

Effect of Support on the Performance of CoMoRe Catalyst in Thiophene and Benzothiophene Hydrodesulfurization

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This work is aimed at selection of a suitable support for CoMoRe catalyst in hydrodesulfurization (HDS) of thiophenes. γ -Al₂O₃ and γ -Al₂O₃-HMS were used as a support for CoMoRe catalyst with 4%Co, 8%Mo and 0.5%Re loading. The metal loading was incorporated by using the pore volume impregnation method, employing aqueous solutions of cobalt (II) nitrate, ammonium molybdate and rhenium (VII) oxide. The catalysts were sulfided with dimethyl disulphide at 250 °C for 10 h and finally tested in the HDS reaction of thiophene and benzothiophene in different temperature and pressure conditions. The catalysts were characterized by determining the adsorption isotherms, the pore size distribution and the acid strengt, FTIR, XRD and SEM. The catalyst supported on γ -Al₂O₃ displayed higher activity than catalyst supported on γ -Al₂O₃-HMS. The results suggest that activity is favoured by the suitable textural and acidic properties of the support.

Keywords: hydrodesulfurization, catalyst, thiophenes

To minimize the negative effects of sulfur compounds on health and the environment, new strategies have been adopted worldwide to reduce sulfur emissions by imposing low sulfur concentrations in fuels. The desulfurization of refined petroleum products is usually accomplished by catalytic hydrodesulphurisation (HDS) processes in fixed bed reactors. Sulfur bonded to various organic species present in fuels is thus converted to H₂S, which is eliminated and then converted to elemental sulfur through the Claus process. The concern for improving the performance of hydrodesulfurization catalysts is found in the large number of published papers that address this process [1-7].

In a recent paper [8], Gomez-Orozco studied the dibenzothiophene hydrodesulfurization reaction on NiMoW / SBA-15 type catalysts in the presence of Ti and without Ti. The authors highlighted an increase in yield in hydrogenated products for the Ti-containing catalyst, termed CAT / 60TiS15. The superior activity for CAT / 60TiS15 and CAT / S15 was explained by the presence of a lower concentration of tetrahedral structures and by a higher dispersion of the Mo (W) S₂ phase. The lower catalytic activity of the CAT / 40TiS15 catalyst could be due to the smaller specific surface area, pore volume and pore diameter. Hysteresis H₂ type isotherms are also likely to affect the diffusion of the reactant / products in the pores. Despite the acidity associated with the catalyst structure and the formation of different types of acidic centers, it was observed that not only acidity affects the selectivity and catalytic activity but also the textural properties and superficial species have an important role in the catalytic activity of the NiMoW ternary catalyst deposited on the SBA- 15 and modified with varying amounts of Ti.

Dibenzothiophene hydrodesulfurization (HDS) and hydrodenitrication (HDN) of carbozole were studied in the presence of hydrogen (P = 55 bar) at 310 °C in a batch reactor on NiMo / Al-HMS catalysts modified with phosphorus at various concentrations (0.5-2.0% by weight) [9]. Based on the study, it was found that modifying the support with an optimized amount of P (1%) decreased inhibition of the HDS reaction due to the presence of carbazole. Regardless of the studied reaction, all P-

containing catalysts exhibited greater activity than those without P. The modified P-modified catalyst showed the best HDS activity and the lowest tendency to inhibit HDS simultaneously with HDN, activity that was close to that of a NiMo / Al₂O₃ commercial catalyst sulfurized. This behavior was probably determined by the formation of irregular MoS₂ structures having a high concentration on the marginal catalytic centers as well as the high concentration of Brønsted and Lewis acid centers. The decrease in catalyst activity when P concentration increased to 2.0% by weight can be explained by an increase in the degree of polymerization of Mo species by Mo-O-Mo linkages. An increase in the concentration of Mo species resulted in harmful effects on the formation of the active phase during the sulphurization as well as on the dispersion of the active phase. José Escobar et al. [10] also prepared Ni-Mo/ alumina catalyst doped with P, for hydrodesulfurization using sucrose as a reducing agent precursor.

Recently Obeso-Estrella et al. [11] prepared a series of CoMoW trimetallic catalysts deposited on Al₂O₃-TiO₂ support in order to study the effect of the partial substitution of Mo with W on the performance of the catalyst in the dibenzothiophene (DBT) hydrodesulphurisation reaction. The study demonstrated that the partial substitution of Mo with W on the CoMo / Al₂O₃-TiO₂ catalyst leads to improved catalyst activity and density of acidic centers. Thus, the CoMoW catalyst containing W at an atomic W / Mo ratio of 1.2 exhibited a catalytic activity of 2.5 times greater than that without W, and a higher hydrogenation selectivity than HDS for DBT conversion than the CoMo catalyst.

