

Synthesis of microporous molecular sieves by surfactant decomposition†

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Microporous molecular sieves can be synthesized under the high temperatures of 165–180 °C and high pH of 10–12.5, using surfactant cetyltrimethylammonium bromide (CTAB) as a template. It was found that various factors, such as temperature, alkalinity, Si:Al ratio and the presence of a small amount of organic alkylammonium species (TMA⁺, TPA⁺) can affect the nature of the microporous materials obtained. In the wide range of Si:Al ratios, we can obtain such zeolites as sodalite, omega, ZSM-35, mordenite, ZSM-5 and silicalite. The experimental results suggest that the decomposition products of CTAB act as templates instead of surfactant CTAB itself. The synthesis condition of high pH (>10) and high temperatures (≥ 165 °C) can ensure the decomposition of CTAB, which is quite essential for the formation of microporous molecular sieves.

1 Introduction

Recently, a new family of mesoporous molecular sieves has been synthesized in a wide range of temperatures and pH *via* supramolecular self-assemblies of surfactants.¹ With the increase of synthesis temperature, however, the ordered supramolecular self-assembly is gradually dissociated to many single surfactant molecules, which lose the role as supramolecular templates. Beck *et al.*² systematically explored the role of alkyltrimethylammonium surfactants of the type $C_nH_{2n+1}(CH_3)_3NBr$ ($n=6-16$) over the entire range of synthesis temperatures, 100–200 °C, for the formation of various porous molecular sieves. They found that the formation of ZSM-5 (Si:Al= ∞) was favored under the conditions of temperatures higher than 150 °C and surfactants with shorter alkyl chain lengths like $n=6$ and 8. When increasing the temperature to 200 °C, mixtures of ZSM-5, ZSM-48 and dense phases were obtained by using the surfactants with longer alkyl chain lengths ($n=8-14$), whereas only an amorphous phase was formed for surfactant cetyltrimethylammonium bromide (CTAB). They suggested that single surfactant molecules direct the formation of microporous materials at higher temperatures. Similarly, Borade and Clearfield³ successfully synthesized ZSM-35 (Si:Al=10) at 165 °C in the presence of CTAOH ion-exchanged from CTAB, with a small amount of mordenite and Nu-3 as impurities. They also suggested that the surfactant CTAOH molecule itself act as a structure-directing agent in this synthesis. We also found that when increasing the crystallization temperature to 165 °C, high siliceous ZSM-5 could be obtained from the gel system containing CTAB.⁴⁻⁶ The gel system containing surfactant CTAB was used to synthesize mesoporous MCM-41, and has received wide attention in recent years. Therefore, it would be

interesting to enter into further study on the synthesis of microporous molecular sieves using surfactants, because it would give us a full understanding of the role of the surfactants in both synthesizing microporous materials and synthesizing mesoporous materials. In the present paper, we chose surfactant CTAB as a template and systematically investigated the effects of temperature, alkalinity, Si:Al ratio and the presence of small amounts of tetramethylammonium ions (TMA⁺) and tetrapropylammonium ions (TPA⁺) on the nature of the products obtained. The role of surfactant CTAB in the synthesis of microporous materials was also discussed.

2 Experimental

2.1 Synthesis

Water glass (Na₂O 7.4 wt%, SiO₂ 25.4 wt%, H₂O 67.2 wt%) and sodium aluminate were used as the Si and Al sources, respectively. A typical hydrothermal crystallization procedure was as follows: 4 g water glass was added dropwise to a surfactant CTAB solution (1 g CTAB dissolved in 10 ml H₂O) with vigorous stirring at room temperature. After this, the surfactant–silicate gel mixture was continuously stirred at room temperature for 30 min, a required amount of sodium aluminate solution being added dropwise with vigorous stirring. The whole mixture was also stirred at room temperature for 30 min more. The molar composition of this surfactant–aluminosilicate gel mixture was $(0.29 + 1/2x) Na_2O : SiO_2 : 1/2x Al_2O_3 : 0.16 CTAB : (26 + 100/x) H_2O$ ($x=Si:Al$). In several cases, a small amount of alkylammonium species such as tetramethylammonium hydroxide (TMAOH, 25 wt%) or tetrapropylammonium bromide (TPABr) was added into the above gel to study their effects on the products obtained (alkylammonium ions: SiO₂=0.039). The pH of the gel was adjusted by the addition of 50 wt% acetic acid. Then, the gel mixture was sealed in a 40 ml stainless steel autoclave and heated in an oven at 100–200 °C for 4 h–10 d. Before the synthesis, the stainless steel autoclaves were thoroughly cleaned by hot alkaline solution to avoid the seeding effect of residue during the hydrothermal treatment. The precipitated products were recovered by filtration, washed

†Electronic supplementary information (ESI) available: IR spectra and assignments for CTAB and its decomposition product; decomposition of CTAB in the presence of SiO⁻ or OH⁻. See <http://www.rsc.org/suppdata/jm/b0/b005770n/>

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in distilled water and dried in air at 100 °C. The as-synthesized products were calcined at 540 °C for 1 h in a nitrogen flow followed by 6 h in air.

