Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Fe_2O_3 Hollow Microspheres as Highly Selective Catalysts to α-olefins

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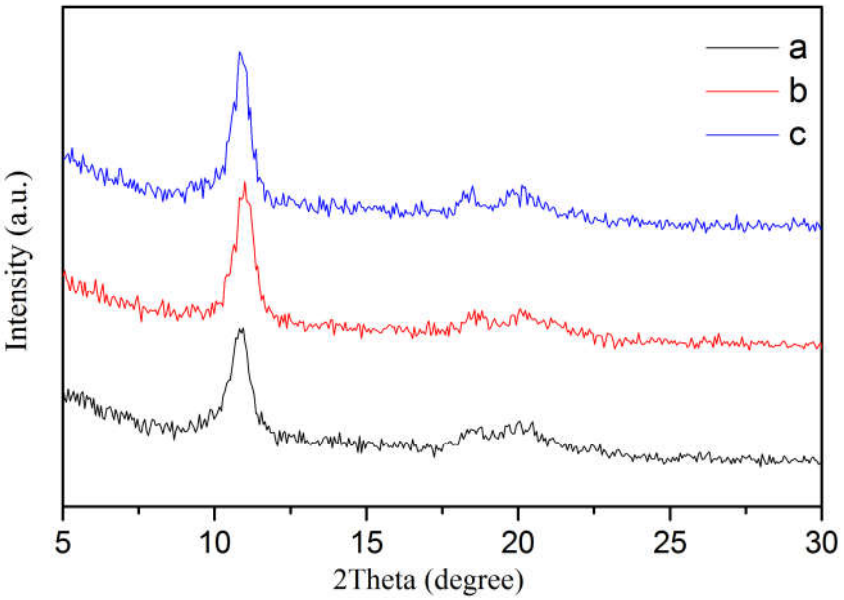

Figure S1. XRD patterns of the Fe–glycerate solid spheres (a), yolk-shell spheres (b) and hollow spheres (c) precursors.

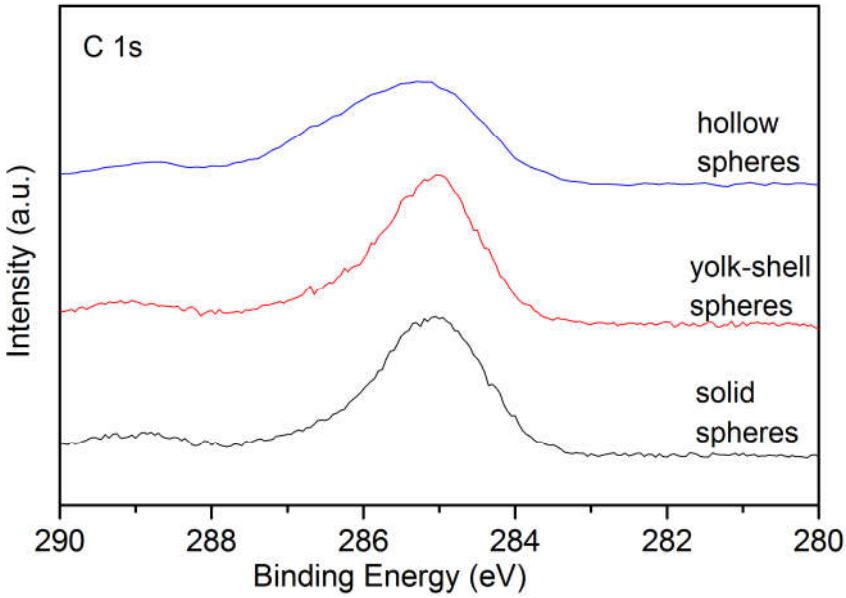

Figure S2. C1s spectra of the Fe_2O_3 solid spheres, yolk-shell spheres and hollow spheres.

