

Supporting Information for

The catalytic relevance of hydrothermally substituted Zn on the zeolite ZSM-5 during the methanol-to-aromatics process

Xin Zhang, Xinyu You, Yunfan wang, Hexun Zhou, Xue Zhou, Abhishek Dutta Chowdhury

S1. Experimental section

S1.1 Catalyst preparation

The synthesis of zeolite in this work is inspired by the recent reports from the Mintova's group.¹⁻⁴ The parent unmodified zeolite ZSM-5 was synthesized based on the following recipe: 1SiO₂:0.4TPAOH:0.004Al₂O₃:20H₂O. The obtained mixed slurry was aged for 18h on an orbital shaker. The aged precursor was then transferred into a 50 mL Teflon-lined autoclave and crystallized at 150 °C for 72 h in a static oven. The obtained solid was washed and dried overnight at 110 °C and then calcined in air at 550 °C for 6 h, which was denoted as the parent ZSM-5. The Zn_F-ZSM-5 zeolite was synthesized using the hydrothermal post-synthesis treatment method¹⁻⁴ ("F" represents the metallic position on the zeolite framework). The details are as follows: 0.18-0.55g Zn(NO₃)₂·6H₂O was dissolved in 10 mL H₂O in a 50 mL polypropylene bottle, and followed by 2g parent as-synthesized ZSM-5 zeolite was added. The as-prepared mixture was stirred overnight and then transferred into a 50 mL Teflon-lined autoclave and then heated at 90 °C for 5 days under autogenous pressure. The resulting solids were centrifuged, washed, and then dried at 80 °C overnight and calcined at 550 °C for 6 h. The final obtained powder was denoted as "Zn_F-ZSM-5 zeolite". It should be noted that, despite varying the initial Zn precursor loading significantly, the final Zn content in the zeolite consistently remained low and within a specific range. This aspect indicates an optimal loading range achievable with this synthesis method.

S1.2 Catalyst Characterization

Powder X-ray diffraction (XRD) patterns were conducted with a German Bruker D8 Advance diffractometer using Cu K α radiation. The data was collected in a 2θ range of 5-60 $^\circ$ using a step size of 0.02 $^\circ$ and a scan speed of 2 $^\circ$ ·min $^{-1}$. Scanning electron microscopy (SEM) imaging was obtained by Hitachi-SU8010, Japan. N $_2$ physisorption measurement was performed on an automated gas sorption system Micromeritics ASAP 2460 instrument. The samples were degassed under vacuum for 10 h at 573 K before the measurement. The total surface areas were obtained based on the BET equation, while the micropore volumes and micropore surface areas were evaluated using the t-plot method. The elemental contents of samples were analyzed using an inductively coupled plasma optical emission spectroscopy (ICP-OES). The crystal morphologies were observed using a scanning electron microscope (Hitachi-SU8010, Japan). Temperature-programmed desorption of ammonia (NH $_3$ -TPD) was measured on a MicrotracBEL (BELCAT-B, Japan) chemical adsorption instrument. Each sample (50mg) was loaded into a quartz reactor and pre-treated at 823 K for 1 h in flowing He. After the pretreatment, the sample was cooled to 373 K for 30 minutes and saturated with NH $_3$ gas. Then, NH $_3$ -TPD was carried out in a constant flow of He (30 mL·min $^{-1}$) from 323 K to 1023 K at a heating rate of 10 K·min $^{-1}$. Brønsted and Lewis acid site concentrations of FER zeolites were investigated by studying pyridine adsorption on an FTIR spectrometer (Thermo IS50). The samples were put into the cell and pretreated at 450 $^\circ$ C under vacuum for 1 h to remove impurities. After cooling to 30 $^\circ$ C, the cell was scanned, and obtained data were used as background. Then pyridine was adsorbed at 30 $^\circ$ C to reach equilibrium. Then the cell was

vacuumed for 30 min to remove excess pyridine. The desorption spectrum was obtained by scanning IR when the cell was heated at 150 °C and 250 °C, respectively. Spectra were recorded in the 1400-1700 cm⁻¹ range at a resolution of 4 cm⁻¹ and co-addition of 64 scans. The following formulas were used to quantify the Brønsted (BAS) and Lewis acid sites (LAS):⁵

$$C_{BAS} = 1.88 \times I_B \times R^2/W$$

$$C_{LAS} = 1.42 \times I_L \times R^2/W$$

Where I_B and I_L are the integrated absorbance of BAS and LAS, respectively. R is the radius of catalyst disk (cm), and W is the mass of catalyst (mg).

Thermogravimetric tests were performed on a TGA/DSC instrument manufactured by Mettler Toledo STAR System. The test conditions were as follows: ca. 5 mg of sample was stripped under a flow of N₂ (50 ml/min) initially at 200 °C for 1 hour, followed by heating up to 800 °C at a heating rate of 4 °C/min. The sample was kept under the flow of N₂ at 800 °C for 30 mins, then switched to air (50 ml/min), keeping the sample at 800 °C under a flow of air for 90 mins. From the thermogravimetric data, the amount of coke precursors (%) and hard coke (%) were calculated as follows:

$$\text{Coke precursors (\%)} = \frac{m_0 - m_e}{m_z} \times 100$$

$$\text{Hard coke (\%)} = \frac{m_e - m_z}{m_z} \times 100$$

where m_0 is the mass of the sample after the stripping step at 200 °C, m_e is the mass after keeping the sample at 800 °C for 30 mins under a flow of N₂, and m_z is the mass of the sample at the end of the 90 min treatment of the sample under air at 800 °C.

