3802 © *1993 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.,* ***66****, 3802—3805(1993)* [Vol. 66, No. 12

Mechanism of Silica Gel Dissolution in Water in the Presence of Pyrocatechol

Tadashi MIZUTANI,*,# Koji TAKAHASHI, Tsutomu KATO, Jiro YAMAMOTO,
Nasuo UEDA, and Ruka NAKASHIMA
Department of Materials Science, Faculty of Engineering, Tottori University, Koyama, Tottori 680

(Received May 24, 1993)

The rates of dissolution of silica gel in aqueous alkaline solutions containing pyrocatechol were measured. At pH 10, all of the silica gel was dissolved in the presence of pyrocatechol at 25 °C for 48 h (SiO_2 0.3 g and pyrocatechol 0.04 mol in 15 ml of water). The rates of silica-gel dissolution increased with increasing pyrocatechol concentration. Four moles of pyrocatechol were needed to dissolve one mole of SiO_2. The rate of dissolution was first order in solid SiO_2 concentration. Langmuir-type adsorption of pyrocatechol to the silica-gel surface was assumed to explain the rate dependence on the pyrocatechol concentration.

The reactions of silica with catechol have been investigated by many researchers, and several coordination complexes have been identified.[1—4] These reactions are interesting from the following two points of view (material science and biological science): (1) a model reaction for the silica dissolution process during silica synthesis or processing,[5] and (2) a model process for the biological silica formation and dissolution.[6] From the view point of material science, the control of silica or silicate crystallization in water is not fully understood, although considerable efforts are being made to clarify the mechanism of nucleation of zeolite or clay mineral crystals. In these processes, the solubilization of silica is one of the key steps. The solubilization reaction of silica in water is also interesting in relation to the biochemical roles of silicon.[7] The surface properties and absorption characteristics of these biological silica attracted interest in relation to metabolism of silicon. The biological silica was found to be amorphous.[7b] We can assume that some organic compounds, or possibly an enzyme, may play a role in transforming these silica. An investigation into the interaction between silica and organic compounds is also important in relation to the desertification process. Hydrated silica or phyllosilicates play important roles in preserving water, inorganic ions, and organic materials in soil, all of which are essential for plants to grow. The possible roles of plant metabolites in preventing the desertification should have a close relationship with the interaction between silica and organic molecules.

Most studies have focused on the structural aspects of silicon–organic ligand chemistry, and only little attention has been paid to the mechanism of the reactions. An investigation of the mechanism of the reaction between silica and organic compounds would help in designing a good "catalyst" for the transformation reactions of silica, since the low solubility of silica[8] in water in the neutral pH range (100 ppm at 25 °C) results in difficulties in silicate synthesis and silicate processing under mild conditions. The aim of this study was to clarify basic aspects of the reaction between silica and organic compounds. We examined the reaction between silica gel and various organic compounds in aqueous solutions and found that pyrocatechol, protocatechuic acid and gallic acid accelerated the dissolution of silica gel at pH 10 at 25 °C.[9] In this paper we report on the reaction mechanism of the dissolution process based on a kinetic study of the reactions.[10]

Experimental

All of the chemicals were of reagent grade and used without purification. Pyrocatechol was purchased from Tokyo Kasei Kogyo Co., Ltd. The silica-gel samples (CARiACT-10, CARiACT-30, CARiACT-50, CARiACT-100) were gifts from Fuji-Davison Chemical Ltd. The surface area of CARiACT-10, 30, 50, and 100, determined by porosimetory, were 263, 131, 76, and 13 $m^2 g^{-1}$, respectively.

In a typical experiment, 0.3 g of silica gel (Fuji-Davison Chemical Ltd. CARiACT-10, 30—200 mesh) was suspended in 15 ml of distilled water and 0.01 mol of organic materials was dissolved. The pH of the suspension was adjusted at 10 by adding aqueous sodium hydroxide. The suspension was left at 25 °C for 24 h; it was then filtered and the solid was dried at 100 °C for 3 h. From the weight difference, the amount of dissolved silica was calculated. In a control experiment, the same procedure was followed, except that the organic materials were not added.

