Role of Interface and pH Effect for Ordered Microstructure Formation in Laurylamine/Tetraethoxysilane System

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Various morphologies of microstructure were synthesized by pH variation in silica nano-structure formation by templating mechanism in laurylamine/tetraethoxysilane system. The formation processes in various pH conditions were investigated. Integrated ordered structure such as hexagonal array or bicontinuous cubic phases were formed only in the narrow pH region from 10 to 11. Liquid-liquid interface between the organic and the aqueous phases played an important role for the formation of the integrated ordered structure.
Key words: role of interface, pH effect, ordered microstructure, laurylamine, mesoporous silica

1. INTRODUCTION

We presented and elucidated the formation processes of silica nanotubes and bundles of a few of them by measuring the evolution of the shape and size of the produced materials at pH 4.5 in laurylamine hydrochloride (LAHC) /tetraethoxysilane (TEOS) system by SAXS, together with transmission electron microscopy (TEM) images, scanning electron microscopy (SEM) images, isotherms of nitrogen adsorption and ^{29}Si NMR measurements [1,2]. Although we succeeded in the formation of silica-nanotubes, integrated ordered silica materials such as hexagonal array or bicontinuous cubic phase could not be produced at pH 4.5 in the above system.

The hydrolysis and condensation reaction rates have been reported to depend strongly on pH-values as shown in Figure 1 [3,4].
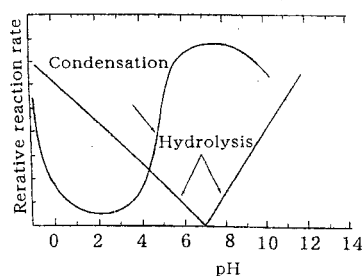

Figure 1 Dependence of hydrolysis and condensation reaction rates on pH

MCM41 was synthesized using cetyltrimethylamonium bromide (CTAB) as template surfactant at high pH region[5,6]. Laurylamine (LA) used in the present work is primary amine and has different properties in comparison with quaternary ammonium compounds such as CTAB. Especially, LA has dissociation equilibrium between cationic (LA$^+$) and nonionic states (LA$_{non}$). Thus, it is interesting to investigate the microstructure change with pH-value for the produced nano-scale materials in primary amine system.

First, we present the effect of pH on the microstructure of mesoporous materials produced by templating mechanism using LAHC/TEOS system and discuss the formation processes. Then, we present the important role of liquid-liquid interface between the

organic and the aqueous phases for the formation of the integrated ordered structure. There are some reports concerning with the formation of integrated ordered structure using air-liquid [7] or liquid-liquid interface [8,9]. Only Schacht et al. [8] reported the mechanistic consideration about the formation of MCM41 at liquid-liquid interface, using CTAB as templating reagent in strong acid conditions. There is still no sufficient mechanistic understanding, however, which can explain the reason why MCM41 was produced at the interface only in the strong acid conditions and why MCM41 could not be produced at the interface in the alkaline conditions, in which MCM41 was produced in the bulk aqueous phase.

In LAHC/TEOS system, we could produce integrated ordered silica materials both at the liquid-liquid interface and in the bulk aqueous phase in alkaline conditions. We discuss the necessary conditions for formation of integrated ordered materials in LAHC/ TEOS system and present the important role of the liquid-liquid interface and pH values.

2. EXPERIMENTAL SECTION

We used a laurylamine (LA) /TEOS system. TEOS was contacted with a 0.1 M LA aqueous solution with various pH-values either in the stirring cell, or quietly through the still liquid/liquid interface. We adjusted the pH values of LA aqueous solutions by adding 2M NaOH or 2M HCl aqueous solution to the LA solutions. Temperature was kept at 313 K. In case of contact through the still liquid-liquid interface, TEOS solution in cyclohexane was used instead of pure TEOS in some experiments. The mole ratio of TEOS to LA was mostly 4 and in some cases was changed in the range from 0.5 to 8. The produced materials was characterized by SAXS, TEM, SEM, isotherm of adsorption of nitogen and ^{29}Si-NMR measurements. The mole ratio of Si/LA in the produced materials was determined from the mass balance between the feed concentrations of LA and Si species and those remaining in the aqueous phase after precipitation.

