JOURNAL OF CATALYSIS **103**, 228–231 (1987)

Effect of Calcination Temperature on the Surface Exposure of Promoters in NiCo–Mo/Al_2O_3 Catalysts

INTRODUCTION

Recently, it has been reported (*1, 2*) that alumina-supported molybdena catalysts with both Co and Ni promoters can render higher hydrodesulfurization (HDS) activity than the single Co- or Ni-promoted catalysts. The effect has been found at different ratios r = Co/(Co + Ni), i.e., at $r \sim 0.7$ (*1*) and $r \sim 0.3$ (*2*). In a following work (*3*) on characterization of those two series of NiCo–Mo/Al_2O_3 catalysts it was shown that the observed differences in HDS activity and optimum atomic ratio r were certainly related to differences in surface exposure caused by the preparation. Furthermore, it was seen that the difference in HDS activity between both series of catalysts was not due to a variation in the dispersion of Mo but rather to changes in the fraction of promoter (Co and Ni) atoms exposed at the surface.

As the final calcination temperature is an essential step in the catalyst preparation and particularly for the distribution of the different Co and Ni species, it is of interest to investigate whether such parameter could be responsible for the observed difference between the referred NiCo–Mo/Al_2O_3 catalyst series. In the case of single Co- or Ni-Mo/Al_2O_3 catalyst, various authors (*4–9*) have shown that the calcination temperature affect to both surface structure and catalytic properties.

EXPERIMENTAL

Two series of NiCo–Mo/Al_2O_3 catalysts were prepared identically except in calcination temperature. The preparation consisted in a double impregnation of γ-Al_2O_3 (0001.5 EHP Azko Ketjen, S_{BET} = 213 m^2g^{-1}) with solutions of ammonium heptamolybdate (first impregnation) and cobalt and/or nickel nitrate (second impregnation). The procedure of preparation has been described in detail previously (*2, 3*). After it was dried at 120°C, the impregnated samples were divided in two portions and calcinated separately at 500 and 600°C in air for 24 h. All the catalysts contain 10.4 wt% MoO_3 and 3.3 ± 0.2 wt% CoO + NiO. The r = Co/(Co + Ni) atomic ratio varying from 0 to 1.

Infrared spectra of NO adsorbed on catalysts were obtained as described previously (*3*), using a Perkin–Elmer 680 double-beam grating spectrometer. The powdered catalysts, pressed into wafers, were pretreated either under high vacuum at 500°C for 15 h (these will be referred hereafter to as oxidized catalysts) or in hydrogen at 500°C for 1 h (these will be referred hereafter to as reduced catalysts) and then cooled down to room temperature before NO admission. Spectra were recorded at room temperature after gaseous NO was condensed in a trap at liquid-nitrogen temperature.

RESULTS AND DISCUSSION

Figure 1 shows the spectra of NO adsorbed on both oxidized (Fig. 1A) and reduced (Fig. 1B) forms of the catalysts calcined at 500° (from Ref. (*3*)). The spectra corresponding to the catalyst series calcined at 600°C are shown in Fig. 2. The most prominent modifications resulting from the increase in calcination temperature were: (i) a pronounced decrease in the intensity of the bands located at about 1888 cm^{-1} (NO adsorbed on Co^{2+} and/or Ni^{2+})

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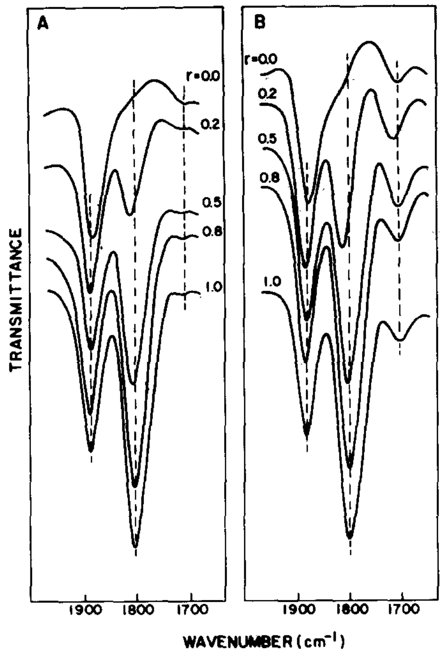

FIG. 1. Infrared spectra of NO adsorbed on NiCo-Mo/Al_2O_3 catalysts calcined at 500°C: (A) after evacuation for 15 h at 500°C, (B) after 1 h reduction in H_2 at 500°C.

