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Study of the Polymerization of Silicic Acid Adsorbed on Iron(III) Hydroxide by Trimethylsilylation-Gas Chromatography

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Synopsis. Polymerization of silicic acid adsorbed on iron (III) hydroxide from dilute monosilicic acid solutions in the concentration range 5—40 ppm (SiO_2) was studied over the pH range 6—12. Silicic acid species formed on the hydroxide were trimethylsilylated and trimethylsilyl derivatives were detected by gas chromatography. Monosilicic acid adsorbed polymerized, and dimer ($Si_2O_7^{6-}$), linear trimer ($Si_3O_{10}^{8-}$) and tetramer ($Si_4O_{13}^{10-}$), and cyclic tetramer ($Si_4O_{12}^{8-}$) were found as polymeric species.

Monosilicic acid adsorbed on or coprecipitated with iron (III) hydroxide rapidly polymerizes.[1,2] Polymerization of silicic acid adsorbed on iron (III) hydroxide has been studied by colorimetry and gel chromatography.[3] Although gel chromatography is useful to study the formation of relatively large polysilicic acids, no information is available on the formation of low-molecular-weight silicic acids such as dimer, trimer, *et al.* Lentz[4] described a chemical technique for the study of silicate structures based on trimethylsilylation of silicic acids. Trimethylsilyl (TMS) derivatives of silicic acids were isolated[5] and the method for the determination of TMS derivatives by gas chromatography was established.[6] The method proposed for the trimethylsilylation of the silicic acids assured that side reactions such as polymerization and depolymerization hardly proceed during the silylation and good reproducible results were obtained.[7] The change with time in the distribution of silicic acids in aqueous solutions was measured.[8]

In this work, the formation of low-molecular-weight silicic acid species in the early stage of polymerization of monosilicic acid adsorbed on iron (III) hydroxide was studied by trimethylsilylation-gas chromatography (TMS-GC).

Experimental

Samples and Reagents. All the reagents except hexamethyldisiloxane (HMDS; $(CH_3)_3Si\text{-}O\text{-}Si(CH_3)_3$) were of analytical reagent grade. HMDS was purified by distillation four times at 120 °C. A stock solution of monosilicic acid was prepared by dissolving silica gel (Mallinckrodt Chemical Works) in sodium hydroxide solution. A monosilicic acid solution of the desired concentration was prepared by diluting a stock solution before use. Iron(III) hydroxide was precipitated by adding sodium hydroxide solution to iron (III) chloride solution and then washed with distilled water. Iron (III) hydroxide was prepared immediately before each experiment.

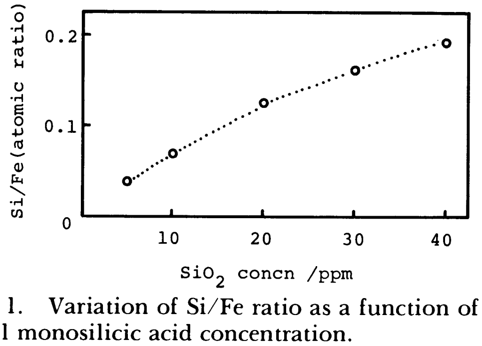

Fig. 1. Variation of Si/Fe ratio as a function of initial monosilicic acid concentration.
pH: 8.

