Preparation of Boron-containing TON-Type Zeolite by Self-transformation of Porous Glass in a Vapor Phase

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Pure phase of boron-containing TON-type zeolite with high crystallinity was prepared by self-transformation of porous glass granules in a vapor phase of methylamine and water. XRD and ^{11}B, ^{27}Al and ^{29}Si MAS NMR spectra proved that the atoms of B, Al and Si in the raw glass have been essentially completely incorporated into the zeolite framework.

As a novel high silica zeolite, TON was first reported in 1981 named as Theta-1 (diethanolamine as template).[1] Since then several kinds of crystalline molecular sieves of aluminosilicate, which possess same framework topology identified by the similar XRD patterns, were reported to be synthesized with various organic templates. They are NU-10 (diaminoethane as template, 1982),[2] CF-2 (diethanolamine and glycerine as template, 1983),[3] KZ-2 (diethylamine or 1-aminobutane, 1,4-diaminohexane, 2,2′-diaminodiethylamine as template, 1983).[4] ISI-1 (methanol as template, 1983),[5] and ZSM-22 (N-ethylpyridine as template, 1984).[6]

Some significant catalysis reactions were performed over TON-type zeolite, such as the conversion of dimethyl ether and monofunctional alcohols to lower olefins,[2] methanol conversion to hydrocarbon for producing high yields of aromatics,[4,7] alkylation of toluene with methanol to p-xylene,[8] xylene isomerization,[9] catalytic dewaxing of petroleum feed stock,[10] 1-butene isomerization to isobutene,[11] conversion of n-butane to aromatic hydrocarbons etc.[12] Because of the one dimensional 10-ring channel in the structure and mild solid acidity, TON-type zeolite shows good shape-selective properties and lowers cracking reaction in isomerization reactions,[11] leading to its potential as industrial catalysts. Therefore, the preparation of the zeolite with various framework compositions for modification is an attractive topic. So far, the synthetic methods of TON-type zeolite in the literature available are mainly conventional hydrothermal synthesis using alumina-silicate gel as the starting material.[3,4,6–8,11–15] No B-containing TON-type zeolite was reported. In this paper, we report the preparation of B-containing TON-type zeolite by using self-transformation of porous glass granules in the vapor phase of water and methylamine, the smallest molecules of organic amine. The method of self-transformation has been successfully used to synthesize B-containing MFI-type zeolite membrane on the substrate of porous glass in our lab.[16]

The granules of B-containing porous glass, with particle sizes smaller than 1.76 mm (>20 mesh, i.e. through 20 mesh sifter), were used as an initial raw material. The chemical composition of the glass is: $SiO_2 = 95.93$ wt%, $B_2O_3 = 3.20$ wt%, $Al_2O_3 = 0.35$ wt%, and $Na_2O = 0.52$ wt%. (Si and Al measured by chemical titration; B by ICP; Na by atomic absorption). The molar ratios are: $SiO_2/B_2O_3 = 34.7$ and $SiO_2/(B_2O_3 + Al_2O_3) = 32.3$. The most probable pore size, the BET surface area and the pore volume of the initial porous glass are 7.5 nm, 155 m^2/g and 0.32 cm^3/g, respectively. A 25–30 wt% reagent grade methylamine aqueous solution (Shanghai Third Reagent Factory) was used for the synthesis. The chemical composition of the as-synthesized TON-type zeolite is: $SiO_2 = 94.96$ wt%, $B_2O_3 = 3.95$ wt%, $Al_2O_3 = 0.68$ wt% and $Na_2O = 0.41$ wt%. The molar ratios are: $SiO_2/B_2O_3 = 27.8$ and $SiO_2/(B_2O_3 + Al_2O_3) = 24.9$ (Si, B, Al, and Na measured by Field Emission Auger Microprobe).

