

# Synthesis of FER type zeolite with tetrahydrofuran as the template

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**FER (ferrierite) zeolite was hydrothermally crystallized in a gel system of sodium aluminosilicate with tetrahydrofuran (THF), a nitrogen-free organic compound, as the template; characterization by using TG/DTG/DTA and <sup>13</sup>C MAS NMR shows that THF is incorporated in the pores of the as-synthesized FER zeolite.**

FER type zeolite is an aluminosilicate molecular sieve with medium pore openings. It has a variety of uses in catalytic processes, such as hydrocarbon cracking and isomerization. In particular, in recent years it has been found that FER zeolite possesses excellent shape selectivity for the isomerization of *n*-butene to isobutene. The latter is a raw material for manufacturing MTBE (methyl *tert*-butyl ether), an additive in lead-free gasoline.<sup>1</sup> What is more, it can be used as a catalyst for skeletal isomerization of *n*-olefins to iso-olefins.<sup>2</sup> Thus, the development of a novel method to synthesize FER zeolite in a cheap way will be a decisive step for the commercialization of these industrial processes.

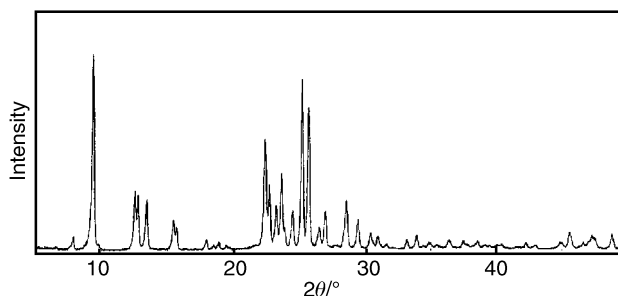
FER zeolite can be prepared in an inorganic reactant system in the presence of Na<sup>+</sup> and K<sup>+</sup> simultaneously. However, the reaction temperature is usually high.<sup>3</sup> It is difficult to exchange K<sup>+</sup> in the zeolite synthesized from this system, leading to limited applications as catalysts and adsorbents. FER type zeolite was firstly synthesized by using an organic compound as the structure-directing reagent (template) in 1977.<sup>4</sup> Up to now more than 30 organic compounds have been employed as templates,<sup>5</sup> most of which are nitrogen-containing organic compounds, and some of which are large organic molecules, such as bis[*N*-methylpyridyl]ethylinium.<sup>6</sup>

Quite a lot of efforts have been made to synthesize various zeolites using oxygen-containing organic compounds. It is known that three types of organic compounds have been used as the templates: (1) ethers, such as 15-crown-5 and 16-crown-6;<sup>7</sup> (2) alkyl oxide compounds, such as trioxane and poly(ethylene oxides);<sup>8</sup> and (3) alcohols, such as ethanol and butan-1-ol.<sup>9</sup> Zeolites FAU, EMT, MAZ, MFI, TON, *etc.*, have been synthesized in the presence of the above templates. One method was disclosed that FER zeolite can be prepared by using 2,4-diketones as the organic templates.<sup>10</sup> In this paper a novel process of using THF as the template<sup>11</sup> for the synthesis of FER zeolite is reported.

