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The Reaction of Magnesium Hydroxide with Soluble Silica under Hydrothermal Conditions below the Critical Temperature

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$Mg(OH)_2$ powder packed into a basket was placed apart from solid SiO_2 in an autoclave so that the SiO_2 might react with the solid $Mg(OH)_2$ in the state of soluble silica. At given temperatures of 250—360 °C, the $Mg(OH)_2$ changed into talc($Mg_3Si_4O_{10}(OH)_2$) through serpentine($Mg_3Si_2O_5(OH)_4$): the reaction was a first-order consecutive-irreversible reaction which can be represented as:

$$Mg(OH)_2 \xrightarrow{+SiO_2} Mg_3Si_2O_5(OH)_4 \xrightarrow{+SiO_2} Mg_3Si_4O_{10}(OH)_2.$$

The reaction rate of serpentine into talc as a single reaction was also first-order. The formation of serpentine was much faster than that of talc. The reaction rate depended on the silica concentration in the hydrothermal solution rather than on the reaction temperature. In the course of the reaction, the crystallite size of the $Mg(OH)_2$ and the serpentine was hardly changed. In addition, the crystallite size of $Mg(OH)_2$ did not affect that of the resulting serpentine. From these results, the rate-limiting step is presumed to be the formation of the crystal nuclei of the serpentine or talc.

The mechanism of the synthetic reaction of silicates under hydrothermal conditions is of interest, but it has not been investigated except for the syntheses of zeolite below 100 °C.[1–5] The purpose of this study is to gain some insight into the mechanism of silicate formation under high temperatures and high pressures. From this point of view, the rate of the formation of serpentine and talc from $Mg(OH)_2$ powder and soluble silica has been investigated at the vapor pressures of hydrothermal solutions.

In the previous investigations[6–9] of the synthetic reaction of the $MgO–SiO_2–H_2O$ system, mixtures of solid MgO (or $Mg(OH)_2$) and solid SiO_2 were used as the starting materials. In this study, in order to observe more simply the reaction process, solid $Mg(OH)_2$ is placed apart from solid SiO_2 in an autoclave so that the SiO_2 may react with the solid $Mg(OH)_2$ surely in the state of soluble silica.

Experimental

The apparatus used for separating the two starting materials from each other is shown in Fig. 1. The silica gel or α-quartz powder used as the silica source was placed at the bottom of a modified Morey-type autoclave with a capacity of 30 ml, while the $Mg(OH)_2$ powder, packed naturally into a basket which was mounted on a holder, was placed above the silica source: distilled water was then introduced into the autoclave to fill it by 60%. The reaction was carried out in the temperature range of 250—360 °C at an autogeneous pressure of the autoclave. The heating rate up to a fixed temperature was 75 °C/h. After a definite time of heating, the autoclave was quenched rapidly with water. The reaction products were taken out of the basket and dried at 110 °C for 12 h. The products were identified by the use of the X-ray diffractometer and DTA. Their quantities could be determined with the gravimetric technique (TG), as will be shown in the following section. The solution was filtered off, and the soluble silica and magnesium ion in the solution were determined by means of the silico molybdate method[10] and EDTA titrimetry[11] respectively. The crystallite size of the reactant and products was measured by the X-ray diffraction method.[12] These methods have also been described fully in previous papers.[13,14]

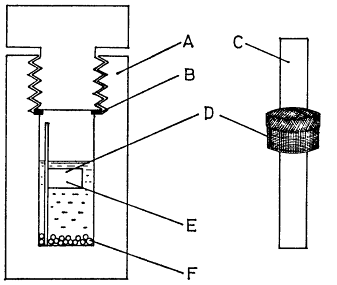

Fig. 1. Hydrothermal apparatus.
A: Hydrothermal vessel (stainless steel), B: silver gasket, C: basket holder, D: sample container (netted stainless steel basket, 160 mesh), E: reactant ($Mg(OH)_2$), F: reactant (SiO_2).

