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Kinetic Study on Hydrolysis of Silicon Phosphate in Aqueous Alkaline Solutions[1)]

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Kinetic study of the hydrolysis of silicon phosphate, $Si_3(PO_4)_4$ (hexagonal), was carried out in borax buffer solutions (pH 5—12, temperature 20—50 °C) to investigate how it acts as a hardener for alkali silicate adhesive. The silicon phosphate was found to be hydrolyzed with a resulting release of orthophosphate ion, soluble silicate ions, and colloidal silica under mild conditions; the decomposition rate increased with decreasing the particle size of the phosphate and with increasing the pH and temperature of the buffer solution. From the analysis of the decomposition rate on the basis of the shrinking core model, it was found that the decomposition rate could be adequately expressed by the rate equation based on the mixed control of diffusion through a residual layer and surface chemical reaction. This indicates that a part of the colloidal silica which resulted from the hydrolysis remains on the surface of the silicon phosphate particle and then partially limits the overall rate of the hydrolysis. The dependence of both rate-determining steps for the decomposition rate was quantitatively indicated according to the reaction conditions.

Because of the advantages of being heat-stable, incombustible, and solvent-resistant, inorganic adhesives are increasingly being used in many fields. A silicate adhesive using alkali silicate solution (generally referred to as "water glass") as a binder is most widely utilized.[2,3)] However, it still has some weak points; for instance, the hardened silicate materials at room temperature show water sensitivity. Since the adhesive properties of the hardened silicate materials are known to be predominantly dependent on the kind of hardeners used, a number of substances such as metal powders, oxides, hydroxides, mineral acids, borates, and phosphates are now being employed.[4,5)] However, no hardener having excellent properties, especially sufficient water resistance, has yet been obtained.

The present authors[1)] have prepared silicon phosphates such as $Si_3(PO_4)_4$ and SiP_2O_7 by calcination of silica gel impregnated with a small amount of phosphoric acid at temperatures up to 1000 °C and have shown that they can be used as a satisfactory hardener for silicate adhesives. The most important feature was that these phosphates with silicate adhesives showed excellent water resistance even without heat-treatment. Although the synthesis of silicon phosphates in a large excess of phosphoric acid has been done by earlier workers,[6,7)] no information is at present available on these chemical properties. Therefore, to investigate the mechanism of the enhancement in the water insensitivity by using silicon phosphates, an understanding of the hydrolysis behavior of silicon phosphates is desirable.

In this study, the kinetics of the hydrolysis of pure silicon phosphate ($Si_3(PO_4)_4$) in aqueous alkaline solutions was investigated in detail. As a model solution, borax buffer solution having the desired pH value was used here.

Experimental

Materials. In the preparation of $Si_3(PO_4)_4$, analytical reagent grade orthophosphoric acid (P_2O_5: 63%) and commercial silica gel for chromatography (200—300 mesh) were used. A buffer solution was prepared using analytical reagent grade sodium tetraborate decahydrate and sodium hydroxide. The pH of the buffer solution was adjusted to the desired value by mixing 0.2 mol dm^{-3} $Na_2B_4O_7$ with 1.0 mol dm^{-3} NaOH.

Preparation of $Si_3(PO_4)_4$.[6)] First, 17.5 g of orthophosphoric acid was transferred to a 30 cm^3 platinum crucible and heated for 30 min at 150 °C. Subsequently, 1.0 g of dried silica gel (P_2O_5/SiO_2 molar ratio: 5.0) was added to the crucible, which was then heated again for 5 h at 220—230 °C. After cooling, the suspension was centrifuged, and the resulting white powder was washed repeatedly with ethanol to remove adsorbed acid and then dried over P_2O_5 under reduced pressure. Since $Si_3(PO_4)_4$ is hygroscopic, it was well-dried before being used for the hydrolysis experiment. Although the spontaneous particle size of $Si_3(PO_4)_4$ was different in all runs, uniform-sized particles were obtained for each run. In this investigation, four different-sized $Si_3(PO_4)_4$ (hexagonal)[8)] were used without further pulverization. As

