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NOTES

Determination of Zero-Valent Molybdenum after Moderate Temperature Reduction of Alumina-Supported Catalysts

Molybdenum is an important component of commercial hydrotreating catalysts. Numerous studies dealing with the oxidation state of the molybdenum species in the reduced sulfided catalysts have been carried out in order to elucidate the sites responsible for catalytic activity. ESCA studies of a moderately reduced (800 K), 8 wt% Mo/Al_2O_3 catalyst revealed the predominant reduction species to be Mo(4+): no lower oxidation state species were detected (*1*). Under more extreme reduction conditions (1173 K), oxygen chemisorption and benzene hydrogenation studies show that metallic molybdenum species formed (*2, 3*). It was also found that metallic molybdenum could be titrated using benzene hydrogenation regardless of whether the Mo/Al_2O_3 catalyst had been prepared by conventional methods or by using $Mo(CO)_6$ deposition (*3*). More recently, Mo(0) has been observed by IR from samples prepared by the decomposition of $Mo(CO)_6$ on alumina of various degrees of dehydroxylation (*4*).

We have reported that the use of an infrared technique can be used to observe Mo(0) on moderately reduced conventional alumina-supported molybdenum catalysts (*5*). This study illustrates the variables that are important in the formation of Mo(0) on these materials.

A series of Mo/Al_2O_3 samples were prepared with molybdenum loadings of 3, 6, 9, and 12 wt%, by the incipient wetness technique. The alumina was a gamma type from Norton, No. 6375 (40 mesh), and had a surface area of 216 $m^2\ g^{-1}$, and a pore volume of 1.1 ml g^{-1}. After impregnation with appropriate solutions of ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$), the samples were dried at 393 K for 16 h, and then calcined under flowing air at 773 K for 3 h.

A 0.7 wt% Co–3 wt% Mo–Al_2O_3 sample was also prepared, by impregnating the 3 wt% Mo/Al_2O_3 sample with a solution of $Co(NO_3)_2 \cdot 6H_2O$. The resulting sample was dried at 393 K for 16 h.

IR spectra were collected using a Nicolet 170 SX FT–IR spectrometer with a liquid nitrogen-cooled MCT detector. All spectra were recorded after 100 scans, at a resolution of 4 cm^{-1}. Spectra were measured using a quartz cell with NaCl windows, that was attached to a glass gas handling/vacuum system.

Hydrogen (ultrahigh purity), and carbon monoxide (99% purity) were passed through molecular sieve traps prior to use. Self-supporting wafers were prepared, mounted in the cell, evacuated for 12 h at approximately 1×10^{-5} Torr before reduction in flowing hydrogen (60 cc/min) for 1 h. The reduced samples were evacuated at 673 K for 0.5 h, and then cooled to room temperature. All spectra were measured after the reduced wafers had been first exposed to 100 Torr CO for 0.5 h, and then evacuated for 0.5 h at 20 Torr.

CO adsorption on freshly calcined, reduced 3 wt% Mo/Al_2O_3 produced a band at 2205 cm^{-1} which can be assigned to Mo(5+) (Fig. 1). CO adsorption on 9 and 12 wt% Mo/Al_2O_3 samples results in bands at 2175, 2130, and 1997: due to Mo(4+), physisorbed CO, and fully reduced Mo(0), respectively (*5, 6*). Our recent XPS investigations of 673 K reduced Mo/Al_2O_3 samples show reduction to Mo(5+), and Mo(4+), but no lower

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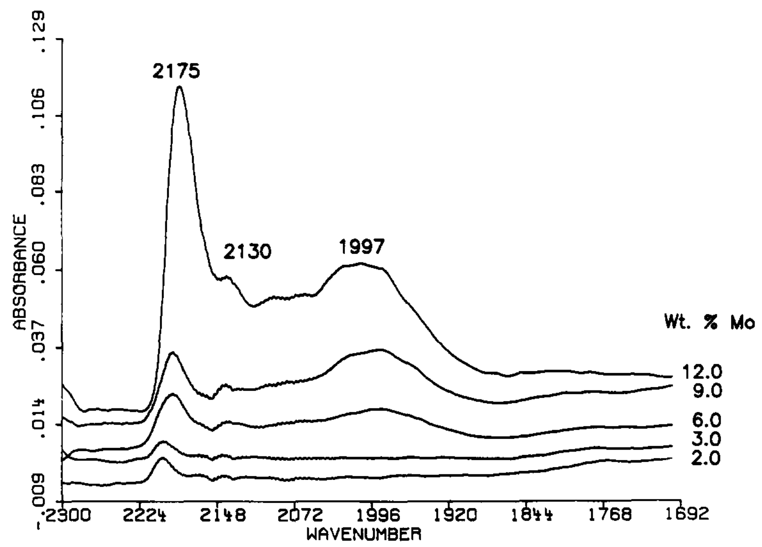

FIG. 1. Infrared spectra of the carbonyl region after CO adsorption on freshly calcined, 673 K reduced Mo/Al_2O_3.

oxidation states (7). It is only with the more sensitive FT–IR technique that Mo(0) is observed.

