

Electronic Supplementary Information (ESI)

Nanocrystalline SSZ-39 zeolite as efficient catalyst for the Methanol-to-Olefins (MTO) process

Nuria Martín,¹ Zhibin Li,^{1,2} Joaquín Martínez-Triguero,¹ Jihong Yu,³ Manuel Moliner,^{1*}
Avelino Corma^{1*}

¹ Instituto de Tecnología Química (UPV-CSIC), Universidad Politécnica de Valencia,
Consejo Superior de Investigaciones Científicas, Valencia, 46022, Spain

² School of Chemistry and Materials Science, Heilongjiang University, Harbin 150080,
China

³ State Key Laboratory of Inorganic Synthesis and Preparative Chemistry
College of Chemistry-Jilin University, 2699 Qianjin Street, Changchun 130012 China

*Corresponding authors: E-mail addresses: acorma@itq.upv.es; mmoliner@itq.upv.es

1.- OSDA and zeolite syntheses

1.1.- Synthesis of the SSZ-13 zeolite

Synthesis of N,N,N-trimethyl-1-adamantamonium (TMAda)

29.6 g of 1-Adamantamine (Sigma-Aldrich) and 64 g of potassium carbonate (Sigma-Aldrich) were mixed with 320 ml of chloroform. At this point, 75 g of methyl iodide was added dropwise while the reaction was stirred in an ice bath. The reaction was maintained during 5 days under agitation at room temperature. The mixture was filtered and washed with diethyl ether, and the resultant solid further extracted with chloroform. The final product was N,N,N-trimethyl-1-adamantammonium iodide. This iodide salt was anion exchanged using an ion exchange resin achieving the hydroxide form.

Synthesis of SSZ-13 zeolite using TMAda

Conventional SSZ-13 was synthesized with the following gel composition: 0.1 Na₂O : 1 SiO₂ : 0.025 Al₂O₃ : 0.2 TMAdaOH : 44 H₂O. TMAdaOH was firstly mixed with NaOH and deionized water at room temperature until it was completely dissolved. Then, SiO₂ (Aerosil) was added to the TMAdaOH solution. Finally, Al₂O₃ was dissolved into the solution mentioned above, and the resulting gel was stirred at room temperature for 1 hour to obtain a homogeneous gel. The gel was transferred into a Teflon-lined steel autoclave and kept statically in an oven at 160°C for 6 days. The product was separated by filtration, washed with deionized water and dried at 100°C. The catalyst was calcined in air at 580°C to remove the template. H-SSZ-13 was obtained by ion exchange of calcined sample with 2.5 M NH₄Cl solution (80°C and liquid to solid ratio of 10) for 2 hours. Finally, the NH₄-exchanged material was calcined at 500 °C for three hours in air.

1.2.- Synthesis of the SSZ-39 zeolites

Synthesis of N,N-dimethyl-3,5-dimethylpiperidinium (DMP)

N,N-dimethyl-3,5-dimethylpiperidinium (DMP): 10 g of 3,5-dimethylpiperidine (C₇H₁₅, Acros Organics, 96%, cis-trans mixture) was mixed with 140 ml of methanol (CH₃OH, Scharlab, 99.9%) and 19.5 g of potassium carbonate (KHCO₃, Sigma Aldrich, 99.7%). 54 g of methyl iodide (CH₃I, Sigma Aldrich, 99.9%) was added dropwise, and the resultant

mixture maintained under stirring for 7 days. After this time, MeOH was partially removed under vacuum, and the iodide salt was precipitated by addition of diethyl ether. For its use in the synthesis of zeolites, the final product was ion exchanged to the hydroxide form using a commercially available hydroxide ion exchange resin (Dowex SBR).

