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Hydrothermal synthesis of mono-dispersed quartz powders

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The hydrothermal method was first used for crystallization of quartz in the middle of 19th century, and has been developed to grow large single crystals of quartz industrially [1]. On the other hand, the hydrothermal method has been recognized as an excellent method to prepare ceramic powders [2]. Though the large single crystals of quartz are artificially grown due to their application as piezoelectric materials, few studies to get fine powders of quartz have been reported. If a quartz powder with a controlled particle size distribution is prepared, it can be used as a cheap source for abrasives and additives to plastics because quartz has high hardness [3] and the earth's crust consists of a large amount of silicon [4].

Lee *et al.* [5] prepared quartz powders (1–10 μm in size) from amorphous silica by adding seed crystals under hydrothermal conditions (240–450 °C, 100–300 atm). Seed crystals might not be necessary, because homogenous nucleation and crystal growth can be expected under hydrothermal conditions due to the difference in solubility of amorphous silica and quartz. They found that KOH was the most effective mineralizer in various alkali hydroxides and alkali halides. Though they showed that quartz crystals were formed at high temperatures over 260 °C in 0.5 wt% KOH solution, most of the results shown in their report were obtained at 350 or 400 °C. The necessity of high temperatures and KOH solutions are not desirable for industrial preparation. We intended to develop a method to prepare quartz powders with finer particle size under milder hydrothermal conditions using a NaOH solution. In this study, the mono-dispersed fine quartz particles with an average diameter of 0.6 μm were prepared by the hydrothermal reaction in 0.33 M NaOH solutions at 300 °C.

The starting material was the commercial silica gel (Nipsil-VN3, $SiO_2$98.63 wt%, Nippon Silica Industrial Co. Ltd., Japan), which consisted of fine spherical particles with the average diameter of 18 nm. The specific surface area determined by the BET method was 160 m^2/g and the amount of absorbed water was 9.1 wt%. It was used without drying for hydrothermal treatments.

Hydrothermal treatments were carried out in a Hastelloy C lined autoclave with the inner volume of 20 cm^3. The silica gel (0.5–1.5 g) was mixed with a NaOH solution (15 cm^3, 0.1–0.5 M) and ultrasonically dispersed for 15 min. The slurry was placed in the autoclave and heated in an air oven at a desired temperature (220–350 °C) for various reaction times (0–24 h). The content of the autoclave was agitated during hydrothermal treatments by rotating the autoclave in the oven. The heating rate was about 10 °C per minute. After the hydrothermal treatments, the products were washed with water, ultrasonically dispersed in acetone, and then vacuum dried. The crystalline phases of the products were identified by X-ray diffraction (XRD) and their morphology was observed by a scanning electron microscope (SEM).

After a few experiments, the standard condition (Silica gel: 1 g, reaction temperature: 300 °C, reaction time: 12 h, NaOH concentration: 033 M) was selected and one reaction factor was changed from the condition to estimate its effect. The standard condition gave a quartz powder consisting of mono-dispersed fine particles (Fig. 2b).

Fig. 1 shows XRD patterns of the products prepared varying reaction temperature. At 220 °C, low-cristobalite was obtained with low-quartz (Fig. 1a). At higher temperatures over 240 °C (Fig. 1b and c), the products consisted of single phase low-quartz. SEM photographs of quartz powders prepared at different temperatures are shown in Fig. 2. In all cases, mono-dispersed quartz particles were obtained. The particle size of the quartz powder obtained at 240 °C (Fig. 2a) was in the range from 0.3 to 0.9 μm with an average of 0.6 μm and similar to that obtained at 300 °C (Fig. 2b). However, the surface morphology of the particles was different. The particles obtained at 240 °C had rough surface, but those obtained at 300 °C had rounded shape with smooth surface. When the reaction temperature increased to 350 °C (Fig. 2c), the particle size remarkably increased to 1.5 μm.

Fig. 3 shows XRD patterns of the products prepared by varying reaction time. The product obtained by cooling down to room temperature just after the temperature of the autoclave reached 300 °C, consisted of amorphous silica with a very small amount of low-quartz (Fig. 3a). As the reaction time increased to 0.5 h (Fig. 3b), the broad peak of the amorphous silica disappeared and high crystalline low quartz phase was obtained. The rate of crystallization of amorphous silica to low-quartz was very fast. It is concluded that low-quartz directly nucleated at 300 °C and the quartz nuclei grew to larger particles from the amorphous silica. The increase in reaction time did not have a large effect on particle size distribution and morphology.

