JOURNAL OF CATALYSIS 90, 368–370 (1984)

$[Mo(CH_3CN)_4(NO)_2](BF_4)_2$ as a Model for NO on a Reduced MoO_3/Al_2O_3 Catalyst

Recently, there has been growing interest both in the use of chemisorption to aid in understanding active sites (*1*) and in supporting homogeneous transition metal complexes to use as model, active catalysts (*2, 3*). Thus, on supported molybdena catalysts which have been activated either by reduction or sulfiding, nitric oxide chemisorption has been shown to be an effective poison for propene hydrogenation (*4*). Infrared studies have shown that the poisoned sites contain two molecules of nitric oxide (*5–8*). There is, however, a question as to whether the best description of the chemisorbed NO is as a dimer or as a dinitrosyl species. Therefore, we have carried out experiments using a transition-metal complex $[Mo(CH_3CN)_4(NO)_2](BF_4)_2$ (*9*) to help clarify this question and provide a model for the poisoned sites on molybdena catalysts.

The catalysts were prepared by dip-impregnating pressed ir platelets. The platelets were prepared by pressing Ketjen CK-300 γ-Al_2O_3 (A_s = 192 m^2/g) at 25,000 psi; the resulting thickness was 10 mg/cm^2. The platelets were then pretreated in flowing dry O_2 for 18 hr at 500°C and evacuated for 2 hr at temperature followed by cooling under vacuum. The impregnation was carried out with the platelet mounted in the ir cell holder and immersed into an approximately 0.1 *M* acetonitrile solution of the complex under a N_2 atmosphere. The platelets were then dried under vacuum at ambient temperature. This treatment resulted in analyzed loadings of 1.6 wt% Mo on alumina. The resulting catalyst had the infrared spectrum shown in Fig. 1B. Also shown as Fig. 1A is the spectrum of $[Mo(CH_3CN)_4(NO)_2](BF_4)_2$ prepared by mixing the solid molybdenum complex with Davison Grade 62 silica gel. The spectrum of NO on a reduced molybdena–alumina catalyst (8% MoO_3/γ-Al_2O_3) is shown in spectrum (C). The similarity in all three spectra suggests that NO is bound to a common type of Mo center and supports the dinitrosyl description of NO chemisorbed on a reduced molybdena–alumina catalyst.

To further clarify the question on the mode of interaction of NO with molybdena–alumina catalysts, ^{15}NO-exchange experiments were carried out on the supported complexes. The results of the exchange reaction on the supported inorganic dinitrosyl complex shown in Fig. 2B can be compared with those from the exchange of ^{14}NO adsorbed on molybdena-alumina which are shown in Fig. 2A. Clearly both materials behave in the same manner to the exchange, exhibiting a decrease in the ^{14}NO–^{14}NO species and an increase in the ^{15}NO–^{15}NO species with little or no evidence of the mixed ^{14}NO–^{15}NO species.

In the above experiments we have used a supported inorganic compound to more fully understand the nature of the active sites on the supported metal oxide catalyst. All Mo dinitrosyl complexes are known to be *cis* and approximately linear (10–12); therefore, the strong similarity in the infrared spectrum of the supported inorganic complex with that of NO on the supported oxide suggests that they also are similar and possesses a dinitrosyl structure. Additionally, the bond angle between *cis* dinitrosyl ligands in an octahedron should be approximately 90° and such is the case found for $Mo(NO)_2(bipy)Cl_2$ (*12*). Yao (*6*) has derived an equation to calculate the bond angle for supported $(NO)_2$ complexes from which we calculate values of 116° for the supported inorganic complex and 105° for NO on the supported oxide; note that both are greater than 90°. A smaller bond angle might be expected for the dimer model possessing a structure such as that shown in **A**, than for a dinitrosyl shown as **B** (due to the N---N interaction).

0021-9517/84 $3.00

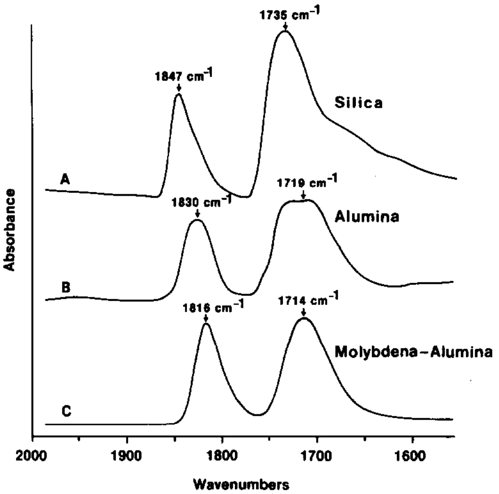
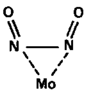
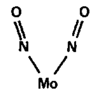


