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NOTE

Low Temperature Chemisorption of CO on Supported Molybdena–Alumina Catalysts

Molybdena–alumina catalysts have been widely used in the petroleum industry (1). Site-selective chemisorption of carbon monoxide (2, 3) is one of several techniques used for monitoring the surface coverage of these catalysts (3–7). Based on their IR results, Knözinger and co-workers (2) showed that CO adsorption, at 77 K on alumina, gave rise to a strong band at 2152 cm^{-1} and a shoulder at 2188 cm^{-1}. The former band, assigned to hydrogen bonded CO molecules, disappeared upon evacuation at the same temperature. The latter band was attributed to carbon monoxide held by coordinatively unsaturated Al^{+3}, and it was modified to a weak band (~2198 cm^{-1}) upon evacuation at 77 K. The absence of the high frequency band for a 12 wt% $\mathrm{MoO_3}$–alumina catalyst suggested an almost unrestricted spreading of the supported molybdates over the support.

Ballinger and Yates (8) have recently used CO adsorption at low temperature (180 K) to probe Al^{+3} Lewis acid sites created upon dehydroxylation of γ-alumina at high temperatures. The IR results showed an approximate linear correlation between the number of OH groups removed by dehydroxylation and the amount of adsorbed CO.

Diaz and Bussell (3) used the selective low temperature adsorption of CO to quantify the coverage of $\mathrm{MoO_3}$ on γ-alumina, employing IR spectroscopy and temperature programmed desorption (TPD). CO adsorption occurred selectively on the uncovered free alumina portion of the surface (Al^{+3} sites). A linear correlation was observed between the CO adsorption capacity of the catalysts and the metal loading. Monolayer growth of $\mathrm{MoO_3}$ occurred on the support surface up to a saturation coverage of $(42 \pm 3) \times 10^{13}$ Mo/cm^2. The calculated monolayer coverage was $(46 \pm 4) \times 10^{13}$ Mo/cm^2.

The main purpose of this work is to re-evaluate the low temperature chemisorption of CO as a method of assaying surface coverage in molybdena–alumina catalysts. In order to achieve this goal, the data obtained in this work, using a simple BET system, is compared to that shown in the work of Diaz and Bussell (3).

γ-alumina (Ketjen CK-300), surface area 210 m^2/g, was used as the support. The catalysts were prepared by impregnation of the support with aqueous solutions of $\mathrm{(NH_4)_6Mo_7O_{24} \cdot 4H_2O}$(BDH, reagent grade) (1, 3). The solids were dried for 2 h at 100°C and calcined for 5 h at 500°C. Surface areas were determined in a Micromeritics Flowsorb II 2300 system. The chemical analysis was performed using atomic absorption spectroscopy. The analytical data are summarized in Table 1.

CO chemisorption experiments were performed in a conventional BET system, similar to that used in Refs. (9) and (10). Catalyst samples were placed in a quartz microreactor and oxidized *in situ* with pure oxygen (60 cm^3 (STP)/min) for 16 h at 500°C. After evacuating the catalysts at 927°C for 3 h($< 1 \times 10^{-5}$ Torr) the CO adsorption isotherms were obtained at 77 K. The double isotherm method (11) was used to measure the amount of irreversibly held CO. The latter was calculated as the difference between the first and the second isotherm, which were parallel and smooth. The catalytic experiments (isomerization and metathesis of 1-butene) were performed at 58°C, after evacuation of the catalysts at 500°C. The experimental details are fully described elsewhere (17).

Table 1 shows a decrease in the amount of chemisorbed CO as the molybdenum loading is increased. This result agrees with other reports (2, 3) and can be understood in terms of coverage of the Al^{+3} sites (free alumina surface) by the molybdenum species. The latter are known to replace the hydroxyl groups of the support, thus decreasing the number of OH groups that can be dehydroxylated at high temperature to generate Al^{+3} species, necessary for the low temperature CO chemisorption. The evacuation temperature of 927°C was selected since previous reports (3, 12) have shown that the alumina surface is totally dehydroxylated at this temperature, thus reflecting the true adsorption capacity of the catalysts and allowing the calculation of the corresponding surface coverage.

