Porous Structure Formed by the Decomposition of the Surface Product on ZnO Preserved in the Atmosphere

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The slow reaction of ZnO with CO_2 and water in the atmosphere is investigated by following the changes in both the surface area of the structure formed and the amounts of CO_2 and water evolved, by heating the product *in vacuo* at increasingly elevated temperatures. The results obtained show that ZnO reacts extremely gradually with CO_2 and water cooperatively in the atmosphere to produce an amorphous surface product with a composition approximate to $Zn_5(OH)_6(CO_3)_2$, and that this product is decomposed by heating *in vacuo* to release the CO_2 and water, leaving a porous structure on the ZnO. The surface area of the product was found to change upon heating: first it increases, passes a prominent maximum value at 200 °C, recovers the original value at 500 °C, and further decreases at higher temperatures; this reflects the initial growth and subsequent destruction of the porous structure. Furthermore, it was confirmed that the destruction of such a honeycomb-like structure is promoted by the adsorption of water.

Recently, it has become clear that ZnO chemisorbs water molecules to produce surface hydroxyl groups, on which a further physisorption of water occurs, and that the adsorption isotherm of water on ZnO reveals a sudden jump around the relative pressure of 0.2—0.3.[1-4] On the other hand, the chemisorption of CO_2 occurs on the dehydroxylated surface of ZnO, but not on the surface hydroxyl groups.[5] The chemisorption force of CO_2 is weaker than that of water, so the substitutional chemisorption of water for prechemisorbed CO_2 takes place on ZnO in contact with water vapor of 4.6 mmHg at 25 °C.[6] All these results are those obtained after equilibrating the system for several hours at most.

The present investigation is intended to examine the naturally-occurring reaction of ZnO with CO_2 and water present in the atmosphere for a much longer time. Another purpose of this work is to investigate the porous structure formed by heating the product *in vacuo* through the measurement of the surface area.

Experimental

Material. The original sample of ZnO used in this study was made by the Sakai Chemical Co. by burning Zn metal in air. The sample was stored in a bottle with a usual ground-glass stopper. The bottle was opened from time to time in order to use the sample for the measurements of the surface properties. The humidity in the laboratory varied within the range from 50 to 85%, the content of CO_2 in the atmosphere, from 0.030 to 0.041%, and the room temperature, from 5 to 32 °C.

Measurement of Surface Area. The specific surface area of ZnO was determined by applying the BET method to the N_2 adsorption data at −196 °C, in which the molecular area of N_2 was assumed to be 16.2 Å^2.

Determination of the Amounts of Water and CO_2 which Reacted with the ZnO Surface. The amounts of water and CO_2 which reacted with the ZnO surface were determined by analysing the gases evolved when the product was decomposed by heating at increasingly elevated temperatures. The sample from the stock bottle was first evacuated at room temperature for 10 hr in a vacuum of 10^{-5} Torr in order to remove the physisorbed molecules; then it was heated at 100 °C for 4 hr to permit the evolution of gases, which were introduced into a trap kept at −196 °C. The total gas volume of water and CO_2 condensed was determined volumetrically after evaporating at room temperature. The gas was recondensed at −78 °C and evacuated at the same temperature, which left water in the solid state; the volume of water was determined after reevaporation at room temperature as before. By subtracting the amount of water from the total gas volume, the amount of CO_2 could be obtained. Then the sample, was subjected to the next gas-evolution at 150 °C, and the determination of the CO_2 and water present was carried out in the same way. A similar set of procedures was repeated successively after each gas evolution at increasingly elevated temperatures up to 1100 °C. Mass-spectroscopic analysis showed that the gas evolved by heating the ZnO samples contained both CO_2 and water, and that the separation of them was accomplished by the above procedure. Thus, the amounts of CO_2 and water absorbed in ZnO during preservation in the atmosphere can be obtained by the summation of the gas volumes evolved at all the stages of heat treatment.