²⁷Al MAS NMR spectra were recorded at a spinning rate of 20 kHz using one pulse

sequence with 3.2 mm CPMAS probe, 4k scans were accumulated, with a $\pi/12$ pulse width of 0.312 μ s and a 1 s recycle delay, where chemical shifts were externally referenced to Al (NO₃)₃ (liquid). The details of the experimental section regarding operando UV-vis coupled to online mass spectrometry solid-state NMR spectroscopy are included in the Supplementary Information.

S1.3 Catalytic Tests

Methanol-to-hydrocarbons (MTH) reactions were performed in a fixed-bed reactor (Xiamen Hande Engineering Co., Ltd.) with a 10 mm inner diameter quartz tubular reactor. The calcined zeolite catalysts were pelletized and crushed into 45-110 mesh, and the obtained catalysts (0.5 g) were mixed with SiC (3 g) at a weight ratio of 1:6 (catalyst/SiC). Before the reaction, the catalytic bed was pretreated with Argon at 550 °C for 2 h. After pretreatment, the temperature decreased to reaction temperature (400-500 °C), and WHSV was set from 4.0~0.5 h⁻¹, with methanol being diluted in Ar to a constant molar MeOH/Ar ratio of 1:2 at a pressure of 1 bar. The reaction products were analyzed online using gas chromatography (GC-8850, Lunan Ruihong Co., Ltd.) with three detectors: two flame ionization detectors (FIDs) and one thermal conductivity detector (TCD). The permanent gas (Ar, N₂, CH₄, CO, and CO₂) was detected by TCD through GDX-104 and TDX-101 columns. The separation of methanol, dimethoxy ether (DME), and C₁-C₄ hydrocarbons was carried out on a KB-PLOT Q column (30m*0.53mm*40um), while the separation of C₅₊ hydrocarbons was carried out on a KB-5 column (60m*0.32mm*1.0um). Methanol conversion (X, %) and selectivity (S, %) of each product are defined as follows:

$$X = \frac{n_{C,MeOH_{in}} - n_{C,MeOH_{out}} - 2 \cdot n_{C,DME_{out}}}{n_{C,MeOH_{in}}} \cdot 100\% \quad (1)$$

$$S_i = \frac{i \cdot n_{Ci}}{n_{C,MeOH_{in}} - n_{C,oxy_{out}}} \cdot 100\% \quad (2)$$

S2. Operando and ssNMR study

S2.1 Operando UV-Vis Diffuse Reflectance Spectroscopy (DRS) Study Coupled with Online Mass Spectrometry (MS)

All the catalytic operando studies were performed using a Linkam cell (THMS600) equipped with a temperature controller (Linkam TMS94), and its lid was equipped with a quartz window compatible with UV-Vis detection (See Fig. S1 for the details of our set-up). The UV-Vis diffuse reflectance spectroscopy (DRS) measurements were performed with an AvaSpec-ULS2048L-USB2-UA-RS micro-spectrophotometer from Avantes (see <https://www.avantes.com/products/spectrometers/starline/avaspec-uls2048cl-evo/>). Halogen and deuterium lamps were used together for illumination. The online gas phase product analyses were performed by Pfeiffer OmniStar GSD 350 O3 (1-200 amu) mass spectrometer, which was directly connected to the outlet of the Linkam cell. The National Institute of Standards and Technology (NIST) mass spectrometry database was consulted for assignment and referencing purposes. Herein, the signals identified at 26 amu, 41 amu, 56 amu, 78 amu, 92 amu and 106 amu were attributed to ethylene, propylene, butene, benzene, toluene and xylene, respectively.⁶⁻⁸ Due to the overlapping of certain intermediates with the reactant methanol or other effluent species, the secondary base peak was considered for identifying

formaldehyde and butadiene. In contrast, other species were corroborated by their highest intense primary base peaks.^{9,10} During operando studies, all reactions were performed without pressing and sieving the zeolite materials. Operando UV-Vis DRS reactions were performed using ca. 40 mg of the catalyst material. Initially, it was placed on the heating stage of the Linkam cell, which was further connected to a water cooler. The inlet of the cell was connected to the N₂ gas line, via a liquid saturator (containing ¹²C-methanol (MeOH, AR, Sinopharm Chemical Co. Ltd.) or ¹³C-methanol (99 atom % ¹³C, Cambridge Isotope Laboratories). The outlet was either connected to the Pfeiffer mass spectrometer or vented out. The lid of the Linkam cell is equipped with a quartz window to monitor the reaction by UV-vis DRS. Before each UV-vis DRS, the material was further pre-treated/activated according to the following procedure under an N₂ environment (flow rate of 20 ml/min): heating to 673 K at 10 K/min and keeping the sample at this temperature for the next 10 min; then, heating the sample to 823 K at a rate of 5 K/min and hold there for the next 30 min. Next, the sample was cooled down to the reaction temperature with a rate of 10 K/min under a flow of N₂ gas (flow rate of 20 ml/min). The starting time of the reaction was considered when the inward N₂ flow goes through the liquid saturator. Finally, the reaction was quenched by rapidly cooling the Linkam cell using a Linkam TMS94 temperature controller. During these experiments, the UV-vis DRS was recorded every 15 s intervals during the MTH experiment, which typically took 20 min. The Operando UV-vis spectra were collected every minute, with 300 accumulations of 50 ms exposure time each. Other relevant details are mentioned in the figure captions.

