

Surface Properties and Hydration of Cadmium Oxide

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Some surface properties of cadmium oxide have been studied by measuring the adsorption of cyclohexane, carbon tetrachloride, and methyl alcohol on the products obtained by the dehydration of crystalline $\text{Cd}(\text{OH})_2$ under vacuum. The effect of temperature of dehydration has been examined. The surface area of products increases with rise of temperature of preparation to a maximum at 200° and then decreases. The size of the adsorbate molecule seems to be a prime factor in determining its ability to penetrate into small pores. Measurements of the sorption isotherms of water at 35° and the color changes attending hydration show that the water uptake by the oxide is not merely a surface phenomenon but rather a bulk effect. This is confirmed by X-ray analysis of the hydrated samples. Results on the rate of hydration of CdO suggest that the initial stage in uptake of water by the oxide is essentially a rapid physical adsorption together with chemisorption, and is followed by a diffusion process to the inside of the solid. The last stage is the recrystallization of the $\text{CdO}\cdot\text{H}_2\text{O}$ complex yielding the $\text{Cd}(\text{OH})_2$ lattice.

INTRODUCTION

The study of the texture of an active solid is of importance especially when dealing with heterogeneous catalytic investigations. In general, little work has been done on the surface properties of cadmium oxide (1). Recently Low and Kamel (2) studied the thermal decomposition of cadmium hydroxide with special reference to the sorption of nitrogen on the dehydration products. Moreover, they showed that the reduction of the oxide by hydrogen, which was attended by a decrease in surface area, occurred even below 100° , and that the water formed during reduction was retained by the surface.

The retention of sorbed water is familiar in some oxide-water systems. It has been shown that the values of water retained by silica, alumina, titanium oxide, and iron oxide gels are low in comparison with those retained by magnesium oxide (3). This phenomenon has been attributed to the fact that in the former case the water remains

attached at the surface with very little penetration effect and probably no chemical reaction at all, while in the case of MgO the water uptake is not merely a surface phenomenon, but rather a bulk effect. For the $\text{CdO}\cdot\text{H}_2\text{O}$ system, hardly any information has been given.

The object of the present investigation is to seek more information on the texture of cadmium oxide as well as its hydration from the vapor phase. The effect of the temperature of calcination on the activity of cadmium oxide prepared by the dehydration of crystalline cadmium hydroxide under vacuum has been examined by studying the adsorption of nonpolar cyclohexane and carbon tetrachloride as well as polar methyl alcohol. The sorption isotherms of water vapor and the rate of water uptake by the products obtained by dehydration of $\text{Cd}(\text{OH})_2$ have also been studied in order to investigate the mode of combination of water with the oxide. The nature of the solid phases has also been investigated by means of X-ray analysis.

EXPERIMENTAL

Apparatus and technique. Cyclohexane, carbon tetrachloride, and methanol adsorption measurements were carried out using a conventional volumetric system. The adsorption of water was measured gravimetrically with a stainless steel spring balance (sensitivity 15.5 cm/g). The rate of hydration was followed by exposing the adsorbent, mounted on the spring balance, to the saturation vapor pressure of water at different temperatures. X-Ray diffraction patterns were obtained with the aid of a Philips (114.23 mm diameter) Debye-Scherrer powder camera using Ni-filtered Cu radiation.

Materials. Cadmium hydroxide was prepared (4) by the slow addition of 1 *N* cadmium nitrate solution to 1 *N* potassium hydroxide solution. The precipitate was then washed thoroughly with water till alkali and nitrate free. Drying was carried out in a vacuum desiccator over P₂O₅. The water content was 16.14% as compared with 12.30% for Cd(OH)₂.

Adsorption measurements were carried out on the parent material and its dehydration products. The dehydration was done *in vacuo* for 5 hr at 150°, 200°, 250°, 300°, 350°, and 500°C.

Cyclohexane, carbon tetrachloride, and methanol were purified by known methods. Water used in adsorption and rate of hydration processes was always freshly distilled.