Synthesis of the SSZ-39 zeolite using DMP as OSDA (SSZ-39_1)

First, the aqueous solution of N,N-dimethyl-3,5-dimethylpiperidinium (DMP) hydroxide was mixed with a 20%wt aqueous solution of sodium hydroxide (NaOH granulated, Scharlab). Then, the crystals of USY zeolite (CBV-720 with $\text{SiO}_2/\text{Al}_2\text{O}_3=21$)^[1] were introduced in the above solution, and the resultant mixture was stirred until complete homogenization. The chemical composition of the synthesis gel was $\text{SiO}_2 : 0.045 \text{ Al}_2\text{O}_3 : 0.2 \text{ NaOH} : 0.2 \text{ DMP} : 15 \text{ H}_2\text{O}$. The gel was transferred into a stainless steel autoclave with a Teflon liner. The crystallization was then conducted at 135°C for 7 days under static conditions. The solid product was filtered, washed with water and dried at 100°C. The sample was calcined in air at 550°C for 4h. The acid form of the N-SSZ-39 material was obtained by ion exchange of the calcined sample with 2.5 M NH_4Cl solution (80°C and liquid to solid ratio of 10) for 2 hours. Finally, the NH_4 -exchanged sample was calcined at 500 °C for three hours in air.

Synthesis of the SSZ-39 zeolite using TEP as OSDA (SSZ-39_2)

First, the aqueous solution of tetraethylphosphonium (TEP) hydroxide was mixed with a 20%wt aqueous solution of sodium hydroxide (NaOH granulated, Scharlab). Then, the crystals of USY zeolite (CBV-720 with $\text{SiO}_2/\text{Al}_2\text{O}_3=21$)^[1] were introduced in the above solution, and the resultant mixture was stirred until complete homogenization. The chemical composition of the synthesis gel was $\text{SiO}_2 : 0.045 \text{ Al}_2\text{O}_3 : 0.1 \text{ NaOH} : 0.2 \text{ TEP} : 5 \text{ H}_2\text{O}$. The crystallization was conducted at 150°C for 9 days under static conditions. The solid product was filtered, washed with water and dried at 100°C. The sample was calcined under a hydrogen atmosphere at 800°C for 4h to assure the complete decomposition of the phosphorous-containing species, followed by a new

^[1] The $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of the USY zeolite used as precursor to overcome the SSZ-39 syntheses has been measured by ICP and EDX.

calcination in air at 550°C for 2 hours. The acid form of the P-SSZ-39 material was obtained by ion exchange of the calcined sample with 2.5 M NH₄Cl solution (80°C and liquid to solid ratio of 10) for 2 hours. Finally, the NH₄-exchanged sample was calcined at 500 °C for three hours in air.

2.- Characterization

The crystallinity of the samples was measured by powder X-ray diffraction (PXRD) with a Panalytical CUBIX diffract meter with monochromatic CuK_{α1,2} radiation ($\lambda=1.5406$, 1.5444 Å; K α 2 / K α 1 intensity ratio=0.5). The morphology and particle size of the zeolites were characterized by Scanning Electron Microscope (SEM, JEOL JSM-6300). The MAS NMR spectra were recorded with a Bruker AV400 spectrometer. Solid state ²⁷Al MAS NMR spectra were recorded at 104.218 MHz with a spinning rate of 10 kHz at a 90° pulse length of 0.5 μs with 1 s repetition time. Solid-state ³¹P NMR spectra were recorded at 161.9 MHz with a spinning rate of 10 kHz, a π/2 pulse of 5 μs with 20 s repetition time. ²⁷Al and ³¹P chemical shifts were referred to Al(H₂O)₆ and H₃PO₄, respectively. Chemical composition was determined by inductively coupled plasma atomic absorption spectroscopy (ICP-OES) using a Varian 715-ES. The BET surface area, micropore volume and pore volume distribution were measured by N₂ adsorption in a Micromeritics ASAP2000. NH₃-TPD experiments were carried out in a Micromeritics 2900 apparatus. A calcined sample (100 mg) was activated by heating to 400°C for 2 h in an oxygen flow and for 2 h in argon flow. Subsequently, the samples were cooled down to 176°C, and NH₃ was adsorbed. The NH₃ desorption was monitored with a quadrupole mass spectrometer (Balzers, Thermo Star GSD 300T) while the temperature of the sample was ramped at 10°C min⁻¹ in helium flow. Total ammonia adsorption was measured by repeated injection of calibrated amounts of ammonia at 176°C until saturation. Ammonia desorption was recorded by means of the mass 15, since this mass is less affected by the desorbed water.

