Fischer-Tropsch synthesis over a 3D foamed MCF silica support: towards a more open porous network of cobalt catalysts

Liang Wei^a, Yanxi Zhao^b, Yuhua Zhang^b, Chengchao Liu^b, Jingping Hong^b, Haifeng Xiong^{c}, Jinlin Li^{b*}*

^a College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou, China

^b Key Laboratory of Catalysis and Materials Science of the State Ethnic Affairs Commission and Ministry of Education, South-Central University for Nationalities, Wuhan, China

^c Center for Microengineered Materials, Department of Chemical & Biological Engineering, University of New Mexico, Albuquerque, 87131 NM, United States

*Corresponding author.

Email: hfxiong@unm.edu (H.Xiong); jnlinli@aliyun.com (J. Li)

Abstract: 3D mesoporous cellular silica foams (MCFs) were prepared and used as supports for cobalt Fischer-Tropsch synthesis (FTS) catalysts (Co/MCF). The silica foam MCFs have 3D mesostructure that large spherical cell pores interconnected with small window pores, which provides an open porous network for Co FTS catalysts. The effects of catalyst structure parameters (cell pore diameter and cobalt particle size) on the performances of the Co/MCF catalysts were investigated. It was found that the Co/MCF catalyst with average pore size of 7-12 nm (window and cell pores) showed the highest reactivity. The MCF not only provided a cavity to suppress the growth of cobalt particles, but also enhanced the reducibility and cobalt dispersion. The Co/MCF catalyst having large and open pore structure is favorable for the transport of reactants and the occurrence of secondary reactions, leading to the high C₅₊ hydrocarbon selectivity. A Co/MCF catalyst with Co particle size of 6.9 nm presented the highest activity in FTS reaction due to the highest dispersion and an appropriate reduction degree. Compared to the Co catalysts supported on other ordered silicas SBA-16, KIT-6 and SBA-15, Co/MCF catalyst showed higher activity and C₅₊ hydrocarbon selectivity, which was attributed to the 3D open porous structures of MCF. The Co/MCF catalysts are stable under low temperature FTS conditions (210 °C). Under harsh FTS reaction conditions (250 °C, 1.0 MPa), the Co/MCF catalyst underwent a rapid deactivation due to cobalt sintering and the formation of interacted Co-silica compound, while the stability of Co/MCF catalyst can be improved by functionalizing the MCF using carbon-coating and Al-doping.

Keywords: Fischer-Tropsch synthesis; Co catalysts; MCF silica; 3D pore structure; Catalyst stability

1. Introduction

Fischer-Tropsch synthesis (FTS) is an efficient route to convert syngas (CO/H_2) derived from coal, natural gas and biomass into liquid fuels and value-added chemicals [1-3]. Cobalt catalysts are preferred due to the low water-gas shift activity, the low deactivation rate and the high selectivity to long-chain hydrocarbons. Ordered mesoporous materials, such as MCM-41[4], MCM-48 [5], SBA-15 [6-8] and HMS [9-11], have been used as supports in FTS. These mesostructured materials not only enhanced the dispersion of active phase, but also decreased the deactivation rate [12].

The porous characteristics of catalysts, such as average pore size [6, 13-15], pore size distribution [16] and pore length [17], have been found to significantly affect the activity and hydrocarbon selectivities in FTS. For example, catalysts supported on SBA-15 with average pore diameter of 6-10 nm were reported to have the highest activity and heavy hydrocarbon selectivity [6, 18]. The catalysts supported on short-pore SBA-15 have a higher metal dispersion, resulting in higher Co-time-yield and C_{5+} selectivity [17]. On the other hand, cobalt catalysts with double pore size distributions (mesopores and macropores) showed higher catalytic activity and C_{5+} selectivity than the catalysts supported on unimodal mesoporous silica. This was explained by that the macropores created an open porous structure, which enhanced the mass transfer of reactants in the hierarchical pores [19].

Different from the porous materials with 1D and 2D pore channels (carbon nanotubes and SBA-15, respectively), catalysts with 3D pore channels have multi-pore size distributions and interconnected pore networks (Fig. 1). These novel pore structures minimize the mass transfer limitation of reactants during catalyst preparation and reactions, which improves the metal dispersion and the contacting frequency between reactants and active sites, leading to improved catalytic performances [20]. Mass transfer limitation is an important factor affecting the catalyst performances (activity and hydrocarbon selectivity) in FTS because a CO/H_2 ratio gradient may exist due to the different diffusion rates of CO and H_2 along a long and small pore channel. We recently found that the catalysts supported on a mesostructure silica SBA-16 having 3D pore channels showed the significantly improved activity and stability in FTS reaction [21, 22].

Fig. 1.

Mesoporous cellular silica foams (MCFs) have porosity with 3D pore channels that aerogel-like, uniformly large spherical cell pores interconnected with uniformly small window pores (a pore model of MCF is shown in Fig. 2d). The average pore sizes of MCF can be adjusted in the range of 5-50 nm and the specific surface area of MCF is up to 1000 m²·g⁻¹. Furthermore, the MCF materials exhibited high hydrothermal stability [23]. These novel pore characteristics of MCF provide more open porous networks than the other conventional porous supports, making the contacting of reactants and active sites much easier in catalysis. The MCF has been used as support in catalysis recently and it was found that these catalysts exhibited high catalytic performance in the esterification of acetic acid [24] and oxidative dehydrogenation of propane [25].

The objective of the present study is to comprehensively investigate the catalytic performances of cobalt catalyst supported on MCF in FTS. The synthesized MCFs have double pore size distributions and the 3D pore structure of MCF was adjusted using microemulsion method. The FT reaction was carried out under reaction temperatures of 210-250 °C and space velocity of 4-50 SL·h⁻¹·g⁻¹. The influence of catalyst structure parameters, i.e. cell pore size (6.3-42.1 nm) and cobalt particle size (3.9-9.4 nm), on catalytic performances of Co/MCF catalysts were firstly investigated in FTS. Then, the FTS performances of Co/MCF were compared with that of the cobalt catalysts supported on other ordered silicas SBA-16, KIT-6 and SBA-15. Furthermore, the stability of the Co/MCF catalyst was investigated under harsh FTS reaction conditions (250 °C).

2. Experimental

2.1. Supports and catalysts preparation

2.1.1. Supports preparation

3D mesoporous cellular silica foams (MCFs) were synthesized using Pluronic P123 (EO₂₀PO₇₀EO₂₀, average molecular weight = 5800, Sigma Aldrich) as a template. Tetraethyl orthosilicate (TEOS, AR, Aladdin) was used as silica source and benzene (C₆H₆, AR, Aladdin) was added to the aqueous solution to form microemulsion. The detailed synthesis procedures are as follows: 10.0 g of P123 and 350 mL of HCl (2 M) were mixed at 35 °C, then appropriate amount of benzene (see Table 1) was added to adjust the pore structures of MCF.

Subsequently, 21.0 g of TEOS was gradually added to the solution under stirring and kept at 35 °C for 24 h at ambient pressure. Then, the mixture was placed in a Teflon bottle and kept at 100 °C for 24 h in an oven. After that, the product was filtered using a Büchner funnel (the pore size of filter paper: 30-50 µm) and washed with deionized water (5000 mL). Then, the solid was dried at 100 °C for 12 h in an oven and calcined at 550 °C for 5 h in flowing air at ambient pressure. The supports were denoted as MCF-1, MCF-2, MCF-3 and MCF-4, corresponding to the samples with average cell pore size of 6.3 nm, 11.5 nm, 26.4 nm and 42.1 nm, respectively.

Mesostructure silicas SBA-16, KIT-6 and SBA-15, were synthesized according to previous methods. For SBA-16 [22, 26], 1.2 g of P123 ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$, average molecular weight = 5800, Sigma Aldrich) and 6.0 g of Pluronic F127 ($\text{EO}_{106}\text{PO}_{70}\text{EO}_{106}$, average molecular weight = 12600, Sigma Aldrich) were dissolved in HCl solution (340 mL, 2M) at 35 °C at ambient pressure. Tetraethylorthosilicate (28.3 g) was then added to the mixture, followed by stirring at 35 °C for 24 h at ambient pressure. The mixture was placed in a Teflon bottle and aged at 100 °C for 24 h in an oven. After that, the solid product was filtered using a Büchner funnel (the pore size of filter paper: 30-50 µm) and washed with distilled water (5000 mL), followed by calcining at 550 °C for 5 h in air at ambient pressure. The KIT-6 support was synthesized as follows: 8.0 g of Pluronic P123 was dissolved in 300 mL of HCl solution (0.5 M). Then 9.9 mL of n-butyl alcohol (AR, Aladdin) was added to the above solution. After stirring at room temperature for 1 h, 18.4 mL of TEOS (AR, Aladdin) was gradually added to the solution and kept at room temperature for 24 h under stirring. Then, the mixture was placed in a Teflon bottle and kept at 120 °C for 24 h in an oven. After filtration and washing with deionized water (5000 mL), the solid was dried at 100 °C for 24 h in flowing air at ambient pressure. Finally, the obtained materials were calcined at 550 °C for 5 h in air at ambient pressure. The synthesis procedure of SBA-15 support has been reported in our previous study [18].

