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Journal of Catalysis 242 (2006) 299–308
JOURNAL OF CATALYSIS
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Catalytic oxidative desulfurization (ODS) of diesel fuel on a continuous fixed-bed reactor

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Received 15 March 2006; revised 30 May 2006; accepted 13 June 2006

Abstract

The oxidative desulfurization (ODS) of model sulfur-containing compounds (thiophene, 2-methylthiophene, benzothiophene, 2-methylbezothiophene, dibenzothiophene, 4-methyldibenzothiophene, and 4,6-dimethyldibenzothiophene) with *tert*-butyl hydroperoxide on different metal-containing molecular sieves has allowed the study the role of the electronics and geometry of the reactant as well as the pore dimensions, topology, and adsorption properties of the catalyst on the rate of desulfurization. The best catalysts were then studied for the ODS of simulated and industrial diesel in a continuous fixed-bed reactor. MoO_x/Al_2O_3 catalysts were active, but rapid deactivation occurs due to metal leaching and sulfone adsorption. Calcined Ti-MCM-41 was more active, did not leach Ti, and deactivated more slowly than MoO_x/Al_2O_3. The amount of adsorbed sulfone was strongly reduced by decreasing the polarity of the Ti-MCM-41 by silylation, with the corresponding increase in catalyst activity and lifetime.

Keywords: Oxidative desulfurization with organic peroxides; Ti-MCM-41 oxidative desulfurization catalyst; Silylation of mesoporous materials

1. Introduction

Sulfur in transportation fuels is a major source of air pollution. Ultra-deep desulfurization of fuels is a matter of major interest not only because of increasing environmental concern and legal requirements, but also because ultra-low-sulfur fuels is a key requirement for fuel cell applications [1–3]. Liquid hydrocarbons are considered a potential fuel for automotive and portable fuel cells [2] due to their higher energy density and readily existing infrastructure for production, delivery, and storage. However, the levels of organic sulfur present in the liquid fuels, particularly gasoline and diesel, are sufficient to considerably reduce the activity and lifetime of the catalysts used in the fuel processor [4]. Furthermore, existing hydrodesulfurization processes (HDSs) for reducing sulfur in gasoline and diesel (particularly light cycle oil [LCO]) require harder than desired processing conditions to remove the last 100 ppm of sulfur, with the corresponding penalty in gasoline octane, investment, and hydrogen consumption. This is due to the presence in LCO of refractory sulfur compounds, such as benzothiophenes or dibenzothiophenes, that require higher hydrogen pressures, temperatures, and/or contact times to achieve fuels with S concentration <10 ppm. In particular, 4-methyldibenzothiophene (4-MDBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) are very difficult to convert by HDS due to their steric hindrance [5]. It must be pointed out, however, that oxidation of these compounds by formic acid and peroxides can be performed under mild reaction conditions [6–12]. During the oxidative desulfurization, sulfur compounds can be oxidized by the electrophilic addition of oxygen atoms to the sulfur to form sulfoxides (1-oxides) and sulfones (1,1-dioxides). The chemical and physical properties of sulfoxides and sulfones are significantly different from those of hydrocarbons in fuel oil, and consequently they can be removed by distillation, solvent extraction, or adsorption.

Potential catalytic oxidative routes to produce low-S fuels include various types of oxidants, including nitrogen oxides [13–15], nitric acid [16,17], hydrogen peroxide [6,18–21], ozone [22], organic hydroperoxides [23], molecular oxygen [24], peracids [3,25], and others. The oxidation of thio-

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doi:10.1016/j.jcat.2006.06.013

phene derivatives with H_2O_2 is known to occur over various catalytic system, such as HCOOH [26,27], CF_3COOH [28,29], methyltrioxorhenium(VII) [30], phosphotungstenic acid [30], and metal supported on alumina [31] or molecular sieves [7, 10–12,32,33].

The use of transition-metal (Ti, Mo, Fe, V, W, Re, Ru) complexes as active catalysts for selective oxidation of sulfur compounds in homogeneous condition has also been reported [34–37]. In the case of metal-containing molecular sieves, the pore dimensions of the material, as well as the metal coordination, oxidizing agent, and solvent, play critical roles in catalyst activity and life for the oxidative desulfurization (ODS) of industrial feeds [7,10–12]. In this sense, Hulea et al. [7] and Corma et al. [38] studied the reaction of sulfides by hydrogen peroxide on TS-1 and Ti-Beta and by H_2O_2 and *tert*-butyl hydroperoxide (TBHP) on Ti-Beta and Ti-MCM-41, respectively, using various organic solvents. TS-1 was less active for sulfur compounds with large molecular size due to the restricted access of these molecules to the zeolite pores. In contrast, molecular sieves with large pore size, such as Ti-Beta and Ti-MCM-41, were very active in liquid phase when large amounts of protic solvents (methanol, ethanol, or acetonitrile) to facilitate H_2O_2 solubility were used. However, the presence of large amounts of solvent in this process may introduce limitations for industrial applications. We believe that ODS can have industrial applications if the process involves a fixed-bed reactor with one phase feed in the absence of any added solvent. To do this, we prepared well-designed large and extralarge pore molecular sieves, as well as other meso-macropore systems, using organic peroxides as oxidants and performed the experiments in a fixed-bed reactor system that also allows the study of catalyst deactivation and regeneration. Thus, we report here the activity, selectivity, and stability, using organic peroxides as oxidants, of mesoporous materials containing Ti in which the surface can be modified by silylation to diminish the adsorption of the more polar sulfones that will strongly contribute to catalyst deactivation. We also explored a MoO_x/Al_2O_3 that has been reported by UOP to be an active oxidation catalyst [39,40], suitable for oxidation of thiophenic compounds with *tert*-butyl hydroperoxide using a flow-type reactor [41,42].

