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Preventing the deactivation behavior of Co-based catalyst is a significant challenge during the Fischer-Tropsch synthesis reaction. In this study, a series of catalysts with Co nanoparticles embedded in matrix of porous carbon is directly synthesized via a unique melting approach. It is demonstrated in this work that the loading of Co is highly controllable, which ranges from 20.6 wt% ~ 44.0 wt% in the as-prepared samples. The catalyst shows a higher selectivity towards heavy hydrocarbons and a lower selectivity towards methane when compared to the MOFs-derived Co@C catalyst tested at similar CO level. Notably, no obvious deactivation of the catalysts is observed at high operating temperature of 260 $^{\circ}$ C, with high CO conversion levels recorded. The special carbon rich environment of catalyst could inhibit the oxidized and agglomeration of the active phase to prevent deactivation.

1. Introduction

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Fischer-Tropsch synthesis (FTS) is a promising strategy for converting coal, natural gas, and biomass into clean fuels and chemicals via syngas (H₂+CO).¹⁻³ Being the earliest industrial FTS catalyst, Co-based catalyst possesses numerous advantages such as high activity and high selectivity for heavy hydrocarbons, low CO₂ selectivity, and reasonable cost.⁴⁻⁵ Generally, the catalytic performance of Co catalyst is highly dependent on the dispersion and reduction of Co species, which is determined by the specific nanostructure of the catalyst. As such, this would mean that manipulating the nanostructure of the material may lead to enhanced catalytic performance.

In the past decades, carbon-based nanomaterials have been widely used as catalysts or catalyst scaffolds in various application as such energy-related or environmental-related fields. This is largely due to their fascinating properties such as well-developed pore structures, high surface areas, and suitable interaction with the active metals.⁶⁻⁸ Recently, MOFs(metal-

organic frameworks)-derived carbon-based catalysts have been used in the catalytic conversion of syngas to hydrocarbons with unparalleled performances reported.9-11 For instance, Gascon et al. synthesized a series of Fe@C catalysts with excellent catalytic activity and high selectivity via direct pyrolysis of Basolite Fe300 precursor. The resultant Fe@C was comprised of well-dispersed θ -Fe₃C which were confined within a porous carbon matrix.¹² Qiu et al. obtained a Co@CN catalyst through the pyrolysis of ZIF-67. The catalyst possessed large pore size and good dispersity, and it was able to demonstrate excellent catalytic activity.¹³ By regulating the ratio of CTAB (cetyltrimethylammonium bromide) and Co precursor in the MOFs, Chen et al. developed a series of Co@C catalysts with high Co loading (ca. 50 wt%) and high degree of dispersion.¹⁴ MOFs is a type of coordination polymer that is formed by the self-assembly of organic ligands and transition metal ions. During the pyrolysis process at high temperature, the organic ligands are destroyed and the metal species are reduced by the surrounding free carbon, simultaneously. The porous M@C construction would benefit from the reconstruction of the carbon which is catalyzed during the reduction of the ions species. The synthesized materials possess rich porous structure, with highly dispersed nanoparticles, and high reduction degree.15

Thus, motivated by the specific generative process of M@C derived from MOFs, we report the design of a series of Co@C catalysts via an innovate melting technique. The as-synthesized catalysts exhibit excellent physical and chemical properties, while at the same time demonstrating remarkable catalytic performance during FTS. Even when the catalysts are exposed to harsh conditions, they are still able to show good stability, which can be attributed to their special encapsulated structure.

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2. Experimental

2.1. Materials

The Co@C catalysts with different Co loadings are prepared using a melt method. 3 g glucose and 5 g urea are mixed and stirred at 140 $^{\circ}$ C to form a clear molten solution. Then 2.18 g Co(NO₃)₃·6H₂O (0.0075 mol) is added into the solution and stirred for 5 min to achieve a transparent solution. The solution is then dried at 180 $^\circ\!\mathrm{C}$ for 20 h. After which, the black dried sample is ground into powder and calcined at 750 $^\circ C$ for 2 h under N2 atmosphere to obtain the catalyst, denoted as 35-Co@C. By adjusting the amount of $Co(NO_3)_3 \cdot 6H_2O$ to 0.0043 mol, 0.01mol and 0.14 mol we have prepared a series of catalysts, and they are denoted as 20-Co@C, 50-Co@C, and 65-Co@C, respectively.

