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The CoO–MoO_3–γ-Al_2O_3 Catalyst

VII. Influence of the Support

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The thiophene hydrodesulfurization activity was measured under continuous flow conditions at 400°C and atmospheric pressure for Mo- and Co-containing catalysts supported on different materials (γ- and η-Al_2O_3 and SiO_2) and using different methods of preparation.

The results showed that all supports having a high specific surface area are suitable in HDS catalyst preparation. Alumina is to be preferred because it inhibits the formation of $CoMoO_4$, and thus exerts a beneficial influence on catalyst preparation. The main function of the support is to stabilize a high degree of dispersion of the actual active component MoS_2. In addition the carrier may facilitate hydrogenation and isomerization reactions.

INTRODUCTION

Among the various models proposed for hydrodesulfurization catalyst systems the role assigned to the support differs in important aspects.

In both the "intercalation model" and "synergy model" described, respectively, by Farragher and Cossee (*1*) and Hagenbach *et al.* (*2*) the carrier plays no role in the actual HDS reaction. Consequently there is no necessity to assume chemical interaction between the active species and the surface of the support. The carrier function remains limited to increasing the degree of dispersion of both the active component and the promoter.

However, in the "monolayer model" proposed by Schuit and Gates (*3*) the molybdenum species are supposed to be present in a monolayer chemically bonded to the surface of the γ-Al_2O_3 support, the monolayer being epitaxial to the support. The function of the promoter is also strongly related to the structure of the carrier. Several versions of this monolayer model have been proposed by other investigators, for instance Lo Jacono *et al.* (*4*), Kabe *et al.* (*5*), Armour *et al.* (*6*), Mitchell and Trifirò (*7*), Sonnemans and Mars (*8*), Seshadri and Petrakis (*9*), and Massoth (*10*).

Ahuja *et al.* (*11*) have studied the influence of the support on the hydrodesulfurization properties of sulfided catalysts containing, *inter alia*, Mo and Co. This was done at 350°C and 60 kg cm^{-2} H_2 pressure using a feed which contained thiophene, toluene and cyclohexane. They found Al_2O_3 and SiO_2–Al_2O_3 (85–15 wt%) to be better supports than pure SiO_2 at the optimum Co/Mo ratio, which was explained in terms of acid functions of the carrier. From this model one might expect that the support will influence not only the typical HDS reactions, but also hydrogenation, isomerization, and cracking reactions. Indeed some data given by Ahuja *et al.* (*11*) and

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by van Sint Fiet (*12*) seem to confirm such an influence.

In the investigation reported here the carrier effect was mainly characterized by thiophene desulfurization activity measurements at 400°C and "atmospheric" pressure, on catalysts containing only Mo or both Mo and Co. The supports used were γ- and η-Al_2O_3 and SiO_2.

EXPERIMENTAL METHODS

The supports used were:

γ-Al_2O_3: Ketjen, high purity, CK-300-1.5E; surface area, 181 $m^2\ g^{-1}$; pore volume, 0.50 $cm^3\ g^{-1}$; average pore radius, 55 Å.

η-Al_2O_3: prepared according to MacIver *et al.* (*13*); surface area, 154 $m^2\ g^{-1}$; pore volume, 0.30 $cm^3\ g^{-1}$; average pore radius, 39 Å.

SiO_2: Ketjen, fluid silica, F-2, surface area 397 $m^2\ g^{-1}$, pore volume, 1.1 $cm^3\ g^{-1}$; average pore radius, 55 Å. In order to obtain catalyst samples with high specific surface area the silica support was treated with excess ammonia (4.5 *N*), washed with demineralized water, dried at 110°C (24 hr) and calcined in air at 600°C (2 hr), before being used in catalyst preparation.

Unless otherwise stated, the catalysts were prepared according to the standard impregnation method described earlier (*14*), with the only difference for the SiO_2 supported samples being a calcination temperature of 450°C instead of 600°C. A list of oxidic catalysts prepared by this standard method is given in Table 1. Some samples were presulfided *in situ* during 2 hr at atmospheric pressure and 400°C in a H_2S/H_2 flow; volume ratio $\frac{1}{6}$ and flow rate, 50 $cm^3\ min^{-1}$. Part of these samples were analyzed for their sulfur content as described by de Beer *et al.* (*15*).

X-Ray diffractograms were recorded on a Philips diffractometer, PW 1009, with a proportional counter using both Cu $K\alpha$ and Co $K\alpha$ radiation in combination with, respectively, a Ni- and Fe-filter. The diffractograms recorded showed nearly always weak and broad lines, many of which are similar to those reproduced by Lo Jacono *et al.* (*4*).

Optical reflectance spectra from oxidic samples were recorded at room temperature. The wave number range 4000–11,500 cm^{-1} was measured with a Zeiss spectrophotometer PMQII in combination with monochromator M.M. 12 and reflectance attachment RA 3. A Unicam ultraviolet spectrometer SP 800D fitted with expansion attachment SP 850 and diffuse reflectance unit SP 890 was used for the spectral range 11,500–52,500 cm^{-1}. All the samples were ground in a ball mill before use.

