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Effect of a potassium promoter on the Fischer–Tropsch synthesis of light olefins over iron carbide catalysts encapsulated in graphene-like carbon†

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Iron carbide catalysts encapsulated in graphene-like carbon were synthesized *via* a facile method by pyrolysis of an iron-glucose precursor. Different amounts of potassium (0–5 wt%) were *in situ* doped into the catalyst simultaneously. Glucose played a role both as the precursor to form a carbon support and a reducing agent that reduced iron oxides to θ -Fe₃C during the catalyst preparation. θ -Fe₃C underwent a phase transformation to χ -Fe₅C₂ as the active phase in Fischer–Tropsch synthesis. Characterization of the structural and chemical properties of the prepared catalysts revealed a core-shell structure with iron carbides enwrapped by several graphene-like layers. The addition of a potassium promoter increased the amount of defects on graphene-like layers and facilitated the formation of iron carbides during the catalyst preparation. Fischer–Tropsch synthesis under typical reaction conditions (320 °C, 20 bar, H₂/CO = 1, GHSV = 15 000 ml g_{cat}^{−1} h^{−1}) was carried out in a fixed bed reactor. A higher light olefin selectivity was obtained than that on common iron catalysts, probably because of the electron-rich surfaces of the prepared catalysts that made it hard for hydrogen to hydrogenate the unsaturated intermediates. A volcano-like evolution of light olefin selectivity was observed on the catalysts with different contents of K, and the highest olefin selectivity reached 41.9% on the 2K-Fe₃C@C catalyst (*i.e.*, doped with 2 wt% of K). The induction period of the catalyst was shortened by K addition. No drastic changes in the catalyst morphology and performance during 100 h time on stream can be ascribed to the protection of graphene-like carbon layers that prevented the supported iron particles from migration and aggregation under harsh conditions in Fischer–Tropsch synthesis.

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1 Introduction

Fischer–Tropsch synthesis (FTS) is a typical catalytic reaction that converts syngas (H₂ and CO) to hydrocarbons such as light olefins/paraffins, gasoline and diesel. Syngas can be widely derived from coal, natural gas, petroleum and biomass. Specifically, Fischer–Tropsch synthesis of light olefins (FTO) including ethylene, propene and butene is an important process in the upstream of production of fuels, polymers and fine chemicals.^{1,2} In this reaction, iron-based catalysts have been widely studied and commercially applied due to

their low cost, high FTO reaction activity, and better light olefin selectivity than Co, Ru, *etc.*³ They show excellent durability to a lower H₂/CO ratio of the feed gas derived from biomass and coal because of the regulation of the water-gas shift reaction (WGS reaction: CO + H₂O → CO₂ + H₂).⁴ However, harsh FTO reaction conditions (250–350 °C, 10–35 bar) tend to induce sintering and aggregation of iron nanoparticles (NPs) supported on inert materials such as carbon and non-metallic oxides due to the weak metal–support interaction.⁵ Using multitudinous carbon materials as the catalyst support provides many advantages toward catalytic performance, including: (1) better dispersion and smaller size of the active iron particles due to the large specific surface area, (2) rich and modifiable surface functional groups and (3) relatively weak metal–support interaction that makes it easier to carburize iron precursors to iron carbides. Accordingly, activated carbon,^{6,7} carbon nanotubes (CNT),^{8–11} carbon nanofibers (CNF),^{12,13} reduced graphene oxide^{14,15} and other forms of carbon supports^{16–18} have been widely studied in the FTO reaction. These carbon supported catalysts showed high light olefin selectivity (over 60%) and thermal stability (over 100 h)

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in the FTO reaction. Although the relatively weak bonding force between iron particles and these carbon supports facilitates the reduction and carburization procedure to form iron carbides, iron NPs are inclined to migration and aggregation during the FTO reaction at high temperatures and pressures. It leads to catalyst deactivation on account of the decrease of the contact area between the active sites and reactant, which remains as one major challenge with the carbon-supported iron catalysts despite their high FTO activity. Besides, as the catalytic active sites, iron carbides are mainly obtained from the reduction of iron oxides (Fe_2O_3 and Fe_3O_4) by H_2 or syngas.¹⁹ Although this reduction is facilitated over carbon supports, it is accompanied by drastic changes in morphology and structure.²⁰ The olefin/paraffin (O/P) ratio over Fe_2O_3 supported on carbon catalysts in FTO has been reported to be very low.²¹ In this case, a series of carbon-encapsulated metal NP catalysts have been proposed to enhance the structure integrity and applied to the oxygen evolution reaction, oxygen reduction reaction, hydrogen evolution reaction, solar cells, batteries, and catalytic hydrogenation, *etc.* in recent years.²² As for FTS, Wezendonk *et al.*²³ synthesized an Fe@C catalyst by pyrolysis of an iron-based metal-organic framework (Fe-MOF) precursor and found that a high product yield and catalyst stability were achieved due to the small iron particle size and the protection of the carbon matrix on internal particles. Potassium promotion effects of the KFe@C catalyst on the CO conversion and O/P ratio were discussed as well. Yan *et al.*²⁴ used biochar as the support precursor to synthesize carbon-encapsulated iron NPs. Iron carbide (mainly $\theta\text{-Fe}_3\text{C}$) was formed on the interface between the graphitic shell and iron core. As high as 95% CO conversion and 68% liquid hydrocarbon selectivity in FTS were maintained over 1500 h time on stream. The structural and catalytic properties of Fe@G (G stands for graphene) were studied by Wang *et al.*²⁵ 2–5 layers of graphene encapsulated iron NPs with a 5–15 nm diameter were *in situ* prepared *via* the arc-discharge method. The space time yield of $\text{C}_2\text{--C}_4$ olefins in the FTO reaction over the Fe@G catalyst was about 3.2 times that over Fe_2O_3 NPs, and they have better stability than common iron catalysts. They considered that graphene layers could in one way affect the electrical conductivities and have confinement effects on iron particles to suppress particle growth, and in another way protect the catalyst from being oxidized or fractured.

