Electronic Supplementary Information

High stable boron-modified hierarchical nanocrystalline ZSM-5 zeolite for methanol to propylene reaction

Zhijie Hu,‡ Hongbin Zhang,‡ Lei Wang, Hongxia Zhang, Yahong Zhang, Hualong Xu, Wei Shen* and Yi Tang*

Department of Chemistry, Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Laboratory of Advanced Materials, and Collaborative Innovation Center of Chemistry for Energy Materials, Fudan University, Shanghai 200433 (P.R. China).

*Corresponding Author. Emails: yitang@fudan.edu.cn; wshen@fudan.edu.cn.
Synthesis procedure:

1. Silicalite-1 seed

The seed with crystal size of 200 nm was synthesized from clear solution method. The gel composition was 4.4TPAOH: 0.1Na2O 25SiO2: 756H2O: 100EtOH. Typically, the TEOS was added into the mixture aqueous solution of TPAOH, NaOH and H2O. Then, the mixture was transferred to a polypropylene bottle and hydrothermally treated at 373 K for 3 days. The obtained gel solution was directly used as the seed without any further treatment.

2. Conventional ZSM-5 (denoted as C-Z5)

In a typical run, Na2SiO3, NaAlO2 and TPABr (tetrapropylammonium bromide) were dissolved in deionized water to prepare a precursor solution. Then, the pH was adjusted to 9.5-10 by dropwise adding sulfuric acid into the mixture. The obtained solution with the molar composition of 400SiO2: 1Al2O3: 120TPABr: 12000H2O was stirred for 5 h and then was transferred into a teflon-lined stainless-steel autoclave for crystallization at 180 ºC for 48 h.

3. Hierarchical nanocrystalline ZSM-5 (denoted as N-Z5)

In a typical run, a starting aluminosilicate mixture with a molar ratio of 400SiO2: 1Al2O3: 60Na2O: 120KF: 40TPABr: 20000H2O was prepared using Al2(SO4)3•18H2O as alumina source, 40% colloidal silica as silica source. Thereafter, the pre-prepared silicalite-1 seed solution with crystal size of 200 nm was added under stirring. The addition quantity of seed typically equals to 7.0 wt% of total SiO2 weight in starting gel. Then, the mixture was stirred at ambient temperature for 3 h and hydrothermally treated at 180 ºC for 2 h.

4. Boron-modified conventional ZSM-5 (denoted as B-C-Z5)

In a typical run, Na2SiO3, NaAlO2, H3BO3 and TPABr were dissolved in deionized water to prepare a precursor solution. Then, the pH was adjusted to 9.5-10 by dropwise adding sulfuric acid into the mixture. The obtained solution with the molar composition of 400SiO2: 1Al2O3: 1B2O3: 120TPABr: 12000H2O was stirred for 5 h and then was transferred into a teflon-lined stainless-steel autoclave for crystallization at 180 ºC for 48 h.

5. Boron-modified hierarchical nanocrystalline ZSM-5 zeolite (denoted as B-N-Z5)

In a typical run, a starting aluminosilicate mixture with a molar ratio of 400SiO2: 1Al2O3: 1B2O3: 60Na2O: 120KF: 40TPABr: 20000H2O was prepared using Al2(SO4)3•18H2O as alumina source, 40% colloidal silica as silica source and H3BO3 as boron source. Thereafter, the pre-prepared silicalite-1 seed solution with crystal size of 200 nm was added under stirring. The addition quantity of seed typically
equals to 7.0 wt% of total SiO\textsubscript{2} weight in starting gel. Then, the mixture was stirred at ambient temperature for 3 h and hydrothermally treated at 180 °C for 4 h.

Finally, the obtained four samples were separated by filtration, washed with deionized water, dried at 90 °C for 12 h and finally calcined under static air for 5 h at 550 °C. Then, these acidic samples were obtained by ion-exchange for three times with NH\textsubscript{4}NO\textsubscript{3} aqueous solution at 90 °C for 3 h and then calcined at 550 °C for 5 h.

