## **Electronic Supplementary Information (ESI)**

# Fluoride-assisted synthesis of bimodal microporous SSZ-13 zeolite

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# **Experimental Section**

### 1. Synthesis of zeolites

Hierarchical SSZ-13 zeolites were synthesized as follows: sodium hydroxide (EMSURE, 50 wt%), TMAdaOH (SACHEM Inc. 25 wt%) were mixed in deionized water and stirred for 10 min, to the template solution aluminium hydroxide (Aldrich, reagent grade) and sodium fluoride (EMSURE,  $\geq$ 99.5 %) were added and then stirred for another 30 min. Ludox AS 40 (Aldrich, 40 wt%) was added quickly into the clear solution. The final gel has a molar composition of 20 TMAdaOH : 7.5 Na<sub>2</sub>O : 2.5 Al<sub>2</sub>O<sub>3</sub> : 100 SiO<sub>2</sub> : x NaF : 4400 H<sub>2</sub>O (x = 0, 5, 10, or 20). After vigorous stirring at room temperature for 2 h, the resulting gel was transferred into a 45 mL Teflon lined steel autoclave and crystallized at 160 °C for 10 days. The obtained solids are denoted as SSZ-13-xF with x = 0, 5, 10, or 20. The conventional SSZ-13 was prepared from the same gel without NaF and crystallized at 160 °C for 6 days. After crystallization, the zeolite products were filtered, washed with distilled water and dried in air at 110 °C. The zeolites were calcined at 550 °C for 10 h under flowing air and subsequently ion-exchanged three times with 1.0 M NH<sub>4</sub>NO<sub>3</sub> solutions followed by calcination at 550 °C for 4 h in flowing air in order to obtain their proton forms.

### 2. Characterization

**Basic characterization:** X-ray diffraction patterns were recorded on a Bruker D4 Endeavor diffractometer using Cu K $\alpha$  radiation in the 2 $\theta$  range of 5–60°. Elemental analyses were carried out by ICP-OES on a Spectro Ciros CCD ICP optical emission spectrometer with axial plasma viewing, samples were digested in a mixture of HF/HNO<sub>3</sub>/H<sub>2</sub>O. Surface area and porosity of zeolites were determined by Argon physisorption at –186 °C on a Micromeritics ASAP 2020 instrument in static mode. The samples were outgassed at 400 °C for 8 h prior to the sorption measurements. Langmuir surface area of SSZ-13 zeolite was obtained in the relative pressure range ( $p/p_0$ ) of 0.05–0.20, the total pore volume was calculated at  $p/p_0$ = 0.97, the mesopore volume and the micropore volume were calculated from the *BJH* method and the *t*-plot method (thickness range 0.336–0.380 nm), respectively. The micropore size distribution and diameter was calculated by the NLDFT model. Use was made of the model for Ar on oxides in cylindrical pores at –186 °C. Regularization was not applied.

**Electron microscopy:** Scanning electron microscopy (SEM) images were taken on a FEI Quanta 200F scanning electron microscope at an accelerating voltage of 3 kV. The zeolites were coated with gold prior to measurements. FIB-SEM measurements were performed on a Helios NanoLab 650. The samples were coated with a layer of gold prior to focused ion beam (FIB) milling. The FIB uses gallium ions, in the rough milling step for which the accelerating voltage and the current were set to 30 kV and 65 nA, respectively. The fine milling on the chosen crystal of SSZ-13-0F was carried out at 30 kV and 0.43 nA. In the case of the SSZ-13-10F crystal, the settings for polishing were 30 kV and 0.3 nA. The EDX line scan was performed with an Ametec-EDAX EDX system. Transmission electron microscopy (TEM) images of SSZ-13 zeolite crystals were acquired using a FEI Tecnai 20 (type Sphera) transmission electron microscope operating at 200 kV with a LaB<sub>6</sub> filament. Prior measurement the samples were suspended in ethanol and dispersed over a Cu grid with holey carbon film.

**Thermogravimetric analysis:** The carbonaceous deposits formed during MTO were analyzed by thermogravimetric analysis (TGA) on TGA/DSC 1 STAR system of Mettler Toledo. The temperature was increased to 850 °C at a rate of 5 °C min<sup>-1</sup> under flowing air (50 ml min<sup>-1</sup>). The weight loss between 300 °C and 600 °C was considered as the total carbonaceous deposit content. To evaluate differences in diffusion in zeolites, methanol, propylene, *n*-butanol, *i*-butanol, and oxylene adsorption was performed on TGA apparatus at 30 °C. The samples were dehydrated at 550 °C before the exposure. For the liquid adsorbents, a He flow was led through a thermostated saturator. The gaseous adsorbents were mixed with a He flow. The partial pressures of the adsorbents were 2.8 mbar for methanol, 6.9 mbar for *n*-butanol, 4.3 mbar for *i*-butanol, 10 mbar for *o*-xylene, 47 mbar for propylene.

