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# Molybdenum–Support Interaction and Its Effect on Nitric Oxide Chemisorption and Temperature-Programmed Desorption

Nitric oxide chemisorption has been used by a number of researchers to characterize $Al_2O_3$-supported molybdenum catalysts. Millman and Hall (*1*) and Peri (*2*) have reported that NO chemisorbs on reduced molybdenum in the form of a dinitrosyl species as determined by infrared spectroscopy. Millman and Hall (*3*) have also reported that NO chemisorbs on the same coordiantively unsaturated molybdenum sites as oxygen. More recently, Jung *et al.* (*4*) reported a linear relationship between NO chemisorption and catalytic HDS activity for a series of $Al_2O_3$-supported molybdenum catalysts of varying metal loadings. In addition, they reported that on TPD the chemisorbed NO desorbed as both NO and $N_2O$.

As a consequence of the TPD results reported by Jung *et al.* (*4*), we initiated a study to define the significance of the TPD gas composition. Specific emphasis was directed toward examining the effects of molybdenum–support interaction.

The supports used were γ-alumina (American Cyanamid), $SiO_2$ (Fisher), and MgO (Alfa) with BET surface areas of 258, 725, and 25 $m^2/g$, respectively. Catalysts were prepared by the incipient wetness technique using an aqueous solution of ammonium heptamolybdate followed by drying at 120°C and calcination at 500°C for 1 h.

NO chemisorption/TPD studies were performed in a flow apparatus equipped with a thermal conductivity detector and a quadrupole mass spectrometer as previously described (*4*). All catalyst samples were presulfided *in situ* at 400°C for 1 h with 10 vol% $H_2S$ in $H_2$ prior to NO chemisorption.

After saturation of the catalyst with NO the sample was heated in a helium stream (50 $cm^3$/min) to 400°C at a rate of 20°C/min. The composition of the effluent gas was measured at 1-min intervals using the online quadrupole mass spectrometer. The ratio of $N_2O$/NO was determined from the sum of the intensities of the $N_2O$ and NO peaks.

As previously reported (*4*) for $Al_2O_3$-supported catalysts, NO chemisorption increases linearly with $MoO_3$ loading up to 16 wt% where it appears to level off (Fig. 1). A similar trend was also observed in this study for a series of $SiO_2$-supported catalysts. However, as illustrated in Fig. 1, NO chemisorption for the $SiO_2$-supported catalysts levels off at 6 wt% $MoO_3$. In addition, the maximum NO chemisorption for the $SiO_2$-supported catalysts is less than that of the $Al_2O_3$-supported catalysts, 106 versus 332 μmol/g, respectively. XRD analyses suggest this difference in NO chemisorption to be related to the greater dispersion of molybdenum on $Al_2O_3$, a consequence of the stronger metal–support interaction, as previously reported by Massoth *et al.* (*5*).

Ratios of $N_2O$/NO on TPD for the $Al_2O_3$ and $SiO_2$-supported catalysts are illustrated in Figs. 2–3. For the $Al_2O_3$-supported catalysts the ratio decreases from 1 to 4 wt% $MoO_3$ and then increases from 4 to 16 wt% after which it appears to level off at a value of 0.21. A high $N_2O$/NO ratio for $Al_2O_3$ without $MoO_3$ (1.39), suggests that the decrease in the ratio from 1 to 4 wt% $MoO_3$ is a consequence of the metal blocking reactive $Al_2O_3$ sites. Above 4 wt% the $N_2O$/NO ratio reflects the nature of the Mo sites. For the $SiO_2$-supported catalysts (Fig. 3) the $N_2O$/NO ratio increases from 1 to 10 wt% $MoO_3$ after which it also appears to level off at a value of 0.14.

Formation of $N_2O$ is proposed to be a consequence of a multistep reaction. NO reacts with a reduced $Mo^{n+}$ species bound

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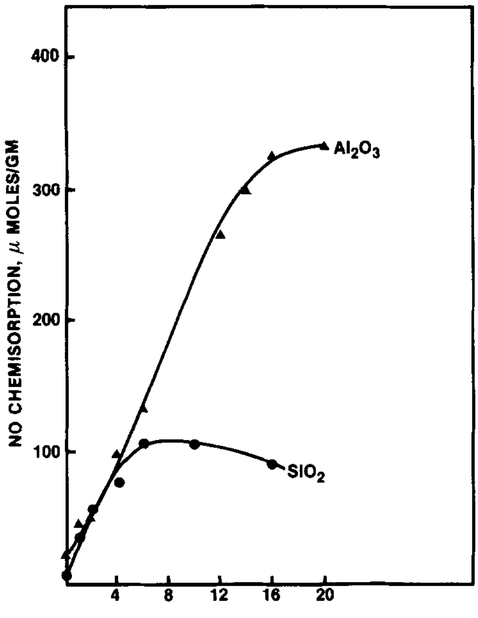

FIG. 1. The effect of MoO$_3$ loading on the amount of NO chemisorbed. (▲) Al$_2$O$_3$; (●) SiO$_2$.

to the support to form a dinitrosyl (*1*, *6*). On TPD a disproportionation reaction occurs yielding $N_2O$ and a $Mo^{(n+2)+}$ species. Based on reaction kinetics, it seems reasonable to assume that the rate of NO disproportionation to $N_2O$, as measured by the $N_2O/NO$ ratio, should be related to the NO concentration or level of uptake.

