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#### 1 Introduction

Fischer–Tropsch (FT) technology is well known as an effective method for the production of liquid fuel or petrochemicals from the reforming of natural gas or biomass (coal) gasification.<sup>1–4</sup> Cobalt and iron are two conventionally used catalysts in FT synthesis.<sup>5</sup> In comparison with cobalt catalysts, iron-based FT catalysts display higher conversions of syngas, with lower H<sub>2</sub>/CO ratios, lower selectivity to undesirable CH<sub>4</sub> from the H<sub>2</sub>-rich syngas, and lower cost.<sup>1</sup> Therefore, there is a great interest in the FT synthesis of liquid fuels with Fe-based catalysts. As for FT synthesis, the development of novel catalysts with high activity and selectivity, especially selectivity, is key to improving FT technology.

Supports are expected to improve the dispersion of active phases and facilitate mass or heat transfer.<sup>1</sup> Moreover, the support may also change the electronic state of the active metal, and thus affect the CO dissociation ability.<sup>6</sup> Furthermore, the pore structure of the support determines the size and

# Mesoporous Fe-based spindles designed as catalysts for the Fischer–Tropsch synthesis of C<sub>5+</sub> hydrocarbons<sup>†</sup>

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Conventional mesoporous catalysts are generally obtained through the dispersion of active phases on porous supports to enhance catalytic performance. However, metal-support interactions can suppress the activation of iron oxides, and this can lead to lower catalytic activity. Moreover, the effects of supports on catalytic performance are complicated for Fischer–Tropsch (FT) synthesis. Herein, we developed novel mesoporous Fe-based spindles and the pores are self-assembled *via* active phases. This unique structure effectively avoids metal-support interactions during activation and FT synthesis, thus improving the FT activity. More importantly, the selectivity for  $C_{5+}$  hydrocarbons is found to be correlated with the pore size. It is identified that Fe/2CTAB, which has the largest pore volume among the three mesoporous spindles (Fe, Fe/CTAB, and Fe/2CTAB), affords the optimum  $C_{5+}$  selectivity, up to 65 wt%. This value is much higher than those for traditional co-precipitation catalysts and supported Fe-based catalysts. Moreover, FT synthesis over Fe/2CTAB leads to the lowest CH<sub>4</sub> selectivity.

morphology of the active metal particles. Fe-Based catalysts are usually sensitive to the structure of iron and/or iron carbides. Therefore, much more attention has been focused on studying the influence of support species on catalytic performance.<sup>3,4</sup> It is accepted that the pores of catalysts play a key role in dispersing the products and reactants, which can significantly affect the selectivity to target products. Thus, pore structures are crucial in determining FT catalytic behaviour. Nevertheless, it is difficult to balance the interactions between the support and the active phase. The effects of supports on catalytic behaviour are complicated in the FT reaction. Interactions that are too weak may lead to the poor dispersion of the active phase, while interactions that are too strong will cause difficulties in the reduction of the precursor of the active phase.<sup>1</sup> Although supports with well-defined nanoporous structures have provided new possibilities for tuning catalytic properties, few studies have contributed to elucidating the sole effects of pore size in FT synthesis.1,7-9

As for the FT synthesis reaction, it is generally accepted that pore size is related to the confinement effect and the active site density. The former is the key to enhancing the reabsorption of  $\alpha$ -olefins that can give rise to C<sub>5+</sub> hydrocarbons through chain growth. The latter is a vital factor in improving the dispersion of the active metal and increasing CO conversion. Thus, the effects of pore size on catalytic behaviour should not be ignored. Catalysts with controllable pore sizes are crucial for high activity and selectivity in FT synthesis. Moreover, overcoming rapid



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#### Paper

catalyst deactivation is also a big challenge for Fe-based catalysts. The current FT reaction mainly focuses on producing long-chain hydrocarbons that can be subsequently hydrocracked into liquid fuels through hydrocracking technology. For this purpose, our work focuses on the design and preparation of unsupported porous Fe-based catalysts for producing  $C_{5+}$  hydrocarbons *via* FT synthesis.

