

Supporting information

The catalytic effects of sulfur in ethane dehydroaromatization

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Experimental Procedures

Synthesis

Conventional ZSM-5 was synthesized from sodium aluminate (NaAlO_2 , Sigma-Aldrich, anhydrous), tetrapropylammonium hydroxide (TPAOH, Sigma-Aldrich, 1.0 M in H_2O) and tetraethyl orthosilicate (TEOS, Sigma-Aldrich, $\geq 99.0\%$). In the synthesis procedure, 0.04 g sodium aluminate was dissolved in 7.2 ml of TPAOH and then 4.4 ml of TEOS was added dropwise while stirring in a Teflon beaker. After stirring for 1 h, the mixture was transferred to a Teflon-lined stainless steel autoclave, heated at $180\text{ }^\circ\text{C}$ and left for 24 h. The product was filtered, washed with distilled water and dried at $80\text{ }^\circ\text{C}$ overnight. Finally, the white powder was calcined for 20 hours at $550\text{ }^\circ\text{C}$ to achieve NaZSM-5. The sample was ion-exchanged by adding 1.0 g of NaZSM-5 in 80 ml of 1 M ammonium nitrate aqueous solution and stirring the solution at $80\text{ }^\circ\text{C}$ for 1 h. Afterwards, the solid was separated from the liquid by centrifugation and the same procedure for ion-exchange was repeated two more times. Finally, the solid was separated, washed and dried for 12 h at $80\text{ }^\circ\text{C}$. The final product was calcined at $550\text{ }^\circ\text{C}$ for 20 h in air and assigned as ZSM-5.

Catalytic test

The catalyst powders were pressed, crushed and sieved to obtain fraction size between 0.6-1 mm. Then 1.5 g of the catalyst was loaded in a continuous fixed-bed stainless steel reactor with an inner diameter of 9 mm to perform ethane dehydroaromatization at $550\text{ }^\circ\text{C}$ and under 2 barg pressure. The reactor and thermowells were coated with SilcoNert®1000^[30] (Silicosteel®, thickness of 100-500 nm). Prior to the catalytic reaction, the catalyst was pretreated 2 h under 12 NL h^{-1} flow of N_2 at $150\text{ }^\circ\text{C}$ followed by heating up to $350\text{ }^\circ\text{C}$ with a heating ramp of $0.5\text{ }^\circ\text{C min}^{-1}$ under 12 NL h^{-1} N_2 with 500 ppmv H_2S in the flow. The catalyst was sulfided for 4 h at $350\text{ }^\circ\text{C}$ and heated up again to the reaction temperature of $550\text{ }^\circ\text{C}$ with a heating ramp of $5\text{ }^\circ\text{C min}^{-1}$ under the same gas flow. When the temperature of the catalyst bed reached $550\text{ }^\circ\text{C}$, the flow was switched to 10% ethane in N_2 and 60 ppmv H_2S with a total flow of 4.5 NL h^{-1} , resulting in a GHSV of $0.3\text{ NL/g}_{\text{cat}}/\text{h}$. It is worth mentioning that for testing the sulfur-free catalysts the samples were pretreated in 12 NL h^{-1} 1% O_2 in N_2 for 2 h at $550\text{ }^\circ\text{C}$ and the reaction was performed at $\text{GHSV}=0.3\text{ h}^{-1}$. The outlet gases were analyzed online in an Agilent 7890B gas chromatograph equipped with two capillary columns of CP- Al_2O_3 -KCl ($25\text{m}\times 0.32\text{mm}\times 5\mu\text{m}$) and HP-INNOWax, ($30\text{mm}\times 0.32\text{mm}\times 0.25\mu\text{m}$), a thermal conductivity detector (TCD) and two flame ionization detectors (FID). The conversion and product selectivity were calculated based on carbon mol balance.

Catalyst characterization

Crystallinity of the samples was evaluated by XRD using a Huber G670 diffractometer operated in transmission mode with $\text{Cu K}\alpha_1$ irradiation from a focusing quartz monochromator.

Energy-dispersive X-ray spectroscopy (EDS) was performed using SEM-EDS elemental mapping by studying the sample with electron scanning microscope (Quanta 200 ESEM FEG) operated at 20 keV and equipped with an Oxford Instruments X-Max 50mm² EDS analyzer using Aztec 3.3 Service Pack 1 software for data analysis.

