The Effect of Sulfiding on the Structure of a Cobalt–Molybdenum–Alumina Hydrodesulfurization Catalyst

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Ultraviolet, visible, and infrared spectra and magnetic properties of a fresh and sulfided cobalt–molybdenum–alumina hydrodesulfurization catalyst are reported. The fresh and sulfided catalyst both contain oxomolybdenum(VI) species. Properties of the fresh catalyst are consistent with the presence of linked [MoO$_4$] tetrahedra and [CoO$_6$] octahedra. Spectroscopic changes on sulfiding indicate that sulfide *adds* to [MoO$_4$] and that no more than one or two oxide ions, probably bridging between molybdenum and cobalt, are replaced by sulfide. There is no evidence for discrete sulfides, e.g., MoS$_2$ and Co$_9$S$_8$, in the sulfided catalyst. Aerial reoxidation of the sulfided catalyst gives a product identical with the fresh catalyst.

INTRODUCTION

Cobalt–molybdenum–alumina (CMA) hydrodesulfurization (HDS) catalysts contain oxospecies of cobalt(II) and of molybdenum(VI) on a carrier of γ-alumina (1). In use, some sulfiding of the catalyst occurs and it is possible that sulfided species are responsible for the catalysis. Speculation about the presence of well-defined sulfides of cobalt and molybdenum in the sulfided catalyst has been based on assumptions about compounds in the fresh catalyst and their known reactions with hydrogen sulfide (1). Cobalt aluminate, CoAl$_2$O$_4$, does not react with hydrogen sulfide, and cobalt molybdate, with 2% hydrogen sulfide in hydrogen at 400°C, gives Co$_9$S$_8$ and MoOS (which is probably a mixture of MoO$_2$ and MoS$_2$). Formation of Co$_9$S$_8$ is in agreement with equilibrium data on the reduction of cobalt sulfides in the presence of a few percent of hydrogen sulfide (2). Richardson (3) considered that the true catalyst was MoS$_2$ promoted with "active cobalt"

which was cobalt in octahedral coordination neither reduced nor sulfided. Unsupported molybdenum and cobalt sulfides catalyze hydrogenations and hydrogenolyses but have lower activity than supported CMA catalysts (4). In an earlier paper we described preliminary work on sulfiding the catalyst and model CMA systems (5). We concluded that cobalt and molybdenum were only partly sulfided. In this paper we describe work directed towards determining the nature of the molybdenum and cobalt species in a sulfided catalyst which was taken from a commercial test reactor while still at maximum activity.

EXPERIMENTAL METHODS

The sulfided catalyst was derived from the fresh (i.e., unsulfided) catalyst studied previously (6) and was taken from a test reactor while still at maximum HDS activity. The composition was: C, 5.8; Co, 2.6; Mo, 7.5; S, 5.9; SO$_4^{2-}$, 0.6; Al$_2$O$_3$, 77.6%. Oxides and sulfides of cobalt and

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molybdenum were prepared by published methods or obtained commercially and were characterized by chemical analysis and by their X-ray diffraction patterns.

Ultraviolet and visible reflectance spectra of powdered solids were recorded on a Unicam SP 700 spectrophotometer against magnesium oxide, lithium fluoride and γ-alumina. Infrared spectra of catalyst samples in potassium bromide pellets were recorded on a Unicam SP 200 spectrophotometer. The effect of absorbance due to γ-alumina was eliminated by placing in the reference beam of the spectrophotometer a potassium bromide pellet containing sufficient γ-alumina (determined by trial and error) to compensate for γ-alumina in the catalyst. The pellets contained ca. 2 mg catalyst or γ-alumina and 130 mg potassium bromide. Magnetic susceptibilities were measured on a Newport Instruments Ltd. variable temperature Gouy balance system calibrated with CoHg(SCN)₄.