Al-doped MCF (AMCF) was prepared by the following procedures: 10.0 g of P123 and 350 mL of HCl (2M) were mixed at 35 °C, followed by the addition of 16.0 g of benzene (Benzene to P123 mass ratio is 1.6). After stirring at 35 °C for 1 h, 2.04 g aluminum isopropoxide ($\geq 99.99\%$, Aladdin) was added into the above solution and the mixture was stirred at 35 °C for 2 h. Subsequently, 21.0 g of TEOS was gradually added to the solution

and stirred at 35 °C for 24 h. The mixture was then transferred into a teflon bottle and kept at 100 °C for 24 h in an oven. After that, ammonia (anhydrous, $\geq 99.99\%$, Aladdin) was added dropwisely into the solution to adjust the pH = 7.5, followed by aging the mixture in the teflon bottle at 100 °C for 24 h in an oven. The solid was collected after filtration using a Büchner funnel and washing with deionized water (5000 mL). Then, the sample was dried at 100 °C for 24 h and calcined at 550 °C for 5 h in air at atmospheric pressure.

Carbon-coated MCF was prepared by incipient wetness impregnation using furfuryl alcohol ($>98\%$, Aladdin) as carbon source, the mass ratio of furfuryl alcohol and MCF-3 is 10 wt.%. Furfuryl alcohol solution (0.2 g) was impregnated to the MCF-3 (2 g) directly at room temperature. After the impregnation, the sample was dried at 60 °C for 12 h in a vacuum oven (DZF-6050, Shanghai Jinghong instrument LLC), followed by pyrolysis at 800 °C for 2 h in a flow of high purity nitrogen ($> 99.999\%$, 100 mL·min⁻¹) in a quartz tube at ambient pressure. The obtained grey powder was collected and denoted as C/MCF.

2.1.2. Catalysts preparation

Series of cobalt catalysts supported on MCFs were prepared to investigate the effect of pore structure, cobalt particle size and support properties on the catalytic performances in FTS. All catalysts were prepared by incipient wetness impregnation using cobalt nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, AR, Sigma Aldrich) as precursor.

Co/MCF catalysts (15 wt.%Co) with different pore structures were prepared using the synthesized MCFs (MCF-1, MCF-2, MCF-3, MCF-4) as supports. Desired amount of cobalt nitrate was added into an anhydrous ethanol/water solution (v/v: 10%), and then, the mixed solution was impregnated into the supports at room temperature at ambient pressure. The samples were evaporated at 80 °C in a rotary evaporator(RE-52AA, Shanghai Yarong instruments) and dried at 100 °C for 24 h in an oven at atmospheric pressure, followed by calcination at 350 °C for 5 h in flowing air at ambient pressure. The catalysts were denoted as Co/MCF-1, Co/MCF-2, Co/MCF-3 and Co/MCF-4, respectively.

Co/MCF catalysts (15 wt.%) with different cobalt particle sizes (3.9-9.4 nm) were obtained using citric acid (AR, Aladdin) as a controlling agent [21], all catalysts were prepared using the same MCF support (MCF-3). Briefly, the desired amount of citric acid (see Table 2) was added into an ethanol/water solution (v/v: 10%).

Then appropriate amount of cobalt nitrate was dissolved in the mixture. After that, the mixture was directly impregnated to the MCF-3 at room temperature. The sample was then dried at 100 °C for 24 h in an oven and calcined at 350 °C for 5 h in air at atmospheric pressure. The obtained catalysts were denoted as Co/MCF-3-a, Co/MCF-3-b and Co/MCF-3-c, which correspond to cobalt particle sizes of 6.9 nm, 4.8 nm and 3.9 nm, respectively.

Co/SBA-15, Co/SBA-16 and Co/KIT-6 catalysts (15 wt.%Co) with similar average pore size (ca. 8.0 nm) were prepared to compare with Co/MCF in order to investigate the effect of support porosity on FTS performances. The catalyst preparation procedures are the same as above. Desired amount of cobalt nitrate was dissolved in an anhydrous ethanol/water solution (v/v: 10%) and the obtained solution was directly impregnated into the supports (SBA-15, SBA-16 and KIT-6). The solvents (water and ethanol) were slowly evaporated at 80 °C in a rotary evaporator. After dried at 100 °C for 24 h in an oven at atmospheric pressure, the samples were calcined at 350 °C for 5 h in flowing air (100 mL·min⁻¹) at atmospheric pressure.

Co/MCF, Co/AMCF and Co/C/MCF catalysts (20 wt.%Co) were prepared by incipient wetness impregnation. Briefly, desired amount of cobalt nitrate was dissolved in water. Then, the solution was directly impregnated into the supports (MCF, AMCF and C/MCF) at room temperature. After evaporating at 80 °C to remove the solvent (water) in a rotary evaporator, the solid was dried at 100 °C for 24 h in air in an oven. Subsequently, the Co/MCF and Co/AMCF samples were calcined at 350 °C for 5 h in flowing air (100 mL·min⁻¹), while Co/C/MCF was calcined at 350 °C in flowing N₂ (100 mL·min⁻¹) at ambient pressure. The three catalysts were prepared to investigate the stability of the Co catalyst supported on MCF under harsh FT reaction conditions.

2.2. Supports and catalysts characterization

Surface area, pore size and total pore volume of supports and catalysts were measured by nitrogen physisorption at -196 °C using a Quantachrome Autosorb-1-C-MS instrument. Before the measurement, the sample was degassed at 200 °C for 6 h. The surface area was obtained using the Brunauer-Emmett-Teller (BET) model. The cell pore size and window pore size were determined by the Barrett-Joyner-Halenda (BJH) method from the adsorption and desorption branches of the isotherm, respectively. The total pore volume was determined at a relative pressure of 0.99.

X-ray diffraction (XRD) patterns were recorded using a Bruker Advanced D8 diffraction instrument with monochromatized Cu-K α radiation ($\lambda=1.54056$ Å) equipped with a VANTEC-1 detector. The scan was ranged from 20° to 80° with a step of 0.0163°. The average crystallite size of Co₃O₄ was calculated using the Scherrer equation from the most intense Co₃O₄ peak ($2\theta = 36.9^\circ$) [27]. The average Co particle size was calculated by the equation [28]: $d(\text{Co}^0)=0.75\times d(\text{Co}_3\text{O}_4)$.

Transmission electron microscopy (TEM) images were obtained with a FEI Tecnai G²20 S-Twin instrument. The catalysts were firstly reduced under high purity H₂ (> 99.999%) at 450 °C for 10 h and passivated under 1% O₂/N₂ at 30 °C for 5 h. Then, the passivated catalysts were directly suspended in ethanol with ultrasonic treatment and loaded onto a copper grid covered with perforated carbon. The average cobalt particle size was obtained from at least 300 ‘shaped objects’ per sample and the TEM images were randomly chosen. Surface averaged Co particle sizes (d_{avg}) were calculated from TEM according to the formula: $d_{\text{avg}}=\Sigma_i d_i^3/\Sigma_i d_i^2$, where d_i is measured diameters of the particles. It should be mentioned that the passivation procedure may create CoO layer on the metallic cobalt. Thus, the measured cobalt size from TEM is a relative value and not an absolute one. Scanning electron microscopy (SEM) was carried out on a ULTRA PLUS-43-13 instrument with a 30 kV beam. In order to avoid the effect of charge, the sample was coated with gold prior to analysis.

H₂-TPR experiment was carried out with a Zeton Altamira AMI-200 instrument. Prior to the TPR measurement, the catalyst (0.15 g) was flushed with high purity argon (> 99.999%) at 150 °C for 1 h, and then cooled down to 50 °C. 10% H₂/Ar (flow rate: 30 mL·min⁻¹) was switched on and the temperature was raised from 50 to 800 °C (ramping rate 10 °C·min⁻¹) in the flowing 10% H₂/Ar. Finally the temperature was held at 800 °C for 30 min.

Hydrogen TPD was carried out with the Zeton Altamira AMI-200 instrument. The sample (0.10 g) was reduced at 450 °C for 10 h using a flow of high purity hydrogen (> 99.999%, 30 mL·min⁻¹) and then cooled down from 450 to 100 °C in flowing hydrogen. Then hydrogen was switched to high purity Ar (> 99.999%, 10 mL·min⁻¹) and swept the sample till the TCD signal showed a stable baseline (30 min). Subsequently, the temperature was increased from 100 to 450 °C with a rate of 10 °C·min⁻¹ and kept at 450 °C for 2 h in flowing Ar (30 mL·min⁻¹). The TCD signal (desorbed H₂) was recorded by a PC automatically. Oxygen pulse

reoxidation experiment was performed after the H₂-TPD. The catalyst was reoxidized at 450 °C by injecting pulses of high purity oxygen (> 99.999%) in flowing He [29]. All flow rates were set to 30 mL·min⁻¹. The signal of O₂ consumption was recorded automatically by TCD. The calculation formulas of the reduction and dispersion are shown in supporting information.

H₂ chemisorption measurements were carried out with a Micromeritics ASAP 2020C. The sample was first reduced at 450 °C for 10 h in high purity H₂ (> 99.999%). After reduction, the sample was evacuated at that temperature for 30 min. Then, the temperature was cooled down to 150 °C. The H₂ adsorption isotherms and Co dispersion were measured at 150 °C [30, 31]. The total H₂ uptake was obtained by extrapolating the linear part of the isotherm to zero pressure. The calculation was performed by hypothesizing one hydrogen atom per cobalt surface atom. The dispersion was calculated as follow: $\text{dispersion} = 1.179X/Wf$, where X, W and f stand for the total H₂ uptake, the weight percentage of cobalt and the reduction degree from the O₂ titration, respectively. The Co particle diameter was estimated from the dispersion, assuming spherical metal particles of uniform diameter with a site density of 14.6 atom/nm² for the supported cobalt particles. Thus, the diameter of supported cobalt nanoparticles is expressed as: $\text{diameter} = 0.96/\text{dispersion}$.

