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Preparation and Charactrization of Fibrous Crystals of Boron-containing MTW-type Zeolite

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Fibrous crystals of boron-containing MTW-type zeolite have been hydrothermally synthesized in B_2O_3-SiO_2-HF-H_2O gel system at 170 ℃ in 20 to 28 d by using 1,4-diazabicyclo[2,2,2]octane (DABCO) and methylamine as the co-template, and characterized with XRD, SEM, TEM, HRTEM and SAED. The results of characterizations show that B atoms are incorporated into the zeolite framework as tetrahedron of $B(OSi)_4$. The fibrous single crystals of 5—50 μm in length and 100—500 nm in width inter-grow along the *c*-axis of the zeolite, and the one dimension 12 oxygen ring channels are perpendicular to the fibber axis.

Keywords MTW zeolite, B-ZSM-12, fibrous crystal, orientation

Zeolite with MTW structure named ZSM-12 was first reported in 1974[1] and has been described since then in a series of papers.[2-5] MTW-type zeolites, including ZSM-12, TEA silicate, CZH-5, Nu-13 and TPZ-12,[6,7] have been applied in catalysis due to their mono-dimensional 12-membered ring linear channel system with window size of 0.56 nm×0.77 nm. Therefore many efforts have been contributed to the synthesis of the zeolite. A variety of organic molecules, such as methyltriethylammonium cation,[2] *N*,*N*-dimethylpiperidinium cation,[6] 6-azonia-spiro[5,5]undecane,[7] *n*-alkylquinuclidium[8] and DABCO-based quarternary ammonium compound,[9] have been used to induce the crystallization of MTW type zeolites including hetero-atom containing types such as Ga-MTW, B-MTW and Ti-MTW.

Zeolite, an important industrial material, is usually used in numerous processes as catalysts, adsorbents and ion-exchangers. Depending upon the application of the material, factors such as mechanical strength, shape of the bodies, or porosity (pore size and its distribution) may have great influence on the lifetime of the materials, the pressure drop over the vessel in which the material is contained, and on the effects of diffusion. Fortunately, fibres of zeolite can improve the diffusion rate of molecules in reactants and in products, and reduce the pressure drop over the vessel as well. Several methods for synthesizing zeolite coated fibres and hollow zeolite fibres have been reported.[10-13] In these methods, colloidal nano-size crystallites of MFI type zeolite should be prepared firstly. Then, fibrous zeolite agglomerates composed of nano-size crystallites can be prepared after several times of synthesis.

In this paper, we report the crystallization of single crystal fibres of boron-containing MTW-type zeolite (B-MTW), and the orientation of the fibre crystals investigated with SEM, TEM, HRTEM and SAED.

The sample of B-MTW zeolite fibres was hydrothermally synthesized in a reactant system of DABCO-CH_3NH_2-SiO_2-B_2O_3-HF-H_2O. Fumed silica was used as the silica source. In a typical preparation, 5.658 g of DABCO (ACROS Organics), 2.530 g of distilled water and 5.778 g of aqueous solution of methylamine (MA, CH_3NH_2, 25%—30%, Shanghai Reagent Co.) were mixed with stirring in a plastic vessel. 5.00 g of HF aqueous solution (40%), 1.542 g of boric acid (Shanghai FE-DA Co.) and 3.11 g of fumed silica (Shanghai Electro-Chemical Plant) were then added subsequently, and the mixture was stirred at ambient temperature till a homogeneous white gel was formed. The final molar composition of the gel was $1.0SiO_2$ •$0.25B_2O_3$ •1.0DABCO •1.0MA •2.0HF •$16H_2O$. The gel was sealed in a 40-mL Teflon-lined stainless-steel autoclaves and reacted under autogenous pressure at 170 ℃ for 20 to 28 d. The product was filtered, washed with distilled water, and dried in air at room temperature.