2. Experimental

2.1. Materials

Ti-MCM-41 samples were obtained from a gel with the following molar composition [43]:

SiO_2:0.015 $Ti(OEt)_4$:0.26 CTABr:0.26 TMAOH:24.3 H_2O,

where CTABr is cetyltrimethylammonium bromide (Merck) and TMAOH tetramethylammonium hydroxide (Aldrich). The silica source, Aerosil-200, was obtained from Degussa and Ti source, $Ti(OEt)_4$, was supplied by Alpha Products. The crystallization was performed at 373 K for 48 h in Teflon-lined stainless steel autoclaves. After the solid was washed and dried at 363 K overnight, it was separated in two fractions. In the first fraction, the occluded surfactant was completely removed by heating at 813 K for 1 h in a flow of N_2 (2.5 $cm^3\ s^{-1}$), followed by 6 h of treatment in a flow of air (2.5 $cm^3\ s^{-1}$) at the same temperature. This calcined sample is referred to as Ti-MCM-41C. In the second fraction, the surfactant was removed following two step extraction procedure as described previously [44]. After this, the sample was silylated with hexamethyldisilazane (HDMS; ABCR GmbH & Co.) as the silylating agent. The silylation was carried out at 393 K for 2 h with a solution of HMDS in toluene under inert atmosphere. Subsequently, the samples were filtered and washed with 250 cm^3 of toluene. The silylated sample is referred to as Ti-MCM-41S. Sample was silylated to increase their hydrophobicity [45] with the aim of decreasing the adsorption of sulfones on the surface.

TS-1 was prepared following a previously reported synthesis method [46]. Al-free Ti-Beta zeolite was prepared in F^- medium with tetraethylammonium cations (TEA^+) as the organic structure-directing agent as described previously [47]. CoAPO-5 material was synthesized as outlined previously [48].

Al_2O_3-supported MoO_3 was prepared by incipient wetness impregnation of γ-Al_2O_3 (Degussa, AG, 101 $m^2\ g^{-1}$) with a solution of $(NH_4)_6Mo_7O_{24}$ (Aldrich, 99%) at a pH of 5. The impregnated sample was dried overnight in ambient air at 393 K and then treated in flowing dry air (Airgas, zero grade) at 773 K for 3 h.

2.2. Characterization techniques

XRD was performed using Cu$K\alpha$ radiation with a Phillips PW 1830 diffractometer equipped with a graphite monochromator. The position of the peaks was measured after dehydration of the samples for 1 h at 383 K and further rehydration over a $CaCl_2$-saturated solution (35% relative humidity) for 16 h. Si was used as internal standard. XRD of Ti-MCM-41 as synthesized, calcined, and silylated is shown in Fig. 1.

Textural properties and chemical compositions of materials used in this work are shown in Tables 1 and 5. Surface

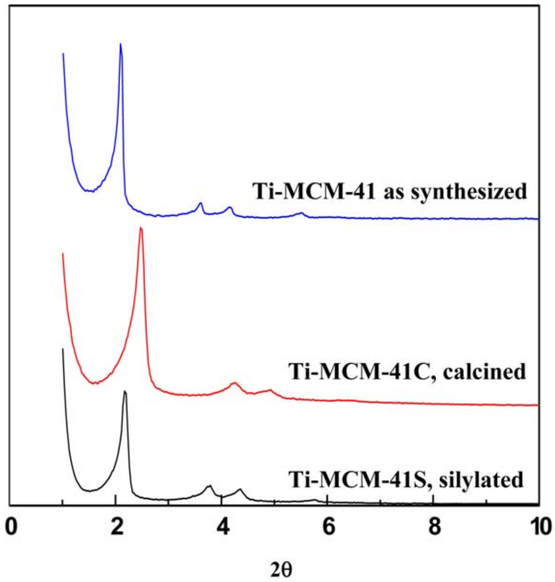


Fig. 1. XRD patterns of Ti-containing MCM-41 samples.

Table 1
Properties of catalytic materials used in batch experiments

Catalyst	Me (wt%)	BET area ($m^2\ g^{-1}$)	Pore volume ($cm^3\ g^{-1}$)
Ti-MCM-41C	1.26[a]	884	0.67
Ti-MCM-41S	1.26[a]	805	0.44
TS-1	2.40[a]	455	0.18
Ti-Beta	1.18[a]	454	0.19
CoAPO-5	2.40[b]	310	0.14
12Mo/Al_2O_3	11.5[c]	98	–

[a] Amount of Ti expressed as wt% Ti.
[b] Amount of Co expressed as wt% Co.
[c] Amount of Mo expressed as wt% Mo.

Table 2
Composition of the simulated diesel fuels used in this work

Compounds	Composition
Simulated Diesel-40	
n-Dodecane	80 wt%
Toluene	20 wt%
Benzothiophene (BT)	10 ppm
Dibenzothiophene (DBT)	10 ppm
4-Methyldibenzothiophene (4-MDBT)	10 ppm
4,6-Dimethyldibenzothiophene (4,6-DMDBT)	10 ppm
Total S (ppm)	40
Simulated Diesel-200	
n-Heptane	80 wt%
Toluene	20 wt%
Benzothiophene (BT)	70 ppm
2-Methylbenzothiophene (2-MBT)	70 ppm
Dibenzothiophene (DBT)	60 ppm
Total S (ppm)	200
Simulated Diesel-200B	
n-Heptane	80 wt%
Toluene	20 wt%
Benzothiophene (BT)	100 ppm
2-Methylbenzothiophene (2-MBT)	100 ppm
Dibenzothiophene (DBT)	100 ppm
Total S (ppm)	300

areas were measured by N_2 adsorption at 77 K in an ASAP-2000 equipment (Micromeritics) after pretreating the samples at 673 K and vacuum overnight. Mo and Ti content were determined by atomic absorption spectrometry (AAS) in a Varian Spectra A-10 Plus apparatus.

2.3. Catalytic experiments

The ODS reactivity of individual sulfur compounds was first studied in a 50-mL glass batch reactor equipped with a temperature controller, a condenser, and magnetic stirrer. Typically, 10 g of *n*-heptane containing 0.10 g of the model sulfur compound, with a molar ratio of TBHP/S of 2.5, was heated at 80 °C, then 0.025 g of catalyst were added. *n*-Decane (0.075 g) was added as an internal standard.

Reaction products were analyzed by gas chromatography (GC) in a Varian 3400 gas chromatograph equipped with a Petrocol-100 fused silica column connected to two detectors (FID and PFPD) in parallel at the outlet of the column. This equipment allows simultaneous determination of the detailed composition of the liquid hydrocarbons and the sulfur compounds. Initially, the products were identified by GC–mass spectroscopy (GC-MS) (Hewlett-Packard 5890) with a 5 wt% methyl-phenyl-silicone capillary column (60 m long, 0.25 mm i.d., 0.25 µm film thickness) and compared with available standard compounds. When necessary, the sulfones were isolated from the reaction media or synthesized by alternative methods and analyzed by ^1H nuclear magnetic resonance (NMR) spectroscopy (Bruker AV-300).

