Electronic Supplementary Information (ESI)

ZSM-5 with controllable acidity as an efficient catalyst for highly adjustable propene/ethene ratio in the 1-butene cracking

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Catalyst preparation

The zeolites were carried out in a quartz glass tube steel, with a thermocouple in the center of the catalyst bed. Typically, 4.0 g of sample was pre-treated in nitrogen stream (30 mL min⁻¹) at 550 °C for 2 h. Then, at the predetermined temperature, methyldiethoxy-silane (MDES) vapor was carried by nitrogen stream (5 mL min⁻¹) into catalyst bed. The SCS treatments over dehydrated zeolites were performed using temperature-controlled experimental device by altering the temperature (x=150-450 °C) and duration time (y=0.5-6h). All samples were swept with nitrogen at elevated temperature 450 °C for 3 h and then calcined at 550 °C (5 °C min⁻¹) for 6 h prior to characterization and catalytic evaluation.

Catalyst characterization

The catalysts were characterized by various techiques. X-ray diffraction (XRD) patterns were recorded on a Rigaku Ultima IV X-ray diffractometer (35 kV and 25 mA) using Cu K α radiation (λ =1.5405 Å). N₂ adsorption was carried out at 77 K on a BELSORP-MAX instrument after outgassing the samples for 10 h under vacuum at 573 K. The specific surface area was calculated with Brunauer-Emmett-Teller method. The crystal morphology and size were measured by scanning electron microscopy (SEM) on a Hitachi S-4800 microscope. The amounts of Si and AI in the catalysts were quantified by inductively coupled plasma (ICP) on a Thermo IRIS Intrepid II XSP atomic emission spectrometer after dissolving the samples in HF solution.

Acidity was measured by temperature-programmed desorption of ammonia (NH₃-TPD) with a Micromeritics tp-5080 equipment equipped with a thermal conductivity detector (TCD). Typically, 100 mg of sample was pre-treated in helium stream (30 mL min⁻¹) at 550 °C for 2 h. The adsorption of NH₃ was carried out at 50 °C for 0.5 h. The catalyst was flushed with helium at 100 °C for 2 h to remove physisorbed NH₃ from the catalyst surface. The TPD profile was recorded at a heating rate of 5 °C min⁻¹ from 100 °C to 550 °C.

The Brønsted and Lewis acid sites of the catalysts were investigated by FTIR of adsorbed pyridine in an in situ cell with CaF₂ windows. 25 mg and radius 6.5 mm wafers degassed 1 h under vacuum at 550 °C. Then pyridine was admitted, and, after equilibration, the samples were outgassed for 0.5 h at increasing temperatures (150, 200, 250, 350 and 450 °C). The spectra were recorded on a Nicolet iS50 FT-IR spectrometer.

The reaction of MDES with the acid sites of dehydrated HZSM-5 was monitored by in situ FTIR spectroscopy. 25 mg and radius 6.5 mm wafers degassed 2 h under vacuum at 550 °C. Then MDES was admitted for 0.5 h at 210 °C, and evacuated for 0.5 h at 210 °C in N₂, followed by subsequent heating procedure in N₂ at 250, 300, 350, 400, 450 and 500 °C.

²⁷Al and ²⁹Si solid-state MAS NMR spectra were recorded on a VARIAN VNMRS-400WB spectrometer under one pulse condition. ²⁷Al NMR spectra were recorded with a frequency of 104.18 MHz, a spinning rate of 10.0 kHz, and a recycling delay of 4 s. KAl(SO₄)₂•12H₂O was used as the reference for chemical shift. The ²⁹Si MAS NMR spectra were measured at a frequency of 79.43 MHz, a spinning rate of 3 kHz, a recycling delay of 60 s. The chemical shift was referred to Q_8M_8 ([(CH₃)₃SiO]₈SiO₁₂).