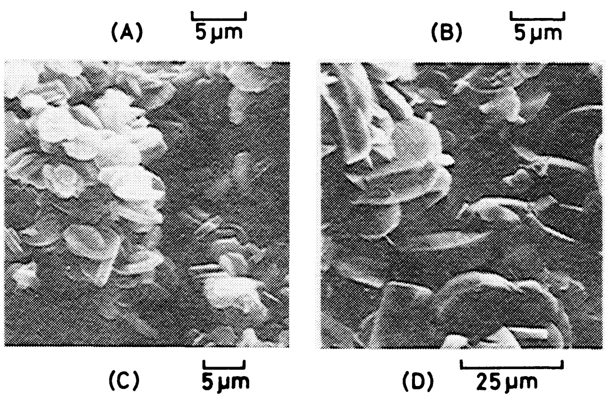

Fig. 1. Scanning electron micrographs of silicon phosphate ($Si_3(PO_4)_4$) used in this experiment.
Mean particle diameter (µm) —— A: 1.0, B: 2.2, C: 3.7, D: 22.6.

can be seen in Fig. 1, these phosphate particles were all disk-shaped. No differences in their crystal forms and chemical compositions were observed. The particle size was measured using a scanning electron microscope (Hitachi-Akashi MSM 4C-102) and the cylindrical shape equivalent diameter[9] was used as the mean particle size. The chemical composition was: Found: SiO_2, 36.6±3.2, P_2O_5, 59.5±1.9; Calcd for $Si_3(PO_4)_4$: SiO_2, 38.8, P_2O_5, 61.2%.

Measurement of Hydrolysis Rate. As the first step, 200 cm^3 of the buffer solution was transferred to a 300 cm^3 three-necked flask equipped with a mechanical stirrer (crescent shaped impeller, 60 mm×20 mm), a reflux condenser, and a thermometer and maintained at 20—50 °C. Then, a weighed amount of $Si_3(PO_4)_4$ was suspended in the buffer solution with vigorous agitation. The decomposition rate of $Si_3(PO_4)_4$ was determined by pipetting about 3 cm^3 of the suspension from the flask as regular time intervals, filtering out the insoluble residues, and chemically analyzing the supernatant solution for orthophosphate ion by colorimetric method.[10] In all experiments, no changes in the pH of the buffer solution were observed from before to after the hydrolysis.

Results and Discussion

Effect of Amount of $Si_3(PO_4)_4$ Added. Figure 2 shows the effect of changes in the amount of $Si_3(PO_4)_4$ on the decomposition rate of $Si_3(PO_4)_4$ conducted in the buffer solution of pH 11.0 at 30 °C with a stirring speed of 300 min^{-1}. The particle size of $Si_3(PO_4)_4$ used was 2.2 µm. Since the maximum difference in the percentage decomposition was only 4%, it cannot be said that there is any effect of amount of $Si_3(PO_4)_4$ under the conditions tested.

Effect of Stirring Speed. Figure 3 shows the effect of stirring speed on the decomposition rate of $Si_3(PO_4)_4$ under the same conditions as those conducted above. 0.2 g of $Si_3(PO_4)_4$ was used here. The decomposition rate was maximum at 300 min^{-1} and slightly decreased at 200 and 400 min^{-1}. When different-sized $Si_3(PO_4)_4$ were tested, the effect of stirring speed was also hardly observed under stirring speeds of 200—300 min^{-1}.

Effect of Particle Size. The decomposition rate was determined using 0.4 g of four different-sized $Si_3(PO_4)_4$, shown in Fig. 1, under the same conditions as those employed above. The result is given in Fig. 4. The decomposition rate obviously increased with de-

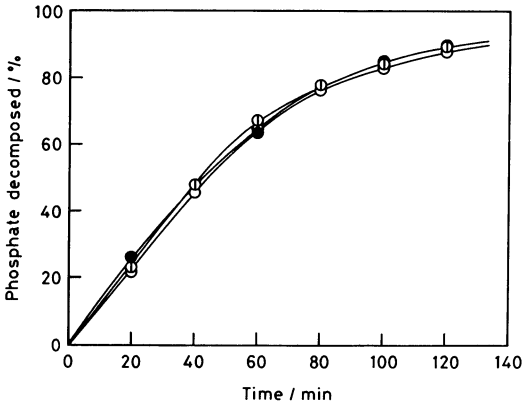

Fig. 2. Effect of amount of silicon phosphate on the decomposition rate of silicon phosphate in aqueous alkaline solution.
Particle diameter: 2.2 µm, pH: 11.0, temperature: 30 °C, stirring speed: 300 min^{-1}, amount of silicon phosphate added (g)—— ●: 0.1, ○: 0.2, ⦶: 0.4.

