JOURNAL OF CATALYSIS **144**, 636–640 (1993)

A Study of the CO_2 Chemisorption on Supported Molybdena–Alumina Catalysts

A series of molybdena–alumina catalysts (1.3–8.2 wt% Mo) was prepared by the adsorption equilibrium method. The solids were studied using IR spectroscopy and CO_2 chemisorption to establish the feasibility of using the latter as a convenient method for determining surface coverage in molybdena–alumina catalysts. The volumetric results showed a strong decrease in the amount of chemisorbed CO_2 as the metal loading was increased. The IR data showed that the decrease in CO_2 chemisorption, with Mo loading, does not correlate with a decrease in the total alumina surface area. Rather, it correlates with a decrease in the number of high-frequency hydroxyl groups to which carbon dioxide and the molybdena species are selectively chemisorbed. These results strongly suggest that the use of CO_2 chemisorption to measure the surface coverage by molybdena leads to an overestimation of the latter. © 1993 Academic Press, Inc.

The importance of molybdena–alumina catalysts in the petroleum industry is well established (*1*). A commonly used technique for monitoring the surface coverage of these catalysts is the chemisorption of carbon dioxide (*2–5*). Segawa and Hall (*2*) reported that CO_2 was selectively chemisorbed on the uncovered alumina portion of the surface of an 8% molybdena–alumina catalyst. For the pure alumina, the chemisorption of CO_2 almost completely eliminated the high-frequency band present in the hydroxyl region of the infrared spectrum. The infrared bands of other alumina hydroxyls were not greatly affected by the chemisorption of carbon dioxide.

Millman *et al.* (*3*) and O'Young *et al.* (*4*), working with a series of molybdena–alumina catalysts with varying metal loading, observed a strong decrease for the CO_2 chemisorption at low metal loading (3–4 wt% Mo); a less pronounced decrease was observed for higher molybdenum contents. These results were used (*4*) to determine the fraction of free alumina surface as a function of Mo loading.

Okamoto and Imanaka (*5*) studied a series of molybdena–alumina catalysts with varying metal loading, using IR spectroscopy and the chemisorption of CO_2. The results for the latter indicated a decrease in the 1237-cm^{-1} (bicarbonate species) band with Mo loading, suggesting a concomitant lowering of the free alumina surface area. Complete elimination of the band occurred for a loading of ca. 26×10^{13} Mo/cm^2.

Recently, Mulcahy *et al.* (*6*) suggested that interactions of Mo, W, V, Cr, and Re oxyanions with alumina occur first at the same alumina sites and that these sites are the same as those at which CO_2 was selectively chemisorbed. Thus, the use of CO_2 chemisorption could lead to an overestimation of the surface coverage.

The main purpose of this work is to reevaluate the chemisorption of CO_2 as a method for assaying surface coverage in molybdena–alumina catalysts. Volumetric chemisorption measurements, as well as quantitative IR data on the effect of CO_2 on the different hydroxyl groups present on the catalysts, are used as characterization tools.

The catalysts were prepared by the adsorption equilibrium method devised by Wang and Hall (*7*). Preparation details are given elsewhere (*8*). The analytical data are given in Table 1. The CO_2 volumetric measurements were performed by two different

0021-9517/93 $5.00

TABLE 1

CO_2 Chemisorption Measurements[a] and Fraction of Total Hydroxyl Groups of the Support Left after Addition of Molybdena Species (f_{tot})[b]

Mo loading		Amount of CO_2 chemisorbed		f_{vol}[e]	f_{tot}
Wt% Mo	(Mo/cm^2) $\times 10^{-13}$	Molec/nm^2[c]	Molec/nm^2[d]		
0.0	0.0	0.42	0.43	1.00	—
1.3	3.8	0.28	0.29	0.67	0.80
3.9	11.3	0.17	0.16	0.39	0.71
6.0	17.4	0.030	0.030	0.071	0.65
8.2	23.8	0.026	0.026	0.061	0.58

[a] CO_2 chemisorption measured volumetrically. For more details, see text.

[b] Fraction of free hydroxyl groups left before the addition of CO_2, determined by IR spectroscopy. For more details, see text.

[c] CO_2 chemisorption results obtained by method 1. See text for details.

