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V-Mo based catalysts for oxidative desulfurization of diesel fuel

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ABSTRACT

Catalytic oxidative desulfurization (ODS) of a Mexican diesel fuel on a spent HDS catalyst, deactivated by metal deposits, was carried out during several reactive-batch cycles in order to study the catalytic performance to obtain low sulfur diesel. To explain catalytic activity results, Mo and/or V oxides supported on alumina pellets were prepared and evaluated in the ODS of a model diesel using *tert*-butyl hydroperoxide (TBHP) or H_2O_2 as oxidant. The catalytic results show that V-Mo based catalysts are more active during several ODS cycles using TBHP. The performance of the catalysts was discussed in terms of reduced species of vanadium oxide, prevailing on the catalysts, which increase the sulfone yield of refractory HDS compounds (DBT, 4-MDBT and 4,6-DMDBT).

1. Introduction

Due to worldwide environmental mandates, refineries are facing the challenge of producing increasingly cleaner fuels [1,2]. The primary focus of the new regulations is the reduction of sulfur in gasoline and diesel. Other rules stipulate to reduce levels of aromatics, especially benzene, benzene derivatives, olefins, and oxygenates. In 1998, the European Union ordered new sulfur specifications for a drastic reduction of sulfur levels that started to be phased in beginning of the year 2000 [3]. Soon similar regulations were legislated in the United States and elsewhere. The Environmental Protection Agency (EPA) Tier II regulations required reductions of sulfur in diesel from the current average of 500 to 15 ppm by June 2006, and in gasoline from 350 to 30 ppm by January 2005 [1]. In Mexico like in most of the world, similar regulations will be imposed. Detailed sulfur standards are complicated because different statutes are applied to individual refinery, corporate pool, and per gallon basis. Removal of sulfur-containing compounds is an important operation in petroleum refining. It is achieved by catalytic processes operated at elevated temperatures (>300 °C) and pressures (20–100 atm H_2) using Co-Mo/Al_2O_3 or Ni-Mo/Al_2O_3 catalyst [4]. The hydrodesulfurization (HDS) process is highly efficient in removing thiols, sulfides, and disulfides, but less effective for thiophenes and thiophene derivatives. Thus, the sulfur compounds that remain in transportation fuels are mainly benzothiophene (BT), dibenzothiophene (DBT), and their alkylated derivatives. The least reactive derivatives are the DBT with methyl groups at the 4 and 6-positions, which are the refractory sulfur compounds that make extremely difficult a deep desulfurization by HDS. To reduce the sulfur content of diesel from 500 to 15 ppm, an estimate showed that the HDS reactor size should be increased by a factor of seven [5]. Another estimate showed that in order to reduce the sulfur level in diesel from 300 to less than 10 ppm, the HDS reactor volume should be increased by a factor of about 15 at 600 psi, or by a factor of five at 1000 psi [6]. This makes HDS an inappropriate solution and thus the search of alternative technologies [2], as the oxidesulfurization (ODS), has gained importance. ODS is a current process and has been discussed recently in previous publications [7–24]. It is an excellent option after HDS process, since the alkyl-substituted dibenzothiophenes (DBTs) are easily oxidized under low temperature and pressure conditions to form the corresponding sulfones. Organic peroxides can supply oxidant species and there is no hydrogen consumed in this reaction. The sulfones are highly polar compounds and are easily separated from the fuel product by extraction [7]. Sulfur compounds such as disulfides are easy to hydrodesulfurize, but they are oxidized slowly. For this reason, ODS can be utilized as a second stage after existing HDS units, taking a low sulfur diesel (~500 ppm) down to ultra low sulfur diesel (<10 ppm) levels.

On the other hand, deactivation of hydroprocessing catalyst occurs time-on-stream. The main causes of catalyst deactivation are deposition of coke [25] and metals on the catalyst [26]. Whereas coke deposition under sufficiently high hydrogen pressure reaches a steady state level, the amount of metal deposited on the catalyst does not reach a steady state. It is continuously deposited on the catalyst during run [27]. The presence of V and Ni is of particular concern because of the poisoning effect during HDS and cracking of the feeds. These metal compounds are accumulated as metal sulfides into the pore mouth

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or into the pore cavity depending on the pore diameter of the catalyst. These sulfides can block the way to the entrance of reactants or cover the active sites causing deactivation of catalyst. Then, during hydroprocessing, metals deposition occurs on the catalyst, which has already lost a substantial portion of its original porosity and surface area [28]. This is generally true for petroleum and coal derived feeds as well as other feeds. Thus, in order to maintain design activity, temperature is raised to offset deactivation, but metals deposition affects the lifetime of the catalyst, and finally it has to be substituted by fresh catalyst. The fresh catalyst (0 wt.% V) has very high HDS activity, but the addition of only 0.87 wt.% of V causes a huge decrease in the HDS activity [29]. Catalysts that are severely contaminated by metal deposits from residue and heavy vacuum gas oil applications are usually not regenerated at all and they have to be disposed of [30]. Environmental legislations require comprehensive solutions for the disposal of spent catalysts [31] since today only "ultimate" wastes may be dumped.

