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Critical size and shape of CdO ex-Cd(OH)$_2$ crystallites

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The present paper reports the extent to which the size and shape of oxide crystallites resulting from a decomposition reaction depend on the crystallite size of the initial material. If those sizes are sufficiently large i.e. higher than "critical sizes", the resulting oxide crystallites assume exactly these "critical sizes". They are the maximum size that can be reached by oxide crystallites in the absence of any evolution process such as ageing or sintering and are specific to a particular shape of these crystals, which is independent of initial crystallite size. Alternatively, if the initial material crystals are below these "critical sizes", at least in one direction, then the dimensions and shape of the oxide crystallites depend on the size of the initial crystallites. These results were interpreted within the framework of the structural conversion mechanism related to the decomposition reaction and showing great similarities with a shear transformation.

1. Introduction

Much work has been devoted to the formation of finely divided oxides resulting from the decomposition of the corresponding hydroxide or carbonate. A fresh viewpoint on the mechanism of such a transformation has been given; decomposition of Cd(OH)$_2$ into CdO. Contrary to previous reports we have shown that the structural transformation did not exhibit any growth step of the oxide crystallites [1, 2], but shows the structural and morphological characteristics of a transformation without diffusion [3, 4] i.e. the piling order of the initial crystalline solid constituents is preserved during transformation.

Experimental results reported here supplement the study of this mechanism. A hydroxide with flat hexagonal prismatic crystallites was used (Mean thickness = 680 Å, mean diameter = 3500 Å), and in all experimental conditions, the size of the crystallites obtained was far smaller than that of the initial crystallites [5]. Now, in a transformation without diffusion, e.g. a martensitic transformation, the division state of the product is quite characteristic and is caused by initial solid fragmentation, which is more or less important and related only to the difference between both crystalline structures.

Our purpose was to determine the extent to which fragmentation depends on the initial solid granulometry, in this Cd(OH)$_2$ → CdO reaction. It will thus be determined whether the oxide division state agrees with a mechanism without diffusion.

2. Experimental

2.1. Materials

Two criteria underlay the preparation of the hydroxide samples: (1) obtaining samples whose crystallite size is larger than that of the previously obtained oxide and others whose size is the same or even smaller; (2) using samples which would, as far as possible, differ in granulometry only. The same reagents, CdI$_2$ and KOH, were always used; only the solvent and mixing rate of both solutions were changed for each preparation. The precipitates were collected by centrifugation after repeated washing with the same solvent. They were then dried and stored in a vacuum desiccator to obviate air carbonation. The preparation conditions of each Cd(OH)$_2$ sample, subsequently termed A, B

TABLE I Preparation conditions and mean crystallite sizes of the $Cd(OH)_2$ samples.

Sample	Solvent	Mixing mode of the solutions	e_H (Å)	ϕ_H (Å)
A	Unknown Prolabo	Unknown Prolabo	680	3500*
B	Distilled water free from CO_2	Slow diffusion	346	590
C	Distilled water free from CO_2	rapid	257	590
D	Ethyl Alcohol	rapid	54	268
E	Butyl Alcohol	rapid	21	103

*ϕ_H of $Cd(OH)_2$ A was measured on a distribution curve obtained from various electron micrographs of these crystals.

etc, are listed in Table I. The mean thickness e_H, listed in the table, was calculated from the half-width of the 0 0 1 hydroxide peak and the mean diameter ϕ_H from the 1 0 0 peak (except for A).

2.2. Decomposition conditions

The samples were decomposed in a thermobalance under similar experimental conditions (T = temperature, P = water vapour pressure, t = time and q = weight). As a result, the oxides obtained, *a priori*, differed in the initial hydroxide granulometry only. Under the given experimental conditions no superficial phenomenon associated with, or subsequent to, formation occurred [5]. The present results were obtained in vacuum, below 300° C; above this value oxide sintering occurs.

2.3. Crystallite size determination

Pure CdO can be kept easily in normal conditions of temperature and pressure. The X-ray diffraction peaks of each sample could thus be recorded after preparation in the thermobalance without any particular apparatus. The conditions were as folflows: Siemens–Kristalloflex IV Generator, Ni Filtered Cu*Kα* radiation, Siemens Goniometer with entrance slit = 1 mm, analysis slit = 0.05 mm, Söller slit = ±4°, Step scanning $0.02° 2\theta/120$ S. count, plot scale 160 mm/°2θ. Comparative results were sufficient for this study and half-peak breadths $\Delta 2\theta_{hkl}$ allowed the various samples to be classified in terms of their mean apparent size without ambiguity. An order of crystallite size is given by the Scherrer equation [6] after correction of the half-widths by the Warren method [7]. Instrumental broadenings were obtained with a BDH sample of CdO sintered at 700° C for 36 h.

