

Supporting information for:

Methanol-to-Olefins Catalysis with Hydrothermally Treated Zeolite SSZ-39

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Fig. S1-21: Additional PXRD, solid state NMR, N₂-physisorption, ¹H-NMR, TGA and MTO reaction data.

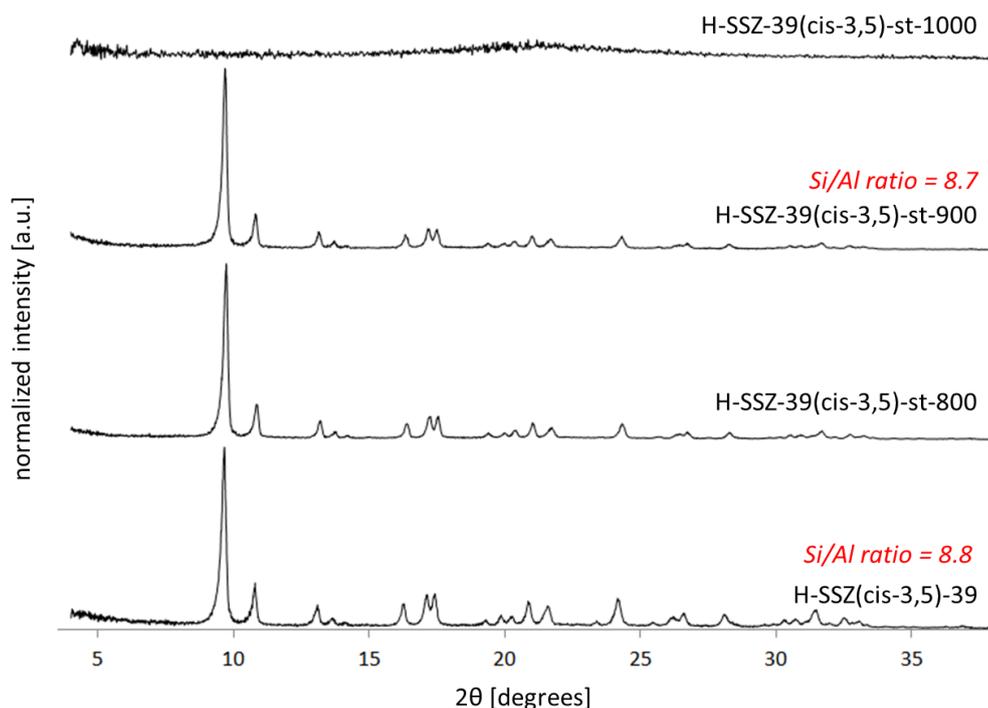


Fig. S1: PXRD of the MTO-ready control catalyst made with *cis*-3,5-dimethylpiperidinium hydroxide OSDA (H-SSZ-39). The gel recipe was: 1Si:0.033Al:0.14OSDA:0.71OH⁻:0.57Na:28H₂O, and the synthesis ran statically for 3 days at 140 °C. Impurity removal with HCl as described under Experimental was performed (more information, see *Chem. Mater.* **2015**, 27, 2695). MTO-ready here denotes successive washing, HCl treatment, washing, calcination, NH₄-exchange and calcination. Also found: PXRD of the same material, but steamed 800 °C, 900 °C and 1000 °C in its NH₄-form.

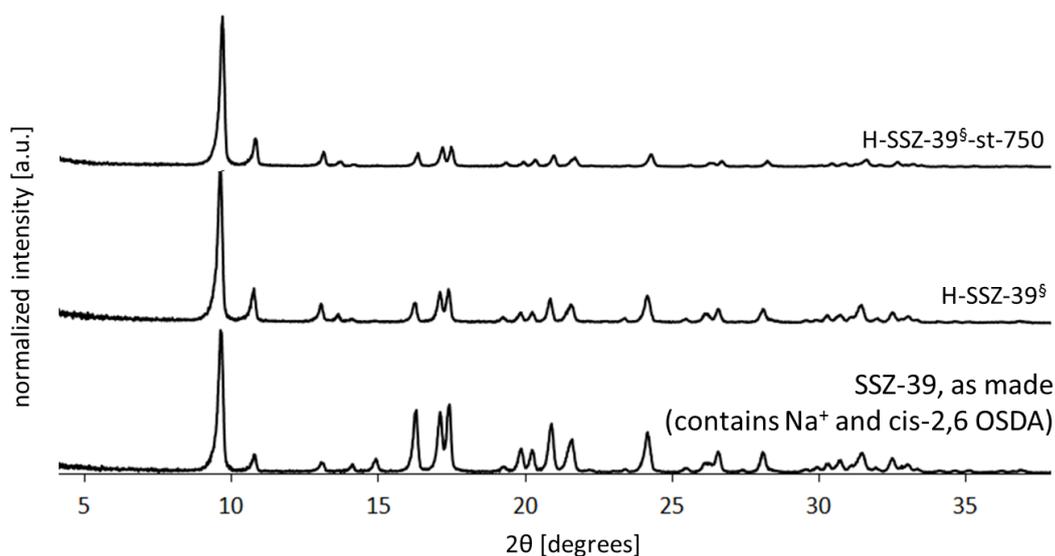


Fig. S2: PXRD of the MTO-ready control catalyst (H-SSZ-39[§]) made with pure *cis*-2,6-dimethylpiperidinium hydroxide OSDA[§] using the following recipe: 1Si:0.033Al:0.07OSDA:0.65OH⁻:0.58Na:12.3H₂O in a rotating oven at 140°C for 4 days. Sodium silicate and CBV-500 as Si and Al sources. Here, HCl washing was not necessary as the batch was essential phase-pure. Also found: PXRD of the as-made material before OSDA removal, and the steamed one at 750 °C. The micropore volume of H-SSZ-39[§] was measured (N₂) and mounted to 0.26 cc.g⁻¹ and the Si/Al ratio was 8.7.

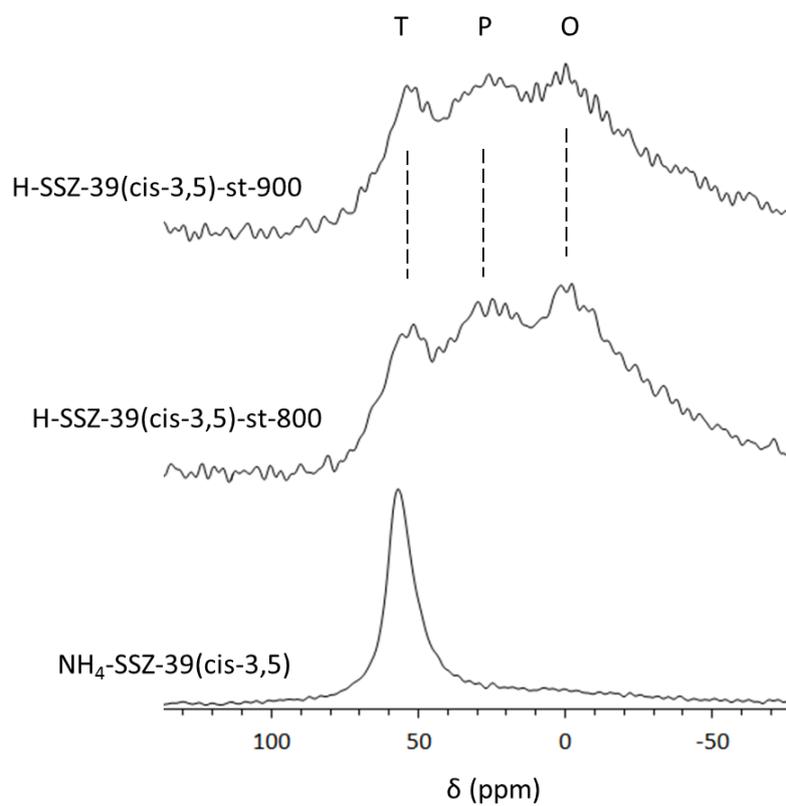


Figure S3: ^{27}Al -NMR of control MTO catalyst and 2 steamed materials of Fig S1 (cis-3,5 OSDA).

