

Supplementary Information

Efficient hydrogen isotopic analysis with Cu-Fe/ZSM-5 zeolite as cryogenic chromatographic stationary phase

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Experimental section

Chemicals

Tetrapropylammonium hydroxide aqueous solution (TPAOH, 25 wt% in water) and tetraethyl orthosilicate (TEOS) were obtained from Aladdin Industrial Corporation. Other reagents of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, NaOH, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, anhydrous $\text{Cu}(\text{CH}_3\text{COO})_2$ powder and fumed silica were received from Beijing Chemical Works. The ZSM-5 (Si/Al=100) with 300 nm particle size was supported by Rao Dong (Liaoning) New Material Co., Ltd. High-purity helium (99.999%), neon (99.999%), He-H₂-D₂ (50%:25%:25%) and H₂-D₂ (50%:50%), H₂-D₂ (90%:10%), H₂-D₂ (10%:90%) were offered by Sichuan Messer gas products Co, Ltd. The ternary mixture of H₂-HD-D₂ was yielded by Pt catalysis of H₂-D₂ (H₂: D₂=50%: 50%) to HD equilibrium conversion at room temperature.

Cu-Fe/ZSM-5 preparation

The ZSM-5 zeolite in size of 600 nm was prepared by a seeded growth method using 6.25Na₂O: 8.35SiO₂: 0.03Al₂O₃: 116H₂O as the synthesis solution under hydrothermal crystallization at 180 °C for 10 h. The recipe for the seed preparation was 1.0TPAOH: 3.64TEOS: 33.8H₂O. Cu/ZSM-5 was prepared by ion exchange: 1 g ZSM-5 was dispersed in 0.04 mol L⁻¹ Cu(CH₃COO)₂ solution and first stirred for 2 h

at 50 °C with subsequent stirring at room temperature for 24 h.¹ The filtrated sample was washed for three times to remove impurities with deionized water, and thus Cu/ZSM-5 was yielded. Cu/ZSM-5 was dispersed in 50 mL 0.001 mol L⁻¹ Fe(NO₃)₃ solution (molar ratio of Cu over Fe was 40 in the synthesis). The ion exchange and post treatment were identical as Cu/ZSM-5. The cleaned zeolite was first dried at 100 °C and then activated at 550 °C in air for 4 h to produce Cu-Fe/ZSM-5.

Characterization

Cu, Fe, Si and Al contents in Cu-Fe/ZSM-5 were analyzed with inductively coupled plasma optical emission spectrometer (ICP-OES). The powder X-ray diffraction (PXRD) measurements were recorded on X-ray diffractometer (Haoyuan Inc., DX2700) with Cu-K α radiation ($\lambda=0.154$ nm) with a 2θ range of 5°-50° at 40 kV and 30 mA. The Micromeritics ASAP 2469 instrument was used to record N₂ adsorption-desorption isotherms at 77 K. The samples were degassed at 150 °C for 12 h before sorption measurements. Specific surface area and pore width were calculated according to Brunauer-Emmett-Teller (BET) and density functional theory (DFT) models. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy images were obtained on SEM (Thermo Scientific Apreo 2C, OXFORD ULTIM Max65), and transmission electron microscopy (TEM) images were obtained on TEM (TALOS F200S). X-ray photoelectron spectroscopy (XPS) (Escalab, 250Xi) was used to measure Cu state in Cu/ZSM-5 and Cu-Fe/ZSM-5 zeolites.

Thermal desorption spectroscopy (TDS) was used to obtain D₂ and H₂ desorption curves at 77 K. In detail, around 5 mg zeolite powder was packed in a sample tube and then subjected to in-situ activation at 100 °C for 10 h. Then, the tube was cooled down to 77 K and soaked in a H₂-D₂ (50%:50%) mixture at 1000 Pa for 10 minutes. Subsequently, the surplus gas in the tube was pumped gently, the tube was cooled down to 20 K and desorption signals of H₂-D₂ mixture from 20 K to 180 K were recorded by a quadrupole mass spectrometer (QMS).

Gas chromatographic separation of H₂/D₂ and H₂/HD/D₂

The home-made gas chromatographic separation device was built with pressure-controlled sampling system, thermal conductivity detector (TCD) and 10 μ L injection loop. Helium and neon were used as driven gas and carrier gas, respectively. The zeolite of Cu-Fe/ZSM-5 was packed in a stainless steel tube in length of 1.5 m and diameter of 1.59 mm (outer) and 0.75 mm (inner). The sample in the column was

activated at 180 °C for 6 h as continuous neon purging with a rate of 17.0 mL min⁻¹. After activation, the sample filled column was cooled to room temperature and then kept at 77 K in a liquid nitrogen container.