The apparatus, method, and conditions employed for thiophene hydrodesulfurization activity measurements (continuous flow) were similar to those described before (*14*), except for presulfided samples, which were not reduced in H_2 prior to the activity test. Thiophene conversion was calculated as reported earlier (*16*).

RESULTS

ALUMINA-SUPPORTED CATALYSTS

HDS Activities

Figure 1 shows the thiophene conversions measured after 1.5 and 8 hr run time for the MoO_3–γ-Al_2O_3, CoO–MoO_3–γ-Al_2O_3, and MoO_3–η-Al_2O_3 catalyst series (Table 1, numbers 1–8, 9–12 and 13–20).

Starting with the conversions measured after 1.5 hr it was found that up to 4 wt% MoO_3 the γ-Al_2O_3-supported samples were inactive. Increasing the MoO_3 concentration led to a gradual activity increase which was highest between 4 and 8 wt% MoO_3. Addition of 4 wt% CoO to the MoO_3–γ-Al_2O_3 samples containing, respectively, 4, 6, 8, and 12 wt% MoO_3 increased the thiophene conversion levels substantially.

With the exception of the catalyst with the highest MoO_3 content all the η-Al_2O_3-supported catalysts were found to be more active than those supported on γ-Al_2O_3.

TABLE 1

List of Oxidic Catalysts Prepared

No.	Support	Composition[a]		Color	Surface area (m^2 g^{-1})	Atomic ratio S_{total}/Mo[b]
		MoO_3	CoO (wt%)			
1	γ-Al_2O_3	2		White	162	1.41[c]
2	γ-Al_2O_3	4		White	160	1.26
3	γ-Al_2O_3	6		White	170	1.73
4	γ-Al_2O_3	8		White	159	1.81
5	γ-Al_2O_3	10		White	155	1.92
6	γ-Al_2O_3	12		White	152	2.00
7	γ-Al_2O_3	14		White	145	
8	γ-Al_2O_3	16		White	143	2.14
9	γ-Al_2O_3	4	4	Gray	153	
10	γ-Al_2O_3	6	4	Gray	150	
11	γ-Al_2O_3	8	4	Blue-gray	147	
12	γ-Al_2O_3	12	4	Blue	144	2.38
13	η-Al_2O_3	2		White	120	1.12
14	η-Al_2O_3	4		White	119	1.56
15	η-Al_2O_3	6		White	121	
16	η-Al_2O_3	8		White	124	1.89
17	η-Al_2O_3	10		White	117	
18	η-Al_2O_3	12		White	112	1.97
19	η-Al_2O_3	14		White	96	
20	η-Al_2O_3	16		White	89	2.08
21	η-Al_2O_3	12	4	Blue	105	2.36
22	SiO_2	2		Yellow-white	272	1.82
23	SiO_2	4		Pale-yellow	270	1.92
24	SiO_2	6		Pale-yellow-green	261	1.99
25	SiO_2	8		Pale-yellow-green	247	1.95
26	SiO_2	10		Pale-yellow-green	244	1.81
27	SiO_2	12		Pale-yellow-green	249	1.92
28	SiO_2	14		Pale-yellow-green	227	1.68
29	SiO_2	16		Pale-yellow-green	222	1.42
30	SiO_2	12	2	Brown-pink	220	2.08
31	SiO_2	12	4	Violet-gray	223	2.40
32	SiO_2	12	6	Dark-gray	217	2.61

[a] Balanced by the support.

[b] Analyzed after sulfidation: 50 cm^3 min^{-1} NTP H_2S/H_2, volume ratio 1/6, 400°C, 2 hr.

[c] MoO_3–γ-Al_2O_3 samples used for sulfur analysis were supported on Ketjen fluid powder γ-alumina grade B.

Even for the lowest MoO_3 concentration an activity could be measured, though it was very low. Because of the fact that the reactor density of the η-Al_2O_3 used was about 30% higher than that of the γ-Al_2O_3, the η-Al_2O_3 runs had a shorter contact time. This, however, was compensated to some extent by a somewhat higher flow resistance of the η-Al_2O_3-supported samples caused by smaller average particle size. (Increase of the flow resistance at a given flow rate leads to an increase of the reactor pressure and consequently to an activity increase.) The amount of MoO_3 added in excess of 4 wt% turned out to be highly effective if the total MoO_3 content did not exceed

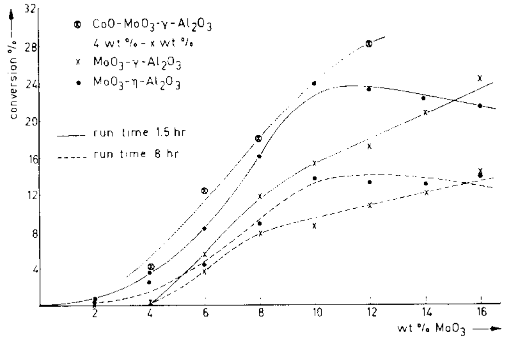

FIG. 1. Thiophene desulfurization as a function of MoO_3 content. Conditions: 180 mg catalyst, 1.5 hr prereduced in hydrogen at 400°C, 50 cm^3 min^{-1} NTP H_2 with 6 vol% thiophene, during 1.5 and 8 hr, 400°C.

