

TREATMENT OF CdO AT ROOM TEMPERATURE AND 150 °C IN A WATER-VAPOUR-SATURATED ATMOSPHERE. PART I.

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ABSTRACT

The behaviour of different CdO samples in a water-vapour-saturated atmosphere was studied by X-ray powder diffraction (XRD), IR spectroscopy and thermogravimetry (TG, DTG). The results indicate three steps during the course of the CdO hydration process at room temperature: (i) γ -Cd(OH)₂ is formed initially; its concentration (67%) does not change over a period of 5–31 days, indicating that the hydration reaction has reached equilibrium; (ii) after 31 days, the unhydrated CdO and γ -Cd(OH)₂ are carbonated; (iii) the carbonation increases with time; CdCO₃ is formed at the end of the process.

When the temperature of treatment is 150 °C, β -Cd(OH)₂ is mainly formed together with γ -Cd(OH)₂ and CdCO₃. The carbonation does not increase with time and the γ -hydroxide is transformed into β -Cd(OH)₂.

INTRODUCTION

It is well known that atoms, ions and molecules located at surfaces suffer from an imbalance of chemical forces. This imbalance may be expressed in terms of surface energy. A finely dispersed solid phase thus tends to lower its surface energy either by reducing its surface area or by adsorbing molecules and ions from adjacent phases. From the point of view of coordination chemistry, the above-mentioned imbalance of chemical forces may be understood as coordinative unsaturation.

Therefore, at the surface layer of a metal oxide, the metal ions have a reduced coordination number and thus behave as Lewis acids. In the presence of water, the surface metal ions may first tend to coordinate H₂O molecules. For most of the oxides, dissociative chemisorption of water molecules seems energetically favoured. The concentration of surface hydroxyl groups has been estimated from the weight loss on heating; from

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BET treatment of water vapour adsorption and from D_2O exchange, etc. The actual numbers depend on the geometry of the crystal structure, the nature of the cleavage planes and the pretreatment of the sample [1].

Bohem [2] first introduced the idea of two different OH groups: hydroxyl groups bound to one metal ion (a type) and hydroxyl groups bound to two (or more) metal ions (b type). The latter seem to be acidic when compared with the basic a-type groups. IR spectroscopy has provided evidence for different types of hydroxyl groups, as in the case of $\gamma-Al_2O_3$, where five different groups have been found [3].

The influence of surface structure, through defects such as edges, corner or vacancy sites, on the reactions that take place at the surface of ionic oxides is well established. Thus, Boudart et al. [4] have shown that the chemisorption of H_2 by MgO depends on the presence of an Mg^{2+} ion vacancy at a cube corner, leaving a micro {111} face consisting of three O^{2-} ions in a triangular array.

Mackrodt and coworkers [5–7] have revealed that the bonding of both CO and H atoms to all low-coordination sites is much greater than to fivefold-coordinated {001} surface sites.

Jones et al. [8], in agreement with Mackrodt, have concluded from IR, electron microscopy and BET studies that perfect fivefold-coordinated sites in {100} surfaces of MgO smoke cubes do not appear to form OH groups after exposure to H_2O vapour. In contrast, $\nu(OH)$ and $\nu(CO_3)$ absorptions are observed in identical MgO preparations subjected to prior abrasion through pressure or light grinding.

We are interested in the reactions that take place with water molecules at the surfaces of oxides because, as we have seen previously [9,10], the reactivity of CdO and V_2O_5 considerably increases when the mixture is treated in a water-vapour-saturated atmosphere. At room temperature, it is possible to obtain α -cadmium metavanadate which evolves with time to the high temperature β allotropic form.

The first part of this paper deals with the behaviour of CdO samples in the same experimental conditions as mentioned above. The study was carried out using IR spectroscopy, X-ray powder diffraction (XRD) and thermogravimetry (TG). The second part reports a similar study with MgO samples.

From an industrial point of view, the reaction of cadmium oxide with water presents a twofold interest: firstly, to study the hardening mechanism and binding properties related to cement and concrete [11–14], and secondly to control the reactions that take place in alkaline-battery electrodes [15].

Fahim and Kolta [16] have studied the hydration of CdO in saturated water vapour at $35^\circ C$. The oxide adsorbs the water almost stoichiometrically to form the hydroxide.

Niepce [17] has pointed out that rehydration of CdO, obtained from heating $Cd(OH)_2$, is possible if the latter contains traces of a salt such as KI.

Nevertheless, rehydration is impossible if the oxide is derived from a relatively pure hydroxide.