Herein, based on previous studies on iron-carbon catalysts, a series of graphene-like carbon encapsulated iron carbide (Fe_3C) NPs with different potassium promoter contents were *in situ* synthesized from an iron-glucose precursor and applied to FTO reaction under industrial conditions (*e.g.* 320 °C, 20 bar). No previous studies about the potassium promotion effect on the graphene-like carbon encapsulated iron carbide catalyst in FTO reactions were carried out comprehensively as far as we know. A facile catalyst synthesis strategy *via* pyrolysis of the iron-glucose precursor was proposed, which allowed the preparation of (potassium promoted) iron carbide catalysts with a core-shell structure. A series of catalyst characterization studies were applied to illustrate the

unique graphene-like carbon shell structure properties and the phase transformation of the iron core during the catalyst synthesis, reduction and reaction. The protective effect of the graphene-like carbon shell and K promotion on FTO performance were investigated as well, in comparison with the performance over various carbon-supported iron catalysts in the literature. The catalyst stability was tested in FTO and interpreted with the aid of the morphology characterization of the fresh and spent catalysts.

2 Experiment section

2.1 Materials

Iron(III) nitrate nonahydrate and potassium nitrate were of analytical grade and obtained from Tianjin Kemiou Chemical Reagent Co., Ltd. D-Glucose was purchased from Sigma-Aldrich. Syngas was purchased from Guangzhou Yigas Gases Co., Ltd. All chemicals were used as received without any purification.

2.2 Catalyst preparation

Catalysts were prepared by a pyrolysis procedure at a flowing N_2 atmosphere following evaporation of water from the precursor.²⁶ Typically, 0.2 g iron(III) nitrate nonahydrate was firstly dissolved in 100 ml deionized water under continuously stirring. 0.5 g D-glucose was then added to form a mixed solution. A desired amount of potassium promoter (in the form of potassium nitrate) was added as well into the above solution. Under constant stirring, the formed light yellowish solution was heated in an oil bath of 80 °C to remove the excess water to obtain a viscous brown mixture. It was transferred and placed in a 60 °C oven overnight to remove its water as much as possible. After that, the foamy precursor was sealed in a tube furnace and heated at 800 °C for 2 hours with a heating rate of 3 °C min^{-1} in a N_2 flow. The as-prepared catalysts were carefully ground to powder for further use and denoted as $x\text{K-Fe}_3\text{C@C}$ ($x = 0, 0.5, 1, 2, 3$ and 5 being the weight percentage of the potassium promoter in the catalyst).

2.3 Catalyst characterization

X-ray diffraction (XRD) patterns of the as-prepared catalysts (before and after the reaction test) were obtained on an X'Pert Pro MPD (Philips, the Netherlands) with $\text{Cu K}\alpha$ radiation at a scanning angle $2\theta = 5\text{--}80^\circ$. The morphology of the catalysts was obtained using a transmission electron microscope (TEM, JEOL-2100F, Japan) at 200 kV accelerating voltage. The surface functional groups of the catalyst were analyzed by Fourier transform infrared spectroscopy (FT-IR, Nicolet 6700, Thermo Fisher Scientific, USA) with KBr pellets. Spectra in the optical range of 400–4000 cm^{-1} were obtained by averaging 32 scans at a resolution of 2 cm^{-1} . Raman spectra were measured on a Raman microscope (LabRAM HR800-LS55, HORIBA, France) using 532 nm laser excitation at ambient temperature to compare the graphitization degrees of catalysts. X-ray photoelectron

spectroscopy (XPS, Thermo Fischer ESCALAB 250XI, USA) was carried out to determine information about the valence state and interaction of different elements. The metal contents of the catalysts were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, OPTIMA 8000DV, USA). The surface areas and structural properties of the catalysts were measured by the Brunauer-Emmett-Teller (BET) method (Micromeritics ASAP 2010 instrument, USA). The pore size distribution and pore volume therein were evaluated by the Barret-Joyner-Halenda (BJH) method. All the catalyst samples were degassed at 200 °C for 10 h before N₂ physisorption. CO temperature programmed desorption (CO-TPD) was conducted after CO adsorption on *in situ* reduced catalysts at 25 °C for 60 min in syngas (H₂/CO/N₂ = 47.5/47.5/5) with a flow rate of 50 ml min⁻¹. Hydrogen temperature programmed reduction (H₂-TPR) was performed in a U-shape quartz tube reactor with a thermal conductivity detector (Quantachrome CPB-1, USA).

2.4 FTO reaction test and product analysis

FTO reaction tests over different catalysts were carried out in a stainless steel fixed bed reactor with an inner diameter of 5 mm. 0.2 g catalyst (200–300 mesh powder), diluted with 0.8 g quartz sand homogeneously, was sealed in the reactor with quartz wool before reaction. The catalyst bed length is *ca.* 12 mm, within the isothermal area of the reactor. Firstly, the catalyst was *in situ* reduced by syngas (H₂/CO/N₂ = 47.5/47.5/5, N₂ as the internal standard gas) at 350 °C and atmospheric pressure for 12 h. Then, the FTO reaction was tested using the same syngas feed at 320 °C and 20 bar (gauge pressure). The gas hourly space velocity (GHSV) was varied by changing the feed gas flow rate with a mass flow controller (Brooks 5850E, USA). Products were cooled down by a cold trap and were separated into the gas and liquid phases. The gas phase was analyzed online using a gas chromatograph (GC7890B, Agilent, USA) with a GS-ALUMINA column (50 mm × 0.530 mm, Agilent, USA). The column temperature was firstly increased from 60 °C to 80 °C at a rate of 20 °C min⁻¹, and then increased to 190 °C (at a rate of 30 °C min⁻¹) and retained for 10 min. The liquid phase was analyzed by an offline gas chromatograph (GC2010, Shimadzu, Japan) with an SE-30 column (50 mm × 0.320 mm, Shimadzu, Japan). The column temperature was firstly held for 5 min at 60 °C, increased to 260 °C at a rate of 5 °C min⁻¹, and then retained for 30 min. The catalyst activity was measured in terms of CO conversion (*X*_{CO}) and iron time yield (FTY). CO conversion was calculated as

$$X_{\text{CO}} = \frac{N_{\text{CO, in}} - N_{\text{CO, out}}}{N_{\text{CO, in}}} \times 100\% \quad (1)$$

where *N*_{CO, in} and *N*_{CO, out} represent the molar flow rates of CO at the inlet and outlet of the reactor. FTY was calculated as the mole number of CO molecules converted per gram of iron per hour:

$$\text{FTY} = \frac{N_{\text{CO, in}} - N_{\text{CO, out}}}{M_{\text{Fe}}} \quad (2)$$

where *M*_{Fe} represents the actual iron weight in the loaded catalyst.

