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Supporting information

Structural evolution of large Fe₃O₄ microspheres on graphene oxide for efficient conversion of syngas into α-olefins

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Fig. S1 XRD patterns of the fresh GO, Fe_3O_4 and Fe/GO catalysts.



Fig. S2 XPS spectra of the fresh catalysts: (a) wide-survey spectra; (b) Fe2p XPS spectra; (c-f) O1s spectra.



Fig. S3 Mössbauer spectra of spent catalysts. Reaction conditions: 0.1 g of catalyst, $H_2/CO/N_2 = 48.5/48.5/3$, 1 MPa, GHSV = 22.2 L g_{cat}⁻¹ h⁻¹, and 340°C.



Fig. S4 TEM images of the spent Fe/GO-25 catalysts.



Fig. S5 The thicknesses of carbon deposition shells with Gaussian analysis fittings: (a) Fe/GO-50 and (b) Fe₃O₄.



Fig. S6 XRD patterns of the reduced Fe_3O_4 and Fe/GO catalysts.



Fig. S7 TEM images of the spent Fe/GO-50 catalyst.

Table S1 Textural properties of the as-prepared catalysts

Catalysts	Surface area	Pore volume Pore size		Particle size, d(Fe ₃ O ₄)	
	$(m^2 g^{-1})$	$(cm^3 g^{-1})$	(nm)	(nm) ^a	
Fe ₃ O ₄	6.7	0.04	3.8	30.8	

^a Calculated using the Scherrer's equation.

Table S2 Mösst	bauer spectra	of the spent	catalysts ^a
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Catalyst	H(KOe)	IS(mm s ⁻¹)	QS(mm s ⁻¹)	Γ/2(mm s ⁻¹)	Phase ascription	Area (%)
Fe ₃ O ₄ -340	216	0.25	-0.11	0.18	χ -Fe ₅ C ₂ (I)	39.3
	186	0.18	-0.06	0.23	χ -Fe ₅ C ₂ (II)	44.1
	111	0.21	-0.11	0.16	χ-Fe ₅ C ₂ (III)	16.5
Fe/GO-25	438	0.06	0.74	1.37	$Fe_3O_4(A)$	13.3
	218	0.26	-0.07	0.21	χ -Fe ₅ C ₂ (I)	35.7
	184	0.20	0.02	0.21	χ-Fe ₅ C ₂ (II)	24.8
	100	0.14	-0.05	0.30	χ -Fe ₅ C ₂ (III)	26.2
Fe/GO-50		0.50	1.07	0.68	Fe(II)/Fe(III)	16.1
	169	0.38	-0.11	0.15	Fe _{2.2} C	44.8
	219	0.40	-0.06	0.20	χ -Fe ₅ C ₂ (I)	15.0
	182	0.38	0.06	0.22	χ-Fe ₅ C ₂ (II)	19.8
	103	0.11	-0.07	0.12	χ-Fe ₅ C ₂ (III)	4.3
Fe/GO-75	168	0.24	-0.11	0.14	Fe _{2.2} C	29.9
	219	0.25	-0.09	0.17	χ -Fe ₅ C ₂ (I)	23.2
	186	0.21	0.04	0.22	χ-Fe ₅ C ₂ (II)	26.1
	102	0.14	-0.05	0.37	χ-Fe ₅ C ₂ (III)	20.8

^a Reaction conditions: catalyst = 0.1 g, T = 340°C, P = 1 MPa, $H_2/CO = 1$, GHSV = 22.2 L g_{cat} ⁻¹ h⁻¹, time on stream = 50 h.

Table S3 Composition of fresh GO, Fe_3O_4 and Fe/GO catalysts measured by ICP-OES

Sample	Fe (wt.%)	S (wt.%)	K (wt.%)
Fe ₃ O ₄	77.85		
GO		1.52	2.21
Fe/GO-25	25.84	1.53	2.05
Fe/GO-50	44.87	0.87	1.47
Fe/GO-75	62.50	0.35	0.76

Table S4 Surface composition of fresh GO, Fe_3O_4 and Fe/GO catalysts analyzed by XPS

Sample	Fe (at.%)	C (at.%)	O (at.%)	S (at.%)	K (at.%)	Mn (at.%)
Fe ₃ O ₄	24.47	31.18	44.35			
GO		64.94	32.59	0.89	1.64	
Fe/GO-25	2.90	60.35	34.94	0.73	1.12	
Fe/GO-75	11.87	46.96	40.33	0.30	0.54	

Experimental methods

Catalyst preparation

Synthesis of Fe_3O_4 microsphere. Fe(NO₃)₃•9H₂O (7.27 g, 18 mmol) was dissolved in reducing agent of ethylene glycol (180 mL) to form a clear solution, followed by the addition of NaAc•3H₂O (12.96 g, 95 mmol). The mixture was stirred vigorously for 30 min and then sealed in a Teflon-lined stainless-steel autoclave (300 mL). The autoclave was heated to and maintained at 200 °C for 12 h, and allowed to cool to room temperature (RT). The black products were washed several times with deionized water and ethanol, respectively, and then dried at 60 °C for 12 h.

