1610 © *1981 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, *54, 1610—1616 (1981)* [Vol. 54, No. 6

The Thermal and Hydrothermal Behavior of Silica-adsorbed Magnesium Hydroxide

Haruto Muraishi
Department of Chemistry, Fukuoka University of Education, Munakata-cho, Fukuoka 811-41

(Received July 14, 1980)

Silica-adsorbed $Mg(OH)_2$ was treated thermally and hydrothermally. The resulting change in the adsorption layer was followed, and the effects of the adsorbed silica on the change in the bulk ($Mg(OH)_2$, MgO) were examined. (1) Thermal treatment: The dehydration temperature of $Mg(OH)_2$ increased with an increase in the amount of silica adsorbed, and it was higher by 25 °C for $Mg(OH)_2$ adsorbing silica above 0.4 mmol/g than for pure $Mg(OH)_2$. The amorphous silicate of the adsorption layer on the $Mg(OH)_2$ surface was transformed into forsterite (Mg_2SiO_4) and chain or sheet-like silicate over the temperature range of 870—1100 °C, and the presence of the silica inhibited the sintering and crystallite growth of the MgO grains. At 1400 °C, these products were all transformed into forsterite, and the presence of the silica had little effect on the crystallite growth. (2) Hydrothermal treatment: Below 360 °C, the amorphous silicate on the surface crystallized as serpentine ($Mg_3Si_2O_5(OH)_4$), and the crystallite growth of $Mg(OH)_2$ was inhibited. Above 420 °C, on the other hand, the silicate was transformed into forsterite through serpentine-like silicate, and the crystallite growth of $Mg(OH)_2$ was promoted. The change in the crystallite size of the bulk by the treatment was interpreted mainly in terms of the behavior of the silicate on the surface.

Our previous works[1,2] have shown that soluble silica was chemisorbed at temperatures under 100 °C, forming –Mg–O–Si– bonds on the $Mg(OH)_2$ surface, and that the resulting surface had properties like magnesium silicate gels, *e.g.*, a relatively large amount of acidity and adsorptive properties for Methylene Blue and Methyl Red. The behavior of the silica-adsorbed $Mg(OH)_2$ upon the thermal and hydrothermal treatment is interesting from the viewpoint of the process of the formation of ceramics and the mechanism of producing magnesium silicate minerals.

In this work, the transformation of the magnesium silicate on the $Mg(OH)_2$ surface by thermal and hydrothermal treatment was observed. In addition, the effects of adsorbed silica were investigated on: (1) the dehydration temperature of $Mg(OH)_2$, (2) the crystallite growth of the dehydration product, MgO, upon the thermal treatment, and (3) the crystallite growth of the $Mg(OH)_2$ upon the hydrothermal treatment.

In some of the earlier works the effect of impurities on the dehydration temperature of $Mg(OH)_2$[3,4] and the effects of the addition of foreign materials on the sintering of MgO[5–8] have been investigated. However, there has been no investigation placing emphasis on the behavior of the silicate.

Experimental

Samples. The silica-adsorbed $Mg(OH)_2$ used as the starting material was prepared in a previously reported way.[2] The silica gel used for chromatography (Wako Pure Chemicals) was dissolved in hot water, and then the silica solution was adjusted to a concentration of about 100 ppm. $Mg(OH)_2$ powder (Kanto Kagaku) was suspended in this solution and was allowed to adsorb the soluble silica while being stirred at 500 rpm at 80 °C. The amount of silica adsorbed was determined by the decrease in the silica concentration in the solution. The silica concentration was determined colorimetrically by the usual molibdate yellow method. The aqueous silica was soluble in monomeric unit form, $Si(OH)_4$, since the value of the silica concentration did not vary when the solution was treated with a 0.1 mol/l NaOH solution. The non-adsorbed $Mg(OH)_2$ which was used as a reference standerd was immersed in distilled water at 80 °C for 8 h before use in order to have the same history as the silica-adsorbed $Mg(OH)_2$. Its surface area was about 30 m^2/g.

Experimental Procedures and Apparatus. The thermal treatment were carried out by the use of an electric furnace in the air at 430 °C for 4 h, 870 °C for 3 h, 1000 °C for 2 h, 1200 °C for 1 h, and 1400 °C for 1 h respectively. The hydrothermal treatment was carried out using a modified Morey-type autoclave with a fill ratio of water of 50% and a heating rate up to a fixed temperature of 75 °C/h.

The dehydration temperatures of the samples was measured by differential thermal analysis (DTA). The DTA was carried out using a Rigaku 8002 Thermal Analyser with a thermobalance. The sample (about 10 mg) was packed in a platinium dish, while the same weight of Al_2O_3 was packed in a reference dish; the heating rate was 10 °C/min.

