JOURNAL OF CATALYSIS 64, 235–237 (1980)

Infrared Study of Sulfided Co–Mo/Al_2O_3 Catalysts: The Nature of Surface Hydroxyl Groups

The preparation of Co–Mo/Al_2O_3 hydrodesulfurization catalysts usually involves several steps. First the active metals are deposited on the alumina by means of impregnation. The impregnated catalyst is then dried and calcined. The active state of the catalyst is, however, first attained by sulfiding the calcined precursor. This sulfidation can either be carried out in a H_2/H_2S mixture or directly in the reaction mixture. Hence, it is the sulfided state of the catalyst which is of most interest catalytically. Nevertheless, despite the vast number of spectroscopic studies aimed at elucidating the structure of this type of catalyst, only a few have dealt with studies of the sulfided state of the catalyst under *in situ* conditions. Specifically, infrared spectroscopy has been widely used to characterize different states of Co–Mo/Al_2O_3 type catalysts (e.g., (*1–6*)); however, to our knowledge no *in situ* infrared studies have been published dealing with the surface structure of sulfided catalysts. The present note, preceding a series of studies of sulfided catalysts to be reported later, reports an infrared study of sulfided Co/Al_2O_3, Mo/Al_2O_3, and Co–Mo/Al_2O_3 catalysts with respect to the nature of the surface hydroxyl groups. Some implications these results may have on the interpretation of the structure of sulfided catalysts will be considered. The many different structural models which have been proposed for such catalyst systems have recently been reviewed by Massoth (*7*).

The catalysts studied were prepared by depositing the active materials onto η-Al_2O_3 (surface area, 220 m^2/g) via impregnation followed by drying and calcining at 773 K in air for 2 hr. The Co/Al_2O_3 sample contained 2.0 wt% Co, whereas the Co–Mo/Al_2O_3 sample contained 1.8 wt% Co and 8.4 wt% Mo. The two Mo/Al_2O_3 samples contained 3.0 and 8.0 wt% Mo. The samples were studied in the form of thin self-supporting wafers placed in an *in situ* ir cell which allows samples to be treated either in high vacuum or in a flowing gas mixture at temperatures between 300 and 770 K. Infrared spectra were recorded with a Perkin–Elmer 180 grating spectrometer. The reference beam was appropriately attenuated to give reasonably good signal levels. Sulfiding of samples was carried out at 653 K for 2 hr in a flowing gas mixture consisting of 1.7% H_2S in H_2. After sulfiding, the H_2S gas mixture was removed by flushing the cell with purified N_2 at the same temperature for 16 hr. For comparison, spectra were also obtained for the corresponding catalysts in the oxidic state and which had been evacuated at 773 K for 16 hr to remove weakly bound water and hydroxyl groups. Oxidic samples evacuated at 653 K for 16 hr result in essentially the same spectra as those evacuated at 773 K except for slightly greater band intensity.

The ir spectra in Fig. 1 show the hydroxyl group region of the alumina support and the Co/Al_2O_3, Mo/Al_2O_3, and Co–Mo/Al_2O_3 catalysts both in their initial oxidic state and after sulfiding. The close similarity of the spectra obtained for the Co/Al_2O_3 (Fig. 1b) and Al_2O_3 support (Fig. 1a) shows that the surface hydroxyl structure is not affected to any appreciable extent by the presence of cobalt ions. On the other hand, the addition of Mo to Al_2O_3 (Figs. 1c and d) is accompanied by the

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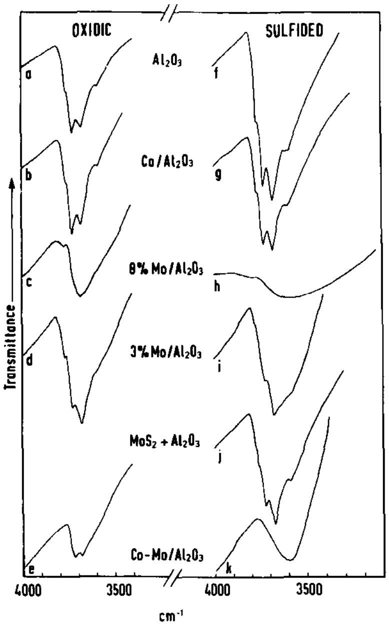

FIG. 1. Infrared spectra of the hydroxyl group region of Al_2O_3 support, Co/Al_2O_3, Mo/Al_2O_3, and Co–Mo/Al_2O_3 catalysts in the oxidic and sulfided states. A spectrum of a physical mixture of MoS_2 and Al_2O_3 in the sulfided state is also included.

disappearance of hydroxyl groups. For the Mo/Al_2O_3 catalyst with the low Mo loading (3% Mo/Al_2O_3 (Fig. 1d)) some well-resolved hydroxyl groups still remain whereas for the 8% Mo/Al_2O_3 catalyst (Fig. 1c) only the high-frequency OH band is discernable beside the broad band centered around 3680 cm^{-1}. The spectrum of the oxidic catalyst containing both Co and Mo (Fig. 1e) shows, in addition to the band at 3680 cm^{-1}, another band resolved at 3720 cm^{-1}. These findings as well as the infrared results reported by previous investigators (*5*, *6*) agree with the generally accepted view that Mo in the oxidic state is very well dispersed on the Al_2O_3 surface. This state of Mo, formed by interaction of Mo with surface hydroxyl groups, is often referred as the "molybdate monolayer" (*7*). The effect of Co on the hydroxyl groups in Co–Mo/Al_2O_3 is unclear but it does appear to cause a more selective interaction of Mo with the OH groups of alumina. In view of the results on the Co/Al_2O_3 catalyst, which show no influence on the surface OH groups, the results on the Co–Mo/Al_2O_3 catalysts may be taken as evidence for interaction of some of the Co with Mo in these catalysts.