10 wt%. For higher MoO_3 concentrations a steady activity decrease was observed which runs more or less parallel with a decrease in surface area (see Table 1).

The results obtained after 8 hr run time were similar to those described above. There are, however, two essential differences. In the first place both the γ- and η-Al_2O_3-supported catalysts showed a substantial activity decrease, and secondly the absolute as well as the relative activity differences between samples with the same MoO_3 content became smaller. The latter phenomenon was even more pronounced for presulfided γ- and η-Al_2O_3-supported samples containing 8 and 10 wt% MoO_3. The steady state conversion levels measured for these catalysts, No. 4, 5, 16, and 17 from Table 1, were, respectively, 7.6, 8.0, 8.2, and 9.8%.

The same applies to the $CoO-MoO_3-\gamma-Al_2O_3$ and $CoO-MoO_3-\eta-Al_2O_3$ catalysts both containing 12 wt% MoO_3 and 4 wt% CoO (Table 1, 12 and 21). When measured in the initially oxidic state the η-Al_2O_3-supported sample was found to be substantially more active than the γ-Al_2O_3-supported one, while for the presulfided samples no significant difference could be observed.

Sulfur Analyses

The results of the sulfur analyses given in Table 1 show that there is no significant difference in sulfurizability between the γ- and η-Al_2O_3-supported catalysts. [Note that the S/Mo ratios of the $MoO_3-\gamma-Al_2O_3$ series are the same as those presented earlier for catalysts prepared on Ketjen fluid powder γ-alumina grade B, (*15*).] The sulfurizability of $MoO_3-\gamma-Al_2O_3$ samples with low MoO_3 content (2 and 4 wt%) was found to be relatively low, which was similar to the findings for comparable η-Al_2O_3-supported samples.

For the laboratory prepared $CoO-MoO_3-\gamma-Al_2O_3$ and $CoO-MoO_3-\eta-Al_2O_3$, S/Co ratios of, respectively, 0.59 and 0.61 were found assuming the S/Mo ratio to be the same as for the corresponding $MoO_3-\gamma-Al_2O_3$ and $MoO_3-\eta-Al_2O_3$ samples. This is in fairly good agreement with the S/Co ratio of 0.63 calculated for the Ketjen $CoO-MoO_3-\gamma-Al_2O_3$ (*15*).

Reflectance Spectra

The optical reflectance spectra obtained for the alumina-supported catalysts are essentially the same as those reported by other investigators (*4*, *17*, *18*). The uv reflectance spectra demonstrated the presence of molybdenum tetrahedrally coordinated by oxygen (peaks at ca. 46,000 and 38,500 cm^{-1}) for all oxidic samples supported on alumina. No indications were found for the presence of MoO_6 octahedra; i.e., no significant broadening of the 38,500 cm^{-1} charge transfer band towards lower wave numbers was observed (*17*).

The spectra of the oxidic $CoO-MoO_3-Al_2O_3$ catalysts (9–12 and 21, Table 1) were typical for tetrahedrally coordinated oxo Co^{2+} species in a spinel system. Two intense (triple) bands, ${}^4A_2 \rightarrow {}^4T_1(F)$ and ${}^4A_2 \rightarrow {}^4T_1(P)$, with maxima, respectively, at 6600, 7400, and 8000 and at 16,000, 17,000, and 18,300 cm^{-1} were observable. A third, relatively weak, band around 4500 cm^{-1} probably originates from both the ${}^4A_2 \rightarrow {}^4T_2$ ligand field transition of tetrahedral Co^{2+}

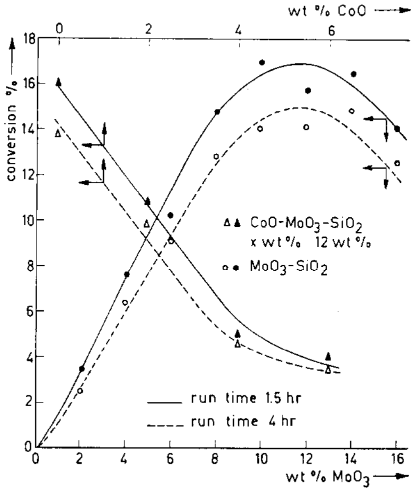

FIG. 2. Thiophene desulfurization as a function of MoO_3 and CoO content for initially oxidic SiO_2-supported catalysts. Conditions: see Fig. 1 run time 1.5 and 4 hr.

and a water peak (*4*). In addition to this, a very weak band at 21,000 cm^{-1} could be distinguished for the cobalt-containing samples with 12 wt% MoO_3. This band might be ascribed to the octahedral cobalt transition $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (*19, 20*). The remaining bands from octahedral cobalt were not observed because of their relatively low extinction coefficients and the fact that their positions are very close to the bands of tetrahedral Co^{2+}. No significant differences were found for the spectra of the corresponding Co- and Mo-containing catalysts supported on γ- and η-Al_2O_3 (12 and 21, Table 1).

Some indications for the presence of the black colored compound Co_3O_4 could also be obtained from the spectra, especially from those with 4, 6, and 8 wt% MoO_3 and 4 wt% CoO (9–11, Table 1). The pertinent observations were a band shoulder at about 14,000 cm^{-1} and a broad absorption starting around 21,000 cm^{-1}, the maximum of which is covered by the strong and broad absorption band of the molybdenum species. The Co_3O_4 band intensities decreased with increasing MoO_3 concentration.

