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Citation for published version (APA):

Scheffer, B., Oers, van, E. M., Arnoldy, P., Beer, de, V. H. J., & Moulijn, J. A. (1986). Sulfidability and HDS activity of Co-Mo/Al₂O₃ catalysts. *Applied Catalysis*, 25(1), 303-311. [https://doi.org/10.1016/S0166-9834\(00\)81248-8](https://doi.org/10.1016/S0166-9834(00)81248-8)

DOI:

[10.1016/S0166-9834\(00\)81248-8](https://doi.org/10.1016/S0166-9834(00)81248-8)

Document status and date:

Published: 01/01/1986

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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SULFIDABILITY AND HDS ACTIVITY OF Co-Mo/Al₂O₃ CATALYSTS

B. Scheffer, E.M. van Oers¹, P. Arnoldy², V.H.J. de Beer¹ and J.A. Moulijn

Institute of Chemical Technology, University of Amsterdam

1) Lab. of Inorganic Chemistry and Catalysis, Eindhoven University of Technology

2) present address: Koninklijke/Shell Laboratory, Amsterdam

ABSTRACT

A series of Co-Mo/Al₂O₃ catalysts were investigated using Temperature-Programmed Sulfiding and HDS activity measurements. The effect of changing the cobalt content and the temperature of calcination on sulfidability, catalyst structure and thiophene HDS activity was studied in detail.

It is found that the effect on the HDS activity of higher temperatures of calcination depends on the Co content: at low Co content the activity drops sharply, for intermediate Co loadings the decline is not as pronounced, while at high Co contents an increase in HDS activity is found when the temperature of calcination is raised above 785 K.

The typical "synergistic" maximum observed when HDS activity is plotted versus Co content (or Co/Mo ratio) does not occur when catalysts are calcined above 785 K. Instead HDS activity rises monotonously with an increase in Co content.

At least five Co species can be present in sulfided Co-Mo/Al₂O₃ catalysts but HDS activity can mainly be attributed in all catalysts to one particular phase which contains sulfided Mo and Co. After calcination at 1125 K the activity is increased because the interaction between the active phase and the support has weakened.

INTRODUCTION

Co-Mo/Al₂O₃ catalysts are widely used commercially as hydrotreating catalysts and they continue to be the subject of much research. Knowledge of the influence of metal content and preparation conditions on the structure of Mo/Al₂O₃ [1-5] and Co/Al₂O₃ [5-8] catalysts, both in the sulfided state and as oxidic precursor, can contribute to a better understanding of the parameters which control the structure of Co-Mo/Al₂O₃ catalysts.

The importance of Co in sulfided Co-Mo/Al₂O₃ catalysts is demonstrated by the observation that Co can be almost as active a catalyst as Mo when it is not supported [13,29], or even more active on a carbon support, thus raising the question whether Co-Mo/Al₂O₃ catalysts should be considered as Co catalysts promoted, or supported, by Mo [6,14,27]. For the sulfided Co-Mo/Al₂O₃ catalyst the

CoMoS model [15] has been applied with much success. In this model a high HDS activity is ascribed to sites which consist of sulfided Co on the edges of MoS_2 crystallites ("CoMoS").

However, it is not quite clear how the composition of the oxidic catalysts and the preparation conditions affect the amounts and activities of sulfided species. The relative abundance of Co-containing species is very sensitive to these parameters [6,7,8,16] and since high HDS activity is believed to be connected to the presence of a sulfided Co species it is of importance to know how the composition and preparation of the oxidic Co-Mo/ Al_2O_3 catalyst affect the sulfidability of Co and the abundance of different Co species in the sulfided Co-Mo/ Al_2O_3 catalyst.

To exclude effects caused by the heterogeneity of the Mo monolayer [1,2] we have fixed the Mo content of the catalysts. The Co content and temperature of calcination were varied over a wide range. Since these same catalysts have been subjected to XRD, TPS [17], TPR and UV/VIS [18] studies, a detailed description of the relationships between the oxidic- and the sulfided catalysts, and HDS activity is possible.

EXPERIMENTAL

Catalyst Preparation

Catalysts were prepared by pore volume impregnation of a Ketjen High-Purity $\gamma\text{-Al}_2\text{O}_3$, followed by drying and calcination. Mo was added first, and the catalyst was dried and calcined before addition of Co. The preparation of the catalysts is described in more detail elsewhere [17,18]. Co loadings in Co-Mo catalysts were 1.6%, 3.5% and 8.1% (g CoO/g Al_2O_3). Catalysts will be denoted by the number of metal atoms/nm² Al_2O_3 ; e.g. 1.6% CoO-9.9% $\text{MoO}_3/\text{Al}_2\text{O}_3$ as Co(.8)Mo(2.5).

