

Synthesis of zeolite EMT with a novel route promoted by surfactants and its benefit in catalytic performance

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Zeolite EMT with small crystal size, which was catalytically active in the alkylation of isobutane with butenes, was synthesized via a novel route promoted by surfactants with a low molar ratio of 18-crown-6 to Al_2O_3 and a short crystallization time.

Zeolite EMT, which is constructed by the linkage of sodalite cages through double six-rings, is the hexagonal analogue of faujasites. The two dimensional direct channel system with 12-ring aperture in EMT is unique and of great interest in catalysis and adsorption.^{1–4} Pure EMT was first synthesized by Delprato and coworkers⁵ using 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6) as template, which plays a key structure-directing role, in the form of the $[\text{Na-18-crown-6}]^+$ complex, during crystallization. In a traditional synthetic system, not all the 18-crown-6 molecules can participate in the templating effect because the molar ratio of 18-crown-6 to Al_2O_3 needed is higher than 0.7.^{5–10} Although the ratio can be decreased to 0.4–0.5 with a low content of water,^{11–12} the starting hydrogels are not easy to work with. It is well known that the solvent plays a vital role during crystallization of zeolites and other microporous materials. One of the most effective synthetic strategies is the introduction of surfactant to the solvent because it can help to change the properties of the solvent greatly. del Val *et al.*¹³ demonstrated that a cationic surfactant favors the replacement of P by Si in the VPI-5 framework. Franco *et al.*¹⁴ found that a cationic surfactant also leads to deep changes in crystal morphology, *etc.* However, these authors did not focus on the effect of surfactant on the improvement of structure-directing efficiency. Here we report a novel synthetic route to produce the EMT phase promoted by surfactant and explain its effect in detail. In addition, the catalytic properties of H-EMT were also explored for the alkylation of isobutane with butenes.

In our study, the surfactants used were dodecylbenzyltrimethylammonium chloride (DBDMACl), sodium lauryl sulfate (SLS), dioctadecyltrimethylammonium chloride (DODMACl), alkyl glycoside (AG, C_{12-14}) and polyoxyethylene (15) ether lauric monoethanolamide (POE (15) LMEA). The reaction mixture was obtained by dissolving one of the surfactants, sodium aluminate (43 wt% Al_2O_3), sodium hydroxide (96 wt%) and 18-crown-6 (99 wt%) in distilled water in turn. Finally, colloidal silica (25 wt% SiO_2 , <0.5 wt% Na_2O) was added to the mixture dropwise with stirring. The resulting hydrogel was continuously stirred for 2 h, and aged for one day at room temperature without agitation. The molar composition of the hydrogel was as follows: 10 SiO_2 : 1 Al_2O_3 : 2.2 Na_2O : x 18-crown-6: y surfactant: 160 H_2O . The crystallization was carried out in a PTFE-lined stainless-steel autoclave at 373 K for 3–30 days. The solid obtained was filtered off, washed thoroughly with distilled water and then dried at 353 K overnight. In order to remove the organic molecules, the as-synthesized EMT was calcined at 523 K for 2 h followed at 773 K for 5 h in air. The H-EMT was prepared by ion exchange with 2 M NH_4NO_3 solutions at 353 K (three times for 3 h each) and the following calcination at 813 K for 7 h in air.

Fig. 1 shows the XRD patterns of the products synthesized by using the surfactant alkyl glycoside (AG) with different ratios of 18-crown-6 to Al_2O_3 (x) and crystallization time (t). When $x =$

0.37 and $t = 3$ d, the three characteristic peaks of the EMT phase in the 2θ region $5\text{--}7^\circ$, which are indexed as 100, 002 and 101 reflections, can be observed. It indicates that there is a significant amount of EMT in the product, but some amorphous substance still exists [Fig. 1(a)]. The pure EMT can be obtained when t is increased to 5 d [Fig. 1(b)]. This result means that the structure-directing efficiency of 18-crown-6 molecules is improved by adding surfactant to the starting hydrogels. It was also found that the intergrowth of EMT and FAU, deduced from the increased intensity of the central peak in the $5\text{--}7^\circ$ 2θ region, was produced when x was further decreased to 0.19 even if t was long enough [Fig. 1(c)]. The SEM photograph reveals that EMT crystals synthesized in the presence of AG are hexagonal plates with an average size below $2\ \mu\text{m}$ [Fig. 2(a)], smaller than those synthesized without surfactant [Fig. 2(b)]. Different categories of surfactant have also been used to synthesize EMT in a more efficient manner (Table 1). This demonstrates that, no matter what kind of surfactant is used, the EMT phase can be

