

Nonionic emulsion-mediated synthesis of zeolite beta

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Abstract. Zeolite beta synthesis was first carried out in a newly developed emulsion system containing nonionic polyoxyethylated alkylphenol surfactant, which showed interesting non-conventional features. Compared to the conventional hydrothermal synthesis of zeolite beta, the reported nonionic emulsion system showed a faster nucleation rate. Furthermore, the emulsion system could stabilize the beta product and retarded its further transformation to ZSM-5 even under the high crystallization temperature at 453 K. Additionally, the beta particle size could be tuned by the adoption of different lengths of alkyl chain in the surfactant and cosurfactant. Control experiments showed each emulsion component played a crucial role in the zeolite beta growth. The approach proposed in this paper might be extended to apply for the syntheses of other types of zeolites with particle size under control.

Keywords. Zeolite beta; zeolite ZSM-5; nonionic emulsion system; particle size; crystal transformation.

1. Introduction

Zeolite beta was firstly synthesized using tetraethylammonium hydroxide as a structure directing agent (SDA) by Wadlinger of Mobile Corp in 1967, which was the first example of a tridirectional large-pore zeolite with low aluminum content (Wadlinger *et al* 1967). It is widely used in hydrocracking, hydroisomerization, aromatic alkylation, disproportionation and other organic synthesis processes at present (Cambor *et al* 1996). Usually, zeolite beta is synthesized by hydrothermal method at mild conditions (Cambor *et al* 1991). Besides the conventional method, many other methods have been explored such as dry gel conversion method (Hari Prasad Rao *et al* 1998), F-system synthesis (Liu *et al* 2001), steam-assisted crystallization method (Matsukata *et al* 2002) and special silicon source technique (Sun *et al* 2007).

Recently, microemulsion has been used to synthesize zeolite A and Silicalite-1 and the ability of microemulsion to induce rapid crystallization and control crystal morphology has been elaborately demonstrated (Lee and Shantz 2004; Carr and Shantz 2005; Lee and Shantz 2005a, b). However, microemulsion has not yet been applied to synthesize other types of zeolites, especially those crystallized with the templating of SDAs such as beta and ZSM-5. The presence of SDAs would complicate the microemul-

sion system and might interfere with the emulsion components and weaken the effects of microemulsion.

Previously, we have described zeolite beta synthesis in an anionic emulsion system containing sodium dodecylbenzenesulfonate (SDBS) surfactant for the first time (Jin *et al* 2009). As an extension of our previous work, here we synthesized zeolite beta in a nonionic emulsion system composed of polyoxyethylated alkylphenol surfactant stabilized zeolite synthesis mixture droplets dispersed in cyclohexane. To the best of our knowledge, this report represents the first use of nonionic emulsion system to prepare zeolite beta.

2. Experimental

The nonionic emulsion synthesis of zeolite beta involved the following steps. Firstly, polyoxyethylated alkylphenol surfactant (OP), alkanol cosurfactant and cyclohexane were mixed under stirring. Then the conventional zeolite beta synthesis mixture with the molar composition of TEAOH : Al₂O₃ : SiO₂ : H₂O to 9 : 0.25 : 25 : 490 was prepared following the procedure reported (Modhera *et al* 2009) and subsequently added to the first mixture containing OP to obtain the emulsion system. Finally, the emulsion system was transferred to Teflon-lined stainless steel autoclaves and crystallized at 413 K for 48 h and then 443 K for 48 h. For comparison, the conventional zeolite beta synthesis was also carried out under the same crystallization conditions. Notably, when the crystalliza-

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tion curves were investigated, syntheses were carried out at 413 K for 0–170 h and when the transformation of beta to ZSM-5 was investigated, syntheses were carried out at 413 K for 48 h and then 433, 443, 448 or 453 K for 48 h. In the final results, the compositions of the emulsion systems were described using weight fractions of emulsion components. As an example, 50H:40S:10Z represents 50 wt.% of cyclohexane, 40 wt.% of OP + alkanol and 10 wt.% of zeolite mixture and H is cyclohexane, Z is zeolite mixture and S is OP plus alkanol with the weight ratio of OP : alkanol to 2 : 1.

3. Results and discussion

3.1 Effect of nonionic emulsion

Figure 1 shows the XRD patterns of the two samples synthesized from the conventional synthesis system and the nonionic emulsion system. The calculated interplanar spacings of both samples match well with the reported values of zeolite beta (Wadlinger *et al* 1967). The presence of both broad and sharp peaks at 7.8 and 22.7° (marked by “♦”) is the typical characteristic of beta structure (Cambor *et al* 2001). Notably, the beta sample synthesized from the nonionic emulsion system shows stronger peak intensity than that of the conventional beta sample, indicating the nonionic emulsion system favours the crystallization of zeolite beta. Figure 2 shows the crystallization curves of the beta samples synthesized at 413 K for different crystallization times. It can be found that the nucleation rate of the nonionic emulsion system sample is greatly shortened. The conventional beta sample nucleates within 0–50 h, while the emulsion system sample finishes nucleation after 30 h. To determine the effect of individual emulsion component on the nucleation

