Supplementary information

Conversion of methanol to propylene over hierarchical HZSM-5: effect of Al spatial distribution

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Experimental section

Catalyst preparation

ZSM-5 crystals were synthesized with two silicon sources: tetraethyl orthosilicate (TEOS) and silica sol, and the zeolites were named as T-Z and S-Z, respectively.

T-Z: Defined amount of TEOS was added into the solution containing deionized water, tetrapropylammonium hydroxide (TPAOH), sodium hydroxide (NaOH), and sodium aluminate ($NaAlO_2$). The resulting gel was stirred at 80 °C for 24 h. The molar ratio of mother gel was $1SiO_2:0.005Al_2O_3:0.15TPAOH:0.02NaO_2:20H_2O$. The prepared mother gel was crystallized at 170 °C for 48 h. The solid product was separated by centrifugation, washed with deionized water until neutral, dried at 110 °C for 12 h and calcined at 550 °C for 6 h.

Seed suspension: Defined amount of TEOS was added into the solution containing deionized water and tetrapropylammonium hydroxide (TPAOH). The resulting clear solution was stirred at 80 °C for 24 h, and then crystallized at 170 °C for 24 h. The molar ratio of clear solution was $1SiO_2$: 0.2TPAOH: $20H_2O$. The solid product was separated by centrifugation, washed with deionized water until neutral, and dispersed in deionized water, obtaining silicalite-1 seed suspension.

S-Z: Deionized water, TPAOH, NaOH, and $NaAlO_2$ were mixed homogeneously with vigorous stirring. Silica sol was slowly dropped into the solution under vigorous stirring. Subsequently, 4 wt% seed suspension was added into the mixture and stirred at room temperature for 6 h. The molar ratio of mother gel was $1SiO_2:0.005Al_2O_3:0.15TPAOH:0.01NaO_2:30H_2O$. The prepared mother gel was crystallized at 170 °C for 48 h. The solid product was separated by centrifugation, washed with deionized water until neutral, dried at 110 °C for 12 h and calcined at 550 °C for 6 h.

T-Z and S-Z were alkali treated with different concentration NaOH solution (0.1 and 0.2 M, 30 ml/g zeolite) for 0.5 h at 65 °C. Afterwards, the zeolite suspension was cooled down in an ice-bath, separated by centrifugation, washed with deionized water until neutral, and dried at 110 °C for 12 h. The prepared samples were denoted as T-Z-xAT and S-Z-xAT (x=0.1, 0.2).

T-Z, S-Z, T-Z-xAT and S-Z-xAT were ion-exchanged with 1 M NH_4Cl aqueous solution at 80 °C for 3 h. The process was repeated three times. Consequently, the zeolites were washed with deionized, dried at 110 °C for 12 h and calcined at 550 °C for 6 h. Then, HZSM-5 zeolite samples (T-HZ, S-HZ, T-HZ-xAT and S-HZ-xAT) were obtained.

HZSM-5 zeolite samples were exchanged with 1 M $NaNO_3$ aqueous solution at 80 °C for 7 h. Then, the samples were ion-exchanged with 0.05 M $Co(NO_3)_2$ aqueous solution at room temperature for 24 h. The exchange procedure was repeated three times to obtain over exchanged Co-type samples. After the Co ion exchange, the samples were washed with deionized water and dried at 110 °C for 12 h before measurement of Ultraviolet-visible diffuse reflectance spectra.

Catalyst characterization

X-ray diffraction (XRD) patterns were measured on a Rigaku D/MAX 2550 VB/PC X-ray diffractometer with Cu Kα radiation at 40 kV and 100 mA. The data were collected in the 2θ range of 5-50° with a step size of 0.02°. The relative crystallinity was calculated according to intensity of three peaks at 2θ=22-25°, and the crystallinity of S-HZ was referenced at 100%.

N_2 adsorption was conducted at -196 °C using a Micrometrics ASAP 2020 instrument. Prior to N_2 adsorption, the samples were outgassed at 350 °C under vacuum for 4 h. Total surface area was determined from BET model, external surface area and micropore volume were derived from T-plot method, total pore volume was derived from a single point measured at $p/p_0=0.99$ and mesopore volume was calculated by subtracting micropore volume from total volume. The pore size distribution was calculated by BJH algorithm using the adsorption branch.

