Crystal Growth of Magnesium Oxide Prepared by the Thermal Decomposition of Magnesium Hydroxide

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It is well known that active metallic oxides are prepared by the thermal decomposition of hydroxide or carbonate and that their physicochemical properties are determined by the temperature at which they are formed and by the duration of the calcination. It is, therefore, important to clarify the process which occurs during the decomposition of such a compound as hydroxide or carbonate and the subsequent calcination. We select the crystal growth of magnesium oxide prepared from hydroxide for this purpose, because this process, especially in a relatively low temperature range, has not been studied so much as have its surface properties[1-3]. It is pointed out in our study that the growth is rather complex and that it might nevertheless be possible to clarify that mechanism which is important in the preparation of magnesium oxide.

The present work is an attempt to examine the effect of the temperature of calcination, and of the duration of heating at a fixed temperature, on the crystal growth of magnesium oxide prepared by the dehydration of precipitated magnesium hydroxide and native brucite. The growth is discussed in the light of kinetics, and the activation energy calculated is compared with that for other oxides.

Experimental

Materials.—Two series of magnesium hydroxides have been examined; one of them was prepared by precipitation from a 0.1 N solution of reagent-grade magnesium chloride with a 2.5 N solution of reagent-grade sodium hydroxide, while the other was a piece of native brucite from Nevada, U. S. A.

In the preparation of former series, care was taken to ensure that all air coming in contact with the carbonate-free sodium hydroxide solution and with the mixture of this solution and the magnesium chloride solution had been freed from carbon dioxide. The precipitate obtained by the reaction between the two solutions was washed until a test for chloride ions with a silver nitrate solution gave only a faint milkiness; it was then decanted. Drying of the precipitate was carried out at 60°C for 50 hr. in a vacunm obtained by means of a water pump. The native brucite contains the following impurities:

CaO : 0.82%, Fe_2O_3 : 0.79%, Al_2O_3 : 0.23%, SiO_2 : 0.14%.

Apparatus and Procedure.—The samples of magnesium hydroxide were ground into fine powder by a mortar and calcined in air at a definite temperature ranging from 500 to 900°C for varying periods. The fluctuation of the calcination temperature was kept within ± 5°C by means of an automatic temperature controller. After calcination, the products were cooled in a desiccator.

The X-ray specimens of magnesium oxide were smeared on a microscopic slide to give a flat surface approximately 2 cm. square. A Rigaku Denki "Geigerflex" (Geiger counter X-ray diffractometer) was employed to determine the mean apparent crystal sizes of the samples on the basis of the broadening of their X-ray diffraction lines. Measurements were made on the magnesium oxide (200) line using copper radiation. The calculation of particle size was carried out following the procedure of Birks and Friedman[4].

Experimental Results

Calcination at Temperatures Ranging from 500 to 900°C. — Precipitated magnesium hydroxide and brucite were calcined at 500, 600, 700, 800 and 900°C for periods ranging from 5 min. to 24 hr. The mean apparent crystal sizes, d, of the magnesium oxide thus obtained are plotted against the time of calcination, t, in Figs. 1 and 2 for precipitated magnesium hydroxide and for brucite respectively. From these results it can be seen that the crystal growth proceeds during the calcination, its rate being highest immediately after the end of dehydration and decreasing with the increase in the time of heating. In Figs. 3 and 4 the relation between the crystal size and time is plotted on a logarithmic scale. In these figures for all calcination temperatures, the curves are composed of two straight lines intersecting at about 100 min. It is concluded from these results that the calcination process is divided into earlier and later stages for all calcination temperatures. Further, it is possible to divide

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[1] S. J. Gregg, R. K. Packer and K. H. Wheatley, *J. Chem. Soc.*, **1955**, 46.

[2] D. T. Livey, B. M. Wanklyn, M. Hewitt and P. Murray, *Trans. Brit. Ceram. Soc.*, **56**, 217 (1957).

[3] R. I. Razouk and R. Sh. Mikhail, *J. Phys. Chem.*, **61**, 886 (1957); **63**, 1050 (1959).