In a previous work, we synthesized hierarchical porousstructured Fe<sub>3</sub>O<sub>4</sub> microspheres in the absence of porous supports and explained the effects of pore size on the selectivity to  $C_{5+}$  hydrocarbons in FT synthesis.<sup>9</sup> In particular, the pore size of Fe<sub>3</sub>O<sub>4</sub> microspheres results from self-assembly from neighbouring active Fe<sub>3</sub>O<sub>4</sub> nanoparticles. The as-prepared porous catalyst revealed relatively higher  $C_{5+}$  selectivity (59.0 wt%) and CO conversion (93.2%) than traditional co-precipitation catalysts and supported Fe-based catalysts.<sup>10–12</sup> As reported, the utilization of active phase assembled mesoporous structures as FT catalysts may provide a new possibility for tuning catalytic performance, particularly product selectivity. Nevertheless, the catalyst displayed low mechanical stability, and CO conversion decreased from 93.2% (24 h) to 80.1% (48 h) with increased time on stream.<sup>9</sup>

Herein, to overcome problem of low mechanical stability,  $Fe_2O_3$  spindles were fabricated using deionized water as a solvent through a one-pot hydrothermal method. Subsequently, mesoporous spindles were synthesized through reducing  $Fe_2O_3$  spindles in syngas, which can thus avoid the reconstruction of Fe-based catalysts during the catalytic reaction. For comparison, catalysts with different pore sizes were synthesized to further explore the effects of pore size on catalytic performance. In the FT synthesis, the catalytic activity and  $C_{5+}$  hydrocarbon selectivity over the as-prepared mesoporous catalysts were investigated.

## 2 Experimental

#### 2.1 Preparation of porous spindle catalysts

Fe<sub>2</sub>O<sub>3</sub> spindles were synthesized via a hydrothermal method. Typically, FeCl<sub>3</sub>·6H<sub>2</sub>O (2.0 g) and sodium acetate anhydrous (Na·Ac, 2.0 g) were dissolved in 30 mL of deionized water to form a homogeneous solution under vigorous stirring, followed by the addition of 2.0 g of cetyl trimethyl ammonium bromide (CTAB). The mixture was stirred vigorously for 15 min, and then sealed in a Teflon lined stainless autoclave (100 mL capacity). The autoclave was placed in an oven that was heated to 200  $^\circ$ C and kept there for 10 h, and then was cooled to room temperature. After washing several times with deionized water, the sample was then dried at 60 °C for 6 h. Next, 1.0 g of the Fe<sub>2</sub>O<sub>3</sub> spindle sample was transferred to a fixed-bed reactor, and then the furnace temperature was raised to 300 °C at a heating rate of 10 °C min<sup>-1</sup> under a flow of syngas ( $H_2/CO = 1$ ), where it was kept for 12 h. After the reduction treatment, the resulting iron carbide spindles were denoted as Fe/2CTAB. On the basis of this, Fe/CTAB and Fe catalysts was prepared with (1.0 g) and without the addition of CTAB. This was then followed by

the same conditions and procedures being applied as for the synthesis of Fe/2CTAB.

#### 2.2 Fischer-Tropsch synthesis

The FT experiments were performed in a fixed-bed reactor at 20 bar and 280 °C under syngas ( $H_2/CO = 1$ ). Typically, 1.0 g of the  $Fe_2O_3$  spindles (particle size = 40–60 mesh) were diluted with 1.0 g of quartz powder (particle size = 60 mesh), and then reduced under syngas ( $H_2/CO = 1$ ) at 300 °C and 2 bar at a heating rate of 10 °C min<sup>-1</sup> for 12 h. After the reduction treatment, the FT synthesis reaction was performed at 280 °C and 20 bar using synthesis gas (H<sub>2</sub>/CO = 1, GHSV = 3000 mL  $g_{cat}^{-1}$  h<sup>-1</sup>). The CO conversion and product selectivity were determined after 72 h of reaction. CO conversion was calculated depending on the variation in moles of CO before and after the FT reaction (CO conversion = 100 - (the amount of substance in the tail gas  $\times$  the amount of CO in the tail gas – the amount of substance in the feed gas  $\times$  the amount of CO in the feed gas)  $\times$  100). Product selectivity was calculated according to the equivalent amount of carbon atoms in a product with respect to the total number of carbon atoms present in the hydrocarbons produced (product selectivity = (the weight of hydrocarbons by carbon number/the total weight of all the hydrocarbons)  $\times$  100). Gas phase data were collected using an Agilent 7890A gas chromatograph (GC), while long chain hydrocarbons (C<sub>4</sub>-C<sub>22</sub>) in liquid were collected (Fig. S1, ESI<sup>+</sup>) and analyzed using an offline GC (Shimadzu, 2010).