Figure 1 shows a linear correlation (correlation coefficient = 0.992) between θ_{exp} and the molybdenum loading. θ_{exp} is defined as the experimental surface coverage, calcu-

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TABLE 1

CO Chemisorption Measurements and Catalytic Activities for the Metathesis of 1-butene[a]

Mo loading		CO chemisorption		Catalytic activity	
Wt% Mo	(Mo/cm^2) × 10^{-13}[b]	μmoles/g_{cat}	θ_{exp}[c]	[d]	[e]
0.0	0.0	1043	0.00	—	—
1.7	5.2	889	0.12	n.d.[f]	n.d.[f]
3.9	12.4	716	0.27	28	2.2
5.5	17.9	554	0.42	68	5.3
8.8	30.3	372	0.59	67	5.2
13.5	50.6	—	—	61	4.7
17.5	70.9	—	—	30	2.3

[a] CO chemisorption temperature = 77 K. Catalysts were previously evacuated at 927°C. For more details see text.

[b] Mo atoms/cm^2 of alumina, calculated as %Mo $6.274 \times 10^{15}/(210(1 - 1.5\%$ Mo/100)). The term in parentheses is the weight fraction of support in the catalyst based on three oxygens per Mo in the calcined catalyst.

[c] Experimental surface coverages. For more details see text.

[d] Initial rates for the production of ethylene, given in (Molecules/min · g_{Mo}) × 10^{18}.

[e] Initial rates for the production of ethylene, given in (Molecules/min · cm^2 of Mo) × 10^{12}. These values are calculated from d/ by assuming 20.6 Å^2/Mo.

[f] n.d., not detected.

lated according to

$$\theta_{exp} = 1 - \frac{Q_{cat}}{Q_{alumina}\,(1 - 1.5\%\,\text{Mo}/100)} \qquad [1]$$

where Q_{cat} and $Q_{alumina}$ are the chemisorption values of CO for the catalyst (μmoles/g_{cat}) and the support (μmoles/$g_{alumina}$), respectively. Equation [1] is similar to that used by Zmierczak *et al.* (19). The term in parentheses is the weight fraction of support in the catalyst based on three oxygens per Mo in the calcined catalyst.

Extrapolation of the line in Fig. 1 to $\theta_{exp} = 1$ yields a value of 48.6×10^{13} Mo/cm^2 for the Mo loading required for complete surface coverage, or 20.6 Å^2/Mo for the molybdenum species cross-sectional area. These values agree with other reports (3–5, 7), particularly with those given in Ref. (3) (46×10^{13} Mo/cm^2).

The isomerization and metathesis of 1-butene was carried out in order to establish a possible link between the surface coverage measurements and catalytic activities. Only the initial rate of production of ethylene (internal metathesis) is shown in this work. Table 1 shows a large increase in the catalytic activity per cm^2 of Mo, with increasing molybdenum loading up to ~17.9×10^{13} Mo/cm^2. For higher loadings, up to 50.6×10^{13} Mo/cm^2, the catalytic activity remains basically constant, while showing a decrease for the 70.9×10^{13} Mo/cm^2 catalyst.

Previous studies (13, 17) have shown that for catalysts activated by thermal treatment at moderate temperatures (≤500°C), the more easily reducible the catalyst is, the easier it would be to effect olefin metathesis. The low loading catalyst contains predominantly tetrahedrally coordinated monomeric species (18). These difficult to reduce monomers are basically inactive for the metathesis reaction. As the metal loading is increased, octahedrally coordinated polymeric molybdate species appear on the

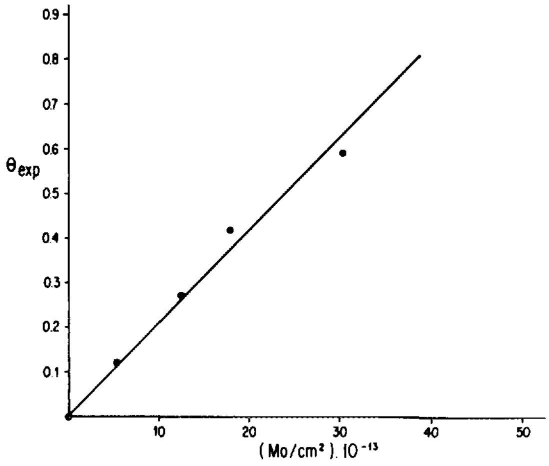

FIG. 1. Plot of θ_{exp} vs molybdenum loading.

