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Effect of MoS_2 morphology on the HDS activity of hydrotreating catalysts

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Mo/Al_2O_3 and Mo/ZrO_2–Y_2O_3 catalysts sulfided at different temperatures were tested in thiophene hydrodesulfurization (HDS) and examined by high resolution electron microscopy (HERM). Higher activities observed for the Mo/ZrO_2–Y_2O_3 sample appear to be correlated to a lower stacking of the layers in the MoS_2 crystallites, solely the top edge sites being catalytically active. Moreover the results suggest that a dual vacancy site is required for the thiophene HDS.

Keywords: alumina; zirconia; molybdenum sulfide; hydrodesulfurization; electron microscopy

1. Introduction

Catalysts based on sulfided Mo (or W) promoted by Ni (or Co) are widely used in the petroleum industry for the hydrotreatment of petroleum feedstocks and over the past twenty years considerable effort has been devoted to the study of the properties of alumina supported catalysts. However, in spite of their wide and longstanding use, a complete explanation of the nature of the active sites still awaits formulation. It appears that the first requirement for an active catalyst is the generation and stabilization of highly dispersed MoS_2 which is then modified in some way by the promoter atoms. The genesis of the MoS_2 on the support is therefore of vital importance.

Due to the necessity to develop hydrotreating catalysts with enhanced properties, other supports have been studied and in several cases it was claimed that higher activities were obtained than those of alumina supported catalysts. Explanations of the role of the support have been recently reviewed [1,2]. Among those, the morphology of the sulfide phase is often considered.

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Following previous investigations [3,4], in this study the morphology of the MoS_2 on two supports (Al_2O_3, ZrO_2) has been investigated at different temperatures of sulfidation and observations are discussed in relation with catalytic activities for thiophene hydrodesulfurization. In this first approach, the study was limited to unpromoted molybdenum catalysts.

2. Experimental

2.1. CATALYST PREPARATION

The support materials used were: Al_2O_3 GFSC from Rhône Poulenc and a ZrO_2 stabilized by Y_2O_3 (97 mol% ZrO_2–3 mol% Y_2O_3) prepared by the molten salt method as previously described [5]. The surface areas of these supports were 236 and 140 $m^2\,g^{-1}$ respectively. All the catalysts were manufactured using the incipient wetness method. After impregnation of the desired molybdenum loading (2.8 atMo/nm^2) using $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, the solids were left at room temperature for 2 h, then dried at 373 K for 2 h and finally calcined at 623 K. These preparations correspond to Mo(9.6 wt%)/Al_2O_3, and Mo(6 wt%)/ZrO_2–Y_2O_3.

Prior to the characterization studies and the catalytic tests, the catalysts were sulfided in a flow reactor under a H_2/H_2S(15%) mixture (heating rate 0.16 K s^{-1}) and an additional 4 h at constant temperature (573 to 973 K). After cooling to room temperature, the reactor was flushed with a N_2 flow, and the samples were stored in sealed bottles under argon in order to preserve the catalysts from oxidation.

2.2. CATALYTIC ACTIVITY

The thiophene hydrodesulfurization (HDS) activity measurement was carried out in the vapour phase using a fixed bed atmospheric pressure flow microreactor ($P_{H_2} = 101$ kPa, $P_{\text{thiophene}} = 2.4$ kPa). The experiments were performed at conversions below 15% and the rates were calculated assuming differential reactor behaviour, at pseudo stationary state after an overnight time on stream.

The global reaction rate (specific rate), was calculated according to the following equation:

$$R_T = F_{TO} X_T / W ,$$

where R_T is the reaction rate (mol s^{-1} g^{-1}) of thiophene consumption, F_{TO} is the molar flow rate of thiophene (mol s^{-1}), X is the conversion and W is the weight of catalyst.

The intrinsic rate (R_{Mo}) was defined as molecules of thiophene converted per second per atom of molybdenum.

2.3. HIGH RESOLUTION ELECTRON MICROSCOPY

Classical transmission electron microscopy was performed using a Jeol 100CX microscope equipped with an ultra high resolution polar piece, allowing for a theoretical point per point resolution of 0.26 nm. The samples were ultrasonically dispersed in ethanol and the suspension was collected on carbon-coated copper grids.