The separation resolution (R) between components of i and j was calculated by Eq.

(1):

$$R_{i/j} = \frac{1.17(t_{Rj} - t_{Ri})}{w_{1/2i} + w_{1/2j}}$$

(1)

where t_{Ri} and t_{Rj} were the retention time of peak i and peak j respectively, $w_{1/2}$ was the full width at half maximum of the peak.

The number of theoretical plates (N) was calculated by Eq. (2):

$$N = 5.54 \left(\frac{t_R}{w_{1/2}} \right)^2 \quad (2)$$

The theoretical plate height was calculated by Eq. (3):

$$H = \frac{L}{N} \quad (3)$$

where L refers to the length of column with a sample.

Supplementary Tables and Figures

Table S1. The materials as column stationary phase in hydrogen isotopes analysis by gas chromatography.

Material	Column temp/K	R (D ₂ /H ₂)	Analysis duration/min
Cu-Fe/ZSM-5	77	1.70	3.8 (This work)
ZIF-67@NH ₂ -SiO ₂	77	1.52	10.2 ²
ZIF-67@NH ₂ - γ -Al ₂ O ₃	77	1.79	5.5 ³
MnCl ₂ @CPL-1@ γ -Al ₂ O ₃	77	1.62	6.5 ⁴
Ni ₂ (adc) ₂ (dabco)@ γ -Al ₂ O ₃	77	2.85	6.0 ⁵
20 wt% MnCl ₂ / γ -Al ₂ O ₃	77	~1.50	7.0 ⁶
Fe(III)/glass	77	1.10	8.2 ⁷

Material	Column temp/K	R (H ₂ /HD)	R (HD/D ₂)	Analysis duration/min
Cu-Fe/ZSM-5	77	1.34	2.23	5.0 (This work)
Molecular Sieve 5A	113	1.17	1.29	~68.0 ⁸
Molecular Sieve 4A	83	1.23	1.81	~27.0 ⁸
Molecular Sieve 3A	93	1.29	1.60	~15.0 ⁸
Ni ₂ Cl ₂ BBTA@ γ -Al ₂ O ₃	77	1.57	2.38	11.0 ⁹
Ni ₂ (adc) ₂ (dabco) @ γ -Al ₂ O ₃	77	1.31	3.26	12.0 ⁵
5A Molecular Sieve/Al ₂ O ₃	77	---	---	16.0 ¹⁰
Al ₂ O ₃ /MnCl ₂	77	1.10	1.95	2.5 ¹¹

Table S2. Average peak area (S) and mean separation resolution (R) of six repetitive experiments for Cu-Fe/ZSM-5 at 77 K with various H₂-D₂ proportions measured on gas chromatography.

Feed gas	\bar{S}_{H_2}	\bar{S}_{D_2}	\bar{R}_{D_2/H_2}
10%H ₂ -90%D ₂	71874.8	459087.5	0.97

50%He-25%H ₂ -25%D ₂	189935.2	127528.2	1.85
50%H ₂ -50%D ₂	372299.7	256605.5	1.66
90%H ₂ -10%D ₂	668561.8	42128.7	2.55

Table S3. Retention time of H₂, HD and D₂ and separation resolution (R) on Cu-Fe/ZSM-5 at various injection loop pressures with a 10.8 mL min⁻¹ flow rate.

Injection loop pressure	Retention time (min)			R	
	H ₂	HD	D ₂	R _{H₂/HD}	R _{HD/D₂}
5.0 kPa	2.83	3.31	4.28	1.34	2.23
7.2 kPa	2.84	3.31	4.30	1.08	2.31
15.2 kPa	2.84	3.29	4.28	1.03	2.24
30.1 kPa	2.82	3.26	4.25	0.97	2.16
60.5 kPa	2.63	2.95	3.81	0.78	1.69
95.6 kPa	2.64	2.90	3.82	0.53	1.64

Table S4. The elemental contents of Cu-Fe/ZSM-5 zeolite measured by EDX.

