Synthesis of ceramics in MO_{n/2}-SiO_2 systems through sol-gel processing under coexistence of polyethylene glycol and in vitro evaluation of their bioactivity

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Sol-gel processing from tetraethoxysilane (TEOS) under coexistence of polyethylene glycol (PEG) allows controlled morphology of the formed silica because of the phase separation during the polycondensation of the hydrated sol. The presence of PEG controlled the morphology effectively in preparation of the ceramics, even in the CaO–SiO_2 binary system, starting from TEOS and Ca(NO_3)_2. In the present study, some ceramics were prepared using the MO_{1/2}-SiO_2 binary systems, where M is given as Na\(^+\) (n = 1), Mg\(^{2+}\) (n = 2) and Al\(^{3+}\) (n = 3), through sol-gel processing in the presence of PEG, to compare the compositional changes in the morphology of the ceramics. In the case of NaO_{1/2}-SiO_2, the framework size increased remarkably with increasing amounts of Na\(^+\) in the starting compositions up to 30 mol%, while continuous pores of approximately 10 \(\mu\)m were observed at 5 mol% of Na\(^+\). In the case of MgO-SiO_2, the framework size increased with increasing amounts of Mg\(^{2+}\) up to 20 mol% in the starting composition. Aggregation of particles with approximately 3 \(\mu\)m in size was observed at 25 mol% and more. The trend in morphological change with addition of Mg\(^{2+}\) was quite similar to that with Ca\(^{2+}\). With AlO_{1/2}-SiO_2, particles were obtained when the starting composition was more than 10 mol% Al\(^{3+}\). The size of the particles appeared to decrease with increasing amounts of Al\(^{3+}\). The morphology and phase separation behavior are strongly affected by the charge value of the metal ions, because the number of non-bridging oxygens coordinated to the metal ion increased with increasing charge value in the sol-gel processing. A specimen prepared with starting composition 20NaO_{1/2}·80SiO_2 and heated at 600°C formed hydroxyapatite on the particle surfaces within 7 d after soaking in a simulated body fluid (SBF), suggesting a potential for bioactivity on application of bone repair.

Key-words: Sol-gel processing, Silicate, Polyethylene glycol, Morphology

1. Introduction

Sol-gel processing has been widely studied for the production of silica particles and porous ceramics from tetraethoxysilane (TEOS). Nakaniishi and his colleagues\(^1,2\) reported that silica gel with controlled size and morphology can be synthesized using sol-gel processing in the presence of polyethylene glycol (PEG). The morphology of the synthesized silica gel was governed by phase separation in solutions containing water-soluble polymers during the polycondensation that forms the siloxane network.

We expected that sol-gel processing in the presence of PEG could be applied to fabrication of bioactive ceramic particles, because calcium silicate is reported to act as a material that could induce bone-like apatite deposition on its surface after exposure to body fluids, and because of results in osteoconduction through the surface bone-like apatite layer. Osteoconduction, the so-called bioactivity of ceramics for bone repair, is the property whereby newly formed bone tissue grows directly on the surface of materials implanted in bone defects, and hence may be useful in assessing novel biomaterials for bone reconstruction. We have previously reported the preparation of calcium silicate with a form of micrometer- and nanometer-sized particles, through a modified process starting from TEOS and Ca(NO_3)_2.\(^3\) The sol-gel behavior in the TEOS-Ca(NO_3)_2-PEG system shows a decrease in gelation time with increasing Ca(NO_3)_2 in the starting composition. The compositional range in which interconnected pore structures could be fabricated in the TEOS-Ca(NO_3)_2-PEG was smaller than that for TEOS-PEG. This suggests that additives for producing metal oxides to modify the siloxane network strongly affect the morphology of the resultant gels. However, the effects of such additives have not been investigated in sol-gel processing in the presence of PEG.

