

Study of Silanolate Groups ($\equiv\text{SiO}^-$) in Synthesis of Micelle Templated Silica with Various Condition of Cationic Surfactant

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ABSTRACT: *Based on the $\{S^+, \Gamma\}$ pathway, the concentration of surfactant and surface charge density of silanolate groups control the phase transition from lamellar, to hexagonal through cubic form. The high surface charge density of silanolate groups was observed for the lamellar phase. With decrease of molar concentration of surfactant on the gel, the yield of reaction decreases and the stability of mesophase increase. The silanolate groups of surface are approximately constant when the hydrocarbon length chain of surfactant changes. The disorder mesophase forms for surfactant with short hydrocarbon length chain and the surface charge density decreases. The yield of reaction decreases with decrease of hydrocarbon length chain of surfactant.*

KEY WORDS: *Mesophase, Mesoporous materials, Surface charge density, Silanolate, Cationic surfactant, Lamellar phase, Hexagonal phase, Cubic phase.*

INTRODUCTION

Micelle templated silica (MTS) are definite inorganic solid phase having a regular unimodal pore system in which the pore size typically ranges from 2 to 50 nm. These materials have attracted vast interest because of their potential application as catalysts [1], metal scavengers [2-4], carbon paste modified electrodes [5], preconcentration of metals [6,7], and green chemistry [8,9]. They can easily be modified and functionalized by incorporation of organic groups in the silica structure [10,11]. They are synthesized using surfactant assemblies as templates, thus ensuring the formation of ordered meso-structure materials [12]. These processes were originally started with cationic [13] and later with anionic

[14] and neutral [15] surfactant. In MCM-41 type materials, the hexagonal array of mesopore is templated using cationic surfactants, S^+ (usually, quaternary amines such as cetyltrimethylammonium, CTMA⁺). Their positive charges are counterbalanced by negative charges of silica surface, denoted as Γ^- according to the $\{S^+ \Gamma^-\}$ pathway, where Γ^- stands for silanolate group, $\equiv\text{SiO}^-$, in silica [16]. In the modified pathways, it was proposed that any anions and cations present in the synthesis are not innocent spectators and they affect the silanolate concentration as well as the long range order in the Mesoporous templated silica (MTS) [17]. The latter route is known to generate more stable materials in which the

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surfactant counterion plays an important role on the long-range order, the nature of the phase and on the hydrophobicity of the organic-inorganic interface [18]. The effects of surfactant concentration on the properties of mesoporous silica prepared from both micellar and liquid crystal phases have been studied. An ordered hexagonal phase can be obtained through both routes and the order depends much on the surfactant concentration [19].

It has been shown that carbon chain length and quantity of surfactant had many effect in mesophase type pore, diameter and morphology [20-22]. On the other hand, synthesis of these materials using low carbon chain of surfactant (lower than 12 carbons) showed disorder hexagonal form of channels [20-22]. In this investigation we have studied the effect of carbon chain length and quantity of surfactant on surface density of silanolate groups in as-synthesized MTS.

EXPERIMENTAL

Materials

The surfactants, Octadecyltrimethylammonium bromide (C_{18} TMAB), cetyltrimethylammonium bromide (C_{16} TMAB), myristyltrimethyl-ammonium bromide (C_{14} TMAB), dodecyltrimethylammonium bromide (C_{12} TMAB) and decyltrimethylammonium bromide (C_{10} TMAB) were obtained from Merck, Aldrich and TCI and used without further purification. The silica gel, NaOH, di-sodium benzene -1,3-disulfonate were from Merck.

Synthesis procedure

To prepare the silica source, silica gel was dissolved in 1M NaOH at 80 °C for 8 h. The molar composition of clear solution of sodium silicate was 1 SiO_2 : 0.5 NaOH: 33 H_2O . The MTS was synthesized in three series. In A series the molar composition of final gel was 1 SiO_2 : x C_{16} TMAB: 0.5 NaOH: 104 H_2O (X=0.05, 0.07, 0.1, 0.18, 0.2 and 0.4). The index A-x corresponding to the A series with various molar concentrations of surfactant. In B series the molar composition of final gel was 1 SiO_2 : 0.1 C_x TMAB: 0.5 NaOH: 104 H_2O (X=10, 12, 14, 16 and 18). The index B-x corresponding to the B series with various numbers of carbons in tail of surfactant. In C series the organic salt (di-sodium benzene-1,3-disulfonate) (DSBS) was added to the gel and the final