A non-supported cobalt and molybdenum sulfide type catalyst was prepared by Jacob Sollner [12] using ammonium heptamolibdate, cobalt nitrate and elemental sulfur under reflux in ammonium hydroxide. The synthesized catalyst was tested in the hydrodesulfurization process of dibenzothiophene at 350 °C. Studies have shown that a highly active CoMoS₂ biphasic catalyst, composed of the Co₉S₈ and MoS₂ phases, has been obtained. It has also been shown that during the synthesis process a CoMoO₄ type intermediate was obtained irrespective of whether the process resulted in the presence or absence

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of elemental sulfur. Probably the elemental sulfur acts as a support for precipitation of the CoMoO_4 intermediate. Thus, the elemental sulfur at 450 °C in the presence of H_2 is converted to H_2S and determines the formation of the Co_9S_8 and MoS_2 phases. The products obtained from the reaction indicate that the reaction takes place through a first stage of desulphurisation.

Morales-Ortuno et al. [13] prepared NiMo catalysts on titanium-containing SBA titans (Ti-SBA-15 and Ti-SBA-16) and titanium nanotubes with different pore diameters, which were tested in the hydrodesulfurization process of a diesel oil. It has been found that the Ni and Mo species are well dispersed in all Ti-containing catalytic supports. However, the TPR characterization showed that there were some differences in the characteristics of Mo species on Ti-SBA media and on nanotubular titanium supports. The above was mainly attributed to the differences in the chemical composition of the supports, which led to some differences in their acidity and the interactions between the metal supports. The Ti-SBA-15 and Ti-SBA-16 NiMo catalysts showed similar selectivity to the NiMo/ $\gamma\text{-Al}_2\text{O}_3$ catalyst. These catalysts have desulfurized 4,6-dimethyldibenzothiophene (DMDBT) by a first hydrogenation step. On the contrary, catalysts on titanium nanotubes have been able to achieve high conversion of 4,6-DMDBT by desulfurization not only by hydrogenation but also through the desulphurisation pathway.

Wang et al. [14] synthesized a mesoporous FDU-12 silica with a particular morphology, under low temperature conditions and by the addition of compounds with high acidity. The sulfurized NiMo / F-HP catalyst showed a high degree of dispersion and sulphurization that favored the increase in the content of active sites for HDT reactions of DBT.

Based on literature data analysis, it has been observed that catalytic support can contribute to improving the distribution of acidic centers and, implicitly, to increased concentration of acidic centers. In this study, the influence of the presence of mesoporous silica on Co-Mo-Re / $\gamma\text{-Al}_2\text{O}_3$ catalyst activity was studied.

Experimental part

Catalyst preparation

The catalysts were prepared by simultaneous impregnation using the pore filling method. In summary, the cylindrical extrudates supports: $\gamma\text{-Al}_2\text{O}_3$ (surface area, pore volume) and $\gamma\text{-Al}_2\text{O}_3$ -HMS (40:60, surface area, pore volume) were impregnated with aqueous solutions of ammonium heptamolybdate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$, Aldrich 99%), cobalt (II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and rhenium (VII) oxide (Re_2O_7) and the resulting samples were subsequently dried for 4 h and at 120°C calcined at 450°C for 4 h. The catalysts are denoted as CoMoRe/ $\gamma\text{-Al}_2\text{O}_3$ and CoMoRe/ $\gamma\text{-Al}_2\text{O}_3$ -HMS with the metal loading was 8% Mo, 4% Co and 0.5% Re.

Catalysts characterization

Temperature programmed desorption using diethyl amine as a probe molecule (DEA-TPD) was used to study the strength of acid sites available in catalysts. DEA-TPD experiments were performed using a DuPont Instrument Thermal Analyst 2000/2100 coupled to a module 951 Thermogravimetric Analyzer. The catalysts structure and morphology was defined from textural characteristics (surface area, pore volume, average pore diameter, pore-size-distribution) and SEM analysis. Textural characteristics were determined by nitrogen adsorption at low temperature (77 K) on a Autosorb 1 Quantacrome instrument. Scanning Electron Microscope FEI Inspect,

S model was used to examine the morphology of the studied catalysts at an accelerating voltage from 200V to 30 kV. X-ray diffraction was used to detect the presence and size of Co, Mo and Re crystallites, confirmed by FTIR analysis. XRD patterns were recorded with a BRUKER D8 Advance X-ray powder diffractometer, using $\text{CuK}\alpha$ radiation ($\lambda = 0.154$ nm). Fourier transform infrared spectroscopy (FT-IR) was used to identify the functional groups of the catalysts using Jasco 610 spectrometer (in an ATR mode), with a scanning range from 4000 to 550 cm^{-1} at a speed of 4 $\text{cm}^{-1} \cdot \text{s}^{-1}$ and with an average of 128 measurements in the final spectrum.