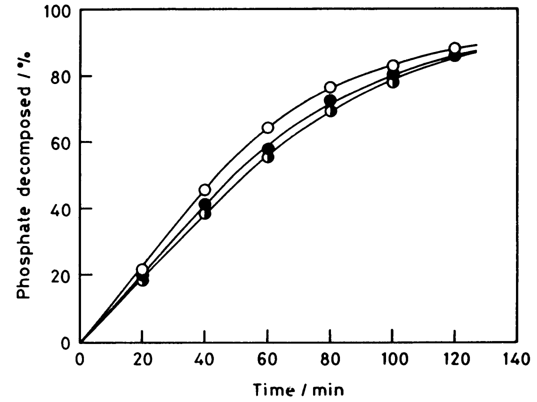

Fig. 3. Effect of stirring speed on the decomposition rate of silicon phosphate in aqueous alkaline solution.
Amount of silicon phosphate added: 0.2 g, particle diameter: 2.2 µm, pH: 11.0, temperature: 30 °C, stirring speed (min^{-1}) —— ●: 200, ○: 300, ◑: 400.

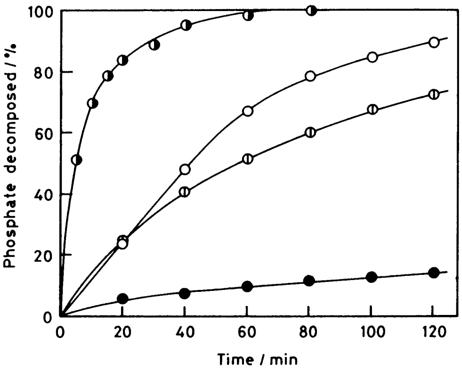

Fig. 4. Effect of phosphate particle diameter on the decomposition rate of silicon phosphate in aqueous alkaline solution.
Amount of silicon phosphate added: 0.4 g, pH: 11.0, temperature: 30 °C, stirring speed: 300 min^{-1}, particle diameter (µm) —— ◑: 1.0, ○: 2.2, ⦶: 3.7, ●: 22.6.

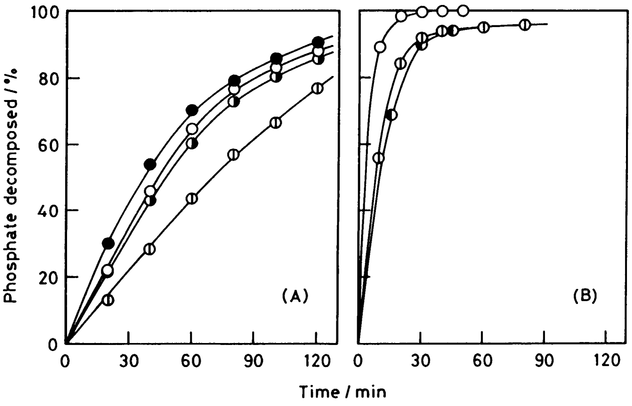

Fig. 5. Effect of pH on the decomposition rate of silicon phosphate in aqueous alkaline solution.
Amount of silicon phosphate added: 0.2 g, particle diameter: 2.2 µm, temperature: (A) 30 °C (B) 50 °C, stirring speed: 300 min^{-1}, pH —— ◐: 5.0, ⦶: 8.0, ◑: 9.5, ○: 11.0, ●: 12.0.

creasing particle size. The relationship between particle size and decomposition rate will be quantitatively discussed later.

On the basis of the data, subsequent experiments were carried out under the following conditions; particle diameter of $Si_3(PO_4)_4$, 2.2 µm; amount of $Si_3(PO_4)_4$, 0.2 g; stirring speed, 300 min^{-1}.

Effect of pH. Figure 5 shows the effect of pH on the decomposition rate of $Si_3(PO_4)_4$ at 30 °C (A) and 50 °C (B). At both temperatures, the decomposition rate increased with increasing the pH, although its effect was not so appreciable. In the experiments at 50 °C, more than 90% of the total quantity of $Si_3(PO_4)_4$ was hydrolyzed at all pH values tested.

Effect of Temperature. Fiure 6 shows the effect of temperature on the decomposition rate of $Si_3(PO_4)_4$ at pH 8.0 (A) and 11.0 (B). At both pH values, the temperature affected predominantly the decomposition rate, which increased significantly with increasing temperature.