Results

Effects of Amount of Silica and $Mg(OH)_2$ *on the Reaction Rate.* Approximately 0.2 g of $Mg(OH)_2$, packed into a basket, was allowed to react with various amounts of 0.5—6.0 g of the silica source at 330 °C for 3 h. After each run, the conversion fraction was determined from the amount of remaining $Mg(OH)_2$. The results are shown as a function of the amount of silica in Fig. 2(a). It was found that, when 1 g or more of silica was used, the conversion fraction was independent of the amount of silica: it was 0.4 for silica gel and 0.2 for α-quartz under these conditions. The silica concentration in the solution during the reaction was about 1200 ppm for silica gel and 400 ppm for α-quartz: these values are approximately equal to their equilibrium solubilities at that temperature.[15,16] The distinction between the conversion fractions for silica gel and α-quartz can be explained in terms of the difference between their solubilities.

On the other hand, various amounts of $Mg(OH)_2$ (0.05—0.60 g) were allowed to react with a fixed amount of 2.0 g of silica at 360 °C for 6 h. The results were shown in Fig. 2(b). The conversion fraction diminished with an increase in the amount of $Mg(OH)_2$. In addition, it was found, from the deter-

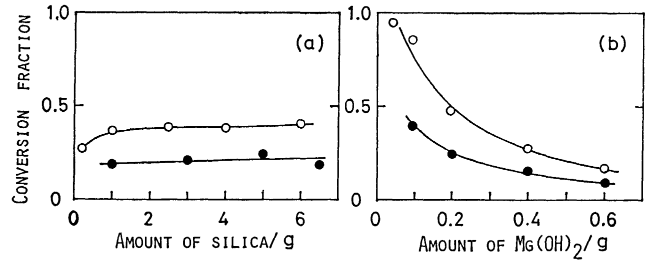

Fig. 2. Effect of amount of SiO_2 and $Mg(OH)_2$ on the conversion of $Mg(OH)_2$.
Silica gel (○) and α-quartz powder (●) were used as silica source. (a) is for a fixed amount of $Mg(OH)_2$ (0.2 g) and treatment at 330 °C for 3 h, and (b) for a fixed amount of SiO_2 (2.0 g) and treatment at 360 °C for 6 h.

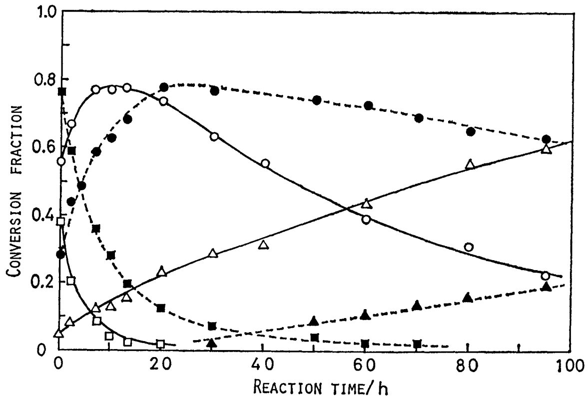

Fig. 3. Conversion curves for reaction of $Mg(OH)_2$ with soluble silica at 250° (----) and 360 °C (——). Silica source: silica gel. ■,□: $Mg(OH)_2$, ●,○: $Mg_3Si_2O_5(OH)_4$(serpentine), ▲,△: $Mg_3Si_4O_{10}(OH)_2$ (talc).

mination of silica concentration in the solution during the reaction, that the silica concentration decreased with an increase in the amount of $Mg(OH)_2$. The decrease in the silica concentration is explicable as a result of the faster rate of taking out of silica by $Mg(OH)_2$ than the rate of dissolution of silica. The relation between the silica concentration and the conversion was examined in detail. In the case of an amount of $Mg(OH)_2$ of 0.2 g or less, the solution was saturated with silica during the reaction (about 1400 ppm for silica gel and 500 ppm for α-quartz). The conversion fraction, however, was decreased with the amount of $Mg(OH)_2$. The drop in the conversion may be due to the fact that soluble silica penetrates slowly into the interior of the pack of $Mg(OH)_2$ powder. When the amount of $Mg(OH)_2$ was 0.05 g or below, the reaction went to completion too rapidly for us to measure the reaction rate. Therefore, 0.2 g of $Mg(OH)_2$ and 2.0 g of silica were employed as the standard amounts of reactants in order to keep the silica concentration constant throughout the reaction and in order to allow the reaction to proceed steadily and at a moderate speed.