3. Results

3.1. CATALYTIC ACTIVITY STUDIES

Table 1 summarizes the catalytic activity results for catalysts sulfided at different temperatures. Comparison of catalyst activities in terms of global rates (R_T) per gram of catalyst are misleading when dealing with different supports having varying amounts of Mo. More proper comparisons are intrinsic rates per Mo atom (R_{Mo}), also given in table 1. It is seen that the intrinsic activity of the Mo/ZrO_2–Y_2O_3 catalyst is about three times that of the Mo/Al_2O_3 sample, in good agreement with other results [4,6]. Moreover a gradual decrease in activity with increasing sulfidation temperature is observed above about 773 K.

3.2. HREM EXAMINATIONS

Typical micrographs of Mo/ZrO_2–Y_2O_3 and Mo/Al_2O_3 catalysts sulfided at 673 K are shown in figs. 1a and 1b respectively. The black lines arise from crystals viewed along the basal plane direction and represent the lattice images from MoS_2 with a lamellar structure one to several layers thick. The observed spacing of about 0.6 nm is consistent with the interplane spacing of bulk MoS_2 (0.62 nm). It should be noted that the morphology of MoS_2 is very similar over the two supports

Table 1
Activity for HDS of thiophene at 623 K[a]

Catalyst	Sulfidation temperature				
	573 K	673 K	773 K	873 K	973 K
Mo/Al_2O_3					
A_s	30.4	30.4	26	22	17
A_{Mo}	2.7	2.7	2.4	2	1.6
Mo/ZrO_2–Y_2O_3					
A_s	56	54	49	43	–
A_{Mo}	9	8.7	7.8	6.8	–

[a] $R_T = 10^{-8}$ mol s^{-1} g^{-1}; $R_{Mo} = 10^{-4}$ molec. s^{-1} $atMo^{-1}$.

