

Electronic Supplementary Information

Selective Methanethiol-to-Olefins Conversion over HSSZ-13 Zeolite

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Experimental section

Catalysts preparation

Commercial zeolite powders NH₄ZSM-5 (Si/Al = 40) and NH₄FER (Si/Al = 10) were purchased from Alfa Aesar and zeolite NH₄BEA (Si/Al = 12) was purchased from Akzo Nobel. Zeolite NaSSZ-13 (Si/Al = 18.7) was synthesized according to a previously reported procedure.^[1] The proton forms of the commercial zeolites were obtained by calcination in a shallow-bed configuration at 550 °C for 4 h. The proton form of SSZ-13 was obtained by 3 consecutive ion-exchange steps with a 1.0 M solution of NH₄NO₃ for 3 h at 70 °C, followed by drying overnight at 110 °C and calcination at 550 °C for 4 h. Prior to catalytic activity measurements, the zeolite catalysts were pelletized, crushed and sieved to obtain particles with a size in the range of 0.25 – 0.5 mm.

Catalytic activity measurements

An amount of 0.1 g zeolite powder was loaded between two quartz wool plugs in a tubular quartz reactor (i.d. = 4 mm, o.d. = 8 mm, l = 250 mm). The zeolite catalyst was first calcined in a flow of 20 vol% O₂ in He at 550 °C for 1 h. Two different reaction feed mixtures were used, either CH₃SH and N₂ or CH₃OH and N₂. CH₃SH and N₂ were fed to the reactor using thermal mass flow controllers. CH₃OH (Merck, 99%) was introduced into the reactor by flowing the N₂ stream through a thermostated saturator containing CH₃OH. The gas-phase products were analyzed by an online gas chromatograph (CGC, Interscience) equipped with 2 columns and detectors: (i) Rtx-1 column: l = 15 m, i.d. = 0.32 mm, FID: CH₃SH, CH₃SCH₃ and hydrocarbons; (ii) Rt-QBond column, l = 12 m, i.d. = 0.32 mm, TCD: N₂; (iii) Molsieve 5A column (l = 7 m, i.d. = 0.32 mm) TCD: H₂S. In order to analyze heavier products, the effluent stream was directed to a diethylene glycol trap. The obtained solution was analyzed by offline gas chromatography-mass spectrometry (GC-MS, Shimadzu GC-17A) equipped with a Stabilwax column (l = 30 m, i.d. = 0.32 mm).

Catalysts characterization

XRD. X-ray diffraction (XRD) patterns of zeolite catalysts were collected on a Bruker D2 Phaser using Cu K α radiation in the 2θ range of 5 - 50° with a step size of 0.02° s⁻¹ and time step size of 0.4 s.

Ar physisorption. Ar adsorption/desorption isotherms were measured at -186 °C with a Micromeritics ASAP-2020 instrument. The zeolite catalysts were pretreated at 500 °C for 6 h under vacuum prior to the measurements. The *t*-plot method was used to calculate the microporous volume. The BET surface area was determined in the relative pressure range 0.05 - 0.25.

SEM. Scanning electron microscopy (SEM) images of the zeolites were taken on a FEI Quanta 200F scanning electron microscope at an accelerating voltage of 2 kV.

Pyridine-adsorption IR spectroscopy. Pyridine-adsorption IR spectra of zeolites were recorded on a Bruker Vertex 70v spectrometer in the range of 4000 - 800 cm⁻¹. Spectra were acquired at 4 cm⁻¹ resolution as an average of 64 scans. The samples were prepared as thin wafers with a density of ~ 9 mg/cm² and placed inside a controlled-environment transmission IR cell with CaF₂ windows. After calcination at 530 °C in air flow, a background spectrum was collected at 150 °C and a pressure < 10⁻⁵ mbar. Then, pyridine was introduced into the cell. Desorption was carried out under vacuum at 150 °C, 300 °C and 500 °C using a dwell time of 1 h at each temperature. The IR spectra were collected at 150 °C.