Hydrocarbon selectivity (*S*_{C_nH_m}) was calculated on a carbon basis without CO₂. It was calculated as the weight percentage of C_nH_m:

$$S_{\text{C}_n\text{H}_m} = \frac{M_{\text{C}_n\text{H}_m}}{\sum_i M_{\text{C}_n\text{H}_m}} \times 100\% \quad (3)$$

where *M*_{C_nH_m} represents the weight of specific hydrocarbons with a carbon number *n* in the products.

Chain growth probability (*α*) was calculated based on the Anderson-Schulz-Flory distribution model.²⁷

$$\ln\left(\frac{W_n}{n}\right) = n \ln \alpha + \ln \frac{(1-\alpha)^2}{\alpha} \quad (4)$$

where *W_n* is the mass fraction of hydrocarbons in the product with a carbon number *n*. The value of ln *α* can be obtained from the slope of the linear fit between ln(*W_n/n*) and *n*. And then *α* was calculated.

Considering the experimental uncertainty, the FTO reaction results were reliable if the carbon balance obtained in the experiments was close to 100%.

3 Results and discussion

3.1 Catalyst phase and morphology

The XRD patterns (Fig. 1a) of the calcined catalysts (*i.e.*, obtained after the pyrolysis step) illustrate that the amount of potassium promoter has no significant effect on the crystal phase in Fe₃C@C catalysts. The peak intensities of the unpromoted Fe₃C@C catalyst are higher than those of K-promoted catalysts, indicating that the size of crystallites in Fe₃C@C is larger than those of K-promoted catalysts according to the Scherrer equation.²⁸ *In situ* doped potassium restricts the growth of iron carbides during the water evaporation and pyrolysis process. A broad peak at 26.1° is assigned to the graphitic carbon (002) generated from the glucose precursor. The relatively weak diffraction peaks at 30.1° and 35.4° are attributed to Fe₃O₄ (JCPDS No. 01-089-2335). Two sharp and intense diffraction peaks at 44.7° (110) and 65.0° (200) are assigned to α-Fe (JCPDS No. 01-087-0721). These peak intensities of Fe₃O₄ and α-Fe gradually decrease with the increasing content of the K promoter, suggesting the facilitation of phase transformation of iron oxides to iron carbides during catalyst preparation. Five contiguous peaks at 42.9°, 43.7°, 44.6°, 45.0° and 45.9° are in accordance with the (211), (102), (220), (031) and (112) planes of cementite θ-Fe₃C (JCPDS No. 00-034-0001).²⁹ These results imply that ferric ions in the precursor were firstly incorporated with glucose during the mixing step and the following water evaporation

Fig. 1 XRD patterns of (a) the calcined catalysts and (b) the reduced catalysts with different qualities of the potassium promoter (0–5 wt%). XRD patterns of the reduced catalysts were obtained after reduction by a $\text{H}_2/\text{CO} = 1$ syngas flow for 12 h at 350 °C and passivation by a 1% O_2/N_2 gas flow for 2 h in a quartz tube (of similar size to the reactor). Standard XRD patterns of $\alpha\text{-Fe}$, $\theta\text{-Fe}_3\text{C}$ and $\chi\text{-Fe}_5\text{C}_2$ are provided for comparison.

step. After that, as a weak reducing agent, carbon in glucose reduced the iron precursor and helped to form cementite during the pyrolysis step at 800 °C under a N_2 atmosphere.³⁰ However, the observed hybrid of iron oxides, metallic Fe and $\theta\text{-Fe}_3\text{C}$ loaded on the graphitic carbon suggests that it was not possible to completely turn the iron precursor into cementite by carburization. From the results in Fig. 1b, it was found that no peaks attributed to iron oxides and metallic iron were detected on the reduced catalysts, and all iron atoms existed in the form of Hägg carbide ($\chi\text{-Fe}_5\text{C}_2$, JCPDS No. 00-036-1248). This indicates that the $\theta\text{-Fe}_3\text{C}$ phase in the calcined catalyst was transformed into $\chi\text{-Fe}_5\text{C}_2$ during reduc-

tion, in line with the literature results.³¹ The most probable existing forms of the potassium promoter are K_2O , KOH and K_2CO_3 , rather than metal potassium. It should be noted that no obvious diffraction peaks were attributed to the potassium promoter, which is due to its low content and high dispersion in the catalyst.^{7,32}

To analyze the promotion effect of the alkali additive on the catalyst structure, $2\text{K}-\text{Fe}_3\text{C}@C$ was used as the example of a potassium-promoted catalyst to compare with the unpromoted $\text{Fe}_3\text{C}@C$ catalyst. TEM images and high resolution TEM (HRTEM) images of both catalysts and their iron carbide particle size distributions are shown in Fig. 2. From

Fig. 2 TEM and HRTEM images of (a) and (b) the as-prepared unpromoted $\text{Fe}_3\text{C}@C$ catalyst and (c) and (d) the as-prepared $2\text{K}-\text{Fe}_3\text{C}@C$ catalyst. The insets in (a) and (c) depict the corresponding iron carbide particle size distribution (based on counts of more than 400 random particles shown as black spots).

Fig. 2a and c, the average particle size was seen to change from 42.7 ± 19.9 nm in the unpromoted catalyst to 29.9 ± 13.9 nm in the promoted one (more than 400 random particles were counted). The particle size of the iron carbides shifted to a lower size range due to the K promotion on iron carbide formation. More specifically, a slight amount of potassium promoter in the catalyst enhanced carburization of iron species.⁸ The HRTEM images over both catalysts (Fig. 2b and d) reveal a unique structure with the graphene-like carbon shell encapsulating iron carbide nanoparticles, which dispersed on thin carbon sheets.²⁶ The shell structure

was formed by about 5–20 layers of graphene. The distance between the consecutive layers is approximately 0.34 nm, which agrees with the (002) plane of graphite. The core-shell structure limited the further growth of the iron core as well. These TEM results are in accordance with the XRD patterns (Fig. 1). That is, there is no difference in the morphology between the promoted and unpromoted catalysts, except the average particle size. When the mixed solution of iron nitrate and glucose was stirred and heated during the catalyst preparation, a metal-organic hybrid was formed between Fe^{3+} and the lone electron pair of O atoms in glucose.³³ After the water

Fig. 3 Deconvolutions of XPS spectra: Fe2p, C1s and O1s spectra of $\text{Fe}_3\text{C}@C$ (a, c and e) and $2\text{K}-\text{Fe}_3\text{C}@C$ catalysts (b, d and f).

evaporation and pyrolysis steps, glucose was dehydrated and enwrapped iron particles and the precursor turned into black spongiform catalysts. Iron atoms were embedded into the carbon framework forming a core-shell structure. This unique structure helped in stabilizing iron carbides and keeping the catalyst morphology.