3.- Catalytic experiments

The catalyst was pelletized, crushed and sieved into 0.2-0.4 mm particle size. 50 mg of sample was mixed with 2 g quartz (Fluka) before being introduced into the fixed-bed

reactor (7mm diameter). N_2 (30mL/min) was bubbled in methanol hold at -17°C , giving a $WHSV=0.8\text{ h}^{-1}$. The catalyst was first activated with a nitrogen flow of 80 ml/min for 1 h at 540°C , and then the temperature was decreased to reaction conditions (350°C). Each experiment was analyzed every 5 minutes with an online gas chromatograph (Bruker 450GC, with PONA and Al_2O_3 -Plot capillary columns, and two FID detectors). After reaction, the catalyst was regenerated at 540°C in 80ml of air for 3h and the reaction was repeated again. Preliminary experiments were carried out at constant $WHSV$, different amount of catalyst and increasing flow rates, and later with catalyst with in different particle sizes, to check that, at the selected reaction conditions the process is not controlled by either external or intraparticle diffusion. Conversion and selectivities were considered in carbon basis and methanol and dimethylether were lumped together for calculation of conversion.

Figure S1: Phase diagrams achieved with the selected OSDAs

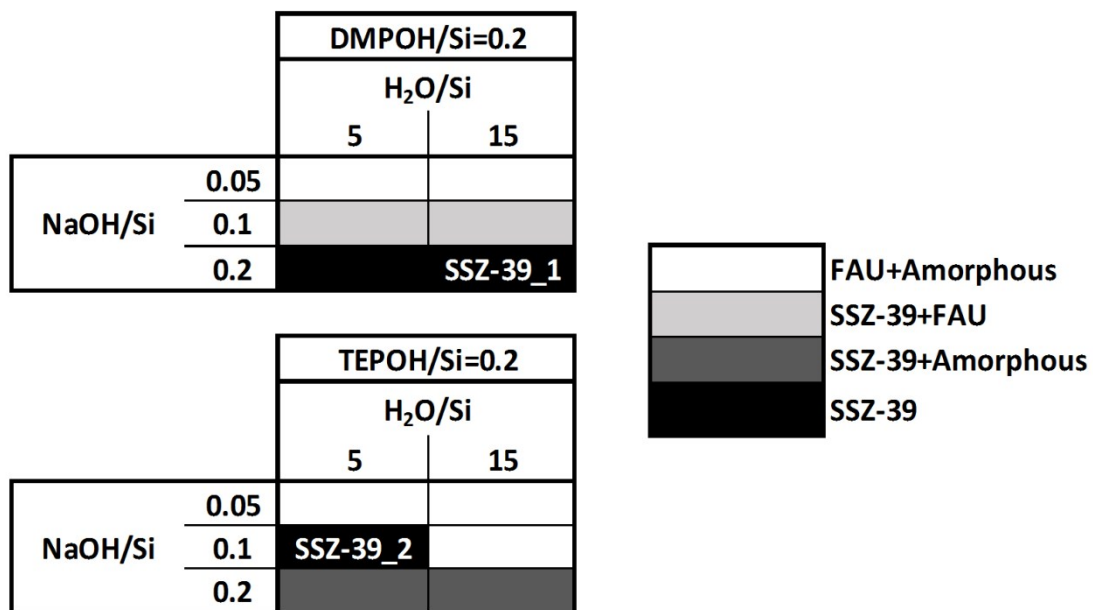


Figure S2: ^{31}P MAS NMR spectra of the as-prepared and calcined SSZ-39 material synthesized using TEP as OSDA