Analysis of Hydrolysis Rate. The electron micrographs of the insoluble residues obtained from the suspensions after the decomposition of 30% and 70% of $Si_3(PO_4)_4$ are shown in Fig. 7. It was observed that the particles shrunk with progress of the hydrolysis. The profile of the residue was quite similar: the same percentage decomposition and independence of the reaction conditions were found. The colloidal silica was gradually suspended in the buffer solution during the hydrolysis. According to Alexander *et al.*,[11] the solubility of the different forms of amorphous silica in water is 0.011—0.015 wt% at pH 6—9 and 25 °C, and increases to 0.2—0.4 wt% at pH 11. It also increases with a rise in temperature, but its effect is not appreciable compared to that of pH. Since the buffer solution used here contains a large amount of borate, the resulting silicate species should be present mainly as colloidal silica in it. Although the colorimetric determination of soluble silicate ion using ammonium molybdate was not so exact because of the coexistence of phosphate ion, the formation of the soluble silicate ion was identified in the buffer solution. From the results reported by Busey *et al.*,[12] the soluble silicate ions were thought to be $SiO(OH)_3^-$ and $Si(OH)_4$. Paper chromatography[13] also revealed that the phosphate ions in the buffer solution which originated from $Si_3(PO_4)_4$ were all orthophosphate ions, PO_4^{3-}. Thus $Si_3(PO_4)_4$ reacts with H_2O or OH^-, and decomposes in aqueous alkaline solution, which leads to the release of orthophosphate ion, soluble silicate ions, and colloidal silica.

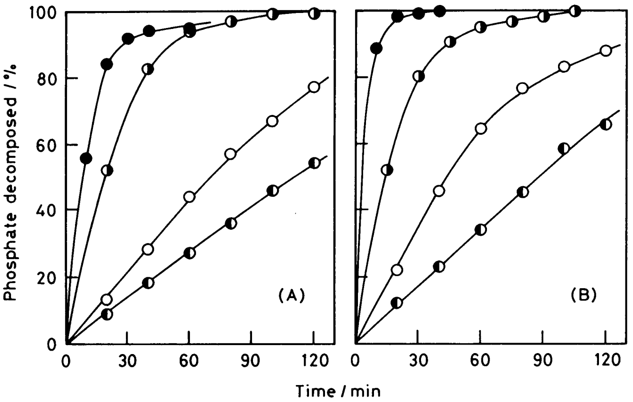

Fig. 6. Effect of temperature on the decomposition rate of silicon phosphate in aqueous alkaline solution.
Amount of silicon phosphate added: 0.2 g, particle diameter: 2.2 µm, pH: (A) 8.0, (B) 11.0, stirring speed: 300 min^{-1}, temperature (°C) —— ◐: 20, ○: 30, ◑: 40, ●: 50.

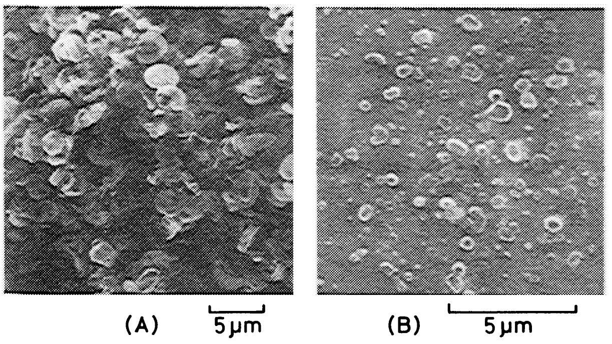

Fig. 7. Scanning electron micrographs of the decomposition residues.
Percentage decomposition (%) —— A; 30, B; 70.

Therefore, the hydrolysis reaction of $Si_3(PO_4)_4$ in aqueous alkaline solution is written as:

$$Si_3(PO_4)_4 + 6H_2O = 3SiO_2(\text{soluble and colloidal}) + 4PO_4^{3-} + 12H^+. \quad (1)$$

The decomposition rates of $Si_3(PO_4)_4$ were analyzed on the basis of the shrinking core model under the assumption that the phosphate particles form a homogeneous spherical solid phase.