In our recent ODS studies, V-based catalysts with different supports have been evaluated [32], showing high S-removal of an actual Mexican Diesel and a model diesel with N-compounds [22] using mainly H_2O_2, which is the most common oxidant agent [15]. *Tert*-butyl hydroperoxide (TBHP) has shown interesting ODS results when it was employed with Mo, V, Ni or W/alumina catalysts and it has been suggested for continuous processes [10,14,18]. Therefore, in order to approach a continuous process, our V-based catalysts have been tested in several ODS-batch cycles using TBHP or H_2O_2 as oxidant. Also, bimetallic V-Mo catalysts have been prepared and tested, as references of a spent HDS catalysts deactivated with vanadium. These catalysts contain mainly Mo, Ni, and V oxide species on alumina, so they can be used as ODS catalysts [33]. Finally, as changes in V oxidation state are most likely during ODS process, reduced VOx phases were evaluated to explain how catalyst acts in presence of each oxidant.

2. Experimental

All compounds were purchased from Sigma–Aldrich and used without further treatment. Hexadecane (99.8%) was used as solvent of model compounds: dibenzothiophene (DBT, 98%), 4-methyl dibenzothiophene (4-MDBT, 96%) and 4,6-dimethyl dibenzothiophene (4,6-DMDBT, 97%). This model diesel was prepared with 610 S ppm: 220 of DBT, 201 of 4-MDBT and 189 of 4,6-DMDBT, and the commercial-Mexican diesel fuel had 350 ppm of total S. Diesel specifications: 34° API, specific gravity = 0.854, initial and final boiling point = 264 and 343 °C. Acetonitrile (99.9%) was used as extraction solvent. Aqueous solutions of hydrogen peroxide (30 wt.% H_2O_2) and *tert*-butyl hydroperoxide (70 wt.% TBHP) were used as oxidant agents.

2.1. Catalyst preparation and characterization

Mo and/or V oxides were supported on pellets (gamma-alumina) of cylindrical shape, 6 mm height, 5 mm diameter and internal walls thickness of 200–250 μm (Fig. 1). Bimetallic and monometallic catalysts were prepared by wet-impregnation method. To prepare V monometallic catalyst (V/A), the required amount of ammonium metavanadate was dissolved in oxalic acid solution (2 M) and mixed with the support in continuous stirring. Then the solvent was slowly evaporated. In the case of Mo, an aqueous solution containing the desired amount of ammonium heptamolybdate was mixed with the support. After that, all

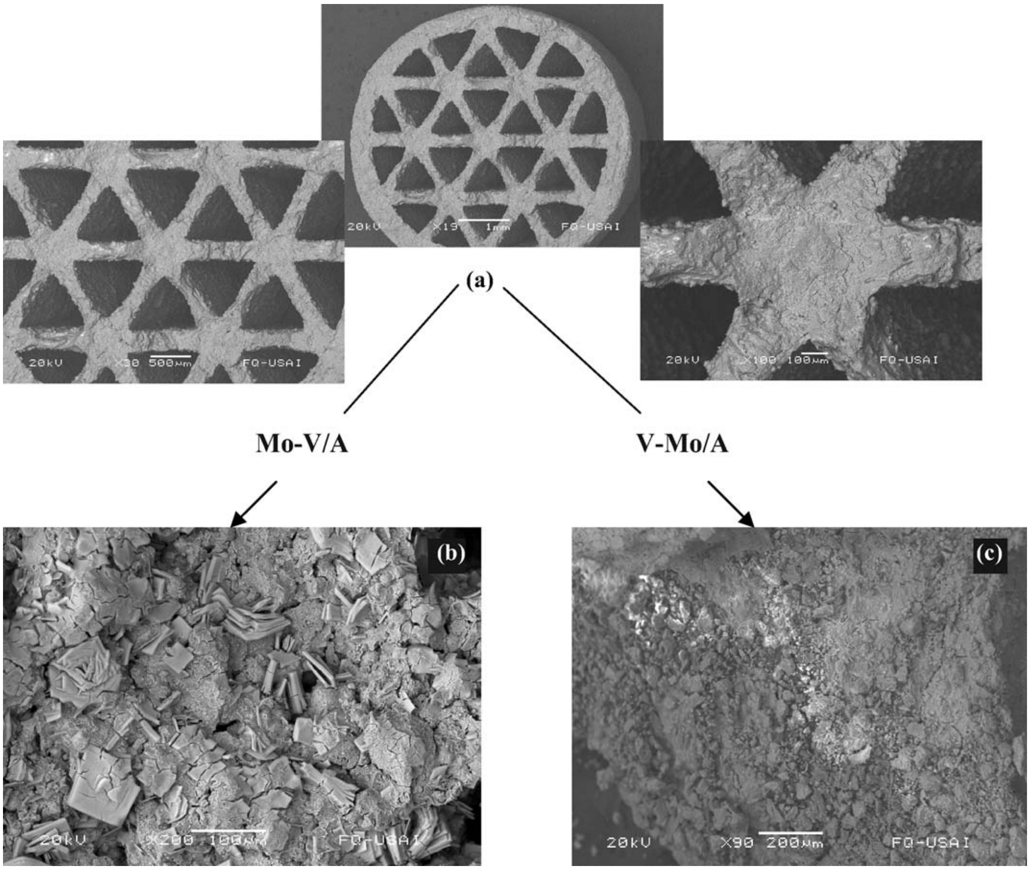

Fig. 1. SEM-EDX micrographs of (a) fresh pellet and, the impregnated catalysts; (b) first V and after Mo (Mo-V/A) or (c) first Mo and after V (V-Mo/A).