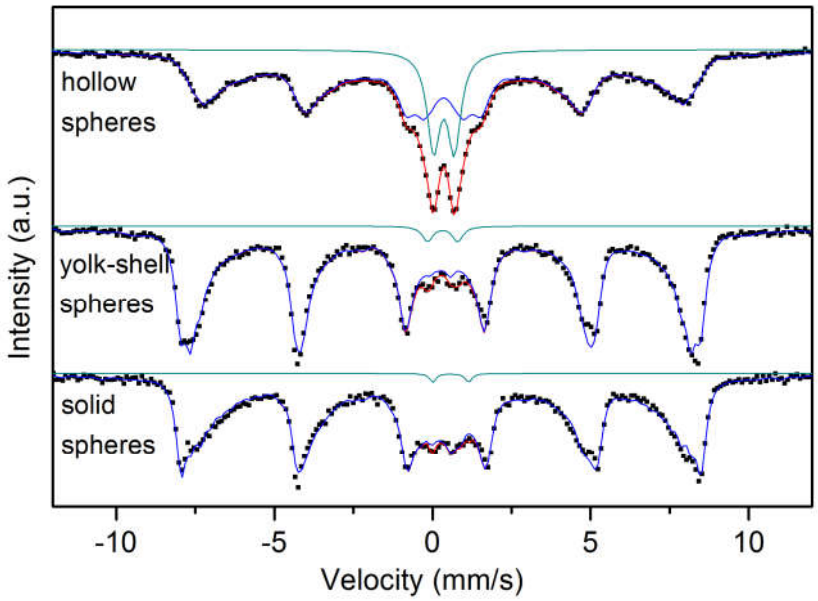

Figure S3. Mössbauer spectra of the Fe_2O_3 solid spheres, yolk-shell spheres and hollow spheres.

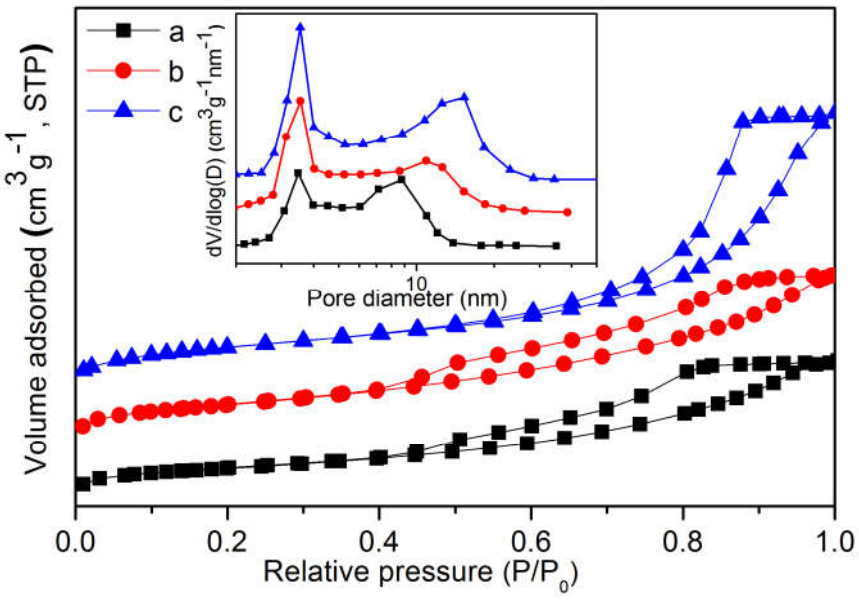

Figure S4. Nitrogen adsorption–desorption isotherms and pore size distributions (inset) of the Fe–glycerate solid spheres (a), yolk-shell spheres (b) and hollow spheres (c) precursors.