#### 2.3 Catalyst characterization

Scanning electron microscope (SEM) images were taken using a Hitachi S-4800 microscope. Transmission electron microscopy (TEM) images of the samples were obtained with an FEI Tecnai G20 instrument. Conventional powder X-ray diffraction (XRD) patterns were obtained using an X'Pert Pro MPD instrument. X-ray fluorescence (XRF) data were acquired using an AxiosmAX Petro instrument to determine the iron loading and the elemental compositions of freshly prepared samples. X-ray photoelectron spectroscopy (XPS) studies were carried out using a Thermo ESCALAB 250XI spectrometer. After degassing at 200 °C for 10 h, surface area and pore size distribution measurements on the catalysts were performed via N2 adsorption-desorption techniques at 77 K on an automated surface area and porosity analyzer (Quantachrome, SI-MP-10). Temperature-programmed desorption (TPD) studies of CO and H<sub>2</sub> were conducted on an automatic temperature programmed chemisorption system (Quantachrome, CPB-1), and helium was used as the carrier gas.

#### 3 Results and discussion

# 3.1 Synthesis and characterization of the as-prepared catalysts

The crystal structures of the as-prepared catalysts were investigated *via* XRD. The XRD patterns of Fe, Fe/CTAB, and Fe/2CTAB are shown in Fig. 1a. As can be seen, the labeled diffraction peaks are well-matched with two Hägg-carbide



Fig. 1 XRD patterns (a) and XPS spectra of Fe-based spindles (b) and high-resolution Fe2p XPS spectra (c).

phases (JCPDS no. 36-1248 and 51-0997; space group, C2/c), thus suggesting that the synthesized catalysts consist of iron carbide particles. As for Fe-based FT synthesis, iron carbides are believed to be the active species.<sup>13</sup> No significant differences between the three catalysts were observed from the XRD patterns. Moreover, no diffraction peaks due to metallic iron or iron oxide were identified, indicating that iron oxide is thoroughly reduced to iron carbide via the reduction treatment. XPS studies were used to evaluate the surface species of the as-prepared Fe, Fe/CTAB, and Fe/2CTAB catalysts. As shown in Fig. 1b, all three catalysts display a similar full-survey-scan spectrum, including characteristic C1s, O1s, and Fe2p peaks. No obvious signals from other elements can be detected. Moreover, the positions of the detected peaks in the XPS spectra are almost identical. This suggests that the compositions of the prepared catalysts remained unchanged when the amount of CTAB is changed. Furthermore, high-resolution Fe2p XPS spectra were also analyzed. As can be seen in Fig. 1c, the Fe2p peaks occurring at around 719.5 eV and 706.4 eV can be attributed to  $\text{Fe}_5\text{C}_2$ ,<sup>14</sup> which is in line with the XRD results (Fig. 1a). In addition to  $Fe_5C_2$ , peaks centered at binding energies of 709.8 eV (Fe2p<sub>3/2</sub>) and 724.2 eV (Fe2p<sub>1/2</sub>) can be ascribed to iron oxide, suggesting the slight surface oxidation of the highly active Fe5C2 nanoparticles. This effect has been reported, because iron carbides with a lower Gibbs energy can easily be oxidized to iron oxide.<sup>2</sup>