**FT-IR spectroscopy:** FT-IR spectra of samples were recorded on a Bruker Vertex 70v instrument. The spectra were acquired at 2 cm<sup>-1</sup> resolution and 64 scans. The samples were prepared as thin wafers of ~ 10 mg and placed inside a controlled environment infrared transmission cell, capable of heating and cooling, gas dosing and evacuation. For CO adsorption, the wafer was heated to 550 °C at a rate of 10 °C min<sup>-1</sup> under evacuation. Subsequently, the sample was cooled to -196 °C. CO (Praxair, 99.999 %) was introduced into the sample cell via a sample loop (5 µL) connected to a Valco six-port valve. FT-IR spectra of propylene were performed at 30 °C and a 10 µL sample loop was used. IR Spectra were normalized by the weight of catalyst wafer.

**NMR spectroscopy:** Nuclear Magnetic Resonance (NMR) spectra were recorded on an 11.7 Tesla Bruker DMX500 NMR spectrometer, operating at 500 MHz for <sup>1</sup>H, 470 MHz for <sup>19</sup>F, 99 MHz for <sup>29</sup>Si, and 132 MHz for <sup>27</sup>Al measurements. <sup>27</sup>Al MAS NMR was performed using a Bruker 2.5 mm MAS probe head spinning at 20 kHz. The MAS NMR measurements were carried out using a 4 mm MAS probe head with sample rotation rates of 10 kHz for <sup>1</sup>H and <sup>19</sup>F, and 5-8 kHz for <sup>29</sup>Si NMR measurements, respectively. The <sup>1</sup>H measurement was carried out using a 4 mm MAS probe head with sample rotation rate of 10 kHz. Quantitative <sup>29</sup>Si NMR spectra were recorded using a high power proton decoupling direct excitation (DE) pulse sequence with a 54° pulse duration of 3 µs and an interscan delay of 120 s. Higher interscan delay did not show any significant increase in signal intensity. <sup>19</sup>F MAS NMR spectra were recorded applying a Hahn-echo pulse sequence and a delay time of 5 s. <sup>27</sup>Al 3QMAS NMR spectra were recorded by use of the three-pulse sequence  $p_1-t_1-p_2-\tau-p_3-t_2$  for triple-quantum generation and zero-quantum filtering (strong pulses  $p_1 = 3.4 \mu s$  and  $p_2 = 1.4 \mu s$  at  $v_1 = 100 \text{ kHz}$ ; soft pulse  $p_3 = 11 \mu s$  at  $v_1 = 8 \text{ kHz}$ ; filter time  $\tau = 20 \mu s$ ; interscan delay 0.2 s). <sup>1</sup>H NMR spectra were recorded with a Hahn-echo pulse sequence  $p_1-\tau_1-p_2-\tau_2$ -aq with a 90° pulse  $p_1 = 5 \ \mu s$  and a  $180^{\circ}$  p<sub>2</sub> = 10 µs. The interscan delay was set to 120 s for quantitative spectra. <sup>1</sup>H NMR shifts were calibrated using tetramethylsilane (TMS) and a saturated aqueous Al(NO<sub>3</sub>)<sub>3</sub> solution was used for <sup>27</sup>Al NMR shift calibration.

In-situ visible light microspectroscopy: The measurements were performed on an Olympus BX41 upright microscope using a 50 × 0.5 NA long working distance microscope objective lens. A 75 W tungsten lamp was used for illumination. In addition, the microscope has a 50/50 double viewport tube, which accommodates a CCD video camera (ColorViewIIIu, Soft Imaging Systems GmbH) and an optical fibre mount. A 200  $\mu$ m core fibre connects the microscope to a CCD Vis spectrometer (AvaSpec-2048TEC, Avantes BV). The in-situ Vis measurements were conducted in a Linkam FT-IR 600 in-situ cell. A pinch of the zeolite crystals were placed in the in-situ cell and exposed to a methanol containing nitrogen flow at a total flow rate of 10 ml min<sup>-1</sup>. The reaction temperature was 350 °C. In this geometry, we cannot accurately determine the weight hourly space velocity in this configuration, but it is expected to be much higher than in the fixed-bed catalytic activity measurements. Before the MTO reaction, the catalysts were heated to 550 °C in 50 ml min<sup>-1</sup> N<sub>2</sub> flow with a rate of 10 °C min<sup>-1</sup> and kept for 1 h. Then the temperature was lowered to 350 °C and methanol was introduced to the in-situ cell by leading a

flow of 10 ml min<sup>-1</sup>  $N_2$  through liquid methanol kept at room temperature. The resulting spent samples were further investigated by confocal fluorescence microscopy.

