Supplementary Information (SI) for ChemComm.

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Supporting Information

Tuning Ruthenium States for Enhanced Polyethylene Hydroconversion over HZSM-5 Catalysts

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1. Materials and Methods

1.1 Materials

HZSM-5(38) was purchased from Meryer, $RuCl_3 \cdot 3H_2O$ was purchased from Alfa Aesar, and Polyethylene (LDPE, average Mw ~4000 and Mn ~1700 by GPC) was purchased from Sigma Aldrich. alkane standard solution C_7-C_{40} (1000 mg/L each in hexane) was purchased from Sigma Aldrich.

1.2 Characterizations

X-ray diffraction patterns were recorded on a Bruker D8 ADVANCE Focus diffractometer with Cu Kα (λ=1.54056 Å) as the radiation source. The test was operated at 40 kV and 40 mA with scattering angels of 5–80°. Transmission electron microscopy images of samples were obtained on a Hitachi HF5000 electron microscopy at 12 kV. X ray photoelectron spectroscopy (XPS) spectra were recorded on a AXIS Ultra DLD system with monochromatic Al Kα radiation.

1.3 Catalytic performance

The catalytic hydroconversion processes were performed in a 100 mL stainless-steel autoclave equipped with a quartz liner. In a typical procedure, 50 mg catalyst and 1000 mg polyethylene were mixed in the liner. The reactor was sequent purged three times with N_2 and H_2 before heating to 250 ℃ at 650 rpm. With a period of 6 hours, the products were collected upon cooling to room temperature.

Gaseous products were collected in gas bags and analyzed using an Agilent 7890 GC equipped with an FID detector for qualitative and quantitative determination. Liquid products were extracted with dichloromethane and characterized by Agilent 8890A GC-MS with C_7-C_{40} n-alkanes as standards. Quantitative analysis was performed on an Agilent 8890A GC using 1,3,5-tri-tert-butylbenzene as an internal standard. A DB-5HT capillary column (30 m, 0.25 mm i.d.×0.25 μm) was employed for separation. Residual solids were dissolved in *o*-dichlorobenzene at 80 °C. The conversion, yield of products, and carbon balance were calculated using the corresponding equations in Eq. (1)-(4).

$$Gas\ Yield = \frac{Carbon\ amount\ in\ gas(mol)}{Carbon\ amount\ in\ Substrate_{in}(mol)} \times 100\% \quad (1)$$

$$Liquid\ Yield = \frac{Carbon\ amount\ in\ liquid(mol)}{Carbon\ amount\ in\ Substrate_{in}(mol)} \times 100\% \quad (2)$$

$$Conv. = \frac{Substrate_{in} + Catalyst_{in} + Solid_{out}}{Substrate_{in}} \times 100\% \quad (3)$$

$$Carbon\ Balance = (Gas\ Yield + Liquid\ Yield + 1 - Conv.) \quad (4)$$

2. Synthetic Procedures

2.1 Preparation of 5 wt% Ru/HZSM-5-1, Ru/HZSM-5-2, Ru/HZSM-5-3, and Ru/HZSM-5-4

In a typical preparation, 10 mL of ruthenium chloride solution containing 50 mg of ruthenium was added dropwise to 20 ml deionized water containing 950 mg HZSM-5(38) at room temperature. The mixture was then stirred at room temperature for 6 h, followed by overnight drying at 100 °C to obtain the precursor. The precursor was then calcined in a muffle furnace at 400 °C for 4 h to produce 5 wt% Ru on HZSM-5, which labelled as 5 wt% Ru/HZSM-5-1. Alternatively, the precursor was reduced in a tubular furnace under H_2 atmosphere at 400°C for 2 h to yield 5 wt% Ru/HZSM-5-2. 5 wt% Ru/HZSM-5-1 was further reduced in a tubular furnace under H_2 atmosphere at 200 °C for 2 h to obtain 5 wt% Ru/HZSM-5-3 and reduced at 400 °C for 2 h to obtain 5 wt% Ru/HZSM-5-4, respectively.

2.2 Preparation of Ru/HZSM-5-3-200℃, Ru/HZSM-5-3-400℃, Ru/HZSM-5-3-700℃:

10 mL of ruthenium chloride solution containing 50 mg of ruthenium was added dropwise to 20 ml deionized water containing 950 mg HZSM-5(38) at room temperature. The mixture was then stirred at room temperature for 6 h, followed by overnight drying at 100 °C to obtain the precursor. The precursor was then calcined in a muffle furnace at 200 °C, 400 °C and 700 °C for 4 h to produce 5 wt% Ru on HZSM-5, which were then reduced in a tubular furnace under H_2 atmosphere at 200 °C for 2 h to obtain Ru/HZSM-5-3-200℃, Ru/HZSM-5-3-400℃ and Ru/HZSM-5-3-700℃, respectively.:

2.3 Preparation of 2 wt% Ru/HZSM-5-3, 5 wt% Ru/HZSM-5-3 and 10 wt%

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Ru/HZSM-5-3:

10 mL of ruthenium chloride solution containing 20 mg, 50 mg and 100 mg of ruthenium was added dropwise to 20 ml deionized water containing 980 mg, 950 mg and 900 mg HZSM-5(38) at room temperature. The mixture was then stirred at room temperature for 6 h, followed by overnight drying at 100 °C to obtain the precursor. The precursor was then calcined in a muffle furnace at 400 °C for 4 h to produce 5 wt% Ru on HZSM-5, which were then reduced in a tubular furnace under H_2 atmosphere at 200 °C for 2 h to obtain 2 wt% Ru/HZSM-5-3, 5 wt% Ru/HZSM-5-3 and 10 wt% Ru/HZSM-5-3, respectively.