2.3. Fischer-Tropsch synthesis (FTS)

FTS reaction was performed in a fixed bed reactor with inner diameter of 12 mm. For the measurements with CO conversion of 20-65%, the catalyst (0.5 g, particle diameter = 50-150 μm) was mixed with 5.0 g carborundum (100-200 μm) and reduced in high purity H₂ (> 99.999%) with a space velocity of 6 NL·h⁻¹g⁻¹ (NTP, normal temperature and pressure, 25°C, 0.1 MPa) at 450 °C for 10 h. After reduction, the catalyst was cooled down to 100 °C in flowing H₂, a flow of syngas with molar ratio of H₂/CO=2 was introduced and the pressure was increased to 1.0 MPa. The temperature of reaction was 210-250 °C and the space velocity of syngas was 4-8 SL·h⁻¹g⁻¹ (STP, standard temperature and pressure, 0 °C, 0.1 MPa). The reaction measurements at differential mode was carried out at 210 °C in the same fixed-bed reactor. Typically, 20 mg of catalyst (50-150 μm) was diluted with 200 mg of SiC particles (100-200 μm). After the catalyst was reduced at 450 °C for 10 h in a flow of high purity H₂ (>99.999%), the temperature of the reactor was cooled to 100 °C and the syngas

was introduced, followed by increasing the reaction temperature from 100 to 210 °C (ramping rate: 10 °C·min⁻¹). The syngas space velocity was kept at 50 SL·h⁻¹·g⁻¹ to achieve the CO conversion of < 5%. The product selectivity of the catalyst was also compared at the same CO conversion (around 5%) by adjusting the syngas space velocity. All the catalytic data were collected after 24 h of operation (under steady state). The wax and water products were collected in a hot trap (100°C), and the oil and water products were collected in a cold trap (-2°C). After removing the water, the wax and oil were analyzed every 24 h by an Agilent 7890A GC and an Agilent 6890N GC, respectively. The outlet gas was analyzed by an online Agilent 3000A Micro GC. Data analysis was performed following the procedures as described elsewhere [32], including the calculation of the alpha value obtained from C₃ to C₁₂ hydrocarbons ($\log(W_n/n) = n \log \alpha + \log (1-\alpha)^2/\alpha$, n is carbon number, W_n is the hydrocarbon weight and α is the carbon chain growth probability).

3. Results and discussion

3.1. Cobalt catalysts supported on mesoporous MCF with 3D pore structures in Fischer-Tropsch synthesis

3.1.1. Preparation and structure characteristics of 3D mesopores MCF supports

The 3D mesoporous structure of MCF was investigated by electron microscopy. The representative SEM and TEM images of a MCF are shown in Fig. 2. The SEM image (Fig. 2a) shows that the 3D MCF has uniform mesopores. The TEM images shows the high-magnification mesostructure of the MCF (Fig. 2b and c), and the 3D model of a MCF showing interconnected porous structure is illustrated in Fig. 2d. The MCF support has large cell pores connecting with small window pores (Fig. 2c and d). The formation of 3D mesoporous structure of MCF is due to the existence of P123-coated benzene droplets after adding benzene into the P123/HCl solution [33].

Fig. 2.

The 3D mesopore structure of MCF was tailored by varying the amount of benzene added. An increase in the benzene/P123 ratio increased the large cell pore size from 6.3 to 42.1 nm, accompanied by an increase of the small window pore size from 5.7 to 11.4 nm (Table 1). The isotherm curves and pore size distributions of four MCFs are shown in Fig. 3. All samples display the type IV isotherm and show steep hysteresis of type H1, indicating that all samples are mesoporous structure (Fig. 3a). The hysteresis loop shifts to the higher relative pressure with increasing benzene content, reflecting the increase in the cell pore size. Fig. 3b shows double pore size distributions of MCF that the large cell pores interconnect with uniform window pores. The cell pore size distribution of MCF-1 is broad and partly overlapped with the window pore size distribution. It suggests that MCF-1 is less ordered due to the less amount of benzene adding, as compared to the other three MCFs. The pore size distributions become narrow with increasing pore sizes (i.e. increasing benzene amount), indicating the improved long-distance ordering of MCF.

Fig. 3.

N₂ physisorption data of MCF with different pore structures are shown in Table 1. All MCFs have high surface areas of 590~690 m²·g⁻¹. The increase of the mass ratio of benzene/P123 from 0.8 to 2.0 led to the increase in average cell size from 6.3 to 42.1 nm and total pore volume from 0.88 to 2.38 cm³·g⁻¹, respectively. Furthermore, the surface area of MCF was found to be insensitive to the mass ratios of benzene/P123 (Figure S1), although both the average cell and window pore sizes of MCF increased.

Table 1

The representative TEM images of MCF with different pore structures are shown in Fig. 4. As can be seen, all MCFs show well-defined pore structure, which is consistent with the N₂ physisorption data. For MCF-4, it is clearly seen that the large cell pores are separated by thin silica walls. In addition, the cell pore size of MCF-4 estimated from TEM image is around 40 nm (Fig. 4d), which agrees with the value obtained from the N₂ physisorption (Table 1).

Fig. 4.

3.1.2. Characterization of Co/MCF catalysts with different pore structures and cobalt particle sizes

The surface area, average pore size and total pore volume of the Co/MCF catalysts decreased remarkably after cobalt introduction, as compared to the corresponding MCF supports (Table 1). It suggests that cobalt species **are** mainly deposited inside the MCF pores. XRD patterns of Co/MCF-1, Co/MCF-2, Co/MCF-3 and Co/MCF-4 catalysts are shown in Figure S2. The main cobalt phase on the catalysts is Co_3O_4 and the average Co_3O_4 crystallite sizes data are shown in Table 2. The Co_3O_4 crystallite sizes obtained from XRD varied between 11.2 nm and 18.5 nm when the corresponding cell pore size changed from 6.3 to 42.1 nm, indicating that an increase in the pore size (cell and window) of 3D MCF support resulted in an increase in the Co_3O_4 crystallite size. A similar trend was observed in cobalt catalysts supported on silica having 2D pore channels [6].

As shown in Fig. 5, cobalt clusters (labeled by circles) were formed on Co/MCF-1 and Co/MCF-2, while no such cluster was found on Co/MCF-3 and Co/MCF-4. This means that more cobalt species locate inside the MCF for Co/MCF-3 and Co/MCF-4, which **is** evidenced by the significantly decreased pore volumes of the two catalysts after cobalt impregnation (Table 1).

Fig. 5.

The surface areas of the Co/MCF catalysts with different cobalt particle sizes varied between 399 and 480 $\text{m}^2\cdot\text{g}^{-1}$ (Table 1). The XRD patterns of Co/MCF-3, Co/MCF-3-a, Co/MCF-3-b and Co/MCF-3-c catalysts with different cobalt particle sizes are shown in Figure S3. The average Co_3O_4 crystallite sizes calculated from the peak at $2\theta = 36.9^\circ$ are listed in Table 2. With the increase of citric acid to cobalt precursor ratio (from 0.09 to 0.54), the average Co_3O_4 crystallite sizes decreased from 10.7 to 6.1 nm. Thus, the addition of citric acid significantly affected the Co_3O_4 particle size and enhanced the dispersion of cobalt on the MCF-3 surface. The representative TEM images of the catalysts with different cobalt particle sizes are shown in Fig. 6 and Figure S4. The histograms of the average cobalt particle sizes for the four catalysts are shown in Figure S5. The cobalt

particles are well dispersed on the catalysts (shown by the black dots in Fig. 6). Compared to the raw Co/MCF-3 (Fig. 6a), no large cobalt particles/**clusters** are formed on the Co/MCF-3 catalysts pretreated by citric acid (Figs. 6b-d).

Fig. 6.

3.1.3. Reduction and dispersion of Co/MCF catalysts **having** 3D pore structures

Fig. 7 shows the H₂-TPR profiles of the Co/MCF catalysts **having** different 3D pore structures and cobalt particle sizes. For the catalysts with different 3D pore structures, there are three reduction regions located at 200-320 °C, 320-600 °C and > 600 °C, corresponding to the reduction of Co₃O₄→CoO, CoO→Co⁰, and unreducible Co₂SiO₄, respectively [34]. Increasing the 3D cell size of the catalysts from 6.3 to 42.1 nm, no significant difference was found on the temperatures of the reduction peaks of Co₃O₄ (α and β peaks, Fig. 7a). This is different from the results obtained from cobalt catalysts supported on porous materials with 2D pore channels that pore size significantly affected the reduction behaviors of Co₃O₄ phase [6]. However, **with the increase of cell sizes**, the intensity of the high temperature peak at about 705 °C decreased firstly and then disappeared when the cell pore size is 42.1 nm, indicating that a weak interaction existed between the large cobalt oxide particles and large pore MCFs.

For the Co/MCF catalysts with different cobalt particle sizes (Fig. 7b), the shape and location of the reduction peak at 250-320 °C are similar. It suggests that the first-step reduction of Co₃O₄ to CoO **is** not influenced by the cobalt particle sizes. However, the temperature of the second reduction peak (peak β; the reduction of CoO to Co⁰) shifted gradually from 417 to 440 °C when decreasing the cobalt particle sizes. Furthermore, the relative intensity of peak γ at about 750 °C increased with decreasing cobalt particle sizes. The increased intensity is attributed to a strong interaction between the cobalt and the MCF and to the formation of cobalt-silica species, which is difficult to be reduced [5]. Thus, the 3D MCF supported cobalt catalysts contain smaller cobalt particles, which are more difficult to reduce.