RESULTS

1. Structural Changes Accompanying Dehydration

X-Ray diffraction patterns were obtained for the parent material and its dehydration products. Comparison with the ASTM cards (5), shows that the parent material is cadmium hydroxide. Heating *in vacuo* at 150° for 5 hr reduces the water content to 13.7%. This value is still higher than the stoichiometric value for the hydroxide-oxide conversion. It is probable that the excess amount of water in the parent material is present mainly as solution in the

lattice (6) and it is expelled regularly and simultaneously during the decomposition of the hydroxide. For the 150° sample, most of the lines which give the characteristic *d* spacings of the hydroxide still remain clear and also a few more lines, which correspond to a limited conversion to the oxide, appear. At 200°, the water content falls to 6.3% and most of the lines are those of the oxide. For products obtained at higher temperatures, the few remaining lines of the hydroxide disappear gradually, and finally, at and above 300° we get only a pattern of the oxide.

2. The Effect of Temperature of Calcination on Adsorption

Results of experiments on the adsorption of cyclohexane at 35° on the parent material and its dehydration products are shown in Fig. 1. The isotherms are of type II in Brunauer's classification (7). Thorough outgassing at room temperature brings about complete removal of the adsorbate, indicating physical adsorption. Small hysteresis loops are formed which indicate a broad pore spectrum of the adsorbents (8). The corresponding adsorption and desorption isotherms of CCl₄ as well as CH₃OH give almost the same picture already described in the case of cyclohexane.

The isotherms are found to obey the BET equation (9) in the normal range of pressure. The specific surface areas of the various samples were calculated from the monolayer capacity taking the cross sectional area of C₆H₁₂, CCl₄, and CH₃OH molecules as 39 Å² (10), 30 Å² (11), and 18.1 Å² (12), respectively. The values obtained are plotted in Fig. 2 as a function of the dehydration temperature. As calcination *in vacuo* for 5 hr at temperatures up to 500° does not bring about complete dehydration of the parent material, the percentage decomposition at various temperatures of dehydration is also inserted in Fig. 2 (curve b).

It is evident that the specific surface areas calculated from the isotherms of the various adsorbates differ widely in absolute value but not in their dependence on the dehydration temperature. In all cases, the