The oxidative desulfurization reaction of the model and industrial diesel fuels was performed in a fixed bed stainless-steel reactor (6.35 mm i.d., 20 cm long). Typically, the reactor was loaded with 0.1 g of catalyst. Before the catalytic experiments, the catalysts were dried in situ at atmospheric pressure in nitrogen flow at 398 K for 1 h, after which the temperature was decreased to the reaction temperature (353–373 K). The feed was introduced into the reactor by a precision syringe pump (Cole Palmer 74900). Oxidation reaction was carried out at atmospheric pressure, a WHSV of 51.5–134 h^{-1}, an oxidant/S molar ratio of 6, and a reaction temperature of 353–373 K. *tert*-Butyl hydroperoxide was added to each diesel fuel before it was fed into the reactor. The composition of model and industrial diesel fuels is shown in Table 2 and Fig. 6, respectively. Each sample was analyzed for 30 min by GC in a Varian 3400 device equipped with a Petrocol-100 capillary column (100 m, 0.25 mm i.d., 0.5 µm film thickness) and connected to FID and PFPD detectors. Unreacted *tert*-butyl hydroperoxide and *tert*-butyl alcohol formed were analyzed; the oxygen balance was always >93%.

3. Results and discussion

3.1. Oxidation of pure sulfur compounds in batch reactor

It is well known that sulfur-containing hydrocarbons can be oxidized to sulfoxides and sulfones with Ti-Beta and Ti-MCM-41 catalysts using H_2O_2 and *tert*-butyl hydroperoxide (TBHP) as oxidants in acetonitrile as solvents [7,48]. More recently, Hulea et al. [33], in very interesting work, expanded this to the oxidation of a large number of sulfur compounds and kerosene fractions using H_2O_2 as oxidant and relatively large amounts of acetonitrile as solvent. It appears to us that for an ODS process using solid catalysts, the use of solvent should be avoided, and, consequently, organic peroxides could be an alternative to H_2O_2 [10–12,49]. The organic peroxides could be generated by controlled hydrocarbon oxidation of an adequate industrial fraction following a process reported previously [9]. Thus, for simplicity, here we use *tert*-butyl hydroperoxide as oxidant and a series of molecular sieves as catalysts. In a first approximation to the problem, the reaction was performed in a batch reactor using single sulfur compounds. Then the selected catalysts were studied with simulated and industrial feeds in a continuous fixed-bed reactor.

Ti-Beta, TS-1, and CoAPO-5 [49] micropore molecular sieve samples were studied with different sulfur compounds; the results are given in Table 3. The table shows that TS-1 has much lower activity than Ti-Beta, probably due to diffusional limitations in the former that make the Ti sites at the external

Table 3
Oxidation of model sulfur compounds in *n*-heptane with *tert*-butyl hydroperoxide (TBHP) over different microporous catalytic materials[a]

Sulfur compound	Initial rate, $r_0 \times 10^{-5}$ (mol h^{-1})			TOF (mol (mol Me)$^{-1}$ h^{-1})		
	Ti-Beta	TS-1	CoAPO-5	Ti-Beta	TS-1	CoAPO-5
Thiophene (T)	0.5	0	5.2	0.8	0	5.1
2-Methylthiophene (2-MT)	3.9	0	3.7	6.3	0	3.6
2,5-Dimethylthiophene (2,5-DMT)	3.2	1.8	3.0	5.2	1.4	2.9
Benzothiophene (BT)	20.1	11.9	1.5	32.7	9.5	1.5
2-Methylbenzothiophene (2-MBT)	14.6	5.4	0.4	23.8	4.3	0.4
Dibenzothiophene (DBT)	5.0	0.8	0	8.1	0.6	0
4-Methylbenzothiophene (4-MDBT)	2.1	0	0	3.4	0	0

[a] Reaction conditions: 0.1 g of substrate, 0.025 g of catalyst, TBHP/S molar ratio of 2.5, 10 g of *n*-heptane, at 353 K during 0.5 h.

Table 4
Oxidation of model sulfur compounds in *n*-heptane with *tert*-butyl hydroperoxide (TBHP) over Ti-MCM-41S silylated catalyst[a]

Sulfur compound	Conversion (mol%)	Initial rate $r_0 \times 10^{-5}$ (mol h^{-1})	TOF (mol (mol Me)$^{-1}$ h^{-1})
Thiophene (T)	0.4	1.0	1.5
2-Methylthiophene (2-MT)	2.9	5.9	9.0
2,5-Dimethylthiophene (2,5-DMT)	7.5	13.4	20.4
Benzothiophene (BT)	16.7	24.9	37.9
2-Methylbenzothiophene (2-MBT)	20.0	27.0	41.1
Dibenzothiophene (DBT)	11.0	12.0	18.2
4-Methylbenzothiophene (4-MDBT)	8.4	8.5	12.9

[a] Reaction conditions: 0.1 g of substrate, 0.025 g of catalyst, TBHP/S molar ratio of 2.5, in 10 g of *n*-heptane, at 353 K during 0.5 h.

Table 5
Properties of catalytic materials used in fixed bed continuous experiments

Catalyst	Ti or Mo (wt%)	BET area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})
Ti-MCM-41C	1.61	960	0.68
Ti-MCM-41S	1.40	850	0.46
12Mo/Al_2O_3	11.5	98	–

zeolite surface the only active ones. On the other hand, a material with larger pores (CoAPO-5) is somewhat more active than TS-1 and even more active than Ti-Beta for the oxidation of thiophene. However, it should be taken into account that thiophene can react to form dimmers, instead of sulfoxides and sulfones, generated through the fast reaction of 1,1-di-oxide thiophene molecules via a Diels-Alder condensation process catalyzed by Lewis solid acids [33,50]. Nevertheless, the oxidation activity of Ti-Beta for formation of sulfones is much higher than that of CoAPO-5, especially with larger sulfur-containing molecules. This can be a consequence of the pore topology of Ti-Beta. Indeed, the tridimensionality of Ti-Beta with respect to the monodimensionality of CoAPO-5 should increase the diffusion of reactants and products in the former. Nevertheless, diffusional limitations are also encountered with Ti-Beta, as demonstrated by the decreased TOF when introducing alkyl groups in the benzothiophene or dibenzothiophene molecules (see Table 3). Taking this into account, we have prepared a Ti-MCM-41 molecular sieve with 4.0 nm pore size [51] that should present much lower diffusion limitations than Ti-Beta for substituted benzothiophenes and dibenzothiophenes. Oxidation results with the Ti-MCM-41 sample, given in Table 4, support this hypothesis because this sample gives activities for sulfone production generally between one and two orders of magnitude higher than CoAPO-5 and between two and four times higher than Ti-Beta.