As illustrated in Fig. 4, a linear correlation exists between the $N_2O/NO$ ratio and the total NO uptake for both the $Al_2O_3$- and $SiO_2$-supported catalysts. However, the slopes ($R_d$) of these plots are different, 6.7 × $10^{-4}$ and 2.1 × $10^{-3}$ for the $Al_2O_3$- and $SiO_2$-supported catalysts, respectively.

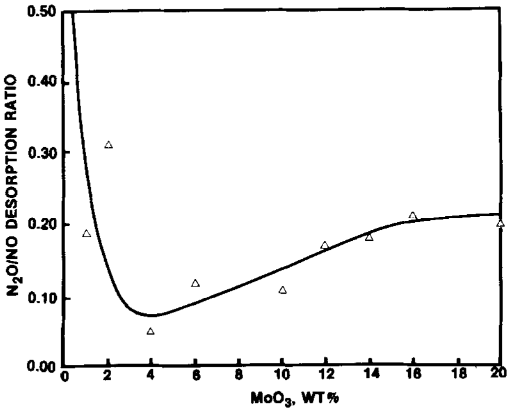

FIG. 2. The effect of MoO$_3$ loading on the $N_2O$/NO temperature-programmed desorption ratio for $MoO_3/Al_2O_3$ catalysts.

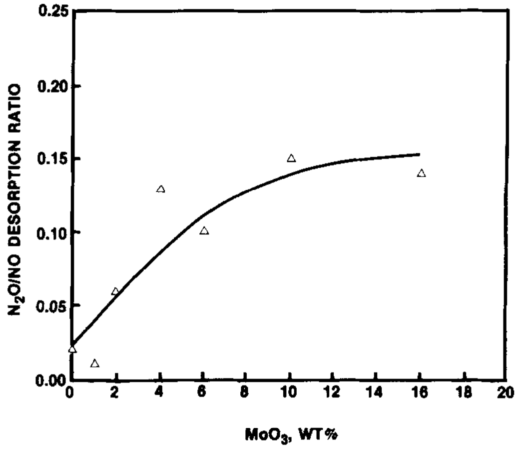

FIG. 3. The effect of MoO$_3$ loading on the $N_2O$/NO temperature-programmed desorption ratio for $MoO_3/SiO_2$ catalysts.

The proposed reaction for the disproportionation of NO to $N_2O$, yielding a $Mo^{(n+2)+}$ species would also suggest that the level of NO chemisorbed should be lower on readsorption if the catalyst is not resulfided. The following equation has been derived to predict this value.

$$NO_{n+1} = NO_n(1 - F_d).$$

The number of the chemisorption–desorption cycle is represented by $n$. $F_d$, the fraction of $Mo^{n+}$ sites oxidized to $Mo^{(n+2)+}$, is equal to

$$\frac{2N_2O/NO}{2N_2O/NO + 1}$$

where the value of the $N_2O/NO$ ratio is for the $n$th cycle.

As presented in Table 1, a 16 wt% $MoO_3/Al_2O_3$ catalyst with an initial NO chemisorption value of 325 μmol/g and a $N_2O/NO$ ratio of 0.21 has a predicted NO chemisorption value for the second cycle of 229 μmol/g. This is in good agreement with the experimental value of 195 μmol/g. The lower

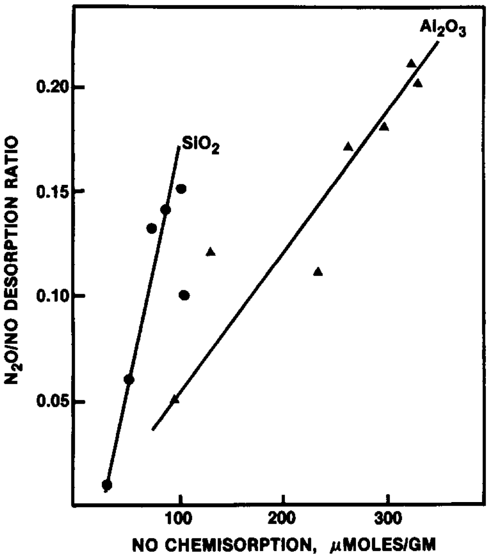

FIG. 4. Correlation of $N_2O/NO$ temperature-programmed desorption ratio to NO chemisorption. (▲) $Al_2O_3$; (●) $SiO_2$.

