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Support effects in the hydrotreatment of model molecules

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Abstract

The support effect on the activity of hydrotreating catalysts using model molecules was analyzed for catalysts supported on TiO_2, SiO_2 and MgO. The results reported in the literature indicate that adequate design of the characteristics of the catalytic support is of great importance in the development of better hydrotreating catalysts. It was shown that by means of an adequate support design it is possible to increase significantly the HDS, HYD and HDN functionalities of hydrotreating catalysts. Semiconducting supports like TiO_2 can improve the HDS and HYD activities by exerting electronic effects on the active phase, helping in this way the formation of sulfur vacancies. Alumina supports modified by SiO_2 can facilitate the sulfidation of the active species, leading to better-promoted type II active sites with increased HDS and HYD catalyst functionalities. The nature of the support affects the sulfidation and dispersion of the catalysts even when chelating agents are used during catalyst preparation.

Keywords: Support effect; Hydrotreating catalysts; Hydrodesulfurization; TiO_2; SiO_2; MgO

1. Introduction

Development of better hydrotreating catalysts is necessary in view of the stringent regulations on the contents of sulfur compounds in transportation fuels. However, to achieve sulfur contents close to zero requires the hydrodesulfurization of the most refractory sulphur-containing molecules such as 4,6-dimethyldibenzothiophene. To obtain catalysts with high HDS activity, it is necessary to achieve high dispersion, complete sulfidation of the Mo and Co (Ni) precursor oxide phases, and high level of promotion of the Mo (or W) phase by the Co or Ni promoters. For this, the nature of the catalyst support plays an important role.

It is now known that compounds like 4-MDBT and 4,6-DMDBT can be hydrodesulfurized through several reaction routes [1,2]. The direct hydrodesulfurization route is a slow one for these compounds due to the steric hindrance of the methyl groups, which hinder an adequate interaction of the sulfur atom with the catalytic active site. The pre-hydrogenation route, in which one of the aromatic rings adjacent to the sulfur atom is hydrogenated, is the main route for hydrodesulfurization of these compounds. When the catalyst has an important acid function like in zeolite-containing catalysts, several other reaction routes are also possible. The acid function allows either the breaking of a C–C bond in the sulfur ring [3,4] or the isomerization or elimination of the methyl groups in the 4 and 6 positions, thus allowing a better interaction of the sulfur atom with the active site.

Several approaches are being used to develop new more active HDS catalysts with adequate functionalities to perform adequate HDS of refractory molecules. The use of new active phases such as carbides, nitrides, phosphides, or transition metal sulfides other than Mo and W, promoted by Ni or Co, has been proposed. The performance of these phases continues to be explored for practical applications. Other approach which appears promising and has been widely investigated is the use of different catalyst supports.

In the past it was considered that the hydrotreating catalyst support was inert so far as the active component was concerned. However, we know now that this is not always the case and that in many cases the support interacts with the active component leading to beneficial or detrimental interactions to catalytic activity The earlier view that the role of the support in hydrotreating catalysts was just to stabilize the active component as small particles, thus increasing the dispersion

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without influencing the catalyst activity has drastically changed in the light of different studies that have shown that the rate and selectivity of hydrotreating reactions over sulfided NiMo(W) or CoMo(W) catalysts are significantly affected by the support nature [5–9]

In general, the studies in this field present the relationship between different physical and chemical properties of the support with the activity of different hydrotreating reactions. Some studies concentrated on the acidic and basic nature of support and its effect on the nature of interaction with the active metal [10–12]. Many of the studies carried out with model molecules have demonstrated that it is possible to obtain better catalytic performance by changing the nature of the support. Benefits have been reported with the use of different supports such as TiO_2, ZrO_2, MgO, carbon, CeO_2, SiO_2, zeolites, SiO_2–Al_2O_3, SiO_2–MgO, ZrO_2–Y_2O_3, ZrO_2–Al_2O_3, ZrO_2–SiO_2, TiO_2–SiO_2, Al_2O_3–B_2O_3, ZrO_2–TiO_2, MCM-41, SBA-15, natural minerals clays, TiO_2–Al_2O_3, etc. [13–46].