2.2 Characterization

Powder X-ray diffraction (XRD) patterns were recorded with a Rigaku D/MAX-IIA X-ray diffractometer system equipped with Ni-filtered Cu-K α radiation and operated at 40 kV and 20 mA. The solid-state MAS NMR spectra were recorded at room temperature on a Bruker MSL-300 spectrometer with resonance frequencies of 78.21 MHz for ^{27}Al NMR and 59.63 MHz for ^{29}Si NMR. The magnetic field was 7.05 T. The spin rate of the sample was 4.0 KHz and the number of scans was *ca.* 1500–2500. The chemical shifts were referenced to tetramethylsilane for ^{29}Si and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ for ^{27}Al . IR spectra were obtained on a Nicolet 55XC FTIR spectrometer with KBr as reference. Differential thermogravimetric (DTG) analysis was performed on a Rigaku PTC-10A thermal analyzer under argon flow with a heating rate of 10 °C min^{-1} . The pH was measured with a homemade pH meter. Because the pH of the gel gradually increased with the aluminosilicate polymerization moving towards equilibrium during the crystallization, we should distinguish between pH and initial pH in this paper. The initial pH here refers to the pH of the gel that was adjusted and measured before hydrothermal crystallization, while the pH here was measured after the crystallization.

3 Results and Discussion

3.1 Synthesis conditions of microporous molecular sieves templated by CTAB—temperature and alkalinity

It is well known that with an increase of concentration above critical micelle concentration (CMC), surfactant molecules tend to aggregate as ordered self-assemblies, from which the mesoporous materials can be obtained. However, the synthesis of microporous materials follows a single molecular templating mechanism, which is quite different from the supramolecular templating mechanism for synthesizing mesoporous materials. That is to say, the surfactant aggregate should be dissociated to many single surfactant molecules for the synthesis of microporous molecular sieves. In general, the dissociation of surfactant aggregate depends much on temperature. Therefore, the possible products crystallized at various temperatures were firstly investigated when using CTAB as a template. Fig. 1 shows the XRD patterns of the products crystallized from the CTAB–aluminosilicate mixture (Si : Al = 15) at pH 12 for 4 d. Figs. 1a and 1b show four resolved peaks indexable as (100), (110), (200) and (210) reflections in a $P6m$ space group. The results indicate that well-ordered hexagonal MCM-41 can be obtained at 100–125 °C. While increasing temperature to 150 °C, Fig. 1c reveals two diffraction peaks indexable as (001) and (002) reflections, which can be attributed to a lamellar form of mesoporous M41S type. Only when the temperature increases up to 170 °C, the final product becomes quite different from the mesoporous phases. Fig. 1d shows several diffraction peaks in the 2θ ranges of 9–10, 12–14, 22–23 and 25–26°, which are characteristic of microporous ZSM-35 phase. Meanwhile, the peaks in the 2θ range of 1.5–10° totally disappear, indicating the destruction of the mesoporous phase. In addition, when the above mesoporous MCM-41 product, which was obtained at the lower temperature of 100 °C, was re-crystallized at the higher temperature of 170 °C along with its mother liquid, the MCM-41 phase was also transformed into the microporous ZSM-35 zeolite. When increasing the temperature to 200 °C (Fig. 1e), the final main products become the thermodynamically most stable α -quartz and α -cristobalite phases. The above results indicate that the