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3. Supplementary Figures and Tables

Table S1. the calculated Ru particle size with different preparation method

Catalysts	Ru (nm)
Ru/HZSM-5-1	60
Ru/HZSM-5-2	18
Ru/HZSM-5-3	28
Ru/HZSM-5-4	34

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Table S2. XPS fitting parameter details

Name		Peak BE	Height CPS	Height Ratio	Area CPS. (eV)	Area Ratio	FWHM fit param (eV)	L/G Mix (%) Product	Tail Mix (%)	Tail Height (%)	Tail Exponent
A	C1s	284.8	10924.04	1	27581.86	1	1.89	30	100	0	0
							0.5: 3.5	fixed	fixed	fixed	fixed
B	C1s	286.26	7034.79	0.64	11385.99	0.61	1.8	30	100	0	0
							0.5: 3.5	A*1	fixed	fixed	fixed
C	C1s	288.42	2650.92	0.24	6138.34	0.29	2.22	30	100	0	0
							0.5: 3.5	A*1	fixed	fixed	fixed
D	Ru^0 $3d_{5/2}$	280.2	3281.6	0.3	2876.33	0.13	0.84	30	100	0	0
		280.10: 280.20					0.5: 3.5	fixed	fixed	fixed	fixed
E	Ru^4 $3d_{5/2}$	280.6	3024.68	0.28	2907.67	0.14	0.92	30	100	0	0
		280.60: 280.80					0.5: 3.5	D*1	fixed	fixed	fixed
F	Ru^{4+a} $3d_{5/2}$	281.63	3184.72	0.29	10151.56	0.47	3.06	30	100	0	0
		281.08: 284.08					0.5: 3.5	D*1	fixed	fixed	fixed
G	Ru^0 $3d_{3/2}$	284.4	1789.8	0.15	2157.25	0.23	2.88	30	100	0	0
		D+4.20			D*0.75		0.5: 3.5	D*1	D*1	D*1	D*1
H	Ru^4 $3d_{3/2}$	284.8	1433.34	0.14	2180.75	0.26	3.5	30	100	0	0
		E+4.20			E*0.75		0.5: 3.5	E*1	E*1	E*1	E*1
I	Ru^{4+a} $3d_{3/2}$	285.83	1877.36	0.15	7613.67	0.27	3.5	30	100	0	0
		F+4.20			F*0.75		0.5: 3.5	F*1	F*1	F*1	F*1

** Note: C 1s components (A, B, C) were included in the fitting to account for carbon contamination, with binding energies referenced to adventitious carbon at 284.8 eV.*

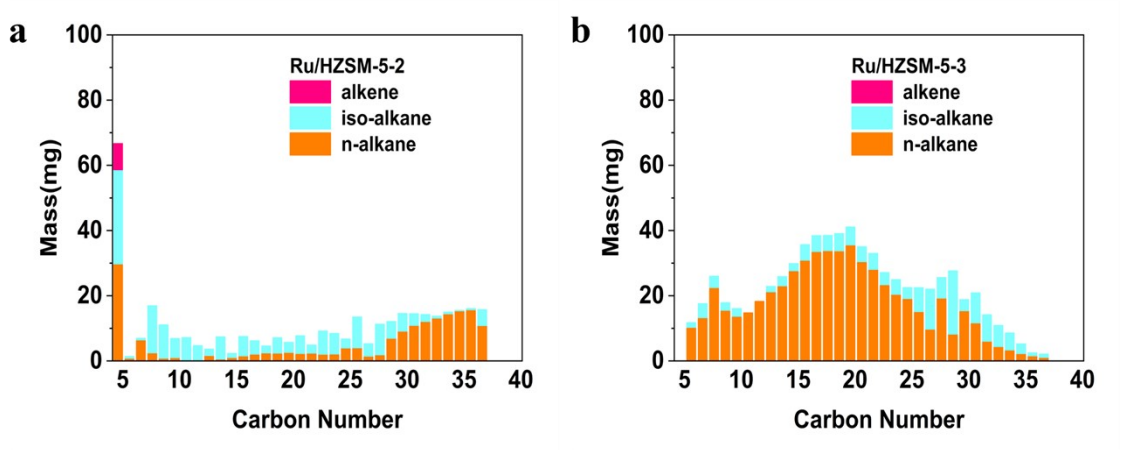

Fig. S1. Liquid product distribution over Ru/H-ZSM-5-2 and Ru/H-ZSM-5-3

Reaction condition: 2 MPa H_2, 250℃, 6 h.