Molybdenum oxide impregnated on γ-Al_2O_3 has been reported to be an active catalyst for the oxidation of dibenzothiophenic compounds [39–42]. To compare the activity of this catalyst with our Ti-MCM-41S silylated material, we prepared a series of MoO_x/Al_2O_3 samples with varying Mo content (2, 6, and 12 wt% of Mo) and found the best results for a sample containing 12 wt% of Mo (Fig. 2). We compared these results with those with Ti-MCM-41S silylated and Ti-Beta for ODS simulated diesel feed. The results, shown in Fig. 3, demonstrate that the Mo catalyst is less active than Ti-MCM-41S and more active than Ti-Beta for benzothiophenes, while also achieving 100% conversion of dibenzothiophene after 7 h of reaction time. These results indicate that the molybdenum catalyst is less active than Ti-MCM-41S but it is a catalyst worth studying within a fixed-bed reaction system and exploring its lifetime as potential oxidation catalyst.

3.2. *Oxidation of model diesel fuels in a continuous fixed-bed reactor*

We investigated the oxidation of benzothiophene (BT), 2-methylbenzothiophene (2-MBT), dibenzothiophene (DBT), 4-methyldibenzothiophene (4-MDBT), and 4,6-dimethyldibenzothiophene (4,6-DMDBT) contained in two different simulated diesel fuels (Diesel-40 and Diesel-200; Table 2). We carried out the oxidation of the organosulfur compounds with *tert*-butyl hydroperoxide using Ti-containing mesoporous catalysts (Ti-MCM-41) and MoO_x/Al_2O_3. The physicochemical properties of these catalysts are given in Table 5. Under our experimental conditions, the catalytic oxidation of aromatic sulfur compounds with *tert*-butyl hydroperoxide led to the corresponding sulfones (1,1-dioxide) as the sole product and *tert*-butyl alcohol as the stoichiometric byproduct (Scheme 1). Products of dodecane, heptane, or toluene oxidation were not detected.

Results shown in Fig. 4 demonstrate total conversion of sulfur compounds and no deactivation of the catalysts when working with Ti-MCM-41, either calcined or silylated. On the contrary, the molybdenum catalyst clearly deactivates after 2 h on stream, although the initial conversion was also 100%. Never-

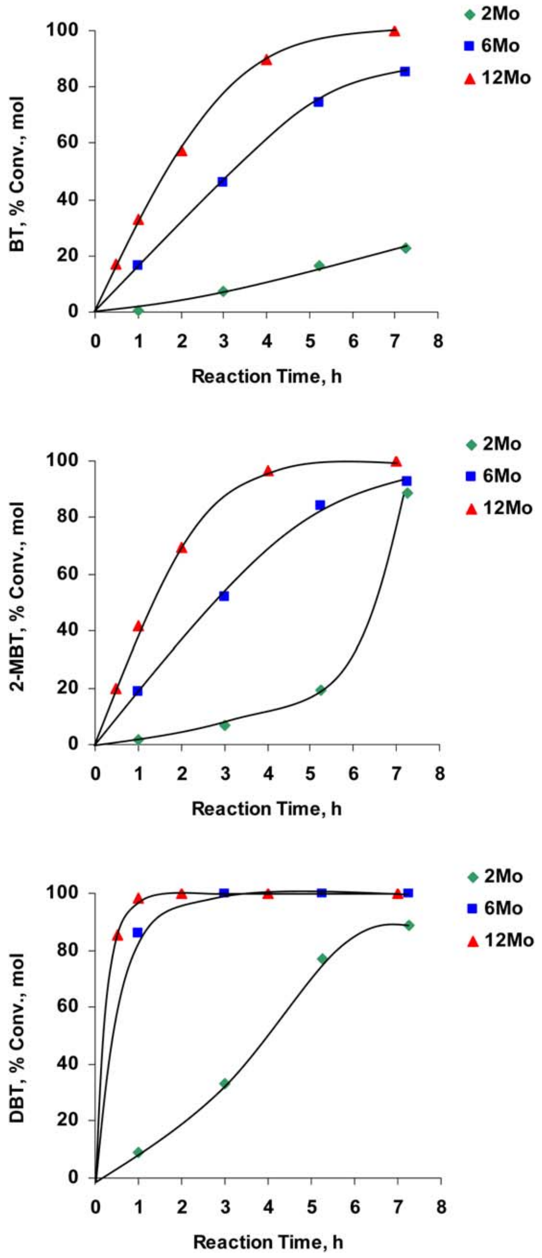


Fig. 2. Comparative study of the selective oxidation of sulfur compounds present in the simulated Diesel-200 over Mo/Al_2O_3 with different amount of Mo. Reaction conditions: 15 g of Diesel-200, 353 K, 0.025 g of catalyst, and oxidant/S ratio of 4 $\text{mol}\,\text{mol}^{-1}$.

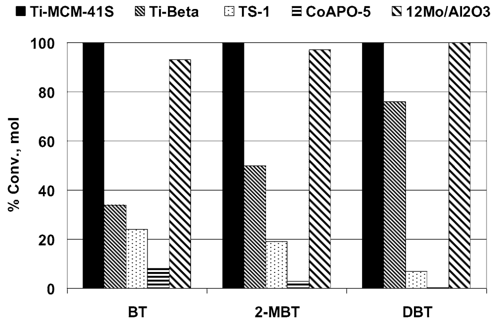


Fig. 3. Comparative selective oxidation of S compounds present in the simulated Diesel-200B over different metallic solid catalysts with TBHP as oxidant. Reaction conditions: 15 g of feed, 0.025 g of catalyst, TBHP/S molar ratio = 4 $\text{mol}\,\text{mol}^{-1}$, at 353 K during 7 h.