SEM and TEM images were used to investigate the morphologies of the Fe, Fe/CTAB, and Fe/2CTAB catalysts. All these synthesized spindles have a hierarchical porous structure. As shown in Fig. 2a–d, each spindle is composed of closely packed  $Fe_5C_2$  nanoparticles. Moreover, pores result from the interspaces between adjacent  $Fe_5C_2$  nanoparticles throughout the spindle. The formation mechanism of the mesoporous spindles is shown in Scheme 1. During the hydrothermal reaction, Na·Ac was used as the medium to accelerate the hydrolysis of  $Fe^{3+}$ to form FeOOH, and then  $Fe_2O_3$  spindles were synthesized



Fig. 2 SEM and TEM images of (a) Fe, (b and c) Fe/CTAB, and (d) Fe/2CTAB.



**Scheme 1** Schematic diagram of mesoporous Fe-based spindle formation during synthesis.

through a dehydration reaction. On the other hand, bubbles, such as HAC and H<sub>2</sub>O, are produced during the hydrolysis of Fe<sup>3+</sup>, which can serve as "soft" templates to promote nucleation and self-assembly into a Fe<sub>2</sub>O<sub>3</sub> spindle, and as such can leave nanospaces between the Fe<sub>2</sub>O<sub>3</sub> nanoparticles in each spindle. Then, the neighbouring nanoparticles in each spindle can aggregate and grow into Fe<sub>2</sub>O<sub>3</sub> spindles. During the reduction process, Fe<sub>2</sub>O<sub>3</sub> spindles are reduced to Fe<sub>5</sub>C<sub>2</sub> porous spindles in syngas. As for the FT reaction, the pores of the catalysts can be expected to regulate product selectivity.<sup>1</sup>

Specific surface areas and pore sizes of the synthesized catalysts are calculated from  $N_2$  physisorption data, using the BET and BJH methods. As shown in Table 1, the surface areas of the Fe, Fe/CTAB, and Fe/2CTAB catalysts are calculated to be 31.8, 12.8, and 45.3 m<sup>2</sup> g<sup>-1</sup>, respectively. In addition, a capillary condensation step above 0.8 in the adsorption branch is observed in Fig. 3a, which is attributed to the presence of slit-shaped pores. This indicates that the pores throughout the spindles result from interparticle voids between adjacent iron carbide particles that assemble into a spindle, which agrees with the phenomenon observed in SEM images (Fig. 2). Fig. 3b shows

Table 1 The performance of Fe-based catalysts

Performance	Fe	Fe/CTAB	Fe/2CTAB
Surface area $(m^2 g^{-1})$	31.8	12.8	45.3
Pore volume $(cm^3 g^{-1})$	0.13	0.08	0.16
Pore diameter (nm)	3.71	3.75	3.81
CO chemisorbed <sup><i>a</i></sup> ( $\mu$ mol <sub>CO</sub> g <sub>cat</sub> <sup>-1</sup> )	95.6	130.7	80.9
Fe dispersion <sup><math>b</math></sup> (%)	1.5	2.0	1.4
$TOF^{c} (10^{-2} s^{-1})$	7.71	5.87	9.11
$H_2$ chemisorbed <sup>d</sup> (mmol <sub>H<sub>2</sub></sub> g <sub>cat</sub> <sup>-1</sup> )	3.0	3.1	2.6
Fe loading <sup>e</sup> (wt%)	71.8	71.7	67.3

<sup>*a*</sup> Determined *via* CO-TPD. <sup>*b*</sup> Dispersion =  $2 \times$  CO chemisorbed/Fe atoms. <sup>*c*</sup> TOF = CO reaction rate/ $(2 \times$  CO chemisorbed). <sup>*d*</sup> Determined *via* CO-TPD. <sup>*e*</sup> Determined *via* X-ray fluorescence (XRF, Table S1, ESI).