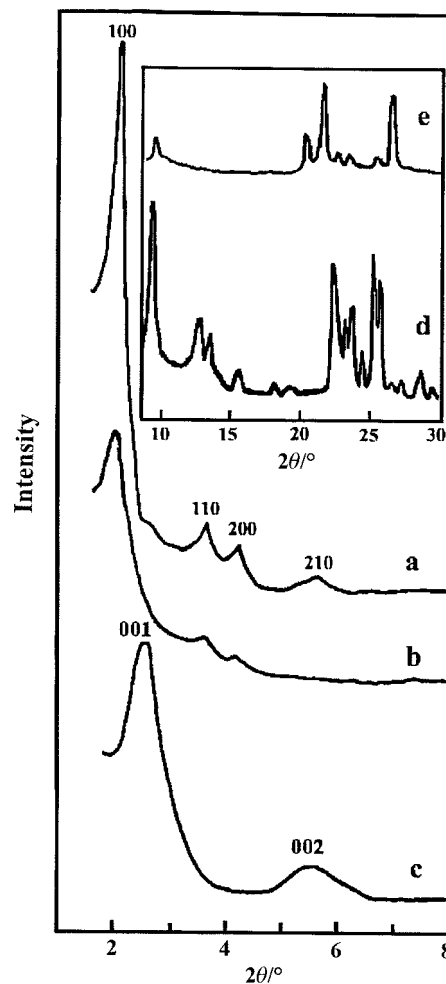


Fig. 1 Crystalline phases obtained from the gel mixture of CTAB–aluminosilicate (Si : Al = 15) at pH 12 and various temperatures. (a) 100 °C; (b) 125 °C; (c) 150 °C; (d) 170 °C and (e) 200 °C.

temperature is a very important factor in the synthesis of mesoporous and microporous phases.

Furthermore, in order to reveal the effects of temperature and alkalinity on the synthesis of porous materials from CTAB–aluminosilicate mixture, detailed studies on the relationship among phase transformation and crystallization temperature and alkalinity were carried out. The results are summarized in Fig. 2. It was found that the hexagonal mesoporous MCM-41 is obtained in the temperature range of 100–150 °C and pH range of 10–11. When the pH increases to 12 in the same temperature range, lamellar M41S phases are finally obtained, although hexagonal MCM-41 phases are

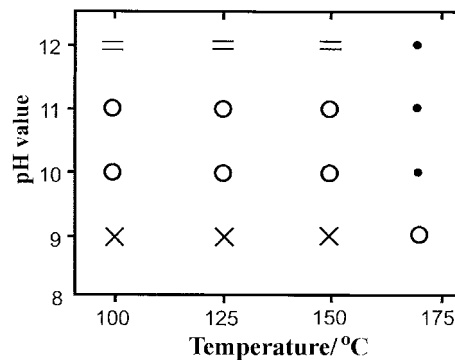


Fig. 2 Thermodynamically stable phases as a function of temperature and pH for the gel mixture of CTAB–aluminosilicate. × : amorphous; O : hexagonal mesoporous; = : lamellar mesoporous; ● : microporous.

produced at the early stage of the crystallization. In Fig. 2, the microporous phases can be synthesized only when increasing temperature to above 165 °C and pH above 10 simultaneously. For example, at the crystallization temperature of 170 °C, only the mesoporous phase is produced when the gel pH was kept at 9, whereas a microporous product is obtained if increasing pH to above 10. Moreover, the presence of surfactant CTAB is undoubtedly most important for the synthesis of both microporous and mesoporous materials. For comparison, when CTAB was not included in the above gel system, only amorphous phase or dense SiO₂ were finally obtained in the above range of temperatures and pH. Therefore, it is concluded that from the CTAB–aluminosilicate gel system, microporous materials can be crystallized in the range of temperatures of 165–180 °C and pH of 10–12.5.

Furthermore, it is notable that various kinds of microporous materials can be obtained by controlling different synthetic conditions in this temperature and pH range from the CTAB–aluminosilicate gel system. The details are described below.

3.2 Effects of various factors on the synthesis of zeolites from the CTAB–aluminosilicate gel system

3.2.1 Crystallization time. The XRD patterns of the as-synthesized products crystallized from the gel system with Si:Al=15 at 170 °C and pH 12 are shown in Fig. 3. One can see that under short crystallization time of 4 and 12 h, the products are hexagonal MCM-41 (Fig. 3a) and the lamellar phase (Fig. 3b), respectively. In Figs. 3a and 3b, although there are small peaks in the high 2θ range beyond 10°, they disappear after calcination, indicating no other phases exist except the mesoporous phase. With the increase of crystallization time to 24 h (Fig. 3c), the diffraction peaks in the 2θ range of 1.5–8° totally disappear, showing the destruction of the mesoporous phase. Meanwhile, several peaks appear in the 2θ ranges of 9–10, 12–14, 22–23 and 25–26°, respectively, which are characteristic of microporous ZSM-35 zeolite. Moreover, the

