

## The CoO-MoO<sub>3</sub>-γ-Al<sub>2</sub>O<sub>3</sub> Catalyst

### V. Sulfide Catalysts Promoted by Cobalt, Nickel, and Zinc

V. H. J. DE BEER, T. H. M. VAN SINT FIET, G. H. A. M. VAN DER STEEN, A. C. ZWAGA, AND G. C. A. SCHUIT

*Department of Inorganic Chemistry and Catalysis, Eindhoven University of Technology, Eindhoven, The Netherlands*

Received December 12, 1973

Cobalt-, nickel-, and zinc-promoted as well as nonpromoted catalysts based on MoO<sub>3</sub>, MoS<sub>2</sub>, and WS<sub>2</sub> supported on γ-Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> have been prepared in three essentially different ways. Their thiophene hydrodesulfurization activities have been determined under continuous flow conditions at atmospheric pressure and 400°C.

Experimental evidence is reported for the relevance of both the monolayer and intercalation model to the preparation and operation of active catalysts. In actual operation the best description of the catalyst is given by the intercalation model.

#### INTRODUCTION

Recently two structural models for the CoO-MoO<sub>3</sub>-γ-Al<sub>2</sub>O<sub>3</sub> hydrodesulfurization catalyst were proposed, viz., the "intercalation model" and the "monolayer model."

In an ideal situation, intercalation involves the accommodation of metal atoms (such as Cu and Ag) in the empty cation sites between the double layers of sulfur occurring in disulfides of, for instance, Nb and Ta. These disulfides have layer structures in which the metal is surrounded by six sulfur atoms in a trigonal prismatic coordination. The intercalation model is discussed in detail by Voorhoeve and Stuiver (1, 2), Voorhoeve (3), and Farragher and Cossee (4). They postulated that, although intercalation of Co and Ni in ideal crystals (bulk) of MoS<sub>2</sub> and WS<sub>2</sub> (with trigonal prismatic structure) is energetically unfavorable, it does occur at the layer edges of these sulfide crystals. The intercalated Co<sup>2+</sup> and Ni<sup>2+</sup> cations are then octahedrally surrounded and their special promoter function is to increase the number of exposed Mo<sup>3+</sup> or W<sup>3+</sup> ions which are believed to be the active centers. Farragher and Cossee calculated that because of the

small dimensions of the crystallites that occur in supported sulfide catalysts the intercalation might increase to values of Co/Mo or Ni/W between 0.3 and 1.0, which correspond to the optimum ratios found in commercial catalysts.

From benzene and cyclohexene hydrogenation experiments in combination with ESR measurements and electron microscope observations, all limited to the system WS<sub>2</sub>-Ni, two active sites were postulated—namely, a single W<sup>3+</sup> ion connected to a vacancy, and a combination of two W<sup>3+</sup> ions with interconnecting sulfur being absent.

CoMo<sub>2</sub>S<sub>4</sub> might be considered as an ideal intercalation compound [Van den Berg (5) and Chevrel *et al.* (6)], yet it was found by Hagenbach *et al.* (7) to be almost inactive as a catalyst. This result is ascribed by Farragher and Cossee to the different type of S-coordination, octahedral instead of trigonal prismatic. On the other hand, in a series of experiments with mixed sulfides a combination of Co<sub>9</sub>S<sub>8</sub> and MoS<sub>2</sub> was found to have a higher activity for thiophene hydrogenolysis than MoS<sub>2</sub> alone (7). A higher activity of this combination was also found for cyclohexene hydrogenation.

tion and cyclohexane isomerization. However, these studies did not yield any conclusive indication concerning the nature of the active species.

A monolayer model was discussed in some detail by Schuit and Gates (8) for both the oxidic and sulfided CoO-MoO<sub>3</sub>- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> system. In this model  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is assumed to consist of particles formed by alternating stacking of two different layers in the direction of the (110) crystallographic plane. According to Lippens (9), the (110) plane is preferentially exposed to the surface in the case of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Moreover, the surface of a particle is assumed to consist entirely of two different types of surface layers with their ratio being unity.

Based on the findings of Dufaux *et al.* (10) and Lipsch *et al.* (11), molybdenum is supposed to be present in a monolayer, chemically bonded to the surface of the support  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, the monolayer being epitaxial to the support in such a manner that the alternating layer stacking is continued at the surface. Charge effects due to the presence of Mo<sup>6+</sup> ions are assumed to be compensated by O<sup>2-</sup> ions, situated in a so-called capping layer on top of the monolayer. The maximum number of these O<sup>2-</sup> ions per unit mesh is four, just as for  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

Incorporation of Co<sup>2+</sup>, for instance, as CoO, is assumed to result in the location of this cation in a tetrahedral position somewhere within the solid, hence below the surface layer of the support. Its accompanying O<sup>2-</sup> ion is forced to remain in the capping layer. Penetration of Co<sup>2+</sup> ions in the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> must be accompanied by expulsion of Al<sup>3+</sup> ions from the bulk of the support to either its surface layer or the Mo-containing monolayer.

