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The anion sequence in the phase transformation of mesostructures templated by non-ionic block copolymers†

Jiawei Tang, Chengzhong Yu,* Xufeng Zhou, Xiaoxia Yan and Dongyuan Zhao
Department of Chemistry, Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Fudan University, Shanghai, 200433, P. R. China. E-mail: czyu@fudan.edu.cn

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A *p6m* to *Ia3d* mesophase evolution is achieved by simply adjusting the acidity and/or anion species in the presence of block copolymers; the unusual anion sequence that affects the phase behavior of block copolymer templated mesostructured solids is revealed to be SO_4^{2-}(HSO_4^-) > NO_3^- > Br^- > Cl^-.

Ionic surfactants[1] and non-ionic surfactants/block copolymers[2] are two classes of commonly used templates in the synthesis of ordered mesoporous materials. The molecular structure as well as the packing behavior of the template is one of the most important factors that may direct the final solid mesostructure. Similar to the well-known surfactant packing parameter (g; $g = v/al$, where v is the chain volume, a is the hydrophobic/hydrophilic interfacial area and l is the chain length), the hydrophilic/hydrophobic volume ratio V_H/V_L is also suggested especially in block copolymer templating systems to account for the formation of different mesophases.[3] Other factors that may affect the phase transformation of mesostructures, *e.g.* the effect of anions, have also been studied in a cationic surfactant templating system.[4] However, the effect of the anions is much weaker in a block copolymer templating system considering their ability to induce phase transformation; an anion sequence in this regard has not been reported until now.

Recently, the synthesis of mesoporous silica with a bicontinuous *Ia3d* structure in the presence of non-ionic block copolymers has drawn a lot of attention.[5–9] These syntheses were carried out with organosiloxane or with organic compounds as additives by a solvent-evaporation method,[5] a laboratory-synthesized copolymer,[6] a very high concentration of NaI salt,[7] a solvothermal treatment[8] or a copolymer–butanol mixture as the structure directing agent.[9] Here, we demonstrate that a *p6m* to *Ia3d* phase evolution is achieved by simply adjusting the acidity and/or anion species in the presence of block copolymers. More importantly, an unusual anion sequence that affects the phase behavior of block copolymer templated mesostructured solids is revealed. This is the first report where the effect of a series of anions has been investigated on the structural change of non-ionic block copolymer templated mesoporous materials.

Mesoporous materials were synthesized by using $EO_{20}PO_{70}EO_{20}$ [denoted P123, BASF. EO is poly(ethylene oxide) and PO represents poly(propylene oxide)] and *n*-BuOH as co-templates and the synthesis procedures were similar to KIT-6.[9] The weight ratio of P123, *n*-BuOH, the silica source tetraethyl orthosilicate (TEOS) and the acid was kept at 1.00 : 1.00 : 2.08 : 40.00 g (X M) in all experiments and the concentrations of the desired acids and inorganic salts were systematically studied. Acid solutions with different concentrations were diluted from a stock solution of 2.0 M. The mixture was allowed to react at 35 °C with stirring for 1 day and then moved to a 100 °C oven for 1 day. The resultant white precipitates were filtered and dried in air. Surfactants were removed by calcination in air at 550 °C for 6 h.

The influence of HCl concentration upon the final mesostructure was examined first (X = 0.5, 1.0, 1.1, 1.2, 1.3, 1.4, 1.5 and 2.0 M) and representative X-ray diffraction (XRD) patterns of as-synthesized samples are shown in Fig. 1a. When $X \leqslant 1.2$, the resultant product has a bicontinuous 3D-cubic *Ia3d* mesophase[9] with a unit cell parameter (a) of 243.0 Å at $X = 1.2$. When $X \geqslant 1.3$, a 2D-hexagonal *p6m* mesophase[2] is obtained with a = 99.2 Å at $X = 1.3$. The above observation has been confirmed by transmission electron microscopy (TEM). The sample synthesized at 1.2 M HCl shows a typical lattice array along the [111], [311] and [531] directions for an *Ia3d* symmetry (Fig. 2a, 2b and 2c, respectively). The typical stripe-like TEM image recorded with the $X = 1.3$ sample is also in accordance with the *p6m* structure as concluded from the XRD results (Fig. 2d).