samples were dried at 100 °C for 12 h and calcined at 500 °C overnight under air. Bimetallic catalysts were obtained by successive impregnation, with intermediate calcination after the first impregnation. When V was the first impregnation, the catalyst was labeled Mo-V/A. Inverse successive impregnation corresponding to V-Mo/A catalyst. The spent HDS catalyst (SHC) was obtained and activated according to the patent [33].

Composition of vanadium species ($V^{5+}/V^{4+}/V^{3+}$) in the catalysts was evaluated by permanganometric titration and titration of iron (II) ammonium sulfate, after dissolving the samples in small amount of H_2SO_4 (1:1) solution, as described in [34]. Chemical analysis was followed potentiometrically with ORP Redox Meter Hanna Instruments.

Catalysts were characterized by X-ray diffraction (XRD) using 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. Average pore size was evaluated from the desorption branch of the isotherm using the BJH model. 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.

2.2. Catalytic experiments

All ODS cycles were performed in a glass-batch reactor, fitted with condenser, mechanical stirrer and a thermocouple. The reactor was immersed in a thermostatically controlled water bath to carry out the reactions at 60 °C, since previous results showed this is the proper temperature [7,21]. In a typical reactive cycle, the water bath was first heated up and stabilized to the desired reaction temperature, and the mixture diesel-solvent (1:1 vol. ratio) was added to the reactor. Then oxidant agent and catalyst (pellet) were introduced into the reactor with vigorous stirring, the pellet was placed in a fix point. An ODS reactive cycle lasts 60 min, then spent solutions (diesel and solvent) are removed and fresh solutions are added to perform a new reactive cycle. The catalysts were submitted to several ODS reactive cycles (4 or 6), using a catalyst concentration of 3.3 g/L of diesel for each cycle. After each ODS cycle, samples of diesel and solvent phases were withdrawn and injected (auto sampler) to the GC-FID after cooling at 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).

TBHP or H_2O_2 was used as oxidant, with an initial O/S molar ratio of 11, 13 or 16. TBHP was measured during reaction by standard permanganometric titration and GC-FID. H_2O_2 content was measured by standard iodometric titration. Oxidant agent was added in small doses to reduce thermal decomposition, according to previous results [21]. Also, in order to evaluate the intrinsic activity of V_2O_5, V_2O_4, and V_2O_3, and take them as reference, DBTs in acetonitrile (610 S ppm) were used as reactive mixture, to evaluate only the liquid phase oxidation [35], and no diesel phase was used. ODS tests with unsupported vanadium oxides were carried out with vanadium (V) oxide (98%), vanadium (IV) oxide (99.9% base metal) and vanadium (III) oxide (98%), employing H_2O_2 or TBHP as oxidant. To avoid excess of water in these experiments a ratio of O/S = 4 was used. These ODS tests were carried out with a ratio of catalyst weight to volume diesel equal 2.0 g/L.

Table 1
Textural properties and elemental composition of the catalysts and support.

Sample	V (wt.%)	Mo (wt.%)	Surface area (m^2/g)	Pore volume (cm^3/g)	Average pore diameter (Å)
Alumina	0	0	207	0.015	71
V/A	19	0	126	0.007	89
Mo-V/A	16	15	125	0.006	89
V-Mo/A	16	14	125	0.006	89
SHC[a]	13	13	99	0.140	85

[a] Spent HDS catalyst with 3 wt.% of Ni.

3. Results and discussion

First we will present the characterization results of the catalysts. Second, we will analyze the ODS activity of the catalysts during 4 or 6 reactive cycles. Then, the effect of oxidant agent on ODS will be discussed. Finally, we will present the ODS performance of a spent HDS catalyst and unsupported vanadium oxides (V_2O_5, V_2O_4, and V_2O_3).

3.1. Characterization of catalysts

Table 1 shows textural properties and elemental analysis of the catalysts, obtained by N_2 physisorption and SEM-EDX. As expected, metal impregnation into pellets reduce surface area and pore volume, while average pore diameter increases. Textural properties of bimetallic catalysts (Mo-V/A and V-Mo/A) are similar, and this result suggests that the impregnation order is unimportant. SHC presents smaller surface area and higher pore volume, and similar metal composition of V and Mo as that of bimetallic catalysts. Chemical analysis by titrimetric method shows that the catalysts have mainly V^{5+} species. V/A has 85.5% of V^{5+} and 6% of V^{3+}, and bimetallic catalysts have more than 95% of V^{5+}. According to these results, XRD patterns of the catalysts (not shown) present the main reflections attributable to vanadium and molybdenum oxides: V_2O_5 (JCPDS 41-1426), MoO_3 (JCPDS 89-5108), and Al_2O_3-gamma (JCPDS 10-0425).