Table S3. the calculated Ru particle size with different calcined temperatures and loadings

Catalysts	Ru (nm)	Catalysts	Ru (nm)
Ru/HZSM-5-3-200℃	20	2wt%-Ru/HZSM-5-3	25
Ru/HZSM-5-3-400℃	31	5wt%-Ru/HZSM-5-3	31
Ru/HZSM-5-3-700℃	100	10wt%-Ru/HZSM-5-3	84

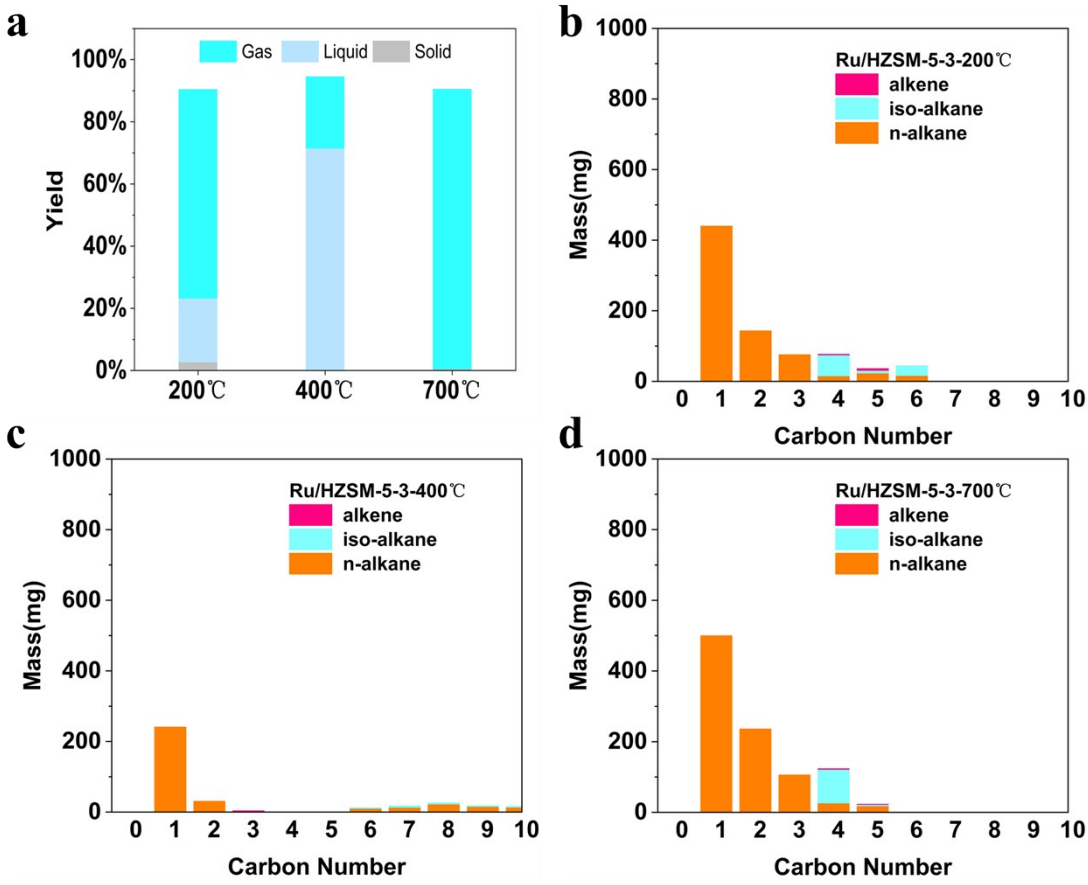

Fig. S2. (a) Catalytic performance and (b)-(d) distribution over Ru/HZSM-5-3 catalysts calcined at 200, 400 and 700 ℃. Reaction condition: 2 MPa H_2, 250 ℃, 6 h.

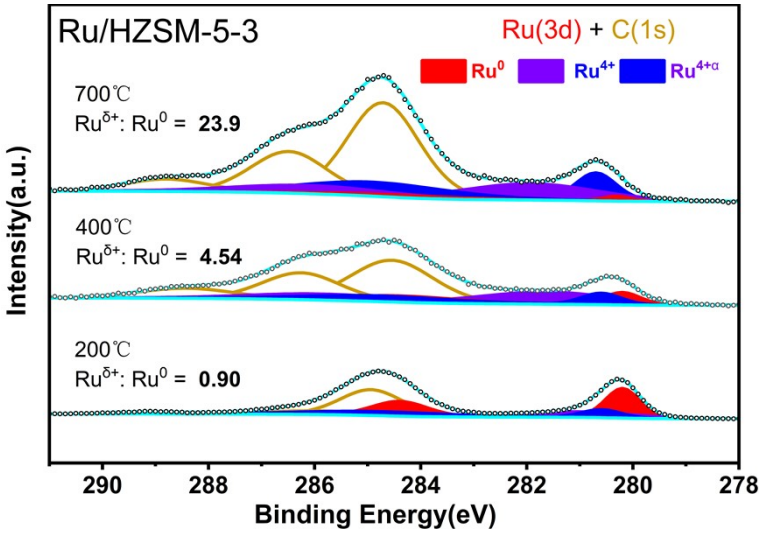

Fig. S3. Ru 3d and C 1s XPS spectra of Ru/H-ZSM-5-3-200°C, Ru/H-ZSM-5-3-400°C and Ru/H-ZSM-5-3-700°C catalysts