The primary effect of Co promotion is the incorporation of tetrahedrally coordinated Al<sup>3+</sup> ions in the monolayer, their presence increasing the stability of this layer because part of the task of binding the monolayer to the surface layer is taken over by a nonreducible Al cation. Combination of all different ways for Co incorporation, possible in this model, makes

Co/Mo ratios between 0.5 and 1.0 acceptable. This is within the range of the Co/Mo ratio for several catalysts described in literature (12).

Sulfiding of the catalyst is assumed to be restricted to removal or exchange of the O<sup>2-</sup> ions located in the capping layer. Since S<sup>2-</sup> is much larger than O<sup>2-</sup>, the maximum of S<sup>2-</sup> ions in this layer is fixed at two instead of four per unit mesh. This implies that in the "mixed" monolayer the maximum value for the S/Mo ratio is 1.0. Removal of S<sup>2-</sup> ions, for instance, by means of hydrogen reduction, results in the formation of an isolated Mo<sup>3+</sup> ion or a pair of Mo<sup>3+</sup> ions which are supposed to be the active sites similar to the situation in the intercalation model. Formation of the single Mo<sup>3+</sup> sites is only possible in the presence of Co. So in the monolayer model the function of the promoter is primarily to increase the reduction of Mo and to a lesser but still significant degree to stabilize the monolayer.

In contrast with the intercalation model, the monolayer model stresses the preference of the promoter for tetrahedral site occupation. With respect to this, de Beer *et al.* (13) measuring the thiophene conversion under continuous flow conditions on various oxide catalysts of the type MeO-MoO<sub>3</sub>- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (with Me standing for Mn<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, and Zn<sup>2+</sup>) have found the tendency to occupy tetrahedral position to be relevant in making a transition metal cation a promoter. The outcome of past structural investigations on fresh oxidic CoO-MoO<sub>3</sub>- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts appears to be predominantly in favor of the monolayer model (11, 14-16). Actually, no proof has been given so far for the existence of the Co-MoS<sub>2</sub> intercalated system or that Co could indeed promote MoS<sub>2</sub> in the manner as shown for Ni-WS<sub>2</sub>. It appears reasonable to assume the parallelism to hold but an experimental proof would be desirable, the more so since the compound CoMo<sub>2</sub>S<sub>4</sub> was shown to possess a different structure (5, 6) and to be almost inactive (7).

A second problem is given by the consideration that a change in structure, for instance, from monolayer to intercalated

structure, might be feasible in actual operation, viz., in relatively short periods of the order of hours or days. This would involve a mobility of  $\text{Co}^{2+}$  because the promoter cation has to migrate from the bulk of the  $\gamma\text{-Al}_2\text{O}_3$  to the  $\text{MoS}_2$ . Experiments to check such a mobility would be desirable.

Granting the existence of a certain promoter mobility, an interesting situation arises. In the two models the preference of the most effective promoter ions for this surrounding is different, being tetrahedral for the monolayer and octahedral for the intercalation model. The promotion effect of some cations ( $\text{Zn}^{2+}$ ) would then decrease with time of operation, while for others ( $\text{Ni}^{2+}$ ) it might increase.

It was now planned to compare the thiophene hydrogenolysis activity of oxidic and sulfidic catalysts prepared in three different ways. The first method of preparation applied here was the more conventional one, viz., sequential impregnation of the carrier with Mo and Co solutions; it could be reasonably expected to result in an intrinsically ideal monolayer system (type I catalysts).

A second method was designed to furnish catalysts (type II) which were supposedly intermediate between the monolayer and intercalation systems. It was attempted here to keep the active Mo compound initially separated from the promoter. The latter may be present either as a separate oxidic or sulfidic phase or incorporated in the support.

In addition, a third method yielding true intercalation systems (type III catalysts) was designed. This situation was believed to occur when (i) the sulfide was already present as  $\text{MoS}_2$  or  $\text{WS}_2$ —for instance, by slurrying the sulfide with a carrier before the promoter was added—or (ii) a carrier was chosen which under the preparation conditions applied here was not able to accommodate Co in the solid—for instance, silica (17).