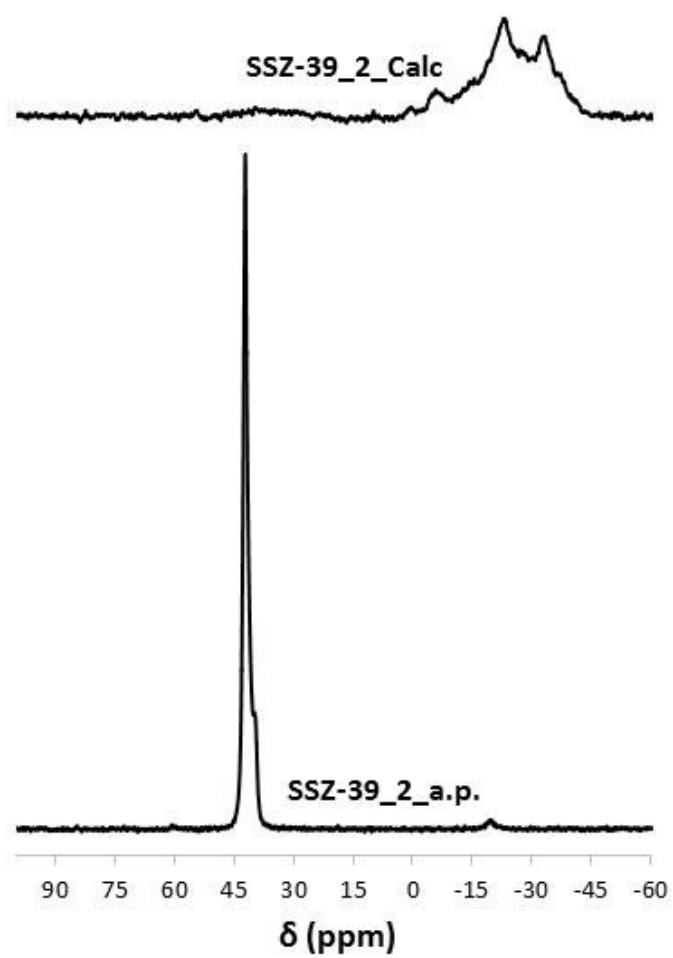


Figure S3: ^{27}Al MAS NMR spectra of the as-prepared and acid SSZ-39 SSZ-13 materials