Element	wt%	atom%
C	14.81	23.54
O	38.24	45.62
Al	0.65	0.46
Si	43.35	29.48
Fe	0.32	0.11
Cu	2.63	0.79
Total	100	100

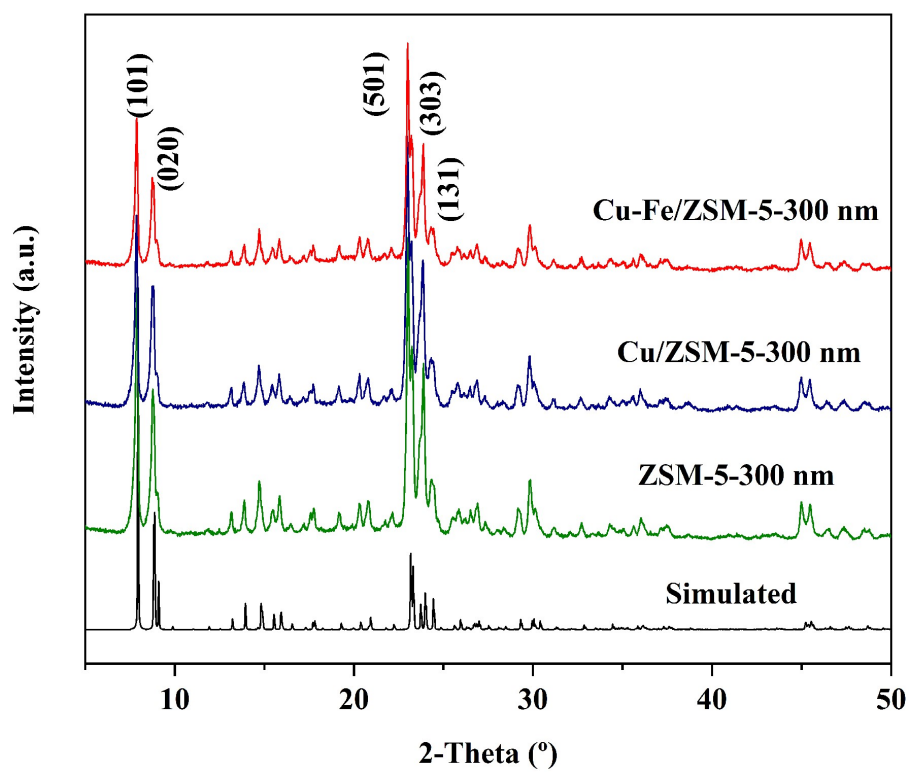


Fig. S1 PXRD patterns for a commercial ZSM-5 zeolite with particle size of 300 nm.

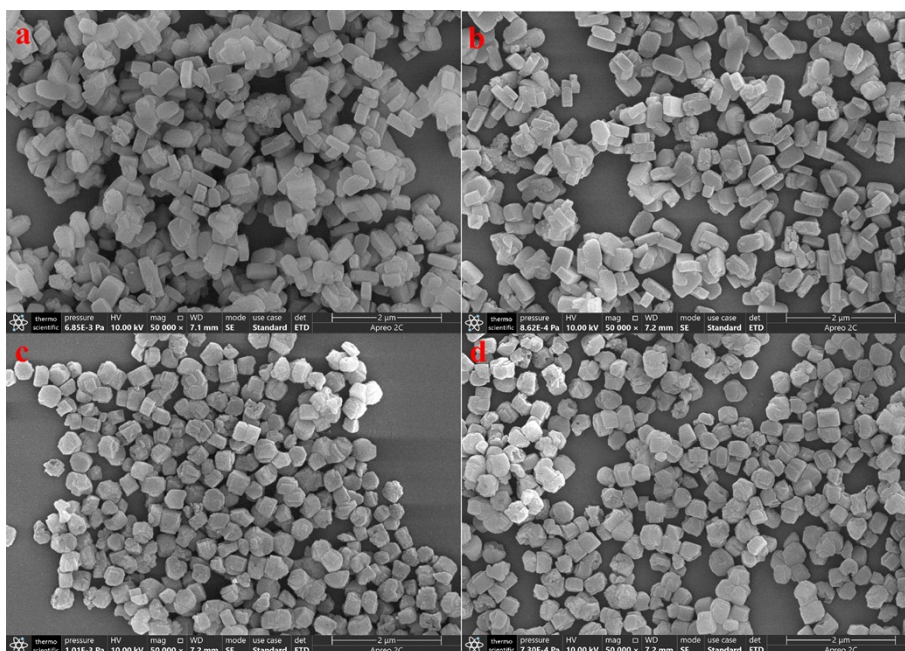


Fig. S2 SEM images of prepared ZSM-5 (a) and Cu-Fe/ZSM-5 (b) in size of 600 nm, and commercial ZSM-5 (c) and Cu-Fe/ZSM-5 (d) in size of 300 nm.

