Pinpointing basic sites formed upon incorporation of iron in hierarchical SAPO-11 using catalytic model reactions

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Supplementary information

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1.0 General characterization

1.1 Experimental information

The experimental information regarding N₂-physisorption, scanning electron microscopy (SEM), inductively coupled plasma - mass spectrometry (ICP-MS), Fourier-transform infrared spectroscopy (FTIR) and thermogravimetric analysis with mass spectrometry (TGA-MS) is based on previous reports and has been detailed below.^{1,2}

Nitrogen physisorption analyses were carried out on a Micromeritics Tristar 3000 Surface Area and Porosity Analyzer at -196 °C. In order to remove water and other volatile adsorbates, the materials were degassed under vacuum at 250 °C prior to measurements using a Micromeritics VacPrep 061 Sample Degas System. The specific surface area was determined by the BET (Brunauer-Emmett-Teller) method while the micropore and external area were estimated using the t-plot method. Finally, the pore size distribution was obtained by BJH (Barrett-Joyner-Halenda) analysis whereas the specific pore volumes were obtained by using the t-plot method in combination with the Gurvich rule ($p \cdot p_0^{-1} = 0.98$).

Scanning electron microscopy (SEM) was performed on a Hitachi S–3400 N with a precentered tungsten hairpin type filament electron source. The samples were gold coated by sputtering using an Edwards Sputter Coater (S150B) prior to imaging. Images were captured in secondary electron (SE) mode using an Everhart-Thornley secondary electron detector and an acceleration voltage of 10 kV. Particle sizes were determined from single images constituting at least 100 particles per sample using the software ImageJ (version 1.52a).³

Thermogravimetric analyses coupled with mass spectrometry (TGA-MS) were carried out with 10 - 15 mg of filtered particle size (212 - 425 μ m) on a Netzsch Jupiter STA 449 equipped with a QMS 403 Aëlos quadrupole mass spectrometer. The flow consisted of 45 mL min⁻¹ air and 25 mL min⁻¹ argon while the temperature program started at 35 °C, subsequently heated to 850 °C at a rate of 2 °C min⁻¹, and held for 6 hours before finally cooling down to room temperature at a rate of 2 °C min⁻¹. Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) was conducted using an Agilent 8800 Triple Quadropole ICP-MS (ICP-QQQ) with a SPS 4 Autosampler. The samples (20 - 40 mg) were decomposed with concentrated nitric acid (HNO₃, 1.5 mL, 65%) and concentrated hydrofluoric acid (HF, 0.5 mL, 40%). The final solution was diluted with deionized water and filled into a 16 mL sample tube. Before analysis, the samples were re-diluted in 5% HNO₃ and ¹¹⁵In was added as an internal standard. Standards from Inorganic Ventures were used for quantification.

Carbon monoxide (CO) adsorption was performed with a Bruker Vertex 80 FTIR spectrometer equipped with an LN-MCT detector from Kolmar Technologies and a custombuilt transmission cell. Measurements were conducted at an aperture setting of 2 mm, a scanner velocity of 20 kHz and a resolution of 4 cm⁻¹. Samples were pressed into selfsupported wafers (10 - 15 mg) and were pre-treated for 1 hour at 500 °C under vacuum to remove adsorbed water and impurities. Subsequently, the cell was cooled to -196 °C before slowly introducing CO (AGA). Finally, stepwise desorption of CO was conducted by gradually lowering the pressure in the system until the initial spectrum was recovered.

1.2 Phase purity, composition and morphology



Fig. S1-1: XRD of as-prepared FeSAPO-11 and FeCTAB-11 with the AEL structure as a reference.

 Table S1-1: Detailed results from ICP-MS elemental analysis including data for a conventional

 SAPO-11 reference (C-SAPO-11) without metal.¹

	Al (wt.%)	Si (wt.%)	P (wt.%)	Fe (wt.%)
FeSAPO-11	17.1	1.8	20.4	1.9
FeCTAB-11	18.3	1.9	22.0	2.0
C-SAPO-11 ^a	19.3	1.5	20.9	-

^aThe synthesis procedure and properties of the reference C-SAPO-11 have been detailed elsewhere.¹



Fig. S1-2: SEM micrographs of the as-prepared FeSAPO-11 (1) and FeCTAB-11 (2).



Fig. S1-3: Additional, high-magnification SEM micrographs of FeSAPO-11 (1) and

FeCTAB-11 (2), illustrating the smaller plates of FeCTAB-11 compared to FeSAPO-11.