Catalysts reactivity in thiophenes hydrodesulphurization activity test

In this study the hydrodesulphurization of thiophene and benzothiophene on CoMoRe/ $\gamma\text{-Al}_2\text{O}_3$ and CoMoRe/ $\gamma\text{-Al}_2\text{O}_3$ -HMS catalysts have been studied, at different temperatures from 200°C to 275°C and pressures from 30 bar to 60 bar, at 2h⁻¹ liquid hourly space velocity.

Oxidic catalyst samples have been activated with hydrogen, for two hours, at 250°C and 5 bar. After two hours, the temperature has been increased to 450°C, and the activation continued for 6 h. After activation, the catalysts have been sulphided for 8 h, at 250°C and 5 bar, in a flow of 1ml/min dimethylsulphide 1% in hexane.

The conversion of thiophenes was monitored by gas chromatography coupled with mass spectrometry. The activity data given are those obtained after 2 h on stream. The conversion of thiophene and benzothiophene have been calculated by reporting the amount of the converted reactant (thiophene or bezothiophene) to the amount of the reactant introduced in the reactor. The product yield resulted in hydrodesulfurization have been calculated by reporting the amount of reactant transformed in a product to the amount of the reactant introduced in the reactor.

The catalytic tests have been performed in a standard fixed bed reactor, described in our previous work [1]. The feedstock consisted of 0.625 wt% thiophene (or 1 wt% benzothiophene) solution in hexane, was used to simulate a FCC gasoline with a sulphur concentration of 2380 ppm. The feedstock was introduced by a metering pump and vaporized, mixed with hydrogen and preheated to a desired temperature before entering into the reactor. The hydrogen/thiophene (benzothiophene) molar ratio was 60:1. The influence of the support on hydrodesulfurization activity of CoMoRe catalyst was studied at different temperatures from 200°C to 275°C and pressures from 30 bar to 60 bar.

Results and discussions

Catalysts characterization

Thermal desorption curves of diethylamine for CoMoRe catalysts (on $\gamma\text{-Al}_2\text{O}_3$ and $\gamma\text{-Al}_2\text{O}_3$ -HMS support) show that the catalytic centers are mainly weak acidic centers, before (A) and after sulphurization (B), as presented in figures 1. After sulphurization, it was observed that the total concentration of acidic catalytic centers, decreased for both catalysts CoMoRe/ $\gamma\text{-Al}_2\text{O}_3$ and CoMoRe/ $\gamma\text{-Al}_2\text{O}_3$ -HMS. For CoMoRe/ $\gamma\text{-Al}_2\text{O}_3$ the total concentration of acidic catalytic centers decreases from 0.731 meq/g to 0.685 meq/g and from 0.884 meq/g to 0.655 meq/g for CoMoRe/ $\gamma\text{-Al}_2\text{O}_3$ -HMS. The acid strength distribution results, based on weak, medium and strong acidic centers are summarized in table 1.

After sulphurization, the acid strength of the catalysts should increase because MoS_3 is strongly acidic than MoO_3 [15], but in this case, the acidic strength after sulphurization

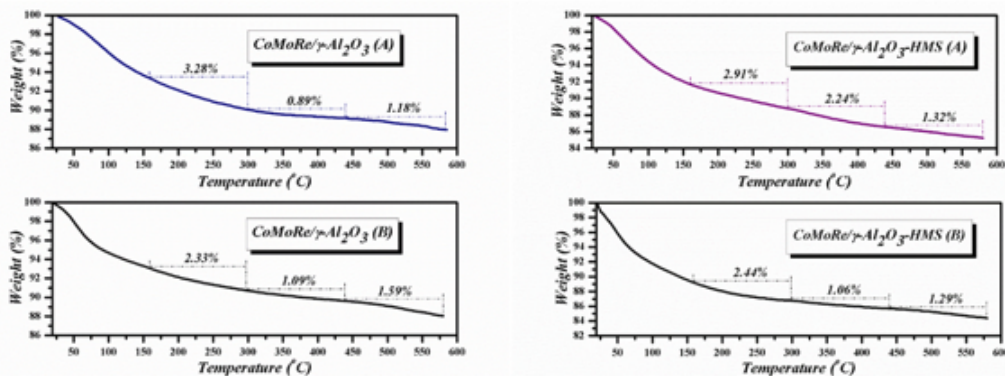


Fig. 1. Temperature-programmed desorption curves of diethylamine for catalysts before (A) and after sulphurization (B)