#### EXPERIMENTAL

All the materials used for preparing and testing the catalysts are listed in Table 1. A list of the catalysts studied is given in Table 2 together with catalyst composi-

TABLE 1  
LIST OF MATERIALS USED

<u>Catalyst preparation</u>	
Supports: $\gamma\text{-Al}_2\text{O}_3$	Ketjen, fluid powder alumina, grade B, surface area $255 \text{ m}^2 \text{ g}^{-1}$ , pore volume $1.8 \text{ cm}^3 \text{ g}^{-1}$
SiO <sub>2</sub>	Davison, grade 12, surface area $600 \text{ m}^2 \text{ g}^{-1}$ , pore volume $0.40 \text{ cm}^3 \text{ g}^{-1}$
Zn(NO <sub>3</sub> ) <sub>2</sub> · 4H <sub>2</sub> O	Merck "extra pure"
Co(NO <sub>3</sub> ) <sub>2</sub> · 6H <sub>2</sub> O	Merck "for analysis"
Ni(NO <sub>3</sub> ) <sub>2</sub> · 6H <sub>2</sub> O	Merck "for analysis"
MoS <sub>2</sub>	Schuchardt München, purity $\geq 98.5\%$ , <sup>a</sup> average particle size $0.5 \mu\text{m}$ <sup>a</sup>
WS <sub>2</sub>	Schuchardt München, purity $\geq 99.8\%$ , <sup>a</sup> particle size $1.5 \mu\text{m}$ <sup>a</sup>
H <sub>2</sub>	Loosco, purity 99.9% <sup>a</sup>
H <sub>2</sub> S	Matheson, CP grade
<u>Activity test</u>	
Thiophene	Merck "for synthesis"
H <sub>2</sub>	Loosco, purity 99.9% <sup>a</sup> with additional purification over B.T.S. catalyst (BASF, R.3-11) activated in H <sub>2</sub> at 150°C and over molecular sieves (Union Carbide 4 A) activated in H <sub>2</sub> at 250°C.
<u>glc Analysis</u>	
1-Octadecene	B.D.H.
Gaschrom (50-60 mesh)	Applied Science Laboratories Inc.

<sup>a</sup> According to the manufacturer.

TABLE 2  
LIST OF CATALYSTS TESTED

Number	Catalyst <sup>a</sup>		Composition: mole % balanced by the support					Surface area m <sup>2</sup> g <sup>-1</sup>	Preparation method <sup>d</sup>	Thiophene conversion at 100 min run time (%)	
	Type <sup>b</sup>	Notation <sup>c</sup>	MoO <sub>3</sub>	CoO	MoS <sub>2</sub>	WS <sub>2</sub>	NiO				ZnO
1	I	Mo - Al	8.8						227	Ketjen type 120-3E	15
2		Mo - Al	8.8						221	Catalyst 1: presulfided <sup>e</sup>	9
3		Co - Mo - Al	8.7	5.5					217	Ketjen type 124-1.5E	27
4		Co - Mo - Al	8.8	5.5					213	Catalyst 3: presulfided <sup>e</sup>	38
5	II	Co - Mo - Al	8.8	5.5					209	A	39
6		Zn - Mo - Al	8.8				6.9		204	A	8
7		Ni - Mo - Al	8.8				5.2		210	A	46
8		Co - Al		6.7					220	B	3
9		Co - Al		6.7					215	Catalyst 8: presulfided <sup>f</sup>	5
10		MoS <sub>2</sub> + (Co - Al)		5.6	17.5				166	C	6
11		MoS <sub>2</sub> + (Co - Al)		5.6	17.5				162	Catalyst 10: presulfided <sup>f</sup>	22

12	III	MoS <sub>2</sub> + Al	18.5		186	D	1
13		Co - (MoS <sub>2</sub> + Al)	17.5		178	E	53
14		MoS <sub>2</sub>	100	5.6	7.8	Sehuchardt München	6
15		WS <sub>2</sub>			2.6	Sehuchardt München	4
16		WS <sub>2</sub> + Al			162	D	<1
17		Co - (WS <sub>2</sub> + Al)		6.4	151	E	38
18		Ni - (WS <sub>2</sub> + Al)			154	E	36
19		MoS <sub>2</sub> + Si			295	D	2
20		Co + Si	14.3		331	B	2
21		Co + Si		4.4	324	Catalyst 20: presulfided/	14
22		MoS <sub>2</sub> + (Co - Si)		3.9	270	C	33
23		MoS <sub>2</sub> + (Co - Si)		3.9	263	Catalyst 22: presulfided/	37

<sup>a</sup> All catalysts were black or dark grey except numbers 1, 3, and 8, which were, respectively, light grey, blue, and greyish blue.

<sup>b</sup> A description of these types is given in the Introduction.

