

Electronic Supplementary Information

Highly Selective Raney Fe@HZSM-5 Fischer–Tropsch Synthesis Catalyst for Gasoline Production: One-Pot Synthesis and Unexpected Effect of Zeolite

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1. Preparation

(1) Preparation of the Fe₅₀Al₅₀ alloy

The Fe₅₀Al₅₀ alloy (Fe/Al, w/w) was provided by Changling Catalyst Corp., Sinopec. The alloy was prepared by a single roller melt-spinning method. Equal weights of metallic Fe and Al were melted and kept at 1573 K in a vacuum induction furnace for 30 min to ensure the homogeneity of the melt. Alloy ribbons with a cross section of $\sim 0.02 \times 2 \text{ mm}^2$ were obtained by spraying the melt onto a high-speed rotation water-cooled copper roller under the blanket of Ar. The ribbons were ground, sieved, and the 40-80-mesh fraction was used throughout the experiments. All other chemicals were of analytical grade (A.R., Sinopharm) and without further purification prior to use.

(2) Preparation of the R-Fe@HZSM-5 Catalyst

1.0 g of Fe₅₀Al₅₀ alloy was mixed with 45 mL of zeolite synthesis solution containing distilled water and ethanol, with TPAOH (60% solution) as the template, tetraethyl orthosilicate (TEOS) as the Si source, and transferred into a 50 mL-capacity Teflon-lined stainless steel autoclave. The molar ratios of the reactants were TPAOH: TEOS: EtOH: H₂O = 1: 4: 16: 240. The autoclave was sealed and heated at 453 K for 48 h. The resulting powders were filtered off, washed several times with distilled

water to pH value below 8. The sample was then dried at 373 K for 10 h, followed by calcination at 823 K for 4 h.

(3) Preparation of the Raney Fe Catalyst

A 1.0-gram portion of the Fe₅₀Al₅₀ alloy was added to an aqueous solution of KOH (8.0 M, 12 mL) at 343 K under gentle stirring for 2 h. The black powders were washed thoroughly with distilled water to neutrality, followed by washing with absolute ethanol to replace water. When removing the liquid, one must ensure that a thin layer of liquid always covers the pyrophoric Raney Fe powders. The as-prepared Raney Fe catalyst was stored under ethanol for activity testing and characterization.

(4) Preparation of the Physically Mixed R-Fe–HZSM-5 Catalyst

For the preparation of the physically mixed R-Fe–HZSM-5 catalyst, pure HZSM-5 with Si/Al ratio identical to that in the R-Fe@HZSM-5 core–shell catalyst was synthesized. TPAOH was used as the template, TEOS as the Si source, and aluminum isopropoxide as the Al source. The composition of HZSM-5 zeolite precursor solution was at a molar ratio of 22.5TPAOH: 63SiO₂: 1Al₂O₃: 36EtOH: 540H₂O. The Teflon-lined stainless autoclave was sealed and heated at 453 K for 48 h. The resulting powders were filtered off, washed several times with distilled water until its pH value was below 8. The sample was then dried at 373 K for 10 h and calcined at 823 K for 4 h. The R-Fe–HZSM-5 catalyst was prepared by evenly mixing the as-synthesized HZSM-5 with the above-prepared Raney Fe in a weight ratio similar to that in the R-Fe@HZSM-5 core–shell catalyst.

2. Characterization

(1) N₂ Physisorption

The Brunauer–Emmett–Teller (BET) surface area (S_{BET}) and porosity were acquired by N₂ physisorption at 77 K on a Micromeritics TriStar3000 apparatus. Prior to the measurements, the catalysts were degassed at 423 K under a N₂ flow for 2 h.

(2) Temperature-Programmed Desorption of NH₃ (NH₃-TPD)

NH₃-TPD was performed in a flow system. The catalyst was activated in He at 673 K for 1 h, after which the catalyst was saturated by 10 vol% NH₃/He gas flow at

393 K for 2 h. Then, the sample is purged with He for 2 h in order to remove gaseous and physisorbed NH₃. The catalyst was heated in He at a rate of 20 K min⁻¹ for NH₃ desorption. The amount of NH₃ desorbed was monitored by TCD.

(3) X-Ray Diffraction (XRD)

Powder XRD pattern was acquired on a Bruker AXS D8 Advance X-ray diffractometer using Ni-filtered Cu K α radiation ($\lambda = 0.15418$ nm). The tube voltage was 40 kV, and the current was 40 mA.

