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Performance of molybdenum oxide in spent hydrodesulfurization catalysts applied on the oxidative desulfurization process of dibenzothiophene compounds

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Abstract In order to understand the role of Mo in spent hydrodesulfurization catalysts, which could be used as catalysts for oxidative desulfurization (ODS) process, the preparation method of Mo based catalysts was modified to change the stability of Mo species anchored to support. Mo-supported catalysts were prepared by the impregnation of ammonium heptamolybdate solutions at acidic and near neutral pH on alumina and pseudoboehmite, and were tested in the batch ODS process, using different oxidants such as *tert*-butyl hydroperoxide, H_2O_2 or cumene hydroperoxide (CHP). The activity of the catalysts and their performance is discussed in terms of the Mo species evaluated by temperature-programmed reduction. The results show that H_2O_2 was the best oxidant in the two-phase system (L–S) and three-phase system (L–L–S), whereas CHP presents evident oxidation in the homogeneous phase without a solid catalyst. The best oxidant was selected to study the catalytic stability in a continuous fixed-bed ODS reactor. Two activity contributions of the Mo species were determined: supported Mo-tetrahedral species are the main participant in the oxidation-heterogeneous reactions, and Mo-octahedral species are partially leached into the extraction-solvent and contribute to the homogeneous catalytic reaction.

Keywords Oxidative desulfurization · Mo-based catalysts · Dibenzothiophene · Cumene hydroperoxide · TPR · Leached Mo-species

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Introduction

Fuel regulations will continue to tighten worldwide in response to the need for cleaner air. Refiners will reach the ultra-low sulfur diesel (ULSD) regulations at a significant cost. In most cases, either a new high pressure hydrotreating unit or a major revamp of low/moderate pressure hydrotreating units will be necessary [1]. A combination of several factors, such as the increase of the catalyst volume (with an additional reactor), the replacement of the old generation catalyst with highly active hydrotreating catalysts of the new generation, the increased hydrogen partial pressure, the removal of H_2S from the recycle gas by scrubbing, the use of high efficiency feed distributors in the reactor, and the use of feedstocks that are easy to desulfurize could be considered in hydrotreater revamps for ULSD production. Thus, sulfur removal by alternative technologies is one of the approaches that can potentially be used after the hydrodesulfurization (HDS) unit in the near future [1–7]. Oxidative desulfurization (ODS) has been considered as a new technology for the deep desulfurization of transport fuels, which is not a replacement process to HDS but is a complementary process to HDS, because the refractory compounds in HDS, including alkyl dibenzothiophene (DBT) compounds [e.g., 4,6-dimethyl DBT (4,6-DMDBT)], show the highest oxidation rate in ODS [3] and can achieve a sulfur content of <10 ppm (ULSD).

There are several ODS methodologies available and the process generally consists of three sections: an oxidant supply section, a sulfone generation section and a sulfone separation section [1–5]. Another option is a three-phase reactor system (L–L–S), where the hydrotreated diesel is mixed with an extraction solvent (polar phase), the oxidant and an active solid catalyst for the oxidation of sulfur compounds. After the oxidation, the extraction solvent is separated from the solvent mixture and oxidized compounds by a simple distillation for recycling.

The oxidation of sulfur compounds with peroxides occurs successfully in the presence of solid catalysts. The active center of these catalysts is a transition metal in a high oxidation state with Lewis acidity, such as Mo(VI), Ti(IV), V(V), and W(VI) [3, 8]. Some of the studies have focused on molybdenum oxide based catalysts, heteropolyoxometalates or polymolybdophosphates. However, these catalysts are not very stable, and molybdenum tends to be leached into the reaction medium due to the low Mo–support interaction.

Few studies with molybdenum catalysts have been realized with different oxidants and supports: MoO_3/Al_2O_3 in light gas oil with *tert*-butyl hydroperoxide, TBHP [9], MoO_3/TiO_2, $MoO_3/Al_2O_3–SiO_2$ in kerosene with TBHP [8], $MoO_3/Al_2O_3–MgO$ promoted with Bi in light cycle oil with TBHP [10], MoO_3/Al_2O_3 with H_2O_2 using *n*-octane as model diesel [11], and polymolybdates supported on alumina in diesel fuel with H_2O_2 [12]. Among all of the catalysts examined, MoO_3/Al_2O_3 exhibited the highest conversion for DBT compounds (DBTs). Prasad et al. [10] reported that the catalyst with a monolayer of Mo (around 14–16 MoO_3 wt%) supported on alumina shows better catalytic properties than Mo oxide in the post monolayer region.

Our interest in studying the ODS process with molybdenum oxides on alumina as a catalyst is based on previous works [13] that refer to the use of spent HDS catalysts deactivated with deposited vanadium. These catalysts contain mainly Mo, Ni, and V oxide species on alumina [1] and can be used as ODS catalysts after an activation process. Thus, to understand the role of Mo in spent HDS catalysts reused as ODS catalysts, Mo oxides on alumina with different loadings were prepared in acidic or neutral media and tested in the ODS reactions of a model solution containing DBTs that prevail in diesel fuels using different oxidants: cumene hydroperoxide (CHP), H_2O_2 or TBHP.

Experimental

All compounds were purchased from Sigma-Aldrich and used without further treatment. Decane (99.8 %) and acetonitrile (99.9 %) were used as the solvents of the sulfur compounds (DBTs): DBT (98 %), 4-methyl DBT (4-MDBT, 96 %) and 4,6-DMDBT (97 %). The model S-compounds for the ODS reaction (DBTs in decane or DBTs in acetonitrile) was prepared with 610 S ppm: 220 of DBT, 200 of 4-MDBT and 190 of 4,6-DMDBT. To simulate the movement of DBTs into the extraction phase, DBTs were dissolved in acetonitrile and mass transfer problems were avoided. CHP (70 wt%, CHP), hydrogen peroxide (30 wt%, H_2O_2) and TBHP (70 wt%) were used as oxidant agents.