Here, some of the works concerning the support effect in hydrodesulfurization catalysts are reviewed in order to highlight the importance of the support design. Special emphasis will be placed on catalysts containing TiO_2, SiO_2, MgO and Al_2O_3. Therefore, no effort has been made to review all the work done in the field.

2. TiO_2 and TiO_2-modified catalysts supports

Table 1 shows the specific and intrinsic rates of reaction found during the hydrodesulfurization of thiophene when equal metal surface density of 2.8 atoms of Mo/nm^2 is used [16,22].

The observed changes in catalytic activity for the TiO_2- and ZrO_2-supported catalysts in Table 1 could not be explained solely on the basis of increased dispersion of the MoS_2 phase. An additional interesting finding in the same study was that the promotion of Mo by Co was smaller for the TiO_2 supported catalyst compared with that of the alumina supported catalyst. In spite of this, the activity of the TiO_2-supported catalyst was 2.2 times that of CoMo/Al_2O_3. These results suggested that TiO_2 was not an inert support for HDS catalysts and that its presence modified the catalyst activity. The main beneficial effect of TiO_2 being on the Mo phase rather than on the promoter.

Soon it was evident that in addition to the textural and mechanical properties, the acid-base and electronic properties of the support were also important to the catalyst activity.

Electronic effects due to the use of semiconducting supports such as TiO_2 have been disclosed in the past. J. Ramírez et al. demonstrated that increasing the amount of Ti in the Al_2O_3–TiO_2 support increases the hydrodesulfurization and hydrogenation rates of NiMo and NiW catalysts supported on Al_2O_3–TiO_2 mixed oxides due to an electronic promotion effect of the Ti present in the support over the Mo or W sulfided active phase [18 and references therein, 46]. So, an electronic interaction between the support and the active component can alter the activity and selectivity of the catalysts. The support can also influence the active component by favoring the exposure of some crystallographic planes in preference to others. Morphological changes of the active phase induced by the support may also cause a change in the active metal-support interaction.

Table 1
Specific and intrinsic HDS rates of reaction for thiophene hydrodesulfurization when equal metal surface density of 2.8 atoms of Mo/nm^2 is used [16,22]

Catalyst	$R_s \times 10^7$ (mol-s^{-1}-g^{-1})	$R_i \times 10^4$ (molecule-s^{-1}(atom Mo)$^{-1}$)
Mo (2.8)/Al_2O_3	3.2	3.3
Mo (2.8)/ZrO_2	5.4	8.7
Mo (2.8)/TiO_2	3.3	14.5
Mo (2.8)/SiO_2–Al_2O_3	2.4	1.5

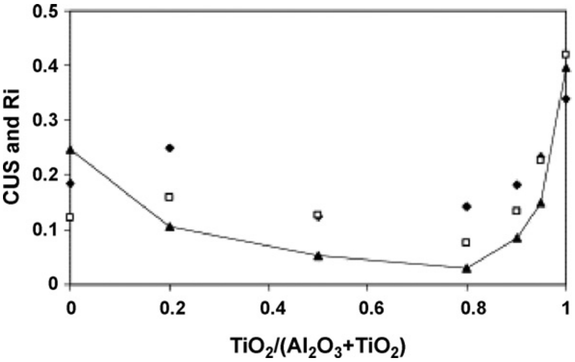

Fig. 1. Activity (▲) of CoMo/Al–Ti(x) catalysts at 513 K ($R_i \times 10^3$ = thiothiophene molecules, Mo atom^{-1} s^{-1}) and CUS vs. Ti content. CUS before (◆) and after (□) reaction test [49].

