



Effect of Benzyltrimethylammonium Ion as a Co-directing Agent on Phase Transitions in a Nanostructure Silica/Surfactant Composite

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Abstract: Effect of benzyltrimethylammonium ion as a co-directing agent in phase transition from hexagonal to cubic and lamellar mesophases was studied in the constant pH at 130 °C. This phase transformation was carried out in constant surface charge and pore size distribution (2 nm). Influence of BTMA⁺ ions between head and tail of surfactant and phase transformation were observed by using the XRD and elemental analysis.

Keywords: Benzyltrimethylammonium ion, Co-directing agent, Phase transition, Hexagonal, Cubic, Lamellar.

Introduction

Order forms of nanoporous materials have been synthesized in a variety of hexagonal, cubic, and lamellar phases through the reaction of inorganic species in the presence of surfactant self-assemblies as supramolecular templates¹. These materials have attracted vast interest because of their potential application as catalysts²⁻⁵, solid phase micro extraction (SPME)^{6, 7}, metal scavengers⁸, preconcentration of metals^{9,10} and in the modified electrodes¹¹⁻¹³. The more understanding of the formation mechanism should finally lead to a more rational approach to synthesis of mesoporous materials. The proposed models have explained the formation of these materials¹⁴. In M41S type materials, cationic surfactant molecules and surface silanolates, $\equiv\text{Si}-\text{O}^-$, are implicated the so-called $\{\text{S}^+, \Gamma\}$ pathway¹⁵. In this pathway, the associated silica oligomers with surfactant head groups can polymerize and a highly ordered rigid framework forms. The overall topology of this nanostructure is determined by surfactant curvature which can be described by the dimensionless effective surfactant

packing parameter (g)¹⁶. This model explains favored phase transition from lamellar to cubic and hexagonal phases. The effect of lipophilic nature of surfactant counter ion was reported in phase transitions^{17,18}. The solid state transformation from MCM-41 to MCM-48 and MCM-50 was recently studied by transmission electron microscopy (TEM) and scanning electron microscopy (SEM) methods¹⁹. Here, for the first time we reported the effect of benzyltrimethylammonium ion as a co-surfactant for phase transitions from hexagonal to cubic and lamellar.

Experimental

To prepare the silica source, colloidal silica, Ludox HS40 (Aldrich), was dissolved in 1 M NaOH at 80 °C for 8 h. The molar composition of clear solution of sodium silicate was 1 SiO₂: 0.5 NaOH: 33 H₂O. The solution was stored in a polypropylene bottle until used as the silica source.

In a typical synthesis batch, 60 g of the silica source was slowly added to clear solution of 4.4 g cetyltrimethylammonium bromide (CTMABr), 10.2 g benzyltrimethylammonium chloride (BTMACl) (60% in water) (Aldrich) and 57.1 g distilled water with vigorous magnetic stirring for 30 min. The resulting gel, with a molar composition of 1 SiO₂: 0.13 CTMABr: 0.35 BTMACl: 66.30 H₂O, was mixed for 1 h, then it was heated at 130 °C in a Teflon-lined autoclave for 24-120 h. The amount of surface silanolate groups (SiO⁻/SiO₂) was determined by acid-base titration as described in details earlier²⁰. The weight loss was measured after calcination at 550 °C. The amount of CTMA/SiO₂ was determined by spectrophotometer as described in details earlier²⁰. The total amount of Cl⁻ and Br⁻ was determined by conductometric titration of 0.01 M silver nitrate solution.

Characterization techniques

The nitrogen adsorption-desorption isotherms were measured at -196 °C using a Belsorp mini-II system. The samples were vacuum dried at 150 °C overnight. The powder x-ray diffractograms were recorded by Bruker AXS D8 diffractometer with nickel filtered Cu-K α ($\lambda = 1.5418 \text{ \AA}$) where the x-ray tube was operated at 40 KV and 30 mA, the spectra were scanned at 0.02 step size.