Catalyst preparation and characterization

Alumina (Sasol, 207 m^2/g) and pseudoboehmite (bh) were used as supports. MoO_3 supported catalysts with various Mo contents were prepared by the incipient impregnation method. The support was impregnated with an aqueous solution (at near neutral pH) or an oxalic-acid (Ox) solution (at pH 0) with the required concentration of ammonium heptamolybdate (AHM) and then maintained for 24 h at room temperature. Differences in the impregnation conditions were realized in order to modify the distribution and the interaction of Mo species on alumina. The impregnated samples were dried overnight at 100 °C in the presence of air, and the resulting solid was calcined in air at 500 °C for 5 h. The MoO_3 load level was varied from 5 to 25 wt% to have Mo content above and below of the monolayer and the catalysts were labeled according to this amount as Mo_5, Mo_8, Mo_{12} and Mo_{25}; additional letters were included to distinguish the preparation method: Ox for the oxalic-acid solution (e.g., Mo_5Ox), H for the aqueous solution (e.g., Mo_5H), and bh for catalysts prepared by impregnation on pseudo-bh (e.g., Mo_5bh).

The catalysts were characterized by X-ray diffraction (XRD) using a Siemens D500 powder diffractometer with Cu K_α radiation. The elemental composition was determined by SEM–EDX (energy-dispersive X-ray) in a Jeol JSM-5900 LV microscope equipped with an EDX elemental analysis system. An ultraviolet (UV)–visible spectrophotometer (Varian-Cary 50 Conc) was used to identify the Mo species in solutions of acetonitrile, water, and model diesel after reaction with H_2O_2 as oxidant. A conventional temperature programmed reduction (TPR) apparatus was used to study the reducibility of the catalysts. The TPR of the catalysts was performed using a flow of a H_2/Ar mixture [30 % H_2 (v/v), 25 cm^3/min] at atmospheric pressure, and a heating rate of 10 °C/min from room temperature up to 900 °C.

Catalytic experiments

ODS reactions were first performed in a glass-batch reactor, fitted with condenser, mechanical stirrer and a thermocouple, that was immersed in a thermostatically controlled water bath to carry out the reactions at 60 °C. In a typical reactive cycle, the model S-compounds (50 cm^3 of DBTs in either decane or acetonitrile) were added to the reactor. Then, the oxidant and the catalyst (100 mg) were introduced, and vigorous stirring started the reaction. This system is a two-phase system (L–S). In a three-phase system (L–L–S), equal volumes of model diesel (DBTs in decane) and extraction solvent phase (acetonitrile) were added to the reactor. Small samples of model diesel and/or 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 GC-PFPD (Varian CP-3800) and GC–MS (HP5890 Series II with MS detector). TBHP, H_2O_2 or CHP were used as oxidants with an initial O/S molar ratio of 6 and were added to the reactor gradually in small doses to reduce the thermal decomposition, according to previous results [13, 14]. TBHP was measured during the reaction by standard permanganometric titration and GC-FID. The H_2O_2 content was measured by standard iodometric titration. CHP and by-products were measured by GC-FID and GC–MS.

Additionally, in order to evaluate the stability of the catalysts, ODS reactions in continuous reactor were performed. These experiments were carried out with a fixed-bed flow reactor (6 mm i.d., 30 cm long) immersed in a thermostatted bath, glass tube packed with 1 g of catalyst and inert particles (1:1). The model diesel was fed into the reactor at the reaction temperature by a liquid pump (Coleparmer MasterFlex 7553-70). Typical ODS reaction conditions were as follows: atmospheric pressure, WHSV = 50 h^{-1}, O/S molar ratio = 6, and reaction temperature = 60 °C. The liquid products were collected every 30 min and analyzed by GC-FID, after cooling at room temperature.

Results and discussion

First, we will present the characterization of the catalysts prepared with different AHM solutions, supports and Mo loading. XRD, SEM–EDX and TPR were used to study the existence of crystalline species, elemental analysis and different Mo species prevailing in the catalysts. Afterwards, the ODS activity was analyzed in terms of the sulfone yields of DBTs for: (1) several oxidants, such H_2O_2, TBHP and CHP, and (2) Mo-based catalysts prepared with different conditions. UV spectroscopy was used to study the Mo species leached and their contribution to the ODS reaction. Finally, the Mo species stability was determined in a continuous fixed-bed ODS reactor.

Table 1 Nomenclature of the catalysts, preparation conditions (pH of AHM solution and used support), Mo loading obtained by SEM–EDX and quantitative TPR results as Mo species ratio

Catalysts	pH/support	MoO_3 (wt%)	$Mo(oct)^{6+}/Mo(th)^{6+}$
Mo_5H	~7/Al_2O_3	5.0	0.13
Mo_8H	~7/Al_2O_3	8.5	0.29
$Mo_{12}H$	~7/Al_2O_3	12.3	0.50
$Mo_{25}H$	~7/Al_2O_3	24.8	0.84
Mo_5Ox	0/Pseudoboehmite	5.3	0.94
Mo_8bh	0/Pseudoboehmite	8.3	0.36
$Mo_{12}bh$	0/Pseudoboehmite	12.6	1.09

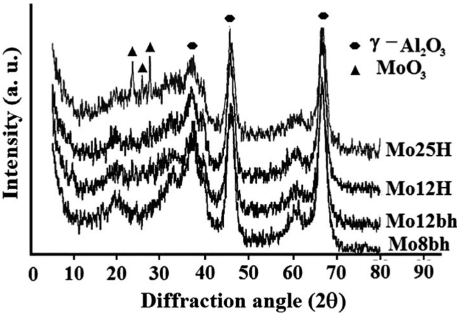


Fig. 1 XRD patterns of the catalysts prepared at near neutral pH ($Mo_{25}H$ and $Mo_{12}H$) and acid pH on pseudoboehmite (Mo_8bh and $Mo_{12}bh$)

Characterization

Similarly to previously reported preparations [13], the textural properties of the catalysts show that the Mo-oxide deposition did not induce any remarkable decrease in the properties of the supported catalysts compared with alumina. Similarly, the catalysts prepared by different methods in this paper did not show an important loss of textural properties with respect to the support. The quantitative SEM–EDX results shown in Table 1 confirm that the Mo contents were similar to the nominal Mo loading for all catalysts prepared.