surface. The latter are more easily reducible, upon contact with 1-butene, than the monomeric entities (17, 18), thus rendering a more active catalyst. Once the reduction requirement is fulfilled, no significant changes in the catalytic activity are observed up to a loading similar to that calculated for monolayer coverage. This result is expected for monolayer-type catalysts, since there is no significant change in the degree of exposure of the metal phase with increasing loading. For Mo contents above the monolayer capacity, the catalytic activity per cm^2 of Mo decreases (20) due to the formation of poorly dispersed bulklike Mo phases (3, 5, 7), which show little activity for the metathesis reaction.

The data obtained in this work show that CO chemisorption, using a very simple BET apparatus, is a simple and useful technique for assaying surface coverage in molybdena–alumina catalysts. These results are very different from those obtained by site-selective chemisorption of carbon dioxide (6, 14). The latter interacts preferentially with the high-frequency hydroxyl groups to which the molybdena species are selectively chemisorbed, thus leading to an overestimation of the molybdena surface coverage (15, 16, 21).

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REFERENCES

1. Massoth, F. E., *in* "Advances in Catalysis" (D. D. Eley, P. H. Selwood, and P. B. Weisz, Eds.), Vol. 27, p. 265. Academic Press, New York, 1978.
2. Zaki, M. I., Vielhaber, B., and Knözinger, H., *J. Phys. Chem.* **90,** 3176 (1986).
3. Diaz, A. L., and Bussell, M. E., *J. Phys. Chem.* **97,** 470 (1993).
4. Mulcahy, F. M., Houalla, M., and Hercules, D. M., *Anal. Chem.* **62,** 2232 (1990).
5. Cheng, C. P., and Schrader, G. L., *J. Catal.* **60,** 276 (1979).
6. Segawa, K. I., and Hall, W. K., *J. Catal.* **77,** 221 (1982).
7. Dufresne, P., Payen, E., Grimblot, J., and Bonnelle, J. P., *J. Phys. Chem.* **85,** 2344 (1981).
8. Ballinger, T. H., and Yates, J. T., Jr., *Langmuir* **7,** 3041 (1991).
9. Goldwasser, J., and Hall, W. K., *J. Catal.* **71,** 53 (1981).
10. Goldwasser, M. R., Rojas, D., and Goldwasser, J., *J. Catal.* **135,** 596 (1992).
11. Ramakrishnan, N. R., and Weller, S. W., *J. Catal.* **67,** 237 (1981).
12. Goldwasser, J., Houalla, M., Fang, S. M., and Hall, W. K., *J. Catal.* **115,** 34 (1989).
13. Thomas, R., and Moulin, J. A., *J. Mol. Catal.* **15,** 157 (1982).
14. O'Young, C., Yang, C., DeCanio, S. J., Patel, M. S., and Storm, D. A., *J. Catal.* **113,** 307 (1988).
15. Mulcahy, F. M., Kozminski, K. D., Slike, J., Ciccone, F., Scierka, S. J., Eberhardt, M. A., Houalla, M., and Hercules, D. M., *J. Catal* **139,** 688 (1993).
16. Gonzalez, L., Galavís, J. L., Scott, C., Pérez Zurita, M. J., and Goldwasser, J., *J. Catal.* **144,** 636 (1993).
17. Pantoja, A., Sarrín, J., Gonzalez, L., Noguera, O., Pérez Zurita, M. J., Galavís, J. L., and Goldwasser, J., *J. Catal.* **142,** 110 (1993).
18. Hall, W. K., *in* "Proceedings of the 4th International Conference on Chemistry and Uses of Molybdenum" (H. F. Barry and P. C. Mitchell, Eds.), p. 224. Climax Molybdenum Co., Ann Arbor, MI, 1982.
19. Zmierczak, W., Qader, Q., and Massoth, F. E., *J. Catal.* **106,** 65 (1987).
20. Giordano, N., Padovan, M., Vaghi, A., Bart, J. C. J., and Castellan, A., *J. Catal.* **38,** 1 (1975).
21. Topsøe, N-Y., and Topsøe, H., *J. Catal.* **139,** 631 (1993).

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