Preliminary experiments with H_2S/H_2 sulfided MoO_3–γ-Al_2O_3 and CoO–MoO_3–γ-Al_2O_3 catalysts yielded reflectance spectra with bands at, respectively, 15,200, 16,700, and 28,000 cm^{-1}, and at 15,200, 16,700, and 28,500 cm^{-1}, provided the samples were sulfided *in situ.* These results, different from those reported by Mitchell and Trifirò (*7*), indicate the presence of MoS_2 which showed bands at 15,200–16,900 and 29,500 cm^{-1}.

X-Ray Analyses

For the γ- and η-alumina-supported catalyst series, only the MoO_3–η-Al_2O_3 samples with 14 and 16 wt% MoO_3 showed X-ray diffraction patterns significantly different from those of the support. These diffraction patterns indicated the formation of $Al_2(MoO_4)_3$ (ASTM 20–34) in both samples and possibly that of Mo_4O_{11} (ASTM 5-337) in the sample with the highest MoO_3 content which showed diffraction lines at *d*-values (in sequence of decreasing intensity) of 3.77, 3.80–3.39, 4.01, 4.24, 3.50, 2.90, 3.18, and 5.69 Å. With respect to the possible presence of MoS_2 and or Co_9S_8 no conclusive information was obtained from the X-ray diffractograms of H_2S/H_2 sulfided alumina-supported catalysts.

SILICA-SUPPORTED CATALYSTS

HDS Activities

For a series of oxidic MoO_3–SiO_2 catalysts (22–29 Table 1) a maximum conversion level of about 17% was measured after 1.5 hr run time for samples with a MoO_3 content around 12 wt% (Fig. 2). In comparison with the alumina-supported samples the effectiveness of small amounts of MoO_3 (2- and 4 wt%) was higher for the silica-supported ones. In addition to this, silica seemed to improve the stability. In this respect Fig. 3 shows that as a result of presulfiding in H_2S/H_2 there was some decrease in conversion of the 12 wt% MoO_3–SiO_2, albeit not to anywhere near the same extent as observed earlier (*15, 16*) for a corresponding γ-Al_2O_3-supported sample.

This stability effect is also demonstrated by the results of long run experiments given in Figs. 1 and 2.

As shown in Fig. 2 introduction of, respectively, 2, 4, and 6 wt% CoO in a 12 wt% MoO_3-SiO_2 (30–32 Table 1) led to a gradual activity decrease. These initially oxidic $CoO-MoO_3-SiO_2$ catalyst systems were found to be relatively stable when judged from the thiophene hydrodesulfurization activities measured after 1.5 and 4 hr run time. However, as an example, for the catalyst containing 12 wt% MoO_3 and 4 wt% CoO a substantial activity decrease was observed during the first 45 min of the run (Fig. 3). When this $CoO-MoO_3-SiO_2$ catalyst was presulfided the steady state activity increased by 5 conversion % (Fig. 3). Although this absolute increase is much smaller than found for the corresponding $\gamma-Al_2O_3$-supported sample the relative increase is higher (*16*).

The results obtained for $CoO-MoO_3-SiO_2$ catalysts, all containing 4 wt% CoO and 12 wt% MoO_3, prepared by a method essentially different from the standard double impregnation method (*14*) is described below. The main results are presented in Fig. 3. No significant improvement of the thiophene hydrogenolysis activity could be measured when Co was introduced into the MoO_3-SiO_2 system by impregnation and drying at 110°C alone (the calcination step being omitted). For such a catalyst, both prereduced in H_2 at 400°C and unreduced, a steady state conversion level of, respectively, 6 and 4% was found. However, when the $CoO-MoO_2-SiO_2$ catalyst under consideration was sulfided in H_2S/H_2 at 400°C right after the drying step its activity was substantially increased (Fig. 3, curve B).

A similar result (19 conversion %) was obtained for a presulfided $MoO_3-CoO-SiO_2$ sample prepared according to the standard preparation method, but with reversed impregnation sequence (Fig. 3, curve C). It should be mentioned that the oxidic $MoO_3-CoO-SiO_2$ catalyst was black instead of violet-gray, the color observed for the comparable $CoO-MoO_3-SiO_2$ catalyst (31, Table 1). Moreover, this $MoO_3-CoO-SiO_2$ catalyst did not stabilize during the period of testing.