The transformation of metal oxide to metal sulfide was monitored using transmission electron microscopy (TEM) before and after sulfidation. The TEM imaging and sulfidation reaction was carried out on a Philips CM300 FEG TEM instrument equipped with a differentially pumped gas cell dedicated to sulfur reaction experiments.^[1] The TEM sample was prepared

by grinding the catalyst precursor materials in a mortar and subsequent dispersion in dry state onto a plasma-cleaned FEI NanoEx e-chip.^[2] TEM imaging was done at a primary electron energy of 300 keV, and using a fixed electron dose rate of $30 \text{ e}^- \text{Å}^{-2} \text{s}^{-1}$. Moreover, the charge coupled device camera (Tietz FastScan F114) was used to record images at a sampling rate of 0.182 nm/pixel. 6 image areas (186 nm x 186 nm) from 4 different catalyst precursor agglomerates protruding from the holes in the e-chip membrane were imaged prior to sulfidation in base vacuum ($<2.1 \times 10^{-6}$ mbar) and at room temperature. Each image area was exposed to the electron beam for about 5 minutes to allow for searching and focus of the sample, and then the beam was blanked. The sulfidation reaction was initiated by introducing 0.7 mbar of H_2S into the microscope and heating the sample at 10 °C/s to 350 °C over 2 hours. After sulfidation, the image areas were imaged again in the base vacuum and at room temperature and 9 additional reference areas not previously exposed to the electron beam was imaged as well, as outlined in Fig. S3.

Temperature programmed desorption of ammonia (NH_3 -TPD) was measured on a Mettler Toledo TGA-DSC1. First, the samples were heated to 500 °C in a mix flow of nitrogen and argon. Then the samples were cooled to 150 °C and ammonia was introduced for 30 min followed by flushing with inert gases for 3 hours to remove physically adsorbed ammonia. Lastly, desorption of NH_3 was carried out by increasing the temperature to 500 °C with a heating ramp of 5 °C/min .

Nitrogen physisorption was performed at liquid nitrogen temperature on a Micromeritics 3Flex surface area and porosimetry analyzer. Prior to the measurement, samples were outgassed under vacuum at 400 °C overnight. The specific surface area (S_{BET}) was calculated from the N_2 adsorption data by BET method in the relative range (P/P_0) of 0.05-0.3. Micropore volume (V_{micro}) was determined using t -plot method. Finally, the total pore volume (V_{total}) was calculated from the amount of adsorbed nitrogen at the relative pressure of $P/P_0=0.95$.

X-ray photoelectron spectroscopy (XPS) analysis was performed with a Thermo Scientific K-Alpha X-ray photoelectron spectrometer equipped with a hemispherical analyser and an Al K α micro-focused monochromator. We made the measurements in ultra-high vacuum conditions and used Thermo Avantage software for analysis. In addition, binding energy was calibrated by using C1s peak.

Elemental analysis was performed by inductively coupled plasma optical emission spectroscopy (ICP-OES) applying an Agilent 720 ICP-OES spectrometer. Furthermore, LECO carbon/sulfur analyzer (model CS-230) was used to determine carbon and sulfur contents.

