Formation of Aluminosilicate by Adsorption of Silicic Acid on Aluminium Hydroxide

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(Received February 15, 1984)

Synopsis. When monosilicic acid was adsorbed on aluminium hydroxide, allophane-like compound rapidly formed and the monosilicic acid adsorbed was consumed by the formation of the allophane-like compound until the Si/Al mole ratio of the sample reached 0.33—0.39. Above these ratio, the formation of polysilicic acid occured.

Some reports have been published on the formation of surface products by adsorption of silicic acid on solids. Huang[1] suggested the formation of phyllite sheets on γ-alumina from a kinetic study. Muraishi and Kitahara[2] confirmed the formation of magnesium silicate on the surface of magnesium hydroxide by differential thermal analysis (DTA) and infrared absorption.

In a previous paper,[3] the authors reported that aluminium hydroxide, which had adsorbed monosilicic acid, showed an endothermic peak between 100 and 300 °C and an exothermic peak at around 1000 °C on the DTA curve. The DTA curve is similar to the thermal curve of allophane, indicating amorphous aluminosilicate.[4]

In this paper, the formation of an allophane-like compound by the adsorption of monosilicic acid on aluminium hydroxide and the effect of the composition of the samples on the exothermic peak intensity are discussed.

Experimental

All the reagents used were of analytical reagent grade. Monosilicic acid solution and aluminium hydroxide were prepared as described previously.[3,5]

Adsorption experiments were carried out using a batch method[3] and a continuous flow method.[5] In the batch method, a known amount of aluminium hydroxide was introduced into a monosilicic acid solution (500 cm^3) of pH 5. In the continuous flow method, aluminium hydroxide was introduced into a flask and then 150 ppm (SiO_2) monosilicic acid solution of pH 5 was continuously flowed through the flask with a flow rate of 2 dm^3/d. Adsorption experiments were carried out at 25 °C. In both methods, after 5 h or at appropriate intervals, an aliquot of aluminium hydroxide, which had adsorbed silicic acid, was pipetted and filtered, and the composition of the sample was determined. The sample dried at 25 °C for 10 d was used for differential thermal analysis. Si(M)/Al(A) and Si(T)/Al(A) ratios are the mole ratios of monosilicic acid and total silicic acid to aluminium in the sample, respectively. The difference between the two ratios indicates the formation of polysilicic acid on the aluminium hydroxide. Si/Al(MR) ratio is the mole ratio of monosilicic acid to aluminium hydroxide in the initial solution in the batch method.

Differential thermal analysis was performed using a Rigaku Denki Thermoflex 8002 H/D thermoanalyzer. The sample (13.5 mg) in a shallow platinum crucible was heated in air at a heating rate of 10 °C/min. The water content was almost the same in all samples (*ca.* 40%). The reference material was γ-alumina.

Results and Discussion

In a preliminary experiment, it was found that the exothermic peak height decreased steeply with increasing pH of the mother solutions over the pH range 5—10. Therefore, the adsorption experiments were carried out at pH 5. A DTA curve of the sample prepared at pH 5 is shown in Fig. 1. In this study the exothermic peak similar to that of allophane was observed for all samples.

The adsorption experiment (batch method) was carried out under the condition of a 2.1 Si/Al(MR) ratio. The results of the differential thermal analysis of the samples are shown in Fig. 2. The exothermic peak height increased with adsorption time and attained a constant value after 2 h. This indicates that the allophane-like compound rapidly formed by the reaction of the adsorbed monosilicic acid and aluminium hydroxide.

In order to examine the effect of the Si(T)/Al(A) ratio of a sample on the exothermic peak height, adsorption experiments (batch method) were carried out by changing the Si/Al(MR) ratio in 100 and 300 ppm (SiO_2) monosilicic acid solutions. Figure 3 shows the variation of the exothermic peak height with the Si(T)/Al(A) ratio. The maximum peak height occurred at a 0.33 Si(T)/Al(A) ratio. The sample (Si(T)/Al(A)=0.36, Si(M)/Al(A)=Si(T)/Al(A))

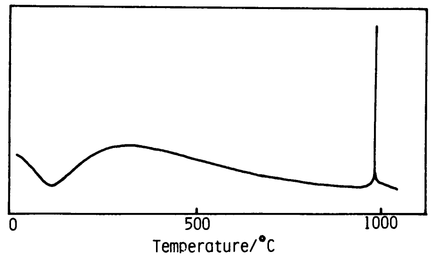

Fig. 1. DTA curve of the sample prepared at pH 5.