This study focuses on the compositional dependence of the structural changes of silica gels after incorporation of some types of metal oxides, through sol-gel processing in the presence of PEG. Ceramics were prepared from MO_{1/2}-SiO_2 binary systems, where M may be Na\(^+\) (n = 1), Mg\(^{2+}\) (n = 2) and Al\(^{3+}\) (n = 3), using sol-gel processing in the presence of PEG, to compare the composition-based changes in the morphology of the resulting ceramics. The potential for bone-like apatite formation was also preliminarily evaluated in vitro using the simulated body fluid (SBF) proposed by Kokubo et al.\(^4,5\) The microstructure and characteristics of the materials were investigated with comparisons to those of the CaO–SiO_2 system.
The binding energy of O 1s of the specimens was measured.

Nacalai Tesque Inc., Japan

7.46–4.76 cm³ for AlO₃

drante glycol

Table 1

Table 1. Starting Compositions of Solutions Containing Metal Nitrate, TEOS and PEG

<table>
<thead>
<tr>
<th>Sample</th>
<th>Metal nitrate</th>
<th>TEOS</th>
<th>PEG/TEOS</th>
</tr>
</thead>
<tbody>
<tr>
<td>No metal</td>
<td>0</td>
<td>100</td>
<td>0.002</td>
</tr>
<tr>
<td>5M95Si</td>
<td>5</td>
<td>95</td>
<td>0.002</td>
</tr>
<tr>
<td>10M90Si</td>
<td>10</td>
<td>90</td>
<td>0.002</td>
</tr>
<tr>
<td>15M85Si</td>
<td>15</td>
<td>85</td>
<td>0.002</td>
</tr>
<tr>
<td>20M80Si</td>
<td>20</td>
<td>80</td>
<td>0.002</td>
</tr>
<tr>
<td>25M75Si</td>
<td>25</td>
<td>75</td>
<td>0.002</td>
</tr>
<tr>
<td>30M70Si</td>
<td>30</td>
<td>70</td>
<td>0.002</td>
</tr>
</tbody>
</table>

TEOS: tetraethoxysilane, PEG: polyethylene glycol.

xM(100–x)Si: x (Metal nitrate) (100 – x) (TEOS) in molar ratio at starting compositions.

M: Na, Mg, Al

2. Experimental

2.1 Synthesis of the specimens using sol–gel processing

Tetraethoxysilane (TEOS, Si(C₂H₅O)₄, Nacalai Tesque Inc., Japan) was used as a silica source. Some metal nitrates such as sodium nitrate (NaNO₃), magnesium nitrate tetrahydrate (Mg(NO₃)₂(4H₂O) and aluminum nitrate enahydrate (Al(NO₃)₃(9H₂O) were purchased as metal sources from Nacalai Tesque Inc., Japan. Nitric acid (HNO₃, Nacalai Tesque Inc., Japan) was used as a catalyst. Polyethylene glycol (PEG, Aldrich, USA) with a molecular weight of 10,000 was used. All the chemicals were used for the preparation of the gels without further purification. The starting compositions for preparation of the gels are summarized in Table 1.

All the gels were prepared using methods described previously. PEG and metal nitrates were dissolved in appropriate amounts of distilled water (7.71–4.76 cm³ for NaO₁₂–SiO₂ gels, 7.54–5.27 cm³ for MgO–SiO₂ gels and 7.46–4.76 cm³ for AlO₂–SiO₂ gels), and 6% mass% nitric acid solution (0.56–0.41 cm³) was added. Then TEOS was added to the aqueous solution with vigorous stirring. After stirring for 20 min, the resultant solution was transferred into a polystyrene square case (10 × 6.5 × 2.8 cm³), with its top tightly sealed, and then kept at 40°C for 1 d for gelation and aging. The gelation time was determined by simply tilting the container to discover the time at which the bulk fluidity of the solution was lost. The wet gel obtained was immersed in distilled water for washing for 3 h to remove PEG. The distilled water was renewed every 1 h. The wet gel was then dried at 40°C for 7 d and then heated at 600°C for 2 h.

