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CoMo/Al₂O₃ and CoMo/TiO₂-Al₂O₃ catalysts in hydrodesulfurization : relationship between the promoting effect of cobalt and the nature of the support.

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Abstract

Molybdenum and cobalt-molybdenum catalysts have been prepared over Al₂O₃ and a TiO₂-Al₂O₃ mixed oxide in order to get more insight on the relation between the nature of the support and the promoting effect of cobalt. These catalysts were characterized by UV-visible diffuse reflectance spectroscopy (DRS), analyzed by energy dispersive spectroscopy (EDS) and evaluated in dibenzothiophene hydrodesulfurization. For the unpromoted catalysts, the Mo/TiO₂-Al₂O₃ sample presented a very high activity as compared to the Mo/Al₂O₃ catalyst. However, over the titania based support a limited activity enhancement by Co promotion was observed. Such a drawback of the TiO₂-Al₂O₃ support was correlated to a large amount of cobalt involved in the formation of CoMoO₄; moreover, variations observed in the stability of the sulfide phase support these explanations.

1. INTRODUCTION

Sulfided CoMo catalysts are used for a long time for hydrotreating processes and these catalysts have generally been prepared over alumina. However, recent environmental specifications regarding the diminution of sulfur and aromatics in transportation fuels have spurred active development of investigation to improve activity and selectivity of such industrial catalysts. As reported in reviews, several studies suggested that changing the support could improve catalyst activity [1,2] .

In this way, a lot of work has been done on TiO₂ since it has been shown that molybdenum disulfide supported over such oxide present an intrinsic activity three up to four times higher than over alumina [3,6]. Such interest in the use of TiO₂ has been also demonstrated using mixed oxide supports with a

rich TiO_2 content [7-9]. In the case of MoS_2 supported over $\text{TiO}_2\text{-Al}_2\text{O}_3$ 5%, a support with the composition $\text{TiO}_2(95\%)\text{Al}_2\text{O}_3(5\%)$, the very high activity as compared to MoS_2 supported over Al_2O_3 could not be correlated simply with variations in the morphology (length and stacking) of the MoS_2 crystallites. Large variations in the reducibility of the supported sulfide were observed, the reducibility of the MoS_2 phase being higher when supported over the mixed oxide [8].

Although such oxides appeared promising when used as supports of MoS_2 , the promoting effect induced by cobalt or nickel is generally lower than that observed over Al_2O_3 , which fact is still to be understood.

The present contribution deals with the comprehension of the level of this synergetic effect by comparison of Mo and CoMo catalysts prepared over a commercial Al_2O_3 and over a $\text{TiO}_2\text{-Al}_2\text{O}_3$ 5% mixed oxide prepared by coprecipitation of aluminium and titanium isopropoxydes.

These catalysts were characterized by UV-visible spectroscopy, analyzed by energy dispersive spectroscopy and evaluated in the hydrosulfurization of dibenzothiophene (DBT).

2. EXPERIMENTAL

2.1. Supports and catalysts preparation

Preparation of the $\text{TiO}_2\text{-Al}_2\text{O}_3$ support with the molar ratio $\text{Al}_2\text{O}_3/(\text{TiO}_2+\text{Al}_2\text{O}_3)=0.05$ has been described in detail previously [9]. Briefly, the method involved the coprecipitation of aluminium and titanium isopropoxydes dissolved in n-propanol by adding acidified water in a large excess. The precipitate was left under slow agitation for 24 h, filtered, washed with demineralized water, dried at 383 K during 24 h and then calcined for 4 h at 823 K. The resulting solid was named $\text{TiO}_2\text{-Al}_2\text{O}_3$ 5% and presented a surface area of 160 m^2/g as determined by nitrogen physisorption using an automated BET apparatus.

Molybdenum was deposited on the carrier by the pore volume method using an aqueous solution of ammonium heptamolybdate of appropriate concentration in order to obtain a solid with 2.8 atoms of molybdenum per square nanometer of support. The impregnated sample was then dried at 393 K and later calcined at 673 K for 4 h (heating rate 2 K/min). In the case of CoMo catalyst cobalt was introduced by coimpregnation using cobalt nitrate, and the molar promoter to molybdenum ratio $r = \text{Co}/[\text{Co}+\text{Mo}]$ was equal to 0.3.

The $\text{Mo}/\text{Al}_2\text{O}_3$ catalyst was prepared according to the same procedure using an industrial $\gamma\text{-Al}_2\text{O}_3$ support (surface area 232 m^2/g) and the $\text{CoMo}/\text{Al}_2\text{O}_3$ catalyst was an industrial sample ($\text{MoO}_3=14$ wt%, CoO 3 wt%) having the same Al_2O_3 support.

