

The CoO-MoO₃-gamma-Al₂O₃ : VI. Sulfur content analysis and hydrodesulfurization activities

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The CoO-MoO₃- γ -Al₂O₃ Catalyst

VI. Sulfur Content Analysis and Hydrodesulfurization Activities

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The sulfur uptake of commercial and laboratory prepared catalysts of the type MoO₃- γ -Al₂O₃, CoO- γ -Al₂O₃ and CoO-MoO₃- γ -Al₂O₃ was studied at 400°C using H₂S/H₂ and thiophene/H₂ as sulfiding gases. The temperature, time, and H₂S partial pressure of sulfiding were varied, and the fraction of sulfur removable by H₂ reduction at 400°C was determined. The influence of the sulfur content on the activity for hydrodesulfurization of thiophene was also measured.

Based on these findings the formation of MoS₂ and Co₉S₈ as a result of the sulfidation is considered to be the most likely process, although the presence of small amounts of other sulfur-containing species cannot be excluded. Experimental evidence is reported for the diffusion of Co²⁺ ions from the bulk towards the surface of the γ -Al₂O₃ support during the sulfiding process. The hydrogenolysis activity was found to decrease with increasing sulfur content for the MoO₃- γ -Al₂O₃ catalyst, while on CoO-MoO₃- γ -Al₂O₃ the reverse effect was observed.

INTRODUCTION

The various forms of lattice and surface sulfur present in hydrodesulfurization catalysts, and their involvement in the actual hydrodesulfurization reactions is not entirely understood. This can be illustrated by the different structure models for sulfided catalyst systems given in the literature. Richardson (1) proposed that the true catalytic agent was MoS₂. It is promoted by "active" Co in octahedral coordination which could be neither reduced nor sulfided. Other Co-species assumed to be present were CoAl₂O₄, which was resistant to sulfiding, and Co₉S₈. His model leads one to expect the ratio of lattice sulfur-to-molybdenum atoms to approach 2. On the basis of their intercalation model for the Ni-WS₂ and Co-MoS₂ systems Voorhoeve and

Stuiver (2, 3), and Farragher and Cossee (4) predicted approximately the same S/Mo ratio. Following physicochemical investigations and measurements of catalytic activity on crystalline molybdenum sulfide and cobalt sulfide mixed catalysts, Hagenbach *et al.* (5) ascribed their HDS activity to a synergetic effect of strongly interacting MoS₂ and Co₉S₈ phases. Much more sulfur was present in the mixed catalysts than required by stoichiometry. According to these authors this was probably a requirement of the synergetic system.

In the monolayer model proposed by Schuit and Gates (6) MoO₃ was assumed to be partially sulfided to such an extent that the maximum S/Mo ratio is 1. The Co-species was thought not to be accessible to sulfur in this model. A study of the kinetics of the reduction and sulfidation of CoO-MoO₃-Al₂O₃ led Kabe *et al.* (7) to describe the sulfided catalyst by the formula CoS·MoO_{1.5}S_{1.5}-Al₂O₃. Free MoO₃ present

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in the catalyst samples was found to be barely sulfided.

Armour *et al.* (8a), and Mitchell and Trifirò (8b) took a position intermediate between the last two. From spectroscopic and magnetic measurements on oxidic and sulfided CoO-MoO₃- γ -Al₂O₃ catalysts these authors concluded that sulfur adds to Mo-tetrahedra and that no more than one or two of the oxide ions, probably those bridging between Mo and Co, are replaced by sulfide. They found no evidence for discrete Mo- and Co-sulfides, although the sulfur content of their samples allows one to assume that MoS₂ and Co₉S₈ are present.

Recent X-ray photoelectron spectroscopy measurements on sulfided CoO-MoO₃- γ -Al₂O₃ and MoO₃- γ -Al₂O₃ by van Sint Fiet (9), who found a spectrum reminiscent of that of Na₂S₂O₃, suggest the presence of both S²⁺ and S⁰. An interesting question is whether or not both these species are involved in the HDS reaction. There has also been some evidence for the occurrence of S-polymers on the catalyst (10, 11) and for the conversion of Al₂O₃ to a form of surface sulfide (12, 13).

Considering this great variety of observations, and the uncertainty still connected with the role of sulfur in HDS reactions, we undertook a systematic study of the sulfiding process of CoO- γ -Al₂O₃, MoO₃- γ -Al₂O₃ and CoO-MoO₃- γ -Al₂O₃ catalysts, followed by measurement of thiophene hydrogenolysis activity as a function of their sulfur content.