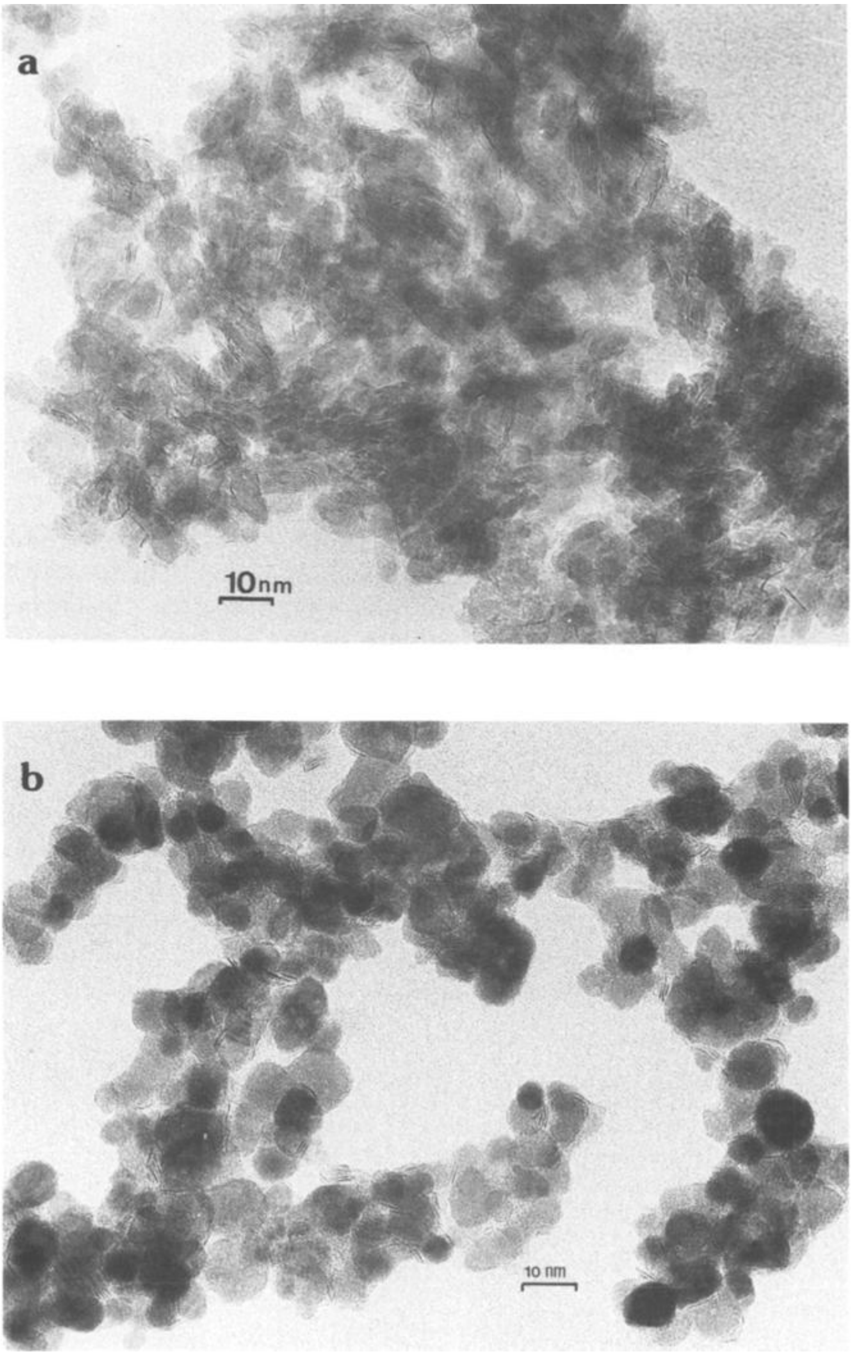

Fig. 1. HREM photographs: (a) Mo/Al_2O_3, (b) Mo/ZrO_2 catalysts sulfided at 623 K.

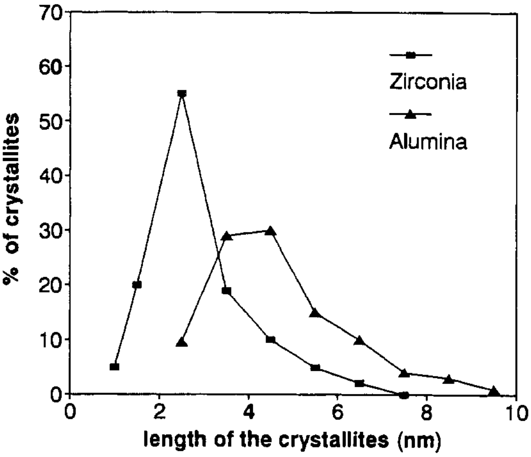

Fig. 2. Crystallite length distribution for Mo/ZrO_2 and Mo/Al_2O_3 catalysts sulfided at 623 K.

and always seems to occur with its basal plane parallel to the oxide surface. These observations are in agreement with those recently reported by Srinivanan et al. [7]. These authors also indicated that the observed bookend morphology of MoS_2, deduced by previous workers [8,9] on high surface area supports, arose from a possible artefact in the electron microscopy examination of such materials.

Size distributions of the crystallites were determined from measurements of more than three hundred crystallites. N, the number of the layers in each particle (also called stacking) was also counted. The distributions of crystallite lengths (L) and number of layers (N) are schematized in figs. 2 and 3. Similar determinations were also made for several other catalysts. Though a rapid examination of the micrographs would indicate similar catalysts, the average results, summarized in table 2, indicate significative variations of crystallite lengths and stacking in rela-

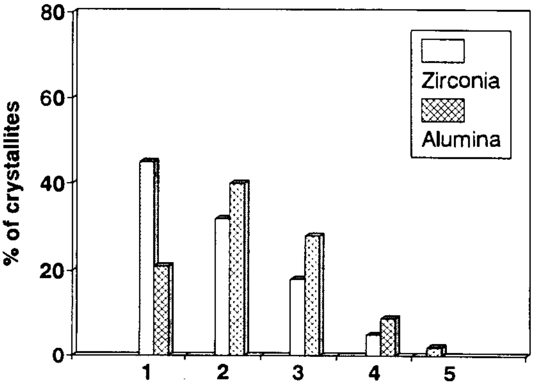

Fig. 3. Distribution of the number of layers for Mo/ZrO_2 and Mo/Al_2O_3 catalysts sulfided at 623 K.