Table 6
Ti and Mo content on the catalysts before and after 8 h of oxidation reaction. Reaction conditions: Diesel-40, 373 K, atmospheric pressure, 0.1 g of catalyst, WHSV of 51 h^{-1} and oxidant/S ratio of 6 $\text{mol}\,\text{mol}^{-1}$[a]

Catalyst	Before reaction wt% (Ti or Mo)	After reaction wt% (Ti or Mo)	Sulfur retained after reaction ($mg_S\,g_{cat}^{-1}$)[b]
Ti-MCM41C	1.61	1.58	2.10
Ti-MCM41S	1.40	1.36	0.20
$12Mo/Al_2O_3$	11.5	9.37	1.57

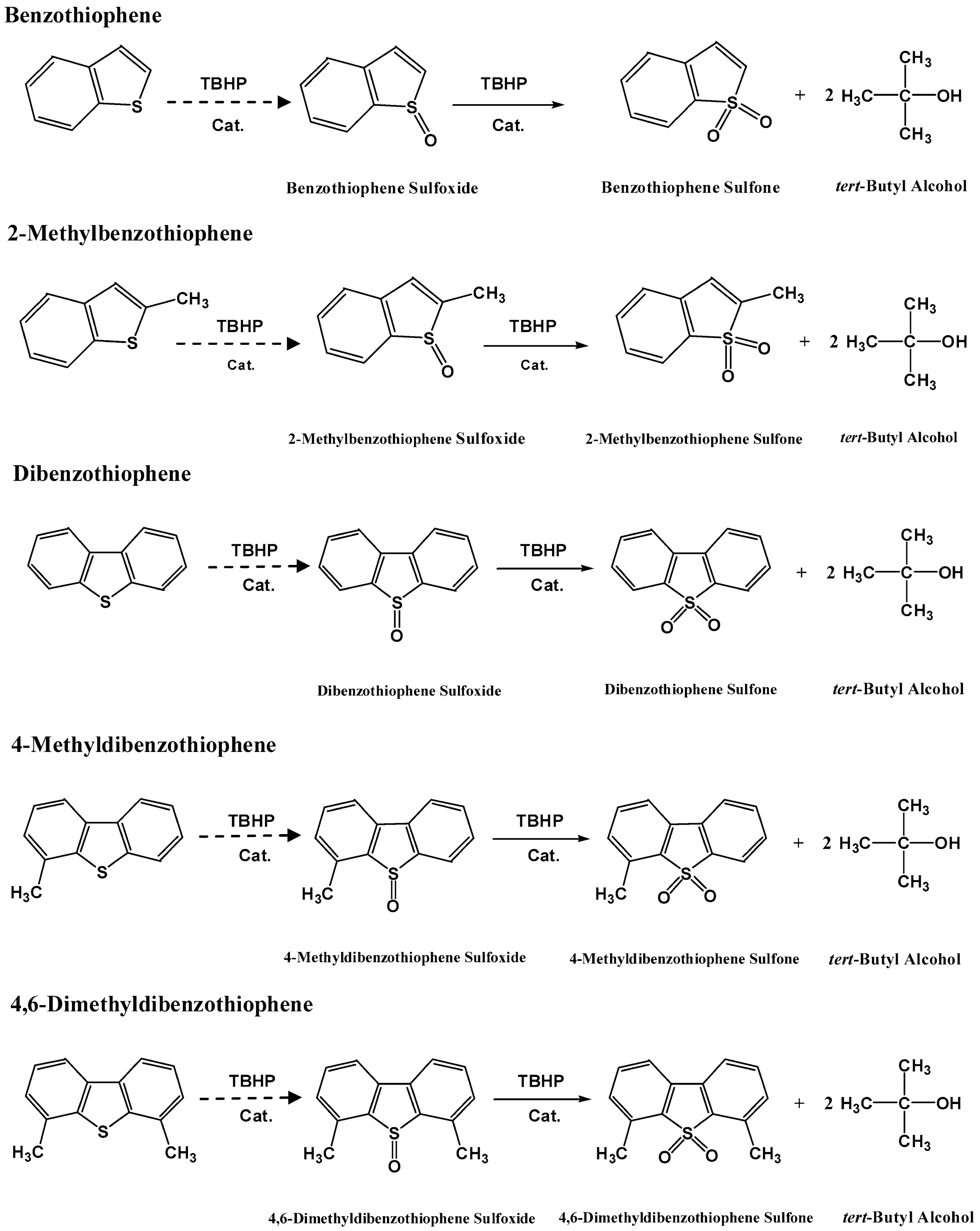
[a] Reaction conditions: Diesel-200, 353 K, atmospheric pressure, 0.1 g of catalyst, WHSV of 134 h^{-1} and oxidant/S ratio of 6 $\text{mol}\,\text{mol}^{-1}$.

[b] Last column shows the amount of sulfur retained on the catalysts after 8 h of reaction time.

theless, considering that the number of moles of Mo per gram of catalyst (1.2×10^{-3} $\text{mol}_{Mo}\,g_{cat}^{-1}$) in the MoO_x/Al_2O_3 is higher than the number of moles of Ti (3.4×10^{-4} $\text{mol}_{Mo}\,g_{cat}^{-1}$) in Ti-MCM-41 materials, it can be concluded that Ti atoms have a higher intrinsic activity than the Mo atoms. Nevertheless, we must consider the possibility that not all of the Mo atoms are accessible or active in the oxidation reaction.

At this point, we decided to increase the level of sulfur in the feed to evaluate the influence of this variable on activity and especially on catalyst deactivation. The results, illustrated in Fig. 5, clearly show that in this case Ti-MCM-41 calcined and silylated can still convert all of the sulfur compounds, but only the more highly hydrophobic silylated sample is able to maintain full conversion with time on stream. The molybdenum sample cannot convert all of the sulfur compounds, and, moreover, very strong catalyst deactivation occurs.

Catalyst deactivation can occur due to metal leaching and/or adsorption of the highly polar sulfones on the catalyst surface. After reaction, the sulfur and metal contents on the catalyst were analyzed; the results are given in Table 6. The table clearly shows that Ti leaching does not occur with Ti-MCM-41 samples, at least at the reaction time studied here, whereas ∼20% of the Mo had already leached out. Furthermore, hydrophilic solids, such as Ti-MCM-41C (with a large number of silanol groups) and MoO_x/Al_2O_3 (with a large number of hydroxyl groups), adsorb much larger amounts of sulfones than the silylated Ti-MCM-41S sample. At this point, we can conclude that for the optimization of an ODS metal-supported catalyst, is not enough to have intrinsically very high catalytic active—the adsorption properties of the solid also must be optimized to increase catalyst life. Controlling the adsorption properties of solid catalysts, especially in microporous and mesoporous molecular sieves, is of paramount importance in controlling activity, selectivity, and catalyst life. Thus, we believe that more emphasis should be given not only to the design of the active site, but also to tuning the adsorption properties of the solid. Further input on this issue is available elsewhere [52,53].



