Crystal Growth of Silicalite and Quartz from Alkaline Solution of Amorphous Silica under Presence of TPA Ion

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TPAイオンを含む非晶質シリカのアルカリ溶液からのシリカライト及び石英の結晶成長

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Silicalite, considered to be a polymorph of SiO₂, was prepared hydrothermally using amorphous silica, tetrapropylammonium bromide (TPA-Br) and NaOH. Silicalite was synthesized in a quartz glass ampoule under the following conditions; [NaOH]/[SiO₂] = 0.2 and [TPA-Br]/[SiO₂] = 0.1. With an increase of [NaOH]/[SiO₂] ratio quartz precipitated gradually instead of silicalite; thus, at 0.9 of [NaOH]/[SiO₂] ratio, the main product was quartz irrespective of the presence of TPA⁺ ion. Several ppm's of aluminium and boron ions were always detected in the crystals. The extra addition of either of the two ions in the starting materials facilitated the formation of silicalite. Silicalite (or ZSM-5 of extra high silica content) is formed in a Pyrex glass ampoule or under the presence of Pyrex glass rods in a silica ampoule, though serious contamination (50-200 ppm) by both ions is unavoidable.

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1. Introduction

Silicalite was synthesized by Flanigen et al. (Union Carbide Co.) in 1978 for the first time and was thought to be one of the polymorphs of SiO₂. The crystal structure of silicalite is topologically related to that of zeolite. It is hydrophobic and organophilic and can absorb organic molecules in the presence of water. Johnson et al. examined thermodynamic properties of silicalite and reported that it is less stable than quartz but more stable than silica glass. They noted also that silicalite has a potential alternative as a reference material for thermochemical measurement on inorganic silicates and silicate minerals because of its ease dissolution in aqueous hydrofluoric acid (application to solution calorimetry).

Silicalite itself has been believed to be aluminium ion free from the preparative condition. However, by 27Al NMR study, it was concluded that small amount of aluminium ion was always included in tetrahedral framework and the difference of silicalite from ZSM-5 (Mobil Oil Co.), synthetic zeolite molecular sieve with limited concentration of aluminium ions, became ambiguous except for the former's extremely low aluminium ion content. Hay et al. investigated 29Si MAS NMR of silicalite, where, silicalite was defined ZSM-5 with [SiO₂]/[Al₂O₃] > 17000. Actually Johnson et al. recognized the presence of 50 ppm aluminium ion in addition to several other metallic impurities by spectrochemical analysis. Unfortunately, the details of physico-chemical properties as well as of preparation of silicalite have not thoroughly been reviewed in the literatures except for a few cases presumably due to a doubt as to “silicalite” as a distinct name of compound and/or its patent. Nevertheless it remained unsolved why the zeolite-like framework is constructed even under the presence of as small amount of as ppm order of aluminium ions. It is important to elucidate the minimum concentration of aluminium ions for the construction of zeolite type crystal structure. It is also interesting to find the best condition of silicalite formation without precipitation of the thermodynamically stable quartz under hydrother-
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2. Experimental

2.1 Synthesis

Instead of fused silica (Cab-o-sil), the original reagent used in the literature, amorphous silica (a-SiO₂) from Nippon Steel Chemical Co. (0.5 µm) was used for preparation. The standard composition of the starting materials per one mol of a-SiO₂ was as follows: 35.2 mol H₂O, 0.115 mol NaOH, 1.37 mol NaCl, and 0.085 mol tetrapropylammonium bromide (TPA-Br), respectively. They were sealed into Pyrex or a silica glass ampoule and inserted into autoclave of stainless steel at 188°C. After 2 days, the powder product was washed by water, dried at 100°-130°C and calcined at 500°C for one day. In some runs, the same starting materials were partitioned into several ampoules in the autoclave and they were sampled consecutively at desired time interval. In order to see the effects of aluminium and boron ions on the yield of the silicalite formation, Al₂O₃, B₂O₃ or Pyrex glass rods (5 mm diameter and 30 mm length) were included into starting mixtures.