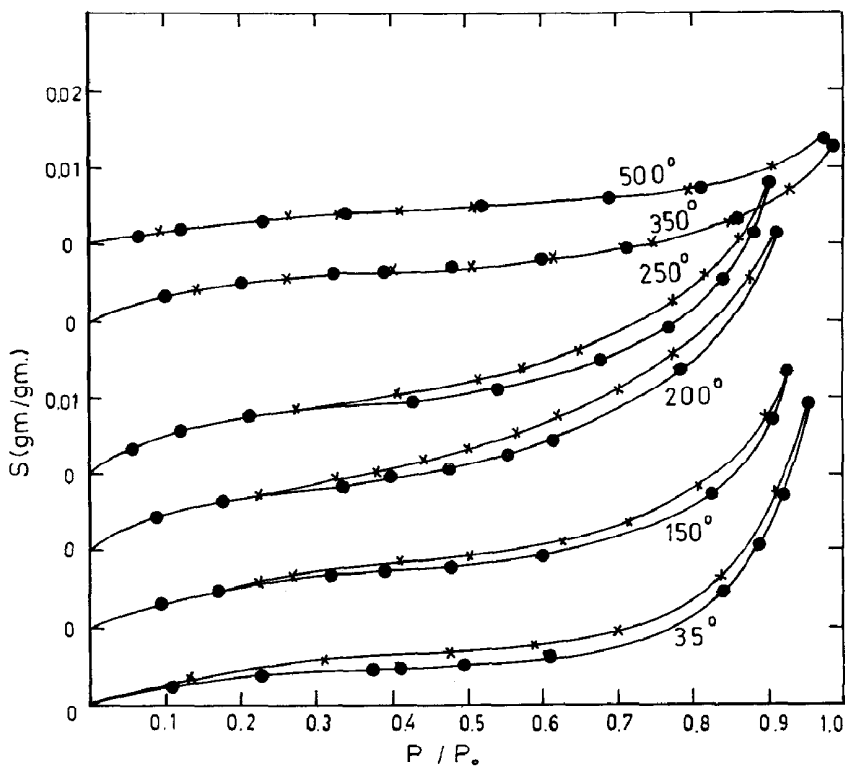


Fig. 1. ●, Sorption isotherms of cyclohexane at 35° on the products obtained by the dehydration of cadmium hydroxide under vacuum during 5 hr at various temperatures; X, desorption.

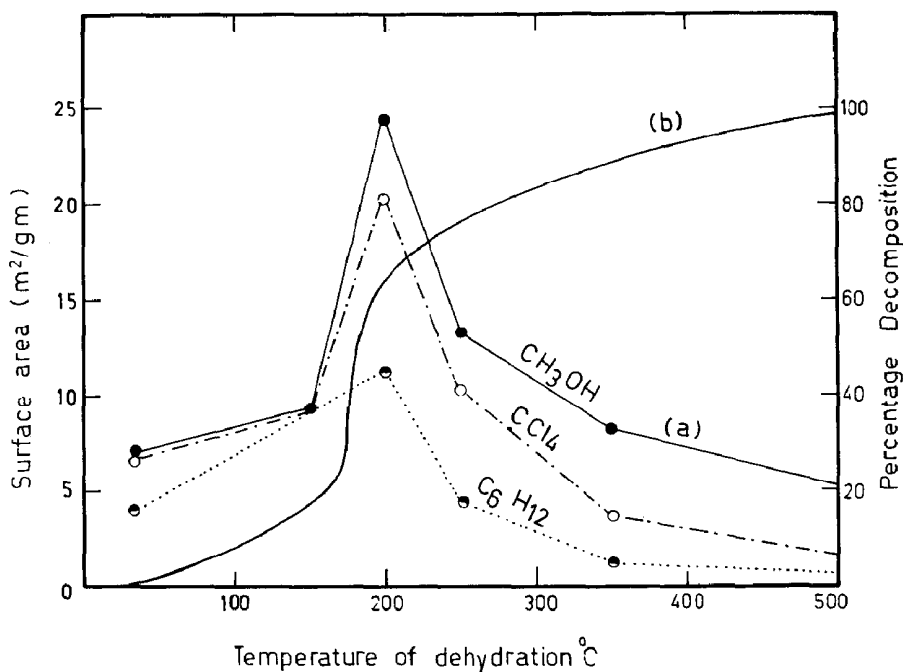


Fig. 2. Effect of temperature of calcination of cadmium hydroxide under vacuum for 5 hr on (a) surface area of product and (b) percentage decomposition.

maximum surface area is at 200°. From Fig. 2, it can be seen that at 150°, the surface areas calculated in the case of the three vapors are nearly the same. At this temperature, the hydroxide is hardly decomposed. Generally, however, the surface area for the same temperature of dehydration is higher the smaller the cross sectional area of the adsorbate molecule. The surface areas determined are of the same order of magnitude as those obtained from nitrogen adsorption by Low and Kamel (2), but the effect of temperature of calcination on the surface area of the dehydration product is different. This disagreement may have its origin in the use of different parent material. The precipitation in their case was affected with ammonia and the water content of the resultant hydroxide is 19.01%.

3. The Hydration of Cadmium Oxide from the Vapor Phase

A. The Adsorption of Water Vapor

Sorption isotherms of water vapor have been determined on the parent material and five specimens of its dehydration products prepared at 150°, 200°, 250°, 300°, and 350°. In all cases equilibrium was attained

slowly and usually successive points on the isotherms were taken at intervals of 24 hr.