In a study on the hydrodesulfurization of thiophene J. Ramírez et al. showed that when using Al_2O_3–TiO_2 mixed oxides prepared by coprecipitation, partial monolayers of alumina enrich the surface of the support and because of this the activity of the catalyst only increases when the TiO_2/$TiO_2 + Al_2O_3$ ratio goes beyond 0.7 [47,48]. The observed activity trends were due to the different electronic nature of the support. It was later demonstrated that the semiconducting nature of TiO_2 had a direct influence on the number and formation of the molybdenum coordinatively unsaturated sites (CUS), which are directly related to the active sites of the catalyst (see Figs. 1 and 2) [49].

Particularly the use of Ti-containing supports has been studied in detail. Besides achieving higher dispersion of the active Mo or W sulfided phases it was found that under reaction conditions some Ti^{4+} transforms into Ti^{3+}, which is capable of transferring electronic charge to the Mo or W sulfided phase leading to an increase in the number of coordinatively unsaturated sites in MoS_2 thus increasing the hydrodesulfurization and hydrogenation activities. In essence, Ti acts as an electronic promoter for the Mo sulfided phase. To produce this effect, it is necessary that the Ti oxide surface species are polymeric (Ti–O–Ti–O) as those in TiO_2 rather than isolated (Al–O–Ti–O–Al) in the alumina matrix. It appears then that the way in which Ti is incorporated to the support has important influence on the activity of the final catalyst. To examine this suggestion J. Ramírez et al. [18] tested CoMo catalysts supported on alumina covered with titania and on TiO_2–Al_2O_3 mixed oxides. The results indicated greater activity for the

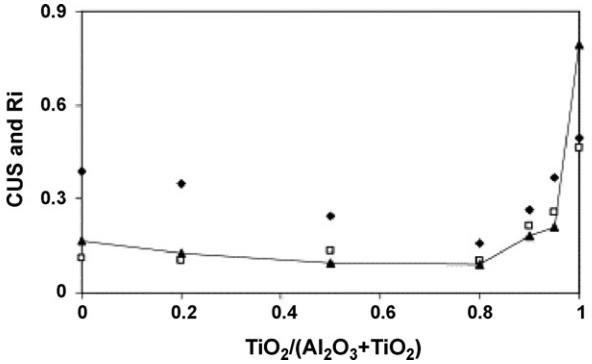

Fig. 2. Activity (▲) of NiMo/Al–Ti(x) catalysts at 433 K ($R_i \times 10^4$ = thio-thiophene molecules, Mo atom^{-1} s^{-1}) and CUS vs. Ti content. CUS before (◆) and after (□) reaction test [49].

catalysts prepared on Ti-covered alumina since in this case TiO_2-like structures were present on the support surface (see Figs. 3 and 4).

In the hydrodesulfurization of 4,6-dimethyldibenzothiophene by depositing TiO_2 on the surface of alumina, 58% greater activity was obtained (Table 2), compared to a catalyst supported on a TiO_2–Al_2O_3 mixed oxide. The former catalyst also displayed higher hydrogenating functionality. These results confirm that the way in which TiO_2 is incorporated to the catalyst support is of greater importance to the activity of the catalyst [50].

To distinguish between the effect of the support and the effect of the precursor salt used to prepare the catalyst J. Ramírez et al. [18] performed a study in which NiW catalysts supported on Al_2O_3, TiO_2 and $TiO_2(x)$–Al_2O_3 mixed oxides with variable amounts of TiO_2 were prepared using $(NH_4)_6H_2W_{12}O_{40}$, (AM), and $(NH_4)_2WS_4$ (AT) as active phase precursors. In this way, the W phase prepared with the latter thiosalt was properly sulfided in all cases since for this particular precursor salt the calcination step was skipped. The results in Table 3 show that the effect of the support on the catalytic activity (12.6 → 38.2) is greater than the effect of the precursor salt (7.8 → 12.6 and 32.4 → 38.2).

