Some Observations on the Calcination Process of Precipitated Magnesium Hydroxide

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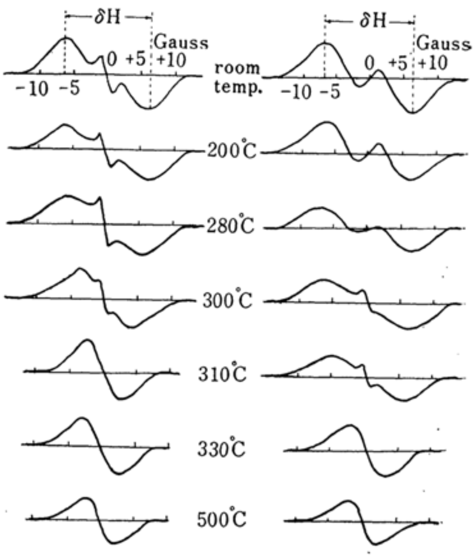
It has previously been reported[1] that the particle size of magnesium oxide crystals prepared by the thermal decomposition of pure precipitated magnesium hydroxide and of native brucite increases with the calcination temperature and the duration of heating at a fixed temperature according to the equation: $d=Kt^n \exp(-E/\boldsymbol{R}T)$, where d is the average crystal diameter determined from the broadening of the X-ray diffraction line, t is time, E is the activation energy, $\boldsymbol{R}$ is the gas constant, T is the absolute temperature, and K and n are constants. The present paper presents microscopic and atomic observations on the calcination process of precipitated magnesium hydroxide.

Experimental

The materials used were the same as those described in a previous paper[1]. Their NMR spectra were obtained by means of a Varian DP 60 spectrometer equipped with an RF unit of 40 Mc., the modulation frequency and width on operation being 40 c. p. s. and 1.1 gauss respectively. The electron microscopic photographs were taken by means of a Nippon Denshi electron microscope TEM-5G.

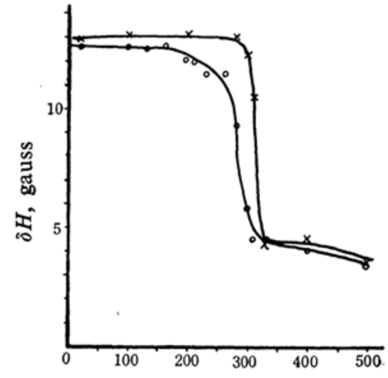
Experimental Results and Discussion

NMR spectra were obtained for samples which had been dehydrated in a vacuum from precipitated magnesium hydroxide and brucite for 3 hr. at 100, 200, 280, 300, 310, 330, 400 and 500°C. The results are shown in Fig. 1, where the (a)'s are the spectra of precipitated magnesium hydroxide and the (b)'s, those of brucite. It may be seen in Fig. 1 that there is a great difference between (a) and (b) below 280°C. The spectra of precipitated magnesium hydroxide are rather complex, having the central peak, while those of brucite have the typical two-proton shape. Figure 2 shows the variations in line width of the NMR spectra with the change in calcination temperature. The decrease in line width began at a lower temperature (at about 200°C) for precipitated magnesium hydroxide than for brucite. To clarify the effect of water vapor on dehydrated samples, these samples were prepared from brucite by means of calcination in a vacuum for 3 hr. at 200, 300, 330, 360, 400 and 500°C, and then reacted with water vapor by succesive exposure to an atmosphere saturated with this vapor at room temperature. After the exposure, rehydrated samples were evacuated at room temperature for 12 hr. in order to remove any excess adsorbed water. In Fig. 3 NMR spectra are shown for dehydrated (a) and rehydrated (b) samples. The central peaks seen in Fig. 3 (b) may be a result of the presence of a trace of movable water adsorbed by the samples and not re-



(a) (b)

Fig. 1. NMR spectra of proton in the thermally dehydrated products in vacuo.
(a) Samples of precipitated $Mg(OH)_2$ series
(b) Samples of brucite series



Calcination temp., °C

Fig. 2. Variations of line width (δH) of NMR spectra in Fig. 1.
○—○, Precipitated $Mg(OH)_2$ series
×—×, Brucite series

