JOURNAL OF SOLID STATE CHEMISTRY **68**, 214–218 (1987)

Time-Resolved X-Ray Diffraction by Synchrotron Radiation: The Thermal Decomposition of Cd((OH)$_2$) Powders

ÖRJAN SÄVBORG, J. R. SCHOONOVER, S. H. LIN, AND L. EYRING

Department of Chemistry, Arizona State University, Tempe, Arizona 85287

Received March 31, 1986; in revised form August 1, 1986

The application of time-resolved X-ray diffraction by synchrotron radiation to thermal decomposition of Cd(OH)$_2$ is reported. In this demonstrative and preliminary work, we follow the reaction by measuring the (100) reflection of Cd(OH)$_2$ and the (111) reflection of CdO as a function of time. The results are consistent with the reported martinsitic nature for the formation of the oxide. The Cd(OH)$_2$ (100) reflection undergoes narrowing that is not consistent with a diffraction domain size effect alone.

1. Introduction

In a previous paper (*1*), we presented a theoretical study of the feasibility of using time-resolved X-ray diffraction (TRXD) to determine the kinetics and mechanisms of solid state reactions and phase transitions. We showed that TRXD can provide valuable information about the size and shape of the crystallites of the reaction product as a function of time; such information is not available from conventional techniques such as thermogravimetry (see, for example, Ref. (*2*)) or HREM (*3*). The present communication reports the preliminary results of a demonstrative TRXD study of the thermal decomposition of Cd(OH)$_2$ powders (see, for example, Ref. (*4*)).

2. Experimental

The Cd(OH)$_2$ powder was prepared by the slow mixing of hot 0.5 *M* Cd((NO)$_3$)$_2$ and decarbonated 0.5 *M* KOH solutions; the water loss kinetics of the decomposition were examined by isothermal thermogravimetry (TGA) using a Cahn 1000 electrobalance.

The TRXD experiment was performed at the Stanford Synchrotron Radiation Laboratory (SSRL) at an eight pole wiggler side station with an unfocused Si(220) monochrometer at 8428.20 eV. The Germanium detector (Ortec GLP 16230/10-5) was stepped scanned at $2\theta = 0.050°$ intervals, with a 2-sec count time and a 0.5-sec wait between steps. The Cd(OH)$_2$ (100) line and the CdO (111) line were alternately scanned. All experiments were performed under a rough vacuum (10^{-3} Torr) and at several temperatures (100 to 150°C).

3. Results and Discussion

Figure 1 shows the decomposition curves of Cd(OH)$_2$ as determined by TRXD. The extent of reaction, 1-α, is approximately the ratio of the integrated intensity of the reacted hydroxide to that of the unreacted hydroxide. Since the final extent of the re-

0022-4596/87 $3.00

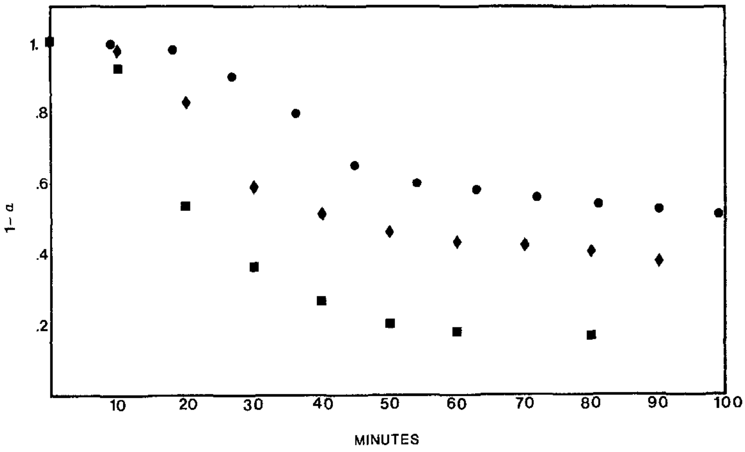

FIG. 1. Decomposition curves for $Cd(OH)_2$ as determined by TRXD. The extent of the reaction α is the ratio of the initial integrated intensity to the intensity of time t. The approximate temperatures are: 130°C, ●; 135°C, ◆; 148°C, ■.

action is uncertain, there has been no attempt to calculate α from the oxide TRXD line. Comparison of the shape of the hydroxide and oxide curves indicates that within the time resolution there is direct conversion of the hydroxide to the oxide without passing through an intermediate phase.