In the study of block copolymer templated mesoporous materials, mesostructure evolution from *p6m* to *Ia3d* induced simply by a slight change in acidity (from 1.3 to 1.2 M HCl) has not been reported before. It is suggested that with the decrease of acidity, the protonation of the EO moieties decreases,[10] resulting in a decrease in V_H/V_L and therefore a phase transformation from the relatively hydrophilic *p6m* to the more hydrophobic *Ia3d* phase.[3] N_2 sorption results indicate that calcined mesoporous materials obtained at X = 2.0 and 0.5 have a mean pore size of 7.3 and 8.0 nm, respectively, suggesting a certain degree of increasing of V_L induced by the relatively weaker protonation at low acidic conditions.

The delicate phase transformation behavior induced by a slight change in acidity in the butanol/P123 templating system makes it a sensitive "balance" to measure some "weak" effects upon phase transformation which cannot be differentiated under normal conditions. When 2.0 M H_2SO_4 is used instead of HCl in the system, the *Ia3d* mesostructure is obtained according to the TEM and XRD results (SI 1, see ESI†). This result suggests that the anions are also important in the phase transformation in addition to the acidity effect.

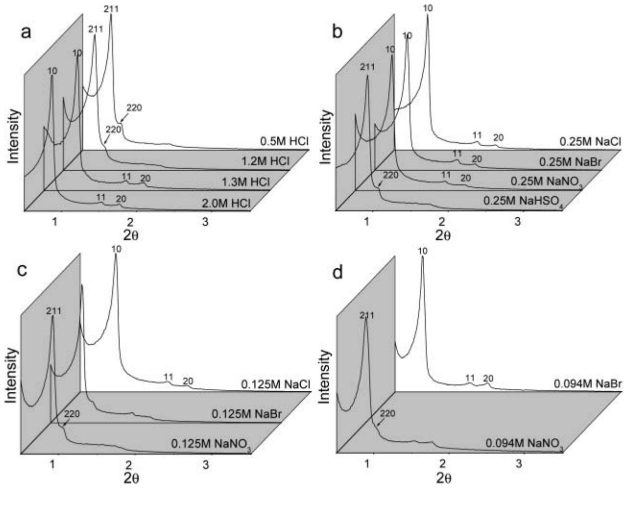

Fig. 1 Powder XRD patterns of as-synthesized mesoporous materials synthesized at various concentrations of HCl (X M) and anions (Y M): (a) X = 0.5–2.0 and Y = 0; (b) X = 1.5 and Y = 0.25; (c) X = 1.4 and Y = 0.125 and (d) X = 1.4 and Y = 0.094.

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† Electronic Supplementary Information (ESI) available: TEM images and XRD patterns of materials synthesized by 2.0 M H_2SO_4; detailed explanation on the reported anion sequence in cation surfactant systems.[4] See http://www.rsc.org/suppdata/cc/b4/b408100e/

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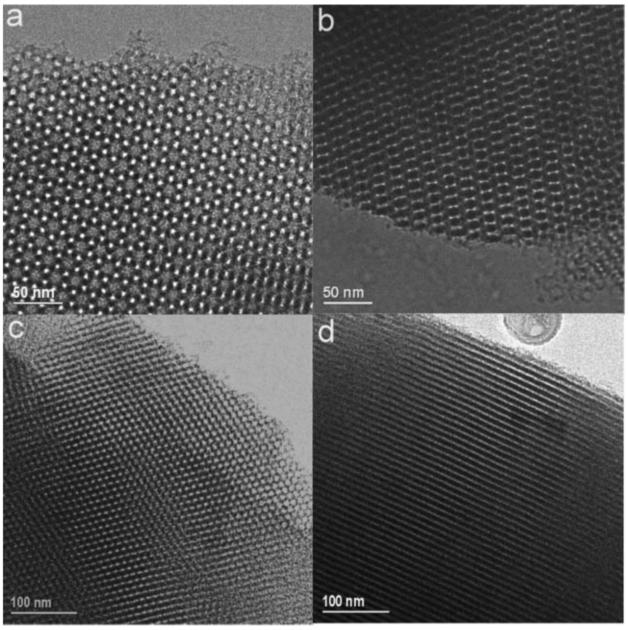

Fig. 2 TEM images (a), (b) and (c) of calcined *Ia*3*d* mesoporous silica ($X = 1.2$) taken along the [111], [311] and [531] directions, respectively. TEM image (d) of calcined *p*6*m* mesoporous silica ($X = 1.3$) taken along the [10] direction.

