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Electronic Supplementary Information

DME carbonylation over a HSUZ-4 zeolite

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Experimental

Catalyst preparation

SUZ-4 was prepared by a hydrothermal method.[1] Appropriate amounts of KOH (96%, Sinopharm Chemical Reagent), Al powder (96%, Sinopharm Chemical Reagent), tetraethylammonium hydroxide (TEAOH, 35%, Energy Chemical), SiO_2 colloid (Ludox AS-40, Sigma Aldrich) and de-ionized water were mixed with a gel composition of $6.43KOH:Al_2O_3:16SiO_2:338H_2O:1.66TEAOH$. The mixture was stirred for 3 h at room temperature, transferred into a Teflon-lined stainless-steel autoclave and hydrothermally treated at 150 ^{0}C under tumbling conditions for 3 days. The solid product was collected by filtration, washed with distilled water, dried at 110 ^{0}C overnight, and finally calcined at 550 ^{0}C in air for 10 h.

ZSM-57 was prepared according to a classical method.[2] The initial gel with a composition of $30SiO_2$: $0.5Al_2O_3:6.9Na_2O:3.0(Et6\text{-}diquat\text{-}5):1200H_2O$ was stirred for 12 hours at room temperature, transferred into a Teflon-lined stainless-steel autoclave and hydrothermally treated for 7 days at 160 °C under tumbling conditions. The solid product was collected by filtration, washed with distilled water, dried at 110 ^{0}C overnight, and finally calcined at 550 ^{0}C in air for 10 h.

To prepare the H-form zeolites, the as-calcined zeolites were ion-exchanged with a 1.0 M NH_4NO_3 aqueous solution at 80 ^{0}C for 6 h. After repeating such a procedure for three times, the sample was dried at 110 ^{0}C overnight and calcined at 540 ^{0}C for 5 h in a flowing 20% O_2/N_2 mixture. For further reducing the residual K^+ in the HSUZ-4 zeolite, the sample after each ion-exchange was calcined at 540 ^{0}C for 5 h in a flowing 20% O_2/N_2 mixture, and the operation was repeated three times.[3]

HZSM-35 was obtained by directly calcining a commercial NH_4-FER (Zeolyst International, CP 914C, SiO_2/Al_2O_3=20) at 540 ^{0}C for 5 h in a flowing 20% O_2/N_2 mixture.

Characterization

Elemental analysis was performed using inductively coupled plasma atomic emission spectroscopy (ICP-AES) with a Plasma-Spec-II spectrometer.

N_2 adsorption-desorption isotherms were recorded on a Micromeritics ASAP-2020 adsorption analyzer at -196 ^{0}C. Before the measurement, the sample was outgassed at 300 ^{0}C for 5 h. The total pore volume was calculated from the adsorption isotherms at $P/P_0 = 0.99$. The micropore surface areas and pore volumes were calculated using the t-plot method.

Powder X-ray diffraction (XRD) patterns were recorded on a D/MAX 2500/PC diffractometer (Rigaku, Japan) using a Cu Kα (λ=0.154 nm) radiation source that was operated at 40 kV and 200 mA. Field-emission scanning electron microscopy (FESEM) images were taken on a Philips FEI Quanta 200F microscope operated at 20 kV. High-resolution transmission electron microscopy (HRTEM) images were taken on JEM-F200 operated at 200 kV.

Temperature-programmed desorption of ammonia (NH_3-TPD) was conducted with a U-shaped quartz tube reactor. 100 mg sample was heated to 500 ^{0}C at a rate of 5 ^{0}C/min and maintained at this temperature for 1 h under He flow (30 mL/min). After cooling down to 200 ^{0}C, the sample was purged with a 10 vol. % NH_3/He mixture (30 mL/min) for 30 min. The physically adsorbed ammonia was removed by consecutively purging the sample at 200 ^{0}C with He for 1 h, a 0.6 vol.% H_2O/He mixture for 1 h and again He for 1 h.[4] Desorption of ammonia was then performed by heating the sample to 650 ^{0}C at a rate of 10 ^{0}C /min under He flow (30 mL/min), and the amount of NH_3 desorbed was monitored by a thermal conductivity detector (TCD).