EXPERIMENTAL

The CdO employed was of AnalaR grade (Riedel de Haën); it was heated to eliminate the CO₂ and H₂O impurities. The heating temperature used was as low as possible to prevent sintering, which reduces both porosity and surface area, thus increasing crystal size. The purity of the samples after heating was checked by XRD, IR spectroscopy and TG.

One set of samples (1 g) of grain size < 0.05 mm was exposed to a water-vapour-saturated atmosphere at room temperature for periods of time ranging between 2 and 90 days.

A second set of CdO samples was heated at 150 °C in a pressure reactor (Phase 2005 of 100 ml capacity) in a water-vapour saturated atmosphere for 24–48 h.

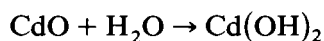
The thermal evolution of each sample (TG and DTG) was observed using a Mettler TA 3000 analysis system with a CTC10TA processor. Samples of approximately 20 mg were heated at a rate of 10 °C min⁻¹ in an air stream, using alumina crucibles.

X-ray diffraction patterns were recorded on a Siemens D500 diffractometer using Cu K α radiation and a graphite monochromator K805. The IR study was carried out on a Perkin–Elmer 599B instrument. KBr pellets of concentration 0.6% of sample were used.

RESULTS AND DISCUSSION

X-ray diffraction analysis

During the first days of treatment at room temperature, the formation of a new crystalline phase was clearly detected, whose X-ray diffraction pattern corresponded to γ -Cd(OH)₂ [18] (Fig. 1(b)). The concentration of this hydroxide was about 67% according to the TG data (see later). This concentration did not change up to the 31st day of treatment, indicating that the CdO hydration reaction reached equilibrium despite an excess of water molecules



At the 31st day of treatment, CdCO₃ appeared (Fig. 1(c)). Its concentration increased with time as both CdO and γ -Cd(OH)₂ decreased (Fig. 1(d)). At 90 days only CdCO₃, was present (Fig. 1(e)).

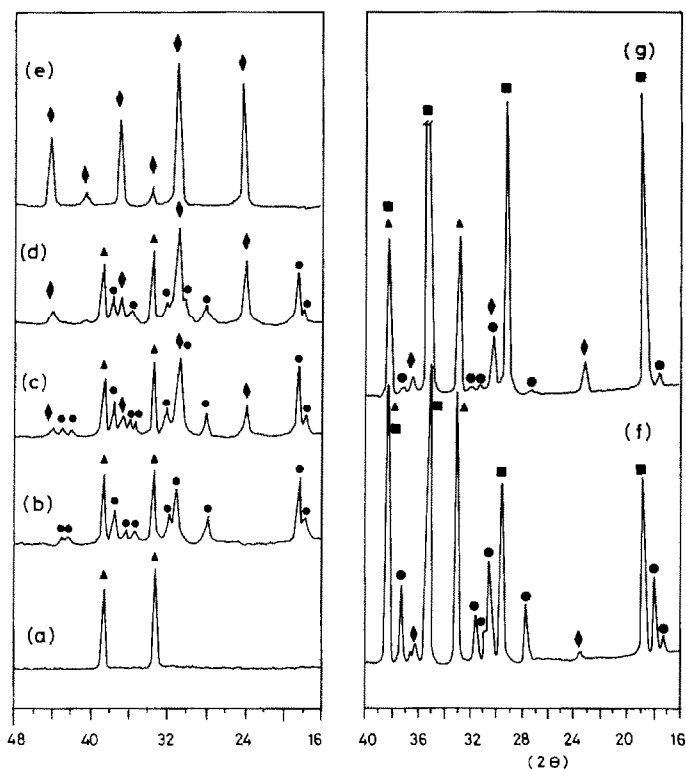


Fig. 1. X-ray diffraction patterns of CdO samples treated at room temperature in a water-saturated atmosphere for different times: (a) untreated; (b) 5 days; (c) 48 days; (d) 67 days; (e) 90 days; (f) CdO treated at 150 °C for 24 h; (g) for 48 h. \blacktriangle , CdO; \bullet , γ -Cd(OH)₂; \blacklozenge , CdCO₃; \blacksquare , β -Cd(OH)₂.

The behaviour of CdO was different when the temperature of humidic treatment was 150 °C. Thus, at 24 h, the X-ray diffraction patterns corresponded to both β - and γ -Cd(OH)₂, and, in addition CdCO₃ (as an impurity) could be seen (Fig. 1(f)). The hydroxide content (64%) remained stable despite the higher temperature of treatment.