molar composition was 1 SiO_2 : 0.1 C_x TMAB: 0.1 DSBS: 0.5 NaOH: 104 H_2O (x=10, 12, 14, 16 and 18). The index C-x corresponds to the C series with various numbers of carbons in tail of surfactant in the presence of organic salt. In a typical synthesis batch, surfactant was dissolved, by heating and magnetic stirring if necessary, and then the above silica source was added dropwise with vigorous magnetic stirring to this clear solution of surfactant at room temperature. The resulting gel mixture was stirred for 1 h and then was heated for 24 h at 100 °C in teflon lined autoclave. The as-synthesized materials were obtained after filtration, washing three times with distilled water and, drying at room temperature.

The amount of silanolate groups of surface was determined by acid base titration as described in details earlier [17]. The weight loss was measured after calcinations at 600 °C. The yield of reaction (R_{SiO_2}) was calculated based on the silica in as-synthesized product.

CHARACTERIZATION

The XRD was obtained from a Bruker AXS D8 diffractometer employing nickel filtrated $Cu K\alpha$ ($\lambda = 1.5418 \text{ \AA}$) where the X-ray tube was operated at 40 kV and 30 mA and spectra were scanned at 0.02° step size.

RESULTS AND DISCUSSION

Chemical analyses and XRD results of as-synthesized MTS of series A obtained from various molar concentrations of surfactant are shown in table 1. The phase transfer was observed in the XRD patterns of as-synthesized MTS materials of series A obtained with increasing the molar concentration of surfactant (C_{16} TMABr) (Fig. 1). The hexagonal phase was observed in low concentration of cationic surfactant (below molar ratio SiO_2/C_x TMABr = 0.18). As previously reported, at molar ratio SiO_2/C_x TMABr = 0.15 to 0.2, or more, the cubic phase and lamellar phase form, respectively [13]. In A-0.18 the mix of two phases was observed due to phase transfer from hexagonal to cubic. In series A the final pH (after hydrothermal treatment) was equal. Thus, in this series, the pH has no parameter effect of the silanolate of surface, because the charge density of silica surface is controlled by pH [18]. The progressive concentrations of surfactant gel produced hexagonal, cubic and lamellar mesophase according to XRD patterns as previously reported in literature [21]. However, the silanolate of

Table 1: Chemical analyses and XRD characteristics of as-synthesized MTS of series A obtained from various molar concentration of surfactant ($C_{16}TMABr$).

sample	phases ^a	d_{hkl}^b $\pm 0.2 \text{ \AA}$	SiO/SiO ₂ $\pm 0.1\%$	$R_{SiO_2}^d$ $\pm 0.1\%$	pH ± 0.1
A-0.05	H	42.1	14.8	36.2	12.3
A-0.07	H	42.0	17.4	41.2	12.2
A-0.1	H	42.1	18.5	53.1	12.2
A-0.18	H+C ^c	41.1	21.4	63.9	12.1
A-0.2	L	33.4	27.7	66.7	12.3
A-0.4	L	33.6	29.1	67.7	12.2

a) L= lamellar, H= hexagonal and C=cubic, b) 100 for lamellar and hexagonal and 211 for cubic, c) contains cubic and hexagonal phase, d) The yield of reaction based on the silica in as-synthesized product.

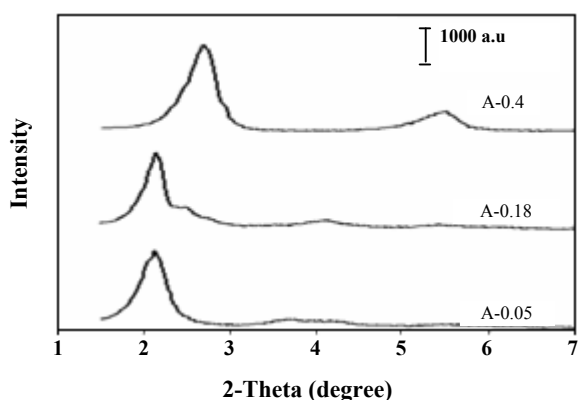


Fig. 1: XRD patterns of as-synthesized MTS materials of series A obtained from various molar concentration of surfactant ($C_{16}TMABr$).

surface have a jump with changing mesophase. In this series, the most negative charge on the surface belongs to the lamellar phase.