0.36 g tetrabutyl titanate and 0.40 g Al(NO₃)₃·9H₂O was coadded with 2.18 g Co(NO₃)₃·6H₂O for Ti and Al promoted catalyst respectively, other steps remain the same. Denoted as 35-Co@C-Ti and 35-Co@C-Al, respectively.

The Co@C-M catalyst was prepared using ZIF-67 as a sacrifcial template according to the following procedure: ZIF-67 was heated to 600 $^\circ\!\!\!\mathrm{C}$ in a quartz tubular reactor by flowing Ar at 80 mL/min with heating rate 3 $^\circ\!\mathrm{C}$ /min and kept at 600 $^\circ\!\mathrm{C}$ K for 2 h.

2.2. Characterization

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The Powder X-ray diffraction (XRD) spectrum is collected by using a Bruker D8 powder diffractometer (Cu-Ka radiation, 40 kV and 40 mA, with a Vantec-1 detector). The morphologies of the samples are investigated under a FEI Tecnai G2 F20 transmission electron microscope (TEM), with an accelerating voltage of 200 kV. The precise mass loading is characterized with thermogravimetric analysis (TGA) by using a NETZSCH TG 209F3 instrument with a ceramic crucible as the sample holder. The TGA is conducted according to the following program: temperature increases from 30 to 900 °C with a ramping rate of 10 °C•min⁻¹ in the presence of continuous flow of air (flow rate 30 mL • min⁻¹). A Zeton Altamira AMI-300 instrument which is equipped with a thermal conductivity detector (TCD) is used to carry out the H₂ temperature-programmed reduction (TPR). Before the testing, the catalyst (0.05 g) is firstly purged with high purity argon (>99.99%) at 120 °C for 1 h, and the catalyst is then cooled to 70 °C. 5% H₂/Ar (flow rate of 30 ml•min⁻¹) is used during the temperature increment from 70 to 750 °C (with a ramping rate of 10 °C • min⁻¹), and the temperature is held at 750 °C for 30 min, in this process, Tilon LC-D200M mass spectroscopy instrument is used to test the tail gas (MS). The amount of H₂ dispersion and dispersity of cobalt were measured by hydrogen temperature programmed desorption (H₂-TPD) using the Zeton Altamira AMI-200 unit. The catalysts were reduced at 450 $^\circ\!\mathrm{C}$ for 10 h and cooled to 100 $^\circ\!\mathrm{C}$ in flowing hydrogen. Prior to increasing the temperature from 100 $^\circ\mathrm{C}$ to 450 $^\circ C$ at a rate of 10 $^\circ C$ /min, the samples were held at 100 $^\circ C$ for 1 h under an argon stream. Then the catalysts were held at 450 $^\circ C$ for 2 h. Meanwhile, the TCD detector began to record the signal until it returned to the baseline. The amount of desorbed hydrogen was calculated by comparing the integrated TPD spectrum with the mean areas of calibrated hydrogen pulses. Micromeritics Tristar 3000 surface area and porosity

analyzer is used to investigate the surface area, poresize, and total pore volume of the catalyst by nitrogen physisorpetion atta 196 °C. Prior to the measurement, the sample is degassed at 200 °C for 6 h. The total pore volume is obtained at a relative pressure of 0.99. The Brunauer-Emmett-Teller (BET) method is used to acquire the surface area of the samples. The pore size distributions are assessed from the desorption curves of the isotherms by utilizing the Barrett–Joyner–Halenda (BJH) method. The laser Raman spectroscopy (LRS) spectra of the samples are collected by a confocal Renishaw Raman microprobe RM-1000. A continuous wave argon ion laser (Ar⁺, 514.5 nm) is projected through the samples in the exposure to air at room temperature. A 30 s focus duration with a $50 \times$ objective lens, and a scanning range of 80 to 4000 cm⁻¹ with a resolution power of 2 cm⁻¹ are used. X-ray Photoelectron Spectroscopy (XPS) is conducted using a VG Multilab 2000 system with Al-K α radiation as the X-ray source. All binding energies are calibrated using the C 1s peak (284.6 eV).