EXPERIMENTAL METHODS

For this investigation the commercially manufactured catalysts Ketjen MoO₃- γ -Al₂O₃ type 120-3E and Ketjen CoO-MoO₃- γ -Al₂O₃ type 124-1.5E were used. The former contained 11.7 wt% MoO₃ and its specific surface area was 227 m² g⁻¹. The CoO and MoO₃ contents of the latter catalyst were 4.1 and 12.4 wt%, respectively, and its specific surface area was 217 m² g⁻¹. MoO₃ (Merck, purity \geq 99.5%; surface area, 0.5 m² g⁻¹) and MoS₂ (Schuchardt,

purity \geq 98.5%; surface area, 7.8 m² g⁻¹) were also used for some experiments. In addition to this a series of MoO₃- γ -Al₂O₃ samples, with different MoO₃ content, and a series of CoO- γ -Al₂O₃ catalysts, calcined at different temperatures and containing various amounts of CoO, were prepared for studying the sulfiding process. Ketjen, fluid powder γ -alumina grade B (surface area, 255 m² g⁻¹) was used as support. The method of preparation was described before (14). MoO₃ and CoO contents, calcination temperatures and surface areas are given in Table 2. The catalyst samples were sulfided at "atmospheric" pressure in a flow of H₂S (Matheson, C. P. grade) and purified H₂ (15), with a H₂S/H₂ volume ratio of 1/6 and a flow rate of either 50 or 175 cm³ min⁻¹ NTP. The following parameters were varied: sulfiding time, temperature, and the H₂S pressure. In some experiments the catalyst was reduced in pure H₂ (50 cm³ min⁻¹ NTP, at 400°C for 2 hr) in order to see how much sulfur could be removed. Thiophene (6 vol%) mixed with H₂ was also used as a sulfiding agent under experimental conditions described earlier (14).

Four types of (pre-)treatment (*a*, *b*, *c* or *d*) have been employed, namely:

- a.* Sulfidation with H₂S/H₂;
- b.* Reduction in pure H₂;
- c.* Sulfidation with C₄H₄S/H₂.
- d.* Oxidation with air.

Successive application of these (pre-)treatments will be indicated by a + sign; for example, (*a* + *b*) means sulfidation in H₂S/H₂ followed by reduction in H₂.

All samples used for sulfur analysis were heated to the desired temperature in purified N₂ (15), sulfided, cooled quickly to room temperature in the sulfiding gas mixture, and flushed again with N₂ for about 10 min. Sulfur was analysed titrimetrically using an all-glass apparatus. Catalyst samples (200-300 mg on dry basis) covered with quartz wool were heated from room temperature to 800°C in a continuous flow of O₂ (10 cm³ min⁻¹ NTP) over a period of

2 hr. The SO₂/SO₃ mixture obtained was passed through a tube filled with quartz wool and chips, in which was maintained a temperature gradient from 800 to 400°C. The emerging gas mixture was trapped in two vessels in series containing ice-cooled aqueous solutions of H₂O₂ (3 vol%). In order to avoid leakage of SO₂ and SO₃ the operating pressure was kept below 1 atm by means of an aspirator at the exit. After the oxidation the whole apparatus was rinsed with water which was collected in the first two H₂O₂ vessels. The amount of sulfuric acid obtained was determined by titration with 0.1 N NaOH using methyl red as an indicator (pH 4.2–6.3).

The accuracy of our method was tested with pure MoS₂ (sample size 20–40 mg) and mixtures of 7–12 mg elemental sulfur and 200 mg pure grade γ -Al₂O₃ (Ketjen CK300). In both cases 98 ± 1.5% of the sulfur could be analyzed. All sulfur deter-

minations were corrected for sulfur initially present in the oxidic samples probably as a sulfate impurity in the γ -Al₂O₃. All samples used for sulfur analysis except the Ketjen MoO₃- γ -Al₂O₃ catalyst were sulfided *in situ*. No significant differences were found when the *in situ* procedure was followed for the latter catalyst as well.

X-Ray diffractograms were recorded using Cu K α and Co K α radiation in combination with, respectively, a Ni- and Fe-filter. They did not yield significant information about the formation of new Mo- or Co-species arising from sulfidation. The relation between sulfur content and thiophene hydrogenolysis activity, as well as the removal of sulfur by means of H₂ reduction were also studied under experimental conditions as described in an earlier paper (14). All the samples used in thiophene hydrodesulfurization tests were sulfided and reduced *in situ*.