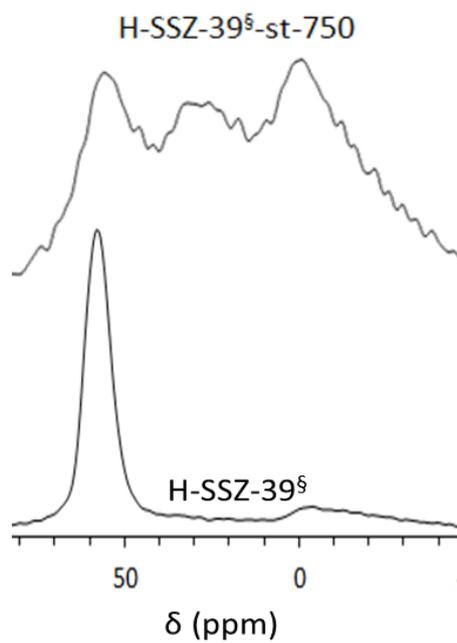


Figure S4: ^{27}Al -NMR of the control MTO catalyst and the steamed material of Fig S2 ($\S = \text{cis-2,6}$).

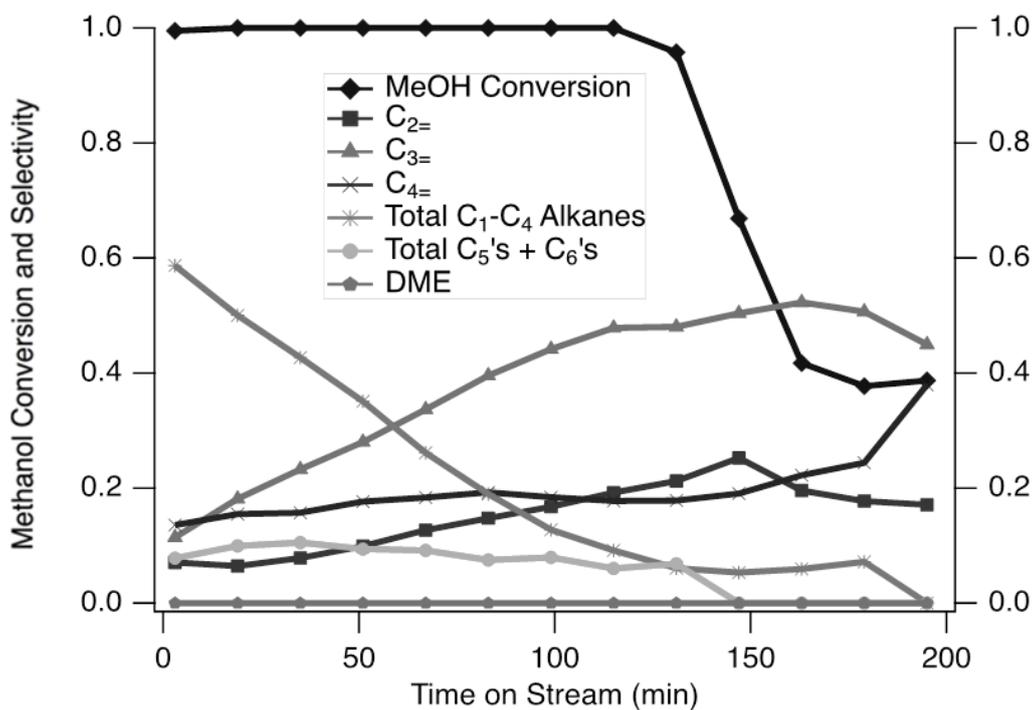


Figure S5: MTO results for the control H-SSZ-39 material of Fig. S1 (made with cis-3,5 OSDA).

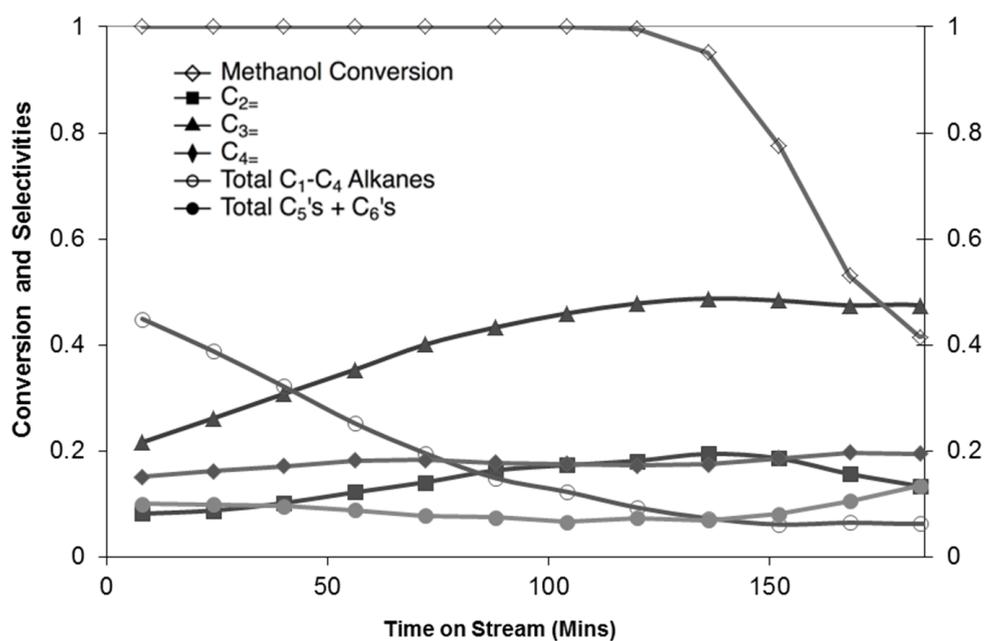


Figure S6: MTO results for the control H-SSZ-39⁸ material of Fig. S2 (made with cis-2,6 OSDA).