At 48 h (Fig. 1(g)), the γ -hydroxide had almost disappeared, and was replaced by the β -hydroxide, which was the major component of the sample together with minor amounts of CdO and CdCO₃. The hydration of CdO was not complete even after 3 days of treatment.

The results obtained seem to indicate that the unstable monoclinic γ -hydroxide (the first to appear) evolves on heating into the more stable hexagonal β -hydroxide.

IR spectroscopic analysis

The evolution of the IR spectra as a function of time at room temperature is shown in Fig. 2.

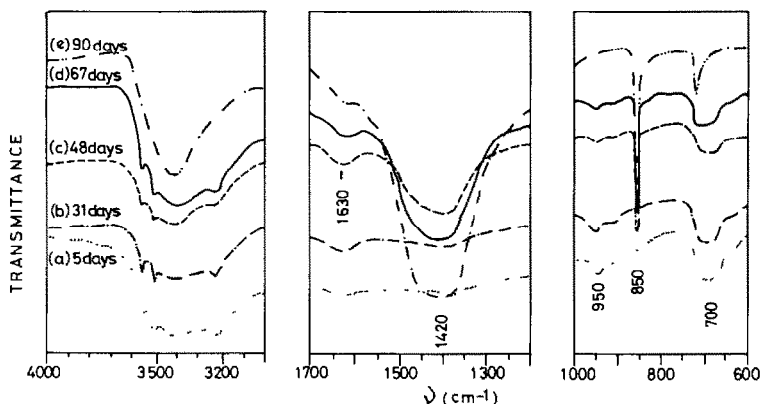


Fig. 2. IR spectra of CdO samples treated at room temperature in a water-saturated atmosphere for different times: (a) 5 days; (b) 31 days; (c) 48 days; (d) 67 days; (e) 90 days.

As can be seen, in the hydroxyl-stretching region ($3100\text{--}4000\text{ cm}^{-1}$), the $\nu(\text{OH})$ vibrations appear at 3230 , 3520 and 3570 cm^{-1} , which indicate hydroxyl groups bonded by weak hydrogen bonding. The bands which appear at 950 and 700 cm^{-1} may be attributed to $\delta(\text{OH})$ and $\gamma(\text{OH})$ vibrations (Figs. 2(a) and 2(b)). All these bands correspond to $\gamma\text{-Cd}(\text{OH})_2$, according to previous IR studies of Tugushev et al. [19]. These workers have distinguished two types of OH groups, bonded by hydrogen bonds, for the γ -hydroxide modification. The first type are weakly bonded groups of effective radii 1.39 , 1.37 and 1.36 \AA , which are indicated by the corresponding $\nu(\text{OH})$ stretching vibrations at 3590 , 3565 and 3525 cm^{-1} and $\gamma(\text{OH})$ at 650 , 687 and 716 cm^{-1} . The effective radii of the other group are 1.34 and 1.33 \AA and the corresponding $\nu(\text{OH})$ vibrations are observed at 3268 and 3224 cm^{-1} and $\delta(\text{OH})$ at 927 and 965 cm^{-1} .

At 48 days of treatment (Fig. 2(c)), the cadmium carbonate absorption bands at 1420 , 850 and 720 cm^{-1} start to appear. The intensity of these bands increases with time, whereas those corresponding to $\gamma\text{-Cd}(\text{OH})_2$ decrease. At 90 days (Fig. 2(e)), the spectrum corresponds exclusively to CdCO_3 .

The interaction of adsorbed carbonate species with adsorbed water or surface hydroxyls may occur through hydrogen-bonding interaction or through the production of an adsorbed bicarbonate species. The relatively small hydroxyl perturbation observed in our case indicates the formation of a weak hydrogen bond. Furthermore, there was no evidence of bicarbonate species from either XRD or TG.

The IR spectrum of CdO treated at 150°C (Fig. 3) shows a sharp $\nu(\text{OH})$ stretching vibration at 3580 cm^{-1} which corresponds to the β -hydroxide modification. In addition, the presence of carbonate is clearly seen by the bands at 720 , 855 and 1420 cm^{-1} (Fig. 3(b)).