Temperature-Programmed Sulfiding

More information on the Temperature-Programmed Sulfiding (TPS) technique is given elsewhere [3,17]. At the beginning of the TPS experiment the sulfiding mixture (3.3% H_2S , 28.1% H_2 and 68.6% Ar) is led through the reactor at ca 295 K and the composition of the gas leaving the reactor is monitored. When no more sulfiding or adsorption takes place at 295 K the temperature of the reactor is raised continuously by 10 K/min up to ca 1270 K.

HDS Activity

Thiophene HDS was carried out in a flow microreactor operating at atmospheric pressure. Details of the equipment are given elsewhere [19]. The catalysts were sulfided in situ in a 10 mol% $\text{H}_2\text{S}/\text{H}_2$ mixture (flow rate ca $45 \cdot 10^{-6}$ mol/s). The

temperature was raised to 675 K and maintained for 2 h. TPS results show that no more sulfiding takes place after this time. Then a 6.2 mol% thiophene/H₂ mixture was fed into the reactor at a total rate of 37.10^{-6} mol/s. After 2 h the HDS rate per gram of catalyst and Turn Over Number (TON, defined per mol Co present) were calculated from thiophene conversion assuming the HDS reaction is first order in thiophene. When reactant and product inhibition were taken into account [20,21] essentially the same values were obtained.

RESULTS

Calcination at 1125 K of a Co(1.6)Mo(2.5) catalyst leads to a drop in surface area of more than a factor 4. In a separate experiment calcination of the support at high temperature did not cause such drastic effects.

FIGURE 1 TPS patterns of Co(.8)Mo(2.5)/Al₂O₃ catalysts calcined at 895 K (a) and 1125 K (b).

FIGURE 2 Amount of sulfided Co (at/nm²) in Co-Mo/Al₂O₃ catalysts. ● Co(.8)Mo(2.5), □ Co(1.6)Mo(2.5), ▼ Co(4.1)Mo(2.5).

Temperature-Programmed Sulfiding

The TPS patterns of some Co-Mo/Al₂O₃ catalysts are shown in figure 1. For clarity only the H₂S pressures are plotted. The general features of these TPS patterns are the same as those reported previously in more detail [17]:

- H_2S uptake at room temperature. The colour change from various shades of blue to brown-black indicates that besides physical adsorption of H_2S also sulfiding takes place for most catalysts. Only the catalysts calcined at 1125 K remained blue at room temperature.
- H_2S uptake and H_2O production up to ca 500 K caused by sulfiding of Mo and Co species via O-S exchange. It has been shown that the effect of calcining on Mo sulfiding is small [17], however H_2S consumption is smaller for catalysts calcined at 1125 K because of loss of MoO_3 during calcination
- H_2S production and H_2 consumption at ca 500 K because of hydrogenation of S. This is formed by the rupture of bonds between sulfur and Mo in oxy-sulfides [3]
- H_2S uptake and H_2O production in a broad pattern from 500 K to ca 800 K caused by further sulfiding of mainly Mo
- H_2S uptake and H_2O production at ca 1000 K from sulfiding of subsurface Co (CoAl_2O_4 -like) species [7]
- H_2S production and H_2 consumption at ca 1200 K pointing to reduction of Co sulfides

Co sulfidability will be defined in this context as the fraction of Co which is sulfidable below 675 K in a TPS experiment. Since both some Mo- and Co species are sulfidable below 675 K Co sulfiding can not be observed independently from Mo sulfiding in this temperature range. It has been found that for $\text{Co/Al}_2\text{O}_3$ catalysts with different contents of Co and temperatures of calcination the total consumption of H_2S in a TPS experiment up to 1270 K corresponds to a ratio of .8 $\text{H}_2\text{S/Co}$ [7]. Assuming the same ratio holds for Co in $\text{Co-Mo/Al}_2\text{O}_3$ catalysts sulfided up to 1270 K, Co sulfidability is determined by subtracting the amount of H_2S used for sulfiding of CoAl_2O_4 -like species at ca 1000 K in a TPS experiment from the H_2S consumption which is calculated for complete sulfiding of Co.

It can be seen in figure 2 that essentially all Co is sulfidable after calcination at 785 K. Co sulfidability drops after calcination at 995 K and is still smaller after calcination at 1125 K. After calcination at higher temperatures sulfidabilities converge to a value of ca .4 at/nm^2 for all Co contents.