Differential Thermal Analysis. The apparatus used for the simultaneous measurements of the weight loss (TGA) and differential thermal analysis (DTA) was of the YGHD type made by the Rigaku Electric Co. The apparatus was operated in air, and the temperature was raised at the rate of 10 °C/min.

Results and Discussion

On the ZnO samples preserved for different periods of time in the atmosphere, the surface area was measured after degassing for 4 hr; they are plotted against the degassing temperature in Fig. 1. It can be seen from Fig. 1 that the surface area of the sample changes remarkably with the degassing temperature: it remains almost unchanged up to 150 °C, increases steeply to reach a maximum value at 200 °C, and decreases to recover the original value at 500 °C. A further decrease in surface area was observed upon heating at temperatures higher than 600 °C, suggesting the occurrence of sintering. Here, it should be noted that the longer the preservation period of the sample, the larger the maximum value of the surface area observed; the highest value obtained is about 2.3 times greater than the initial value, although the initial values are almost equal to one another irrespective of the preservation period of the sample.

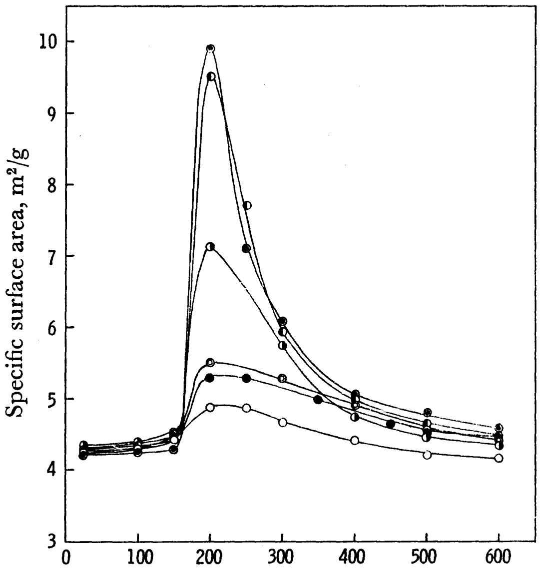

Fig. 1. Relation between specific surface area and degassing temperature on ZnO samples preserved for different periods: ○ 2, ● 30, ◎ 54, ◑ 60, ◐ 84, ◉ 90 months.

The amounts of water and CO_2 evolved are represented as functions of the heating temperature in Figs. 2 and 3 respectively, both expressed in the number of molecules expelled per 100 Å² of the initial surface of ZnO. It may be found from Figs. 2 and 3 that the evolution of CO_2 from ZnO reaches a maximum on heating at 200 °C, and is mostly finished by 300 °C, whereas the evolution of water occurs in two stages, corresponding to the two maxima at 200 and 300 °C, and that the gas evolution increases gradually with the time of preservation.