The sorption isotherm for the parent material is sigmoid in nature, belonging to type II of Brunauer's classification (7). The hysteresis extends to the lowest pressures and thus forms an open loop. Thorough outgassing at room temperature removes the adsorbate molecule from the surface completely, and hence the same isotherm was obtained during a second cycle of measurements. For a sample prepared at 150°, the picture is nearly the same but it was noticed that the adsorbent retained some water on outgassing at room temperature. On repeating the cycles of adsorption-desorption, incremental amounts of water were retained by the surface.

In case of samples prepared at 200°, 250°, 300°, and 350° the sorption isotherm followed similar behavior. Sorption continued to be relatively low till a relative vapor pressure of 0.5, where it started to show a significant rise. After desorption till very low pressures and on outgassing thoroughly at room temperature, the adsorbent did not lose any of the retained water and there appeared a marked hysteresis. The repeated cycles of adsorption-desorption showed a

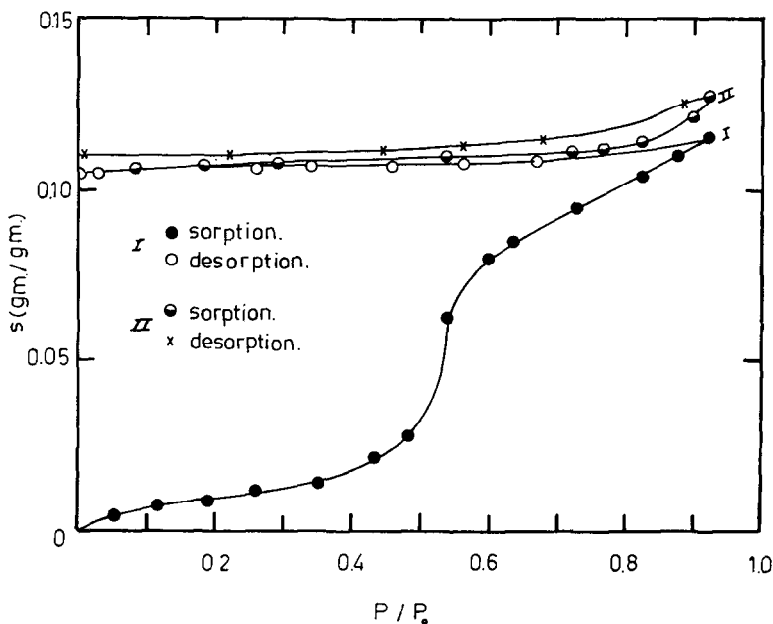


FIG. 3. Sorption isotherm of water vapor at 35° on sample prepared at 200°.

relatively small increase in retention of water towards limiting values. The sorption isotherm of water vapor on sample prepared at 200° is shown in Fig. 3.

The color changes that occurred during the process of hydration are of interest. On hydration, sample prepared at 150° did not show much change from its pale yellow color. Samples prepared at 200°, 250°, and 300° changed from dark brown to pale yellow. The dark brown color of sample prepared at 300° got lighter.

This value is near to the water content of the parent material, viz., 0.161 g H₂O/g material. This fact has shown that every product of dehydration has retained water which is almost equivalent to that being lost on dehydration. This is not followed in the case of sample prepared at 350° which was inactive towards water vapor due to the pronounced sintering effect.

The above-mentioned phenomenon as well as the color changes accompanying hydration indicate that a process of bulk