Procedure. Monosilicic acid solution (0.5 dm^3) of an appropriate concentration was adjusted to the desired pH with hydrochloric acid and sodium hydroxide solution. Sodium chloride concentration was adjusted to 0.1 mol dm^{-3}. Iron (III) hydroxide (0.95×10^{-3} mol) was then introduced into the solution and the pH was readjusted. The suspension was stirred vigorously. The experiments were carried out in a thermostated bath at 25°C. After 30 min, the suspension was rapidly filtered. The concentration of monosilicic acid in the filtrate was determined by colorimetry. For the trimethylsilylation of silicic acid adsorbed on iron(III) hydroxide, the solid sample was added to a mixture of water (5 cm^3), concentrated hydrochloric acid (7.5 cm^3), 1-propanol (15 cm^3), HMDS (12 cm^3), which had been stirred for 1 h at 28°C. The mixture was then stirred for 1 h. The siloxane layer was separated from the aqueous layer and washed with water. The aqueous layer and the washed water were combined, and the water was vigorously shaken with 10 cm^3 of HMDS to extract the remaining TMS derivatives and the siloxane layer was separated and washed with water, then the two siloxane layers were combined. The siloxane layer was stirred for 4 h at room temperature in the presence of Amberlyst 15 cation-exchange regin (2 g). After filtration, the filtrate was evaporated to less than 10 cm^3 by distillation at 120—130°C, and adjusted to 10 cm^3 with isopropyl alcohol. TMS derivatives of silicic acid in the sample solution were analyzed by GC.[6]

Results and discussion

The effect of the initial concentration of monosilicic acid on the amount and polymerization of silicic acid adsorbed on iron (III) hydroxide was examined at pH 8. Figure 1 shows the variation of Si/Fe atomic ratio of monosilicic acid adsorbed to iron (III) hydroxide as a function of the initial concentration of monosilicic acid. The ratio is an indicator of the amount of silicic acid adsorbed on the hydroxide. The Si/Fe ratio increased with an increase in the initial concentration of monosilicic acid. The silicic acid adsorbed on iron (III) hydroxide was trimethylsilylated and the TMS derivatives were analyzed by GC. The results are shown in Fig. 2. Each silicic acid species is expressed in its anionic form. It was found to contain dimer ($Si_2O_7^{6-}$), linear trimer ($Si_3O_{10}^{8-}$) and tetramer ($Si_4O_{13}^{10-}$), and cyclic tetramer ($Si_4O_{12}^{8-}$) in addition to the monomer (SiO_4^{4-}). Figure 2 shows the variation of proportion of each silicic acid species as a function of the initial concentration of monosilicic acid. The proportion

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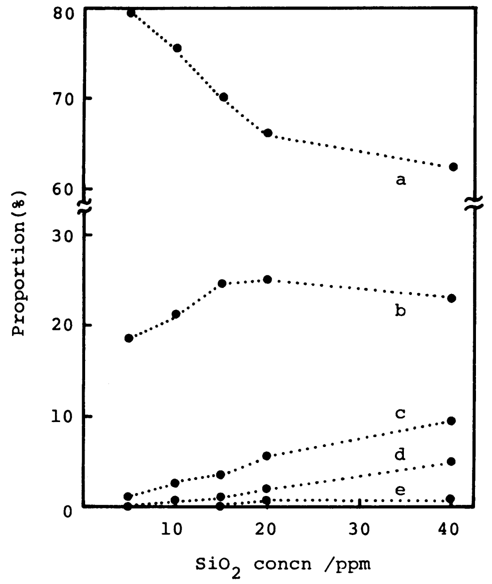

Fig. 2. Effect of initial monosilicic acid concentration on the proportion of various silicic acid species.
pH: 8.
a: SiO_4^{4-}, b: $Si_2O_7^{6-}$, c: $Si_3O_{10}^{8-}$, d: $Si_4O_{12}^{8-}$, e: $Si_4O_{13}^{10-}$.

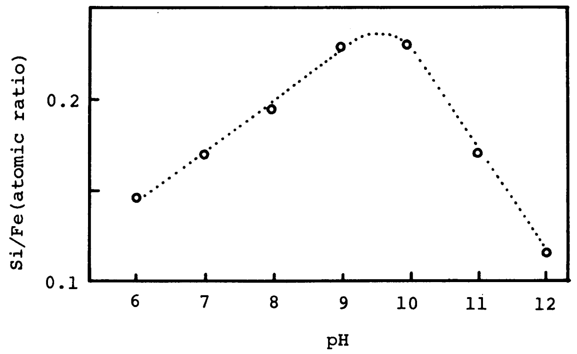

Fig. 3. Variation of Si/Fe ratio with pH.
Initial monosilicic acid concentration: 40 ppm (SiO_2).