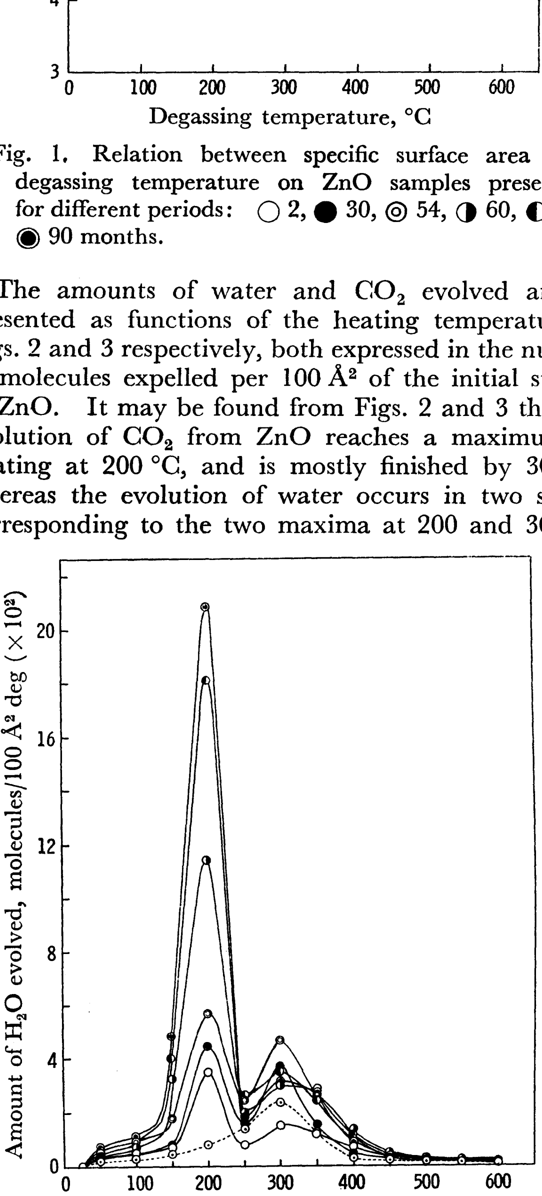

Fig. 2. Differential amount of water evolved against degassing temperature. Samples preserved for 2 (○), 30 (●), 54 (◎), 60 (◑), 84 (◐), 90 (◉) months. Dotted line means the desorption curve of chemisorbed water.

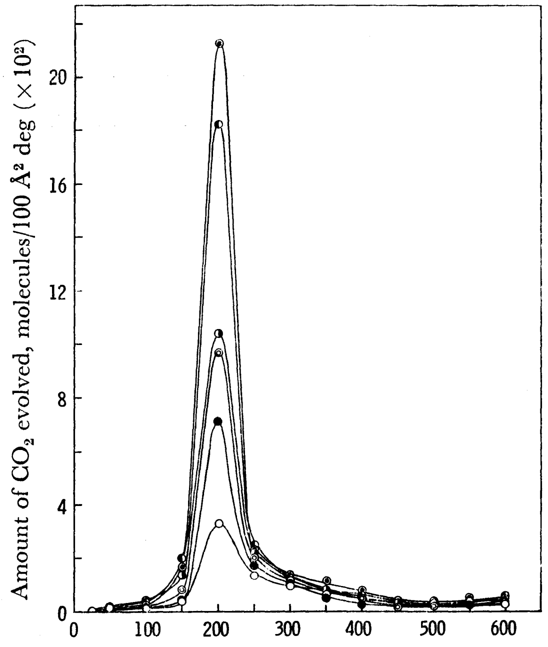

Fig. 3. Differential amount of CO_2 evolved against degassing temperature. Samples preserved for 2 (○), 30 (●), 54 (◎), 60 (◑), 84 (◐), 90 (◉) months.

A comparison of the results in Fig. 1 with those in Figs. 2 and 3 makes it possible to infer that the increase in the surface area of ZnO originates from the formation of pores after the evolution of gases. During the preservation of ZnO in the atmosphere, the surface layer will react with water and CO_2 cooperatively to produce a complicated compound; on subsequent heating *in vacuo,* the compound decomposes to recover the ZnO, accompanied by the evolution of water and CO_2, thus resulting in the formation of a porous structure, *i.e.*, presumably of a honeycomb-like structure, in the surface layer. The reaction of the surface layer will proceed more deeply with the time of preservation, so the depth of the honeycomb structure resulting from the decomposition will be increased. The increment of the surface area obtained can thus be considered to correspond to that of the inner wall in the honeycomb structure. The decrease in the surface area at temperatures higher than 200 °C will be due to the destruction of the honeycomb structure or the recrystallization of the wall in the structure upon heating.