3.2 Catalyst structure and surface properties

Fig. 3 shows the XPS spectra and the corresponding deconvolution of Fe2p, C1s and O1s of Fe₃C@C and 2K-Fe₃C@C catalysts. The weak intensity of the Fe2p spectra of both catalysts (Fig. 3a and b) is probably because carbon enwrapped iron particles and thus led to a low response in the XPS spectrum.²⁶ Peaks at 712.0 eV and 725.1 eV for the Fe₃C@C catalyst (Fig. 3a) are assigned to Fe2p_{3/2} and Fe2p_{1/2} of Fe³⁺, respectively, and peaks at 716.9 eV and 729.8 eV to the Fe³⁺ satellite. These results are correlated with the XRD patterns (Fig. 1) and illustrate the existence of a slight amount of iron oxides. Two small peaks at 708.2 eV and 721.1 eV in Fig. 3a are assigned to iron carbide species according to previous studies,^{34,35} which again proves the formation of iron carbides by carburization during the pyrolysis process. The Fe2p spectrum of the 2K-Fe₃C@C catalyst (Fig. 3b) shows a similar result to that of the Fe₃C@C catalyst, except a shift of 0.5 eV to lower binding energy. This shift suggests that the incorporation of potassium into the catalyst favored the formation of iron carbides.³⁶ In the meantime, the C1s spectra of both catalysts (Fig. 3c and d) are deconvoluted into four peaks, which are attributed to the bonds of C=C (284.8 eV), C-O (285.3 eV), C=O (286.2 eV)¹⁴ and Fe-C (284.0 eV).^{36,37} Particularly, the Fe-C groups indicated the existence of iron carbides, which agrees with the XRD and XPS Fe2p results. Since the C=C bond normally exists in the form of hexagon ring carbon, the ratio of the C=C bond peak area to that of all the surface carbon-containing groups represents the graphitization degree of carbon materials. And other oxygen-containing groups are regarded as the defects in graphite carbon.³⁸ A slight decrease in graphitization degree in the K-promoted catalyst with increasing K content was observed from the result of the *I_D/I_G* ratio in the Raman spectra (shown in Table 1). The Raman spectrum of carbon materials exhibits two characteristic peaks that are assigned to the D band (1350 cm⁻¹) and G band (1580 cm⁻¹), which can be observed in the Raman spectra of xK-Fe₃C@C catalysts (Fig. S1†). The D band is attributed to the structural disorder at defect sites. The G band is derived from the vibration of the sp² C-C

bond. The ratio of these two peaks intensities, denoted as *I_D/I_G*, is regarded as a measure of the graphitization structure.¹⁵ The *I_D/I_G* ratio of the Fe₃C@C catalyst is 0.91, indicating a better graphite structure was achieved without the addition of potassium. However, with the increasing content of K, the *I_D/I_G* ratio firstly increased to 1.13 and then slightly decreased. No obvious changes were observed while the amount of potassium exceeded 1 wt%. This result indicates that the addition of K before the pyrolysis step during the catalyst preparation has changed the surface groups and the structure of the carbon support. It introduced more defects into the carbon matrix, which could facilitate the CO associative adsorption and dissociative adsorption during the initiation steps of the FTS reaction. This variation tendency of the *I_D/I_G* ratio with increasing K content is consistent with previous studies on FeK/rGO (rGO stands for reduced graphene oxide) catalysts.¹⁴ From the comparison of the O1s spectra of Fe₃C@C (Fig. 3e) and 2K-Fe₃C@C (Fig. 3f), an enhancement in the relative content of C=O in all oxygenated groups was observed with the addition of K, which verifies the effect of the potassium promoter on introducing more defects into the carbon support.

The FT-IR spectra of xK-Fe₃C@C catalysts with different contents of potassium promoters are shown in Fig. S2†, which exhibit similar peaks assigned to the stretching vibrations of O-H (3443 cm⁻¹), aromatic C=C (1627 cm⁻¹) and C-H (1385 cm⁻¹). No other characteristic peaks of D-glucose were observed,³⁹ which implies that D-glucose was decomposed during the pyrolysis process.

Table 1 further shows the textural properties of xK-Fe₃C@C catalysts (*x* = 0, 0.5, 1, 2, 3 and 5). The actual iron and potassium loadings were determined by ICP-AES analysis and were close to the target values showing the reliability of the catalyst preparation. Besides, the porous structure and specific area of the as-prepared catalysts were investigated by the nitrogen adsorption-desorption method. All the adsorption-desorption isotherms of these catalysts (Fig. 4a) show a typical IUPAC IV type curve with a hysteresis loop in the medium relative pressure range, indicating the existence of mesopores in these catalysts.⁴⁰ The corresponding pore size distributions shown in Fig. 4b confirm that the pore diameters are within the mesoporous range (2–50 nm).⁴¹ Based on the BJH method, the hysteresis loops that close sharply at *P/P₀* = 0.45 are probably attributed to the presence of “ink-bottle” pores with a narrow entrance and a larger internal cavity which is emptied by cavitation (common in carbon materials).^{42,43}

Table 1 Textural properties of the as-prepared xK-Fe₃C@C catalysts (*x* = 0, 0.5, 1, 2, 3 and 5)

Catalysts	Fe ^a (wt%)	K ^a (wt%)	Surface area ^b (m ² g ⁻¹)	Pore volume ^b (cm ³ g ⁻¹)	Pore size ^b (nm)	<i>I_D/I_G</i> ^c
Fe ₃ C@C	20.6	0	238	0.35	3.41	0.91
0.5K-Fe ₃ C@C	22.4	0.43	233	0.35	3.40	1.13
1K-Fe ₃ C@C	21.8	0.96	229	0.31	3.43	1.06
2K-Fe ₃ C@C	18.8	1.83	202	0.32	3.42	0.99
3K-Fe ₃ C@C	21.6	2.70	240	0.30	3.42	1.06
5K-Fe ₃ C@C	20.7	4.53	212	0.27	3.07	0.99

^a Determined by ICP-AES. ^b Determined by the N₂ adsorption-desorption method. ^c Calculated from Raman spectra.