[d] CO_2 chemisorption results obtained by method 2. See text for details.

[e] Fraction of free alumina surface area given as the average between the values obtained for both methods. For calculation details, see text.

methods in a conventional BET system (*8*). The procedures are described in full detail in Ref. (*9*). In short, the first method involved treatment with flowing O_2 (60 cm^3 (NTP)/min) for 12 h at 500°C before cooling to room temperature under high vacuum ($<1 \times 10^{-5}$ Torr). The catalyst was then exposed to 100 Torr of CO_2 for 30 min. The excess of gas was measured and the amount of chemisorbed CO_2 was obtained from the difference. The temperature was then raised to 500°C and the desorbed gas was measured in a similar fashion (second method).

The IR data were recorded on a Perkin–Elmer 1760X FT spectrometer with a resolution of 2 cm^{-1}. The IR cell was described previously (*8*). Samples were mounted in the cell as wafers having a thickness of approximately 20 mg/cm^2. The infrared studies were carried out after the pretreatment procedure described above. The spectra were recorded in the region 3000–4000 cm^{-1}. The sample was contacted with 100 Torr of CO_2 for 30 min and then evacuated for 1 h at room temperature. The spectra with chemisorbed CO_2 were then taken. Integrated intensities (absorbances) were normalized to unit wafer thickness and corrected for small differences in surface areas. The results are given in arbitrary units/cm^2 of surface area (A.U./cm^2). The quantification for the individual hydroxyl bands was made for the alumina and the 1.3 and 3.9% Mo catalysts. For the other catalysts the individual bands were virtually impossible to resolve and quantify.

Table 1 shows the amounts of chemisorbed CO_2 as a function of the molybdenum loading. The two methods of measuring the chemisorbed CO_2 were in excellent agreement. The values obtained compare favorably with those reported in the literature (*3*, *4*). The fraction of free alumina surface (f_{vol}), calculated as the ratio between the chemisorption values for each catalyst and that for pure alumina, shows a strong decrease with Mo loading up to 6.0% Mo; a less pronounced decrease is observed for the 8.2% Mo catalyst.

The IR spectra of the hydroxyl regions (before adsorption of CO_2) are shown in Fig. 1a. Strong bands at ca. 3768, ca. 3729, and ca. 3677 cm^{-1} are observed together with broad bands extending to lower frequencies. These frequency values agree with other reports (*10*). As the Mo loading is increased, the intensity of the bands decreases, indicating a replacement of the alumina hydroxyl groups by molybdate species (*2*, *5*). The quantitative information is summarized in Tables 1 and 2. The fraction of total hydroxyl groups of the support left uncovered by the addition of molybdenum oxyanions (f_{tot}), calculated as the ratio between the area for the total hydroxyl region (3000–4000 cm^{-1}) for each catalyst and that for alumina, is shown in Table 1 (last column). The results are within 20% of those obtained for similar preparations by ion scattering spectroscopy (*11*). These results do not correlate well with f_{vol}.

The data shown in Table 2 (third column) show a totally different behavior. The results indicate a selective disappearance of the high-frequency hydroxyl groups of the support upon addition of molybdenum oxyanions, as suggested by other studies (*5*, *6*, *12*). The f_{vol} correlates fairly well with the