2.2. Catalysts characterization

Diffuse reflectance spectra (UV-vis DRS) of the catalysts in their oxidic form were obtained in Perkin-Elmer Lambda 9 spectrophotometer using BaSO_4 as a reference.

EDS analyses were performed on a JEOL 2010 FEG electron microscope equipped with a Link Isis microanalysis system. The H₂-H₂S sulfided catalyst was dispersed in an ethanol solution and a droplet of the suspension was deposited over a holey carbon film supported on a copper grid. The K lines of S, Co, O, Al and the L lines of Mo were selected for quantitative analyses.

2.3. Catalytic activities

The HDS of dibenzothiophene was carried out in a continuous flow high pressure microreactor working under a total pressure of 30x10⁵ Pa, with a partial pressure of DBT of 4.80x10² Pa and H₂S added to the feed (252x10² Pa). Experiments were performed between 533 and 588 K.

The HDS activity was expressed by the pseudo first order rate constant calculated after 16 h time on stream at the pseudo stationary state, by the following equation :

$$k = -\frac{F_0}{m \times C_0} \times \ln(1 - x),$$

where k is the rate constant of the reaction (l.g⁻¹.s⁻¹), F₀ the molar flow rate of DBT (mol/s) at the inlet, x the conversion of reactant, m the weight of catalyst (g) and C₀ the concentration of DBT (mol/l).

Prior to catalytic tests the samples were sulfided ex situ under H₂-H₂S (10%) mixture for 4 h at 673 K.

3. RESULTS AND DISCUSSION

3.1. Activities :

Results given in Figure 1 indicate that in the Mo series, the TiO₂ rich support leads to a catalyst with a high activity as compared to the Mo/Al₂O₃. For the CoMo samples, we observed a dramatic decrease of the promoting effect of Co when the TiO₂-Al₂O₃5% support is used.

Figure.1. HDS activities compared at 573 K .

These results confirm previous ones obtained for NiMo catalysts prepared over the same supports and evaluated in aromatic ring hydrogenation (8). Such a low synergetic effect could be explained by a difficult formation of the CoMoS phase during the sulfidation. To answer that question the catalysts have been characterized by UV diffuse reflectance spectroscopy and EDS analysis.

3.2. Diffuse reflectance spectroscopy :

The DRS spectra of catalysts in their oxidic state, supported on TiO₂-Al₂O₃5 % and Al₂O₃, are presented in Figure 2. The intense adsorption band at about 240-340 nm, recorded for all samples, could be in first analysis attributed to the ligand-metal charge transfer $O^{2-} \rightarrow Mo^{6+}$ [10, 11]. For the alumina-supported sample, this band would correspond to tetrahedral (250-280 nm) and octahedral (290-330 nm) forms of Mo(IV). However, in the TiO₂-Al₂O₃ supported catalyst, the adsorption at 365 nm is due to the absorption edge of the $O^{2-} \rightarrow Ti^{4+}$ charge transfer band [9], and it is not possible to clearly determine the changes occurring in the molybdenum species, which appear in the 250-330 nm wavelengths range.

For the CoMo/Al₂O₃ catalyst a broad triple band in the 500-700 nm region is observed. This band could be attributed to ligand field transition of tetrahedral Co(II) [12, 13]. In this catalyst this band has been assigned to tetrahedral Co(II) in CoAl₂O₄. For the TiO₂-Al₂O₃5% support, the probability to incorporate cobalt into the Al₂O₃ to form CoAl₂O₄ is strongly reduced due to the low content of this oxide. This could explain why this band is very weak for the titania based support.

In the region 1100-1800 nm, the bands appearing correspond to both octahedral Co(III) and tetrahedral Co(II) in oxygen surrounding. For the CoMo/Al₂O₃ catalyst, this octahedral Co(III) could not be attributed to the presence of oxide compounds like CoO, Co₃O₄ or CoMoO₄ [14 - 17]. This point is confirmed by the blue colour of the catalyst. This octahedral Co(III) would be located near the surface in strong interaction with the molybdates. That interaction is not well defined and Topsøe and Topsøe [15] proposed that the octahedral Co(III) would be present as CoO₆ octahedra associated with the octahedrally coordinated Mo atoms located in one dimensional chains on the alumina surface.

The spectrum of CoMo/TiO₂-Al₂O₃5% is very different from the one of CoMo/Al₂O₃. A very weak band is observed between 1100 and 1800 nm and only a little shoulder appears in the region 400-700 nm.

