JOURNAL OF SOLID STATE CHEMISTRY 25, 205–206 (1978)

NOTE

Adsorption of Water Vapor on ZnO: Effects of Annealing and Grinding

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Received January 3, 1978

TG, DTA, and DTGA study of water vapor adsorption on ZnO showed that the water vapor was adsorbed reversibly at 500°C (0.12 mg/g ZnO). Irreversible desorption of water vapor was also found at approximately 270°C. Both the specific surface area and the amount of water vapor adsorbed reversibly decreased with increasing annealing temperature above 500°C. When as-received ZnO was ground, the amount of water vapor adsorbed reversibly decreased sharply before any significant change took place in the specific surface area. At longer grinding time, the specific surface area increased but the amount of water vapor adsorbed reversibly increased only slightly with the grinding time. When the specimen was ground after annealing, the reversible adsorption of water vapor was not affected by the thermal history before grinding.

Adsorption of water vapor on zinc oxide (*1*, *2*) and mechanochemical effects on the adsorption behavior (*3*) have been reported. In this paper, the adsorption of water vapor on zinc oxide was studied with TG, DTA, and a highly sensitive new analytical tool, differential thermal gas analysis (DTGA). The effects of grinding and annealing on the adsorption characteristics of zinc oxide were also studied.

Commercial ZnO powder (Merck, purity 99·95%) was used. A grinding machine with an agate mortar and a pestle was used. For annealing, the powder was heated for 24 hr at various temperatures in air. Details of DTGA have been reported (4). Three hundred milligrams of specimen was placed in a platinum boat and was heated with a constant rate of heating (10°C/min). Oxygen carrier gas from a commercial gas cylinder was passed over the specimen (volume flow rate 40 ml/min at room temperature). The thermal conductivity of carrier gas prior and after passing over the specimen was measured with thermal conductivity detectors. Evolution and/or adsorption of gas could be determined from the change in thermal conductivity of the carrier gas. A P_2O_5 trap may be inserted between the specimen and the detector to remove water vapor selectively. The equipment was calibrated with $CaC_2O_4 \cdot H_2O$ to determine the amount of water vapor quantitatively. The specimen was also analyzed with a TG-DTA[1] in air (heating rate: 10°C/min, specimen weight 100 mg).

The results of DTA, TG, and DTGA on as-received ZnO are presented in Fig. 1. On heating the specimen, the evolution of gas was found around two temperature regions (275 and 500°C). The weight losses of specimen were found around 270°C (1.3 mg/g ZnO) and around 500°C (0.12 mg/g ZnO). Each weight loss was accompanied with an endothermic peak in DTA. On cooling the sample, adsorption of gas was found around 485°C.

[1] Model M8076 Rigaku Denki, Ltd., Tokyo, Japan.

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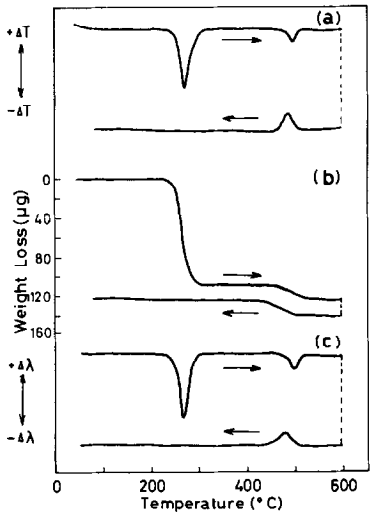

FIG. 1. DTA (a), TG (b), and DTGA (c) on ZnO. Arrows indicate the direction of temperature change.

The weight gain (0.12 mg/g ZnO) occurred and an exothermic peak appeared in DTA. The amount of gas adsorbed at this temperature was equal to that evolved around 500°C on heating. However, the change corresponding to the evolution around 270° on heating was not found. When the heating–cooling cycle was repeated, only the change around 500°C occurred reversibly. All specimens quenched after being heated above or below this temperature showed sharp X-ray powder diffraction lines of ZnO, indicating the absence of structural change in the bulk. Diffraction lines due to the presence of impurity or reaction products were not found. When dry gas, instead of one containing water vapor as an impurity, was used as carrier for these experiments, no adsorption of gas was detected. When a P_2O_5 trap was placed between the specimen and the detector of DTGA, evolution of gas was not detected; the gas was absorbed by P_2O_5. These results showed that a small amount of water vapor was adsorbed reversibly on ZnO around 500°C.

The effects of annealing and grinding on the reversible adsorption of water vapor on ZnO are presented in Fig. 2. The data are plotted

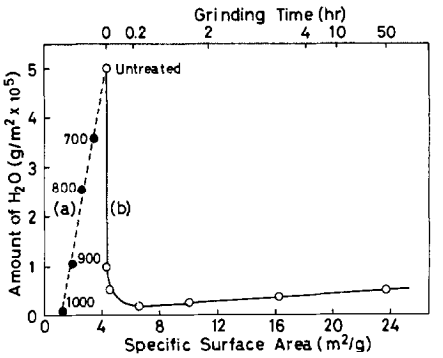

FIG. 2. Effects of annealing and grinding on the amount of water vapor adsorbed reversibly. The broken (a) and solid (b) lines show the amount of water vapor adsorbed reversibly on the annealed and ground specimens, respectively. The annealing temperatures are presented in the figure (°C).

against the specific surface area. Both the specific surface area and the amount of water vapor adsorbed reversibly decreased with increasing annealing temperature above 500°C. When as-received ZnO powder was ground, the amount of water vapor adsorbed reversibly decreased sharply before any significant change took place in the specific surface area. At longer grinding time, the specific surface area increased but the amount of water vapor adsorbed reversibly increased only slightly with the grinding time (Fig. 2b). When the well-annealed specimen was ground, the relation between the specific surface area and the amount of water vapor adsorbed reversibly was essentially the same as that shown in Fig. 2 except the initial short period after the start of grinding. This result shows that the adsorption of water vapor adsorbed reversibly was virtually unaffected by the thermal history before annealing.

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