Fig. 4 (a) Nitrogen adsorption-desorption isotherms and (b) pore size distributions of $x\text{K-Fe}_3\text{C@C}$ catalysts ($x = 0, 0.5, 1, 2, 3$ and 5).

Fig. 5 (a) H₂-TPR profiles and (b) CO-TPD profiles of Fe₃C@C and 2K-Fe₃C@C catalysts.

Table 2 FTO performance over graphene-like carbon encapsulated iron carbide catalysts with different contents of the K promoter^a

Catalysts	Fe ₃ C@C	0.5K-Fe ₃ C@C	1K-Fe ₃ C@C	2K-Fe ₃ C@C	3K-Fe ₃ C@C	5K-Fe ₃ C@C
CO conversion (%)	64.4	74.8	54.0	48.5	47.1	47.4
H ₂ conversion (%)	46.8	43.6	29.8	27.3	21.6	23.2
H ₂ /CO usage ^b	0.72	0.55	0.52	0.53	0.43	0.46
CO ₂ selectivity (% C)	60.3	73.4	79.5	62.8	65.9	66.7
FTY (mol _{co} g _{Fe} ⁻¹ h ⁻¹)	0.83	0.97	0.68	0.76	0.65	0.67
Product selectivity ^c (wt%)						
CH ₄	29.4	24.3	25.7	24.1	27.9	25.4
C ₂ =C ₄ ⁼	31.0	36.7	36.5	41.9	39.4	36.0
C ₂ ⁰ -C ₄ ⁰	22.7	12.7	13.9	13.0	14.1	12.8
C ₅ ⁺	16.9	26.3	23.9	21.0	18.6	25.8
O/P ^d	1.21	2.53	2.39	2.95	2.58	2.58
Chain growth probability (α)	0.48	0.49	0.54	0.59	0.56	0.55
Carbon balance (%)	94.9	101.6	100.8	96.4	92.8	93.6

^a Reaction conditions: 320 °C, 20 bar, H₂/CO = 1 and GHSV = 15 000 ml g_{cat}⁻¹ h⁻¹. Time on stream (TOS) = 24 h. ^b The molar ratio between the converted H₂ and CO. ^c Calculated on a carbon basis without CO₂. ^d The molar ratio of olefins to paraffins in the product.

Herein the adsorption branch was used to calculate the pore size distribution. A relatively narrow pore size distribution in the mesoporous range implies that the pyrolyzed carbon materials in this study have more regular pore structures than activated carbon with a three-dimensional nanostructure containing micropores, mesopores and macropores.⁴⁴ The specific surface area of the Fe₃C@C catalyst is 238 m² g⁻¹ according to the BET method (Table 1), which proves the porous structures of the catalyst. A large surface area enables

more adsorption sites to the reactant. No obvious changes in the specific area and pore volume among catalysts with different potassium contents were observed. This signifies that the addition of a K promoter had no significant influence on the porous structure of the prepared carbon support. As interpreted before, the Fe₃C@C catalyst with a structure of iron carbide nanoparticles encapsulated in several graphene-like layers was prepared by a facile pyrolysis method. The potassium promoter was expected to be decorated and

Fig. 6 (a) Correlation between the CH₄ selectivity and O/P ratio of C₂–C₄ over xK-Fe₃C@C catalysts ($x = 0, 0.5, 1, 2, 3$ and 5); (b) the FTO reaction activity for the first 24 h reaction time on stream over xK-Fe₃C@C catalysts ($x = 0, 0.5, 1, 2, 3$ and 5). Reaction conditions: 0.2 g catalyst, 320 °C, 20 bar, H₂/CO = 1, GHSV = 15 000 ml g_{cat}⁻¹ h⁻¹.

Table 3 Comparison of FTO performance over various carbon-supported iron catalysts

Catalyst	Fe% (wt%)	T (°C)	P (bar)	GHSV (L g _{cat} ⁻¹ h ⁻¹)	H ₂ /CO	FTY (mol _{co} g _{Fe} ⁻¹ h ⁻¹)	X_{CO} (%)	S_{CH_4} (wt%)	S_{olefin} (wt%)	O/P	Ref.
Fe/AC	20	340	20	9	1.0	N.A. ^a	17.2	17.5	6.0	0.19	17
20Fe/O-CNT	20	340	25	50	1.0	1.5	26.5	6	N.A.	N.A.	51
Fe/CNT	10	340	20	9	1.0	N.A.	24.3	24.2	9.0	0.34	17
Fe@BCNNS ^b	20.9	320	20	1	2.0	N.A.	88.9	22.7	15.7	0.47	64
Fe@C	N.A.	310	67	2	0.9	N.A.	92.3	7.1	N.A.	N.A.	24
Fe@GO-0.25	N.A.	340	10	22.2	1.0	N.A.	91.5	16.5	31.2	2.62	21
Fe/PANI ^c	11	350	20	9	1.0	N.A.	79	24	47	3.4	65
9FeP	16	340	20	54	1.0	1.08	16	8	60	12	66
Fe–Ru–K/CNT	9.8	275	8	N.A.	2.0	0.40	25	14.5	N.A.	N.A.	67
Fe-2K-AC	10	320	20	3	1.0	0.53	93.6	14.9	26.1	5.9	7
Fe ₃ C@C	20.6	320	20	15	1.0	0.83	64.4	29.4	31.0	1.21	This work
2K-Fe ₃ C@C	18.8	320	20	15	1.0	0.76	48.5	24.1	41.9	2.95	This work

^a Not available. ^b BCNNS stands for boron carbon nitride nanosheets. ^c PANI stands for polyaniline.

Fig. 7 (a) The FTO reaction activity and product selectivities over the 2K-Fe₃C@C catalyst during the 100 h time on stream. Reaction conditions: 0.2 g catalyst, 320 °C, 20 bar, H₂/CO = 1, GHSV = 15 000 ml g_{cat}⁻¹ h⁻¹. (b) XRD patterns of the used xK-Fe₃C@C catalysts ($x = 0, 0.5, 1, 2, 3$ and 5) after 100 h on stream in the FTO reaction test. The used catalysts were sieved to remove quartz sand as much as possible.

embedded within the core–shell structure during the preparation process. Though a certain amount of potassium was detected in the promoted catalyst by ICP-AES, no obvious evidence was found in XRD and TEM results possibly due to its high dispersity. Generally, from the characterization results of XRD, TEM, XPS and N₂ adsorption–desorption, the pre-

pared catalysts have the same textural properties with traditional carbon-supported catalysts,⁴⁵ except that the active iron nanoparticles are surrounded and protected by the graphene-like carbon.