2.2 Characterization of silicalite

X-ray powder diffraction (Cu Kα) was applied to identify the silicalite. Figure 1 shows the typical X-ray powder pattern of silicalite obtained in this work. The degree of crystallization was estimated from the peak area over the 2θ range 22°–24° of the diffraction pattern referred to NaCl as an internal standard. A scanning electron microscope (SEM, Akashi ISI-DS 130) was used to see the size as well as direction of crystal growth. Figure 2 shows SEM image of typical silicalite crystals from the standard mixture. It consists of crystals in the form of slab. Contents of aluminium and boron ions were determined by ICP analysis.

3. Results and discussion

3.1 Effects of aluminium and boron ions

Figure 3 represents the effects of aluminium or boron ions on the crystallization of silicalite. When either of the two ions was introduced into the starting mixture, yields of silicalite reached
about 90% within two days at 188°C. When the reaction proceeded in a Pyrex glass ampoule, the similar yield was attained without addition of extra Al₂O₃ or B₂O₃. On the other hand, in a silica glass ampoule under limited supply of the two ions, the degree of crystallization was low (about 60%). In Fig. 4 the degree of silicalite formation was plotted against number of Pyrex glass rods in a silica glass ampoule. In this case the reaction was proceeded over 5 days. The yield of silicalite increased, whereas the formation of quartz was suppressed, with an increase of the number of glass rods. These two set of data reveals clearly that the presence of aluminium or boron ions is essential for the formation of silicalite. In Table 1 analytical results are shown. The name “silicalite” may not even be adequate for the samples No. 1 to No. 6 because of high content of the two ions. Even when contamination of aluminium or boron ions were avoided as far as possible, several ppm of Al and B ions were always observed, which might be brought from the reagents. Here it is to be noted that considerable quantity of boron ion was included in silicalite, when one uses the Pyrex glass. The effects of boron ion seems rather predominant, SEM observation showed that silicalite crystals were formed on the surface of the Pyrex glass rod. This indicate that Pyrex glass may offer the site suitable for silicalite nucleation.

### 3.2 Kinetics of the silicalite formation

Figure 5 shows the time dependence of the silicalite formation when Pyrex and silica glasses were used. When reaction was conducted in a Pyrex glass ampoule, a retention time is shorter and silicalite crystals could be obtained without exception after 40 h at 188°C. On the other hand, the reaction could not be complete in a silica glass ampoule under the same condition. It was also shown that in the crystallization of ZSM-5 the retention time and reaction rate become longer and slower with an increase of [Si]/[Al] ratio.

The Avrami equation was applied to this kinetic behavior. The degree of crystallization can be expressed by the following equation:

\[
X = 1 - \exp(-kt^n)
\]  

(1)

where \(X\) is degree of the crystallization, \(k\) is the reaction constant, \(t\) is time and \(n\) is constant which determines the dimension of the crystal growth. Taking the double logarithm after rearrangement of Eq. (1), one obtains the following equation:

\[
\ln \ln \left(1/(1-X)\right) = n \ln t + \ln k
\]  

(2)

If the left-hand side of Eq. (2) is plotted against \(\ln t\), one finds the growth mechanism of the crystallization from the slope, \(n\). Within the limit of the experimental errors the values of both lines

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**Table 1.** The content of Al and B ions in the silicalite cited in Figs. 3 and 4.

<table>
<thead>
<tr>
<th>No.</th>
<th>Al₂O₃ (added mol)</th>
<th>B₂O₃</th>
<th>Al (found, ppm)</th>
<th>B (found, ppm)</th>
</tr>
</thead>
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<tr>
<td>1</td>
<td>0.0065</td>
<td>-----</td>
<td>2040</td>
<td>20</td>
</tr>
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<td>0.032</td>
<td>-----</td>
<td>19800</td>
<td>135</td>
</tr>
<tr>
<td>3</td>
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</tr>
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<td>0.0334</td>
<td>12000</td>
<td>36200</td>
</tr>
<tr>
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</tr>
<tr>
<td>7</td>
<td>0.060</td>
<td>0.0334</td>
<td>12000</td>
<td>36200</td>
</tr>
</tbody>
</table>

* Partly including unreacted Al₂O₃

** Pyrex: SiO₂ (81 wt. %), B₂O₃ (13 %), Al₂O₃ (2 %), Na₂O (4 %)

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**Fig. 4.** Effect of Pyrex glass rod on the formation of silicalite (●) and quartz (■). 188°C, 2 days.