IR investigations have shown that the hydroxyl groups are eliminated by molybdate species loaded on alumina supports (8). The IR spectra obtained here of the hydroxyl regions of the reduced Mo/Al_2O_3 samples reveal only very weak adsorptions for 9 and 12 wt% materials. For molybdenum load-

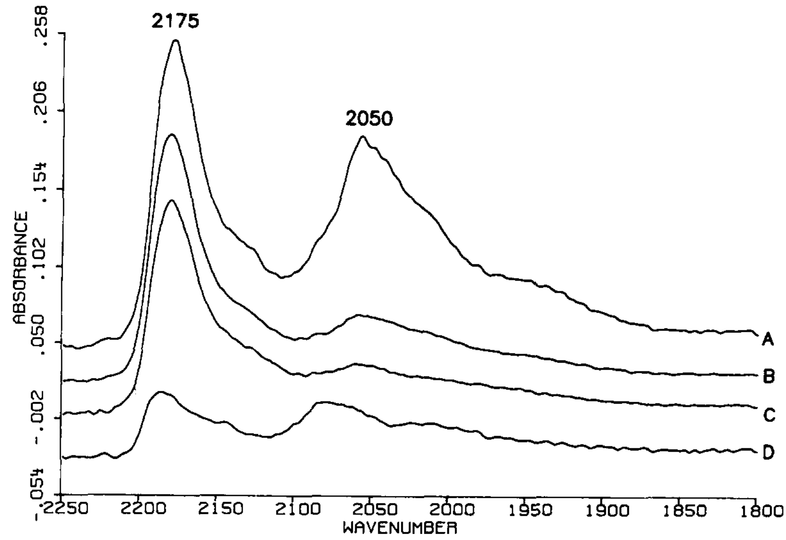

FIG. 2. Infrared spectra of the carbonyl region after CO adsorption on aged, reduced 12 wt% Mo/Al_2O_3 samples: (A) after H_2 reduction at 703 K; (B) after H_2 reduction at 673 K; (c) after H_2 reduction at 643 K; (d) 703 K reduced sample, after evacuation to 5×10^{-5} Torr.

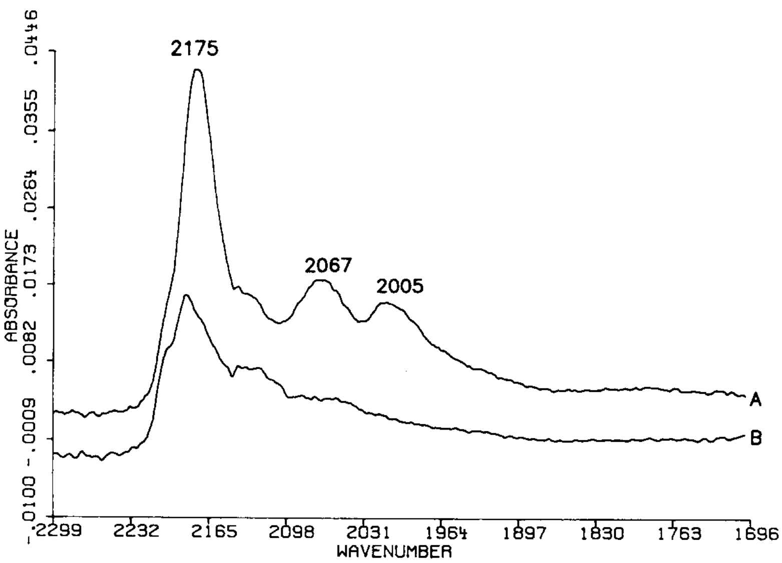

FIG. 3. Infrared spectra of the carbonyl region after CO adsorption on: (A) 3 wt% Mo–0.7% wt% Co/Al_2O_3; and (B) 3 wt% Mo/Al_2O_3, samples after 673 K H_2 reduction.

ings less than 9 wt% there are surface hydroxyl groups present that may act as oxidizing agents for any Mo(0) species formed during the reduction. It is, therefore, reasonable that Mo(0) is only observed on the 9 and 12 wt% samples.