Crystalline phases of the specimens were analyzed by X-ray diffraction (XRD, RINT PC 2100, Rigaku Co., Japan). The binding energy of O 1s of the specimens was measured using an X-ray photoelectron spectrometer (XPS, JPS–9000MC, JELOL, Japan). In the XPS measurements, AlK₀X-rays were used as an excitation source. The measured binding energies were corrected with reference to the binding energy of C 1s (284.6 eV) of the hydrocarbon adsorbed on the sample surfaces. The morphology of the prepared specimens was observed using a scanning electron microscope (SEM, JSM5600, JELOL Ltd., Japan), after coating the specimens with platinum. To analyze the metal content of the gels after heating at 600°C for 2 h, elemental characterization was carried out using energy-dispersive spectroscopy (EDS, EX–54140, JELOL Ltd., Japan).

2.2 In vitro evaluation of bioactivity

Formation of a bone-like apatite layer in the simulated body fluid proposed by Kokubo and his colleagues was examined for some specimens to evaluate the osteoconduction potential of the materials. Rectangular specimens with dimensions of 10 × 10 × 2 mm³ were cut from the bulk after heat treatment at 600°C. The specimens were then soaked in 30 cm³ of a simulated body fluid (SBF, Na⁺ 142.0, K⁺ 5.0, Mg²⁺ 1.5, Ca²⁺ 2.5, Cl⁻ 147.8, HCO₃⁻ 4.2, HP0₄²⁻ 1.0, SO₄²⁻ 0.5 mol m⁻³) with ion concentrations nearly equal to those of human blood plasma with pH 7.25 at 36.5°C. After the specimens were soaked in SBF for predetermined periods of 1 and 7 d in the incubator at 36.5°C, they were removed from the SBF, and gently washed with distilled water and then dried at room temperature. The surface structures of the specimens were analyzed by XRD. The surface morphology of the specimens was observed under SEM.

3. Results

All the prepared solutions remained transparent during stirring for 20 min, and there were no appearances of precipitates. Figure 1 shows the gelation times of the solutions, when they were prepared without or with the presence of PEG. When the solution was prepared without PEG, the gelation time of the solution decreased with increasing the added amounts of magnesium (Mg²⁺) and aluminum (Al³⁺) increased, but increased with increasing sodium (Na⁺). The decreasing degree of gelation time of the Al³⁺ added solution is larger than that of the Mg²⁺ added solution. When the solutions were prepared with PEG present, the gelation time of the Na⁺ added solution also decreased with increasing amounts of Na⁺ in the starting composition. The gelation times of Mg²⁺ added solutions and Al³⁺ added solutions decreased with increasing amounts of Mg²⁺ and...
Al$^{3+}$ with the similar degree of decreases, while the decrease in gelation time for the Na$^+$ added solution was smaller than those of the Mg$^{2+}$ and Al$^{3+}$ added solutions.

After gelation and aging, all the gels were white opaque and crack-free, irrespective of their starting compositions. The specimens prepared with the addition of sodium nitrate looked partially black after heating at 600°C. Figure 2 shows SEM photographs of the NaO$_{1.2}$–SiO$_2$ specimens after heating at 600°C for 2 h. It can be seen from Fig. 2 that the size of the frameworks and particles of the specimens prepared with sodium nitrate increased with increasing sodium content up to 30 mol% Na$^+$. It is evident that the size of the frameworks increased remarkably with increasing amounts of Na$^+$ in the starting compositions from 10 mol%, while continuous pores of approximately 10 μm were observed at 5 mol% Na$^+$. In a previous study on the effect of calcium nitrates (Ca(NO$_3$)$_2$·2H$_2$O), the aggregation of spherical particles could be obtained with the addition of 25% calcium content in the CaO–SiO$_2$ system. In contrast, spherical particles could not be obtained with the addition of sodium nitrate in the range of starting compositions from 0 to 30% molar ratio in the NaO$_{1.2}$–SiO$_2$ system.