1.3 Nitrogen physisorption

Table S1-2: Nitrogen physisorption characterization results for the FeSAPO-11s with a conventional

 SAPO-11 without metal (C-SAPO-11)¹ included as a reference.

Sample	Surface area (m ² g ⁻¹)			Pore ve	plume (cm ³ g ⁻¹)
	S _{BET}	S _{micro}	S _{ext}	V _{micro}	V _{meso}
FeSAPO-11	198	135	63	0.07	0.06
FeCTAB-11	247	123	124	0.06	0.13
C-SAPO-11 ^a	211	135	76	0.07	0.07

^aThe synthesis procedure and properties of the reference C-SAPO-11 have been detailed elsewhere.¹



Fig. S1-4: Nitrogen physisorption isotherms (A) and BJH pore size distributions (B) for both FeSAPO-11s as well as a conventional SAPO-11 without metal (C-SAPO-11)¹ included as a reference. For the pore size distributions, the adsorption branch of the BJH method was used.

1.4 Acid characterization by CO-FTIR spectroscopy

While the main manuscript focuses on conventional and hierarchical iron-incorporated SAPO-11, this section will briefly look at the main interactions between CO and a reference conventional SAPO-11 without metal (C-SAPO-11). The details regarding the synthesis and properties of C-SAPO-11 have been reported elsewhere.¹

Similar to the FeSAPOs, the typical bands for SAPO-11 were displayed by C-SAPO-11 both prior to and after exposure to CO. Here, Table S1-3 and Fig. S1-3 give an overview of the observed bands in the Brønsted region, whereas Table S1-4 and Fig. S1-4 show the bands in the CO region. Altogether, the results indicate that the acid strength of C-SAPO-11 was comparable to the FeSAPOs in this study. On the other hand, the surface group density of C-SAPO-11 (isolated silanols, P-OH groups) as well as the Brønsted acid site (BAS) density was slightly lower (0.3 and 0.7, respectively) when compared to the conventional FeSAPO-11 (1).

The reduced surface group density for C-SAPO-11 compared to the iron-incorporated SAPO-11s is in contrast to previous reports on metal-incorporated SAPO-11 and SAPO-34,^{4,5} where the metal-incorporated SAPOs had a reduced surface group density compared to the corresponding non-metal containing SAPO. For metal-incorporated SAPO-34, the reduced density was attributed to a decreased incorporation of Si, which might also be the case for the non-metal containing conventional SAPO-11 reference in this study as it contained less silicon (1.5%) than the FeSAPOs (1.8-1.9%) (Table S1-1). It should however be mentioned that the reduced Brønsted acid site (BAS) density for C-SAPO-11 (compared to FeSAPO-11) was consistent with a previous report on nickel-incorporated SAPO-11,⁵ where the metalincorporated SAPO-11 had a higher BAS density compared to the SAPO-11 without metal.

Interestingly, despite having a much lower density of P-OH sites, C-SAPO-11 contained slightly more phosphorous (20.9%) than the conventional FeSAPO-11 (20.4%) (Table S1-1). This might be an additional indication at the presence of additional Fe-OH groups underneath the P-OH band of the FeSAPOs.

1.4.1 Tables

Sample	v _{Si-OH}	V _{P-OH}	$v_{Brønsted}$	VSi-OH-Al 6	$v_{Brønsted}*$	Δv_{OH}
			cm ⁻¹			cm ⁻¹
FeSAPO-11	3746	3678	3632	3517	3366	266
FeCTAB-11	3746	3677	3628	3516	3368	260
C-SAPO-11	3743	3677	3635	3522	3374	261

Table S1-3: Location of the bands in the Brønsted region (3800 - 3200 cm⁻¹) of the FeSAPO samples and C-SAPO-11 reference¹ at 77 K and their acid shifts after perturbation by CO^a.

^aThe high frequency BAS are denominated as $v_{Brønsted}$, where an asterisk ($v_{Brønsted}$ *) denotes acid sites perturbed by CO, the shift being given as Δv_{OH} . The hydroxyl bands interacting with lattice oxygens (low frequency Brønsted sites) have been given as $v_{Si-OH-Al\,6}$.

Table S1-4: Location of the bands in the CO region (2200 - 2100 cm⁻¹) of the FeSAPO samples and C-SAPO-11 reference¹ at 77 K after CO adsorption.