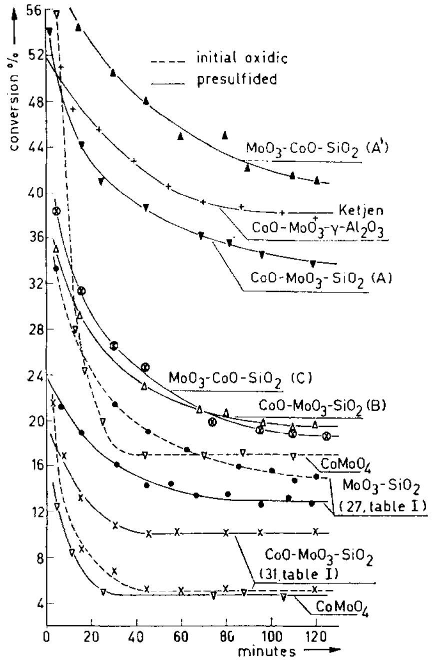

FIG. 3. Thiophene desulfurization as a function of run time. Conditions: see Fig. 1, only the initially oxidic catalysts (except $CoMoO_4$) were prereduced in H_2. Presulfiding: 50 $cm^3\ min^{-1}$ NTP H_2S/H_2; volume ratio, 1/6; 400 or 450°C during 2 hr. (A) Preparation method A described earlier (*16*). (A′) Same as A but with reversed impregnation sequence. (B) Calcination step omitted after Co introduction. (C) Standard preparation method (*14*) but with reversed impregnation sequence.

The best activities were obtained with Co-containing samples prepared according to method A [described earlier (*16*), with the precursor MoO_3-SiO_2 being calcined at 450°C], and method A′, a variant of method A. [Method A′: impregnation of a calcined (500°C) and sulfided $CoO-SiO_2$ with ammonium paramolybdate solution, drying and additional sulfidation at 400°C]. The conversion levels measured after 1.5 hr run time were 35 and 43%, respectively. As can be seen in Fig. 3, these catalysts were less stable than the presulfided Ketjen $CoO-MoO_3-\gamma-Al_2O_3$. This phenomenon was even more pronounced during long run experiments where the activity decrease in the period between 1.5 and 4 hr run time was found to be, respectively, 1.5 and 8 conversion % for Ketjen $CoO–MoO_3–\gamma–Al_2O_3$ and $CoO–MoO_3–SiO_2$ A.

Activity tests of these type A, SiO_2-supported catalysts with different CoO contents, viz, 1, 2, 3, and 4 wt%, showed that 1 wt% CoO is enough to accomplish the same promoter effect as demonstrated in Fig. 3 for the $CoO–MoO_3–SiO_2$ A sample containing 4 wt% CoO. As demonstrated before (*14*) for $MoO_3–\gamma–Al_2O_3$ catalysts with 12 wt% MoO_3 the optimum HDS activity was reached at a CoO content of 4 wt%.

When compared with the alumina-supported catalysts the silica-supported ones were found to have poor hydrogenation properties. For instance, samples with about the same steady state thiophene conversion showed the following differences at 1.5 hr run time. Initially oxidic $MoO_3–SiO_2$ and $MoO_3–\gamma–Al_2O_3$ (12 wt% MoO_3) produced, respectively, 9 and 14% butane in the total amount of C_4-products. For the presulfided $CoO–MoO_3–SiO_2$ A, $MoO_3–CoO–SiO_2$ A′ and Ketjen $CoO–MoO_3–\gamma–Al_2O_3$, 5, 8 and 19% butane was analyzed, respectively.

Sulfur Analyses

Sulfur contents were analyzed for the silica-supported catalysts after sulfiding *in situ* with H_2S/H_2. As can be seen in Table 1 (Nos. 22–27) an average S/Mo atomic ratio of 1.90 is found for $MoO_3–SiO_2$ samples with a MoO_3 concentration up to 12 wt%. For increasing MoO_3 content a decrease of the S/Mo ratio to 1.42 was measured.

For the $CoO–MoO_3–SiO_2$ catalysts (30–32, Table 1) prepared according to the standard impregnation method, S/Mo ratios higher than 2 were found. Assuming that 1.92 sulfur ions are bonded to a molybdenum ion (see catalyst 27, Table 1) S/Co ratios of 0.50, 0.75, and 0.72 can be calculated for the samples containing 2, 4, and 6 wt% CoO, respectively. This indicates that, under the sulfidation conditions applied, the Co present in the SiO_2-supported samples can be sulfided more completely than it can in the alumina-supported ones.

Reflectance Spectra

Optical reflectance spectra recorded for $MoO_3–SiO_2$ catalysts showed a significant broadening of the 38,500 cm^{-1} band towards lower wave numbers, when compared with the alumina-supported samples. In addition, at MoO_3 concentrations higher than 10 wt% a weak shoulder around 33,000 cm^{-1} could be observed, indicating the presence of octahedrally coordinated Mo, viz, free MoO_3 (*17*). Some spectra in the visible region recorded for cobalt-containing silica-supported samples are given in Fig. 4. The spectrum obtained for the $CoO–MoO_3–SiO_2$ sample, containing 4 and 12 wt% CoO and MoO_3, respectively, prepared according to the standard preparation method, showed bands at 17,500 and 19,500 cm^{-1}, a shoulder around 13,500 cm^{-1} and a broad charge transfer band (*18, 19*) starting at about 21,000 cm^{-1}. This spectrum was very similar to the one recorded for a mechanical mixture of β-$CoMoO_4 + SiO_2$ (16 wt% β-$CoMoO_4$), whereas it was significantly different from the spectrum obtained for a mixture of α-$CoMoO_4 + SiO_2$ (16 wt% α-$CoMoO_4$), as shown in Fig. 4. This led to the conclusion that β-$CoMoO_4$ is the main cobalt-containing compound formed during the preparation of $CoO–MoO_3–SiO_2$ [see also its color (31, Table 1)]. This is not the case for the black $MoO_3–CoO–SiO_2$ C catalyst (reversed impregnation sequence) which showed a ligand field band at 14,000 cm^{-1} and a broad charge transfer band starting around 16,500 cm^{-1} (*4, 21*), like its precursor, $CoO–SiO_2$ (4 wt%). The main cobalt compound formed here is very probably Co_3O_4.