(4) Scanning Electron Microscopy (SEM)

The morphology and microstructure were observed a Philips XL30 scanning electron microscope operating at 20 kV, to which an EDX analyzer was attached.

(5) ⁵⁷Fe Mössbauer Spectroscopy

⁵⁷Fe Mössbauer spectrum was recorded on a spectrometer constructed by the Key Laboratory of Nuclear Analysis Techniques, Chinese Academy of Sciences, using a ⁵⁷Co/Rh irradiation source. All spectra were acquired using the constant acceleration transmission mode at room temperature. The velocity was calibrated by a 25 μ m-thick α -Fe foil, and the *IS* value was referenced to α -Fe at room temperature.

3. Activity Testing

Prior to the FTS reaction, the R-Fe@HZSM-5 sample (1.0 g) diluted with quartz powder (80-100 mesh, 1.0 g) was reduced *in situ* in 5% H₂/Ar (50 mL min⁻¹) for 16 h at 723 K (ramping rate 2 K min⁻¹). Catalytic testing was conducted on a tubular fixed-bed reactor with inner diameter of 10 mm under reaction conditions of 2: 1 (v/v) H₂/CO (flow rate 33.3 mL min⁻¹), 543 K, and 2.0 MPa, if not specified. FTS products were analyzed on line with two gas chromatographs equipped with two high-temperature Valco six-port valves. A TDX-01 packed column connected to a thermal conductivity detector (TCD) was used to analyze H₂, N₂, CO, CH₄, and CO₂. Hydrocarbons (C₁–C₃₀) were analyzed with a PONA capillary column connected to a flame ionization detector (FID). The hydrocarbon selectivities were calculated on carbon basis.

Table S1 Textural and chemical properties of Raney Fe, R-Fe-HZSM-5, and R-Fe@HZSM-5 catalysts

Catalyst	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_{pore} ($\text{cm}^3 \text{g}^{-1}$)	d_{pore} (nm)	Fe/Zeolite (weight ratio)	NH_3 uptake ($\mu\text{mol g}^{-1}$)	$\text{SiO}_2/\text{Al}_2\text{O}_3$ (Molar ratio)
Raney Fe	60	0.16	10.5	-	-	-
R-Fe-HZSM-5	199	0.17	7.8	87.0/13.0	64.5	63
R-Fe@HZSM-5	171	0.12	6.5	87.5/12.5	56.1	63

Table S2 Comparison of the selectivity to gasoline-range hydrocarbons over R-Fe@HZSM-5 catalyst with those over literature FTS catalysts containing Fe and HZSM-5 and typical industrial iron-based FTS catalyst

Catalyst	Reaction conditions	Selectivity (C ₅ -C ₁₁)	Yield (C ₅ -C ₁₁)	Ref.
R-Fe@HZSM-5	$T = 543 \text{ K}, P = 2.0 \text{ MPa}, H_2/CO = 2,$ $W_{\text{cat.}}/F_{(\text{CO}+\text{H}_2)} = 10 \text{ g h/mol}$	71%	66%	This work
R-Fe@HZSM-5	$T = 543 \text{ K}, P = 2.0 \text{ MPa}, H_2/CO = 1,$ $W_{\text{cat.}}/F_{(\text{CO}+\text{H}_2)} = 10 \text{ g h/mol}$	73%	65%	This work
HZSM-5/fused-iron	$T = 573 \text{ K}, P = 1.0 \text{ MPa}, H_2/CO = 1,$ $W_{\text{cat.}}/F_{(\text{CO}+\text{H}_2)} = 10 \text{ g h/mol}$	48%	46%	[S1]
Fused-iron/HZSM-5-mix	$T = 573 \text{ K}, P = 1.0 \text{ MPa}, H_2/CO = 1,$ $W_{\text{cat.}}/F_{(\text{CO}+\text{H}_2)} = 10 \text{ g h/mol}$	40%	38%	[S1]
FeCuMgCaK-HZSM-5	$T = 553 \text{ K}, P = 1.0 \text{ MPa}, H_2/CO = 1,$ $W_{\text{cat.}}/F_{(\text{CO}+\text{H}_2)} = 10 \text{ g h/mol}$	52%	59%	[S2]
Fe-Cu-K/ZSM-5	$T = 573 \text{ K}, P = 1.0 \text{ MPa}, H_2/CO = 2,$ $W_{\text{cat.}}/F_{(\text{CO}+\text{H}_2)} = 11.2 \text{ g h/mol}$	58%	45%	[S3]
FeCuLa/HZSM-5	$T = 603 \text{ K}, P = 2.5 \text{ MPa}, H_2/CO = 1,$ $W_{\text{cat.}}/F_{(\text{CO}+\text{H}_2)} = 7.2 \text{ g h/mol}$	56%	–	[S4]
FeKCu/SiO ₂ (Ruhchemie LP33/88)	$T = 523 \text{ K}, P = 2.4 \text{ MPa}, H_2/CO = 2,$ $W_{\text{cat.}}/F_{(\text{CO}+\text{H}_2)} = 6.2 \text{ g h/mol}$	50%	21%	[S5]

