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A PROBLEM OF HYDROXIDE PURITY: REHYDRATION OR NON-REHYDRATION OF CdO ex-$Cd(OH)_2$

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ABSTRACT

The present experimental results are qualitative evidence that minute traces of a salt such as potassium iodide in cadmium hydroxide enormously accelerate the decomposition reaction and make rehydration of the oxide obtained possible, the latter being impossible if the resulting oxide is derived from a relatively pure hydroxide.

INTRODUCTION

The present results were obtained by investigating the influence of experimental conditions and of the crystallite sizes of the initial hydroxide upon that of the cadmium oxide produced[1, 2].

It has been shown that the smaller the initial crystallites, the slower the water vapour loss during the decomposition reaction of $Cd(OH)_2$[3]. Also, a tremendous increase in the reaction rate has been observed for one of the samples with very small granulometry[4].

In addition, another difficulty has been met during the decomposition, under water vapour pressure, of this divided sample: systematic rehydration of the resulting oxide during cooling. Cadmium oxide rehydration is a surprising phenomenon for, none of the other samples investigated behaved in this way. Cadmium oxide rehydration has been observed by Fahim only[5].

The purpose of this study was to find out the reasons for both unusual phenomena.

EXPERIMENTAL

Materials

The purpose was to investigate some characteristics of the oxide produced versus initial hydroxide granulometry, which required a set of samples differing from

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TABLE 1

PREPARATION CONDITIONS AND MEAN CRYSTALLITE SIZES OF THE β-$Cd(OH)_2$ SAMPLES

Sample	*Solvent*	*Mixing mode of the solutions*	e_{H}*(Å)*	ϕ_{H}*(Å)*
A	Conc. KOH	Dissolution 140°C and slow cooling	1 μm < e < 100 μm	0.1 mm a 2 mm
B		unknown Prolabo	680	3500[a]
C	Distilled water free from CO_2	Slow diffusion	346	590
D	Distilled water free from CO_2	rapid	257	590
E	Ethyl alcohol	rapid	65	347
F	Ethyl alcohol	rapid	54	268
G	Butyl alcohol	rapid	21	103

[a] ϕ_{H} of $Cd(OH)_2$ B was measured on a distribution curve obtained from various electron-photomicrographs of these crystals.

one another in granulometry only. The samples were obtained by precipitation from solutions of cadmium iodide and of potash. By changing the rate of mixing of both solutions and the nature of the solvent, the hydroxide granulometry is modified. The most divided samples were prepared by rapid mixing of both solutions made from ethyl or butyl alcohol. The apparent mean size of the crystallites obtained and the corresponding preparation mode are listed in Table 1. Each sample will be designated by the reference letter which appears in this table.

Experimental decomposition conditions

Decomposition was carried out in a thermobalance, under dynamic vacuum or constant water vapour pressure by connecting the reaction vessel to a "cold spot" containing water whose regulated temperature is lower than that of the reactor. 11 mg hydroxide were spread over a platinium crucible 15 mm in diameter.

In each rehydration test, the sample, once the weight-loss step is reached, is brought back to room temperature while being kept under constant water vapour pressure.

Sample characterization

Identification of solid phases is performed by X-ray diffraction (Siemens, powder diffractometer, K_{α}Cu radiation) and i.r. spectroscopy (Perkin-Elmer 325 Cesium iodide faces–Nujol dispersif).

FIRST RESULTS: REHYDRATION OF CdO ex-$Cd(OH)_2$

A slight weight gain within a few hours was observed when trying samples B, C, D rehydration. This weight excess may be removed by heating the sample slightly. In each case, the resulting material is CdO alone. The weight excess, is thus, probably due to water adsorption on the divided oxide.

Alternatively, a large weight gain, even larger than the loss noticed during decomposition, was observed for the oxide resulting from the decomposition of E. The final material was white, slightly yellowish (the hydroxide is white and the oxide more or less dark brown depending on preparation temperature). The solid obtained consisted of two phases: β-$Cd(OH)_2$ hydroxide (similar to initial material) and γ-$Cd(OH)_2$ the other allotropic species, far less common and reported by Glemser[6]. Both phases occur in almost equal proportions.

