Supplementary information

Synthesis of CZ5

The reactants used in the synthesis were tetraethylorthosilicate (TEOS, Beijing Modern Eastern Fine Chemicals Co., Ltd), tetrapropylammonium hydroxide (TPAOH, 25% in water, Zhejiang Ken Te Chemical Co., Ltd.), Aluminium nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$, Beijing Chemical Works) , Urea (Beijing Chemical Works), NaOH (Beijing Chemical Works), iso-propanol (IPA, Beijing Chemical Works) and ammonium nitrate (NH_4NO_3, Beijing Chemical Works). MZ5 was commercial ZSM-5 catalyst produced by Nan Kai University. In a typical synthesis of short b-axis nano CZ5, 13.1 g TPAOH, 11.2 g TEOS, 2.0 g urea, 0.3 g $Al(NO_3)_3 \cdot 9H_2O$, 0.1 g NaOH and 0.1 g IPA were added into 18.4 g H_2O under stirring. After stirring at room temperature for 1-2 h, the resulting solution was transferred into an autoclave for further crystallization. The autoclave was placed into a temperature programming oven. The oven was heated from room temperature to 180 ^oC with a rate of 15 $^oC/h$, and then hold on for 48 h. The crystallization reaction was subsequently quenched by cold water. The obtained crystals were separated by filtration and washed by deionized water for three times, subsequently dried at 90 ^oC in air, then calcined at 550 ^oC for 5 h to remove the template. The obtained Na-ZSM-5 was converted to the ammonium form by cation-exchange in a NH_4NO_3 solution. 10 g Na-ZSM-5 was dispersed in 100 mL NH_4NO_3 solution (1 M) and vigorously stirred for 6 h. The exchange process was performed repeatedly for 3 times to complete the exchange reaction, and NH_4-ZSM-5 was formed. The H-CZ5 was obtained by calcining the NH_4-ZSM-5 powder at 550 ^oC for 5 h.

The as-prepared H-CZ5 was hydrothermally treated at 660 ^oC or 760 ^oC in 100% water vapor for 4 h to obtain the aged H-CZ5 designated as 660 H-AZ5 or 760 H-AZ5, respectively.

The corresponding Zn-modified HZSM-5 with mass loading of Zn of 3% was prepared by traditional incipient wetness impregnation of HZSM-5 using aqueous solutions of $Zn(NO_3) \cdot 6H_2O$. After drying and calcinating in air at 550 ^oC for 5 h, the resultant catalyst was designated as Zn/CZ5. If using660/760 H-CZ5 as the starting materials, the resultant catalysts were designated as 660/760 AZ5.

Synthesis of molded Zn/CZ5-M or Zn/MZ5-M

For molding of the zeolite, zeolite (Hydrogen form CZ5 or MZ5) was mixed with silica sol (as binder) and kaolin clay (as mechanical additive) in a solution with solid concentration of 15%. Weight ratio of zeolite, whether is CZ5 or MZ5, were controlled to 30% for fair comparison. The solution was quickly sprayed into a granulator with temperature of 300-350 ^oC. Water was quickly heated into vapor and the solid condensed to become powder. To test the catalytic performance of MFI in model reaction of methanol to aromatics, 3wt% Zn was doped based on the weight of ZSM-5 by an incipient wetness impregnation method using aqueous solutions of $Zn(NO_3)_2 \cdot 6H_2O$. After drying and calcinating in air at 550 ^oC for 5 h, Zn/CZ5-M and Zn/MZ5-M were obtained

Characterization

X-ray diffractions (XRD) were recorded on a Rigaku D/Max-RB diffractometer with Cu $K\alpha$Radiation at 40 kV and 120 mA. Scanning electron microscope (SEM) images were obtained by a high-resolution scanning electron microscope (JEOL, JSM-7401) at 3.0 kV. TEM, EDX and STEM experiments were performed on high-resolution transmission electron microscopes (Titan Themis^3 300, exited at 300 kV and JEOL, JEM-2010, exited at 120 kV). Brunauer-Emmett-Teller (BET) surface area were recorded in a Quantachrome automated surface area and porosity analyzer with Ar as the adsorption gas. NH_3-TPD was recorded in a Quantachrome automated chemisorption analyzer from room temperature to 700 ^oC with a ramp of 10 ^oC/min. The Si/Al of the zeolite was obtained by an inductively coupled plasma optical emission spectrometer (ICP-OES, IRIS Intrepid II XSP). NMR spectra were obtained on a Bruker AVANCE III 600 spectrometer. Brønsted acid sites and Lewis acid sites were determined by pyridine adsorption. The samples were first dried, *in situ*, by heating to 420 ^oC under vacuum, and then were cooled to 100 ^oC. At this temperature, the samples were exposed to pyridine vapor using an equilibration time of 30 min. After the physically adsorbed pyridine molecules were removed by outgassing at 200 ^oC for 1 h, IR spectra were collected at 200 ^oC with 4 cm^{-1} resolution using a Bruker Tensor 27 FTIR spectrometer. After the collection was done, the samples were heated to 350 ^oC to desorb pyridine molecules adsorbed at weak acid sites for 30 min. IR spectra were collected at 350 ^oC.