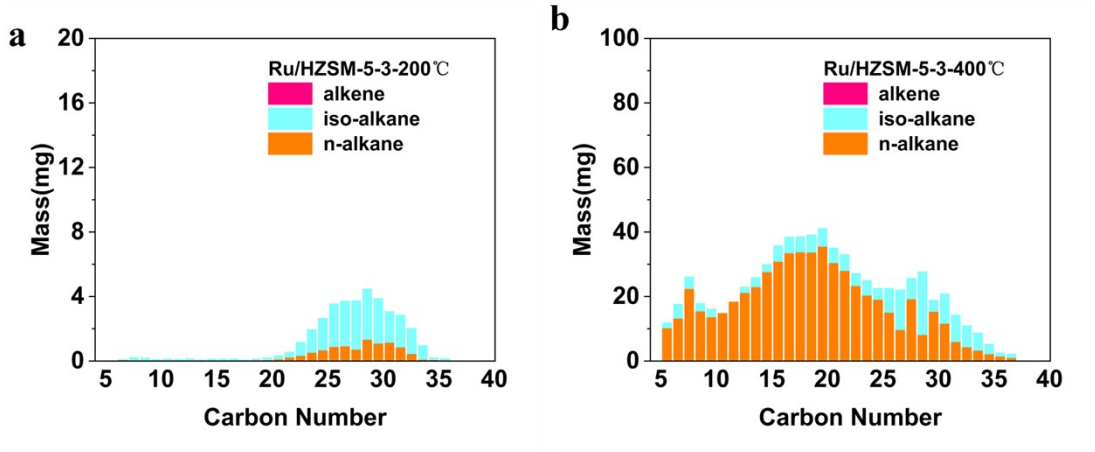

Fig. S4. Liquid product distribution over Ru/H-ZSM-5-3-200℃ and Ru/H-ZSM-5-3-400℃. Reaction condition: 2 MPa H_2, 250℃, 6 h.

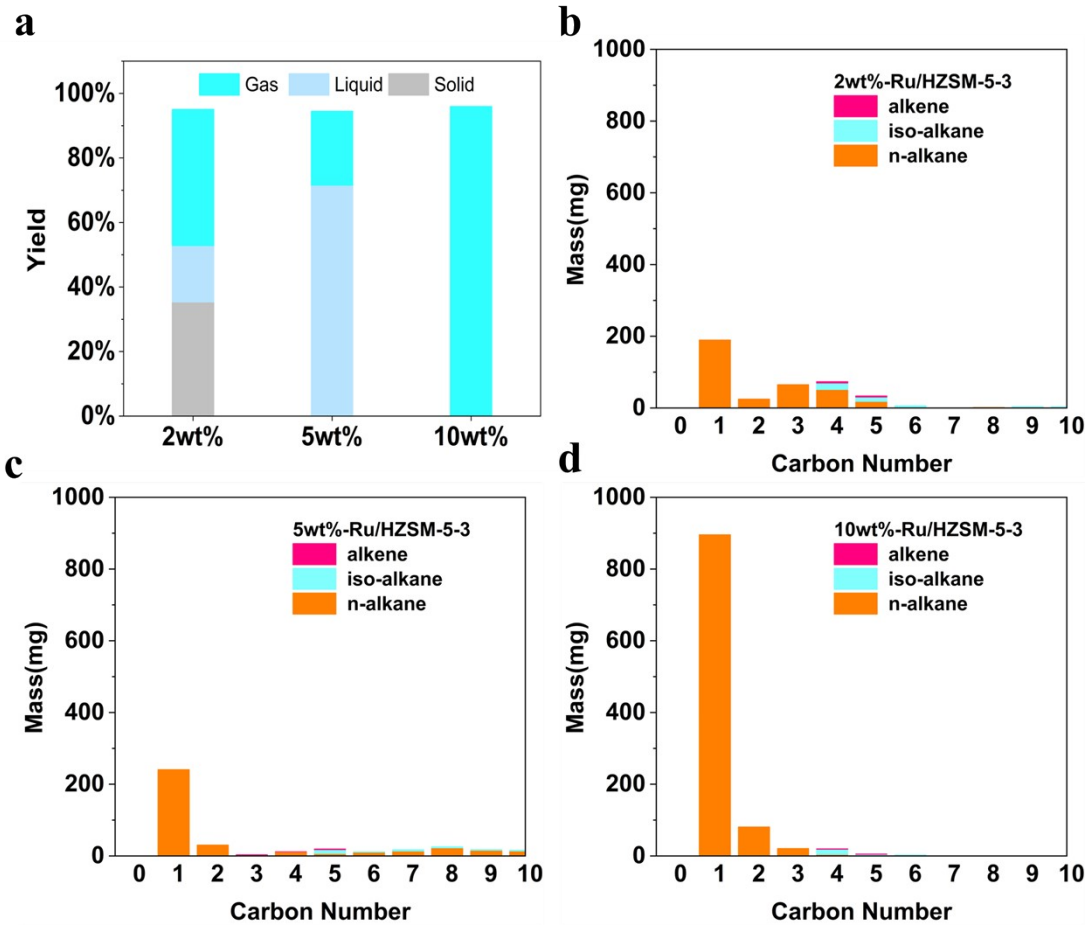

Fig. S5. (a) Catalytic performance and (b)-(d) distribution over Ru/HZSM-5-3 catalysts of 2, 5, and 10% Ru loading. Reaction condition: 2 MPa H_2, 250 °C, 6 h.