RESULTS AND DISCUSSION

Infrared Spectra

Infrared spectra (650–1000 cm⁻¹) are shown in Fig. 1. Absorption in this region is due to metal–oxygen vibrations of γ-alumina and oxomolybdenum species; molybdenum and cobalt sulfides and cobalt oxides do not exhibit absorption in this region. When the absorption due to alumina bands in this region was eliminated by placing in the reference beam of the spectrophotometer a pellet containing alumina, bands were observed in the fresh catalyst at 960 cm⁻¹ and ca. 725 cm⁻¹ and in the sulfided catalyst at 945 cm⁻¹. These bands are assigned to Mo–O vibrations (7). The positions of the band maxima (±5 cm⁻¹) depended on the concentration of alumina in the reference pellet: as the concentration increased the bands appeared to shift slightly to higher wavenumbers. So, although oxomolybdenum(VI) species are clearly present in the fresh and sulfided catalysts, it is difficult to deduce the nature of the species from the band positions. The catalyst apparently does not contain appreciable quantities of molyb-
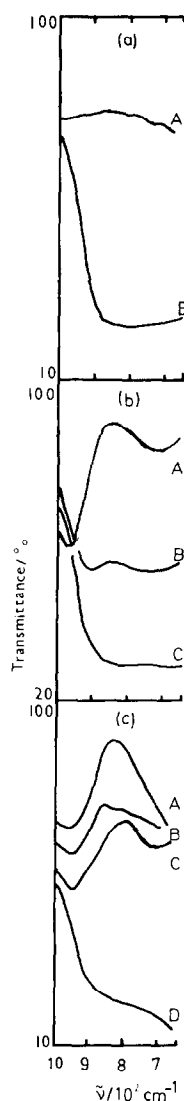

FIG. 1. Infrared spectra (KBr discs). (a) γ-Alumina: (A) after compensation in the reference disc; (B) before compensation. (b) Fresh catalyst: (A) after compensation; (B) partially compensated; (C) not compensated. (c) Sulfided catalyst: (A) sulfided; (B) partially reoxidized (1 hr, 500°C); (C) fully reoxidized (2 hr, 500°C) (all compensated); (D) sulfided catalyst not compensated.

denum trioxide (no band at >960 cm⁻¹) or ionic molybdate (MoO₄²⁻: no band at ca. 800 cm⁻¹). Bands in the region 900–950 cm⁻¹ indicate either tetrahedral or octahedral oxomolybdenum(VI) species bridged through oxide to a second metal

with one or two terminal oxygens on the molybdenum. The spectrum is different from that of cobalt molybdate (bands in cm^{-1} at 940s, 850m, 775m) and resembles the spectra of copper and zinc molybdates (bands in cm^{-1} at 950s, 725s and 750s, respectively) which have structures based on linked $[MoO_6]$ octahedra and $[MoO_4]$ tetrahedra (8).

In the spectrum of the sulfided catalyst there was only one strong band (945 cm^{-1}) whereas for the fresh catalyst there were two bands (960 and 725 cm^{-1}). Thus sulfiding affects the molybdate spectrum. This shows that sulfur interacts with molybdenum. However, the shift of the main band to lower wavenumbers cannot be explained by replacement of ligand oxide by sulfide since this would be expected to increase the wavenumber of the molybdenum–oxygen vibration (cf. MoO_4^{2-}, 810; $MoO_2S_2^{2-}$, 834; $MoOS_3^{2-}$, 859 cm^{-1}) (9). We attribute the shift to an increase in the coordination number of molybdenum caused by addition of sulfide to a tetrahedral oxomolybdenum(VI) species. The absence from the sulfided catalyst of the 725 cm^{-1} band which, in the fresh catalyst, is assigned to vibrations of a Co–O–Mo system (10), suggests that sulfide may also replace this bridging oxide. [Compare our earlier suggestion that, in reduction of iron(III) molybdate catalysts, bridging oxide and not terminal oxide, is first removed (11).] Progressive reoxidation of the sulfided catalyst by heating in air at 500°C gradually restores the ir spectrum of the fresh catalyst (see Fig. 1).