NMR spectroscopy. Solid-state magic-angle spinning nuclear magnetic resonance (MAS NMR) spectra were recorded using an 11.7 Tesla Bruker DMX500 NMR spectrometer, operated at 132 MHz, 500 MHz and 125 MHz for ^{27}Al , ^1H and ^{13}C , respectively. ^{27}Al MAS NMR spectra were recorded with a spinning rate of 25 kHz and a single excitation pulse length of 1 μs with a 1 s repetition time. The reference signal for the ^{27}Al chemical shift was a saturated solution of $\text{Al}(\text{NO}_3)_3$. One-dimensional $^{13}\text{C}\{^1\text{H}\}$ cross polarization (CP) and two-dimensional $^1\text{H}\text{-}^{13}\text{C}\{^1\text{H}\}$ HETCOR (Heteronuclear Correlation) MAS NMR spectra were recorded with a ramped contact pulse of 3 ms and an interscan delay of 3 s. ^{13}C Direct Excitation (DE) spectra were measured using a high power proton decoupling Hahn Echo pulse sequence p1- τ 1-p2- τ 2-aq with a 90° pulse p1=5 μsec , a 180° pulse p2=10 μsec and an interscan delay of 10 sec. ^{13}C NMR spectra were recorded at spinning rate of 8 kHz. ^1H shifts were calibrated using tetramethylsilane (TMS). Solid adamantane was used for the ^{13}C NMR shift calibration.

XPS. X-ray photoelectron spectroscopy (XPS) was performed using a Thermo Fischer K-Alpha spectrometer, equipped with a monochromatic X-ray source ($\text{Al K}\alpha = 1486.6 \text{ eV}$), and a delay line detector. Used catalysts were dispersed on alumina sample holders coated with carbon tape in a nitrogen-filled glovebox ($\text{H}_2\text{O} < 1 \text{ ppm}$, $\text{O}_2 < 1 \text{ ppm}$). The samples were transferred to the XPS apparatus using a protective atmosphere transport vessel. The background pressure prior to analysis was 2×10^{-9} mbar. Survey scans were collected at a constant pass energy of 160 eV, region scans at 40 eV. The spectra were fitted using the CasaXPS software. The main C 1s signal served as an energy reference and was set at 284.8 eV.

TG-MS. The thermal gravimetric and mass spectrometry (TG-MS) analysis of used catalysts was performed with a Mettler Toledo TGA-DSC 1 instrument coupled to a mass spectrometer (Pfeiffer Vacuum, OmniStar GSD 300). The used catalysts (~10 mg) was placed in an alumina crucible and then heated up to 700 $^\circ\text{C}$ with a ramp rate of 5 $^\circ\text{C}/\text{min}$ in 40 mL/min He and 20 mL/min O_2 flow.

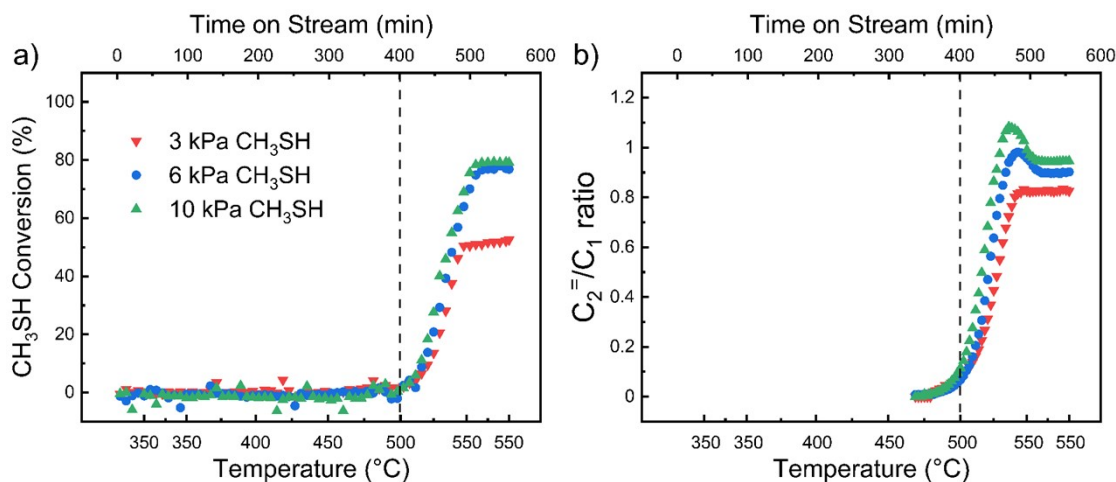


Figure S1. (a) CH₃SH conversion and (b) C₂⁻/C₁ ratio (carbon-based) during thermal decomposition of CH₃SH (3 kPa, 6 kPa, and 10 kPa CH₃SH in N₂). The total flow rate was 5 mL/min, the temperature was increased from 350 °C to 550 °C at a rate of 0.5 °C/min.