<sup>c</sup> Al and Si are abbreviations for  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>. Impregnation and mechanical mixing are indicated by - and +, respectively.

<sup>d</sup> An explanation of the preparation methods A-E is given in the text.

<sup>e</sup> Conditions: 2 hr, 400°C, 175 cm<sup>3</sup> min<sup>-1</sup> NTP H<sub>2</sub>S/H<sub>2</sub> volume ratio 1/6.

<sup>f</sup> Conditions: the same as <sup>e</sup>, except for the temperature 450°C.

tions, specific surface areas, and indications as to the preparation method.

#### Method A

The standard  $\text{MoO}_3\text{-}\gamma\text{-Al}_2\text{O}_3$  catalyst, Ketjen type 120-3E, was sulfided during 2 hr at  $400^\circ\text{C}$  in a flow of  $\text{H}_2\text{S}$  and  $\text{H}_2$ , with  $\text{H}_2\text{S}/\text{H}_2$  volume ratio of 1/6 and a flow rate of  $175\text{ cm}^3\text{ min}^{-1}$  (NTP).

After sulfiding, the sample was impregnated with an aqueous solution of cobalt, nickel, or zinc nitrate of the desired concentration. The incipiently wetted catalyst was dried in  $\text{N}_2$  (12 hr at  $100^\circ\text{C}$ ) and calcined (2 hr at  $450^\circ\text{C}$ ) in a  $\text{H}_2\text{S}/\text{H}_2$  flow with the volume ratio and flow rate being the same as mentioned above.

#### Method B

The support was incipiently wetted with an aqueous solution of cobalt nitrate of the desired concentration. The sample was then dried (12 hr at  $110^\circ\text{C}$ ) and calcined (2 hr at  $600^\circ\text{C}$ ) in air.

#### Method C

$\text{CoO-}\gamma\text{-Al}_2\text{O}_3$  and  $\text{CoO-SiO}_2$  samples were mechanically mixed with  $\text{MoS}_2$  as an aqueous slurry. This was followed by drying in  $\text{N}_2$  for 12 hr at  $100^\circ\text{C}$ .

#### Method D

This involved mixing  $\gamma\text{-Al}_2\text{O}_3$  with  $\text{MoS}_2$  or  $\text{WS}_2$  in the same way as described for method C.

#### Method E

Catalysts prepared according to method D were impregnated with cobalt or nickel nitrate as described for method A.

Method A is expected to lead to catalysts of type II (intermediate). Methods B and C on  $\gamma\text{-Al}_2\text{O}_3$  furnish type II and on  $\text{SiO}_2$  type III (intercalation) catalysts. Methods D and E are supposed to result in systems of type III.

X-ray diffractograms were recorded using  $\text{CuK}\alpha$  radiation and a Ni filter. They did not yield significant additional information about the structure of the catalysts.

Unless otherwise stated the catalysts

were prerduced in  $\text{H}_2$  at  $400^\circ\text{C}$  during 1 hr and their thiophene hydrodesulfurization activity was measured at  $400^\circ\text{C}$  under continuous flow conditions, similar to those described by de Beer *et al.* (13). The same applies for the apparatus and the glc analyses system used here.

The experiments with catalysts 1-7 were carried out with a reactor charge of 180 mg. Due to the relatively low specific activity of the other samples, the reactor charge was enlarged to 750 mg for catalysts 8-9, to 700 mg for catalysts 20-21, and 1000 mg for catalysts 10-19 and 22-23 (see Table 2).

The reaction products were the same as those described earlier (13). Thiophene conversion ( $\eta$ ) was calculated from the total amount of  $\text{C}_4$ -hydrocarbon produced and the amount of unconverted thiophene using for  $\text{C}_4$ -hydrocarbons and thiophene, respectively, 1.0 and 0.73 as katharometer sensitivity factors (estimated by calibration).

If necessary, as for instance in the case of  $\text{MoS}_2 + \gamma\text{-Al}_2\text{O}_3$ , corrections were made for relatively large amounts of cracking products formed, viz., methane, ethane, ethene, propene, and propane.

The reproducibility for the steady-state conversion (at 100 min run time) was found to be better than  $\pm 1.0$  conversion percentages.