Sample	V _{CO-OH}	V _{CO}	V _{CO-Fe}
		cm ⁻¹	
FeSAPO-11	2171	2137	2181
FeCTAB-11	2171	2137	2181
C-SAPO-11	2171	2137	-

Table S1-5: Integration results from normalized FTIR vacuum spectra of the FeSAPO samples and C-SAPO-11 reference (Fig. S1-8), displaying the relative density of acid sites^a.

Active site	Relative density of acid sites per sample (a.u.)					
-	FeSAPO-11	FeCTAB-11	C-SAPO-11 ¹			
Si-OH	1	1.2	0.3			
P-OH	1	1.1	0.3			
Brønsted	1	0.31	0.7			
Si-OH-Al	1	0.64	0.9			

^aThe values have been normalized with respect to the conventional FeSAPO-11. The hydroxyl bands interacting with lattice oxygens (low frequency Brønsted sites) have been denoted as Si-OH-Al.

1.4.2 Figures



Fig. S1-5: Normalized FTIR difference spectra of the FeSAPO-11 samples and a reference SAPO-11 without metal (C-SAPO-11)¹ with similar amounts of CO adsorbed. The hydroxyl bands interacting with lattice oxygen (low frequency Brønsted sites) are denoted as Si-(OH)-Al, while the high frequency BAS and their perturbed counterparts are denoted as Brønsted and Brønsted*, respectively. α_1 and α_2 denote perturbed Si-OH and P-OH groups, respectively.



Fig. S1-6: Normalized FTIR spectra of the CO region for FeSAPO-11, FeCTAB-11 and a reference C-SAPO-11.¹ Band number 1 is situated at 2171 cm⁻¹ and corresponds to a CO-OH adduct. Number 2 is situated at 2137 cm⁻¹ and corresponds to liquid-like (physically adsorbed) CO. Finally, band 3 is situated at 2181 cm⁻¹ and is in this study ascribed to an Fe²⁺-CO interaction.



Fig. S1-7: Results from Gaussian peak fitting of the CO-OH and CO-Fe²⁺ bands in the normalized CO-region for FeSAPO-11 (top) and FeCTAB-11 (bottom). Here, 'CO – Fe²⁺' corresponds to the 2181 cm⁻¹ band whereas 'CO – OH' corresponds to the 2171 cm⁻¹ band (also given in Table S1-3). Peak fitting and integrations were done with MatLab (v. R2018b).



Fig. S1-8: Normalized, clean vacuum spectra of FeSAPO-11, FeCTAB-11 and a reference SAPO-11 without metal (C-SAPO-11)¹ used for calculating the relative density of acid sites in Table S1-5. The hydroxyl bands interacting with lattice oxygen (low frequency Brønsted sites) are denoted as Si-(OH)-Al, while the high frequency BAS are denoted as Brønsted.

1.5 Base characterization by CO₂-TPD

Table S1-6: Summary of CO_2 -TPD analyses on FeSAPO-11 and FeCTAB-11. CO_2 -TPD results from a conventional SAPO-11 without metal (C-SAPO-11^a) have also been provided as a reference. The values have been normalized with respect to the area of FeSAPO-11.

Sample	Peak center	Relative peak area	Peak height (a.u.)
	(temperature, °C)	(a.u.)	
FeSAPO-11	653	1	0.22
FeCTAB-11	679	1.5	0.36
C-SAPO-11	635	0.31	0.08

^aThe synthesis procedure and properties of the reference C-SAPO-11 have been detailed elsewhere.¹

2.0 X-ray absorption spectroscopy

X-ray absorption spectroscopy (XAS) was conducted in order to verify the incorporation of Fe(III) into the SAPO-11 structure. Based on the work of Sørli et al.⁶ on CuSAPO-34, the main criterion for considering Fe to be successfully incorporated into the AEL structure of SAPO-11 was that there should be no Fe...O...Fe backscattering contributions in the EXAFS.^{6–8} As this has been discussed in the main manuscript, this section will focus on the XANES as well as an evaluation of the thermal stability of the samples.

The XANES spectra of the calcined samples are compared to the references in Fig. S2-1, where the absorption edge energy (7125 eV) and pre-edge feature (7114 eV) for both calcined samples suggests that iron is indeed present as Fe^{3+} in a non-centrosymmetrical tetrahedral environment.^{9–11} The oxidation state and local environment of FeSAPO-11 and FeCTAB-11 were studied by comparing the XANES region to references where Fe(III) is present in an octahedral form (Fe₂O₃)¹² and a tetrahedral form (Fe₃O₄)¹³.