The bulk atomic composition of HZSM-5 catalysts was determined by X-ray Fluorescence Spectrometer (XRF, XRF-1800, SHIMADZU). The surface atomic composition of HZSM-5 catalysts was determined by X-ray photoelectron spectra (XPS, ESCALAB 250Xi, Thermo Fisher).

Scanning electron microscopy (SEM) images were obtained on a field emission scanning electron microscope (FE-SEM, NOVA Nano SEM450, FEI). Transmission electron microscopy (TEM) images were collected on a transmission electron microscopy (TEM, JEM-2100, JEOL) after samples were deposited onto a carbon coated copper grid.

Ultraviolet-visible diffuse reflectance spectra (UV-vis DRS) of Co ion-exchanged ZSM-5 samples were recorded on a Cary 500 spectrometer equipped with a 110 mm integrating sphere attachment. The absorption intensities were extracted from reflectance data using the Schuster-Kubelka-Munk equation.

^{27}Al magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectra were obtained on a Bruker AVANCE III 600 spectrometer at a magnetic field of 14.1 T with a 14 kHz spinning rate, a

0.65 μs pulse width and a 1 s recycle delay. The chemical shifts were referenced to $[Al^{3+}(H_2O)_6]$.

Fourier transform infrared (FTIR) of adsorbed pyridine was carried out on a Nicolet Nexus 470 spectrometer equipped with an in-situ cell containing CaF_2 windows. Self-supporting wafer with a diameter of 2 cm and a weight of about 10 mg was activated at 300 °C for 4 h under 10^{-2} Pa, and then cooled to room temperature. Consequently, pyridine were admitted, and after equilibration the sample was outgassed at 150 °C for 0.5 h to evacuate the excess pyridine. The IR spectra of catalysts were recorded with a resolution of 2.0 cm^{-1}.

Catalytic test

The performance of zeolite catalysts in MTP was evaluated in a fixed-bed flow reactor with 10 mm inner diameter. 0.5 g of the catalyst (40-60 mesh) was loaded into the reactor. Before the reaction, the catalyst was heated at 550 °C for 2 h in nitrogen. Consequently, MTP reaction was conducted at 450 °C under atmospheric pressure by pumping methanol to the preheating section where it was gasified to pass through the reactor. The WHSV of methanol was 6 h^{-1}, and the methanol was diluted in nitrogen to a concentration of 14%. The gas products were analyzed by Agilent GC 6890 equipped with a flame ionization detector (FID) and a HP-PLOT Al_2O_3 capillary column. The liquid oil products were analyzed by Agilent GC 7890 equipped with a flame ionization detector (FID) and a HP-5 capillary column. The liquid aqueous products were analyzed by Agilent GC 6820 equipped with a thermal conductivity detector (TCD) and a HP-PLOT Q capillary column. Dimethyl ether was considered reactant when calculating methanol conversion.

