NOTE

HYDROTHERMAL SYNTHESIS OF SEPIOLITE

Sepiolite is a fibrous magnesium silicate with a well characterized structure (Bailey, 1980; Newman & Brown, 1987), a feature of which is the presence of tunnels 3.7 Å × 10.6 Å running along the fibrous structure. Consequently, the surface area of sepiolite is as large as that of zeolites and silica gels. Although the synthesis of sepiolite has been attempted by many researchers (Glass, 1936; Hast, 1956; Wiegmann & Horte, 1960; Siffert & Wey, 1962; Wollast et al., 1968; Nesterchuk & Makarova, 1973; Abtahi, 1985), it has not been synthesized on a practical scale. This seems to be due to the fact that (1) sepiolite is unstable under hydrothermal conditions above 300°C (Frank-Kamenetskii et al., 1970, 1972; Otsuka et al., 1974; Güven & Carney, 1979; Komarneni, 1989); (2) sepiolite is also unstable in either acidic or alkaline solutions at elevated temperatures (Golden et al., 1985); (3) smectites instead of sepiolite crystallize more easily from magnesium silicate gel in alkaline solutions.

We have investigated the crystallization reaction of magnesium silicate gels under hydrothermal conditions and found that crystallization of magnesium silicate gel to sepiolite was induced by the addition of sepiolite seeds.

Experimental

The sepiolite used as seeds was from Anatolia, Turkey (Fukushima & Shimosaka, 1987). Polyvinylalcohol (Mw = 22,000) and polyallylamine hydrochloride (Mw = 10,000) were purchased from Wako Pure Chem. Ind. and Nittoboseki Co., respectively.

Preparation of magnesium silicate gel. Sodium orthosilicate (Nacalai Tesque Co.) (15.12 g) was dissolved in 840 ml of deionized water, acidified to pH 3.0 by the addition of 2 ml hydrochloric acid and 48.4 g magnesium chloride hexahydrate (Wako Pure Chem. Ind.) added. Aqueous sodium hydroxide (1 M, 41.3 ml) was added to the resultant solution at the rate of 0.3 ml/min, and during this addition the solution became turbid due to precipitation of magnesium silicate gel. The suspension was aged at room temperature for one day and the gel was collected by suction filtration, thoroughly washed with deionized water and used for the hydrothermal reactions.

The Si : Mg ratio in the gel can be controlled by changing the amount of sodium hydroxide added (Mizutani et al., 1990). The Si : Mg ratio in the gel was determined by atomic absorption spectroscopy, and a gel with a ratio of 1.9 was used.

Hydrothermal crystallization of the gel. The magnesium silicate gel (0.3 g, dry weight) and the sepiolite seed were suspended in 60 ml of deionized water and the suspension was probe-sonicated with the microtip of a Sonifier B-12 (Branson Sonic Power Co.) for 3 min. The suspension was then heated at 100–200°C for 10–100 h in a Teflon-lined stainless steel bottle (100 ml volume). After the reaction mixture was cooled to room temperature, a precipitate was collected by suction filtration, washed with deionized water and dried at 60°C in vacuo overnight.

Characterization of hydrothermal reaction products. Infrared (IR) spectra were recorded on a JASCO FT/IR-5M spectrometer. X-ray diffraction (XRD) data were obtained using a Rigaku RAD-B diffractometer with Co-Kα radiation. For quantitative determination of
sepiolite in the products, a calibration curve of XRD intensities vs. sepiolite contents was obtained by measuring XRD patterns of mixtures of silicon powder (National Bureau of Standards, 640b), Turkish sepiolite, and the dried magnesium silicate gel. Differential scanning calorimetry (DSC) curves were recorded on a Seiko DSC 10 at a heating rate of 5°C/min.

Results and discussion

The XRD patterns of the products heated at 100°C, 150°C and 200°C as well as the starting gel-sepiolite mixture are shown in Fig. 1. As the reaction temperature was raised to 200°C, the XRD peaks of sepiolite intensified, indicating that the magnesium silicate gel had crystallized as sepiolite. In the XRD pattern of the product prepared at 200°C, the 110 peak of sepiolite at 12 Å did not shift, and as no peak appeared in 20-12 Å region upon ethylene glycol treatment, formation of smectites was negligible.