2.4. Crystallite shape characterization

In exceptional cases such as those of hexagonal crystallites of $Mg(OH)_2$ or $Cd(OH)_2$, the ratios of the half-peak breadths of a same diffractogram give direct information about crystallite shape. More generally, this is not possible but these ratios are always shape-dependent, even if the latter is unknown. Thus for samples of a similar origin, it is reasonable to think these ratios constant if the shape is conserved. Alternatively they vary if the shape is not the same. In this sense, we have calculated the ratio values k_1 and k_2 of the half-peak breadths of 1 1 1, 2 0 0, 2 2 0 diffraction peaks for each CdO sample obtained.

$$k_1 = \Delta 2\theta_{111}/\Delta 2\theta_{200}$$

and

$$k_2 = \Delta 2\theta_{111}/\Delta 2\theta_{220}$$

3. Results and discussion

The results in Table II were obtained after decomposition in the best conditions for investigation of the mechanism (vacuum, $T < 300°$ C). The half-peak breadths $\Delta 2\theta_{hkl}$ and the mean apparent crystallite *dimensions* D_{hkl} are listed for each CdO sample.

The oxide crystallites obtained from $Cd(OH)_2$, A, B and C, show the same mean apparent *dimen-*

TABLE II Crystallite sizes of various CdO samples obtained by decomposition of different $Cd(OH)_2$ samples in vacuum at T = 161° C for 4.50 h. $\Delta 2\theta_{hkl}$ is the half width of the diffraction peak $h\,k\,l$; D_{hkl} is the mean size calculated from the diffraction peak $h\,k\,l$; $e_{0(111)}$ is calculated from relation 1, $e_{0(200)}$ from 2 and $\phi_{0(111)}$ from 1 and 3.

$Cd(OH)_2$ Sample	e_H (Å)	$\Delta 2\theta_{111}$ (mm)	$\Delta 2\theta_{200}$ (mm)	$\Delta 2\theta_{220}$ (mm)	D_{111} (Å)	D_{200} (Å)	D_{220} (Å)	$e_{0(111)}$ (Å)	$e_{0(200)}$ (Å)	$\phi_{0(111)}$ (Å)
A	680	104	114.5	144	134	122	104	54	70	142
B	346	101	114.5	140.5	138	122	106	55	70	144
C	257	103	115	137	135	122	109	54	70	152
D	54	180	208	195–202	75	66	75–72	30	38	107–114
E	21	606	522	336–360	22	26	43–40	9	15	69–76

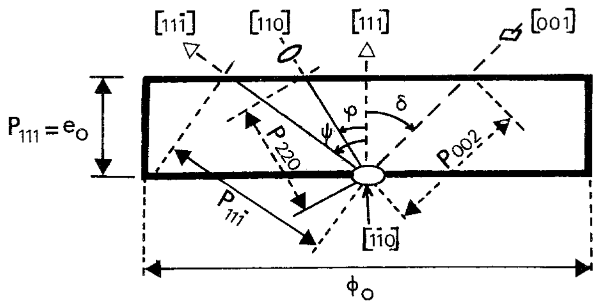

Figure 1 (1 $\bar{1}$ 0) Section of a platelet CdO crystallite.

sions, which are smaller than those of the A, B, C crystallites. Alternatively, for D and E the oxide crystallite size is of the same order of magnitude as that of the hydroxide; but in the latter case the D and E crystallites are smaller than those of the oxides obtained from A, B and C. The mean apparent size of D_{111}, D_{200} and D_{220} gives no information as to the shape of the crystallites; these are probably small hexagonal platelets parallel to the (1 1 1) plane of the oxide [8, 9].

It would be interesting to compare the actual mean sizes of the hydroxide crystallites to those of the oxide crystallites but their determination is made quite impossible by the particular shape of the latter. Indeed, the 1 1 1 peak, for instance, results from X-ray reflections on (1 1 1), ($\bar{1}$ 1 1), (1 $\bar{1}$ 1) and (1 1 $\bar{1}$) planes, and crystallite size is different perpendicular to each of these plane families (Fig. 1). In such a case, it is very hard to deduce the profile of each component peak from the recorded peak and therefore each corresponding crystallite size.