The partition equilibrium of LA between cyclohexane and the aqueous phase with various pH-values was also measured. The interfacial tension

between cyclohexane and the aqueous phase was measured by Wilhelmy plate method.

3. RESULTS AND DISCUSSION

3.1 Variation in the ratio of $[LA_{non}]/[LA^+]$ and partition coefficient of LA

The ratio of the concentration of non-charged LA_{non} to that of cationic LA^+, $[LA_{non}]/[LA^+]$, changes with pH-value as shown in Figure 2 at dilute conditions, because pKa of LA was reported as 10.63 [10]. In the acidic conditions at pH<7, LA^+ is decisively predominant. At pH=10.63, $[LA_{non}]=[LA^+]$. LA_{non} becomes predominant at pH>11.5.

$$[LA^+]/([LA_{non}] \cdot [H^+])=10^{10.63} \qquad (1)$$
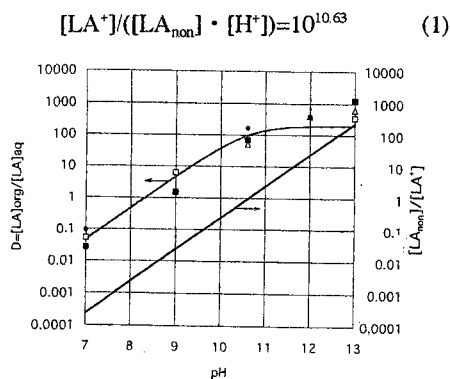

Figure 2 Variation of the concentration ratio of non-charged state of laurylamine LA_{non} to that of cationic state LA^+ and dependence of partition coefficient D of LA between cyclohexane and the aqueous phase with variation in pH. Volume ratio $V_{org}/V_{aq}=1$. Total concentration of LA: ■ 0.1M, △ 0.05M, □ 0.01M, ● 0.001M. Solid curves are calculated ones by Eq.(1) and $D=200/(1+[H^+]/10^{-10.63})$.

In the absent of organic phase, 0.1 M aqueous solution of LA became turbid at pH=7.8 when sodium hydroxide solution was added to the solution of LA, which was used as the aqueous phase in the present experiments. When pH of the aqueous solution became around 10.5, the oil droplets of LA_{non} appeared in the solution. We inferred that LA_{non} made oil droplets, because no structure was detected for the aqueous solution containing globules of LA_{non} by SAXS. At higher pH, LA_{non} became predominant, existing as oil droplets.

We measured also the partition coefficient D of LA between cyclohexane and the aqueous phases with various pH-values by changing the total concentrations of LA. There were no oil droplets of LA_{non} in the aqueous phase in the cyclohexane/aqueous two phase system. As shown in Figure 2, partition coefficient D decreased logarithmically with decreasing pH in the range pH<10, because LA^+ does not dissolve into the organic phase, and LA_{non} decreases logarithmically with decreasing pH. On the other hand, almost all LA existed as LA_{non} at pH>11.5, and D became constant value, which was determined by the equilibrium partition of LA_{non} between cyclohexane and the aqueous phase.