Fig. 7.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26

H₂-TPD and O₂ titration data for Co/MCF catalysts are shown in Table 2 and Table S1. It revealed that the 3D pore structure (cell/window) has great influence on the reduction degree, dispersion and cobalt particle size. With an increase in the pore size of catalyst, cobalt dispersion and hydrogen consumption decreased from 15.3% to 8.7% and 122.3 to 74.5 $\mu\text{mol}\cdot\text{g}^{-1}$, respectively, whereas the reduction degree of the catalysts increased from 62.9% to 67.2%. The cobalt particle size of the catalysts increased from 6.7 to 11.9 nm with the increase of the cell pore size (Table S1), **which is** consistent with the results of XRD and TEM. The amount of H₂ adsorbed on the reduced Co/MCF catalysts were also measured using H₂-chemisorption at 150 °C (Table 2). The results showed that the amount of chemisorbed H₂ on Co/MCF obtained from H₂ chemisorption ranged from 62.1 to 97.7 $\mu\text{mol}\cdot\text{g}^{-1}$, which are similar to the data obtained from H₂-TPD measured at 100-450 °C. This indicated that both H₂-TPD and H₂-chemisorption are reliable to measure the chemisorbed H₂ on Co/MCF catalysts.

For the Co/MCF catalysts with different cobalt particle sizes, the reduction and dispersion of four catalysts are in the range of 49.6-63.5% and 10.2-24.6% (Table 2), respectively. The amount of desorbed H₂ increased from 82.5 to 155.7 $\mu\text{mol}\cdot\text{g}^{-1}$ with decreasing cobalt particle size, **suggesting** more active sites exposed. Thus, we concluded that the decrease in the cobalt particle sizes led to the higher dispersion and the lower reduction degree.

Table 2

3.1.4. Fischer-Tropsch synthesis performances for Co/MCF catalysts having 3D mesoporous

3.1.4.1. Relation of catalyst pore structure with performances over Co/MCF catalysts

Table 3 shows the data of the activity, product selectivity and TOF for Co/MCF catalysts with different cell pore sizes in FTS. The Co/MCF-2 catalyst showed the highest CO conversion and the Co/MCF-4 showed the lowest CO conversion. Only a slight change in metal-time-yield from 5.4 to 4.0 $\text{mol CO}\cdot\text{g}_{\text{Co}}^{-1}\text{s}^{-1}$ was observed for the four catalysts as the cell pore size of the 3D MCF increased from 6.3 to 42.1 nm. The C₅₊ selectivity varied in the range of 82.0-85.9% with increasing cell pore size (6.3-42.1 nm). Meanwhile, all the Co/MCF

catalysts showed the low methane selectivity of 8-10.5 %, indicating that the MCFs are good FTS catalyst supports. The chain growth probability (α value) did not change significantly (around 0.9).

The Co/MCF-2 catalyst has a 3D pore structure with the average cell pore diameter of 11.5 nm and the interconnected window pores with average diameter of 7.4 nm. Under the same FTS conditions, this catalyst showed the highest CO conversion for the Co/MCF catalysts with different 3D pore structures. This indicated that the average pore diameters of 7-12 nm are the optimal sizes of Co/MCF catalysts having the highest reactivity in FTS. Likewise, the cobalt catalyst with a 2D pore channel with average pore size of 6-10 nm was suggested to be the most active in FTS [6].

Table 3

Fig. 8 shows the relationship between the cell pore size and performances of the Co/MCF catalysts with 3D open mesopores. The specific activity was calculated at low CO conversion under differential conditions. As can be seen, the turnover frequency (TOF) kept constant with the increase of the cell pore size of Co/MCF catalysts. C_{5+} selectivity passed through a maximum for the catalyst with average cell pore size of 11.5 nm and then kept constant. These trends are more distinct when the CO conversion is high (Figure S6). It is explained that for the catalysts with large cell pore sizes, the reactant gas could easily access to the catalyst cavity and contact with the active sites, as a result alkenes is much easier to be readsorbed, enhancing the chain growth probability, i.e. increased C_{5+} selectivity.

Fig. 8.

3.1.4.2. Relation of cobalt particle size with catalytic performances over Co/MCF catalysts

The above discussion shows that the pore structure of 3D MCF affects the cobalt particle sizes and performances of Co/MCF catalysts in FTS. In order to investigate the role of cobalt particle size on activity and selectivity of Co/MCF catalysts without the interference from pore structure, MCF-3 with large cell pore size

was used as support to prepare cobalt catalysts with different cobalt particle sizes since Co/MCF-3 catalyst exhibited the lowest CH₄ selectivity in FTS.

The cobalt particle sizes of the Co/MCF catalysts were calculated by XRD, TEM and H₂-chemisorption (Table 2). The surface-average particle sizes from TEM are larger than the data obtained from the H₂ chemisorption, which is possibly due to the formation of surface CoO layers through the passivation process. Table 4 shows the data of the activity and selectivity for Co/MCF-3 catalysts with different cobalt particle sizes. With the increase of particle sizes from 3.9 to 9.4 nm, the cobalt time yield increased initially from 6.0 to 6.9 molCO·g_{Co}⁻¹s⁻¹ and then decreased to 5.1 molCO·g_{Co}⁻¹s⁻¹. The Co/MCF-3-a with cobalt size of around 6.9 nm showed the highest FTS activity. With the decrease of cobalt particle size, methane selectivity increased from 7.9% to 9.4% and C₅₊ selectivity dropped from 85.3% to 81.3%.

The highest activity over Co/MCF-3-a catalyst (average cobalt particle size: 6.9 nm) was attributed to the high dispersion of the cobalt particles and a reasonable reduction degree. Although the Co/MCF-3-b and Co/MCF-3-c catalysts have much higher dispersion, the reduction degrees of the two catalyst are much lower than that of Co/MCF-3-a. The low reduction extent is attributed to a strong interaction of small cobalt particle with the framework of 3D MCF support, revealed by both TPR and O₂ titration.

Table 4

Fig. 9 shows the relationship between the cobalt particle size and the TOF and selectivities of cobalt catalysts supported on MCF and other silicas (data were shown in Table 5). TOF was measured at low CO conversion (< 5%, Table S1, supporting information). There is a linear relationship between TOF and cobalt particle size from 3.9 to 8.0 nm. When the cobalt particle size is larger than 8.0 nm, the TOF remains constant at about 54.4×10⁻³ s⁻¹. It suggests that TOF is almost independent of the large cobalt particle size (> 8.0 nm) for the Co/MCF catalysts. At high CO conversion, the C₅₊ selectivity increased initially from 81.3 to 84.4% and then became constant at about 85% with the increase in the cobalt particle size (Fig. 9b). CH₄ selectivity was in the opposite trend to the C₅₊ selectivity. The same trends between hydrocarbon selectivities and cobalt particle size were also observed at a CO conversion of ca. 5% for these catalysts (Table S2 and Figure S7). Furthermore, similar

relationships between cobalt particle size and TOF value, hydrocarbon selectivity were also found on cobalt catalyst supported on carbon materials with 1 D pore channel and nonporous carbon (carbon nanofibers, carbon nanotubes and carbon spheres) [36, 37].

Fig. 9.

3.2. Comparison of Co/MCF, Co/SBA-16, Co/KIT-6 and Co/SBA-15 catalysts with different mesopore structures

Co/MCF catalysts have 3D mesoporous structure, and the porous networks are more open (i.e. short pore length) than that of cobalt catalysts supported on other silicas such as SBA-15, KIT-6 and SBA-16. We synthesized cobalt catalysts supported on SBA-15, KIT-6 and SBA-16 and these catalysts have average pore sizes of 7-8 nm (Table 1), which are similar to the average pore size of 8.8 nm for Co/MCF-2 (denoted as Co/MCF in this section. It should be mentioned that the average pore size (d_a) for catalysts with bimodal distributions was calculated by $d_a = (d_{cell} + d_{window})/2$ in order to compare with cobalt catalysts having unimodal pore size distribution (see Table 1). The structures and catalytic performances of these catalysts were then compared in FTS.

3.2.1. Characterization of cobalt catalysts supported on MCF, SBA-16, KIT-6 and SBA-15

The small-angle XRD (SAXRD) patterns of mesoporous silicas MCF, SBA-16, KIT-6 and SBA-15 are displayed in Fig. 10a. All samples showed diffraction peaks at the range of 0.5~2.0°, indicating that all materials have well-ordered pore structure. The presence of a diffraction peak at 0.5-1.0° in the SAXRD pattern of MCF indicated that the size distribution of the 3D spherical pore is narrow [33, 38]. SBA-16 exhibited an intense peak and two weak peaks that correspond to the (110), (200) and (211) reflection of the cubic ($Im\bar{3}m$) cage mesostructure [39]. The SAXRD pattern of KIT-6 showed one peak corresponding to (211) plane and a very weak shoulder peak for (220) plane, which belong to cubic $Ia\bar{3}d$ symmetry and bicontinuous mesostructure [40]. For SBA-15, three diffractions corresponding to the (100), (110) and (200) planes of 2D hexagonal ($p6mm$) mesostructure were displayed [39]. The isotherm curves of N₂ physisorption for different silicas are shown in

Figure S8. SBA-16 showed a type-IV isotherm pattern with a H2 hysteresis loop, whereas KIT-6 and SBA-15 were type-IV isotherm with H1 hysteresis loop. These results indicated that SBA-16 has cage-like mesopores [41], KIT-6 has cubic mesopores [42] and SBA-15 has cylindrical mesopores [43]. Thus, each sample has its unique porous structure. The N₂ physisorption data of these supports are shown in Table 1. SBA-16 has double pore size distributions (5.8 and 8.9 nm) and the average pore sizes for KIT-6 and SBA-15 are about 8.0 nm. Furthermore, the pore volumes of these materials are 1.0-1.40 cm³·g⁻¹. TEM images of MCF, SBA-16, KIT-6 and SBA-15 materials (Fig. 4b and Fig. 10b-c) confirmed that MCF, SBA-16, KIT-6 and SBA-15 have different ordered porous structures, consistent with the SAXRD and N₂ physisorption results.

