

# Counterion and alcohol effect in the formation of mesoporous silica

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## Abstract

The adsorption of silicate anions onto the cationic micellar surface and the slow condensation of silicate species control the early phase of the alkaline synthesis of mesoporous materials. We found that there exists a well-defined induction time ( $t_p$ ) of the transition from clear solution to white precipitation gel. The induction time  $t_p$  increases with the concentration of added salt NaX. At a fixed concentration of the salts, the  $t_p$  decreases in the order:  $\text{ClO}_3^- > \text{NO}_3^- > \text{Br}^- > \text{SO}_4^{2-}$ ,  $\text{SO}_3^{2-} > \text{Cl}^- > \text{F}^-$ , with  $\text{F}^-$  being the most effective ion in forming the hexagonal phase gel. The order in induction time reflects the strength in counter-ion binding of  $\text{X}^-$  to micelles. The stronger adsorbing  $\text{X}^-$  would block the adsorption of silicate ions on micelles and delay the formation of the silica–surfactant mesophases. The order of the ion series agrees with the Hofmeister series in many lyotropic systems such as in ion–protein and ion–surfactant interactions. Surfactant chain length and the addition of 1-alkanols affects the counterion adsorption behavior and they also have strong influences on the rate of formation of the silicate–surfactant mesophase. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Mesoporous; Hexagonal phase; Hofmeister; Lyotropic; Counterion

## 1. Introduction

Mesoporous silica is formed by condensing silicate anions in a structural template of surfactant followed by calcination [1,2]. It can be synthesized by either the alkaline route [1,2] or the acidic route [3,4]. In the synthesis of mesoporous silica MCM-41, cationic surfactant and silicate polyanion

combine in alkaline solution to form the hexagonal phase. In the alkaline route, surfactant and silicates organize by the strong  $\text{S}^+\text{I}^-$  electrostatic interaction where  $\text{S}^+$  is the positively charged surfactant organization and  $\text{I}^-$  is the negatively charged silicate polyanion. Although the counterion  $\text{X}^-$ , either from the surfactant or from salt added to the initial solution, is not present in the final mesoporous materials, it plays an important role in the initial formation of the surfactant–silicate mesophase. It has been known the counterion species  $\text{X}^-$  has effects on the structural order [5]

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and morphology [6] of the final product. It is the purpose of this paper to investigate such counterion effects from the point of view of surfactant–counterion interactions. The close resemblance between the mesophase observed in the inorganic–surfactant composite and the aqueous surfactant–counterion system suggests that the formation processes are similar in both cases.

In the initial gel of synthesizing MCM-41, two processes are simultaneously in operation: (1) the exchange of polysilicate anions against  $X^-$  for the surface of micelles while elongating it to rod form [7], (2) the micelle-catalyzed silica condensation leading to mesophase of hexagonal symmetry [8]. Different  $X^-$  anion offers different competition and the rate of micelle catalyzed silicate condensation would be expected to be different.

On the other hand, in the acid route the interaction is different. The surfactant ( $S^+$ )-silica ( $I^+$ ) interaction in  $S^+X^-I^+$  is mediated by the counterion  $X^-$  [4]. Recently, we investigated the kinetics of formation of the surfactant–silica composite under acid condition by using various acid sources HX [9]. There is a well-defined induction time  $t_p$  for the formation of meso-structural precipitation [8] and it is a good indicator of the binding strength of the counterion. We found  $t_p$  increases according to the lyotropic series:  $NO_3^- < Br^- < Cl^-$  under the same pH value. The induction rates were analyzed with a micelle-catalyzed reaction scheme. The order in induction time reflects the strength in counter-ion binding of  $X^-$ . Nitric acid with the highest binding strength of counterion  $NO_3^-$  tends to form very long micelles. We found the dependence of structure quality and morphology on the counterion concentration  $[X^-]$  can be understood as a consequence of counterion binding.