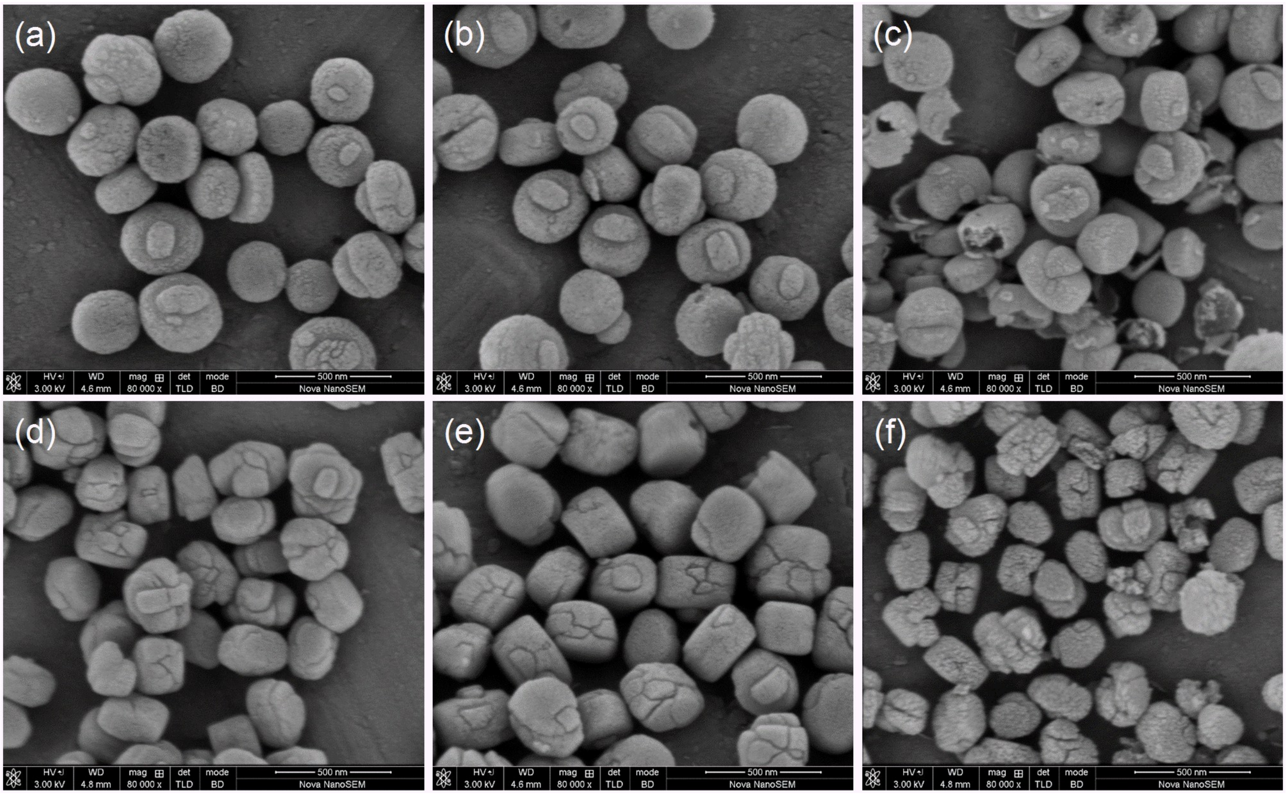

Fig. S1 SEM images of (a) T-HZ, (b) T-HZ-0.1AT, (c) T-HZ-0.2AT, (d) S-HZ, (e) S-HZ-0.1AT, and (f) S-HZ-0.2AT.