Thermal gravimetric (TG) analysis of the spent catalyst was conducted using a Diamond TG/ DTA6300 instrument (PerkinElmer). The sample was heated from room temperature to 800 ^{0}C at a rate of 10 ^{0}C · min^{-1} under flowing air.

The soluble components of coke over the spent catalyst were determined by gas chromatography-mass spectrometer equipped with a capillary HP-5MS column (GC-MS, Agilent Technologies 5977A MSD).[5] 100 mg sample was dissolved into 2 mL aqueous HF solution (40%), and 14 mL dichloromethane (CH_2Cl_2) were added to extract the soluble compounds that were analyzed by GC-MS. Compounds were identified by comparing mass spectra with NIST library data.

DME adsorption was performed over an intelligent gravimetric analyzer (IGA-100, Hiden Isochema). 60 mg sample was loaded into the analysis cell and outgassed at 350 ^{0}C for 4 h under the pressure of less than 10^{-3} Pa to remove the adsorbed impurities. The sample was then cooled down to 50 ^{0}C, and DME adsorption was done by introducing a 1 vol.% DME/He mixture until the equilibrium was reached at a setting pressure, which was judged by the mass change of less than 0.001 mg within 1 min. The adsorption at each pressure step was recorded to give the adsorption isotherm as a function of pressure.

IR spectra were recorded over a Bruker Tensor 27 spectrometer with a resolution of 4 cm^{-1}. For the NH_3-IR, 15mg sample was pressed into a self-supporting wafer (R = 0.65 cm) and loaded into an IR cell. Before the measurement, the sample was evacuated to 2×10^{-2} Pa at 400 ^{0}C (the spent HSUZ-4 catalyst was evacuated at 200 ^{0}C) for 60 min to remove the physically adsorbed water. After cooling down to room temperature, the background spectrum was recorded. NH_3 adsorption was then conducted at 30 ^{0}C for 10 min, and the sample was evacuated for 60 min to eliminate the physically adsorbed NH_3 before recording the spectrum. IR spectra of DME carbonylation on the HSUZ-4 catalyst was performed using a 1 vol% DME/99 vol% CO mixture at 220 ^{0}C and under atmospheric pressure.

Catalytic test

DME carbonylation was carried out with a continuous flow fixed-bed reactor (i.d. 8 mm). 300 mg catalyst (40−60 mesh) was loaded into the reactor and treated with N_2 (30 mL/min) at 500 ^{0}C for 1 h. After cooling down to the reaction temperature, a mixture of 5 vol.% DME/50 vol.% CO/2.5 vol.% Ar/42.5 vol.% He was introduced via a mass-flow controller (6.25 mL/min) and the reactor was pressurized to 2.0 MPa. The effluent from the reactor was analyzed online using a gas chromatograph (Agilent 7890A) equipped with a 100% dimethylpolysiloxane column (HP-PONA, 50 m×0.20 mm×0.50 µm) that connected to a flame-ionization detector.

In order to accelerate the deactivation, the reaction was performed at 230 ^{0}C for 30 hours, during which the conversion of DME dropped to around 20%. The catalyst was then exposed to a 20 vol% O_2/He mixture and heated to 450 or 500 ^{0}C at a rate of 2 ^{0}C/min and maintained at that temperature for 4 h. Thereafter, the reaction was continuously tested at 230 ^{0}C.

Tables and Figures

Table S1. Textual properties and chemical compositions of the zeolites

Sample	S_{micro} ($m^2 \cdot g^{-1}$)	V_{micro} ($cm^3 \cdot g^{-1}$)	Si/Al	K(Na)/Al
HSUZ-4	245	0.13	5.1	0.296
HZSM-35	259	0.14	9.6	0.06
HZSM-57	290	0.14	17.1	0.08

Table S2. Acidic properties of the zeolites

Sample	[a]Total amount of acid site ($mmol \cdot g^{-1}$)	[b]Fraction of acid site within the 8-MR pores (%)	Amount of acid site within the 8-MR pores ($mmol \cdot g^{-1}$)
HSUZ-4	1.87	37.7	0.70
HZSM-35	1.50	47.3	0.71
HZSM-57	0.94	29.8	0.28

[a]Derived from the NH_3-TPD profiles (Fig. S7); [b]Estimated from the NH_3-IR spectra (Fig. S8).