It is interesting to ask whether an analogous counterion specific effect would exist for the alkaline synthesis process. If it does exist, we would like to know the trend and effect it will give on the process. We will investigate the effect of various counterions on the induction time of forming the liquid crystalline phase.

In the alkaline synthesis of mesoporous silica, the initial micelle formation is fast but the silica condensation is slow. Cheng et al. have found that

the surfactant micelles catalyze the polymerization of the silicates based on the  $^{29}Si$ -NMR observation [8]. Here we examine the catalytic action by reporting the kinetically well-defined “induction period” for forming the observable mesophase of surfactant–silicate. In this paper, we study the kinetics of induction stage by varying the counterion species with well-defined solution condition.

According to Huo et al. [4], the formation of the  $S^+I^-$  mesostructure intermediates is driven by the electrostatic interaction of the positively charged  $S^+$  and the counterion  $X^-$ . The surfactants adsorb the counterion (provided by the sodium salts NaX) to form the  $S^+X^-$  micelles. Theory of micelle-catalyzed chemical reactions has been developed in the past for many chemical reactions [10]. It applies to reactions taking place predominantly on the micellar surface. The enhanced reaction is a result of increased of local concentration of reactants by counterion adsorption or solubilization [11,12].

With enough neutralization of surface charges, one observes the onset of mesophase after a certain induction period. Previously, White and coworkers [11] have studied the slow mesoporous silicate film growth at air–water interface by X-ray reflectivity. They found that the formation of an organized mesophase of surfactant–silicate layer after the induction period. Other in situ X-ray diffraction studies also confirm that the precipitation formed after the induction period is the hexagonal mesophase [13].

In this paper, we examine the variation in induction rates by changing both the  $S^+$  (surfactant and cosurfactant) and  $X^-$  (counterion) species. The incorporation of cosolvents or cosurfactants, such as 1-alkanols, changes the micelle–counterion interaction, it also changes the rate of silica–surfactant mesophase formation. The co-solvent and cosurfactant effects will also be discussed.

## 2. Experimental

### 2.1. Materials

The silica source was tetraethylorthosilicate (TEOS, 98%) from Acrôs. The quaternary

ammonium surfactants  $C_nH_{2n+1}(CH_3)_3NBr$  ( $n = 10-16$ ) were obtained from Aldrich. Ethanol, 1-propanol, 1-butanol, 1-pentanol and NaOH are from Acrôs or Merck. Sodium salts are purchased from Acrôs. All chemicals were used directly without further purification.

## 2.2. Kinetic measurement

The structural-directing agent  $C_n$ TMABr was dissolved in a proper amount of water and then one added a suitable amount of 1.0 M NaOH aqueous solution and 1-alkanols to give a clear solution. We used the sodium salts,  $NaNO_3$ , NaBr, NaCl,  $Na_2SO_3$ ,  $Na_2SO_4$ , NaF, and  $NaClO_3$ , to adjust the ionic strength and the counterion concentration  $[X^-]$ . Then the silica source TEOS was added under stirring. Initially, one obtained a clearly solution immediately. At a well-defined time  $t_p$ , the white precipitate appears. We measured the induction time  $t_p$  for various counterion concentrations. The composition of the solution is chosen as 1  $C_n$ TMABr:177  $H_2O$ :0–11 NaX:0.5 NaOH:1 TEOS:(0–6.0) 1-alkanols.

## 3. Results and discussions

In this section, we discuss the effects of counterion, alcohol, and surfactant chain length on the rate of formation of inorganic silica–surfactant mesophase.

### 3.1. Counterion effect

Fig. 1 shows the relationship between the induction time for the formation of the mesophase and the concentration of the counterion  $[X^-]$ . The induction time  $t_p$  increases with the concentration of added salt NaX. This is because the more  $X^-$  ions the harder for the silicate oligomers to compete to adsorb on the micellar surface. The catalytic polymerization of the silicates becomes less effective at higher  $[X^-]$ .