3.2 Change in microstructure with variation in initial pH of the aqueous solutions of LA

Silica nanotubes or bundles of a few of them were formed in acidic conditions (1<pH<6), because the packing parameter [11,12] of the complex composed of

LA^+ and hydrolyzed TEOS led to the formation of cylinders. Since the hydrolysis reaction rate is more rapid than the condensation one as shown in Figure 1, the shape of the molecular assemblies was determined by the packing parameter of the complex composed of LA^+ and hydrolyzed TEOS. The mole ratio of Si/LA in the produced materials was equal to that of feed, because homogeneous gelation occurred in this condition. The detail formation processes of silica nanotubes has been reported already elsewhere [2].
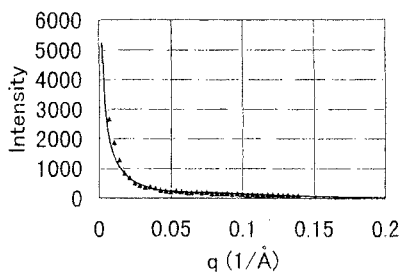

Figure 3 SAXS spectrum for the solution at initial pH 7. [LA]=0.1M, [TEOS]=0.4M, 25 min.

At pH=7, precipitation started after about 30 min from the addition of TEOS to the LA aqueous solutions. The mole ratio of Si/LA in the produced materials was 8 for the feed ratio being 4. pH value became 6.6 after the precipitation. Formation of small spheres (diameter 3.3 nm) and the rod like structures (diameter 12 nm and length 100 nm) were obtained by the analysis of SAXS results (shown in Figure 3) of the aqueous phase taken about 25 min after the addition of TEOS. Adsorption isotherm of nitrogen for this precipitates after calcination at 773 K (shown in Figure 4) showed the same pattern as IUPAC type III [4,13], indicating the formation of open microstructure characterized by aerogel. Since the hydrolysis reaction rate is slowest and the condensation reaction rate is very rapid at pH 7, hydrolyzed TEOS combined with each other by the rapid condensation reaction before rearranging the shape of the aggregate, when the TEOS were adsorbed on the aggregates of LA, and formed spherical shape. The spheres connected with each other to yield rod like structure, which formed open structure like aerogel by attaching mutually. The BET surface area was determined as 79 m²/g, which was much smaller than that of silica-nanotubes produced at pH 4.5.
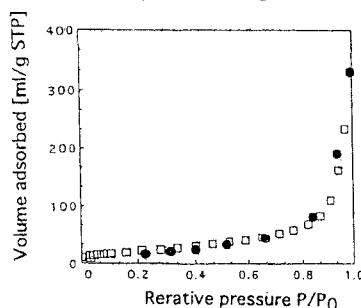

Figure 4 Isotherm of nitrogen adsorption for the calcined materials at 773 K obtained at pH 7.

At pH 10.3, the initial LA aqueous phase contained oil droplets of LA_{non}. When TEOS was added in the stirring cell, the oil droplets disappeared, because TEOS and LA_{non} dissolved mutually. After 1.5 min from the

addition of TEOS, precipitates were formed from the uniformly emulsified liquid phase. The mole ratio Si/LA in the produced materials was equal to that of feed ratio, because almost no LA was detected in the aqueous phase after precipitation. The pH value after precipitation was 9.1. The SAXS results of these precipitates (shown in Figure 5) showed many peaks in the mesopore region, indicating the formation of periodical ordered structure. In case of Figure 5, the produced structure was identified as gyroid (space group Ia3d) from the peak-values [14]. Nitrogen adsorption isotherm of these materials gave the non-hysteresis curves, i.e., coincidence of adsorption curve with desorption one. This was found first for MCM41 [5,6]. The pore size distribution was determined from the isotherm and showed sharp peak at pore radius of 1.5 nm. BET surface area was 733 m^2/g. The integrated ordered structure such as gyroid was obtained only in the narrow initial pH region from 10 to 11, where both hydrolysis and condensation reaction rates are rapid. The formation processes of the ordered structure are discussed in detail later.
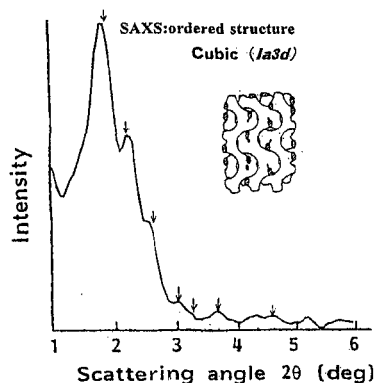

Figure 5 SAXS spectrum of the precipitates at initial pH 10.3.