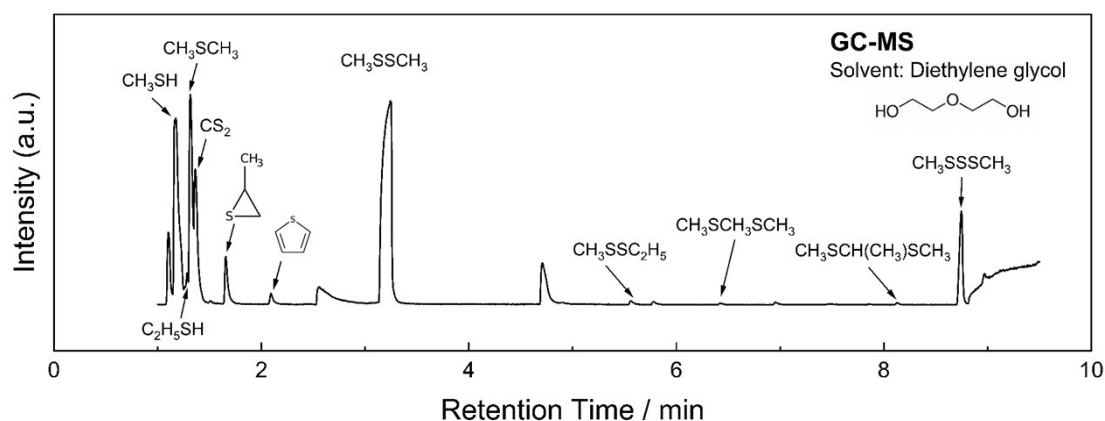


Figure S2. GC-MS analysis of the products of CH₃SH thermal decomposition (reaction at 550 °C) collected in diethylene glycol.

Below 500 °C (Fig. S1), the non-catalytic conversion of CH₃SH is negligible, while conversion strongly increase from 5% to 75%, when the temperature is raised from 500 °C to 550 °C. Under these conditions the main hydrocarbon products in the gas phase are CH₄ and C₂H₄. The carbon-based C₂H₄/CH₄ ratio reached a maximum value of ~1 at a CH₃SH partial pressure of 10 kPa and a temperature in the range of 520 – 530 °C. The C₂H₄/CH₄ ratio increased with the CH₃SH partial pressure. Analysis of the condensable gases (Fig. S2) showed a range of other products such as CS₂, CH₃SCH₃, CH₃SSCH₃, CH₃SSSCH₃, C₂H₅SH, CH₃SSC₂H₅ and thiophene. A representative gas chromatogram is shown in Fig. S2. These findings demonstrate that selective catalytic conversion of CH₃SH can only be achieved below 500 °C where thermal decomposition can be avoided.

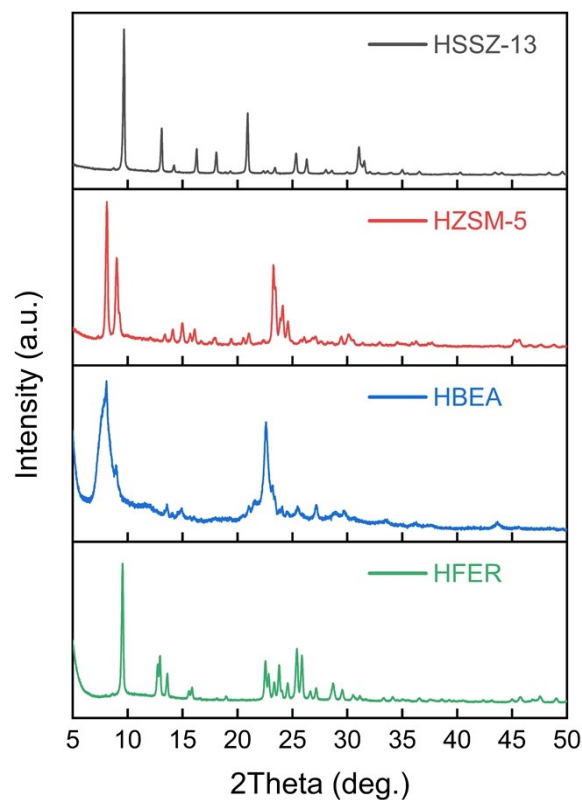


Figure S3. XRD patterns of calcined zeolite catalysts.