Table 1

ACID STRENGTH DISTRIBUTION FOR CoMoRe/γ-Al₂O₃ AND CoMoRe/γ-Al₂O₃-HMS CATALALYSTS, BEFORE SULPHURIZATION(FRESH) AND AFTER SULPHURIZATION (SULPHIDED)

Catalyst	Weak acidic centers meq/g		Medium acidic centers meq/g		Strong acidic centers meq/g		Total acidity	
	fresh	sulphided	fresh	sulphided	fresh	sulphided	fresh	sulphided
CoMoRe/γ-Al ₂ O ₃	0.448	0.319	0.122	0.149	0.161	0.217	0.731	0.685
CoMoRe/γ-Al ₂ O ₃ -HMS	0.398	0.334	0.306	0.145	0.180	0.176	0.884	0.655

has decreased, as seen in table 1. This may be due to the low availability of diethylamine in the pores of the catalysts, as a result of specific area decrease, due to the clogging of the small pores.

The specific surface area, pore volume and average pore diameter were determined to obtain information on the diffusion rate of the reactants and reaction products into and out of the pores and the deposition of coke and other contaminants. The textural characteristics interrelated with the pores of the catalysts were determined by the adsorption and physical desorption of nitrogen by determining the moment when the surface is covered with a monolayer of gas molecules. The textural properties (BET surface area, pore volume and average pore diameter) of the catalysts are summarized in table 1. After sulphurization, the textural characteristics of the catalysts change by decreasing the specific surface, the pore volume and the average pore diameter. These changes are due to the replacement of oxygen from molybdenum oxide (MoO₂) with sulfur and the formation of molybdenum sulfide (MoS₂). The sulfur molecule is bigger than oxygen molecule so, MoS₂ will have a higher volume than MoO₂, reducing the pore dimensions.

The adsorption desorption isotherms and the pore-size distribution curves of CoMoRe/γ-Al₂O₃ and CoMoRe/γ-Al₂O₃-HMS catalysts, before sulphurization (A) and after sulphurization (B), are presented in figure 2.

CoMoRe/γ-Al₂O₃ catalyst exhibits a IV isotherm with a H4 hysteresis loop, characteristic for bottle neck pores. After sulphurization, the isotherm type and shape is the same, resulting only a decrease of the adsorbed volume (fig. 2). Similar pattern of behaviour is observed for CoMoRe/γ-Al₂O₃-HMS catalyst (fig. 2). The difference between the two catalysts is that CoMoRe/γ-Al₂O₃-HMS has wider pore volume than CoMoRe/γ-Al₂O₃ so the nitrogen adsorbed volume is higher for CoMoRe/γ-Al₂O₃-HMS.

SEM analysis shows that there are differences between the shape and size of the catalysts particles. The SEM images for sulphided CoMoRe/γ-Al₂O₃ and CoMoRe/γ-Al₂O₃-HMS catalysts are presented in figure 3. Figure 3a (1000 magnification) shows the non-homogeneity of CoMoRe/γ-Al₂O₃ catalyst and in figure 3b (a higher magnification, 1500x) different particle shapes can be observed - elongated and conglomerates. The same can be observed for CoMoRe/γ-Al₂O₃-HMS catalyst (fig. 3 c,d).

Table 2

TEXTURAL PROPERTIES OF CoMoRe/γ-Al₂O₃ AND CoMoRe/γ-Al₂O₃-HMS CATALALYSTS, BEFORE SULPHURIZATION (FRESH) AND AFTER SULPHURIZATION (SULPHIDED)

Catalyst	S _{BET} (m ² /g)		Pore volume (cm ³ /g)		Average pore diameter (nm)	
	fresh	sulphided	fresh	sulphided	fresh	sulphided
CoMoRe/γ-Al ₂ O ₃	180.33	145.67	0.294	0.247	3.42	3.31
CoMoRe/γ-Al ₂ O ₃ -HMS	273.50	211.69	0.419	0.332	3.63	3.46