promotion, six control experiments were performed including syntheses containing (i) butanol only, (ii) butanol and OP-10 only, (iii) OP-10 only, (iv) cyclohexane only, (v) OP-10 and cyclohexane only, and (vi) cyclohexane and butanol only. The syntheses (i) and (ii) both produced amorphous XRD patterns, suggesting that the existence of butanol suppresses the crystal formation. The syntheses (iii)–(vi) all produced weak XRD patterns compared to the emulsion sample containing all the three components, which had the highest crystallinity. The above results indicate that each emulsion component plays a critical role in the growth enhancement of the beta material. The cyclohexane may act to solvate the hydrophobic chain of the surfactant, the butanol to lower the interfacial tension, and the surfactant (and butanol) to interact with the aluminosilicate species in solution via van der Waal's forces. The emulsion inducing rapid growth was also reported by Shantz *et al* when they investigated the nonionic-microemulsion mediated growth of zeolite A (Carr and Shantz 2005). They believed that the nonionic surfactant interacted with the aluminosilicate precursors, which led to the increase of local concentration of these precursors and the final quick growth of zeolite crystal.

3.2 Particle size control

To investigate the influence of surfactant identity on the zeolite morphology, we have used three kinds of polyoxyethylated alkylphenol surfactants with ethoxy (EO) numbers of 7.5, 10 and 15 (denoted as OP-7.5, OP-10 and OP-15) respectively as the surfactants to synthesize the zeolite beta. Figure 3 shows the SEM images of the beta samples synthesized using different surfactant systems with the emulsion composition of 40H:50S:10Z. From

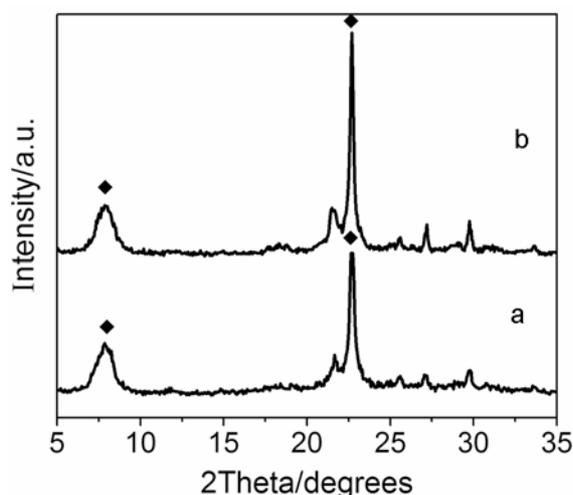


Figure 1. X-ray diffraction patterns of beta samples synthesized from (a) the conventional synthesis system and (b) the nonionic emulsion system of 40H:50S:10Z.

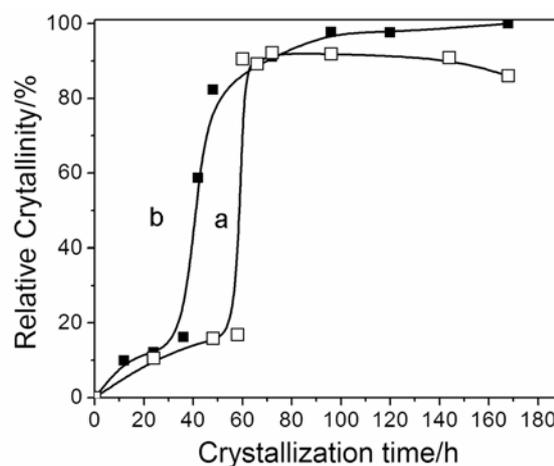


Figure 2. The crystallization curves of the beta samples crystallized at 413 K from (a) the conventional synthesis system and (b) the nonionic emulsion system of 40H:50S:10Z.