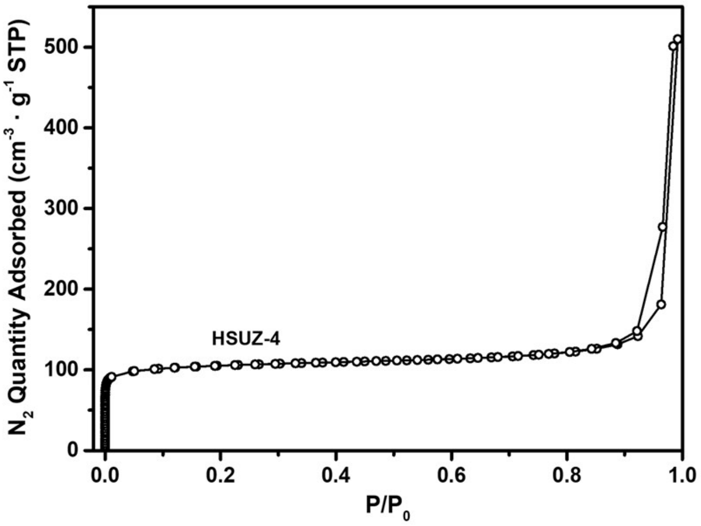

Fig. S1 N_2 adsorption-desorption isotherm of the HSUZ-4 zeolite.

SUZ-4 has a 3-dimensional pore system with 10-MR channels (5.2 × 4.1 Å, along [001] axis) intersected by two arrays of 8-MR channels (4.8 × 3.2 Å and 4.8 × 3.0 Å, along [010] and [110] axis, respectively).

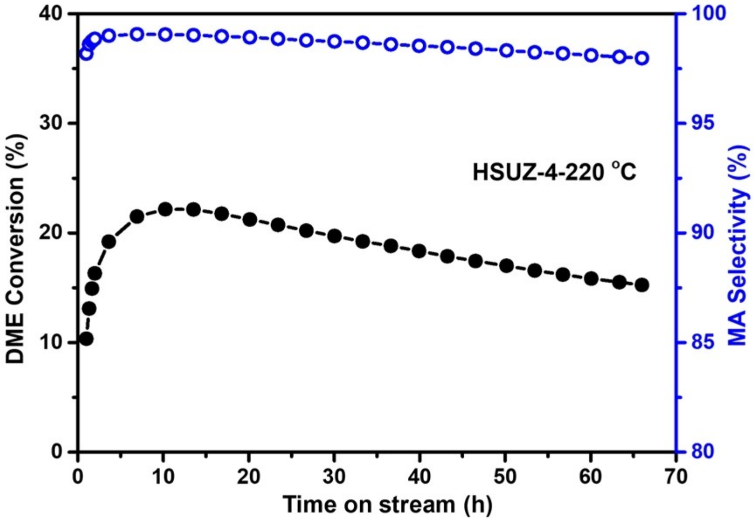

Fig. S2. DME carbonylation over the HSUZ-4 catalyst at 220 ^{0}C. Reaction conditions: 5 vol.% DME/50 vol.% CO/2.5 vol.% Ar/42.5 vol.% He, 1250 ml·g^{-1}·h^{-1}, 2.0 MPa.