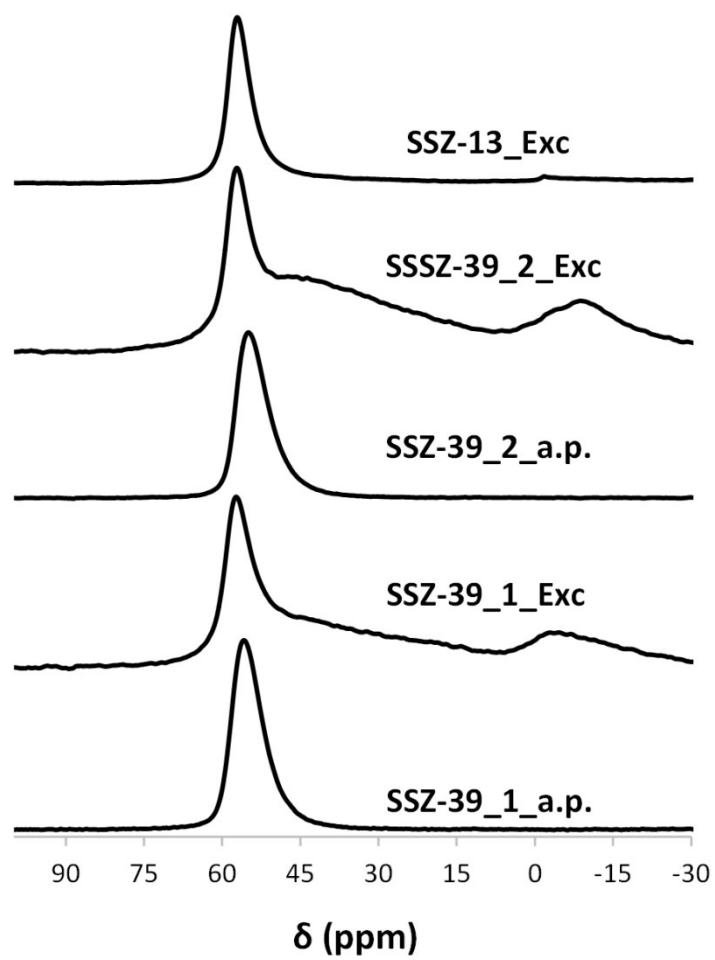


Figure S4: NH₃-TPD profiles of the acid SSZ-13 and SSZ-39 materials

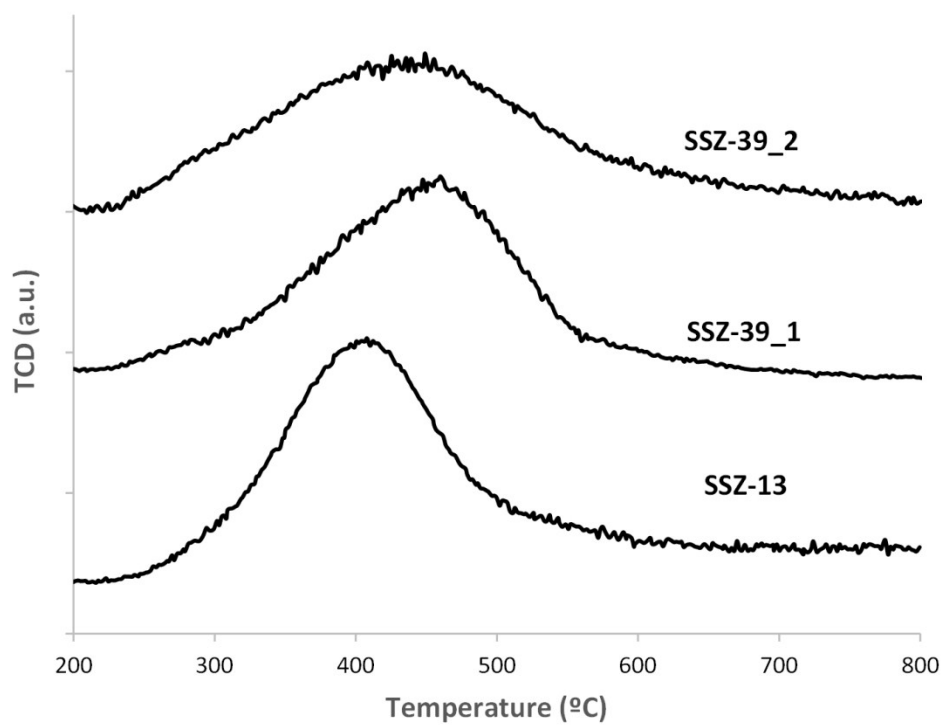


Figure S5: Yields to C2, C3, C4 and C5+ hydrocarbons at different methanol conversions at 350°C and WHSV=0.8 h⁻¹ for the different catalysts.