About 1.0–1.5 g granules of the porous glass were put in a small Teflon cup with many pinholes on the bottom and the wall, and supported on a Teflon holder in an a 35 ml autoclave. The raw material was reacted with the mixed vapor of about 10 ml of a 25–30 wt% methylamine aqueous solution in the bottom of the autoclave at 473 K for 240 h. The cup was located at a position, where the granules did not directly come into contact with the upper surface of the solution under it at both room temperature and 473 K. After completion of the vapor/solid reaction, the granules were removed from the autoclave, dried at 373 K for 12 h, and then ground prior to characterization.

The initial porous glass was amorphous [Figure 1. (A) (a)] and the as-synthesized sample showed a typical XRD pattern of TON-type zeolite with high crystallinity and free from amorphous material and impurities [Figure 1. (A) (b)] [XRD by Rigaku D-MAX/II-A X-ray powder diffractometer, Cu-Kα radiation ($\lambda = 0.15418$ nm)].

^{11}B qualitative MAS NMR (^{11}B, ^{27}Al and ^{29}Si MAS NMR were measured using Bruker DMX-300 spectrometer) spectra of the as-synthesized B-containing TON-type zeolite and the initial porous glass granules are shown in Figure 1. (B). The resonance peak positioning at $\delta = -1.6$ ppm is assigned to the heterogeneously distributed tetrahedral BO_4 units in the network of the porous glass. A pair of twin peaks appearing at about $\delta = 5.3$ and -14.7 ppm are attributed to the trigonal BO_3 units [Figure 1. (B) (a)].[17] Hence, there are two types of the coordination geometry for B atoms in the network of the porous glass: tetrahedral coordinated BO_4 units and trigonal coordinated BO_3 units [Figure 1. (B) (a)]. These three peaks coupled together to form a broad peak, indicating that the chemical environments around these two B-O units are quite uneven. Only one very sharp, narrow and symmetric resonance peak (at about $\delta = -3.7$ ppm) remained on the spectrum of the as-synthesized zeolite sample [Figure 1. (B) (b)]. The peak is ascribed to tetrahedral BO_4 units quite orderly arranged in the framework of the TON-type zeolite [Figure 1. (B) (b)].[17] This datum indicates that B atoms have been

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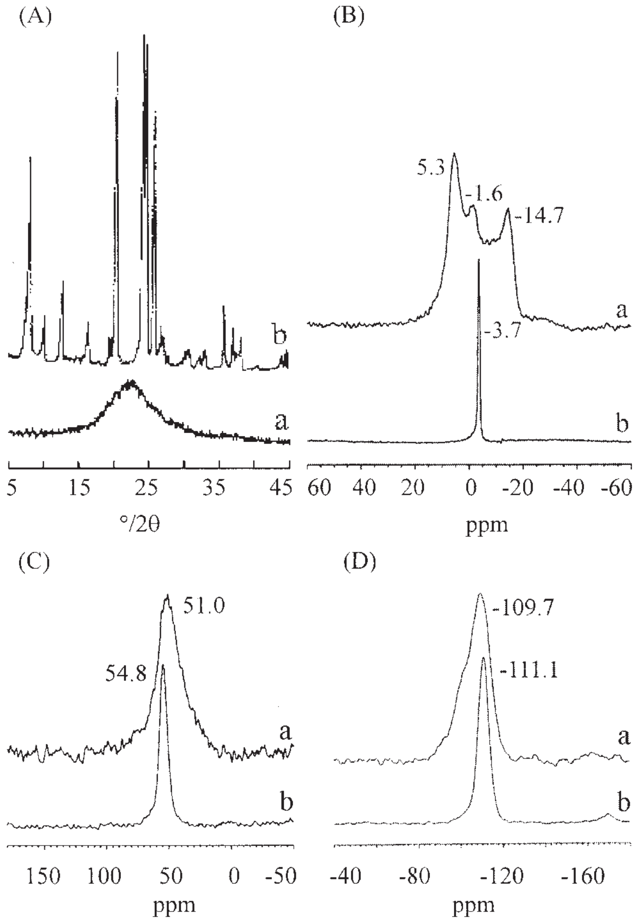

Figure 1. (A). XRD patterns, (B). ^{11}B MAS NMR spectra, (C). ^{27}Al MAS NMR spectra, and (D). ^{29}Si MAS NMR spectra. a. Initial porous glass granules. b. The as-synthesized B-containing TON-type zeolite.

essentially completely incorporated into the framework, and the as-synthesized sample is B-containing zeolite.