Fig. 10.

The wide-angle XRD patterns for the four Co catalysts are shown in Figure S9. Diffraction peaks at 2θ of 31.2°, 36.9°, 44.7°, 59.3° and 65.2° corresponds to the different crystalline planes of Co₃O₄ [44]. The average Co₃O₄ crystallite and cobalt metal sizes of the catalysts are shown in Table 2. It is noted that the average Co₃O₄ crystallite sizes on different catalysts are similar (~11.8 nm), which is ascribed to the similar average pore size of the four supports.

TEM images of the four catalysts with different pore structures are shown in Fig. 11. It can be seen that the ordered structure of different supports were maintained after impregnating cobalt species and the following calcination. Cobalt clusters were found on all catalysts, whereas part of small cobalt particles are clearly seen inside the MCF pore and separated by thin MCF walls for Co/MCF catalyst (Fig. 11a), indicating that the 3D open pore structure is beneficial to the dispersion of cobalt particles. For Co/SBA-15 catalyst with a 2D pore channels, cobalt species aggregated in the pore and formed cobalt nanorods aligned to the central axis of the pore channel (Fig. 11d).

Fig. 11.

TPR spectra of Co/MCF, Co/SBA-16, Co/KIT-6 and Co/SBA-15 catalysts are shown in Fig.12. The four Co catalysts showed the completely different reduction behaviors. Two reduction regions for the four catalysts are observed in the temperature range of 200-550 °C and > 550 °C, respectively, which correspond to the reduction of Co_3O_4 ($\text{Co}_3\text{O}_4 \rightarrow \text{CoO} \rightarrow \text{Co}^0$) and the reduction of cobalt silicate [45], respectively. The reduction temperature of Co_3O_4 to CoO for the Co/MCF is lower than that of the other three catalysts, which is ascribed to the novel pore structure of MCF. The temperatures of reduction peaks of Co/MCF, Co/SBA-16, Co/KIT-6 catalysts appearing at 200~600 °C ($\text{Co}_3\text{O}_4 \rightarrow \text{Co}^0$) are lower than those of Co/SBA-15 catalyst, indicating that cobalt species supported on materials having 3D pore structure are easier to be reduced than those on material having 2D hexagonal mesostructure.

Fig. 12.

The improved reduction behavior of Co/MCF in comparison to Co/SBA-16, Co/KIT-6 and Co/SBA-15 was also evidenced by O_2 -titration (Table 2). The reduction degree of the Co/MCF catalyst (63.1%) is higher than that of Co/KIT-6 and Co/SBA-15. Thus, the cobalt oxide in Co/MCF with 3D mesostructure is readily reduced due to the weaker interaction between the cobalt and support and to a more open pore structure. Furthermore, the amount of adsorbed H_2 for Co/MCF is significantly higher than that adsorbed on other catalysts, indicating that more active sites are exposed on Co/MCF, i.e. high dispersion.

3.2.2. Fischer-Tropsch synthesis performances for Co/MCF, Co/SBA-16, Co/KIT-6 and Co/SBA-15 catalysts

FTS performances of Co/MCF, Co/SBA-16, Co/KIT-6 and Co/SBA-15 catalysts were compared under 1.0 MPa and 210 °C and the data are listed in Table 5. Co/SBA-15 catalyst with a 2D mesopore exhibited the lowest activity by contrast with Co catalysts supported on 3D mesopore MCF, SBA-16, KIT-6, indicating that 3D pore structure catalysts are more active than 2D pore structure catalysts. The CO conversion of Co/MCF catalyst (49.4%), is higher than that of Co/SBA-16 and Co/KIT-6 catalysts (about 46%). Furthermore, the Co/MCF

catalyst showed the highest chain growth probability (α value), which was ascribed to the open 3D porous networks.

Table 5

Hydrocarbon selectivity data of the four catalysts are shown in Fig. 13. Co catalysts supported on 3D mesopore MCF, SBA-16, KIT-6 presented higher C_{5+} selectivity than Co/SBA-15 catalyst with a 2D mesopore. Furthermore, the C_{5+} selectivity for Co/MCF catalyst is higher than that of Co/SBA-16 and Co/KIT-6 catalysts (Fig. 13a). The detailed hydrocarbon distribution of the catalyst with carbon number > 20 showed that the Co/MCF catalyst has much larger amount of heavy hydrocarbon at each carbon than Co/SBA-16 and Co/KIT-6 catalysts (Fig. 13b). Furthermore, Table 5 shows that the selectivities for total heavy hydrocarbons with carbon number > 20 over Co/MCF catalyst (31.5%) was two-fold higher than that over Co/SBA-16 and Co/KIT-6 catalysts (14.7~15.8%).

Fig. 13.

In summary, MCF, SBA-16 and KIT-6 have well-ordered 3D pore structure, whereas SBA-15 has 2D-hexagonal pore structure. Cobalt catalysts supported on MCF, SBA-16, KIT-6 and SBA-15 have similar average pore size and cobalt particle size, however, the pore orientation are significantly different. The catalytic activity for the catalysts with 3D pore structure (Co/MCF, Co/SBA-16 and Co/KIT-6) are much higher than that of the catalyst with 2D-hexagonal structure (Co/SBA-15) due to a lower reducibility of the latter. The Co/MCF showed higher activity than Co/SBA-16 and Co/KIT-6 because the Co/MCF has the high dispersion and reduction extent (Table 2), albeit all the three catalysts have the 3D pore structure. Furthermore, the open 3D pore structure of Co/MCF catalyst suppressed the diffusion limitation of syngas in the pore, resulting in lower methane selectivity and higher C_{5+} selectivity, as compared to the other two catalysts having long 3D pore channels.

3.3. The stability of the Co catalysts supported on 3D mesopores MCF during FTS

The Co/MCF catalyst (15 wt.%) showed very stable reactivity during the 200 h run under 210 °C, 1 MPa and a space velocity (SV) of 4 SL·h⁻¹·g⁻¹. This indicated that the MCF mesoporous structure is stable under the above FT conditions. In order to observe the deactivation of the Co/MCF catalyst and to investigate the stability of the Co/MCF catalyst, we chosen a relatively harsh FT reaction condition (1.0 MPa and SV=8 SL·h⁻¹·g⁻¹) to rapidly deactivate the Co/MCF catalyst. The function of activity of a Co/MCF catalyst (20 wt.%Co) with time on stream under this harsh FT condition is shown in Fig. 14. It can be seen that the Co/MCF catalyst underwent rapid deactivation in the first 60 h and then deactivated slowly (Fig. 14).

The spent Co/MCF catalyst after reaction was investigated by H₂-TPR and TEM. Prior to the H₂-TPR and TEM, the residual oil and wax on the spent Co/MCF catalyst was removed by a step of Soxhlet extraction using toluene as solvent (supporting information). H₂-TPR pattern of fresh Co/MCF catalyst before reaction shows the complete reduction of cobalt species before 500 °C (Figure S10a). Thus, after the reduction in H₂ at 450 °C for 12 h and the following FTS reaction, the main cobalt phase on the spent Co/MCF catalyst is expected to be metallic cobalt. However, the H₂-TPR pattern of the spent Co/MCF catalyst shows a large reduction peak located at 450-600 °C (Figure S10b), corresponding to the reduction of cobalt compound from the interaction of cobalt and silica. This indicated that more interacted compound was formed on the Co/MCF catalyst in FTS. On the other hand, the TEM image of the spent Co/MCF catalyst after reaction showed the marked sintering of cobalt particles (Figure S11a). Thus, the deactivation is due to the cobalt sintering and the formation of cobalt-silica compound, which resulted from the harsh reaction condition at the high conversion and high reaction temperature [46, 47]. The TEM image of the spent Co/MCF catalyst showed that the mesoporous structure of MCF was maintained after reaction under this harsh condition, again indicating that the MCF is a stable catalyst support. However, more studies must be done in future to investigate the stability of MCF mesostructure under harsher reaction conditions (i.e. higher vapor pressures and higher reaction temperatures).

Carbon-coating and hybrid atom doping have been used to improve catalyst stability in heterogeneous catalysis [48-50]. In this study, we preliminary investigated two methods in order to improve the stability of the 3D mesopore MCF supported Co catalysts in FTS carried out at high temperatures. Cobalt catalysts supported

on carbon-coating and Al-doping MCF (20 wt.%Co) were prepared and the stability of the two catalysts (denoted as Co/C/MCF and Co/AMCF, respectively) were compared to the Co/MCF catalyst under the same FTS conditions (250 °C, 1.0 MPa and SV=8 SL·h⁻¹g⁻¹). The physical and chemical properties of the two catalysts synthesized were shown in Table S3. The Co/C/MCF and Co/AMCF catalysts maintained the 3D porous structure with the high surface areas. However, the Co/Al/MCF catalyst showed larger pore diameters than Co/MCF and Co/C/MCF, which is attributed to the effect of the doping Al atoms on the MCF structures. As can be seen in Fig. 14, both the carbon-coating Co/C/MCF and Al-doping Co/AMCF catalysts showed improved stability during the whole run under 250 °C and 1 MPa.

