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The CoO–MoO_3–γ-Al_2O_3 Catalyst

VI. Sulfur Content Analysis and Hydrodesulfurization Activities

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The sulfur uptake of commercial and laboratory prepared catalysts of the type MoO_3–γ-Al_2O_3, CoO–γ-Al_2O_3 and CoO–MoO_3–γ-Al_2O_3 was studied at 400°C using H_2S/H_2 and thiophene/H_2 as sulfiding gases. The temperature, time, and H_2S partial pressure of sulfiding were varied, and the fraction of sulfur removable by H_2 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 MoS_2 and Co_9S_8 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 Co^{2+} ions from the bulk towards the surface of the γ-Al_2O_3 support during the sulfiding process. The hydrogenolysis activity was found to decrease with increasing sulfur content for the MoO_3–γ-Al_2O_3 catalyst, while on CoO–MoO_3–γ-Al_2O_3 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 MoS_2. It is promoted by "active" Co in octahedral coordination which could be neither reduced nor sulfided. Other Co-species assumed to be present were $CoAl_2O_4$, which was resistant to sulfiding, and Co_9S_8. 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–WS_2 and Co–MoS_2 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 MoS_2 and Co_9S_8 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*) MoO_3 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–MoO_3–Al_2O_3 led Kabe *et al.* (*7*) to describe the sulfided catalyst by the formula $CoS \cdot MoO_{1.5}S_{1.5}$–$Al_2O_3$. Free MoO_3 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–MoO_3–γ-Al_2O_3 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 MoS_2 and Co_9S_8 are present.

Recent X-ray photoelectron spectroscopy measurements on sulfided CoO–MoO_3–γ-Al_2O_3 and MoO_3–γ-Al_2O_3 by van Sint Fiet (*9*), who found a spectrum reminiscent of that of $Na_2S_2O_3$, suggest the presence of both S^{2+} and S^0. 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 Al_2O_3 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-Al_2O_3, MoO_3–γ-Al_2O_3 and CoO–MoO_3–γ-Al_2O_3 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 MoO_3–γ-Al_2O_3 type 120-3E and Ketjen CoO–MoO_3–γ-Al_2O_3 type 124-1.5E were used. The former contained 11.7 wt% MoO_3 and its specific surface area was 227 $m^2\ g^{-1}$. The CoO and MoO_3 contents of the latter catalyst were 4.1 and 12.4 wt%, respectively, and its specific surface area was 217 $m^2\ g^{-1}$. MoO_3 (Merck, purity $\geqslant 99.5\%$; surface area, 0.5 $m^2\ g^{-1}$) and MoS_2 (Schuchardt, purity $\geqslant 98.5\%$; surface area, 7.8 $m^2\ g^{-1}$) were also used for some experiments. In addition to this a series of MoO_3–γ-Al_2O_3 samples, with different MoO_3 content, and a series of CoO–γ-Al_2O_3 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 $m^2\ g^{-1}$) was used as support. The method of preparation was described before (*14*). MoO_3 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 H_2S (Matheson, C. P. grade) and purified H_2 (*15*), with a H_2S/H_2 volume ratio of 1/6 and a flow rate of either 50 or 175 $cm^3\ min^{-1}$ NTP. The following parameters were varied: sulfiding time, temperature, and the H_2S pressure. In some experiments the catalyst was reduced in pure H_2 (50 $cm^3\ min^{-1}$ NTP, at 400°C for 2 hr) in order to see how much sulfur could be removed. Thiophene (6 vol%) mixed with H_2 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 H_2S/H_2;
b. Reduction in pure H_2;
c. Sulfidation with C_4H_4S/H_2.
d. Oxidation with air.

Successive application of these (pre-)-treatments will be indicated by a + sign; for example, ($a + b$) means sulfidation in H_2S/H_2 followed by reduction in H_2.

All samples used for sulfur analysis were heated to the desired temperature in purified N_2 (*15*), sulfided, cooled quickly to room temperature in the sulfiding gas mixture, and flushed again with N_2 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 O_2 (10 $cm^3\ min^{-1}$ NTP) over a period of