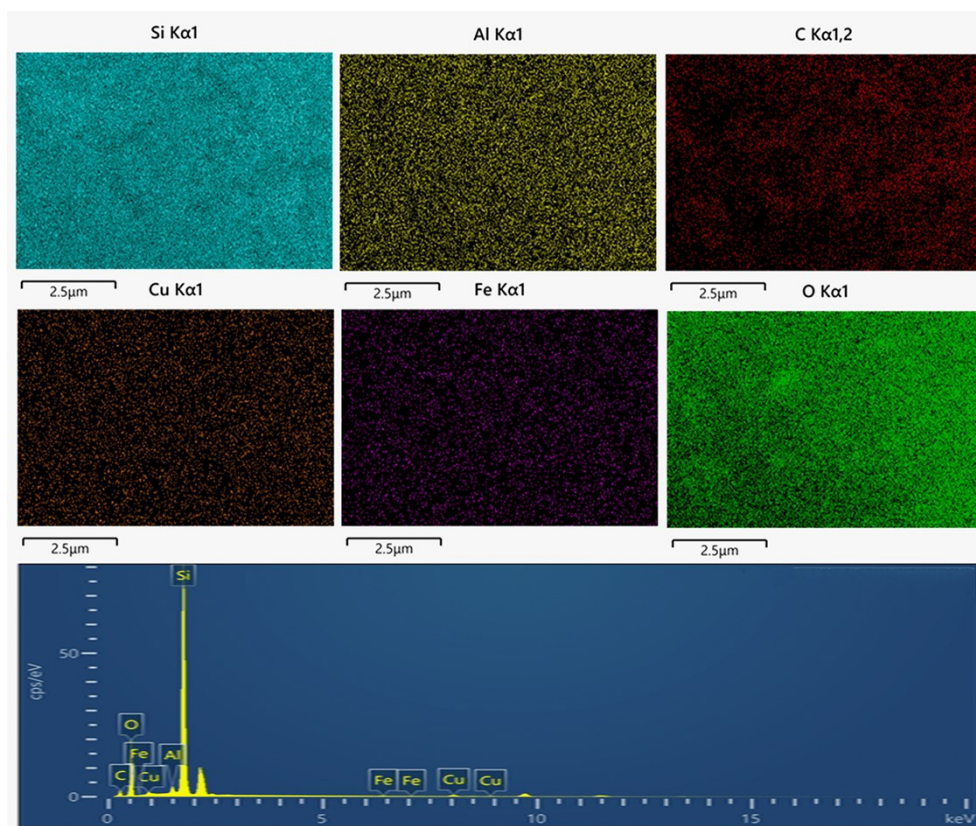


Fig. S3 EDX mapping and analysis of the Cu-Fe/ZSM-5 zeolite.

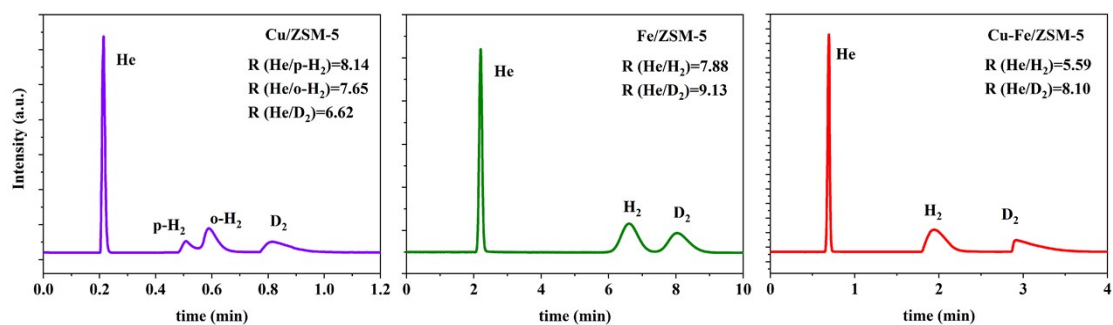


Fig. S4 Gas chromatographic signals of Cu/ZSM-5, Fe/ZSM-5 and Cu-Fe/ZSM-5 as stationary phase materials in He-H₂-D₂ (50%:25%:25%) mixture.