The above mentioned comparison was attempted using a rough hypothesis that the mean apparent crystallite size calculated from the recorded peak is the arithmetical mean of the sizes which could be calculated from each component peak. This assumption is not strictly valid and can only be used when the various structural factors are the same for the various planes, but it can, however, yield an approximation of the crystallite actual size.

If we let p_{hkl} = size perpendicular to (h k l), $\mathscr{D}_{hkl}$ = mean size perpendicular to $(h\,k\,l)$ = mean of p_{hkl}, and D_{hkl} = mean apparent size calculated from the $h\,k\,l$ peak, then from Fig. 1 we can write the following relations.

$$\mathscr{D}_{111} = p_{111} = e_0.$$

$$\mathscr{D}_{\bar{1}11} = \mathscr{D}_{1\bar{1}1} = \mathscr{D}_{11\bar{1}} \simeq e_0/\cos\psi$$

because in the largest part of the crystallite

$$p_{111} = e_0/\cos\psi.$$

$$\mathscr{D}_{200} = \mathscr{D}_{020} = \mathscr{D}_{002} \simeq e_0/\cos\delta$$

because in the largest part of the crystallite

$$p_{002} = e_0/\cos\delta.$$

$$\mathscr{D}_{220} = \mathscr{D}_{202} = \mathscr{D}_{022} \simeq e_0/\cos\varphi$$

because in the largest part of the crystallite

$$p_{220} = e_0/\cos\varphi.$$

and finally we call the mean diameter ϕ_0 of the oxide crystallites

$$\mathscr{D}_{20\bar{2}} = \mathscr{D}_{\bar{2}20} = \mathscr{D}_{0\bar{2}2} = \phi_0.$$

From the above hypothesis

$$D_{111} = \tfrac{1}{4}(\mathscr{D}_{111} + \mathscr{D}_{\bar{1}11} + \mathscr{D}_{1\bar{1}1} + \mathscr{D}_{11\bar{1}}) = \frac{e_0}{4}(1 + 3/\cos\psi) \quad (1)$$

$$D_{200} = \tfrac{1}{3}(\mathscr{D}_{200} + \mathscr{D}_{020} + \mathscr{D}_{002}) = e_0/\cos\delta \quad (2)$$

$$D_{220} = \tfrac{1}{6}(\mathscr{D}_{220} + \mathscr{D}_{202} + \mathscr{D}_{022} + \mathscr{D}_{20\bar{2}} + \mathscr{D}_{0\bar{2}2} + \mathscr{D}_{\bar{2}20}) = \tfrac{1}{2}(\phi_0 + e_0/\cos\phi) \quad (3)$$

From these relations, the values of the mean size of e_0 and ϕ_0 of the various oxides, were calculated (Table II); it was verified that e_0 is overvalued from the above approximation. From these results, Fig. 2 shows how the oxide crystallite size values e_0 and ϕ_0 are related to the thickness e_H of the hydroxide crystallites from which they derive. If e_H is larger than a value comprised between 70 and 120 Å, e_0 and ϕ_0 are independent of e_H. Alternatively e_0 is very close to e_H when the latter is smaller than the above value.

These results are readily accounted for in the case of a structural transformation whose characteristics are very close to those of a transformation without diffusion such as a shear transformation.