2 hr. The SO_2/SO_3 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 H_2O_2 (3 vol%). In order to avoid leakage of SO_2 and SO_3 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 H_2O_2 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 MoS_2 (sample size 20–40 mg) and mixtures of 7–12 mg elemental sulfur and 200 mg pure grade γ-Al_2O_3 (Ketjen CK300). In both cases 98 ± 1.5% of the sulfur could be analyzed. All sulfur determinations were corrected for sulfur initially present in the oxidic samples probably as a sulfate impurity in the γ-Al_2O_3. All samples used for sulfur analysis except the Ketjen MoO_3–γ-Al_2O_3 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 $K\alpha$ and Co $K\alpha$ 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 H_2 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]	*b*	1.88		0.95
	b + *c*	1.96		0.98
MoO_3[d]	*a*	0.11		0.06
	a + *b* + *c*	0.25		0.13
Ketjen	*a*	2.04		1.02
MoO_3–γ-Al_2O_3[d]	*a* + *b*	1.23		0.62
	a + *b* + *c*	1.72		0.86
	b + *c*	1.36		0.68
Ketjen	*a*	2.44	0.63	0.95
CoO–MoO_3–γ-Al_2O_3	*a* + *b*	1.51	0.44	0.59
	a + *b* + *c*	2.07	0.55	0.81
	a + *c*	2.68		1.05
	c	2.51		0.98
	c + *b*	1.35		0.53

[a] (*a*) Sulfidation in H_2S/H_2: 175 $cm^3\ min^{-1}$ NTP H_2S/H_2, volume ratio $\frac{1}{6}$; 400°C, 2 hr. (*b*) Reduction in H_2: 50 $cm^3\ min^{-1}$ NTP H_2, 400°C, 2 hr. (*c*) Sulfidation in thiophene/H_2: 50 $cm^3\ min^{-1}$ NTP H_2 with 6 vol% thiophene, 400°C, 2 hr.

[b] Assuming the S/Mo ratio to be the same as for the corresponding MoO_3–γ-Al_2O_3 sample.

[c] Based on the formation of MoS_2 and Co_9S_8.

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

RESULTS

γ-Al_2O_3

The sulfur uptake of the alumina support alone was found to be 0.6 wt% after standard H_2S/H_2 treatment at 400°C. The color changed from white to light gray.

MoS_2

A small fraction of the sulfur could be removed from crystalline MoS_2 by hydrogen reduction for 2 hr at 400°C. Following the thiophene/H_2 treatment the sulfur content increased, while the S/Mo ratio remained only just below that for pure MoS_2.

MoO_3

Sulfidation of bulk MoO_3 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 H_2S/H_2 at temperatures between 300 and 500°C and that the products formed were MoS_2 and MoO_2, of which the latter reacts slowly with H_2S. This might explain the twofold increase in sulfur content after additional H_2 reduction followed by thiophene/H_2 treatment.

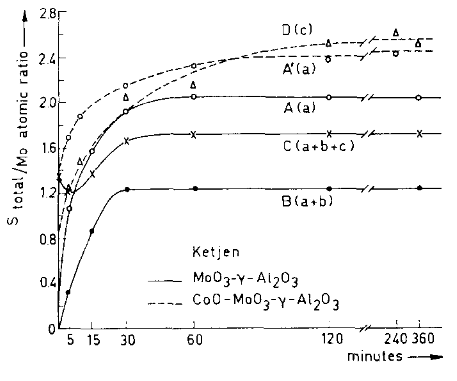

FIG. 1. Sulfur content as a function of sulfidation time. Sequence of treatments is added in parentheses. Conditions: (*a*) Sulfidation in H_2S/H_2: 175 cm^3 min^{-1} (MoO_3-γ-Al_2O_3) and 50 cm^3 min^{-1} (CoO-MoO_3-γ-Al_2O_3) NTP H_2S/H_2, volume ratio 1/6, 400°C. Length of treatment given by abscissa. (*b*) Reduction in H_2: 50 cm^3 min^{-1} NTP H_2, 400°C, 2 hr. (*c*) Sulfidation in thiophene/H_2: 50 cm^3 min^{-1} NTP H_2 with 6 vol% thiophene, 400°C, 2 hr (curve C) and *x* hr (curve D).

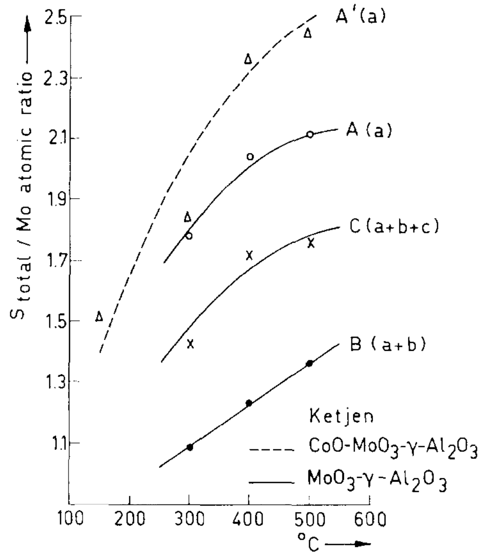

FIG. 2. Sulfur content as a function of sulfidation temperature. Sequence of treatments added in parentheses. Conditions: (*a*) Sulfidation in H_2S/H_2: see Fig. 1, 2 hr. (*b*) Reduction in H_2: see Fig. 1. (*c*) Sulfidation in thiophene/H_2: see Fig. 1, 2 hr.