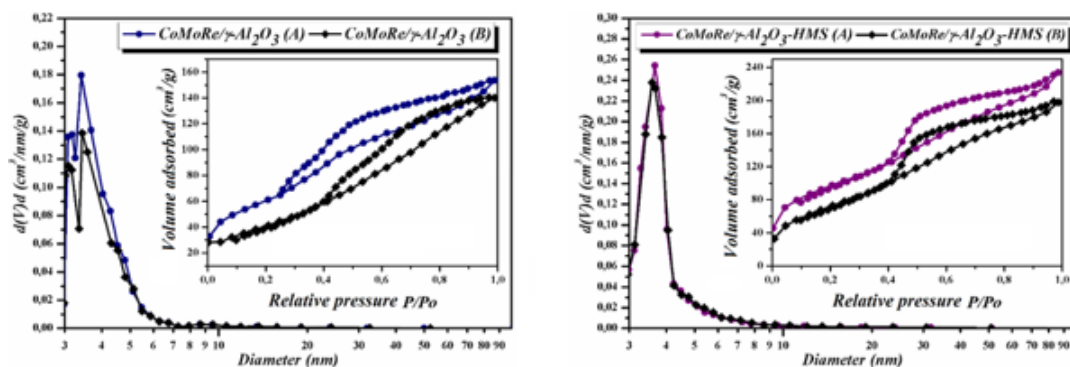


Fig. 2. Pore size distributions and adsorption desorption isotherm for catalysts before (A) and after sulphurization (B)

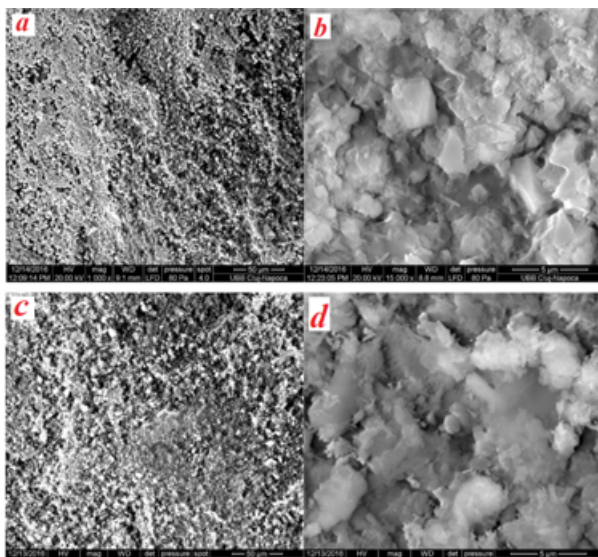


Fig. 3. SEM images for sulphided CoMoRe/ γ -Al₂O₃ (a,b) and CoMoRe/ γ -Al₂O₃-HMS (c,d) catalyst

FTIR analysis of the catalysts was to identify functional groups on the prepared materials. The spectra were obtained with the ATR method, ranging from 4000 to 400 cm⁻¹.

The IR spectra for the catalysts (fig. 4) show similar spectral bands at aprox. 3420 cm⁻¹ and 1630 cm⁻¹ corresponding to stretching and bending O-H bonds vibrations, which can be attributed to the adsorbed water molecules [15]. The bands in the 500-750 cm⁻¹ and 800 cm⁻¹ regions are characteristic of the stretching vibrations of the AlO₆ and AlO₄ in the -Al₂O₃ support [16]. Between 500-1000 cm⁻¹ are the characteristic bands for Co, Mo and Re oxides. An exactly identification is imposible because of the bands overlapping. The Co-O stretching vibration is assigned between 500-590 cm⁻¹, depending on cobalt oxidation number. CoOH shows spectral band at 585 cm⁻¹, CoO at 505 cm⁻¹, and Co₃O₄ at 570 cm⁻¹ [17]. FTIR spectra of CoMoRe/ γ -Al₂O₃-HMS catalyst (fig. 4), in the range of