The reaction in Eq. 1 can be represented simply as Eq. 2:

$$A(l) + \sigma S(s) \longrightarrow P(l). \quad (2)$$

When the reaction percentage of component P was represented as x and the steady state of the reaction was assumed, the following Eq. 3 was obtained as the rate equation:

$$\frac{dx}{dt} = \frac{3C_A V}{r_0} = \frac{1}{\dfrac{1}{k_L} + \dfrac{\sigma r_0}{D_e}\{(1-x)^{-1/3}-1\} + \dfrac{1}{k_C}(1-x)^{-2/3}}. \quad (3)$$

Three rate-determining steps were studied: The diffusion in liquid film, the diffusion in residual layer, and the surface chemical reaction.[14] However, the diffusion in liquid film should not be the rate-determining step because the decomposition rate of $Si_3(PO_4)_4$ was not affected by the stirring speed but was significantly influenced by temperature, as described previously. Therefore, the following two equations were obtained for each rate-determining step by integration of Eq. 3:

i) For diffusion in residual layer (k_L, $k_C \gg D_e/r_o$)

$$1 - \frac{2}{3}x - (1-x)^{2/3} = \frac{2C_A D_e V}{\sigma r_0^2}t, \quad (4)$$

ii) For surface chemical reaction (k_L, $D_e/r_o \gg k_C$)

$$1 - (1-x)^{1/3} = \frac{C_A k_C V}{r_0}t, \quad (5)$$

In the first place, the results for the hydrolysis of $Si_3(PO_4)_4$ shown in Figs. 4 and 5 were replotted according to the rate equations shown in Eqs. 4 and 5. However, it was found that neither rate equation could express the decomposition rates satisfactorily. In general, the rate of heterogeneous reaction of a solid-liquid system is often dependent on both the rate of diffusion through residual layer and the surface chemical reaction. According to Habashi[15] and Sohn *et al.*,[16] a mixed control rate equation can be derived by combining the diffusion and chemically controlled expressions as shown in Eq. 6:

iii) For mixed control ($k_L \gg D_e/r_o$, k_C)

$$[1-\frac{2}{3}x-(1-x)^{2/3}]+\beta[1-(1-x)^{1/3}]=kt, \qquad (6)$$

where

$$\beta=\frac{2D_e}{k_C\sigma r_0},$$

$$k=\frac{2C_AD_eV}{\sigma r_0^2}.$$

The results for the hydrolysis of $Si_3(PO_4)_4$ shown in Figs. 4 and 5 are replotted according to Eq. 6 as Fig. 8. A good linear dependence of $[1-2/3x-(1-x)^{2/3}]+\beta[1-(1-x)^{1/3}]$ on time was obtained. The values of β and k used for replotting Fig. 8 were conveniently given by the slope and intercept of the straight line drawn between $[1-2/3x-(1-x)^{2/3}/t]$ and $[1-(1-x)^{1/3}/t]$ at constant temperature.[17] The values for the constants β and k for the four different-sized particles used are given in Table 1. If Eq. 6 describes the reaction conversion adequately, then the ratio of the values of k for two essentially monosized fractions should be equal to the square of the ratio of the radii. The comparison is shown as Table 2. Agreement between the expected results and those actually obtained is observed, and hence the suggestion that the hydrolysis of $Si_3(PO_4)_4$ is under mixed diffusion through residual layer and chemical reaction control is reasonable. A part of the resulting colloidal silica remains on the surface of $Si_3(PO_4)_4$ and the diffusion of the reactant through the silica layer partially controls the overall rate of the hydrolysis.

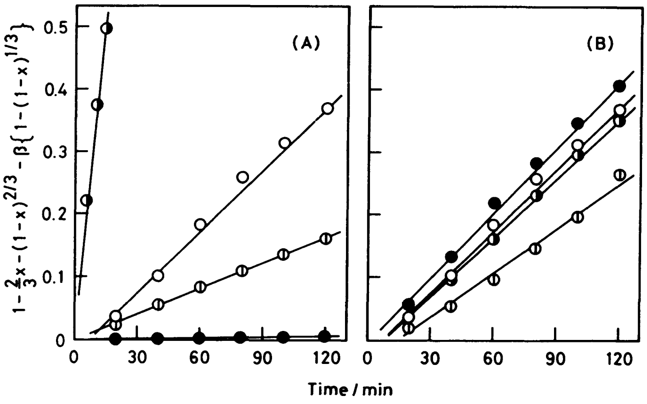

Fig. 8. Plots of decomposition data according to shrinking core model with mixed surface chemical and diffusional kinetics.
(A) Effect of phosphate particle diameter (Fig. 4), (B) Effect of pH (Fig. 5-A) (Symbols are the same as those in each Fig.).