We have found that it is important to have freshly calcined Mo/Al_2O_3 samples in order to observe the band at 2000 cm^{-1} due to Mo(0). Figure 2B shows the IR spectrum of CO adsorbed on a 12 wt% Mo/Al_2O_3 sample which has been stored for several months after calcination. Bands are observed at 2205, 2175, and 2050 cm^{-1}, but no signal is seen at 2000 cm^{-1}. The spectral features observed around 2050 cm^{-1} may be assigned to Mo(2+) species. The hydroxyl regions of the "freshly calcined" reduced 12 wt% Mo/Al_2O_3 and the samples which had been stored for several months before reduction, reveal that the "stored" sample has an additional hydroxyl band at 3745 cm^{-1}. Also, the "stored" sample contains a higher total concentration of hydroxyl groups. This is consistent with data that show that strongly dried alumina chemisorbs at least a monolayer of water when exposed to moisture at room temperature (9). These hydroxyl groups likely act as oxidizing agents for any Mo(0) produced during these moderate temperature reductions.

The reduction temperature has also been found to be important. "Stored" samples reduced at 643 and 673 K produce bands at 2175 and 2050 cm^{-1} (due to Mo(4+) and Mo(2+) species respectively) but no Mo(0) (Fig. 2). Reduction at 703 K results in a slight increase in the intensity of the band centered at 2175 cm^{-1}, a large increase in intensity of the band centered at 2050 cm^{-1}, and the appearance of a small Mo(0) signal at 1975 cm^{-1}. Upon evacuation (Fig. 2D), the band at 2175 cm^{-1} shifts to 2190 cm^{-1}, due to changes in the dipole interactions between the chemisorbed CO molecules, and small bands are still observed at 2070 and 2010 cm^{-1}, again revealing the presence Mo(0) in addition to Mo(2+).

The presence of 0.7 wt% Co in 3 wt% Mo/Al_2O_3 greatly facilitates the reducibility of Mo (Fig. 3). After reduction at 673 K, followed by CO adsorption, 3 wt% Mo/Al_2O_3

produces bands at 2201 and 2175 cm^{-1} due to Mo(5+) and Mo(4+). CO adsorption on reduced 3 wt% Mo–0.7 wt% Co/Al_2O_3 gives rise to a larger band at 2175 cm^{-1}, with very significant signals at 2070 and 2000 cm^{-1} which indicate the presence of Mo(2+) and Mo(0) species.

In conclusion, it has been demonstrated that Mo(0) is observable on conventional Mo/Al_2O_3 samples which have been reduced under relatively mild conditions using infrared analysis of adsorbed CO. Reduction of Mo(0) is dependent upon efficient removal of the hydroxyl groups by calcination, and may require a specific minimum reduction temperature (i.e., 703 K in the 12 wt% "aged" sample described here). Cobalt effects the reduction to Mo(0), even in samples of low Mo loading that do not typically show the presence of Mo(0).

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REFERENCES

1. Zingg, D. S., Makovsky, L. E., Tidcher, R. E., Brown, F. R., and Hercules, D. M., *J. Phys. Chem.* **84,** 2898 (1980).
2. Redey, A., Goldwasser, J., and Hall, W. K., *J. Catal.* **113,** 82 (1988).
3. Nakamura, R., Pioch, D., Bowman, R. G., and Burwell, R. L., Jr., *J. Catal.* **93,** 388 (1985).
4. Goldwasser, J., Fang, S. M., and Hall, W. K., *J. Catal.* **115,** 34 (1989).
5. DeCanio, E. C. and Storm, D. A., submitted for publication.
6. (a) Peri, J. B., *J. Phys. Chem.* **86,** 1615 (1982); (b) Delgado, E., Fuentes, G. A., Hermann, C., Kunzmann, G., and Knozinger, H., *Bull. Soc. Chim. Belg.* **93,** 8 (1984).
7. DeCanio, S. J., Cataldo, M. C., DeCanio, E. C., and Storm, D. A., *J. Catal.* **119,** 256 (1989).
8. Okamoto, Y., and Toshinobu, I., *J. Phys. Chem.* **92,** 7102 (1988).
9. Peri, J. B., *J. Phys. Chem.* **69,** 211 (1965).

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