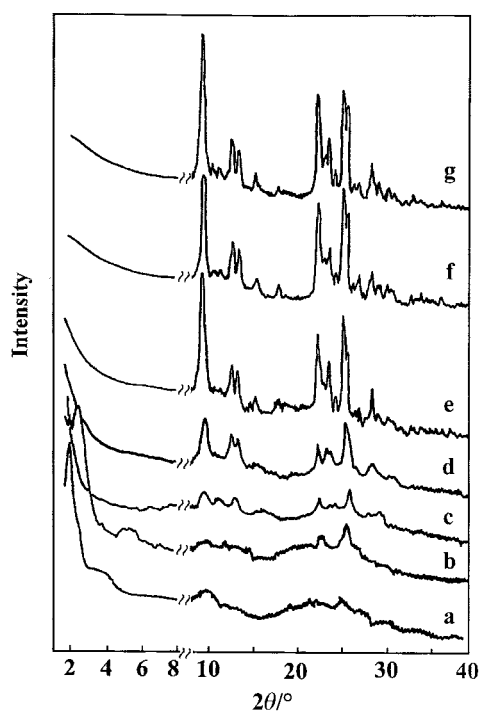


Fig. 3 XRD patterns of as-synthesized products obtained from the gel mixture of CTAB–aluminosilicate (Si:Al=15) at pH 12 and 170 °C for (a) 4 h; (b) 12 h; (c) 24 h; (d) 48 h; (e) 96 h; (f) 144 h; (g) 240 h.

crystallinity of ZSM-35 gradually increases with increasing crystallization time and it achieves a maximum at 144 h. No other phases are detected as impurities during the course of this crystallization.

The XRD results show that structure transformation occurs from mesoporous MCM-41 phase to lamellar phase and then to microporous ZSM-35 phase with the increase of crystallization time. Once the diffraction peaks for ZSM-35 appear, the peaks for the lamellar phase completely disappear. That is to say, lamellar M41S and ZSM-35 phase do not exist simultaneously during the crystallization. However, it is a different case for the synthesis from the gel system of CTAB–silicate. The co-crystallization products of lamellar M41S and silicalite phase were observed when the crystallization time was less than 3 d at 170 °C.⁶ In addition, the thermodynamically most stable phase, α-quartz or α-cristobalite, was also produced along with the silicalite phase when increasing the crystallization time to above 6 d. Therefore, for the CTAB–silicate system, the crystallization proceeded at 170 °C following the order of MCM-41→lamellar→lamellar + silicalite→silicalite silicalite + α-cristobalite or α-quartz.

Further characterization of the corresponding samples was done by ²⁹Si and ²⁷Al MAS NMR. Fig. 4 is the ²⁹Si NMR spectra of the calcined samples obtained from the gel mixture of CTAB–aluminosilicate (Si:Al=15). In Fig. 4a, a broad resonance with maximum at around -106 ppm can be observed for product crystallized for 12 h, showing a wide distribution of Al(Si)–O–Si bond angles in hexagonal or lamellar mesoporous phase.¹ With the formation of ZSM-35, the signals at -107.5 and -99.6 ppm, which result from Q⁴[Si(0Al)] unit and overlapping of Q³[Si(0Al)] and Q⁴[Si(1Al)]

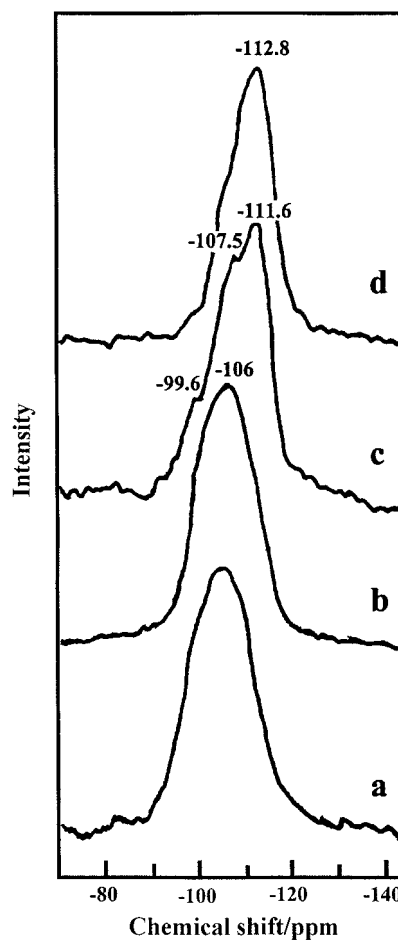


Fig. 4 ²⁹Si NMR spectra of the calcined products obtained from the CTAB–aluminosilicate gel mixture (Si:Al=15) at pH 12 and 170 °C for (a) 12 h; (b) 24 h; (c) 48 h and (d) 240 h.

units of the mesoporous phases respectively, gradually decrease their intensities (Fig. 4b–4c). Meanwhile, the main resonance shifts toward higher field at -111.6 ppm, which can be assigned to $Q^4[\text{Si}(0\text{Al})]$ units of a crystal structure. As for well-crystallized ZSM-35, Fig. 4d shows one unsymmetrical resonance with maximum at -112.8 ppm. By Gaussian simulation, this resonance can be deconvoluted to various signals corresponding to the crystallographic sites of Si with different Al coordination numbers, *i.e.* $Q^4\text{Si}(0\text{Al})$, -112.8 ppm; $Q^4\text{Si}(1\text{Al})$, -104 ppm and $Q^4\text{Si}(2\text{Al})$, -100 ppm. According to the integrated intensities of 68, 30 and 2% respectively, the $(\text{Si}:\text{Al})_{\text{NMR}}$ is calculated to be 15.8, which is well close to the Si:Al ratio in the gel composition.