Fig. 1 shows SEM-EDX micrographs of the support and bimetallic catalysts. Mo impregnation after vanadium (Mo-V/A) generates stacking of MoO_3 (see Fig. 1b), but if V is impregnated after Mo (V-Mo/A), these species are dispersed (see Fig. 1c). Probably, this dispersion is due to dissolution of Mo agglomerates when pellets were immersed to carry out the second impregnation. SEM-EDX elemental analysis map of Mo-V/A (not shown) presents Mo agglomerates and good V distribution. And for all other catalysts, good metallic distribution was obtained.

3.2. ODS of DBTs, using H_2O_2 or TBHP as oxidant agent

The reactive system consists of two phases (diesel and solvent phase) and a solid catalyst (L–L–S system). The sulfone yield of DBTs was defined as the fraction of DBTs sulfone (only present in solvent phase) respect to the initial concentration of DBTs in the feedstock.

First comparative tests were done using the monometallic system (V/A), employing H_2O_2 and TBHP (O/S = 13), during four ODS cycles (240 min, 60 min/cycle). After each cycle new phases (solvent and model diesel) were used. Results of sulfone yield using H_2O_2 are presented in Fig. 2. It is clear that the catalyst suffers a deactivation in subsequent cycles, where H_2O_2 decomposes in water and reactive oxygen. Reactive oxygen participates in the oxidation of DBTs compounds, but adsorbed water on catalyst increases with the number of reactive cycles. It produces deactivation of the catalysts, according to previous results [21,22]. Then, a different behavior must be submitted using TBHP, because it decomposes producing *tert*-butanol and reactive oxygen.

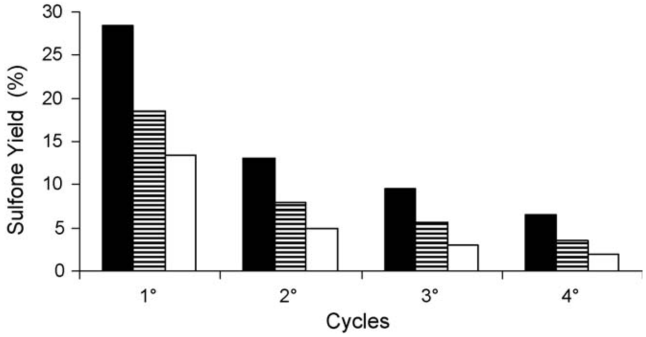

Fig. 2. Sulfone yield of DBT (■), 4-MDBT (▤) and 4,6-DMDBT (□), in four reactive cycles, using V/A and H_2O_2.

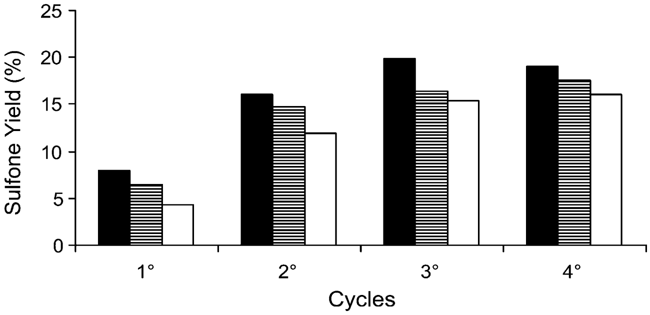

Fig. 3. Sulfone yield of DBT (■), 4-MDBT (▤) and 4,6-DMDBT (□), in four reactive cycles, using V/A and TBHP.

Fig. 3 shows sulfone yield of DBTs using TBHP. Contrary to the behavior presented with H_2O_2, TBHP does not show deactivation during reactive cycles, and sulfone yields increase with each cycle. To explain these results, V_2O_5 (15 wt.%)/Al_2O_3 was prepared by thermal spreading as reported in [32] and calcined at 500 °C for 6 h. After that the catalyst (V15) was dried or wet for 48 h, in air atmosphere at 100 °C or in a chamber (with 90% of humidity) at room temperature (r.t.), respectively. DTA/TG results of wet catalyst indicate a continuous weight loss from r.t. to 150 °C, which is due to dehydration. Total weight loss was 22.5 wt.%, where 2.5 wt.% was lost in the range of 90–150 °C.