In order to study the effect of the anions individually, NaCl, NaBr, $NaNO_3$ and $NaHSO_4$ with the same concentration (Y M) were added to an X M HCl solution in one batch of synthesis. When $X = 1.5$ and $Y = 0.25$, the use of $NaHSO_4$ gives rise to an *Ia*3*d* structure while the use of the other three anions results in a *p*6*m* mesostructure (Fig. 1b). If $X = 2.0$ and $Y = 0.25$, a mixture phase of both *Ia*3*d* and *p*6*m* is observed only in the case of $NaHSO_4$ and the use of the other three anions gives rise to a *p*6*m* mesophase, as expected. These results suggest that the anion SO_4^{2-}–HSO_4^- induces a more hydrophobic mesophase than the other three anions (referred to as a more hydrophobic anion hereafter). By carefully tuning the acidity and the concentration of the salts, the hydrophobic anion sequence of the other three anions is characterised. When $X = 1.4$ and $Y = 0.125$ (Fig. 1c), the use of NO_3^- leads to the formation of a *Ia*3*d* mesophase, Br^- induces a mixture phase of both *Ia*3*d* and *p*6*m* (also confirmed by TEM) and Cl^- still gives rise to a *p*6*m* structure. When $X = 1.4$ and $Y = 0.094$, the use of NO_3^- results in the formation of a mixture phase (*Ia*3*d* and *p*6*m*) and Br^- leads to a *p*6*m* mesophase (Fig. 1d). The hydrophobic anion sequence is therefore determined to be $SO_4^{2-}(HSO_4^-) > NO_3^- > Br^- > Cl^-$ and is consistent in all experiments.

It is surprising to note that the hydrophobic anion sequence determined in our experiments does not obey the classic Hofmeister sequence ($SO_4^{2-} > Cl^- > Br^- > NO_3^-$),[11] nor its reverse, or the reversed hydrated anion radii sequence suggested by Che *et al.* ($NO_3^- > Br^- > Cl^- > SO_4^{2-}$).[4] Considering the strong acid nature of H_2SO_4 and the dissociation constant of HSO_4^- ($K_a = 1.2 \times 10^{-2}$), the HSO_4^- and SO_4^{2-} species coexist in H_2SO_4 solution: the dominant anionic species in 2.0 M H_2SO_4 solution is HSO_4^- and the fraction of SO_4^{2-} increases when the acid concentration decreases. For this reason, the effect of SO_4^{2-} and HSO_4^- is represented together in our discussion. Indeed, a more accurate hydrophobic anion sequence in Che's report is most likely represented as $NO_3^- > Br^- > SO_4^{2-}(HSO_4^-) > Cl^-$ (SI 2, see ESI†).[4] Nevertheless, the anion sequence that induces structural change is obviously different between the non-ionic block copolymer and ionic surfactant templating systems.

Table 1 Effect of anions and the corresponding hydrophobic-hydrophilic sequence in non-ionic copolymer templated systems

	Hydrophobic → Hydrophilic
A: radii effect	$NO_3^- > Br^- > HSO_4^- > Cl^-$
+	
B: dehydration effect	$SO_4^{2-} > Cl^- > Br^- > NO_3^-$
⇓	
C: observed sequence	$SO_4^{2-}(HSO_4^-) > NO_3^- > Br^- > Cl^-$

In the study of the common Hofmeister anion effect, the system is usually under neutral conditions, while in block copolymer templated synthesis (our system) and Che's report, strong acidic conditions were employed. In Che's case, it is suggested that the counter-anions with smaller hydrated radii may bind more closely and strongly with the head group of the cationic surfactant and therefore decrease the hydrophilic volume ratio, leading to a phase transformation to more hydrophobic phases. In our synthesis with non-ionic block copolymer templates under strong acidic conditions, it is now believed that the interaction at the inorganic/organic interface is through a $(\text{–}EO^0H^+)(X^-H_2^+OSi\text{–})$ pathway.[2] In this regard, the partially charged EO head group is indeed not "non-ionic" in the assembly process; the effect of the counter-anion radii should be considered (Table 1A). On the other hand, anions with large hydration ability greatly dehydrate the EO group and decrease the V_H/V_L ratio (the normal Hofmeister sequence, Table 1B). It is noted that SO_4^{2-} possesses a hydration free energy that is ~3 times larger than that of NO_3^-, Br^- and Cl^-.[12] The interplay of the radii effect and the dehydration effect gives rise to the observed anion sequence (Table 1C) in our experiments.

In general, an abnormal anion sequence that affects the phase transformation behavior of mesostructured composites has been determined in non-ionic block copolymer templating systems. The faithful effect of anions is important to better understand the formation mechanism of mesoporous materials in different systems and is also useful in other research areas such as physical and biological chemistry.

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