S2.2. Solid-state nuclear magnetic resonance study on spent ¹³C-enriched zeolite

catalysts

All ^1H and ^{13}C related (both 1D and 2D) magic angle spinning (MAS) solid-state nuclear magnetic resonance (ssNMR) spectroscopic experiments were performed on Bruker AVANCE NEO spectrometers operating at 400 MHz frequency for ^1H using a 4 mm CPMAS H/X/Y probe (CP: Cross-polarization). NMR chemical shifts are reported with respect to the external reference adamantane. Herein, samples were prepared using fully enriched $^{13}\text{CH}_3\text{OH}$ at our typical experimental conditions (as discussed in the previous section) to increase the solid-state NMR sensitivity. All NMR measurements were performed at room temperature (298 K) and the magic angle spinning rate was set to 10 kHz. Note that effective sample temperatures can be 5-10 degrees higher due to frictional heating. The 1D ^1H - ^{13}C CP/MAS NMR experiments were recorded using a 2.0 s recycle delay, an 18 ms acquisition time, and an accumulation of 2000 scans. The Hartmann-Hahn condition was achieved using hexamethylbenzene (HMB), with a contact time of 3000 μs . The 2D ^{13}C - ^{13}C PDS (proton-drive-spin-diffusion) spectra were recorded at 10 kHz MAS, a 70% ramp for the ^1H CP pulse with a 3000 μs CP contact time, 2 s recycle delay, 15 ms and 10 ms acquisition times for direct and indirect ^{13}C dimensions, respectively. The 2D ^{13}C - ^1H CP HETCOR spectra used a ^1H $\pi/2$ pulse width of 4.51 μs . The cross-polarization step was performed using a contact time of 3000 μs . A total of 320 t1 FIDs were recorded at increments of 20 ms using the States-TPPI method to achieve sign discrimination in F1. ^1H SPINAL-64 decoupling was applied during the t2 acquisition with a RF-field amplitude of 55kHz. In all cases, other relevant acquisitions/experimental parameters were described in figure captions. All NMR spectra were processed and analyzed

using Bruker TopSpin 4.4.

S3. Supplementary Tables and Figures

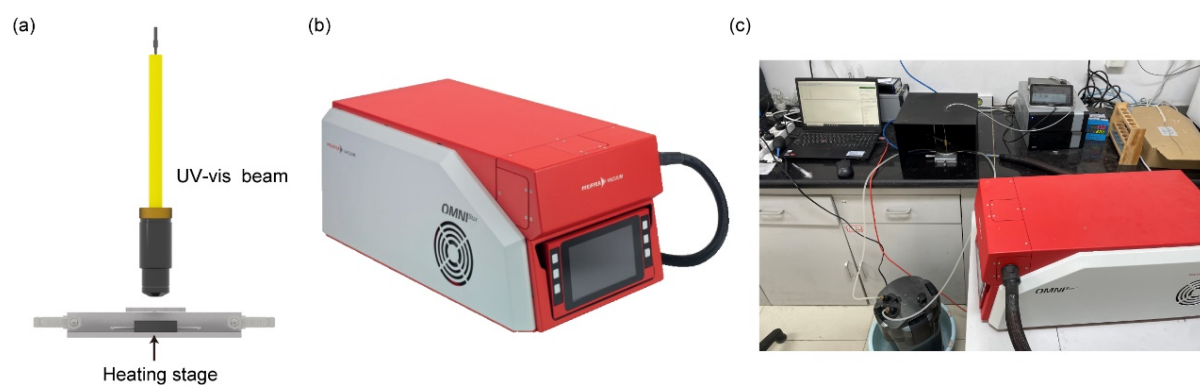


Fig. S1 The operando set-up consists of UV-Vis diffuse reflectance spectroscopy (UV-Vis DRS) coupled with online mass spectrometry (MS): (a) Illustration of the UV-vis DRS working principle along with images of (b) online MS, and (c) the whole working set-up. See experimental Section S1.4 for the technical details.

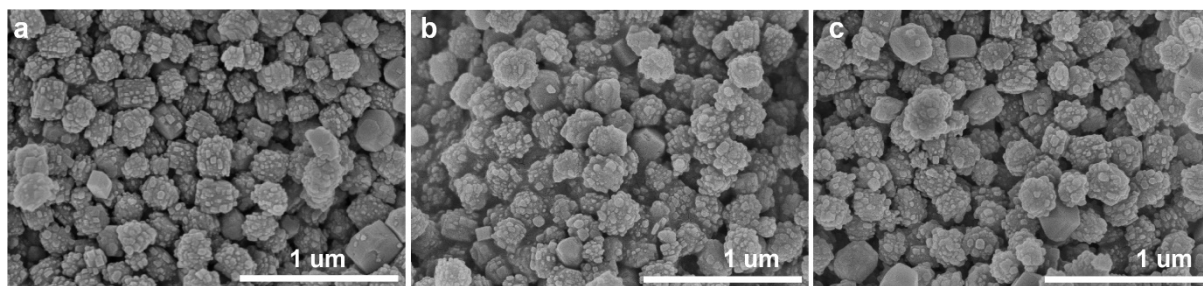


Fig. S2. SEM images of (a) parent-ZSM-5, (b) $0.19\text{Zn}_F\text{-ZSM-5}$, and (c) $0.22\text{Zn}_F\text{-ZSM-5}$ zeolites.

