Supplementary Information (SI)

Synthesis, Characterization, and Catalytic Performance in 1-Butene Cracking of ZSM-5 Zeolites Prepared with Different Cross-Linked Silicon Species

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Preparation of S-1 zeolite

S-1 zeolite was synthesized via a hydrothermal method using tetraethyl orthosilicate (TEOS) as the silicon source and a 25 wt% aqueous solution of tetrapropylammonium hydroxide (TPAOH) as the structure-directing agent (SDA). The initial gel molar composition was 1.0 TEOS : 0.25 TPAOH : 18 H_2O. The mixed sol system was accurately weighed and transferred to a constant-temperature water bath for sequential treatment: (1) pre-hydrolysis at 323 K for 30 min; (2) heating to 353 K to evaporate alcohol until the mass of the sol system stabilized (indicating complete alcohol removal); (3) transfer of the alcohol-free sol to a stainless-steel crystallization reactor lined with polytetrafluoroethylene (PTFE), followed by dynamic crystallization at 443 K for 48 h. After crystallization, the reactor was rapidly cooled to room temperature using a cold-water bath. The solid product was isolated by filtration, thoroughly washed with deionized water, and the filter cake was dried at 353 K overnight. Finally, calcination at 823 K for 6 h in a muffle furnace yielded the target S-1 zeolite.

Characterization of samples

The infrared (IR) spectra were collected on Nicolet Nexus 670 FT-IR spectrometer at a spectral resolution of 2 cm^{-1}. Pyridine adsorption coupled with IR spectroscopy (Py-IR) was performed using a Nicolet iS50 FT-IR spectrometer equipped with a vacuum cell to quantify Brønsted (BAS) and Lewis (LAS) acid sites on catalysts. A 13 mm-diameter self-supporting catalyst wafer was inserted into the cell, evacuated, and activated at 450℃ for 1 h. For pyridine adsorption, the probe was dosed at 150℃ to 0.1 mbar, adsorbed for 30 min, and physisorbed pyridine was removed under vacuum. BAS/LAS site densities were calculated from peak areas using extinction coefficients of 1.23 and 1.73 cm μmol^{-1}.

^{29}Si NMR spectra were recorded on a Bruker BioSpin GmbH spectrometer at 298.2 K. The spectra was obtained with a frequency of 119.24 MHz, a relaxation delay of 5 s and D_2O as the solvent.

XRD was performed on a Rigaku Ultima IV X-ray diffractometer equipped with

CuKα radiation (λ= 1.5405 Å) under the operation condition of 35 kV and 25 mA. Scanning electron microscopy (SEM) images were taken on a Hitachi S-4800 microscope.

X-ray photoelectron spectroscopy (XPS) measurements were conducted on a Thermo Scientific ESCALAB 250Xi spectrometer equipped with a monochromated X-ray source, operating at a constant power of 200 W. The acquired spectra were analyzed using the Casa XPS curve-fitting software, with the C1s peak at 284.8 eV serving as the binding energy reference. The measurement was performed with a 650 μm monochromated X-ray spot. Depth profiling of heteroatom contents was carried out via argon ion sputtering at 5000 eV, where the etching rate was calibrated to 5 nm/min using a Ta_2O_5 standard.

The pore structure characteristics of the zeolite were analyzed via nitrogen adsorption-desorption (BET) using an Autosorb-3B automatic adsorption instrument manufactured by Quantachrome Instruments, USA. Prior to testing, the zeolite powder was first compressed and sieved to obtain a 40–60 mesh fraction. Approximately 0.1 g of the sieved sample was loaded into a test tube and subjected to vacuum activation at 573 K for 3 hours to remove residual moisture and impurities. Immediately after activation, the sample was transferred to a liquid nitrogen bath maintained at 77 K for the adsorption-desorption measurements. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) model, while the external specific surface area and micropore volume were derived from the t-plot method.

Inductively coupled plasma atomic emission spectroscopy (ICP) analyses were conducted using a Thermo Fisher Scientific IRIS Intrepid II XSP spectrometer. Approximately 0.01 g of each sample was accurately weighed and digested with 0.3–0.4 g of 65 *wt.*% hydrofluoric acid (HF) solution. **Caution**: HF is highly corrosive and can cause severe, irreversible damage to human tissue; appropriate personal protective equipment (including acid-resistant gloves, lab coats, and goggles) must be worn, and all operations should be performed in a certified fume hood. After complete digestion, the resulting solution was diluted with 9 g of deionized water to adjust the concentration

to a range suitable for ICP detection.