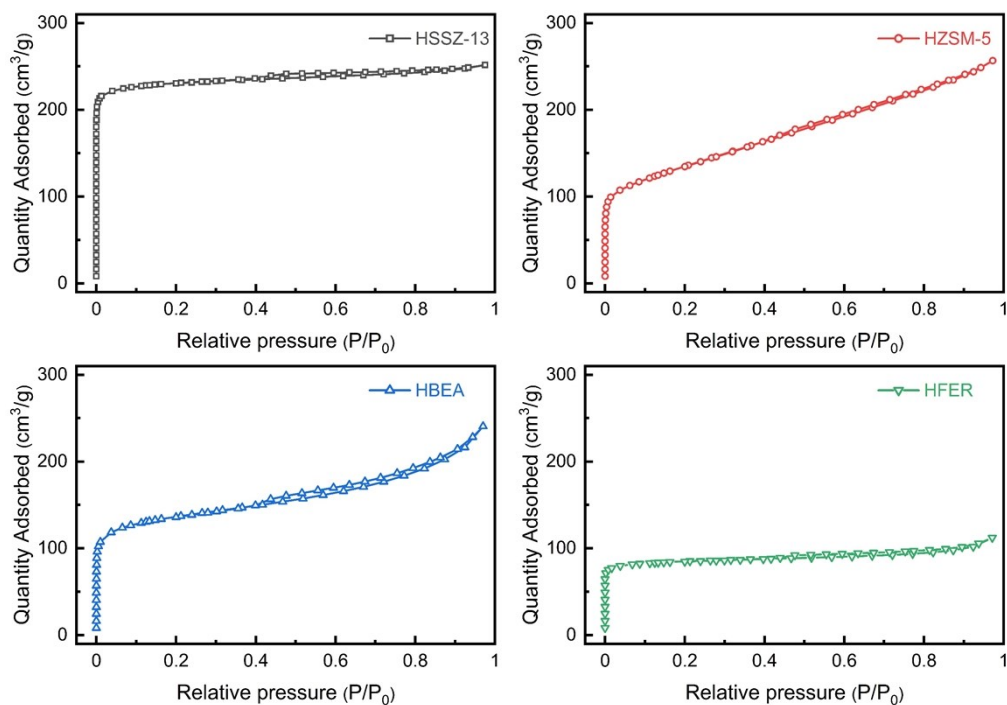


Figure S4. Ar physisorption isotherms of calcined zeolite catalysts.

Table S1. Textural properties of calcined zeolite catalysts determined by Ar physisorption.

Sample	V_{tot} ($\text{cm}^3 \text{g}^{-1}$)	V_{micro} ($\text{cm}^3 \text{g}^{-1}$)	S_{BET} ($\text{m}^2 \text{g}^{-1}$)
HSSZ-13	0.32	0.26	701.6
HZSM-5	0.33	0.05	418.4
HBEA	0.31	0.11	420.5
HFER	0.14	0.09	258.8

V_{tot} total pore volume at $p/p_0 = 0.95$

V_{micro} micropore volume calculated by the *t*-plot method

S_{BET} Brunauer-Emmett-Teller (BET) surface area ($p/p_0 = 0.05$ - 0.25)