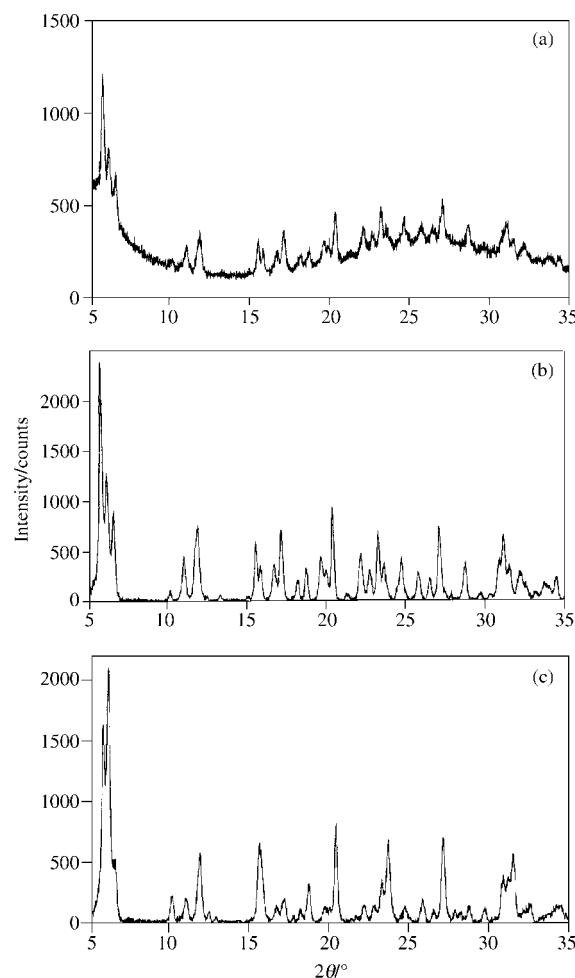
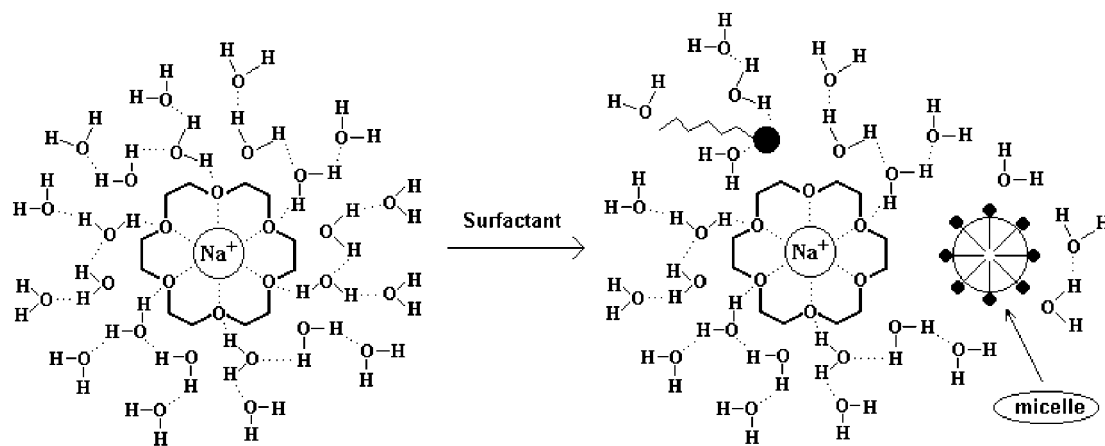


Fig. 1 Powder X-ray diffraction patterns of the as-synthesized products prepared using the surfactant AG. (a) $x = 0.37$, $y = 0.043$, $t = 3$ d; (b) $x = 0.37$, $y = 0.043$, $t = 5$ d and (c) $x = 0.19$, $y = 0.042$, $t = 30$ d.