Reaction Products. Under these experimental conditions, serpentine($Mg_3Si_2O_5(OH)_4$) and talc ($Mg_3Si_4O_{10}(OH)_2$) were identified as the products.

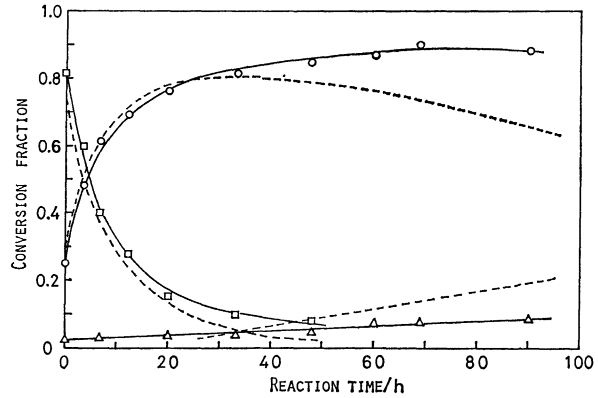

Fig. 4. Effect of temperature on the reaction rate.
Reaction temperature: ----, 250 °C;[a] ——, 360 °C.
Silica gel and α-quartz powder were used as silica source at 250 and 360 °C, respectively, and the silica concentration in the solution was 900 and 500 ppm. Symbols are the same as in Fig. 3.
a) This curve has been already shown in Fig. 3.

The results were compatible with the phase boundary in the phase diagram of the $MgO-SiO_2-H_2O$ system presented by Bowen and Tuttle.[17] These silicates possess a layer structure and essential water analogues with $Mg(OH)_2$. It was found, from the TG and DTA curves of $Mg(OH)_2$ and synthesized serpentine and talc, that the essential water was quantitatively dehydrated and that the dehydration temperatures were 400, 640, and 860 °C respectively. These silicates, therefore, could be determined gravimetrically from mixtures of reactant and products.

Effect of the Temperature and Silica Concentration on the Reaction Rate. Figure 3 shows the conversion curves plotted against the time for the formation of serpentine and talc at the temperatures of 250 and 360 °C. When the autoclave reached a prescribed temperature (0 h of the reaction time), the reaction had proceeded considerably. Although the real initial stage could not be observed, it was found that both conversion curves obtained for serpentine reach a maximum in a certain time, and that for talc increases monotonously with the time throughout the reaction. Therefore, the reaction can be written as:

$$\mathrm{Mg(OH)_2} \xrightarrow{+\mathrm{SiO_2}} \text{serpentine} \xrightarrow{+\mathrm{SiO_2}} \text{talc}.$$

This is a typical consecutive two-stage reaction.

The two conversion curves at 250 and 360 °C shown in Fig. 3 are those obtained at different concentrations of silica as well as at different temperatures, since the equilibrium solubility of silica gel is dependent on the temperature (*e.g.*, the silica concentrations at 250 and 360 °C were about 900 and 1400 ppm respectively). As long as silica gel is used as the silica source, it is difficult to control the experimental conditions so as to keep the same silica concentration at the different reaction temperatures. Therefore, α-quartz powder, which has a different solubility[15] from silica gel, was also used as a silica source. The effect of the reaction temperature on the reaction rate was measured semiquantitatively under the conditions of a somewhat similar silica concentration but at dif-

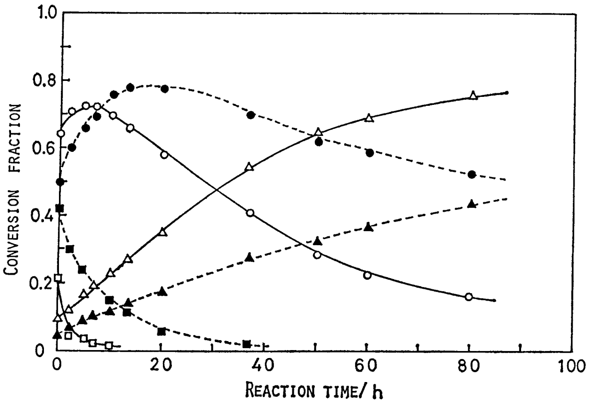

Fig. 5. Conversion for different parts of briquette of reactant in sample container.
Reaction temperature: 360 °C, Silica source: silica gel. ——: outer parts of the pack, ----: inner parts of the pack. Symbols are the same as in Fig. 3.