Figure 1. (C) shows the ^{27}Al MAS NMR spectra of the samples. The strong resonance appearing at about 51 ppm is assigned to the four-coordinated Al-O groups [Figure 1. (C) (a)]. The weak shoulder positioning at about 0 ppm is from non-structural six-coordinated Al-O groups.[17] The fact indicates that the atoms of Al exist mainly as four-coordinated Al-O groups in the initial porous glass. Its broad peak indicates that the chemical environments around four-coordinated Al atoms are not uniform. The narrow and symmetric peak at 54.8 ppm [Figure 1. (C) (b)] indicates that all Al atoms have been essentially completely incorporated into the framework of the as-synthesized zeolite.

The spectra of ^{29}Si MAS NMR of the samples are shown in Figure 1. (D). The spectrum (D) (a) is a broad and asymmetric peak in the range of -85 to -125 ppm with a shoulder at about -101 ppm. There is a tail in the range of -85 to -93 ppm, which was caused mainly by Si-OH or four-coordinated silicon atoms bonded with only three tetrahedra of Si-O and one oxygen atom bearing a negative charge.[17] The spectrum (D) (a) indicates that the chemical environments around Si atoms are variable and there are a great number of Si-OH groups in the initial porous glass granules. The spectrum (D) (b) is a narrow and symmetric peak at about -111.1 ppm, indicating that the four-coordinated SiO_4 units were rearranged more orderly and the atoms of Si in the raw material have been essentially completely incorporated into the framework.

The SEM photographs (taken on PHILIPS XL SERIES, XL 30) of the samples are shown in Figure 2. These show that the granules of the initial porous glass are irregular in morphology with particle size from 1.76 mm (not shown the largest granules in the Figure) to very small, and no zeolite crystals within [Figure 2 (a)]. The granules of the porous glass spontaneously completely transformed to the crystals of TON-type zeolite after the reaction in a vapor of 25–30 wt% methylamine aqueous solution at 473 K for 240 h. The as-synthesizsed crystals of TON-type zeolite are rectangular rod-shaped [Figure 2 (b)]. Some of the crystals are individuals and the others are aggregates. The size of the crystals is about $(0.43\text{–}1.7)\times(1.5\text{–}12)\mu$m. The SEM photo gives further evidence that the as-synthesized sample is a pure TON-type zeolite without visible impurity and amorphous phase, in agreement with the results of XRD and NMR. The further and deep studies on the properties of the zeolite are in progress.

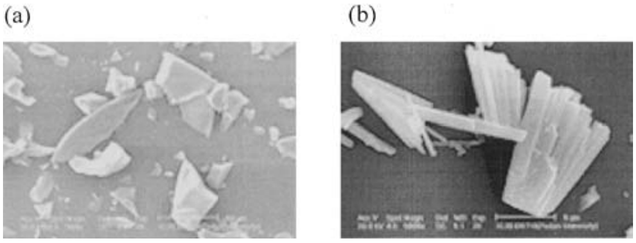

Figure 2. SEM Photographs of the samples. a. Initial porous glass granules. b. The as-synthesized B-containing TON-type zeolite.

In summary, B-containing porous glass can spontaneously transform to pure phase of TON-type zeolite with higher content of heterogeneous boron atoms in the framework and high crystallinity in the vapor of water and methylamine.

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