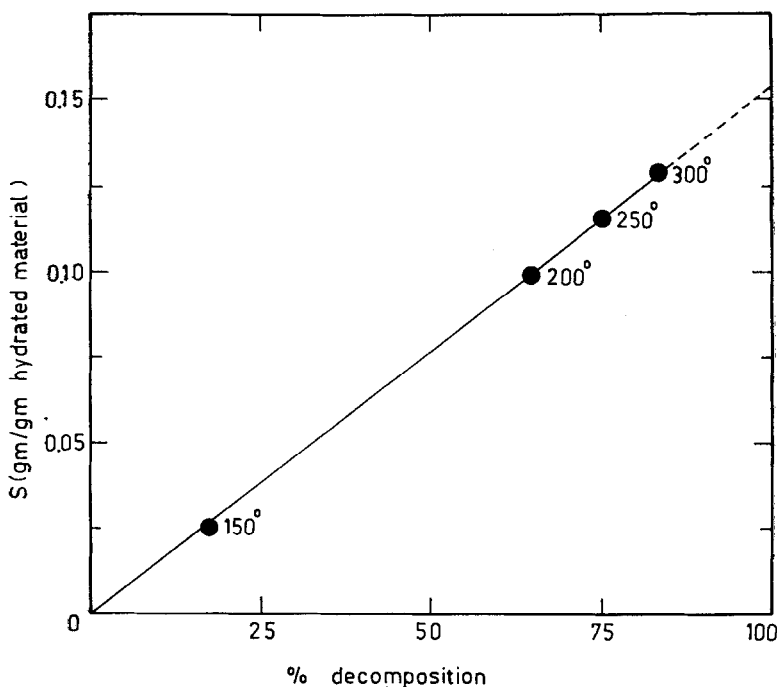


FIG. 4. The relation between the amount of water retained by the adsorbent and the percentage decomposition.

Due to the fact that sorption of water gets very slow the more we approach the saturation vapor pressure, the adsorbents were directly exposed to the saturation vapor pressure at 35° for enough time thus ensuring a state of equilibrium; then the sample was degassed thoroughly till constant weight, hence evaluating the limiting value of retained water. The plot of water retained against percentage decomposition is a straight line (Fig. 4) which on extrapolation gives a value of 0.154 g H₂O/g hydrated material at 100% decomposition.

interaction between CdO and H₂O, which finally results in the formation of the hydroxide, is occurring. This idea is confirmed by X-ray analysis of the hydrated samples which proved to display the hydroxide structure. This is with the exception of hydrated sample prepared at 350° which was found to be a mixed oxide-hydroxide.

B. The Rate of Hydration of CdO from the Vapor Phase

The study of the rate of water uptake might give valuable information concern-

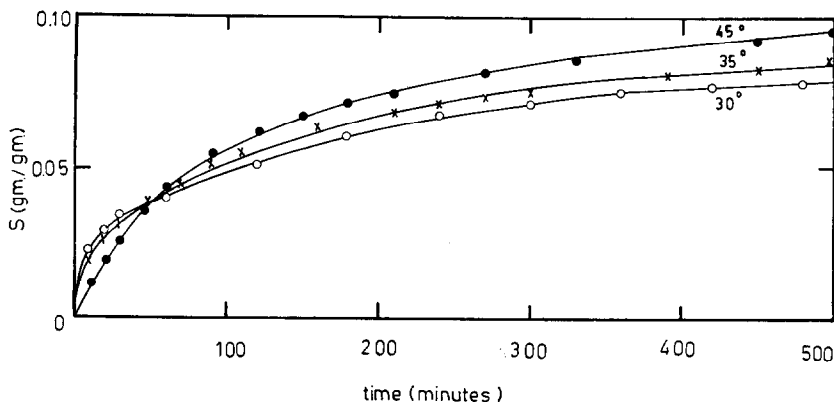


Fig. 5. Amount of adsorbed water, on sample prepared at 300°, as a function of time; at saturation vapor pressure and at different temperatures.

ing the mechanism of hydration of the oxide. Rate experiments were carried out on samples prepared at 200°, 250°, and 300° in the temperature range 25–45°. A typical set of experiments for sample prepared at 300° are shown in Fig. 5. It is clear that the rate of water uptake decreases with rise of temperature in the initial stage, while in the later stages the effect is reversed. The rate of uptake at lower temperatures is less than that at higher temperatures.