The H₂-TPR patterns of the spent Co/C/MCF and Co/AMCF catalysts (Figure S10b) showed weak reduction peaks at temperature of < 450 °C, corresponding to the reduction of CoO phase, which was formed when the catalyst was exposed to the air through the ex-situ treatment. It is noted that no reduction peak at temperature of > 450 °C was observed in the TPR patterns of the two spent catalyst, as compared to the TPR pattern of the spent Co/MCF catalyst, indicating that no strongly interacted compound was formed for the functionalized catalysts through the FTS reaction. Furthermore, the representative TEM images of the two functionalized catalysts after reaction showed no sintering of cobalt particles (Figure S11b and c). Thus, we concluded that the stability of Co/MCF catalyst under harsh FTS condition can be improved by functionalizing the MCF using carbon-coating and Al-doping.

Fig. 14.

The activity and product selectivity data for the Co/MCF, Co/C/MCF and Co/AMCF catalysts in FTS are shown in Table 6. Both the Co/C/MCF and Co/AMCF catalysts showed higher CO conversion and C₅₊ hydrocarbon selectivity than the Co/MCF. It is seen that CO₂ was formed in the products for the three catalysts under this FTS condition. This indicated that water gas shift reaction (WGS) took place in the reaction at 250 °C. However, functionalization of the MCF support by the carbon-coating and Al-doping decreased the CO₂ selectivity of the obtained catalysts. The characterization of the spent catalysts by H₂-TPR showed that interacted compound was found on the Co/MCF catalyst, while no interacted compound was formed on

Co/C/MCF and Co/AMCF catalysts. Thus, the functionalization of MCF by C or Al decreased the interaction of cobalt and support in FTS reaction, which suppressed the occurrence of WGS reaction.

Table 6

4. Conclusions

3D mesoporous cellular silica foams (MCFs) with open porous networks, were synthesised and used to prepare cobalt catalysts in Fischer-Tropsch synthesis (FTS). The 3D pore structure of MCFs (cell pore diameter: 6.3-42.1 nm; window pore diameter: 5.7-11.4 nm) significantly affects the FTS performances of Co/MCF catalysts. The results showed that the Co_3O_4 crystallite size and the catalyst reducibility depended on the 3D pore diameter of MCF. The catalysts with larger pore diameter have larger Co_3O_4 crystallites and higher reducibility than those with small pore diameter. The Co/MCF catalysts with different cobalt particle size (3.9-9.4 nm) were synthesized and the catalyst with crystallite size of 6.9 nm showed the highest activity and good stability for FTS due to good dispersion and appropriate reduction degree. Furthermore, the Co/MCF catalyst exhibited higher activity and heavy hydrocarbon selectivity, as compared to cobalt catalysts supported on SBA-16, KIT-6 and SBA-15 having similar pore diameters (7-9 nm). The good performances of the Co/MCF catalyst is attributed to the 3D mesostructure of MCF, which providing a more open porous network for mass transportation and carbon chain growth. The Co/MCF catalyst is stable under low temperature FTS reaction conditions (210 °C, 1.0 MPa and 4 $\text{SL}\cdot\text{h}^{-1}\text{g}^{-1}$), while it underwent deactivation under harsh FTS reaction conditions (250 °C, 1.0 MPa and 8 $\text{SL}\cdot\text{h}^{-1}\text{g}^{-1}$). The stability of the Co/MCF catalyst can be remarkably improved by functionalizing the MCF support using carbon-coating or Al-doping. The present study evidenced that the 3D foam MCF is a good catalyst support in FTS due to their open porous networks.

Acknowledgements

This work was supported by Key Program project of the NSFC and China Petrochemical Corporation Joint Fund (Grant No. U1463210), the National Natural Science Foundation of China (Grant Nos. 21473259 and 21203253). Dr. H.F. Xiong would like to thank the financial supports from NSF GOALI grant CBET-1438765 and from the Center for Biorenewable Chemicals (CBiRC) supported by NSF under grant EEC-0813570.

References

- [1] A.Y. Khodakov, W. Chu, P. Fongarland, *Chemical Reviews*, 107 (2007) 1692-1744.
- [2] H.F. Xiong, L.L. Jewell, N.J. Coville, *ACS Catalysis*, 5 (2015) 2640-2658.
- [3] T.J. Fu, Z.H. Li, *Chemical Engineering Science*, 135 (2015) 3-20.
- [4] O. González, H. Pérez, P. Navarro, L.C. Almeida, J.G. Pacheco, M. Montes, *Catalysis Today*, 148 (2009) 140-147.
- [5] H.L. Li, S.G. Wang, F.X. Ling, J.L. Li, *Journal of Molecular Catalysis A: Chemical*, 244 (2006) 33-40.
- [6] H.F. Xiong, Y.H. Zhang, K.Y. Liew, J.L. Li, *Journal of Molecular Catalysis A: Chemical*, 295 (2008) 68-76.
- [7] Y. Ohtsuka, Y. Takahashi, M. Noguchi, T. Arai, S. Takasaki, N. Tsubouchi, Y. Wang, *Catalysis Today*, 89 (2004) 419-429.
- [8] L.A. Cano, M.V. Cagnoli, J.F. Bengoa, A.M. Alvarez, S.G. Marchetti, *Journal of Catalysis*, 278 (2011) 310-320.
- [9] J.H. Li, Y. Xu, D. Wu, Y.H. Sun, *Catalysis Today*, 148 (2009) 148-152.
- [10] L.F.F.P.G. Bragança, M. Ojeda, J.L.G. Fierro, M.I.P. da Silva, *Applied Catalysis A: General*, 423-424 (2012) 146-153.
- [11] D.H. Yin, W.H. Li, W.S. Yang, H.W. Xiang, Y.H. Sun, B. Zhong, S.Y. Peng, *Microporous and Mesoporous Materials*, 47 (2001) 15-24.
- [12] J.S. Jung, S.W. Kim, D.J. Moon, *Catalysis Today*, 185 (2012) 168-174.
- [13] D.C. Song, J.L. Li, *Journal of Molecular Catalysis A: Chemical*, 247 (2006) 206-212.
- [14] A.Y. Khodakov, A. Griboval-Constant, R. Bechara, V.L. Zholobenko, *Journal of Catalysis*, 206 (2002) 230-241.
- [15] K. Cheng, M. Virginie, V.V. Ordonsky, C. Cordier, P.A. Chernavskii, M.I. Ivantsov, S. Paul, Y. Wang, A.Y. Khodakov, *Journal of Catalysis*, 328 (2015) 139-150.
- [16] J.G. Wang, D.B. Li, B. Hou, L.T. Jia, J.G. Chen, Y.H. Sun, *Catalysis Letters*, 140 (2010) 127-133.
- [17] G. Prieto, A. Martínez, R. Murciano, M.A. Arribas, *Applied Catalysis A: General*, 367 (2009) 146-156.
- [18] H.F. Xiong, Y.H. Zhang, S.G. Wang, K.Y. Liew, J.L. Li, *Journal of Physical Chemistry C*, 112 (2008) 9706-9709.
- [19] N. Tsubaki, Y. Zhang, S. Sun, H. Mori, Y. Yoneyama, X. Li, K. Fujimoto, *Catalysis Communications*, 2 (2001) 311-315.

- [20] D. Merino, I. Pérez-Miqueo, O. Sanz, M. Montes, *Topics in Catalysis*, (2015) 1-12.
- [21] J. Chen, J.L. Li, Y.X. Zhao, Y.H. Zhang, J.P. Hong, *Journal of Natural Gas Chemistry*, 21 (2012) 673-679.
- [22] Y.X. Zhao, Y.H. Zhang, J. Chen, J.L. Li, K.Y. Liew, M.R.B. Nordin, *ChemCatChem*, 4 (2012) 265-272.
- [23] Q. Li, Z.X. Wu, B. Tu, S.S. Park, C.S. Ha, D.Y. Zhao, *Microporous and Mesoporous Materials*, 135 (2010) 95-104.
- [24] Y.M. Liu, J. Xu, L.C. Wang, Y. Cao, H.Y. He, K.N. Fan, *Catalysis Letters*, 125 (2008) 62-68.
- [25] Y.M. Liu, W.L. Feng, L.C. Wang, Y. Cao, W.L. Dai, H.Y. He, K.N. Fan, *Catalysis Letters*, 106 (2006) 145-152.
- [26] T.W. Kim, R. Ryoo, M. Kruk, K.P. Gierszal, M. Jaroniec, S. Kamiya, O. Terasaki, *Journal of Physical Chemistry B*, 108 (2004) 11480-11489.
- [27] B. Cullity, Addison-Wesley, Reading, MA, (1978).
- [28] D. Schanke, S. Vada, E. Blekkan, A. Hilmen, A. Hoff, A. Holmen, *Journal of Catalysis*, 156 (1995) 85-95.
- [29] M. Voß, D. Borgmann, G. Wedler, *Journal of Catalysis*, 212 (2002) 10-21.
- [30] R.C. Reuel, C.H. Bartholomew, *Journal of Catalysis*, 85 (1984) 63-77.
- [31] R.D. Jones, C.H. Bartholomew, *Applied Catalysis*, 39 (1988) 77-88.
- [32] H.F. Xiong, Y.H. Zhang, S.G. Wang, J.L. Li, *Catalysis Communications*, 6 (2005) 512-516.
- [33] P. Schmidt-Winkel, J. W. Lukens, Wayne , P.D. Yang, D. I. Margolese, J. S. Lettow, J.a. Y. Ying, G. D. Stucky, *Chemistry of Materials*, 12 (2000) 686-696.
- [34] E.V. Steen, G.S. Sewell, R.A. Makhothe, C. Micklethwaite, H. Manstein, M.D. Lange, C.T. O'Connor, *Journal of Catalysis*, 162 (1996) 220-229.
- [35] D.G. Mustard, C.H. Bartholomew, *Journal of Catalysis*, 67 (1981) 186-206.
- [36] G.L. Bezemer, B. Johannes H, K. Herman P C E, H. Oosterbeek, H. Johannes E, X.D. Xu, K. Freek, A.J. Van Dillen, J.K.P. De, *Journal of the American Chemical Society*, 128 (2006) 3956-3964.
- [37] H.F. Xiong, M.A.M. Motchelaho, M. Moyo, L.L. Jewell, N.J. Coville, *Journal of Catalysis*, 278 (2011) 26-40.
- [38] P. Schmidt-Winkel, J. W. Lukens, Wayne , D.Y. Zhao, P.D. Yang, B. F. Chmelka, G. D. Stucky, *Journal of the American Chemical Society*, 121 (1999) 254-255.
- [39] D.Y. Zhao, Q.S. Huo, J.L. Feng, C. Bradley F, S. Galen D, *Journal of the American Chemical Society*, 120 (1998) 6024-6036.
- [40] T. Harun, C.W. Lehmann, B. Hans, T. Bernd, S. Roland, S. Ferdi, *Journal of the American Chemical Society*, 130 (2008) 11510-11517.
- [41] Y.X. Zhao, J.L. Li, Y.H. Zhang, S.F. Chen, K.Y. Liew, *ChemCatChem*, 4 (2012) 1926-1929.