Table 2
HREM data and deduced calculations. L: mean length of the crystallites; N: mean number of slabs; a: (Mo edge atoms)/(total Mo atoms)

Catalyst	Sulfidation temp. (K)	L	N	a	a/N
Mo/Al_2O_3	673	4.0	2.3	0.27	0.117
	973	4.1	2.5	0.26	0.100
$Mo/ZrO_2-Y_2O_3$	673	2.9	1.8	0.36	0.200
	873	3.1	1.9	0.34	0.178

tion to the nature of the support and the temperature of the sulfidation. The ZrO_2 support gives significantly smaller microcrystallites having a lower stacking of the layers than the Al_2O_3 support. For each catalyst series, an increase in the length of the particles due to an increase in the sulfiding temperature was generally accompanied by an increase in the number of layers.

4. Discussion

High resolution electron microscopy observations reported here are in agreement with many previous studies and there is no doubt as to the existence of small "MoS_2-like" slabs, isolated or somewhat stacked together along their c axis, and well dispersed on the supports. The reactivity data may now be examined in the light of these HREM results. In order to rationalize and to quantify in simple terms the relationships existing between these active phase solid state crystallographic features and the macroscopic catalytic properties, we will use the "geometrical model" proposed by Kasztelan et al. [10]. We will discuss first the effect of the size of the crystallites and in a second part the influence of the stacking on catalytic activity.

4.1. EFFECT OF THE SIZE OF THE PARTICLES

The small MoS_2 slabs can be described as fragments of a MoS_2 single layer of this layered compound. Modelling MoS_2 single slabs with different geometrical shapes (chain, triangle, rhomb, hexagon), and taking into account the Gibbs–Curie–Wulf law, Toulhoat and Kasztelan [11] have shown that hexagonal slabs are the most stable among the various shapes. By energy minimization calculations, Drew et al. [12] have shown that there is no optimum slab size. However, if small slabs are less stable, their existence results from a stabilizing effect of the support. Their catalytic role has been much debated, but it is now generally admitted that they bear the active sites located at the slab edges, as previously emphasized by the experiments of Tanaka and Okuhara on cut and uncut MoS_2 single crystals [13].

Assuming that the average length (L) determined from HREM measurements is the longest dimension of the hexagonal crystallites, the number of Mo edge atoms (Mo_e) presumed to be catalytically active, and the total number of Mo atoms in the slab (Mo_t), can be calculated. These values can be expressed in relation to the number of Mo–Mo bonds (n) at the edge of the crystallites, n being equal to one for the smallest entity. These values are given by the following equations:

$$Mo_t = 3n^2 + 3n + 1, \quad Mo_e = 6n.$$

Moreover, the length of the slab is related to n by

$$L = 2n \times 3.2\ \text{Å} \quad (d_{\text{Mo–Mo}} = 3.2\ \text{Å}).$$

Fig. 4 gives the variation of the fraction of edge sites, $a = Mo_e/Mo_t$ in relation to the length of the slabs. It can be seen that for catalysts in which particle sizes vary from 3 to 5 nm, this ratio does not greatly change.

A plot of the intrinsic activity versus a, presented in fig. 5, clearly shows a lack of correlation of these parameters. A direct true relationship should not only be linear but also go through the origin. The results of fig. 5 would imply no catalytic activity for an (Mo edge)/(Mo total) ratio below about 0.22, which is inconsistent with the concept of active edge sites. Thus, intrinsic activities are not directly related to total edge Mo sites, i.e. cannot be explained solely by differences in the length of the slabs of the crystallites.