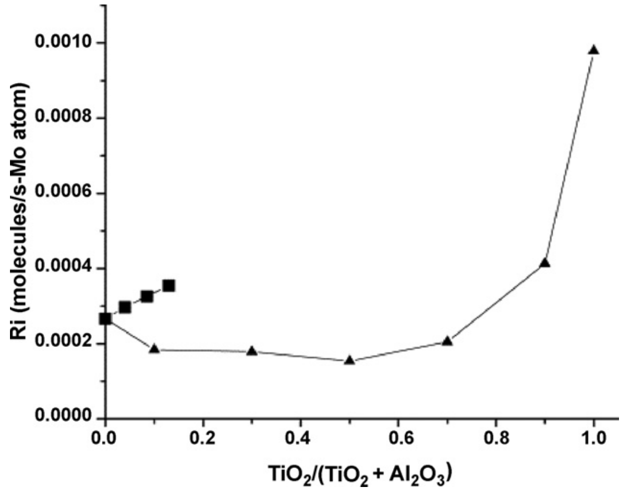

Fig. 3. Catalytic activity at 593 K in thiophene HDS for Mo catalysts supported on (▲) co-precipitated Al_2O_3–$TiO_2(x)$ and (■) impregnated $TiO_2(x)/Al_2O_3$ supports [18].

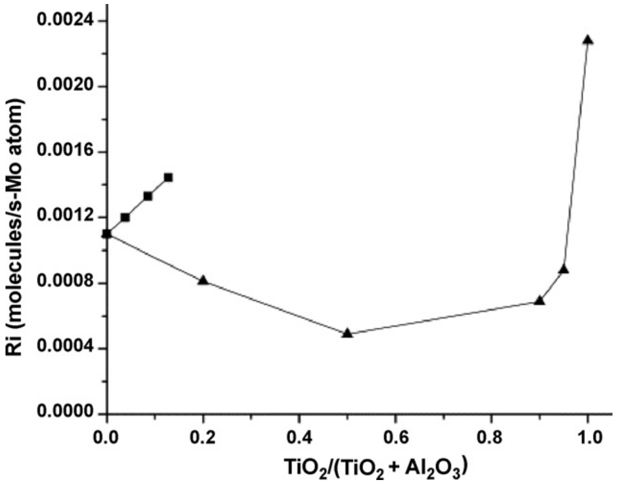

Fig. 4. Catalytic activity at 553 K in thiophene HDS for NiMo catalysts supported on (▲) co-precipitated Al_2O_3–$TiO_2(x)$ and (■) impregnated $TiO_2(x)/Al_2O_3$ supports [18].

3. Support effects in catalysts prepared with chelating agents

The use of chelating agents during the preparation of Co (Ni) Mo (W) hydrodesulfurization catalysts delay the sulfidation of the Ni and Co promoter to assure that the formation of the Ni and Co sulfides occurs after the sulfidation of the Mo phase and in this way a proper promotion of the latter is achieved. At the same time, a lower support-active phase interaction is induced leading to the formation of the highly active CoMoS or NiMoS type II structures. So when chelating agents are used it is expected that the support influence on the activity of the catalyst will be minimized.

However, it has been found recently that even when chelating agents are used during the preparation of HDS catalysts, the nature of the support has an important influence on the activity of the catalyst [51]. It was reported that a CoMo catalyst prepared using EDTA as chelating agent, supported on Al_2O_3–MgO was more active than a catalyst supported on SiO_2 and this in turn more active than one supported on Al_2O_3 (see Fig. 5). The differences in HDS activity with the support were found to be due to changes in the dispersion of the active phase

Table 2
Hydrodesulfurization of 4,6-dimethyldibenzothiophene over NiW catalysts supported on Ti(x)–alumina (mixed oxides) and Ti(x)/alumina (TiO_2 over alumina)

Catalyst	$k \times 10^4$ (g/h m^2)	HYD/DDS (DMCHB/DMBF)*
NiW/Ti (4.5%)-Al	5.4	0.2759
NiW/Ti (9%)-Al	6.4	0.2763
NiW/Ti (9%)/Al	10.1	0.3049
NiW/Ti (14.5%)/Al	13.0	0.4215

x = wt% TiO_2. Experiments at T = 325 °C; 1100 psi.