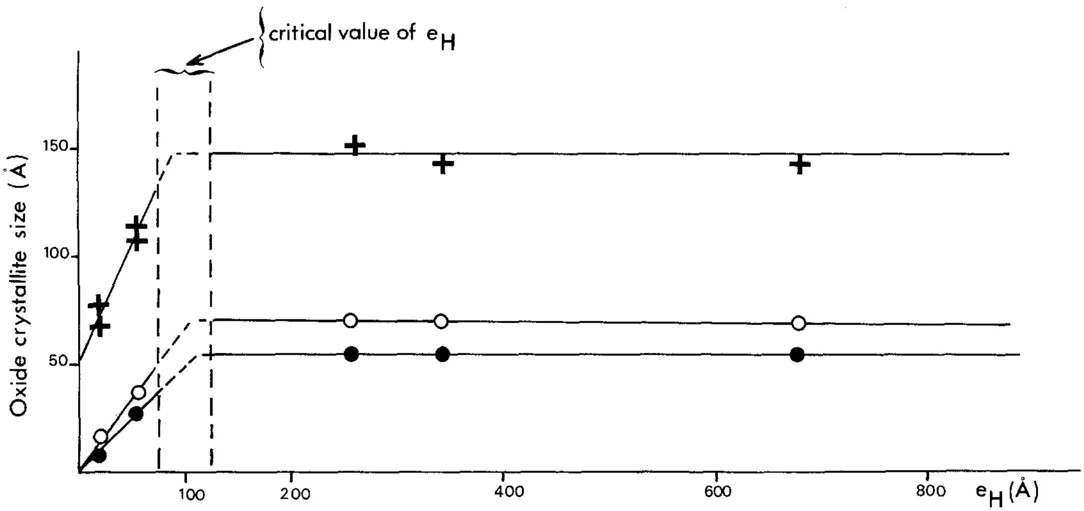

Figure 2 Mean crystallite sizes e_0 and ϕ_0 related to the thickness e_H of the hydroxide crystallites from which they derive: ● e_0 calculated from 1 1 1 peak, ○ e_0 calculated from 2 0 0 peak, + ϕ_0 calculated from 1 1 1 and 2 2 0 peaks.

In such a case, only mechanical stresses* or initial crystallite size limit the product crystallite size.

If the initial crystallite is sufficiently large the fragmentation of the initial solid occurs when stresses* balance exactly the interatomic forces. Neglecting crystal defects, this happens for the same size in a given crystallographic direction; that size is the maximum that the crystallites produced can reach in this direction. It was termed "maximum critical size" of the oxide.

When the initial crystallite size is smaller than this "maximum critical size", fragmentation cannot occur; the crystallite size of the product is very close to that of the initial crystallite.

Our results and their interpretation are in good agreement with those obtained by Guilliat and Brett [10] (Table III), who determined the mean crystallite size of MgO resulting from the decomposition of $Mg(OH)_2$ of variable granulometry. They explained the small variation in MgO crystallite size by the growing importance of "relics" as the thickness of the hydroxide platelet decreases. But critical size occurrence would require using magnesium hydroxide whose crystallite thickness would be smaller than the crystallite mean size of the oxide listed in Table III.

In addition, the higher value obtained for brucite platelets (sample 11) may certainly be explained

TABLE III The correspondence of crystallite size between parent, $Mg(OH)_2$, and product, MgO. The hydroxide crystals are assumed to be lamellar and the oxide crystallites to be octahedral (From Guilliatt and Brett 1971).

Sample	Crystallite size (Å)			
	$Mg(OH)_{2\,(00\cdot1)}$	$MgO_{(200)}$		
	Fourier integral breadth	Slope of the variance function	Fourier coefficients	Fourier integral breadth
1	96	40	54	47
2	99	41	54	47
3	112	40	56	48
4	137	41	57	50
5	182	42	58	51
6	203	44	60	55
7	218	49	62	60
8	231	54	68	65
9	235	55	73	69
10	243	59	77	71
11	>2000	74	96	100

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*In a decomposition reaction, such as that of $Cd(OH)_2$, mechanical stresses arise either from H_2O vacancies in the initial structure or distortions generated by the conversion of the hydroxide structure into the oxide structure [3]

TABLE IV Mean apparent sizes and ratios k_1 and k_2 characteristic of the shape of CdO crystallites obtained in various experimental conditions.

p_{H_2O} (torr)	T (° C)	D_{111} (Å)	D_{200} (Å)	D_{220} (Å)	k_1	k_2
5×10^{-5}	100	139	124	108	0.89	0.72
	250	138	125	108	0.90	0.73
	325	154	140	116	0.91	0.71
1	152	178	164	137	0.92	0.73
	250	171	150	133	0.89	0.73
	310	189	169	147	0.90	0.73
2	160	197	173	151	0.89	0.73
	250	184	159	141	0.88	0.72
	311	199	178	153	0.90	0.73
5	180	215	189	166	0.89	0.72
	250	199	176	148	0.89	0.71
	330	250	216	184	0.89	0.71
17.5	193	239	212	177	0.90	0.70
	250	213	191	162	0.90	0.72
	295	237	205	171	0.89	0.70

differently. Similar results were obtained with $Cd(OH)_2$ monocrystals of about 1 mm. The temperature used by these authors, i.e. 350° C, causes the hydroxide to decompose rapidly and a non-negligible water vapour pressure is liable to be exerted within the sample. It has been shown elsewhere that the crystallites obtained under pressure were bigger than those obtained in vacuum.