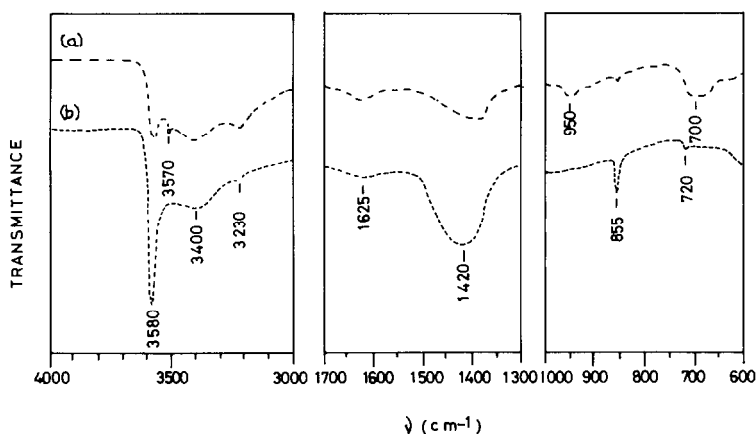


Fig. 3. IR spectra of CdO samples treated at 150 °C in a water-saturated atmosphere for different times: (a) 24 h; (b) 48 h.

Thermogravimetric analysis

The quantitative analysis of the different compounds formed during the humidic treatment of CdO at room temperature can be easily calculated from the TG curves, since they clearly show an inflection point between the two weight losses observed (one due to the removal of water molecules from structural OH groups of γ -Cd(OH)₂, and the other due to the elimination of CO₂ from carbonate decomposition).

At 5 days, the TG curve (Fig. 4) shows a weight loss (8.2 %) between 150 and 550 °C corresponding to removal of chemisorbed water (structural OH groups). The maximum of the DTG peak is centred at 210 °C. Between 25

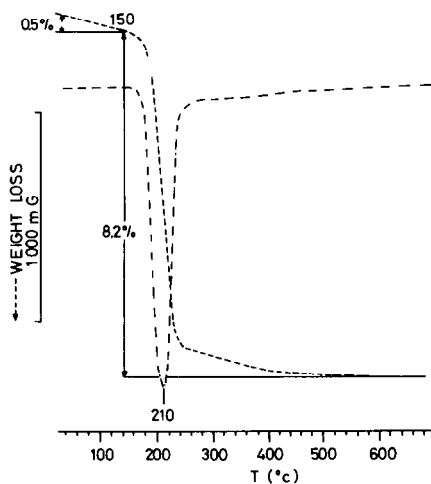


Fig. 4. TG and DTG curves of CdO treated for 5 days.

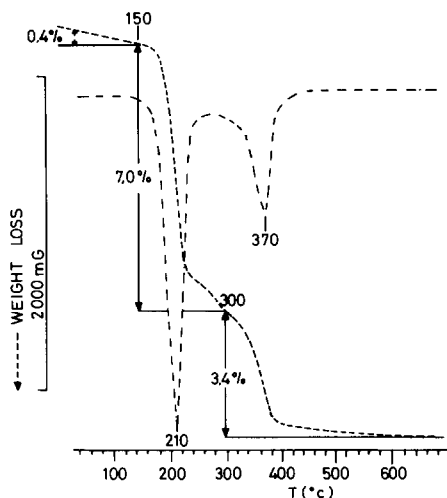


Fig. 5. TG and DTG curves of CdO treated for 48 days.

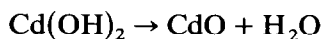
and 150 °C, the removal of physisorbed water (0.5%) takes place. The content of this does not change with an extension of treatment.

Up to 38 days, the TG curves are identical in shape. When the treatment is extended to more than 38 days, the carbonation of the samples can be clearly seen. Thus between 300 and 500 °C, a second weight loss appears, which is due to the elimination of CO₂ from the carbonate ions. The maximum of the DTG peak is centred at 370 °C (Fig. 5).

The carbonation increases with time, and therefore so does the second weight loss. The maximum of the DTG peak is shifted to higher temperatures (Fig. 6). In contrast, the first weight loss, corresponding to the removal of the structural OH groups of γ -Cd(OH)₂, decreases and its DTG peak is shifted to lower temperatures.

At the end of treatment, the γ -Cd(OH)₂ and unreacted CdO are transformed completely into CdCO₃. The TG curve (Fig. 7) shows a unique weight loss between 230 and 500 °C; its DTG peak maximum is centred at 420 °C. Before this, a much smaller peak can be detected which may be due to the decomposition of more labile carbonate ions.

