# NO Chemisorption as a Probe of the Active Precursors in Co–Mo/Al$_2$O$_3$ Catalysts

Recently, ir studies of NO adsorption have shown some interesting possibilities for characterizing the surface structures of alumina-supported and silica-supported Co, Mo, and Co–Mo catalysts in their calcined state (*1, 2*). For the Co–Mo catalysts these studies confirm previous findings (e.g., (*3, 4*)) that interactions occur between Co and Mo atoms. For the alumina-supported catalysts the ir results suggest that the cobalt atoms in the surface interaction phase have octahedral coordination. Furthermore, the molybdenum atoms seem to be interacting strongly with the alumina surface as in the case of Mo/Al$_2$O$_3$ catalysts. This conclusion is supported by EXAFS measurements (*5*).

Several earlier studies (e.g., (*6—10*)) have presented results which show that the catalytic activity of the sulfided catalysts may be related to different properties of the calcined catalysts. These studies do not, however, agree on the origin of the various observations and also widely different views on the nature of the active phase were presented.

The interpretation of such correlations may be further complicated by the presence of many different species simultaneously. Mössbauer emission spectroscopy (MES) studies have recently shown (e.g., (*11–14*)) that in sulfided Co–Mo/Al$_2$O$_3$ catalyst, Co is generally present in three different types of phase, namely, cobalt associated with the alumina, Co$_9$S$_8$, and Co associated with a highly dispersed MoS$_2$-like phase (the so-called Co–Mo–S phase). The latter was found to be responsible for the Co promotion of the hydrodesulfurization (HDS) activity (*13, 14*).

The presence of a Co–Mo interaction phase in calcined catalysts is interesting in relation to the structure of the sulfided catalysts. In particular, the presence of such a phase at the surface before sulfiding seems to be a favorable situation for the formation of the active Co–Mo–S phase, since upon sulfiding only a minimum rearrangement of the atoms would be required.

In order to check the validity of this hypothesis, infrared and volumetric adsorption experiments using NO as a selective probe molecule have been carried out on a series of calcined alumina-supported catalysts whose activity and amount of Co–Mo–S have been measured (*13*) after sulfiding. The catalysts had different Co/Mo atomic ratios and were prepared by impregnating the same batch of Mo/Al$_2$O$_3$ catalyst (8.6 wt% Mo, and calcined at 773 K) with different amounts of cobalt and finally recalcining at 773 K. Thus, only the concentration of the promoter atoms was varied and the level of molybdenum was kept constant. The procedures used in the ir experiments have been given in detail previously (*1*). In short, the sample wafers (70 mg in all cases) were evacuated at 703 K before contacting with NO at room temperature. Spectra were recorded at room temperature on a Perkin–Elmer 180 spectrometer after the excess gaseous NO and the physisorbed NO had been evacuated. A pretreatment temperature of 703 K was chosen since at this temperature the amount of NO adsorbed on Mo is negligible (*1*). The ir spectra obtained in the present study confirmed this since mainly NO absorption bands associated with cobalt atoms are observed. The volumetric chemisorption of NO was

carried out in a constant-volume system after similar pretreatments.

Two absorption bands are seen for all the catalysts at approximately 1885 and 1800 cm$^{-1}$. The frequencies and relative intensity ratio appear to be quite constant for most of the catalysts in the range of Co loadings studied here and they are quite similar to those observed for the Co–Mo/Al$_2$O$_3$ catalysts (1) prepared by co-impregnation. This shows that the Co–Mo interaction phase is not specific to the preparation method and that it is also the dominating surface phase in the sequentially impregnated Co–Mo/Al$_2$O$_3$ catalysts studied here.

For the very high Co loading catalysts, small changes in the relative intensity of the absorption bands are observed. These changes may be attributed to the formation of some Co$_3$O$_4$. Nevertheless, contribution from this phase to the bands appears to be small. This is probably due to the poor dispersion of Co$_3$O$_4$. In contrast to the present results for Co–Mo/Al$_2$O$_3$ catalysts, Co$_3$O$_4$ is readily observed in the Co/Al$_2$O$_3$ catalysts with quite low Co loadings (1). The Co–Mo interaction phase appears therefore to decrease the tendency towards Co$_3$O$_4$ formation.

Information about the variation in the amount of Co atoms involved in the Co–Mo interaction phase is obtained from a plot (Fig. 1a) of the absorbance of the ir band at 1800 cm$^{-1}$ as a function of the Co/Mo ratio (a plot of the absorbance of the 1885-cm$^{-1}$ band shows a similar dependence on the Co/Mo ratio). Figure 1b shows the thiophene hydrodesulfurization activity (expressed as the first-order rate constant) of the same catalysts after they have been sulfided. It is quite clear from a comparison of Figs. 1a and b that there exists a parallelism between the NO adsorption results on the calcined catalysts and the activity of the sulfided catalysts. The much debated "synergistic" behavior which is often observed for supported Co–Mo (or Ni–Mo) catalysts does, therefore, appear to be linked with
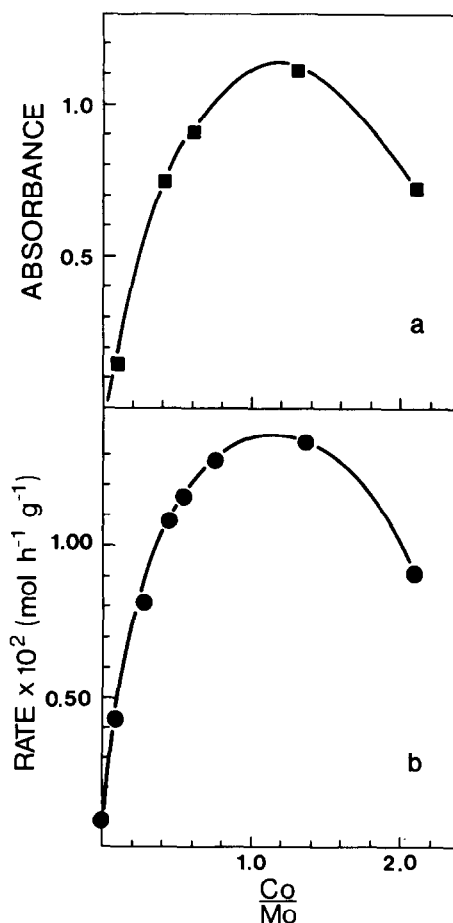