Figure 3 shows SEM photographs of the MgO–SiO$_2$ specimens after heating at 600°C for 2 h. The framework and particle sizes increased with increasing magnesium content. Aggregation of particles to sizes of approximately 3 μm was observed at 25 mol% and more in the MgO–SiO$_2$ system, while an interconnected porous structure was observed for compositions of less than 20%. The trend in morphological change with the addition of Mg$^{2+}$ was quite similar to that with Ca$^{2+}$. Figure 4 shows SEM photographs of the AlO$_{1.2}$–SiO$_2$ specimens after heating at 600°C for 2 h. The interconnected porous structure changed to the aggregation of particles by addition of aluminum nitrate at 10% and more in the
Al\textsubscript{2}O\textsubscript{3}/SiO\textsubscript{2} system. Particles were obtained with starting compositions of more than 10 mol\%. The size of the particles appears to decrease slightly with increasing amounts of Al\textsuperscript{3+}.

From these morphological observations, the structures of the formed gels varied from porous products to the aggregation of spherical particles, depending on the kinds and amounts of added metal (M) ions. With magnesium, the aggregation could be obtained at the starting composition, Mg/Si = 25/75 molar ratio, while with aluminum, it was obtained at the starting composition, Al/Si = 10/90. In contrast, there are no suitable compositions to obtain sphere particles in the NaO\textsubscript{1.2}/SiO\textsubscript{2} system up to Na/Si = 30/70 molar ratio at starting compositions.

Figure 5 shows XRD patterns of NaO\textsubscript{1.2}/SiO\textsubscript{2} gels after heating at 600°C for 2 h. It is apparent that the specimens crystallized to form cristobalite with this heat treatment. From the intensity of the peaks assigned to cristobalite, it seems that the crystallization temperature decreased with increasing amounts of added sodium nitrate. In the SEM
In this study, we obtained crack-free monoliths of $\text{MO}_{n/2}-\text{SiO}_2$ systems through sol-gel processing under coexistence of polyethylene glycol and in vitro evaluation of their bioactivity.
SiO$_2$ binary systems through sol–gel processing. In the presence of PEG, the gelation time of all the compositions decreased with increasing metal content. The effects of the addition of metal ions on gelation time were confirmed. From the results of SEM observations (see Figs. 2, 3 and 4), the effects of the metal ions on the structural change of the gel increased with increasing ionic charge of the cations. Higher charge values of metal additives may allow formation of particles of the resultant gels with lower amounts of additives. For example, the required addition of sodium ions is estimated to be 50\% in molar ratio to obtain spherical particles, because calcium is a divalent cation having twice the charge of the sodium ion. Bansal et al.\(^8\) reported the influence of the addition of several metal ions on the preparation of silica gel through sol–gel processing. They classified the added metals (Cu$^{2+}$, Al$^{3+}$, La$^{3+}$, Y$^{3+}$, Li$^+$, Na$^+$, Mg$^{2+}$, Ca$^{2+}$, Sr$^{2+}$) ions into two groups. One group results in a decrease of gelation time and has ions that are generally classified as glass network modifiers. The other group results in an increase of gelation time and has ions that are classified
as glass intermediates. Our previous study reported that the gelation time of the CaO–SiO$_2$ system decreased with increasing amounts of added calcium compound. The present study also showed that the gelation times of the gels in the systems NaO$_{1.2}$–SiO$_2$, MgO–SiO$_2$ and AlO$_{1.2}$–SiO$_2$ decreased with increasing metal ion concentrations when the sol–gel processing is conducted in the presence of PEG.