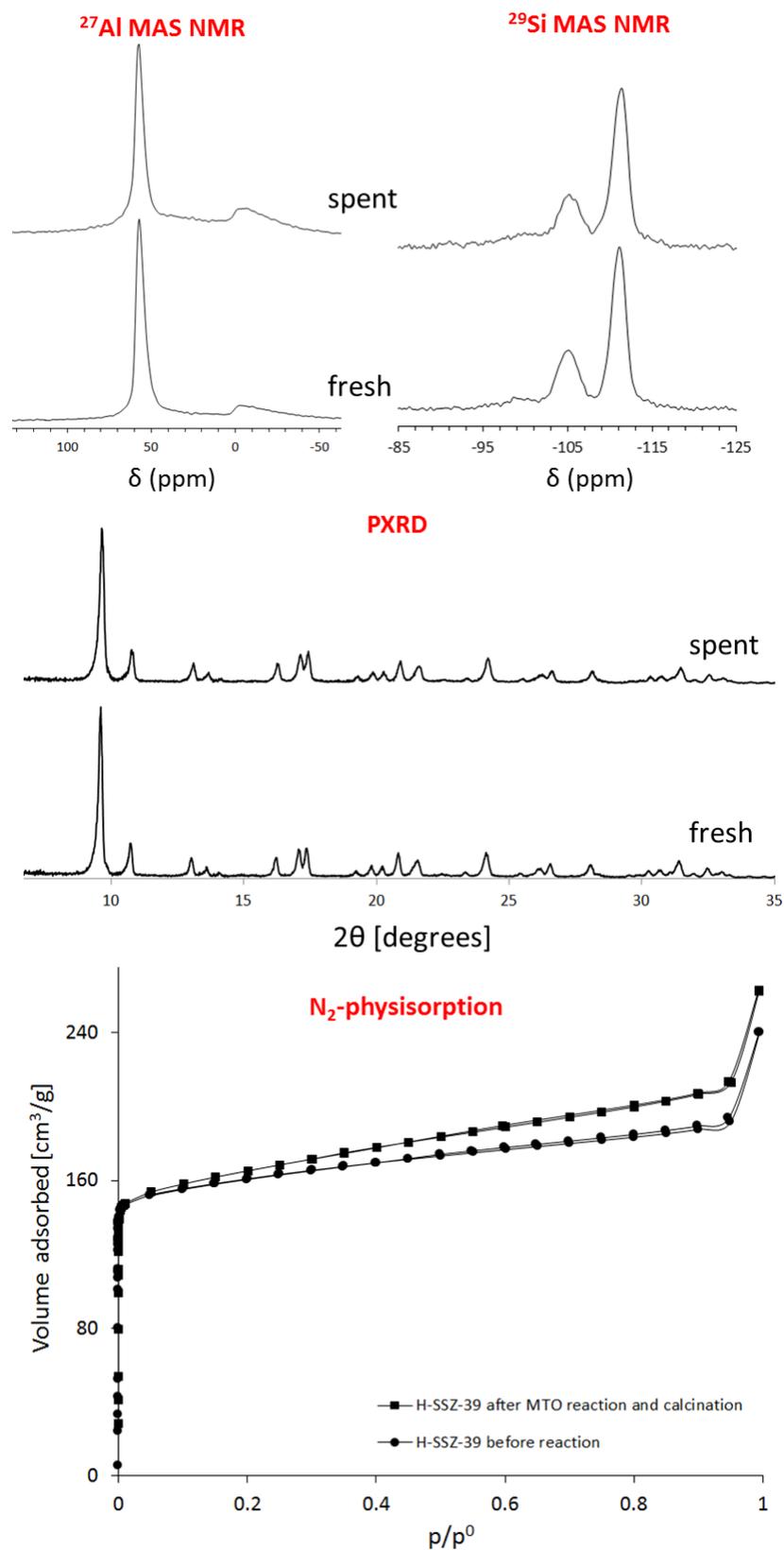
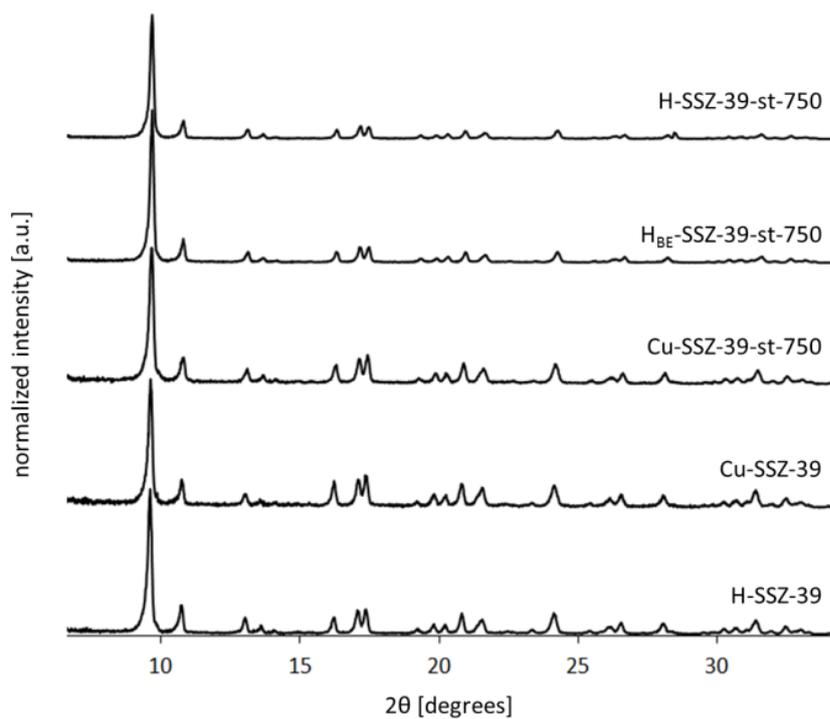


Fig. S7: Comparing PXRD, ^{29}Si , ^{27}Al -NMR patterns and physisorption before and after MTO reaction on H-SSZ-39 control (cis-trans-3,5 isomer, MTO results see main manuscript Fig. 1). All characterization of spent-catalyst performed after calcination.

A) overview



B) Detailed comparison between H-SSZ-39 and H-SSZ-39-st-750.

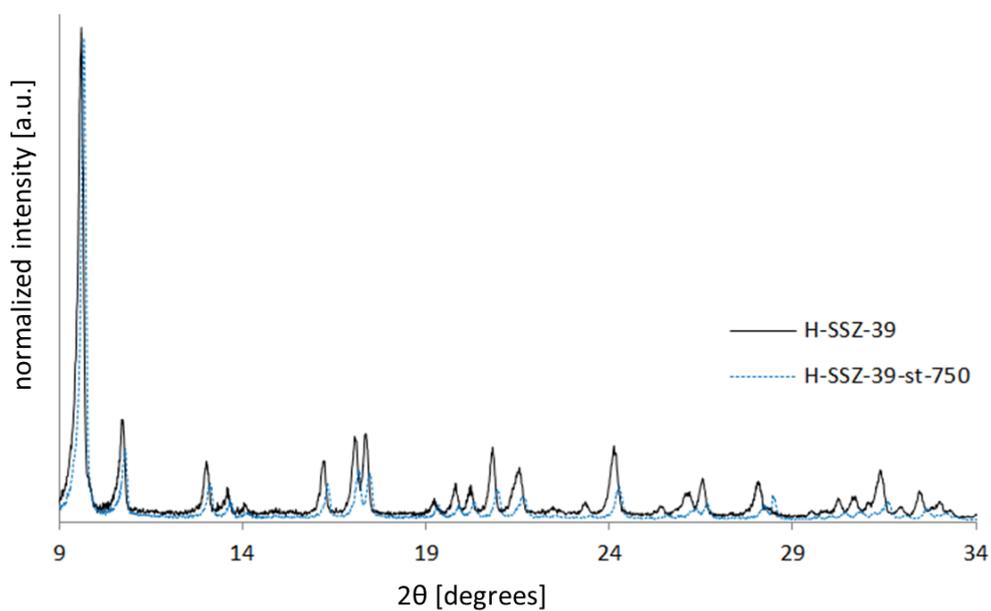


Fig. S8 PXRD patterns for the series of SSZ-39 materials described in Fig. 2 of the main paper.