At a fixed concentration (greater than 0.1 M) of the salt, the  $t_p$  value decreases roughly in the order:  $ClO_3^- > NO_3^- > Br^- > SO_4^{2-} \sim SO_3^{2-} > Cl^- > F^-$ , with  $F^-$  being the most effective ion in forming the

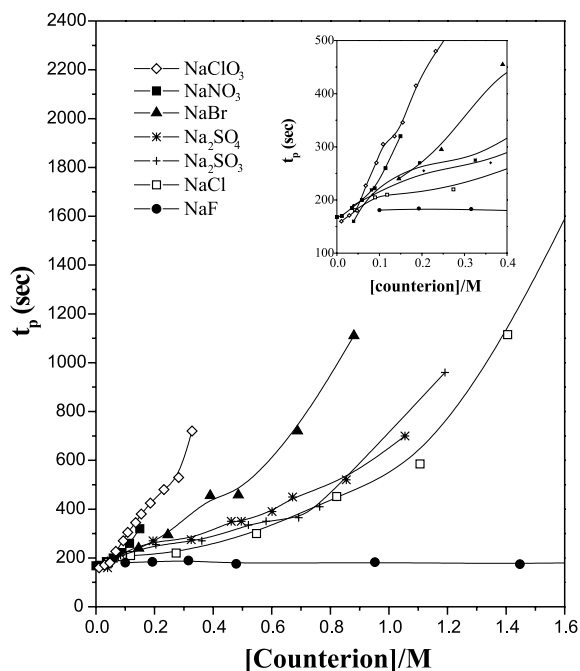


Fig. 1. Plots of  $t_p$  vs.  $[X^-]$  for  $C_{16}$ TMABr–NaX–TEOS– $H_2O$  systems at 30°C. The composition of the solution is chosen as 1.0  $C_{16}$ TMABr:177  $H_2O$ :(0–11) NaX:0.5 NaOH:1.0 TEOS.

hexagonal phase gel. The order in the anions in the formation of mesophase is consistent with the well-known Hofmeister series in the binding of counterion to cationic surfactant [14,15]. For example, recent results obtained from direct electrochemical potential EMF measurement of degree of counterion association also follow the above Hofmeister (lyotropic) order [16]. One should note that the bivalent sulfate and sulfite ions show rather weak binding tendency. This is also consistent with the corresponding behavior in micelle–sulfate interaction [17].

In our previous study of the acidic synthesis [9], we add both the acid HX and the salt NaX in order to investigate the effects of  $[X^-]$  and  $[H^+]$ . We found  $t_p$  decreases with the increase the concentration  $[X^-]$  while keeping  $[H^+]$  constant. The values of  $t_p$  decrease in the order:  $Cl^- > Br^- > NO_3^-$ . The order (in anions) of  $t_p$  that we found for the alkaline synthesis is opposite to those found in the acid synthesis. However, they just reflect the same order of the binding strength of counterion

to surfactant. In the alkaline synthesis route, the counterion  $X^-$  acts as a block to the adsorption of silicate ions to micellar surface. The stronger adsorbing ion such as nitrate would delay the silicate adsorption and its polymerization the most. From the considerations of counterion effects, the formation mechanisms of the mesoporous silica in acid and alkaline conditions can be compared schematically in Fig. 2.