It has been proposed that the low promoting effect of cobalt on CoMo/TiO₂ could be explained by a migration of cobalt in the titania lattice, to form an inactive surface phase, probably anamorphous titanate [3]. To check that possibility a CoTiO₃ titanate was prepared as a reference. The spectrum of CoTiO₃ is given on Figure 2 and, comparison with that of CoMo/TiO₂-Al₂O₃5% clearly indicates that cobalt atoms do not migrate in the titania structure.

A Co/TiO₂-Al₂O₃5% sample with the same amount of cobalt than the CoMo/TiO₂-Al₂O₃5% was also prepared and its spectrum given in Figure 2 appears very different. In the region 1100-1800 nm, bands prove the presence of tetrahedral and octahedral cobalt confirmed by the large band near 700 nm and the shoulder near 400 nm [7].

Figure 2. DRS spectra of various catalysts supported on Al_2O_3 or $\text{TiO}_2\text{-Al}_2\text{O}_3$ 5%

This spectrum confirms that cobalt is not incorporated in the titania lattice but that cobalt oxide Co_3O_4 is formed. This point is proved by the black colour of this catalyst. When Co and Mo are coimpregnated on $\text{Co/TiO}_2\text{-Al}_2\text{O}_3$ 5% only small

changes in the 400-800 nm region are observed. The same compound as in CoMo/TiO₂-Al₂O₃5% is formed. It could be CoMoO₄ species in which cobalt has an octahedral structure (low intensity). This compound is known to be difficult to sulfide and to give low activity catalysts [16, 18-19]. This result could explained the low promoting effect for the catalysts supported on TiO₂-Al₂O₃5% by a difficult formation of the CoMoS phase due to the presence of CoMoO₄ in the oxidic precursor. This oxide is easily detected by its light green colour.

3.3. EDS analysis of sulfided catalysts.

Our DRS experiments have clearly demonstrated that in calcined CoMo precursors the cobalt atoms located at the surface of the support change with the nature of this oxide. Therefore, variations in the nature of the actives species of the sulfided catalysts are expected. To check that point our samples have been analyzed by EDS. The use of probe size of 2nm allow to focus the beam over the MoS₂ slabs.

Results given in Figure 3 indicate the Co/(Co+Mo) ratios obtained for numerous analyses over the two samples. It is clear that the cobalt is not so homogeneously dispersed over the TiO₂-Al₂O₃5% support than over the alumina, suggesting that on the former support the formation of the CoMo surface phase precursor of the active CoMoS phase is more difficult than over alumina.

Figure.3. EDS analyses of CoMo sulfided catalysts.

Moreover, it was noticed that over Al₂O₃ the S/(Co+Mo) atomic ratio decreases after the first analysis upon beam exposure under the small probe size used in these studies. On the contrary, over TiO₂-Al₂O₃5% the phenomenon was considerably less pronounced. That fact, which has never been previously

reported, could be related to the energy required to form sulfur vacancies which are believed to be the active sites for many hydrotreating catalysts.

Indeed, several works have been done to try to correlate the HDS activity of sulfides with the metal-sulfur bond energy [20,21]. For promoted catalysts, Byskov et al [22] have recently reported that the presence of cobalt (or nickel) atoms at the edge of MoS₂ leads to a significant lowering of the metal sulfur binding energy, and therefore to an increase in the concentration of the active sites for the reaction (promoting effect).

Our DRS results and the EDS analysis appear therefore in good agreement since the lower stability of the sulfur phase observed over Al₂O₃ (leading to more uncoordinated molybdenum active sites) is associated with a high dispersion of cobalt in close contact with molybdenum in the oxidic state.

4. CONCLUSION

The aim of the present work was to understand the effect of the nature of the support of CoMo hydrotreating catalysts over the level of the promotion induced by cobalt. From the UV-vis data presented above, it is demonstrated that in the case of the CoMo/TiO₂-Al₂O₃5% catalyst cobalt is not lost into the titania matrix, but mainly involved in the formation of CoMoO₄ (hardly sulfided compound). The formation of a CoMo interaction in the oxidic state, assumed to be the precursor of the active CoMoS phase is therefore reduced, in agreement with the lower synergetic effect observed. Moreover, during EDS analysis of the sulfided samples a lower stability of the CoMo/Al₂O₃ was noted. This fact is in line with recent proposals on the effect of cobalt on the lowering of the metal-sulfur bond energy, leading therefore to an increase in the concentration of active sites.

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