Table S3 Room-temperature ^{57}Fe Mössbauer parameters for Raney Fe, R-Fe-HZSM-5, and R-Fe@HZSM-5 catalysts after *ca.* 150 h on stream

	Parameter ^a	Raney Fe	R-Fe-HZSM-5	R-Fe@HZSM-5
Sextet 1	IS (mm s^{-1})	0.18(2)	0.17(3)	0.17(7)
$(\gamma\text{-Fe}_5\text{C}_2)$	QS (mm s^{-1})	0.07(2)	0.07(8)	0.07(8)
	H (T)	18.3(5)	18.4(1)	18.2(9)
	Γ (mm s^{-1})	0.43(9)	0.43(7)	0.35(8)
	A (%)	8.9	10.5	16.4
Sextet 2	IS (mm s^{-1})	0.25(7)	0.25(3)	0.23(1)
$(\gamma\text{-Fe}_5\text{C}_2)$	QS (mm s^{-1})	0.18(5)	0.11(6)	0.11(3)
	H (T)	22.9(6)	23.3(1)	23.0(8)
	Γ (mm s^{-1})	0.29(4)	0.38(2)	0.38(2)
	A (%)	9.9	10.2	17.0
Sextet 3	IS (mm s^{-1})	0.26(9)	0.26(4)	0.27(3)
$(\gamma\text{-Fe}_5\text{C}_2)$	QS (mm s^{-1})	0.04(6)	0.04(4)	0.03(5)
	H (T)	10.4(6)	10.4(4)	10.4(2)
	Γ (mm s^{-1})	0.32(8)	0.32(9)	0.29(4)
	A (%)	5.7	7.7	8.7
Sextet 4	IS (mm s^{-1})	-0.01(8)	-0.02(8)	-0.01(4)
(Fe^0)	QS (mm s^{-1})	0.09(9)	0.09(7)	0.09(3)
	H (T)	33.3(1)	33.3(8)	33.2(4)
	Γ (mm s^{-1})	0.33(5)	0.29(1)	0.35(9)
	A (%)	7.8	5.8	3.9

Sextet 5	<i>IS</i> (mm s ⁻¹)	0.65(4)	0.64(8)	0.64(3)
(Fe(II/III); Fe ₃ O ₄)	<i>QS</i> (mm s ⁻¹)	-0.02(5)	-0.03(2)	-0.02(4)
	<i>H</i> (T)	45.4(4)	45.7(8)	45.8(5)
	<i>Γ</i> (mm s ⁻¹)	0.49(4)	0.45(6)	0.50(1)
	<i>A</i> (%)	33.8	32.8	33.6
Sextet 6	<i>IS</i> (mm s ⁻¹)	0.28(3)	0.28(2)	0.19(4)
(Fe(III); Fe ₃ O ₄)	<i>QS</i> (mm s ⁻¹)	-0.01(5)	-0.01(1)	-0.01(7)
	<i>H</i> (T)	49.0(3)	48.9(6)	48.9(9)
	<i>Γ</i> (mm s ⁻¹)	0.30(1)	0.30(2)	0.29(5)
	<i>A</i> (%)	23.5	21.5	14.2
Sextet 7	<i>IS</i> (mm s ⁻¹)	0.34(9)	0.33(6)	
(Fe(III) in iron oxide)	<i>QS</i> (mm s ⁻¹)	0.01(5)	0.02	
	<i>H</i> [T]	50.9(5)	50.2	N/A
	<i>Γ</i> (mm s ⁻¹)	0.49(3)	0.54(5)	
	<i>A</i> (%)	10.4	11.5	
Doublet	<i>IS</i> (mm s ⁻¹)			0.33(4)
(superparamagnetic	<i>QS</i> (mm s ⁻¹)			0.79(1)
(spm) Fe(III))		N/A	N/A	
	<i>H</i> (T)			0.57(2)
	<i>Γ</i> (mm s ⁻¹)			6.2

