Interaction between Carbon Dioxide and the Zinc Oxide Surface

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The adsorption of carbon dioxide has been measured at 25 °C on zinc oxide surfaces with different amounts of preadsorbed carbon dioxide. As a result, it has been found that carbon dioxide molecules are chemisorbed more weakly to zinc oxide surfaces than water; the desorbability of carbon dioxide is almost complete upon evacuation at temperatures higher than 300 °C, whereas upon evacuation at 25 °C 80% of the carbon dioxide remains on the surface. Also, the adsorption isotherms of carbon dioxide have been obtained at 25 °C on differently-hydroxylated surfaces of zinc oxide. On such surfaces, the adsorption amount of carbon dioxide decreases linearly with an increase in the amount of surface hydroxyl groups. This suggests that most of the carbon dioxide is adsorbed strongly on the vacant sites formed by dehydroxylation, and not on the surface hydroxyl groups.

Recently, it has been reported that surface hydroxyl groups react with carbon dioxide to form bicarbonate species on a variety of metal oxides.[1–5] Especially, Boehm has applied the adsorption measurement of carbon dioxide to the titration of basic hydroxyl groups on η-Al_2O_3.[2] On the other hand, Taylor and Amberg[6] and Hockey *et al.*[7] have discovered, from IR studies, that absorption bands due to surface hydroxyl groups on zinc oxide are not disturbed by the chemisorption of carbon dioxide. It would probably be difficult to ascertain the formation of bicarbonate species on zinc oxide surfaces from such IR spectra, since the perturbation in the surface hydroxyl region due to bicarbonate formation is very small.

Consequently, it seems that it would be interesting to examine the adsorption of carbon dioxide on zinc oxide in connection with the population of surface hydroxyl groups. Hitherto, though many authors have measured the adsorption isotherms of carbon dioxide on zinc oxide, most of them have been concerned with the measurements to obtain isosteric heats of adsorption at elevated temperatures.[8–11] Very recently, it has been found[12,13] that surface hydroxyl groups on zinc oxide can be removed by degassing at rather higher temperatures, and that a two-dimensional condensation of water occurs on such hydroxylated surfaces. In relation to these problems, the measurements of the adsorption of various gases on well-defined zinc oxide surfaces are desirable.

This work will deal with the interaction between carbon dioxide and zinc oxide surfaces covered with controlled amounts of preadsorbed carbon dioxide or surface hydroxyl groups, on the basis of the adsorption measurements of carbon dioxide at room temperature.

Experimental

Materials. Zinc oxide was prepared by burning zinc metal in air in our laboratory. The purity of the zinc metal used was, according to the maker's assay, 0.01% Pb, 0.002% Cu, 0.005% Cd and Fe, 0.00005% As, and traces of S and P. X-ray analysis showed that the zinc oxide thus prepared was highly crystalline. Carbon dioxide gas from dry ice was purified by trapping and degassing at the temperature of liquid nitrogen and by following to sublimation at the temperature of the dry ice-ethanol mixture.

Adsorption of Carbon Dioxide. The adsorption of carbon dioxide was measured volumetrically by means of a conventional adsorption apparatus equipped with an oil manometer. Prior to the adsorption measurements, a zinc oxide sample of *ca.* 6 g was degassed at 600 °C under a reduced pressure of 10^{-5} Torr for 30hr in order to remove the chemisorbed water and carbon dioxide.

The adsorption isotherm of carbon dioxide was first measured at 25 °C on a fresh surface of a sample degassed at 600 °C. After this, the sample was degassed for 4 hr at 25 °C and was then applied to the second adsorption isotherm at 25 °C. By increasing the degassing temperatures, the adsorption isotherms on the surfaces with partially-preadsorbed carbon dioxide were obtained at 25 °C by using the same sample.

In order to examine the influence of surface hydroxyl groups upon the adsorption of carbon dioxide, the sample was degassed for 30 hr at 600 °C and was then exposed to the saturated water vapor over night at room temperature. This sample was again degassed for 4hr at different temperatures (100, 300, 350, and 400 °C) to prepare differently-hydroxylated surfaces. On these surfaces, the adsorption of carbon dioxide was measured at 25 °C.

Measurement of the Water Content. The surface water content was measured by the successive-ignition-loss method on a sample which had been pretreated at 600 °C, exposed to the saturated water vapor overnight at room temperature, and degassed for 4 hr at 30 °C in a vacuum of 10^{-5} Torr in order to remove the physisorbed water. A small amount of carbon dioxide expelled from the sample together with the water vapor was removed from the mixture by evacuating the mixture in a condensed state at −78 °C.[14]

Measurement of the Surface Area. The surface area of zinc oxide was measured by the BET method with nitrogen as an adsorbate. The specific surface area of the sample evacuated at 600 °C for 30 hr was 3.5 m^2/g.