DISCUSSION

The activity of some metal oxides prepared by the thermal decomposition of the corresponding hydrous oxides or hydroxides has been studied extensively in the light of the adsorption capacity (13). It is believed that the main factor responsible for the activity is the presence of an extensive surface area in the solid as the water is expelled on heating the parent material, thus leaving behind capillaries, vacancies, cracks, and so forth.

From the study of the surface properties of oxides prepared by thermal decomposition of crystalline hydroxides, it is believed that the mechanism which determines the surface area–temperature relationship is governed by three processes, viz., decomposition, recrystallization, and sintering. A maximum in the surface area–temperature curve is expected; the rising part of the curve being due to the first two processes while the descending part must be ascribed

to sintering. The three processes overlap around the maximum.

The change in crystal structure attending the cadmium hydroxide–oxide conversion is marked. Cadmium hydroxide forms a layer structure (14) in which every Cd is surrounded by six OH's. Every OH forms three bonds to Cd atoms in its layer and is in contact with three OH's of the adjacent layer. According to Low and Kamel (2), two overall steps are involved in the rearrangement from the layer structure of Cd(OH)₂ to the rock salt structure of CdO: (i) dehydration, whereby H₂O is lost, O²⁻ is formed, and OH vacancies are made in the anion sub lattice; (ii) rearrangement where the depleted layer lattice collapses to form the rock salt lattice.

The adsorption measurements of the different organic vapors on Cd(OH)₂ and its dehydration products indicate that the calculated specific surface areas increase regularly with the decrease of the cross sectional area of the adsorbate molecule. This suggests that the size of the adsorbate molecule seems to be a prime factor in determining its ability to penetrate into the micropores, while polarity of the molecule plays a minor role. In this respect, it is known that the specific surface area is obtained primarily by the volume and dimensions of the pores. Almost all the surface area of gas adsorbent is provided by the micropores, the majority of which are less than 10 Å in diameter (15) and probably approach molecular dimensions in order of magnitude

(16). Hence, the molecules of CH_3OH , which possess a relatively small size, can penetrate more through the fissures, cracks, and interstices; consequently their adsorption measures almost the total surface area of the adsorbent. Generally, it can be concluded that because the specific surface area increases the size of the adsorbate molecule decreases, therefore almost all the surface is provided by the walls of the micropores.

The retention of water by some oxides has been reported occasionally (17). However, in the case of MgO (3), from the presence of permanent hysteresis loops in the sorption-desorption isotherms and the stoichiometric uptake of water vapor by the oxide prepared from brucite at temperatures below 650° , it was suggested that the phenomenon was a bulk interaction between the oxide and water and not merely a surface process.

In the present investigation, the sorption of water on $\text{Cd}(\text{OH})_2$ seems to be physical in nature. The sorption of water on the dehydration products of $\text{Cd}(\text{OH})_2$ revealed certain facts: (i) the presence of wide hysteresis on desorption, (ii) the color change, attending hydration, from dark brown to pale yellow, and (iii) the linear relationship between percentage decomposition and amount of retained water. These facts suggest that CdO prepared from the hydroxide at temperatures below and at 300° follows almost the same lines as MgO with respect to the bulk character of water uptake. This phenomenon, which causes the conversion of CdO to the hydroxide, was revealed by X-ray examination of the system $\text{CdO}-\text{H}_2\text{O}$.

In the light of the experimental results on the rate of hydration of CdO at various temperatures, it is possible to suggest that the initial stage in the uptake of water vapor by the oxide is essentially physical adsorption together with slower chemisorption which makes its appearance and becomes more significant as the temperature gradually rises. The initial stage is followed by a diffusion process, to the inside of the solid, which is endothermic in contrast with the early water uptake, which is generally

exothermic. As shown before, the last stage in the hydration process is the recrystallization of the $\text{CdO}-\text{H}_2\text{O}$ complex, formed by the interaction of the H_2O molecules with the CdO crystallites, to yield the $\text{Cd}(\text{OH})_2$ lattice.

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