The crystallite size of MgO and $Mg(OH)_2$ obtained was determined by the X-ray line-broadening method,[9] using diffraction peaks from the (110) and the (0001) planes respectively. The aspect of the samples was observed by means of an Hitachi S-430 scanning electron microscope (SEM). The samples submitted to treatment were examined by IR spectroscopy and X-ray diffractometry. The IR spectra were observed by the KBr tablet method; the tablet was made up of 2 mg of the sample and 150 mg of KBr. A Hitachi EPI-G IR Spectrometer and a Rigaku XGC-20 X-ray Diffractometer were used for the measurement.

The specific surface area of the sample was determined by applying the BET method to the nitrogen-adsorption data obtained at the temperature of liquid nitrogen, assuming the cross-sectional area of a nitrogen molecule to be 16.2 Å^2.

Results and Discussion

Part 1. Thermal Behavior

The Effect of Adsorbed Silica on the Dehydration of $Mg(OH)_2$. Figure 1 shows DTA and TG curves for pure $Mg(OH)_2$ and a typical silica-adsorbed $Mg(OH)_2$. The position of the endothermic peaks shows that the dehydration of the latter takes place at a higher temperature than that of the former. In addition to the rise of the dehydration temperature, the DTA curve for the silica-adsorbed sample had a small exothermic peak at about 850 °C which was assigned to the reaction of MgO with silica. Both the TG curves

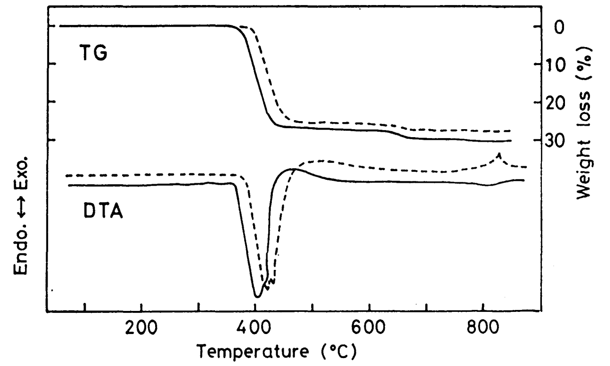

Fig. 1. TG and DTA curves for pure Mg(OH)$_2$ (——) and silica-adsorbed Mg(OH)$_2$ (------).

gradually declined with an increase in the temperature after the dehydration occurred at about 400 °C. Such a phenomenon has often been observed in various hydroxides and minerals containing water; it can be attributed to residual essential water or OH groups.

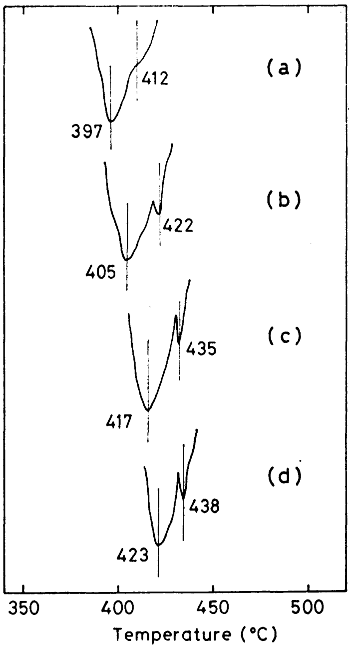

Fig. 2. DTA curves for pure Mg(OH)$_2$ and Mg(OH)$_2$ with various amount of adsorbed silica. Amount of adsorbed silica (mmol/g): (a), Non adsorption; (b), 0.097; (c), 0.34; (d), 1.26.

Figure 2 shows the change in the position and shape of the endothermic peak with a variation in the amount of silica adsorbed. The dehydration temperature increased with the increase in the amount of silica adsorbed, and the shape of the endothermic peak apparently varied from singlet to doublet for these silica-adsorbed Mg(OH)$_2$. This peak separation suggests that the two-step dehydration of Mg(OH)$_2$ was induced by the adsorption of silica. Weber and Rustum Roy[10] have observed a two-step dehydration of Mg(OH)$_2$ and presumed it to result from the formation of an intermediate phase in the dehydration process. Ball and Taylor[11] asserted the formation of an intermediate phase with a spinel-like structure (*e.g.*, (MgO)$_3$·H$_2$O) resulting from cation migration during dehydration. In this study, the intermediate phase was not observed by means of X-ray diffractometry. This bimordal DTA curve, therefore, is not ascribed to the structure change, but it indicates that the dehydration process following the release of the resulting H$_2$O from the Mg(OH)$_2$ particle is surely affected by the adsorbed silica.

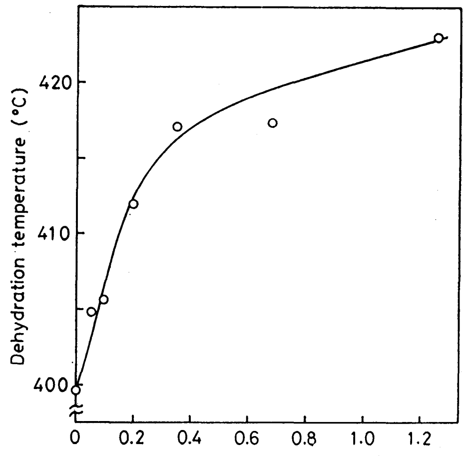

Fig. 3. Effect of amount of adsorbed silica on dehydration temperature of Mg(OH)$_2$.