In order to evaluate the adsorbed water effect, dried V15 and wet V15 were tested in ODS reaction at the same conditions (described above), using H_2O_2 or TBHP as oxidant. Table 2 presents the sulfone yield obtained after 60 min of ODS reaction with these catalysts and O/S = 11. Dried catalysts had better performance, but using TBHP as oxidant this difference becomes more important. Using H_2O_2 (30%) the initial amount of water is higher respect to that of TBHP (70%) furthermore H_2O_2 decomposes into water. According to previous results [21,22], activity is strongly affected by the presence of water in the reaction system; in this case deactivation is more observable with TBHP. Water effect can be attributed to organic compounds, which are less soluble in water and the solvent performance depends on the solubility of the sulfones in the reaction mixture [13]. But it is not the unique factor because Hulea et al. also stated that in hydrophilic materials, water is strongly adsorbed and the inner substrate concentration will be very low, thus hindering catalytic performance. In our experiments, solutions did not accumulate water during batch cycles and deactivation cannot be attributed to lower solubility of DBTs in extraction solvent, because spent solutions (diesel and solvent) are removed and fresh solutions are added to perform a new reactive cycle. On the other hand, leaching is common on liquid phase reaction but in our system liquid solutions did not show the characteristic color of leached vanadium with TBHP and only a faint coloration was observed with H_2O_2, and considering leaching results with similar catalysts [35], leaching is not the principal reason of deactivation with H_2O_2. Thus, during ODS cycles with H_2O_2, inhibition by water dominates the ODS reaction since sulfone yield decreases steadily with each cycle. In contrast, when TBHP is used as oxidant the sulfone yield increases. The cause of this behavior will be discussed further below.

Table 2
Sulfone yield of DBTs with V15 pretreated.

Catalyst.	Oxidant	Sulfone yield (%)		
		DBT	4-MDBT	4,6-DMDBT
Dried	H_2O_2	76	48	26
Wet		73	45	23
Dried	TBHP	48	33	18
Wet		14	12	8

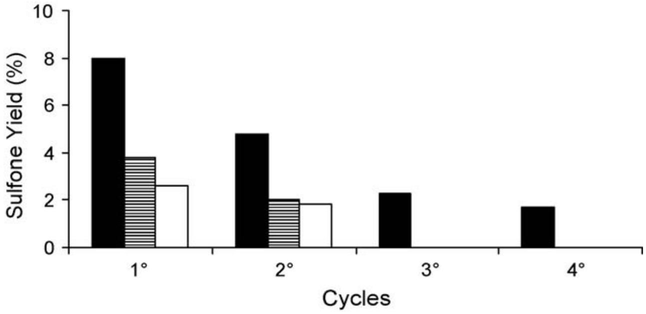

Fig. 4. Sulfone yield of DBT (■), 4-MDBT (▤) and 4,6-DMDBT (□), in four reactive cycles, using V-Mo/A and H_2O_2.

The activity trend obtained, with bimetallic catalysts, is qualitatively analogous to that obtained with V/A. Figs. 4 and 5 present the sulfone yield obtained with V-Mo/A. ODS cycles were also carried out with Mo-V/Al and no differences were observed, which suggests again that the impregnation order is not important. In the case of H_2O_2 (Fig. 4), sulfones of 4-MDBT and 4,6-DMDBT were not produced beyond the second cycle. In contrast, when TBHP was used, sulfones yield increases with reactive cycles (Fig. 5). Using H_2O_2, the incorporation of Mo did not improve ODS activity. ODS results of monometallic catalyst Mo/A (not included), using TBHP, show sulfone yields between 15% and 20%, in a similar trend to V/A and V-Mo/A. This means that in a continuous ODS process, TBHP must be used as oxidant agent.

A comparison of the activities of bimetallic and monometallic catalysts, suggest that the metal oxides act independently without synergistic interactions. When TBHP was used, along with V/A and V-Mo/A (Figs. 3 and 5, respectively), sulfone yields were similar. Then the sum of the individual activities of the monometallic

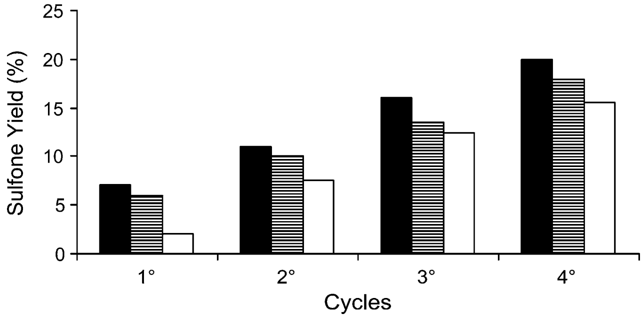

Fig. 5. Sulfone yield of DBT (■), 4-MDBT (▤) and 4,6-DMDBT (□), in four reactive cycles, using V-Mo/A and TBHP.

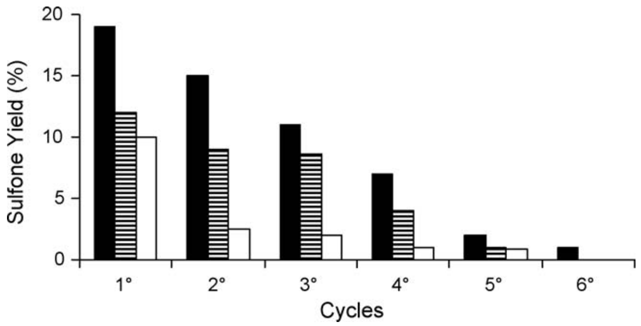

Fig. 6. Sulfone yield of DBT (■), 4-MDBT (▤) and 4,6-DMDBT (□), in six reactive cycles, using SHC and H_2O_2.