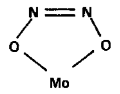
FIG. 1. Infrared spectra in the nitrosyl region of the inorganic and supported inorganic Mo complex along with the spectrum of NO adsorbed on a reduced MoO_3/γ-Al_2O_3 catalyst. (A) $[Mo(CH_3CN)_4(NO)_2](BF_4)_2$ as a silica wafer. (B) $[Mo(CH_3CN)_4(NO)_2](BF_4)_2$ supported on γ-Al_2O_3. (C) Adsorption of NO on a reduced molybdena–alumina catalyst. The catalyst had been reduced at 500°C for 1 hr in H_2 followed by evacuation at 500°C for 30 min and cooled to 25°C under vacuum. After the pretreatment the catalyst was exposed to 5 Torr of NO for 30 min at 25°C followed by evacuation at 25°C for 30 min.



A



B



C

This provides additional support for the dinitrosyl model. Ghiotti *et al.* (*13*) have recently proposed that the species formed on silica-supported chromia is a chromium *cis* dinitrosyl complex. They argued that there are no NO inorganic dimer structures known, and that the hyponitrite structure, C, suggested by Kugler and Gryder (*14*) should have a significant shift in the nitrosyl stretching frequency. In fact, one such complex is known and its X-ray structure has been determined (*15*). This structure is a hyponitrite ligand arrangement bound to a bis(triphenylphosphine) platinum center. As predicted by Ghiotti *et al.* the infrared bands are all below 1300 cm^{-1} (*16*) which are indeed significantly lower than the observed frequencies. Thus, this hyponitrite structure is not a good model for the actual surface species.

The ^{15}NO exchange experiments have provided the impetus for the dimer description of NO on both molybdena (*7*, *8*) and

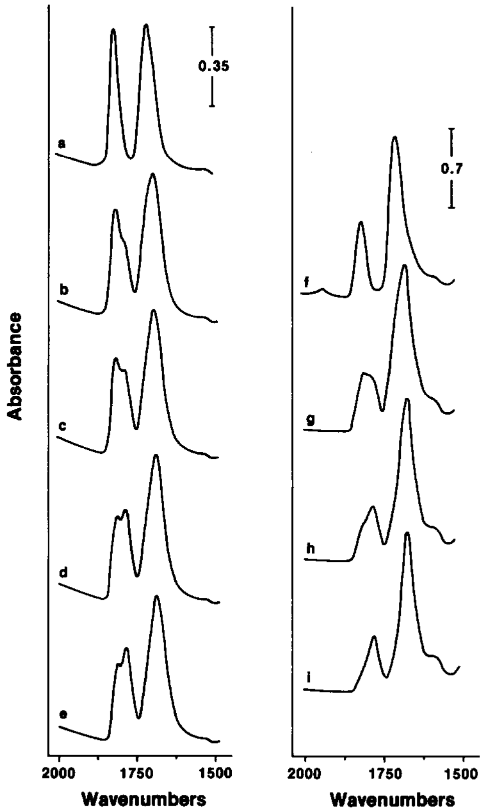


FIG. 2. Infrared spectra of ^{15}NO exchange on the supported catalysts. (a–e) Addition of 20 Torr of ^{15}NO (12.0 cm^3 NTP) to a catalyst reduced as in Fig. 1C. Following the reduction the catalyst was exposed to ^{14}NO as in Fig. 1C. This resulted in 0.12 cm^3 NTP/g NO chemisorbed. After this pretreatment the catalyst was exposed to the labeled NO and spectra recorded at 0, 0.75, 2, 5, and 20 hr following the introduction of the NO. All exposures to NO were carried out at 25°C. (f–i) Addition of 22 Torr of ^{15}NO (13.2 cm^3 NTP) to the catalyst containing $[Mo(CH_3CN)_4(NO)_2](BF_4)_2$ on alumina. Spectra were recorded after 0, 1, 4, and 16 hr with the catalyst maintained at 100°C throughout the time in contact with the labeled NO except while spectra were being recorded (25°C). The band maxima in (a–e) are at 1817 and 1714 cm^{-1} in (a) and 1782 and 1684 cm^{-1} in (e). Spectrum (b) through (d) contain both the 1817- and 1782-cm^{-1} bands while the other band exhibits a smooth transition between 1714 and 1684 cm^{-1}. In spectra (f–i) the bands are at 1816 and 1705 cm^{-1} and/or 1779 and 1674 cm^{-1} as the surface species changes from ^{14}NO–^{14}NO to ^{15}NO–^{15}NO.