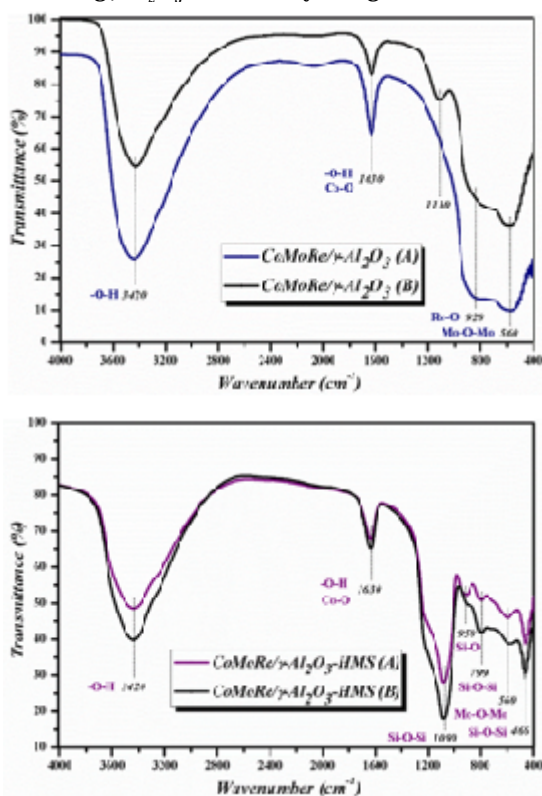


Fig. 4. FTIR spectra for catalysts, before (A) and after sulphurization (B)

500 cm⁻¹ and 1000 cm⁻¹, show specific customized spectral bands from silica, due to Si-O-Si bonds [18].

Figure 5 shows the X-ray diffractogram of the catalyst before and after the sulfurization. Both catalysts prior to sulfurization exhibit intense XRD peaks at $2\theta \sim 36.7^\circ$; 45.5° and 66.8° which are specific for γ -Al₂O₃ support. ReO₃ has assigned specific peaks at $2\theta \sim 38^\circ$; 40° ; 42.8° ; 44° and 65° . HMS shows specific peaks in the region $2\theta \sim 20$ - 30° which corresponds to the amorphous state of HMS [19-20].

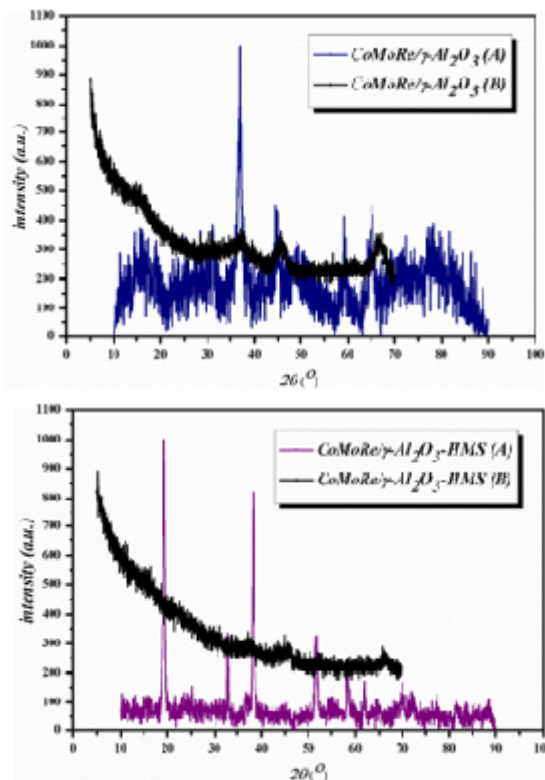


Fig. 5. XRD spectra for catalysts, before (A) and after sulphurization (B)

The catalysts have undergone structural changes after sulfurization, either by decreasing the peak intensity or by dropping the specific peaks, indicating that the present species has been amorphous, or crystallites are too small to record a RX signal.

Catalysts hydrodesulphurization activity

a. Effect of reaction temperature

Studies of thiophene and benzothiophene conversion as a function of temperature are presented in Figure 6 and the results show that the activity of both catalysts increased with the temperature. The hydrodesulfurization of thiophene and benzothiophene on CoMoRe/ γ -Al₂O₃ and CoMoRe/ γ -Al₂O₃-HMS, proved to be efficiently in the range of 200°C-275°C, at 30 bar and LHSV of 2h⁻¹.

Thiophene conversion with temperature, follows a similar slope for both catalysts, between 200-225°C, but is higher by about 20% over CoMoRe/ γ -Al₂O₃. At higher temperatures of 275°C, thiophene is converted more than 99% over both catalysts. On CoMoRe/ γ -Al₂O₃ catalyst, thiophene conversion increased from 54.54% (at 200°C) to 85% at 225°C and reached almost 100% at 275°C. On CoMoRe/ γ -Al₂O₃-HMS, thiophene conversion was 35% at 200°C but also reached almost 100% at 275°C.