Results and Discussion

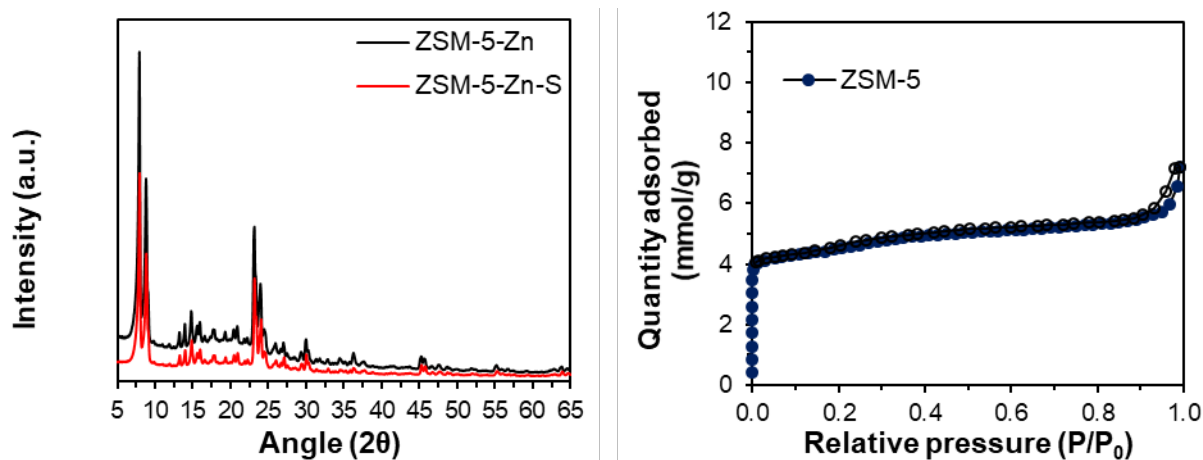


Fig. S1. (left) XRD patterns of synthesized HZSM-5 with 5% zinc loading before (ZSM-5-Zn) and after sulfidation (ZSM-5-Zn-S), (right) nitrogen adsorption-desorption isotherms for ZSM-5 sample.

Table S1. Textural properties of synthesized ZSM-5 zeolite.

Sample name	S_{BET} (m^2/g)	S_{ext} (m^2/g)	V_{micro} (cm^3/g)	V_{tot} (cm^3/g)
ZSM-5	358	94	0.114	0.199

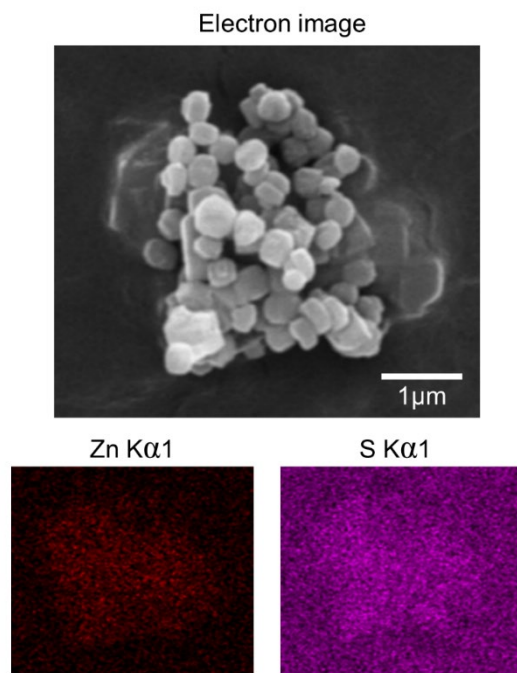


Fig. S2. SEM-EDS of ZSM-5-5%Zn-S catalyst after sulfidation in the reactor and before reaction.

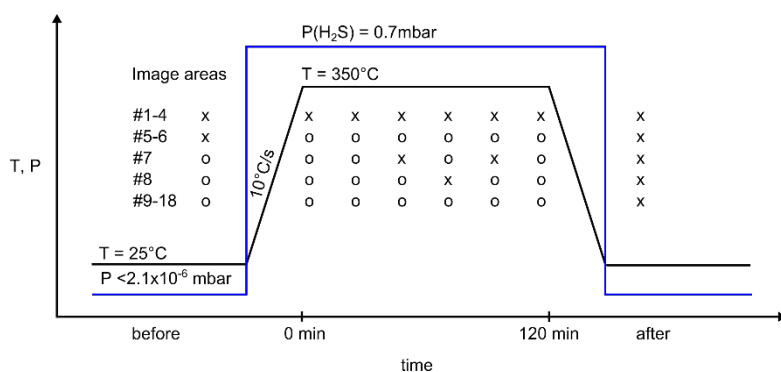


Fig. S3. Outline of the TEM sulfidation experiment. The 'x' denotes imaging (i.e. acquisition of one TEM image) and 'o' denotes no exposure to the electron beam. During sulfidation a few areas were imaged *in situ* including two areas not exposed to the electron beam prior to sulfidation. During each acquisition the sample area was exposed to the electron beam for about 2 min per acquisition for relocating the sample area and refocusing and in the intermittent period between acquisitions the beams was blanked.

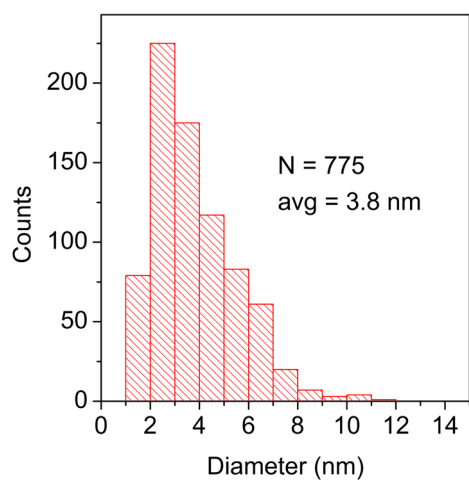


Fig. S4. Distribution of particles size based on 775 particles from image areas #9-18, not previously exposed to electron beam.