Results and Discussion

The adsorption amount of carbon dioxide at 300 °C on the zinc oxide evacuated at 600 °C for 30 hr changes with the time, as is shown in Fig. 1. It can be seen from Fig. 1 that the initial fast adsorption is followed by a slow process for every dose of carbon dioxide, and that the slow adsorption increases linearly with the time and that its rate is proportional to the pressure. The adsorption at the initial stage is too rapid to pursue accurately by means of an oil manometer, and it largely finishes within a few minutes. The same trend also appears in adsorption experiments at different temperatures, but the lower the adsorption temperature, the shorter the time required for the attainment of

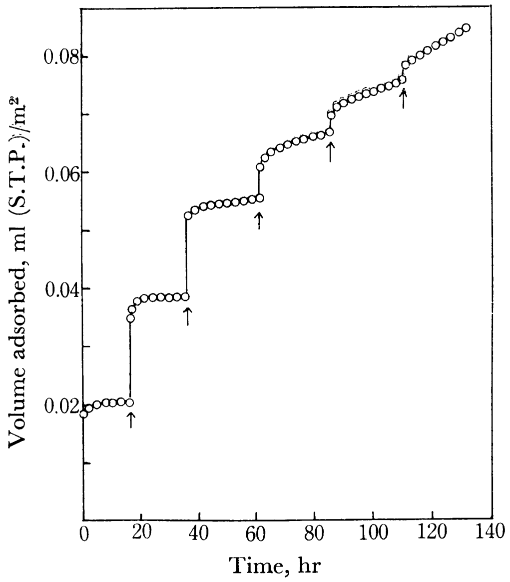

Fig. 1. Change in the amount of adsorbed CO$_2$ with time; arrows indicate admissions of small amount of CO$_2$.

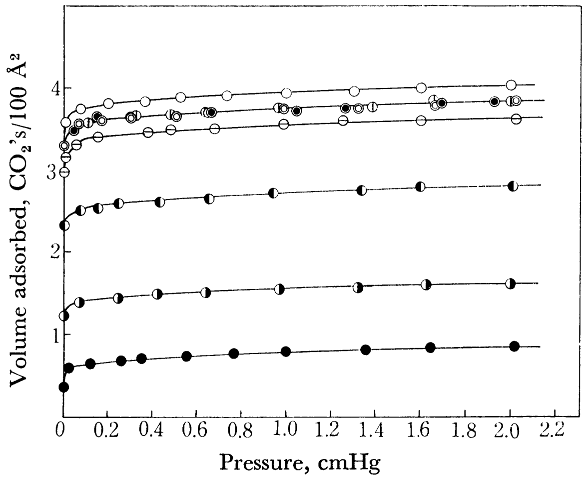

Fig. 2. Adsorption isotherms (25 °C) of CO$_2$ on ZnO pretreated at various temperatures. ○: after initial degassing at 600, ●: after degassing at 25, ◑: 100, ◐: 200, ⊖: 300, ◎: 400, ⊙: 500, ⦶: 600 °C.

the adsorption equilibrium. Thus, it follows that the adsorption measurements based on the pressure reading within one or two hours after every dose of carbon dioxide should refer only to the fast adsorption.

Figure 2 is an example of the adsorption isotherms of carbon dioxide obtained at 25 °C over various surfaces with preadsorbed carbon dioxide; the ordinate is expressed in the number of carbon dioxide molecules adsorbed per 100 Å^2 of the surface. The isotherm obtained on a fresh surface degassed at 600 °C is much higher than that obtained on a sample degassed at 25 °C after the first adsorption experiment. The amount of carbon dioxide adsorbed on the surfaces with preadsorbed carbon dioxide increases with the evacuating temperature, and approaches that on the fresh surface when the surfaces are evacuated above 300 °C. All the adsorption data thus obtained can be expressed approximately by the Langmuir equation, which makes it possible to calculate the saturated values of adsorbed carbon dioxide, as is shown in Fig. 3. It may be seen clearly from Fig. 3 that the higher the degassing temperature before the second adsorption, the larger the second adsorption amount of carbon dioxide; the amount of adsorption on the zinc oxide degassed at 300 °C is approximately equal to that on the zinc oxide degassed at 600 °C. In other words, the carbon dioxide adsorbed on zinc oxide is almost completely desorbed at temperatures higher than 300 °C, while about 20% of the adsorbed carbon dioxide can be removed by evacuation at 25 °C.