Both of the two mechanisms include: (I) binding of the counterion and surfactant; (II) the hydrolysis of TEOS; (III) preferred polymerization of silicate species at the surfactant–silicate interface; and (IV) charge-matching combination of the surfactant and silicate oligomers. The primary distinction of the two formation processes is in the cooperative interaction between surfactant and silica species. In alkaline condition, the silica spe-

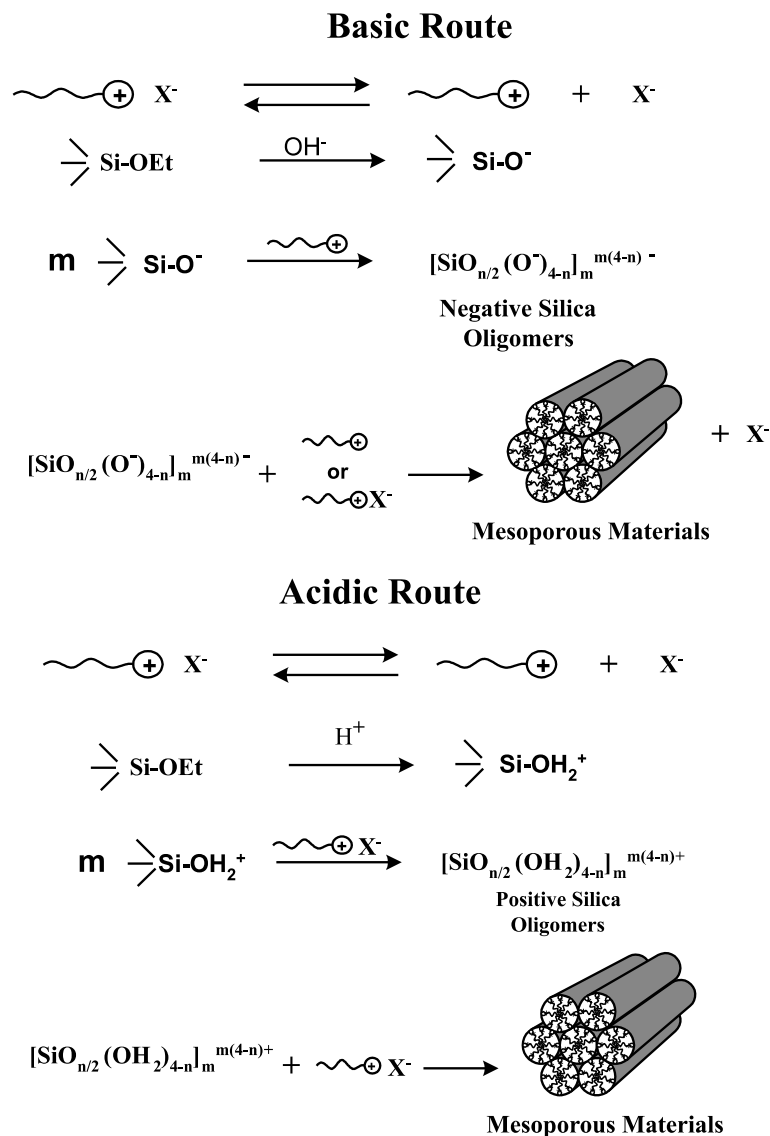


Fig. 2. The comparison of the formation processes of the mesoporous materials in base and acid conditions.

cies are negatively charged and thus energetically favored to condense at the surface of the positive-charged surfactant ( $S^+$ ) through the strong electrostatic interactions ( $S^+I^-$ ). Thus the addition of counterion with stronger binding affinity would decrease the number of active site ( $S^+$ ) and increase the  $t_p$ . However, in acid synthesis ( $pH < 1$ ), the dominating cationic silica precursor ( $I^+$ ) combines with  $S^+X^-$  type active sites on the surfactant micelles through a weaker electrostatic interactions. The stronger binding ion  $X^-$  tends to bind to the active sites ( $S^+X^-$ ) to promote the silica condensation in  $S^+X^-I^+$  and thus decrease the  $t_p$ . Therefore, the counterion effect in the alkaline synthesis is in opposite to the acidic synthesis.