Figure 3 shows the relation between the amount of silica adsorbed and the dehydration temperature. The dehydration temperature rose greatly with the increase in the amount of silica up to about 0.4 mmol/g, although above this amount it rose only slightly. The Mg(OH)$_2$ particles used were observed microscopically to be disk-like crystals with a well-developed (0001) plane. Consequently, it may be said that the crystal consists only of an approximate (0001) plane with respect to the estimate of its surface area. The number of Mg atoms exposed on the surface can, therefore, be calculated from the specific surface area and the array of Mg atoms on the (0001) plane.[12] On the other hand, it can reasonably be considered from the structure of the (0001) plane that two silica molecules combine with three Mg atoms on the surface of Mg(OH)$_2$. Thus, the amount of silica adsorbed required to form a monolayer on 1 g of the used Mg(OH)$_2$ is calculated to be 0.34 mmol/g. This amount corresponds to the quantity of about 0.4 mmol g^{-1} observed as a characteristic amount in the relation between the dehydration temperature and the amount of silica adsorbed. In other words, it can be said that the dehydration temperature of silica-adsorbed Mg(OH)$_2$ rose appreciably until the surface was completely covered with a monolayer of silicate, while it rose only slightly when the surface had an excess of silica. The rise in the dehydration temperature may be accounted for as follows. The dehydration of Mg(OH)$_2$ has been interpreted as an inhomogeneous mechanism in which the reaction takes place through the two steps of nucleus formation and growth.[13] The nucleus formation is known to be mainly initiated at such sites as grain boundaries or defects on the surface (*i.e.*, step, kink, and pit).[14] Since these sites are also atcive in the adsorption of silica, some of them are occupied by the silica molecules in the case of silica-adsorbed $Mg(OH)_2$. The decrease in the active sites forces a delay in the rate of nucleus formation. In addition, the grain surface covered with the silica obstructs the release of the H_2O molecules formed by the decomposition. This effect may be compared with the rise in the decomposition temperature of $Mg(OH)_2$ due to an increase in the water-vapor pressure.[15)]

The Change in Surface Products. In a previous study,[2)] it has been found that the silica-adsorbed $Mg(OH)_2$ has surface properties and a structure similar to those of magnesium silicate gel. In addition, when magnesium silicate gels were calcined above 870 °C, forsterite (Mg_2SiO_4) and a small amount of enstatite ($MgSiO_3$) were produced in the case of a SiO_2/MgO ratio below 1, while mainly enstatite was produced in the case of a ratio above 1. Since the silica-adsorbed samples have a large excess of MgO, the silicate layer on the surface is presumed to be transformed into forsterite by thermal treatment.

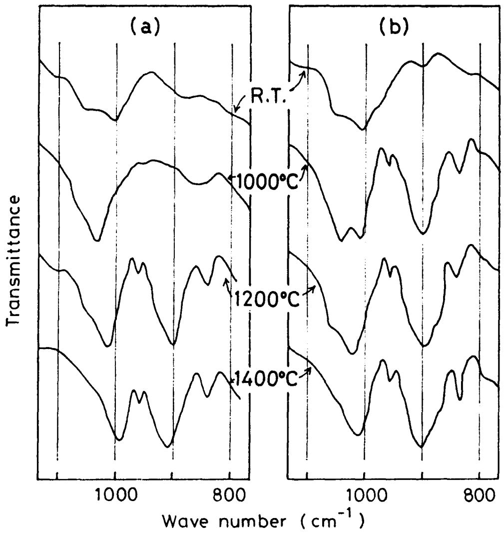

Fig. 4. The changes of IR spectra of silica-adsorbed $Mg(OH)_2$ by thermal treatment. Amount of adsorbed silica (mmol/g): (a), 0.19; (b), 1.26.

Figure 4 shows the change in the IR spectra by thermal treatment for $Mg(OH)_2$ with a different amount of the silica. It was found from the IR spectra that, when the samples were heated at 1000 °C, forsterite, which is composed of nesosilicates, was formed. In addition to the absorption spectrum for forsterite, some additional bands were observed in the region from 1000 to 1100 cm^{-1}. It is known that nesosilicates with a three-dimensional structure of single SiO_4^{4-} usually exhibit their absorption in the region of 800—1000 cm^{-1},[16)] while chain silicates (*i.e.*, enstatite) or sheet silicates (*i.e.*, talc ($Mg_3Si_4O_{10}(OH)_2$)) do so in the region of 1000—1100 cm^{-1}. In order to examine the route of the appearance of the additional bands in the region of 1000—1100 cm^{-1}, the following procedure was carried out. The silica-adsorbed samples heated above 1000 °C were treated with a 5% NH_4Cl solution until the bulk MgO had been removed completely. This treatment is based on the fact that an amorphous material consisting of a –Mg–O–Si– bond, forsterite, and enstatite is insoluble in a NH_4Cl solution, but MgO is soluble.[17)] The residue in the solution was filtered and dried. The residue was identified by IR spectroscopy and X-ray diffractometry. When the spectrum for the residue is compared with that for the parent sample, the absorption pattern in the region of 800—1000 cm^{-1} which was assigned to forsterite did not change; the slight absorption peaks in the region of 1000—1100 cm^{-1}, however, changed to larger, broad absorption bands ranging from 1010 to 1090 cm^{-1}. On the other hand, the X-ray diffraction pattern of the residue was assigned to forsterite and an amorphous material. Therefore, it is reasonable to assume that the additional bands are due to an amorphous material, which is an incomplete chain or sheet-like silicate.