The XRD patterns of the catalysts shown in Fig. 1 exhibit the main diffraction peaks of gamma-Al_2O_3 and only the catalyst with 25 % MoO_3 ($Mo_{25}H$) presented small diffraction peaks attributed to MoO_3. The MoO_3 diffraction peaks were not observed for the catalysts with lower Mo loading, which can be attributed to small crystallites well dispersed on alumina. In addition, the elemental mapping obtained by SEM–EDX showed a good distribution of Mo species on the support surface.

TPR analysis of the catalysts

TPR has provided very useful information on the nature and strength of the interaction between supported species and support, and it has been shown to be a sensitive technique to study the reducibility of different Mo species prevailing on

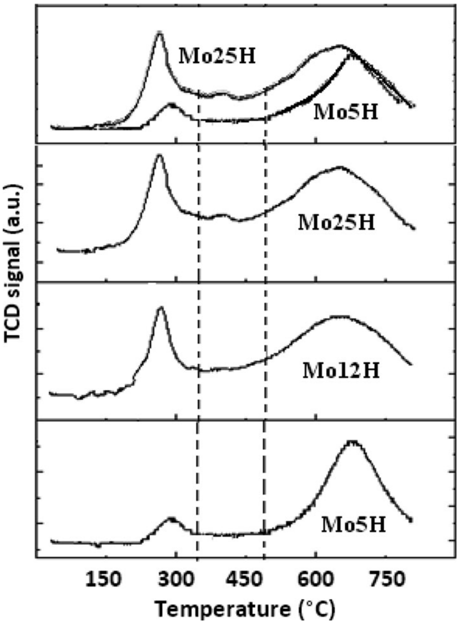


Fig. 2 TPR profiles of the catalysts prepared with different Mo loadings by incipient impregnation with aqueous solutions of AHM on alumina. Experimental conditions: H_2/Ar mixture [30 % H_2 (v/v), 25 cm^3/min], and heating rate of 10 °C/min from room temperature up to 900 °C

the catalyst [15, 16]. Fig. 2 shows the TPR profiles of the catalysts prepared with various Mo contents by incipient impregnation with aqueous solutions on alumina. The TPR profiles of the catalysts were similar to that previously reported in the literature [16, 17]. In general, they exhibit two well-defined reduction peaks ascribed to the reduction of two different Mo^{6+} species.

The first peak at approximately 280 °C is attributed to the first reduction step (Mo^{6+}–Mo^{4+}) of octahedrally coordinated molybdenum species weakly bound to Al_2O_3, predominantly as multilayer molybdenum domains, with some polymolybdates in monolayer patches [15, 16]. As observed in Fig. 2, the intensity of the first peak increased according to Mo loading increases up to a Mo monolayer ($Mo_{12}H$). A small peak was obtained at 400 °C only for higher Mo contents ($Mo_{25}H$), which is related to the presence of crystalline MoO_3, as observed in XRD (Fig. 1). Finally, the peak at 650–700 °C is ascribed to the partial reduction of Mo-species (Mo^{6+}–Mo^{4+}) strongly bound to the support, which corresponds to tetrahedral molybdenum, Mo(th) species. Additionally, a second reduction of octahedrally coordinated molybdenum species, Mo^{4+}, can be observed for $Mo_{12}H$ and $Mo_{25}H$ as a shoulder at 500–650 °C. In these TPR profiles and Table 1, it can be observed that the ratio Mo(th)/Mo-octahedral, Mo(oct) is different for each catalyst and this one depends on the Mo loading and preparation method. The Mo(th) amount is constant in all catalysts, due to the Mo atoms adopt this coordination when they interact with the Al_2O_3 surface during the impregnation step, therefore the Mo(oct) amount increases for high Mo loadings in the catalyst.

Fig. 3 shows the TPR profiles of the catalysts prepared by the incipient impregnation of aqueous solutions of AHM at near neutral pH (Mo_5H) and AHM in Ox solution at pH 0 (Mo_5Ox), as it is described in the experimental section. The

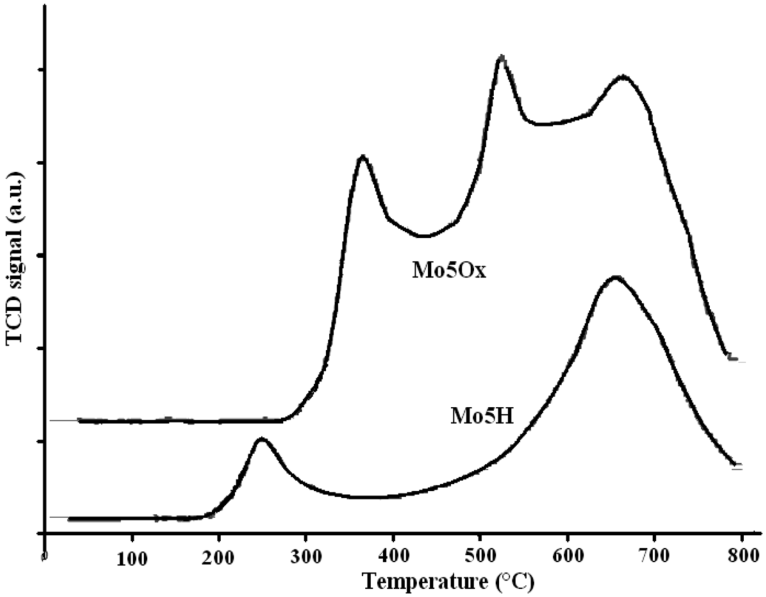


Fig. 3 TPR profiles of the catalysts prepared by the incipient impregnation of an aqueous solution of AHM (Mo_5H) and an oxalic acid solution (Mo_5Ox). Experimental conditions: H_2/Ar mixture [30 % H_2 (v/v), 25 cm^3/min], and heating rate of 10 °C/min from room temperature up to 900 °C

