benzothiophenic compounds. When quinoline was present, a higher effect was obtained, decreasing the yield to sulfone up to 78% for 4,6-DMDBT and in less proportion for other benzothiophenic compounds.

ODS activity trend of S-compounds prevails, in presence or absence of N-compounds: DBT > 4-MDBT > 4,6-DMDBT > BT. Thus, the presence of N-compounds does not influence the ODS reaction mechanism. Since only indole is oxidized, and all N-compounds inhibited ODS reaction, this poisoning effect is attributed not only to competitive adsorption between sulfur and nitrogen compounds for catalytic sites, but also to their basic character.

Acknowledgements

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