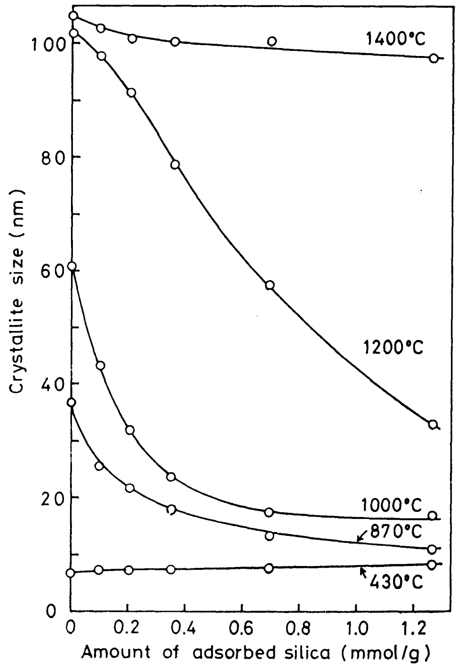

Fig. 5. Effect of amount of adsorbed silica on crystallite size of bulk MgO at various treatment temperatures.

The Effect of Adsorbed Silica on the Crystallite Growth of the Dehydration Product MgO. Figure 5 shows the crystallite size of MgO at various treatment temperatures. The crystallite size of MgO was not influenced by the adsorbed silica at a little above the dehydration temperature of $Mg(OH)_2$, but over the temperature range of 870 to 1200 °C it became smaller with an increase in the amount of silica adsorbed. At a temperature of 1400 °C, at which sintering evidently begins,[18)] it became independent of the adsorbed silica.

Moreover, the thermal changes in pure $Mg(OH)_2$ and silica-adsorbed $Mg(OH)_2$ were observed comparatively by the use of the SEM. As may be seen from the photographs in Fig. 6, there was no difference between pure $Mg(OH)_2$ and silica-adsorbed $Mg(OH)_2$ before heat treatment (Figs. 6(a) and 6(d)). After the treatment at 1000 and 1400 °C, the apparent grain of MgO from pure $Mg(OH)_2$ grew; it was much larger than