[4] L. S. Birks and H. Friedman, *J. Appl. Phys.*, **17**, 687 (1946).

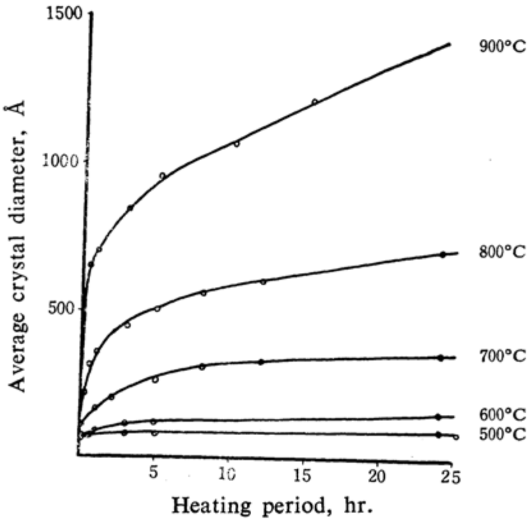

Fig. 1. Diameter change during heating of MgO prepared from ppt. $Mg(OH)_2$ at various temperatures.

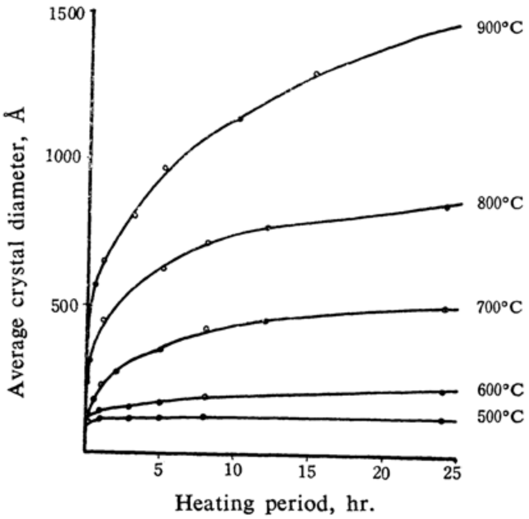

Fig. 2. Diameter change during heating of MgO prepared from brucite at various temperatures.

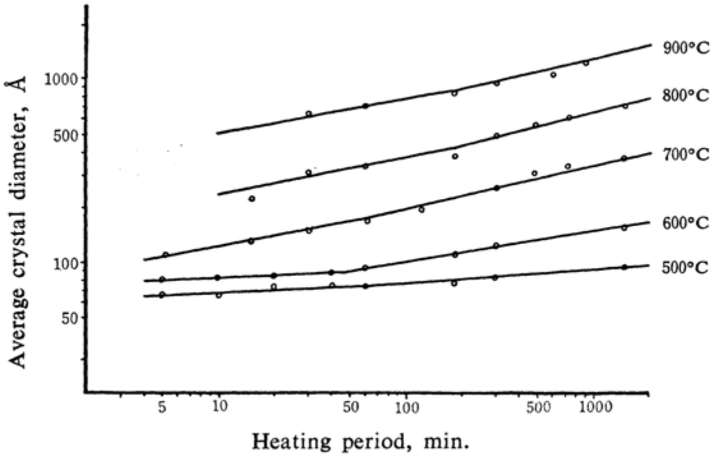

Fig. 3. Logarithmic plot of diameter change during heating of MgO prepared from ppt. $Mg(OH)_2$.

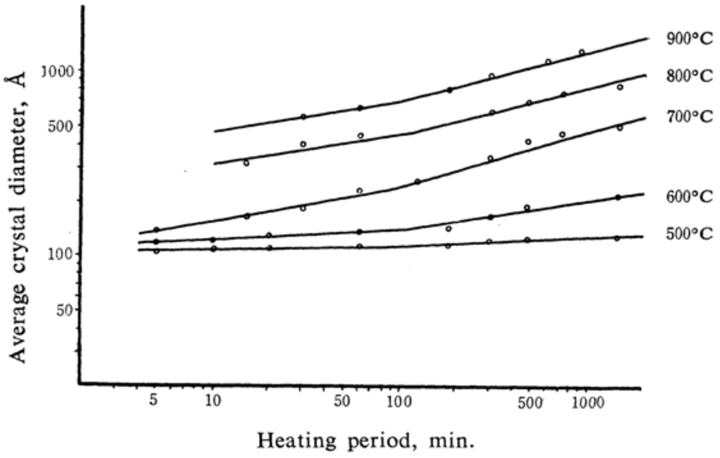

Fig. 4. Logarithmic plot of diameter change during heating of MgO prepared from brucite.