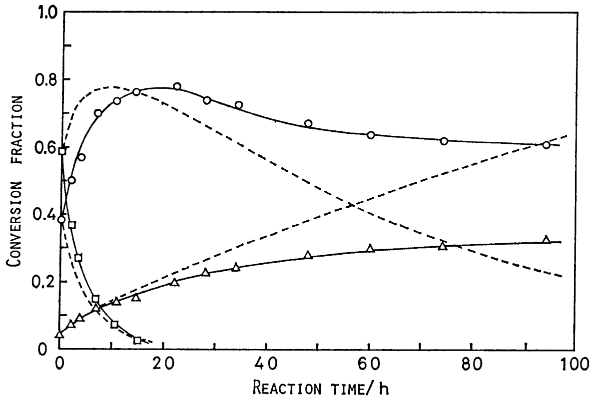

Fig. 6. Effect of crystallite size of starting $Mg(OH)_2$ on the reaction rate.
Reaction temperature: 360 °C, Silica source: silica gel. Crystallite size of starting $Mg(OH)_2$: ----, 16.4 nm;[a] ——, 58.0 nm. Symbols are the same as in Fig. 3.
a) This curve has been already shown in Fig. 3.

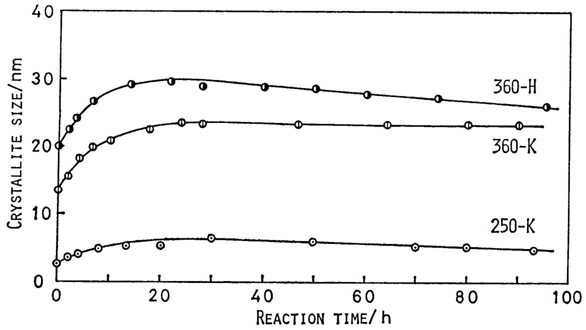

Fig. 7. Effect of reaction temperature and crystallite size of starting $Mg(OH)_2$ on the crystallinity of product (serpentine).
Silica source: silica gel.

Symbol	Reaction temperature	Crystallite size of starting $Mg(OH)_2$	Shorthand
⊙:	250 °C	16.4 nm	250-K
⦶:	360 °C	16.4 nm	360-K
◑:	360 °C	58.0 nm	360-H

ferent temperatures. The results are shown in Fig. 4. There was no difference in the mode of the two conversion curves in the initial stage of the reaction, but in the later stage the position of the maximum of the curve for serpentine was shifted to the right in the case of lower silica concentrations, while the slope of the curve for talc became more gentle. In other words, the rate of the reaction of serpentine into talc may be more affected by the silica concentration than by the reaction temperature.

Effect of Diffusion of Soluble Silica. Since the two starting materials were separated from each other in the autoclave, and since $Mg(OH)_2$ powder was packed into the basket, there may be a concentration gradient of soluble silica in the solution and in the pack of $Mg(OH)_2$ powder. Therefore, two processes of the diffusion of soluble silica may be considered; one is the diffusion through the solution (intrasolution diffusion), and the other is the diffusion across the interstice constructed by $Mg(OH)_2$ particles (interstice diffusion). In order to study the effect of the former, the distance between the silica on the bottom of the autoclave and the $Mg(OH)_2$ powder in the container was allowed to vary. The variation in the distance between them did not enable us to distinguish the conversion. In order to study the effect of the latter, a large amount of $Mg(OH)_2$ powder was used. The pack of $Mg(OH)_2$ powder was, after the reaction, divided into several parts beginning with the outside, and the conversion fraction of each part was measured. Consequently, the conversion fraction decreased with an increase in the distance from the outside, and thus the reaction rate was found to be influenced by the interstice diffusion. Some typical conversion curves obtained for the outside and inner parts of the pack are shown in Fig. 5.