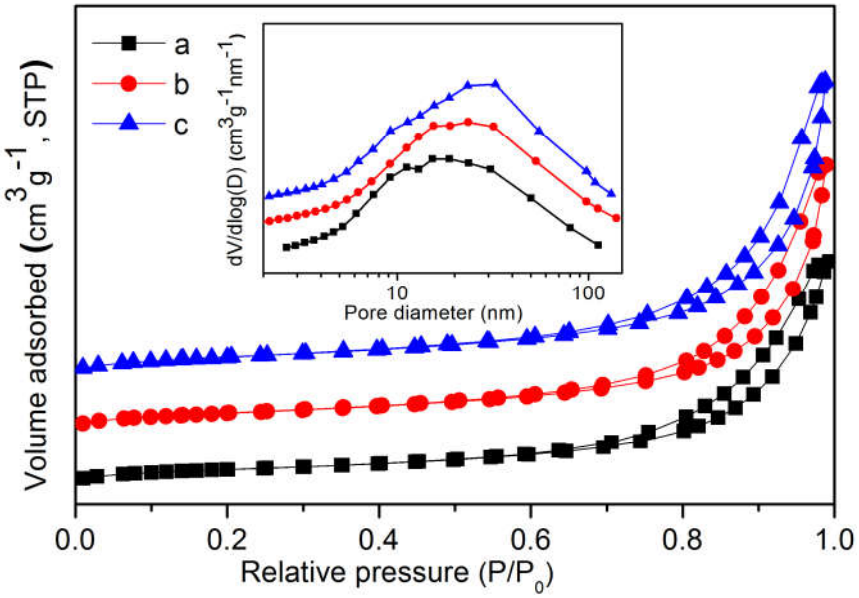

Figure S5. Nitrogen adsorption–desorption isotherms and pore size distributions (inset) of the Fe_2O_3 solid spheres (a), yolk-shell spheres (b) and hollow spheres (c).

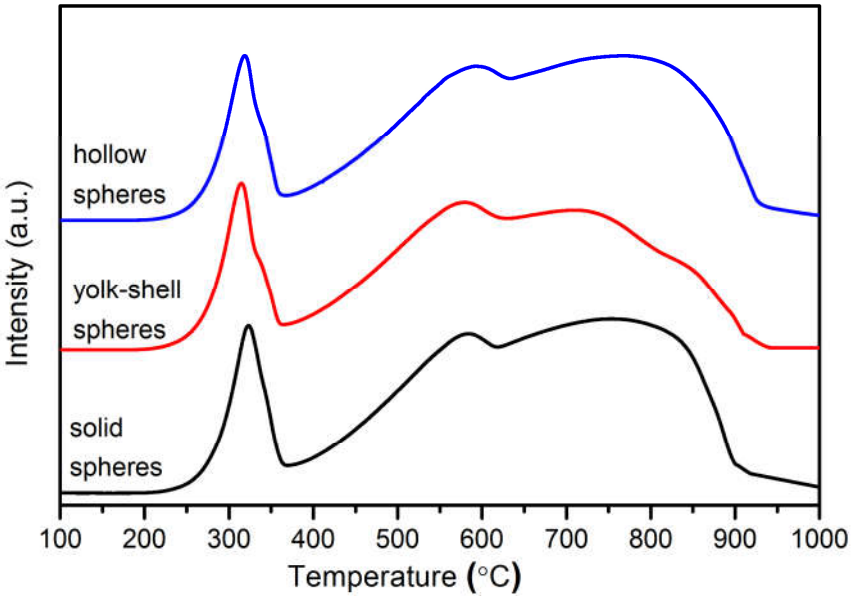

Figure S6. H_2-TPR profiles of the Fe_2O_3 solid spheres, yolk-shell spheres and hollow spheres.