The phenomenon is not due to a crystallite size effect

It was first thought that this phenomenon of rehydration might be attributed to the small dimensions of the hydroxide crystallite E. This is not so; hydroxide F, whose dimensions were very similar to that of E and whose preparation is identical, behaved in the same way as samples B, C and D.

The phenomenon is due to an impurity effect

Careful analysis of hydroxide E by X-ray diffraction (step scanning 0.02°2θ/2 mn-Analysis slit 0.02°) shows minute amounts of potassium iodide (a few percent). This salt, a by-product from hydroxide preparation, is relatively little soluble in ethyl alcohol used as solvent, it was hardly removable by washing. Whether those KI traces might be the cause of the particular behaviour of hydroxide E was worth investigating. For this purpose, a small amount of hydroxide E was first washed several times with alcohol to remove any remaining potassium iodide. The hydroxide thus purified and whose granulometry had not changed was decomposed and the oxide obtained placed under suitable rehydration conditions: no rehydration occurred. Secondly, 1 to 2% weight potassium iodide was added to the hydroxide samples B and C. They resulted in an oxide which rehydrated into a mixture of both hydroxide β- and γ-$Cd(OH)_2$ in proportions which varied largely from one sample to the other.

The potassium iodide traces within the initial sample, thus, seem to be the cause of the possible rehydration of the cadmium oxide obtained through thermal decomposition of the hydroxide β-$Cd(OH)_2$. Oxide rehydration also occurred when the potassium iodide was directly added to the oxide.

It has also been reported that $Cd(OH)_2$ E decomposition rate is very high compared to that of D or F in similar experimental conditions. The various tests made to find out the cause of the possibility of rehydration showed that the potassium iodide traces are also the cause of this increase in dehydration rate. Addition of tiny amounts of KI to the pure hydroxides B, C or D enormously accelerates their decomposition reaction.

FURTHER RESULTS: INFLUENCE OF THE NATURE OF IMPURITY

To understand the influence of potassium iodide, various salts containing either the K^+ cation or the I^- anion or neighbour ions (e.g., KBr, KCl, KOH, NaI, NaBr, NaCl, NaOH . . .) were added to a pure hydroxide. The results obtained depend on the nature of the impurity, the amount added and the hydroxide sample used together.

Analysis of the relative influence of addition in equal percents of KI, KBr, KCl and KOH led to the following:

– Dehydration rates increase differently depending on the impurity nature; they rank as follows: $\nu_{KOH} > \nu_{KI} > \nu_{KBr} > \nu_{KCl} \simeq \nu_{pure}$, where ν_i is the dehydration rate when the impurity added is i.

– Rehydration rates rank in the same way. The presence of KCl does not seem to involve the reversibility phenomenon; the hydroxide behaves as if it were pure.

– Nature and amount of impurity not only affect the rehydration or dehydration rates but also the proportions of both β- and γ-$Cd(OH)_2$ in the ultimate product.

Hydroxide γ-$Cd(OH)_2$ alone or β-$Cd(OH)_2$ alone was sometimes obtained but these results were not reproducible.

X-ray diffractogrammes and i.r. adsorption spectra of various hydroxides, of hydroxides insufficiently washed, of potassium iodide alone and of hydroxides containing various potassium iodide amounts, were recorded. Measurement errors taken into account, no change in the pure phases was observed, X and i.r. spectra of the insufficiently washed hydroxides or to which potassium iodide was added were the superimposition of the spectra of both phases.

CONCLUSION

The experimental results reported are qualitative evidence that traces of a salt such as potassium iodide with cadmium hydroxide: accelerate tremendously the hydroxide decomposition reaction and make rehydration of the resulting oxide possible.

These results, however, do not allow these observations to be interpreted. But we think that they might be related to those obtained by Berg and Kovyrzina[7]. These authors showed that a lowering of the decomposition reaction temperature of $CdCO_3$ into CdO depends on the nature of the impurity introduced, i.e., NaCl, AgCl or even CdO, the latter resulting in a maximum lowering.

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