Such significant shifts were not seen for any of the other materials of the design of experiment (Fig.2, main manuscript). The shift toward higher 2theta values indicates a shrinking unit cell, confirming the Al T-atom removal by Al and Si NMR.

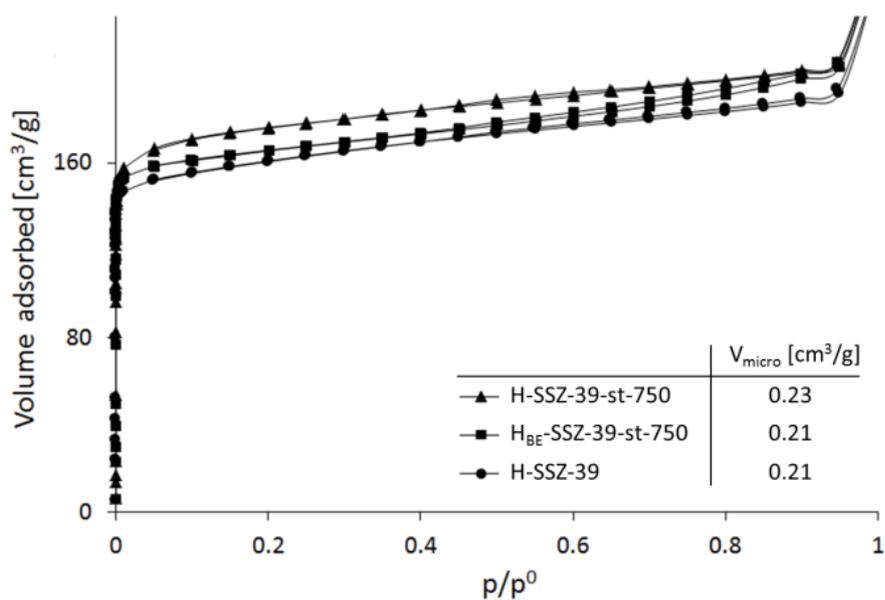


Fig. S9. N_2 -physorption isotherms for patterns for as-made, back-exchanged and steamed samples of SSZ-39 as described in Fig. 2.

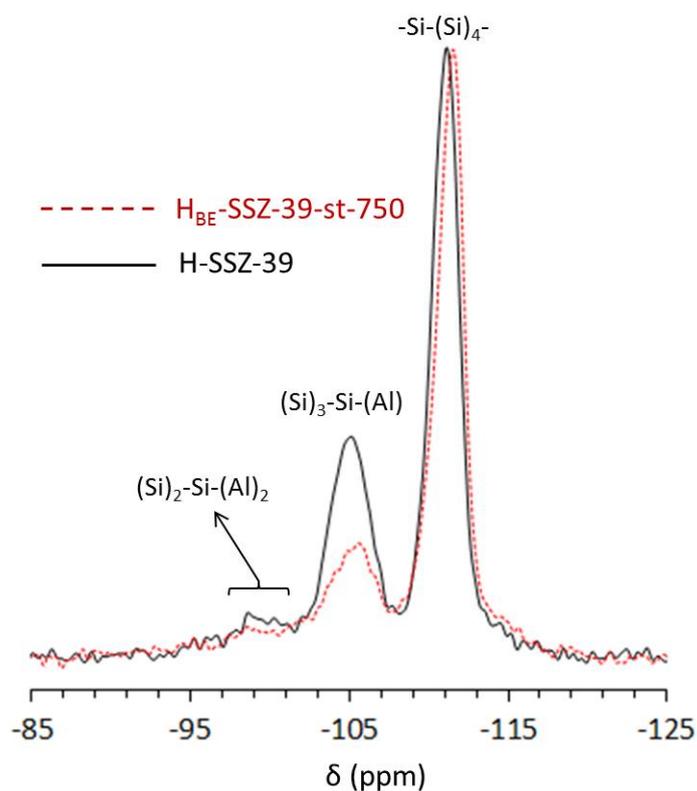


Fig. S10: Detailed comparison of ^{29}Si NMR of H-SSZ-39 and H_{BE} -SSZ-39-st-750, normalized on $\text{Si}-(\text{Si})_4$ -signal (of main manuscript Fig. 3, cis-trans-3,5 synthesis, Si/Al 8-8.5).

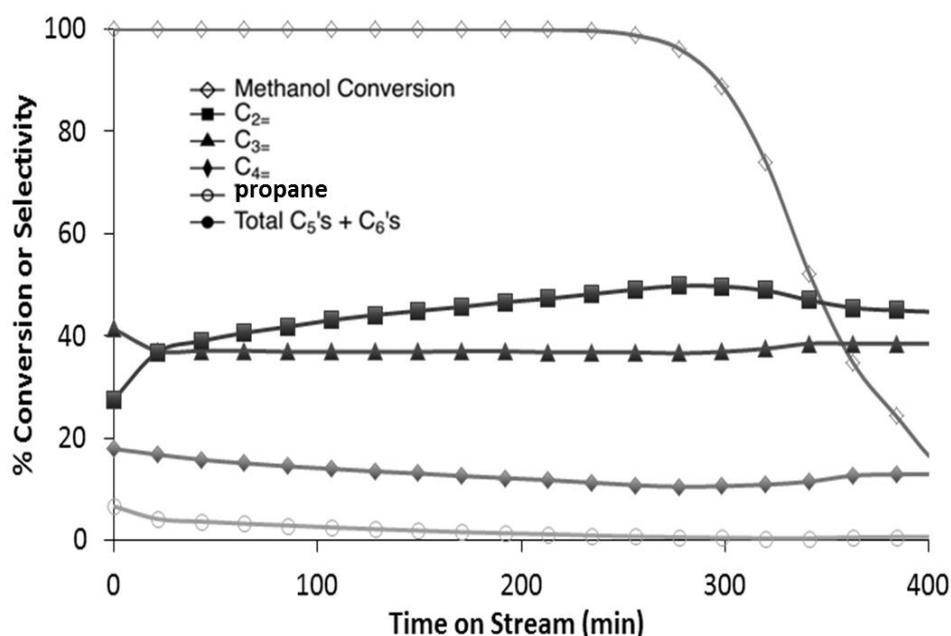


Figure S11: MTO results of an SSZ-13 (CHA) zeolite with Si/Al 55, made with trimethyladamantammonium hydroxide as OSDA. Details, see Deimund, M. A.; Harrison, L.; Lunn, J. D.; Liu, Y.; Malek, A.; Davis, M. E., 'Effect of Heteroatom Concentration in SAPO-34 and SSZ-13 on the Methanol-to-Olefins Reaction' in revision stage at ACS Catalysis 2015. Note the different propylene/ethylene/butylene distribution with Fig. 4 in the main manuscript.