Catalytic conversion of methanol to aromatics

The MTA reactions were performed at the conditions of 1 atm, 475 ^oC and WHSV=0.8 h^{-1} (under N_2 flow (10 mL/min)) in a conventional fixed bed stainless steel reactor (13.0 mm i.d.) equipped with a thermocouple in the middle of the catalyst bed. 1.0 g catalyst was placed in the fixed bed reactor. The flow rate of the pure methanol and N_2 was controlled using a dual micro-plunger pump and the mass flow controllers, respectively. The products (hydrocarbons) were analyzed using two flame ionization detectors (FIDs). The conversion of methanol and the selectivity of the different products were calculated (carbon base) by considering the oxygenates (methanol and dimethylether) as the unconverted reactants.

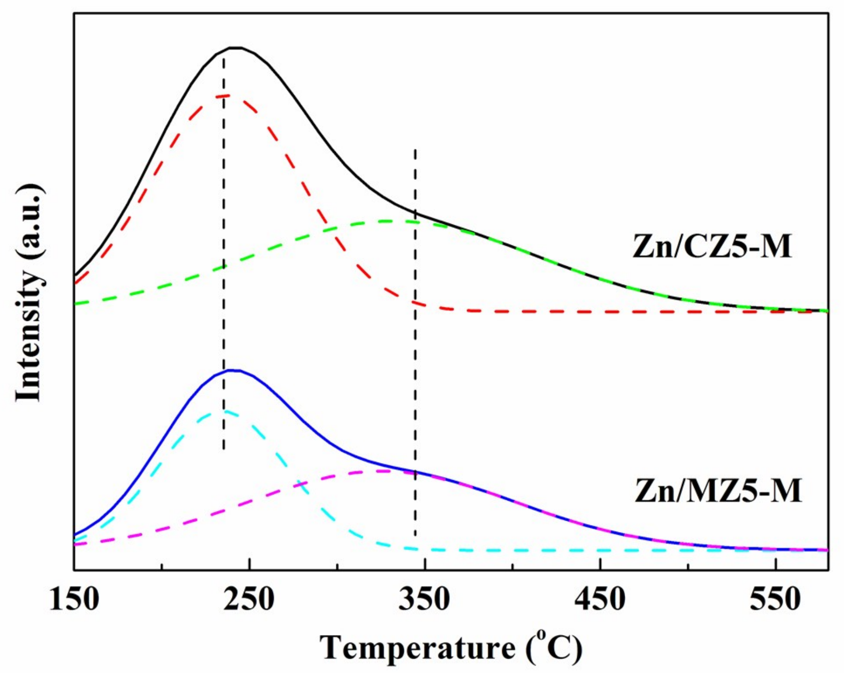

Fig. S1 NH_3-TPD spectra of Zn/CZ5-M and Zn/MZ5-M catalysts.

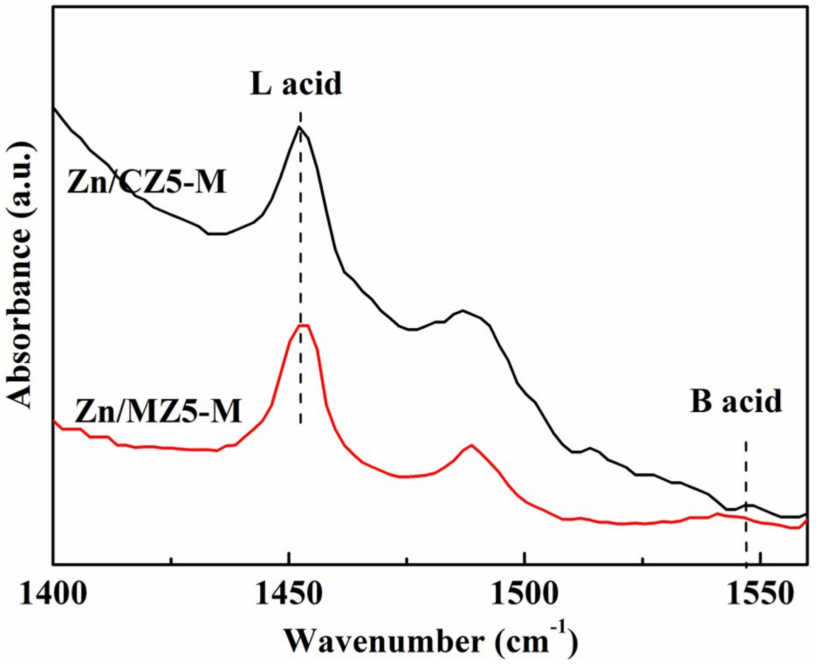

Fig. S2 Py-FTIR spectra of Zn/CZ5-M and Zn/MZ5-M catalysts.