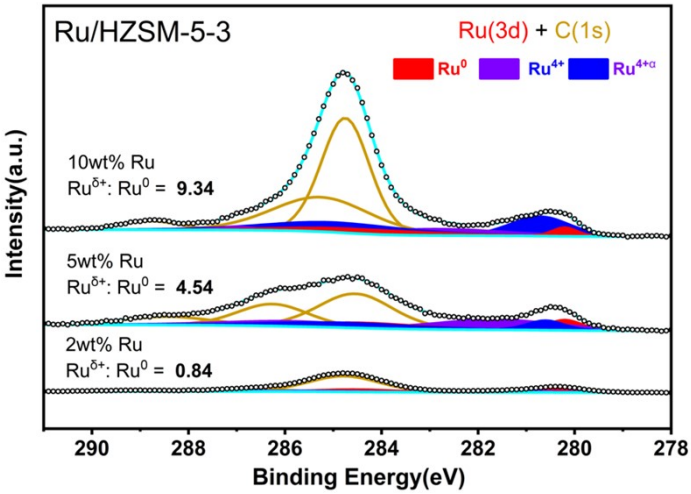

Fig. S6. Ru 3d and C 1s XPS spectra of 2wt%-Ru/H-ZSM-5-3, 5wt%-Ru/H-ZSM-5-3 and 10wt%-Ru/H-ZSM-5-3 catalysts

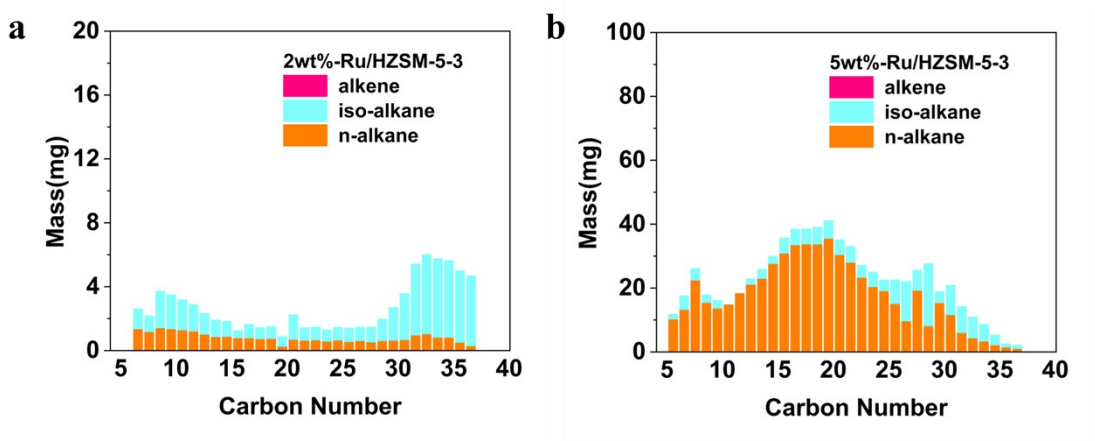

Fig. S7. Liquid product distribution over 2wt%-Ru/H-ZSM-5-3 and 5wt%-Ru/H-ZSM-5-3. Reaction condition: 2 MPa H_2, 250 ℃, 6 h.