HDS Activity

Mo/Al₂O₃. The effect of a rise of the temperature of calcination up to 995 K is a small loss of activity whereas activity drops sharply after calcination at 1125 K (figure 3b). However, when loss of MoO_3 during calcination is taken into account, the activity per mole Mo present is higher.

Co/Al₂O₃. The catalysts with the lower loading of Co exhibit the highest turn-over numbers. A detailed account of the activity of $\text{Co/Al}_2\text{O}_3$ catalysts will be given elsewhere [22].

Co-Mo/Al₂O₃. Figure 3a shows clearly the promoting effect of Co: the Co-Mo catalysts are up to 6 times more active than the Mo catalysts, and 10 times more active than the Co catalysts. A typical synergistic curve is obtained which displays a maximum when the activity is plotted versus the Co content (or Co/Mo ratio) for the Co-Mo/Al₂O₃ catalysts calcined at 785 K. However, the curves are quite different for the catalysts calcined at higher temperatures: no maximum in activity is found. Instead the activity rises monotonously with Co content.

FIGURE 3a. Rate of thiophene HDS (mmol/g.h) of Co-Mo/Al₂O₃ catalysts calcined at 785 K (▲), 895 K (●), 995 K (△) and 1125 K (○).

FIGURE 3b. HDS turn-over numbers (mmol/mol.s) of Co-Mo/Al₂O₃ catalysts. ▲Co(.8)Mo(2.5), ●Co(1.6)Mo(2.5), ◆Co(4.1)Mo(2.5), ▽Mo(2.5), ◇Co(.8), ○Co(3.7).

Figure 3b shows that there is a sharp drop in activity of the Co(.8)Mo(2.5) catalysts as the temperature of calcination is raised from 785 to 895 K. A further decrease occurs at 995 K, but an increase is seen at 1125 K with respect to calcination at 995 K. For the Co(1.6)Mo(2.5) catalysts the trend is the same, but not as pronounced. The highest loading (Co(4.1)Mo(2.5)) catalysts display an increase in activity when the temperature of calcination is raised from 785 to 895 K. The activity becomes fairly constant at higher calcination temperatures. The order of activity per gram catalyst is reversed upon calcination above 895 K, where the highest loading catalyst becomes more active than the lowest loading catalyst.

DISCUSSION

Mo/Al₂O₃

Loss of MoO₃ is found by TPR [18] for catalysts calcined at 1125 K. Surprisingly, mainly the monolayer Mo species ("MoI") are lost while it is expected that the amount of multilayer MoO₃ ("MoII") decreases more, since it has a weaker interaction with the support. However, this is explained by the loss of surface area which necessarily brings about a reduction of the amount of the highly disperse MoI species [18].

While TPS results indicate that sulfiding is not greatly affected, figure 3b shows that the TON is somewhat smaller at calcination temperatures of 895 and 995 K, as is also found by others [23]. However, the TON actually increases after calcination at 1125 K, which suggests that the MoII species is more active than the MoI species. A higher dispersion of the sulfided MoII species is not likely in view of the smaller surface area. It is concluded that the increased activity is caused by a weaker interaction with the support of the sulfided species, as is confirmed by the finding that Mo catalysts are more active when supported on a more inert support e.g. carbon [24,27]. Moreover, it can be concluded that support interactions found in the oxidic catalyst may persist in the sulfided phase for Mo/Al₂O₃ catalysts.

Co/Al₂O₃

The TON decreases at higher temperatures of calcination due to formation of non-sulfidable CoAl₂O₄ species [16]. The activities observed indicate that Co can be present as an HDS active surface phase different from inactive CoAl₂O₄-like species, as has also been found by TPR [6], TPS [7] and NO adsorption [9].

TPS results indicate that not Co₉S₈ but another sulfided Co species is present [7], as was proposed earlier [4]. We suggest that a CoS-like phase is present, and also Co₉S₈ at higher loadings. This is analogous to the oxidic Co/Al₂O₃ catalysts where a CoO surface phase is found and the thermodynamically more stable Co₃O₄ is formed at higher loadings [6, 7].

Co-Mo/Al₂O₃

It has recently been shown by TPR that the reducibility of Co is greatly affected by the presence of Mo [18]. Also from other techniques the conclusion that an interaction or even an interaction phase ("CoMoO") exists in oxidic Co-Mo/Al₂O₃ catalysts [4,5,9,10,11,12,23,25,28] has been drawn. This "CoMoO" phase might well be the precursor for the CoMoS phase in the CoMoS model [8,9]. Moreover, TPS has shown that active Co-Mo/Al₂O₃ catalysts are well sulfidable at low temperatures, where, of course, large structural rearrangements during sulfiding are unlikely [17].