- [42] M.K. Gnanamani, G. Jacobs, U.M. Graham, W. Ma, V.R.R. Pendyala, M. Ribeiro, B.H. Davis, *Catalysis Letters*, 134 (2009) 37-44.
- [43] A.Y. Khodakov, V.L. Zholobenko, R. Bechara, D. Durand, *Microporous & Mesoporous Materials*, 79 (2005) 29-39.
- [44] Q. Cai, J.L. Li, *Catalysis Communications*, 9 (2008) 2003-2006.
- [45] C. López, F. Márquez, *Journal of Catalysis*, 220 (2003) 486-499.
- [46] G. Kiss, C.E. Kliewer, G.J. DeMartin, C.C. Culross, J.E. Baumgartner, *Journal of Catalysis*, 217 (2003) 127-140.
- [47] A.K. Dalai, B.H. Davis, *Applied Catalysis A: General*, 348 (2008) 1-15.
- [48] H.F. Xiong, H.N. Pham, A.K. Datye, *Green Chemistry*, 16 (2014) 4627-4643.
- [49] H.N. Pham, A.E. Anderson, R.L. Johnson, S.R. Klaus, A.K. Datye, *Angewandte Chemie*, 124 (2012) 13340-13344.
- [50] H.F. Xiong, T.J. Schwartz, N.I. Andersen, J.A. Dumesic, A.K. Datye, *Angewandte Chemie*, 127 (2015) 8050-8054.

Figure captions

Fig. 1. Schematics of 1D, 2D and 3D pore channels.

Fig. 2. Representative SEM/TEM images (a-c) and a model illustration of MCF support showing 3D pore structures (d).

Fig. 3. N₂ physisorption results of 3D mesoporous MCF materials: (a) N₂ physisorption isotherms; (b) window size distributions obtained from desorption branches and cell size distributions obtained from adsorption branches.

Fig. 4. TEM images of MCF with different pore structures: (a) MCF-1; (b) MCF-2; (c) MCF-3 and (d) MCF-4.

Fig. 5. TEM images of passivated Co/MCF catalysts (a) Co/MCF-1, (b) Co/MCF-2, (c) Co/MCF-3 and (d) Co/MCF-4 after reduction in high purity H₂ at 450 °C for 10 h.

Fig. 6. TEM images of passivated Co/MCF catalysts with different Co particle sizes: (a) Co/MCF-3; (b) Co/MCF-3-a; (c) Co/MCF-3-b and (d) Co/MCF-3-c.

Fig. 7. H₂-TPR profiles for the Co/MCF catalysts with (a) different cell pore sizes and (b) different cobalt particle sizes.

Fig. 8. Catalyst cell pore size as a function of (a) TOF and (b) C₅₊ and CH₄ selectivity at low CO conversion (< 5%).

Fig. 9. TOF and hydrocarbon selectivity as a function of cobalt particle size (obtained from H₂ chemisorption) for cobalt catalysts supported on porous silica: (a) the TOF value was obtained at low CO conversion (< 5%); (b) these data were obtained at CO conversion of 20-60 % and the data at low CO conversion (ca. 5%) was shown in Figure S7.

Fig. 10. (a) SAXRD patterns of different supports and TEM images of (b) SBA-16, (c) KIT-6 and (d) SBA-15.

Fig. 11. TEM images of passivated cobalt catalysts after reduction at 450 °C for 10 h in H₂: (a) Co/MCF, (b) Co/SBA-16, (c) Co/KIT-6 and (d) Co/SBA-15.

Fig. 12. H₂-TPR profiles for the cobalt catalysts with different mesostructures.

Fig. 13. The hydrocarbon distribution on Co/MCF, Co/SBA-16, Co/KIT-6 and Co/SBA-15 catalysts in FTS: (a) hydrocarbon selectivity comparison for different cobalt catalysts; (b) C₂₀₊ hydrocarbon selectivity as a function of carbon number for cobalt catalysts.

Fig. 14. CO conversion as a function of time on stream for Co/MCF, Co/C/MCF and Co/AMCF in FTS under 250 °C and 1.0 MPa and a space velocity of 8 SL·h⁻¹·g⁻¹.

Table 1

Pore structure properties of the supports and cobalt catalysts obtained from N₂ physisorption.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20

Table 2

Dispersion, reduction, average Co_3O_4 crystallite size and cobalt particle size data of Co catalysts supported on mesoporous materials.

Table 3

The performances of Co/MCF catalysts with different cell and window pore sizes in FTS

Table 4

The performances of Co/MCF catalysts with different cobalt particle sizes

Table 5

The performances of cobalt catalysts supported on silicas with different pore structures in FTS

Table 6

The performances of Co/MCF and cobalt catalysts supported on MCF functionalized by carbon-coating and Al-doping in FTS

Table 1

Pore structure properties of the supports and cobalt catalysts obtained from N₂ physisorption.

Samples	R (g/g) ^a	S _{BET} (m ² ·g ⁻¹)	Window diameter (d _w , nm) ^b	Cell diameter (d _c , nm) ^c	AVD (nm) ^d	TPV (cm ³ ·g ⁻¹) ^e
MCF-1	0.8	594.0	5.7	6.3	6.0	0.88
MCF-2	1.2	663.2	7.4	11.5	9.5	1.30
MCF-3	1.6	683.7	10.4	26.4	18.4	1.93
MCF-4	2.0	645.6	11.4	42.1	26.8	2.38
SBA-16	—	549.3	5.8	8.9	7.4	1.03
KIT-6	—	681.4	8.1	—	8.1	1.38
SBA-15	—	634.1	7.9	—	7.9	1.26
Co/MCF-1	—	525.5	5.4	6.2	5.8	0.77
Co/MCF-2	—	470.9	6.4	11.1	8.8	0.91
Co/MCF-3	—	472.3	9.3	23.3	16.3	0.98
Co/MCF-4	—	498.6	10.8	38.3	24.6	1.57
Co/MCF-3-a	—	452.7	10.2	26.1	18.2	1.32
Co/MCF-3-b	—	399.2	10.1	25.8	18.0	1.04
Co/MCF-3-c	—	432.0	10.1	25.9	18.0	1.19
Co/SBA-16	—	427.8	5.8	8.8	7.3	0.77
Co/KIT-6	—	484.2	7.5	—	7.5	0.91
Co/SBA-15	—	527.5	7.7	—	7.7	1.02
STDEV ^f	—	11.2	0.8	1.3	1.0	0.2

^a R: Benzene to P123 mass ratio;

^b The small window pore size (d_w) was determined from the desorption branches of the isotherms;

^c The large cell pore size (d_c) was determined from the adsorption branches of the isotherms;

^d **AVD = average pore diameter**; Average pore size (d_a) for sample with unimodal distribution was determined from the desorption branches of the isotherms; average pore size (d_a) for sample with bimodal distribution was calculated by d_a = (d_c+d_w)/2;

^e **TPV = total pore volume**;

^f **Standar deviation.**

Table 2

Dispersion, reduction, average Co₃O₄ crystallite size and cobalt particle size data of Co catalysts supported on mesoporous materials.