TABLE 1. INTEGRATED VALUES OF CO_2 AND H_2O EVOLVED

Preservation period, month	CO_2 amount, molecules/ 100 Å²	H_2O amount, molecules/ 100 Å²	CO_2/H_2O	Number of ZnO layers
2	4.02	5.94	0.68	1.17
30	4.98	6.14	0.81	1.31
54	7.70	10.68	0.72	2.16
60	9.68	14.42	0.67	2.84
84	13.19	16.70	0.79	3.52
90	14.94	21.35	0.70	4.27

Table 1 gives the integrated values of water and CO_2 which are obtained from the data in Figs. 2 and 3. Though the numerical values of the ratio of CO_2 to water are widely dispersed, as is shown in Table 1, they approximate the 2: 3 ratio, suggesting the formation of $Zn_5(OH)_6(CO_3)_2$.[7] In order to ascertain more definitely the composition of the compound formed on the surface of ZnO in the atmosphere, an experiment was attempted: a few grams of ZnO, which had been newly prepared in our laboratory by burning metallic Zn in the atmosphere,[5] was allowed to react in a mixed gas of 760 mmHg CO_2 and 23 mmHg H_2O at room temperature. Though the reaction, when the ZnO sample was kept in a vessel containing one component of the mixed gas, did not proceed even after 3 months, all the ZnO sample was consumed in the mixed gas within 2 months to produce an amorphous product. This product was then subjected to differential thermal analysis; the results obtained are shown in Fig. 4. It may be found from Fig. 4 that the product decomposes in the temperature range from 230 to 260 °C, accompanied by heat absorption; the weight decrease amounts to 25.6%, which corresponds to the composition of $Zn_5(OH)_6(CO_3)_2$ (theoretical, 25.98%).[7]

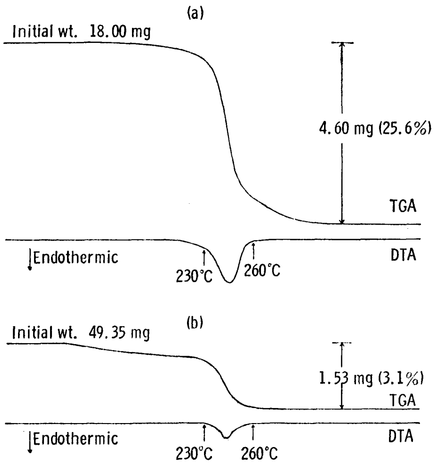

Fig. 4. DTA and TGA curves of ZnO samples. (a) completely converted sample, (b) partially modified sample in the atmosphere for 7 years.

In Fig. 4, the data on a sample preserved in the atmosphere are also added; the decomposition temperature of the sample is found to be the same as that of the completely-converted compound, which testifies that the two substances are the same, though the weight of the former is considerably smaller than that of the latter because of the smaller portion of the modified part in the former sample. These results indicate that the composition of the basic carbonate prepared from the reaction of ZnO in a gaseous atmosphere is $Zn_5(OH)_6(CO_3)_2$, though the product in this investigation was found to be amorphous by X-ray diffraction measurement.

It is interesting to consider why the second peak of water appears at 300 °C, as is shown in Fig. 2, contrary to the absence of the second peak in the case of CO_2. Undoubtedly, this peak area is included in the integration of the value of water in Table 1. In order to clarify this phenomenon, another test was made as follows. The ZnO sample, which had been treated at 450 °C *in vacuo* to remove most of the water and CO_2 absorbed, was exposed to saturated water vapor for 24 hr, degassed at room temperature for 12 hr, and then subjected to the analysis of water by means of the method described above. The results obtained are illustrated by the dotted line in Fig. 2. It shows that the position of the peak agrees well with that of the second peak of the other samples, and that the integrated value of water on this sample amounts to 8.2 OH's/100 Å^2. This indicates that the second peak of water originates from the chemisorbed water on ZnO. It may thus be reasonable to conclude that part of the water evolved by the decomposition of the complicated product is chemisorbed instantly on the ZnO surface newly developed.