Fig. 4 shows XRD patterns of the products prepared varying NaOH concentration. When the NaOH concentration was lower than 0.1 M (Fig. 4a), low-cristobalite

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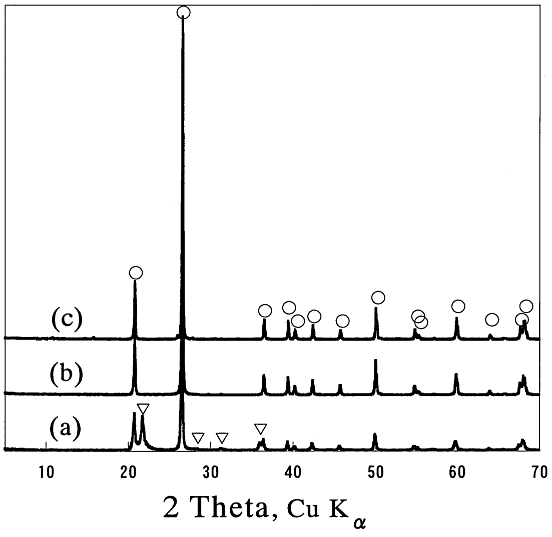

Figure 1 XRD patterns of the products obtained from silica gel of 1 g in 0.33 M NaOH solution by hydrothermal treatments at: (a) 220 °C, (b) 240 °C, and (c) 300 °C for 12 h.

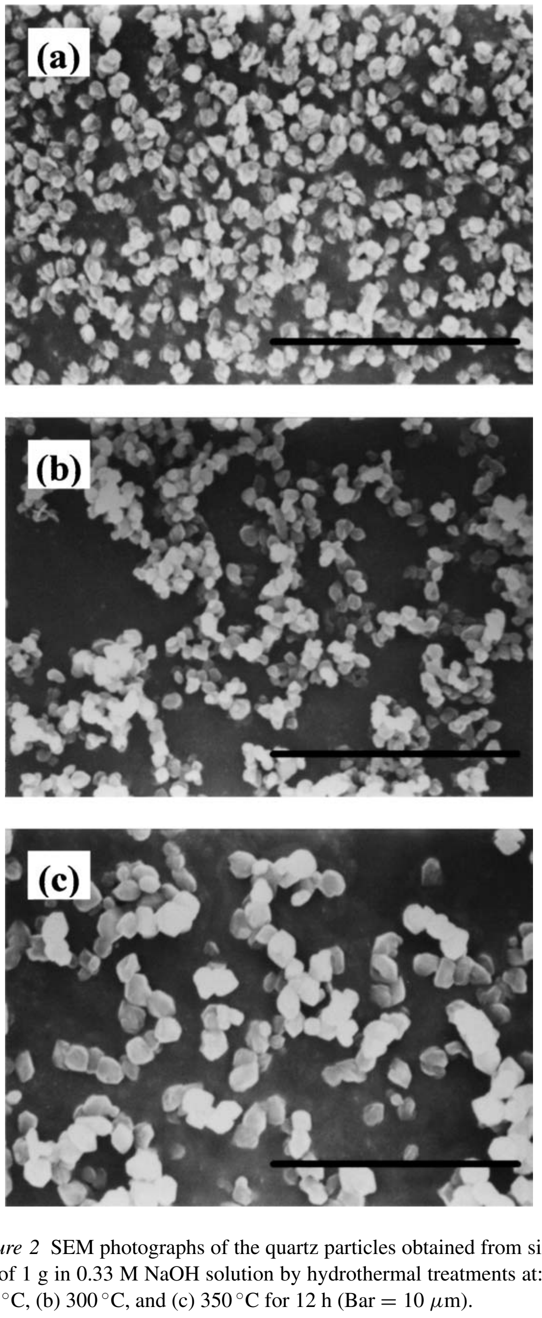

Figure 2 SEM photographs of the quartz particles obtained from silica gel of 1 g in 0.33 M NaOH solution by hydrothermal treatments at: (a) 240 °C, (b) 300 °C, and (c) 350 °C for 12 h (Bar = 10 μm).