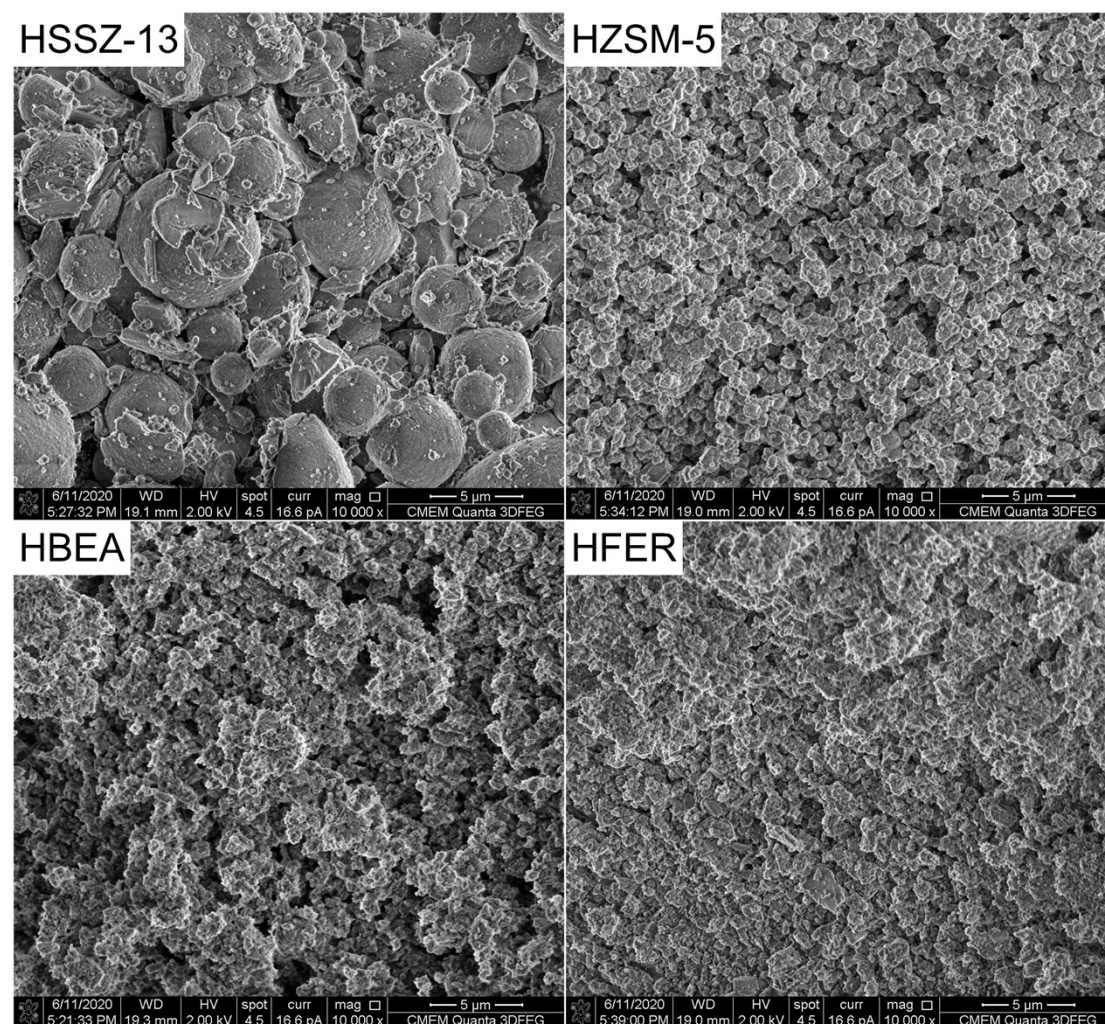


Figure S5. SEM images of calcined zeolite catalysts.