Results and Discussion

Figure 1 shows the small angle x-ray diffraction patterns of as-made and calcined silica mesophases at 130 °C for 24, 48, 72 and 120 h reaction times. The phase transformation of silica mesophase was observed with the increasing of reaction time of gel according to small angle x-ray diffraction patterns. After 24 h of the reaction time (so-called MTS-24 h), three diffraction peaks were observed that can be indexed to a $p6mm$ two-dimensional hexagonal phase (MCM-41 type). When this sample (MTS-24 h) was calcined at 550 °C, the (100) reflection was shifted to high angle and the FWHM (Full Width at Half-Maximum) of the reflection increases. This observation can be attributed to the 19% shrinkage of the silica walls as previously reported for MCM-41²¹. It can be due to lower condensation of silica framework and the partial collapse of the hexagonal ordered phase²¹. After 48 h hydrothermal treatment (so-called MTS-48h), the XRD showed the diffraction patterns of cubic nanostructure (MCM-48 type) with $Ia3d$ space group. All characterization peaks of hexagonal array were disappeared at this reaction time. The XRD patterns of calcined MTS-48 h indicated that the (211) reflection was shifted to the high angle and the nanostructure cubic phase was stable after removal of the surfactant. On the other hand, the intensity

increases in the XRD reflections that correspond to high order cubic phase with 10% shrinkage of silica framework. However, it shows that there is higher condensation of silica framework in the cubic phase than in the hexagonal phase. Therefore, this process can be due to change of silica walls curvature in nanostructure mesophase. This curvature depends on the packing factor (g) of directing agent and the surface charge on silica surface^{17, 20}. When BTMA⁺ ions are not presence in the composition reaction, this phase transformation did not observe and the hexagonal phase was obtained. Therefore, BTMA⁺ ions have an important role as a co-directing agent. This effect was observed when the gel was treated for more time (72 h) (so-called MTS-72 h), the intensity of d_{211} reflection was decreased and lamellar phase was appeared (peak at $2\theta = 2.7$ degree). The lamellar phase collapsed when the directing agent (surfactant) was calcined at high temperature or was removed during the treatment with acid in ethanol¹. Thus, the characterization peak of this phase was not observed in XRD pattern after calcination. Finally, the pure lamellar phase with two diffraction peaks (MCM-50 type) was observed in the XRD pattern after 120 h (so-called MTS-120 h). The two characterization peaks of MTS-120 h were disappeared after calcination.

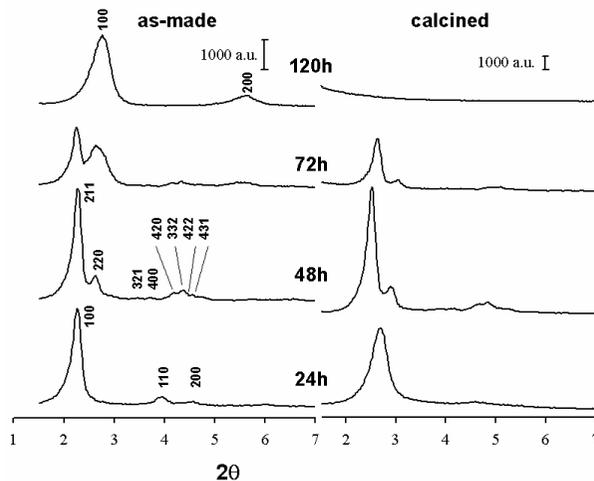


Figure 1. Small angle powder XRD patterns of as-made (left) and calcined (right) silica mesophases obtained at 130 °C for 24, 48, 72 and 120 h reaction times