and about 1805 cm^{-1} (NO adsorbed on both Co^{2+} and $Mo^{\delta+}$ ($\delta \simeq 4$); (ii) and a marked increase in the intensity of the band near 1707 cm^{-1}, which is associated only to NO adsorbed on $Mo^{\delta+}$. These changes are more clearly seen in the catalyst containing only Ni and Mo ($r = 0$). Thus, for example, the band near 1880 cm^{-1} decreased by a factor of about 5 (oxidic sample) or 3 (reduced sample) and shifted to about 1875 cm^{-1} when the calcination temperature was increased from 500 to 600°C; and the bands associated to $Mo^{\delta+}$ (1805 and 1707 cm^{-1}), which appeared only as broad shoulders in the oxidic sample calcined at 500°C, are well resolved in the corresponding sample calcined at 600°C. In the case of catalysts containing Co the behavior is similar, except that the change of the composed band near 1805 cm^{-1} is minor because the two contributions from NO adsorption on both Co^{2+} and $Mo^{\delta+}$ to this band act contrary, but as the Co contribution is dominant it then result in a net decrease in intensity.

The variation in the absorbance of the bands associated to the promoter and $Mo^{\delta+}$ for the reduced samples as a function of r and calcination temperature is shown in Figs. 3A–C. The dashed lines correspond to the theoretical values expected when the promoter and $Mo^{\delta+}$ ions act independently as in the Co–Mo/Al_2O_3 and Ni–Mo/Al_2O_3 catalysts. It is noteworthy that the absorbances of the bands at about 1707 and 1888 cm^{-1} reach maxima at low r for samples calcined at 500°C or high r for samples calcined at 600°C. The tendency of the band about 1805 cm^{-1} for the series calcined at 600°C is similar to the other bands, but for the series calcined at 500°C the maximum absorbance occurred apparently at a medium promoter atomic ratio, this being probably due to a contrary contribution from both Co^{2+} and $Mo^{\delta+}$ ions to such band. From the spectra of NO chemisorbed on oxidic and reduced catalysts is evident that the concentration of exposed Co^{2+} and/or Ni^{2+} ions at the surface of the catalysts decreased markedly, although not proportionally for all of them, by increasing the calcination temperature. This decrease indicates, in agreement with other authors

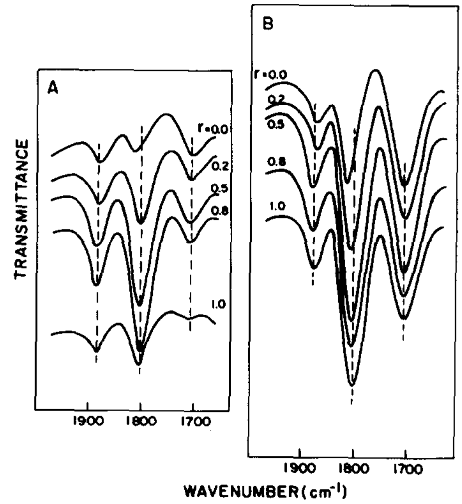

FIG. 2. Infrared spectra of NO adsorbed on NiCo-Mo/Al_2O_3 catalysts calcined at 600°C: (A) after evacuation for 15 h at 500°C, (B) after 1 h reduction in H_2 at 500°C.

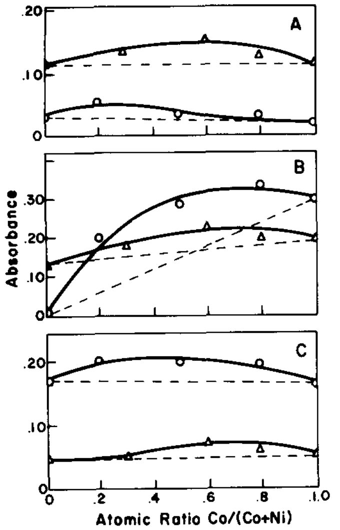

FIG. 3. Absorbance of the bands of (A) NO adsorbed on Mo (~1707 cm^{-1}), (B) Mo and Co (~1805 cm^{-1}), and (C) Co and/or Ni (~1888 cm^{-1}) on catalysts reduced at 500°C. Catalysts calcined at: (○) 500°C, (△) 600°C.