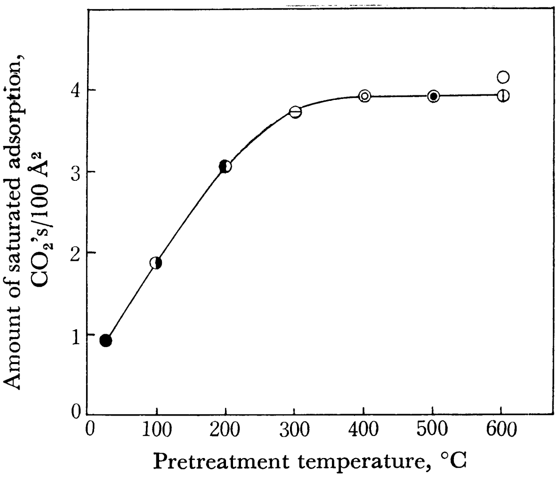

Fig. 3. Dependence of the amount of adsorbed CO$_2$ at 25 °C upon degassing temperature, ○: after initial degassing at 600, ●: after degassing at 25, ◑: 100, ◐: 200, ⊖: 300, ◎: 400, ⊙: 500, ⦶: 600 °C.

Infrared studies performed by Taylor and Amberg[6] point out that the adsorption of carbon dioxide on zinc oxide at room temperature can be classified into three types of adsorption: physisorption, and weak and strong chemisorption, and that the former two are desorbable by degassing at room temperature. Therefore, the 80% of the carbon dioxide remaining on zinc oxide surfaces may be the strong chemisorption of Taylor's classification.

TABLE 1. WATER CONTENT OF ZINC OXIDE (OH's/100 Å^2)

Treatment	Initial 600 °C[a]	After hydration[b]	Temperature (°C)					
			100	200	300	350	400	500
Water content	0.34	9.13	8.82	7.17	7.00	4.86	2.63	1.53

a) Degassed at 600 °C for 30 hr.

b) Exposed to the saturated water vapor overnight at room temperature, and then degassed at 30 °C for 4 hr.

The water content of zinc oxide is given in Table 1, which is the number of surface hydroxyl groups remaining on 100 Å^2 of the surfaces pretreated at the temperatures indicated. It is known that only a small amount of the surface hydroxyl groups on zinc oxide can be desorbed by evacuation up to 300 °C, while most of them can be removed at temperatures ranging

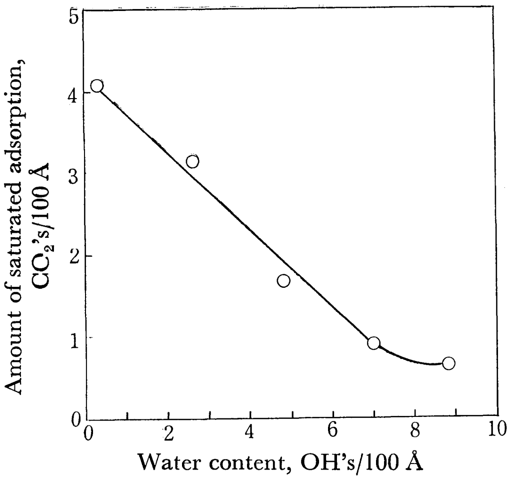

Fig. 4. Relation between amount of adsorbed CO_2 and water content on ZnO.

from 300 to 400 °C.[13] On the other hand, a large part of the strongly-adsorbed carbon dioxide can be removed by evacuating up to 300 °C, as may be seen from Fig. 3. This indicates that water is chemisorbed more strongly than carbon dioxide on the surface of zinc oxide. The adsorption isotherms of carbon dioxide, which were of the same type as those shown in Fig. 2, were also obtained at 25 °C on such differently-hydroxylated zinc oxides as are listed in Table 1. The amounts of the saturated adsorption of carbon dioxide computed from the isotherms are plotted against the water content in Fig. 4. It can be seen from Fig. 4 that the amounts of adsorbed carbon dioxide decrease linearly with an increase in the amount of the remaining surface hydroxyl groups. This suggests that carbon dioxide can be chemisorbed on the vacant sites free from hydroxyl groups; accordingly, under the conditions studied at least most of the chemisorbed carbon dioxide is not combined with the surface hydroxyl groups to form bicarbonate species, contrary to the results reported for the other systems of metal oxide-carbon dioxide.[1-5]

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