TABLE 1
Degree of Sulfiding after Different Treatments

Sample	Treatment ^a sequence	Atomic ratio		Total degree of sulfiding ^c
		S _{total} /Mo	S/Co ^b	
MoS ₂ ^d	<i>b</i>	1.88		0.95
	<i>b</i> + <i>c</i>	1.96		0.98
MoO ₃ ^d	<i>a</i>	0.11		0.06
	<i>a</i> + <i>b</i> + <i>c</i>	0.25		0.13
Ketjen	<i>a</i>	2.04		1.02
	<i>a</i> + <i>b</i>	1.23		0.62
MoO ₃ - γ -Al ₂ O ₃ ^d	<i>a</i> + <i>b</i> + <i>c</i>	1.72		0.86
	<i>b</i> + <i>c</i>	1.36		0.68
Ketjen	<i>a</i>	2.44	0.63	0.95
	<i>a</i> + <i>b</i>	1.51	0.44	0.59
CoO-MoO ₃ - γ -Al ₂ O ₃	<i>a</i> + <i>b</i> + <i>c</i>	2.07	0.55	0.81
	<i>a</i> + <i>c</i>	2.68		1.05
	<i>c</i>	2.51		0.98
	<i>c</i> + <i>b</i>	1.35		0.53

^a (a) Sulfidation in H₂S/H₂: 175 cm³ min⁻¹ NTP H₂S/H₂, volume ratio $\frac{1}{6}$; 400°C, 2 hr. (b) Reduction in H₂: 50 cm³ min⁻¹ NTP H₂, 400°C, 2 hr. (c) Sulfidation in thiophene/H₂: 50 cm³ min⁻¹ NTP H₂ with 6 vol% thiophene, 400°C, 2 hr.

^b Assuming the S/Mo ratio to be the same as for the corresponding MoO₃- γ -Al₂O₃ sample.

^c Based on the formation of MoS₂ and Co₉S₈.

^d These samples had been in contact with air at room temperature between the sulfidation and analysis steps (see text also).

RESULTS

 γ -Al₂O₃

The sulfur uptake of the alumina support alone was found to be 0.6 wt% after standard H₂S/H₂ treatment at 400°C. The color changed from white to light gray.

MoS₂

A small fraction of the sulfur could be removed from crystalline MoS₂ by hydrogen reduction for 2 hr at 400°C. Following the thiophene/H₂ treatment the sulfur content increased, while the S/Mo ratio remained only just below that for pure MoS₂.

MoO₃

Sulfidation of bulk MoO₃ appeared to be a slow process (Table 1). Seshadri *et al.* (10), Coleuille and Trambouze (16) and Gautherin and Colson (17) have found that this compound decomposes rather rapidly when treated with H₂S/H₂ at temperatures between 300 and 500°C and that the products formed were MoS₂ and MoO₂, of which the latter reacts slowly with H₂S.

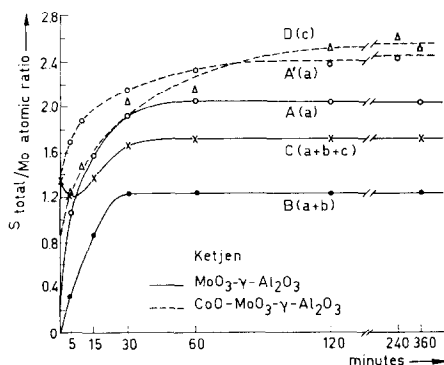


FIG. 1. Sulfur content as a function of sulfidation time. Sequence of treatments is added in parentheses. Conditions: (a) Sulfidation in H₂S/H₂: 175 cm³ min⁻¹ (MoO₃- γ -Al₂O₃) and 50 cm³ min⁻¹ (CoO-MoO₃- γ -Al₂O₃) NTP H₂S/H₂, volume ratio 1/6, 400°C. Length of treatment given by abscissa. (b) Reduction in H₂: 50 cm³ min⁻¹ NTP H₂, 400°C, 2 hr. (c) Sulfidation in thiophene/H₂: 50 cm³ min⁻¹ NTP H₂ with 6 vol% thiophene, 400°C, 2 hr (curve C) and x hr (curve D).

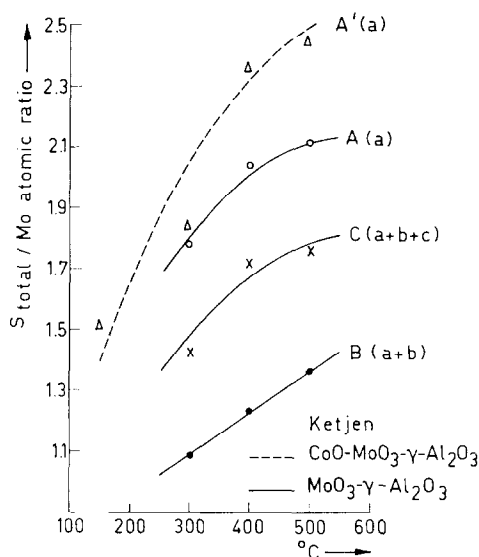


FIG. 2. Sulfur content as a function of sulfidation temperature. Sequence of treatments added in parentheses. Conditions: (a) Sulfidation in H₂S/H₂: see Fig. 1, 2 hr. (b) Reduction in H₂: see Fig. 1. (c) Sulfidation in thiophene/H₂: see Fig. 1, 2 hr.