4.2. EFFECT OF THE STACKING OF THE MoS_2 LAYERS

The effect of the stacking of the layers on catalytic activity has been previously reported for a $NiMo/Al_2O_3$ catalyst [14,15]. Therefore, an attempt was made to

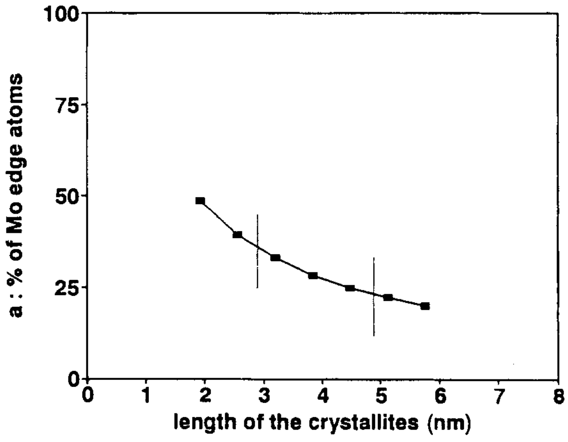

Fig. 4. Evolution of the percentage of Mo edge atoms versus the length of the crystallites for hexagonal shape slabs.

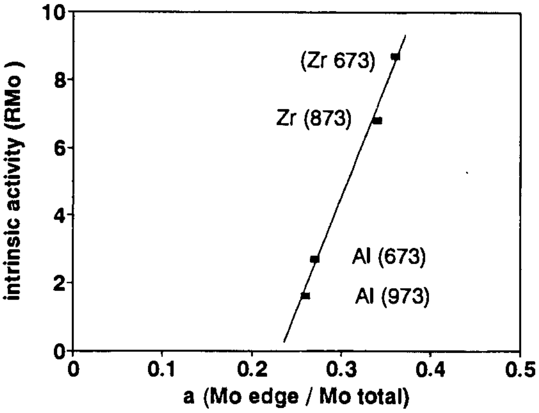

Fig. 5. Intrinsic activity ($R_{Mo} = 10^{-4}$ molec. s^{-1} $atMo^{-1}$) versus a ((Mo edge sites)/(Mo total)).

correlate this parameter with thiophene HDS. In order to eliminate the influence of the length of the slabs on catalytic activity (see section 4.1), corrections of the intrinsic rates were made taking into account only the number of edge Mo atoms present in a sample with crystallites of length L, using the Mo_e/Mo_t ratios (fig. 4). Fig. 6 gives the corrected intrinsic rates versus the stacking of the MoS_2 layers and shows that, regardless of the support or the sulfidation temperature, all activities follow a continuous decrease with an increase of the number of the layers in the microcrystallites.

4.3. INFLUENCE OF THE POSITION OF THE SLAB

Considering first the influence of the stacking of the layers on catalytic activity, a decrease in activity could in a first approach be explained by a lower accessibility

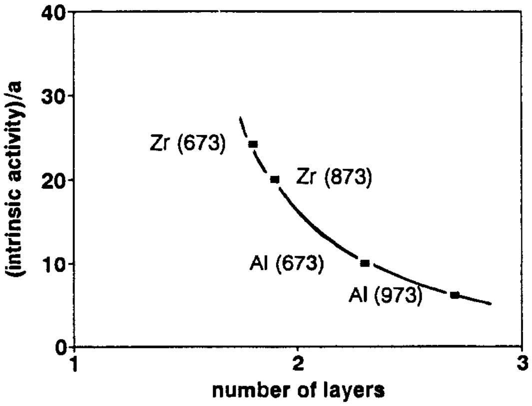

Fig. 6. Intrinsic activity of edge Mo sites ($R_{Mo} = 10^{-4}$ molec. s^{-1} $atMo^{-1}$) versus the number of layers of the crystallites for catalysts sulfided at various temperatures (activities are corrected by the length of the slabs).

of the thiophene molecule to the underlayered edge Mo atoms. Adsorption of a thiophene molecule at an edge site of MoS_2 lying flat on the support may be sterically hindered, and as a consequence only the upper layer of the MoS_2 crystallite would be involved in the catalytic act.

Such considerations can be applied to the geometrical model described above, allowing calculation of the fraction of molybdenum atoms located in the edge position of the upper MoS_2 slab, i.e. $a/N =$ (Mo edge on top layer)/(Mo total edge), values reported in table 2, and therefore the number of Mo atoms assumed to be potentially active sites in each sample characterized by electron microscopy. Fig. 7 gives the variations of specific activities in relation to the number of these Mo atoms. If only geometrical effects occur, all activity data should fall on the same straight line, which would go through the origin. Such is clearly not the case.