Preliminary experiments with H_2S/H_2 sulfided $MoO_3–SiO_2$ and $CoO–MoO_3–SiO_2$

samples yielded similar spectra as described already for the corresponding alumina-supported catalyst, indicating again the formation of MoS_2 as a result of sulfidation.

X-Ray Analyses

X-Ray analysis of oxidic MoO_3-SiO_2 samples (22–29, Table 1) produced evidence for the existence of MoO_3 (ASTM 5-0508) in samples with a MoO_3 content of 12 wt% or higher. The diffraction patterns contained lines at the following *d*-values (in order of decreasing intensity): 3.26, 3.45, 3.81, 2.30, 2.65, and 1.85 Å.

For all oxidic $CoO-MoO_3-SiO_2$ catalysts prepared according to the standard double impregnation method (30–32, Table 1), diffraction patterns ascribable to β-$CoMoO_4$ (ASTM 21–868) were obtained. For the sample containing 6 wt% CoO the *d*-values of the complete set of diffraction lines observed were (in sequence of decreasing intensity): 3.36, 3.80, 3.29, 2.44, 2.66–4.66, and 1.57–1.65–2.02–2.32–2.80–2.84–3.13 Å. This indicates that Co_3O_4 (ASTM 9-418) was also present. Both $CoO-SiO_2$ and $MoO_3-CoO-SiO_2$ contained Co_3O_4 (lines at *d*-values of 2.43, 1.56–1.43, and 2.02–2.88 Å), while in the latter catalyst some β-$CoMoO_4$ and MoO_3 might have been present (very weak lines at *d*-values of 3.36 and 3.26–3.81 Å, respectively).

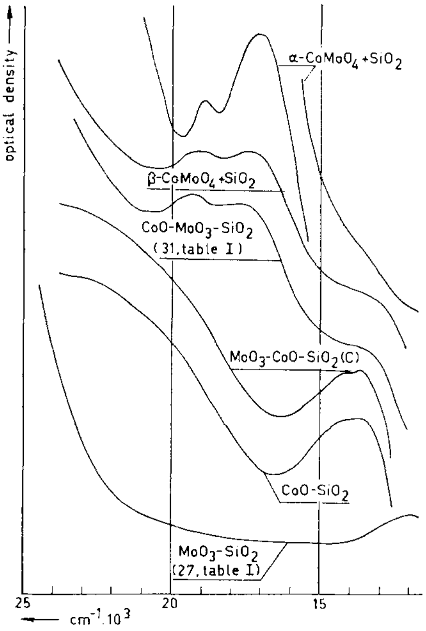

FIG. 4. Reflectance spectra for oxidic silica-supported catalysts. (C) see Fig. 3.

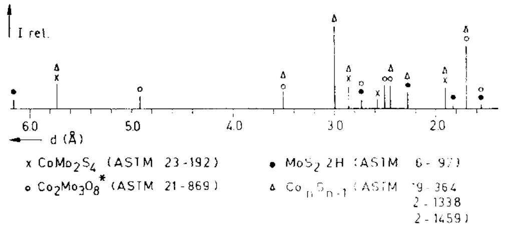

FIG. 5. X-Ray diagram of sulfided β-$CoMoO_4$. Conditions: H_2S/H_2; volume ratio, 1/6; 50 cm^3 min^{-1} NTP; 400°C; 2 hr. *$CoMoO_3$ mentioned in the ASTM file should very probably be $Co_2Mo_3O_8$.

From the series of H_2S/H_2 sulfided MoO_3-SiO_2 catalysts only the sample with the highest Mo content showed a very weak line at $d = 6.14$ corresponding with the strongest line of MoS_2 (ASTM 6–97).

The H_2S/H_2 sulfided $CoO-MoO_3-SiO_2$ (32, Table 1) as well as $CoO-MoO_3-SiO_2$ A and $MoO_3-CoO-SiO_2$ A′ (see Fig. 3) might contain some Co_9S_8 (ASTM 19–364), while for the two last mentioned catalysts the presence of MoS_2 may also be inferred from the X-ray diffractograms. The lines observed were attributable to the strongest lines of Co_9S_8 and MoS_2 at $d = 1.76$ and 2.99 and $d = 6.15$, respectively.

COBALT MOLYBDATE

The thiophene HDS activity of 180 mg violet $CoMoO_4$ (surface area 6.2 m^2 g^{-1}) was also measured (see Fig. 3). The prereduced initially oxidic sample showed an extremely high starting activity which decreased within a period of 40 min to a steady state conversion level of 17%. H_2S/H_2 presulfiding followed by reduction in H_2 led to a considerable activity decrease. The steady state conversion level reached within 30 min was 5%.