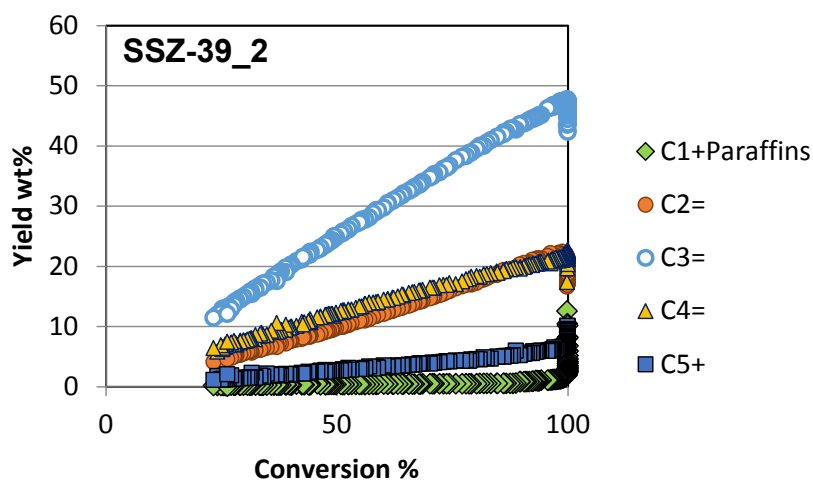
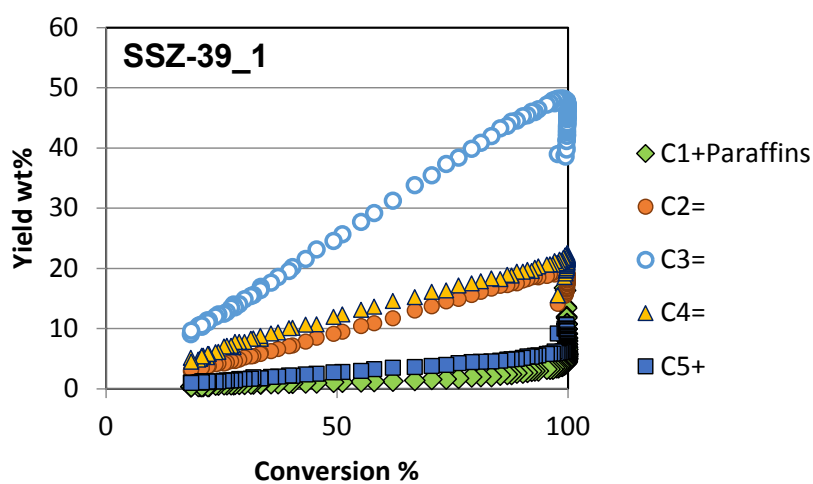
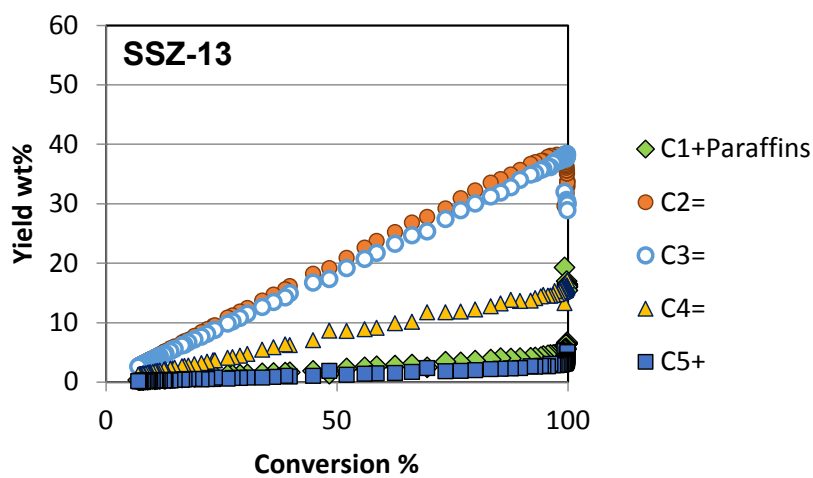


Figure S6: Selectivities to C2, C3, C4 and C5+ hydrocarbons at different methanol conversions for the different catalysts