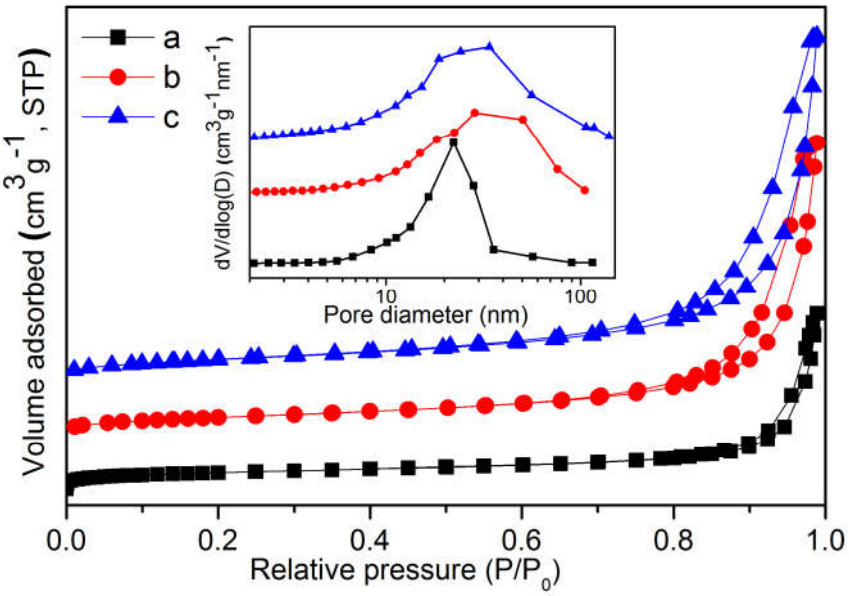

Figure S7. Nitrogen adsorption–desorption isotherms and pore size distributions (inset) of the Fe_2O_3 solid spheres (a), yolk-shell spheres (b) and hollow spheres (c) after 400 h on stream.

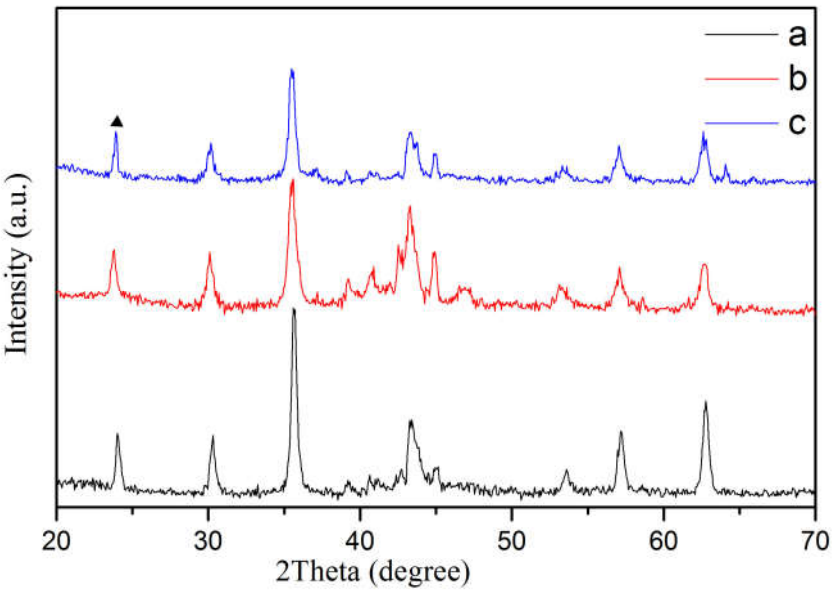

Figure S8. XRD patterns of the Fe_2O_3 solid spheres (a), yolk-shell spheres (b) and hollow spheres (c) after 400 h on stream.

Table S1. Mössbauer spectroscopy parameters of the as-prepared Fe_2O_3 spheres.[a]

Samples	IS (mm/s)	QS (mm/s)	Hhf (T)	Area (%)	Phase
Fe_2O_3 solid spheres	0.35	-0.17	39.1	98.9	α-Fe_2O_3
	0.58	1.13	-	1.1	γ-Fe_2O_3 (spm)
Fe_2O_3 yolk-shell spheres	0.35	-0.13	42.55	98.1	α-Fe_2O_3
	0.34	0.95	-	1.9	γ-Fe_2O_3 (spm)
Fe_2O_3 hollow spheres	0.38	0	35.8	83.4	α-Fe_2O_3
	0.39	0.66	-	16.6	γ-Fe_2O_3 (spm)

[a] IS: isomer shift (relative to α-Fe); QS: quadrupole splitting; Hhf: hyperfine magnetic field.