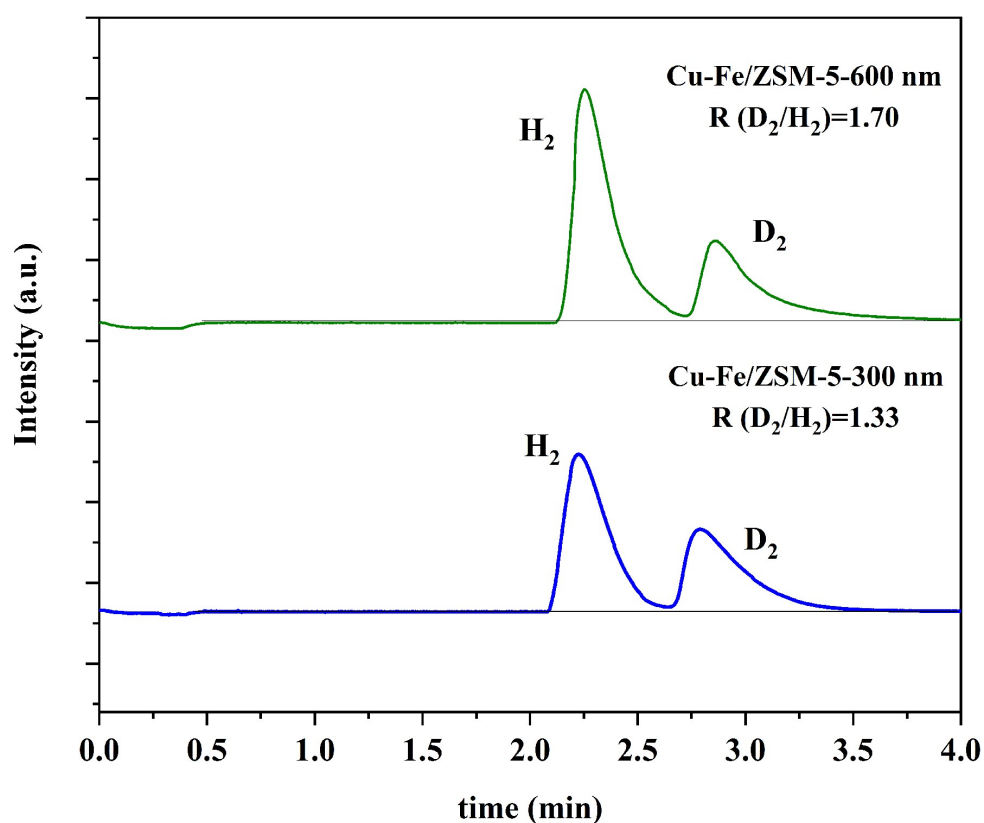


Fig. S5 Gas chromatographic peaks of H₂ and D₂ for Cu-Fe/ZSM-5 zeolites with particle sizes of 300 nm and 600 nm in H₂-D₂ (50%:50%) mixture. Injection loop pressure was set at atmospheric pressure (95.6 kPa) and flow rate was set at 17.0 mL min⁻¹. Cu-Fe/ZSM-5 in 600 nm prepared in this study can separate D₂/H₂ with

resolution of 1.70 which is higher than that of 1.33 for commercial ZSM-5 in 300 nm.

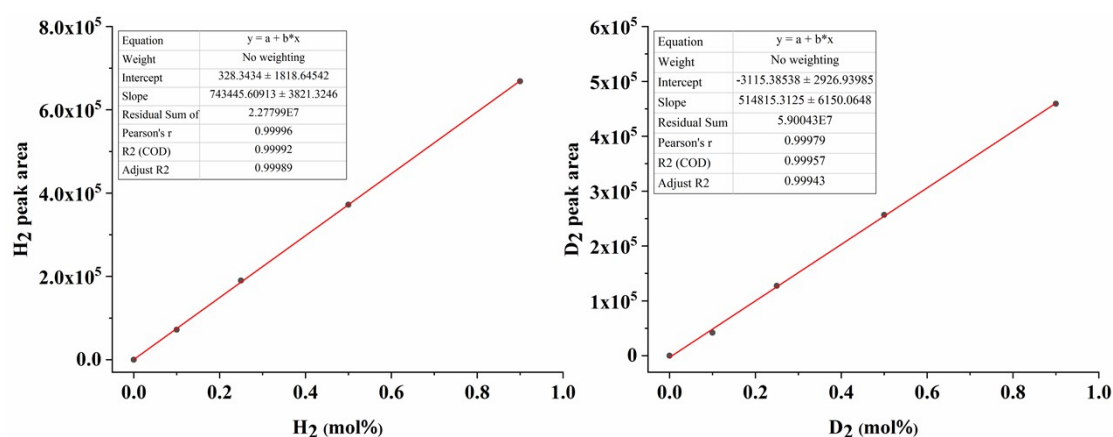


Fig. S6 The linear relationship between gas proportion and peak area for H₂ and D₂, respectively. Injection loop pressure was set at atmospheric pressure (95.6 kPa) and flow rate was set at 17.0 mL min⁻¹.

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