## RESULTS

Figure 1 shows the thiophene hydrodesulfurization conversion as a function of the run time for the Ketjen catalysts and those prepared according to method A (Table 2, catalysts 1-7 inclusive). Under the conditions applied here all samples showed a relatively high initial activity (at 5 min run time) followed by an activity decrease in the first 60-80 min of the experiment. After this period a so-called steady-state activity level could be observed for all catalysts except the initially oxidic  $\text{MoO}_3\text{-}\gamma\text{-Al}_2\text{O}_3$ , which showed a gradual activity decrease down to 8% conversion during a period of about 7 hr (see Fig. 2A). In this figure the same phenomenon is shown for a double impreg-

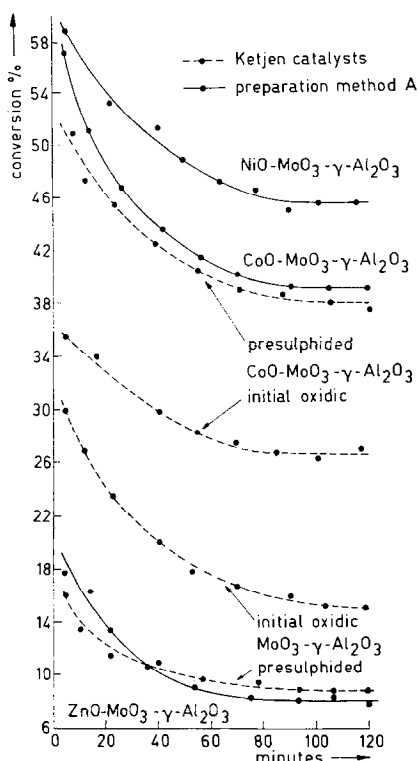


Fig. 1. Thiophene desulfurization as a function of run time. *Conditions*: 180 mg catalyst, 1.5 hr reduced in hydrogen at 400°C, 50 cm<sup>3</sup> min<sup>-1</sup> NTP H<sub>2</sub> with 6 vol% thiophene, 400°C. a. Catalysts prepared according to Method A were not reduced prior to the activity test.

nated ZnO-MoO<sub>3</sub>-γ-Al<sub>2</sub>O<sub>3</sub> catalyst containing 12 wt% MoO<sub>3</sub> and 4 wt% ZnO.

The decrease in activity during the first period of the run is very probably connected with the establishment of a new reduction-oxidation equilibrium under reaction conditions. However, a contribution from a poisoning effect cannot be entirely excluded.

As reported earlier (13), introduction of cobalt in the MoO<sub>3</sub>-γ-Al<sub>2</sub>O<sub>3</sub> system resulted in a considerable increase of the steady-state conversion level. Sulfidation decreased the steady-state level of MoO<sub>3</sub>-γ-Al<sub>2</sub>O<sub>3</sub> by a factor of 0.6, while the effect of the same pretreatment on the CoO-MoO<sub>3</sub>-γ-Al<sub>2</sub>O<sub>3</sub> system was found to be a substantial increase of the steady-state activity.

When a MoO<sub>3</sub>-γ-Al<sub>2</sub>O<sub>3</sub> sample was suc-

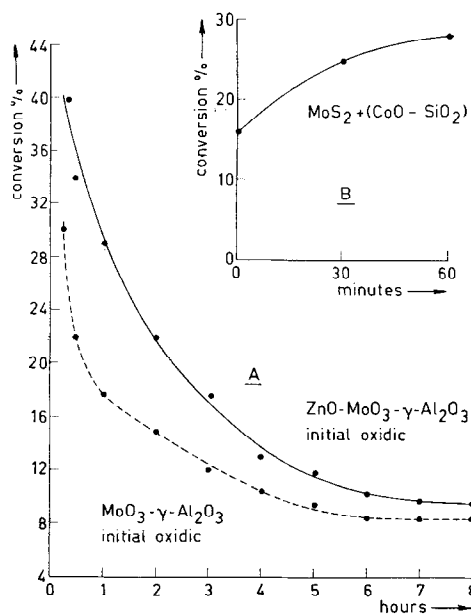


Fig. 2A. Thiophene desulfurization as a function of run time. *Conditions*: see Fig. 1. B. Initial thiophene conversion (run time 5 min) as a function of reduction time. *Conditions*: see Fig. 1, 1000 mg catalyst.

cessively sulfided, impregnated with cobalt nitrate, dried in N<sub>2</sub>, and calcined at 450°C in a H<sub>2</sub>/H<sub>2</sub>S flow (CoO-MoO<sub>3</sub>-γ-Al<sub>2</sub>O<sub>3</sub> preparation, method A), the thiophene conversion appeared to be increased substantially when compared with the initial oxidic CoO-MoO<sub>3</sub>-γ-Al<sub>2</sub>O<sub>3</sub> sample. About the same steady-state level as for the presulfided catalyst was reached.

In a similar catalyst system, Ni was found to be much more effective as promoter than Co while Zn did not show any promoter effect at all.