MoO_3-γ-Al_2O_3

The results of the sulfidation of Ketjen MoO_3-γ-Al_2O_3 with H_2S/H_2 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 MoS_2 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 H_2S/H_2, volume ratio $\frac{1}{6}$, 2 hr.

[b] Balanced by the support.

even higher percentage of the sulfur was removed by H_2 reduction. After further treatment (*c*) with a 6 vol% mixture of thiophene in H_2 (2 hr at 400°C) the sulfur content of these presulfided and prereduced 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 MoO_3–γ-Al_2O_3 was successively reduced in H_2 and sulfided in thiophene/H_2 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 H_2S/H_2 during the same period. Whether this phenomenon is ascribable to the substantially lower partial pressure of the sulfur-containing agents during thiophene/H_2 treatment was checked by decreasing the H_2S/H_2 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 MoO_2 formed as a result of H_2 reduction of the free MoO_3 that could have been present in the MoO_3–γ-Al_2O_3 catalyst (*10*). The temperature effect on the sulfidation of MoO_3–γ-Al_2O_3 (H_2S/H_2 = 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 MoO_3–γ-Al_2O_3 catalysts are given in Table 2. A relatively low sulfur uptake was found for samples containing 2- and 4 wt% MoO_3, and from 6 up to 16 wt% a slight increase in S/Mo ratio was observed. For the highest MoO_3 content a S/Mo ratio significantly higher than that for MoS_2 was found.

As was demonstrated earlier (*15*) a substantial HDS activity decrease results from presulfiding the MoO_3–γ-Al_2O_3 catalyst (see also Fig. 4). In addition to this the influence of the time of H_2S/H_2 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 MoO_3–γ-Al_2O_3 sulfided at different H_2S concentrations at constant time and temperature (2 hr, 400°C); likewise for samples sulfided under standard conditions (H_2S/H_2 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 H_2 in order to activate the MoO_3-γ-Al_2O_3 catalyst, no matter whether presulfided 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-Al$_2$O$_3$

With respect to the sulfurizability of Co in CoO-γ-Al_2O_3 samples by means of H_2S/H_2 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 Co_9S_8. As demonstrated earlier (*15*) the sulfiding process of initially oxidic CoO-γ-Al_2O_3 can be "visualized" by measuring 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 Co^{2+} from the interior of the carrier to its surface. Presulfidation in H_2S/H_2 at 400°C would enhance such a diffusion process.

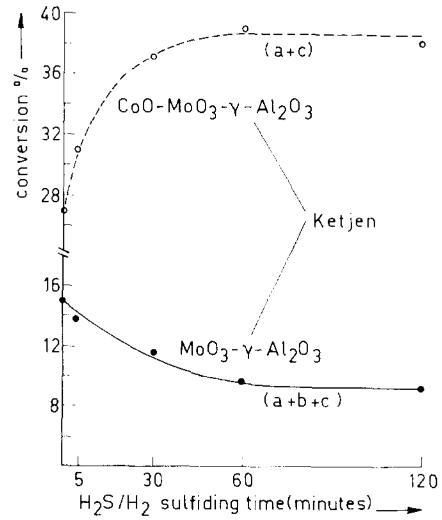

FIG. 3. Thiophene conversion after 2 hr run time vs sulfiding time in H_2S/H_2. Sequence of treatments added in parentheses. Conditions: see Fig. 1, 200 mg catalyst.