chromia (*14*). The argument has been made that the presence of a dinitrosyl should lead to a smooth transition from the $^{14}NO-^{14}NO$ species to the $^{14}NO-^{15}NO$ species and finally to the $^{15}NO-^{15}NO$ species. The dimer on the other hand should result in the disappearance in the $^{14}NO-^{14}NO$ species and the appearance of the $^{15}NO-^{15}NO$ species without going through the mixed $^{14}NO-^{15}NO$ species. Peri (*7, 8*), however, has pointed out that this argument is not unequivocal. The data presented here show a supported dinitrosyl complex exhibits the same exchange behavior as that expected for a dimer and indicates the following scheme may represent the exchange reaction

$$2NO + M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} M\text{–}NO + NO \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} M\text{–}(NO)_2.$$

In this scheme $k_2 \gg k_1$, $k_{-1} \gg k_{-2}$ and furthermore since the exchange is slow even in substantially excess gas phase NO and the NO is difficult to desorb, it is likely that $k_{-1} > k_2$. This, of course, results in the exchange appearing to involve NO dimers. The fact that both the catalyst and the supported complex respond in the same way in the exchange (Fig. 2) validates these ideas.

Additionally, the similarities between the inorganic complexes and the catalyst suggests that the oxidation state is the same. The oxidation state of Mo in $[Mo(CH_3CN)_4(NO)_2](BF_4)_2$ is *formally* Mo(0) (*17*). It is, however, evident that the above compound can be written $[Mo(CH_3CN)_4(NO)_2]^{2+}(BF_4^-)_2$. The corresponding dichloride is also known. Moreover, it is of interest that the only known dinitrosyl compounds of molybdenum are those where the *apparent* valence is Mo^{2+}. Thus, the data support our suggestion (*1*) that the oxidation state of the catalytic sites for hydrogenation is Mo^{2+}. After adsorption of two molecules of NO, however, the *formal* oxidation state may be regarded as Mo(0), in accordance with the electron counting rules of the inorganic chemist.

ACKNOWLEDGMENTS

The authors thank Richard Thomas and Ayusman Sen for providing us with samples of the molybdenum complex, Roger Schneider for helpful discussions, and the National Science Foundation for support of this work under Grant CHE-8019309.

REFERENCES

1. Valyon, J., and Hall, W. K., *J. Catal.* **84,** 216 (1983), and references therein.
2. Li, X. J., and Gates, B. C., *J. Catal.* **84,** 55 (1983).
3. Watters, K. L., Howe, R. F., Chojnacki, T. P., Fu, C. M., Schnieder, R. L., and Wong, N. B., *J. Catal.* **66,** 424 (1980).
4. Lombardo, E. A., Lo Jacono, M., and Hall, W. K., *J. Catal.* **64,** 150 (1980).
5. Millman, W. S., and Hall, W. K., *J. Phys. Chem.* **83,** 427 (1979).
6. Yao, H. C., and Rothschild, W. G., *in* "Proceedings, 4th International Conference, The Chemistry and Uses of Molybdenum, Golden, Colorado" (H. F. Barry and P. C. H. Mitchell, Eds.), pp. 31ff. Climax Molybdenum Company, Ann Arbor, Michigan, 1982.
7. Peri, J. B., *J. Phys. Chem.* **86,** 1615 (1982).
8. Peri, J. B., *Div. Pet. Chem. Amer. Chem. Soc.* **23,** 1281 (1978).
9. Sen, A., and Thomas, R. R., Organometallics **1,** 1251 (1982).
10. Visscher, M. O., and Caulton, K. G., *J. Amer. Chem. Soc.* **94,** 5923 (1972).
11. Diebold, T., Schappacher, M., Chevrier, B., and Weiss, R., *J. Chem. Soc. Chem. Commun.* 693 (1979).
12. Ballivet-Tkatchenko, D., Bremard, C., Abraham, F., and Nowogrocki, G., *J. Chem. Soc. Dalton Trans.* 1137 (1983).
13. Ghiotti, G., Garrone, E., Della Gatta, G., Fubini, B., and Giamello, E., *J. Catal.* **80,** 249 (1983).
14. Kugler, E. L., Kadet, A. B., and Gryder, J. W., *J. Catal.* **41,** 72 (1976).
15. Bhaduri, S., Johnson, B. F. G., Pickard, A., Raithby, P. R., Sheldrick, G. M., and Zuccaro, C. I., *J. Chem. Soc. Chem. Commun.* 354 (1977).
16. Cenini, S., Ugo, R., La Monica, G., and Robinson, S. D., *Inorg. Chim. Acta* **6,** 182 (1972).
17. Wigley, D. E., and Walton, R. A., *Inorg. Chem.* **22,** 3138 (1983).

RICHARD P. ROSEN
KOH-ICHI SEGAWA[1]
WILLIAM S. MILLMAN
W. KEITH HALL[2]

Department of Chemistry
Laboratory of Surface Studies
The University of Wisconsin-Milwaukee
Milwaukee, Wisconsin 53201

Received May 17, 1984

---

[1] On leave from Sophia University, Tokyo, Japan.

[2] To whom all correspondence should be addressed.