* DMCHB = dimethylcyclohexylbenzene; DMBF = dimethylbiphenile.

Table 3
Thiophene HDS activity for NiW catalysts prepared with ammonium tetrathiotunstate (ATT) and ammonium metatungstate (AMT)

$Al_2O_3–TiO_2(x)$	$x = 0$		$x = 0.5$		$x = 0.95$		$x = 1.0$	
	ATT	AMT	ATT	AMT	ATT	AMT	ATT	AMT
553 K	9.4	6.3	11.1	7.1	19.9	13.5	27.3	23.1
563 K	12.6	7.8	13.4	8.5	25.6	17.3	38.2	32.4

Table 4
Promotional effect in CoMo catalysts prepared with EDTA as chelating agent, obtained from NO and CO adsorption experiments [50]

Catalyst	CUS-Co/CUS-Mo (NO adsorption)	CUS-CoMoS/CUS-Mo (CO adsorption)
$CoMoE/Al_2O_3$	4.1	0.6
$CoMoE/Al_2O_3–MgO$	74.3	3.2
$CoMoE/SiO_2$	49.0	1.4

and to changes in the level of promotion estimated from CO and NO adsorption experiments, used to measure the relative number of coordinatively unsaturated sites associated with the promoter and the Mo sulfide phases, as Table 4 shows.

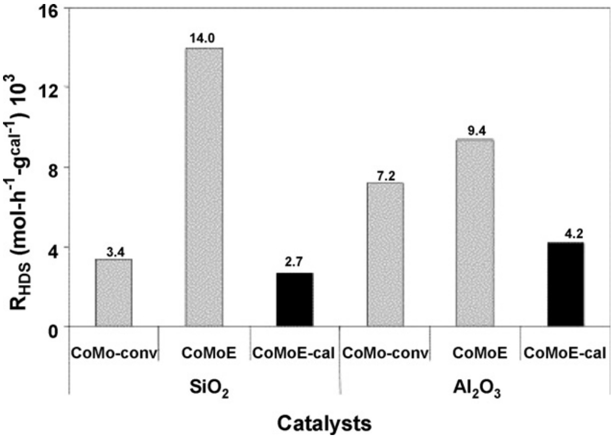

Fig. 5. Thiophene HDS activity for SiO_2- and Al_2O_3-supported CoMo catalysts prepared with and without chelating agent (EDTA). CoMoE-calc was calcined (400 °C, 4 h) prior to sulfidation. CoMo-conv was prepared without EDTA following a conventional preparation method (impregnation–drying–calcination) [50].

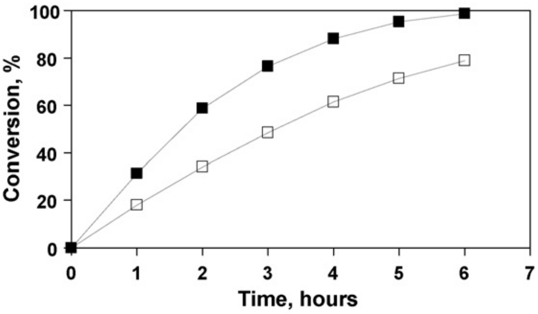

Fig. 6. Hydrodesulfurization of 4,6-dimethyldibenzothiophene over NiMo-SAC 0 (□) and NiMo-SAC 10 (■) catalysts. 1000 ppm S, 1200 psia, solvent decane-xylene 70/30 vol%.

