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Uncovering the role of Lewis and Brønsted acid sites in perforated SAPO-34 with an enhanced lifetime in methanol conversion to light olefins

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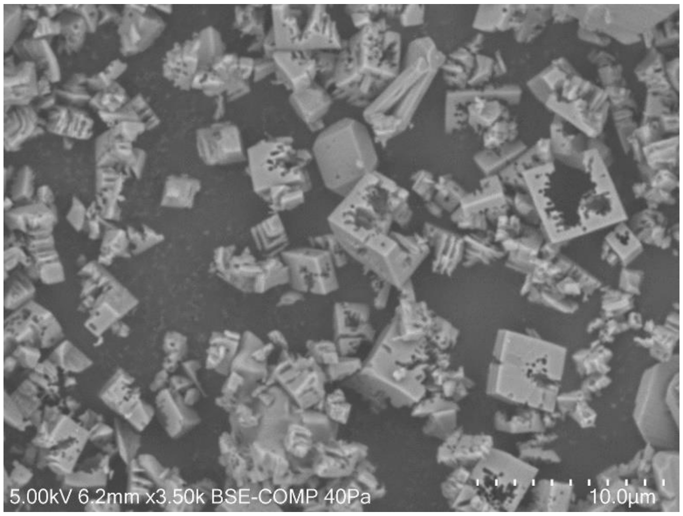

Fig. S1 SAPO-34 treatment by 0.5 molar DEA solution using magnetic bar stirrer for 24 h (the sample has crushed due to long treatment and mechanical mixing)

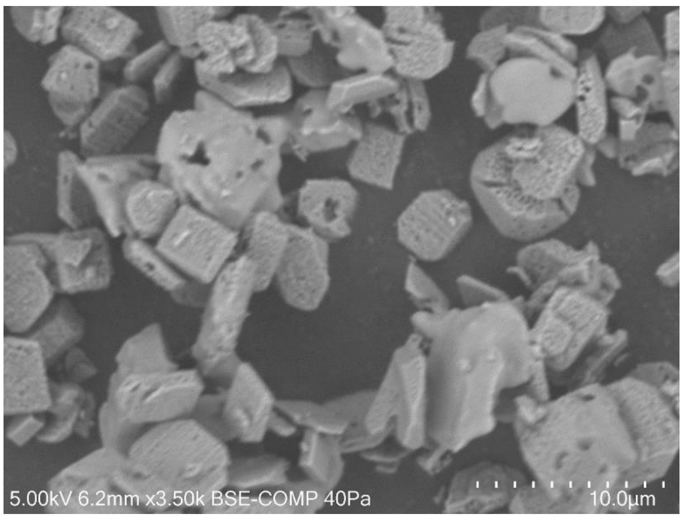

Fig. S2 SAPO-34 treatment by 10 molar DEA solution using an orbital shaker for 5 h (high DEA concentration has corroded the sample and created plate-shape particles along with amorphous phase)