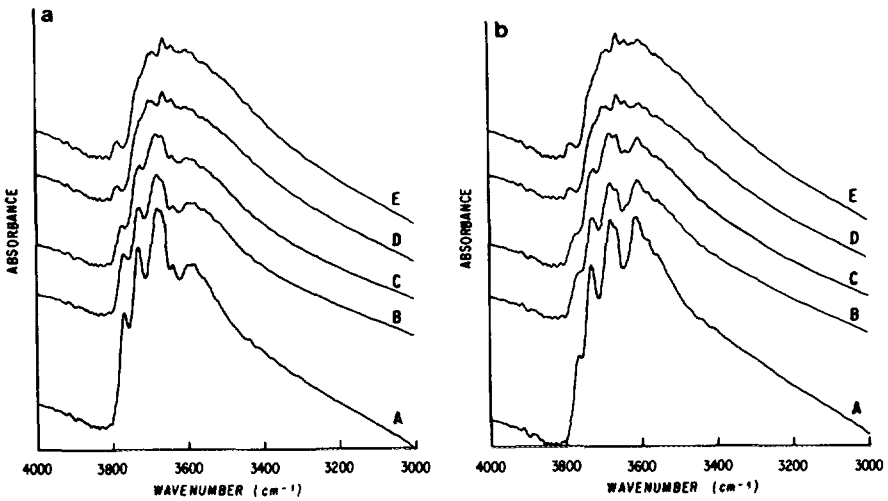

FIG. 1. (a) Infrared spectra of hydroxyl groups for alumina and molybdena–alumina catalysts: (A) γ-alumina, (B) 1.3% Mo, (C) 3.9% Mo, (D) 6.0% Mo, and (E) 8.2% Mo. (b) Infrared spectra of hydroxyl groups for alumina and molybdena–alumina catalysts after chemisorption of CO_2: (A) γ-alumina (B) 1.3% Mo, (C) 3.9% Mo, (D) 6.0% Mo, and (E) 8.2% Mo.

TABLE 2

Integrated Intensities of the Different Hydroxyl Groups of the Alumina and Molybdena–Alumina Catalysts

Catalyst	Vibrational frequency (cm^{-1})	Amount of hydroxyl groups uncovered (A.U./cm^2)		Amount of hydroxyl groups covered by CO_2 (A.U./cm^2)[a]	Fraction of hydroxyls uncovered[b]
		Before CO_2 chemisorption	After CO_2 chemisorption		
Alumina	3766	3.5	2.3	1.2(0.66)[c]	—
	3729	5.2	4.6	0.6(0.89)[c]	—
	3677	6.2	5.8	0.4(0.94)[c]	—
1.3% Mo	3768	2.5(0.72)[d]	1.7	0.8	0.67
	3725	4.0(0.77)[d]	3.5	0.5	0.83
	3679	5.0(0.81)[d]	4.6	0.4	1.00
3.9% Mo	3772	1.9(0.54)[d]	1.4	0.5	0.42
	3722	3.5(0.68)[d]	3.1	0.4	0.67
	3682	4.6(0.74)[d]	4.3	0.3	0.75

[a] Obtained as the difference between the corresponding values in columns 3 and 4.

[b] Fraction of OH groups left uncovered by the chemisorption of CO_2.

[c] Values in parentheses correspond to the fraction of free hydroxyl groups left in the support after CO_2 chemisorption, calculated as the ratio between the values in columns 4 and 3.

[d] Values in parentheses correspond to the fraction of hydroxyl groups uncovered before the adsorption of CO_2. The values for the high-frequency bands are defined as f_b (see text). All values were calculated as the ratio between the amount of hydroxyls uncovered for each catalyst and the corresponding values for alumina.

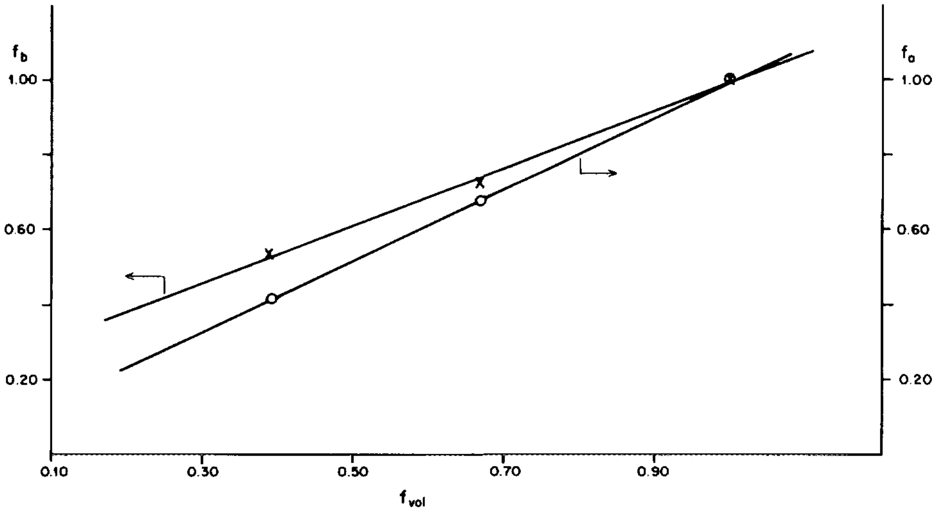

FIG. 2. Plot of f_b and f_a vs f_{vol}. The correlation coefficients obtained were 0.997 (f_b vs f_{vol}) and 0.999 (f_a vs f_{vol}).