Traditional iron-based catalysts require a reduction procedure before use in the reaction test. Iron nanoparticles in the

Fig. 8 TEM images of (a) the unpromoted $\text{Fe}_3\text{C}@C$ catalyst and (b) the K-promoted $2\text{K-Fe}_3\text{C}@C$ catalyst after 100 h on stream in the FTO reaction. Reaction conditions: 0.2 g catalyst, 320°C , 20 bar, $\text{H}_2/\text{CO} = 1$, GHSV = $15\,000\text{ ml g}_{\text{cat}}^{-1}\text{ h}^{-1}$.

oxidized state can be activated by hydrogen, carbon monoxide or syngas. In particular, syngas has been widely used for its better reducibility on iron-based catalysts.⁴⁶ Oxygen atoms are removed by hydrogen or carbon monoxide in syngas and subsequently, the iron oxide turns into metallic Fe. Then, by carburization of CO during the reduction and further in the initial reaction period, it is transformed into a complex mixture of iron carbides including $\epsilon\text{-Fe}_2\text{C}$, $\chi\text{-Fe}_5\text{C}_2$, $\theta\text{-Fe}_3\text{C}$, etc.⁴⁷ The reduction and activation progress is as follows: $\alpha\text{-Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{FeO} \rightarrow \alpha\text{-Fe} \rightarrow \text{Fe}_x\text{C}_y$.^{10,48,49} In this study, a fraction of cementite Fe_3C was directly obtained *via* a facile *in situ* synthesis method (Fig. 1a). It simplifies the deoxygenation and carburization process, which contributed to a more stable morphology of the active iron nanoparticles. Fig. 5a shows the H_2 -TPR profiles of $\text{Fe}_3\text{C}@C$ and $2\text{K-Fe}_3\text{C}@C$ catalysts. The small reduction peaks in the range of $300\text{--}350^\circ\text{C}$ are attributed to $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$, and the peaks in the ranges of $400\text{--}500^\circ\text{C}$ and $500\text{--}600^\circ\text{C}$ are attributed to $\text{Fe}_3\text{O}_4 \rightarrow \text{FeO} \rightarrow$ metallic Fe successively.^{50,51} With the addition of a potassium promoter, the hydrogen reduction peaks shift from 438.2°C to 414.0°C and from 569.5°C to 548.1°C . This implies that the potassium promoter facilitates the formation of iron carbides and shortens the initial period of reaction, which is in agreement with the XRD results in Fig. 1. The CO-TPD profiles of these two catalysts are shown in Fig. 5b. The desorption temperature of CO decreases from 506.5°C to 469.2°C upon the addition of a potassium promoter, which indicates that an increasing K content enhances the adsorption and dissociation of CO molecules on Fe species. The adsorbed CO amount is improved as well (from $331\text{ }\mu\text{mol}_{\text{CO}}\text{ g}_{\text{cat}}^{-1}$ to $569\text{ }\mu\text{mol}_{\text{CO}}\text{ g}_{\text{cat}}^{-1}$), demonstrating that K promotes the adsorption of CO in terms of both bonding strength and adsorption quality. Basically, the addition of K enhances the electron donation between the adsorbed CO and iron active sites. The C–O bond force in carbon monoxide is weakened due to the addition of a K promoter and the electron-rich surface of graphene-like carbon sheets.^{14,52} Fast CO adsorption and dissociation can lead to a higher conversion of reactants in FTO, which means that higher catalytic activity can be achieved over the K-promoted catalyst than the unpromoted catalyst.

3.3 FTO performance

The FTO reaction over the prepared catalysts was performed for 24 h time on stream in a fixed bed reactor at 320°C , 20 bar, $\text{H}_2/\text{CO} = 1$ and GHSV = $15\,000\text{ ml g}_{\text{cat}}^{-1}\text{ h}^{-1}$. The catalyst activities and product distributions are shown in Table 2. It should be noted that the hydrocarbon product selectivities are on a carbon basis without CO_2 . According to the widely accepted iron carbide mechanism, its catalytic activity in FTS is closely related to the dissociation of the adsorbed CO molecules.⁵³ CO molecules in the feed gas are easily adsorbed on the active sites with the help of the defect-rich carbon support. And the large specific surface area of the support increases the amount of the effective adsorption sites by improving the dispersity of iron nanoparticles. From the comparison of the activities of the prepared $x\text{K-Fe}_3\text{C}@C$ catalysts as shown in Table 2, it is noted that with the increase in K content, CO conversion was firstly increased from 64.4% (at $x = 0$) to 74.8% (at $x = 0.5$), and then it gradually decreased to 47–48% (at $x = 2\text{--}5$). This implies that a slight amount of K doped in the $\text{Fe}_3\text{C}@C$ catalyst enhances CO dissociation. In agreement with the XRD results (Fig. 1a), the potassium promoter facilitates the formation of iron carbides and weakens the C–O bonds, which further enhances the catalytic activities. CO conversion declined when the K content was more than 1 wt%. It is because excessive potassium enlarges the nanoparticle size of $\chi\text{-Fe}_5\text{C}_2$ by facilitating its formation,¹⁴ which reduces the contact area between the active sites and feed gas, leading to a slightly lower catalytic activity. Besides, previous studies have found that the addition of an alkali promoter favors the carbon deposition by the disproportionation reaction ($2\text{CO} \rightarrow \text{C} + \text{CO}_2$).^{54,55} The generated by-product CO_2 also reduces the FTS rate because of its competitive adsorption on the active sites. These two additional factors (coking and CO_2 competitive adsorption) further help explain the reduction of catalytic activities with K addition. FTY shows a similar volcano-like evolution with increasing K content, due to the K-promoted CO dissociation on the one hand (advantage) and coking at a high K content as well as CO_2 competitive adsorption on the other hand (disadvantages). With regard to the conversion of hydrogen, there is no

distinct difference between $\text{Fe}_3\text{C}@C$ (46.8%) and $0.5\text{K-Fe}_3\text{C}@C$ (43.6%) catalysts. H_2 conversions over $x\text{K-Fe}_3\text{C}@C$ ($x = 1, 2, 3$ and 5) catalysts, however, significantly decreased to 29.8%, 27.3%, 21.6% and 23.2%, respectively. The deactivation of H_2 dissociation and adsorption in the presence of K retards the hydrogenation of the chemisorbed CO and α -olefins. It suppresses the formation of paraffins and isomerization to internal or branched olefins, which favors the desired light olefin selectivity.⁵⁶