2.3. Catalytic test

Fischer–Tropsch synthesis reaction is carried out in a fixed-bed reactor (stainless steel, id = 9.5 mm). In a typical setup, the catalyst (0.1 g) is firstly mixed with inert quartz sand particles (1 g). Before the measurement, the catalyst is reduced by a pure flowing H₂ stream (GHSV=6 g SL⁻¹ h⁻¹) at 450 $^{\circ}$ C for 10 h. After which, the catalyst is cooled to 100 $^\circ C$. Then, the syngas (H₂/CO = 2, GHSV=4 g SL⁻¹ h^{-1}) is led into the tube and the pressure was increased to 1.0 MPa, the temperature is gradually increased to the target temperature. During the reaction, feed gas and outlet gases such as H₂, CH₄, CO, CO₂, C₂~C₄ products, etc. are tested online using an Agilent Micro GC3000 kitted out with molecular sieves, Plot-Q and Al₂O₃ capillary columns. CO steady state conversion and hydrocarbon selectivity are collected at 15-40 h. The wax and water products are collected in a hot trap (100 $^{\circ}\mathrm{C}$) and the oil and water products are gathered in a cold trap (0 $^{\circ}$ C) after more than 80 h of operation to achieve a good mass balance at close to steady state, typically.

3. Results and discussion

3.1. Synthesis and structure

The synthesis process of Co@C is based on a melting method which is illustrated in Scheme 1. The amount of Co loading is tuned by controlling the amount of cobalt nitrate added in the reaction system. The pyrolysis process is crucial for the formation of the encapsulated structure.



Scheme 1: Melting strategy used in the synthesis of Co@C FTS catalyst. The X-ray diffraction (XRD) patterns of the as-prepared Co@C catalysts with different Co loading are presented in Figure 1. The

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XRD spectra of all Co@C catalysts reveal three prominent diffraction peaks located at 44.5°, 51.9°, and 76.0°, which can be assigned to the (111), (200), and (220) crystalline planes of the FCC-Co (face-centered cubic Co⁰), respectively. Self-reduction behavior during pyrolysis process (calcination) is well documented for Co-based catalyst which uses carbon material as the supporter.¹⁶⁻¹⁷ Thus, based on the XRD result, the Co species presented in Co@C catalysts after pyrolysis at 750 °C is Co⁰. This indicates that the reduction degree of Co species in the as-synthesized catalysts is high after the pyrolysis process. The diffraction peak at 26.5° corresponds to the (002) planes of graphitic carbon, which could be a result of the conversion of free carbon under the catalysis of the Co⁰ particles. Hence, based on the XRD results, it can be confirmed that Co@C is composed of Co⁰ and graphitic carbon.



Figure 1. XRD patterns of Co@C catalysts with different Co loadings.

Figure 2 presents the typical transmission electron microscope (TEM) images of 35-Co@C. Based on Figure 2a, it can be observed that the Co particles located on the carbon matrix are well dispersed. Particle-size histogram obtained from the TEM analysis show an average nanoparticle diameter of 23.5 nm, with a wide size distribution ranging from 7.5 to 30 nm. The high resolution TEM (HRTEM) image, presented in Figure 2b, reveals a few layers graphite coating on the particles. The TEM images of the 20-Co@C, 50-Co@C, and 65-Co@C are shown in Figure S1. As shown in Figure S1, Co particles in 20-Co@C exhibit uniform size distribution in the framework of carbon, which are smaller in size as compared to the Co particles in 35-Co@C. Even though Co particles are dispersed in the 50-Co@C and 65-Co@C, the size distributions of Co particles in these samples are relatively broad, which makes it hard to analysis the statistical data accurately. The precise Co content presented in the various Co@C samples is determined using thermogravimetric (TG) analysis, and the results are shown in Table S1. It can be observed that the Co loading in Co@C increases with the amount of cobalt nitrate added. The Co loading in 65-Co@C is the highest at 44.0 wt%. This Co loading is higher as compared to some of the intricately designed MOFs-derived Co@C.18



Figure 2. (a) Low magnification (inset showing the Co size distribution graph), and (b) High resolution (inset showing the graphite layers) TEM images of 35-Co@C catalyst.