The XRD patterns (Cu Kα radiation, Rigaku D-MAX/II A) of the as-synthesized product are shown in Figure 1. Pure phase of MTW type zeolite without detected impurity crystalline phase was obtained in DABCO-MA-SiO_2-B_2O_3-HF-H_2O reactant system. SEM photo (taken with Philips XL30 Scanning Electron Microscope) shows that the crystals of B-MTW zeolite obtained are in a form of fibres with the length of 20—60 μm and the width of *ca*. 0.5 μm (Figure 2). While in the reactant system of DABCO-MA-SiO_2-Al_2O_3-

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HF-H_2O, the main product was rice-grain shaped agglomerates of Si-Al-MTW-type zeolite, which is similar to the habit of the reported zeolite crystallites.[2,14] A trace of impurity of MFI type zeolite co-crystallized with the main product. On the other hand, MTN type (ZSM-39) zeolite crystallized in the reactant system in the absence of B_2O_3 or Al_2O_3.

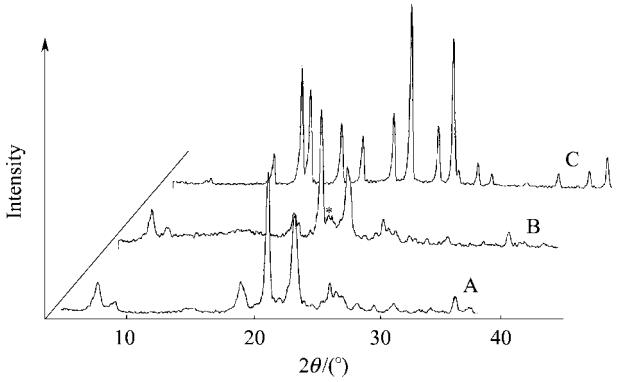

Figure 1 XRD patterns of (A) MTW-type zeolite obtained in a reactant system containing boron and silica, (B) MTW-type zeolite obtained in a reactant system containing aluminum and silica, and (C) MTN-type zeolite obtained in a pure silica reactant system. * Impurity of MFI-type zeolite.

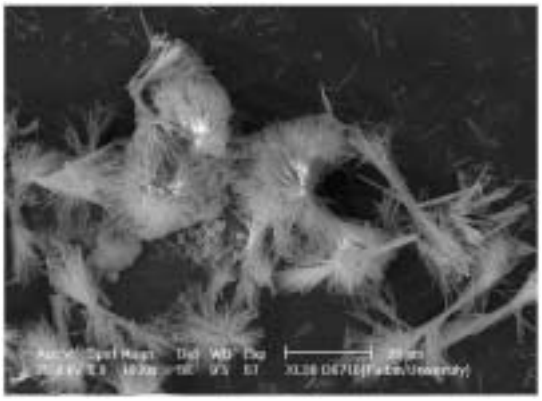

Figure 2 SEM image of the as-synthesized B-MTW zeolite.

The molar ratio of SiO_2/B_2O_3 is 42 for the as-synthesized B-MTW zeolite, in which B was determined by inductively coupled plasma atomic emission spectrometer (ICP) and Si by chemical titration. The ^{11}B and ^{29}Si MAS NMR spectra (see Figure 3, recorded at room temperature with a Bruker MSL-300 spectrometer), which are in agreement with those reported in references,[8,14] show that the atoms of B and Si are incorporated in the framework of the as-synthesized B-MTW zeolite. The main ^{11}B resonance at δ −3.6 and a weak resonance at δ −1.4 are assigned to $B(OSi)_4$ in different crystallography positions of the zeolite, respectively (see Figure 3A). The signals of ^{29}Si MAS NMR for the as-synthesized zeolite are shown in the range of δ −100 to −120 (see Figure 3B), which belong to Si(OB) and Si(1B) (at δ −102.7).