The ^{27}Al NMR spectra of the products are shown in Fig. 5. When the structure is hexagonal or lamellar, there is only one resonance centered at 55.0 ppm corresponding to tetrahedrally co-ordinated Al (Fig. 5a). However, an unsymmetrical resonance with maximum at 65.6 ppm is detected adjacent to the signal at 55.0 ppm during the structure transformation from mesoporous phase to microporous ZSM-35 (Fig. 5b). This resonance, ranging from 60–80 ppm, consists of several overlapping peaks, which have been assigned to various aluminum coordination states with different number of neighboring ($-\text{SiO}-$) and ($-\text{OH}$) groups, such as the structures: $Q^1[\text{Al}(\text{OSi})]$, 70–72 ppm; $Q^2[\text{Al}(\text{OSi})_2]$, 66 ppm; $Q^3[\text{Al}(\text{OSi})_3]$, 61 ppm.⁷ With the formation of ZSM-35, the Q^1 peak vanishes quickly and the peak intensities for Q^2 and Q^3 centered at 65.6 ppm gradually decrease (Fig. 5c). The Q^2 and Q^3 peaks totally vanish and only one peak at 55 ppm remains when the well-

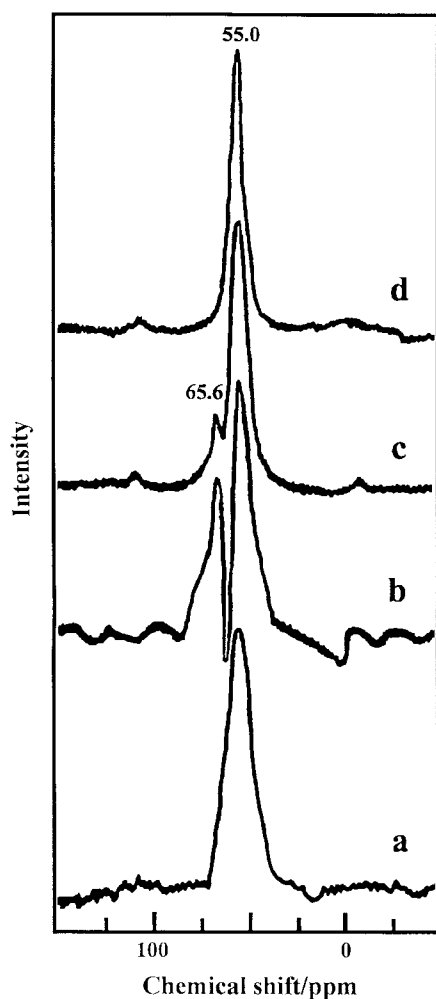


Fig. 5 ^{27}Al NMR spectra of the calcined products obtained from the CTAB–aluminosilicate gel mixture (Si:Al=15) at pH 12 and 170 °C for (a) 12 h; (b) 24 h; (c) 48 h and (d) 240 h.

crystallized ZSM-35 is formed (Fig. 5d). The presence and the absence of the additional resonance ranging from 60–80 ppm also indicates that the $\text{Al}(\text{OSi})_4$ units in mesostructure can be disassociated to different aluminosilicate intermediates, which would be re-organized and re-polymerized to the $\text{Al}(\text{OSi})_4$ units in microporous structure during the structure transformation from M41S to ZSM-35. In addition, the ^{27}Al NMR spectra exhibit no sharp resonances at 0 ppm, indicating that no intermediates appear as octahedrally co-ordinated extra-framework aluminum during the structure transformation (the side signals that appeared symmetrically on each side of the main resonances result from sample spinning).

3.2.2 pH value. The aggregate condition of inorganic precursors is closely associated with the alkalinity in the gel.^{8,9} Generally speaking, relatively low alkalinity favors the presence of highly condensed polysilicate species, whereas it is on the contrary for relatively high alkalinity. Thus, the change of alkalinity may probably change the nature of the microporous products obtained. In Table 1, when crystallized from the gel mixture with Si:Al=15 at 170 °C, the product is mordenite and ZSM-35 if the gel pH is 12.5 and 11, respectively. Likewise, with the decrease of pH, the product is changed from an amorphous phase to pure ZSM-5 for the gel mixture with Si:Al=100 and from analcime or omega to pure ZSM-35 for the mixture with Si:Al=7.5. Combined with the results in Fig. 2, it indicates that in the gel system of CTAB–aluminosilicate, the gel pH not only controls the formation of microporous phases at 170 °C, but also changes the nature of the microporous products obtained.