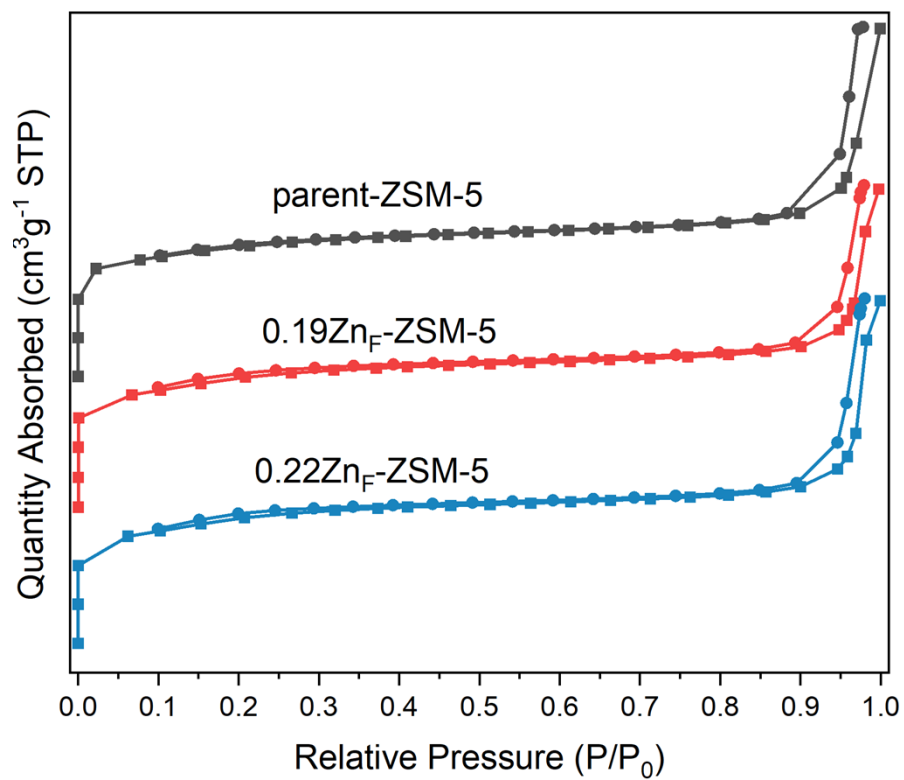


Fig. S3. N₂ sorption isotherms of paren-ZSM-5, 0.19Zn_F-ZSM-5, and 0.22Zn_F-ZSM-5 zeolites used in this study.

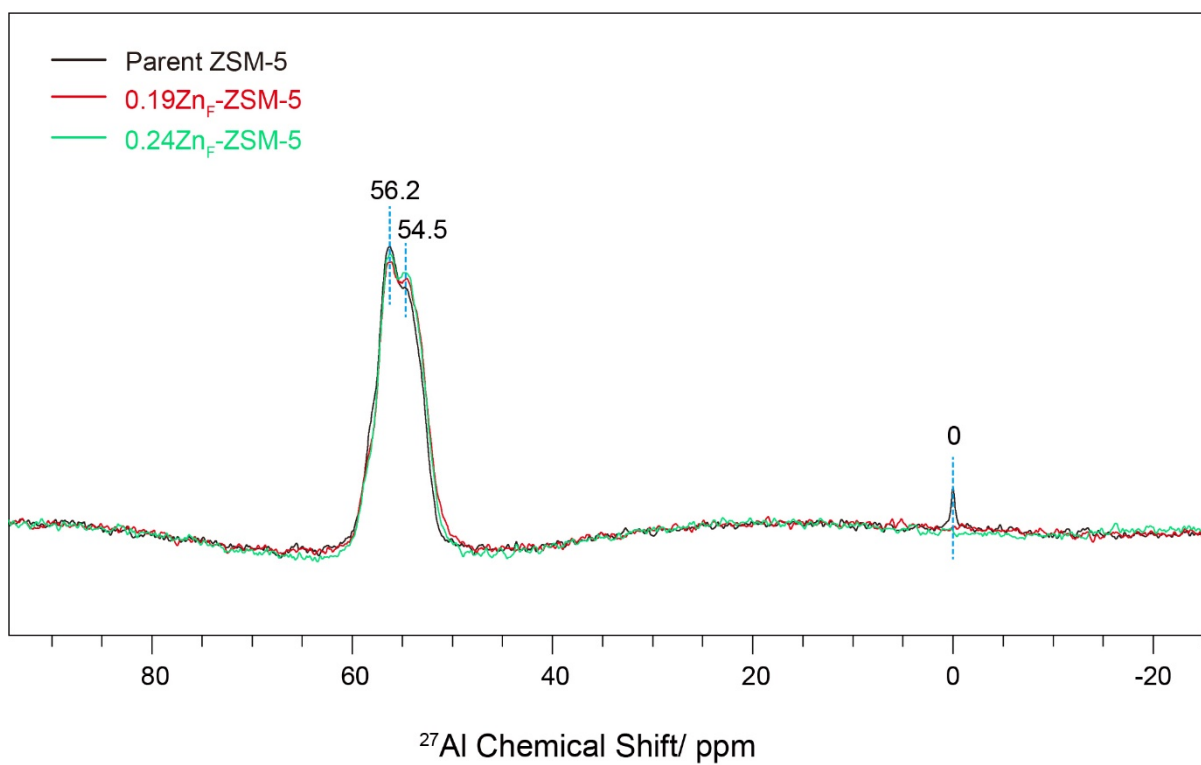


Fig. S4 1D ^{27}Al magic angle spinning (MAS, 20 KHz) solid-state NMR spectra of paren-ZSM-5, $0.19\text{Zn}_F\text{-ZSM-5}$, and $0.22\text{Zn}_F\text{-ZSM-5}$ zeolites used in this study.