Influence of Adsorbed Water on the Destruction of the Porous Structure. Figure 1 demonstrates that the porous structure formed on ZnO is destroyed by heating at temperatures higher than 200 °C. As has just been stated, part of the water evolved by the decomposition is presumably chemisorbed on the newly-formed surface. Here, it appears that the temperature at which the surface area sharply decreases, as is shown in Fig. 1, coincides with that corresponding to the second peak in Fig. 2; this suggests that the decrease in surface area is largely influenced by the adsorption of water. Figure 5 shows the data concerning the influence of adsorbed water upon the change in surface area. In this experiment, part of the 5-year sample was evacuated for 4 hr at 200 or 300 °C, subjected to the measurement of the surface area (Point 1 in Fig. 5), allowed to adsorb water at 25 °C in a vapor of 23 mmHg for 12 hr, and degassed at the same temperature for 4 hr in a vacuum of 10^{-5} Torr to remove the physisorbed water; then the second measurement of the surface area was carried out (Point 2). After the subsequent exposure of the sample to water vapor in the same way as before,

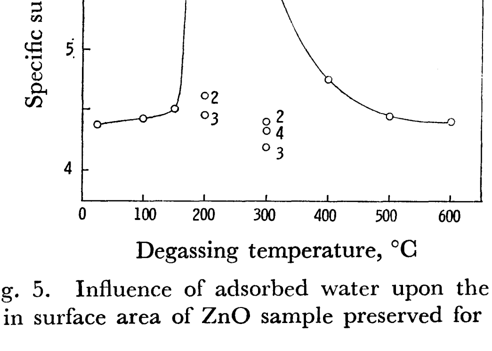

Fig. 5. Influence of adsorbed water upon the change in surface area of ZnO sample preserved for 5 years.

the third value of the surface area was obtained (Point 3). The final measurement of surface area was performed after the reevacuation of the sample at 200 or 300 °C for 4 hr (Point 4). In this series of measurements, the adsorption isotherms of N_2 were found to have no hysteresis, thus indicating the absence of pores with radii larger than about 15 Å.[8]

Figure 5 shows that the surface area of the 200 °C-treated sample drops after the chemisorption of water, but it recovers its original value after the subsequent desorption of the chemisorbed water. On the contrary, in the case of the 300 °C-treated sample, the surface area does not return to the original value even after the evacuation at 300 °C. Furthermore, it should be pointed out that, in both cases, the surface area of the samples covered with chemisorbed water is almost the same as that of the undecomposed sample. The nature of such an apparently similar result, however, is probably different depending on the treatment of the sample. The result obtained for the 200 °C-treated sample suggests that the pore radius in the honeycomb structure is so small as to lock out the adsorption of N_2 after the chemisorption of water on the inner surface of the structure. On the other hand, the walls of the honeycomb structure of the 300 °C-treated sample may be so delicate that they are ruptured and incorporated into the substrate crystals as a result of the adsorption of water, though they cannot be destroyed by the adsorption of N_2. This postulation seems feasible, since water has a large influence on the sintering of metal oxides.[9] However, it is not clear whether the destruction of the honeycomb structure occurs in the stage of water adsorption or in that of the subsequent heating to 300 °C. The reversibility of the surface area of the 200 °C-treated sample may reasonably be thought to be caused by the reinforcement of the pore wall due to the incomplete decomposition of the product.

In conclusion, we can roughly estimate the thickness of the surface layer of ZnO which reacted in the atmosphere. Assuming that, on the actual surface of ZnO, the (0001) and $(10\bar{1}0)$ planes, both excellent in cleavage, appear in equal amounts, the average number of Zn atoms on the ZnO surfaces can be calculated to be 8.5/100 Å^2.[2] Since each molecule of water or CO_2 will react with each atomic pair of Zn and O on the crystal surface, as is expressed in the formula stated above, an average of 3.5 layers of Zn atoms on the ZnO crystal changes during a preservation of about 7 years. Thus, if half the atomic pairs of Zn and O in the surface layer is pulled out to form small pores, the depth of the pores will correspond to about 7 layers of the crystal planes.

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