3.2.3 Adding small alkylammonium ions in the gel. As shown in Table 2, Mordenite can be obtained from the CTAB–aluminosilicate (Si:Al=15) at pH 12.5. When a small amount of TMAOH (TMAOH:SiO₂=0.039 mol/mol) is included in the above synthesis gel, the final product is ZSM-35 instead of mordenite. However, as is well known, the crystallization of ZSM-35 is not directed by TMA⁺ species. Only at the higher ratio of TMAOH:SiO₂=0.12, is the product changed to sodalite, which can be synthesized by TMA⁺ templating. Similarly, at low TPA⁺ content (TPA⁺:SiO₂=0.039 mol/mol, TPA⁺:H₂O=0.001 mol/mol), the final product obtained is mainly the ZSM-5 phase (>80%) instead of mordenite or ZSM-35 phases. It should be noted that it is difficult to synthesize ZSM-5 at such low TPA⁺ content if CTAB is not involved, suggesting that CTA⁺ ion assist the growth of ZSM-5 phase.

Table 1 Effect of pH on final products (obtained from the CTAB–aluminosilicate gel mixture at 170 °C for 10 d)

pH	Si:Al		
	7.5	15	50–200
10–12	ZSM-35	ZSM-35	ZSM-5
12.5	analcime, omega	mordenite	amorphous

Table 2 Products obtained from the CTAB–aluminosilicate gel mixture (Si:Al=15) at 170 °C

Alkylammonium	Alkylammonium:SiO ₂ (mol/mol)	Alkylammonium:CTAB (mol/mol)	Phase obtained
None	0.00	0.0	mordenite (2–10 d)
TMAOH	0.039	0.25	ZSM-35 (2–10 d)
TPABr	0.039	0.25	ZSM-5 > mordenite > ZSM-35 (2–6 d)
			ZSM-5 (>80%) (8 d)

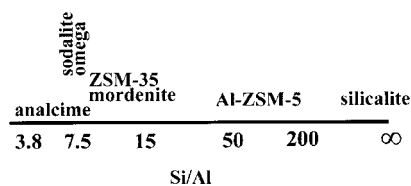


Fig. 6 Various kinds of zeolites obtained at 170 °C with increasing Si : Al ratios.

3.2.4 Zeolites obtained from different Si : Al ratios. From the CTAB–aluminosilicate gel mixture, various possible phases can be obtained over the wide range of Si : Al ratios, as summarized in Fig. 6. It was found that each type of zeolite was synthesized in certain Si : Al regions. For instance, ZSM-5 can be formed with high Si : Al ratios (50–∞), whereas ZSM-35 or mordenite can be formed with middle Si : Al ratios (7–30). When the Si : Al was equal or lower than 7, the product was omega, sodalite or analcime.

Since we used commercially available water glass and sodium aluminate as starting materials, a large number of sodium ions were unavoidably introduced into the gel solution. High levels of Na⁺ ions (Na⁺ : Si = 0.32–0.42) would act as the template to obtain analcime and sodalite,¹⁰ but we are not sure whether the assistance role of surfactant can be totally excluded. While for the synthesis of the other zeolites such as ZSM-35, mordenite and ZSM-35, if no surfactant except sodium ions are included in the solution, the products are only amorphous phase or dense phase. In addition, we have found that ZSM-5 or ZSM-35 can still be obtained if we reduced the content of sodium ions from Na : Si = 0.32 to 0.1 while keeping the pH value in the solution. It suggests that the surfactant plays an important role in the synthesis and sodium ions may partly supply a basic media.

3.3 Role of surfactant CTAB in the synthesis of microporous materials

The role of surfactant CTAB during the crystallization can be understood according to various thermodynamic interactions in the synthesis gel, *i.e.* the interactions of surfactant–inorganic (SI), inorganic–inorganic (II) and surfactant–surfactant (SS).¹¹ If the interaction order is SI > SS > II, an orderly mesoporous phase can be formed, in which anionic inorganic species condenses around the cationic supramolecular aggregate of surfactant. The mesostructure formed corresponds well to the structure of a supramolecular array of surfactant after it is removed with calcination. When the crystallization temperature is high enough to break up the surfactant aggregate, the SS interactions decrease. Thus, the interaction order is changed to SI > SS and II > SS. In this case, every templating organic molecule is encapsulated within a cage and/or pore opening with only secondary van der Waals organic–organic interactions found in the final product. Therefore, microporous phases are finally produced. However, two questions need to be addressed here: one is whether surfactant CTAB itself acts as a template in this synthesis. The second is why microporous phases are only obtained under condition of high temperatures (165–180 °C) and high pH (10–12.5).