Acidity was measured by temperature-programed desorption of ammonia (NH_3-TPD) with a Micromeritics tp-5080 equipment equipped with a thermal conductivity detector (TCD). A 100-mg sample of 40-60 mesh particle size was first flushed with He gas flow (35 ml/min) at 550 °C for 2 h. The adsorption of NH_3 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 NH_3 from the catalyst surface. The TPD profile was recorded at a heating rate of 5 °C/min from 100 °C to 550 °C.

^{29}Si MAS NMR spectra were recorded on a VARIAN VNMRS-400WB spectrometer under a one-pulse condition. The spectra were obtained with a frequency of 79.43 MHz, a spinning rate of 3000 rps, and a recycling delay of 60 s. The chemical shift was referred to $Q_8M_8([(CH_3)_3SiO]_8\text{-}SiO_{12})$.

^{27}Al MAS NMR and spectra were recorded with a frequency of 104.18 MHz, a spinning rate of 10.0 kHz, and a recycling delay of 4 s. $KAl(SO_4)_2\cdot 12H_2O$ was used as the reference for chemical shift.

Calculation formula

The calculation formulas for 1-butene conversion rate, product selectivity, and product yield are shown in (1)~(3).

$$\text{conversion}=\frac{F^0_{C_4H_8}-F^t_{C_4H_8}}{F^0_{C_4H_8}}\times 100\%=\frac{F^0_{N_2}\times\frac{1}{7.82}-F^t_{N_2}\times\frac{X^t_{C_4H_8}}{X^t_{N_2}}}{F^0_{N_2}\times\frac{1}{7.82}}\times 100\%$$

$$=100\%-7.82\times\frac{X^t_{C_4H_8}}{X^t_{N_2}}\times 100\% \qquad \left(F^0_{N_2}=F^t_{N_2}\right) \qquad (1)$$

$$\text{mole selectivity}\left(C_xH_y\right)=\frac{X^t_{C_xH_y}}{\sum X^t_{C_iH_j}}\times 100\% \qquad (2)$$

$$\text{mole yield}=\text{conversion}\times\text{mole selectivity} \qquad (3)$$

In the equation, F^0_{C4H8}, F^t_{C4H8}, F^0_{N2}, and F^t_{N2}, representing 1-butene feed molar flow rate, 1-butene discharge molar flow rate, N_2 feed molar flow rate, and N_2 discharge molar flow rate, respectively, mol/min； X^t_{C4H8}, X^t_{N2}, X^t_{CxHy} and X^t_{CiHj} are the 1-butene

mole fraction, N_2 mole fraction, desired product mole fraction, and any product mole fraction obtained by gas chromatography analysis, respectively, %.

Table S1 The ratio of peak areas for Q^1–Q^3 species to Q^0 species in the ^{29}Si NMR spectra of silicon species A and B

Entry	Variable	[a]$A_Q^{1\sim3}/A_Q^0$			
		$A_Q^{1}{}_{\text{-d}}/A_Q^0$	$A_Q^{1}{}_{\text{-c}}/A_Q^0$	A_Q^2/A_Q^0	A_Q^3/A_Q^0
1	Silicon species A	0.56	0.12	<0.05	<0.05
2	Silicon species B	0.72	0.45	1.52	0.23

[a] Represented that the peak area ratio of $Q^{1\sim3}$ states to Q^0 states.

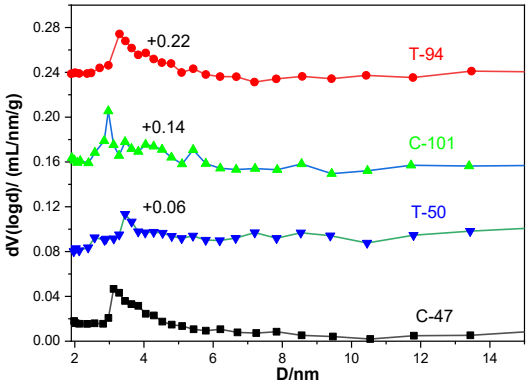

Figure S1 Pore size distribution diagram of C-series and T-series ZSM-5 zeolites.