Catalytic testing

Catalytic cracking of 1-butene over the zeolites were carried out in a stainless steel continuous-flow reactor (10 mm i.d.), with a thermocouple in the center of the catalyst bed. Catalyst (0.8 g) was pressed, crushed, and sorted into grains by 40-60 meshes, and then was activated at 550 °C for 3 h under a nitrogen flow before starting each reaction run. Then 1-butene (99.9%) in diluted nitrogen ($N_2/1-C_4H_8 = 9.07$, mole ratio, analyzed by GC) with a weight hourly space velocity of 7.50 $g_{1-butene}g_{zeolite}$ -1h⁻¹ was passed through the reactor at the 500 °C. The output products were analyzed online by Agilent 7890A gas chromatograph equipped with a Agilent 19095P-M25 column (50 m × 530 µm × 15 µm), a Dikma 2 m × 1/8 5A column, a Dikma 2 m × 1/8 Porapak Q column, two Dikma 1 m × 1/8 Porapak Q columns, a FID detector which was used to detect hydrocarbons and two TCD detectors which were used to detect hydrogen and nitrogen. For simplicity, we grouped all types of butenes as the overall feed. Detailed calculations can refer to the previous article.¹

Calculation procedure of Table 1 and Fig. 2a data

The calculation procedure is as follows. ZSM-5(30): Si/Al=14.45 (ICP); The amount of TASs: 1.083 mmol.g⁻¹ $n_{SiO2} \times M_{SiO2} + n_{AlO2} \times M_{AlO2} = 1000$ mg $n_{AlO2} = 1000/(14.45 \times 60+59) = 1.080$ mmol.g⁻¹ (consistent with the amount of TASs measured by NH₃-TPD)

ZSM-5(30)-S₄₅₀-0.5: Si/Al=14.70 (ICP); The amount of TASs: 0.813 mmol.g⁻¹ $n_{SiO2} \times M_{SiO2} + n_{AlO2} \times M_{AlO2} = 1000$ mg $n_{AlO2} = 1000/(14.70 \times 60+59) = 1.0627$ mmol.g⁻¹ Δn_{Si} (mmol)/ $m_{zeolite}$ (g)=(Si/Al_{Modified}-Si/Al_{Parent}) $\times n_{AlO2} = (14.70-14.45) \times 1.0627 = 0.266$ mmol.g⁻¹ $\Delta n_{Acidity}$ (mmol)/ $m_{zeolite}$ (g)=TA_{Parent}-TA_{Modified}=1.083-0.813=0.270 mmol.g⁻¹

And so forth!



Scheme S1 Schematic diagram of the experimental device for SCS technology.



Scheme S2 Research on the process of the CCS method by thermogravimetric apparatus.²



Fig. S1 In situ FTIR spectra of the reaction of MDES with the acid sites of dehydrated HZSM-5, including the OH (A) and CH (B and C) stretching regions. (a) FTIR spectrum at 210 °C of the dehydrated for 2 h at 550 °C, (b) exposed to MDES for 0.5 h, (c) evacuated for 0.5 h at 210 °C in N₂, followed by subsequent heating procedure in N₂ at (d) 250 °C, (e) 300 °C, (f) 350 °C, (g) 400 °C, (h) 450 °C, (i) 500 °C.

The reaction of MDES with the acid sites of dehydrated HZSM-5 is monitored by in situ FTIR spectroscopy (Fig. S1, including the OH (Fig. S1A) and CH (Fig. S1B,C) stretching regions). The introduction of MDES at 210 °C leads a nearly complete disappearance of all OH bonds including silanol groups (3743 cm⁻¹), Al-OH groups (3657 cm⁻¹) and Brønsted acidic OH groups (3602 cm⁻¹) (spectra a-b in Fig. S1A). Meanwhile, peaks of Si-OC₂H₅ (around 2983 cm⁻¹), Si-H (2123 and 2173 cm⁻¹), and Si-CH₃ (1391 and 1466 cm⁻¹) appear (spectra a-b in Fig. S1B,C). These CH bonds gradually decrease in intensity with increasing the temperature (spectra c-i in Fig. S1B,C), while a small frac-tion of the original OH bond is regenerated (spectra c-i in Fig. S1A). The substitution reactions of Si-OH-Al and other hydroxyl species with silane functional groups, as well as subsequent cracking reactions at elevated temperature have been confirmed.



Fig. S2 NH₃-TPD profiles of parent and SCS-modified ZSM-5(52).



Fig. S3 NH_3 -TPD profiles of parent and SCS-modified ZSM-5(30).



Fig. S4 Normalized area and absolute value relative to BASs versus evacuation temperature over SCS-modified ZSM-5(30).



Fig. S5 XRD patterns of parent and SCS-modified ZSM-5(52).



Fig. S6 XRD patterns of parent and SCS-modified ZSM-5(30).



Fig. S7 ²⁹Si MAS NMR spectra of parent and SCS-modified ZSM-5(52).