Effect of Particle Size of $Mg(OH)_2$ on the Reaction Rate. Two kinds of $Mg(OH)_2$ with different particle sizes were used as reactants. These $Mg(OH)_2$ powders were about 35 and 18 m^2/g in surface area, while the crystallite sizes were about 16 and 58 nm respectively. The distinction of the reaction rate due to different particle size is shown in Fig. 6. The reaction rate for larger particles was slower, but the conversion curves obtained for them differed in form from those for small particles. The alteration in the form of the conversion curves suggests that a part of the reaction process varied in the case of larger particles, as will be described in the following section.

Effect of the Crystallite Size of $Mg(OH)_2$ and the Reaction Temperature on the Crystallinity of Serpentine. It has been reported that the crystallite size of the starting material influences the crystallinity of products in some solid reactions—for example, the hydration of MgO,[18] the oxidation of Fe_3O_4 into γ-Fe_2O_3[19] and the reaction of $MgO+Al_2O_3 \rightarrow MgO \cdot Al_2O_3$.[20] Similar behavior can also be expected for the serpentinization of $Mg(OH)_2$, since serpentine has a layer structure consisting of linked SiO_2 tetrahedra and Mg–O(OH) octahedra sheets,[21] like the structure of $Mg(OH)_2$. In order to examine this tendency, two kinds of $Mg(OH)_2$ with different crystallite sizes were allowed

Table 1. Effect of the crystallite size of $Mg(OH)_2$ on the crystallinity of products (serpentine)
Reaction temperature: 360 °C
Silica source: α-quartz blocks

Reaction time (week)	Crystallite size of serpentine (nm)	
	Starting material	
	$Mg(OH)_2$-K[a]	$Mg(OH)_2$-H[a]
1	25.3	26.4
2	28.0	28.7
3	29.8	30.5
4	31.9	31.3

a) The crystallite sizes of $Mg(OH)_2$-K and $Mg(OH)_2$-H are, respectively, 16.4 and 58.0 nm.

to react at 360 °C. The serpentine produced from large crystals (360-H) was slightly larger than that produced from small crystals (360-K), as is shown in Fig. 7. The distinction of the crystallinity may also have been caused by the variation in the reaction rate due to the different crystallite size. In order to minimize this effect, α-quartz blocks were used as the silica source because their slow dissolution rate may limit the rate of reaction. The results showed that the crystallite size of the resulting serpentine was not affected by that of $Mg(OH)_2$, as is shown in Table 1.

On the other hand, the reaction temperature apparently had an effect on the crystallinity of the products, as may be seen from the curves of 250-K and 360-K in Fig. 7. The crystallite size was about 5 nm at 250 °C and 23 nm at 360 °C for 30 h.

Discussion

As has been described above, the reaction of $Mg(OH)_2$ with soluble silica proceeds consequently in two stages as follows: $Mg(OH)_2 \xrightarrow{\text{(Reaction 1)}} \text{serpentine} \xrightarrow{\text{(Reaction 2)}} \text{talc}$. It is assumed that Reactions 1 and 2 proceed *via* a similar reaction process. The process may consist of the following steps:[22]

(1) Dissolution of silica.
(2) Diffusion of soluble silica in solution.
(3) Diffusion of soluble silica along interstices constructed by $Mg(OH)_2$ (or serpentine) particles.
(4) Adsorption of soluble silica on the $Mg(OH)_2$ (or serpentine) surface.
(5) Formation of crystal nuclei for serpentine (or talc).
(6) Crystal growth.

An excess of the silica source was used in this experiment, and the solution was kept saturated with silica throughout the reaction. As has been described above, under these conditions Steps (1) and (2) are not rate-limiting. Furthermore, Step (4), that is, surface reaction, proceeds much faster than the other steps, as has been reported in a previous paper.[14] Accordingly, Steps (3), (5), or (6) may be considered to be the rate-limiting steps.