In Fig. 8 the percentage evolution of each compound as a function of time of treatment is shown. The data were calculated from comparisons between the corresponding weight losses and the stoichiometric content of both H₂O (12.3%) of γ -Cd(OH)₂ and CO₂ (25.5%) of CdCO₃. The unreacted CdO concentration was determined from the difference between the constant weight of the residue and the CdO formed from both Cd(OH)₂ and CdCO₃, according to the following reactions



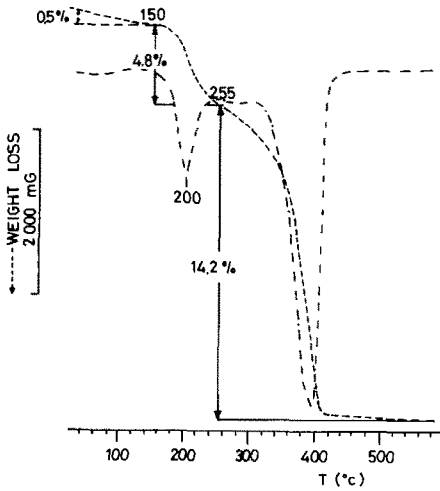


Fig. 6. TG and DTG curves of CdO treated for 67 days.

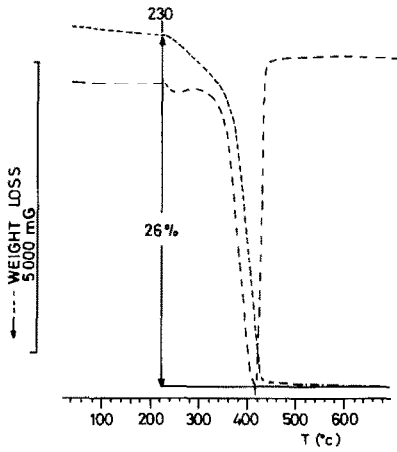


Fig. 7. TG and DTG curves of CdO treated for 90 days.

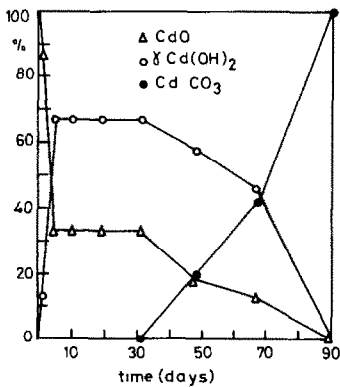


Fig. 8. Evolution of the percentage of compounds formed as a function of time of treatment.

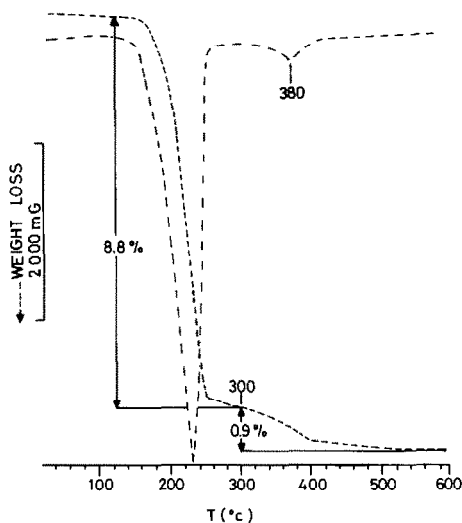


Fig. 9. TG and DTG curves of CdO treated at 150 °C for 48 h.

When the temperature of treatment is 150 °C, β -Cd(OH)₂ is formed. The TG curve (Fig. 9) shows a weight loss (8.8%) between 140 and 260 °C corresponding to the elimination of water molecules from structural hydroxyl groups. The maximum of the DTG peak (230 °C) appears at a higher temperature than that observed for γ -Cd(OH)₂. This fact indicates that the β -modification is more stable than γ -Cd(OH)₂. Between 300 and 600 °C, a second weight loss appears, which is due to CO₂ elimination from carbonate ions (0.9%).

The interpretation of the results obtained in this work is in disagreement with that previously reported by Fahim and Kolta [16]. These workers hydrated CdO samples (prepared from the thermal decomposition of the hydroxide at 300 °C) by directly exposing the oxide to saturated water vapour at 35 °C for a sufficient time. Their TG curve (very similar to Figs. 5 and 6 in this study) showed two weight losses which were clearly differentiated: the first, between 200 and 300 °C, was attributed by these workers to the removal of excess water (7.8%); the second, between 300 and 500 °C, was attributed to the decomposition of the hydroxide to the oxide. Their IR spectrum of hydrated CdO clearly showed the characteristic bands of CdCO₃ at 1450, 860 and 720 cm⁻¹. Fahim and Kolta related these to the water molecules combined with the hydroxide. In our opinion, the sample was partially carbonated. Thus, the second weight loss in the TG curve should be attributed to CdCO₃ decomposition. The presence of carbonate was also clearly shown in the IR spectrum by the characteristic bands at 1500, 860 and 720 cm⁻¹. According to this, the empirical formula proposed (CdO · 1.64H₂O) is not correct.

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