### 3.2. Surfactant chain length

Next, we investigate the effect of surfactant chain length on the rate of formation of the product materials. Fig. 3 shows the relationship of

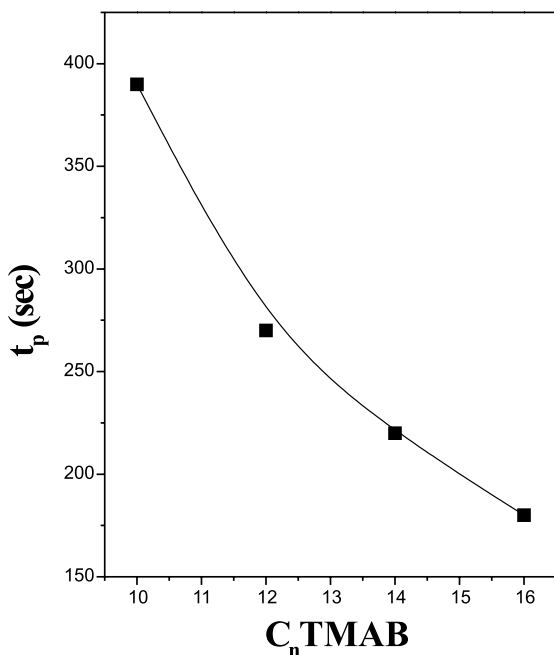


Fig. 3. The relationship between induction time  $t_p$  and the carbon chain length of the surfactants  $C_n$ TMABr at 30°C. The composition of the solution is 1.0  $C_n$ TMABr:177  $H_2O$ :0.5 NaOH:1.0 TEOS.

$t_p$  versus chain length. Surfactants with longer chain length form the mesophase faster. Due to the hydrophobic–hydrophilic balance [18], the longer chain length of the surfactant has a stronger counterion association. Thus, one expects more silicate polyanion association on the micelles made of longer surfactant molecules leading to more catalytic silicate condensations. While under acidic condition, we noted that strong binding anions at higher concentration, such as  $Br^-$  and  $NO_3^-$ , combined with longer chain surfactants to promote the formation of the longer rod micelles which can be aligned under shear flow [19,20]. Good quality mesophases can often be synthesized in this way. On the other hand, weaker binding anions such as  $Cl^-$  often lead to the worm-like micelle and worse order in meso-structures [21].

### 3.3. Alcohol effect

It is known that 1-alkanols as additives in synthesis gel affect the structural order of MCM-41 [22]. The medium chain alcohol,  $C_nH_{2n+1}OH$  ( $n = 4-6$ ), acts as a cosurfactant and leads to better hexagonal order in MCM-41. On the other hand, shorter chain 1-alkanols (ethanol and 1-propanol), acting as polar cosolvents, tends to disrupt the structural order of hexagonal mesophase due to the weaker solvophobic effect [22]. We would like to understand this behavior by studying the alcohol effect on the rate of formation of mesophase. In order to examine the alcohol effect under both types of influences, we chose to study the borderline cases of ethanol, 1-propanol, 1-butanol and 1-pentanol.

Fig. 4 shows the influence of induction time  $t_p$  by the chloride concentration with the addition of 1-alkanols. Compared to the case without alcohol, the addition of ethanol and 1-propanol leads to a shorter induction time, e.g. the reaction goes faster. On the other hand, 1-butanol and 1-pentanol result in a slower rate of formation of the surfactant/silicate composite. Apparently, the longer chain alcohol induces more chloride ion adsorption on micelle which in turn leads to less silicate adsorption and condensation. Acting as cosurfactants, 1-butanol and 1-pentanol are solubilized on the micellar palisade surface, lowering the charge