Table S2. Textural characterization of Fe–glycerate precursors, the Fe–glycerate precursors-derived catalysts and the used catalysts

Samples	S_{BET}[a] (m^2g^{-1})	S_{meso}[b] (m^2g^{-1})	V_{meso}[b] (cm^3g^{-1})	D_{meso}[b] (nm)
Fe–glycerate solid spheres	91	143	0.19	8.5
Fe–glycerate yolk-shell spheres	125	174	0.24	12.0
Fe–glycerate hollow spheres	137	178	0.39	15.0

Fe_2O_3 solid spheres	78	89	0.33	15.0
Fe_2O_3 yolk-shell spheres	87	98	0.39	20.1
Fe_2O_3 hollow spheres	92	106	0.44	20.5
Fe_2O_3 solid spheres used	42	62	0.27	22.0
Fe_2O_3 yolk-shell spheres used	75	81	0.43	35.0
Fe_2O_3 hollow spheres used	88	102	0.50	29.7

[a] Calculated by the BET method.

[b] Mesoporous surface area, volume and average pore diameter of mesopores evaluated by the BJH method from the desorption branches of isotherms.

Table S3. Catalytic performance of iron oxide catalysts after 24 h on stream in FTS.

Catalysts	Fe_2O_3 solid spheres	Fe_2O_3 yolk-shell spheres	Fe_2O_3 hollow spheres	Fe_2O_3 nanotubes [22a]	Fe_3O_4 nanospheres[22b]	Fe_3O_4 microspheres [22c]	Fe_xO_y@C [22d]	Fe-rGO[22e]
FTY ($\mu mol_{CO} g_{Fe}^{-1} s^{-1}$)	7.3	8.7	14.0	11.4	11.0	10.3	23.9	22.5
CO conv. (%)	14.1	17.3	32.4	65.0	70.5	47.0	76	78
CO_2 selectivity (%)	11.7	15.2	26.8	25.7	39.4	42.7	23	12
Hydrocarbon selectivity (C-mol %, CO_2-free)								
CH_4	15.2	4.7	4.9	7.6	7.7	19.6	14	8.1
C_{2-4} olefins	27.4	16.8	16.5	15.2	21.6	35.3	~14	~13.5
C_{2-4} paraffins	17.1	4.1	5.3	5.1	6.5	14.0	~12	~12.5
C_{5+} olefins	23.7	42.5	43.7	35.4		~9	~20	~30.1
C_{5+} paraffins	16.6	31.9	29.6	36.7	64.2 (C_{5+})	~22.1	~40	~35.8

Table S4. Mössbauer spectroscopy parameters of the Fe_2O_3 spheres after FTS.

Catalysts	IS (mm/s)	QS (mm/s)	Hhf (T)	Area (%)	Phase
solid spheres	0.35	0.04	21.8	33.2	χ-Fe_5C_2 (I)
	0.26	0.15	10.6	21.7	χ-Fe_5C_2 (III)
	0.21	0.14	18.4	26.0	ε′-Fe2.2C
	0.33	0.03	48.8	5.1	Fe_3O_4 (A)
	0.71	-0.05	45.5	9.2	Fe_3O_4 (B)
	0.28	1.07	-	4.8	Fe^{3+} (spm)
yolk-shell spheres	0.21	0.14	18.6	33.9	χ-Fe_5C_2 (I)
	0.27	0.15	10.7	19.7	χ-Fe_5C_2 (III)
	0.35	0.03	21.8	32.3	ε′-Fe2.2C
	0.35	0.04	48.9	5.5	Fe_3O_4 (A)
	0.75	-0.07	45.6	5.3	Fe_3O_4 (B)
	0.25	1.07	-	3.3	Fe^{3+} (spm)
hollow spheres	0.35	0.05	21.9	35.1	χ-Fe_5C_2 (I)
	0.26	0.15	10.7	22.0	χ-Fe_5C_2 (III)
	0.21	0.14	18.4	29.3	ε′-Fe2.2C
	0.40	-0.05	48.7	5.5	Fe_3O_4 (A)
	0.75	-0.01	45.3	4.6	Fe_3O_4 (B)
	0.26	1.03	-	3.5	Fe^{3+} (spm)

[a] IS: isomer shift (relative to α-Fe); QS: quadrupole splitting; Hhf: hyperfine magnetic field; A (tetrahedral Fe^{3+}); B (octahedral Fe^{3+}, Fe^{2+})