TPR profile of Mo_5Ox differs from the TPR profile of Mo_5H in the higher intensity of the peak at 670 °C and the absence of the reduction peak at 250 °C, whereas two new peaks at 370 and 550 °C for Mo_5Ox were observed. As the low temperature peak at approximately 250 °C is generally associated with the reduction of Mo^{6+}–Mo^{4+} in dispersed polymeric Mo structures, such Mo structures are favored in the catalyst prepared at neutral pH [17]. However, dispersed polymeric Mo structures on Mo_5Ox are reduced at high temperature due to at high Mo–support interaction.

In the high temperature region, both catalysts showed a large peak at 670 °C. This peak was generally associated with further progress in the reduction of the partially reduced Mo species of the first peak, together with the partial reduction of tetrahedrally coordinated Mo species interacting strongly with Al_2O_3 [17]. In this region, the profiles of the catalysts differed very little, and only greater broadening in the shape of this peak for Mo_5Ox was observed. In general, these TPR results are in excellent agreement with those reporting the effect of the pH of the impregnation solution on the TPR of Mo/Al_2O_3 catalysts, and in this case, the Mo–support interaction is higher. The Mo(oct)/Mo(th) ratio (Table 1) for Mo_5Ox indicates that the Mo(oct) species content in this catalyst is higher than for Mo_5H, but in the former the Mo(oct) species have greater interaction with the support, as it is observed in Fig. 3.

According to the TPR results (Fig. 3), it is evident that the dispersion of Mo was lower in the acidic-prepared catalyst (Mo_5Ox) than in the neutral-prepared one (Mo_5H). The former catalyst exhibits a peak at 550 °C attributed to the reduction of bulk MoO_3, which was not detected by XRD in the latter catalyst. In addition, the

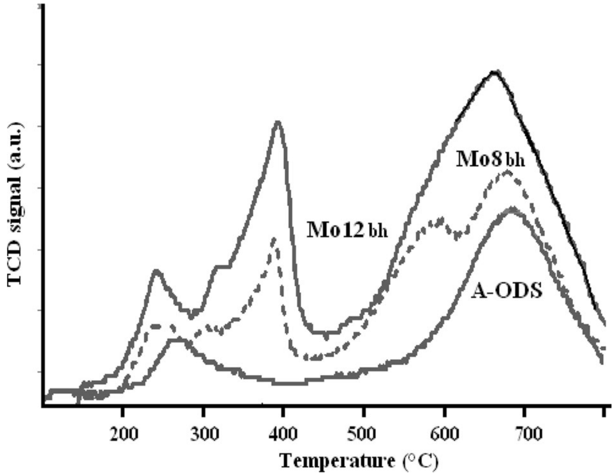


Fig. 4 TPR profiles of the catalysts prepared with different Mo loadings (Mo_8bh and $Mo_{12}bh$) by the incipient impregnation of oxalic acid solutions on pseudoboehmite, and $Mo_{12}bh$ after ODS reaction (A-ODS). Experimental conditions: H_2/Ar mixture [30 % H_2 (v/v), 25 cm^3/min], and heating rate of 10 °C/min from room temperature up to 900 °C

fraction of octahedral Mo, Mo(oct) as polymolybdates (H_2 consumption of the peak at 370 °C) of Mo_5Ox is higher than that of Mo_5H (at 250 °C).

To explain the TPR profile differences of the catalysts prepared in different conditions and to increase the Mo–support interactions, Mo-based catalysts on pseudo-bh were prepared by the impregnation of acidic-oxalic solutions, and the TPR profiles of these catalysts are shown in Fig. 4. The two main peaks of the TPR pattern for the Mo catalysts are presented in these formulations, but another two reduction peaks appear in the range of 300–650 °C, which are similar to those observed for Mo_5Ox (supported on Sasol-alumina, see Fig. 3) and can be interpreted as Mo(oct) species strongly anchored to the support because the alumina surface can be partially dissolved during impregnation at pH 0 and new Mo species can be obtained. In addition, Mo_8bh clearly displays the second reduction step of Mo^{4+} at approximately 600 °C, which corresponds to octahedrally coordinated molybdenum species. For $Mo_{12}bh$, this reduction is overlapped with the reduction of tetrahedrally surrounded Mo^{6+} monolayer species. Besides, as can be observed in Table 1, Mo_8bh and $Mo_{12}bh$ have a higher Mo(oct)/Mo(th) ratio respect to the catalysts prepared at near neutral pH (Mo_8H and $Mo_{12}H$) that indicates the preponderance of Mo(oct) species on the support. Thus, these TPR results suggest that the catalysts prepared in acid solutions or on pseudo-bh promote Mo(oct) species with high Mo–support interaction due to surface-alumina dissolution or the formation of a surface-like pseudo-bh during the impregnation step.

Oxidative desulfurization

The extraction–oxidation system or the ODS process consists of two liquid phases, the model diesel (or actual diesel) and an extraction solvent, and a solid catalyst in a three-phase system (L–L–S). When these phases are mixed, the DBTs present in the diesel phase are partially extracted to the solvent phase, where the oxidant reagent is predominantly present, and the oxidation reaction occurs therein, producing the corresponding sulfone [14]. If DBTs–sulfones are obtained only in the solvent phase, the process consists of two consecutive steps (extraction and reaction). If the liquid–liquid extraction step occurs rapidly, the oxidation of the DBTs is the rate determining step of the ODS process. Otherwise, the transfer of DBTs from the diesel phase to the solvent phase will impose some limitations on the rate of the global process.

