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The $CoO–MoO_3/\gamma$-Al_2O_3 Catalyst

VIII. Analysis of Sulfided Co- and Mo-Containing Catalysts by *in Situ* Reflectance Spectroscopy[1]

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Ultraviolet and visible reflectance spectra were recorded *in situ* for oxidic and sulfided Mo- and/or Co-containing catalysts supported on alumina and silica. In addition, reflectance spectra of certain selected Mo and Co oxides and sulfides have been included for reference purposes. The results show the formation of MoS_2 and Co_9S_8 in supported systems as a result of sulfidation in H_2S/H_2. The effect of oxygen chemisorption on sulfided $CoO–MoO_3/\gamma$-Al_2O_3 and the effect of Co introduction on the MoS_2 phase are discussed.

INTRODUCTION

Reflectance spectroscopy in the uv and visible spectral regions has been widely applied to investigate the structure of the oxidic (precursory) state of hydrodesulfurization (HDS) catalyst systems like $CoO–MoO_3/\gamma$-Al_2O_3. In contrast, few reflectance spectra for the corresponding sulfided catalysts are reported. It is reasonable, however, to expect that application of this analytical technique on sulfided samples may contribute to a better and more reliable description of supported HDS catalysts in their state of actual operation, viz., the sulfided state.

Armour *et al.* (*1a*), and Mitchell and Trifirò (*1b*) have reported a study of both oxidic and sulfided $CoO–MoO_3/\gamma$-Al_2O_3 (taken from an HDS test reactor) catalyst systems by means of magnetic measurements, infrared transmittance spectroscopy, and diffuse reflectance spectroscopy in the ultraviolet and visible spectral regions. These authors came to the conclusion that, during sulfiding, the sulfide adds to the MoO_4 tetrahedra, present in the fresh oxidic catalyst and linked to CoO_6 octahedra. According to these investigators, not more than one or two oxide ions, probably those bridging Mo and Co, are replaced by sulfide. Although no evidence was found for discrete Mo- and Co-sulfides, from the results based on the analysis of the total sulfur content (atomic ratios were Co:Mo:S = 1:1.77:4.18), the presence of MoS_2 and Co_9S_8 cannot be excluded.

It is known that freshly prepared MoS_2 (*2*) as well as freshly sulfided MoO_3/γ-Al_2O_3 and $CoO–MoO_3/\gamma$-Al_2O_3 (*3*) show some reactivity with respect to oxygen, even at room temperature. This interaction with oxygen was found to cause at least a temporary increase in HDS activity.

Since this "oxygen chemisorption effect" is not primarily relevant to a study of HDS catalysts in actual operation, we measured uv and visible spectra of sulfided catalysts of the type $CoO–MoO_3/(\gamma$-Al_2O_3 or $SiO_2)$

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[1] Part V is Ref. (*5*), Part VI is Ref. (*3*) and Part VII is Ref. (*6*) of the present paper.

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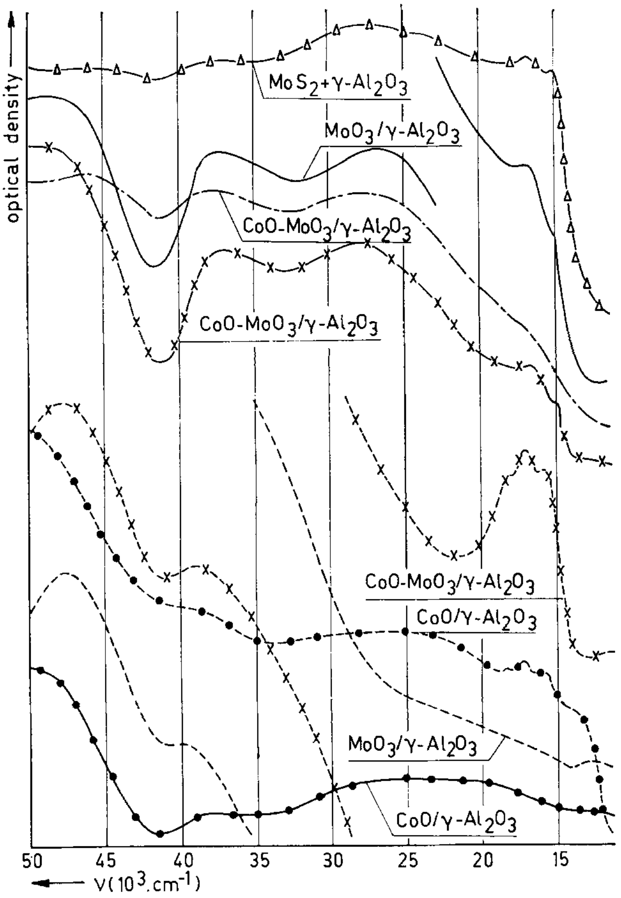