The results obtained for the catalysts containing MoS<sub>2</sub> as the main active compound are given in Fig. 3. Within the first 100 min only pure MoS<sub>2</sub> and the mixture MoS<sub>2</sub> + γ-Al<sub>2</sub>O<sub>3</sub> showed what might be called a steady state conversion. As can be seen from Fig. 3 the conversion over MoS<sub>2</sub> + γ-Al<sub>2</sub>O<sub>3</sub> is improved by a factor of 50 after impregnation with cobalt nitrate and calcination in H<sub>2</sub>/H<sub>2</sub>S.

Although to a somewhat lower extent, a similar effect of Co and Ni was found

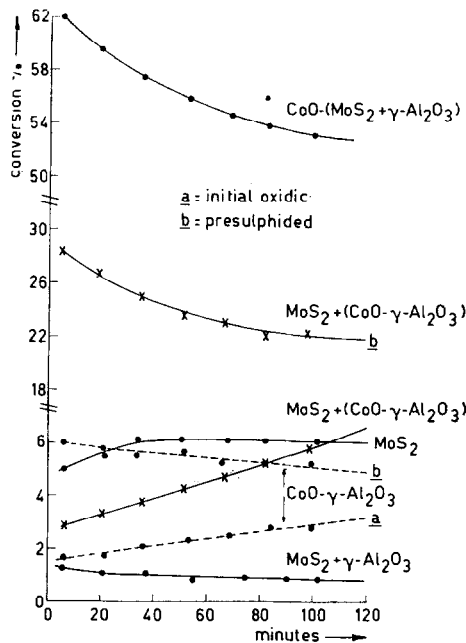


Fig. 3. Thiophene desulfurization as a function of run time. Conditions: see Fig. 1, 1000 or 750 mg catalyst.

for the  $\text{WS}_2 + \gamma\text{-Al}_2\text{O}_3$  catalyst (Table 2, catalysts 16–18).

Returning now to the results presented in Fig. 3, it can be seen that initially oxidic  $\text{CoO}-\gamma\text{-Al}_2\text{O}_3$  containing 5%  $\text{CoO}$  by weight (introduced by impregnation, drying, and calcining in air at  $600^\circ\text{C}$ ) showed an initial activity of 1.5% which increased to 3% at the end of the run. The color of the  $\text{CoO}-\gamma\text{-Al}_2\text{O}_3$  sample (greyish blue instead of blue) used here, indicates the presence of  $\text{Co}_3\text{O}_4$  as demonstrated by Lo Jacono *et al.* (16). Presulfidation of this catalyst resulted in an activity increase of 4.5% at the beginning of the experiment and 2% after 100 min run time. A somewhat higher conversion (7% instead of 5%) was found for a presulfidated  $\text{CoO}-\gamma\text{-Al}_2\text{O}_3$  sample where  $\text{Co}$  was introduced only by impregnation and drying, and not by additional calcination.

When the initially oxidic  $\text{CoO}-\gamma\text{-Al}_2\text{O}_3$  was mixed mechanically with  $\text{MoS}_2$ , the activity of the mixture appeared to increase gradually during the entire period of testing. The rate of this increase was

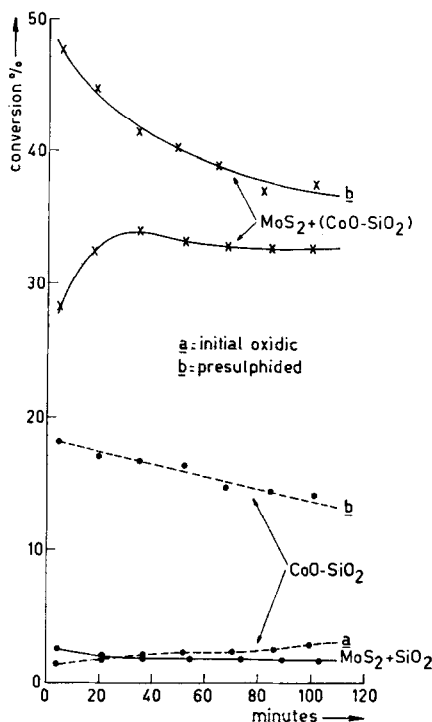


Fig. 4. Thiophene desulfurization as a function of run time. Conditions: see Fig. 1, 1000 or 700 mg catalyst.

such that at the end of the experiment the conversion of the  $\text{MoS}_2 + (\text{CoO}-\gamma\text{-Al}_2\text{O}_3)$  sample (6%) was somewhat but significantly higher than the sum of the ultimate conversions found for  $\text{MoS}_2 + \gamma\text{-Al}_2\text{O}_3$  (1%) and initially oxidic  $\text{CoO}-\gamma\text{-Al}_2\text{O}_3$  (3%).