The hydrothermal reaction was also carried out at 250°C and this resulted in the peak at 4-5 Å being stronger than that at 4-3 Å. As smectite shows a strong reflection at 4-6 Å (020, 110), this suggests that the conversion of sepiolite to smectite occurs at 250°C. This observation is consistent with the results reported by Güven & Carney (1979) who described the hydrothermal transformation of sepiolite to smectite (stevensite). These data suggest that the transformation of sepiolite to smectite is the most undesirable side reaction in the synthesis of sepiolite.

The amounts of sepiolite in the products were determined by measuring the XRD peak intensities, and for some of the products the amounts were also determined from the endothermic peak area at ~300°C on the DSC curves. The yields of sepiolite determined from the XRD method using Si as an internal standard are listed in Table 1. About 10-20% of the starting gel crystallized to sepiolite in these runs. The sepiolite content determined from the DSC peak area in the 200°C run was 32%, in good agreement with the amount determined by XRD.

The effect of addition of magnesium sulphate to the aqueous suspension was to accelerate the formation of sepiolite (Fig. 2). Table 2 shows the effects of several additives on the yields of sepiolite; magnesium sulphate and magnesium chloride improved the yields, whereas the other additives had an adverse effect. The XRD patterns of the products indicated that the addition of sodium fluoride, magnesium acetate, polyallylamine hydrochloride accelerated the transformation of sepiolite seed to smectite.

Table 1. Formation of sepiolite by hydrothermal reaction (50 h) of magnesium silicate gel.

<table>
<thead>
<tr>
<th>Reaction temp. (°C)</th>
<th>Sepiolite content (%)</th>
<th>% Growth</th>
</tr>
</thead>
<tbody>
<tr>
<td>r.t</td>
<td>19.5</td>
<td>0</td>
</tr>
<tr>
<td>100</td>
<td>20.0</td>
<td>2</td>
</tr>
<tr>
<td>150</td>
<td>29.1</td>
<td>49</td>
</tr>
<tr>
<td>200</td>
<td>34.0</td>
<td>74</td>
</tr>
</tbody>
</table>

a The initial gel-seed mixture contained 19.5 wt% sepiolite seed.

b wt% synthesized sepiolite with respect to sepiolite seed.


**Fig. 1.** XRD patterns of (a) initial gel-sepiolite mixture, and the hydrothermal reaction products from magnesium silicate gel and sepiolite treated hydrothermally at (b) 100°C, 60 h, (c) 150°C, 95 h, (d) 200°C, 40 h.

**TABLE 2.** Effects of additives on the yields of sepiolite (150°C, 95 h).

<table>
<thead>
<tr>
<th>Additive</th>
<th>Concentration</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>—</td>
<td>49</td>
</tr>
<tr>
<td>MgSO₄</td>
<td>0.5 M</td>
<td>76</td>
</tr>
<tr>
<td>MgCl₂</td>
<td>0.5 M</td>
<td>67</td>
</tr>
<tr>
<td>NaF</td>
<td>0.5 M</td>
<td>5</td>
</tr>
<tr>
<td>Mg(OAc)₂</td>
<td>0.5 M</td>
<td>—</td>
</tr>
<tr>
<td>Polyvinylalcohol</td>
<td>3 wt%</td>
<td>—</td>
</tr>
<tr>
<td>Polyallylamine hydrochloride</td>
<td>3 wt%</td>
<td>—</td>
</tr>
</tbody>
</table>

* Decomposition of sepiolite seed occurred.
For comparison, the hydrothermal reaction was carried out in the absence of sepiolite seed. The XRD patterns and IR spectra of the gel heated at pH 8–10 at 200°C for 50 h are different from those of sepiolite, and are similar to those of smectite. The DSC curve of the product showed no endothermal peak around 300°C. These results indicated that the gel did not convert to sepiolite in the absence of sepiolite seed.

Conclusions

(1) Hydrothermal treatment of magnesium silicate gel at 150–200°C in the presence of sepiolite seed yielded sepiolite, as confirmed by XRD and DSC.

(2) Hydrothermal treatment of magnesium silicate gel at 200°C at pH 8–10 in the absence of sepiolite seed yielded crystals with different XRD and DSC characteristics from sepiolite.

(3) The hydrothermal conditions of sepiolite formation are determined primarily by the hydrothermal stability of sepiolite.
REFERENCES


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