$N_2O/NO$ ratio of 0.09 on the second desorption cycle yields a predicted NO chemisorption value for the third cycle of 165 μmol/g. The experimental value was 146. Interestingly, these results are in good agreement with the correlation illustrated in Fig. 4 as illustrated in Fig. 5.

Previously, Yamagata *et al.* (*7*) reported that the amount of $MoO_3$ adsorbed onto a support is related to the number of anionic OH groups on the support. Furthermore, they reported that a $MgO-Al_2O_3$ support contained the largest amount of OH groups and adsorbed the largest amount of $MoO_3$. More recently, Lercher and Noller (*8*) reported that the acid strength of OH groups on $Al_2O_3$, $SiO_2$, and MgO is directly related to the Sanderson intermediate electronegativity of the oxide. As proposed by Sanderson (*9*) the intermediate electronegativity of a compound is the geometric mean of the electronegativities of the component atoms.

As a consequence of these results a 16 wt% $MoO_3/MgO$ catalyst was prepared and tested for NO chemisorption and TPD. The NO uptake was 55 μmol/g, while the $N_2O$/No ratio was 0.02. The calculated $R_d$ value was $3.6 \times 10^{-4}$, less than that of the $Al_2O_3$ or $SiO_2$-supported catalysts. However, as presented in Fig. 6, a direct correlation was found between the calculated electronegativity of the support and the $R_d$ value of the catalyst. This correlation is similar to that reported by Lercher and Noller (*7*).

In conclusion, the results presented sug-

TABLE 1

NO Chemisorption/TPD Results for 16 wt% $MoO_3/Al_2O_3$

| Adsorption cycle | $N_2O/NO$ ratio | NO chemisorbed, μmol/g | |
|---|---|---|---|
| | | Experimental | Theoretical |
| 1 | 0.21 | 325 | — |
| 2 | 0.09 | 195 | 229 |
| 3 | 0.07 | 146 | 165 |

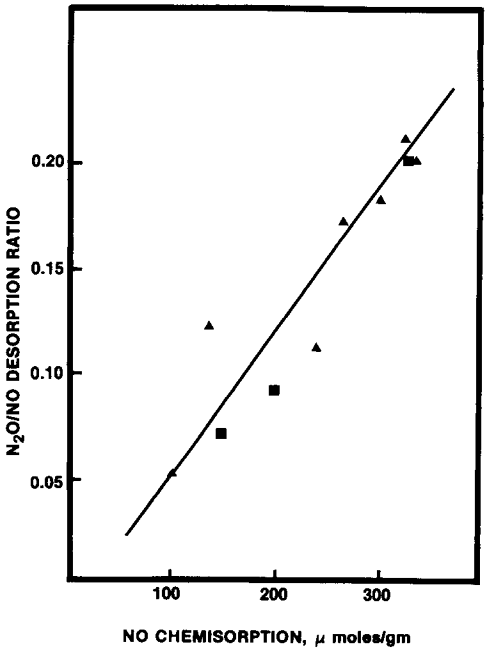

FIG. 5. Correlation of $N_2O/NO$ temperature-programmed desorption ratio to NO chemisorption. (▲) Variation in $MoO_3$ loading; (■) 16 wt% $MoO_3/Al_2O_3$—cycled.

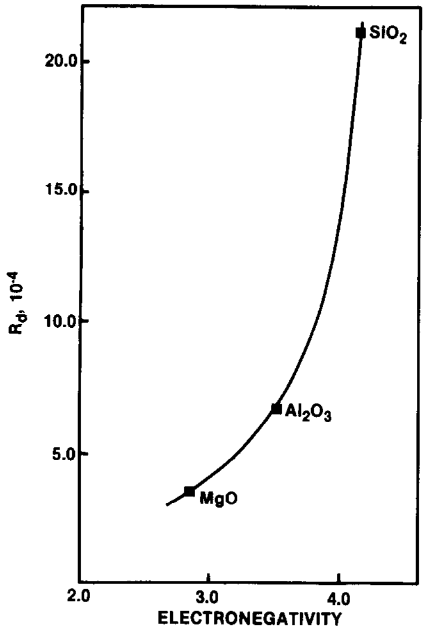

FIG. 6. Relation between ratio ($R_d$) of $N_2O$/NO ratio to NO chemisorption and the Sanderson intermediate electronegativity of the support.

gest that the reactivity of Mo sites for the disproportionation of chemisorbed NO to $N_2O$ may be related to molybdenum–support interaction. Additional experiments are now being pursued to determine the relationship of these results to hydrodesulfurization activity.

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