For the thermal stability, the EXAFS refinements of the as-prepared (AP) FeSAPO-11 (Table S2-1, Fig. S2-2 and S2-3) indicated that after calcination, the number of nearest neighbors (N) was constant (~ 4.5) whereas the bond distance (R) increased from 1.925 to 1.947 Å. Interestingly, the opposite trend was observed for FeCTAB-11-AP, where both N and R decreased after calcination, from 4.2 to 3.7 and 1.940 to 1.929 Å, respectively. To further elucidate these observations, XANES comparisons of the as-prepared and calcined FeSAPO-11 and FeCTAB-11 have been provided in Fig. S2-4 and Fig. S2-5, respectively.

Evidently, both of the as-prepared FeSAPOs had the absorption edge at a slightly lower energy (~7124 eV) compared to the calcined samples. This indicates the presence of a minor fraction of Fe²⁺ in the as-prepared samples which is oxidized to Fe³⁺ during calcination, where similar observations have been reported for iron-incorporated SAPO-34.⁸ Furthermore, whereas the pre-edge intensity for FeSAPO-11-AP was constant, the pre-edge for FeCTAB-11-AP showed an increased intensity after calcination. An increased intensity for the pre-edge is associated both with the presence of Fe(III) and a preference for tetrahedral coordination.¹¹ As such compounds have shorter bond lengths and fewer neighbors than octahedral compounds, the decrease in N and R for FeCTAB-11 is therefore attributed to an increased presence of tetrahedrally coordinated iron after calcination. For FeSAPO-11-AP, there were no changes in coordination number nor pre-edge intensity after calcination, indicating that the local environment of Fe did not change. This is further confirmed by comparing the XANES spectra of calcined FeSAPO-11 to FeCTAB-11 (Fig.S2-6), indicating that the samples have Fe present in a similar tetrahedral environment. Thus, the slightly increased bond distance for FeSAPO-11 after calcination is attributed to a weaker interaction between isomorphously substituted Fe³⁺ and framework oxygen. This may also explain the observations in the main manuscript regarding the increased tendency of the Fe³⁺ in FeSAPO-11 to autoreduce to Fe²⁺ compared to FeCTAB-11 during thermal pre-treatment in inert gas and vacuum.^{14,15}

2.1 Tables

Table S2-1: EXAFS refinements showing the energy correction factor (EF), the Debye-Waller factor $(2\sigma^2)$, coordination numbers (N), bond distances (R), goodness of fit (*R*), k-range of refinement (Δ k) and the amplitude correction factor (AFAC) which was taken from Fe₃O₄ and set to 0.88 for both FeSAPO-11 and FeCTAB-11.

Sample	Shell	EF	$2\sigma^2$ (Å ²)	Ν	R (Å)	R	Δk	AFAC
		(eV)				(%)		
FeSAPO-AP	Fe-O	-4.4(8)	0.014(2)	4.4(3)	1.925(8)	27	2.3-9.5	0.88
FeSAPO-11	Fe-O	-5.7(6)	0.012(1)	4.5(3)	1.947(5)	24	2.3-12	0.88
FeCTAB-AP	Fe-O	-5.3(7)	0.010(2)	4.2(4)	1.940(7)	38	2-13.5	0.88
FeCTAB-11	Fe-O	-4.8(7)	0.012(2)	3.7(4)	1.929(8)	36	2-11.5	0.88

2.2 Figures



Fig. S2-1: Left: Normalized XANES of calcined FeSAPO-11 and FeCTAB-11 compared to an octahedral and a tetrahedral reference (Fe_2O_3 and Fe_3O_4 respectively). Right: Normalized XANES of selected Fe model compounds.



Fig. S2-2: FT-EXAFS of the calcined and as-prepared (AP) FeSAPOs, where (a) FeSAPO-11, (b) FeSAPO-11-AP, (c) FeCTAB-11 and (d) FeCTAB-11-AP.



Fig. S2-3: EXAFS chi-curves of the calcined and as-prepared (AP) FeSAPOs, where (a) FeSAPO-11, (b) FeSAPO-11-AP, (c) FeCTAB-11, (d) FeCTAB-11-AP.



Fig. S2-4: Normalized XANES of calcined FeSAPO-11 and as-prepared FeSAPO-11-AP, where the inset shows a close-up of the pre-edge region.



Fig. S2-5: Normalized XANES of calcined FeCTAB-11 and as-prepared FeCTAB-11-AP, where the inset shows a close-up of the pre-edge region.