Scheme 1 Representation of the interactions between the [Na-18-crown-6]⁺ complex, added surfactant and water solvent. (Dotted lines indicate hydrogen bonds or dipole-ion interactions.)

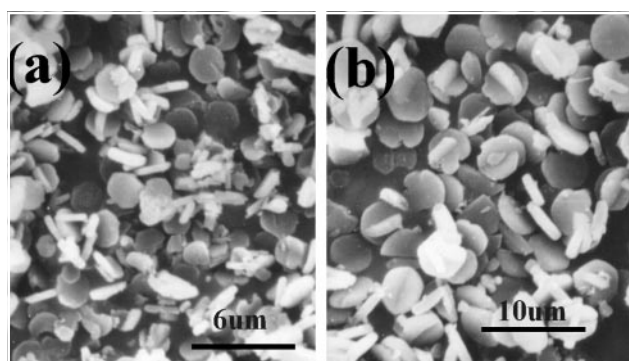


Fig. 2 SEM images of as-synthesized EMT prepared (a) with the surfactant AG ($x = 0.36$, $y = 0.043$, $t = 30$ d) and (b) without surfactant ($x = 0.68$, $y = 0$, $t = 30$ d).

Table 1 Synthesis of zeolite EMT using surfactants other than AG at $x = 0.36$ and $t = 6$ d

Surfactant	y	Product
<i>Cationic</i>		
DBDMACI	0.047	Amorphous
	0.102	EMT
DODMACI	0.035	EMT + Amorphous
	0.061	EMT
<i>Anionic</i>		
SLS	0.051	EMT
<i>Nonionic</i>		
POE (15) LMEA	0.017	EMT + Amorphous
	0.040	EMT

synthesized at low x and t values when the ratio of surfactant to Al_2O_3 (y) exceeds a certain level, which varies according to the surfactant.

Comparison of the ^{13}C CP MAS NMR spectra and the DTA curves of EMT synthesized with or without surfactant reveals that the surfactant molecules do not enter the channels or cages of EMT. Therefore, the surfactant must play an auxiliary role during crystallization, instead of a structure-directing role. In a synthetic system, the interaction between structure-directing agent and solvent would occur, but must not be so strong as to prevent the framework-forming species from interacting with the structure-directing molecules to form the zeolite phase.¹⁵ In the starting hydrogel for producing EMT without surfactant, there is a balance of interactions between the water solvent, framework species and the [Na-18-crown-6]⁺ complex. When surfactant is added to the hydrogel, the balance is upset due to the interactions between the surfactant and solvent and/or other dissolved species. Although this process is very complicated, it is clear that the interaction between the [Na-18-crown-6]⁺ complex and the water solvent is weakened because of the interaction of surfactant with water (Scheme 1). As a result, it becomes more favorable for 18-crown-6 molecules to access the

framework-forming species and direct the formation of the crystal nucleus and the following growth. On the other hand, the surface tension of the water solvent is decreased in the presence of surfactant, *i.e.* the interface energy between the newly-formed EMT phase and the solvent would be lowered, helping to shorten the crystallization time and reduce the particle size of EMT crystals produced.

For the alkylation of isobutane with butenes, the catalytic properties of H-EMT prepared by our method with AG were compared with those of H-EMT synthesized without surfactant under the same reaction conditions. It was found that the former is more selective for the main products, trimethylpentanes (TMPs), than the latter. It shows that the diffusion of bulky TMPs in small crystals is beneficial because the catalytic reaction takes place in the pores of EMT.

In conclusion, we have demonstrated a novel route to synthesize zeolite EMT by using surfactants at a low molar ratio of 18-crown-6 to Al_2O_3 and a short crystallization time. The average crystal size of the product is less than that of EMT synthesized without surfactant, which is more favorable for the alkylation of isobutane with butenes. Our route can be expanded to synthesize other types of zeolite in order to improve the templating effect, a study which is underway in our laboratory.

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