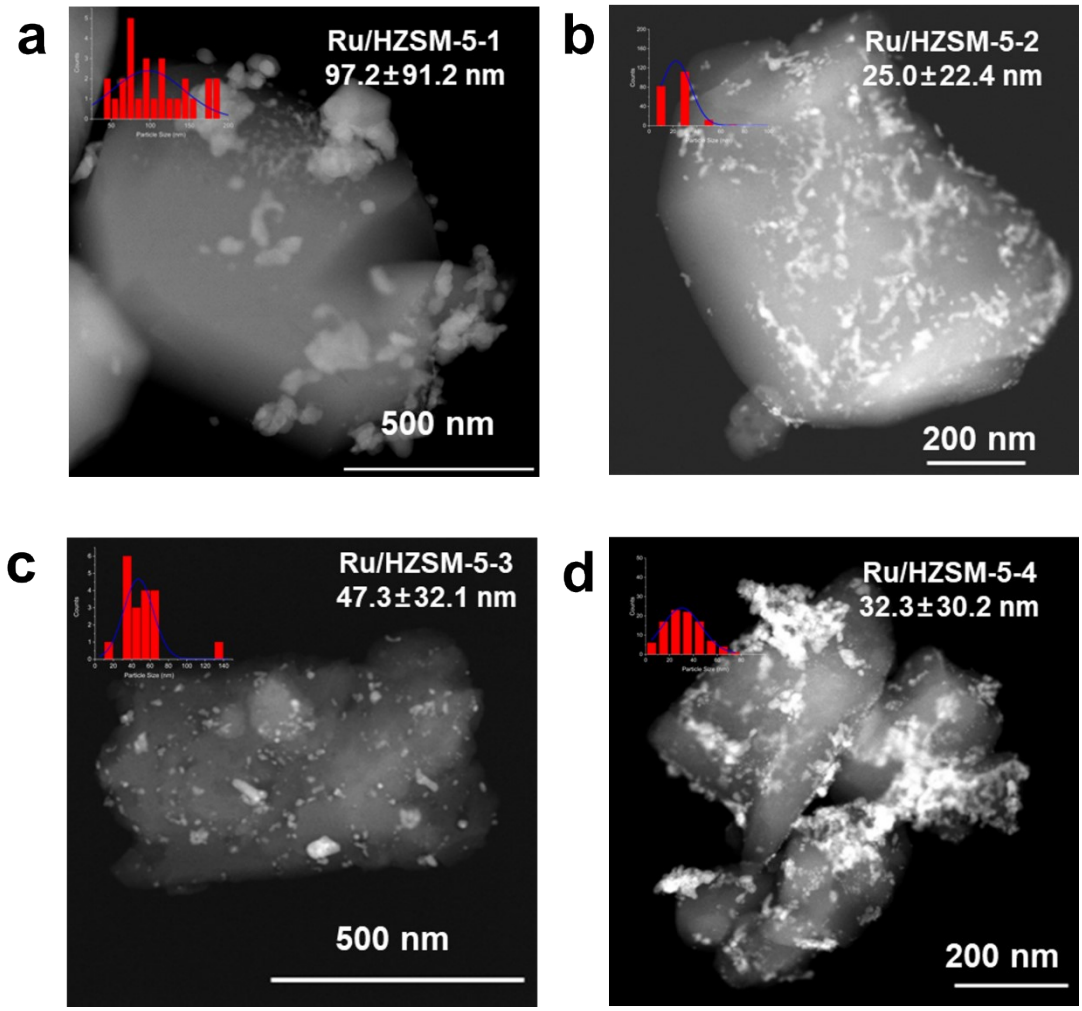

Fig. S8 (a)-(d) ADF-STEM patterns of recycled Ru/H-ZSM-5-1,2,3,4 catalysts

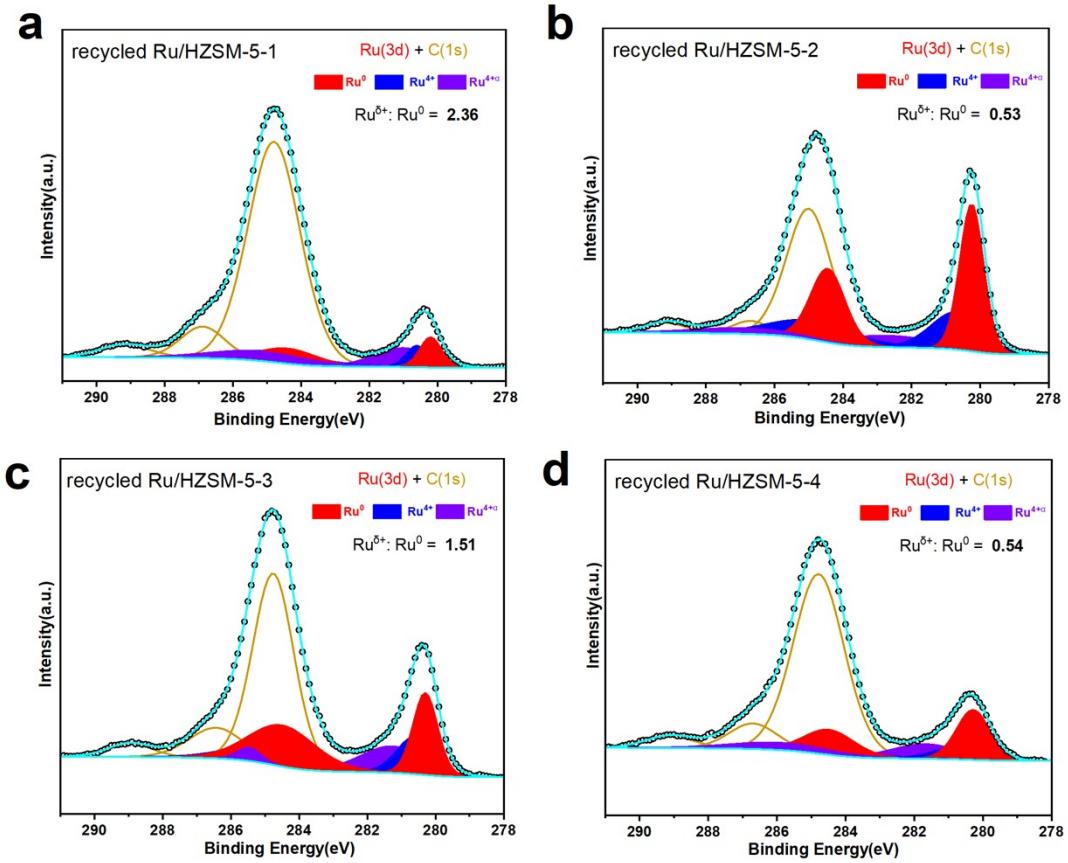

Fig. S9. (a)-(d) Ru 3d and C 1s XPS spectra of recycled Ru/H-ZSM-5-1,2,3,4 catalysts