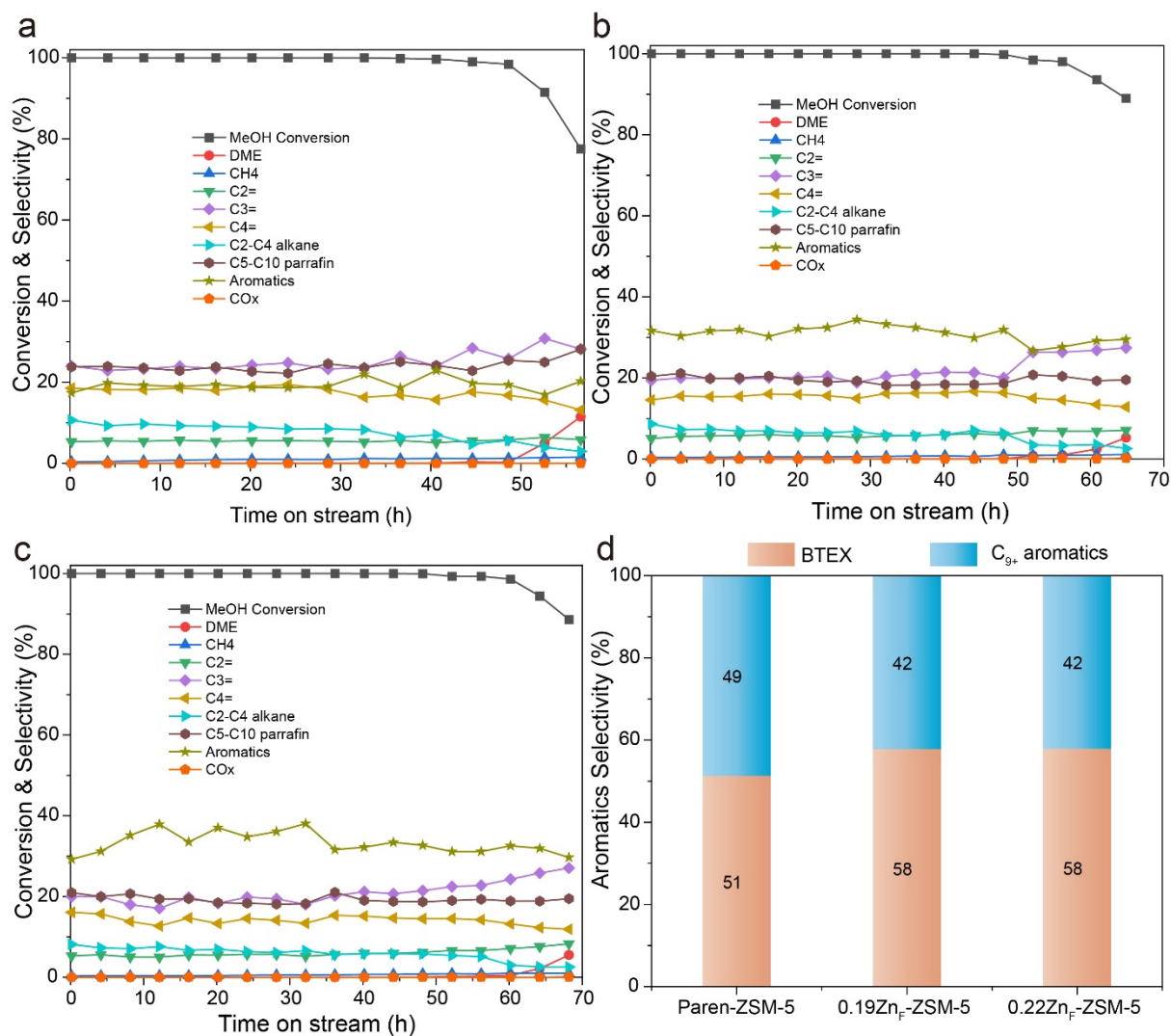
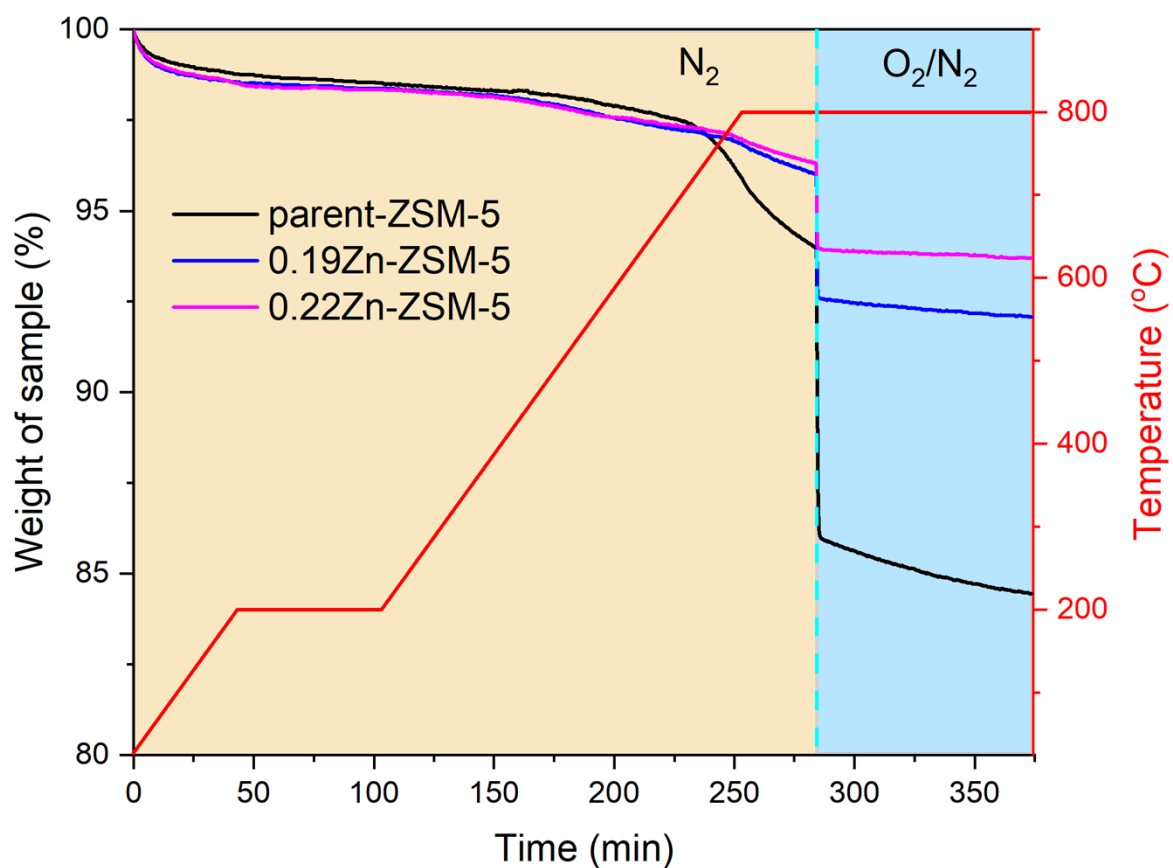