**Confocal fluorescence microscopy:** For the confocal fluorescence microscopy, a Nikon Eclipse LV150 upright microscope with  $50 \times 0.55$  NA dry objective was used for fluorescence microscopy studies. Fluorescence microphotographs were collected using 510–700 nm excitation light from a mercury source. Confocal images were acquired with a Nikon D-Eclipse C1 head connected to 488, 561, and 635 nm excitation lasers. The emission was detected in the ranges 510–550 nm, 570–620 nm, and 662–737 nm, respectively. For the confocal images of SSZ-13 samples after the exposure to propylene, the excitation wavelength of the laser is 561 nm and detection was in the 570–620 nm range. Thiophene oligomerization reactions were performed on the heating element of a Linkam in-situ cell. The samples were heated at 120 °C for 5 min. Subsequently, 15 µl of thiophene was added and then heating was stopped after 10 s. The fluorescent light in the range 570–620 nm.

#### 3. Molecular modelling

A sorption isotherm was modelled using Materials Studio v6.0 (BIOVIA, formerly Accelrys) to estimate the occupation of the CHA cages by Ar atoms using a periodic box consisting of  $2\times2\times2$  CHA unit cells. Charge assignment using the QEq method was combined with the use of the Universal Forcefield and Metropolis algorithm at Fine quality. The temperature was set to -188 °C and the fugacity range was 0 to 5000 kPa. The total loading fluctuated between 48 to 49 Ar atoms – though a loading of 49 became dominant at higher fugacity. It was found that Ar atoms adopt an octahedral geometry in every cage. The same settings were used to create the Ar-loaded CHA periodic structure of  $2\times2\times2$  unit cells.

The Ar-loaded model was used to calculate the distances between different Ar atoms within the same channel – *i.e.* looking through the 8MR windows. For instance, the *x*- and *y*-positions were independently determined in the *xy*-plane yielding the distances  $\Delta x$  and  $\Delta y$  between pairs of Ar atoms. The Van der Waals radius of Ar (1.88 Å) was added twice to the obtained distance, because  $\Delta x$  and  $\Delta y$  only yield core-to-core distances which would in this way significantly underestimate the channel diameter. The procedure of measuring distances and correcting for the Van der Waals radius of Ar was done for eight different pores – four in the *xz* plane and four in

the yz plane – yielding an average of 4.96 Å for the 16 different obtained diameters. This was all done under the assumption that either  $\Delta z$  and  $\Delta x$  (xz-plane) or  $\Delta z$  and  $\Delta y$  (yz-plane) intersect each other at the centre of the channel. This simplification will slightly underestimate the pore diameter. See also Figure S11 for a schematic overview of the procedure.

#### 4. Catalytic tests

The proton form zeolites was pressed into pellets, and then crushed and sieved to obtain particles ranging in size from 250 to 500  $\mu$ m. Catalytic activity measurements were carried out in a quartz tubular fixed-bed reactor with 50 mg catalyst loading. The inner diameter of the quartz tube reactor was 4 mm. The catalyst lifetime is defined as the time to reach a conversion of 50 % ( $t_{50}$ ). Here, the time at which conversion has decreased to 98 % ( $t_{98}$ ) is also employed, as this is more relevant to commercial practice. Before reaction, the catalysts were activated at 550 °C in synthetic air (30 ml min<sup>-1</sup>) for 2 h. The methanol-to-olefins reaction was performed at 350 °C. Methanol (Merck, 99 %) was introduced to the reactor by leading a flow of 30 ml min<sup>-1</sup> of He through a saturator kept at -17.2 °C. The resulting WHSV is 0.8 g g<sup>-1</sup> h<sup>-1</sup>. The product effluent was analysed online by gas chromatography (Compact GC Interscience equipped with TCD and FID detectors with RT-Q-Bond and Al<sub>2</sub>O<sub>3</sub>/KCl columns). The reaction was followed for 24 h. Methanol conversion is based on the inlet and outlet concentrations of methanol as determined by GC analysis of the reactor feed before and after the reaction and the reactor effluent during reaction. Dimethylether was considered as a reactant in these calculations.



