Electronic Supplementary Information

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

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Synthesis procedure:

1. Silicalite-1seed

The seed with crystal size of 200 nm was synthesized from clear solution method. The gel composition was 4.4TPAOH: $0.1Na_2O$ $25SiO_2$: $756H_2O$: 100EtOH. Typically, the TEOS was added into the mixture aqueous solution of TPAOH, NaOH and H_2O. 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, Na_2SiO_3, $NaAlO_2$ 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 $400SiO_2$: $1Al_2O_3$: 120TPABr: $12000H_2O$ 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 $400SiO_2$: $1Al_2O_3$: $60Na_2O$: 120KF: 40TPABr: $20000H_2O$ was prepared using $Al_2(SO_4)_3{\bullet}18H_2O$ 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 SiO_2 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, Na_2SiO_3, $NaAlO_2$, H_3BO_3 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 $400SiO_2$: $1Al_2O_3$: $1B_2O_3$: 120TPABr: $12000H_2O$ 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 $400SiO_2$: $1Al_2O_3$: $1B_2O_3$: $60Na_2O$: 120KF: 40TPABr: $20000H_2O$ was prepared using $Al_2(SO_4)_3{\bullet}18H_2O$ as alumina source, 40% colloidal silica as silica source and H_3BO_3 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_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_4NO_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_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-Kα 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 ^{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 ^{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_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_3-TPD using a Micromeritics 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_3 adsorption was performed under a flow of 10 vol% NH_3/He (30 ml min^{-1}) for 1 h. The NH_3-TPD was promptly started at a heating rate of 10 °C min^{-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_2 for 1 h. The weight hourly space velocity (WHSV) for methanol was 4.0 h^{-1} with a methanol/H_2O 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:

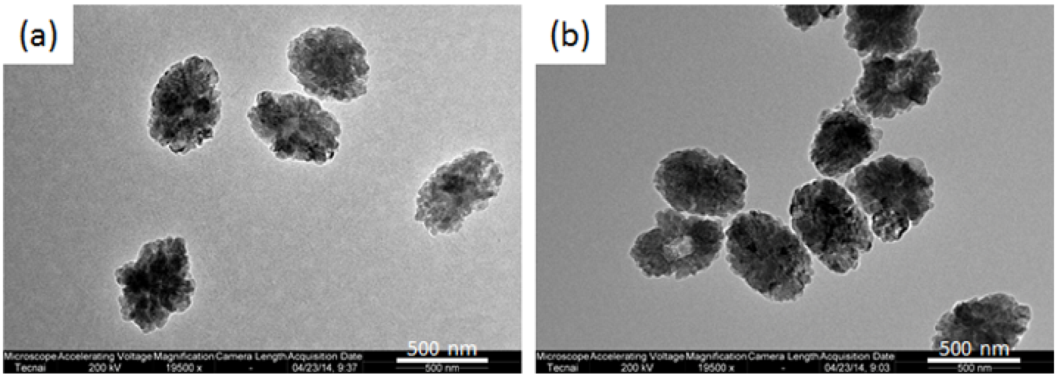

Fig. S1 TEM images of calcined B-N-Z5 a) before and b) after the ultrasound treatment of 180 min.

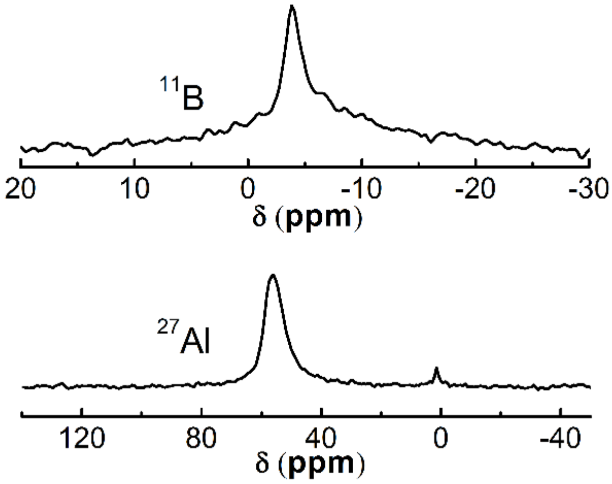

Fig. S2 ^{11}B and ^{27}Al MAS NMR spectra of B-C-Z5.