Electronic Spectra

Diffuse reflectance spectra of the catalysts and cobalt and molybdenum sulfides are shown in Fig. 2. For the fresh catalyst absorption from 35,000 to 20,000 cm^{-1} was weak; the bands are assigned to crystal-field transitions of cobalt(II). For the sulfided catalyst there was a broad, strong band with absorption maxima at ca. 38,000, 31,000, and 25,000 cm^{-1} and a long tail to ca. 10,000 cm^{-1} covering crystal-field bands. Coke in the sulfided catalyst, as shown by measurement of the reflectance spectrum
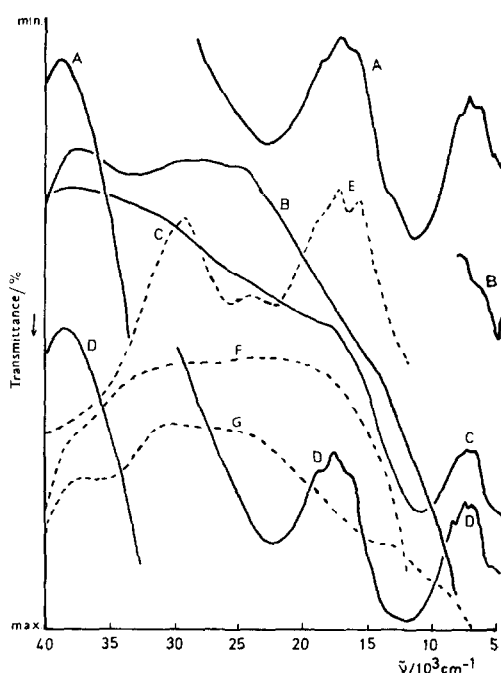

FIG. 2. Ultraviolet and visible reflectance spectra relative to MgO. (—) (A) Fresh catalyst; (B) sulfided catalyst; (C) sulfided catalyst partially reoxidized (1 hr, 500°C); and (D) fully reoxidized (2 hr, 500°C). (– –) (E) MoS_2; (F) MoS_3; (G) Co_9S_8. Transmittance increases downwards on each spectrum. For spectra B, C, E, F, and G transmittance at the uv absorption maxima was ca. 20%. For spectra A, B, and D transmittance at the visible maxima was ca. 70% and at the uv maxima ca. 20%. Breaks in the curves indicate a change of instrument setting.

of a mixture of γ-alumina with 6% charcoal, contributes to the high background absorption which is responsible for the poor resolution of the peaks. The shift of the absorption bands to lower wavenumbers in the sulfided catalyst indicates that the absorption is due to metal–sulfur charge-transfer transitions (12); thus sulfur is coordinated to molybdenum and/or cobalt. The spectrum is different from the spectra of MoS_3 (which absorbs less strongly above 35,000 cm^{-1} and more strongly below 25,000 cm^{-1} even when diluted with alumina), MoS_2 (much weaker absorption above 30,000 cm^{-1} and bands between 15,000 and 20,000 cm^{-1}) and cobalt sulfide (weaker absorption above 30,000 cm^{-1} and stronger

below 25,000 cm⁻¹). The only indication of the possible presence of MoS_2 is a shoulder at ca. 15,000 cm⁻¹. The band at ca. 37,000 cm⁻¹ in the sulfided catalyst is assigned (5) to charge-transfer absorption of oxo-species of molybdenum and/or cobalt since it is observed in the unsulfided catalyst but not in cobalt and molybdenum sulfides.