The diffractogram of H_2S/H_2 sulfided (standard conditions) β-$CoMoO_4$ showed lines at *d*-values given in Fig. 5. A good fit for this line pattern can be made by a composition of the patterns obtained from Co_9S_8 (ASTM 19–364) or Co_4S_3 (ASTM 2–1338) or γ-Co_6S_5 (ASTM 2–1459), MoS_2 (ASTM 6–97), $CoMo_2S_4$ (ASTM 23–192), and molybdite[2] (ASTM 21–869).

After sulfiding which appeared to be incomplete under the standard conditions applied here, an average S/Mo ratio of 2.10 was analyzed.

DISCUSSION

We will start the discussion with the SiO_2-supported catalyst. For relatively low MoO_3 contents a linear relation of Mo-concentration versus HDS activity was found, in contrast with the alumina-supported catalysts. The maximum at about 12 wt% MoO_3 might be caused by pore blocking. Since crystalline MoO_3 was observable by X-rays, the appropriate model for the MoO_3–SiO_2 catalyst is that of small MoO_3 crystals embedded in the pores of the SiO_2 support. These MoO_3 crystals are converted to MoS_2 crystals during presulfidation or in actual operation.

At first sight the action of Co seems rather complicated. As far as could be ascertained by sulfur analysis, activity measurements, X-ray diffraction and reflectance spectroscopy, there was no interaction between Co and the support. Catalysts with excellent properties were prepared by sequential impregnation, drying, and sulfidation of sulfided MoO_2–SiO_2 or CoO–SiO_2 samples (method A or A′), while inferior catalysts were obtained by double impregnation with Mo being the first element added. Somewhat better catalysts, although still rather inferior, were obtained by changing the sequence of impregnation or avoiding the calcination step after Co introduction.

It is not entirely clear why the method of preparation has such a large influence, but it is almost certain that the differences are related to the formation of $CoMoO_4$ in the oxidic precursor stages of the catalyst. Experiments with pure cobalt molybdate showed an initially very high catalytic activity but which rapidly declined and ended up at a very low level. Presulfided $CoMoO_4$ showed an even lower activity. An explanation of this lack of activity might be found in the nature of the reaction products of $CoMoO_4$ sulfidation. The approximate composition after sulfiding was MoS_2 (15%), $CoMo_2S_4$ (25%), Co_nS_{n-1} (45%) and $Co_2Mo_3O_8$ (15%). In the literature $CoMo_2S_4$ (*22*) is mentioned as an inactive compound. Nothing is known of the HDS properties of $Co_2Mo_3O_8$. However, MoS_2 which is the main actual active component is only present in minor quantities.

Any method of preparation that avoids the possibility of $CoMoO_4$ formation—and this is especially valid for methods A and A′—leads to CoO–MoO_3–SiO_2 catalysts with activity similar to that of the Al_2O_3-supported ones. There can be hardly any doubt that those are precisely the catalysts of the Co promoted MoS_2 type. It is noteworthy, however, that SiO_2-supported catalysts invariably had considerably lower hydrogenation activity than the Al_2O_3-supported ones. Perhaps this is connected with their lower stability [see activity decrease as a function of run time (Fig. 3)]. We shall return to this problem below.

With respect to the effectiveness for thiophene HDS measured after 1.5 hr, for both the MoO_3–γ-Al_2O_3 and MoO_3–η-Al_2O_3 catalyst series, three MoO_3 concentration ranges can be distinguished, viz, wt% MoO_3, <4; $4 <$ wt% $MoO_3 < 10$, and wt% MoO_3 >10 (see Fig. 1). In the low concentration range Mo was found to be entirely (γ-Al_2O_3), or largely (η-Al_2O_3), ineffective. A relatively high effectiveness was observed in the second range, while Mo added in excess of 10 wt% MoO_3 was found to be moderately effective (γ-Al_2O_3) or even harmful (η-Al_2O_3), for HDS of thiophene.

These phenomena may be rationalized on the basis of a variation in strengths of

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[2] Mentioned as $CoMoO_3$ in the ASTM file. However, this should very probably be $Co_2Mo_3O_8$.

interaction between Mo and Al surface species. It is reasonable to assume that the surfaces of high area aluminas are largely heterogeneous. When added in small amounts Mo will react preferentially, during catalyst preparation, with the more active surface or possibly subsurface alumina sites, resulting in the formation of a stable compound which contains very probably MoO_4 tetrahedra. This compound cannot be easily reduced (*10*) nor sulfided (*15*) and will therefore be inactive. These Mo species might be barely removable on washing in ammonia (*8*, *23*). Less active alumina sites will form weaker compounds with increasing Mo level. These compounds may contain both MoO_4 tetrahedra and MoO_6 octahedra in registry with the alumina surface (*3*, *4*), resulting in the formation of a monolayer on top of the carrier surface. Based on the great similarity of O–O distances in a γ- and η-Al_2O_3 spinel structure (2.8 Å) and in a molybdate ion (2.8–2.9 Å), both tetrahedral and octahedral site occupation by Mo^{6+} ions are in principle eligible. However, data taken from reflectance spectroscopy showed that the formation of MoO_4 tetrahedra preponderates very strongly. This is in agreement with the findings of other investigators (*17*, *24*, *25*). The readily reducible Mo species in the monolayer are the main precursors of the actual active hydrodesulfurization sites, viz, Mo^{3+} surrounded by sulfur (*16*). Further increase of the Mo concentration leads gradually to the formation of separate crystalline phases.