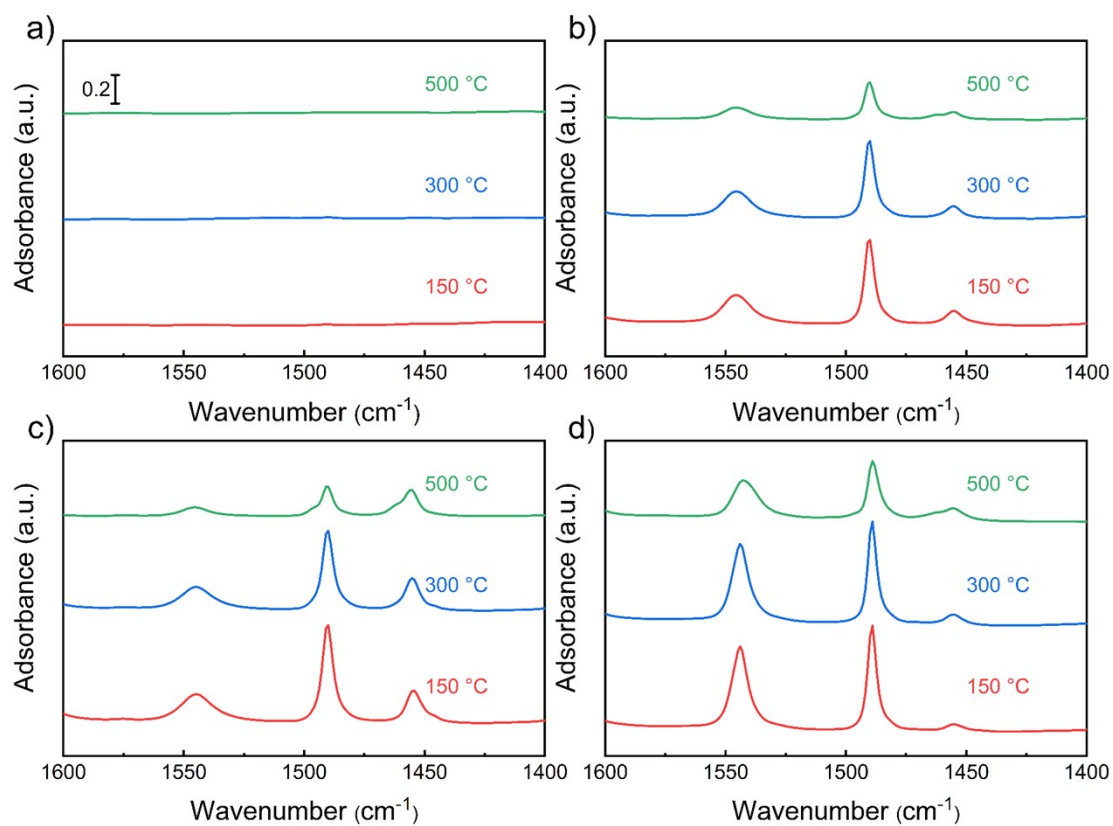


Figure S6. Pyridine adsorbed IR spectra of calcined (a) HSSZ-13, (b) HZSM-5, (c) HBEA, and (d) HFER after evacuation at 150 °C, 300 °C, and 500 °C.

Table S2. Acidic properties of calcined zeolite catalysts based on pyridine IR and ^1H MAS NMR spectroscopy.

Sample	BAS (mmol/g) ^a			LAS (mmol/g) ^a			BAS (mmol/g) _b
	150 °C	300 °C	500 °C	150 °C	300 °C	500 °C	
HSSZ-13	-	-	-	-	-	-	0.70
HZSM-5	0.48	0.44	0.20	0.16	0.14	0.11	-
HBEA	0.81	0.65	0.20	0.47	0.39	0.32	-
HFER	0.47	0.36	0.13	0.03	0.04	0.07	-

^a determined by IR spectroscopy of pyridine adsorption

^b determined from ^1H MAS NMR spectroscopy^[1]

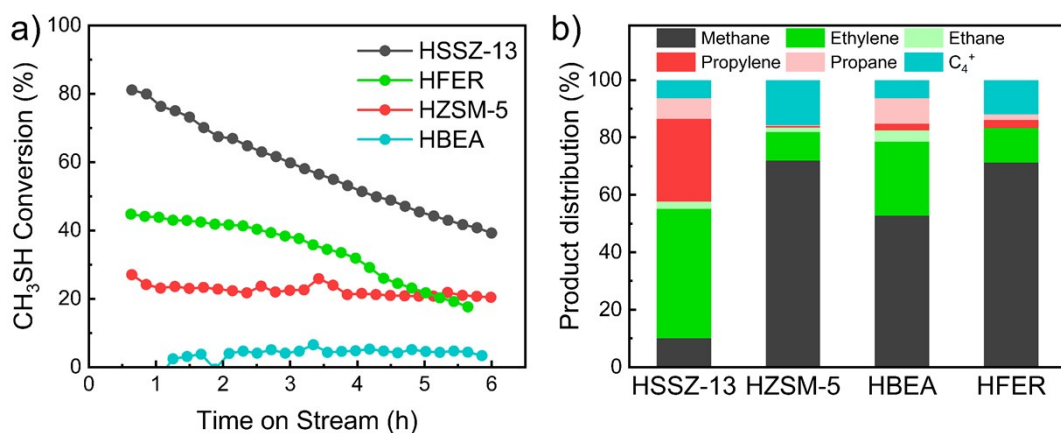


Figure S7. (a) CH₃SH conversion and (b) carbon-based product distribution within first 2 h of respective reactions over HSSZ-13, HZSM-5, HBEA, and HFER. Conditions: 6 kPa of CH₃OH/CH₃SH in N₂ (5 mL/min), 450 °C, 100 mg of catalysts, 6 h.