The thiophene hydrodesulfurization properties of the mixture of  $\text{MoS}_2$  and  $\text{CoO}-\gamma\text{-Al}_2\text{O}_3$  were found to be substantially improved by calcination in  $\text{H}_2/\text{H}_2\text{S}$  (2 hr at  $450^\circ\text{C}$ ), especially when the ultimate conversions are compared.

Besides  $\gamma\text{-Al}_2\text{O}_3$  another support ( $\text{SiO}_2$ ) was applied. For  $\text{SiO}_2$ -supported catalysts the thiophene conversion determined during a run of 100 min is given in Fig. 4. Comparison of their ultimate conversion levels with those of the corresponding  $\gamma\text{-Al}_2\text{O}_3$ -supported catalysts shows similar effects on the activity due to the method of preparation (Table 2, catalysts 8–11 and 20–23). However, the magnitudes of these



effects are different. Very low conversions (2%) were found for  $\text{MoS}_2 + \text{SiO}_2$  and initially oxidic  $\text{CoO-SiO}_2$ . When the latter was presulfided, the activity increased to 14%. A mechanical mixture of  $\text{MoS}_2$  with initially oxidic  $\text{CoO-SiO}_2$  showed a conversion increase from 28 to 34% during the first 30 min, followed by a slight decrease to 33% conversion at 100 min run time. Searching for the reason of this activity increase, the influence of prereduction time ( $\text{H}_2$ ,  $400^\circ\text{C}$ ) on the initial thiophene conversion (at 5 min run time) was measured. The results given in Fig. 2B show a considerable positive effect of prereduction on the initial activity. After being sulfided, the activity of the  $\text{MoS}_2 + (\text{CoO-SiO}_2)$  catalyst was increased from 28 to 47% conversion initially and from 33 to 37% at the end of the run.

#### DISCUSSION

The first point to be discussed is whether Co-Mo $\text{S}_2$  intercalation systems exist, i.e., whether it is indeed possible to produce evidence for promotion of Co in such systems. The answer based on the experiments described is that there are good reasons to accept this situation (type III catalysts).  $\text{MoS}_2$  present as such can be promoted by Co just as  $\text{WS}_2$  can be promoted by Ni in entirely similar experiments. The experiments with  $\text{SiO}_2$  as the carrier (Fig. 4) gave results that were in good agreement with this conclusion.

The second point is whether there are observations that support a diffusion of  $\text{Co}^{2+}$ , from the interior to the surface of the carrier, during catalytic operation. Because of the fact that Co alone possesses some hydrodesulfurization activity, this diffusion did indeed become observable. This effect is also observed, and is even more pronounced, when  $\text{MoS}_2$  is present [see Fig. 3,  $\text{CoO-}\gamma\text{-Al}_2\text{O}_3$  and  $\text{MoS}_2 + (\text{CoO-}\gamma\text{-Al}_2\text{O}_3)$ ].

Presulfiding appears to exert a similar influence; after presulfiding the catalysts are initially more active and no further increase during operation is noticed.

The difference between experiments 10 and 11, listed in Table 2, is that in the first one diffusion to the surface followed

by intercalation becomes apparent during the activity run while in the second both processes were already finished during pretreatment. Obviously the rate of diffusion appears to be so fast as to occur in a time of the order of some hours. This is confirmed by the observations on a Zn-promoted catalyst. Initially it is very active, but after 8 hr its activity is equal to that of the nonpromoted  $\text{MoO}_3\text{-}\gamma\text{-Al}_2\text{O}_3$  system (Fig. 2A).

Actually this experiment produces a beautiful confirmation of quite a number of assumptions. Firstly, the high initial activity of the  $\text{ZnO-MoO}_3\text{-}\gamma\text{-Al}_2\text{O}_3$  catalyst is evidence for the reality of the monolayer model, viz., promotion by tetrahedrally surrounded cations. Secondly, the relatively fast decrease in activity shows the relevance of fast cation diffusion during sulfidation. Finally, the fact that  $\text{Zn}^{2+}$  evidently is no promoter for the intercalated system is in agreement with the predictions of Farragher and Cossee (4).

For  $\text{Ni}^{2+}$  the situation is reversed. Earlier results (13) have shown that this cation is not particularly active in the "initial" state and certainly less so than  $\text{Co}^{2+}$ .