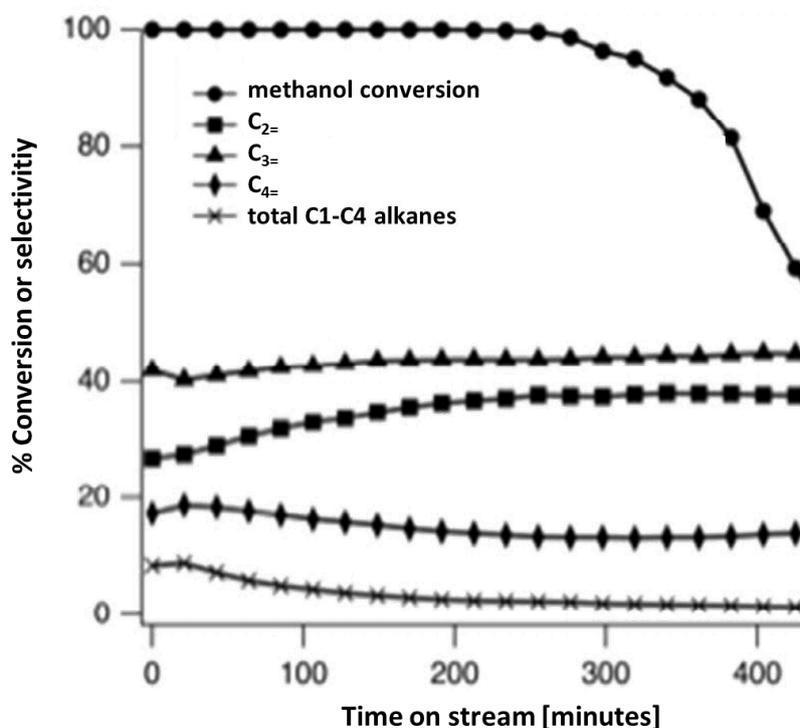


Figure S12: MTO results of a SAPO-34 (CHA) catalyst with Si/(Si+P+Al) = 0.12. Synthesis details, see reference in Fig. S11.

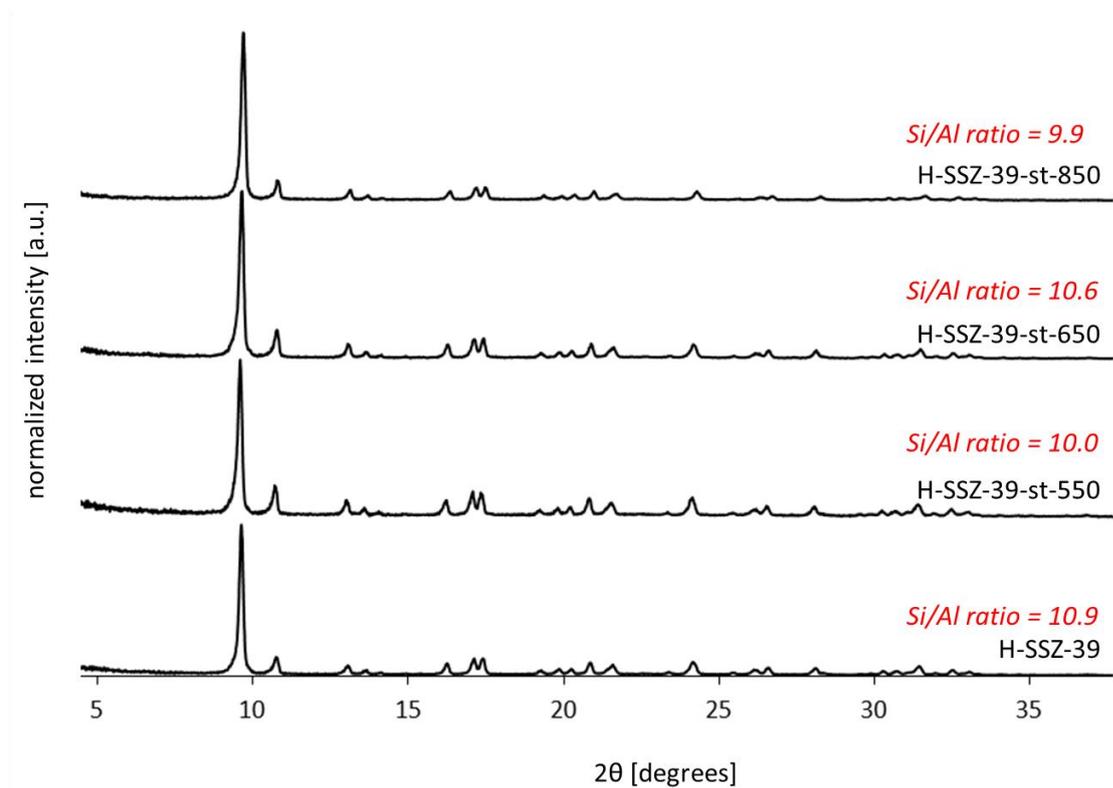


Figure S13: PXRD and Si/Al ratios of second batch of SSZ-39 made with cis-trans-3,5-dimethylpiperidinium hydroxide OSDA and its steaming series. (NMR data, see main manuscript).

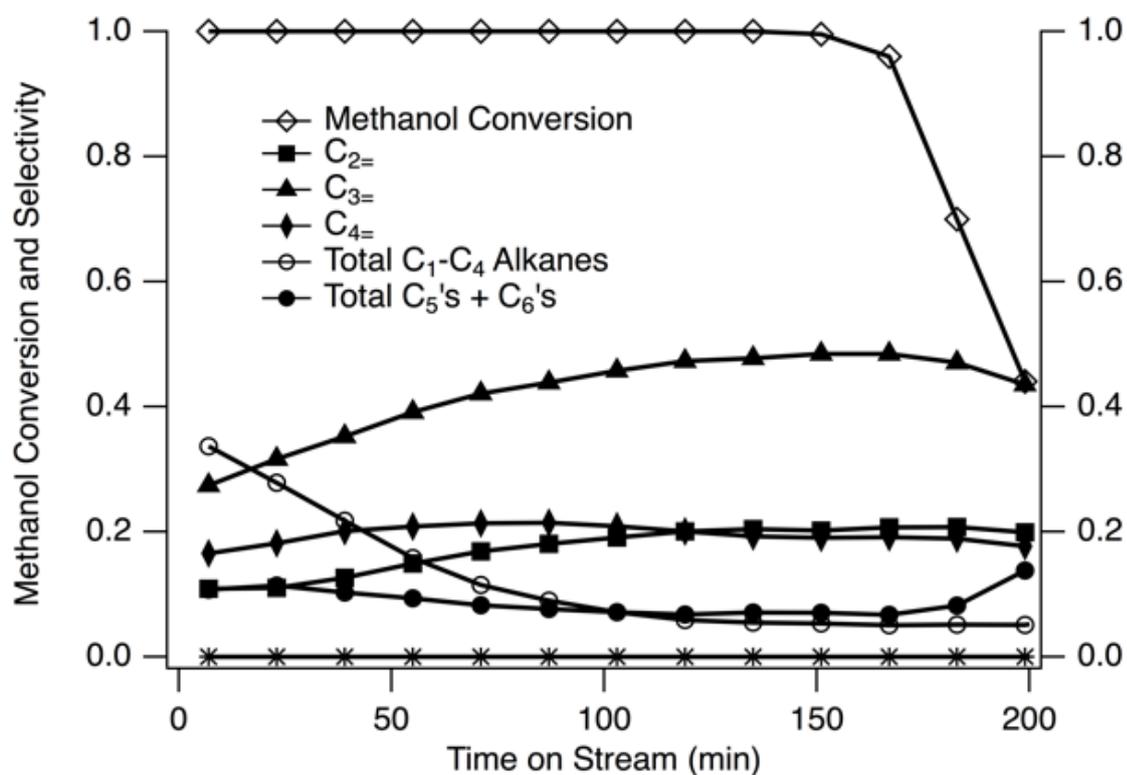


Figure S14: MTO result for the material of Fig S12, steamed at 550 °C (cis-trans-3,5-OSDA).