It is interesting that after sulfiding the spectra of the Al_2O_3 support (Fig. 1f) and Co/Al_2O_3 catalyst (Fig. 1g) remain essentially unchanged. The reversal of the relative intensity of the bands at 3728 and 3678 cm^{-1} upon sulfiding as compared to the oxidic state can possibly be attributed to some selective exchange of OH by SH (*8*) thus lowering the intensity of the high-frequency band more than the low-frequency band. The similarity of these two spectra again verifies that cobalt ions do not interfere with the OH groups of the alumina. The spectrum of the sulfided Mo/Al_2O_3 catalyst (Fig. 1h) shows no distinct OH groups but a very broad band centered around 3580 cm^{-1} extending downward to 3200 cm^{-1}. The significant broadening and downward frequency shift suggest more extensive hydrogen bonding as a result of the sulfiding process. When the Co–Mo/Al_2O_3 catalyst is sulfided, the spectrum (Fig. 1k) also shows a somewhat broadened band centered around 3600 cm^{-1}. However, the broadening is less than in the case of Mo/Al_2O_3. Thus when cobalt is present together with Mo in sulfided catalyst, it appears to have some effects on the structure of the Mo/Al_2O_3 catalyst which could be attributed to a decrease in the extent of hydrogen bonding.

It may be argued that the broadening and the absence of distinct hydroxyl groups observed in the sulfided 8% Mo/Al_2O_3 catalyst are not due to the effects of sulfiding, but could be attributed to the high absorbance of the sulfided catalyst masking the structure of surface species. To test this possibility, a sulfided sample consisting of a physical mixture of 8 wt% MoS_2 (surface area, 38 m^2/g) with the Al_2O_3 support was examined. The ir spectrum (Fig. 1j) is similar to that of the sulfided Al_2O_3 support

(Fig. 1f) and clearly shows the characteristic surface hydroxyl structure of Al_2O_3 and not the broadening feature of the sulfided 8% Mo/Al_2O_3 catalyst (Fig. 1h), thus suggesting that the broadening and the lack of distinct OH structure are not due to the masking of MoS_2 or another compound with high absorbance. Nevertheless, there still remains the possibility that in the physical mixture one may mainly be seeing the transmission through the fraction of the Al_2O_3 which is not covered by MoS_2 hence giving the spectrum of the surface structure of Al_2O_3. The ir spectrum of the 3% Mo/Al_2O_3 catalyst (Fig. 1i) further verifies that the source of band broadening and absence of distinct OH groups observed in the sulfided $Co-Mo/Al_2O_3$ (Fig. 1k) and 8% Mo/Al_2O_3 (Fig. 1h) is due to sulfiding rather than some experimental effects. This is seen in that both the higher-frequency hydroxyl bands of Al_2O_3 due to the incomplete surface coverage by Mo and a distinct broadening towards the lower-frequency side evidently attributed to the effects of sulfiding of the highly dispersed Mo are observed in the spectrum.

In none of the samples could SH species be detected, possibly due to the low molar absorbance of SH bands. However, the finding (*8*) that SH bands were clearly observable when H_2S was adsorbed on alumina suggests that SH species are not present to any appreciable extent in the present case. Also, no regeneration of hydroxyl groups was observed after sulfiding. These results may have some relevance to the much debated question of the fate of the Mo monolayer upon sulfidation (*9*). If, as assumed by some (e.g., (*10*), the Mo monolayer is broken up and is subsequently transformed into bulk MoS_2 crystals, OH (or SH) groups should be regenerated on the alumina surface and ir spectra much like those of the sulfided Al_2O_3 (or Co/Al_2O_3) or the physical mixture of bulk MoS_2 and Al_2O_3 should be observed. Such spectra were, however, not observed, indicating that the present sulfiding conditions do not result in MoS_2 crystals with appreciable three-dimensional character. Rather the results suggest that a strong interaction of the Mo with the alumina surface occurs not only in the oxidic state but also in the sulfided state of Mo/Al_2O_3 or $Co-Mo/Al_2O_3$ catalysts. In order to further elucidate the structure of sulfided Mo/Al_2O_3 and $Co-Mo/Al_2O_3$ catalysts, a better understanding of the origin of the broad 3600-cm^{-1} band would be helpful. Water generated during sulfiding could be strongly adsorbed on the surface to give rise to the broadening and mask the possible presence of OH bands.

ACKNOWLEDGMENTS

The author thanks Henrik Topsøe, Frank Massoth, and Roberto Candia for stimulating discussions and helpful comments.

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NAN TOPSØE

Haldor Topsøe Research Laboratories
DK-2800 Lyngby, Denmark

Received September 25, 1979