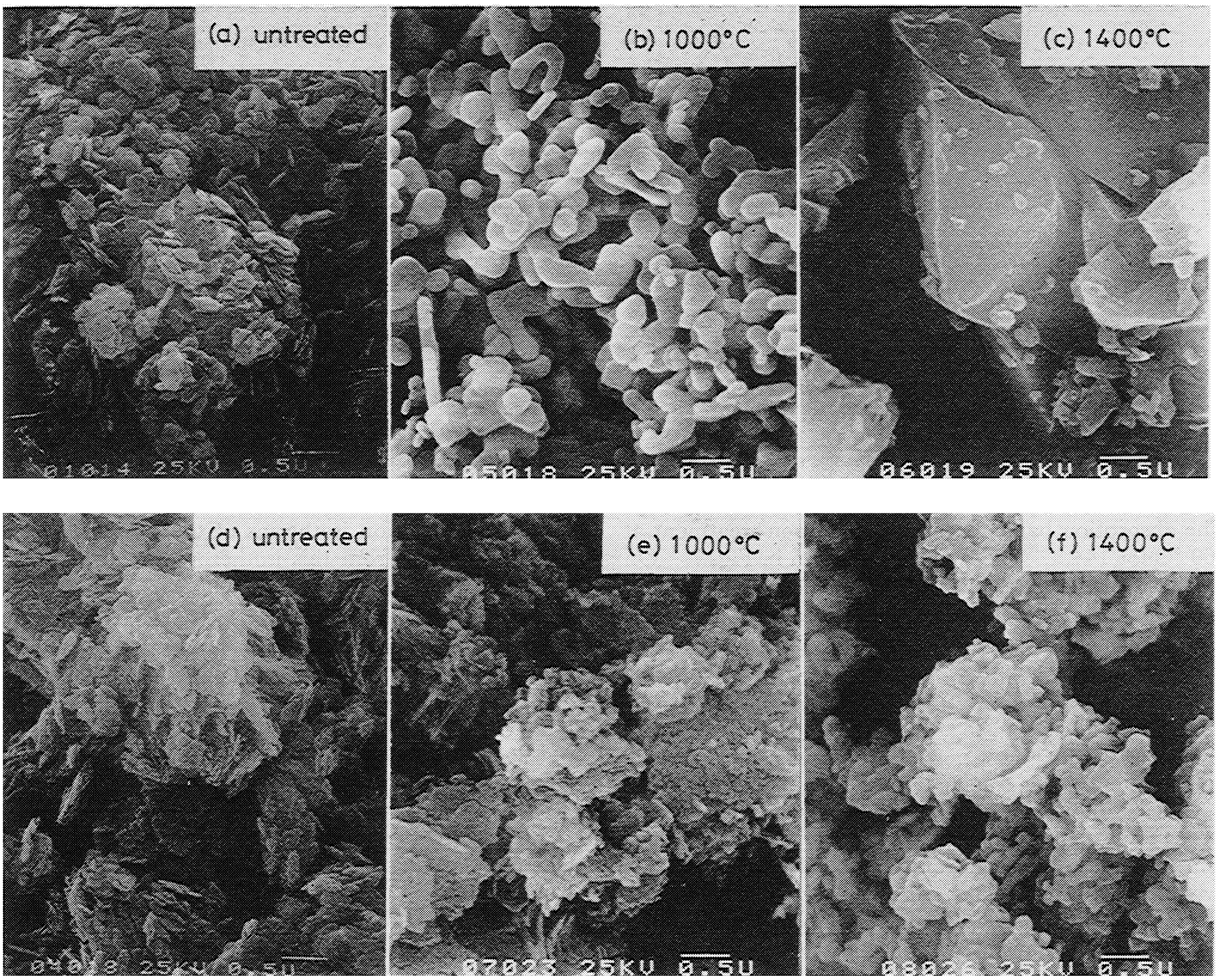

Fig. 6. SEM microphotographs of the samples treated thermally at 1000 and 1400 °C. (a), (b), (c): Non-adsorbed $Mg(OH)_2$. (d), (e), (f): Silica-adsorbed $Mg(OH)_2$.

the crystallite measured by the X-ray method. Therefore, the apparent grain seems to be an aggregate of crystallites formed by their sintering. On the other hand, the size of MgO from silica-adsorbed $Mg(OH)_2$ (amount of silica adsorbed; 1.26 mmol/g) was relatively similar to the crystallite size, as is shown in Fig. 5.

From these results, the thermal behavior of $Mg(OH)_2$ and MgO can be explained as follows. An untreated pure $Mg(OH)_2$ powder was observed by means of the SEM as a layered aggregate of disk-like grains 20 to 50 nm thick in the direction of the c-axis. The thickness of a single grain observed was in good agreement with the crystallite size as measured by the use of the X-ray line broadening method. Therefore, the single grain observed seems to be a single crystal of $Mg(OH)_2$. The dehydration product of the aggregate is also considered to be an aggregate of single crystals keeping the same crystallographic orientation with each other, since the dehydration of $Mg(OH)_2$ is a topotactic reaction.[11,19] The rise in the temperature leads to a grain growth resulting from the disappearance of the grain boundary upon the sintering of these single crystals. This grain growth may be limited to the size of the aggregate consisting of single grains with the same crystallographic orientation. The presence of a silicate layer on the grain surface will result in lowering the motion of the grain boundary because of its hindrance to the surface diffusion and the grain boundary diffusion. This hindrance will depress the grain growth and the formation of a polycrystal by sintering. At temperatures above 1300 °C (the so-called Tamman temperature of MgO (melting point, 2800 °C)), atoms or ions on the surface and in the bulk MgO are easy to diffuse. In addition, the silicate layer has been transformed into a forsterite crystal with a three-dimensional construction. It is, therefore, considered that the grain growth of the silica-adsorbed samples is not distinguishable from that of pure sample, since the silicate can no longer inhibit the motion of the grain boundary.

Part 2. Hydrothermal Behavior

The Change in the Surface Product. The silica-adsorbed $Mg(OH)_2$ indicated the IR absorption spectra of magnesium silicate gels-like material to be as has been described in the previous paper.[2] The hydrothermal treatment at 250 °C for 72 h changed them into absorption bands near 960, 1010, and 1080 cm^{-1}, which are

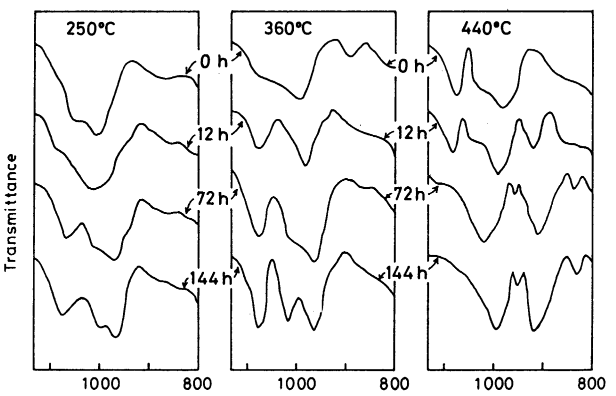

Fig. 7. IR spectra of silica-adsorbed $Mg(OH)_2$ treated hydrothermally at 250—440 °C for 0—144 h.