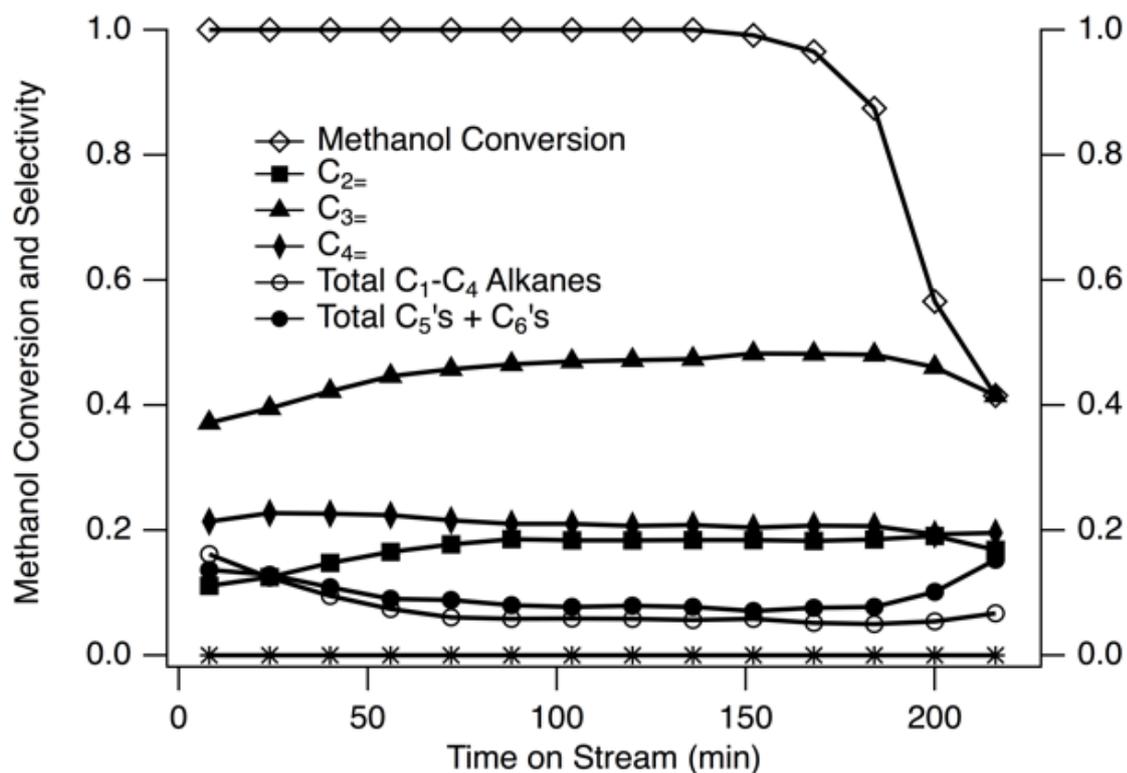


Figure S15: MTO results for the steamed series of Fig S12, steamed at 650 °C (cis-trans-3,5-OSDA).

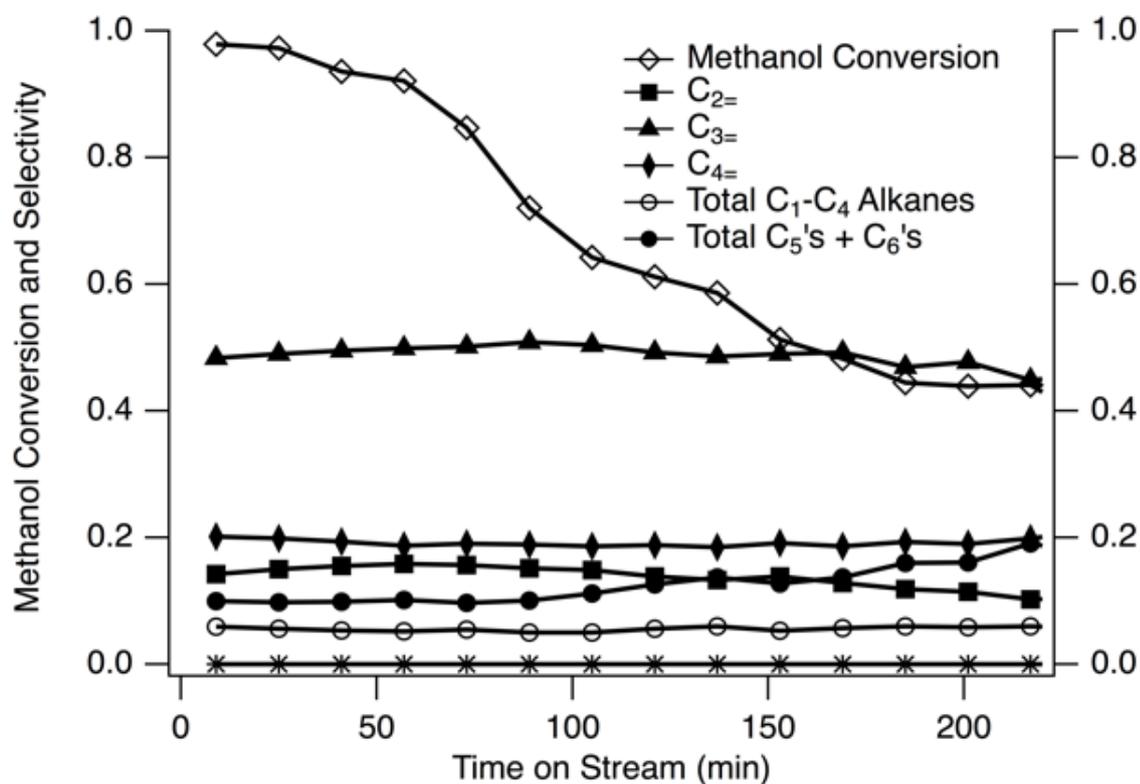


Figure S16: MTO results for the steamed series of Fig S12, steamed at 850 °C (cis-trans-3,5-OSDA).