Fig. S5. Methanol conversion and products selectivity over (a) parent-ZSM-5, (b) 0.19Zn_F-ZSM-5, and (c) 0.22Zn_F-ZSM-5 zeolites, at 400 °C under 6 h⁻¹ WHSV; and (d) the relative fraction of BTEX and C₉₊-aromatics among the all detected aromatics over different catalysts.



Sample	Reaction temperature	Coke precursors (%)	Hard coke (%)
Parent-ZSM-5	400 °C	5.35	11.30
0.19Zn _F -ZSM-5	400 °C	2.55	4.29
0.22Zn _F -ZSM-5	400 °C	2.16	2.80

Fig. S6. TGA profiles of post-reacted parent-ZSM-5, 0.19Zn_F-ZSM-5 and 0.22Zn_F-ZSM-5 zeolites. The left zone in light orange was tested under an N₂ atmosphere to analyze the soft coke, and the right zone in light blue was tested under an O₂ atmosphere to analyze hard coke. The larger amount of hard coke produced over parent-ZSM-5 implies the formation of more hard coke than Zn-modified ZSM-5 zeolites.

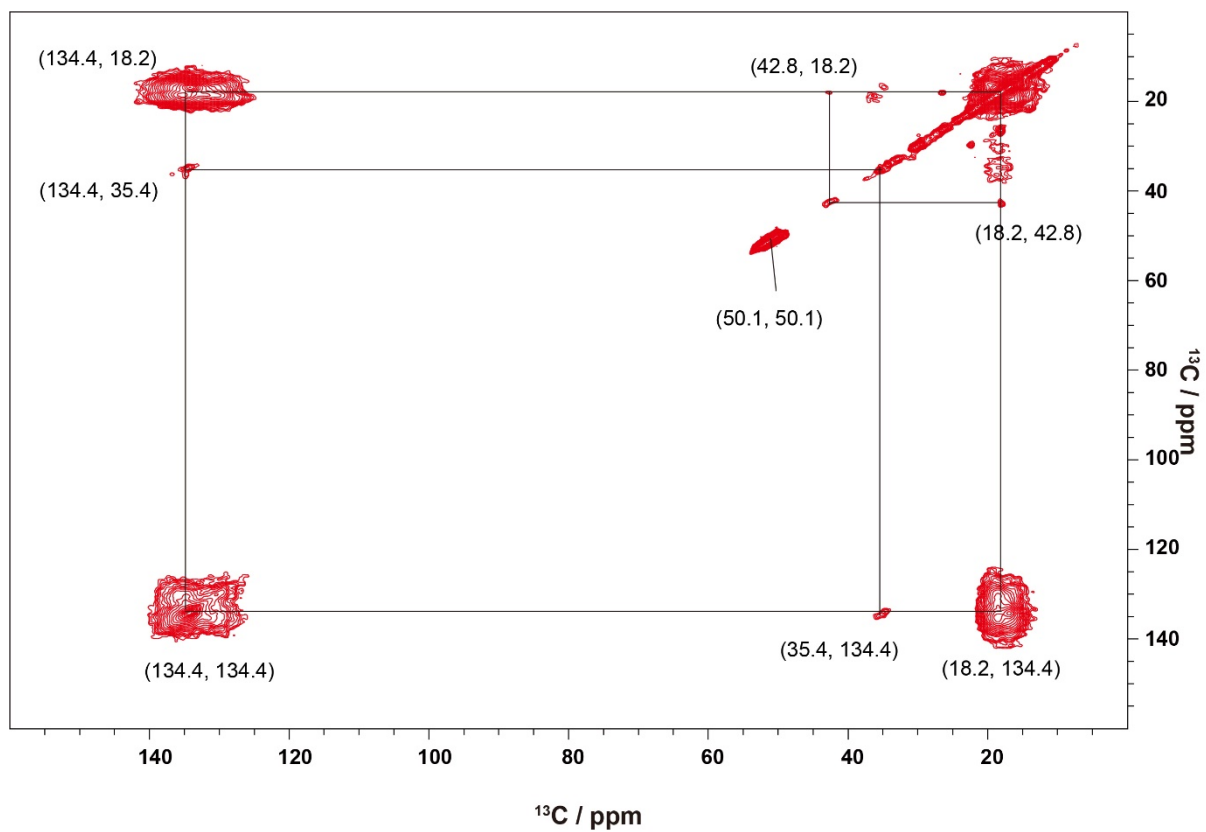


Fig. S7. 2D ^{13}C - ^{13}C (10 kHz MAS) solid-state NMR correlation spectrum of the post-reacted parent-ZSM-5 zeolite. The sample was prepared after ^{13}C -methanol conversion over this catalyst at 400 °C for 20 min [magic angle spinning (MAS)].