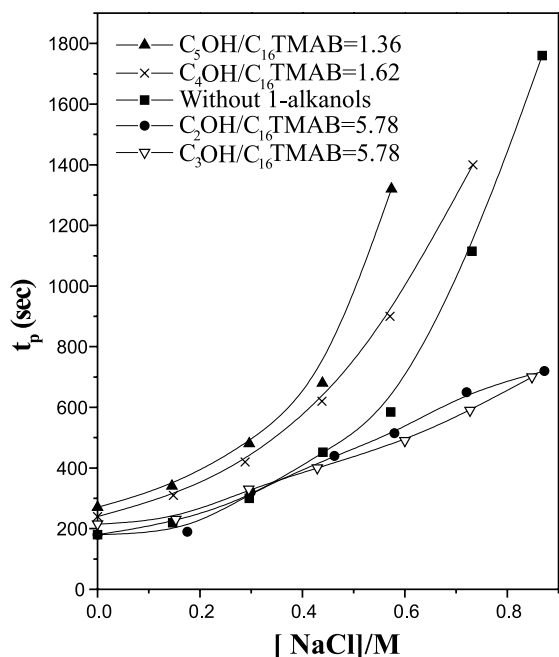


Fig. 4. The relationship between induction time  $t_p$  and chloride concentration with the addition of 1-alkanols for the surfactant  $C_n$ TMABr at 30°C. The composition of the solution is 1.0  $C_{16}$ TMABr:177  $H_2O$ :(0–3.0) NaCl:0.5 NaOH:1.0 TEOS: $X$  1-alkanols.  $X = 1.36$  for 1-pentanol;  $X = 1.62$  for 1-butanol;  $X = 5.78$  for 1-propanol;  $X = 5.78$  for ethanol.

density, and lead to more counterion adsorption. There will be thus less available sites for the silicates.

On the other hand, for ethanol and 1-propanol, compared to the case without alcohol addition, the alcohol effect is not strong at  $[Cl^-]$  less than 0.5 M. Previously, Agren et al. have found that the addition of small amount of 1-alkanols (as cosolvents) does not have a large influence on the kinetics of mesophase formation [23]. They attributed this to the smaller influence on silicate speciation by 1-alkanols. Our data agree roughly with the above observations. At higher concentration of chlorides, they show a shorter induction time than the case without alcohol. Ethanol and 1-propanol acts more like cosolvent. Their presence in solution, leading to less driving force for the formation of surfactant aggregates, results in a lesser counterion adsorption. The polysilicate an-

ions are easier to condense and thus one observes a higher rate of formation of the surfactant/silicate mesophase. The alcohol effect would give us one more control of the association of the surfactant–silicate organization in synthesis [23]. For example, Mou and coworkers [24,25] previously employed 1-butanol as cosurfactant in the  $C_{14}$ TMABr + silicate system to make the hierarchical pillar-within-sphere morphology.

### 3.4. Implications on the synthesis of MCM-41

From this study, one can understand the effects of counterion, surfactant, and the alcohol on the rate of formation of inorganic-silicate composite as its consequence on the adsorption of silicate polyanions and the interionic competition. The counterion specificity follows the well-known Hofmeister series in determining surfactant aggregation. Lower counterion concentration of  $X^-$  leads to fewer competition of silicate and to higher rate of catalyzed silica condensation in alkaline synthesis. The perturbation by alcohol as cosolvent (shorter chain alcohol) or cosurfactant (longer chain than 1-butanol) can also be understood as consequences of changes in counterion adsorption. There has been a lot of works on the micelle-catalyzed chemical reactions, mostly ionic reactions; the kinetic schemes are often parallel [26–28]. Further detailed kinetic studies based on such kind of analysis would be desirable to understand quantitatively the binding competition in the formation of surfactant–silicate composite.

Once we understand the elementary kinetics in surfactant–silicate system, one could further correlate its rich morphologies and structural control with kinetic information. It would be interesting to understand the relationship of counterion binding and particle size [29], shape and wall thickness [30] of the mesoporous product. In the post-synthesis treatments in salt solution [31–33], the surfactant–counterion binding is important in controlling the pore structure and hydrothermal stability. In principle, the many controlling factors of the rate of formation of the mesophase would give one a variety of controls on the rate of its nucleation, growth and aggregation. A better understanding of the kinetics involved would give one better

control of the structural order and morphology of the mesoporous silica materials [9].

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