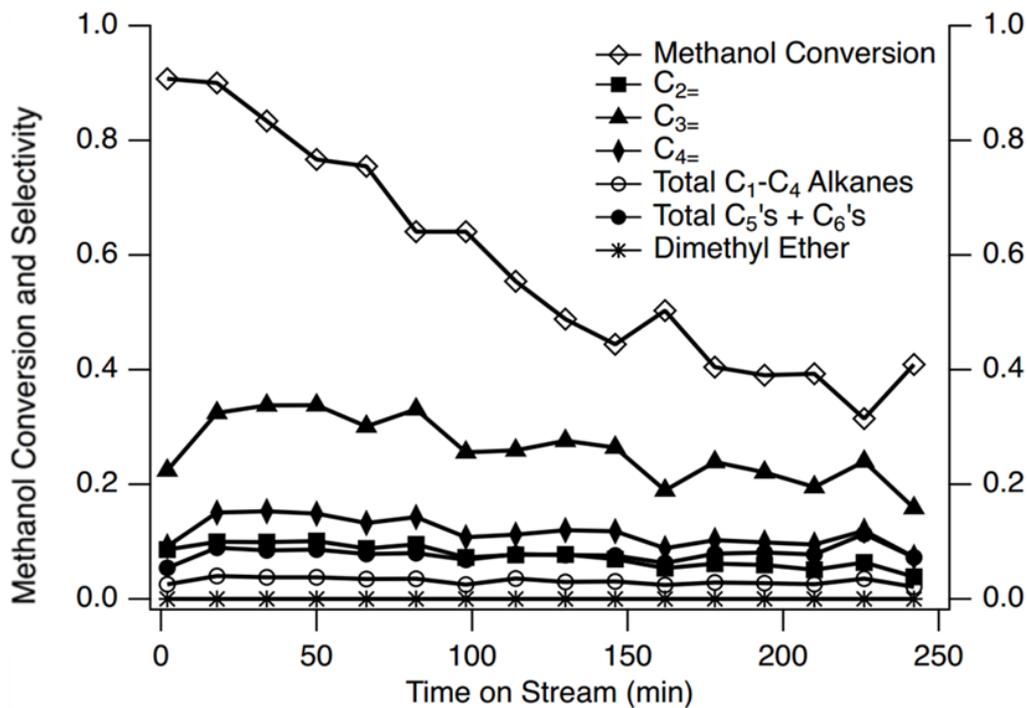


Figure S17: MTO results for the material of Fig. S1 after steaming at 900 °C (cis-3,5-OSDA): H-SSZ-39(cis-3,5)-st-900

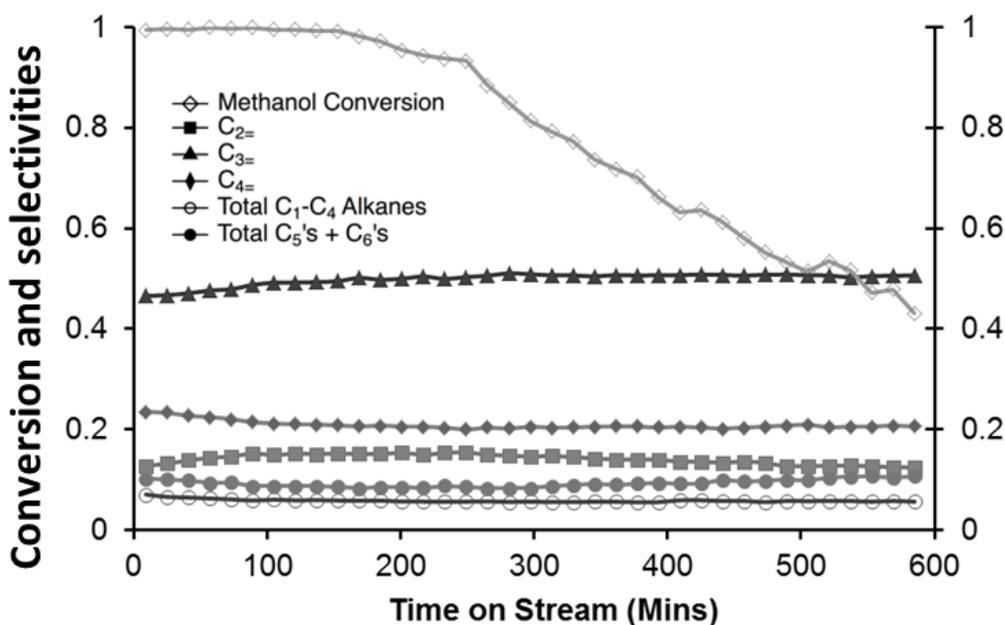


Figure S18: MTO results for the material of Fig. S1 after steaming at 750 °C (cis-3,5-OSDA).

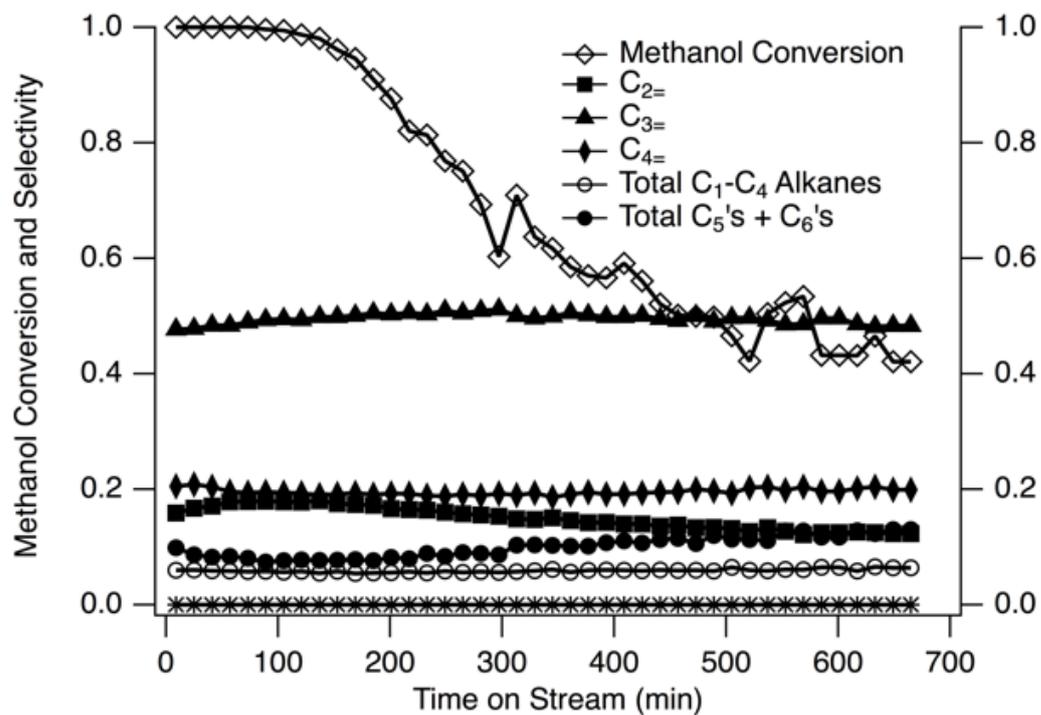


Figure S19: MTO results for the material of Fig. S2 after steaming at 750 °C (cis-2,6-OSDA): H-SSZ-39^s-st-750).