Comparison of results using sodium, magnesium and aluminum ions reveals that aluminum ions bond to oxygen more rapidly than sodium or magnesium ions because of the rapid gelation with aluminum. This can be related to differences in ionic field strength among these metal ions. The ionic field strength, $F$, is defined as:

$$F = \frac{Z}{r^n},$$

where $Z$ is the valence of the ion and $r$ is its ionic radius.$^{9}$

This equation means that metal ions with high positive valences have high ionic field strengths. The ionic field strength of aluminum ions is thus greater than those of sodium and magnesium. The higher ionic field strength allows a higher rate of gelation in sol–gel processing for production of silicate compounds from TEOS.$^{10}$ Therefore, the solutions prepared with the addition of aluminum nitrate gelled faster than the solutions prepared with the addition of magnesium or sodium.

The size and morphology of gels is affected by their rates of gelation.$^{11}$ According to the previous research on the preparation of silica gel through sol–gel processing of silicon alkoxides such as TEOS, the gelation time is affected by the ratio of water and the alkoxide, as well as by the catalyst and its type. These parameters were the same among the examined compositions. However, the gel formation was conducted with various kinds and amounts of the added metal ions. Thus, the metal ions strongly affected the gelation reaction of the binary MO$_{1.2}$–SiO$_2$ system. In our previous study, the morphology of the silica gels prepared with the addition of calcium nitrate changed from the porous interconnected body to an aggregation of spherical particles. In this study, the morphology of the gel prepared with the addition of sodium nitrate did not change; however, the framework increased with increasing sodium content (see Fig. 2). With the addition of magnesium nitrate, the change in the morphology of the gel was similar to that of the gel prepared with the addition of calcium nitrate.$^{12}$ With the addition of aluminum nitrate, the morphology of the gel was changed to spherical particles at lower concentrations than were required with calcium.

These changes in morphology were related to the charge valence of the metal ions, and are similar to the formation of non-bridging oxygen in glass structures. From the viewpoint of glass formation, each divalent cation such as Mg$^{2+}$, Ca$^{2+}$ and Ba$^{2+}$ form two non-bridging oxygen ions, while each monovalent cation such as Li$^+$, Na$^+$, K$^+$ forms one of non-bridging oxygen.$^{11}$ With aluminum ions, the XPS results of the gels prepared with 20 mol% of metal in the starting composition show that the gel containing aluminum ion has a high proportion of non-bridging oxygen compared with specimens prepared with sodium and magnesium (see Fig. 7). It therefore seems that aluminum ions act as a network modifier, making non-bridging oxygen, and that an aluminum ion bonds to three SiO$_4$ tetrahedras.

The present study also showed the potential of using sodium ions for producing bioactive materials. Cho et al. reported$^{11}$ that silica gel porous bodies prepared in the presence of water-soluble polymers formed hydroxyapatite on their surfaces when they were immersed in SBF within 2 weeks. In contrast, silica gel monoliths prepared in the absence of water-soluble polymers did not form it. This suggests that the ability of apatite formation in SBF depends on the porous structure of the silica gel determined by processing. Thus, the bioactivity of pure silica gel is not enough for application as bioactive material, because of its low ability of apatite formation. On the other hand, it was reported$^{7,12,13}$ that CaO–SiO$_2$ and NaO$_{1.2}$–SiO$_2$ glasses have high ability of apatite formation in SBF because the glasses allow increases in degree of supersaturation of the surrounding fluid with respect to hydroxyapatite, attributed to the dissolution of calcium and sodium, as well as the formation of silanol groups on their surfaces. We can conclude that modification of silica gel with calcium or sodium can enhance the ability of apatite formation in the body environment, i.e., bioactivity, even when prepared in the presence of water-soluble polymer.

5. Conclusion

Sol–gel processing in the presence of PEG was conducted to fabricate ceramics in the binary systems MO$_{1.2}$–SiO$_2$ (M = Na, Mg, Al). After sol–gel processing, gels could be obtained in a form with interconnected pores with low metal concentration, and with aggregation of spherical particles with high metal concentrations. The morphological changes of the forms from porous products to spherical particles depended on the charge valences of the metal cations. The products of the system NaO$_{1.2}$–SiO$_2$ showed the ability to form hydroxyapatite in SBF, indicating potential bioactivity for bone repair.

References