Fig. S2-6: Normalized XANES of calcined FeSAPO-11 and FeCTAB-11, where the inset shows a close-up of the pre-edge region.

3.0 Vapor phase isomerization of cyclohexanone oxime model reaction

The conversion and lifetime of FeSAPO-11 and FeCTAB-11 in the vapor phase isomerization of cyclohexanone oxime (BMR) have been provided in Fig. S3-1 and there are two main observations that can be extracted from the figure. Firstly, the initial conversion of FeCTAB-11 was higher than for FeSAPO-11, despite the latter having a higher BAS density than the former. This is contrary to a previous report on the BMR model reaction,¹⁶ which found that the initial conversion typically matches the BAS density distribution. Secondly, the hierarchical FeCTAB-11 deactivated much faster than FeSAPO-11, seemingly contradictory to the presence of a hierarchical pore topology for the former sample. Post-catalysis XRD and nitrogen physisorption (Fig. S3-2 and Fig. S3-3, respectively) indicated that while the samples did not collapse during the reaction, most of the micropore and external surface area was congested. Lastly, TGA-MS on the spent samples (Fig. S3-4) revealed that both FeSAPO-11 and FeCTAB-11 contained almost twice the amount (7.5%) of the microporous FeSAPO-11 (4.9%).

The CO₂-TPD results (Table S1-6) indicated that FeCTAB-11 had a larger number of basic sites (1.5) compared to FeSAPO-11 (1.0). According to previous reports on the BMR,¹⁷ the presence of basic sites on catalysts is accompanied by an increased formation rate of coke due to base catalyzed polymerization reactions. This often results in an increased rate of deactivation due to pore blockages and explains the rapid deactivation and high coke content observed for FeCTAB-11 (Fig. S3-1 and Table S3-2). Thus, rather than the lack of a hierarchical pore system, the increased deactivation and high coke content for FeCTAB-11 is ascribed to the increased accessibility, and high number of basic sites for the hierarchical sample compared to FeSAPO-11.

3.1 Tables

Compounds	Init	ial	After 7	hours
	FeSAPO-11	FeCTAB-11	FeSAPO-11	FeCTAB-11
Conversion	64	79	47	22
ε-Caprolactam	33	14	44	17
Cyclohexanone	44	53	56	66
Aniline	12	20	0	17
5-Cyano-1-pentene	1.5	0.9	0	0
2-Cyclohexen-1-one	1.5	7.3	0	0
Phenol	0	0.6	0	0
2-Cyclohexen-1-ol	1.4	1.6	0	0
2-Cyclohexen-1-one oxime	6.6	1.3	0	0
n-Ethyl aniline	0	1.3	0	0

Table S3-1: Initial and 7-hour conversions and product distributions for the BMR model reaction^a.

^aValues below sample names correspond to initial and 7-hour conversion of cyclohexanone oxime.

Catalyst	Coke (%, mg mg _{cat} ⁻¹)	Time on stream (hours)
FeSAPO-11	4.9	7
FeCTAB-11	7.5	7

 Table S3-2: Post-BMR TGA-MS results for FeSAPO-11 and FeCTAB-11.



Fig. S3-1: Conversion of cyclohexanone oxime as a function of time on stream for FeSAPO-11 and FeCTAB-11.



Fig. S3-2: Post-BMR XRD of FeSAPO-11 and FeCTAB-11. Asterisks denote impurities.



Fig. S3-3: Post-BMR nitrogen physisorption of FeSAPO-11 and FeCTAB-11.



Fig. S3-4: Post-BMR TGA-MS of FeSAPO-11 and FeCTAB-11.

4.0 Methanol-to-hydrocarbons model reaction

4.1 Lifetime and activity

The methanol-to-hydrocarbons (MTH) model reaction was in this study mainly used to elucidate the location of the Brønsted acid sites (BAS) and, combined with the BMR model reaction, the pore topology of the FeSAPOs. The weak acid sites (WAS) in SAPOs may be located based on an increased lifetime for dimethyl ether (DME) production,² however identifying the location of the WAS for SAPO-11 is difficult due to the SAPO's intrinsically long lifetime for the MTH reaction.¹⁸ Thus, in this section, mainly the activity and lifetime of the FeSAPOs will be briefly discussed.