When the CTAB–aluminosilicate gel mixture (Si : Al = 15) was crystallized at 170 °C and pH 12, IR spectroscopy showed that the products contain new organic species different from CTAB at the crystallization time of 12 h and, a layer of colorless or light-yellow oily products were found floating on the surface of the gel solution after a crystallization time of 96 h. The new organic products were detected by GC–MS and IR as a mixture of cetene (C₁₆), cetyldimethylamine (C₁₆(CH₃)₂N) and trimethylamine ((CH₃)₃N), which are supposed to arise from the Hoffmann degradation of surfactant CTAB.^{1,5,12} As discussed above, microporous phases appeared only after the crystallization time of 24 h

(Fig. 3). That is to say, the decomposition products of CTAB already existed prior to the formation of microporous phases.

To verify the decomposition of CTAB, the following experiment was carried out. A water solution of CTAB with the same concentration as that in the synthesis gel was adjusted to various pH with NaOH solution. Then, the CTAB solution was sealed in a stainless steel tube and heated at different temperatures. It was found that CTAB can only be decomposed at temperatures higher than 160 °C and pH higher than 11, which matches the conditions required for synthesizing microporous phases in the CTAB–aluminosilicate mixture. It suggests that the CTAB decomposition is closely related to the synthesis of the microporous phases.

The relationship between CTAB decomposition and microporous phase formation can be further demonstrated by the existence of an ‘induction period’ during the formation of microporous phases, as shown in Fig. 7. It is found that when the pH is maintained at 9 during the whole crystallization, CTAB cannot be decomposed. In this case, the final product is only the mesoporous phase rather than any kind of microporous phase (Fig. 7a). However, it is a different case when the gel pH is adjusted to 9 only at the initial stage of crystallization (Fig. 7b). With the condensation of the aluminosilicate species under alkaline conditions, the gel pH rises gradually to the region where the CTAB surfactant can be easily decomposed on the second day of crystallization. Subsequently, a microporous phase can be produced on the third day of the crystallization. While the pH is adjusted to 12, at which the CTAB surfactant can be quickly decomposed, the ZSM-35 phase is obtained only after one day (Fig. 7c). Therefore, the decomposition rate of CTAB, which is

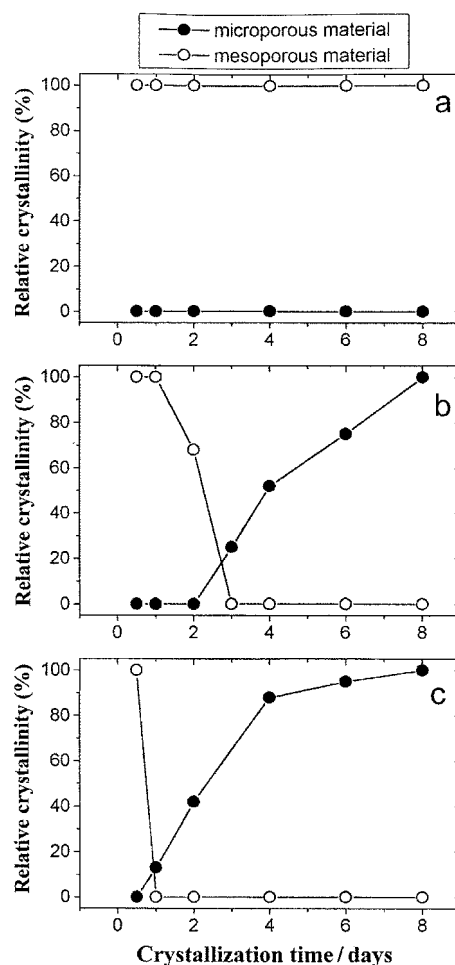


Fig. 7 Crystallization curves from the CTAB–aluminosilicate gel mixture (Si : Al = 15) at 170 °C and different pH values. (a) constant pH = 9, (b) initial pH = 9 and (c) initial pH = 12.