Table S4. ICP-OES Analysis Results for Fresh and Spent Ru/HZSM-5 Catalysts

	Ru/HZSM-5-1	Ru/HZSM-5-2	Ru/HZSM-5-3	Ru/HZSM-5-4
Ru loading, %	5.21	5.09	4.99	5.13
Ratio of SiO_2/Al_2O_3	38.3	37.5	37.2	37.4
	Ru/HZSM-5-1 Recycled	Ru/HZSM-5-2 Recycled	Ru/HZSM-5-3 Recycled	Ru/HZSM-5-4 Recycled
Ru loading, %	5.17	5.10	4.89	4.96
Ratio of SiO_2/Al_2O_3	38.0	37.7	37.2	37.6
	Ru/HZSM-5-3 After cycle 1	Ru/HZSM-5-3 After cycle 4	-	-
Ru loading, %	4.96	4.93	-	-
Ratio of SiO_2/Al_2O_3	37.1	37.1	-	-

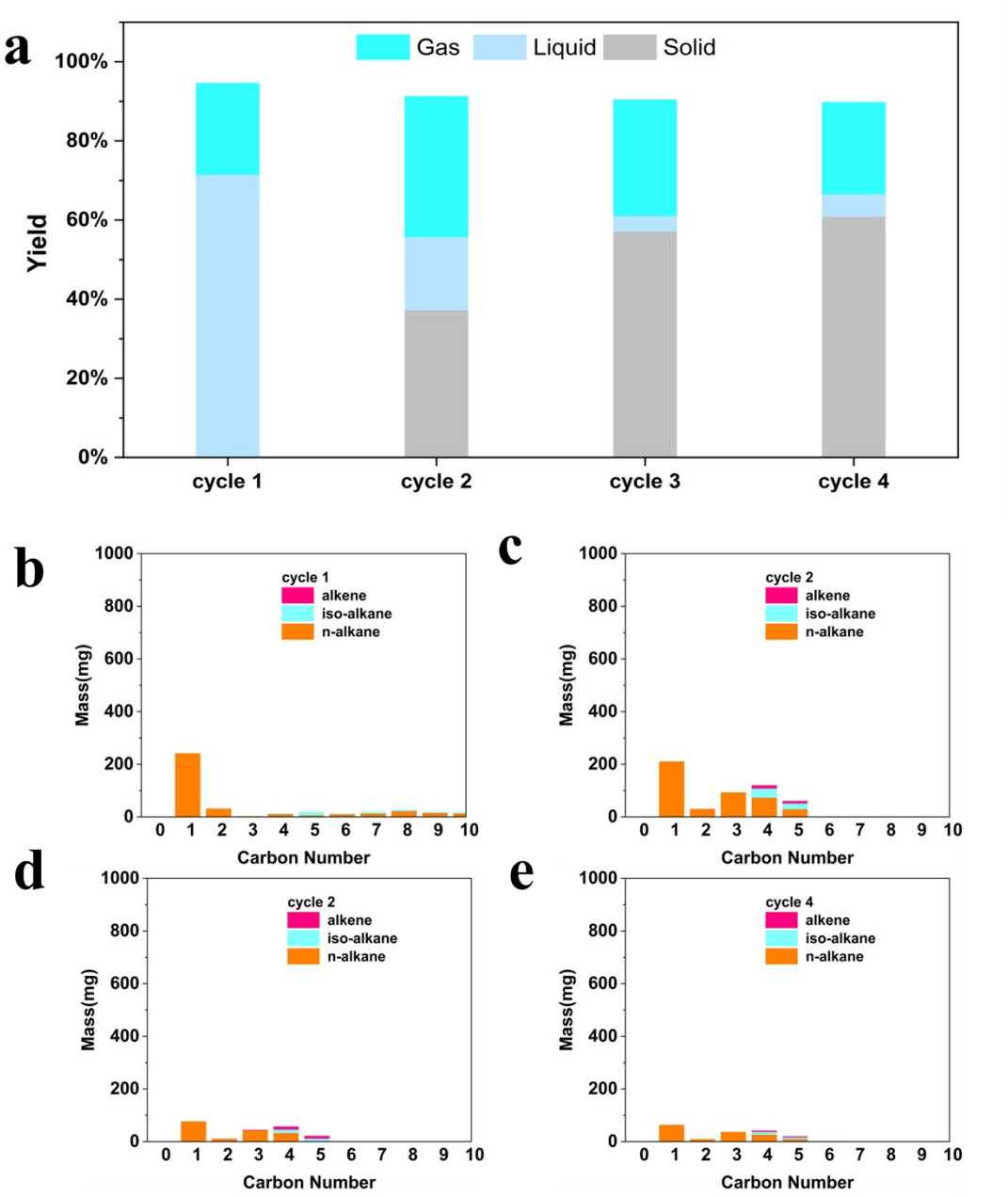

Fig. S10. (a) Catalytic performance and (b)-(d) product distribution over Ru/H-ZSM-5-3 catalysts in 4 cycles. Reaction condition: 2 MPa H_2, 250 ℃, 6 h.