However, the results of experiments 5 and 7 (Table 2) show that  $\text{Ni}^{2+}$  is more active than  $\text{Co}^{2+}$  as a promoter provided it is introduced in the presulfided  $\text{MoO}_3\text{-}\gamma\text{-Al}_2\text{O}_3$ , viz.,  $\text{MoS}_2 + \gamma\text{-Al}_2\text{O}_3$  (see Fig. 1). In this respect it should be mentioned that Farragher and Cossee on the basis of cation radii predicted  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  to be almost equally effective when intercalated in  $\text{WS}_2$ . This is confirmed by the results of experiments 17 and 18 in Table 2.

On the basis of this combined evidence we now postulate that the  $\text{CoO-MoO}_3\text{-}\gamma\text{-Al}_2\text{O}_3$  catalyst starts as a monolayer system but is converted into an intercalated structure in a few hours either when in operation or during the presulfiding treatment. One might conclude from this that the monolayer has no particular importance. We believe, however, that this conclusion is not correct for the following reasons.

The nonpromoted monolayer system  $\text{MoO}_3\text{-}\gamma\text{-Al}_2\text{O}_3$  after presulfiding, as well

as after being 8 hr in operation, has only a small activity. The activity of the Co-promoted monolayer structure CoO-MoO<sub>3</sub>- $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, on the other hand, is substantially improved by presulfidation. We now propose that the stabilization of the monolayer by Co<sup>2+</sup>, a stabilization that can only be destroyed by the reappearance of Co<sup>2+</sup> at the surface, leads to smaller MoS<sub>2</sub> crystals that are immediately intercalated by Co<sup>2+</sup>. The initial monolayer structure thus represents a synthetic route to the formation of finely divided, relatively highly intercalated, and therefore highly active catalysts.

Experiments with catalysts prepared according to preparation method A (Table 2, numbers 5 and 7) make plausible the possibility to prepare highly active catalysts via an alternative, albeit more complicated, synthetic route. This route is probably based then on the action of Co<sup>2+</sup> to break up the already formed relatively large MoS<sub>2</sub> crystals when it intercalates the MoS<sub>2</sub> phase.

#### ACKNOWLEDGMENTS

The authors are indebted to W. van Herpen and R. Lenten for technical and experimental assistance. Thanks are due to Akzo Chemie N.V. for providing commercially manufactured catalyst samples.

#### REFERENCES

1. VOORHOEVE, R. J. H., AND STUIVER, J. C. M., *J. Catal.* **23**, 228 (1971).
2. VOORHOEVE, R. J. H., AND STUIVER, J. C. M., *J. Catal.* **23**, 243 (1971).
3. VOORHOEVE, R. J. H., *J. Catal.* **23**, 236 (1971).
4. FARRAGHER, A. L., AND COSSÉE, P., "Proceedings of the 5th International Congress on Catalysis" (J. W. Hightower, Ed.), p. 1301. North-Holland, Amsterdam, 1973.
5. VAN DEN BERG, J. M., *Inorg. Chim. Acta* **2**, 216 (1968).
6. CHEVREL, R., SERGENT, M., AND PRIGENT, J., *C. R. Acad. Sci. Paris C* **267**, 1135 (1968).
7. HAGENBACH, G., COURTY, PH., AND DELMON, B., *C. R. Acad. Sci. Paris C* **271**, 783 (1970); *J. Catal.* **23**, 295 (1971).
8. SCHUIT, G. C. A., AND GATES, B. C., *AIChE J.* **19**, 417 (1973).
9. LIPPENS, B. C., Ph.D. thesis, Technological University, Delft, The Netherlands, 1961.
10. DUFAUX, M., CHE, M., AND NACCACHE, C., *J. Chim. Phys.* **67**, 527 (1970).
11. LIPSCH, J. M. J. G., AND SCHUIT, G. C. A., *J. Catal.* **15**, 174 (1969).
12. MITCHELL, P. C. H., "The Chemistry of Some Hydrodesulphurisation Catalysts Containing Molybdenum." Climax Molybdenum Company, London, 1967.
13. DE BEER, V. H. J., VAN SINT FIET, T. H. M., ENGELEN, J. F., VAN HAANDEL, A. C., WOLFS, M. W. J., AMBERG, C. H., AND SCHUIT, G. C. A., *J. Catal.* **27**, 357 (1972).
14. ASHLEY, J. H., AND MITCHELL, P. C. H., *J. Chem. Soc. A*, 2821 (1968).
15. ASHLEY, J. H., AND MITCHELL, P. C. H., *J. Chem. Soc. A*, 2730 (1969).
16. LO JACONO, M., CIMINO, A., AND SCHUIT, G. C. A., *Gaz. Chim. Ital.* **103**, 1281 (1973).
17. DALMON, J. A., MARTIN, G. A., AND IMELIK, B., *J. Chim. Phys. Physicochim. Biol.* **70**, 214 (1973).