When the sulfided catalyst was oxidized in a stream of air at 500°C the low wavenumber peaks of cobalt(II) first appeared and ultimately a spectrum identical with that of the fresh catalyst was obtained. This observation is of considerable significance in terms of the possible cobalt and molybdenum sulfide species in the sulfided catalyst. If the sulfided catalyst contained molybdenum disulfide and cobalt sulfides, e.g., Co_9S_8, as has been suggested (4), aerial oxidation would give MoO_3 and Co_3O_4. There is no evidence from the uv and ir spectra for these compounds as distinct phases in the oxidized catalyst.

Magnetic Susceptibilities

The magnetic susceptibility results, which are given in more detail elsewhere (5), showed that μ'_{eff} evaluated from the slope of the linear Curie–Weiss plot over the temperature range 90 to 350 K was 4.79 μ_B for the fresh catalyst and 4.25 μ_B for the sulfided catalyst, with Weiss constants of -7 and 22 K, respectively. The magnetic properties of the sulfided catalyst did not correspond with those of any discrete sulfide of molybdenum or cobalt (13, 14). Our conclusion from these results is that in the sulfided catalyst cobalt(II) is only partially sulfided or not sulfided at all since a much lower magnetic moment than 4.25 μ_B would have resulted from complete sulfiding to a cobalt sulfide and molybdenum sulfides.

Composition of the Sulfided Catalyst

From the analysis of the sulfided catalyst atomic ratios are Co:Mo:S = 1:1.77: 4.18. Complete sulfiding of cobalt and molybdenum to Co_9S_8 and MoS_2 would require 4.43 S. Thus the sulfur content is less than required for complete sulfiding. Moreover sulfur analyses will not differentiate

between MoS_2 and oxosulfide species MoO_xS_2. It is possible also that some sulfur is associated with the carrier.

CONCLUSIONS

We have shown previously (6) that molybdenum in the catalyst is in tetrahedral coordination by oxide ions and cobalt in tetrahedral and octahedral coordination and that these structures are imposed by the alumina carrier. We have suggested that it is misleading to describe the fresh catalyst in terms of well-defined compounds of cobalt and molybdenum, e.g., cobalt aluminate and molybdate (6). Equally we consider it misleading to describe the sulfided catalyst in this way since its magnetic and spectroscopic properties do not correspond with those of any well-defined sulfide of cobalt or molybdenum. We are, in fact, concerned with the specific properties of cobalt(II) and molybdenum(VI) in the environment provided by the γ-alumina carrier. During the hydrodesulfurization process, cobalt and molybdenum in the catalyst are partially sulfided. This is true also for model systems of cobalt and molybdenum on γ-alumina.

On the basis of our results we suggest that the catalyst contains linked molybdenum and cobalt tetrahedra and octahedra. Molybdenum in tetrahedral coordination would be more accessible to the reactant gas than in octahedral coordination because sulfur could be accommodated by expansion of the coordination sphere or by formation of a bond with three-coordinated molybdenum at an anion vacancy, i.e., via addition of the reactant species to molybdenum rather than substitution of oxide ions. We have also shown (6) that molybdenum and cobalt are associated in the catalyst.

Finally we query the assumption (15) that anion vacancies arise by removal of "independently" bonded [terminal (7)] oxide. We have shown (12) that in reactions of binuclear oxomolybdenum(V) complexes with hydrogen sulfide bridging oxide is replaced in preference to terminal oxide and our present results show that

terminal oxides are present in the sulfided catalyst. We consider that, during the HDS reaction, cobalt and molybdenum remain bonded to the alumina carrier via oxide bridges, that sulfiding of the catalyst occurs through addition of sulfide to [MoO_4] species, and that no more than one or two exposed oxide ions, probably bridging between cobalt and molybdenum, are replaced by sulfides. Although the sulfided catalyst may contain some MoS_2 the bulk of the molybdenum is present as an oxosulfide of molybdenum(VI). This is supported by the X-ray photoelectron (ESCA) spectrum of the sulfided catalyst (16) which shows the presence of molybdenum(VI) and a small amount of a reduced molybdenum species.

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