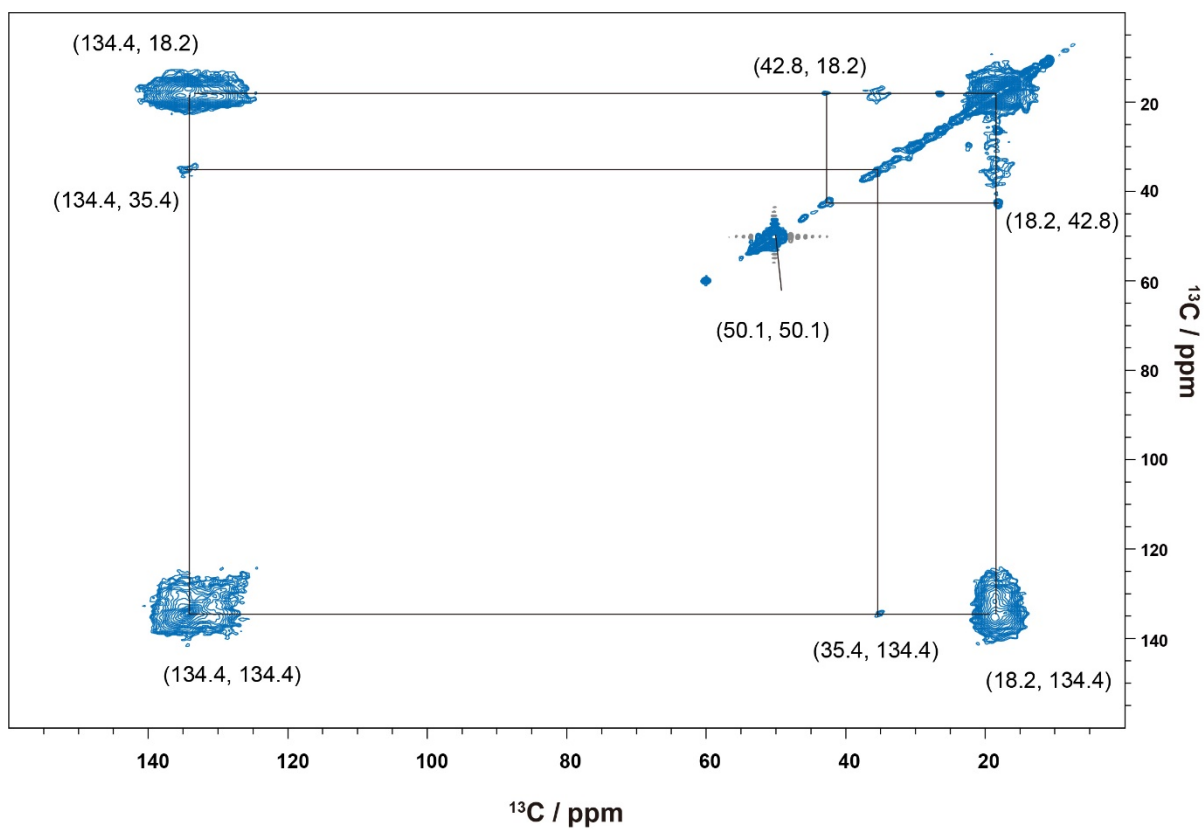


Fig. S8. 2D ^{13}C - ^{13}C (10 kHz MAS) solid-state NMR correlation spectrum of 0.22Zn_F-ZSM-5 zeolite. The sample was prepared after ^{13}C -methanol conversion over this catalytic system at 400 °C for 20 min [magic angle spinning (MAS)].