the results into three groups when the slopes of these straight lines are calculated, the first consisting of a whole period at 500°C and an earlier stage at 600°C, the second consisting of a later stage at 600°C and an earlier at a temperature between 700 and 900°C, and the third, of later stages at a temperature between 700 and 900°C.

Calcination at Temperatures Ranging from 700 to 950°C.—Magnesium hydroxide samples were dehydrated at 700°C for 10 hr. and the magnesium oxide samples thus obtained were used as starting materials to clarify the calcination process at a temperature between 700 and 950°C. Magnesium oxide samples were calcined at 800, 850, 900 and 950°C for periods varying from 1 to 8 hr. When the crystal sizes were plotted on logarithmic scale, Fig. 5 was obtained for magnesium oxide from precipitated magnesium hydroxide, and Fig. 6 for magnesium oxide from brucite. Their sizes before the calcination are 350 Å for the former and 530 Å for the latter. It was found that the crystal size increases exponentially with the reciprocal of the calcination temperature, as is implicit for a typical case in Fig. 7.

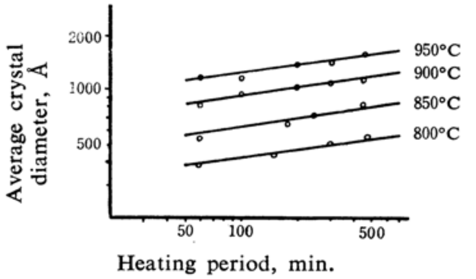

Fig. 5. Logarithmic plot of diameter change during heating between 800 and 950°C for MgO prepared from ppt. $Mg(OH)_2$ at 700°C.

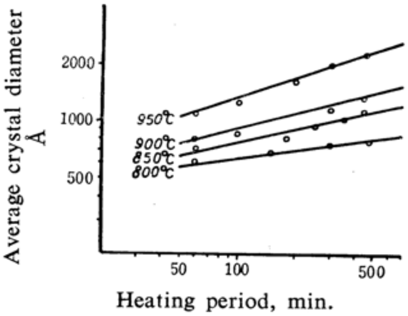

Fig. 6. Logarithmic plot of diameter change during heating between 800 and 950°C for MgO prepared from brucite at 700°C.

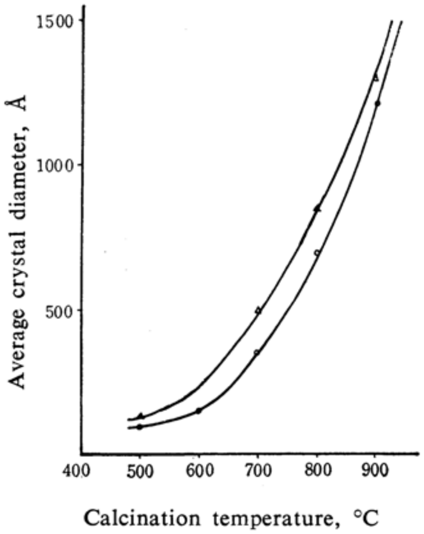

Fig. 7. Average crystal diameter as a function of calcination temperature. (calcination time: 24 hr.)

○—○ MgO prepared from ppt. $Mg(OH)_2$
△—△ MgO prepared from brucite

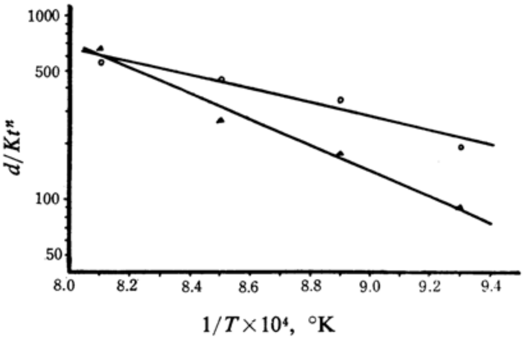

Fig. 8. Arrhenius plot for crystal growth of magnesium oxide samples prepared from ppt. magnesium hydroxide and brucite.