(*4–10*), that Co^{2+} and Ni^{2+} ions diffuse from octahedral positions at the surface to tetrahedral and/or octahedral positions inside the alumina lattice, resulting then in less concentration of exposed promoter atoms in the catalysts calcined at 600°C. This phenomenon of diffusion was probably the reason for the change in color of the Co-containing catalysts which turned bluer calcining at 600°C.

The IR spectra also show that in the series calcined at 600°C the concentration of exposed Mo (Fig. 3A) increased as compared to the series calcined at 500°C. This could be attributed, in principle, to an increase in the dispersion of Mo or to an increase of the Mo exposure able to chemisorb NO, presumably by migration of Co and/or Ni atoms from a Co(or Ni)–Mo interacting phase. In a recent study (*8*) using Raman spectroscopy and low energy ion scattering a spreading and a reorganization of the surface molybdate layer has been shown to occurs at 597°C on Ni–Mo/Al$_2$O$_3$ catalysts. In contrast, other authors (*7*) have reported no significant change in the configuration of the Mo atoms, as a result of increasing the calcination temperature, on Co–Mo/Al$_2$O$_3$ catalysts. As in the present work the intensity of the band near 1705 cm^{-1} increased more by a factor of 2 when increasing the calcination temperature, it seems unlikely that such a large change could be totally due to an increase in the dispersion of Mo. This conclusion is supported by additional measurements of O$_2$ chemisorption on the parent Mo/Al$_2$O$_3$ samples used for the preparation of the NiCo–Mo/Al$_2$O$_3$ catalysts. The amounts of O$_2$ chemisorbed on reduced Mo/Al$_2$O$_3$ samples calcined at 500 and 600°C were quite similar, i.e., 67.6 and 63.3 mg O$_2$ per g MoO$_3$, respectively. Therefore, the dispersion of Mo species may be similar for both series of catalysts calcined at 500 and 600°C. Although the band near 1705 cm^{-1} is slightly broad, the observation that it remained practically at the same position in both series of catalysts seems also to support the above conclusion. It is not excluded, however, that some reorganization in the molybdate layer could also be occurring but without a substantial alteration in the overall dispersion of Mo.

Thus, in view of the above findings, a larger fraction of Mo may be present as a Co(or Ni)–Mo interaction phase in the series calcined at 500°C than in the calcined at 600°C. Such Mo$^{\delta+}$ ions are not adsorbing NO, possibly due to either a shielding effect of the Co^{2+} or Ni^{2+} ions located in the neighborhood of Mo$^{\delta+}$ ions or a minor reducibility of the Mo because their interaction with the promoter atoms. If such Mo atoms exhibit minor reducibility, the degree of coordinative unsaturation required to permit NO adsorption is not very likely achieved.

Interestingly, the fractions of exposed Mo$^{\delta+}$ ions adsorbing NO (Fig. 3A) and of exposed Co^{2+} and Ni^{2+} ions adsorbing NO (Fig. 3C) follow a similar trend as *r* varied. The effect is observed for both series of catalysts. This parallel behavior of the fractions of exposed Mo$^{\delta+}$ and Co^{2+} and Ni^{2+}

ions supports the above conclusion that the appearance of a large fraction of exposed Mo is due to the diffusion of the promoter atoms, presumably those interacting with Mo and forming the precursor of the Co(or Ni)–Mo–S active phase (*11*). A similar conclusion has been recently found for both Co–Mo/Al_2O_3 and Ni–Mo/Al_2O_3 catalysts on the basis of diffuse reflectance spectroscopy and electrophoretic migration measurements (*9*).

As shown in Fig. 3C, the maximum in exposed promoter (Co^{2+} and Ni^{2+}) ions appeared at different r values for the catalysts calcined at 500 and 600°C. This is related to the difference in reactivity between Co and Ni oxides with the alumina. At 500°C, when a large fraction of Ni atoms exposed in incomplete octahedral coordination are present, and the difference in reactivity between Co and Ni oxides with the alumina is smaller, it seems to be reasonable that the net concentration of exposed promoter (Co^{2+} and Ni^{2+}) ions occurs in the region of medium or high Ni content. However, at 600°C, as most of Ni^{2+} ions are located inside the alumina lattice due their higher reactivity relative to Co, it is expected that the higher exposure of promoter ions occurs in the region of high Co content.

ACKNOWLEDGMENTS

The authors thank the Comisión Asesora de Investigación Cièntifica y Técnica (Spain), and the Consejo Nacional de Investigaciones Científicas y Tecnológicas (Venezuela) for support of this work.

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Received March 16, 1986

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