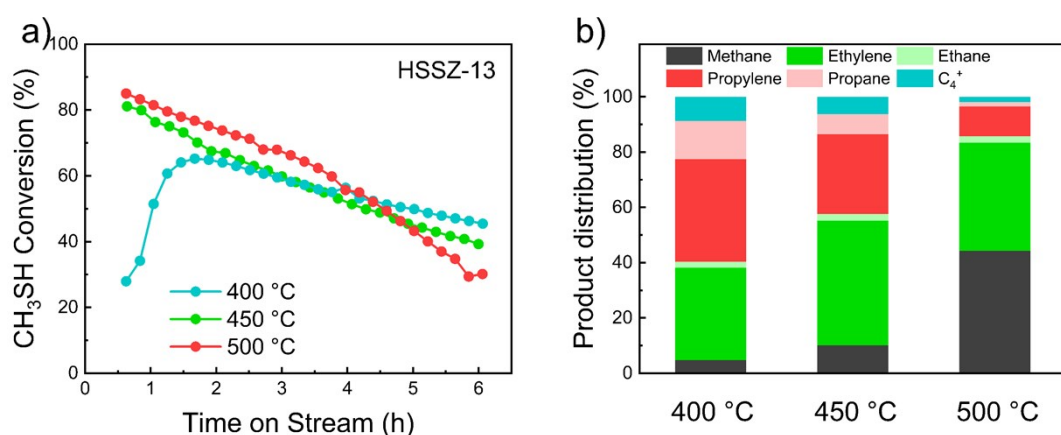


Figure S8. (a) CH₃SH conversion and (b) carbon basis selectivity within first 2 h of HSSZ-13 of 6kPa of CH₃SH in N₂ (5 mL/min) reaction at 400 °C, 450 °C and 500 °C for 6 h.

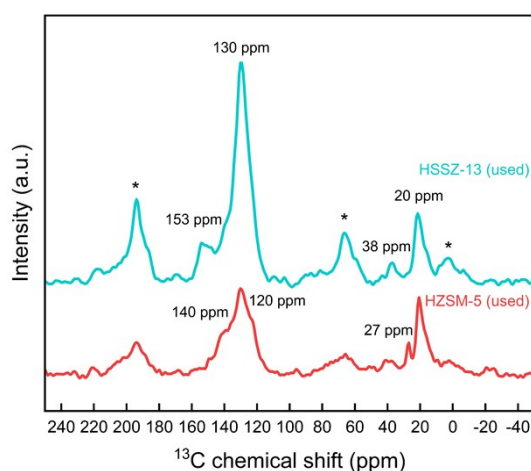


Figure S9. ¹³C cross polarization NMR spectra of used HZSM-5 and HSSZ-13 after 6 h MtTO reaction at 450 °C. Asterisks denote spinning side bands.

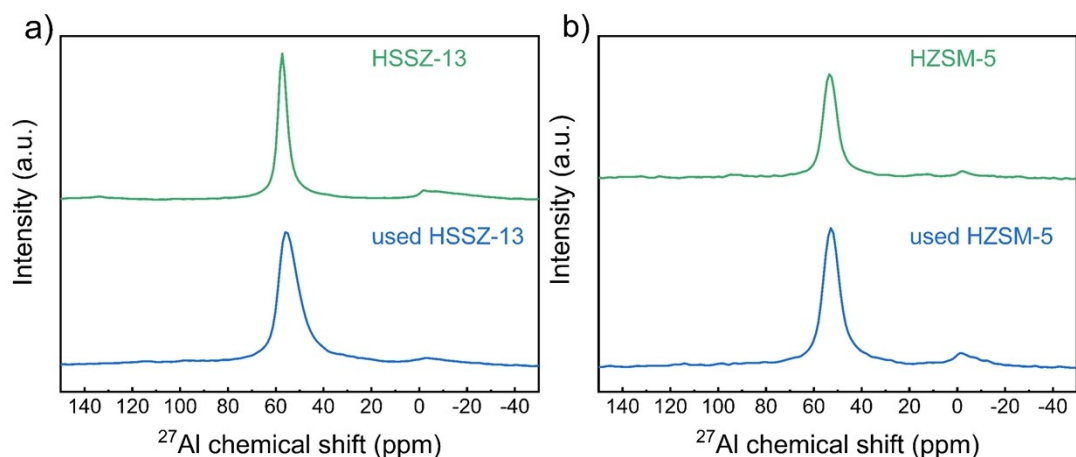


Figure S10. ^{27}Al MAS NMR spectra of calcined and used (a) HSSZ-13 and (b) HZSM-5 zeolites.