In this study, the two-phase system (the extraction solvent and the solid catalyst) uses the same extraction solvent (acetonitrile) as the three-phase system, which contains the different DBTs used to model the sulfur compounds in diesel. In other words, the experiment with the two-phase system (biphasic system, L–S) avoids the mass transfer limitations imposed during the extraction step and will allow an estimate of the rate of the catalytic step.

In the ODS reaction, DBTs first undergo an oxidation to their corresponding DBTs–sulfoxide, and then the sulfoxide is oxidized to its corresponding DBTs–sulfone. However, under the reaction conditions in this study, no sulfoxides were detected. Thus, the catalytic performance was defined according to the sulfone yield and the relative reactivity of DBTs; the sulfone yield for each compound was expressed as DBTs–sulfone produced/initial DBTs. During the batch reaction, the sulfone yield evolution was evaluated every 15 min, and the results show profiles similar to those in previous works [13, 14], where DBTs–sulfone reaches the maximum conversion within a few minutes. However, to compare stable values, the ODS activities are discussed as the sulfone yield obtained at 30 min.

In this case, three different oxidants were used: H_2O_2, TBHP and CHP; the former is a oxidant highly soluble in the polar phase, TBHP is a oxidant moderately soluble in the oil phase and CHP is a oxidant highly soluble in the oil phase [18], in order to estimate whether the oxidant influences leaching Mo species.

H_2O_2 *and TBHP as oxidants*

Table 2 shows the sulfone yields of DBTs of the catalysts prepared on pseudo-bh and bulk catalysts as references, using either H_2O_2 or TBHP as the oxidant. The catalysts with different Mo loading were tested in the ODS of DBTs and in Table 2 this effect is shown. For Mo_Xbh catalysts with H_2O_2 as oxidant, the sulfone yield of DBT enhanced from 44 to 97 % with the increase of MoO_3 loading from 5 to 12 wt%, and then dropped to 89 % over 25 wt% MoO_3 loaded catalyst (Mo_{25}bh). A similar tendency was obtained for other DBTs–sulfones and when TBHP was used as an oxidant. Also, pseudo-bh and Al_2O_3 present low oxidation activity (sulfone yield of DBT of 5 and 10 %, respectively) and when Mo was dispersed on it, an increase in the oxidation activity was observed. The conversion of DBTs increased with increasing Mo content up to about 12 wt% and decreased when Mo content was beyond this value, which is equivalent a monolayer of Mo species. According to the previous reports [11], as the Mo loading increased, more and more polymerization of Mo species was produced, which led to the decrease of the

Table 2 Sulfone yield of DBTs (%) of Mo catalysts prepared by impregnation of AHM solution at near neutral pH on pseudoboehmite, and as references: filtered solution of Mo_{12}bh, Mo_{12}bh reutilized alumina, uncalcined catalysts of Mo_5bh and Mo_{12}bh, and bulk catalysts of AHM and MoO_3

Catalysts	Oxidant agents	DBT–O_2	4-MDBT–O_2	4,6-DMDBT–O_2
Mo_{25}bh	H_2O_2	89	83	71
Mo_{12}bh	H_2O_2	97	93	80
Mo_8bh	H_2O_2	70	65	45
Mo_5bh	H_2O_2	44	27	15
Mo_{25}bh	TBHP	24	20	15
Mo_{12}bh	TBHP	28	22	17
Filtered solution[a]	H_2O_2	26	30	33
Mo_{12}bh reutilized	H_2O_2	65	59	56
Alumina	H_2O_2	14	11	10
AHM	H_2O_2	28	32	36
MoO_3	H_2O_2	16	17	18
Mo_{12}bh uncalcined	H_2O_2	47	38	42
Mo_5bh uncalcined	H_2O_2	24	18	13

Results reported at 30 min, 60 °C, and O/S = 6. ODS in the L–S system, using DBTs in acetonitrile

[a] Without catalyst

activity. Other results show similar DBT conversions to this work, using H_2O_2 in a batch system [8, 11].

The ODS activity depends on the Mo loading and oxidant used; Mo_{12}bh with H_2O_2 presents the highest sulfone yield, whereas for Mo_8bh and Mo_5bh using TBHP as oxidant (not shown) the sulfone yields were minor than 10 %. For these solid catalysts, the usual reactivity order of DBT > 4-MDBT > 4,6-DMDBT is maintained [1–5] and Mo_{12}bh displays the highest sulfone yield in the presence of both oxidants. These catalysts were prepared on pseudo-bh to increase the Mo–support interaction. However, elemental analysis (SEM–EDX) shows that the Mo loadings were diminished after ODS (A-ODS) reaction, i.e. from 11.9 to 8.9 % of MoO_3 (approximately 25 % for Mo_{12}bh), and the TPR results show that Mo(oct) species were lost by leaching in the liquid phase reaction. Fig. 4 shows the TPR profile of Mo_{12}bh A-ODS reaction, where we can observe that Mo(oct) species were leached in the reaction medium and the TPR profile resembles to catalyst of low loading of Mo (i.e. Mo_5H). Thus, the ODS activity results depend on the Mo(th) species in the catalyst. Another possibility is that the leached Mo species are active in the homogeneous reaction.

In this sense, AHM and MoO_3 were used as bulk catalysts in the ODS reaction in similar conditions, and the results show appreciable yields with respect to the supported catalysts (see Table 2). In these tests, different catalyst amounts were used to ensure similar amounts of Mo-species; 10 mg of bulk catalyst and 100 mg of Mo supported catalyst were used in the ODS process, but, if only 25 % of the Mo-species on supported catalysts were leached, the amount of Mo species in solution was actually considerably higher with bulk catalysts, and the ODS activity was lower. In addition, the reactivity order for bulk catalysts was the inverse with respect to that obtained with solid catalysts, showing the usual order for homogeneous reactions [3].