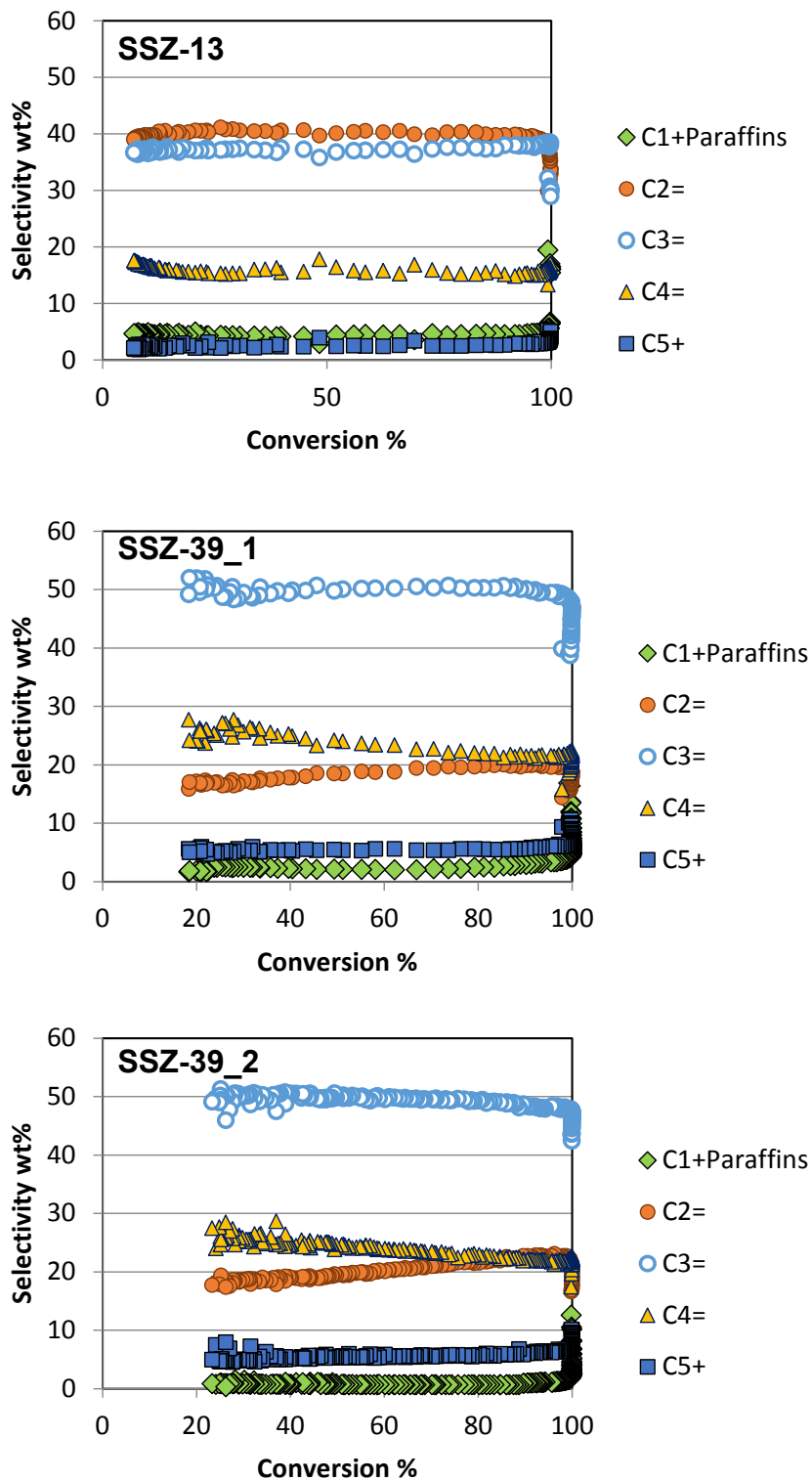


Figure S7: The C2/C3 ratio of the SSZ-13 and SSZ-39 materials in the conversion of methanol at 350°C and WHSV=0.8 h⁻¹.