Preparation of Fe/GO catalysts. Graphene oxide (GO) was prepared using a modified Hummer's method. Typically, GO-modified Fe₃O₄ catalysts were prepared by an ultrasound-assisted deposition method as follows. First, the desired amounts of Fe₃O₄ and GO were dispersed in deionized water and sonicated for 20 min, respectively. Then, the two suspensions were mixed and stirred for 1 h followed by sonicating for another 1 h. The product was then centrifuged before drying at 80 °C for 24 h. The obtained samples were labeled as Fe/GO-x (x = 25, 50, 75), where x represent the weight percentage of Fe₃O₄ in Fe/GO-x.

Fischer-Tropsch synthesis reaction

FTS reaction was carried out in a pressurized fixed-bed reactor (id = 12 mm) where 100 mg of catalyst diluted with 2 g of quartz sand was loaded for each test. Prior to the catalytic reaction, catalyst was reduced in a pure H₂ flow of 37 mL min⁻¹ at 350 °C and 0.2 MPa for 3 h with a heating rate of 2 °C min⁻¹. After the reduction, catalyst bed was cooled down to 280 °C under a H₂ flow. Next, syngas with a H₂:CO:N₂ ratio of 48.5:48.5:3 was switched to reactor, and the system pressure was raised up to 1 MPa. FTS reaction then started at 340 °C. The flow rate of syngas was set at 37 mL min⁻¹, representing a space velocity of 22.2 SL g⁻¹ h⁻¹. Each test was performed for 50 h on stream. The gaseous products were analyzed hourly online using two integrated gas chromatographs (Agilent GC 7820A). A thermal conductivity detector (TCD), equipped with a Porapak Q packed column and a 5A molecular sieve column, was used to analyze CO_2 , H_2 , CO, N_2 and CH_4 . And a flame ionization detector (FID), equipped with a Rt-Q-BOND column, was used to analyze the composition of C_1 - C_7 hydrocarbons. The CO conversion, CO_2 selectivity and gaseous hydrocarbon selectivity were calculated using 3% N_2 as internal standard. Liquid products and wax were collected by a cold trap at 0 °C and a hot trap at 120 °C, respectively, which were analyzed offline using a gas chromatograph (Shimadzu GC-2014 AFSC) equipped with an HP-1 capillary column. The CO conversion and product selectivity was calculated based on carbon molar. The carbon balance was calculated in the range of 95-103%.

Characterization of catalysts

Field emission scanning electron microscopy (SEM) was performed on a S-4800 (Hitachi, Japan) microscopy at an accelerating voltage of 2.0 kV to visualize the morphology and size of sample.

Transmission electron microscopy (TEM) of the fresh and spent catalysts was carried out on JEM-2100 microscope, operated at an accelerating voltage of 200 kV. The samples were prepared by dropwise addition of the dilute catalyst suspension on a 300 mesh copper grid covered with perforated carbon followed by evaporation of the solvent, anhydrous ethanol.

 N_2 adsorption/desorption isotherms were measured on a Quantachrome Autosorb iQ instrument at -196 °C. Before analysis, 150 mg of catalyst was degassed at 200 °C for 4 h under vacuum conditions. The specific surface area was calculated using Brunauer-Emmett-Teller (BET) method. The pore size and pore volume were calculated based on Barrett-Joyner-Halenda (BJH) method using the desorption branches of N_2 isotherms.

X-ray diffraction (XRD) of the fresh and spent catalysts was performed on a Bruker AXS D2 Advance diffractometer equipped with a Cu K α radiation source ($\lambda = 1.5418$ Å) at 30 kV and 10 mA. The scans were taken

with a step size of 0.02° at the range of $5^{\circ} < 2\theta < 90^{\circ}$.

⁵⁷Fe Mössbauer spectra of spent catalysts were collected in a constant acceleration transmission mode on a Wissel 1550 electromechanical spectromter (Wissenschaftliche Elektronik GmbH) using a ⁵⁷Co in Pd matrix irradiation source. The velocity was calibrated using a 25µm thick α-Fe foil. The isomer shift (IS) was referenced to α -Fe at RT. The spectrum was fitted using a least-squares fitting routine that modeled the spectrum as a combination of singlets, quadruple doublets and magnetic sextets with a Lorentzian line shape and constraints in peak width and intensity using the MossWinn 3.0i program. The phase compositions were derived from the areas of the absorption peaks with the assumption of the same recoil-free factor (the probability of absorption of the γ photons) for all kinds of iron nuclei in the catalyst.

The surface composition of fresh catalysts was determined by XPS on a Thermo SCIENTIFIC ESCALAB 250xi X-ray photoelectron spectrometer using AL-K α (1486.8 eV) as the excitation source at 15 kV and 10 mA. The background vacuum of the analysis chamber was 2×10^{-9} mbar. The binding energies were assigned using the C1s peak at 284.8 eV from adventitious carbon. In the experiments, the samples were pressed into self-supported wafers and mounted on a stainless-steel manipulator.

The elemental contents of fresh catalysts were determined by inductively coupled plasma optical emission spectrometry (ICP-OES) on an Agilent 725 instrument. Before measurement, 100 mg of sample was dissolved in aqua regia and diluted with deionized water up to 100 mL, and then the as-prepared solution was injected into ICP spectrometer for recording the elemental content in weight%.