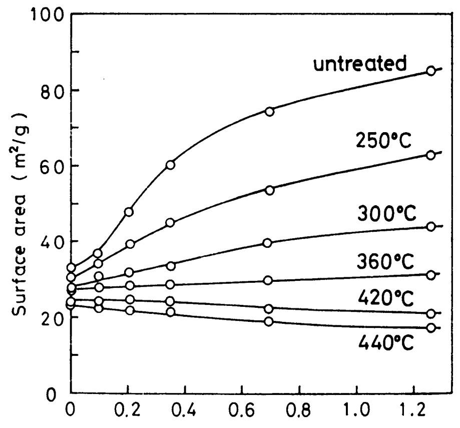

Fig. 8. The change of surface area by hydrothermal treatment for 72 h.

assigned to a compound having the sheet silicate group. The absorption bands became sharp upon treatment at 360 °C for 144 h. The results are shown in Fig. 7. On the basis of the data proposed by Brindley *et al.*[20] and the spectrum of serpentine synthesized in our laboratory, these IR spectra were assigned to serpentine. Above 420 °C, a serpentine-like spectrum was observed in the beginning of the treatment, but it was transformed into the absorption spectra of forsterite, which was characterized by four absorption peaks in the 800—1000 cm^{-1} region, upon subsequent treatment. The surface products obtained below 360 °C were easily isolated by dissolving the bulk $Mg(OH)_2$ with a 5% NH_4Cl solution or a dilute acid solution. The isolated silicate was identified by the use of X-ray diffractometry and IR spectroscopy. The IR spectra of surface products were hardly changed by isolation; therefore, the serpentine-like spectra are attributable to a poor crystalline serpentine.

The phase diagram of the SiO_2–MgO–H_2O system described by Bowen *et al.*[21] shows that, under relatively low water-vapor pressures, serpentine is stable below 380 °C, while above that point forsterite is stable. The phase boundary of the serpentine and forsterite formed hydrothermally from the silica-adsorbed $Mg(OH)_2$ was comparable to the phase boundary presented by Bowen *et al.* Talc was not formed, even if the ratio of the silica molecules and Mg^{2+} ions in the surface layer had the stoichiometric relationship of talc. It was found that the kind of magnesium silicate produced by hydrothermal treatment does not depend upon the composition of the silicate layer on the surface, but upon the composition of the sum of the silicate layer and the bulk.

The Change in the Surface Area. The effects of the amount of silica adsorbed and the treatment temperature on the surface area of silica-adsorbed $Mg(OH)_2$ are shown in Fig. 8. As has been described in the previous paper,[2] the chemisorption of soluble silica on the surface of $Mg(OH)_2$ led to an increase in the surface area; the increase was attributed to the formation of micro pores on the surface (see the "Untreated" curve in Fig. 8). The surface area was more or less decreased by hydrothermal treatment over the temperature range from 250 to 440 °C. It was found, from the measurement of the N_2-adsorption isotherms of the samples and the t-plots[22] derived from this isotherm, that the decrease in the surface area by the treatment is mainly attributable to the disappearance of the micro pores. However, on treatment above 420 °C, the surface area of the silica-adsorbed samples became smaller than that of the non-adsorbed sample. This reduction in the surface area cannot be interpreted only in terms of the disappearance of the micro pores. It will be discussed in the following section.

The Growth of the Crystallite of $Mg(OH)_2$. The change in the crystallite size of the bulk $Mg(OH)_2$ by the treatment was followed as a function of the time at various temperatures. The crystallite size of pure $Mg(OH)_2$ was not appreciably affected by the treatment, while that of silica-adsorbed $Mg(OH)_2$ was dependent on the treatment temperature. The growth of the crystallite of silica-adsorbed $Mg(OH)_2$ did not proceed below 300 °C, but above 360 °C it proceeded with the treatment time. Moreover, the crystallite

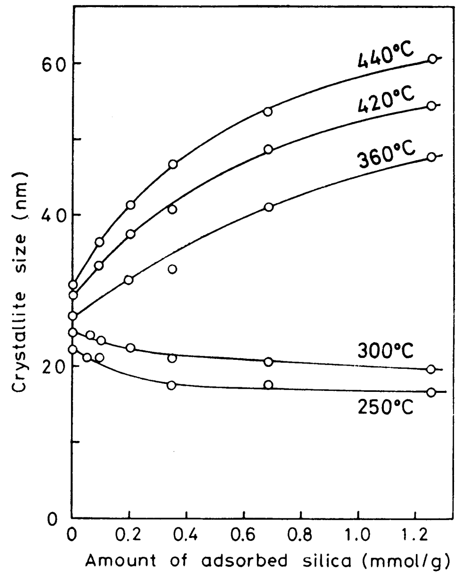

Fig. 9. Effect of amount of adsorbed silica on crystallite size of bulk $Mg(OH)_2$ at various treatment temperature for 72 h.