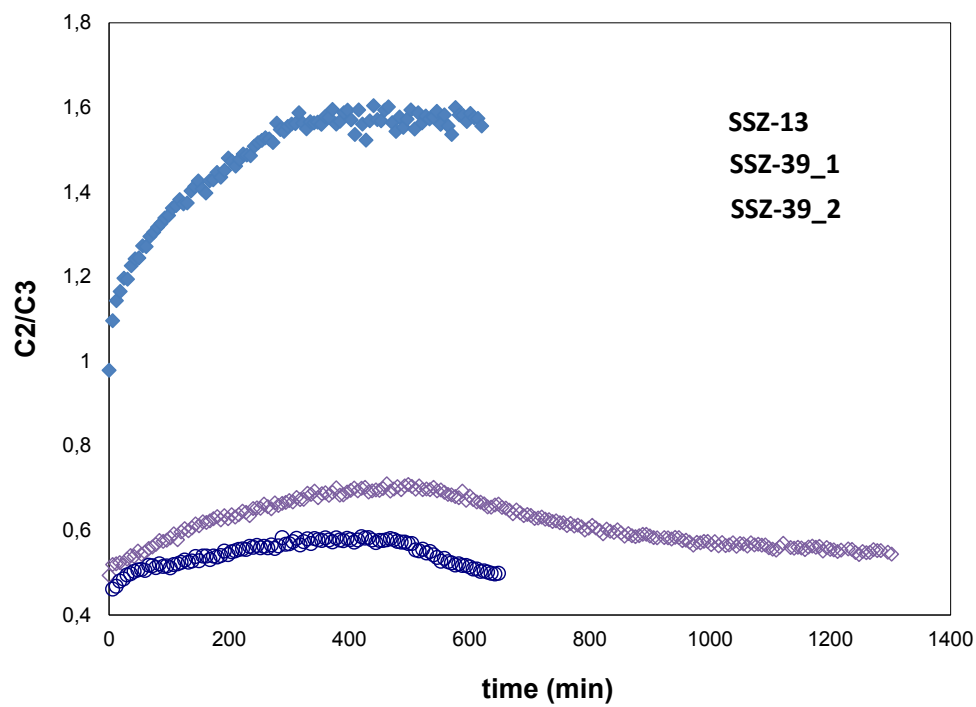


Figure S8: The hydrogen transfer index of the different catalysts against reaction time and methanol conversion

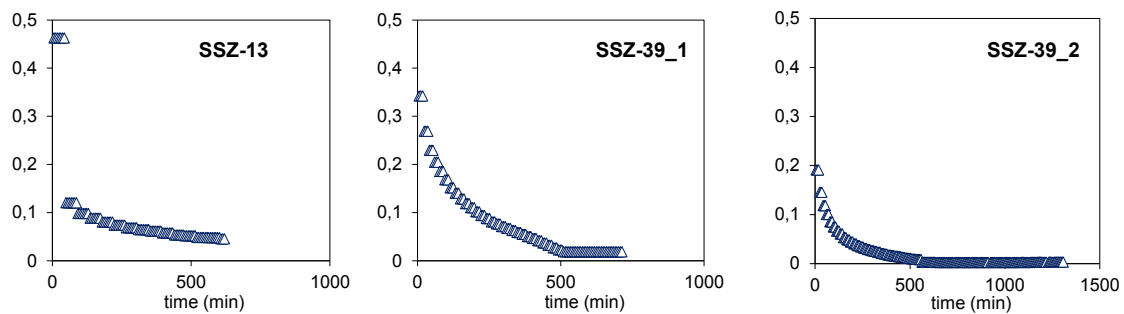


Table S1: Textural properties of the SSZ-13 and SSZ-39 materials

Sample	Si/Al	OSDA	Crystal size (μm)	BET (m^2/g)	$S_{\text{micro}}(\text{m}^2/\text{g})$	$S_{\text{Ext}}(\text{m}^2/\text{g})$	$V_{\text{micro}}(\text{cm}^3/\text{g})$
SSZ-13	15.3	TMAda	1x0.2	520	517	3	0.25
SSZ-39_1	8.3	DMP	0.2-0.4	516	501	15	0.25
SSZ-39_2	8.5	TPA	0.05	526	484	42	0.23

Table S2: Acidity of the SSZ-13 and SSZ-39 materials measured by adsorption of NH_3 at 175°C

Sample	$\text{NH}_3(\text{mmol}/\text{g})$
SSZ-13	0.35
SSZ-39_1	0.54
SSZ-39_2	0.49