The yield of silica product (R_{SiO_2}) in A series (table 1) increases with increasing of surfactant concentration. In the higher concentrations of surfactant, the silica yield slightly increases. The yield of surfactant in A-0.05 was 84 %. It was expected to be more because in this case the molar ratio of surfactant/SiO₂ was very low. It can also be related to equilibrium between surfactant and silica oligomer in the gel [16].

According to XRD patterns, the best hexagonal phase is obtained at the lowest silanolate of surface and also after calcinations of as-synthesized MTS (A-0.05) the position of d_{100} has a small change (42.1 to 41.6 Å) than

Table 2: Chemical analyses and XRD characteristics of as-synthesized MTS of series B obtained from various numbers of carbons in tail of surfactant.

sample	Phases ^a	d_{hkl}^b $\pm 0.2 \text{ \AA}$	SiO/SiO ₂ $\pm 0.1\%$	$R_{SiO_2}^c$ $\pm 0.1\%$	pH ± 0.1
B-10	H _d	31.5	13.7	40.6	12.4
B-12	H _d	33.2	19.9	44.9	12.1
B-14	H	36.8	18.2	52.4	12.2
B-16	H	42.1	18.5	53.1	12.3
B-18	H	43.2	18.3	51.4	12.3

a) H= hexagonal and H_d = hexagonal disorder, b) 100 for lamellar and hexagonal, c) The yield of reaction based on the silica in as-synthesized product.

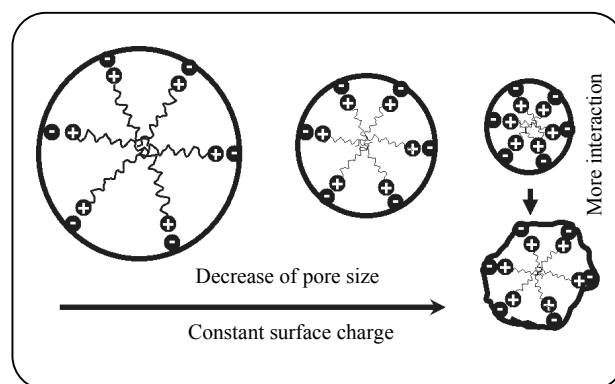


Fig. 2: Schematic presentation of pore form with decrease of carbon chain in tail of surfactant and constant surface charge.

the other in this series. The same effect was observed, when the organic salt was added to the gel (series C), as for C-0.05 the position of d_{100} for the calcinated and as-synthesized was very small (42.1 to 42.0 Å). For construction of MTS at the lowest concentration of surfactant, probably, the head group of surfactant prefer more uniform silica species on the solution [25, 26].

Table 2 shows the chemical analyses and XRD characteristics of as-synthesized MTS of series B obtained from various numbers of carbons in the tail of surfactant. The final pH of all samples in this series were in the same range and XRD patterns shows the hexagonal mesophase form corresponding to typical pattern of P6m space group. The yield of reactions (R_{SiO_2}) decreases for $C_{12}TMAB$ and $C_{10}TMAB$ which can be attributed to

Table 3: Chemical analyses and XRD characteristics of as-synthesized MTS of series C obtained from various numbers of carbons in tail of surfactant with addition of organic salt.

sample	Phases ^a	d_{hkl}^b $\pm 0.2\text{\AA}$	SiO ⁻ /SiO ₂ $\pm 0.1\%$	R _{SiO₂} ^c $\pm 0.1\%$	pH ± 0.1
C-10	H _d	31.4	11.4	36.8	12.3
C-12	H	33.3	17.0	41.2	12.2
C-14	H	36.7	17.2	41.3	12.1
C-16	H	42.1	17.6	46.2	12.3
C-18	H	43.3	18.4	40.7	12.3