○—○ MgO prepared from ppt. $Mg(OH)_2$
△—△ MgO prepared from brucite

From the results obtained it is possible to express the crystal sizes as the function of the temperature, T°K, and of the time, t, by the following equations:

$d=K_1t^{1/6}\exp(-E_1/RT)$ for MgO from precipitated $Mg(OH)_2$ and

$d=K_2t^{1/4}\exp(-E_2/RT)$ for MgO from brucite, where K_1 and K_2 are constans, and E_1 and E_2 are activation energies for the crystal growth of magnesium oxide. It is probable that K_1 or K_2 may depend on the initial value of the crystal size.

In Fig. 8 the relation between $\log(d/Kt^n)$ and $1/T$ is plotted for both magnesium oxide samples; the values of the activation energy calculated from the figure are 17 kcal. for magnesium oxide from precipitated magnesium hydroxide and 32 kcal. for that from brucite.

Discussion

The effect of the conditions of preparation of the active metallic oxide in the thermal decomposition of hydroxide or carbonate upon its physico-chemical properties has been briefly studied. When the surface properties of magnesium oxide prepared from precipitated magnesium hydroxide or from brucite were studied by Gregg et al.[1], Livey et al.[2] and Razouk and Mikhail[3], it was found that these properties depend on the time as well as the temperature of decomposition of a parent substance, viz., precipitated magnesium hydroxide or brucite. Meanwhile, Birks and Friedman[4] studied the particle size determination of magnesium oxide prepared from the carbonate by means of an X-ray line broadening method; they compared the results with direct measurement by means of electron microscopy. They concluded that the results obtained by the two methods agree ± 10 per cent except for particles smaller than 100 Å. Their results show the dependence of particle size on the time and temperature of calcination, but no explanation was given in their study.

In the present study, precipitated magnesium hydroxide was used as a starting material as well as brucite. It might be necessary to compare the results of the former with those of the latter in order to elucidate the disagreement which seems to be present in the results based on the surface properties of magnesium oxide prepared from precipitated magnesium hydroxide[3]. On the other hand, brucite contains more impurities than precipitated magnesium hydroxide, and this fact may make it impossible to obtain accurate results on crystal growth kinetics which depend upon the purity of a parent substance. The naturally-occuring crystalline brucite chosen was as pure as possible, but it still contains the small amount of impurities described above.

The crystal sizes of magnesium oxide prepared from hydroxide increase with a rise in the calcination temperature and with its duration, a tendency similar to that in the case of carbonate. Comparing Birks' results[4] with ours shows that the increase in crystal size with a rise in the temperature is more prominent for oxide from hydroxide than for that from carbonate. The stages found for oxide from hydroxide are not found in the results by Birks, in which the shortest time of calcination carried out was 2 hr. In the study of the sintering of active magnesium oxide, Gregg et al.[1] found that the micellar length calculated under the assumption that the material exists as equal cubelets increases proportional to the square root of the time between 1 and 350 hr. at temperatures between 400 and 600°C. It is probable that the lowering of the temperature may serve to increase the value of the exponent relative to time in the equation expressing the relation between crystal size and calcination time, such a tendency being seen in our experiments. Nevertheless, it seems to be difficult to compare the micellar length calculated from the surface area with the crystal size obtained by the X-ray broadening method.