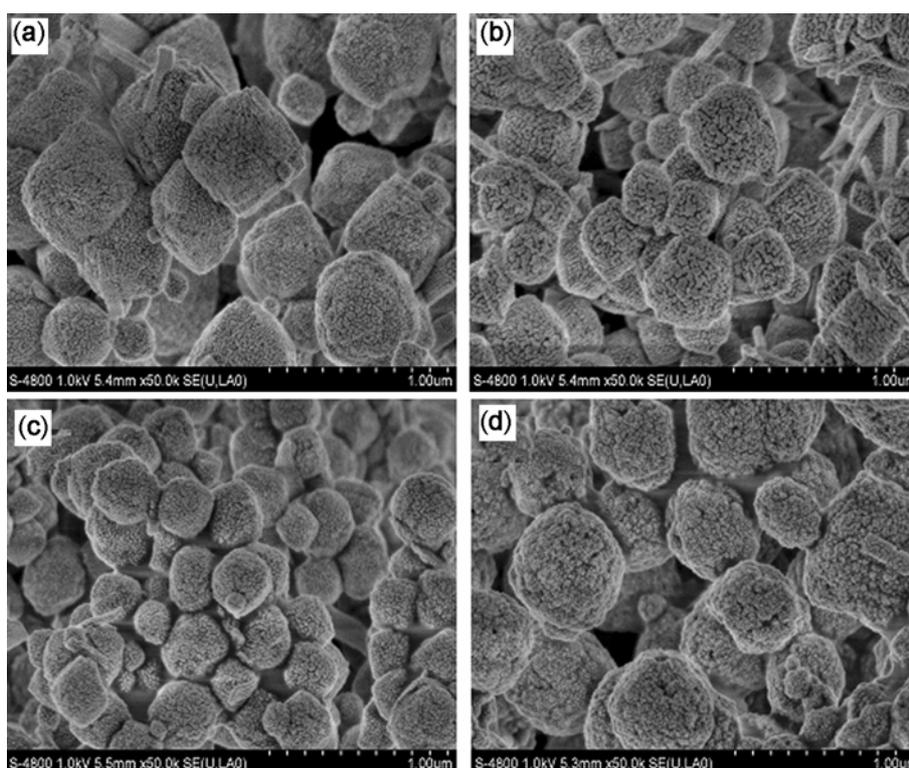


Figure 3. The SEM images of the beta samples synthesized based on the emulsion composition of 40H : 50S : 10Z: (a) butanol + OP-7.5; (b) butanol + OP-10; (c) butanol + OP-15; (d) decanol + OP-10.

the SEM images (figures 3a–c) of the corresponding beta samples using these surfactants, it can be obviously seen that with the increase of the ethoxy (EO) numbers from 7.5 to 10 and 15, the particle sizes of zeolite beta decrease from 600 nm to 400 nm and 300 nm. Similar particle size variation is also observed when the alkyl chain length of the cosurfactant is changed. Specifically, when decanol substitutes for butanol, the particle sizes increase from 400 nm to 600 nm (figures 3b and d). The similar impacts of surfactant identity on the zeolite morphology have been reported in the nonionic microemulsion synthesis of zeolite A (Carr and Shantz 2005). This indicates that in the emulsion-mediated synthesis of zeolite beta, the particle size can be tuned by the adoption of different lengths of alkyl chains in the surfactants and cosurfactants. This approach might be extended to apply for synthesizing other types of zeolites to control particle size.

3.3 The transformation of zeolite beta to ZSM-5

In the zeolite synthesis process, the outcome is most frequently kinetically controlled (Cundy and Cox 2005) and the desired product is frequently at metastable states. Figure 4 is the XRD patterns of beta samples synthesized at different crystallization temperatures. For the conventional zeolite beta synthesis (figure 4A), beta transforms

to thermodynamically stable ZSM-5 when the crystallization temperature is raised to 448 K. However, for the emulsion synthesis of 40H : 50S : 10Z (figure 4B), the beta can be stabilized until the crystallization temperature is up to 448 K and finally transforms to ZSM-5 when the crystallization temperature further increases to 453 K. Surprisingly, for the emulsion synthesis of 40H : 40S : 20Z (figure 4C), even under the crystallization temperature of 453 K, the crystal product still keeps as zeolite beta structure. This result proves that the nonionic emulsion can stabilize the beta product under the high temperature up to 453 K. This stabilizing effect is also observed by Kong *et al* when they synthesized small crystal zeolite beta in a biphasic H₂O–CTAB–alcohol system (Kong *et al* 2009).

4. Conclusions

Well-crystallized beta zeolites are successfully synthesized for the first time in the nonionic emulsions. The presence of nonionic emulsion components quickens the nucleation rate of beta crystallization process and retards the transformation of beta to ZSM-5 even at the higher crystallization temperature of 453 K. Control experiments indicate that all components of the emulsion play important roles in the crystal growth. Additionally, the beta particle size can be tuned by varying the alkyl chain

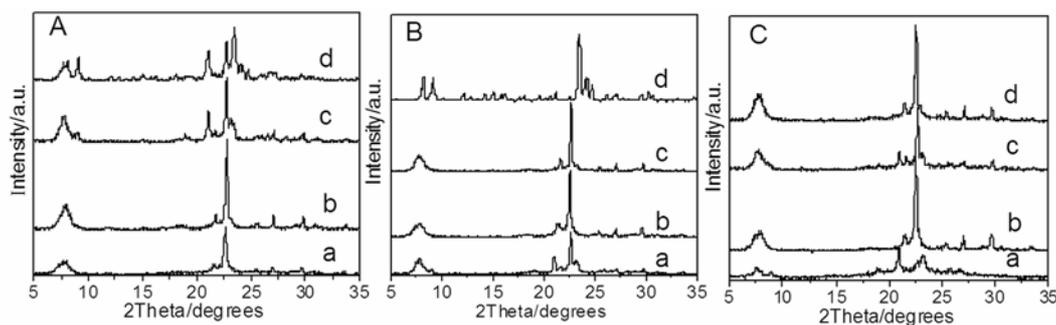


Figure 4. The XRD patterns of the beta samples from (A) the conventional synthesis systems and the nonionic emulsion systems with the composition of (B) 40H : 50S : 10Z and (C) 40H : 40S : 20Z crystallized at 413 K for 48 h and then heated to 433 K (a), 443 K (b), 448 K (c) or 453 K (d) for 48 h.

length of the surfactant and cosurfactant involved in the emulsion synthesis system.

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