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The CoO–MoO$_3$/γ-Al$_2$O$_3$ Catalyst

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

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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$_3$S$_4$ in supported systems as a result of sulfidation in H$_2$S/H$_2$. The effect of oxygen chemisorption on sulfided CoO–MoO$_3$/γ-Al$_2$O$_3$ 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$_3$/γ-Al$_2$O$_3$. 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$_3$/γ-Al$_2$O$_3$ (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$_3$S$_4$ cannot be excluded.

It is known that freshly prepared MoS$_2$ (2) as well as freshly sulfided MoO$_3$/γ-Al$_2$O$_3$ and CoO–MoO$_3$/γ-Al$_2$O$_3$ (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$_3$/γ-Al$_2$O$_3$ or SiO$_2$
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-Al₂O₃ (Ketjen, high purity, CK-300-1.5E), and SiO₂ (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-cm³ min⁻¹ H₂S/H₂ flow (v/v, 1/6), followed by cooling to room tempera-
ture in the sulfiding gas. After this sulfiding procedure was completed, the samples were pressed against the cell window, and the spectra were recorded.

The \( \gamma-Al_2O_3 \) - 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 \([MoS_2 (7, 8), CoS_8 (9), Co_2O_4 (9), CoMoO_4 (10)]\) or were obtained commercially \([MoS_2 (Schuchardt), MoO_3 (Merck)]\) and were characterized by X-ray diffraction analysis.

RESULTS

The reflectance spectra of \( \gamma-Al_2O_3 \)-supported HDS catalyst precursors, oxidic \( MoO_3/\gamma-Al_2O_3 \), \( CoO/\gamma-Al_2O_3 \), and \( CoO-MoO_3/\gamma-Al_2O_3 \) 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\(^{-1}\) \((Mo^{6+} \text{ tetrahedra})\); 16,000, 17,200, and 18,200 cm\(^{-1}\) \((Co^{2+} \text{ tetrahedra})\); 13,500, 25,000, and 40,000 cm\(^{-1}\) \((Co_3O_4\), see also Fig. 2).

After \textit{in situ} sulfiding in \( H_2S/H_2 \), the spectra changed remarkably. Sulfided \( MoO_3/\gamma-Al_2O_3 \) 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 \( CoO-MoO_3/\gamma-Al_2O_3 \) 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 \( CoS_8 \) (see Fig. 2). The spectra recorded for sulfided \( MoO_3/\gamma-Al_2O_3 \) and \( CoO-MoO_3/\gamma-Al_2O_3 \) were very similar to the spectrum obtained from a mechanical mixture of 10 wt% \( MoO_3 \) and \( Al_2O_3 \) \((MoS_2 + \gamma-Al_2O_3)\) 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 \( CoO/\gamma-Al_2O_3 \) \((4 \text{ wt}% \ CoO)\) 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 \( CoS_8 \).

The effect of oxygen chemisorption on sulfided samples (occurring when samples are not sulfided \textit{in situ}) is demonstrated in Fig. 1 for the \( CoO-MoO_3/\gamma-Al_2O_3 \) 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 \textit{et al.} \((1a)\) and Mitchell and Trifirò \((1b)\). It showed features of the spectra recorded for both the oxidic and fresh sulfided \( CoO-MoO_3/\gamma-Al_2O_3 \) 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 \((5)\), in the spectrum of oxidic \( MoO_3/SiO_2 \) \((12 \text{ wt}% \ MoO_3)\), 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 \( CoO-MoO_3/SiO_2 \) \((4 \text{ wt}% \ CoO)\) can be characterized by bands ascribable to \( \beta-CoMoO_4 \) \((17,500 \text{ and } 19,500 \text{ cm}^{-1})\), \( CoO_4 \) (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-
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$_2$S/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$_9$S$_8$.

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$_9$S$_8$, 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 CoS$_2$/NiS$_2$ mixed with MoS$_2$/WS$_2$.

Although there are good reasons to assume that the precursor oxidic state on the $\gamma$-Al$_2$O$_3$ 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$_9$S$_8$ when Co is present.

Based on results obtained from thiophene conversion measurements ($\delta$) and sulfur analysis ($\beta$), 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 $\gamma$-Al$_2$O$_3$-supported catalyst precursor should be preserved during H$_2$S/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$_3$/\(\gamma\)-Al$_2$O$_3$ caused an increase in the

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**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 $\gamma$-Al$_2$O$_3$-supported catalysts prepared in different ways (5) and on a sulfided CoO–MoO$_3$/γ-Al$_2$O$_3$ 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$_x$S$_y$ 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 oxygens 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., $\gamma$-Al$_2$O$_3$ and SiO$_2$.

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