**Figure S1.** XRD patterns of as-synthesized (a) SSZ-13-0F, (b) SSZ-13-5F, (c) SSZ-13-10F, and (d) SSZ-13-20F. \* Impurity quartz.



**Figure S2.** SEM images taken at different magnifications of (a, e, and i) SSZ-13-0F, (b, f, and j) SSZ-13-5F, (c, g, and k) SSZ-13-10F, and (d, h, and l) SSZ-13-20F. TEM images taken at different magnifications of (m, n) SSZ-13-R and (o, p) SSZ-13-10F.



**Figure S3.** <sup>19</sup>F MAS NMR spectra of as-synthesized SSZ-13-10F (green) and calcined SSZ-13-10F zeolite (black). The resonance at -63 ppm is due to F in the D6R cages of the CHA structure as reported before for SSZ-13 synthesized with TMAda<sup>+</sup> in the presence of fluoride at neutral pH.<sup>1</sup> The resonance at  $\sim -121$  ppm is due to free fluoride anions present in the zeolite. Solid NH<sub>4</sub>F and NaF give rise to a single line at  $\sim -116$  ppm and -126 ppm, respectively.<sup>2,3</sup>



**Figure S4.** Methanol conversion versus cumulative amount of methanol that has been converted to hydrocarbons. Extrapolation to zero methanol conversion gives the total methanol conversion capacity for SSZ-13-0F ( $\blacksquare$ ), SSZ-13-5F ( $\blacktriangle$ ), and SSZ-13-10F ( $\bigcirc$ ).



**Figure S5.** Time-resolved in-situ visible light microspectroscopy of (a, b, and c) SSZ-13-0F and (d, e, and f) SSZ-13-10F taken during the MTO reaction at 350 °C. All time-resolved spectra were deconvoluted into two main spectral features (b and e; the black line represents mostly polymethylated benzenes and the red line stands for bulkier multi-ring aromatics) and the evolution of those spectral features with increasing time on stream (c and f) by non-negative matrix factorization analysis.



**Figure S6.** <sup>27</sup>Al MAS NMR spectra and <sup>29</sup>Si MAS NMR spectra of SSZ-13-0F and SSZ-13-10F. The spectra were normalized by the weight of the samples.



**Figure S7.** (a) Decomposition of the different peaks of <sup>1</sup>H MAS NMR spectra of SSZ-13-0F. The spectra was normalized by the weight of the catalyst. (b) Proton T2 filtered spectra of dehydrated SSZ-13-0F at varied echo times 2t = 0.05, 2, 8, 16, 32, and 64 ms (from top to bottom). From the filtered spectra at higher 2t times can be clearly seen that the silanol signal consists of two peaks at 2.0 and 1.8 ppm which are assigned as internal and external silanols, respectively.



**Figure S8.** (left) Hydroxyl and (right) CO stretch regions of FTIR spectra of (a, b) SSZ-13-0F and (c, d) SSZ-13-10F as a function of the CO coverage. The spectra were normalized by the weight of the catalysts.



Figure S9. EDX line scan (Si and Al signals) of FIB cuts of (a) SSZ-13-0F and (b) SSZ-13-10F.



**Figure S10.** (a) High resolution Ar physisorption isotherms of ( $\blacksquare$ ) SSZ-13-0F, ( $\blacktriangle$ ) SSZ-13-5F, and ( $\bigcirc$ ) SSZ-13-10F. (b) All the samples have similar mesopore size distributions. (c) The micropore size distribution analyzed by the NLDFT method points to additional microporosity with a size of ~ 0.5 nm. The native micropore system of SSZ-13 zeolite that is composed of 0.92 nm supercages separated by 0.38 nm apertures gives rise to on average 0.54 nm micropores as also confirmed by molecular simulations.



Figure S11. Molecular modelling. Note that the CPK values of Ar have been downscaled for esthetic reasons.



**Figure S12.** (a) Methanol, (b) *n*-butanol, (c) *i*-butanol, and (d) *o*-xylene uptake experiments performed at 30 °C on zeolite samples ( $\blacksquare$ ) SSZ-13-0F and ( $\bullet$ ) SSZ-13-10F. The samples were dehydrated before the adsorption. Extrapolation of linear part of the uptake curve to zero time gives the initial uptake.