^a *IS*: Isomer shift (relative to α-Fe); *QS*: quadrupole shift for sextet and quadruple splitting for doublet; *Γ*: full line width at half maximum; *H*: hyperfine magnetic field; *A*: relative spectral area. Numbers in parentheses provide the uncertainty in the last digit.

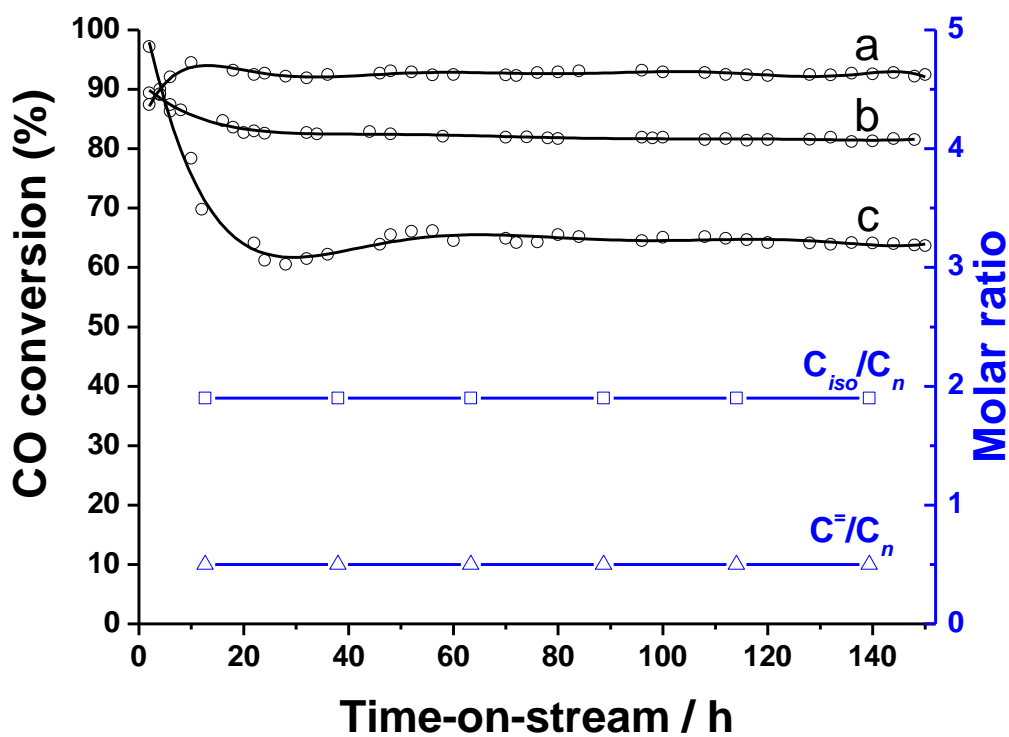


Fig. S1 Evolution of CO conversion versus time-on-stream (TOS) over (a) R-Fe@HZSM-5, (b) R-Fe-HZSM-5, and (c) Raney Fe under reaction conditions of $T = 543$ K, $H_2/CO = 2$, $P = 2.0$ MPa, and $W_{Fe}/F_{(CO+H_2)} = 10$ g h mol⁻¹. \square and Δ represent the C_{iso}/C_n and $C^=/C_n$ molar ratios over (a) versus TOS, respectively.

