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Chemisorption of CO_2 on Alumina-Supported Catalysts

A large number of industrially important catalysts are prepared by contacting a high-surface-area metal oxide support with a solution containing an active phase precursor metal ion. Following this impregnation step, catalysts are dried and then calcined to decompose the precursor to the metal oxide. A catalyst may then be subjected to a pretreatment, such as reduction or sulfidation, before use in a reactor. The coverage of the support by the active phase of a catalyst is important, since it will often determine catalytic activity. Thus, to properly evaluate the effectiveness of a particular preparation, it is useful to monitor the extent to which the active phase covers the support surface.

The techniques used to characterize the surface coverage of supported catalysts depend on the state and structure of the active phase. For a highly dispersed, monolayer-like system like Mo/Al_2O_3, CO_2 chemisorption has been shown to be a useful means for monitoring the coverage of the surface of the support (*1–4*). This method has also been applied to Mo/TiO_2 catalysts (*5*).

One of the limitations in using CO_2 chemisorption to monitor surface coverage is that the method is based on selective chemisorption on the support (*1*). Thus, only certain support–active phase combinations are suitable for characterization using this technique. The objective of the present study is to examine CO_2 chemisorption on a wider variety of catalysts (Mo, W, V, Cr, and Re supported on Al_2O_3). Catalysts are prepared by equilibrium adsorption in order to ensure that the active phase is uniformly distributed over the support.

Catalyst samples were prepared by equilibrium adsorption of ammonium salts of heptamolybdate, metatungstate, metavanadate, dichromate, and perrhenate from solution (0.055 *M* in monomeric anion) on γ-Al_2O_3 (American Cyanamid, BET surface area = 205 m^2/g). The pH of the impregnation solution was adjusted with HNO_3 or NH_4OH. The ratio of the mass (g) of alumina to the volume (ml) of solution was 1 : 58. Adsorption of the metal oxyanions was carried out for 24 h, after which the solutions were filtered. The residue was dried in air overnight at 120°C and calcined in air at 500°C for 16 h.

Chemisorption of CO_2 was carried out at 0°C by passing 0.5-ml pulses of CO_2 at 5-min intervals through an 0.8-g catalyst bed packed in a pyrex tube. Samples were pretreated by purging in helium at 500°C for 1 h. Helium was used as the CO_2 carrier, and the amount of CO_2 in the effluent was measured using the thermal conductivity detector of an HP3700 gas chromatograph. Chemisorption was considered complete when the detector gave the same response for consecutive pulses. When chemisorption was complete, the sample was outgassed by raising the temperature to 450°C. No outgassing was observed above about 300°C. The amount of CO_2 outgassed is the value reported for CO_2 chemisorption.

The amount of CO_2 chemisorbed on the pure support was 0.35 CO_2 molecules/nm^2. This value compares favorably with values obtained by O'Young *et al.* (0.327 molecules/nm^2) (*4*), Zmierczak *et al.* (0.25 molecules/nm^2) (*3*), and Millman *et al.* (0.51 molecules/nm^2) (*2*).

Figure 1 illustrates the change in the number of CO_2 molecules adsorbed/nm^2 of alu-

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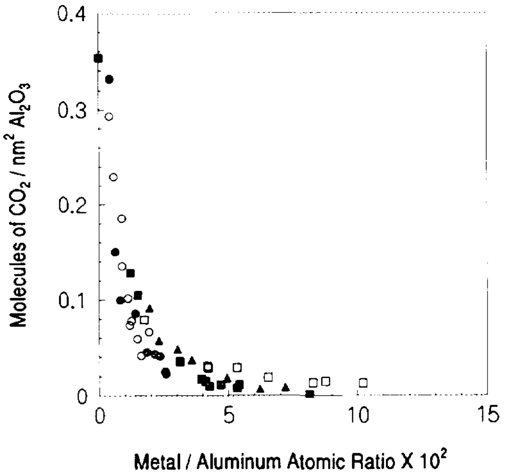

FIG. 1. Variation of CO_2 molecules chemisorbed per unit alumina surface area as a function of metal/bulk Al atomic ratio: (■) Mo, (□) W, (▲) V, (●) Cr, and (○) Re.

mina surface area as a function of the active phase loading, expressed as the metal/bulk Al (M/Al) atomic ratio. From this figure, it may be observed that CO_2 chemisorption decreases sharply with the first small increases in metal loading, almost reaching zero for M/Al ratios of 0.025. These results resemble the qualitative results recently shown by Turek *et al.* (*6*). Also, it is interesting to note that suppression of CO_2 chemisorption depends only on the metal loading and is independent of the type of active phase (Mo, W, V, Cr, or Re).

To rationalize these results, it is important to point out that CO_2, in addition to being selectively adsorbed on alumina, is also selective in the type of alumina sites with which it interacts. Using a value of 4.5 OH/nm^2 for the pure support calcined at 500°C (*7*), and assuming that CO_2 adsorbs primarily on basic hydroxyl groups, the number of hydroxyl groups on which CO_2 adsorbs is only 7.2% of the total number present at 500°C. It is therefore evident that CO_2 chemisorbs on only a fraction of the alumina surface. Okamoto *et al.* (*8*) have shown that the adsorption of CO_2 on alumina results in a decrease in the intensity of the infrared absorption of basic hydroxyl groups, but does not greatly affect the absorption bands of other alumina hydroxyls. Thus, CO_2 chemisorption measurements will only reflect surface coverage if the material covering the surface interacts with surface hydroxyl groups in a nonselective manner.

Active phases like Mo and W, which are derived from metal oxyanions, are believed to interact strongly with the basic hydroxyl groups of alumina (*8–10*). Thus, the sites to which CO_2 binds are also the sites which favor interactions with Mo, W, V, Cr, and Re on oxidic catalysts. The sharp decrease in CO_2 chemisorption observed in Fig. 1 implies that the first sites which are occupied by the supported phases are binding sites for CO_2. This may cause surface coverages determined by CO_2 chemisorption to be overestimated. For instance, monolayer coverage for a Mo/Al_2O_3 catalyst has been variously reported to be between 8 and 12 wt% Mo (Mo/Al atomic ratios of 0.046 and 0.072, respectively) (*2, 11*). If Mo is present as a monolayer on alumina, a catalyst with an Mo/Al atomic ratio of 0.025 (4.5% Mo) should have a coverage of between 35 and 54%. From the CO_2 chemisorption results presented in Fig. 1, the coverage of a catalyst with a Mo/Al atomic ratio of 0.025 is estimated to be 94%.

An additional point which deserves consideration is the fact that suppression of CO_2 chemisorption as a function of metal loading appears to be independent of the nature of the metal (Mo, W, etc.). This indicates that all of these active phases are all bound in similar fashion to the same types of sites on the alumina surface. This behavior is not expected a priori, since the active phase precursors, with the exception of ReO_4^-, can be present as polymeric species ($Mo_7O_{24}^{-6}$, $W_{12}O_{39}^{-6}$, etc.) in the impregnation solutions (*12*). One factor which may explain the similarity of Mo, W, V, Cr, and Re active phases for suppression of CO_2 chemisorption is that for low loadings, monomeric oxyanions predominate. Another factor is that calcination of the samples can lead to redispersion of the active phase. Active phase clusters may decompose into dispersed oxide species, which then interact with alumina hydroxyl groups.

In conclusion, it appears that interactions of Mo, W, V, Cr, and Re with alumina occur first at the same alumina surface sites and that these sites are the same as those at which CO_2 chemisorption occurs. Use of CO_2 chemisorption to determine surface coverage may therefore lead to overestimation of surface coverage.

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