The values for the constants β and k for various pH values and temperatures are summarized in Table 3. The value of k increased with increasing pH. On the other hand, at constant pH the value of β decreased

Table 1. Values of constants in Eq 6 for the decomposition of silicon phosphate in aqueous alkaline solution

Mean particle diameter[a]	β	k
μm		min^{-1}
1.0	0.9	1.6×10^{-2}
2.2	0.4	3.4×10^{-3}
3.7	0.2	1.4×10^{-3}
22.6	0.04	3.2×10^{-5}

a) Since the phosphate particle was disk-shaped, its diameter, d, could be calculated as follows: $d=(f\cdot h)^{1/3}$, where $f=\pi d'^2$.[9]

Table 2. Testing of Eq 6 using data from Table 1

Particle diameters used/μm		Ratio	Ratio
d_i	d_j	k_i/k_j	$(d_j/d_i)^2$
1.0	2.2	4.7	4.8
1.0	3.7	11.4	13.7
1.0	22.6	500	511
2.2	3.7	2.4	2.8
2.2	22.6	106	106
3.7	22.6	43.8	37.3

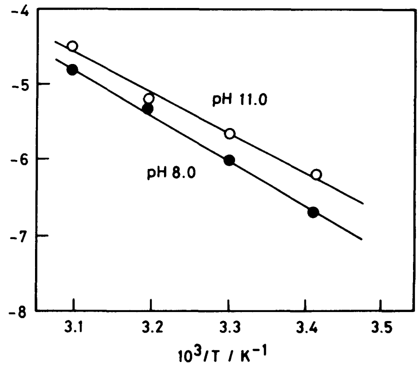

Fig. 9. Arrhenius plots for the decomposition rate of silicon phosphate in aqueous alkaline solution. pH —— ●: 8.0, ○: 11.0.

Table 3. Values of constants in Eq. 6 and Arrhenius activation energy

pH	Temperature/°C								E_a
	20		30		40		50		kJ mol^{-1}
	β	k/min^{-1}	β	k/min^{-1}	β	k/min^{-1}	β	k/min^{-1}	
8.0	0.5	5.7×10^{-4}	0.4	2.5×10^{-3}	0.05	4.9×10^{-3}	0.01	7.9×10^{-3}	48.8
9.5	—	—	0.4	3.2×10^{-3}	—	—	0.01	7.9×10^{-3}	—
11.0	0.5	2.0×10^{-3}	0.4	3.4×10^{-3}	0.05	5.5×10^{-3}	0.01	1.1×10^{-2}	42.7
12.0	—	—	0.4	3.5×10^{-3}	—	—	—	—	—

with increasing temperature, whereas the value of k increased. The decrease in the value of β means that the contribution of the surface chemical reaction to the overall rate of the decomposition becomes smaller. The unusual behavior, that the value of β decreased with increasing temperature in spite of the increase in silica solubility, can be explained by the relative increase of the rate of the chemical reaction.

The Arrhenius plots for the data of pH 8.0 and 11.0 are given in Fig. 9. The dependence of ln k on temperature was approximately the same at both pHs. The apparent activation energies calculated from the Arrhenius plots were 48.8 and 42.7 kJ mol^{-1} at ph 8.0 and 11.0, respectively; these are reasonable values for the mixed control reaction.

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Nomenclature

C_A=Bulk reactant concentration (mol cm^{-3}).
D_e=Effective diffusivity of reactant through the product layer (cm^2 min^{-1}).
d=Mean particle diameter (μm).
d'=Diameter of disk-shaped particle (μm).
h=Height of disk-shaped particle (μm).
k=Overall reaction rate constant (min^{-1}).
k_C=Surface chemical reaction rate constant (cm min^{-1}).
k_L=Mass transfer coefficient (cm min^{-1}).
r_0=Initial particle radius (cm).
t=Reaction time (min).
V=Molar volume of solid reactant (cm^3 mol^{-1}).
x=Fractional conversion (−).
β=Coefficient indicating surface chemical contribution to overall rate (−).
σ=Stoichiometry factor (−).

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