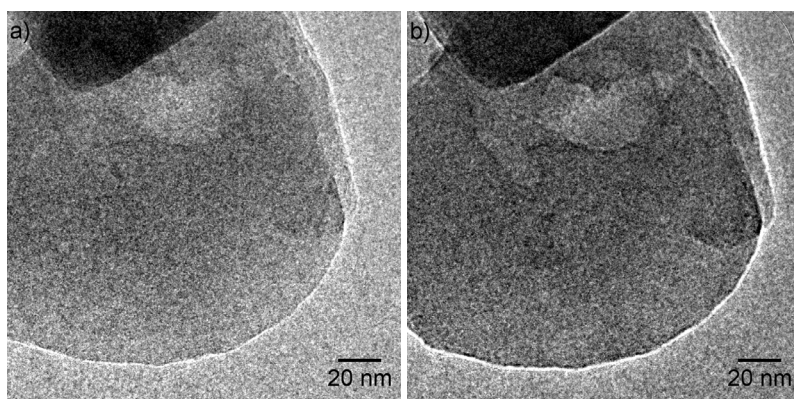


Fig. S5. TEM images of an image area (#5) before and after exposure to 0.7 mbar H₂S at 350 °C for 120 min. No highly dispersed nanoparticles were observed as in other areas not previously exposed to electron beam (main paper Fig. 2b).

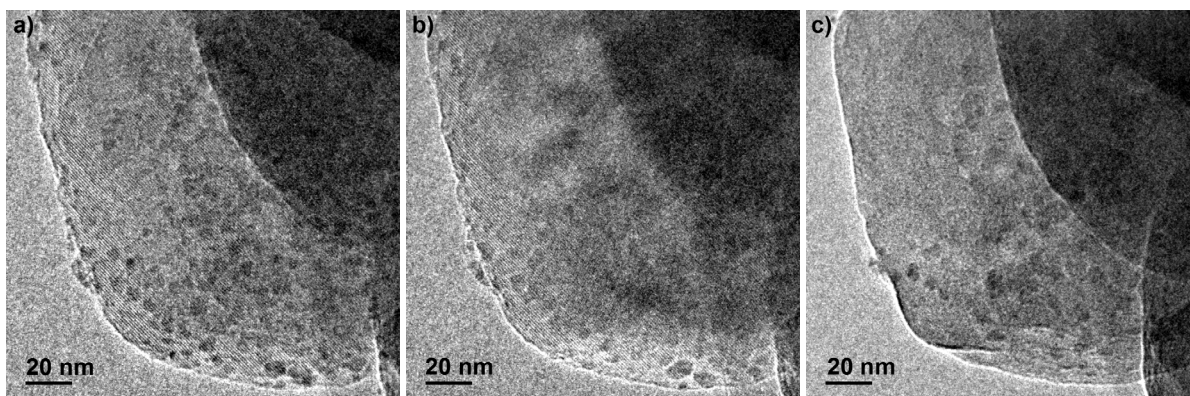


Fig. S6. In situ TEM images of an area (#7) not previously exposed to electron beam during exposure to 0.7 mbar H₂S at 350 °C after a) 42 min and b) 75 min. c) Same area after termination of sulfidation for 120 min by rapid cooling (10°C/s) to room temperature and H₂S pumped out to reach a vacuum level of 8.4×10^{-7} mbar. The repeated imaging under in situ conditions appear to decrease the density of particles and increase the particle sizes.

Table S2. Ammonia TPD results for the samples.

Sample	Weak acid sites (mmol/g) ^a	Strong acid sites (mmol/g) ^b	Calculated Si/Al
ZSM-5	0.04	0.09	175
ZSM-5-Zn	0.10	0.06	
ZSM-5-Zn-S	0.10	0.05	

^a Density of acid sites determined by NH₃-TPD for NH₃ desorbed at 180-280 °C. ^b Density of acid sites determined by NH₃-TPD for NH₃ desorbed at 280-550 °C.