The conversion curves obtained were analyzed on the basis of the kinetics in order to clarify the reaction mechanism. The full reaction scheme is represented as follows:

$$\begin{array}{llll} & Mg(OH)_2 \xrightarrow[+SiO_2]{k_1} & Mg_3Si_2O_5(OH)_4 \xrightarrow[+SiO_2]{k_2} & Mg_3Si_4O_{10}(OH)_2 \\ t=0 & [A]_0 & 0 & 0 \\ t=t & [A] & [B] & [C] \end{array} \tag{1}$$

where k_1 and k_2 are the rate constants, $[A]_0$ is the amount of $Mg(OH)_2$ at $t=0$, and [A], [B], and [C] are, respectively, the amounts of $Mg(OH)_2$, serpentine, and talc at $t=t$. Since the silica concentration is almost constant throughout the reaction, as has been described above, the silica concentration is not contained in the rate equation, but is one of the constant factors that are contained in the rate-constant term. The reaction rate also depends on the surface area of $Mg(OH)_2$ powder. However, the surface area is constant in the same sample.

If the reaction is a first-order reaction, the rate equation is expressed as follows:[23]

$$\frac{d[A]}{dt} = -k_1[A], \tag{2}$$

$$\frac{d[B]}{dt} = k_1[A] - k_2[B], \tag{3}$$

$$\frac{d[C]}{dt} = k_2[B]. \tag{4}$$

The above three simultaneous differential equations are solved as follows:

$$[A] = [A]_0 e^{-k_1 t}, \tag{5}$$

$$[B] = [B]_0 e^{-k_2 t} + \frac{k_1[A]_0}{k_2-k_1}(e^{-k_1 t} - e^{-k_2 t}), \tag{6}$$

$$[C] = [C]_0 + [A]_0(1-e^{-k_1 t}) + [B]_0\left(1-e^{-k_2 t}-\frac{[A]_0/[B]_0}{1-k_2/k_1}\right)(e^{-k_2 t}-e^{-k_1 t}), \tag{7}$$

where $[A]+[B]+[C]=1$ and the initial concentrations are $[A]_0=1$ and $[B]_0=[C]_0=0$. These equations can be simplified by writing $k=k_2/k_1$ and $\tau=k_1 t$:

$$[A] = e^{-\tau}, \tag{8}$$

$$[B] = (e^{-\tau}-e^{-k\tau})/(k-1), \tag{9}$$

$$[C] = \{k(1-e^{-\tau}) - (1-e^{-k\tau})\}/(k-1). \tag{10}$$

The values of [A], [B], and [C] are equal to the conversion fractions. They can be represented as a function of τ by changing the value of k in Eqs. 8, 9, and 10. When an appropriate k value was given, the conversion curves determined from Eqs. 8, 9, and 10 agreed with those obtained from this measurement. Some typical model curves determined to correspond to the experimental curves are shown in Fig. 8. Table 2 shows the experimental conditions under which these experimental conversion curves were obtained and also the k values selected to determine these model curves. From the k values, the conversion into serpentine was proved to be much faster than that into talc. Moreover, the dependence of the k values on the

TABLE 2. k VALUES AND EXPERIMENTAL CONDITIONS OF MEASURED CONVERSION CURVES

Silica source	Reaction temperature (°C)	Silica concentration (ppm)	Crystallite size of $Mg(OH)_2$ (nm)	k value	k_1	Ref.
α-quarts powder	360	500	16.4	0.03	0.080	Fig. 5
Silica gel	250	900	16.4	0.07	0.085	Fig. 4
	330	1200	16.4	0.10	0.102	—
	360	1400	16.4	0.09a) 0.12b) 0.19c)	0.090 0.107 0.114	Fig. 6 Fig. 4 Fig. 6
	360	1400	58.0	—d)	—	Fig. 7

a) Conversion of the inner parts of the sample pack. b) Conversion of whole sample. c) Conversion of the outer parts of the sample pack. d) Disagreement with theoretical conversion curve.