CARiACT-10 was used for all of the data reported, except for the surface area dependence of dissolved silica shown in Fig. 5.

Results and Discussion

Stoichiometry of the Reaction. The amounts of dissolved silica at various pH values in the presence of 2—8 equivalents of pyrocatechol are shown in Fig. 1. Almost all of the silica gel was dissolved in the presence of 4 and 8 equivalents of pyrocatechol after 100 h. However, only 50% of the silica gel was dissolved in the presence of 2 equivalents of pyrocatechol **1** (0.67 M[11]). This indicates that the stoichiometry of the reaction at pH 10 may by summarized as follows:

$$SiO_2 + 4 \text{ pyrocatechol} \rightarrow \text{water soluble complex}$$

#Present address: Department of Synthetic Chemistry and Biological Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto, 606.

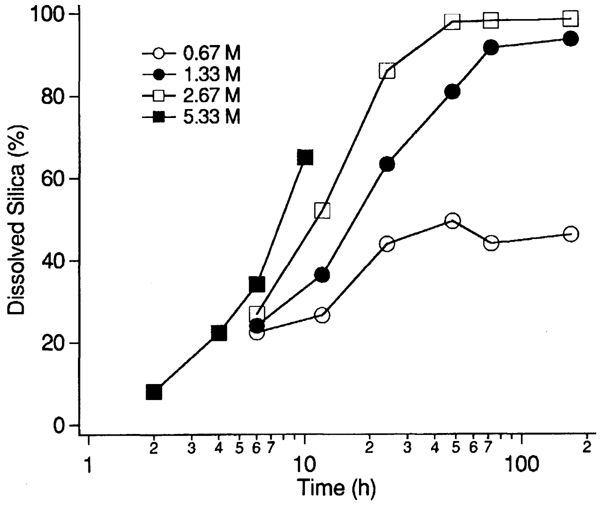

Fig. 1. Rate of dissolution of silica gel (0.3 g) in the presence of pyrocatechol (0.01, 0.02, 0.04, and 0.08 mol) in 15 ml of water at pH 10 and 25 °C.

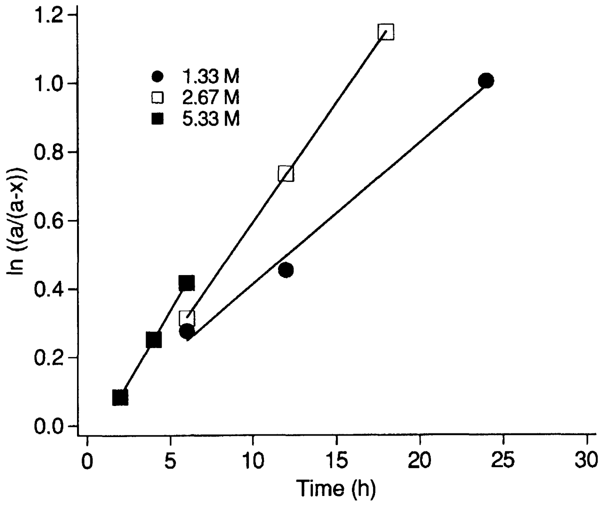

Fig. 2. Pseudo-first-order plot of the dissolution of silica gel in the presence of 1.33, 2.67, and 5.33 M of pyrocatechol at pH 10 and 25 °C.

The same stoichiometry was observed at pH 11. A structural determination of the water-soluble silicon complex was not carried out. Barnum[2] reported that complexes between either 3 moles or 4 moles of pyrocatechol and one mole of silicon were formed in the reaction of aqueous NH_3 and pyrocatechol. Weiss et al. reported that a complex between 3.5 moles of catechol and one mole of silicon was formed.[4] Since these results are based on the isolated crystalline product, the stoichiometry of the complex between catechol and silicon in water may be different from that in the solid states. The stoichiometry observed in this study is close to that of the solid state. As shown in these studies, the chemistry of the orthosilicic acid ester of pyrocathechol is rather complex; it thus seems likely that the dissolving species comprises a mixture of oligomers or polymers of bis(*o*-phenylenedioxy)silane.[10]

Kinetics of the Reaction. All of the kinetic measurements were carried out at pH 10. A control experiment without the addition of pyrocatechol indicated that almost no silica gel was dissolved at pH 10. Therefore, the dissolution of silica gel can be exclusively ascribed to the catalytic action of pyrocatechol.