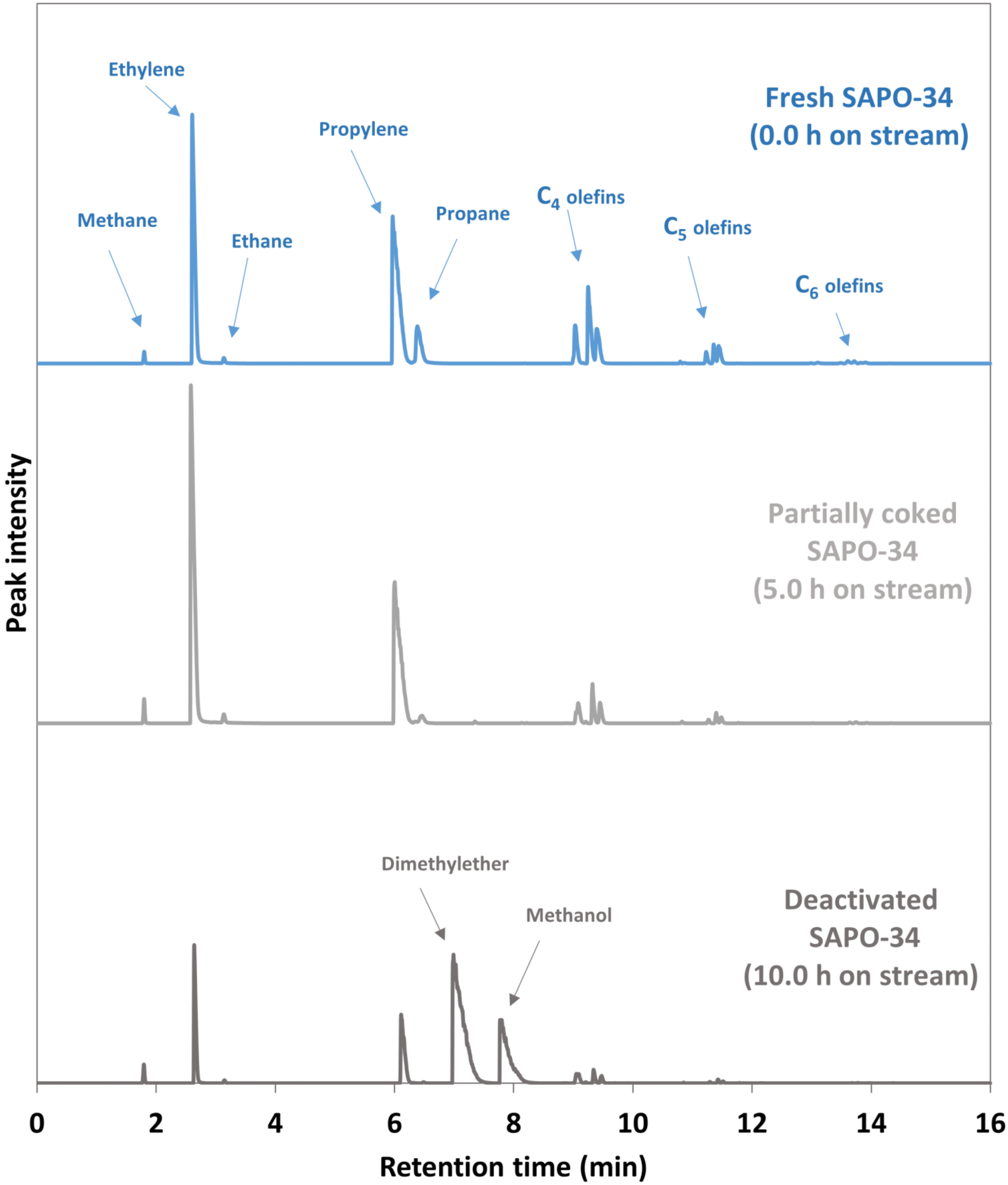

Fig. S3 GC chromatograms over parent SAPO-34 at different times on stream (over the fresh catalyst, partially coked catalyst-half lifetime, and after deactivation)