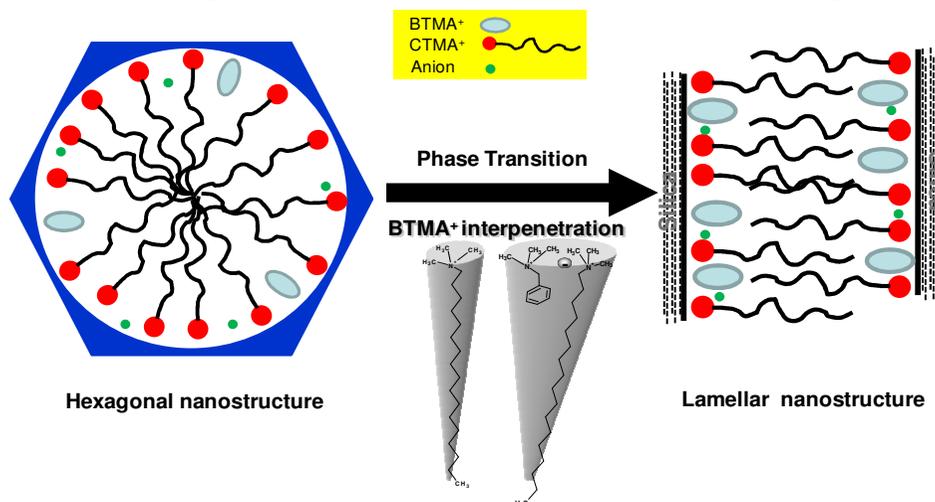
It is necessary to calculate the amount of BTMA⁺ ions in the solids to understand why phase transformation from a higher-curvature hexagonal phase is preferred to a lower-curvature lamellar phase in the presence of BTMA⁺ ions during the reaction time. Table 1 shows the chemical analysis of the as-made silica nanostructure. The final pH of all samples and the obtained silanolate (SiO⁻/SiO₂) were approximately very close. The quantity of CTMA⁺ on the surface was decreased with increase of the reaction time. At the same time, the phase transfers from hexagonal to lamellar, as mentioned above. In contrast, an augmentation was observed for the percentage of anions (Cl⁻ and Br⁻), but with small variations (about 0.2% for each transition phase). In this chemical analysis, there is a deficit in positive charges that could be attributed to both BTMA⁺ and Na⁺. However, the concentration of sodium is very low (at the detection limit of atomic absorption technique) and accounts for less than 0.1% Na⁺/SiO₂. Therefore, the deficit is mainly compensated by BTMA⁺ ion. The percentage of BTMA⁺ is increased from hexagonal to lamellar mesophase (about 1% for each transition phase).

Table 1. Chemical analysis of as-made silica mesophase obtained with titration of 0.1N HCl in absolute ethanol

	pH _{final} ±0.1	SiO ⁻ /SiO ₂ ±0.1%	X ⁻ /SiO ₂ ^a ±0.1%	CTMA ⁺ /SiO ₂ ±0.1%	ΔΣ ^{±b} ±0.3%	a ₀ ^c ±0.1(nm)
MTS-24 h	10.3	22.7	1.0	22.5	1.2	2.1
MTS-48 h	10.2	22.2	1.2	20.7	2.7	2.2
MTS-72 h	10.5	22.1	1.3	20.0	3.4	2.2
MTS-120 h	10.6	22.3	1.5	19.2	3.6	-

^aX⁻ = Cl⁻ + Br⁻, ^bCharge deficit (missing positive charge per SiO₂), ^cAverage pore diameter calculated by BJH method

The phase transition can be understood by applying the simple model of Israelachvili on the conical shape and the space occupied by the hydrophilic and hydrophobic groups of the surfactant^{16,22}. The local effective parameter is defined as $g=V/a_0 l_c$, where V and l_c are the total volume and the length of the hydrophobic portion of the surfactant and a_0 is the polar head area. The aggregate structure depends on the value of the g : the larger the g , the less curvature in the aggregate. The increased tail motion changes the effective volume and shape occupied by a surfactant. In this mesophase transition, over time some BTMA⁺ diffuses between of head and tail of surfactant and increase the V (Figure 2) and mobility of tail, which in turn increases the g and favored mesophase with a lower curvature. However, for the repulsion decreasing between BTMA⁺ and head group of surfactant, the presence of anions was probably admitted beside of BTMA⁺. Penetration of anion leads to a closer Helmholtz planes and a better screening of the positive charges that allows the ammonium heads to move closer one to another and to have a smaller surface area for the same occupied space by the alkyl chains¹⁷. However, the silica framework limits the available space, and thus, surfactants are unable to occupy their preferred volume and/or attain their preferred curvature; the surfactant volume and/or curvature become frustrated. Eventually this packing frustration overcomes the strength of the covalent bonds in the silica network, and the hexagonally packed nanostructure silica transform to lamellar silica (Figure 2).