fraction of high-frequency hydroxyl groups uncovered (f_b) (Fig. 2), and not with the fraction of *total* hydroxyl groups uncovered, suggesting that the same particular surface sites (basic hydroxyl groups) interact with CO_2 and molybdenum oxyanions. As the molybdenum loading increases, the lack of correlation between f_{tot} and f_{vol} becomes more evident, since the specific adsorption sites for CO_2 are progressively blocked by the molybdena species.

The results obtained for the chemisorption of CO_2 followed by IR spectroscopy are summarized in Fig. 1b and Table 2. A new band at ca. 3612 cm^{-1} assigned to bicarbonate species is observed (*5*). The data (Table 2) show a strong selectivity for the interaction of CO_2 with the high-frequency hydroxyl groups of the support, as suggested by other authors (*2, 5*). The fraction of hydroxyl groups left uncovered by the chemisorption of CO_2 is calculated as the ratio between the amount of hydroxyl groups covered by CO_2 (A.U./cm^2) for each catalyst and that amount for pure alumina. This fraction measured for the high-frequency band (f_a) (Fig. 2) shows a strong correlation with f_{vol}, the fraction of alumina surface area. These results quantitatively support the observations concerning the selectivity of molybdenum oxyanions and CO_2 for certain hydroxyl groups of the support.

In conclusion, our quantitative data show that the decrease in CO_2 chemisorption observed in this work, and by other authors (*3–5*), with molybdenum loading does not correlate with a decrease in the total uncovered alumina surface area. Rather, it correlates with a decrease in the number of high-frequency hydroxyl groups to which CO_2 and the molybdena species are selectively chemisorbed. Thus, the use of CO_2 chemisorption to measure the surface coverage by molybdena leads to an overestimation of the latter, as suggested by Mulcahy *et al.* (*6*).

ACKNOWLEDGMENT

The authors are grateful to Consejo Nacional de Investigaciones Científicas y Technológicas (CONICIT) for support of this work through Grant S1-1322.

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. Segawa, K., and Hall, W. K., *J. Catal.* **77**, 221 (1982).

3. Millman, W. S., Segawa, K., Smrz, D., and Hall, W. K., *Polyhedron* **5,** 169 (1986).
4. O'Young, C., Yang, C., DeCanio, S. J., Patel, M. S., and Storm, D. A., *J. Catal.* **113,** 307 (1988).
5. Okamoto, Y., and Imanaka, T., *J. Phys. Chem.* **92,** 7102 (1988).
6. Mulcahy, F. M., Kozminski, K. D., Slike, J. M., Ciccone, F., Scierka, S. J., Eberhardt, M. A., Houalla, M., and Hercules, D. M., *J. Catal.* **139,** 688 (1993).
7. Wang, L., and Hall, W. K., *J. Catal.* **77,** 232 (1982).
8. Pantoja, A., Sarrín, J., Gonzalez, L., Noguera, O., Pérez Zurita, M. J., Galavís, J. L., and Goldwasser, J., *J. Catal.* **142,** 110 (1993).
9. Redey, A., Goldwasser, J., and Hall, W. K., *J. Catal.* **113,** 82 (1988).
10. Turek, A. M., Wachs, I. E., and DeCanio, E., *J. Phys. Chem.* **96,** 5001 (1992).
11. Mulcahy, F. M., Houalla, M., and Hercules, D. M., *Anal. Chem.* **62,** 2232 (1990).
12. van Veen, J. A. R., and Hendricks, P. A. J. M., *Polyhedron* **5,** 75 (1986).

L. GONZALEZ
J. L. GALAVÍS
C. SCOTT
M. J. PÉREZ ZURITA
J. GOLDWASSER[1]

Centro de Catálisis, Petróleo y Petroquímica
Esquela de Química, Facultad de Ciencias
Universidad Central de Venezuela
Apartado 47102, Los Chaguaramos
Caracas, Venezuela

Received March 16, 1993; revised June 28, 1993

---

[1] To whom correspondence should be addressed.