4. Support effects in catalysts modified by SiO_2

The effect of the support nature is revealed for SiO_2-modified NiMo catalysts in experiments with catalysts supported on pure alumina (NiMo-SAC0), and on alumina covered with 10 wt% SiO_2 (NiMo-SAC-10) during the hydrodesulfurization of 4,6-dimethyldibenzothiophene (4,6-DMDBT) in the absence and presence of naphthalene and carbazole. The results, displayed in Figs. 6–8, show that the incorporation of SiO_2 to the alumina support enhances the hydrogenation functionality of the catalyst leading to increasing hydrodesulfurization of 4,6-DMDBT through the hydrogenation-hydrodesulfurization reaction route. Although the HDS activity was diminished by the presence of naphthalene and carbazole, in all cases it was greater for the SiO_2-modified catalyst. Analysis of the Langmuir-Hinshelwood kinetic parameters showed that the inhibition of the HDS reaction rate by naphthalene is due to the high concentration of

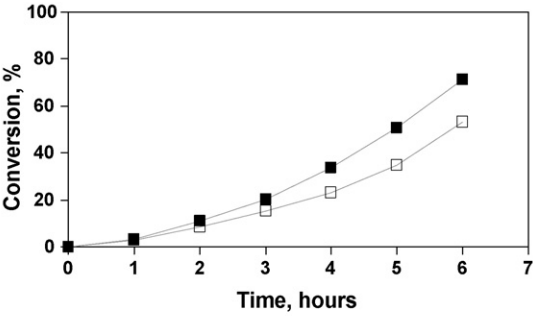

Fig. 7. Hydrodesulfurization of 4,6-dimethyldibenzothiophene over NiMo-SAC 0 (□) and NiMo-SAC 10 (■) catalysts. 1000 ppm S, 1200 psi, solvent decane-xylene 70/30 vol%, 5 vol% naphthalene.

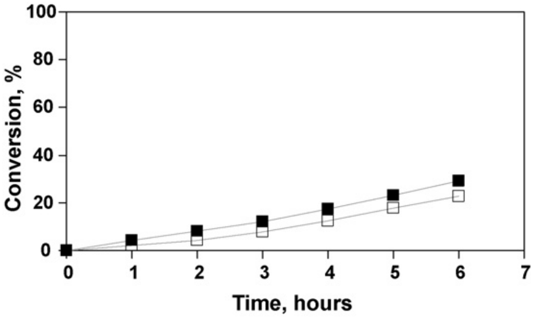

Fig. 8. Hydrodesulfurization of 4,6-dimethyldibenzothiophene over NiMo-SAC 0 (□) and NiMo-SAC 10 (■) catalysts. 1000 ppm S, 1200 psi, solvent decane-xylene 70/30 vol%, 5 vol% naphthalene, 100 ppm N.

naphthalene in the reaction mixture rather than to the magnitude of the adsorption constant, which was the smallest. In contrast, the inhibition caused by the presence of carbazole is due to the high value of the adsorption constant of carbazole (~71), compared to those of naphthalene (~6), and 4,6-DMDBT (~34). High resolution transmission electron microscopy micrographs of the sulfided catalysts showed that the alumina support modified by SiO_2 can facilitate the sulfidation of the CoMo active species, leading to better-promoted type II active sites with increased HDS and HYD catalyst functionalities.

5. Conclusions

It has been shown that the nature of the support is of great importance to the design of hydrotreating catalysts.

By means of an adequate support design it is possible to increase significantly the HDS, HYD and HDN functionalities of hydrotreating catalysts.

Semiconducting supports like TiO_2 can improve the HDS and HYD activities by exerting electronic effects on the active phase, helping in this way the formation of sulfur vacancies.

Alumina supports modified by SiO_2 can facilitate the sulfidation of the active species, leading to better-promoted type II active sites with increased HDS and HYD catalyst functionalities.

The nature of the support affects the sulfidation and dispersion of HDS catalysts even when chelating agents are used during catalyst preparation.

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