This might explain the twofold increase in sulfur content after additional H₂ reduction followed by thiophene/H₂ treatment.

MoO₃- γ -Al₂O₃

The results of the sulfidation of Ketjen MoO₃- γ -Al₂O₃ with H₂S/H₂ are given in Figs. 1 and 2 and Table 1. In Fig. 1 the atomic ratio S/Mo has been plotted versus sulfiding time. As can be seen from curve A at 400°C one-half of the sulfur was taken up already in the first 5 min and the catalyst was optimally sulfided after 1 hr, thereafter apparently remaining in a steady state. The S/Mo ratio at the steady state level was equal to 2 within experimental error, so that there is a strong possibility that all the Mo had been converted to MoS₂ during sulfiding.

At steady state about one third of the sulfur had been removed by hydrogen reduction (treatment b) during 2 hr at 400°C (curve B), leading to a S/Mo ratio of 1.23. For sulfiding times shorter than 30 min an

TABLE 2
Laboratory Prepared Catalysts, Degree of Sulfiding^a

No.	Composition ^b (wt%)		Calcination temp (°C)		Surface area (m ² g ⁻¹)	Sulfidation temp (°C)	Atomic ratio	
	MoO ₃	CoO	MoO ₃	CoO			S/Mo	S/Co
1	2		600		162	400	1.41	
2	4		600		160	400	1.26	
3	6		600		170	400	1.73	
4	8		600		159	400	1.81	
5	10		600		155	400	1.92	
6	12		600		152	400	2.00	
7	16		600		143	400	2.14	
8		4		200	217	400		0.86
9		4		400	224	400		0.80
10		4		400	224	600		0.87
11		4		600	221	400		0.31
12		4		600	221	600		0.78

^a Sulfided in H₂S/H₂, volume ratio $\frac{1}{6}$, 2 hr.

^b Balanced by the support.

even higher percentage of the sulfur was removed by H₂ reduction. After further treatment (c) with a 6 vol% mixture of thiophene in H₂ (2 hr at 400°C) the sulfur content of these presulfided and prerduced samples was increased up to a S/Mo ratio of 1.72 (curve C), but the level found for the freshly sulfided catalyst was never reached. When an oxidic MoO₃- γ -Al₂O₃ was successively reduced in H₂ and sulfided in thiophene/H₂ for 2 hr (treatment b + c in Table 1 and first point curve C in Fig. 1, at which $t = 0$, i.e., in the absence of treatment a) a much lower S/Mo ratio was found than for the sample treated with H₂S/H₂ during the same period. Whether this phenomenon is ascribable to the substantially lower partial pressure of the sulfur-containing agents during thiophene/H₂ treatment was checked by decreasing the H₂S/H₂ ratio from 1/6 to 1/24. The result was only a small decrease of the S/Mo ratio from 2.04 to 1.97 after 2 hr, so that the reason must be sought elsewhere, for instance slow sulfurizability of MoO₂ formed as a result of H₂ reduction of the free MoO₃ that could have been present in the MoO₃- γ -Al₂O₃ catalyst (10). The temperature effect on the sulfidation of MoO₃-

γ -Al₂O₃ (H₂S/H₂ = 1/6, 2 hr) is given in Fig. 2. The tendency found for all three different treatments (a, a + b, a + b + c) is an increase of the degree of sulfiding with increasing temperature. Qualitatively this is in agreement with the findings of Seshadri *et al.* (10).

The S/Mo ratios found for a series of laboratory prepared MoO₃- γ -Al₂O₃ catalysts are given in Table 2. A relatively low sulfur uptake was found for samples containing 2- and 4 wt% MoO₃, and from 6 up to 16 wt% a slight increase in S/Mo ratio was observed. For the highest MoO₃ content a S/Mo ratio significantly higher than that for MoS₂ was found.