**Figure S13.** (a) Propylene uptake experiments performed at 30 °C on zeolite samples ( $\blacksquare$ ) SSZ-13-0F and ( $\bullet$ ) SSZ-13-10F. The samples were dehydrated before the adsorption. (b) Infrared spectra of SSZ-13-0F and SSZ-13-10F after prolonged propylene exposure at 30 °C (bands at 2962 cm<sup>-1</sup>, 2937 cm<sup>-1</sup>, 2871 cm<sup>-1</sup>, 1466 cm<sup>-1</sup>, and 1380 cm<sup>-1</sup> are due to olefinic oligomers). Confocal fluorescence micro-photographs of (c) SSZ-13-0F and (d) SSZ-13-10F crystals collected after uptake of propylene. Images c and d, in false colours, were taken in the middle plane of single crystals. The excitation wavelength of the laser is 561 nm and detection was in the 570-620 nm range.

Zeolite	Coke	$t_{50}^{a}$	$t_{00}^{b}$	$TCC^{c}$	Selectiv	vity (%)				
	(%)	(h)	(h)	$(g g^{-1})$	C <sub>1</sub>	$C_2^{=}$	C <sub>2</sub>	$C_3^{=}$	C <sub>3</sub>	$C_4 - C_6^{d}$
SSZ-13-0F	14.1	5.1	2.1	6.8	0.8	40.6	0.2	41.0	2.7	14.7
SSZ-13-5F	18.1	7.3	3.5	8.8	0.5	42.5	0.6	38.9	1.0	16.5
SSZ-13-10F	19.7	10.1	5.2	12.5	0.7	38.2	0.4	41.7	2.2	16.8

Table S1. Lifetime, product selectivity of MTO reaction after 1 h time on stream over SSZ-13 zeolites.

<sup>*a*</sup> lifetime is defined as the time to reach 50 % of methanol conversion;

<sup>b</sup> lifetime is referred to the time to reach 98 % of methanol conversion;

<sup>c</sup> total methanol conversion capacity.

<sup>*d*</sup> sum of olefins and paraffins selectivity.

Zeolite	Si/Al (ICP)	Si/Al <sup>a</sup> ( <sup>29</sup> Si NMR)	Al <sup>IV</sup> (%)	Al <sup>VI</sup> (%)
SSZ-13-0F	21	22	89	11
SSZ-13-10F	22	25	88	12

**Table S2.** Si/Al ratio determined by ICP-OES elemental analysis and the relative amount of Al species in zeolites was determined by <sup>27</sup>Al MAS NMR.

<sup>*a*</sup> deconvoluted according to the strategy outlined by Eilertsen et al.<sup>4</sup>

Zeolite	BAS		SiO	H <sub>external</sub>	SiOH <sub>internal</sub>		
	[d/ppm]	[mmol g <sup>-1</sup> ]	[d/ppm]	[mmol g <sup>-1</sup> ]	[d/ppm]	[mmol g <sup>-1</sup> ]	
SSZ-13-0F	4.0	0.65	1.8	0.55	2.0	0.22	
SSZ-13-10F	4.0	0.67	1.8	0.55	2.0	0.17	

 Table S3. Integrals of deconvoluted <sup>1</sup>H MAS NMR spectra of dehydrated SSZ-13-0F and SSZ-13-10F.

Zeolite	$S_{ m L}^{\ a}$	$V_{\rm tot}^{\ b}$	V <sub>meso</sub> <sup>c</sup>	V <sub>micro</sub> <sup>d</sup>
	$(m^2 g^{-1})$	$(cm^{3}g^{-1})$	$(cm^{3}g^{-1})$	$(\text{cm}^{3}\text{g}^{-1})$
SSZ-13-0F	677	0.24	0.02	0.20
SSZ-13-10F	763	0.28	0.03	0.23

Table S4. Textural properties of SSZ-13 zeolite samples.

<sup>*a*</sup>  $S_L$  is the Langmuir surface area obtained in the relative pressure range ( $p/p_0$ ) of 0.05–0.20;

<sup>*b*</sup>  $V_{\text{tot}}$  is the total pore volume at  $p/p_0 = 0.97$ ;

 $^{c}V_{meso}$  is the mesopore volume calculated by the *BJH* method;

 $^{d}V_{\text{micro}}$  is the micropore volume calculated by the *t*-plot method.

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