When an excess amount of pyrocatechol is present, plots of ln $([SiO_2]_0/([SiO_2]_0-[SiO_2]_d))$ versus time are linear up to the third half lives (Fig. 2), thus confirming that the reaction is first-order in silica gel. We define the initial concentration of silica gel ($[SiO_2]_0$) as the number of moles of SiO_2 in one liter of water (M). The rate of dissolution should be analyzed on the basis of the surface area of silica gel instead of the number of moles of silica gel. However, we assume that the surface area per mole of the silica-gel sample did not change appreciably during the reaction and that the surface area of the silica gel is proportional to the number of moles of it. Based on this assumption, the pseudo-first-order rate constants (k_{obsd}) is defined by the following equation:

$$\frac{\mathrm{d}[SiO_2]_d}{\mathrm{d}t} = k_{\text{obsd}}([SiO_2]_0 - [SiO_2]_d)$$

where $[SiO_2]_0$ is the initial "silica-gel concentration" and $[SiO_2]_d$ the concentration of dissolved silica.

However, as shown in Fig. 1, the curves of silica-gel dissolution are concave upward up to the second half-lives, rather than convex, although the curve should be convex if the reaction is strictly first order in silica-gel concentration. This indicates that the rate constant (k_{obsd}) becomes slightly larger as the reaction proceeds, which may be tentatively ascribed to a change in the silica-gel surface during the reaction, with the surface being more reactive as the reaction proceeds than during the initial stage.

The dependence of k_{obsd} on the concentration of pyrocatechol is shown in Fig. 3. The relation between k_{obsd} and [pyrocatechol] is not linear, and the value of k_{obsd} is saturated at a high concentration of pyrocatechol. This indicates that the adsorption of pyrocatechol on silica-gel surface, such as Langmuir-type adsorption, occurs first, followed by the reaction of pyrocatechol and silica gel. The concentration range of pyrocatechol (1.3 to 5.3 M) is sufficiently high enough for the monolayer coverage of the silica-gel surface by pyrocatechol, considering that the surface area of the silica-gel sample is 263 $m^2\,g^{-1}$. It is reasonable to assume that only the first layer of pyrocatechol can react with silica gel, even if multi-layer adsorption of pyrocatechol occurs. If we assume that such pre-adsorption occurs and is of the Langmuir-type, the rate equation will be given as follows, where a is adsorption coefficient and b is the monolayer capacity of the initial silica gel, and both a and b are constant:

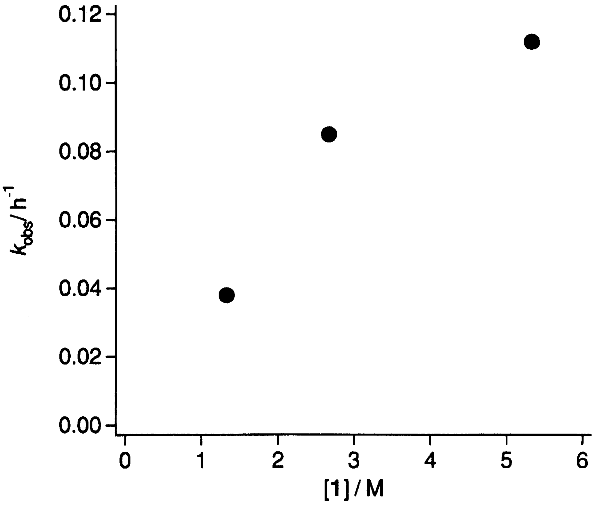

Fig. 3. Plot of k_{obsd} vs. the pyrocatechol concentration (pH 10, 25 °C).

$$\frac{\mathrm{d}[\mathrm{SiO_2}]_\mathrm{d}}{\mathrm{d}t} = k\frac{ab[\mathbf{1}]}{1+a[\mathbf{1}]}([\mathrm{SiO_2}]_0 - [\mathrm{SiO_2}]_\mathrm{d}).$$