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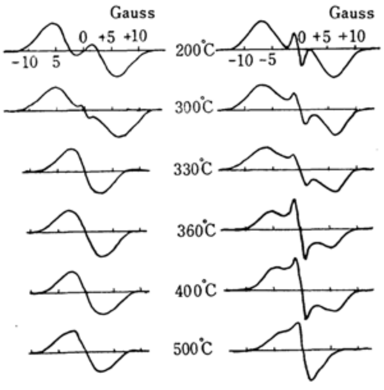
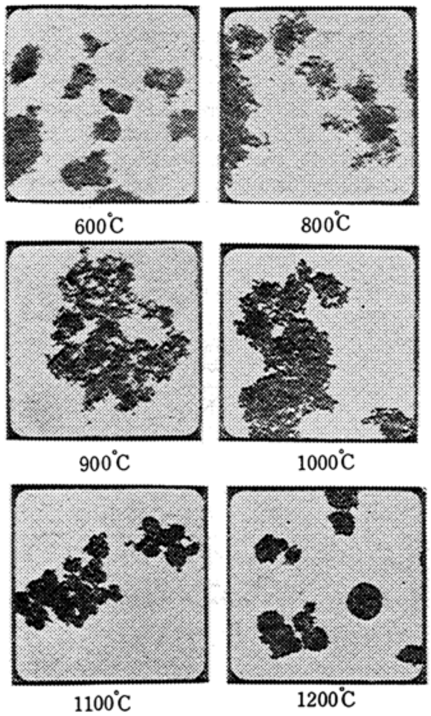
[1] Y. Kotera, T. Saito and M. Terada, This Bulletin, **36**, 195 (1963).

moved by evacuating the samples at room temperature. It was possible to remove it, however, by heating the samples to 110°C and by then evacuating them at this temperature. It is interesting that the spectra of (b) are similar to those of precipitated magnesium hydroxide (Fig. 1 (a)).



(a) (b)

Fig. 3. NMR spectra of proton in the thermally dehydrated products of brucite in vacuo and their rehydrated products.
(a) Samples of dehydration series
(b) Samples of rehydration series



600°C 800°C 900°C 1000°C 1100°C 1200°C

(×1500)

Fig. 4. Electron micrographs of MgO prepared from precipitated $Mg(OH)_2$.

The samples for the electron micrograph were prepared by the calcination of precipitated magnesium hydroxide at 600, 700, 800, 900, 1000, 1100 and 1200°C for durations ranging from 30 min. to 24 hr. The duration had a smaller effect upon the crystal size and the crystal form than the temperature. The effect of the calcination temperature upon the crystal figure is shown in Fig. 4, the rate of magnification being ×1500. From Fig. 4 it may be seen how crystals aggregate with each other until the temperature of 900°C is reached and how they grow to sphere-like particles, the particle size being about 0.1, 1 and 3 μ for the products at 1000, 1100 and 1200°C respectively.

From the results obtained it may be concluded that the precipitated magnesium hydroxide holds the movable water in the interstices between crystal lattice layers or between fine particles and that the structure water is removed only partially from the precipitated magnesium hydroxide by calcination below 280°C. It may also be concluded that the rehydration process is not the reverse reaction of dehydration but proceeds according to the thermal history of the samples. Such a tendency was seen in our experiment, where the water contents of the samples rehydrated by saturated water vapor were measured gravimetrically with the change of storage time; it has also been reported in adsorption experiments carried out for magnesium oxide[2]. The crystal growth of magnesium oxide shown in Fig. 4 would support the conclusion of the preceding paper[1]. A detalied study of these and other aspects will be published elsewhere in due course.

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[2] S. J. Gregg and R. K. Packer, *J. Chem. Soc.*, **1955**, 51; R. I. Razouk and R. Sh. Mikhail, *J. Phys. Chem.*, **59**, 636 (1955); **61**, 886 (1957); **62**, 920 (1958); D. T. Livey et al., *Trans. Brit. Ceram. Soc.*, **56**, 217 (1957).