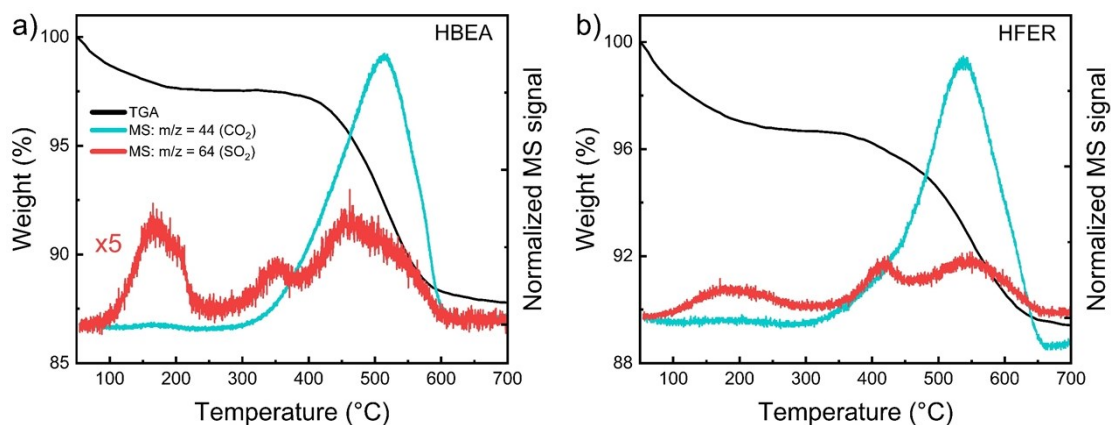


Figure S11. TGA curves and MS signals of CO_2 ($m/z = 44$) and SO_2 ($m/z = 64$) collected under air flow of used (a) HBEA and (b) HFER.

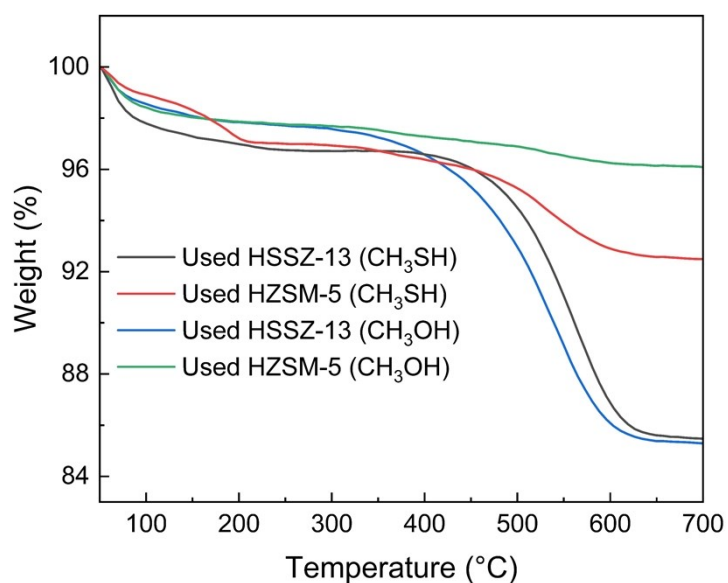


Figure S12. TGA curves of used HSSZ-13 and HZSM-5 after MTO and MtTO reaction.

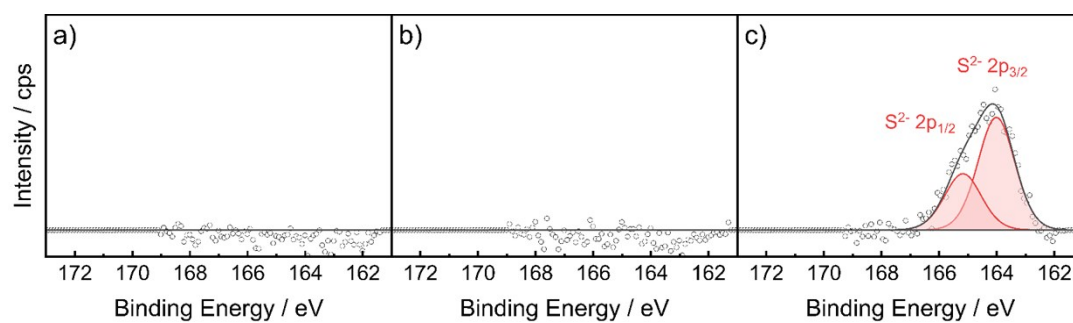


Figure S13. XPS spectra of S 2p region of used HSSZ-13 after 6 h reaction at (a) 400 °C, (b) 450 °C, and (c) 500 °C.

References

- [1] A. Bolshakov, A. J. F. Van Hoof, B. Mezari, N. Kosinov, E. Hensen, *Catal. Sci. Technol.* **2019**, *9*, 6737–6748.