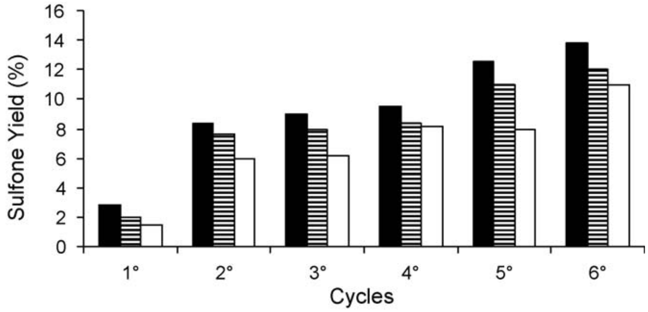

Fig. 7. Sulfone yield of DBT (■), 4-MDBT (▤) and 4,6-DMDBT (□), in six reactive cycles, using SHC and TBHP.

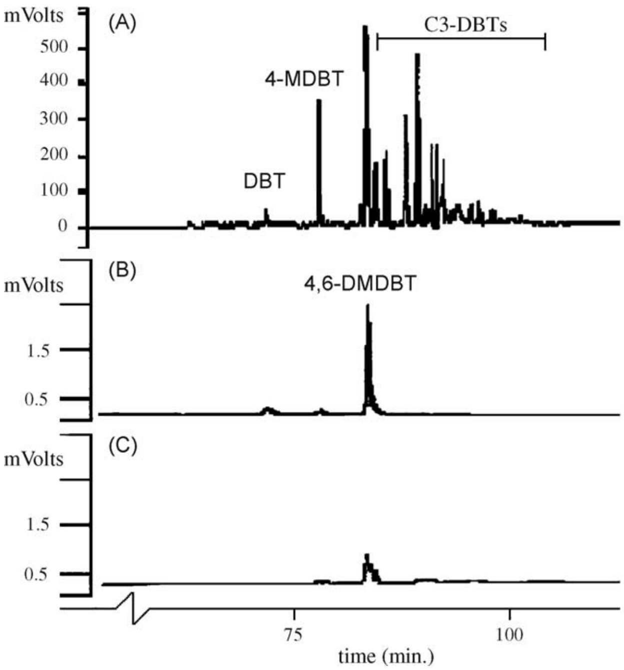

Fig. 8. Sulfur-specific chromatograms (PFPD) of original Mexican diesel (A), and after ODS reaction with H_2O_2 (B) or TBHP (C). With SHC used during four ODS cycles.

catalysts does not correspond to the activity of the V-Mo/A catalyst. The absence of synergistic interactions is expected for single site reactions such as sulfur dioxide oxidation [36], where V-Mo based catalysts were used. However, in this case with H_2O_2, bimetallic catalysts present lower activity than V/A, which suggests an inhibiting effect of the Mo on V catalyst. Possibly due to microcrystals of Mo–alumina species, which were observed by XRD and SEM-EDX. This point will be discussed below.

Having analyzed the performance of bimetallic and monometallic catalysts, we evaluated the spent HDS catalyst (SHC) activated for ODS, during six reactive cycles at the same conditions mentioned above. Results show that total S-compounds removal using H_2O_2 decreases with ODS cycles, this obviously affect sulfone yield (Fig. 6). In the case of TBHP, the re-activation of catalyst during ODS cycles was observed again, and sulfone yield increased (Fig. 7). Also, SHC was tested with actual Mexican diesel, during four ODS cycles, adding new diesel after each cycle of 60 min and employing H_2O_2 or TBHP with O/S = 16. According to previous results [32], GC-FID analyses of the original diesel before and after the catalytic oxidation show that the chromatogram traces were almost the same as those of the original diesel and there were no significant changes in either distribution or intensity of these peaks. In this case, results show similar ODS performance to that of model diesel. In Fig. 8, GC-PFPD chromatograms showed the distribution of DBTs before and after ODS reaction. It is observed that a cluster of peaks exists in the original diesel between 85 and 95 min, which corresponds to alkyl-substituted DBT (C3-DBTs). After oxidation, the whole group of peaks disappeared (notice the scales are different), mainly prevailing small amounts of 4,6-DMDBT. It is the most refractory compound under ODS conditions. But it is evident after ODS reaction that there was a noticeable decrease in the amounts of S-compounds, including 4-MDBT and 4,6-DMDBT. These results suggest that, working in optimal conditions, ultra deep desulfurization of diesel can be achieved by ODS process in presence of vanadium-molybdenum based catalysts, which can be obtained from spent HDS catalysts.