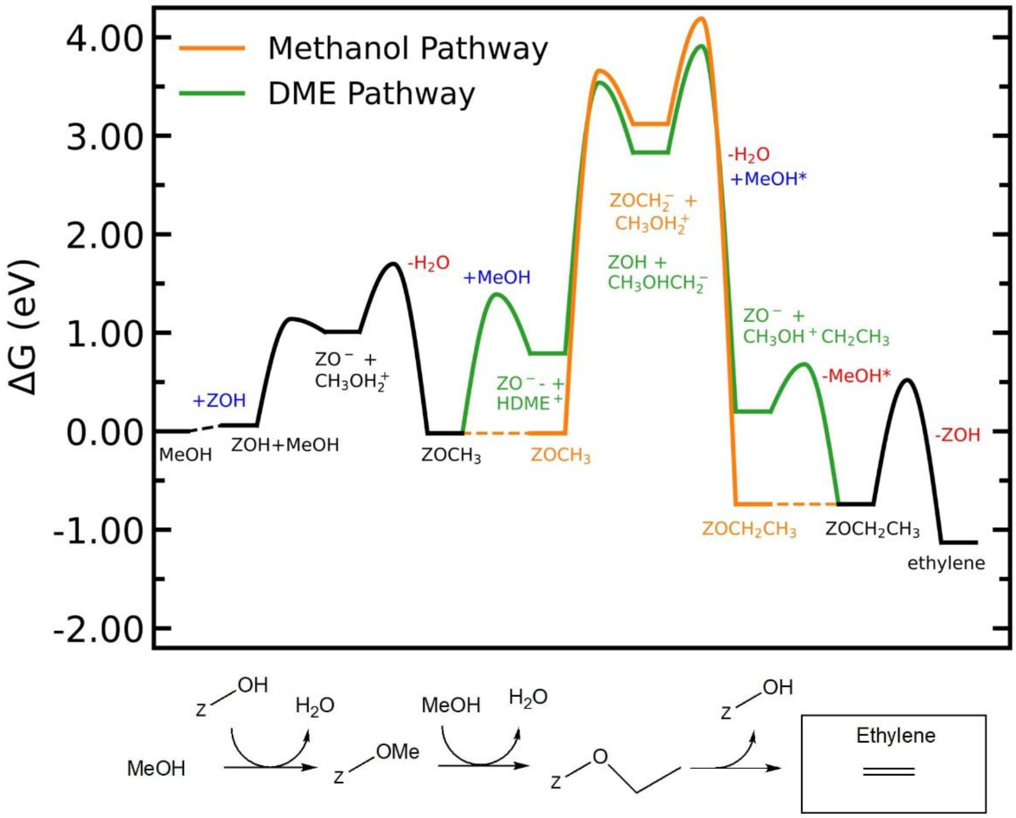

Fig. S4 Gibbs Free energy profile at 400 °C and 1 bar, for the catalytic formation of ethylene. Methanol pathway, depicted in orange, has protonated methanol ($CH_3OH_2^+$) as an intermediate, whereas DME pathway has protonated DME (H^+-DME). Reactants are depicted in blue and products in red. Reactants and products labelled in the diagram correspond to both pathways except when marked with *, which only correspond to reactants and products of the DME pathway, in green.

To assess the ability of BAS in catalyzing olefin formation, the possible reaction mechanisms of ethylene formation (the simplest olefin) were studied (Fig. S*4*) at 400 °C and a pressure of 1 bar through two routes: (1) MeOH insertion and protonation ($CH_3OH_2^+$, orange pathway) and (2) MeOH insertion and methylation (H^+-DME, green pathway). The Brønsted active site ZOH, corresponds to the zeolite framework (Z), that includes the Si-substituted site, followed by the neighboring oxygen, and added proton (OH). The active site then interacts with a methanol molecule (MeOH) by proton transfer, leading to the formation of a nucleophile (ZO^-) that interacts with $CH_3OH_2^+$ by donating an electron and cleaving the C-O bond, forming a methylated active site ($ZOCH_3$) and water. In a similar way, $ZOCH_3$ reacts with a second MeOH by either proton transfer (orange pathway) or methyl transfer (H^+-DME formation, in green). In the former, a proton from the zeolite-bound methyl is transferred to MeOH, eventually producing $ZOCH_2CH_3$ and water, with a barrier of 3.6 eV, whereas in the latter, CH_3 is transferred over to MeOH and then a proton is transferred back to the active site. An additional MeOH molecule will be necessary to form $ZOCH_2CH_3$, however, the barrier is decreased to 2.7 eV. The final reaction involves a concerted reaction step, where a proton from CH_3 is transferred over to another neighboring zeolite-bound oxygen, while CH_2 detaches from the zeolite forming ethylene that returns to the gas phase. Overall, it can be inferred that the DME pathway due to the lower value of the most energy-demanding step is preferred over the MeOH formation pathway.

Table S1. Summary of the previous modification methods on SAPO-34 catalyst and their activity performances