FIG. 1. (a) Absorbance of ir band (1800 cm$^{-1}$, normalized on a standard wafer weight) due to NO adsorbed on Co plotted as a function of the Co/Mo ratio. (b) The rate constant for thiophene conversion (data adapted from (13)) plotted as a function of the Co/Mo ratio.

the structure already present in the calcined state.

The close relation between the properties of the calcined and sulfided catalysts is more directly seen from Fig. 2 in which the rate is plotted as a function of the absorbance. The results of volumetric chemisorption of NO are also included in this figure. Both the ir and volumetric chemisorption results show that the activity increase observed by promoting Mo/Al$_2$O$_3$ catalysts with Co is proportional to the amount of Co atoms adsorbing NO in the calcined state,
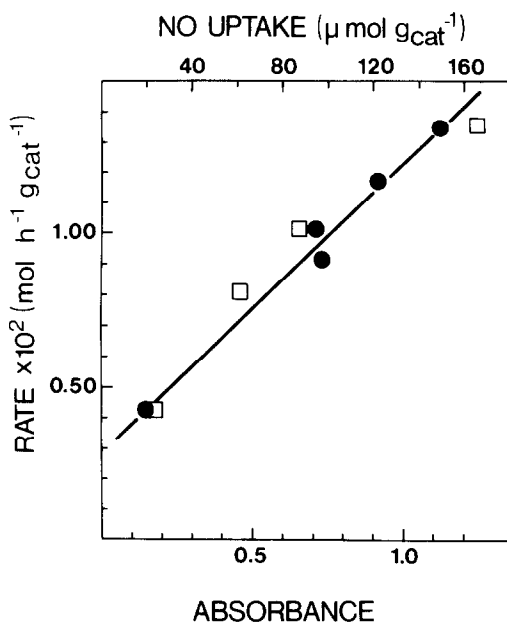
FIG. 2. A plot of the rate of thiophene conversion vs absorbance (●) of ir band due to NO adsorbed on Co. The NO uptake (□) per gram of catalyst for a few samples is also included.
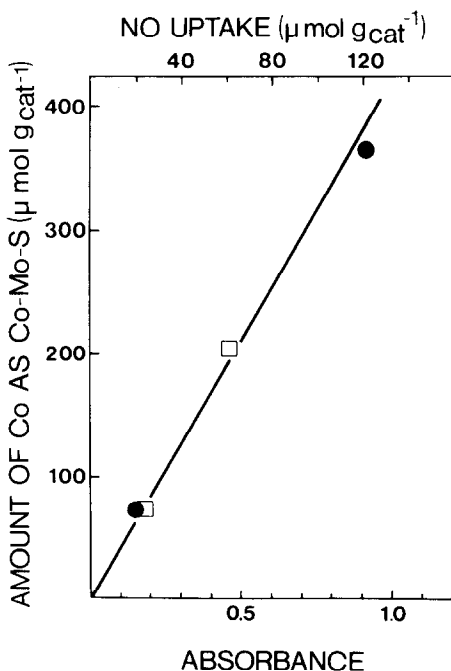


FIG. 3. A plot of the amount of Co present as Co–Mo–S (13) vs absorbance of NO absorption band due to Co (●) and NO (□) uptake.

i.e., those which are present in octahedral coordination in the "Co–Mo–O" surface phase. The observation that the line in Fig. 2 does not pass through the origin simply expresses the fact that catalysts not containing cobalt have some catalytic activity.

The present findings suggest that the "Co–Mo–O" phase is a precursor for the Co–Mo–S phase since other results have shown that the activity of the sulfided catalysts is related to the amount of Co atoms present as Co–Mo–S (13, 14). In more direct support of this, Fig. 3 shows that the amount of Co–Mo–S is proportional to the amount of NO adsorbed.

It is apparent from Fig. 3 that the number of cobalt atoms probed by NO is much smaller than those found in the Co–Mo–S phase. This may indicate that other forms of cobalt (for example, cobalt located in the alumina in the immediate vicinity of the Co–Mo interaction phase) may also be precursors to the Co–Mo–S phase. Alternatively, the discrepancy may be related to the possibility that not all Co atoms in the Co–Mo interaction phase are capable of adsorbing NO (i.e., achieving the proper degree of coordinative unsaturation) under the present pretreatment conditions. These different possibilities are presently being investigated further.

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