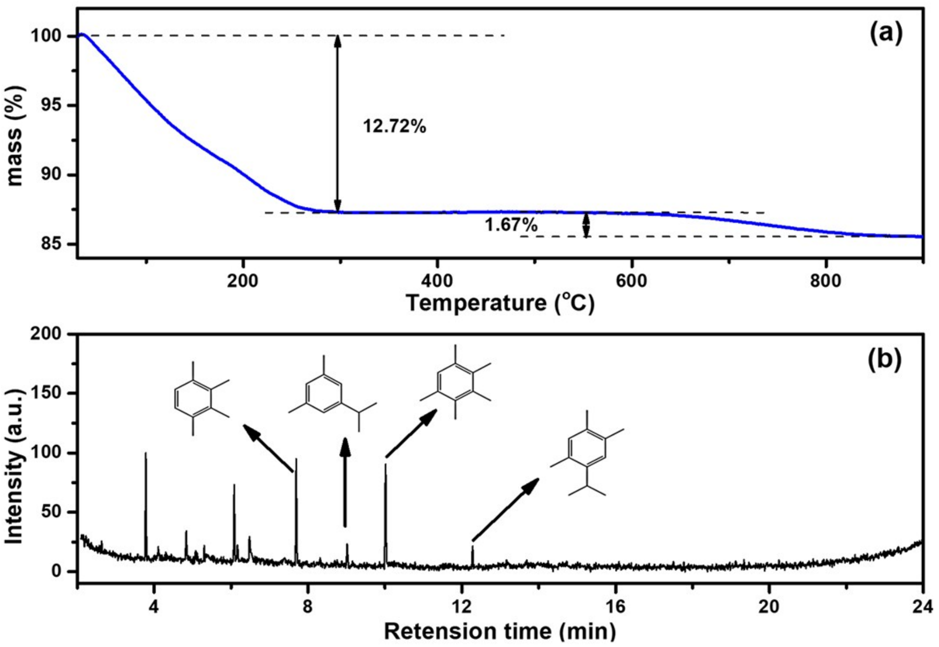

Fig. S3 TG profile (a) of the spent HSUZ-4 catalyst and GC-MS analysis (b) of the coke deposits.

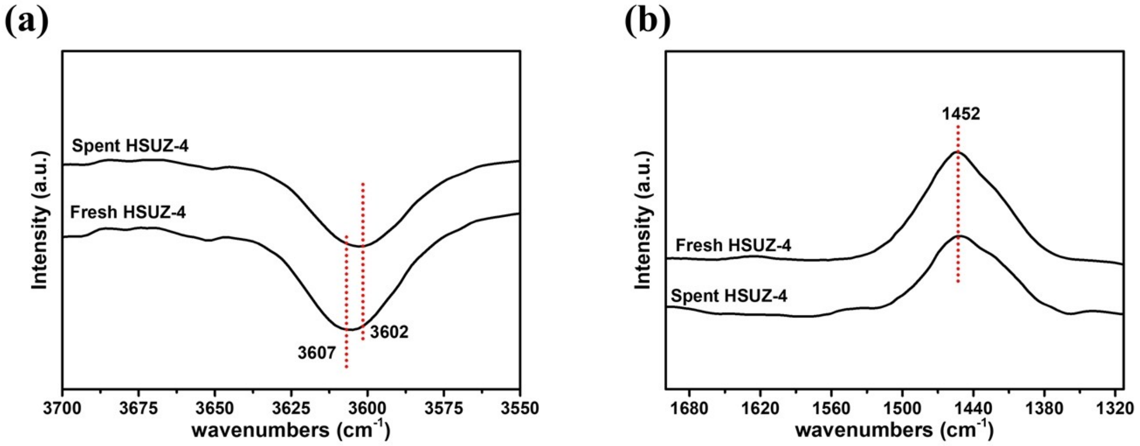

Fig. S4 NH_3-IR spectra of the fresh and spent HSUZ-4 samples: (a) the differential spectra in the OH vibration region and (b) the characteristic vibration region of ammonia adsorbed on the Brönsted acid sites.

The red shift of the OH vibration band from 3607 cm^{-1} over the fresh HSUZ-4 to 3602 cm^{-1} over the spent sample, indicated that the acid sites on the spent sample was disturbed by the coke deposits. The coke species mainly located in the 10-MR channels because the IR absorbance at higher frequency was associated with the bridging hydroxyls in the large channels.[6,7]