FIG. 1. *In situ* reflectance spectra for sulfided (——) and oxidic (– – –) alumina-supported catalysts. (— — — —), A sulfided sample exposed to air at 30°C. The ordinate is an arbitrary optical density scale. In order to reduce overlap, some spectra are presented in two sections by displacement of the optical density scale. Supported catalysts prepared via mechanical mixing are indicated by a plus sign; all others were prepared via impregnation methods.

using an *in situ* reflectance cell. Application of this cell enabled us to avoid interaction of the catalyst samples with oxygen during pretreatment and spectroscopic analysis.

EXPERIMENTAL

A Unicam ultraviolet spectrometer SP 800D, fitted with an expansion attachment SP 850 and a diffuse reflectance unit SP 890, was used in combination with an *in situ* reflectance cell (sample holder) designed by Groeneveld (*4a, b*). The cell was fitted with a quartz glass window. All spectra presented in Figs. 1, 2, and 3 were recorded at room temperature in the range of 11,500–52,500 cm^{-1}, using the same expansion factor. Powdered MgO (Merck, calcined 15 hr at 900°C), γ-Al_2O_3 (Ketjen, high purity, CK-300-1.5E), and SiO_2 (Ketjen, fluid silica, F-2) were used as reference compounds.

All samples were ground in a ball mill before use. The powdered samples were introduced in the reflectance cell and were sulfided *in situ*. The sulfiding conditions were: 2 hr at "atmospheric" pressure and 400°C in a 50-cm^3 min^{-1} H_2S/H_2 flow (v/v, 1/6), followed by cooling to room temperature in the sulfiding gas. After this sulfiding procedure was completed, the samples were pressed against the cell window, and the spectra were recorded.

The γ-Al_2O_3- and SiO_2-supported samples were prepared according to methods described before (*5*, *6*). Sulfides and oxides of Co and/or Mo, used as model compounds, were prepared by published methods [MoS_3 (*7*, *8*), Co_9S_8 (*9*), Co_3O_4 (*9*), $CoMoO_4$ (*10*)] or were obtained commercially [MoS_2 (Schuchardt), MoO_3 (Merck)] and were characterized by X-ray diffraction analysis.

RESULTS

The reflectance spectra of γ-Al_2O_3-supported HDS catalyst precursors, oxidic MoO_3/γ-Al_2O_3, CoO/γ-Al_2O_3, and CoO–MoO_3/γ-Al_2O_3 containing 12 wt% MoO_3 and/or 4 wt% CoO, are given in Fig. 1. In the light of earlier work by several investigators (*11–13*), these spectra can be explained in terms of Mo^{6+} and Co^{2+} tetrahedrally coordinated by oxygen and $Co^{3+}O_6$ octahedra (Co_3O_4). The corresponding band or band shoulder positions are: 39,000 and 47,000 cm^{-1} (Mo^{6+} tetrahedra); 16,000, 17,200, and 18,200 cm^{-1} (Co^{2+} tetrahedra); 13,500, 25,000, and 40,000 cm^{-1} (Co_3O_4, see also Fig. 2).