Scheme 1. Oxidation reaction of the different sulfur compounds contained in the model diesel fuels used in this work (TBHP: *tert*-butyl hydroperoxide, Cat.: catalyst).

3.3. Oxidation of a partially hydrotreated industrial diesel fuel in a continuous fixed-bed reactor

Organosulfur compounds in industrial diesel fuel consist mainly of benzothiophene and dibenzothiophene derivatives. The results presented above show that Ti-MCM-41 calcined and silylated are able to catalyze the continuous selective oxidation of the most refractory sulfur compounds: benzothiophene (BT), 4-methylbenzothiophene (4-MBT), dibenzothiophene (DBT) and especially 4,6-dimethyldibenzothiophene (4,6-DMDBT). However, in complex feeds such as gas oil, competitive adsorption and molecular interactions may occur that can negatively influence activity, selectivity, and catalyst life. Taking this into account, along with the fact that we consider ODS a “polishing” process coupled with hydrotreaters, we carried out ODS of a partially hydrotreated commercial diesel

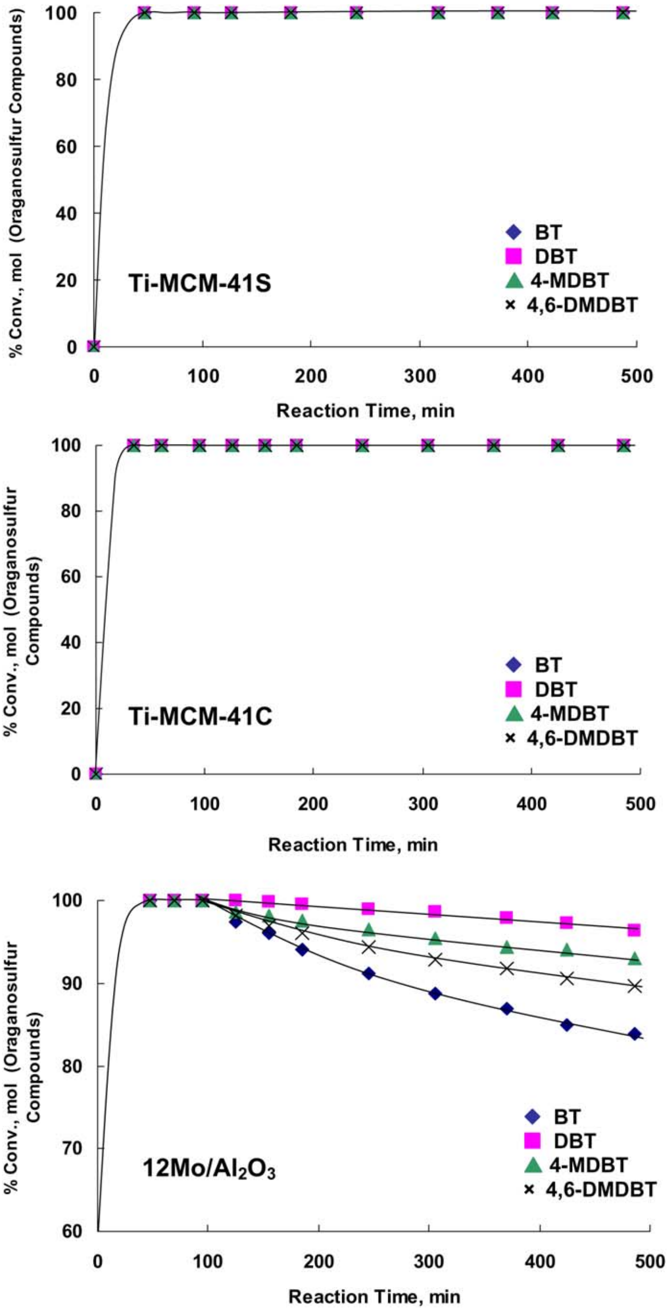


Fig. 4. Oxidation conversion of benzothiophene (BT), dibenzothiophene (DBT), 4-methyldibenzothiophene (4-MDBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) contained in the Diesel-40 with *tert*-butyl hydroperoxide as a function of reaction time over Ti-MCM-41C, Ti-MCM-41S and $12Mo/Al_2O_3$ catalysts. Reaction conditions: 373 K, atmospheric pressure, 0.1 g of catalyst, WHSV of 51.5 h^{-1}, and oxidant/S ratio of 6 mol mol^{-1}.

fuel (LCO) containing 330 ppm of sulfur compounds formed by monomethyl, dimethyl, and trimethyl dibenzothiophenes and other alkyl dibenzothiophenes (see Fig. 6) in a continuous fixed-bed reactor. The results thus obtained (Figs. 6 and 7) show that Ti-MCM-41 calcined and the silylated samples are able to fully oxidize the sulfur compounds into sulfones. However, the Ti-MCM-41C catalyst deactivates much faster than the silylated counterpart, due to the greater adsorption of sulfones in the former, as noted above. However, despite the lower adsorption of the silylated samples, this will also deactivate over time, necessitating catalyst regeneration. Thus, desorption of the polar sulfones could be achieved by washing with a polar hydrocarbon such as methanol. To investigate this possibility, a 50-mg sample of Ti-MCM-41C calcined that had been used in ODS and contained 1.2 wt% of sulfones (expressed as wt% of S re-