Catalysts	R (g/g) ^a	H ₂ desorbed (μmol·g ⁻¹) ^b	Reduction (%) ^c	Dispersion (%)	Particle size (nm)			
					XRD		TEM	H ₂ chemisorption
					D(Co ₃ O ₄) ^d	d ₁ (Co ⁰) ^e	d ₂ ^f	d ₃ ^g
Co/MCF-1	—	97.7 (122.3)	62.9	12.2	11.2	8.4	11.5	7.9
Co/MCF-2	—	89.1 (107.1)	63.1	11.1	11.8	8.9	13.1	8.7
Co/MCF-3	—	82.5 (99.4)	63.5	10.2	13.8	10.4	15.0	9.4
Co/MCF-4	—	62.1 (74.5)	67.2	7.3	18.5	13.9	20.7	13.2
Co/MCF-3-a	0.09	96.3 (115.7)	54.2	14.0	10.7	8.0	10.2	6.9
Co/MCF-3-b	0.36	129.9 (167.3)	51.4	19.9	8.2	6.2	8.7	4.8
Co/MCF-3-c	0.54	155.7 (198.4)	49.6	24.6	6.1	4.6	7.1	3.9
Co/SBA-16	—	77.7 (93.4)	63.7	9.6	12.3	9.2	11.9	10.0
Co/KIT-6	—	80.4 (96.5)	61.7	10.2	11.4	8.6	12.3	9.4
Co/SBA-15	—	54.9 (65.6)	39.1	11.0	11.9	8.9	11.7	8.7
STDEV ^h	—	3.4 (6.8)	0.9	0.4	0.5	0.3	0.8	0.2

^a R: citric acid to Co(NO₃)₂·6H₂O mass ratio;

^b Obtained from H₂-chemisorption at 150 °C; The data in the parenthesis were obtained from H₂-TPD carried out from 100 to 450 °C;

^c Obtained from O₂-titration at 450 °C;

^d The average Co₃O₄ crystallite size was determined by XRD (Scherrer equation) at 2θ = 36.9°;

^e The metallic cobalt particle size was calculated from XRD: d(Co⁰)=0.75×d(Co₃O₄);

^f The surface-average cobalt particle size was obtained from TEM according to the formula: $d = \frac{\sum d_i^3}{\sum d_i^2}$, where d_i is measured diameters of the particles [35];

^g The cobalt particle size calculated using the following equation: d= 0.96/dispersion;

^h Standard deviation.

Table 3

The performances of Co/MCF catalysts with different cell and window pore sizes in FTS ^a

Catalysts	TOF (10 ⁻³ s ⁻¹) ^b	Cobalt-time-yield (10 ⁻⁵ molCO·g _{Co} ⁻¹ ·s ⁻¹) ^c	CO conversion (%) ^c	Products selectivity (mol%)					α	Catalyst pore sizes (nm)	
				CH ₄	C ₂	C ₃	C ₄	C ₅₊ ^d		Window	Cell
Co/MCF-1	51.7	5.0	45.1	10.2	1.0	3.0	3.8	82.0	0.89	5.4	6.2
Co/MCF-2	53.0	5.4	49.4	9.4	0.6	2.5	2.9	84.5	0.90	6.4	11.1
Co/MCF-3	53.8	5.1	48.1	8.4	0.6	2.4	2.7	85.9	0.90	9.3	23.3
Co/MCF-4	53.9	4.0	36.7	8.6	0.8	2.9	3.1	84.5	0.90	10.8	38.3

^a Reaction conditions : 210 °C, 1.0 MPa, H₂/CO= 2 : 1 and 4 SL·h⁻¹g⁻¹;

^b TOF was calculated using the low CO conversion data (supporting information); The standard deviation is 0.5×10⁻³ based on repeated measurements;

^c The standard deviation for CO conversion is 0.8 based on repeated measurements;

^d The standard deviation for C₅₊ selectivity is 0.5 based on repeated measurements.

Table 4The performances of Co/MCF catalysts with different cobalt particle sizes ^a

Catalysts	TOF (10 ⁻³ s ⁻¹) ^b	Cobalt-time-yield (10 ⁻⁵ mol CO·g _{Co} ⁻¹ s ⁻¹)	CO conversion (%) ^c	Products selectivity (mol%)					Cobalt particle sizes (nm) ^e
				CH ₄	C ₂	C ₃	C ₄	C ₅₊ ^d	
Co/MCF-3	53.8	5.1	48.1	8.4	0.6	2.4	2.7	85.9	9.4
Co/MCF-3-a	49.6	6.9	62.7	7.9	0.8	2.8	3.3	85.3	6.9
Co/MCF-3-b	39.7	6.6	60.3	8.1	0.9	3.0	3.6	84.4	4.8
Co/MCF-3-c	36.8	6.0	54.3	9.4	1.0	3.9	4.4	81.3	3.9

^a Reaction conditions: 210°C, 1.0 MPa, H₂/CO= 2 : 1 and 4 SL·h⁻¹g⁻¹;^b TOF was calculated using the low CO conversion (< 5 %, Table S1, supporting information); The standard deviation is 0.6×10⁻³ based on repeated measurements;^c The standard deviation for CO conversion is 1.2 based on repeated measurements;^d The standard deviation for C₅₊ selectivity is 0.4 based on repeated measurements;^e Cobalt particle sizes were obtained from H₂ chemisorption data.

Table 5The performances of cobalt catalysts supported on silicas with different pore structures in FTS ^a

Catalysts	TOF (10 ⁻³ s ⁻¹) ^b	Co-time-yield (10 ⁻⁵ molCO·g _{Co} ⁻¹ s ⁻¹)	CO conversion (%) ^c	Products selectivity (mol %)					C ₂₀₊ hydrocarbon selectivity	α	Structure
				CH ₄	C ₂	C ₃	C ₄	C ₅₊ ^d			
Co/MCF	53.0	5.4	49.4	9.4	0.6	2.5	2.9	84.6	31.5	0.90	Foamed-like
Co/SBA-16	54.1	5.1	46.0	12.9	1.5	4.1	4.9	76.6	14.7	0.88	$\overline{Im3m}$
Co/KIT-6	54.5	5.1	46.7	13.5	1.5	4.0	4.5	76.5	15.8	0.87	$\overline{Ia3d}$
Co/SBA-15	54.4	2.5	22.3	13.9	2.2	6.2	6.0	71.7	7.8	0.80	$p6mm$

^a Reaction conditions: 210 °C, 1.0 MPa, H₂/CO= 2 : 1 and 4 SL·h⁻¹·g⁻¹;^b TOF was calculated at low CO conversion (Table S1); The standard deviation is 0.5×10⁻³ based on repeated measurements;^c The standard deviation is 0.9 based on repeated measurements;^d The standard deviation is 0.8 based on repeated measurements.

Table 6

The performances of Co/MCF and cobalt catalysts supported on MCF functionalized by carbon-coating and Al-doping in FTS ^a

Catalysts ^b	CO conversion (%) ^c	Products selectivity (mol%)					
		CH ₄	C ₂	C ₃	C ₄	C ₅₊ ^d	CO ₂
Co/MCF	28.3	24.3	2.9	7.2	6.5	59.1	0.5
Co/C/MCF	40.5	16.7	2.9	5.7	5.4	69.3	0.2
Co/AMCF	51.3	21.4	2.8	5.5	5.8	64.5	0.2

^a Reaction conditions : 250 °C, 1.0 MPa, H₂/CO= 2 : 1 and 8 SL·h⁻¹g⁻¹;

^b Cobalt loading is 20 wt.%;

^c The standard deviation for CO conversion is 2.3 based on repeated measurements;

^d The standard deviation for C₅₊ selectivity is 2.0 based on repeated measurements.

Fig. 1. Schematics of 1D, 2D and 3D pore channels.

Fig. 2. Representative SEM/TEM images (a-c) and a model illustration of MCF support with 3D pore structures (d).

Fig. 3. N₂ physisorption results of 3D mesoporous MCF materials: (a) N₂ physisorption isotherms; (b) window size distributions obtained from desorption branches and cell size distributions obtained from adsorption branches.

Fig. 4. TEM images of MCF with different pore structures: (a) MCF-1; (b) MCF-2; (c) MCF-3 and (d) MCF-4.

Fig. 5. TEM images of passivated Co/MCF catalysts (a) Co/MCF-1, (b) Co/MCF-2, (c) Co/MCF-3 and (d) Co/MCF-4 after reduction in high purity H_2 at 450 °C for 10 h.

Fig. 6. TEM images of passivated Co/MCF catalysts with different Co particle sizes: (a) Co/MCF-3; (b) Co/MCF-3-a; (c) Co/MCF-3-b and (d) Co/MCF-3-c.

Fig. 7. H₂-TPR profiles for the Co/MCF catalysts with (a) different cell pore sizes and (b) different cobalt particle sizes.

Fig. 8. Catalyst cell pore size as a function of (a) TOF and (b) C₅₊ and CH₄ selectivity at low CO conversion (< 5%).

Fig. 9. TOF and hydrocarbon selectivity as a function of cobalt particle size (obtained from H_2 chemisorption) for cobalt catalysts supported on porous silica: (a) the TOF value was obtained at low CO conversion ($< 5\%$); (b) these data were obtained at CO conversion of 20-60 % and the data at low CO conversion (ca. 5%) was shown in Figure S7.

Fig. 10. (a) SAXRD patterns of different supports and TEM images of (b) SBA-16, (c) KIT-6 and (d) SBA-15.

Fig. 11. TEM images of passivated cobalt catalysts after reduction at 450 °C for 10 h in H₂: (a) Co/MCF, (b) Co/SBA-16, (c) Co/KIT-6 and (d) Co/SBA-15.

Fig. 12. H₂-TPR profiles for the cobalt catalysts with different mesostructures.

Fig. 13. The hydrocarbon distribution on Co/MCF, Co/SBA-16, Co/KIT-6 and Co/SBA-15 catalysts in FTS: (a) hydrocarbon selectivity comparison for different cobalt catalysts; (b) C₂₀+ hydrocarbon selectivity as a function of carbon number for cobalt catalysts.

Fig. 14. CO conversion as a function of time on stream for Co/MCF, Co/C/MCF and Co/AMCF in FTS under 250 °C and 1.0 MPa and a space velocity of 8 SL·h⁻¹g⁻¹.

Graphical abstract