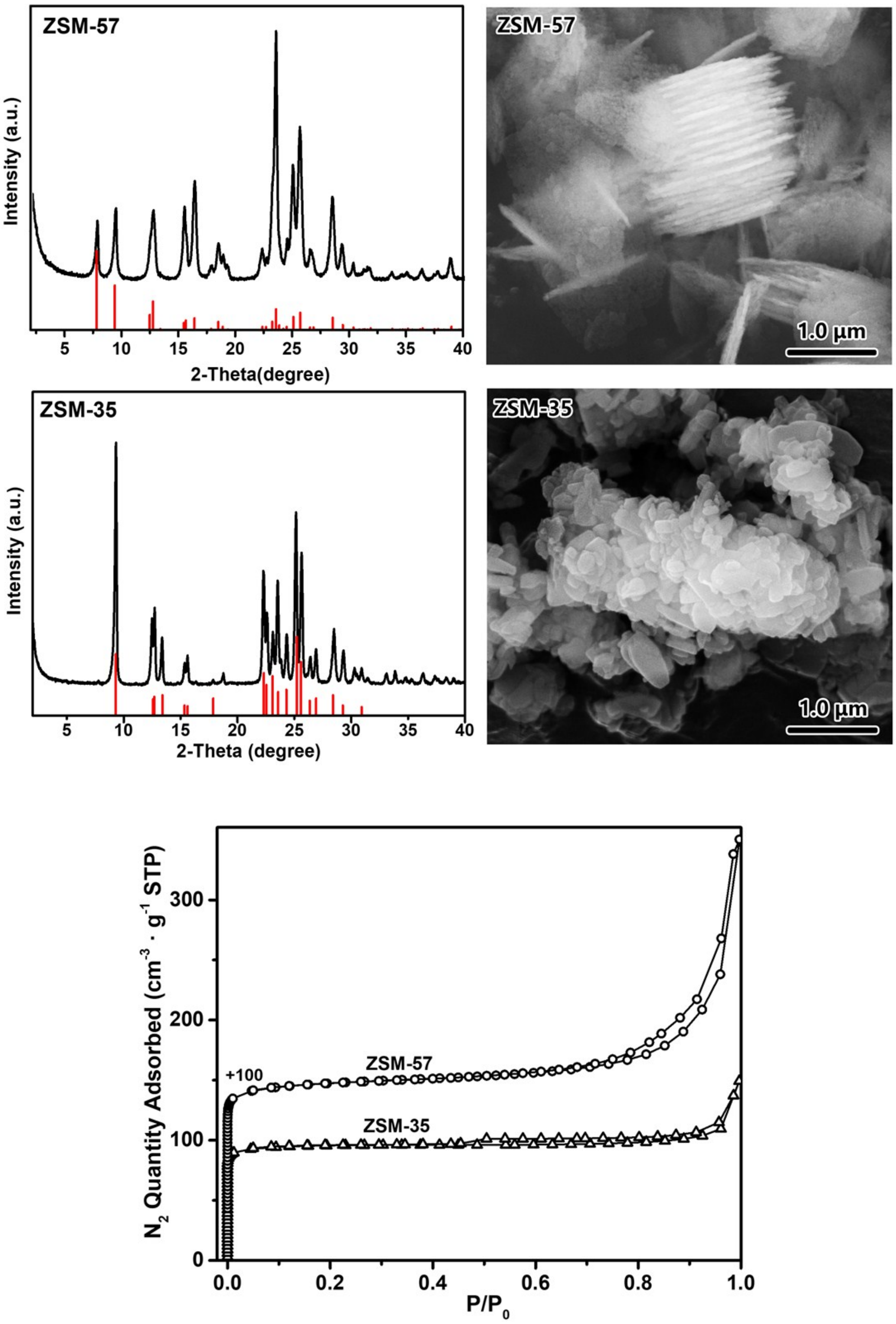

Fig. S5 XRD patterns, SEM images and nitrogen adsorption-desorption isotherms of the ZSM-57 and ZSM-35 zeolites.

XRD patterns of ZSM-57 and ZSM-35 showed characteristic diffraction lines of the respective zeolite; N_2 adsorption of both samples exhibited typical type I isotherm of the microporous materials. Moreover, both samples exhibited plate-like crystal morphology according to the SEM images, which were typically displayed by these zeolites.[8]