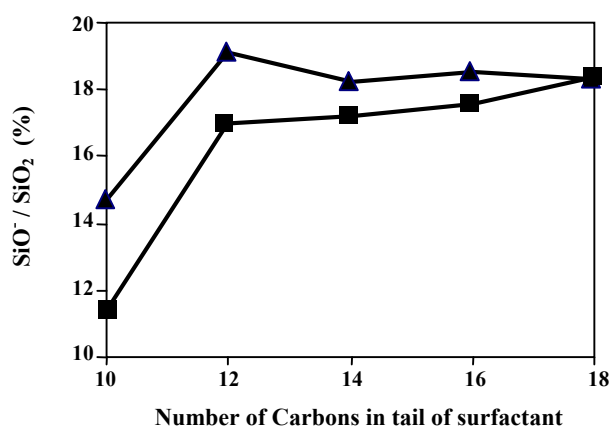


Fig. 3: Silanolate group concentration in as-synthesized MTS [■ with (series B) and ▲ without organic salt (series C)] versus number of carbons in tail of surfactant.

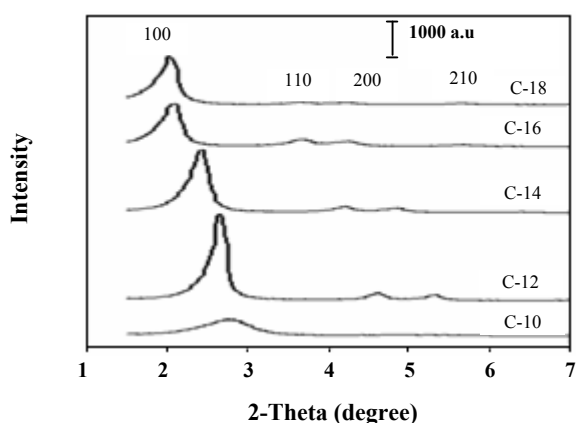


Fig. 4: XRD pattern of as-synthesized MTS of series C obtained from various numbers of carbons in tail of surfactant.

interaction between silica species on the solution and head group of surfactant. This interaction decreases for low hydrocarbon chain in tail of surfactant, because cohesion energy between head group of surfactant and counterion decreases [27]. On the other hand, charge density of surface decreases, and XRD patterns of B-10 and B-12 show a disorder hexagonal mesophase [20]. Decreasing of hydrocarbon chain of surfactant cause to reduce the pore diameter from B-18 to B-10 [20-22]. In this condition, the MTS (B-10 and B-12) have to keep more charge of the surface or the negative charge closer in B10 than B18. Thus, the surface charge falls down and disorder mesophase forms with lower hydrocarbon chain of surfactant (Fig. 2).

As already reported [18, 26], addition of organic counterion reduces the silanolate of surface. Fig. 3 shows silanolate group concentration in as-synthesized MTS with (series B-x) and without organic salt (di-sodium benzene-1,3-disulfonate) (series C-x) versus number of carbons in tail of surfactant. The difference between two points in Fig. 4 increases with decrease of hydrocarbon tail of surfactant in both series B-x and C-x. The competition between silica species and organic anion are minor for long hydrocarbon tail. In the case of the B-12, the organic salt was added to the gel (sample C-12). The results show that the yield and SiO⁻/SiO₂ were reduced to 41.2 % and 17.0 (Fig. 3), respectively. Its XRD pattern shows a high order hexagonal mesophase (Fig. 4 C-12). The XRD patterns of the C series show the hexagonal mesophase form corresponding to typical pattern of P6m space group (Fig. 4).

CONCLUSIONS

Based on the {S⁺, I⁻} pathway, the concentration of surfactant and surface charge density of silanolate groups control the phase transition from lamellar, to hexagonal through cubic form. The high surface charge density of silanolate groups was observed for the lamellar phase. With decrease of molar concentration of surfactant on the gel, the yield of reaction decreases and the stability of mesophase increases. The silanolate groups of surface are approximately constant when the hydrocarbon length chain of surfactant changes. The disorder mesophase forms for surfactant with short hydrocarbon length chain and the surface charge density decreases. The yield of reaction decreases with decrease of hydrocarbon length chain of surfactant.

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