Fig. S8 Results of long-term test of ZSM-5(52)- S_{150} -6 in the 1-butene cracking. Reaction conditions: cat., 0.8 g; temperature, 500 °C; pressure, 0.1 MPa; 1- butene flow rate, 40 mL min⁻¹; N₂ flow rate, 360 mL min⁻¹; WHSV, 7.50 $g_{1-butene}g_{zeolite}$ -¹h⁻¹.

Table S1 Acidity of parent and SCS-modified ZSM-5(52)^a

Entry	Zeolites	Brønsted	acid (~154	0 cm⁻¹) (a.u	.)		Lewis acid (~1450 cm ⁻¹) (a.u.)						
		150°C	200°C	250°C	350°C	450°C	150°C	200°C	250°C	350°C	450°C		
1	ZSM-5(52)	0.153	0.140	0.126	0.094	0.062	0.055	0.048	0.042	0.030	0.020		
2	S ₄₅₀ -2.5	0.069	0.058	0.047	0.027	0.007	0.078	0.068	0.063	0.042	0.033		
3	S ₃₀₀ -3.75	0.065	0.053	0.039	0.019	0.006	0.070	0.061	0.052	0.036	0.023		
4	S ₂₁₀ -5	0.065	0.042	0.025	0.007	0.003	0.064	0.057	0.045	0.031	0.020		
5	S ₁₅₀ -6	0.068	0.015	0.007	0.005	0.004	0.060	0.052	0.043	0.031	0.021		

^a Detected by FTIR spectroscopy after adsorption of pyridine.

Table S2 Acidity^a and Si/Al₂ ratios^b of parent and SCS-modified ZSM-5(30)

Entry	Zeolites	Acidity								
		WA (mmol g ⁻¹)	SA (mmol g ⁻¹)	TA (mmol g ⁻¹)	SA/WA					
1	ZSM-5(30)	0.571	0.512	1.083	0.897	28.9				
2	S ₄₅₀ -0.5	0.430	0.383	0.813	0.891	29.4				
3	S ₄₅₀ -2	0.395	0.351	0.746	0.889	29.6				
1	S ₄₅₀ -3	0.331	0.292	0.623	0.882	29.8				
5	S ₄₅₀ -5	0.254	0.222	0.476	0.874	30.1				

^a Detected by NH₃-TPD. WA, SA and TA represent the amounts of weak, strong and total acid sites, respectively. ^b Detected by ICP.

Table S3 Acidity of parent and SCS-modified ZSM-5(30)^a

Entry	Zeolites	Brønsted acid (~1540 cm ⁻¹) (a.u.)						Lewis acid (∼1450 cm⁻¹) (a.u.)					
		150°C	200°C	250°C	350°C	450°C		150°C	200°C	250°C	350°C	450°C	
1	ZSM-5(30)	0.265	0.237	0.203	0.135	0.084		0.077	0.069	0.061	0.044	0.025	
2	S ₄₅₀ -0.5	0.201	0.179	0.154	0.100	0.063		0.106	0.096	0.085	0.057	0.037	
3	S ₄₅₀ -2	0.183	0.164	0.145	0.096	0.055		0.125	0.112	0.100	0.072	0.041	
4	S ₄₅₀ -3	0.158	0.140	0.124	0.085	0.046		0.167	0.150	0.132	0.087	0.056	
5	S ₄₅₀ -5	0.091	0.080	0.072	0.045	0.026		0.127	0.115	0.101	0.069	0.044	

^a Detected by FTIR spectroscopy after adsorption of pyridine.

Table S4 Textural properties of parent and SCS-modified ZSM-5(52)

Entry	Zeolites	Pore properties	Size♭ (µm)					
	-	S _{BET} (m ² .g ⁻¹)	S _{micro} (m ² .g ⁻¹)	S _{meso} (m ² .g ⁻¹)	V _{total} (cm ³ .g ⁻¹)	V _{micro} (cm ³ .g ⁻¹)	V _{meso} (cm ³ .g ⁻¹)	
1	ZSM-5(52)	401	373	28	0.234	0.168	0.066	0.5-1.5
2	S ₄₅₀ -2.5	307	289	18	0.173	0.131	0.042	0.5-1.5
3	S ₃₀₀ -3.75	313	291	22	0.177	0.133	0.044	0.5-1.5
4	S ₂₁₀ -5	316	293	23	0.180	0.134	0.046	0.5-1.5
5	S ₁₅₀ -6	322	297	25	0.187	0.140	0.047	0.5-1.5

^a measured by N₂ physisorption. S_{BET} : BET surface area; S_{micro} : micropore surface area; S_{meso} : mesoporous surface area; V_{total} : total pore volume; V_{micro} : micropore volume; V_{meso} : mesoporous volume. ^b Obtained from SEM.

