Evidence for the Importance of a Cationic Charge in the Formation of Hollow Fiber Silica from an Organic Gel System

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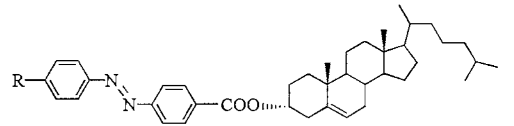
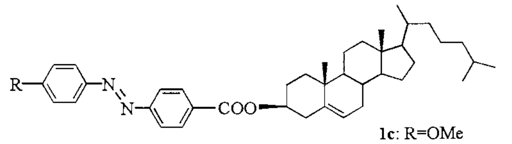
To obtain an insight into the mechanism for the construction of novel hollow fiber silica ("macaroni silica"), sol-gel polymerization of tetraethoxysilane was carried out in the organic gels prepared in the presence of a benzo-18-crown-6-containing cholesterol gelator. Hollow fiber silica was obtained only in the presence of the high concentration of $KClO_4$. The findings support the view that the cationic charge plays a role indispensable to the construction of the tubular structure.

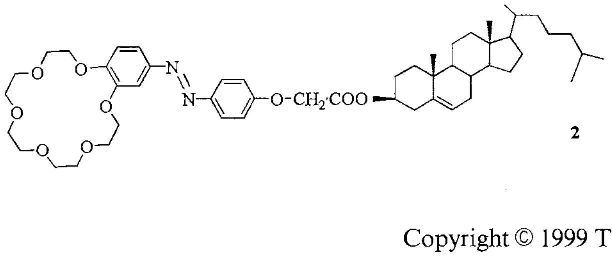
Recently, exploitation of new organic gelators which can gelate various organic solvents has become an active research area of endeavor.[1-12] These organic gels are of particular interest in that being different from polymer gels, fibrous aggregates of low molecular-weight compounds formed by non-covalent interactions are responsible for such gelation phenomena. More recently, it was newly found that sol-gel polymerization of tetraethoxysilane (TEOS) gelated by a cholesterol-based gelator bearing a quaternary ammonium group (**1b**) results in novel silica with a hollow fiber strunture.[1] It was proposed that the unique structure is created by a template effect of the fibrous gelator aggregates which, after calcination, eventually constitute the hollow moiety. In contrast, sol-gel polymerization of TEOS gelated by a cholesterol-based gelator without a quaternary ammonium group (**1a**) did not result in any novel silica structure.[1] The contrasting influence suggests that as frequently seen in conventional cationic surfactants used as templates for sol-gel polymerization, the cationic group in **1b** may play an essential role in the creation of the novel structure. However, it is still ambiguous whether one can attribute the difference solely to this cationic charge, because the gelation properties are largely different between **1a** and **1b**.[1,8] Is there any good system in which the role of the cationic charge can be distinctly estimated?



1a: $R=O(CH_2)_3Me$
1b: $R=O(CH_2)_4NMe_3^+Br^-$



1c: R=OMe



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We previously found that compound **2** bearing a benzo-18-crown –6 moiety also acts as an excellent gelator of organic solvents. With this compound, a "neutral" gelator can be consecutively converted into a "cationic" gelator by the addition of alkali metal salts. We have found that only when the benzo-18-crown-6 moiety binds a significant amount of K^+, the novel hollow fiber silica results.

The sol-gel polymerization was carried out as follows. Compound **2** (5.8×10^{-6} mol) and $KClO_4$ (for the amount see Table 1) were dissolved in dichloromethane (1.0 g). The solution was evaporated to dryness. The residual solid was dissolved in a medium for the sol-gel polymerization: 1-butanol/ TEOS/ water/ benzylamine =95.0/ 15.0/ 5.7/ 5.6 (mg). In Runs 1, 2, 3, 4, and 5 the solutions were gelated at this stage. The samples were sealed in a glass tube and left at 20 °C for a day. Subsequently, they were heated at 200 °C for 1.0 h, 500 °C for 2.0 h under a nitrogen atmosphere, and finally at 500 °C for 4.0 h under aerobic conditions.

Table 1. Conditions for sol-gel polymerization

Run	Gelator[a]	$[KClO_4]$ /mmol dm^{-3}	Major solvent	Silica structure[b]
1	**2**	40	1-Butanol	Tubular
2	**2**	20	1-Butanol	Tubular
3	**2**	10	1-Butanol	Granular
4	**2**	0	Aniline	Granular
5	**1c**	40	1-Butanol	Granular
6	None	40	1-Butanol	Granular

[a] [Gelator]=40 mmol dm^{-3}.
[b] The tubular structure was observed both by TEM and SEM whereas the granular structure was observed only by SEM.