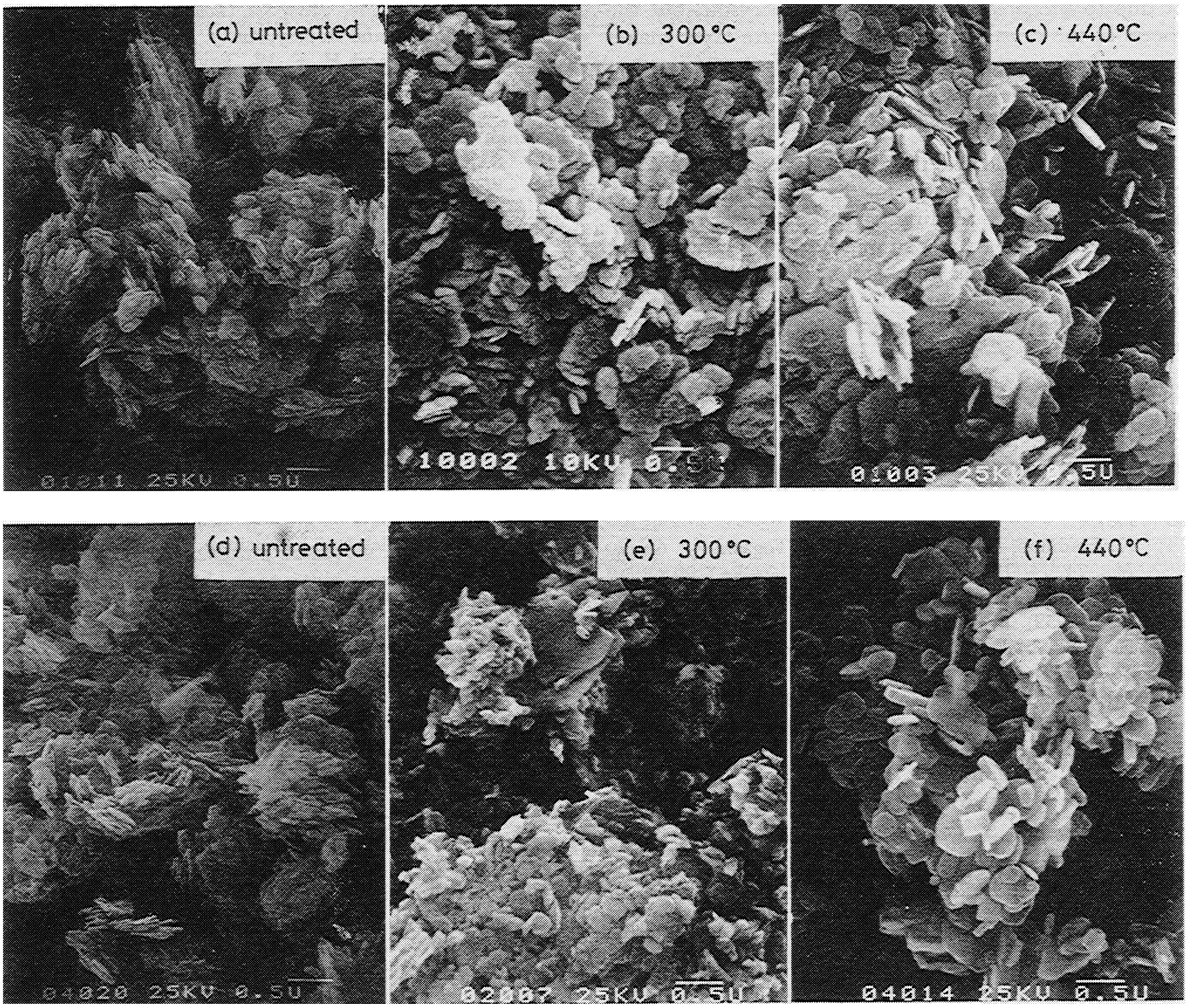

Fig. 10. SEM microphotographs of the samples treated hydrothermally at 300 and 440 °C.
(a), (b), (c): Non-adsorbed $Mg(OH)_2$. (d), (e), (f): Silica-adsorbed $Mg(OH)_2$.

growth at various temperatures was investigated with respect to the effects of the amount of adsorbed silica, as is shown in Fig. 9. The crystallite size at a temperature below 300 °C decreased with an increase in the amount of silica adsorbed, while above 360 °C, on the contrary, the size increased with the amount of silica adsorbed. In other words, the adsorbed silica contributes to inhibiting the growth of the crystallite of $Mg(OH)_2$ up to 300 °C, while above 360 °C it serves to promote it.

The non-adsorbed and the silica-adsorbed $Mg(OH)_2$ treated at various temperatures were observed comparatively by the use of the SEM. The microphotographs are shown in Fig. 10. As may be seen from the photographs, the grain of non-adsorbed $Mg(OH)_2$ did not grow throughout the treatment from 250 to 440 °C, while the grain of silica-adsorbed $Mg(OH)_2$ grew in thickness at the temperature of 440 °C. This increase in grain size corresponds to the change in the crystallite size of $Mg(OH)_2$ shown in Fig. 10, and also to the change in the surface area shown in Fig. 8. Therefore, the grain is considered to be a single crystal.