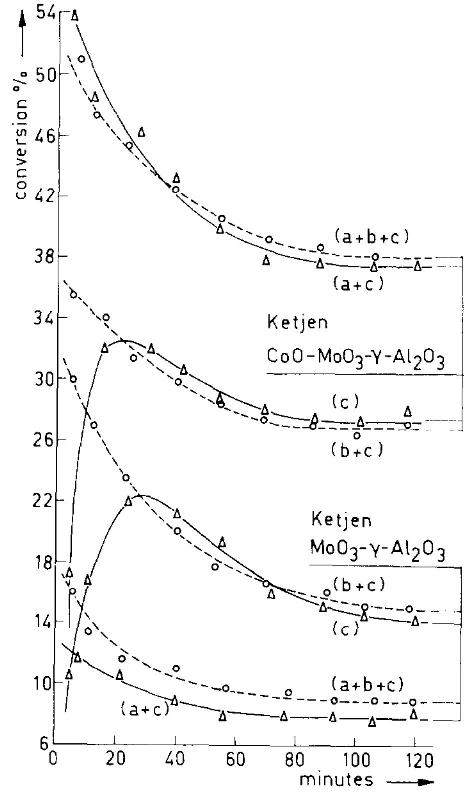

FIG. 4. Thiophene conversion as a function of run time after different treatments. Sequence of treatments added in parentheses. (*a*) Sulfidation in H_2S/H_2: 50 cm^3 min^{-1} NTP, volume ratio 1/6, 400°C, 2 hr over 200 mg catalyst. (*b*) Reduction in H_2: see Fig. 1. (*c*) Conversion of 6 vol% thiophene in H_2, 50 cm^3 min^{-1} NTP, 400°C, run time given by abscissa.

CoO-MoO$_3$-γ-Al$_2$O$_3$

As can be seen in Table 1 and Figs. 1 and 2 the total sulfur uptake of CoO-MoO_3-

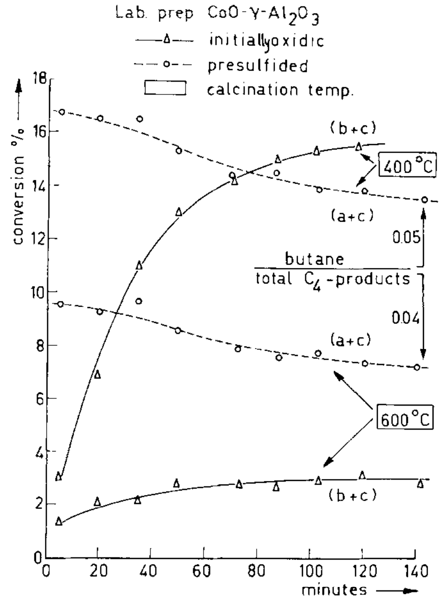

FIG. 5. Thiophene conversion as a function of time. Sequence of treatments added in parentheses. Conditions: (*a*) Sulfidation in H_2S/H_2: 50 cm^3 min^{-1} NTP H_2S/H_2, volume ratio 1/6, 400°C, 2 hr. (*b*) see Fig. 1. (*c*) see Fig. 1, 800 mg catalyst.

γ-Al_2O_3 is significantly higher than that of MoO_3–γ-Al_2O_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 H_2S/H_2 at 400°C for 2 hr. This is an appreciably higher fraction than found for the comparable CoO–γ-Al_2O_3 catalyst calcined at 600°C and sulfided at 400°C in H_2S/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 CoO–MoO_3–γ-Al_2O_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 MoO_3-γ-Al_2O_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 MoO_3–γ-Al_2O_3 the attainment of optimum sulfiding with H_2S/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 H_2S/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 CoO–MoO_3–γ-Al_2O_3 catalyst with respect to the effect of prereduction in H_2 is the same as observed for the corresponding MoO_3–γ-Al_2O_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 CoO–MoO_3–γ-Al_2O_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 $CoO–MoO_3–\gamma$-Al_2O_3 Sulfided in H_2S/H_2

The H_2S/H_2–sulfided $CoO–MoO_3–\gamma$-Al_2O_3 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. SO_2 was formed and color changes could be observed. When the catalyst had been sulfided with thiophene/H_2 these phenomena occurred to a much lesser extent. In order to obtain reproducible sulfur analyses the $CoO–MoO_3–\gamma$-Al_2O_3 samples had to be maintained in an oxygen-free atmosphere. For $MoO_3–\gamma$-Al_2O_3 this *in situ* sulfidation was not necessary. After the freshly sulfided sample had been in contact with pure O_2 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 SO_2 formation noted during the first few minutes of air contact, a temperature increase of up to about 100°C was observed. After three sequential H_2S/H_2 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 $CoO–(MoS_2 + \gamma$-$Al_2O_3)$ 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 be much smaller and the stability was lower. For the Ketjen $MoO_3–\gamma$-Al_2O_3 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.