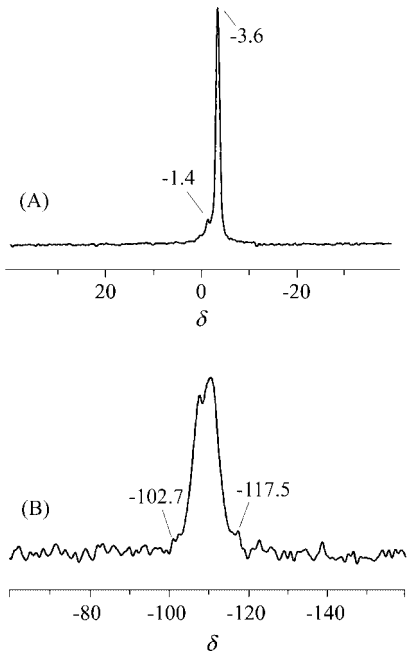

Figure 3 ^{11}B (A) and ^{29}Si (B) MAS NMR spectra of the as-synthesized B-MTW zeolite.

The TEM image (taken with JEOL JEM2011 high-resolution transmission electron microscope) exhibits the habit of the fibrous crystals for B-MTW zeolite (see Figure 4-A). Obviously, the fibrous crystals are composed of several long and thin single crystals, which inter-grow with each other and parallel along the long axis of the fiber. The width and thickness of the single crystals are about 260—680 and 70—130 nm, respectively.

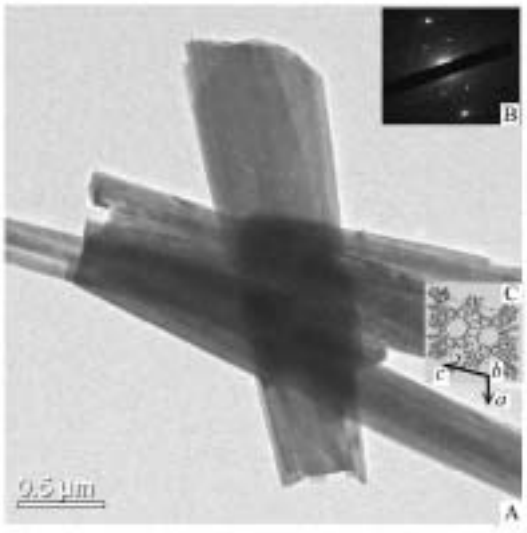

Figure 4 TEM image (A), single crystal SAED pattern of the as-synthesized B-MTW zeolite (B), and crystal structure simulated by program of Powder Cell viewed along [010] (C).

MTW type zeolite possesses monoclinic symmetry, space group of *C*2/*m*, a=2.56 nm, b=0.53 nm, c=1.21 nm and β=109.3°,[15] indicating that the only one L^2

symmetry axis of the zeolite crystal is parallel to *b*-axis of the cell. The SAED (selected-area electron diffraction) taken normal to the long axis of a single crystal of the as-synthesized B-MTW zeolite, presents a pattern of L^2 symmetry (see Figure 4-B). The fact indicates that the 12-MR channels are perpendicular to the direction along the fiber (see Figure 4-C).

A high-resolution TEM image of the as-synthesized B-MTW zeolite, having obtained normal to the long axis of the fibrous crystals, is presented in Figure 5. It can be seen that two or three parallel single crystals inter-grow with each other. The borders of these crystals are along the direction of the fibers, which is the same as that observed by SEM. The interplanar spacing, measured from the pattern of a single crystal, is 1.21 nm, which is very close to 1.184 nm of the calculated value for d_{200}.[16] The fact indicates that *c*-axis of the crystals is parallel to the direction of the fiber.

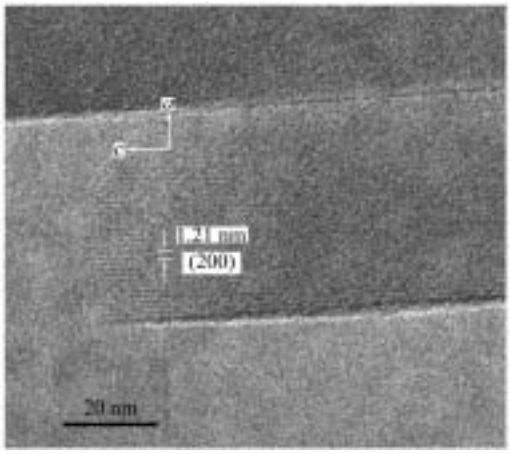

Figure 5 HRTEM image of the as-synthesized B-MTW zeolite fibrous crystals.

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