A striking feature of the curves is that the hydroxide (100) line never shows 100% decomposition and that the kinetics of the water loss and crystallographic conversion do not correspond. The crystallographic changes proceed much more rapidly than is expected from TGA (Fig. 2), and the amount of unreacted hydroxide present af-

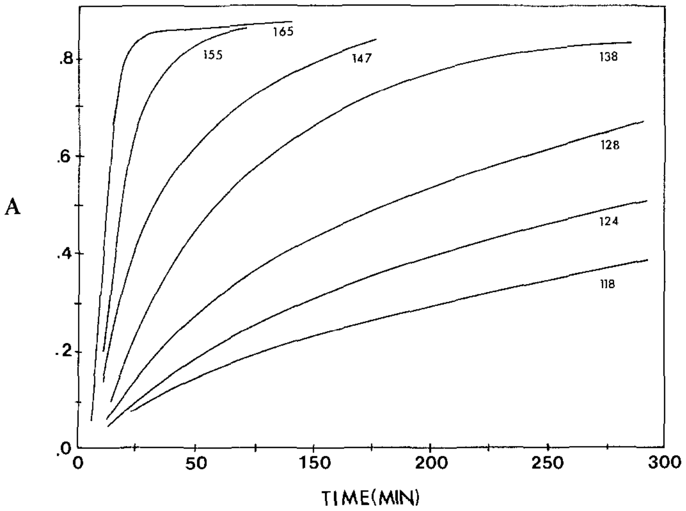

FIG. 2. Isothermal thermogravimetric curves for the decompostion of $Cd(OH)_2$ powders. A is the extent of the reaction.

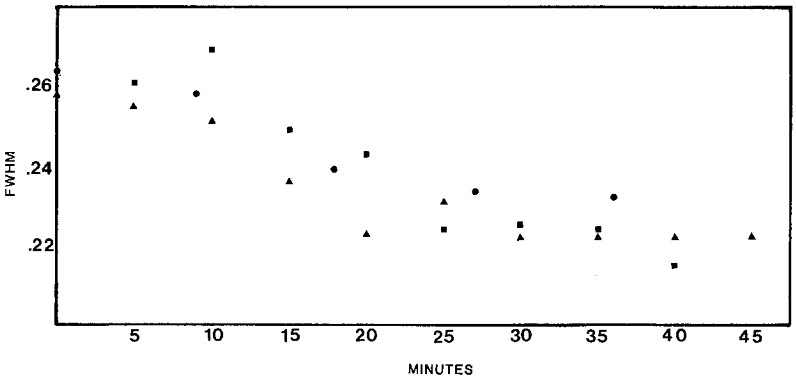

FIG. 3. The full-width at half-maximum (FWHM) of the $Cd(OH)_2$ 100 line as a function of time. The approximate temperatures are: 130°C ●; 135°C ▲; 148° ■.

ter the time when the reaction rate becomes small is larger than is expected from the TGA.

The kinetics as investigated by TGA appear to be diffusion controlled, while the observed kinetics from TRXD are crystallographically controlled. Thus, upon comparison, the two methods of investigation indicate that water loss and the formation of the cubic oxide may not be concomittant temporally, kinetically, or mechanistically. Based on TGA and X-ray diffraction, a highly lacunar structure formed by the dehydration of the hydroxide without an accompanying significant crystallographic change has been postulated for Mg and Ca hydroxides (both are brucite-type hydroxides) (*5*, *6*); such a lacunar structure may be present during the dehydration of $Cd(OH)_2$.

The hydroxide peak width has a complex behavior. Rather than the line broadening expected for nucleation and growth, the half-width decreases as the reaction proceeds (Fig. 3). In our preliminary investigation we have not yet examined higher order lines which are required for obtaining the domain size and strain distributions, but the behavior of the peak widths do provide insight into the nature of the line narrowing. At all temperatures, the $Cd(OH)_2$ linewidth narrows until it approaches the instrumental linewidths; the rate of the narrowing is about -2×10^{-3} 2θ°/min and is weakly temperature dependent. If the peak widths are examined as a function of the extent of reaction (Fig. 4), an interesting behavior is revealed. At low temperatures, the Cd $(OH)_2$ linewidth smoothly approaches the instrumental linewidth, but as the temperature is raised, the curve breaks into two parts: in the first part, the slope is less than that for the lower temperature, while in the second part, there is a sudden drop toward the instrumental linewidth. As the temperature is increased further, the first part of the curve flattens out, the slope going to zero, and in the second, the drop becomes more severe until finally the linewidth reaches the instrumental width; the drop also occurs at a higher extent of reaction. The drop corresponds to the time in the decomposition curves when the rate of the reaction becomes small.