After *in situ* sulfiding in H_2S/H_2, the spectra changed remarkably. Sulfided MoO_3/γ-Al_2O_3 showed a strong increase in absorption in the 15,000- to 35,000-cm^{-1} region with relatively broad bands at 27,000, 37,000, and 48,500 cm^{-1} and a band at 16,700 cm^{-1} with a shoulder at 15,200 cm^{-1}. Sulfided CoO–MoO_3/γ-Al_2O_3 yielded an almost identical spectrum. The only differences were that the 27,000-cm^{-1} band shifted slightly to a higher wavenumber, and both the 16,700- and 15,200-cm^{-1} bands became somewhat better defined, especially the one at the lower wavenumber. In addition, the absorption around 12,500 cm^{-1} was found to be stronger. This observation might indicate the presence of Co_9S_8 (see Fig. 2). The spectra recorded for sulfided MoO_3/γ-Al_2O_3 and CoO–MoO_3/γ-Al_2O_3 were very similar to the spectrum obtained from a mechanical mixture of 10 wt% MoS_2 and γ-Al_2O_3 (MoS_2 + γ-Al_2O_3) and were essentially the same as the spectrum of pure MoS_2 (see Fig. 2). As can be seen in Figs. 1 and 2, sulfidation of CoO/γ-Al_2O_3 (4 wt% CoO) led to the disappearance or fading of the characteristic $Co^{2+}O_4$ tetrahedra and Co_3O_4 bands in favor of those ascribable to Co_9S_8.

The effect of oxygen chemisorption on sulfided samples (occurring when samples are not sulfided *in situ*) is demonstrated in Fig. 1 for the CoO–MoO_3/γ-Al_2O_3 catalyst sulfided in H_2S/H_2 and subsequently exposed to air at 30°C. As reported earlier (*3*), the first observation was a rapid temperature increase up to about 100°C. The spectrum obtained was very similar to that reported by Armour *et al.* (*1a*) and Mitchell and Trifirò (*1b*). It showed features of the spectra recorded for both the oxidic and fresh sulfided CoO–MoO_3/γ-Al_2O_3 sample. This phenomenon indicates the formation of Mo species with mixed O and S ligands as a result of the "oxygen effect."

The spectroscopic data of the SiO_2-supported catalysts are given in Fig. 3. As has been already discussed (*3*), in the spectrum of oxidic MoO_3/SiO_2 (12 wt% MoO_3), in comparison with the alumina-supported sample, there is a significant broadening of the band around 38,500 cm^{-1} toward lower wavenumbers and a weak shoulder around 33,000 cm^{-1}. This indicates the presence of $Mo^{6+}O_6$ octahedra, resulting from the formation of "free" MoO_3 during preparation (*12*). The spectrum of oxidic CoO–MoO_3/SiO_2 (4 wt% CoO) can be characterized by bands ascribable to β-$CoMoO_4$ (17,500 and 19,500 cm^{-1}), Co_3O_4 (increased absorption around 25,000 cm^{-1} and the band shoulder at 13,500 cm^{-1}), and probably some "free" MoO_3.