As was demonstrated earlier (15) a substantial HDS activity decrease results from presulfiding the MoO₃- γ -Al₂O₃ catalyst (see also Fig. 4). In addition to this the influence of the time of H₂S/H₂ presulfiding was now examined. The results (Fig. 3) indicate a correlation between the sulfur content found after different sulfidation times (Fig. 1, curve A) and HDS activity. Such a correlation was also found for MoO₃- γ -Al₂O₃ sulfided at different H₂S concentrations at constant time and temperature (2 hr, 400°C); likewise for samples sulfided

under standard conditions (H₂S/H₂ volume ratio 1/6, 2 hr) but at different temperatures. The general pattern was that the higher the initial sulfur content, the lower was the thiophene conversion found after a 2 hr run. As can be seen in Fig. 4 there is no necessity for prereduction with H₂ in order to activate the MoO₃- γ -Al₂O₃ catalyst, no matter whether prereduced or oxidic. As expected, marked differences show up in the oxidic catalyst only during the initial 30 min, depending on whether the molybdenum is initially in a higher or lower oxidation state. This was also clearly shown in a series of pulse experiments (18).

CoO- γ -Al₂O₃

With respect to the sulfurizability of Co in CoO- γ -Al₂O₃ samples by means of H₂S/H₂ it is shown in Table 2 that the S/Co ratio increased with decreasing calcination temperature and also with increasing sulfiding temperature. For samples 8 and 10 the S/Co ratio is very close to that of Co₉S₈. As demonstrated earlier (15) the sulfiding process of initially oxidic CoO- γ -Al₂O₃ can be "visualized" by measuring

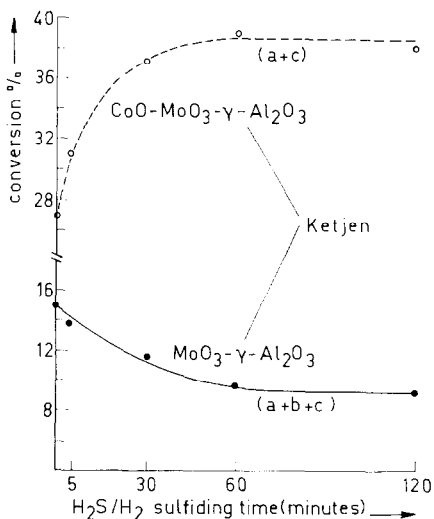


Fig. 3. Thiophene conversion after 2 hr run time vs sulfiding time in H₂S/H₂. Sequence of treatments added in parentheses. Conditions: see Fig. 1, 200 mg catalyst.

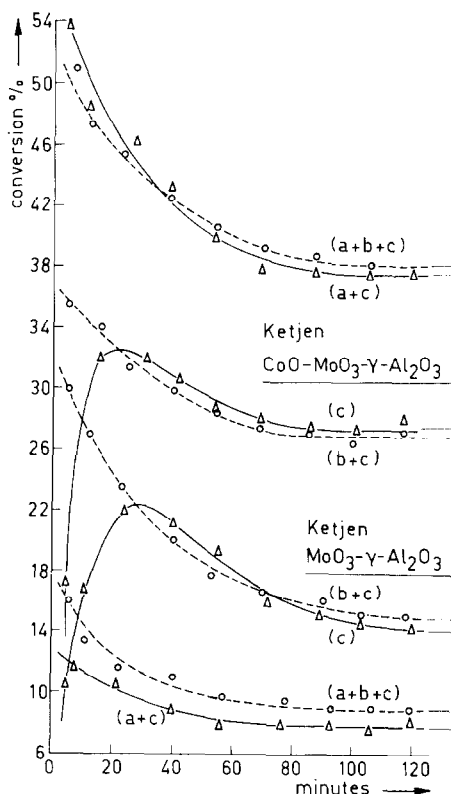


Fig. 4. Thiophene conversion as a function of run time after different treatments. Sequence of treatments added in parentheses. (a) Sulfidation in H₂S/H₂: 50 cm³ min⁻¹ NTP, volume ratio 1/6, 400°C, 2 hr over 200 mg catalyst. (b) Reduction in H₂: see Fig. 1. (c) Conversion of 6 vol% thiophene in H₂, 50 cm³ min⁻¹ NTP, 400°C, run time given by abscissa.

the thiophene conversion as a function of time in a flow experiment. Similar experiments were performed, as shown in Fig. 5 for samples containing 4 wt% CoO, and calcined at 400 and 600°C. The results showed that the lower the calcining temperature the more sulfided cobalt was formed on the catalyst surface, probably aided by diffusion of Co²⁺ from the interior of the carrier to its surface. Prereduction in H₂S/H₂ at 400°C would enhance such a diffusion process.