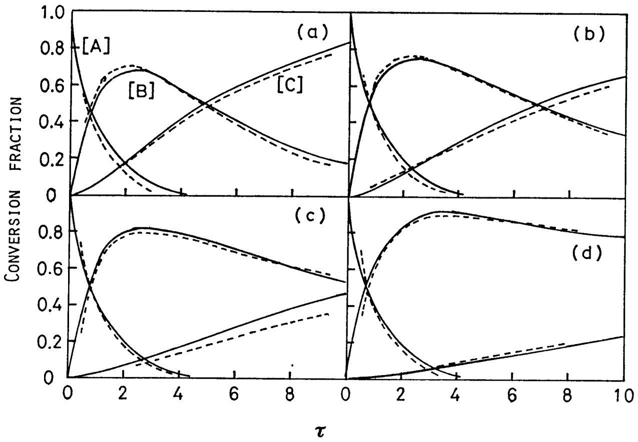

Fig. 8. Typical model curves for the first-order consecutive-irreversible two stage reaction A $\xrightarrow{k_1}$ B $\xrightarrow{k_2}$ C. $k=k_2/k_1$, $\tau=k_1t$. (a) $k=0.19$, (b) $k=0.12$, (c) $k=0.07$, (d) $k=0.03$. ——: Calculated conversion curve, ----: observed conversion curve.

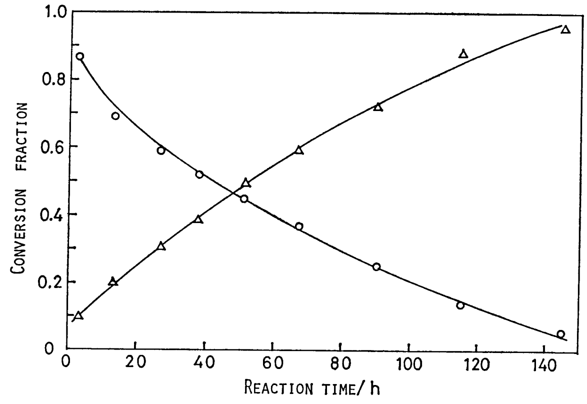

Fig. 9 Conversion curves for the reaction of synthesized serpentine with soluble silica.
Reaction temperature: 360 °C, Silica source: silica gel. Symbols are the same as in Fig. 3.

silica concentration showed that the k values become greater with an increase in the silica concentration. In other words, an increase in the silica concentration accelerates the formation of talc rather than that of serpentine.

When a larger quantity of $Mg(OH)_2$ was packed in the sample container, the rate of the reaction was slowed down toward the center of the pack of $Mg(OH)_2$ powder. Regardless of whether a part or the whole of the sample is involved, these rate equation could be applied only if the k value was varied. The reaction proceeded in a first-order manner at any part of the pack of $Mg(OH)_2$ powder, although there was a concentration gradient attributable to the interstice diffusion. This may be explained as follows. The term referring to the interstice diffusion rate as well as that of the silica concentration is contained in the rate constant k.

In order to measure the reaction rate of serpentine into talc as a single reaction, a synthesized serpentine was used as the starting material. The results are shown in Fig. 9. It was confirmed from the decrease in the amount of serpentine that the reaction of serpentine into talc is also first-order.

These results suggest that diffusion is not a rate-limiting step under the present experimental conditions, since diffusion is not represented by a first-order rate equation.23) Therefore, Step (5), the formation of crystal nuclei, which is considered to be independent of the diffusion,22) seems to be the rate-limiting step.

The change in the crystallite size of $Mg(OH)_2$ and serpentine with the reaction time was followed by the use of an X-ray diffractometer in order to obtain some further information about the reaction mechanism. The results for serpentine can be seen in Fig. 8. The amount of $Mg(OH)_2$ was reduced to one-half of its initial value after 1—5 h, while its crystallite size was hardly changed at all. Thus, in the $Mg(OH)_2 \longrightarrow$ serpentine $\longrightarrow$ talc reaction, the crystallite of the reactions did not decrease despite the decrease in their amount as the reaction proceeded. In the course of the reaction, the reactants may be either completely transformed into products (serpentine or talc) or may still be kept in the initial state. This result suggests that the crystal growth, Step (6), will finish immediately following the formation of the nucleus, Step (5). Thus, this evidence supports the idea that the formation of nuclei is the rate-limiting step. This conception is reasonable, however, only in the case of $Mg(OH)_2$ powder with a small particle size, since the use of larger particles gives rise to an apparent deviation from the typical model curve described above. The reaction mechanism for large particles may be more complex than that for small particles.