These results suggest that the leached Mo species may exhibit activity although lower than activity due to solid catalysts, this implies that our above statement about the homogeneous activity of the leached species may be correct and therefore they contribute to the total activity. Then uncalcined catalysts (only dried) were tested in the ODS process, and the results are shown in Table 2. In this case, the Mo species are not anchored to the support, and they are considerably leached. Thus, the observed activity can be attributed mainly to Mo species in the liquid phase and the contribution of the support, which also participates as a catalyst. Sasol-alumina and alumina impregnated with an Ox solution show similar ODS activity, approximately 10–14 % of DBTs–sulfones, whereas the sulfone yields depend on the AHM amounts impregnated on alumina for uncalcined catalysts. However, these results for uncalcined catalysts are considerably lower than the results for calcined catalysts, showing that the ODS activity is favored for Mo species anchored to the support, which are obtained during the preparation in the calcination step.

Additionally, several tests were performed to confirm that Mo leached species are active in a typical ODS reaction (system L–S) with Mo_{12}bh. Heterogeneity tests were performed as described in [19] and the results are shown in the Table 2, which shows that the activity results of ODS reaction with filtered solution (without catalyst) are important and also is observed that the reactivity order of DBTs is typical of homogeneous ODS reaction: 4,6-DMDBT $>$ 4-MDBT $>$ DBT [1]. These activity results are in agree with the results shown for AHM as bulk catalyst. The activity of Mo_{12}bh decreases when it is reutilized and it is similar to the Mo_8bh (see Table 2), because the Mo species leaching into the reaction medium due to the oxidation reaction.

CHP as oxidant

To modify the distribution and the interaction of Mo species on alumina, Mo_5 catalysts were prepared under different conditions (medium acid or aqueous), and these catalysts were tested in the two-phase system (L–S). Mo_5 was chosen for these tests to diminish the leached-Mo amount for liquid-oxidation reactions because Mo species present on the support are mainly tetrahedrally coordinated molybdenum species.

The sulfone yields of DBTs using either H_2O_2 or CHP as oxidant are shown in Table 3. The catalyst Mo_5H presents lower ODS activity than Mo_5Ox (with H_2O_2 as oxidant) due to its higher dispersion observed by TPR, suggesting that the activity of Mo catalysts is associated mainly with the Mo species that are reduced at high temperature (as observed by TPR). Therefore, it can be stated that the species reduced at low temperatures are the ones that were leached.

Different types of oxidants have been used in the ODS process, such as hydrogen peroxide (H_2O_2), TBHP and CHP [1–5]. Hydrogen peroxide is the most commonly used oxidant among these. Wang et al. [8] used TBHP, and they found that Al_2O_3-supported MoO_3 showed higher catalytic activity than those supported on TiO_2 and

Table 3 Sulfone yield of DBTs (%) at 30 min using H_2O_2 or CHP as oxidant

Catalysts	Oxidant agents	DBT–O_2	4-MDBT–O_2	4,6-DMDBT–O_2
Mo_5H	H_2O_2	60	40	29
Mo_5Ox	H_2O_2	67	59	50
Mo_5Ox	CHP	89	73	97
Mo_5Ox^a	CHP	75	60	66
Mo_5Ox^b	CHP	78	76	78
Without catalyst	CHP	41	46	49

Mo catalysts were prepared by the impregnation of AHM in an oxalic-acid solution (Mo_5Ox) and an aqueous solution at near neutral pH on alumina (Mo_5H). ODS in the L–S system at 60 °C, O/S = 6, and using DBTs in acetonitrile

[a] Using DBTs in decane as model diesel

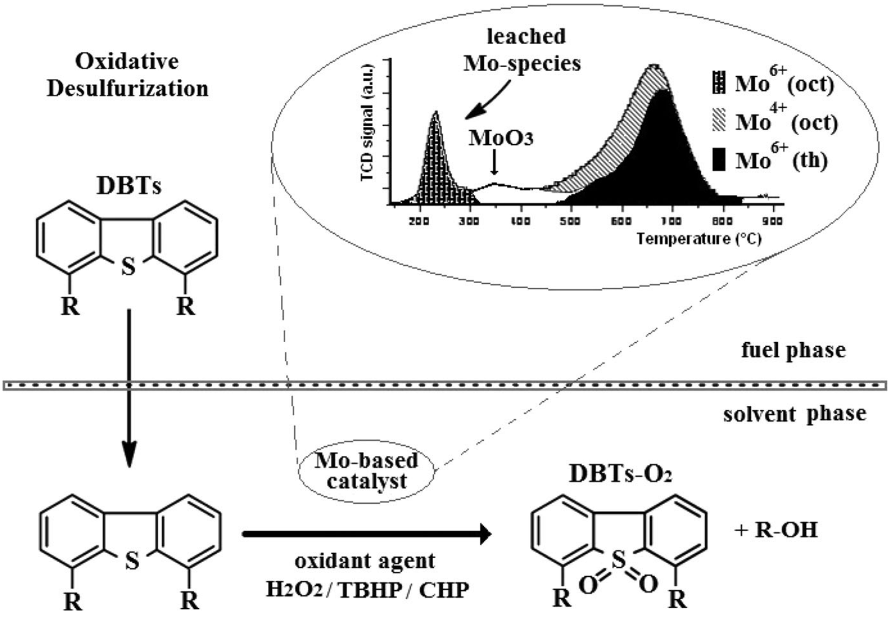
[b] In three phases system (L–L–S)

SiO_2–Al_2O_3. Nevertheless, Chang et al. [18] showed that Al_2O_3-supported MoO_3 was not stable in this system. For this reason, CHP was used as an oil-soluble oxidant to avoid the extraction solvent in the ODS process. However, it is necessary to eliminate the oxidized compounds, and an extraction process is required in a second step. It is known [1] that the polarity of the solvent plays a key role in the extent of the extraction of sulfones. Therefore, the removal of sulfones can be improved using a solvent with a higher polarity. The presence of an extracted agent such as acetonitrile in the oxidation phase has been found to enhance sulfur oxidation [14]. Thus, a three-phase system (L–L–S) is needed, and, in this study, the system could be simulated as a L–S system to estimate only the rate of the catalytic step.