CoO-MoO₃- γ -Al₂O₃

As can be seen in Table 1 and Figs. 1 and 2 the total sulfur uptake of CoO-MoO₃-

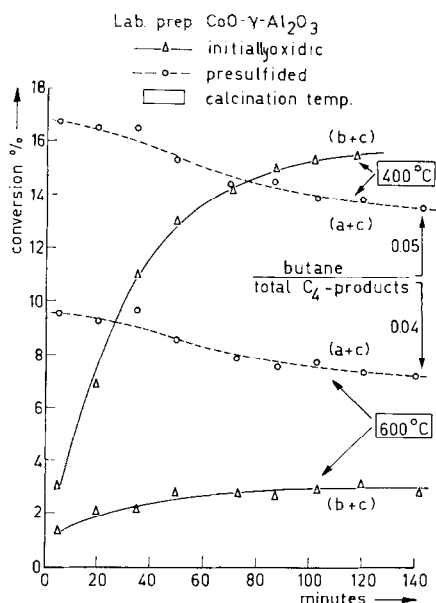


Fig. 5. Thiophene conversion as a function of time. Sequence of treatments added in parentheses. Conditions: (a) Sulfidation in $\text{H}_2\text{S}/\text{H}_2$: $50 \text{ cm}^3 \text{ min}^{-1}$ NTP $\text{H}_2\text{S}/\text{H}_2$, volume ratio 1/6, 400°C , 2 hr. (b) see Fig. 1. (c) see Fig. 1, 800 mg catalyst.

$\gamma\text{-Al}_2\text{O}_3$ is significantly higher than that of $\text{MoO}_3\text{-}\gamma\text{-Al}_2\text{O}_3$. If we assume that the addition of Co has not changed the S/Mo ratios from the values of the corresponding samples without Co, then the results indicate with high probability that 70% of the Co was converted into Co_9S_8 by sulfidation in $\text{H}_2\text{S}/\text{H}_2$ at 400°C for 2 hr. This is an appreciably higher fraction than found for the comparable $\text{CoO-}\gamma\text{-Al}_2\text{O}_3$ catalyst calcined at 600°C and sulfided at 400°C in $\text{H}_2\text{S}/\text{H}_2$ (Table 2, number 11).

The presence of Mo seems to facilitate the sulfurizability of the cobalt species. From Table 1 it can also be seen that the cobalt sulfide species present in $\text{CoO-MoO}_3\text{-}\gamma\text{-Al}_2\text{O}_3$ seem to be sensitive to hydrogen reduction at 400°C (decrease of S/Co ratio after treatment $a + b$) and to subsequent thiophene/ H_2 sulfiding (increase of S/Co ratio after treatment $a + b + c$). This is similar to the phenomena observed for the Mo in $\text{MoO}_3\text{-}\gamma\text{-Al}_2\text{O}_3$.

Sulfidation in thiophene/ H_2 for 2 hr at 400°C (treatment c) led to a relatively high

sulfur content. However, a large fraction of this sulfur could be removed by subsequent reduction in hydrogen, 2 hr at 400°C (treatment b). This might have been due to the formation of sulfur-containing hydrocarbon residues which can be removed by H_2 reduction.

In studying the sulfur uptake at 400°C as a function of time it was found (Fig. 1) that although it was faster in the first 5 min than in the case of $\text{MoO}_3\text{-}\gamma\text{-Al}_2\text{O}_3$ the attainment of optimum sulfiding with $\text{H}_2\text{S}/\text{H}_2$ (curve A') took longer overall. For the samples sulfided in thiophene/ H_2 this period was extended even further (curve D).

The temperature dependence of the sulfur uptake was increased to some extent by the presence of Co, as can be seen by a comparison of curves A and A' in Fig. 2. The results presented in Fig. 2, curve A', are in good agreement with the findings of Wakabayashi and Orito (19) from sulfiding experiments at atmospheric pressure.

The sulfur content appeared to be only weakly dependent on the partial pressure of H_2S . An increase from 1/24 to as much as 1/1 in the $\text{H}_2\text{S}/\text{H}_2$ ratio resulted in corresponding S/Mo ratios of 2.21 and 2.44 after 2 hr of sulfiding, a difference of only 10%. Wakabayashi and Orito (19) have found a somewhat stronger H_2S pressure dependency.

As can be seen in Fig. 4 the behavior of both the oxidic and sulfided $\text{CoO-MoO}_3\text{-}\gamma\text{-Al}_2\text{O}_3$ catalyst with respect to the effect of prerduction in H_2 is the same as observed for the corresponding $\text{MoO}_3\text{-}\gamma\text{-Al}_2\text{O}_3$ samples. Again this was confirmed by pulse experiments (18).

The results presented in Figs. 1 (curve A') and 3 suggest a fairly good correlation between the sulfur content and desulfurization activity of $\text{CoO-MoO}_3\text{-}\gamma\text{-Al}_2\text{O}_3$, as also demonstrated by Wakabayashi and Orito (19). However, for the series of catalysts sulfided on the one hand at different temperatures and on the other at various H_2S partial pressures, such smooth correlations

were not in evidence. Even so, for both series the samples with the lowest sulfur content appeared to be significantly less active than the other ones.