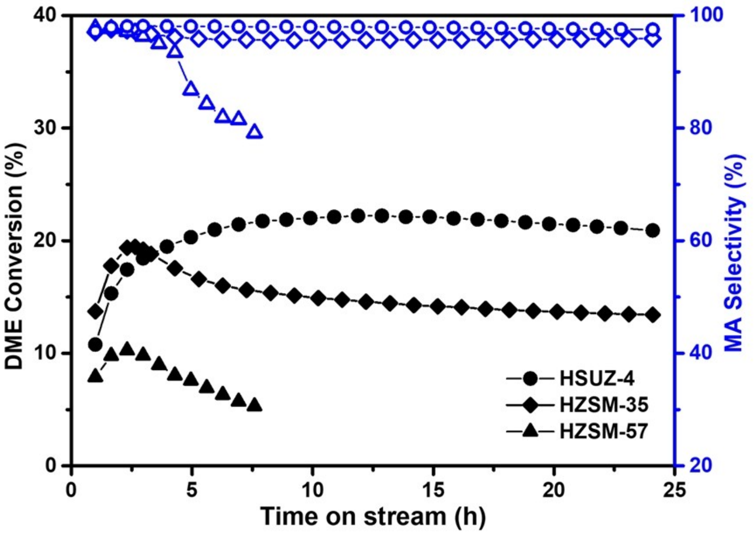

Fig. S6 DME carbonylation over HSUZ-4, HZSM-57 and HZSM-35. Reaction conditions: 220 ^{0}C, 5 vol.% DME/50 vol.% CO/2.5 vol.% Ar/42.5 vol.% He, 1250 ml·g^{-1}·h^{-1}, 2.0 MPa.

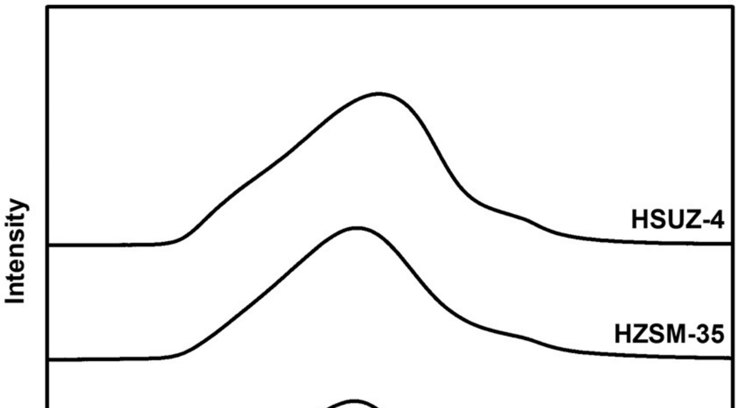

Fig. S7 NH$_3$-TPD profiles of the HSUZ-4, HZSM-35 and HZSM-57 zeolites.

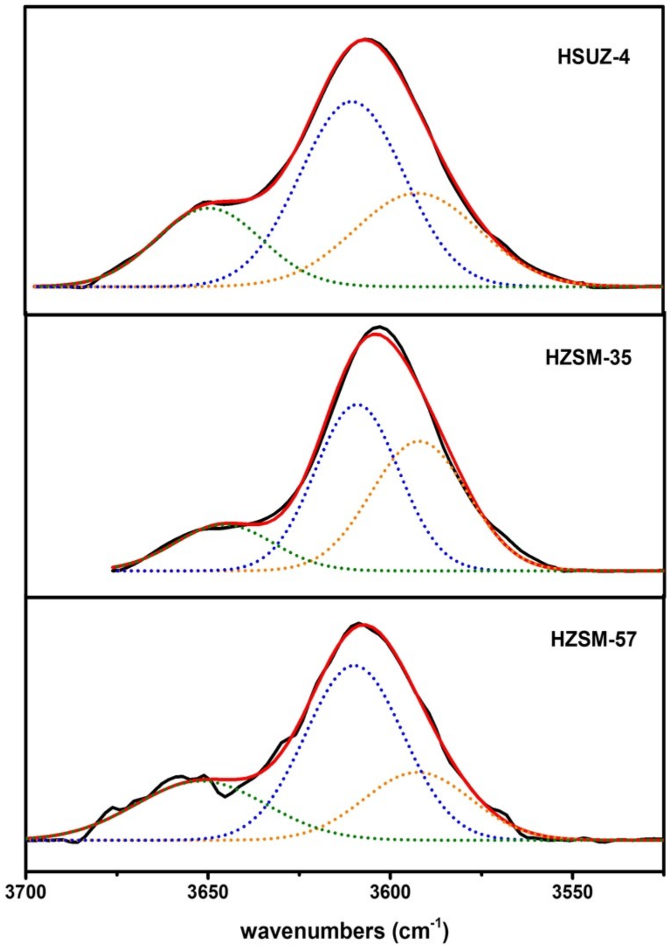

Fig. S8 NH_3-IR spectra of the OH vibration bands in HSUZ-4, HZSM-35 and HZSM-57.