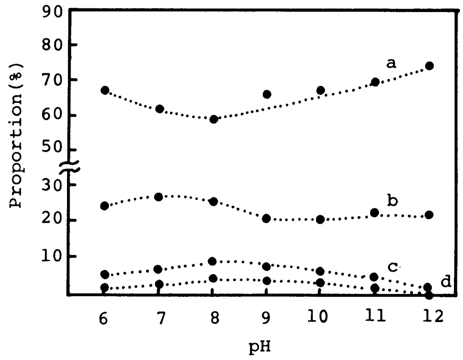

Fig. 4. Effect of pH on the proportion of various silicic acid species.
Initial monosilicic acid concentration: 40 ppm (SiO_2).
a: SiO_4^{4-}, b: $Si_2O_7^{6-}$, c: $Si_3O_{10}^{8-}$, d: $Si_4O_{12}^{8-}$.

was calculated by

$$\text{Proportion (\%)} = 100\ (p_i/\textstyle\sum P_i)$$

where P_i is the peak intensity of the ith TMS derivative on the gas chromatogram. With increasing initial concentration of monosilicic acid, the proportion of monomer rapidly decreased and the proportion of the other silicic acid species increased. The results indicate that although monosilicic acid in solution at concentrations up to about 120 ppm at pH 8 does not polymerize, monosilicic acid adsorbed on iron(III) hydroxide easily polymerizes.

Adsorption of silicic acid by iron (III) hydroxide from 40 ppm (SiO_2) monosilicic acid solution and polymerization of adsorbed silicic acid was examined over the pH range 6—12. Figure 3 shows the variation of the Si/Fe ratio with pH. The maximum adsorption as a function of the pH occurred at around pH 9.5. Figure 4 shows the variation with pH of the proportion of silicic acid species. Although the linear tetramer was detected, it was not plotted in the figure because of its small amount. The polymerization of silicic acid adsorbed occurred at all the pH. It is noteworthy that monosilicic acid adsorbed on iron(III) hydroxide even in strongly alkaline solution (pH 12) polymerizes. Figure 4 suggests that the rate of polymerization of adsorbed silicic acid is most rapid at around pH 8 in the early stage of the adsorption of silicic acid, although the amount of adsorbed silicic acid is largest at around pH 9.5. In colorimetry, only monosilicic acid reacts with molybdic acid to form yellow molybdosilicic acid. As the polysilicic acid species shown in Fig. 4 depolymerize they are determined as monosilicic acid by colorimetry,8) but the formation of such species can not be detected by colorimetry. This work indicates that TMS-GC is useful to study the early stage of the polymerization of silicic acid adsorbed on the surface of a solid.

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References

1) H. Harder and W. Flehmig, *Geochim. Cosmochim. Acta*, **34**, 295 (1970).

2) T. Tarutani and H. Kato, *Mem. Fac. Sci. Kyushu Univ., Ser. C*, **11**, 197 (1978).

3) T. Yokoyama, T. Nakazato, and T. Tarutani, *Bull. Chem. Soc. Jpn.*, **53**, 850 (1980).

4) C. W. Lentz, *Inorg. Chem.*, **3**, 574 (1964).

5) T. Shimono, H. Takagi, T. Isobe, and T. Tarutani, *J. Chromatogr.*, **197**, 59 (1980).

6) T. Shimono, T. Isobe, and T. Tarutani, *J. Chromatogr.*, **205**, 49 (1981).

7) T. Shimono, T. Isobe, and T. Tarutani, *Mem. Fac. Sci. Kyushu Univ., Ser. C*, **13**, 303 (1982).

8) T. Shimono, T. Isobe, and T. Tarutani, *J. Chromatogr.*, **258**, 73 (1983).