At pH 13, the solution was turbid for initial several hours when TEOS was added to the LA aqueous solution. Then, the solution separated to two transparent liquid phases. TEOS was completely hydrolyzed and existed only in the aqueous phase, but condensation reaction did not occur because of the strong electrostatic repulsion. The organic phase was composed of LA_{non} and ethyl alcohol. There was almost no LA in the aqueous phase. Therefore, silica materials were not formed at pH 13.

3.3 Formation processes of the integrated ordered microstructure and the role of liquid-liquid interface

First we tried to produce the integrated ordered materials from silica nanotubes produced at pH 4.5 in various reaction stages by changing the pH to 10.5. Consequently we could not produce the ordered materials by this method.

Liquid-liquid interface provides two-dimensional space. When the reaction products were restricted in the two-dimensional space, there is a good possibility to make ordered structure composed of a unit structure. Thus, formation of ordered structure were tried by contacting pure TEOS or TEOS solutions of cyclohexane with the LA aqueous phase through the still liquid-liquid interface. Precipitates were formed at the interface in both cases after about 3 min from adding TEOS. The SAXS results of both cases are shown in

Figure 6. Hexagonal array structure was obtained for the case of pure TEOS, and gyroid like structure was obtained for TEOS solution of cyclohexane. These results strongly suggest that the liquid-liquid interface play an important role for producing the integrated ordered structure.
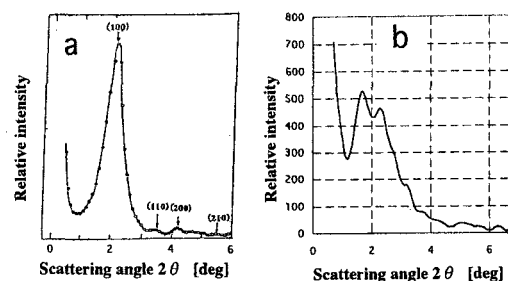

Figure 6 SAXS spectra of the precipitates obtained by contacting 0.1M LA aqueous solution with TEOS (a) or TEOS solution of cyclohexane (b) through the still liquid-liquid interface.
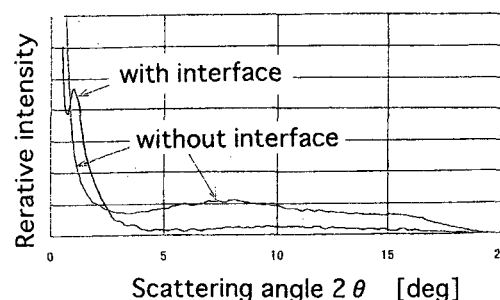

Scattering angle 2 θ [deg]

Figure 7 SAXS spectra of the precipitates obtained with interface and without interface.

Next, we examined the role of interface by checking the difference in the structure of produced materials with interface and without interface. The experiments without interface were performed as follows: LA was extracted from 0.1 M aqueous LA solution of pH 10.5 to cyclohexane. TEOS was added to the LA solution of cyclohexane(W_0=2.5). The mole ratio of TEOS to LA was 4. The experiments with interface were carried out by contacting pure TEOS with 0.1 M LA aqueous solution of pH 10.5 through the still liquid-liquid interface. Both SAXS spectra of the obtained precipitates are shown in Figure 7. The spectrum with interface had a peak in the meso-scale region, indicating the existence of meso-scale periodical structure. On the other hand, the spectrum without interface had no peak in the meso-scale region. This result clearly shows that liquid-liquid interface played the important role for the formation of the integrated ordered structure.