It has been reported that solid-phase reactions, such as the crystallization of zeolite[1)] and the dehydration of $Mg(OH)_2$[24)] and kaolinite ($Al_2Si_2O_5(OH)_4$),[25,26)] are first-order. In these reactions, the mechanism is thought to involve a rate-limiting heterogeneous nucleation. For the dehydration of larger particles of kaolinite,[27,28)] however, the rate-limiting step is taken as the diffusion process and the reaction is not a first-order. These reports seem to support our proposal.

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References

1) G. T. Kerr, *J. Phys. Chem.*, **70**, 1047 (1966).
2) J. Ciric, *J. Colloid Interface Sci.*, **28**, 315 (1968).
3) S. P. Zhdanov, *Adv. Chem. Ser.*, **101**, 20 (1971).
4) R. A. Cournoyer, W. L. Kranich, and L. B. Sand, *J. Phys. Chem.*, **79**, 1578 (1975).
5) H. Kacirek and H. Lechert, *J. Phys. Chem.*, **80**, 1291 (1976).
6) Von. W. Noll, *Z. Anorg. Chem.*, **261**, 1 (1950).
7) J. J. Hemley, J. W. Montary, C. L. Christ, and P. B. Hostetler, *Am. J. Sci.*, **277**, 322 (1977).
8) J. C. Yang, *J. Am. Ceram. Soc.*, **43**, 542 (1960).
9) G. L. Kalousec and D. Mui, *J. Am. Ceram. Soc.*, **37**, 38 (1954).
10) R. K. Iler, "The Chemistry of Silica," John Wiley & Sons, New York (1979), p. 96.
11) "Jikken Kagaku Koza," ed by The Chemical Society of Japan, Maruzen Press, Tokyo (1957), Vol. 15, p. 291.
12) K. Kubo, E. Suito, U. Nakagawa, and S. Hayakawa, "Funtai," Maruzen Press, Tokyo (1962), p. 186.
13) S. Kitahara and H. Muraishi, *Nippon Kagaku Kaishi*, **1978**, 555.
14) H. Muraishi and S. Kitahara, *Nippon Kagaku Kaishi*, **1978**, 1457.
15) A. J. Ellis and W. A. J. Mahon, "Chemistry and Geothermal Systems," Academic Press, New York (1977), p. 145.
16) R. K. Iler, "The Chemistry of Silica," John Wiley & Sons, New York (1979), p. 30.
17) N. L. Bowen and O. F. Tuttle, *Bull. Geol. Soc. Am.*, **60**, 439 (1949).
18) S. Kitahara, unpublished.
19) M. Kiyama, *Bull. Chem. Soc. Jpn.*, **47**, 1646 (1974).
20) R. C. Rossi and R. M. Fulrath, *J. Am. Ceram. Soc.*, **50**, 56 (1967).
21) L. G. Berry and B. Marson, "Mineralogy," W. H. Freeman and Co., San Francisco (1959), p. 504.
22) W. S. Fyfe, N. J. Price, and A. B. Thompson, "Fluids in The Earth's Crust," Elsevior Scientific Publishing Co., Amsterdam (1978), p. 89.
23) C. H. Banford and C. F. H. Tipper, "Chemical Kinetics, Vol. 2," Elsevior Scientific Publishing Co., Amsterdam (1969), p. 17.
24) R. S. Gordon and W. D. Kingery, *J. Am. Ceram. Soc.*, **58**, 8 (1967).
25) G. W. Brindley and M. Nakahira, *J. Am. Ceram. Soc.*, **40**, 346 (1957).
26) F. Toussaint, J. J. Fripat, and M. C. Gaetuche, *J. Phys. Chem.*, **67**, 26 (1963).
27) J. B. Holt, I. B. Culter, and M. E. Wadsworth, *J. Am. Ceram. Soc.*, **45**, 133 (1962).
28) R. E. Carter, *J. Chem. Phys.*, **34**, 2010 (1961); **35**, 1137 (1961).