The Effect of Oxygen on CoO-MoO₃- γ -Al₂O₃ Sulfided in H₂S/H₂

The H₂S/H₂-sulfided CoO-MoO₃- γ -Al₂O₃ catalyst was found to be very sensitive to oxygen. Exposure of a fresh sample to air even at room temperature caused a vigorous exothermic reaction, an effect strongly dependent on the sample temperature at the time of contact. SO₂ was formed and color changes could be observed. When the catalyst had been sulfided with thiophene/H₂ these phenomena occurred to a much lesser extent. In order to obtain reproducible sulfur analyses the CoO-MoO₃- γ -Al₂O₃ samples had to be maintained in an oxygen-free atmosphere. For MoO₃- γ -Al₂O₃ this *in situ* sulfidation was not necessary. After the freshly sulfided sample had been in contact with pure O₂ or air near room temperature, its thiophene desulfurization activity measured after 2 hr under standard continuous flow conditions appeared to be surprisingly high, providing that not too much sulfur had been removed from the catalyst.

As can be seen in Fig. 6 the first air treatment (*d*) at 50°C during 0.5 hr led to an increase of thiophene conversion (at 2 hr run time) from 38 to 44%. In addition to some SO₂ formation noted during the first few minutes of air contact, a temperature increase of up to about 100°C was observed. After three sequential H₂S/H₂ and air treatments (*a* + *d*) a conversion level of 49% was found. The cumulative extent of the "oxygen effect" decreased with the number of air treatments.

From experiments with a CoO-(MoS₂ + γ -Al₂O₃) catalyst prepared according to method E described earlier (15), qualitatively similar results were obtained. However the oxygen effect on thiophene HDS measured after 2 hr run time was found to

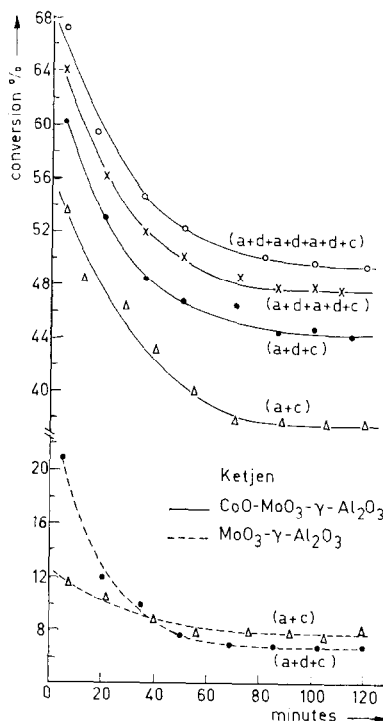


FIG. 6. Thiophene conversion as a function of run time after different pretreatments. Sequence of treatments added in parentheses. Conditions: (*a*) see Fig. 5. (*c*) see Fig. 1, 200 mg catalyst. (*d*) 50 cm³ min⁻¹ NTP air, 50°C 0.5 hr.

be much smaller and the stability was lower. For the Ketjen MoO₃- γ -Al₂O₃ the oxygen effect was very much limited in time (Fig. 6, approximately the first 20 min of the activity test) and therefore did not bring about increased activity under steady-state conditions.

DISCUSSION

From the observed sulfur content in various catalyst systems it can be most plausibly inferred that almost all the sulfur is chemically bonded to molybdenum and cobalt. This results most probably in the formation of MoS₂ and Co₉S₈. Other sulfur species, the formation of which during the sulfiding process cannot be excluded, are "aluminum sulfide" (12), H₂S adsorbed on aluminum hydroxyl groups (13), sulfur-containing hydrocarbon residues in the case of thiophene being the sulfidizing agent (see

Table 1, CoO–MoO₃– γ -Al₂O₃ treatments *c* and *a + c*) and even polymeric sulfur (11), for instance S₂²⁻ and S₃²⁻. However, these sulfur species would occur only to a small extent.

Analysis of the results obtained for the series of MoO₃– γ -Al₂O₃ catalysts indicates that part of the Mo present in the oxidic state cannot be sulfided at all, assuming that the formation of MoO_xS_y compounds can be excluded as stated by Gautherin and Colson (17) for the sulfidation of MoO₃. As will be demonstrated in another paper (20) this unsulfidable Mo is not very active in thiophene hydrodesulfurization, indicating again that it is not easily reducible. These Mo species might be the same as the ones mentioned by Ishii and Matsuura (21) and Sonnemans and Mars (22) as being barely removable on washing in ammonia. All these phenomena may be ascribed to the preferred formation of stable Al₂(MoO₄)₃-like structures at the surface of MoO₃– γ -Al₂O₃ samples with low Mo content (23–25). This surface "compound" contains molybdate ions with tetrahedrally oxygen coordinated Mo⁶⁺, strongly interacting with the support. A similar situation was described by Biloen and Pott (26) for WO₃– γ -Al₂O₃ samples where Al₂(WO₄)₃, which is isomorphous with Al₂(MoO₄)₃, was found to be present.