Fig. 3 BET isotherms (a) and BJH isotherms (b) of the Fe-based spindles

the pore size distributions of the prepared catalysts. It is to be noted that all three catalysts display a peak centered at around 4 nm, indicating that the spindles are a mesoporous material that can enhance catalytic activity and provide efficient diffusion.<sup>15</sup> The average pore diameters of the Fe, Fe/CTAB, and Fe/2CTAB catalysts are calculated to be 3.71, 3.75, 3.81 nm, and the corresponding total pore volumes are 0.13, 0.08, 0.16 cm<sup>3</sup> g<sup>-1</sup> (Table 1). Apparently, the pore diameter and pore volume of the Fe/2CTAB catalyst are larger than those of the Fe and Fe/CTAB catalysts. Interestingly, some early studies demonstrated that catalysts containing larger pores could lead to the rapid transportation of products and reactants, thus improving selectivity for long chain (C5+) hydrocarbons.<sup>1</sup> It is accepted that the nanospaces over the synthesized catalysts limit diffusion effects related to the reactants and products, and thus play a key role in regulating the product distribution, which can give rise to the selectivity for C<sub>5+</sub> hydrocarbons.<sup>1,16</sup> It is a reasonable assumption that the selectivity for C<sub>5+</sub> over the three catalysts would obey the following order: Fe/2CTAB > Fe > Fe/CTAB.

#### 3.2 Interaction with CO and H<sub>2</sub>

As for Fe-based FT synthesis, CO adsorption and dissociation on the surfaces of active phases are key elementary steps.<sup>15</sup> To study the ability for CO adsorption, desorption, and dissociation over the prepared catalysts, CO-TPD data from the synthesized catalysts were measured after the pre-adsorption of CO at 150 °C, and the corresponding CO-TPD profiles are shown in Fig. 4a. As can be seen, Fe/CTAB displays a strong peak at about 558 °C for strongly chemisorbed CO. The CO desorption temperature over the Fe/2CTAB catalyst is shifted to about 553 °C, indicating that the interaction between iron and CO over Fe/CTAB was stronger. Table 1 summarizes the amount of





Fig. 4 (a) CO and (b)  $\rm H_2$  TPD profiles for Fe-based catalysts

adsorbed CO and the dispersion of Fe over the synthesized catalysts. Actually, the CO adsorption capacity is closely related to the number of active sites, which depends on the dispersion of iron species. The calculated results in Table 1 reveal that the order of CO chemisorption is Fe/2CTAB (80.9  $\mu$ mol<sub>CO</sub> g<sub>cat</sub><sup>-1</sup>) < Fe (95.6  $\mu$ mol<sub>CO</sub>  $g_{cat}^{-1}$ ) < Fe/CTAB (130.7  $\mu$ mol<sub>CO</sub>  $g_{cat}^{-1}$ ). This indicates that Fe/CTAB enhanced the adsorption of CO not only in relation to strength but also to capacity, compared with the Fe/2CTAB and Fe catalysts (Table 1). Furthermore, the strong broad peak at a higher temperature is ascribed to the desorption of CO after the recombination of dissociated carbon and oxygen on the surface.<sup>15</sup> This indicates that the Fe/CTAB catalyst can achieve a higher degree of CO dissociation than Fe and Fe/2CTAB, thus promising excellent CO conversion during the FT reaction. Nevertheless, the smaller pore volume and surface area of the Fe/CTAB catalyst may restrain the transportation of products and chain growth in FT synthesis, and this cannot give rise to selectivity for C<sub>5+</sub> hydrocarbons.