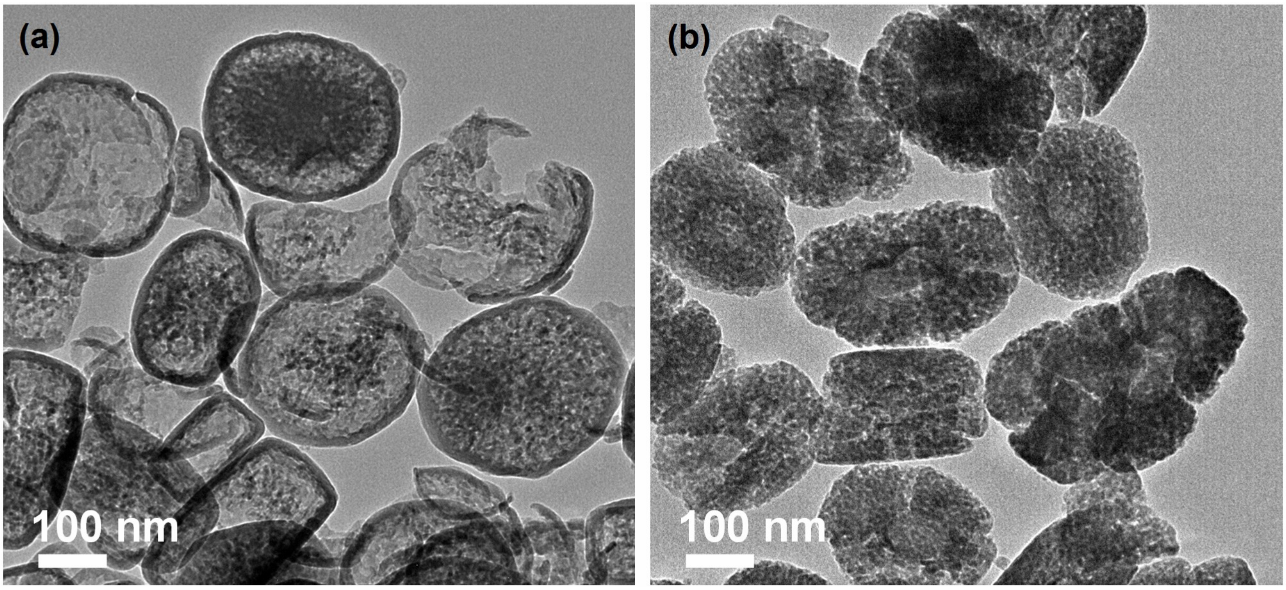

Fig. S2 TEM images of (a) T-HZ-0.2AT and (b) S-HZ-0.2AT.