However, another possibility exists. A number of investigators have proposed a multiple vacancy center as the active site for the HDS of thiophene. Joffre et al. [16] have assumed a triple vacancy site, while Brunier et al. [17] assumed a double vacancy site. Both authors concluded that vertical adsorption through the thiophene molecule was more favorable than flatwise adsorption.

If a dual vacancy site is required, then the top edge sites concentration should be roughly proportional to the square of the number of vacancies. Assuming the number of vacancies to be proportional to the top edge molybdenum atoms, then the intrinsic activity should be proportional to $(a/N)^2$. Such a plot is shown in fig. 8, where it is seen that a good correlation for the series of catalysts is obtained, which goes through the origin.

Although the real nature of the active sites in hydrotreating catalysts remains uncertain, a number of researchers have modeled the adsorption of thiophene on MoS_2 catalysts. Most of these works were reviewed by Harris and Chianelli [18]. It was suggested that initial adsorption might occur through a η^1 vertical mode on a site with two sulfur vacancies [16,19], although subsequent reaction would require the ring to flip over into the η^5 horizontal binding mode [19].

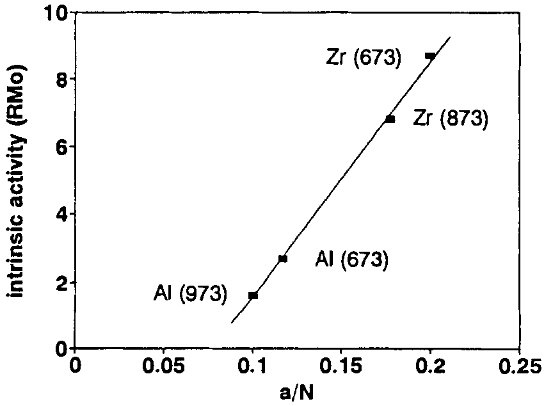

Fig. 7. Intrinsic activity ($R_{Mo} = 10^{-4}$ molec. s^{-1} $atMo^{-1}$) versus top edge Mo sites (a/N).

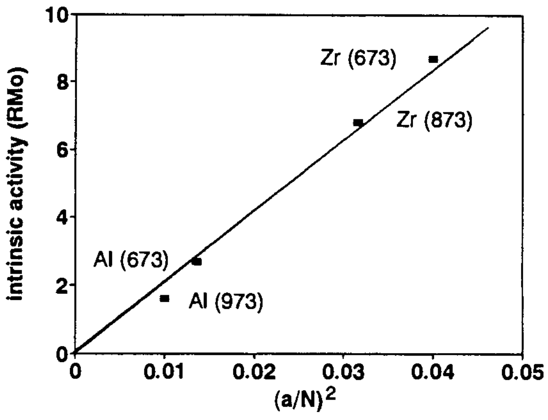

Fig. 8. Intrinsic activity versus square of top edge Mo sites $(a/N)^2$.

The correlation of fig. 8 implies that edge vacancy sites on layers below the top one are not catalytically active for thiophene HDS. Although simple computer models show that adsorption of thiophene on a two-vacancy center at the edge of an intermediate layer should not be geometrically restricted, a special orientation may be required for subsequent reaction with adsorbed hydrogen on an adjacent S atom. Thus, thiophene may adsorb, but not undergo reaction at this site. No such restriction would apply to a similar site on the top edge position.

Daage et al. [20] have recently proposed two different reaction sites for bulk MoS_2, one at top edge sites (called "rim" sites) responsible for hydrogenation of dibenzothiophene, and another at all edge sites responsible for direct HDS of dibenzothiophene. Our results suggest that for supported MoS_2 catalysts only the top edge sites contribute to the hydrodesulfurization.

Studies are continuing to establish if similar effects apply to promoted supported catalysts.

5. Conclusion

Comparison of activities of unpromoted MoS_2 supported on Al_2O_3 and ZrO_2–Y_2O_3 with the same Mo loading per surface area showed the latter to have higher intrinsic activities. The higher activity appears to be correlated to a lower stacking of the MoS_2 layers, as well as to smaller crystallite sizes. Such a stacking would induce a lack of activity of intermediate edge sites for the reaction of thiophene.

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