H2-TPD was also carried out to investigate the H2 adsorption behavior (Fig. 4b), and the corresponding results are summarized in Table 1. As shown in Fig. 4b, the Fe, Fe/CTAB, and Fe/2CTAB catalysts show similar H<sub>2</sub> adsorption curves. The H<sub>2</sub> desorption peak of the three catalysts occurs in two stages, with temperature ranges of 350-450 °C and 510-560 °C. The former peak (350-450 °C) is attributed to the weak desorption of molecular H<sub>2</sub>, while the main peak at higher temperatures (510–560 °C) is attributed to the strong desorption of molecular H<sub>2</sub>. For the Fe/2CTAB catalyst, the main peak is observed at about 520 °C. The Fe and Fe/CTAB catalysts show relatively higher H<sub>2</sub> desorption temperatures of about 556 °C and 550 °C, respectively. Moreover, Fe/2CTAB obtains a lower H<sub>2</sub> chemisorption value, 2.6  $\text{mmol}_{\text{H}_2} \text{g}_{\text{cat}}^{-1}$ , than Fe (3.0  $\text{mmol}_{\text{H}_2} \text{g}_{\text{cat}}^{-1}$ ) and Fe/CTAB (3.1  $\text{mmol}_{\text{H}_2} \text{g}_{\text{cat}}^{-1}$ ). The relatively weak intensity of the binding energy of hydrogen atoms on the active phase and the low amount of adsorbed H<sub>2</sub> over Fe/2CTAB limit the hydrogenation rate, thus favoring chain growth, which cannot give rise to CH<sub>4</sub> production in FT synthesis.

#### 3.3 Catalytic tests

The FT performances of the Fe, Fe/CTAB, and Fe/2CTAB catalysts were tested in a fixed-bed reactor at 20 bar and 280  $^{\circ}$ C under syngas (H<sub>2</sub>/CO = 1, GHSV = 3000 mL g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>). Table 2 summarizes the results of catalytic performance both for CO conversion and product selectivity over the three catalysts after undergoing the FT reaction for 72 h. The activity of Fe-based

Performance	Fe	Fe/CTAB	Fe/2CTAE
CO conversion (%)	94.3	95.3	93.6
Mass balance (%)	98.0	98.2	97.5
$CO_2$ selectivity (%)	45.4	49.2	43.8
Chain growth probability $\alpha$	0.72	0.69	0.75
Product selectivity (wt%)			
CH <sub>4</sub>	16.9	19.1	13.9
$C_2-C_4$	24.2	25.7	21.1
C <sub>5+</sub>	58.9	55.2	65.0

catalysts in FT synthesis depends solely on the number of active sites. Under the selected reaction conditions, Fe/CTAB achieves a higher CO conversion, of 95.3%, than Fe (94.3%) and Fe/2CTAB (93.6%) (Table 2). This is in good agreement with the speculation from the CO-TPD results (Fig. 4a and Table 1). Obviously, the number of active sites depends on the amount of CO chemisorption.

Generally, catalytic activity and stability are vital factors for evaluating the performance of catalysts in FT synthesis. The trend of CO conversion with time on stream over the synthesized mesoporous catalysts was studied, and the corresponding results are shown in Fig. 5a. As can be seen, Fe/2CTAB exhibits a CO conversion of 98.3% after 24 h of reaction, and the value is decreased to 96.9% after 48 h and then decreased further to 93.6% after 72 h. In comparison with Fe/2CTAB, the Fe and Fe/CTAB catalysts display a relatively slow decrease in the CO conversion from 98.3 to 94.3% and from 98.2 to 95.3%, respectively. As for FT synthesis, a slight decrease in CO conversion during the reaction mainly results from a continuous drop in



Fig. 5 The CO conversion (a) and product selectivity (b) of Fe, Fe/CTAB, and Fe/2CTAB catalysts in relation to time on stream.