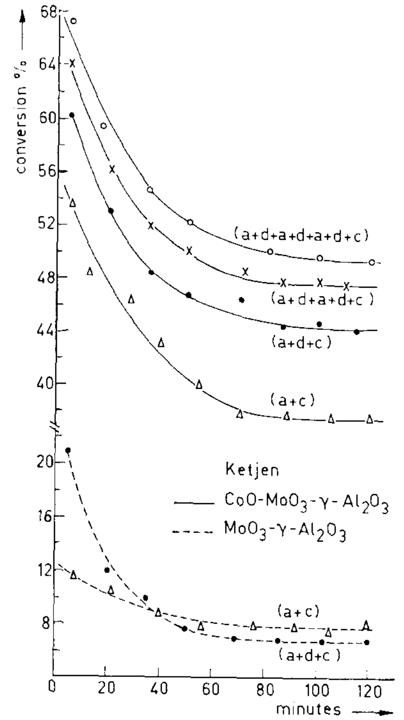

FIG. 6. Thiophene conversion as a function of run time after different pretreatments. Sequence of treatments added in parentheses. Conditions: (*a*) see Fig. 5. (*c*) see Fig. 1, 200 mg catalyst. (*d*) 50 cm^3 min^{-1} NTP air, 50°C 0.5 hr.

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 MoS_2 and Co_9S_8. Other sulfur species, the formation of which during the sulfiding process cannot be excluded, are "aluminum sulfide" (*12*), H_2S adsorbed on aluminum hydroxyl groups (*13*), sulfur-containing hyerocarbon residues in the case of thiophene being the sulfidizing agent (see

Table 1, CoO–MoO_3–γ-Al_2O_3 treatments *c* and *a* + *c*) and even polymeric sulfur (*11*), for instance S_2^{2-} and S_3^{2-}. However, these sulfur species would occur only to a small extent.

Analysis of the results obtained for the series of MoO_3–γ-Al_2O_3 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 MoO_3. 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 $Al_2(MoO_4)_3$-like structures at the surface of MoO_3–γ-Al_2O_3 samples with low Mo content (*23–25*). This surface "compound" contains molybdate ions with tetrahedrally oxygen coordinated Mo^{6+}, strongly interacting with the support. A similar situation was described by Biloen and Pott (*26*) for WO_3–γ-Al_2O_3 samples where $Al_2(WO_4)_3$, which is isomorphous with $Al_2(MoO_4)_3$, was found to be present.

The high sulfur content (S/Mo > 2) analyzed for the laboratory prepared MoO_3–γ-Al_2O_3 catalyst with 16 wt% MoO_3, and the Ketjen MoO_3–γ-Al_2O_3 catalyst, sulfided at 500°C is in agreement with the findings of Hagenbach *et al.* (*5*) for unsupported MoS_2 and MoS_2–Co_9S_8 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-Al_2O_3 system depends on both the calcination and sulfiding temperatures. This could be explained in terms of temperature effect on the diffusion rate of Co^{2+} ions migrating from surface into subsurface layers of the γ-Al_2O_3 or in the reverse direction during the calcination and sulfiding stages, respectively (see also under CoO–γ-Al_2O_3 in Results).

The results obtained for the Ketjen CoO–MoO_3–γ-Al_2O_3 catalyst indicate that part of the Co is present as a sulfide, probably Co_9S_8, and that the remaining part is either incorporated as Co^{2+} in the carrier or intercalated as Co^{2+} in the MoS_2 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 MoO_3–γ-Al_2O_3 and CoO–MoO_3–γ-Al_2O_3 can be removed by reduction in H_2 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 WS_2 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 H_2. However, one would expect this large sulfur removal to influence the catalytic properties of both MoO_3–γ-Al_2O_3 and CoO–MoO_3–γ-Al_2O_3, either positively by complete reduction of Mo^{4+} to Mo^{3+}, or negatively by overreduction of the Mo^{3+} 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 H_2-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 H_2S of MoO_3–γ-Al_2O_3 and CoO–MoO_3–γ-Al_2O_3 is markedly higher than that of unsupported MoO_3 (see Table 1). This can be regarded as strong evidence for the high degree of dispersion of MoO_3 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 MoS_2 in a continuous flow experiment with thiophene/H_2 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 $CoO-(MoS_2 + \gamma-Al_2O_3)$ catalyst, while for a H_2S/H_2 sulfided $MoO_3-\gamma-Al_2O_3$ sample the effect is found to be of short duration (see Fig. 6). In contrast the oxygen effect measured for a $CoO-MoO_3-\gamma-Al_2O_3$ sample, prepared by double impregnation and sulfided in H_2S/H_2 seemed to be permanent under the test conditions applied. A possible explanation for this effect might be the breaking up of the MoS_2 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 MoS_2 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 MoS_2 phase because of the fact that formation of MoO_xS_y crystals is unlikely (*17*).

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