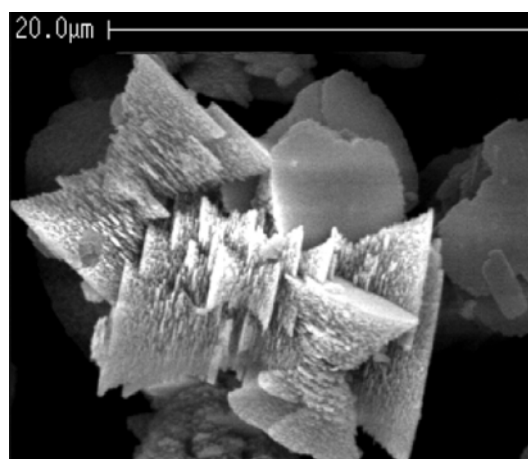
The process of synthesizing FER zeolite was as follows: 24.44 g of silica sol (SiO<sub>2</sub> = 25.07%, Na<sub>2</sub>O = 0.27%, Qingdao Ocean Chemical Plant) was mixed with 6.94 g aqueous solution of aluminium sulfate (Al<sub>2</sub>O<sub>3</sub> = 7.49%, H<sub>2</sub>O = 74.9%, Shanghai Xinxing Material Corp.) to form a mixture in a plastic vessel. Then 1.69 g of NaOH and 13.25 g of deionized water were added to the mixture. A homogeneous gel of the reactant was formed after 3.71 g of THF (analytical grade, Shanghai Chemical Reagent Corp.) were added into the mixture with vigorous stirring. The molar composition of the reactant gel was 0.5THF:0.215Na<sub>2</sub>O:SiO<sub>2</sub>:0.05Al<sub>2</sub>O<sub>3</sub>:20H<sub>2</sub>O. The gel was sealed into a 30 ml stainless steel Teflon lined autoclave, and hydrothermally crystallized in an oven at 200 °C for 8–12 days under static conditions. The spontaneously crystallized product was washed with distilled water, filtered and then dried at

120 °C. A reactant with the same molar composition but without THF remained amorphous for a long time under the same conditions.

The XRD pattern (Cu-Kα radiation, Rigaku D-MAX/II A) indicates that the as-synthesized product is highly crystalline FER type zeolite without any impurity phase (Fig. 1). The cell composition of the as-synthesized FER zeolite is Na<sub>3.42</sub>[Al<sub>3.59</sub>Si<sub>32.41</sub>O<sub>72</sub>]-1.05THF·6.19H<sub>2</sub>O as determined by chemical analysis. The SEM photo (Shimadzu S-520) shows that the morphology of the zeolite is agglomerate with a shape like a spindle (Fig. 2).



**Fig. 1** XRD pattern of FER type zeolite synthesized in the reactant system with THF as the template.



**Fig. 2** SEM photograph of FER type zeolite synthesized in the reactant system with THF as the template.

The TG/DTG/DTA curves (PCT-10A thermal analyzer with a flow of air of 70 ml min<sup>-1</sup> at a rate of 5 °C min<sup>-1</sup> from room temperature to 600 °C) are displayed in Fig. 3. The weight loss below 350 °C is attributed to the loss of water incorporated into the pores of the as-synthesized FER zeolite. The weight loss in the temperature range of 350–550 °C is attributed to the loss of THF. The content of THF in the zeolite calculated from the weight loss is 3.12 wt.%. The maximum temperature in the DTG curve is 393 °C, and an obviously endothermic effect followed by an exothermic one are observed at 415 and 431 °C

respectively in the DTA curve (Fig. 3), indicating the escape of THF from the zeolite and the subsequent oxidation in air. This implies that THF is incorporated in the pores of the as-synthesized FER zeolite.

Fig. 4 shows the  $^{13}\text{C}$  CP and HPDEC MAS NMR spectra (recorded at room temperature with a Bruker MSL-300 spectrometer,  $^{13}\text{C}$  resonance frequency 78.468 MHz, rotor spun at 4.0 KHz, radiofrequency field 50 kHz, recycle time 2 s with an accumulation number of 2000–6000, contact time 2 ms for CP spectrum, decoupling power 50 kHz for HPDEC spectrum, adamantane was used as a second reference). Two peaks are observed in both the CP NMR and HPDEC  $^{13}\text{C}$  NMR spectra of the as-synthesized FER zeolite compared with that of THF in the liquid phase. The chemical shifts of  $\text{C}_1$  (-C-C<sub>1</sub>-C<sub>1</sub>-C-) and  $\text{C}_2$  (-C<sub>2</sub>-O-) are 23.99 and 66.09 ppm respectively for the THF molecules in the liquid state. In comparison, the chemical shifts of  $\text{C}_1$  and  $\text{C}_2$  in the CP spectrum move to 26.55 and 69.67 ppm respectively for the THF molecules trapped in the as-synthesized FER zeolite. The obvious shift to lower field is caused by