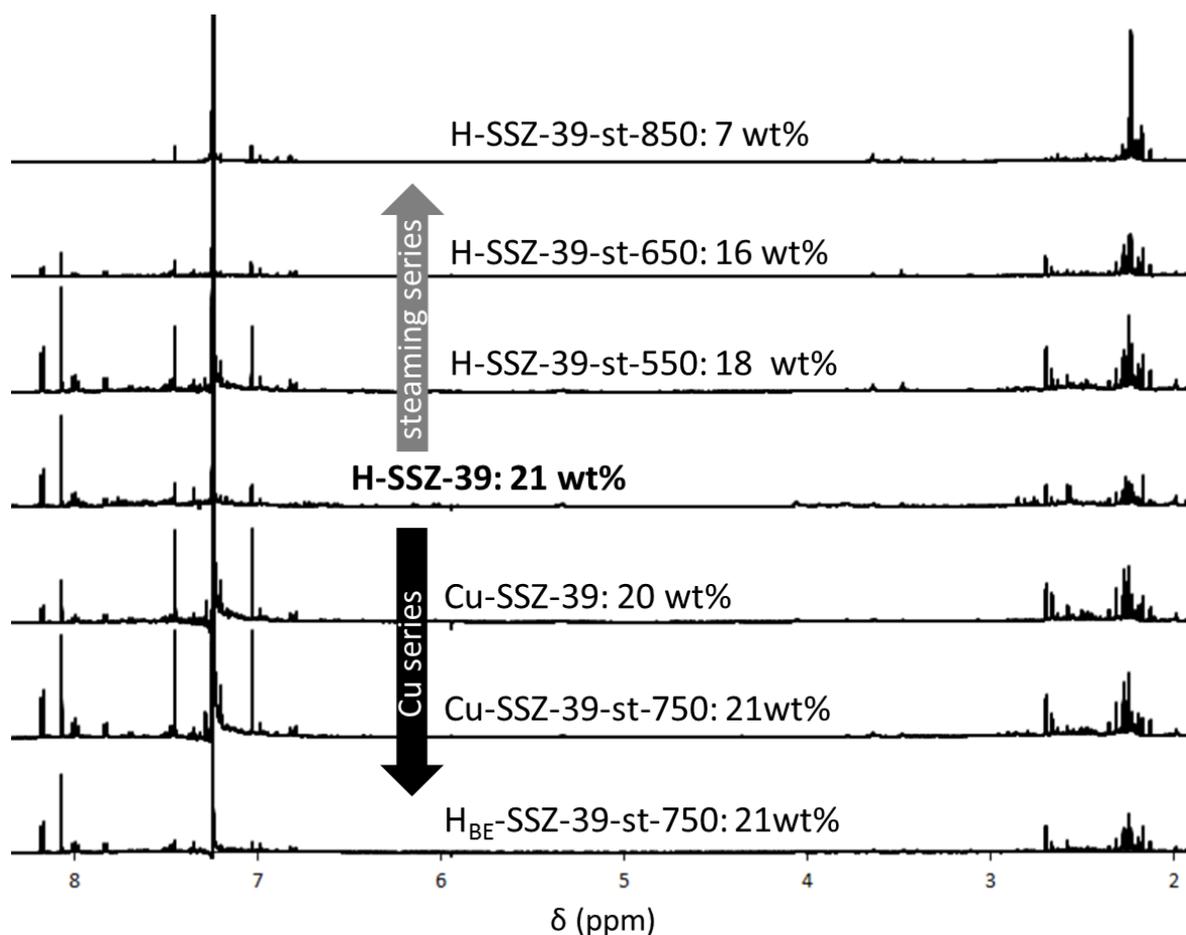


Figure S20. $^1\text{H-NMR}$ analysis of the hydrocarbons occluded in different SSZ-39 samples after MTO reaction and acid digestion, CDCl_3 solvent peak at 7.26 ppm. Amount of coke from TGA (mass loss over 300 $^\circ\text{C}$, relative to the zeolite weight left at 900 $^\circ\text{C}$) indicated.

We analyzed the hydrocarbon fraction occluded in the zeolites after reaction by TGA and by $^1\text{H-NMR}$ (after dissolution of the aluminosilicate framework) in search for influences of the different alkane and olefin production profiles on the amount and nature of the deactivating carbon-containing species deposited. Both the Cu series of Fig. 2 was tested, as well as selected steamed samples. MTO reactions were usually halted when the conversion of methanol dropped below 50%. First, TGA analysis (indicated in Fig. S19) showed that the spent control, H-SSZ-39, was completely filled with organic material (21 wt%). The Cu-series all showed similar coke content, in line with their mid-level alkane make. The extraction experiments confirmed these trends, as peaks in the 7 - 8.3 ppm region, attributed to aromatic species extracted from the cages, were clearly present. Peaks in the 2-3 ppm region are usually attributed to protons of methyl, ethyl or propyl groups on aromatic rings (see M. Deimund, J. Schmidt and M. Davis, *Top. Catal.*, **2015**, 1-8). The steamed series showed that only few aromatic signals were found for the H-SSZ-st-850 material. Likely, this material deactivates fast due to its lack of sufficient active sites ($\text{Si}/\text{Al}_\text{T} > 100$). This is corroborated by TGA, as only 7 wt% of organic material was found, which indicates that not all cages have participated in the hydrocarbon pool mechanism and thus MTO catalysis. The material steamed at 550 $^\circ\text{C}$ showed a similar coking pattern as the control, in line with its similar ^{27}Al NMR spectra (Fig. 6), while the 650 $^\circ\text{C}$ material showed relatively few aromatics but still 16 wt% of organic material. A material steamed at 750 $^\circ\text{C}$ (Fig. S18, cis-2,6) had 13 wt%. It is likely that the mode of deactivation in the case of better performing MTO catalysts is linked to different species.

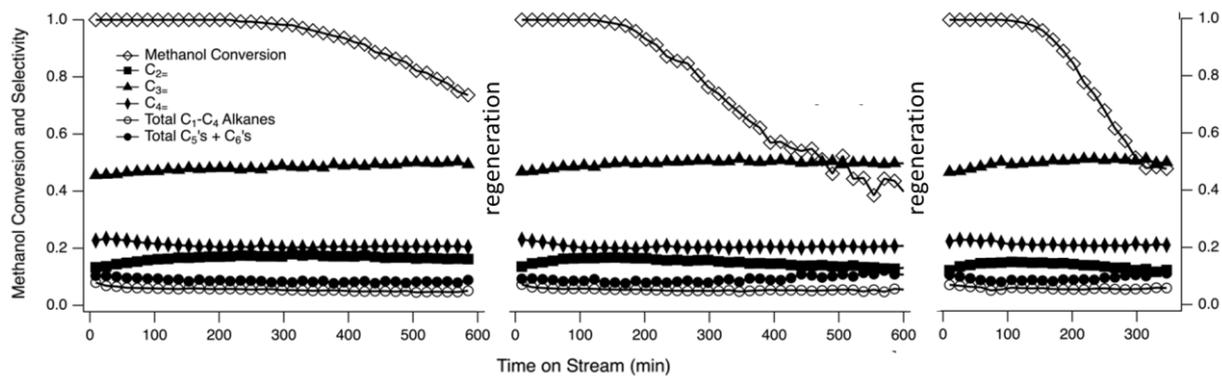


Figure S21. Time on stream plot of three consecutive reactions with H-SSZ-39-750 (cis-trans-3,5 synthesis) with non-optimal, breathing-air calcination at 580 °C