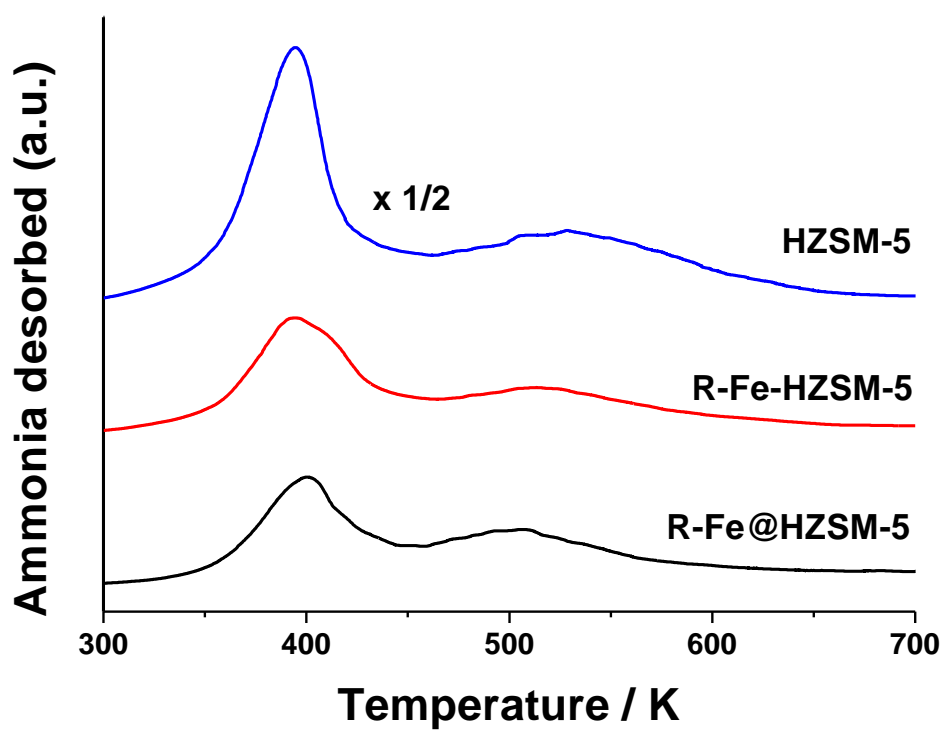


Fig. S2 NH₃-TPD profiles of HZSM-5, physically mixed R-Fe-HZSM-5, and R-Fe@HZSM-5.

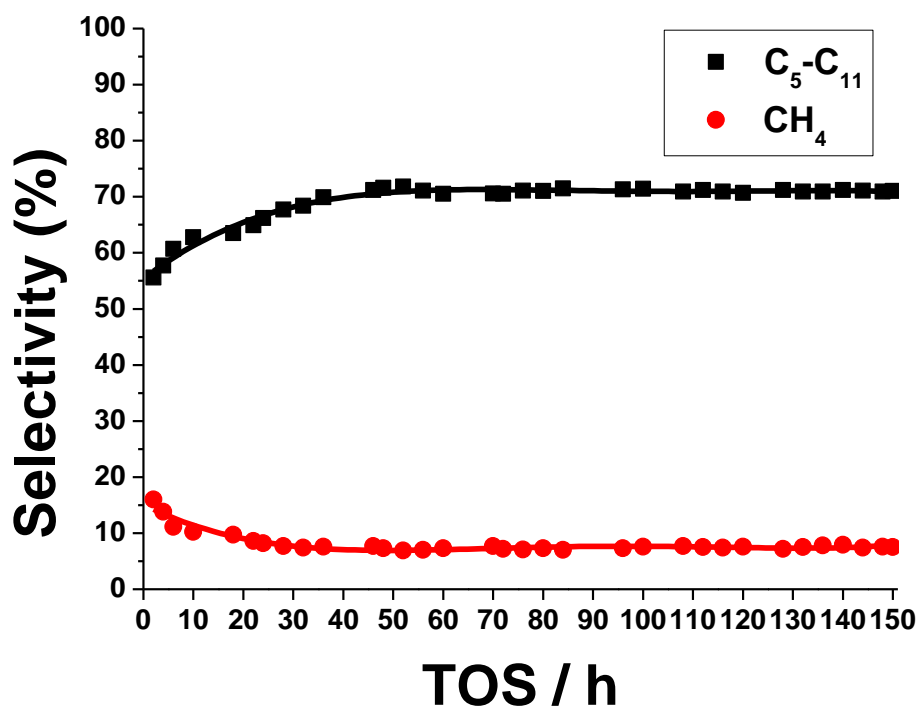


Fig. S3 Hydrocarbon selectivities over R-Fe@HZSM-5 against the reaction time in the FTS reaction.

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