The products from the oxidation of DBTs were their corresponding sulfones, whereas CHP was decomposed to 2-phenyl-2-propanol after donating the oxygen atom. When using TBHP as an oxidant, *tert*-butyl alcohol was obtained as a decomposition product. All of these compounds were confirmed by GC–MS. In addition, other reference tests without catalyst were performed with H_2O_2, TBHP and CHP. Common peroxides in ODS (H_2O_2 and TBHP) without catalyst exhibit very low oxidation of DBTs compounds at 30 min. However, CHP is able to oxidize DBTs without a solid catalyst (see Table 3), which shows that oxidation in the homogeneous phase is important. CHP itself (without a solid catalyst) produces sulfone yields of 41, 46 and 49 % for DBT, 4-MDBT and 4,6-DMDBT, whereas yields of 89, 73 and 97 % were obtained with Mo_5Ox, which corresponded to homogeneous and heterogeneous activity contributions. Chang et al. [18] reported for a catalyst with 15 % of MoO_3 a DBT conversion of 95 % using CHP as oxidant, but they did not discuss about the probability of the homogeneous reaction with this oxidant.

The reactivity of organosulfur compounds in oxidation varies widely, depending on their structure and the local environment of the sulfur atom [1]. The following order of reactivity has been reported for the oxidation of some model sulfur compounds with the homogeneous system: 4,6-DMDBT > 4-MDBT > DBT. It is interesting that the oxidative reactivity of 4,6-DMDBT is higher than that of DBT, which is inverse to their reactivity with the heterogeneous system and has been explained on the basis of a steric hindrance effect due to alkyl groups in the four and six positions. When CHP was used as an oxidant and Mo_5Ox was the catalyst, the homogeneous and heterogeneous reactions were obtained, and the DBTs-reactivity trend depended on each one of the contributions. Therefore, the two different trends matched, and differences in reactivity decreased, showing similar sulfone yields for DBTs.

To evaluate the solvent effect, the oxidation reaction was conducted in a model diesel (DBTs in decane) under conditions similar to those of the other tests. These results are also presented in Table 3, where a higher sulfone yield in polar solvent (acetonitrile) than in decane solvent can be observed. In both solvents, the oxidation reaction is appreciable. Thus, for a three-phase system (L–L–S), the reaction pathway is more complex because a parallel-consecutive scheme is obtained, wherein DBTs can be extracted to the solvent and oxidized in both the fuel phase and the extraction-solvent phase. Then, the sulfones can be extracted to solvent. In a three-phase system using Mo_5Ox and CHP as the oxidant, the sulfone yields were 78, 76 and 78 % for DBT, 4-MDBT and 4,6-DMDBT. The ODS results correspond to the intermediate case between the tests in the polar solvent (acetonitrile) and in the decane solvent, simulating in both cases the biphasic system (L–S). In addition, in this case, as in previous tests, homogeneous and heterogeneous catalytic reactions can be observed, and the system analysis is more complex (Scheme 1).



Scheme 1 Catalytic oxidative desulfurization of diesel fuel using Mo based catalyst in L–L–S system

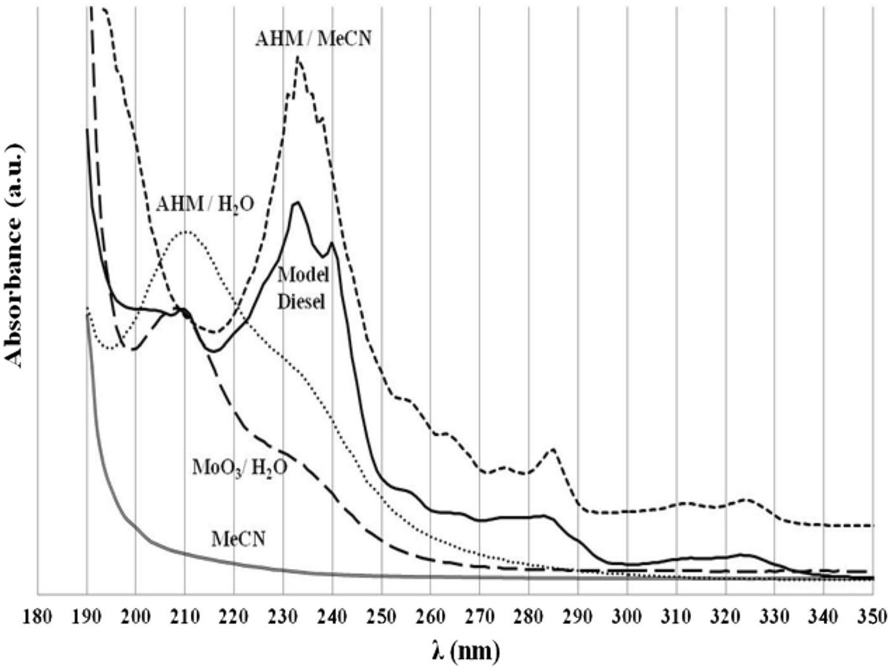


Fig. 5 UV spectra of: AHM dissolved in water (AHM/H_2O) or acetonitrile (AHM/MeCN), MoO_3 dissolved in water (MoO_3/H_2O), and model diesel after ODS process using H_2O_2 as oxidant

Mo species leached and their contribution to ODS reaction

To corroborate that Mo species were leached in liquid solvents, UV spectra were measured for the model diesel A-ODS process, and different solutions of AHM and MoO_3 as references. The results are shown in Fig. 5. The UV spectra of the different samples show three distinctive bands for Mo species in solution at approximately 210, 230–240 and 285 nm. According to the aqueous equilibrium, the original solutions contain exclusively either the *para*molybdate anion ($Mo_7O_{24}^{6-}$) at pH <6 with Mo in an octahedral environment or the tetrahedral MoO_4^{2-} ion at pH >6 [20]. The MoO_4^{2-} species absorbs at 230–240 nm, while the additional band near 290 nm corresponds to the *para*molybdate ion. All solutions shown in Fig. 5 have a pH in the range of 5–6. Thus, these bands correspond to the Mo species in solution or leached Mo species, and both species contribute to a low proportion of the ODS activity.