On the other hand, during ODS reaction color changes were observed in the catalysts, which could be ascribed to different oxidation state of V oxides. It can be attributed to complex formation of an oxometal, which is obtained during activation of the oxidant involving a change in the oxidation state of the metal species [32,35]. In this sense, unsupported vanadium oxides (V_2O_3, V_2O_4, and V_2O_5) were evaluated as catalysts and the results are presented in Figs. 9 and 10. The reaction was carried out using DBTs in acetonitrile as reactive mixture (L–S system), in order to

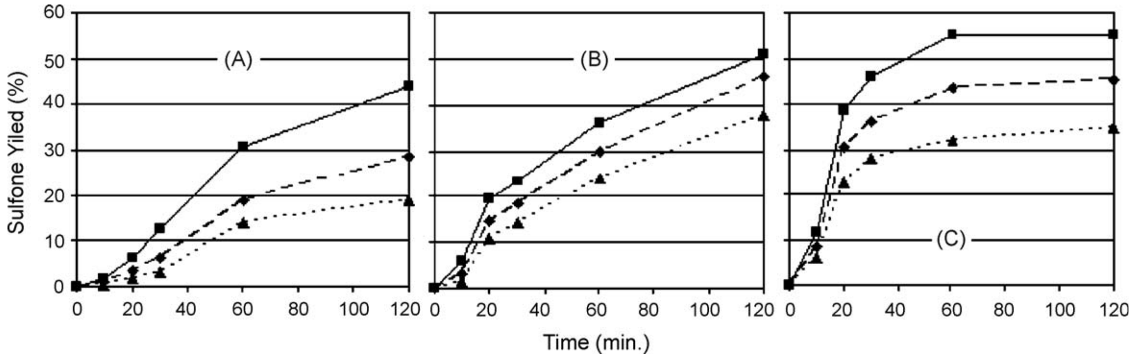

Fig. 9. Sulfone yield of DBT (■, continuous line), 4-MDBT (◆, dashed line) and 4,6-DMDBT (▲, doted line), with V_2O_5 (A), V_2O_4 (B) or V_2O_3 (C), using H_2O_2.

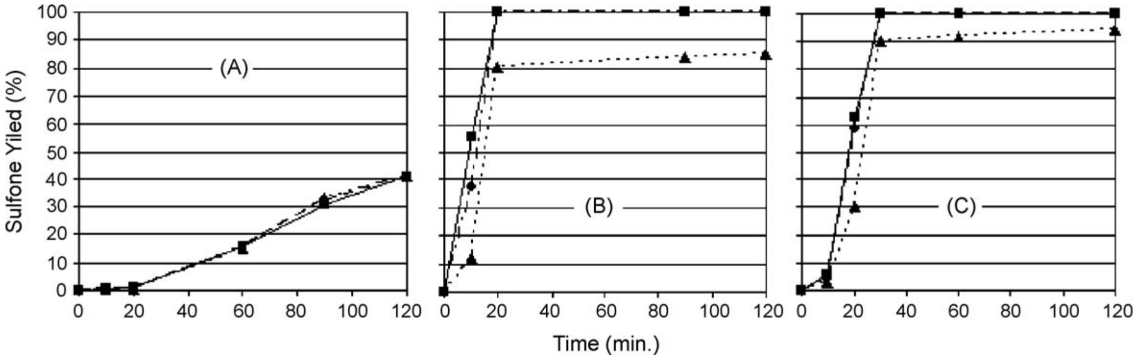

Fig. 10. Sulfone yield of DBT (■, continuous line), 4-MDBT (◆, dashed line) and 4,6-DMDBT (▲, doted line), with V_2O_5 (A), V_2O_4 (B) or V_2O_3 (C), using TBHP.

evaluate only the liquid phase oxidation [35]. With H_2O_2, sulfone yield of DBT reaches 44% in 2 h using V_2O_5 (Fig. 9A). While V_2O_4 (Fig. 9B) produces 51% of DBT sulfone yield, and similar yield is obtained in only 50 min using V_2O_3 as catalysts (Fig. 9C). Also, the initial rate increases considerably with reduced V species showing that these species are more active respect to V_2O_5. When TBHP is used as oxidant (Fig. 10), a better performance of reduced phases is observed and it is possible to obtain sulfone yields (DBT and 4-MDBT) up to 100%, in only 30 min of reaction using V_2O_4 and V_2O_3. These results confirm that reduced V species present better performance, which explains the results during ODS cycles using TBHP, where the presence of VOx reduced phase improves the activity. There are two factors that affect ODS reaction: water, which deactivates the catalyst with both oxidants (Table 2), and reduced V-oxide species prevailing on catalysts. In latter, both oxidants increase the activity, but with TBHP it is more significant than H_2O_2 (Figs. 9 and 10).

In order to corroborate that reduced V species present ODS activity, reduced catalysts of V-Mo/A and V/A were prepared and tested in ODS cycles (L–L–S system). Reduced catalysts were obtained in a conventional TPR apparatus [32], at 10 °C/min up to 700 °C, in flow of H_2/Ar mixture. After that, chemical analysis by titration shows that reduced catalysts have mainly V^{3+} species, more than 98%. Figs. 11 and 12 show sulfone yields of DBTs obtained in four ODS cycles in presence of reduced catalyst of V-Mo/A and V/A (respectively), using the best oxidant, TBHP. These results show similar trends to those obtained with original-oxide catalysts; V/A (Fig. 3), V-Mo/A (Fig. 5) and SHC (Fig. 7). But, if the catalyst is reduced, ODS performance is appreciably higher. We can examine this point, by comparing ODS trends of reduced V-Mo/A (Fig. 11) with the corresponding oxide catalyst (Fig. 5), and Fig. 12 versus Fig. 3 for V/A.