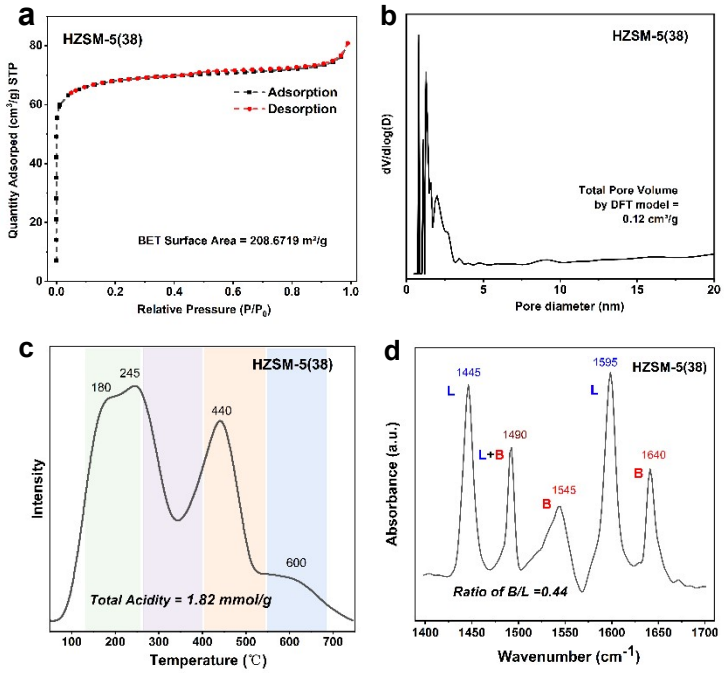

Fig. S11 (a) BET of HZSM-5 (38) and (b) pore diameter by DFT, (c) NH_3-TPD curve and (d) Pyridine *in-situ* IR spectrum

The textural and acidic properties of HZSM-5(38) were characterized by N_2 physisorption (BET), NH_3 temperature-programmed desorption (NH_3-TPD), and pyridine adsorption Fourier-transform infrared spectroscopy (Py-IR). The Brunauer–Emmett–Teller (BET) specific surface area of HZSM-5(38) was determined to be 208.6719 m^2/g (Figure S11a). Pore size distribution and total pore volume were derived from the DFT model (Figure S11b). The total pore volume was 0.12 cm^3/g, and the pore size distribution revealed a hierarchical porous structure with micro/mesopores, rather than a single micropore at 2 nm. The NH_3-TPD profile (Figure S11c) exhibited four distinct desorption peaks at 180 °C, 245 °C, 440 °C, and 600 °C, corresponding to weak, moderate, and strong acid sites, respectively. The peaks at 180 °C and 245 °C were assigned to weak/medium-strength acid sites, while those at 440 °C and 600 °C corresponded to strong acid sites[1]. The total acidity was calculated to be 1.82 mmol/g. The Py-IR spectrum (Figure S11d) confirmed the presence of both Brønsted (B) and Lewis (L) acid sites. Peaks at 1445 cm^{-1} and 1595 cm^{-1} were attributed to Lewis acid sites, while peaks at 1545 cm^{-1} and 1640 cm^{-1} were characteristic of Brønsted acid sites. The peak at 1490 cm^{-1} was assigned to the overlap of Brønsted and Lewis acid signals. The ratio of Brønsted to Lewis acid sites (B/L) was determined to be 0.44.

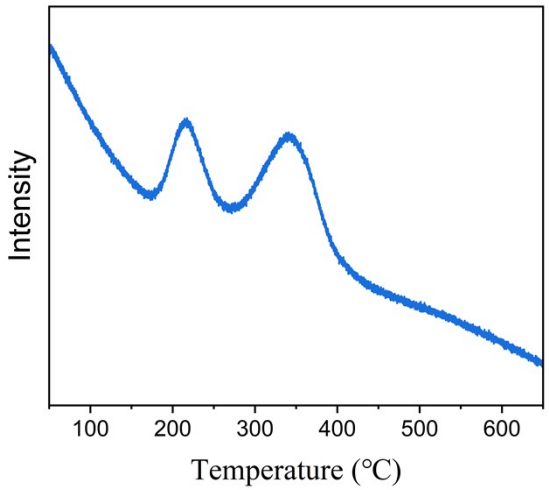

Fig. S12 H_2-TPD of Ru/HZSM-5-3

The H_2 temperature-programmed desorption (H_2-TPD) profile of HZSM-5(38) exhibits two distinct desorption peaks in the temperature ranges of 200–300 °C and 300–400 °C, respectively. The desorption peak centered at approximately 220 °C is ascribed to the reduction of oxidized ruthenium species to metallic Ru^0. The peak at around 340 °C corresponds to the desorption of hydrogen molecules strongly adsorbed on Brønsted acid sites of the zeolite support[2].

Notes and references

1 L. Gao, X. Zhong, J. Liu, J. Chen, Z. Wang, Y. Zhang, D. Wang, M. Shakeri, X. Zhang and B. Zhang, *ChemSusChem*, 2024, **17**, e202400598.

2 J. Long, Y. Mao, Y. Long, G. Chang, L. Chen, W. Zhou, J. Long and Y. Liu, *Bioresour Technol*, 2026, **439**, 133357.