One ineluctable side reaction in Fischer–Tropsch synthesis over iron-based catalysts is the WGS reaction. It contributes to the adjustment of the H_2/CO ratio by consuming CO and generating H_2 , which makes iron-based catalysts suitable for processing the feed gas with low H_2/CO ratios originating from coal, biomass, *etc.*^{7,57} Iron carbides are the active phases for both FTS and WGS reactions.^{52,58} With the doped potassium promoter, the WGS reaction activity (indicated by CO_2 generation in the FTS product) is enhanced. As shown in Table 2, 60.3% of CO_2 selectivity was obtained over the unpromoted $\text{Fe}_3\text{C}@C$ catalyst and generally higher values were found over the K-promoted catalysts. The latter selectivity values are also above those over other iron-based FTS catalysts (45–60%). Owing to the low H_2 dissociation activity over the K-promoted catalysts, the usage ratio of H_2/CO (~ 0.5) is far less than that in the feed gas ($\text{H}_2/\text{CO} = 1$). The insufficiency of activated H_2 that reacted to dissociated CO leads to a low hydrogenation activity. On iron-based catalysts, a higher WGS reaction activity is obtained to generate sufficient activated H_2 . But the co-generation of unwanted CO_2 diminishes the yield of hydrocarbons. The reduction of CO_2 in the product to improve the catalyst efficiency needs further research.

The hydrocarbon product selectivities in relation to the potassium weight fraction over the catalysts are shown in Table 2 as well. Compared with the unpromoted catalyst, a better FTO performance was acquired over the potassium promoted catalysts. From the chain growth probability α in Table 2 and the corresponding fitted ASF plots (Fig. S3†), it can be observed that the hydrocarbon distribution slightly moved to higher carbon numbers and α was increased over the potassium-promoted catalysts. Besides, the methane selectivities fitted the values predicted from the as-obtained ASF models while C2 species were lower than those from the ASF plots. This suggests that the $\text{CH}_2\text{--CH}_2^*$ intermediate adsorbed on the catalyst surface was regarded as the chain initiator where further chain growth occurred.⁵⁹ Methane selectivity, as a vital indicator of the hydrogenation activity in FTO,⁶⁰ was gradually decreased from 29.4% to $\sim 24\%$ with increasing K content in the $x\text{K-Fe}_3\text{C}@C$ catalysts. In the meantime, the C₂–C₄ olefin selectivity was increased and the C₂–C₄ paraffin selectivity declined in general with the addition of a potassium promoter. More precisely, a volcano-like evolution of the desired light olefin selectivity was observed. The light olefin selectivity reached its highest (41.9%) over the $2\text{K-Fe}_3\text{C}@C$ catalyst, and the O/P ratio was increased to the highest value of 2.95, indicating suppression in the hydrogenation of the adsorbed intermediates. As a common al-

kali promoter in the FTO reaction, a potassium promoter increases the content of Hägg carbide and surface basicity, which suppresses the possibility of second hydrogenation by inhibiting the H_2 dissociation.^{14,56} In contrast, the carbon chain growth was stimulated because of the lack of termination by hydrogenation to the saturated hydrocarbons. On the basis of the iron carbide catalytic mechanism,³⁶ the surface carbide species derived from the dissociated CO have two outlets: C–H bond formation or C–C coupling (*i.e.*, the adsorbed C^* can either bond to the dissociated hydrogen atoms or link to the neighboring carbon species). These two competing routes lead to two outcomes as hydrogenation and carbon chain growth, the reaction rates of which determine the final (hydrocarbon) product distribution. To better illustrate this effect, a correlation indicating the hydrogenation ability varying with the carbon chain length over different K-promoted catalysts is provided in Fig. 6a. This correlation is expressed in this figure as CH_4 selectivity with respect to O/P ratios (in C₂, C₃ and C₄ individually). As it grows, all of the O/P ratios of C₂, C₃ and C₄ are gradually decreased. The O/P ratio in C₂ (*i.e.* ethylene/ethane ratio) varies a little with the difference in the K content. This implies that the content of potassium has a minor effect on the hydrogenation of the $\text{CH}_2\text{--CH}_2^*$ intermediate generated on the surface of iron carbides. The decrease in O/P ratios in C₃ and C₄ with respect to the increasing CH_4 selectivity is significant and shows a similar slope. This suggests that potassium has a more crucial effect on the hydrogenation activity and C–H bond formation due to the increasing catalyst basicity with the addition of potassium. The lowest CH_4 selectivity and highest O/P ratio were obtained over the $2\text{K-Fe}_3\text{C}@C$ catalyst.

For iron-based FTS catalysts, generally they undergo an induction period at the beginning of reaction which involves carburization and reconstruction of the active phases until a steady state is reached.³¹ In this work, cementite was *in situ* synthesized during the catalyst preparation process, which shortened the induction period (Fig. 6b). This is in accordance with the XRD and XPS results (Fig. 1 and 3), which show that a large amount of iron oxides has been reduced to iron carbides during the catalyst synthesis. A moderate activation procedure was thus carried out on the $\text{Fe}_3\text{C}@C$ catalyst. This avoids unnecessary phase transformation (*i.e.*, from oxides to iron metal then to carbides involving the removal of oxygen atoms and insertion of carbon atoms) and potential damage of the active phase microscopic morphology during the catalyst reduction and activation of the traditional iron-based catalysts, but only crystalline phase transformation ($\theta\text{-Fe}_3\text{C}$ to $\chi\text{-Fe}_5\text{C}_2$) of the core–shell catalyst in this work. It is believed that the addition of K ($\geq 1\%$) shortened the induction period of the $\text{Fe}_3\text{C}@C$ catalyst to 8–9 hours (Fig. 6b). This is due to the K promotion during the cementite formation on the basis of XRD and H_2 -TPR results (Fig. 1a and 5a). Previous research studies on iron oxide catalysts^{61,62} showed that the potassium promoter weakly inhibits the reduction of Fe_3O_4 to metallic Fe but facilitates the carburization. In summary, it is expected that the active Hägg carbide from

complexation of K/Fe/Fe₃C in this work is easier to obtain than typical K/Fe₂O₃ catalysts.