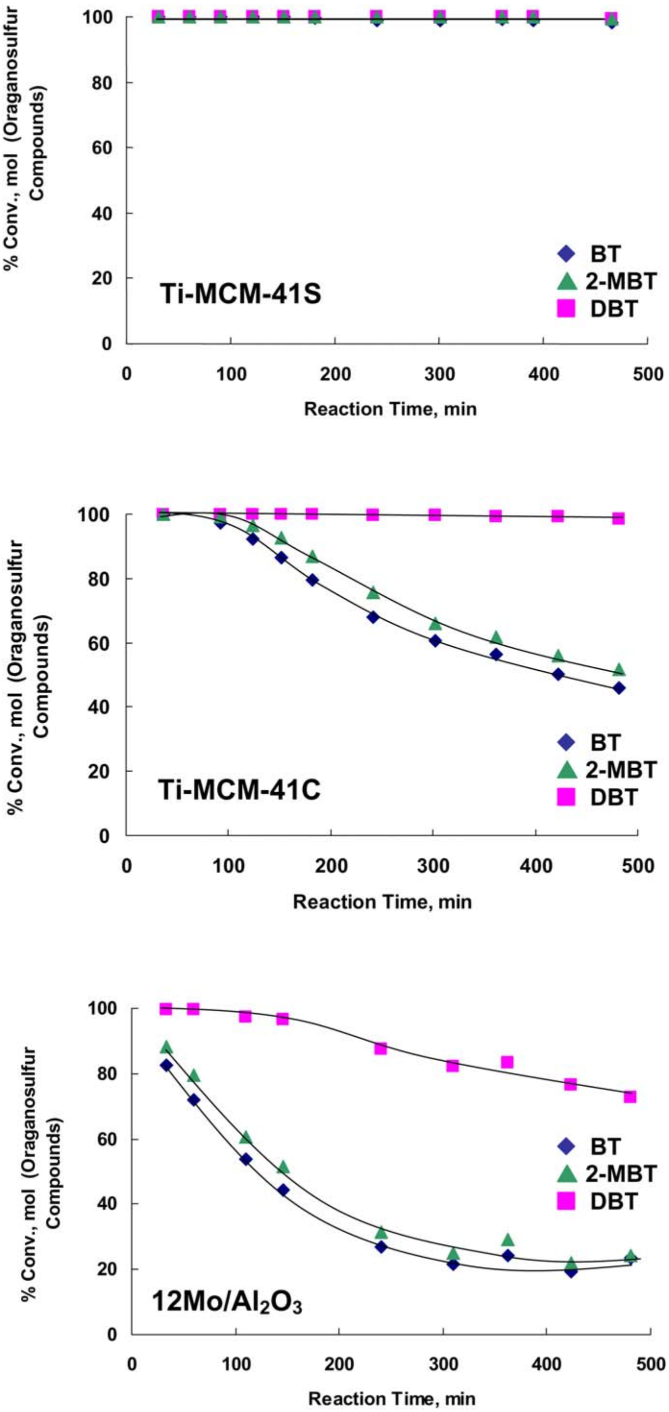


Fig. 5. Oxidation conversion of bezothiophene (BT), 2-methylbenzothiophene (2-MBT) and dibenzothiophene (DBT) contained in the Diesel-200 with *tert*-butyl hydroperoxide as a function of reaction time over Ti-MCM-41C, Ti-MCM-41S and $12Mo/Al_2O_3$ catalysts. Reaction conditions: 353 K, atmospheric pressure, 0.1 g of catalyst, WHSV of 134 h^{-1}, and oxidant/S ratio of 6 mol mol^{-1}.

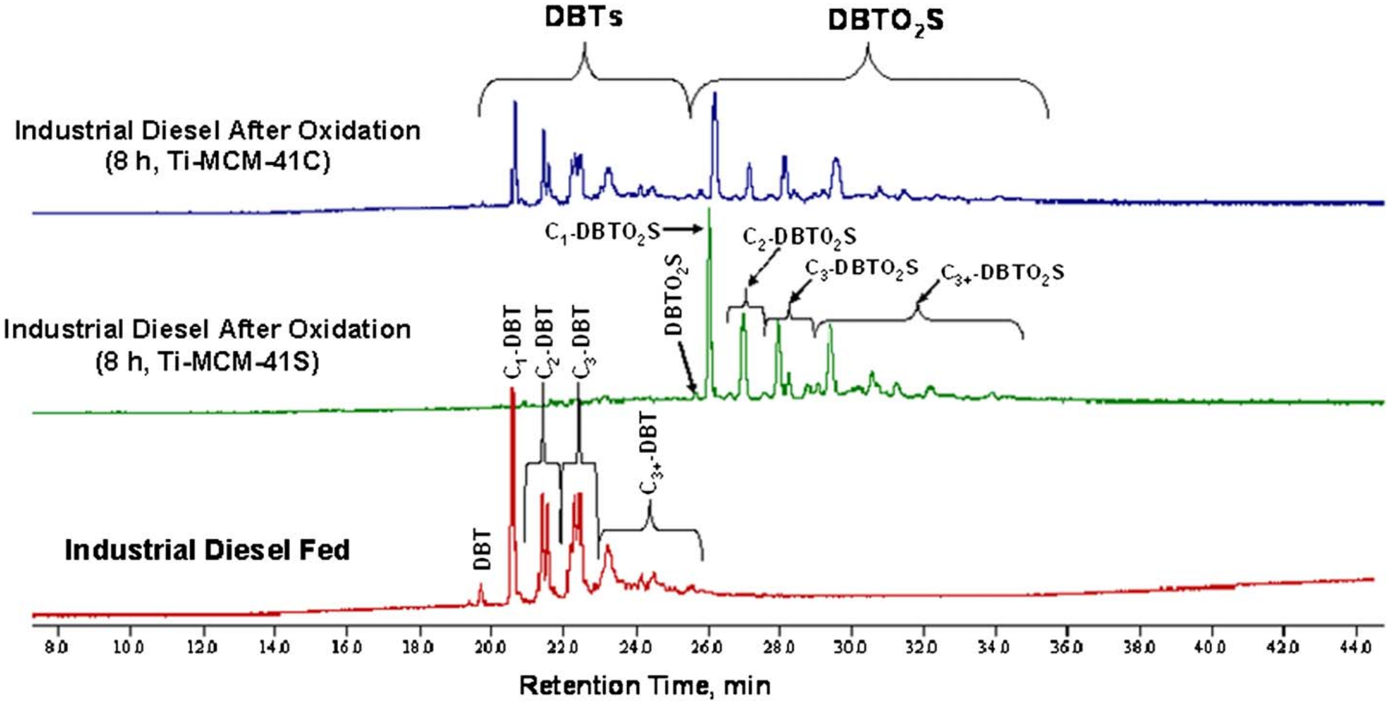


Fig. 6. Sulfur-specific GC-PFPD chromatograms of industrial diesel fed and industrial diesel in the reactor outlet after 8 h of reaction time with Ti-MCM-41C (calcined) and Ti-MCM-41S (silylated) catalysts. Reaction conditions: industrial diesel, 373 K, atmospheric pressure, 0.1 g of catalyst, WHSV of 51.5 h^{-1}, and oxidant/S ratio of 6 mol mol^{-1}.