According to Hüttig's views[5], which have been verified by others, sintering is caused by three processes, viz., surface adhesion, surface diffusion and lattice diffusion. The first process may occur even at room temperature at the points of contact between neighboring micelles. The shearing stress exerted by the micelles near the region of contact leads to the deformation of the micelles and an increase in the area of contact over which adhesion occurs. As the rise in temperature reduces the rigidity of solids, adhesion will increase with the rise in temperature, and so also will sintering. This process occurs at temperatures above one-fourth of the melting point of the solid. Surface diffusion resulting from the mobility of the ions of the solid at its surface becomes sensible at a temperature about one-third of the melting point of the solid, while lattice diffusion, where the ions can move through the bulk of the micelles, occurs only at temperature above half the melting point. The last effect probably does not play an important part in the present work, as the highest temperature used was 950°C, which corresponds to 40% of the melting point (3100°K). Meanwhile, it has been pointed out[6] that there is a period during which surface roughness is destroyed and which is followed by an adhesion period. In the present study, it was found that there are three groups in the results for the calcination between 500 and 900°C; it may be assumed that they correspond to surface smoothing, surface adhesion and surface diffusion. In the explanation of the results concerning the sintering of magnesium oxide at temperatures between 400 and 600°C, Gregg et al.[1] pointed out that the temperature is so low that both surface diffusion and bulk diffusion seem to be ruled out, leaving adhesion alone, but they also pointed out that simple adhesion cannot represent the whole process. It is probable that surface smoothing remains before an adhesion period in their experiments. This

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[5] F. Hüttig, *Kolloid-Z.*, **98**, 263 (1942); **99**, 262 (1942).

[6] F. S. Stone, "Reactivity of Solids", Elsevier, Amsterdam (1961), p. 15.

idea is supported by the fact that the decreasing rate of surface area is very high, even at such a low temperature as 500 or 600°C[1], while the increase in crystal size is not so rapid at such a low temperature (Figs. 1 and 2). However, the later stage at 600°C may be explained as the beginning of surface adhesion. In the second group, viz., the later stage at 600°C and earlier stages at a temperature between 700 and 900°C, surface adhesion would occur. Furthermore, the crystal growth occurs in the last group, viz., the later stages at a temperature between 700 and 900°C, according to the mechanism associated with surface diffusion.

In the last group, the value of the exponent to time in the equation expressing the relation between crystal size and calcination time, as well as the value of activation energy for the crystal growth, are different in magnesium oxide obtained from precipitated hydroxide and that obtained from brucite. The values of activation energy, 17 kcal. for the former and 32 kcal. for the latter, are nearly the same as those of the surface diffusion in other oxides. Latty[7] studied the crystal growth of rutile-type titanium oxide and obtained a value of 16,68 kcal./mol. for alkali-free oxide in the temperature region between 585° and 750°C, where surface diffusion can be expected to be operative. Further, in their study of the sintering reactions of zinc oxide, Lee and Parravano[8] calculated the activation energy of the diffusion of excess zinc ions through the very thin oxidized layer to be about 18 kcal./mol. in the temperature range between 700 and 900°C. It might be assumed that surface diffusion occurs in this case. The difference in activation energy between precipitated magnesium hydroxide and brucite is difficult to explain in this work, and it is probable that lattice diffusion occurs in the case of brucite. That lattice diffusion occurs at such a low temperature might be due to the presence of impurities.

Summary

The particle size of magnesium oxide crystals prepared by the thermal decompositions of pure precipitated magnesium hydroxide and native brucite at various temperatures between 500 and 900°C has been measured by the X-ray line broadening method, and the effect of the calcination temperature and its duration on the crystal size of magnesium oxide has been examined.

It has been found that the particle size of magnesium oxide crystals increasese with the increase in the calcination temperature and that the rate of crystal growth obeys a different law between the earlier stage of the calcination process at a definite temperature and the later stage. It has also been found that the crystal growth of magnesium oxide proceeds proportional to t^n, (t : time), where n is 1/6 for the later stage of the calcination of magnesium oxide from precipitated magnesium hydroxide at temperatures ranging from 700 to 900°C and 1/4 for the same calcination of that from brucite. The values of the activation energy calculated by Arrhenius plot are 17 and 32 kcal./mol. for magnesium oxide obtained from precipitated hydroxide and from brucite respectively.

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[7] J. E. Latty, *J. Appl. Chem.*, **8**, 96 (1958).

[8] V. J. Lee and G. Parravano, *J. Appl. Phys.*, **30**, 1735, (1959).