CH<sub>4</sub> production.<sup>17</sup> As shown in Fig. 5b, the CH<sub>4</sub> selectivity for all the catalysts gradually decreases with time on stream. This can be rationalized using the simplified "surface carbide" or "alkyl" mechanism that is widely accepted for FT synthesis.<sup>17</sup> Following CO dissociation and carbon hydrogenation, the insertion of CH<sub>2</sub> into the adsorbed alkyl species is proposed to accelerate chain growth, thus increasing C5+ selectivity, and not giving rise to CH<sub>4</sub> production. As reported, the lower turnover frequency (TOF) may be attributed to longer CHx residence times, which can likely block the surfaces of the active phase, and then lead to lower C<sub>5+</sub> selectivity.<sup>18</sup> As shown in Table 1, the TOF is in the order of Fe/2CTAB (9.11  $\times$  10<sup>-2</sup> s<sup>-2</sup>) > Fe (7.71  $\times$  $10^{-2} \text{ s}^{-2}$ ) > Fe/CTAB (5.87 ×  $10^{-2} \text{ s}^{-2}$ ). This order is the same for the changing tendency of  $C_{5+}$  selectivity (Table 2 and Fig. 5b). As shown in Fig. 5b, the order of C<sub>5+</sub> selectivity over the asprepared catalysts is Fe/2CTAB > Fe > Fe/CTAB. Obviously, the CH<sub>4</sub> selectivity decreases, in accompaniment with an increase in the C<sub>5+</sub> product fraction, with time on stream. In particular, Fe/2CTAB, with a higher TOF value, obtains a higher C5+ selectivity of 65.0 wt%. Moreover, this value is much higher than the previously reported highest value (59.0 wt%, 24 h) over unsupported mesoporous Fe<sub>3</sub>O<sub>4</sub> microspheres.<sup>9</sup> In the previous work, the selectivity for C5+ decreased (49.5 wt%, 48 h) with time on stream, accompanied by a rapid decrease in CO conversion from 93.2% (24 h) to 80.1% (48 h). In contrast, the Fe/2CTAB catalyst displays good C5+ selectivity, with high and stable CO conversion (Fig. 5). Furthermore, both the activity or C<sub>5+</sub> selectivity over the Fe/2CTAB catalyst are much higher than the reported values for various supported iron nanostructures.4,10,11

Although some challenges still remain, current FT technology generally aims at the development of efficient FT catalysts with a higher selectivity for  $C_{5+}$  hydrocarbons, while limiting CH<sub>4</sub> selectivity to the lowest level possible. It is observed from Table 2 that the Fe/CTAB catalyst exhibits lower selectivity toward C<sub>5+</sub> hydrocarbons (55.2 wt%) while yielding a CH<sub>4</sub> product fraction higher than 19.1 wt%. In contrast, the Fe catalyst shows higher C5+ hydrocarbon selectivity (58.9 wt%), accompanied by a decrease in the CH<sub>4</sub> selectivity (16.9 wt%). In particular, the selectivity for C5+ hydrocarbons over Fe/2CTAB is increased to 65.0 wt%. Meanwhile, the selectivity for undesired  $CH_4$  is decreased to 13.9 wt%. Interestingly, the selectivity for  $C_{5+}$  hydrocarbons over the synthesized catalysts is in the order: Fe/2CTAB (65.0 wt%) > Fe (58.9 wt%) > Fe/CTAB (55.2 wt%). This order is the same as the trend in pore volume: Fe/2CTAB  $(0.16 \text{ cm}^3 \text{ g}^{-1}) > \text{Fe} (0.13 \text{ cm}^3 \text{ g}^{-1}) > \text{Fe/CTAB} (0.08 \text{ cm}^3 \text{ g}^{-1}).$ This indicates that a larger pore volume size corresponds with a higher selectivity for C5+ hydrocarbons and provides a higher chain growth probability ( $\alpha$ ) in this work (Tables 1 and 2). This is mainly because larger pores can contribute to transporting primary products more effectively and to decreasing the CH<sub>4</sub> formation rate from the secondary hydrocracking of olefins.<sup>1,19</sup> It is a reasonable conclusion that the product selectivity in FT synthesis is associated with pore structure. Thus, mesoporous spindles assembled via active phases, without the interference of support effects, can provide a path for the FT synthesis of C<sub>5+</sub> hydrocarbons, particular using Fe/2CTAB.

# 4 Conclusions

Novel mesoporous spindles were synthesized to explore the effects of pore structure on FT performance, and a single spindle is assembled from numerous iron carbide nanoparticles. Interestingly, the mesoporosity of the spindles consists of the interspaces between neighboring nanoparticles. The synthesized catalysts show excellent stability and C5+ selectivity during FT synthesis. This demonstrates that the pore structure plays a key role in regulating the selectivity for C<sub>5+</sub> hydrocarbons. Fe/2CTAB, with a larger pore size, achieves a higher selectivity for  $C_{5+}$ hydrocarbons (65 wt%) than Fe and Fe/CTAB. Meanwhile, it exhibits a lower selectivity for  $CH_4$  (13.9 wt%), with a high CO conversion of 93.6% after undergoing the FT reaction for 72 h. The novel mesoporous Fe-based spindles will allow us to understand the effects of pore size on catalytic performance and to further improve the selectivity for target products, and they may provide a promising strategy for the production of liquid fuels.