**Fig. 5.** The dependence of silicalite yield on the reaction time.

○: in Pyrex glass ampoule, ●: silica ampoule. 188°C.
are approximately 3, which indicate that the crystal growth is three dimensional in nature in accordance with the shape of crystal.

### 3.3 Effects of [NaOH]/[SiO$_2$] ratio

Figure 6 shows the effect of NaOH concentration in the starting materials. Here, the molar ratio of reagents other than NaOH are kept the same as cited previously. With an increase of NaOH content, the yields of silicalite increased and then decreased through maximum around 0.2 of [NaOH]/[SiO$_2$] ratio. On the other hand, the formation of quartz crystal became pronounced with an increase of NaOH concentration. This coincided with the recent results on the formation of ZSM–5 from cristobalite rock. The resulting crystal radii became extremely small (5 μm). The alkali dependence of the crystallization could be explained by the solubility of amorphous silica under the hydrothermal condition. A suitable quantity of NaOH is required; thus only at an appropriate concentration of amorphous silica, silicalite might be precipitated under the presence of TPA$^+$ ion. On the other hand, when the solution is highly basic, solubility becomes large and thermodynamically stable quartz are then formed instead of silicalite. In addition, nuclei of silicalite precursor appear homogeneously over the whole solution. The crystal size then becomes small and homogeneous. The contents of aluminium and boron ions in silicalites cited in Fig. 6 were 6–22 and 9–17 ppm respectively.

### 3.4 Effects of [TPA-Br]/[SiO$_2$] ratio

TPA$^+$ ion is one of the most essential reagent to prepare silicalite. Figure 7 shows the effects of TPA$^+$ ion on the crystallization, where the syntheses were carried out at three temperatures; i.e. 188°C, 198°C and 205°C. At three temperatures, the maximum yields were obtained at 0.085 of [TPA-Br]/[SiO$_2$] ratio. Quartz was also crystallized in the case of low TPA$^+$ concentration and preferably at higher temperature. Silicalite could not be formed without addition of TPA$^+$ ion. The analytical results of Al and B in this series of silicalite are as follows; 6–14 ppm and 8–30 ppm, respectively.

### 3.5 Effects of [NaCl]/[SiO$_2$] ratio

The total yields could not be distinguished between with and without NaCl in the starting mixture. However, it was observed also that the shape of silicalite crystal was somewhat dependent on the presence of Na$^+$ ion; thus the SEM observation showed that direction of the crystal growth is not spherical in the case of low Na$^+$ content in the starting mixtures.

### 3.6 Sequence of silicalite and quartz formation

When the presence of aluminium and boron ions were limited, quartz was formed, especially at higher reaction temperature. Heydemann$^{11}$ reported that quartz was formed from the highly basic solution at 100°–250°C via SiO$_2$–$x$ and cristobalite. In the present experiment the presence of cristobalite crystal could not be detected in the X-ray diffraction pattern. However unidentified crystal (perhaps SiO$_2$–$x$) was detected in some cases. Thus the crystallization should proceed written by the following sequence:

\[
\text{silica} \xrightarrow{\text{OH}} \text{(SiO}_2\text{–}x) \xrightarrow{\text{TPA}^+ \text{ and } \sim 5 \text{ ppm Al}^+ \text{ or } \text{B}^+} \text{quartz}
\]

**Fig. 6.** The dependence of silicalite (●) and quartz (■) formation on the [NaOH]/[SiO$_2$] ratio. 188°C, 2 days.

**Fig. 7.** The yield of silicalite and quartz formation as functions of the [TPA-Br]/[SiO$_2$] ratio.

Silicalite transforms into cristobalite at higher temperature (∼900°C), as observed by DTA experiment.

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References