The conversion results of the MTH model reaction for FeSAPO-11 and FeCTAB-11 are plotted in Fig. S4-1. As the catalysts were assumed to be deactivated after falling below a conversion of 70%, the hierarchical FeCTAB-11 clearly had a significantly longer lifetime compared to the conventional FeSAPO-11. Indeed, while FeCTAB-11 remained active throughout the reaction (95 hours), FeSAPO-11 deactivated after approximately 16 hours on stream.

Post-catalysis XRD (Fig. S4-2) indicated that neither sample collapsed during the MTH model reaction, while post-catalysis nitrogen physisorption (Fig. S4-3) showed that the micropores of both FeSAPO-11 and FeCTAB-11 were congested. On the other hand, FeCTAB-11 retained all of its external surface area and mesopore volume, whereas FeSAPO-11 retained approximately 50% and 60% of both, respectively. This matches the TGA-MS results (Table S4-2 and Fig. S4-4), which showed that FeSAPO-11 produced a larger amount of coke (4.6%) than FeCTAB-11 (3.1%).

The factors that affect the deactivation of a SAPO in the MTH model reaction have been detailed elsewhere,² however specifically for the samples in this study, the acidity (acid strength and density) and particle sizes should be considered.

Whereas the acid strengths of the iron-incorporated samples were similar, the microporous FeSAPO-11 had a higher density of BAS (1.0) compared to FeCTAB-11 (0.31). Previous reports on the MTH reaction,^{19–22} have indicated that a high acid density may lead to rapid

deactivation due to polymerization of products, resulting in blocked pores and a heightened production of coke. The product distribution (Table S4-1) indicated that FeSAPO-11 indeed produced a slightly larger amount of hydrocarbons compared to FeCTAB-11. Furthermore and as previously mentioned, post-catalysis TGA-MS revealed that the microporous FeSAPO-11 contained more coke (4.6%) than FeCTAB-11 (3.1%), indicating that the increased BAS density may have affected the deactivation rate of the microporous sample.

The particle size of FeSAPO-11 ($21 \pm 10 \mu m$) was twice as large as that of FeCTAB-11 ($9 \pm 3 \mu m$), where previous reports have indicated that smaller SAPO particles have a longer lifetime for the MTH reaction.^{23,24} Larger SAPO particles have also been reported to accumulate larger amounts of coke than smaller particles,²⁵ which matches the observation in this study. Thus, the deactivation of FeSAPO-11 in the MTH model reaction is mainly ascribed to the larger particle size of the sample as well as an increased density of BAS when compared to FeCTAB-11.

Finally, as a note on the location of the WAS for FeCTAB-11, the hierarchical sample had an increased lifetime for the MTH model reaction combined with a relatively low formation rate of coke and high retention of texture properties. This may indicate the presence of WAS in mesopores, corroborating the hypothesis from the FTIR characterization results. However, the decreased density of BAS as well as the smaller particle size of FeCTAB-11 compared to FeSAPO-11 may also reasonably explain these findings.

4.2 Tables

Compounds	Ini	tial	After 2	0 hours
-	FeSAPO-11	FeCTAB-11	FeSAPO-11	FeCTAB-11
Conversion	80	79	68	78
C_1	0	0	0	0
C_2	2.8	0.3	0	0
C ₃	3.3	0	0	0
DME	84	99.7	100	100
C_4	3.0	0	0	0
C ₅	2.2	0	0	0
C ₆₊ aliphatics	1.6	0	0	0
PolyMB	2.0	0	0	0
Larger than HMB	1.0	0	0	0

Table S4-1: Initial conversion and product distribution for the MTH model reaction and after 20 hours on stream for FeSAPO-11 and FeCTAB-11^a.

^aValues below sample names correspond to initial and 20-hour conversion of methanol.

Table S4-2: Coke formation in the MTH model reaction as a function of time on stream for the catalysts.

Catalyst	Coke (%, mg mg _{cat} ⁻¹)	Time on stream (hours)	$R_{coke}^{a} (mg hr^{-1})$
FeSAPO-11	4.6	95	0.015
FeCTAB-11	3.1	95	0.010

^aAmount of coke (mg) generated per hour of reaction time.

4.3 Figures



Fig. S4-1: Conversion of methanol as a function of time on stream for FeSAPO-11 and FeCTAB-11.



Fig. S4-2: Post-MTH XRD of FeSAPO-11 and FeCTAB-11. Circles denote missing reflections, while asterisks symbolize impurities.



Fig. S4-3: Post-MTH nitrogen physisorption for FeSAPO-11 and FeCTAB-11.



Fig. S4-4: Post-MTH TGA-MS of FeSAPO-11 and FeCTAB-11.

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