As shown in Table 3, the reaction activities of the promoted and unpromoted Fe₃C@C catalysts are higher than those of conventional carbon-supported iron oxide catalysts (including AC- or CNT-supported catalysts and carbon-coated catalysts). A relatively low interaction between the metal and inert carbon support and a unique core-shell structure in the prepared catalysts ensure better reducibility and FTO reaction activity compared with those over oxide-supported catalysts.⁶³ However, compared with 20Fe/O-CNT and 9FeP (carbon nanofiber as the support) catalysts with <20 nm iron particle size, catalysts in this work have lower FTY, probably because of their relatively large iron particle size and small contact surface area. In this case, decreasing the average particle size to a level comparable to those catalysts prepared by the impregnation method is a possible way to improve the catalyst activity. Meanwhile, the unpromoted Fe₃C@C catalyst shows a much higher light olefin selectivity (31.0%) than other iron oxide catalysts such as Fe/AC and Fe/CNT (Table 3). The C* intermediate and readsorbed α -olefins generated in the course of the reaction tend to be hydrogenated to alkanes over iron oxide nanoparticles supported on the conventional carbon supports. It is known that only a certain amount of iron carbides is formed at the exterior surface of iron oxide particles. The unreduced iron oxide that existed in iron-based catalysts is unfavorable for light olefin generation.²⁰ In this study, Fe/Fe₃C nanoparticles in the prepared catalysts were encapsulated in several graphene-like carbon layers (Fig. 2a). The *in situ* generated iron carbides during the catalyst preparation contributes to a more homogeneous distribution of active sites on the catalyst surface than those generated during reduction by carburization. Besides, Fe₃C is inactive towards CH₄ formation and has a weak hydrogenation activity.⁶⁰ According to the "Chainmail catalyst" theory proposed by Bao's group,²² the electrons of transition metal particles can penetrate through the graphene-like shell to facilitate catalytic reaction on the surface of the shell. The indirect contact of metal particles and reactants can protect the structural properties and chemical environment of the active sites, which guarantees catalyst stability under severe reaction conditions. The sp² hybridized carbon-carbon matrix on the electron-rich surface of graphene-like carbon enhances the electron transfer within the interfaces of the active particles and carbon support. According to the iron carbide catalytic mechanism for the FTS reaction,³⁶ the electron holes of (CH₂)_n* adsorbed on the active sites are possibly occupied by the free electrons that originated from graphene-like layers. It restricts the secondary hydrogenation and promotes the desorption of alkenes. The unpromoted catalysts with carbon sheets as a support and the graphene-like layers that enwrapped iron carbides exhibit a superior olefin selectivity to those with activated carbon, carbon nanotubes and other carbon coated catalysts (Table 3). Besides, rather than some other expensive carbon materials (graphene, MOFs, etc.), the catalyst used in this work features a facile and controllable

preparation strategy and cheap raw materials, which make it more applicable to light olefin production.

3.4 Catalyst stability

To verify the catalyst stability, a 100 h time on stream test was carried out over the 2K-Fe₃C@C catalyst. As shown in Fig. 7a, after a short induction period, CO conversion reached its steady state and this was retained without an obvious decrease, together with a stable hydrocarbon selectivity. As shown in Fig. 7b, the XRD patterns of the used catalysts with different K contents exhibit a typical χ -Fe₅C₂ crystal phase at around $2\theta = 44^\circ$.⁶⁸ The sharp peaks at 20.9°, 21.4°, 26.6°, 50.0°, 59.9° and 68.1° are attributed to the residual quartz sand that existed in the used catalysts.⁶⁹ There are no metallic Fe peaks and iron oxide peaks, implying that no partial oxidation of the iron carbides occurred. The stability of the iron carbide phase contributes to its resistance to possible deactivation.³⁵ By comparison, the crystal phases in the used catalyst are in accordance with the reduced fresh catalysts (Fig. 1b), which indicates that the FTO active phase has no further transformation. The morphologies of the unpromoted and promoted catalysts after 100 h reaction are shown in Fig. 8. The particle size distribution of these used catalysts slightly increased. Compared with the morphology of fresh catalysts (Fig. 2), neither aggregation nor obvious growth of particle size was observed in the used catalysts. Thus, unlike conventional supported iron catalysts, the graphene-like layer-encapsulated iron carbide nanoparticles as prepared in this work have less tendency to migrate because of the protection of the graphene-like shell. Thanks to the weak metal-support interaction, the prepared catalyst is easier to activate than the metal oxide-supported iron catalysts.⁷⁰

4 Conclusions

Graphene-like carbon encapsulated iron carbide catalysts were synthesized by facile pyrolysis of an iron-glucose precursor. Iron carbide (Fe₃C) with a narrow particle size distribution was obtained by reduction and carburization during the catalyst synthesis and was enwrapped by several graphene-like layers. In the FTO reaction, owing to the unique structure of graphene-like carbon layers that encapsulated Fe₃C catalyst, the electron-rich surfaces made it hard for hydrogen to dissociate and hydrogenate the unsaturated intermediates, which enhances the olefin selectivity compared to common carbon-supported catalysts. Compared with the unpromoted Fe₃C@C catalyst, *in situ* K-doped Fe₃C@C catalysts indicated a further decrease in CH₄ selectivity and an increase in the O/P ratio of C₂-C₄ hydrocarbons. By optimizing the K content (0–5 wt%), as high as 41.9% light olefin selectivity and a 2.95 O/P ratio were achieved on the 2K-Fe₃C@C catalyst (with 2 wt% of K). K promoted the formation of iron carbides and retarded the hydrogenation activity by restricting H₂ dissociation and adsorption, which facilitated the catalyst reduction and activation as well as enhanced the desired product yield. From the catalyst life

test and the morphologies of used catalysts, it was found that the protection of the carbon shell prevented the migration and aggregation of iron nanoparticles, which resulted in a better catalyst stability (over 100 h).

Conflicts of interest

There are no conflicts of interest to declare.

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