The high sulfur content (S/Mo > 2) analyzed for the laboratory prepared MoO₃– γ -Al₂O₃ catalyst with 16 wt% MoO₃, and the Ketjen MoO₃– γ -Al₂O₃ catalyst, sulfided at 500°C is in agreement with the findings of Hagenbach *et al.* (5) for unsupported MoS₂ and MoS₂–Co₉S₈ catalysts, viz, that there is a substantial amount of sulfur in excess of the stoichiometric content of the sulfides. The nature of this excess sulfur is not clear.

As demonstrated in Fig. 5 and Table 2 the sulfurizability of the Co present in the CoO– γ -Al₂O₃ system depends on both the calcination and sulfiding temperatures. This could be explained in terms of temperature

effect on the diffusion rate of Co²⁺ ions migrating from surface into subsurface layers of the γ -Al₂O₃ or in the reverse direction during the calcination and sulfiding stages, respectively (see also under CoO– γ -Al₂O₃ in Results).

The results obtained for the Ketjen CoO–MoO₃– γ -Al₂O₃ catalyst indicate that part of the Co is present as a sulfide, probably Co₉S₈, and that the remaining part is either incorporated as Co²⁺ in the carrier or intercalated as Co²⁺ in the MoS₂ phase, thus reducing the Mo ions to the trivalent state. In the two latter situations Co does not contribute to the sulfur uptake.

From the results presented here it can be seen that a large fraction of the sulfur taken up by MoO₃– γ -Al₂O₃ and CoO–MoO₃– γ -Al₂O₃ can be removed by reduction in H₂ at 400°C. In this respect it should be mentioned that according to the findings of Kalechits [discussion part of the paper by Farragher and Cossee (4)] the percentage of mobile sulfur, i.e., about 5% of the total sulfur, in unsupported WS₂ is very close to the calculated amount of surface sulfur. Since in alumina-supported catalysts the Mo is highly dispersed, it is reasonable to accept that 30% of the sulfur can be removed by reduction in H₂. However, one would expect this large sulfur removal to influence the catalytic properties of both MoO₃– γ -Al₂O₃ and CoO–MoO₃– γ -Al₂O₃, either positively by complete reduction of Mo⁴⁺ to Mo³⁺, or negatively by overreduction of the Mo³⁺ active centers. According to the results presented in Fig. 4 this is apparently not the case. Therefore it must be concluded that this mobile sulfur is not involved in the hydrodesulfurization process, or else the sulfur deficiency would have had to be largely made up during the first minutes of the activity test of the H₂-reduced, sulfided, samples. In Fig. 1 it is shown that sulfidation is indeed a fast process. It is worth noting, however, that the reactivity with H₂S of MoO₃– γ -Al₂O₃ and CoO–MoO₃– γ -Al₂O₃ is markedly higher

than that of unsupported MoO₃ (see Table 1). This can be regarded as strong evidence for the high degree of dispersion of MoO₃ on the support and thus for the monolayer model.

An "oxygen effect," in some respects similar to that described above has also been observed by Kolboe and Amberg (27) for unsupported MoS₂ in a continuous flow experiment with thiophene/H₂ at very low conversion (1.2%). However, their activity returned gradually to its initial level over a period of hours. The same might also be the case for the effect observed here on the CoO-(MoS₂ + γ -Al₂O₃) catalyst, while for a H₂S/H₂ sulfided MoO₃- γ -Al₂O₃ sample the effect is found to be of short duration (see Fig. 6). In contrast the oxygen effect measured for a CoO-MoO₃- γ -Al₂O₃ sample, prepared by double impregnation and sulfided in H₂S/H₂ seemed to be permanent under the test conditions applied. A possible explanation for this effect might be the breaking up of the MoS₂ crystals by (partial) reoxidation, resulting in an increase of Mo ions exposed. This situation may be stabilized during the resulfiding step, when there is enough Co available to enter the newly formed MoS₂ crystals by intercalation, preventing them in this way from growing to their original size. Another possibility is that the presence of oxygen ligands improves the specific catalytic properties of some Mo sites. However, this can only be a temporary effect because of the exchange of oxygen by sulfur during the desulfurization reaction. Moreover, it is limited to the surface of the MoS₂ phase because of the fact that formation of MoO₂S_y crystals is unlikely (17).

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