The plot of $1/k_{\mathrm{obsd}}$ versus 1/[pyrocatechol] is linear (Fig. 4), indicating that the pre-adsorption of pyrocatechol to silica-gel surface occurs before the reaction takes place. This observation also excludes the mechanism that the dissolved silica reacts with pyrocatechol, and rather suggests that the reaction between silica and pyrocatechol occurs on the surface of the silica gel. From the slope and intercept of the line, a was found to be 0.057 M^{-1} and kb to be 0.44 h^{-1}. The conclusion that the preadsorption step of pyrocatechol is important is also supported by dissolution experiments with silica gel having various surface areas. The amounts of dissolved silica after the reactions at pH 10 for 48 h are plotted against the surface area of silica-gel samples (Fig. 5). The larger was the surface area, the more silica was solubilized. This result is consistent with the above mechanism, in which only the adsorbed pyrocatechol is effective in the solubilization reaction.

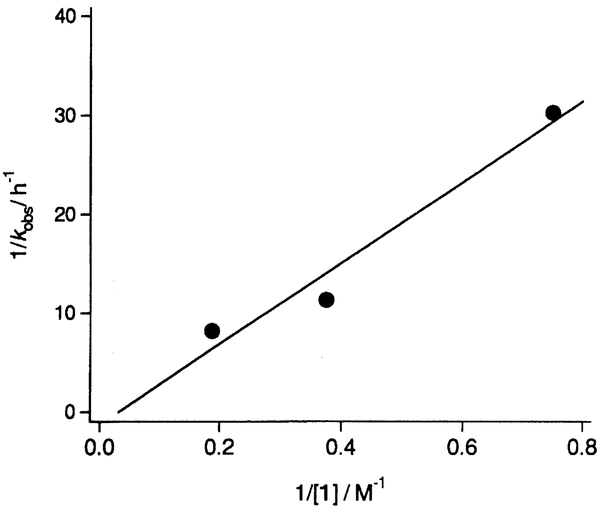

Fig. 4. Plot of $1/k_{\mathrm{obsd}}$ vs. 1/[pyrocatechol].

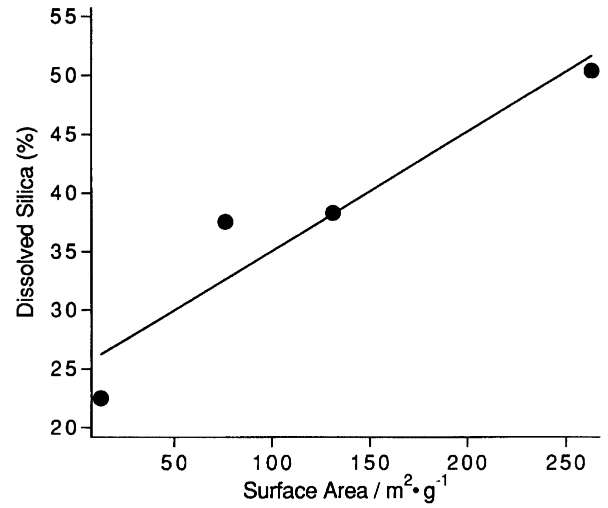

Fig. 5. Plot of the amount of dissolved silica against the surface area of the silica-gel sample (25 °C, 48 h, pH 10.0±0.1).

The mechanism of silica-gel dissolution consists of at least three consecutive steps: (1) adsorption of pyrocatechol to the silica-gel surface, which is either monolayer or multilayer adsorption; (2) a reaction between the adsorbed pyrocatechol and silica gel; and (3) desorption of the silicon complex from the silica-gel surface:

$$\mathrm{SiO_2} + \mathbf{1} \underset{\text{Fast}}{\overset{\text{step 1}}{\rightleftharpoons}} \mathrm{SiO_2}\cdot\mathbf{1} \underset{\text{Slow}}{\overset{\text{step 2}}{\longrightarrow}}$$

$$\mathrm{SiO_2}\text{·silicon complex} \overset{\text{step 3}}{\rightleftharpoons} \mathrm{SiO_2} + \text{silicon complex}$$

In this study, it was demonstrated that the adsorption step (step 1) is fast, and that the following reaction between pyrocatechol and silica gel is rate-determining.