4. Further experiments and discussion

The above study has reported the maximum critical sizes of oxide–ex-hydroxide crystallites and how difficult it is to determine their actual numerical values. The following results and the discussion are related to crystallite shape with maximum critical size; but they deal only with shape evolution versus initial hydroxide granulometry.

Table IV lists mean apparent sizes and the half-width ratios k_1 and k_2 of the most important CdO diffraction peak obtained in various experimental conditions [5]. $Cd(OH)_2$ A was used for this study so the mean apparent sizes in Table IV are characteristic of maximum critical size. The results show that critical size depends on experimental conditions, which is not the case for k_1 and k_2. Thus, in the various experimental conditions, the oxide crystallites remain "homothetic", one to the other, and $k_1 \simeq 0.89$, $k_2 \simeq 0.72$ are two constants specific to the shape of the oxide crystallites produced by hydroxide decomposition with maximum critical sizes.

TABLE V Ratios characteristics of the CdO crystallite shape related to precursor $Cd(OH)_2$ crystallite thickness.

$Cd(OH)_2$		CdO		
Sample	e_H (Å)	k_1	k_2	ϕ_0/e_0
A	680	0.908	0.722	2.63
B	346	0.882	0.719	2.62
C	257	0.896	0.752	2.81
D	54	0.865	0.92–0.88	3.57–3.8
E	21	1.16	1.80–1.68	7.67–8.44

It was, thus, of interest to observe how these ratios vary compared to the initial hydroxide crystallite sizes, i.e. what happens to k_1 and k_2 when the oxide crystallites reach, or do not reach, the maximum critical sizes. k_1 and k_2 values for the various oxides of Table II are listed in Table V, which also contains the ϕ_0/e_0 ratios of the actual mean sizes calculated from the above approximation. These ratios remain constant when the oxide crystallites are of maximum critical size, i.e. when the hydroxide crystallites are sufficiently large for fragmentation to occur in each direction (hydroxides A, B, C). In these conditions the size and shape of the oxide crystallites are the same.

On the other hand, in the case of hydroxides D and E having smaller crystallites the ratio values depend on the hydroxide crystallite thickness, which may be easily explained. The crystallites of both hydroxide samples are too small (at least in one direction); no fragmentation of the solid arrangement occurs in that direction. The shape of the resulting crystallite, thus, depends on initial crystallite size.

These results show that the crystallites with maximum size have a characteristic shape even if the latter cannot be determined accurately. According to the interpretation of the critical sizes and shape of the resulting oxide crystallites those sizes and shape should be closely related to the structural correlation precursor-product, which, in particular, means that for a same product critical sizes and shape depend on the crystalline structure of the precursor. This has actually been experimentally confirmed; CdO was prepared from $Cd(OH)_2$ and from $CdCO_3$; in both cases the dimensions of the precursor crystallites were far greater than those of the oxide crystallites obtained, the latter being of the maximum critical dimensions. The latter as well as the shape of the resulting crystallites were largely different in both cases [9].

5. Conclusion

The fact that Cd hydroxide conversion into the oxide is topotactic and the characteristics of the resulting oxide division state related, on the one hand, to the extent of reaction progress, and on the other to reaction rate, enabled us to show that the oxide formation is related to a shear transformation mechanism.

In such a transformation, mechanical processes cause the initial crystalline arrangement to split as structure changes and generate the resulting crystallites. The mechanical stresses causing this splitting do not depend on the initial size of the crystallites but on the difference between the crystalline structure of the precursor and that of the oxide. However, for these stresses to develop sufficiently and cause the initial arrangement to split, the latter should be of sufficient size, i.e. "critical size". If the initial crystals are far bigger than that value they split into crystallites of roughly this "maximum critical size". In the opposite case no splitting occurs.

Experimental results reported in this paper perfectly support this transformation mechanism.

This concept of "maximum critical size" appears to be of major importance in the preparation of fine particles. When this size is small the solid produced by decomposition will always be very finely divided in the absence of sintering; alternatively when it is large one must start from a precursor with the same granulometry as that required for the final product.

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