The distribution the of acid sites was derived by deconvolution of the OH vibration band around 3600 cm^{-1}. The bands centered at 3590 cm^{-1} and 3610 cm^{-1} were ascribed to the acid sites located in the 8-MR and 10-MR pores,[6,7] respectively. The fraction of the acid site located in the 8-MR pores for HSUZ-4, HZSM-35 and HZSM-57 were 37.7%, 47.3% and 29.8%, respectively.

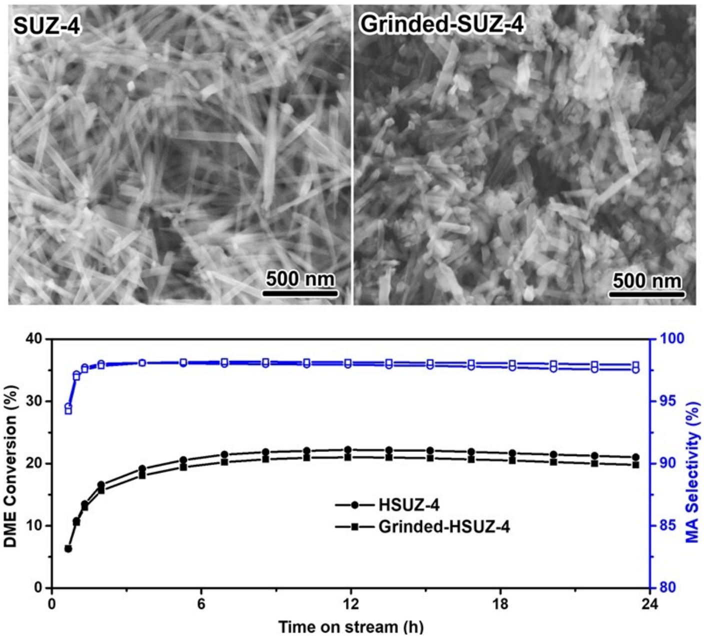

Fig. S9 SEM images (top) of HSUZ-4 and the grinded sample with shortened rods and their catalytic performance (down) for DME carbonylation. Reaction conditions: 220 ^{0}C, 5 vol.% DME/50 vol.% CO/2.5 vol.% Ar/42.5 vol.% He, 1250 ml·g^{-1}·h^{-1}, 2.0 MPa. The selectivity of MA was around 97% in both cases.

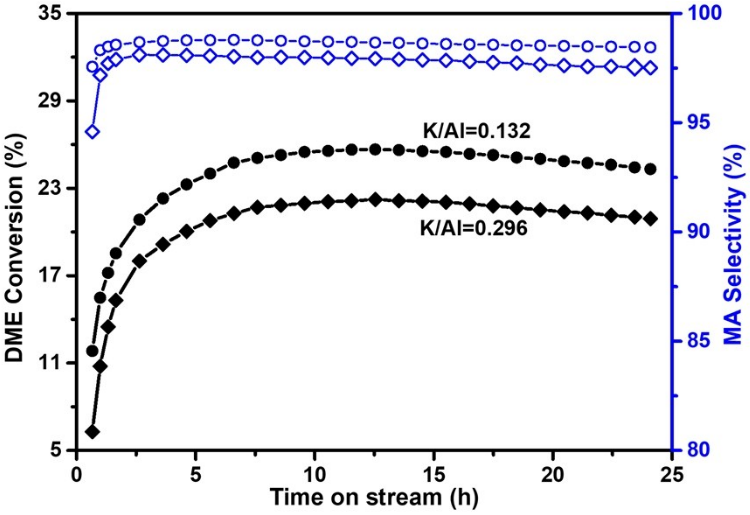

Fig. S10 DME conversion (solid symbols) and MA selectivity (blank symbols) over HSUZ-4 zeolites with K/Al ratios of 0.269 and 0.132. Reaction conditions: 220 ^{0}C, 5 vol.% DME/50 vol.% CO/2.5 vol.% Ar/42.5 vol.% He, 1250 ml·g^{-1}·h^{-1}, 2.0 MPa.

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