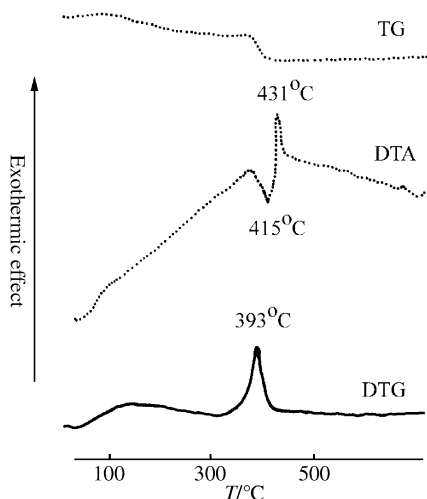


Fig. 3 TG/DTG/DTA curves of as-synthesized FER type zeolite in a flow of air.

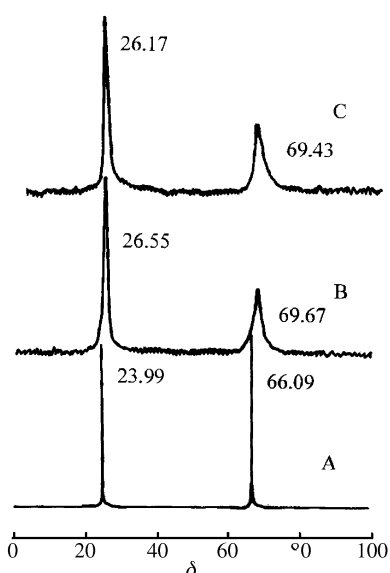


Fig. 4  $^{13}\text{C}$  MAS NMR spectra of THF (A) in liquid state, (B) CP spectrum of as-synthesized FER zeolite, (C) HPDEC spectrum of as-synthesized FER zeolite.

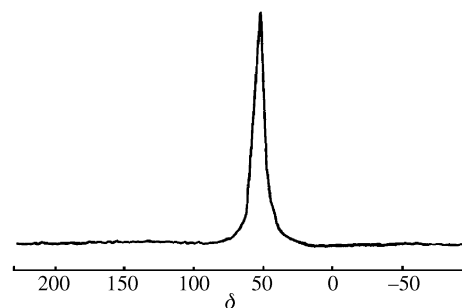


Fig. 5  $^{27}\text{Al}$  MAS NMR spectrum of FER type zeolite synthesized in the reactant system with THF as the template.

electronic deshielding effects of the framework oxygen atoms in the small cage formed by intersection of the 8-ring ( $0.48 \times 0.34$  nm) and 6-ring channels in the cell of FER zeolite. The deduction is consistent with our earlier observation of TMEDA (tetramethylethylenediamine) trapped in the cages of several as-synthesized zeolites, such as MTN, MON and FER.<sup>12</sup>

Fig. 5 shows  $^{27}\text{Al}$  MAS NMR (resonance frequency 78.205 MHz, rotor spun at 3.5 kHz, frequency field 27.8 kHz, recycle time 500 ms,  $\text{AlCl}_3(\text{H}_2\text{O})_6$  as reference). The peak at 53 ppm in the  $^{27}\text{Al}$  MAS NMR spectrum of the as-synthesized FER zeolite corresponds to tetrahedrally coordinated framework aluminium, indicating that the framework of the FER zeolite discussed herein does not include non-framework aluminium.

The nitrogen adsorption isotherm was measured (at 77.35 K using a Micromeritics ASAP 2000 instrument) on the sample of FER zeolite calcined to remove THF and treated by ion-exchange. The adsorption isotherm of  $\text{N}_2$  belongs to the Langmuir type. The microporous volume was  $0.15 \text{ ml g}^{-1}$  calculated from the adsorption isotherm, which is consistent with the value determined for the FER zeolite synthesized by using TMEDA as the template.<sup>13</sup>

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