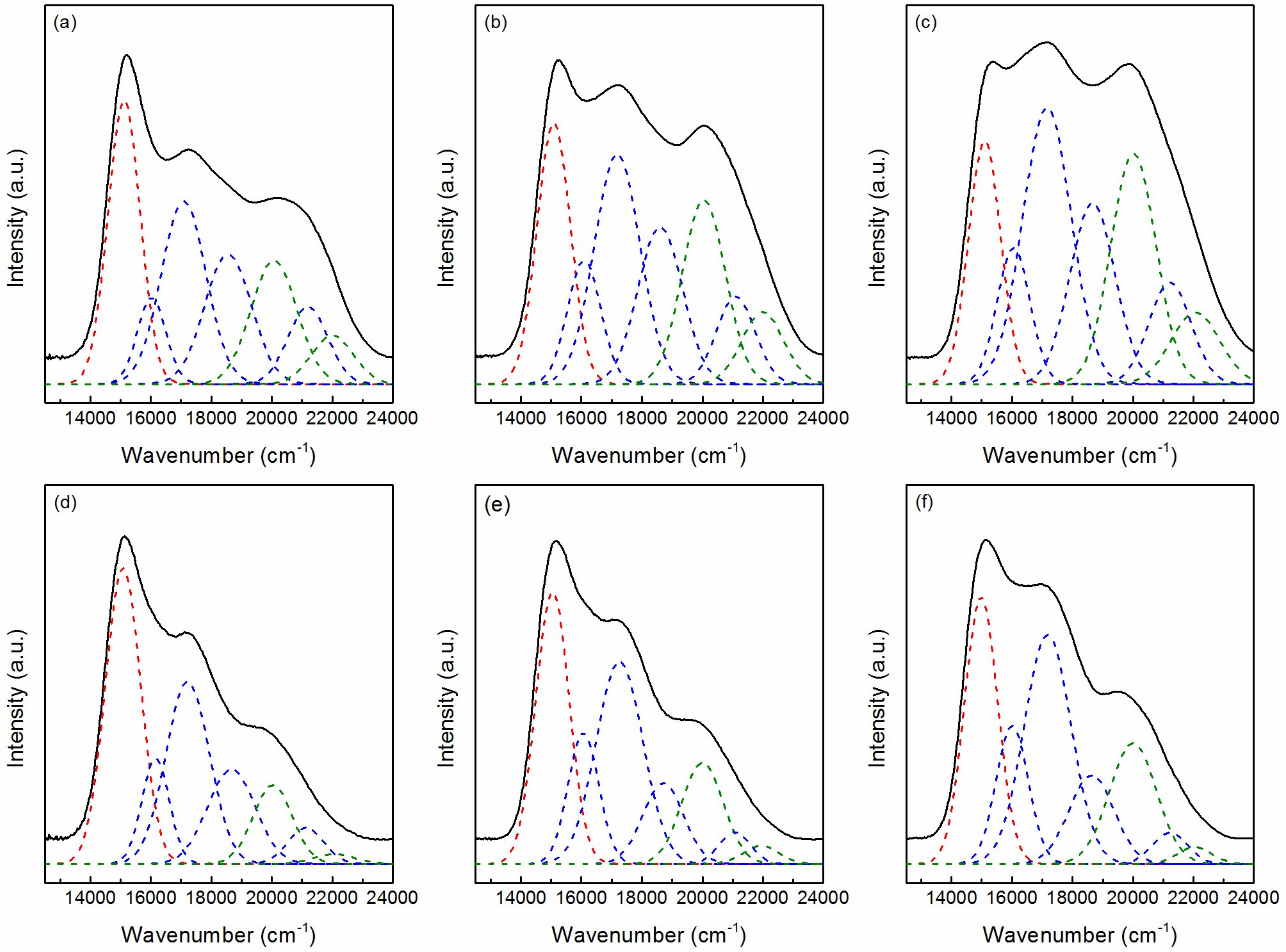

Fig. S3 Deconvolution of Co(II) UV-vis DRS of Co-ion exchanged (a) T-HZ, (b) T-HZ-0.1AT, (c) T-HZ-0.2AT, (d) S-HZ, (e) S-HZ-0.1AT, and (f) S-HZ-0.2AT.

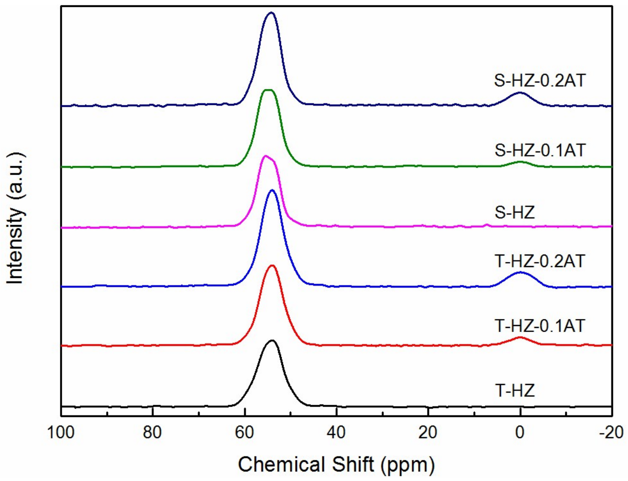

Fig. S4 ^{27}Al MAS NMR spectra of HZSM-5 catalysts.