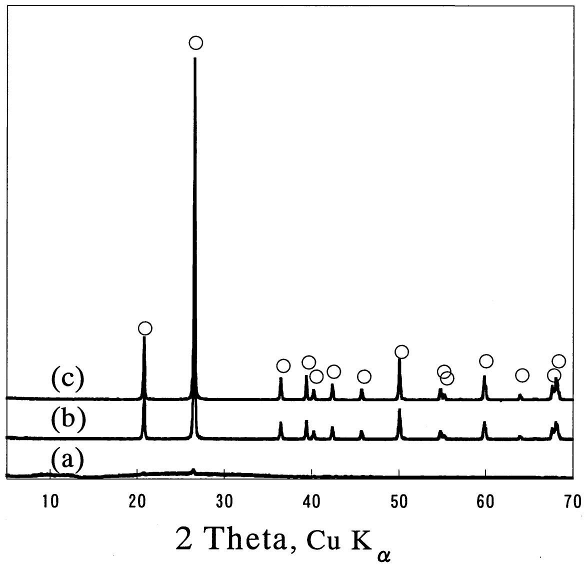

Figure 3 XRD patterns of the products obtained from silica gel of 1 g in 0.33 M NaOH solution at 300 °C for 12 h by varying the reaction times to: (a) 0 h, (b) 0.5 h, and (c) 1 h.

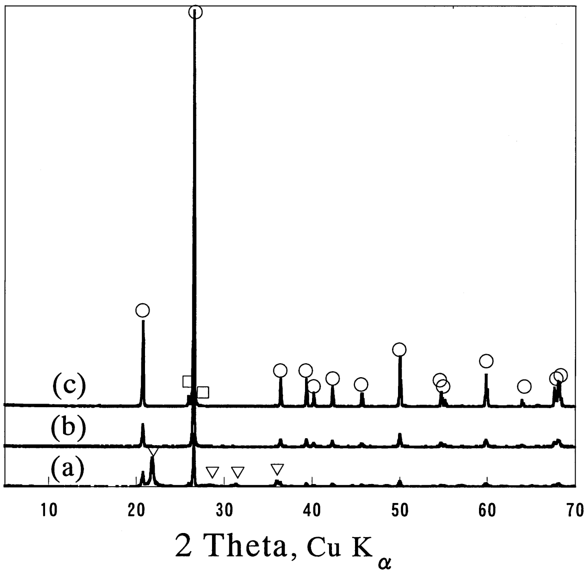

Figure 4 XRD patterns of the products obtained from silica gel of 1 g at 300 °C for 12 h by varying NaOH concentration to: (a) 0.1 M, (b) 0.2 M, and (c) 0.5 M.

crystallized with low-quartz. In the concentrated NaOH solutions over 0.2 M (Fig. 4b and c), the reaction products mainly consisted of low-quartz. The intensity of the peaks of low-quartz produced in 0.2 M NaOH solution (Fig. 4b), was weaker than that in the concentrated NaOH solution (Fig. 4c), which suggested that the product obtained in 0.2 M NaOH solution might include some amorphous silica. In 0.5 M NaOH solution (Fig. 4c), a small amount of the tetragonal phase of SiO_2 was formed with low-quartz. This phase might be formed during cooling to room temperature. The product obtained in 0.2 M NaOH solution (Fig. 5a) consisted of highly agglomerated particles which might include both of the quartz and silica gel particles. As shown in Fig. 2b, the quartz powder obtained in 0.33 M NaOH solution consisted of mono dispersed fine particles. When the concentration of NaOH solution increased to 0.5 M (Fig. 5b), quartz crystals grew larger to 1.8–3.5 μm and were bounded by faceted planes.

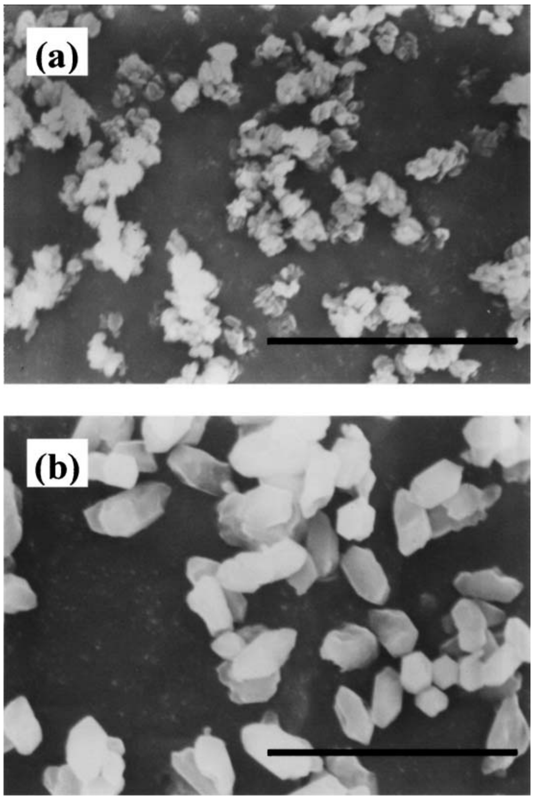

Figure 5 SEM photographs of the quartz particles obtained from silica gel of 1 g in: (a) 0.2 and (b) 0.5 NaOH solution at 300 °C for 12 h (Bar = 10 μm).