Table S5 Textural properties of parent and SCS-modified ZSM-5(30)

Entry	Zeolites	Pore properties ^a									
		S _{BET} (m ² .g ⁻¹)	S _{micro} (m ² .g ⁻¹)	S _{meso} (m ² .g ⁻¹)	V _{total} (cm ³ .g ⁻¹)	V _{micro} (cm ³ .g ⁻¹)	V _{meso} (cm ³ .g ⁻¹)				
1	ZSM-5(30)	367	353	14	0.188	0.160	0.028	0.5-1.5			
2	S ₄₅₀ -0.5	341	321	20	0.179	0.148	0.031	0.5-1.5			
3	S ₄₅₀ -2	334	298	36	0.172	0.138	0.034	0.5-1.5			
4	S ₄₅₀ -3	310	278	32	0.167	0.125	0.042	0.5-1.5			
5	S ₄₅₀ -5	302	272	30	0.163	0.120	0.043	0.5-1.5			

^{*a*} measured by N₂ physisorption. S_{BET} : BET surface area; S_{micro} : micropore surface area; S_{meso} : mesoporous surface area; V_{total} : total pore volume; V_{micro} : micropore volume; V_{meso} : mesoporous volume. ^{*b*} Obtained from SEM.

Table S6 Catalytic Cracking of 1-butene over parent and SCS-modified ZSM-5(30)^a

Entry	Zeolites	TA (mmol g⁻¹) [♭]	Conv. (mol%)	TO F (h ⁻¹)	Sel. (mo	Sel. (mol%)								$(C_2^{=}+C_3^{=}+C_5^{=}+C_6^{=})$ /(C ⁰ +H ₂ +Arom) ^c
				(11)	C ₂ =	C ₃ =	C₅⁼	C ₆ ⁼	C ₁ ⁰ +C ₂ ⁰	C ₃ °~C ₅ °	H ₂	Arom		
1	ZSM-5(30)	1.083	96.5	119	14.0	9.3	0.5	0.6	10.9	24.8	19.4	20.5	0.66	0.32
2	S ₄₅₀ -0.5	0.813	95.8	158	19.5	13.7	0.9	1.7	10.0	23.5	19.1	11.6	0.70	0.56
3	S ₄₅₀ -2	0.746	94.0	169	22.8	17.9	1.1	1.9	8.2	22.4	17.0	8.7	0.79	0.78
4	S ₄₅₀ -3	0.623	90.1	193	25.6	27.0	1.6	2.3	6.4	18.1	10.4	8.6	1.05	1.30
5	S ₄₅₀ -5	0.476	86.3	242	29.7	35.0	3.0	2.7	1.9	14.4	6.1	7.2	1.18	2.38

^{*e*} Reaction conditions: cat., 0.8 g; temperature, 500 °C; pressure, 0.1 MPa; 1- butene flow rate, 40 mL min⁻¹; N₂ flow rate, 360 mL min⁻¹; WHSV, 7.50 g_{1-butene}g_{zeolile}⁻¹h⁻¹; TOS, 1 h. ^{*b*} TA represents the amounts of total acid sites, evaluated from NH₃-TPD results in Table S2. ^{*c*} Employed to roughly describe the relative proportions of main reactions and side reactions of 1-butene cracking.

Table S7 Acidity of parent and SCS-modified Beta(26) a

Entry	Zeolites	Brønsted acid	(~1540 cm⁻¹) (a.u.)		Lewis acid (~1450 cm ⁻¹) (a.u.)					
		200°C	350°C	450°C	200°C	350°C	450°C			
1	Beta(26)	0.896	0.836	0.687	0.333	0.210	0.179			
2	S ₂₀₀ -6.5	0.462	0.178	0.056	0.458	0.283	0.201			
3	S ₃₀₀ -4.5	0.460	0.276	0.134	0.489	0.299	0.210			
4	S ₄₅₀ -3	0.457	0.335	0.279	0.548	0.351	0.267			

^a Detected by FTIR spectroscopy after adsorption of pyridine.

Reference

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