These phenomena may be explained as follows. The surface of the $Mg(OH)_2$ grain will still be covered by the silicate layer under treatment at temperatures below 300 °C. It was found, from the determination of the Mg^{2+} ion in the hydrothermal solutions, that the presence of the silicate layer tends to decrease the rates of the dissolution and solubility of $Mg(OH)_2$. This decrease seems to have resulted in the slower crystal growth of $Mg(OH)_2$, since its growth is considered to be a solution growth based on the dissolution and recrystallization of $Mg(OH)_2$. However, at temperatures above 360 °C, the silicate layer changed into a crystalline silicate (serpentine or forsterite), with a three-dimensional growth. The silicate may exist in the isolated state, and so may no longer coat the surface of $Mg(OH)_2$ grain. In order to confirm whether or not the characteristic crystal growth of silica-adsorbed $Mg(OH)_2$ is due to the presence of the isolated silicate, a mixture of pure $Mg(OH)_2$ and a synthesized serpentine (or forsterite) was treated hydrothermally above 360 °C. It was found that the $Mg(OH)_2$ crystal hardly grows at all under these conditions. Therefore, the growth is not due to the presence of the silicate crystal, but the process of the crystallization of the silicate layer makes some contribution to the growth. Unfortunately, it is difficult to make this phenomenon clearer using our limited experimental procedure.

The author would like to express his hearty thanks to Professor Shigeo Kitahara for his valuable guidance and for his critical reading of this manuscript. The present work was partially supported by a Grant-in-Aid for Scientific Research No. 474205 from the Ministry of Education, Science and Culture.

References

1) S. Kitahara and H. Muraishi, *Nippon Kagaku Kaishi*, **1978**, 555.
2) H. Muraishi and S. Kitahara, *Nippon Kagaku Kaishi*, **1978**, 1457.
3) J. W. Nelson and I. B. Cutlur, *J. Am. Ceram. Soc.*, **41**, 406 (1958).
4) K. Hamano, K. Yoshino, and H. Togashi, *J. Ceram. Assoc. Jpn.*, **74**, 14 (1966).
5) G. K. Layden and M. C. McQuarrie, *J. Am. Ceram. Soc.*, **42**, 89 (1959).
6) H. J. S. Kriek, W. F. Ford, and J. White, *Trans. Brit. Ceram. Soc.*, **58**, 1 (1959).
7) M. H. Leipold, *J. Am. Ceram. Soc.*, **49**, 498 (1966).
8) K. Hamano, K. Yoshino, and H. Togashi, *J. Ceram. Assoc. Jpn.*, **74**, 312 (1966).
9) F. W. Jones, *Proc. Phys. Soc.* (*London*), *A*, **166**, 16 (1938).
10) J. N. Weber and R. Roy, *Am. J. Sci.*, **263**, 668 (1965).
11) M. C. Ball and H. F. W. Taylor, *Mineral. Mag.*, **32**, 754 (1961).
12) L. G. Berry and B. Mason, "Mineralogy," W. H. Freeman, San Francisco (1961), p. 381.
13) S. J. Gregg and R. I. Razouk, *J. Chem. Soc.*, **1949**, S 36.
14) "Chemistry of the Solid States," ed by W. E. Garner, Butterworths, London (1955), p. 221.
15) G. W. Brindley, J. H. Sharp, J. H. Patterson, and B. N. Narahari, *Am. Mineral.*, **52**, 201 (1967); F. Toussaint, J. J. Fripiat, and M. C. Gaetuche, *J. Phys. Chem.*, **67**, 26 (1963).
16) J. A. Gadsden, "Infrared Spectra of Minerals and Related Inorganic Compounds," Butterworth, London (1975), p. 29.
17) S. F. Hulbelt and G. Lane, *Trans. Brit. Ceram. Soc.*, **67**, 391 (1968).
18) D. T. Livey, B. M. Wanklyn, M. Hewitt, and P. Murray, *Trans. Brit. Ceram. Soc.*, **56**, 217 (1957).
19) J. F. Goodman, *Proc. R. Soc. London*, *Ser. A*, **247**, 346 (1958);
20) G. W. Brindley and J. Zussman, *Am. Mineral.*, **44**, 1057 (1959).
21) N. L. Bowen and O. F. Tuttle, *Bull. Geol. Soc. Am.*, **60**, 439 (1949).
22) B. C. Lippens, B. G. Linsen, and J. H. de Boer, *J. Catal.*, **3**, 32 (1964); J. H. de Bore, B. C. Lippens, B. G. Linsen, J. C. P. Broekhoff, A. van den Heuvel, and Th. J. Osinga, *J. Colloid Interface Sci.*, **21**, 405 (1966).