Methanol Processing ability (g_{MeOH} g_{Cat}^{-1})*	**Catalyst Lifetime (min)**	**Template**	**Bulk Si content % (Si/Si+P+Al)**	**Gel formula $Al_2O_3/P_2O_5/SiO_2/T/H_2O$ molar**	**Reaction Temperature (ºC)**	**WHSV (g_{MeOH} g_{Cat}^{-1} h^{-1})**	**Feed dilution (mol%)**	**Employed technique**	**Ref**
5.0 P	150 P	TEAOH (seeds) TEA (secondary catalyst)	16 P	1/1.2/0.8/2/50 1/1/0/1.75/27.5	400	2	0	Nano sized catalyst using seed-assist method	[1]
20.0 T	600 T		10 T						
4.7 P	70 P	DEA (initial)-TEA (secondary)	NA P	1/1/0.8/2/50 1/1/0/1.75/27.5	450	4	H_2O 60%	Using post-synthesis milling and recrystallization method	[2]
20.0 T	300 T		8.8 T						
NA	NA P	TEAOH	NA P	1/1/0.3/1/3	400	1	H_2O 50%	Solvent-free hydrothermal synthesis, hierarchical porosity due to stacked nanocrystals	[3]
15.0 T	900 T		7.6 T						
9.6 P	480 P	TEAOH	13 P	1/1/0.6/6/110	400	1.2	0	Nano sized catalyst using microwave	[4]
18.0 T	900 T		5.6 T						
11.3 P	150 P	TEAOH	17.9 P	0.5/1/0.3/2/70	450	4.5	H_2O 20%	Nano sized catalyst using Ultrasonic mixing	[5]
18.0 T	240 T		19.1 T	1/1/0.6/2/70					
4.0 P	120 P	Morph	18 P	1/1/0.6/3/80	400	2	0	Hierarchical SAPO-34 using Organosilane surfactant	[6]
16.7 T	500 T		16 T						
8.0 P	160 P	DEA	NA P	1/1/0.5/2.3/150	450	3	He 80%	Hierarchical SAPO-34 using Organosilane surfactant	[7]
17.5 T	350 T		14.9 T						
2.2 P	130 P	Morph-TEAOH	12 P	1/1/0.6/1.5+0.5/60	470	1	He 90%	hierarchical SAPO-34 using carbon nano tubes	[8]
5.3 T	320 T		14 T						
4.7 P	140 P	Morpholine	16.9 P	1/1/0.8/2.1/57	400	2	N_2 70%	Hierarchical SAPO-34 using post-treatment with HF-NH_4F mixed aqueous solutions	[9]
3.3 T	100 T		16.1 T						
8.3 P	250 P	TEA	9.9 P	1/1.1/0.4/4.7/70	400	2	N_2 70%	Hierarchical SAPO-34 using post-treatment with HF-NH_4F mixed aqueous solutions	[9]
8.3 T	250 T		9.2 T						

Table S1 Continue. Summary of the previous modification methods on SAPO-34 catalyst and their activity performances

Methanol Processing ability (g_{MeOH} g_{Cat}^{-1})*	**Catalyst Lifetime (min)**	**Template**	**Bulk Si content % (Si/Si+P+Al)**	**Gel formula $Al_2O_3/P_2O_5/SiO_2/T/H_2O$ molar**	**Reaction Temperature (ºC)**	**WHSV (g_{MeOH} g_{Cat}^{-1} h^{-1})**	**Feed dilution (mol%)**	**Employed technique**	**Ref**
25.0 P	375 P	TEAOH	10.1 P	1/2/1/4/138.8	450	4	N_2 50%	Hierarchical SAPO-34 using post-treatment with HF-NH_4F mixed aqueous solutions	[9]
16.7 T	250 T		5.9 T						
4.7 P	140 P	TEA	8.6 P	1/1/0.4/3.5/105	450	2	H_2O 50%	Introducing ordered mesoporous structures using $NaHCO_3$	[10]
7.7 T	230 T		8.6 T						
6.7 P	200 P	TEAOH	11 P	1/2/0.6/4/140	400	2	N_2 70%	Nano sized catalyst using microwave	[11]
28.3 T	850 T		12 T						
10.8 P	540 P	TEAOH	13 P	1/1/0.6/6/110	400	1.2	N_2 50%	Nano sized catalyst using microwave	[12]
15.6 T	780 T		5.7 T						
6.0 P	180 P	TEAOH/ TEA	16 P	1/1.2/0.6/2/40 seed 1/1/0.4/4.7/70 outer layer	400	2	NA	Nano sized catalyst using seeding	[13]
21.7 T	650 T		10 T						
6.7 P	100 P	TEAOH	NA	1/1/0.5/2/65	400	4	N_2 90%	Hierarchical SAPO-34 using Organosilane	[14]
16.7 T	250 T								
6.0 P	300 P	TEAOH	21 P	1/1/0.6/2/40	400	1.2	N_2 50%	Hierarchical SAPO-34 using hexadecyltrimethylammonium bromide (CTAB)	[15]
8.4 T	420 T		20 T						
4.0 P	120 P	TEA	9 P	1/1/0.33/4/100	450	2	50% H_2O	Base-etching post treatment	[16]
7.3 T	220 T		9 T						
3.0 P	180 P	TEA	9 P	1/1/0.4/3/50	400	1	5% H_2O	Citric acid-etching post treatment	[17]
7.5 T	450 T		11 T						
6.7 P	400 P	TEAOH	15.1 P	1/1/0.4/2/70	400	1	70% Ar	Alkali-etching post treatment	This study
9.9 T	595 T		14.1 T						

* Methanol processing ability $=$ WHSV (g_{MeOH} $g_{cat}^{-1} h^{-1}$)) $\times$ (time taken to go down to 95% MeOH conversion (h))
* until 95% methanol conversion , “P” stand for parent catalyst and “T” stands for treated or modified sample

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