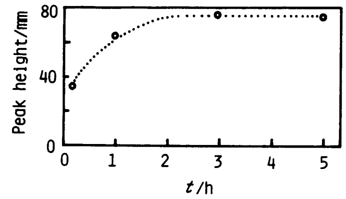

Fig. 2. Variation with adsorption time of exothermic peak height. Initial monosilicic acid concentration: 300 ppm (SiO_2). Si/Al(MR): 2.1. pH: 5.

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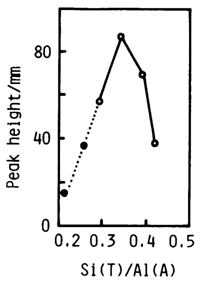

Fig. 3. Variation of exothermic peak height with Si(T)/Al(A) ratio. Initial monosilicic acid concentration: ···●··· 100 ppm, —○— 300 ppm. Reaction time: 5 h. pH: 5.

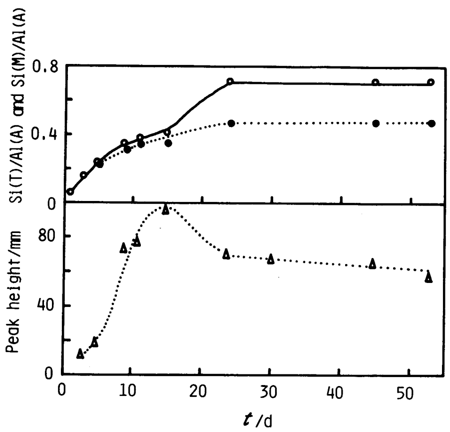

Fig. 4. Variations with time of Si(M)/Al(A) and Si(T)/Al(A) ratios and exothermic peak height. Flowing solution: 150 ppm monosilicic acid solution of pH 5. ···●···: Si(M)/Al(A), —○—: Si(T)/Al(A), ···△···: Exothermic peak height.

was heated at 1000 °C for 5 h and the heated sample was analyzed by powder X-ray diffraction. The diffractogram showed the formation of mullite ($3Al_2O_3 \cdot 2SiO_2$). This result also suggests that the sample is an allophane-like compound.[4)]

The results obtained by the continuous flow method are shown in Fig. 4. The exothermic peak height increased steeply until the Si(T)/Al(A) ratio reached 0.39 and then declined with further increase in the Si(T)/Al(A) ratio. At an early stage of adsorption the Si(T)/Al(A) and Si(M)/Al(A) ratios increased with time, and the Si(T)/Al(A) ratio was nearly equal to the Si(M)/Al(A) ratio below 15 d. Subsequently the Si(T)/Al(A) ratio became larger than the Si(M)/Al(A) ratio with time, indicating that a part of the silicic acid adsorbed on the aluminium hydroxide polymerized.

As shown in Figs. 3 and 4, the exothermic peak height was strongly influenced by the Si(T)/Al(A) ratio of the sample and the maximum peak height occurred at Si(T)/Al(A) ratios of 0.33 and 0.39. These values are similar to that of mullite. In the sample having the 0.33 Si(T)/Al(A) ratio, the largest amount of the allophane-like compound may exist.

The behavior of monosilicic acid adsorbed on aluminium hydroxide can be explained as follows. When monosilicic acid is adsorbed on aluminium hydroxide, the allophane-like compound rapidly forms and the adsorbed monosilicic acid is consumed by the formation of an allophane-like compound until the Si(T)/Al(A) ratio reaches 0.33. Most of the aluminium hydroxide transforms to the allophane-like compound after a short time. Monosilicic acid is still adsorbed on the allophane-like compound formed, and the adsorbed monosilicic acid polymerizes with time above a Si(T)/Al(A) ratio of *ca.* 0.4.

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