**Figure 2.** Influence of BTMA⁺ between head and tail of surfactant and volume increasing, and phase transition from hexagonal to lamellar nanostructure

Conclusion

In conclusion, it was shown that in the nanostructure mesophase synthesis under constant pH conditions, BTMA⁺ ions diffuses between the head and the tail of the surfactant and phase transition occurs from hexagonal to cubic and lamellar mesophases at 130 °C. In this transformation the charge of surface and the pore size (2 nm) were constant.

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References

1. Beck J S, Vartuli J C, Roth W J, Kresge C T, Leonowicz M E, Schmitt K D, Chu C T-W, Olson D H, Sheppard E W, McCullen S B, Higgins J B and Schlenker J L, *J Am Chem Soc.*, 1992, **114**, 10834.
2. Trong On D, Desplandier-Giscard D, Danumah C and Kaliaguine S, *Appl Catal A: Gen.*, 2001, **222**, 299.
3. Gholami J, Badiei A, Abbasi A and Mohammadi Ziarani G, *Int J Chem Tech Res.*, 2009, **1(3)**, 426.
4. Badiei A, Gholami J and Khaniani Y, *E- J Chem.*, 2009, **6**, S324.
5. Darabi H R, Aghapoor K, Mohsenzadeh F, Taala F, Asadollahnejad N and Badiei A *Catal Lett.*, 2009, **133**, 84-89.
6. Hashemi P, Shamizadeh M, Badiei A, Ghiasvand A R and Azizi K, *Chromatographia* 2009, **70**, 1147-1151.
7. Hashemi P, Shamizadeh M, Badiei A, Poor P Z, Ghiasvand A R and Yarahmadi A, *Anal Chem Acta*, 2009, **646(1-2)**, 1-5.
8. Bibby A and Mercier L, *Chem Mater.*, 2002, **14**, 1591-1597.
9. Gangali M R, Hajiagha Babaei L, Badiei A, Mohammadi Ziarani G and Tarlani A, *Anal Sci.*, 2004, **20**, 725.
10. Ganjali M R, Daftari A, Hajiagha Babaei L, Badiei A, Saberyan K, Mohammadi Ziarani G and Moghimi A, *Wat Air Soil Pollut.*, 2006, **173**, 71.
11. Javanbakht M, Badiei A, Ganjali M R, Norouzi P, Hasheminasab A and Abdouss M *Anal Chim Acta*, 2007, **601(2)**, 172-182.
12. Javanbakht M, Khoshsafar H, Ganjali M R, Badiei A, Norouzi P and Hasheminasab A, *Curr Anal Chem.*, 2009, **5**, 35.
13. Javanbakht M, Divsar F, Badiei A, Fatollahi F, Khaniani Y, Ganjali M R, Norouzi P, Chaloosi M and Ziarani G M, *Electrochim Acta*, 2009, **54**, 5381.
14. Ying J Y, Mehnert C P and Wong M S, *Angew Chem Int Ed.*, 1999, **38**, 57.
15. Monnier A, Schuth F, Huo Q, Kumar D, Margolese D, Maxwell R S, Stucky G D, Krisnamurthy M, Petroff P, Firouzi A, Janicke A and Chmelka B F, *Science*, 1993, **261**, 1299.
16. Lapena A M, Gross A F and Tolbert S H, *Langmuir*, 2005, **21(1)**, 470-480.
17. Echchahed B, Morin M, Blais S, Badiei A, Berhault G and Bonneviot L, *Micro Mesopor Mater*, 2001, **53**, 44.
18. Badiei A, Vahidifar R and Hasheminasab A, *Iran J Chem Chem Eng.*, 2008, **27**, 1.
19. Diaz I, Perez-Pariente J and Terasaki O, *J Mater Chem.*, 2004, **14**, 48.
20. Badiei A, Morin M, Cantournet S and Bonneviot L, *Langmuir*, 1998, **14**, 7087.
21. Gomez S, Giraldo O, Garces L J, Villegas J and Suib S L, *Chem Mater.*, 2004, **16**, 2411.
22. Israelachvili J N, Mitchell D J and Ninham B W, *J Chem Soc Faraday Trans.*, 2, 1976, **72**, 1525.



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