Sulfided MoO_3/SiO_2 gave almost the same spectroscopic results as the corre-

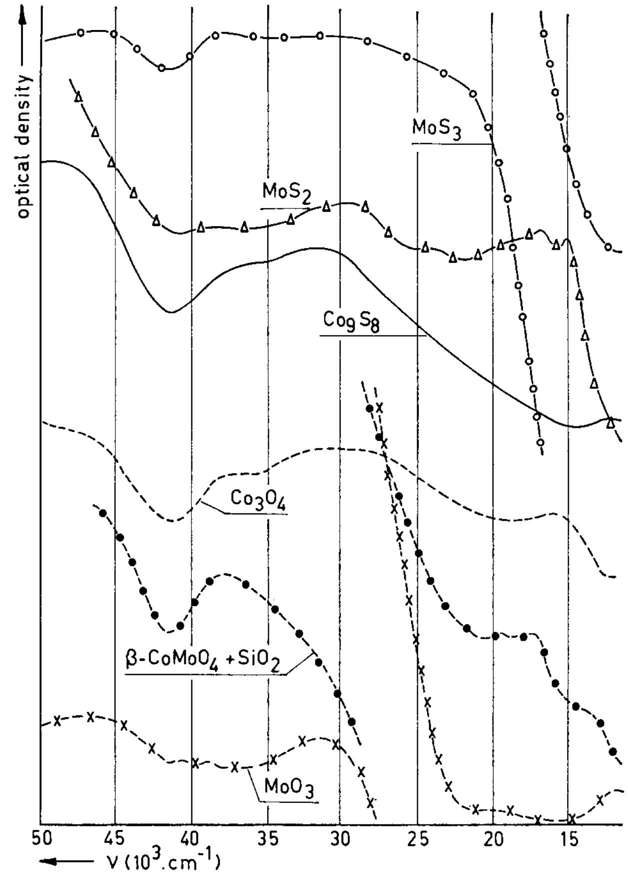

FIG. 2. *In situ* reflectance spectra for sulfidic (——) and oxidic (– – –) reference compounds. For ordinate and catalyst preparation, see Fig. 1.

sponding alumina-supported sample. The only difference was that the band at 16,700 cm^{-1} and the band shoulder at 15,200 cm^{-1} were less pronounced. The spectrum obtained after H_2S/H_2 treatment of the oxidic $CoO–MoO_3/SiO_2$ catalyst, which was prepared according to the standard double-impregnation method (calcination temperature, 450°C) (*5*, *6*), showed mainly MoS_2 bands. The relatively strong absorption around 12,500 cm^{-1}, in comparison with the spectra of oxidic $CoO–MoO_3/SiO_2$ and sulfided MoO_3/SiO_2, indicates the presence of a cobalt sulfide, probably Co_9S_8.

As can be seen in Fig. 3, the strongest evidence for the formation of MoS_2 was obtained for the $CoO–MoO_3/SiO_2$ (A) sample prepared according to method A (*5*), i.e., impregnation of a calcined (450°C) and sulfided MoO_3/SiO_2 with a cobalt nitrate solution, drying, and additional sulfidation at 400°C (*3*). The formation of Co_9S_8, however, remained questionable.

DISCUSSION

In excellent agreement with the results reported earlier on thiophene HDS activity measurements (*5*, *6*, *14*), sulfur content analysis (*3*), and X-ray diffraction (*6*), the present *in situ* uv and visible reflectance data strongly support the significance of the intercalation (*15*) and/or synergetic (*16*) models as a viable description of the structure of HDS catalysts in actual operation. These catalyst models are based on the presence and chemical functions of sulfide phases, respectively, Co/Ni intercalated MoS_2/WS_2 or Co_9S_8/Ni_3S_2 mixed with MoS_2/WS_2.

Although there are good reasons to assume that the precursor oxidic state on the γ-Al_2O_3 support (extensive interaction of the support and MoO_3, viz., "monolayer" formation) differs essentially from that on the SiO_2 support ("free" MoO_3 which sulfides relatively slowly), the results obtained under our standard conditions of sulfidation present strong evidence for the exclusive formation of MoS_2. In addition to this, the spectra in both cases show the formation of Co_9S_8 when Co is present.

Based on results obtained from thiophene conversion measurements (*6*) and sulfur analysis (*3*), it is reasonable to expect that at least part of the $Mo^{6+}O_4$ and $Co^{2+}O_4$ tetrahedra present in the oxidic γ-Al_2O_3-supported catalyst precursor should be preserved during H_2S/H_2 treatment. However, no conclusive information was hitherto obtained from reflectance spectra. The reason for this is very probably the masking of the bands originating from these oxidic species by the spectra of the sulfides formed.

With respect to the influence of Co on formation of the MoS_2 phase, an interesting phenomenon was observed. Addition of Co to MoO_3/γ-Al_2O_3 caused an increase in the