$Al_2(MoO_4)_3$ and possibly Mo_4O_{11}, which contains Mo in both distorted octahedra and tetrahedra (*26*), were observable by XRD in two MoO_3–η-Al_2O_3 catalysts (14 and 16 wt% MoO_3). The presence of $Al_2(MoO_4)_3$, consisting of Mo^{6+} in tetrahedral and Al^{3+} in octahedral environment, is mentioned in several papers (*8*, *24*, and *27*) and also the occurrence of free MoO_3 (distorted MoO_6 octahedra) (*3*, *4*, *10*, *24*). The presence of crystalline phases probably causes pore blocking and therefore lowers the effectiveness of the added Mo (Fig. 1). It should be emphasized that several factors, e.g., surface area of the alumina, calcination temperature and time, as well as the way in which Mo is introduced (*8*), may influence the relative fractions of Mo present respectively in nonreducible compounds, in the monolayer species, and in separate crystalline phases.

When compared after 1.5 hr run time the MoO_3–η-Al_2O_3 catalysts were found to be more active than the corresponding γ-Al_2O_3-supported ones. An explanation for this phenomenon might be found in differences between γ- and η-Al_2O_3 as described by Lippens (*28*) and Krischner *et al.* (*29*). For instance, η-Al_2O_3 is said to contain relatively more tetrahedral Al^{3+} ions and its (111) crystal plane might be the predominant surface plane, while for γ-Al_2O_3 it is the (110) plane. However, long run experiments (8 hr) showed that the influence of the support diminished during operation (Fig. 1) and this was found to be even more pronounced for H_2S/H_2 presulfided samples. These observations combined with the results of sulfur analysis (Table 1) indicate strongly that MoO_3–γ-Al_2O_3 and MoO_3–η-Al_2O_3 catalysts in actual operation consist mainly of small MoS_2 crystals on the external surfaces of the support.

We now return to the problem of the low olefin hydrogenation activity of SiO_2-supported catalysts in comparison with that of Al_2O_3-supported ones. For the sake of convenience further discussion is conducted with the help of Fig. 6. We may interpret the difference in terms of monolayer catalyst systems containing HDS sites M_S (*12*, *14*) as well as hydrogenation sites M_H (*8*, *12*). The presence of both HDS sites I_S and hydrogenation sites I_H in pure sulfide systems follows from the work of Voorhoeve and Stuiver (*30–32*), Hagenbach *et al.* (*2*, *22*), and Kolboe and Amberg (*33*). The I_H and I_S sites are known to be susceptible to poisoning by H_2S and CS_2.

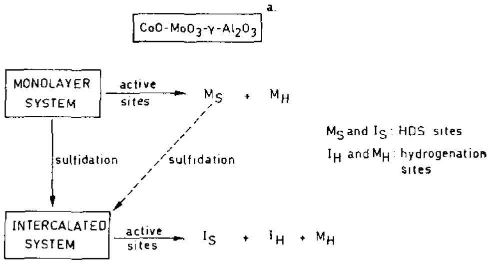

FIG. 6. Scheme of active sites formed in oxidic and sulfided alumina-supported catalysts. (a) $CoO = NiO$, $MoO_3 = WO_3$, $\gamma\text{-}Al_2O_3 = \eta\text{-}Al_2O_3 \neq SiO_2 \neq C$.

It has been demonstrated in the foregoing pages that the greater part of the monolayer is converted into MoS_2 crystals. The remaining part of the Mo species, very strongly bonded to the support, is assumed to be still active for olefin hydrogenation. This is confirmed by the low hydrogenation activity of SiO_2-supported catalysts (no interaction of Mo with the support) and both oxidic and sulfided $CoO–\gamma\text{-}Al_2O_3$ samples (*12*, *15* [Fig. 5]) as well as by the low butane/total C_4-product ratio (about 0.10) found for $CoO–(MoS_2 + \gamma Al_2O_3)$ and $CoO\text{-}(WS_2+\gamma\text{-}Al_2O_3)$ catalysts (*16*, [Table 2]). When Mo is present in the alumina-supported catalysts, olefin hydrogenation is appreciable (*12*).

It is noteworthy that addition of Co to a 4 wt% $MoO_3–\gamma\text{-}Al_2O_3$ catalyst seems to reduce the number of stable Mo sites (Fig. 1). In spinel structures Co^{2+} ions apparently have a stronger preference for tetrahedral site occupation than Mo^{6+} ions.

CONCLUSIONS

1. Any support with a high specific surface area (e.g., γ- and $\eta\text{-}Al_2O_3$, SiO_2, or C) is acceptable for HDS catalyst systems.

2. Alumina is to be preferred because it inhibits the formation of $CoMoO_4$ and thus exerts a beneficial influence on catalyst preparation.

3. Alumina may differ from other supports in preserving, at the surface, specific hydrogenation sites which are less susceptible to sulfur poisoning.

4. The realization that supports, as applied throughout this investigation, do not contribute to the chemistry of the HDS reaction explains the industrial application of supports in which a second function (hydrocracking) is explicitly introduced (*34*). Further experiments in this direction are in progress.

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