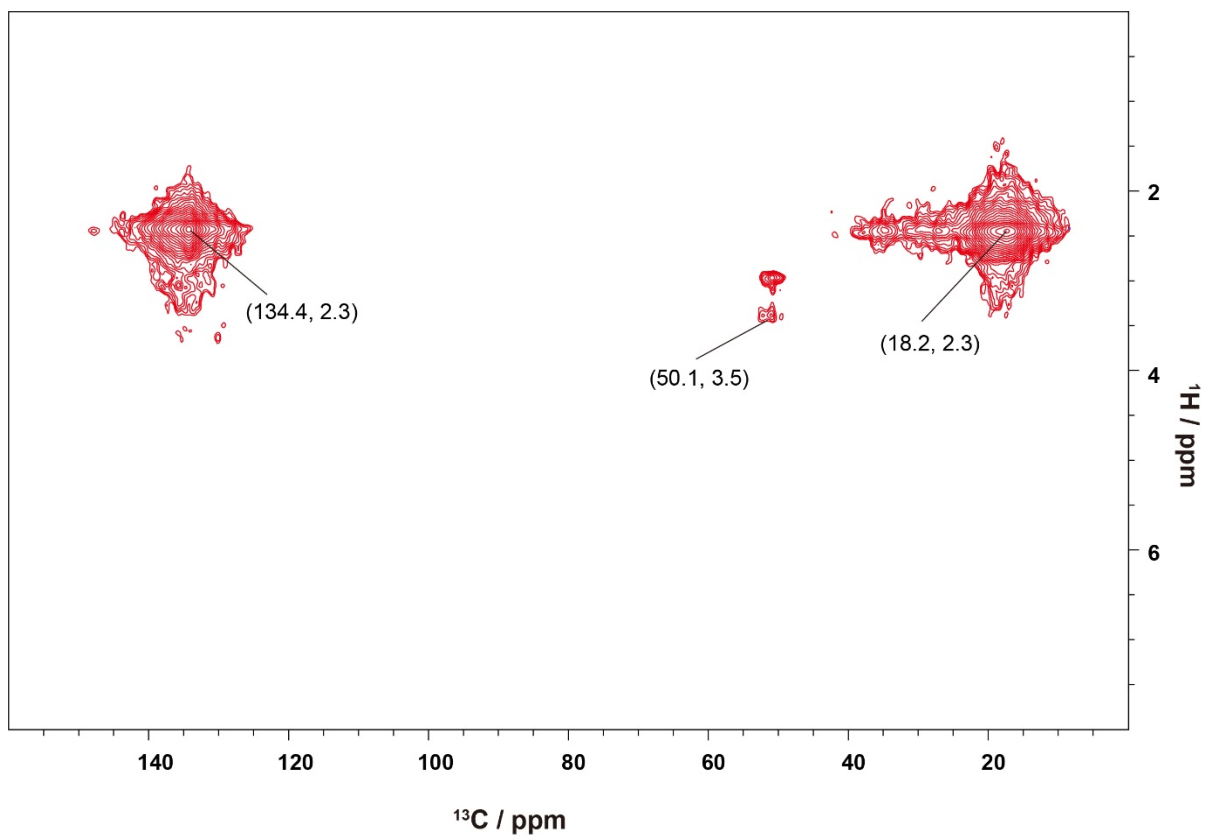


Fig. S9. 2D ^1H - ^{13}C (10 kHz MAS) solid-state NMR correlation spectrum of the parent-ZSM-5 zeolite. The sample was prepared after ^{13}C -methanol conversion over this catalyst at 400 °C for 20 min [magic angle spinning (MAS)].

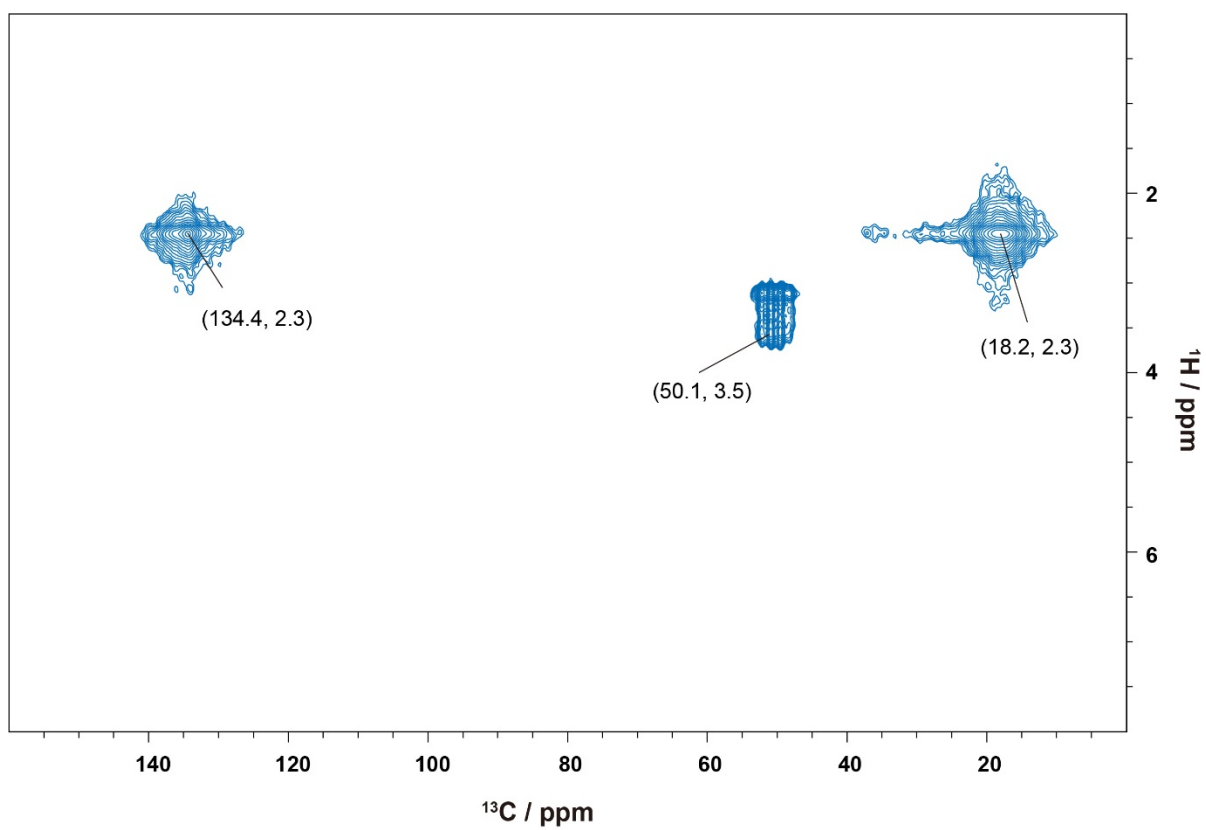


Fig. S10. 2D ^1H - ^{13}C (10 kHz MAS) solid-state NMR correlation spectrum of 0.22Zn_F-ZSM-5 zeolite. The sample was prepared after ^{13}C -methanol conversion over this catalytic system at 400 °C for 20 min [magic angle spinning (MAS)].

S4. Supplementary References

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