# Conflicts of interest

There are no conflicts to declare.

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## References

- 1 Q. Zhang, J. Kang and Y. Wang, *ChemCatChem*, 2010, 2, 1030–1058.
- 2 Y. Zhang, T. Wang, L. Ma, N. Shi, D. Zhou and X. Li, *J. Catal.*, 2017, **350**, 41.

- 3 S. Jang, S. W. Kang, D. H. Chun, H.-T. Lee, J.-I. Yang, H. Jung, H.-Do Jeong, K. M. Nam and J. C. Park, *New J. Chem.*, 2017, **41**, 2756.
- 4 F. Zhang, M. Wang, L. Zhu, S. Wang, J. Zhou and Z. Luo, *Sci. Int. J. Hydrogen Energy*, 2017, **42**, 3667.
- 5 M. Rahmati, B. Huang, M. K. Mortensen Jr., K. Keyvanloo, T. H. Fletcher, B. F. Woodfield, W. C. Hecker and M. D. Argyle, *J. Catal.*, 2018, **359**, 92.
- 6 A. Y. Khodakov, W. Chu and P. Fongarland, *Chem. Rev.*, 2007, **107**, 1692.
- 7 Y. Zhang, L. Ma, J. Tu, T. Wang and X. Li, *Appl. Catal.*, 2015, **499**, 139.
- 8 X. Wang, L. Zhu, Y. Liu and S. Wang, *Sci. Total Environ*, 2018, **625**, 686.
- 9 Y. Zhang, L. Ma, T. Wang and X. Li, *New J. Chem.*, 2015, **39**, 8928.
- 10 W. Chen, Z. Fan, X. Pan and X. Bao, J. Am. Chem. Soc., 2008, 130, 9414.
- 11 W. Wang, M. Ding, L. Ma, X. Yang, J. Li, N. Tsubaki, G. Yang, T. Wang and X. Li, *Fuel*, 2016, **164**, 347.
- 12 Y. Zhang, L. Ma, T. Wang and X. Li, Fuel, 2016, 177, 197.
- 13 J. Aluha, P. Boahene, A. Dalai, Y. Hu, K. Bere, N. Braidy and N. Abatzoglou, *Ind. Eng. Chem. Res.*, 2015, **54**, 10661.
- 14 J. C. Park, S. C. Yeo, D. H. Chun, J. T. Lim, J.-I. Yang, H.-Tae Lee, S. Hong, H. M. Lee, C. S. Kim and H. Jung, *J. Mater. Chem. A*, 2014, 2, 14371.
- 15 K. Keyvanloo, J. B. Horton, W. C. Hecker and M. D. Argyle, *Catal. Sci. Technol.*, 2014, 4, 4289.
- 16 H. Xiong, M. Moyo, M. A. Motchelaho, Z. N. Tetana, S. M. A. Dube, L. L. Jewell and N. J. Coville, *J. Catal.*, 2014, **311**, 80.
- 17 H. M. T. Galvis, J. H. Bitter, C. B. Khare, M. Ruitenbeek, A. I. Dugulan and K. P. de Jong, *Science*, 2012, 335, 835.
- 18 J. P. den Breejen, P. B. Radstake, G. L. Bezemer, J. H. Bitter, V. Frøseth, A. Holmen and K. P. De Jong, *J. Am. Chem. Soc.*, 2009, **131**, 7197.
- 19 Y. Zhang, M. Koike, R. Yang, S. Hinchiranan, T. Vitidsant and N. Tsubaki, *Appl. Catal.*, *A*, 2005, **292**, 252.