Table S2 The properties of ZSM-5 zeolites

Entry	Type	[a]Si/Al	[b]$S_{sur.}$ ($m^2 \cdot g^{-1}$)	[b]$S_{micro.}$ ($m^2 \cdot g^{-1}$)	[b]$S_{exter.}$ ($m^2 \cdot g^{-1}$)	[b]V_{total} ($cm^3 \cdot g^{-1}$)	[b]$V_{micro.}$ ($cm^3 \cdot g^{-1}$)	[b]V_{meso} ($cm^3 \cdot g^{-1}$)	[c]Pore Diameter Dv(d)/nm
1	C-47	53	380.6	326.8	53.8	0.24	0.148	0.092	2.978
2	T-50	105	403.5	334.8	68.7	0.52	0.150	0.370	4.043
3	C-101	94	387.6	338.4	49.2	0.23	0.152	0.078	2.974
4	T-94	254	405.2	322.8	83.1	0.48	0.146	0.334	3.527

[a] detected by XPS. [b] given by N_2 adsorption at 77 K and calculated from t-plot, $S_{sur.}$, $S_{micro.}$, $S_{exter.}$, V_{total}, $V_{micro.}$ and V_{meso} respectively represent the surface area, micropore area, external specific surface area, total pore volume, micropore volume and mesoporous volume of the zeolite. [c] Pore diameter, given by nitrogen-sorption BJH measurement.

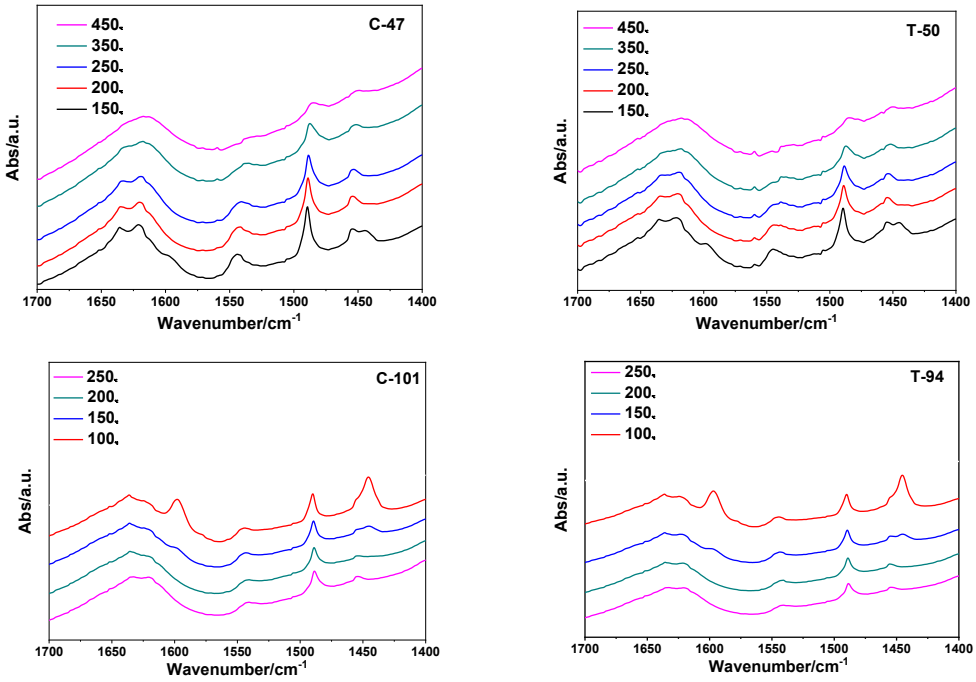

Figure S2 Py-IR spectra of C-series and T-series ZSM-5 zeolites.

Table S3 The calculation of normalized area of ZSM-5 zeolites

T/ ℃	C-47				T-50			
	S_{1880}	S_{1540}	S_{1540}/ S_{1880}	Normalization area	S_{1880}	S_{1540}	S_{1540}/ S_{1880}	Normalization area
150	35.819	2.866	0.080	1.000	38.925	2.336	0.060	1.000
200	36.033	2.525	0.070	0.876	38.925	2.146	0.055	0.919
250	35.623	2.086	0.059	0.732	38.089	1.879	0.049	0.822
350	35.769	1.133	0.032	0.396	37.403	1.261	0.034	0.562
450	36.354	0.000	0.000	0	38.556	0.583	0.015	0.252

Table S4 The calculation of normalized area of ZSM-5 zeolites

T/ ℃	C-101				T-94			
	S_{1880}	S_{1540}	S_{1540}/ S_{1880}	Normalization area	S_{1880}	S_{1540}	S_{1540}/ S_{1880}	Normalization area
100	47.066	1.459	0.031	1.000	44.597	1.739	0.039	1.000
150	46.251	1.232	0.027	0.859	44.080	1.649	0.036	0.959
200	46.249	0.823	0.026	0.574	44.193	1.424	0.034	0.826
250	46.808	0.705	0.020	0.486	43.808	1.017	0.027	0.595