Benzothiophene conversion was higher than thiophene conversion on both catalysts, due to the lower aromatic character of benzothiophene which means a higher activity. At 200°C, benzothiophene conversion on CoMoRe/

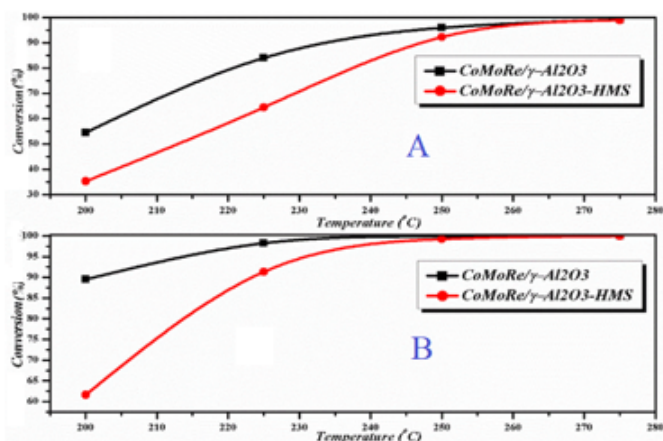


Fig. 6. Influence of temperature on thiophene (A) and benzothiophene (B) conversion at 30 bar and LHSV = 2h⁻¹

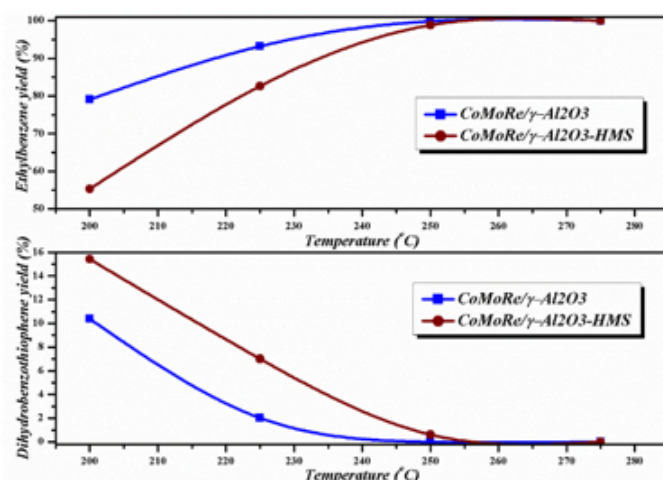


Fig. 7. Influence of temperature on products yield in benzothiophene hydrodesulphurization at 30 bar and LHSV = 2h⁻¹

γ-Al₂O₃-HMS is 60% and on CoMoRe/γ-Al₂O₃ is almost 90%. Over 250°C, the conversion is 100%.

It is noted that for the CoMoRe catalyst, the introduction of mesoporous silica into the γ-Al₂O₃ support decreased the conversions of thiophene and benzothiophene compared to the γ-Al₂O₃ support. However, smaller conversions are only at temperatures from 200 to 250 °C. At 275 °C, the conversions reached almost 100% for CoMoRe supported on both γ-Al₂O₃ and γ-Al₂O₃-HMS.

The tests performed in this work, over CoMoRe catalyst, suggested that benzothiophene is first hydrogenated to dihydro-benzothiophene (DHBT), then hydrodesulfurized to ethylbenzene (EB). Thiophene is first hydrodesulfurized to butadiene and further hydrogenated to butane.

In benzothiophene hydrodesulphurization, the variation of reaction products yields with temperature is represented in figure 7. It is observed that the intermediary reaction product DHBT, is completely converted with the temperature increase from 200 to 275 °C, meanwhile, the yield of the final product, ethylbenzene, increases.

b. Effect of reaction pressure

The influence of pressure on hydrodesulphurization process of thiophene and benzothiophene on the CoMoRe catalysts on both supports were studied in the range of 30-60 bar at 200 °C and 2h⁻¹ liquid hourly space velocity.

The reaction pressure has small influence on the hydrodesulfurization process of thiophene and benzothiophene, on both catalysts studied: CoMoRe/γ-Al₂O₃ and CoMoRe/γ-Al₂O₃-HMS (fig. 8). On CoMoRe/γ-