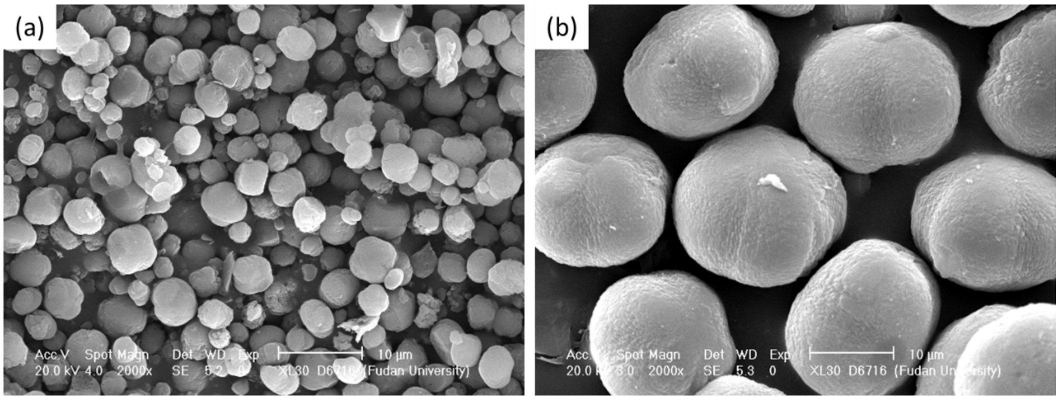

Fig. S3 SEM images of (a) C-Z5 and (b) B-C-Z5.

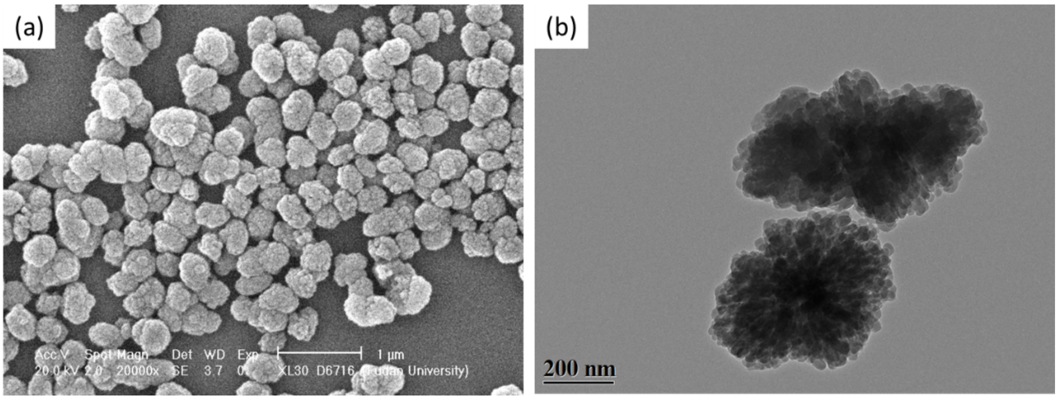

Fig. S4 (a) SEM and (b) TEM images of N-Z5.

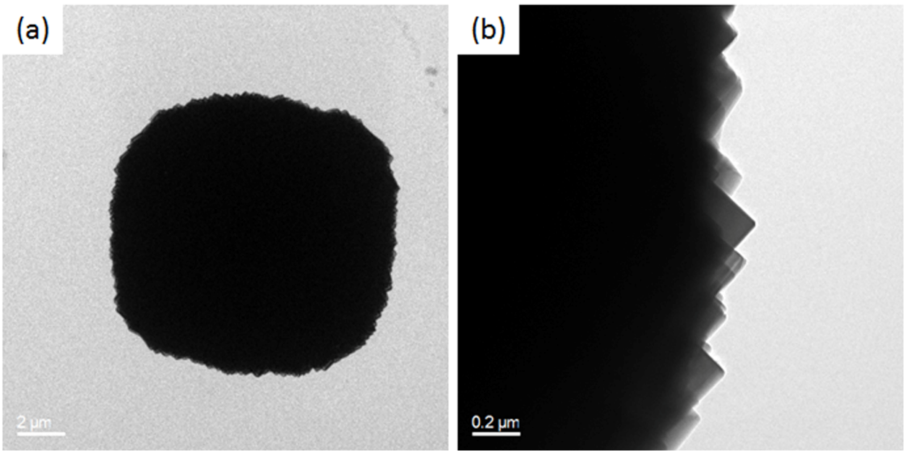

Fig. S5 (a, b) TEM images of B-C-Z5.

