Electronic Supplementary Information:

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Preparation of hierarchical porous-structured Fe_3O_4 microspheres for Fischer-Tropsch synthesis

Yulan Zhang, Longlong Ma, Tiejun Wang,* and Xinjun Li*

Table S1. Properties of fresh prepared Fe_3O_4 microspheres.

Catalyst	Surface area (m^2/g)[a]	Pore diameter (nm)[a]	Microsphere size (nm)[b]
3PFe	45.4	2.39	150
1PFe	41.9	3.71	200
0PFe	48.1	3.70	225

[a]Determined by BET. [b]Determined by SEM (Figure 2).

Table S2. Fe dispersion of the synthesized catalysts.

Catalyst	CO Chemisorbed (μmol/g)[a]	Fe dispersion (%)[b]
3PFe	969	15.0
1PFe	897	13.9
0PFe	527	8.2

[a]Determined by CO-TPD. [b]Dispersion=2×CO chemisorbed/Fe atoms.

Table S3 Mössbauer spectra of 1PFe at different reaction states.

Catalysts	Phases	MES Parameters			
		IS (mm/s)	QS (mm/s)	Γ (mm/s)	Area (%)
fresh	Fe_3O_4 (A)	0.32	-0.03	0.55	57.9
	Fe_3O_4 (B)	0.46	0.00	0.93	42.1
0 h	Fe_5C_2 (A)	0.00	0.70	0.20	6.99
	Fe_5C_2 (B)	0.05	-0.16	0.50	29.5
	Fe_5C_2 (C)	0.29	0.15	0.32	20.9
	Fe_3C	0.32	0.35	0.30	22.5
	Fe^{3+}	0.30	1.00	0.48	20.2
12 h	Fe_5C_2 (A)	0.06	0.13	0.68	9.36
	Fe_5C_2 (B)	0.20	-0.22	0.46	7.36
	Fe_5C_2 (C)	0.48	-0.84	0.25	4.10
	Fe_3O_4 (A)	0.33	0.02	0.43	37.1
	Fe_3O_4 (B)	0.64	-0.04	0.43	34.3
	Fe^{3+}	0.27	1.27	0.58	7.82
24 h	Fe_5C_2 (A)	0.04	-0.07	0.88	12.1
	Fe_5C_2 (B)	0.14	-0.06	0.19	2.65
	Fe_5C_2 (C)	0.46	-0.65	0.32	5.16
	Fe_3O_4 (A)	0.31	0.05	0.39	33.5
	Fe_3O_4 (B)	0.66	-0.08	0.47	39.2
	Fe^{3+}	0.12	1.36	0.58	7.50
48 h	Fe_5C_2 (A)	0.02	1.36	0.61	9.49
	Fe_5C_2 (B)	0.40	-2.00	0.26	5.01
	Fe_5C_2 (C)	0.44	-0.56	0.29	7.10
	Fe_3O_4 (A)	0.30	-0.02	0.34	35.0
	Fe_3O_4 (B)	0.65	-0.04	0.39	41.3
	Fe^{3+}	0.07	1.26	0.21	2.13

Table S4. Catalytic performance of 1PFe after FT reaction.

Performance	24 h	48 h
CO conversion	93.2	80.1
Mass balance (%)	96.0	96.3
Product selectivity (wt%)		
CH_4	11.3	14.8
C_{2-4} paraffins	6.4	8.3
C_{2-4} olefins	23.3	27.4
C_{5+}	59.0	49.5
Olefins/paraffins (wt/wt)		
C_{2-4}	3.64	3.30

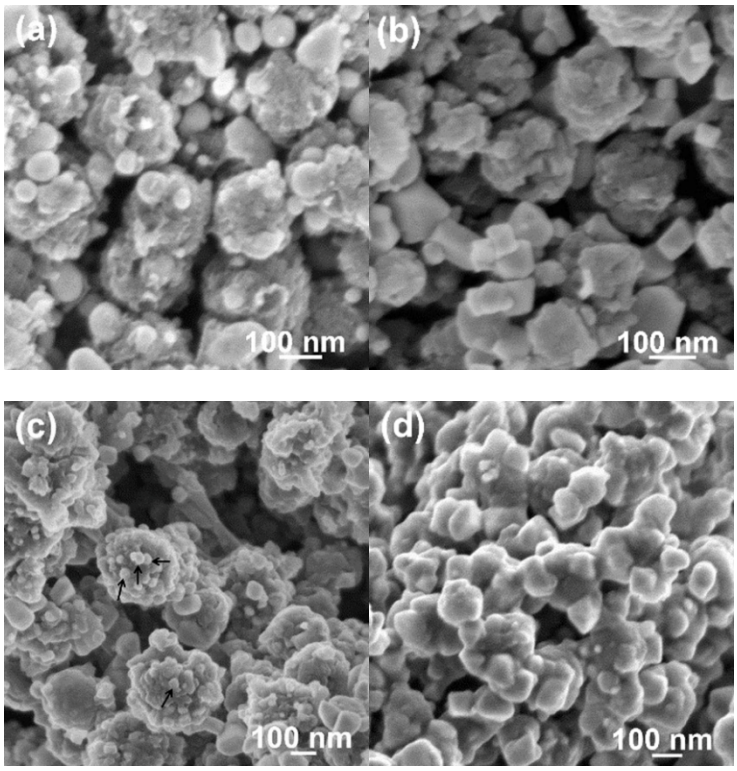

Fig. S1 SEM images of 1PFe after FT reaction for different time: (a) 0 h, (b) 12 h, (c) 24 h, and (d) 48 h.