Surface Exchange Reaction Calorimetry: Measurement of Heats of Chemisorption of CO_2 on ZnO

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Summary The heats of chemisorption of CO_2 on ZnO were measured by immersion of CO_2-covered ZnO in water.

CARBON DIOXIDE molecules chemisorbed on ZnO, which are considered to form carbonate ions,[1] have been found to be desorbed from CO_2-covered surfaces when they are exposed to water vapour at room temperature, resulting in the formation of surface hydroxy-groups.[2,3] It may reasonably be expected that the similar exchange reaction of chemisorbed CO_2 would occur more rapidly in liquid water than in the vapour. If the reaction occurs quantitatively in water, we can calculate the heat of chemisorption of CO_2 on ZnO from heat of immersion measurements in water by determining (i) the heat of immersion of bare ZnO surfaces

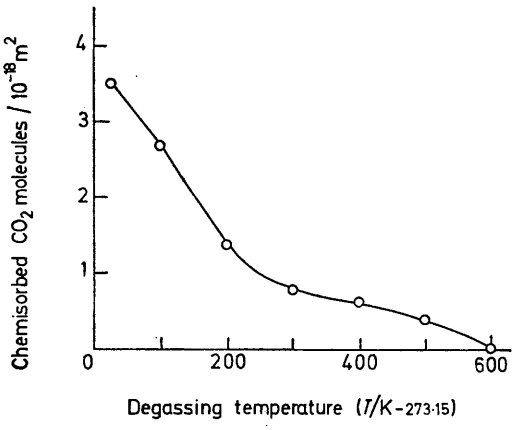

FIGURE 1. Amount of chemisorbed CO_2 remaining on the ZnO surface as a function of degassing temperature.

(H_1) and (ii) the heat of immersion of CO_2-covered ZnO (H_1'). The heat of chemisorption, $Q_a(\Gamma)$, of CO_2 on ZnO can then be obtained by equation (1), where $Q_d(\Gamma)$ is the heat of

$$Q_a(\Gamma) = Q_d(\Gamma) + H_1 - H_1' \quad (1)$$

dissolution of CO_2 in water, and Γ the number of molecules. In deriving equation (1), the assumption is made that all the CO_2 molecules liberated from the exchange reaction are dissolved in water.

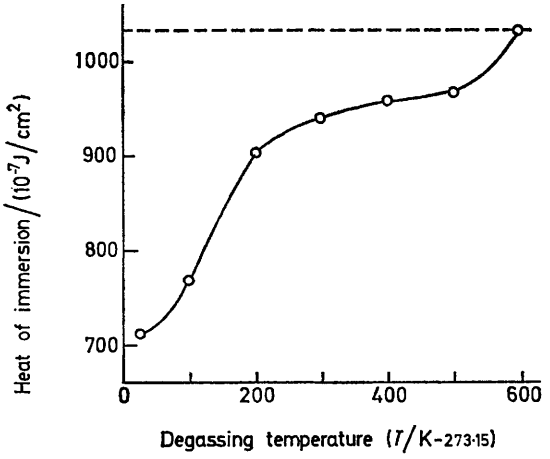

FIGURE 2. Heat of immersion of CO_2-covered ZnO in water as a function of degassing temperature.

We now report the application of immersion calorimetry to the determination of the heat of chemisorption of CO_2 on ZnO. Powdered crystalline ZnO was first evacuated at 873 K and 10^{-5} mmHg for 4 h in order to remove surface impurities such as chemisorbed H_2O and CO_2 molecules,[4] and then the sample was kept in an atmosphere of 50 mmHg of CO_2 for 2 h at room temperature to adsorb CO_2 molecules, followed by evacuation of the sample at room temperature for 2 h. The CO_2-chemisorbed ZnO sample thus formed was re-evacuated at higher temperatures (373—873 K) for 2 h, which produced surfaces with a different covering of chemisorbed CO_2. The amount of chemisorbed CO_2 remaining on the ZnO surfaces was analysed by the successive ignition loss method;[2] the data obtained are shown in Figure 1 as a function of degassing temperature. The heat of immersion[5] of CO_2-covered ZnO in water was measured at 301·15 K, and the data obtained are illustrated in Figure 2. The broken line in Figure 2 represents the heat of immersion of the ZnO sample which had been prepared by the first evacuation of the original material at 873 K for 4 h *in vacuo* and had no chemisorbed CO_2. Figure 2 indicates that the heat of immersion is least on the ZnO sample fully covered with chemisorbed CO_2, it increases with the desorption of CO_2, and reaches the value for the bare sample after degassing at 873 K. All the CO_2 molecules liberated from the ZnO surfaces by the exchange reaction have been found to be dissolved in the water.[6]

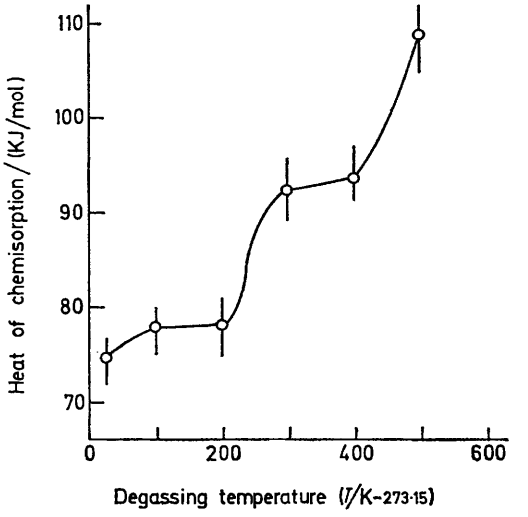

FIGURE 3. Heat of chemisorption of CO_2 on ZnO as a function of degassing temperature.

From the data in Figures 1 and 2 and equation (1), we can calculate the heat of chemisorption of CO_2 on ZnO (Figure 3). It is interesting that the heat of chemisorption of CO_2 on ZnO increases with increasing degassing temperature of the sample, *i.e.* with the ZnO sample which has less chemisorbed CO_2, suggesting that the surface of the sample tested had a particular heterogeneity.

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[6] Unpublished work.