Preparation of Metal-Silicate Microballoons Based on Ion Exchange through Liquid Surfactant Membrane

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Abstract
Inorganic microballoons composed of metal-silicate shell were prepared by ion exchange between internal Na⁺ and external metal cation through liquid surfactant membrane. The effects of metal species and salts concentration on the state of microballoons were examined for a series of alkaline earth and transition metals. The mechanism of balloons formation was discussed based on the ion releasing behavior and the composition of particles.

1 Introduction
Recently, the spherical particles with micron size, called as microparticles, are used in various fields. The microparticles with inner hollow sphere are called as microballoons and applied as a storage space. Inorganic microballoons composed of inorganic shell have excellent advantages such as the endurance against high temperature and organic solvents compared with the conventional organic microballoons made of polymer. Various techniques for preparing inorganic microballoons have been proposed such as mechanical method, solution reaction methods, spray drying methods and so on.[1,2,3] The interfacial reaction method developed by Nakahara applied inorganic precipitation reactions which yield the insoluble shell along the interface between oil and internal aqueous solutions.[4] Ion exchange occurs through a liquid membrane between internal and external aqueous phases according to the mechanism similar to the extraction with liquid surfactant membrane processes.[5,6] In preparing inorganic microballoons by this method, operating conditions influence the particle morphology significantly. It has not been certified under which conditions a hollow particle is formed. In this study, the effects of preparing conditions such as metal species and salt concentrations on the formation of metal-silicate microballoons are discussed to clarify the formation mechanism and stoichiometry.
2 Experimental

Figure 1 shows the experimental procedure to prepare calcium silicate microballoons as an example. An internal aqueous sodium silicate (Na$_2$O·nSiO$_2$, n = 3.2) solution and an organic solution, prepared by dissolving Span 80 as a surfactant and D2EHPA (Di-2-ethylhexylphosphoric acid) as a cation carrier in kerosene, were mixed in a homogenizer at 2500 rpm. W/O emulsion prepared was then poured into an external aqueous solution containing CaCl$_2$ and stirred gently at 200 rpm in a tank. The salt concentrations in both aqueous solutions were made equal to prevent the swelling of emulsion. Microballoons formed were washed with methanol and dried for scanning electron microscopy observations. A wide variety of metal silicates microballoons were prepared by changing the concentration of salts, surfactant and cation carrier.

3 Results and discussion

3.1 Identification of inner structure of microparticles

The influence of preparation conditions on the formation of spherical microballoons was examined by employing various alkaline earth and transition metals. Figures 2 and 3 show the SEM pictures of cross-section of calcium and manganese silicate microballoons, respectively. The particles prepared by the interfacial reaction method are almost spherical in shape with smooth surface and hollow space inside uniform shell. Table 1 summarizes the particle size and state of microballoons formation for various metal-silicate microballoons. The column of “Evaluation” expresses the state of microballoons formation based on the following observation. +++: Particles of over 80 % are sphere. ++: The fraction of spherical particles is from 80 to 50 %. +: The fraction of spherical particles is from 50 to 20 %. -: The fraction of spherical particles is below 20 %. Even though spherical particles were formed, the inner space was not hollow but filled up in a few cases. This is probably because metal
cations diffused to the central zone of internal aqueous droplets before a hard shell was formed on the interface between oil and internal aqueous phases by ion exchange reaction. It was also found that too high salt concentration made an emulsion unstable and inhibited microballoons formation. In general, the salt concentration suitable for preparing stable microballoons was high for transition metal silicates compared with that for alkaline earth metal silicates. The ratio of Na\(^+\) exchanged with metal cation versus initially loaded Na\(^+\) in the internal aqueous solution was close to 100% for alkaline earth metal silicates, whereas it was low in transition metal silicates. Probably the penetration of metal cations through the silicate shell might be suppressed due to hard structure of metal silicate and further growth of shell stopped.

### 3.2 Mechanism of particles formation

Figure 4 shows the time course of cation concentrations after pouring the W/O emulsion into external aqueous solutions of alkaline earth metal chlorides. With the elapse of reaction time, the concentration of metal cations in external aqueous solution decreased smoothly, while Na\(^+\) increased lately compared with the decrease of metal cations. This behavior is explained as follows. At first, a metal cation penetrates into internal aqueous solution through oil...
membrane so as to make the concentration in both aqueous solutions equal. The metal cation transported into internal aqueous solution is exchanged with Na\(^+\) of sodium silicate and metal silicate formed precipitates at the periphery of the interface between oil and internal aqueous phases. After the concentration of Na\(^+\) released becomes high in the internal aqueous solution, Na\(^+\) is gradually transported to the external aqueous solution. Thus, the increase of Na\(^+\) occurred lately than the decrease of metal cation. It is also observed that the decreasing rate of metal cation increases with the order of Mg > Ca > Sr > Ba, which is also true for the increasing rate of Na\(^+\). From this finding, it is suspected that the overall ion exchange rate decreases with the increase of metal cation size for alkaline earth metals. Since the rate of ion exchange between Na\(^+\) and metal cation at internal aqueous phase is considered to be fairly high, the gradual decrease and increase of cations concentration shown in Fig. 4 support the assumption that particle formation process is controlled by the diffusion of cation and carrier complex through oil phase from the outer periphery to the core of W/O emulsion drops.

3.3 Composition of microballoons

The composition of metal-silicates microballoons was determined by three ways, that is, based on Na\(^+\) released to the external aqueous solution, EDX observations and fluorescence X-rays analysis. Table 3 shows the composition of calcium silicate microballoons by the relative fraction of Na, Ca, and Si. From these comparison, the fractions of elements calculated by mass balance and those observed by EDX measurement and fluorescence X-rays analysis agreed well. Also, the fractions of elements at both outer surface and cross-section of microballoons showed no significant difference at reaction times of 180 and 300 min. Therefore, it appears that the composition of inorganic shell formed is almost uniform during the reaction.

<table>
<thead>
<tr>
<th>Element</th>
<th>Reaction time [min]</th>
<th>180</th>
<th>300</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Based on Na(^+) released</td>
<td>EDX observation</td>
<td>Fluorescence X-rays analysis</td>
</tr>
<tr>
<td>Na</td>
<td>1.9</td>
<td>3.1</td>
<td>4.0</td>
</tr>
<tr>
<td>Ca</td>
<td>23.1</td>
<td>25.1</td>
<td>25.1</td>
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<tr>
<td>Si</td>
<td>74.9</td>
<td>71.8</td>
<td>70.9</td>
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</table>

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References