ODS in continuous fixed-bed reactor

In order to evaluate the stability of the catalysts, ODS reactions in a continuous reactor were performed and the results for Mo_5bh and Mo_{12}bh using H_2O_2 as oxidant are shown in Fig. 6. These results demonstrate the deactivation of the catalysts when working in continuous flux. The catalyst clearly deactivates, although the initial DBT conversion for Mo_{12}bh was 47 %, and 25 % for Mo_5bh,

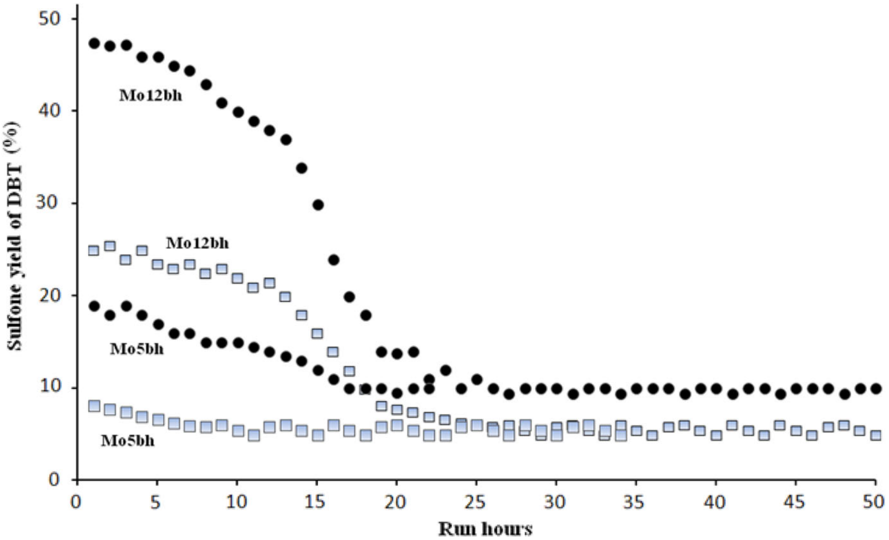


Fig. 6 Sulfone yield of DBT (*filled circles*) and 4,6-DMDBT (*squares*) in a continuous fixed-bed reactor using H_2O_2 as oxidant, and $Mo_{12}bh$ or Mo_5bh as catalyst. ODS reaction conditions: atmospheric pressure, WHSV = 50 h^{-1}, O/S molar ratio = 6 and reaction temperature = 60 °C

finally both catalysts reach the same DBT conversion (∼10 %). Similar trends were observed in the sulfone yield of 4-MDBT (not shown) and 4,6-DMDBT. Under these conditions, the catalysts cannot convert all of the sulfur compounds and catalyst deactivation occurs. If Mo species were leached during the ODS process and Mo(oct) species are easy removed because the interaction with the support is minor, then Mo(th) species prevailing in the catalyst and the ODS activity is similar for catalysts with different Mo loading after the long period of the reaction when only Mo species anchored to support prevail as observed in TPR profiles (see Fig. 4).

Catalyst deactivation can occur due to metal leaching and/or adsorption of the highly polar sulfones on the catalyst surface [21]. A-ODS reaction, the sulfur and metal contents on the catalyst were analyzed by SEM–EDX. The results show that ∼25 % of the Mo has already leached out. As was discussed above, the leached species correspond to Mo(oct) species. Hence, to avoid the catalytic deactivation, it is necessary to find a method for anchoring the Mo(oct) species on the support to obtain a similar behavior as Mo(th) species. Several authors [8–10] have reported high sulfur compound conversions (>85 %) using TBHP as oxidant, for a catalysts with MoO_3 loading nearly to monolayer (∼12 %), in a continuous reactor. It is known that TBHP is better oxidant than H_2O_2 in a continuous system, but few works have studied the reasons why the Mo catalysts are deactivated.

This study has been performed with the aim to determine which are the Mo active species in a heterogeneous system, because it is very important to take in account this information when thinking about the activation and reuse of spent HDS catalyst for the ODS process. This is a first approach about the role of Mo; of course it should be considered that there are other aspects to investigate, which should be study in future works.

Conclusions

Mo oxides on alumina with different loadings were prepared and tested in ODS reactions using different oxidants such as H_2O_2, TBHP and CHP, to evaluate the activity of Mo species in the oxidation reactions. The uncalcined catalysts (only dried), where Mo species are not anchored to the support and are considerably leached, as shown by the ODS activity. Thus, the activity can be attributed mainly to the Mo species in the liquid phase and the contribution of the support. However, the ODS activities for uncalcined catalysts are considerably lower than for calcined catalysts, showing that activity is favored for Mo species anchored to the support, which were obtained during the calcination step. According to the UV–visible spectra, the Mo species in solution are equivalent to leached Mo species and contribute to a low proportion of the ODS activity compared to the stable-solid catalyst, in which Mo(th) species dominate.

CHP presents the highest ODS performance. However, the ODS results show that oxidation in the homogeneous phase is important when using CHP without a solid catalyst. Then, in the presence of a Mo-based catalyst, homogeneous and heterogeneous reactions were obtained, and the reactivity trend of DBTs depended on each of the contributions, where the two different trends were matched and the differences in reactivity are diminished, showing similar sulfone yields for DBT, 4-MDBT and 4,6-DMDBT.

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