It is reported that the activity of a Co-Mo/Al₂O₃ catalyst depends on the calcination temperature [25]. Co/Al₂O₃ catalysts are very sensitive to this parameter [5,6]. The results presented here show that the effect of a change of the calcination temperature depends strongly on the Co content. It can be seen that as the temperature of calcination is raised there is a sharp drop in activity for catalysts with a low Co content, and a slight rise in activity at high Co content. At intermediate Co loadings (such as used in [25]) the effect of raising the temperature of calcination is not so strong.

From figure 3a it is apparent that the well known synergistic curve, with a maximum activity at a fixed Co content, is only obtained for the lowest temperature of calcination. All other curves rise monotonously.

FIGURE 4 Turn-over numbers for sulfided Co (mmol/mol.s) in Co-Mo/Al₂O₃ catalysts calcined at 785 K (○), at 895 or 995 K (●) and at 1125 K (■).

To investigate whether these results can be interpreted in terms of the amount of a single active phase a quantitative approach on the basis of turn-over numbers is chosen. The CoMoS phase is many times more active than other phases present in the sulfided catalyst [21], so all activity can be ascribed to a single phase, which facilitates the interpretation of activity data. In figure 4 the TON' expressed per mole sulfided Co is plotted versus the amount of sulfided Co as determined from TPS experiments. Three regions of activity can be discerned:

- high activity for catalysts calcined at 1125 K
- moderate activity for catalysts calcined at 785-995 K, except for the catalysts with the highest Co loadings calcined at 785 K
- low activity for the Co(1.6)Mo and Co(4.1)Mo catalysts calcined at 785 K

The TON' values of the typical Co-Mo/Al₂O₃ catalysts lie close together. This shows that indeed over a wide range of Co content and temperature of calcination the catalytic activity is caused by a single phase which contains sulfided Co.

The low TON' values which underlie the low activity of the 785 K calcined catalysts, and thereby produce the typical synergistic curve, suggest that there is a

difference in structure with all other catalysts. The factor most likely responsible for this difference is the occurrence of Co_3O_4 crystallites, which are known to be present at higher Co contents in the oxidic catalysts [18]. These are absent because of formation of CoAl_2O_4 -like species at higher temperatures of calcination [5,6,18]. Co_3O_4 sulfides into Co_9S_8 [4,7,8] with a low activity, which makes the TON' lower. However, it is not immediately clear why this should actually lower the HDS activity per gram of catalyst in the case of the catalyst with the highest Co loading (figure 3a). Blocking of HDS sites is not likely since the active phase is more highly dispersed than the Co_9S_8 crystallites. A more plausible explanation is that the amount of active phase is smaller because either the amount of oxidic precursor is smaller [8], or oxidic Co species sulfide into inactive Co_9S_8 , instead of a more active phase. Nucleation is here proposed to be the most difficult step in the formation of Co_3O_4 and Co_9S_8 crystallites, but once nuclei are formed, growth is rapid at the expense of the active Co phase or precursor phase (e.g. CoMoS or CoMoO).

The high TON' obtained for Co-Mo/ Al_2O_3 catalysts calcined at 1125 K shows that structural changes have taken place in the oxidic catalysts. For Mo/ Al_2O_3 catalysts also a higher TON was observed after calcination at 1125 K (this work) and the same interpretation seems applicable for the Co-Mo/ Al_2O_3 catalysts: in accordance with earlier suggestions [18], BET results indicate a lower surface area. This causes a decrease in the amount of Mo in strong interaction with the support, both in the oxidic- and the sulfided state. Because the support interaction of the remaining active phase is weaker, it is a more active species. This is in accordance with the result that on a more inert carrier (carbon) a higher TON is obtained for a Co-Mo/C catalyst (TON = ca 55 mmol thiophene/mol Co.s, calculated from data published by Duchet et al. [24]. TPS shows that even after calcination at high temperature sulfidable Mo- and Co species are present [17]. It is therefore concluded that the active species is structurally similar to the phase obtained at lower temperatures of calcination. I.e. the activity of the CoMoS phase depends on the interaction with the support, as corroborated by findings of Co-Mo/C [24].

It was found that after sulfiding at higher temperatures a "CoMoS II" phase is formed with a higher TON for HDS [26]. We can not yet prove that CoMoS II is identical with the phase formed after calcination at 1125 K, but similar structural characteristics have been proposed. Furthermore, the higher activity of CoMoS II is also attributed to a weaker active phase-support interaction [26].

Further research is necessary to make full use of the higher TON obtained after more rigorous pretreatments, in order to produce catalysts with higher rates of HDS per gram catalyst.

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