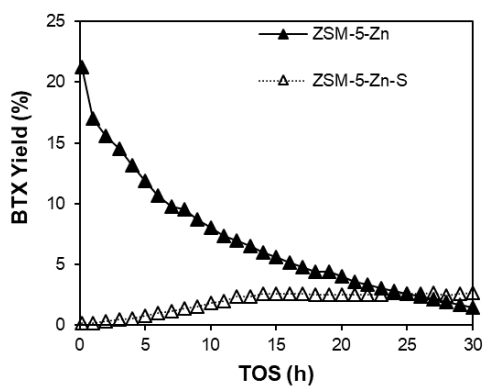


Fig. S7. BTX yield of ZSM-5-Zn in sulfur free ethane feed and ZSM-5-Zn-S in the presence of 60 ppm H₂S in ethane feed for ethane dehydroaromatization at 550 °C, 2 barg and GHSV=0.3 h⁻¹.

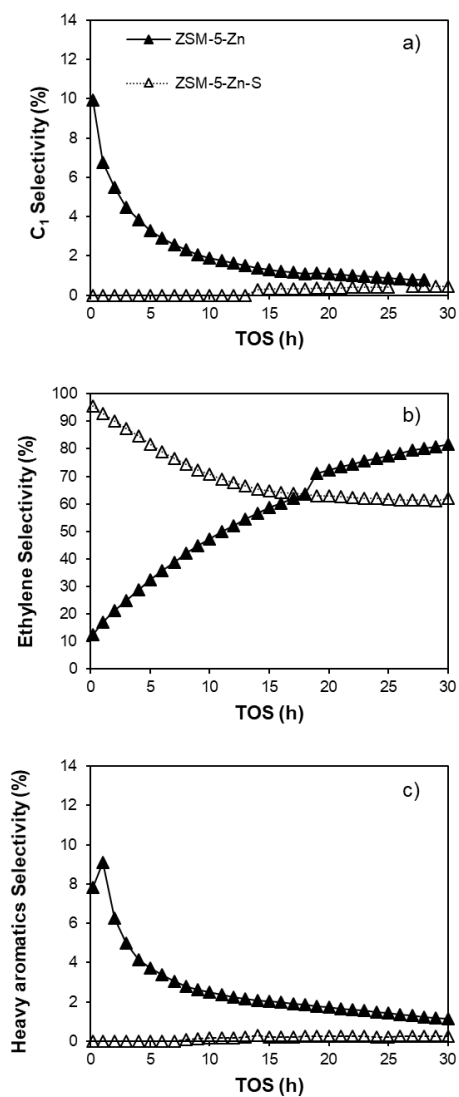


Fig. S8. a) C₁, b) ethylene and c) heavy aromatics selectivity for ZSM-5-Zn in sulfur free ethane feed and ZSM-5-Zn-S in the presence of 60 ppm H₂S in ethane feed for ethane dehydroaromatization at 550 °C, 2 barg and GHSV=0.3 h⁻¹.

Table S3. Elemental analysis results for carbon, sulfur and zinc.

Catalyst	Si/Al	Zn	S	C
Fresh				
ZSM-5-Zn	40	4.47	0	-
Spent				
ZSM-5-Zn	40	2.08	0	2.03
ZSM-5-Zn-S	40	3.94	1.65	0.22

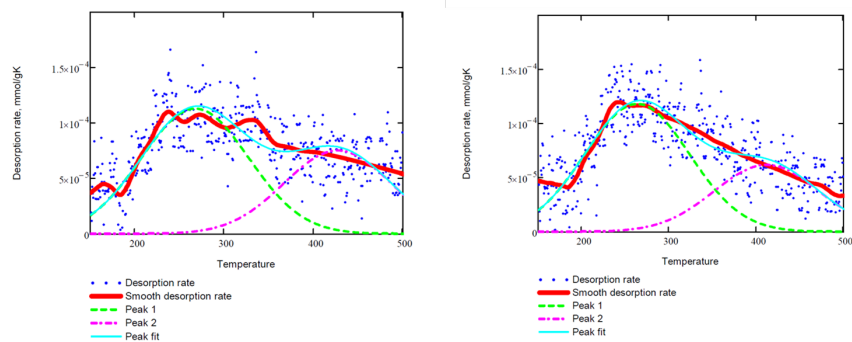


Fig. S9. Ammonia TPD results for ZSM-5-Zn (left) and ZSM-5-Zn-S (right) samples

References

- [1] L. P. Hansen, E. Johnson, M. Brorson, S. Helveg, *J. Phys. Chem. C* **2014**, *118*, 22768–22773.
- [2] L. Mele, S. Konings, P. Dona, F. Evertz, C. Mitterbauer, P. Faber, R. Schampers, J. R. Jinschek, *Microsc. Res. Tech.* **2016**, *79*, 239–250.