Behavior of the linewidths is not readily explained as a size effect alone; temperature dependence of the linewidth makes such an explanation difficult. The rapid narrowing indicates a recrystallization although the nature of the recrystallization, whether a size or an ordering effect, is unknown at this time. The presence of water

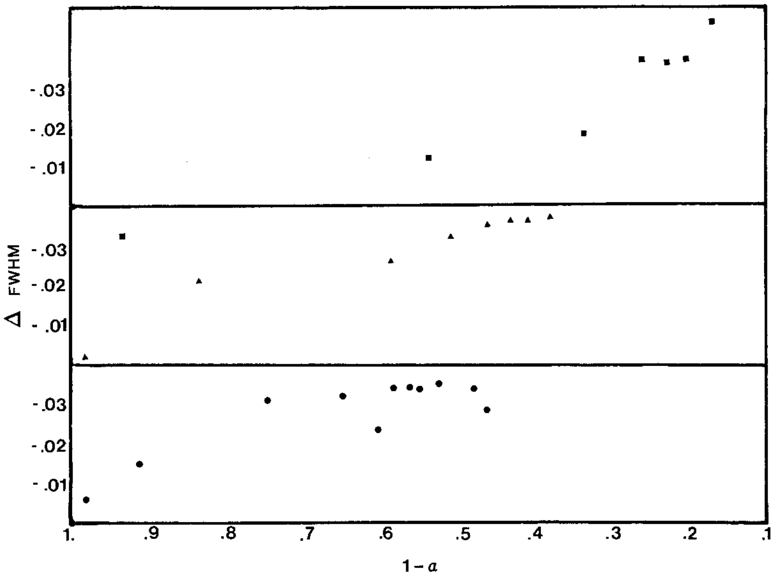

FIG. 4. The change in the peak width as a function of the extent of the reaction and temperature. The approximate temperatures are, from top to bottom, 148°C, 135°C, and 130°C.

may help induce recrystallization, resulting in a smooth narrowing of the lines at low temperatures; at high temperatures, the diffusion and subsequent evaporation of water is rapid, impeding the recrystallization. The influence of water in decomposition reactions in general is well known. The story may be more complex than this though, in that the rate of decomposition abruptly slows when the drop in linewidth occurs. Such a slowdown may not be due to simple annealing, but the role of defects in trapping the rapidly diffusing protons (*5*) (that initiate water formation) and in aiding the diffusion of water to the surface may be the determining factors in decomposition, accounting for the observed behavior. The role of competing effects in the linewidth narrowing cannot be overlooked; indeed, there does seem to be a slight broadening of the linewidth during the first few minutes of the decomposition, indicating that a thermal effect may be disrupting the recrystallization until a critical extent of reaction is reached. This is supported by the Raman spectroscopy of $Ca(OH)_2$, which indicates that during decomposition, fluctuations in atom positions occur (*8*). But the noise level may be as large as the "broadening effect." All of these effects, surface energy effects by absorbed water, thermal disruption of the lattice, and the role of defects in decompositions, may simultaneously play determining roles in the linewidth behavior and decomposition kinetics.

The width of the CdO (111) line is independent of time, extent of reaction, and temperature. There is little strain in the product phase, thus the linewidth gives a reasonable estimate of the average particle size (*7*); from the Scherrer equation, the diffraction domains are found to be approximately 110 Å. The constancy of the particle size distribution has been attributed to a martinsitic transformation (*9*). Temperature independence is a characteristic of the martinsitic transition, as is a strain threshold at which particle fracturing may occur.

Acknowledgments

The National Science Foundation (Grant DMR 81-08306) provided financial support. We thank Karl Ludwig and Dennis Lorentz for their generous assistance at SSRL.

References

1. T. L. Groy, S. H. Lin, S. K. Porter, R. R. Von Dreele, and L. Eyring, *J. Mol. Sci.* **2,** 93 (1982).
2. T. Sugihara, S. H. Lin, and L. Eyring, *J. Solid State Chem.* **40,** 189 (1981).
3. L. Eyring, *in* "The Handbook on the Physics and Chemistry of the Rare Earths" (K. A. Gschneidner and L. Eyring, Eds.), Chap. 27, North-Holland, Amsterdam (1979); L. Eyring, *in* "Nonstoichiometric Oxides" (O. T. Sorensen, Ed.), Chap. 7, Academic Press, New York (1981).
4. P. Dumas, N. Ea, J. C. Niepce, and G. Watelle, *J. Solid State Chem.* **27,** 317 (1979); J. C. Niepce, M. T. Mesnier, and D. Louër, *J. Solid State Chem.* **22,** 341–351 (1977).
5. F. Freund and V. Sperling, *Mat. Res. Bull.* **11,** 621 (1976).
6. O. Chaix-Pluchery, J. Bouillot, D. Ciosmak, J. C. Niepce, and F. Freund, *J. Solid State Chem.* **50,** 297 (1983).
7. D. Louë, M. T. Mesnier, and J. C. Niepce, *J. Mat. Sci.* **19,** 716 (1984).
8. O. Chaix-Pluchery, D. Ciosmak, J. C. Niepce, and M. Peyard, *J. Solid State Chem.* **53,** 273 (1984).
9. J. C. Niepce and G. Watelle, *Chem. Soc. Faraday Trans.* **74,** 1530 (1978).