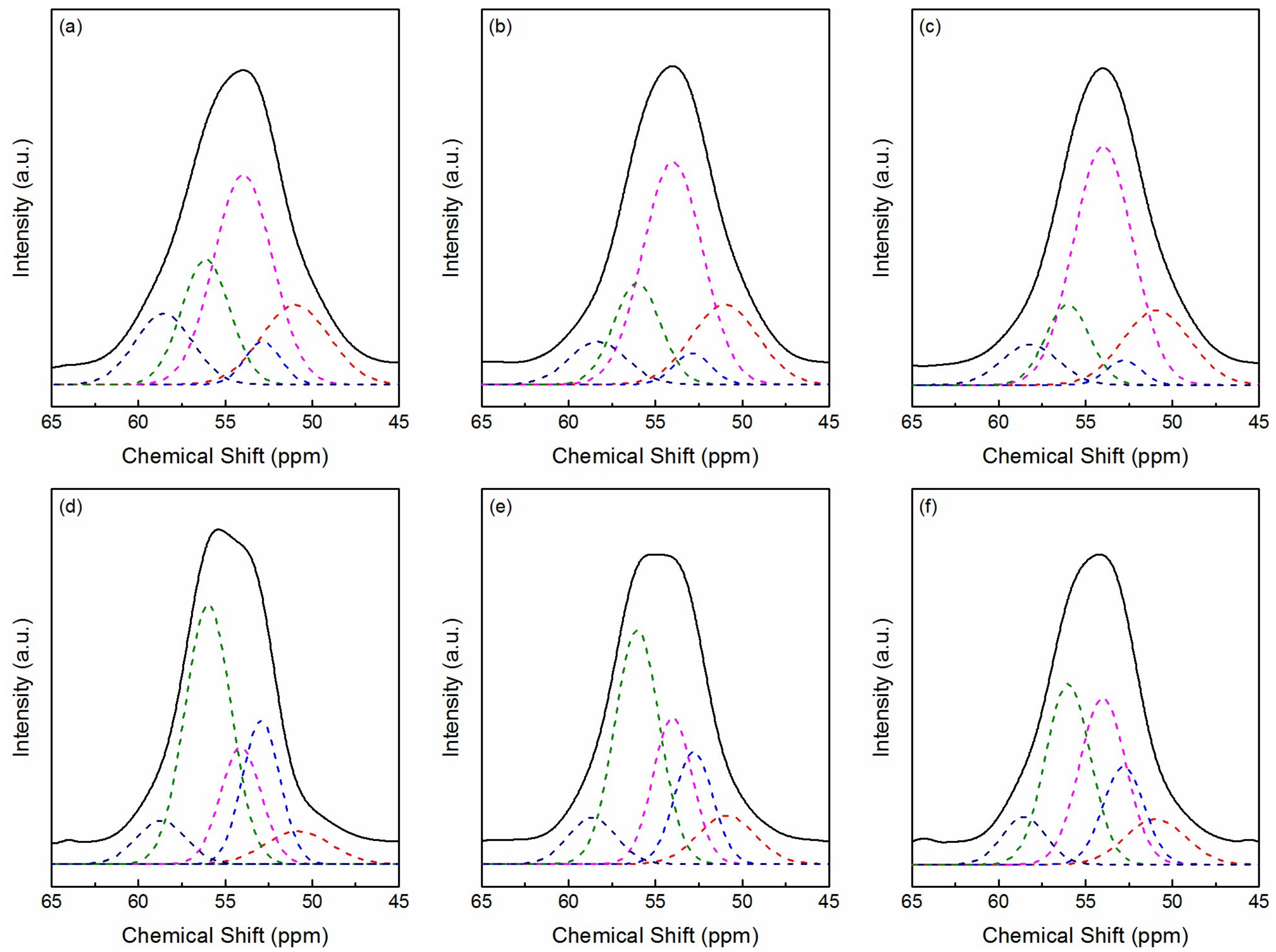

Fig. S5 Curve fittings of the ^{27}Al MAS NMR spectra of (a) T-HZ, (b) T-HZ-0.1AT, (c) T-HZ-0.2AT, (d) S-HZ, (e) S-HZ-0.1AT, and (f) S-HZ-0.2AT.

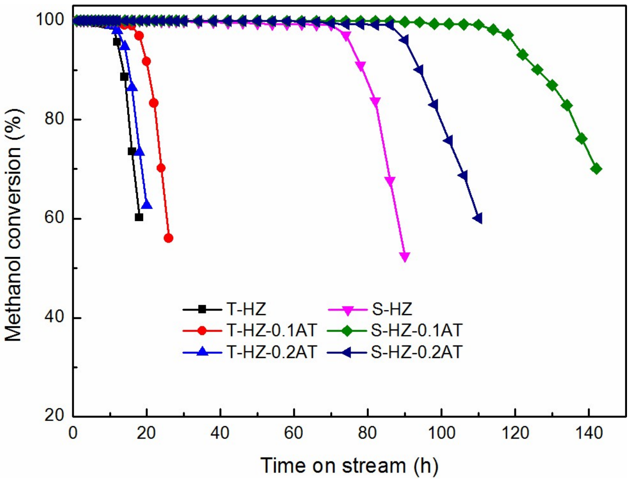

Fig. S6 Methanol conversion as a function of time on stream for MTP over HZSM-5 catalysts, reaction conditions: T = 450 °C, WHSV = 6 h^{-1}.

Table S1 Concentration of Brønsted and Lewis acid sites of HZSM-5 catalysts

Sample	c(B)[a] (μmol g^{-1})	c(L)[b] (μmol g^{-1})
T-HZ	78	51
T-HZ-0.1AT	99	69
T-HZ-0.2AT	126	93
S-HZ	72	48
S-HZ-0.1AT	81	75
S-HZ-0.2AT	114	111

[a] Concentration of Brønsted acid sites

[b] Concentration of Lewis acid sites