The present findings can be applied, for example, to a new method of silicate processing. Because pyrocatechol can be easily modified by introducing substituents on the benzene ring and, consequently, its bulkiness can be changed, a specific site of silicate can be processed with these catalysts. Electronic effects in the reaction between silica and catechol are also interesting, and physical-organic studies on this reaction are now underway in our laboratory.

Summary

In order to clarify the mechanism of silica-gel dissolution in the presence of pyrocatechol, the rates for dissolution of silica gel were measured at 25 °C. The rate of silica-gel dissolution was first order in the silica-gel "concentration". Although the rate increased with increasing the pyrocatechol concentration, it was not linear. This was ascribed to the Langmuir-type adsorp-

tion of pyrocatechol to the silica-gel surface before the dissolution reaction took place.

This work was supported by a grant from the Asahi Glass Foundation to R. N. and T. M. We thank Fuji-Davison Chemical Ltd. for the generous gift of a silica-gel sample, and also providing us with surface-area data.

References

1) A. Rosenheim, B. Raibmann, and G. Schendel, *Z. Anorg. Chem.*, **196**, 160 (1931).

2) a) D. W. Barnum, *Inorg. Chem.*, **9**, 1942 (1970); b) D. W. Barnum, *Inorg. Chem.*, **11**, 1424 (1972).

3) a) A. Boudin, G. Cerveau, C. Chuit, R. J. P. Corriu, and C. Reye, *Angew. Chem., Int. Ed. Engl.*, **25**, 473 (1986); b) A. Boudin, G. Cerveau, C. Chuit, R. J. P. Corriu, and C. Reye, *Angew. Chem., Int. Ed. Engl.*, **25**, 474 (1986).

4) A. Weiss, G. Reiff, and A. Weiss, *Z. Anorg. Allg. Chem.*, **311**, 151 (1961).

5) a) J. P. van den Berg, P. C. de Jong-Versloot, J. Keijsper, and M. F. M Post, "Innovation in Zeolite Materials Science," ed by P. J. Grobet, Elsevier Science Pub. B. V., Amsterdam (1985), p. 85; b) T. Mizutani, Y. Fukushima, A. Okada, and O. Kamigaito, *Bull. Chem. Soc. Jpn.*, **63**, 2094 (1990); c) M. Toba, F. Mizukami, S. Niwa, and K. Maeda, *J. Chem. Soc., Chem. Commun.*, **1990**, 1211.

6) a) L. Addadi and S. Weiner, *Proc. Natl. Acad. Sci. U. S. A.*, **82**, 4110 (1985); b) A. J. Barwise, R. G. Compton, and P. R. Unwin, *J. Chem. Soc., Faraday Trans.*, **86**, 137 (1990).

7) a) R. J. P. Williams and D. W. Xin, "Introduction to Silicon Chemistry and Biochemistry," ed by D. Evered and M. O'Connor, John Wiley and Sons Ltd., Chichester (1986), p. 24; b) S. Mann, C. C. Perry, R. J. P. Williams, C. A. Fyfe, G. C. Gobbi, and G. J. Kennedy, *J. Chem. Soc., Chem. Commun.*, **1983**, 168.

8) G. B. Alexander, W. M. Heston, and R. K. Iler, *J. Phys. Chem.*, **58**, 453 (1954).

9) T. Mizutani, K. Takahashi, J. Yamamoto, N. Ueda, and R. Nakashima, *Chem. Express*, **7**, 365 (1992).

10) For examples of kinetic studies of silica dissolution, see: a) V. P. Malyshev, S. V. Belyaev, N. S. Bekturganov, and A. T. Kul'zhanov, *Zh. Fiz. Khim.*, **58**, 2451 (1984); b) A. Kamatani, J. P. Riley, and G. Skirrow, *J. Oceanogr. Soc. Jpn.*, **36**, 201 (1980).

11) $\mathrm{M=mol\,dm^{-3}}$.

12) H. Meyer and G. Nagorsen, *Angew. Chem.*, **91**, 587 (1979).