As shown in Figure 1, Runs 1 and 2 containing the high concentration of $KClO_4$ resulted in the fibrous silica with a tubular structure which was similar to that obtained from sol-gel polymerization in the presence of **1b**.[1] The silica structure obtained from Run 1(outer diameter ~50 nm, inner diameter ~10 nm) was minuter than that obtained from Run 2 (outer diameter 100 ~200 nm, inner diameter ~50 nm). In Run 3 where sol-gel polymerization was carried out at the low $KClO_4$ concentration, in contrast, the resultant silica only showed the conventional granular structure similar to that prepared from a solution in the absence of the gelator (Run 6) or from an organic gel in the presence of **1a**.[1] The 1-butanol solution was not gelated by **2** in the absence of $KClO_4$. Since **2** could gelate aniline, we performed the same sol-gel polymerization in aniline/ TEOS/ water/

benzylamine =45.0/ 15.0/ 5.7/ 5.6 (mg; Run 4). Again, the product was the granular silica. Run 5 is a reference experiment starting from an organic gel in the presence of **1c** without the crown ether moiety. As shown in Table 1, the tubular structure was not observed.

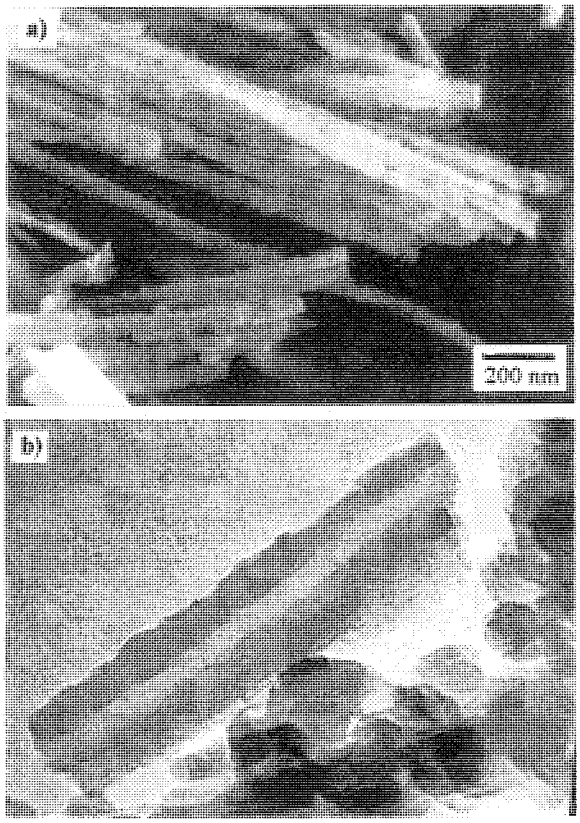

Figure 1. Electron micrographs of the hollow fiber silica, a) SEM image and b) TEM image of Run 1.

We also repeated the sol-gel polymerization in the 1-butanol solution in the presence of LiX (X^- = NO_3^-, SCN^-), NaX (X^- = NO_3^-, SCN^-, ClO_4^-, AcO^-, PF_6^-), RbX (X^- = NO_3^-, ClO_4^-, AcO^-), and CsX (X^- = NO_3^-, ClO_4^-, AcO^-), but the silicas obtained from these experiments all showed the granular structure. The prominent effect of $KClO_4$ is ascribed to the high affinity of the benzo-18-crown-6 moiety with K^+ ion.[13]

The foregoing results consistently support the view that the construction of the hollow fiber silica is profoundly related to the specific K^+-benzo-18-crown-6 interaction.[14] It is now clear, therefore, that the tubular structure is not originated from a difference in the gelation state between **1a** and **1b** but more closely related to the specific influence of the cationic charge on the sol-gel polymerization process. When the sol-gel polymerization is carried out in an alkaline solution, the propagation species is considered to be anionic.[15] Hence, the oligomeric silica species are adsorbed onto the cationic gelator fibrils and the polymerization further proceeds along these fibrils. This propagation mode can eventually yield the fibrous silica with a tubular structure. Since the gelators, the molecular structure of which is similar to gelator **2**, form one-dimensional stacking of the cholesterol moieties, it would have a helical structure in a gel state to displace the direction of crown ether moieties for relaxation of electrostatic repulsion.[8]

In conclusion, the present study has clarified that the silica structure prepared from an organic gel system is transformed from the granular one to the hollow fiber one. The most important factor which governs this transformation is the "cationic charge density" along the organic gel fibers. This concept may be useful to open a doorway to the silica morphology control by added metal cations.

References and Notes

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13 The silicas, which were made under the similar conditions in the presence of KX (X^- = NO_3^-, SCN^-, AcO^-, and PF_6^-), showed the granular structure. It seems that the dissociation constant and the solubility of these salts in the silicate solution are not satisfactory for the production of the expected hollow fiber silica
14 The stabilization constants of 2 for K^+ and Li^+ (used as their picrate salts) in 1-butanol are 1.4×10^4 and 1.7×10^3 dm^3 mol^{-1}, respectively (25℃). If the silicate solution is replaced by 1-butanol, the percentage of the complex would be 96% for Run 1, 50% for Run 2, and 25% for Run 3. One may consider, therefor, that 2 in the sol-gel solution mostly binds K^+ and the hollow fiber silica results when the percentage is higher than *ca.* 50%.
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