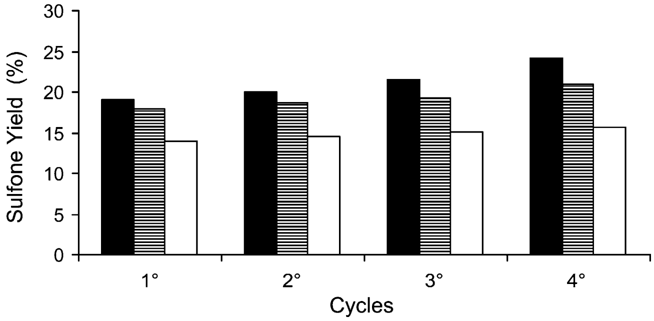

Fig. 11. Sulfone yield of DBT (■) 4-MDBT (▤) and 4,6-DMDBT (□), in four reactive cycles, using reduced catalyst of V-Mo/A and TBHP.

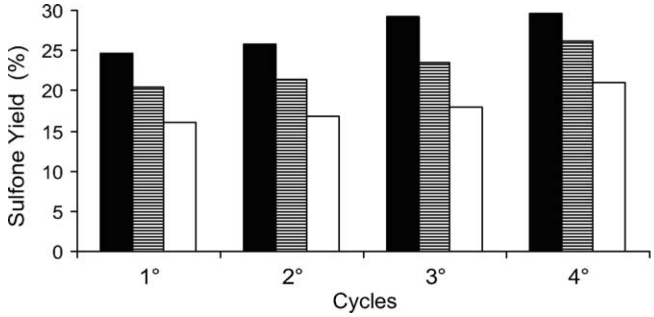

Fig. 12. Sulfone yield of DBT (■, 4-MDBT (▤) and 4,6-DMDBT (□), in four reactive cycles, using reduced catalyst of V/A and TBHP.

Both oxides, vanadia, and molybdena, can be easily reduced but since vanadium has lower reduction potential it is preferentially reduced. Reduction is most frequently accompanied by the formation of shear structures (V_nO_{2n-1} and Mo_nO_{3n-1}, series of oxides). These structural similarities enable the formation of substitutional solid solutions as well as an intermediate compound [37]. Then different phases can exist in the catalysts after TPR treatment that in ODS reactions conditions are not present, and some of which can be active for this reaction.

As it was described elsewhere [38], catalysts for liquid phase oxidations activate oxidant by heterolytic routes, which involve complex formation of oxometal and peroxometal kind, where only the former involves a redox process. Vanadium(5+) complexes have been found to act as catalyst precursors in oxidations of sulfides to sulfoxides and sulfones [39]. The active species has been identified in stoichiometric reactions as mononuclear oxoperoxovanadium(5+) complexes. Vanadium(4+) complexes can also be used as precursors in these oxidation reactions. In the presence of excess peroxide, they are readily converted to these complexes. The actual oxoperoxo catalyst is formed in situ by oxidation of V(4+) to V(5+) with excess of alkylhydroperoxide, yielding an alkylhydroperoxo vanadium(5+) complex. In a proposed mechanism [10,39] the sulfide does not coordinate to the metal centre, but undergoes nucleophilic addition to the peroxide oxygen, i.e. the oxygen is electrophilic in nature. This mechanistic route is also common for peroxometal complexes such as Ti(IV) and Mo(VI) derivatives. In our case, we obtained that the catalytic performance is favored with weaker oxidant (TBHP), which has lower capacity to oxidize V species and they prevail reduced, promoting the formation of active species (oxoperoxo complexes).

4. Conclusions

ODS of DBTs was conducted in presence of V-Mo based catalyst, with H_2O_2 or TBHP as oxidant agent, during several ODS reactive cycles. Also, a spent HDS catalyst deactivated with vanadium, after the adequate activation, was tested as ODS catalyst. Using a model diesel or commercial-Mexican diesel, the ODS performance of the catalysts was similar. After consecutive ODS cycles, with H_2O_2 the yield of DBTs sulfones was decreasing, whereas with TBHP, the ODS activity trend was increased. Water present in the reactive system produces catalytic deactivation, but this effect is more appreciable using TBHP. However, during reactive ODS cycles, this effect is not evident because reduced species of vanadium prevailing on the catalysts are involved in the reaction, working as better active phases. Using H_2O_2, water effect dominates ODS performance, while with TBHP the presence of reduced vanadium species is the important factor.

Reduced vanadium-oxide phases are more active than the oxidized phase, and it is possible to obtain yields of DBTs sulfones up to 100%. Using V-Mo oxide catalysts, the ODS performance is favored with weaker oxidant (TBHP), which has lower capacity to oxidize V species and they prevail as reduced species, promoting the formation of active species, like oxoperoxo complexes.

Spent HDS catalysts present good performance as catalyst for ODS of model and commercial-Mexican diesel. It was possible to obtain high S-compound removals during reactive ODS cycles. These results suggest that ultra deep desulfurization of diesel can be achieved by ODS process in presence of vanadium-molybdenum based catalysts, which can be obtained from spent HDS catalysts.

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