When integrated ordered structure is formed at the liquid-liquid interface, similar ordered structure have to be obtained by contacting the organic phase containing both LA and TEOS with pure water or the aqueous NaOH solution of pH 10.5. Also, the contacting method, i.e., by stirring or quiet contact through the still liquid-liquid interface, does not affect the produced structure significantly. Figure 8 shows the SAXS spectra obtained by the three different conditions. a) The aqueous LA solution was contacted with pure TEOS through the still

liquid-liquid interface. b) The organic phase containing both LA and TEOS was contacted with pure water by the stirring condition. c) The organic phase containing both LA and TEOS was contacted with pure water through the still liquid-liquid interface. These three cases gave the almost same spectra.
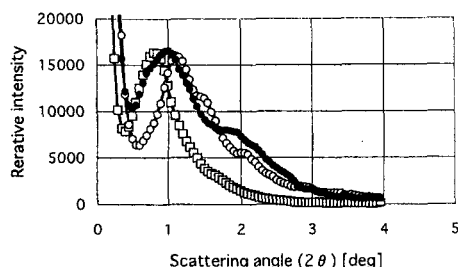

Figure 8 Comparison of SAXS spectra obtained following three conditions: a) ☐ Aqueous LA solution was contacted with pure TEOS through the still liquid-liquid interface. b) ● Organic phase containing both LA and TEOS was contacted with pure water by the stirring condition. c) ○ Organic phase containing both LA and TEOS was contacted with pure water through the still liquid-liquid interface.
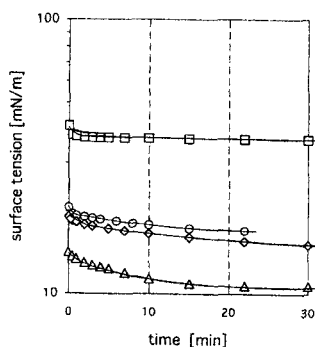

Figure 9 Variation in surface tension with time by adding 3.2×10^{-5} moles of TEOS to the measuring system composed of 80 ml LA solution of cyclohexane and 20 ml aqueous solution of pH 10.5. Key: ☐:[LA]=0, ○:[LA]=1×10^{-4}M, ◇:[LA]=2×10^{-4}M, △:[LA]=5×10^{-4}M

We measured the variation in interfacial tension with time between the cyclohexane solution of LA and the aqueous NaOH solution of pH 10.5 when a constant amount of TEOS was added to the measuring system containing various concentrations of LA. Figure 9 presents the results. When LA was absent, surface tension decreased rapidly within 0.5 min and kept almost constant after 2 min to 30 min. When LA was contained in the system, surface tension decreased within 0.5 min and continued to decrease for 30 min. It decreased more rapidly with increase in the LA concentration. This shows that surface active substances gathered at the interface with proceeding the reactions between surfactant and TEOS.

These findings mentioned above confirm the important role of the liquid-liquid interface, which assists to produce the integrated ordered materials by restricting the reaction products in the two-dimensional space.

Lastly, we tried to find out the necessary

conditions for formation of integrated ordered materials at liquid-liquid interface by changing the pH-value and also surfactant. When the 0.1 M LA aqueous solution of pH<7 was contacted with pure TEOS (mole ratio Si/LA =4) through the still liquid-liquid interface, no reaction was observed for one hour half from the contact. Both phases and interface were transparent, and integrated ordered structure was not formed.

When 0.1 M CTAB aqueous solution of pH 10.5 was contacted with pure TEOS (mole ratio Si/LA=4) through the still liquid-liquid interface, no reaction was observed over one day, and integrated ordered structure was not formed.

These findings strongly suggest that in spite of the existence of liquid-liquid interface, formation of integrated ordered structure does not occur when surfactant is ionized and makes molecular assembly in the bulk aqueous phase. Therefore, it would be indispensable condition for the formation of integrated ordered structure that the reaction products of surfactant and TEOS are restricted on the liquid-liquid interface.

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