Based on the novel “salt-aided seed-induced route” for synthesis of N-Z5 and B-N-Z5 with hierarchical nanocrystalline structure, the TPABr/ SiO\textsubscript{2} ratio of 0.3 can be reduced to lower than 0.1; the crystallization time of 48 h can be decrease to 2-4 h; the yield of products can be increased to >80% by the introduction of 7.0 wt% silicalite-1 seeds, compared with the synthesis of C-Z5 and B-C-Z5.

**Characterization method:**

Scanning electron microscopy (SEM) images were recorded on a JEM-2100F microscope working at 10 kV acceleration voltage. Transmission electron microscopy (TEM) images were taken with a JEOL JEM-2001 microscope operated at 200 kV. The powder X-ray diffraction (XRD) patterns (2θ, 5-50°) were obtained with a Bruker D8-Advanced diffractometer using Ni-filtered Cu-K\textalpha radiation. The elemental compositions of the catalyst samples were measured by ICP-AES using an IRIS Intrepid spectrometer. Solid-state magic angle spinning (MAS) NMR experiments were performed on a Bruker DSX 300 spectrometer at a rotation rate of 12 kHz. The \textsuperscript{27}Al MAS NMR were obtained at a Lamor frequency of 78.2 MHz using a short RF pulse length of 1.0 µs and a recycle delay of 2 s. The \textsuperscript{11}B MAS NMR were obtained at a Lamor frequency of 96.3 MHz using a short RF pulse length of 2.0 µs and a recycle delay of 0.5 s. BET surface area and pore volume were carried out with N\textsubscript{2} adsorption using Micrometrics ASAP 2020. Before analysis, all of samples were degassed in vacuum at 350 °C for 12 h. The acid amount and strength were measured by NH\textsubscript{3}-TPD using a Micrometerics AutoChem 2920 analyzer. The catalyst sample (0.1 g) was heated at 550 °C in a He flow for 3 h and then cooled to 80 °C. NH\textsubscript{3} adsorption was performed under a flow of 10 vol% NH\textsubscript{3}/He (30 ml min\textsuperscript{-1}) for 1 h. The NH\textsubscript{3}-TPD was promptly started at a heating rate of 10 °C min\textsuperscript{-1} from 80 to 600 °C.

**Catalyst test:**

The performance of catalysts for methanol to propylene reaction was measured under atmospheric pressure at 733 K in an automatic fixed-bed micro-reactor with a quartz tube (I.D. = 8 mm). The catalyst particles (0.5 g, 40-60 mesh) were packed into the tube and activated with N\textsubscript{2} for 1 h. The weight hourly space velocity (WHSV) for methanol was 4.0 h\textsuperscript{-1} with a methanol/H\textsubscript{2}O molar ratio of 1 : 3 unless noted. The total products were analyzed by an on-line gas chromatographs (Thermo ULTRA-GC) equipped with a flame ionization detector (FID) and CP-Pora PLOT-Q capillary
column (I.D.=0.32 mm and length =52.5 m). DME was considered as reactant and the carbon balance is above 95%.
References information:

**Fig. S1** TEM images of calcined B-N-Z5 a) before and b) after the ultrasound treatment of 180 min.

**Fig. S2** $^{11}$B and $^{27}$Al MAS NMR spectra of B-C-Z5.

**Fig. S3** SEM images of (a) C-Z5 and (b) B-C-Z5.
Fig. S4 (a) SEM and (b) TEM images of N-Z5.

Fig. S5 (a, b) TEM images of B-C-Z5.

Fig. S6 TG curves of the different coked catalysts after reaction.
Fig. S7 Conversion of methanol, selectivity of total olefin and propylene over zeolite B/N-Z5. Reaction conditions: WHSV = 10 h⁻¹, T = 733 K, n(CH₃OH) : n(H₂O) = 1 : 3, P_{total} = 1 atm.

Fig. S8 XRD patterns of B/N-Z5 and B-N-Z5 before reaction and B/N-Z5-Coke and B-N-Z5-Coke after reaction.
Fig. S9 $^{11}$B and $^{27}$Al MAS NMR spectra of B-N-Z5 after reaction.