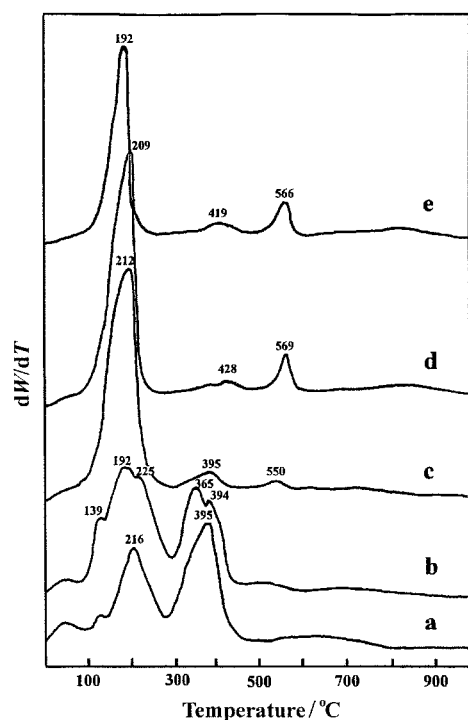


Fig. 8 DTG curves of the as-synthesized products obtained from the CTAB-aluminosilicate gel mixture (Si:Al=15) at pH 12 and 170 °C for (a) 4 h; (b) 24 h; (c) 48 h; (d) 96 h and (e) 240 h.

closely related to the temperature and pH in the gel, would affect the induction period for the synthesis of the microporous phases. It also suggests that CTAB decomposition products play an important role in this synthesis.

Furthermore, DTG results also indicate strong interactions between the surfactant decomposition products and the aluminosilicate framework. The DTG curves of the products crystallized for different times are shown in Fig. 8, and the corresponding weight loss percentages are listed in Table 3. One can see that with the increase of crystallization time, the total weight loss percentages decrease from 48.7 to 25.5%, showing the decrease of the organic species occluded in the product channel. The DTG curves in Figs. 8c–8e become different from those for a mesoporous phase (Fig. 8a). Fig. 8a is a typical DTG curve for the mesoporous phase. The peaks at 216 and 395 °C correspond to the desorption of organic templates associated with Si–O and Al–O groups, respectively.¹ While Figs. 8c–8e show two kinds of weight loss peaks, the peak in the lower temperature region of 120–300 °C may be related to the desorption of intercrystalline water or residual hydrocarbon decomposition products which was not washed away

Table 3 Thermal analysis data of products obtained from the CTAB-aluminosilicate gel mixture (Si:Al=15) at 170 °C for different crystallization times

Cryst. time/h	Total weight loss(%)	Distribution of weight loss							
		<120 °C		120–300 °C		300–500 °C		>500 °C	
		°C	%	°C	%	°C	%	°C	%
4	48.7	63	3.5	139	1.7	395	22.1	662	5.2
24	48.6	63	2.3	216	16.1	364	9.9		4.1
				192	12.2				
48	45.8	0.82	212	225	11.0	395	4.1	550	1.9
					36.5				
96	36.1	0.26	209	216	3.0	428	2.7	569	3.4
					26.4				
240	26.1	0	192	395	4.1	419	2.7	566	4.3
					15.2				

with water. In addition, it is noteworthy that there are two weight loss peaks at higher temperatures, ca. 410 and ca. 560 °C (weight loss 6–7 wt%). They may correspond to the relatively strong interactions between anionic inorganic framework and cationic organic species located at different sites of the ZSM-35 framework. Likewise, similar results can be obtained from the DTG curves for the other zeolites such as mordenite and ZSM-5, etc. In addition, IR results revealed the presence of the decomposition products of CTAB when the samples were heated at 300 °C under the same conditions as for TG analysis. Therefore, the IR and DTG results confirm that the decomposition products are occluded in the channels of microporous materials and tightly connected with the inorganic framework. Another experiment was conducted by displacing CTAB with its decomposition products in the similar synthesis gel followed by hydrothermal treatment at 150 °C. It was found that the final product obtained was of ZSM-35 phase instead of the above-mentioned lamellar M41S phase (Fig. 2) though the crystallization time became longer. In summary, it is concluded that it is the decomposition products of surfactant CTAB that act as structure-directing agents for the preparation of microporous materials.

4 Conclusions

This paper reports the role of surfactant in synthesizing microporous materials. It was found that at 165–180 °C and pH 10–12.5, zeolite sodalite, analcime (Si:Al=3.5–7), omega (Si:Al=7), ZSM-35 (Si:Al=7–30), mordenite (Si:Al=15–30), Al-ZSM-5 (Si:Al=50–200) and silicalite (Si:Al=∞) can be obtained from CTAB-aluminosilicate or CTAB-silicate gel mixtures. High pHs above 10 and high temperatures of no less than 165 °C ensured the quick decomposition of CTAB, which is essential for the formation of microporous phases. Only the mesoporous phase was obtained without the decomposition of surfactant CTAB. The experimental results suggest that the surfactant decomposition products act as structure-directing agents instead of surfactant CTAB itself. These results are different from those reported previously and therefore this paper give a full understanding on the role of the surfactant in synthesizing both microporous materials and mesoporous materials from the same surfactant-containing gel solution.

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