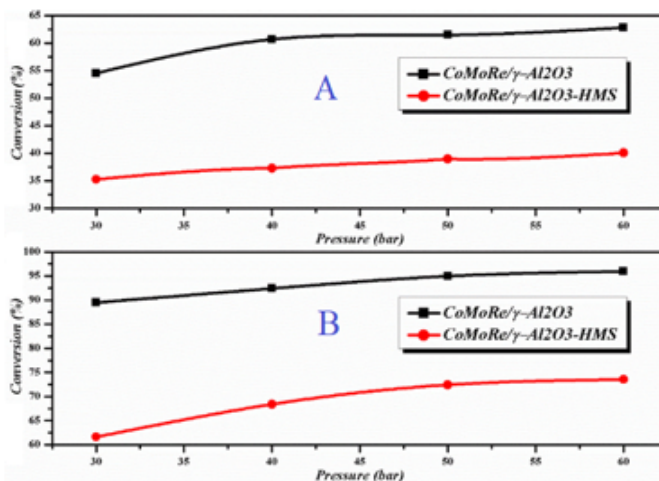


Fig. 8. Influence of pressure on thiophene and benzothiophene conversion at 200°C and LHSV = 2h⁻¹

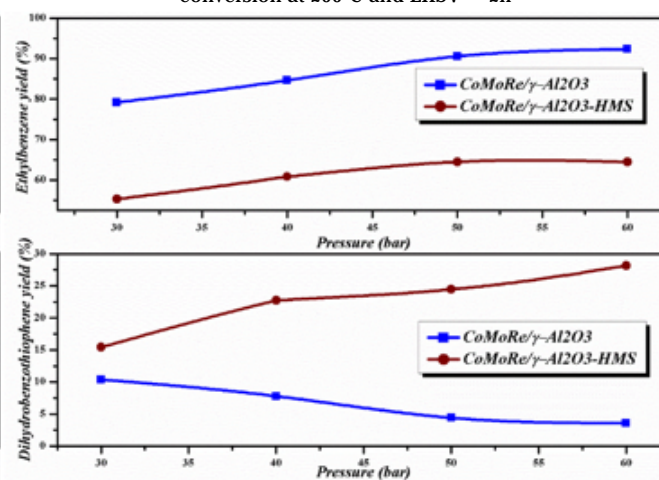


Fig. 9. Influence of pressure on hydrodesulphurization products yield at 200°C and LHSV = 2h⁻¹

Al₂O₃, at 200°C and LHSV of 2h⁻¹, the conversion of thiophene increases from 54.54% to 62.80% (only by 8.14%), when pressure increases from 30 bar to 60 bar. On CoMoRe/γ-Al₂O₃-HMS catalyst, thiophene conversion increment is only by 5%, from 35% to 40%. This may be attributed to larger pores of CoMoRe/γ-Al₂O₃-HMS catalyst.

The benzothiophene conversion increases from 89.49% (30 bar) to 95.96% (60 bar), on CoMoRe/γ-Al₂O₃ catalyst and from 60% (30 bar) to 75% (60 bar), on CoMoRe/γ-Al₂O₃-HMS catalyst. We note that the more active in the hydrodesulfurization reaction the CoMoRe catalyst is, the weaker is the pressure influence on thiophene and benzothiophene conversion.

Figure 9 shows the variation of products yields with pressure. An increase in pressure from 30 bar to 60 bar, favors the formation of final products in the case of benzothiophene hydrodesulfurization. On CoMoRe/γ-Al₂O₃, the yield in ethylbenzene at 30 bar is 79.19% and in 2,3-dihydrobenzothiophene is 10.38%. At 60 bar, the yield in ethylbenzene increases to 92.38% and in 2,3-dihydrobenzothiophene decreases to 3.58%.

On CoMoRe/γ-Al₂O₃-HMS catalyst, the yield in the intermediate product, 2,3-dihydrobenzothiophene, increases with pressure, from 15% (30 bar) to 27% (60 bar), and so the final product does. The yield in ethylbenzene increase from 55 to 65%, with the pressure increase from 30 bar to 60 bar.

Conclusions

The CoMoRe catalyst deposited on the Al₂O₃ and Al₂O₃-HMS supports was prepared simultaneous impregnation

using the pore filling method. The catalysts have been characterized to determine: the textural characteristics, the chemical and the structural properties. The presence of HMS mesoporous silica causes a decrease in CoMoRe/ γ -Al₂O₃ catalyst acidity and increases the textural features. On the other hand the textural features of both catalysts decrease after sulfurization, due to the larger volume of the sulfur atoms compared to the oxygen that it has replaced.

The influence of pressure and temperature on the performance of the HDS process is basically similar on the two catalysts. The presence of HMS type mesoporous silica reduces the performance of the CoMoRe / γ -Al₂O₃ catalyst probably due to the negative influence on the concentration of acidic centers sau HMS structure and catalyst-support interaction.

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