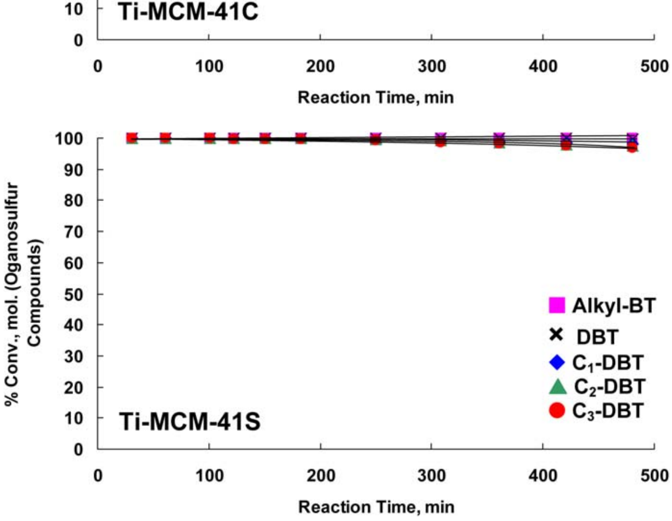


Fig. 7. Oxidation conversion of the sulfur compounds contained in an industrial diesel with *tert*-butyl hydroperoxide as a function of reaction time over Ti-MCM-41C and T-MCM-41S catalysts. Reaction conditions: industrial diesel, 373 K, atmospheric pressure, 0.1 g of catalyst, WHSV of 51.5 h^{-1}, and oxidant/S ratio of 6 mol mol^{-1}.

tained in the catalysts) was washed by passing 20 g of methanol through the fixed-bed reactor at 40 °C. After this treatment, 98 wt% of sulfones was desorbed, and the catalyst recovered its initial oxidation activity. Two reaction–regeneration cycles were carried out with this Ti-MCM-41C catalyst, and the oxidation activity was fully recovered after each cycle (Fig. 8). In a similar way, a Ti-MCM-41S sample containing 0.5 wt% of adsorbed sulfones (expressed as wt% of S retained in the catalysts) was washed with methanol following the procedure reported above, and 99% of the sulfones were removed.

Completing the sulfur removal cycle and producing sulfur-free fuel oils requires that sulfones be removed from the treated diesel. This process is relatively simple, considering that sulfones have physicochemical properties significantly different from hydrocarbons in fuel oil; thus, distillation, solvent extraction, or adsorption may be effective approaches to sulfone removal. We have found that sulfones can be selectively adsorbed on modified aluminas, silicas, sepiolites, or zeolites; consequently, an ultra-deep desulfurized fuel oil could be obtained by coupling the ODS process with the sulfone removal by selective adsorption.

4. Conclusions

1. The most difficult sulfur products to remove by hydrotreatment in diesel can be fully oxidized using an organic peroxide (e.g., TBHP) as oxidant and Ti mesoporous materials as catalysts in the absence of any solvent.
2. CoAPO-5 is an unsuitable catalyst for performing this; Ti-Beta gives a lower activity than the Ti-mesoporous ma-

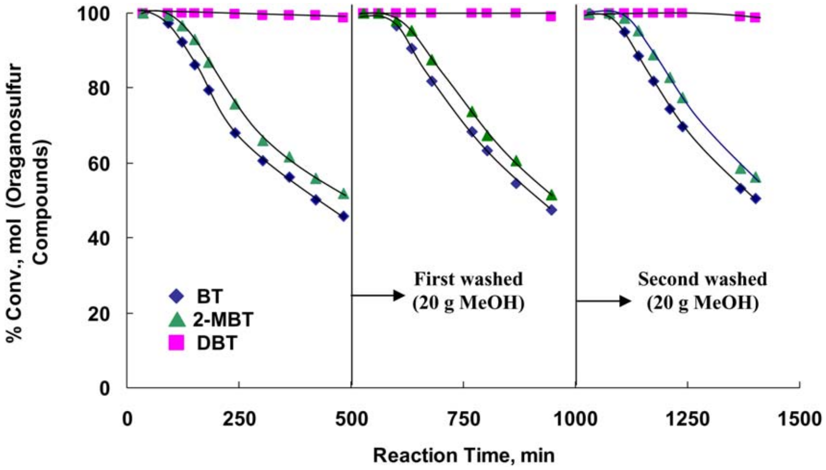


Fig. 8. Regeneration study of Ti-MCM-41C catalyst. Two regeneration cycles have been carried out. Each regeneration step consisted in a washed of the catalyst after reaction with 20 g of methanol at 40 °C following of a dried in flow of nitrogen at 120 °C for 1 h. Each reaction step was carried out at 353 K, atmospheric pressure, Diesel-200, 0.05 g of catalyst, WHSV of 134 h^{-1}, and oxidant/S ratio of 6 mol mol^{-1}.

terial. The lower activity of Ti-Beta is due mainly to diffusional limitations and probably steric effects for the interaction of the sulfur atom with Ti when it is in the pore.

3. Molybdenum supported on γ-Al_2O_3 is able to oxidize benzothiophenes and dibenzothiophenes, but its activity is lower than that of Ti-MCM-41.
4. Continuous fixed-bed experiments clearly show metal leaching in the molybdenum-containing catalysts but no leaching in the case of Ti-MCM-41.
5. The high polar sulfones strongly adsorbed on the hydroxylated surfaces on the Ti-MCM-41C and MoO_x/Al_2O_3 are responsible for catalyst deactivation. However, this adsorption is strongly suppressed by silylating Ti-MCM-41, producing a more hydrophobic catalyst and decreasing the amount of adsorbed sulfones by a factor of 10, significantly increasing catalyst life.
6. Catalysts deactivated during oxidative desulfurization can be regenerated by washing with methanol.

This work shows the possibility of using an ODS process based on Ti-mesoporous materials and organic peroxides as a “polishing” process, working in combination with a hydrotreating unit. This should allow for increasing the throughput of the existing hydrotreating units, while operating under milder conditions.

Acknowledgments

Financial support was provided by MAT2000-1392 and ENIRECHERCHE (2002 grant). M.E.D. and A.C. thank ITQ and MEC for a scholarship and a “Ramon y Cajal” grant, respectively.

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