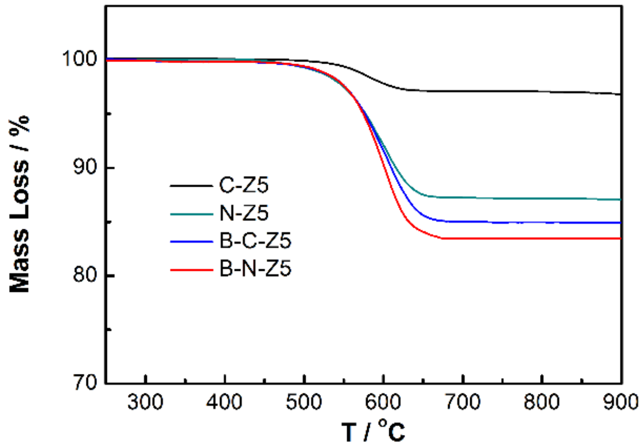

Fig. S6 TG curves of the different coked catalysts after reaction.

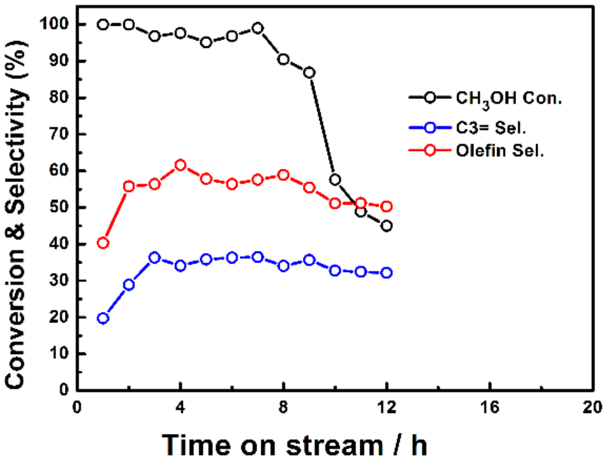

Fig. S7 Conversion of methanol, selectivity of total olefin and propylene over zeolite B/N-Z5. Reaction conditions: WHSV = 10 h^{-1}, T = 733 K, n(CH_3OH) : n(H_2O) = 1 : 3, P_{total} = 1 atm.

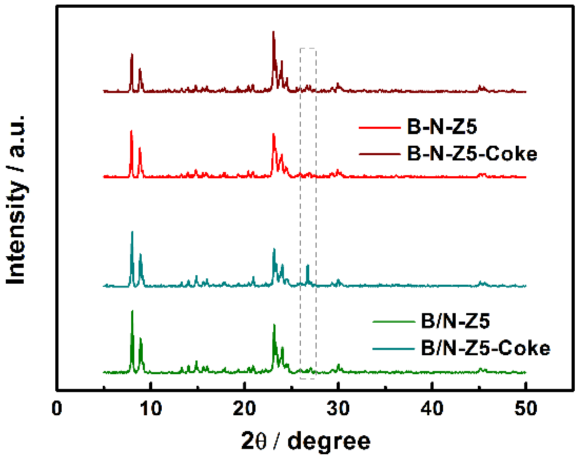

Fig. S8 XRD patterns of B/N-Z5 and B-N-Z5 before reaction and B/N-Z5-Coke and B-N-Z5-Coke after reaction.

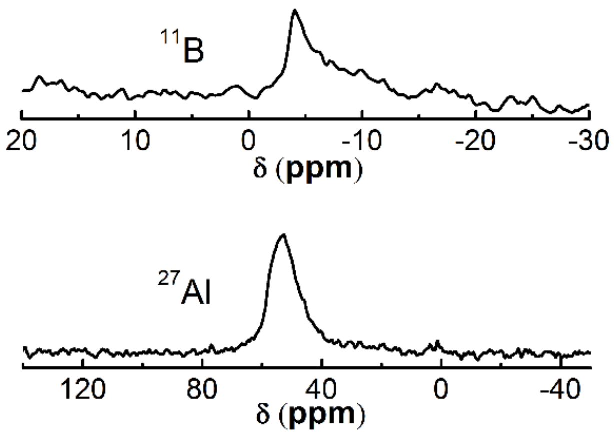

Fig. S9 ^{11}B and ^{27}Al MAS NMR spectra of B-N-Z5 after reaction.