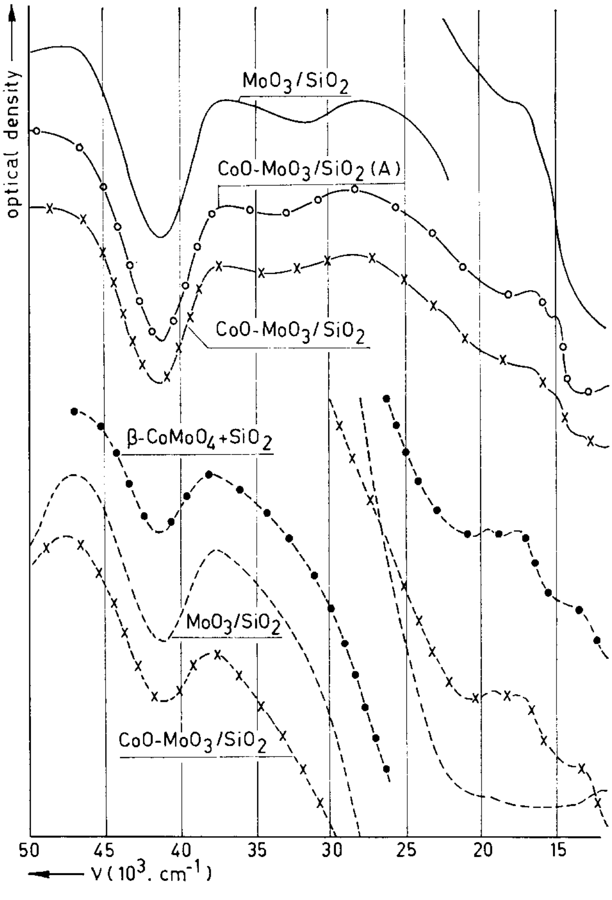

FIG. 3. *In situ* reflectance spectra for sulfided (——) and oxidic (- - - -) silica-supported catalysts. For ordinate and catalyst preparation, see Fig. 1. Sample (A) was twice sulfided, viz., after both the Mo- and Co-impregnation steps.

intensity and sharpness of the two typical MoS_2 bands at 16,700 and 15,200 cm^{-1}. This effect was even more pronounced when Co was added to a sulfided MoO_3/SiO_2 sample [$CoO-MoO_3/SiO_2$(A)]. These observations can be explained by the assumption that Co facilitates the growth of MoS_2 crystals, resulting in a less amorphous sulfide phase. For unsupported systems, this phenomenon has already been described by other investigators. Hagenbach *et al.* (*16*) found that Co facilitates better crystallization of MoS_2 while Voorhoeve and Stuiver (*15*) observed that Ni improves the crystallinity of the WS_2 structure, especially the stacking of the prismatic layers. An essentially different interpretation of the phenomena observed with respect to the effect of Co introduction on the MoS_2 phase was reported earlier (*3*, *5*). This was based on results obtained from thiophene HDS activity measurements on γ-Al_2O_3-supported catalysts prepared in different ways (*5*) and on a sulfided $CoO-MoO_3/\gamma$-Al_2O_3 sample that had been subjected to the "oxygen effect" (*3*). These measurements led us to the assumption that Co, via an intercalation process, was able to break up already formed MoS_2 crystals. In this way, Co could inhibit the formation of a well-defined crystalline MoS_2 phase. Support for this interpretation was found in the work of Furimsky and Amberg (*17*) who observed, for crystalline MoS_2 catalysts impregnated with Co, a fivefold increase in surface area in the Co/Co + Mo composition region 0–0.65 (MoS_2 + Co_9S_8 systems). For the percentage of thiophene conversion, a fivefold increase also was measured, while the intrinsic activity or surface concentration of active sites changed little. In order to explain more precisely the influence of Co/Ni (at various concentrations) on the MoS_2/WS_2 phases (prepared in different ways), further research appears to be necessary.

The general conclusion that can be drawn from the uv and visible reflectance spectroscopy work presented here is that, in order to obtain significant information about the structure of HDS catalysts in actual operation (sulfided state), the application of an in *situ* technique (i.e., exclusion of oxygen) is necessary. When standard (not *in situ*) reflectance techniques are used, the general structural pattern will be dominated by Mo and Co species, with mixed oxygen and sulfur ligands, which are not relevant to HDS catalyst systems in actual operation.

In agreement with our earlier studies (*3*, *5*, *6*), the foregoing work leads to the conclusion that the specific catalytic HDS function is primarily related to the MoS_2 phase and has no basic relationship with the nature of the carrier. Accordingly, the technique of *in situ* reflectance spectroscopy fails to reveal an essential influence of the carrier materials used in this investigation, viz., γ-Al_2O_3 and SiO_2.

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