When silica gel was hydrothermally treated in a diluted NaOH solution, or at low temperatures, low-cristobalite was formed with low-quartz. Similar results were obtained by Campbell and Fyfe [7]. They hydrothermally treated the ignited silicic acid in a dilute NaOH solution with a concentration from 0.1 to 0.012 M at 245 °C. Though cristobalite first crystallized without quartz by a short time reaction, quartz started to crystallize by a longer time reaction and finally the product became a single phase of quartz. When the concentration of NaOH solutions was lower, longer time was necessary to get the quartz single phase. For example, it took 19 and 140 h to get the quartz single phase in 0.1 and 0.012 M NaOH solution, respectively.

In this study, hydrothermal treatments in a concentrated NaOH solution, or at high temperature, gave larger quartz particles. Under these conditions, it is expected that quartz nuclei are directly formed without formation of cristobalite. Quartz particles underwent dissolution and precipitation by the process of Ostwald ripening [6] and grew larger under these conditions with high solubility of quartz.

Well dispersed quartz crystals were obtained by the reaction of the amorphous silica of 1 g in 0.33 M NaOH solution, independent of reaction temperatures. With a small amount of the amorphous silica (0.8 g), low quartz crystals grew larger but they were aggregated (Fig. 6a). With a large amount of the amorphous silica (1.5 g), fine quartz crystals were hardly aggregated (Fig. 6b). The dispersion of quartz crystals may relate to the ratio of the starting amount of the silica gel and that of a NaOH solution. When these amounts increased together in the same ratio, larger and mono-dispersed quartz particles were obtained (Fig. 6c).

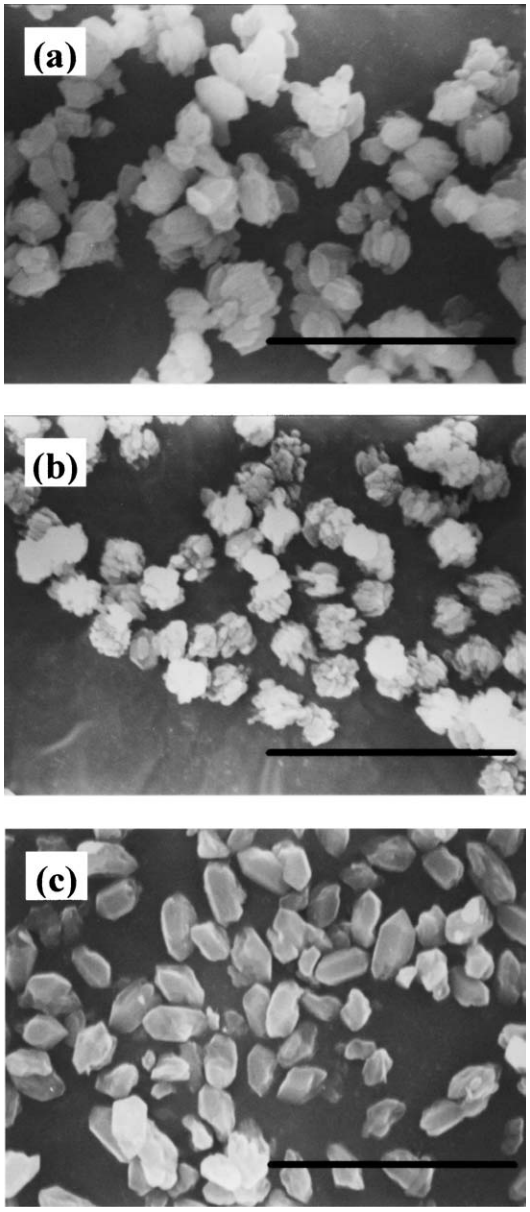

Figure 6 SEM photographs of the quartz particles obtained with different ratios of silica gel and NaOH concentration at 300 °C for 12 h (Bar = 10 μm): (a) Silica gel/concentration = 0.8 g/0.33 M, (b) 1.5 g / 0.33 M and (c) 1.5 g/0.5 M.

It is concluded that mono-dispersed fine quartz particles with a controlled particle size from sub micron to a few micron are formed in a NaOH solution at low temperatures below 300 °C. The results suggest that larger quartz particles might be obtained at higher temperatures in a more concentrated NaOH solution.

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