Surface elemental composition and chemical environment of the as-synthesized Co@C are characterized with X-ray photoelectron spectroscopy (XPS), and the results are shown in Table S2 and Figure 3. There is no clear distinction in the surface elemental composition for Co@C with different Co contents, while it is worth noting that the survey XPS data shows a low Co content of less than 2.7 at% and a high C content over 88 at% for all samples. This result suggests that the abundant Co species is surrounded by C matrix, which is consistent with the TEM results (Figure 2b). The chemical state of the Co is determined based on the Co 2p XPS spectrum. As shown in Figure 3, the presence of the peak at \sim 781.0 eV indicates the existing oxidation state of Co on the surface of particles. On the other hand, the peak at 778.5 eV is ascribed to Co⁰,¹⁹ suggesting that there is a considerable number of accessible active sites on the external surface. Thus, the XPS result is consistent with the XRD results (Figure 1). It is generally known that the Co⁰ particles in nanoscale can be oxidized easily when exposed to air. The unique reducing chemical environment in Co@C catalysts would thus be responsible for its high reducibility.



Figure 3. Co 2p XPS spectra of Co@C catalysts with different Co mass loading.

The reducibility of Co@C catalysts is studied by temperatureprogrammed reduction-mass spectrum (TPR-MS) test. It can be



seen that the Co@C catalysts exhibit three distinct peaks at 210-250 $^{\circ}$ C , 330-360 $^{\circ}$ C , and 510-550 $^{\circ}$ C respectively, which coincide well with the shape of the CH₄ (m/z=16) signal measured by MS. Besides, weak H₂O (m/z=18) signal are also observed for all catalysts at 210-250 $^{\circ}$ C , based on the MS result. The peak at 210-250 $^{\circ}$ C could be ascribed to the overlay of the reduction of cobaltous oxide and the methanation of unstable carbon species. Peaks at 330-360 $^{\circ}$ C and 510-550 $^{\circ}$ C are the methanation of more stable carbon species. Interestingly, the methanation temperature of the third peak decreases with Co loadings, which implies that the methanation of carbon species may be closely related to the catalysis of Co for Co@C catalyst.

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Figure 4. H₂–TPR and MS profiles of different Co@C catalyst. a: 20-Co@C; b: 35-Co@C; c: 50-Co@C; d: 65-Co@C

The pore structure of the as-synthesized Co@C materials are evaluated using the N₂ sorption experiments. The N₂ adsorption-desorption isotherms of the as-synthesized Co@C catalysts are shown in Figure 5, and the detailed pore parameters are listed in Table 1. It is observed that the 65-Co@C exhibits a BET surface area of 218.8 m²g⁻¹ while 20-Co@C possesses a BET surface area of 381.3 m²g⁻¹. With the decrease in the Co loading, the surface area increases significantly. This clearly indicates that the overall structure of the material presented in this work is determined by reaction procedures of the carbon under the catalysis of Co at high-temperature pyrolysis process. All the samples display type IV isotherms and they exhibit a steep N₂ hysteresis, which are the characteristics of non-uniform banded pores or close-packed pores. This pore structure is composed of interlaced graphitic and non-graphitic carbon that are derived from reorganization of free carbon catalyzed by adjacent Co⁰ particles during high temperature pyrolysis.



Figure 5. N₂ adsorption-desorption isotherms of the as-synthesized Co@C catalysts.

Table 1. Surface area, pore volume, and pore diameter of catalysts

Sam	ple	Surface area,	Pore Volume,	Pore diameter,	
		m²/g	cm ³ /g	nm	
20-C	o@C	381.3	0.13	3.1	
35-Co	o@C	284.5	0.06	3.5	
50-Co	o@C	241.6	0.03	3.7	
65-C	o@C	218.8	0.03	3.9	

3.2 Fischer-Tropsch synthesis

The FTS catalytic performance of the Co@C catalysts is investigated in a fixed bed reactor at a temperature of 240 $^\circ\mathrm{C}$ and at a pressure of 1.0 MPa. The overall results are listed in Table 2. CH_4 and C_5^+ selectivity of 20-Co@C are 14.1 % and 73.4%, respectively, with a CO conversion of 19.1%. With the increase in the Co loading, the CO conversion increases without any changes to the selectivity. Another Co@C catalyst derived from MOFs precursor is synthesized as a comparison (Co@C-M). The morphological features of Co@C-M, is characterized using the TEM. As shown in Figure S2, a similar image of a highly dispersed Co nanoparticles are supported onto a carbon matrix. The overall catalytic performances of Co@C-M and 65-Co@C are then compared at similar CO conversion level. The cobalttime-yield (CTY) of Co@C-M is higher than that of 65-Co@C, while the C5⁺ selectivity of Co@C-M is lower at a conversion of ca. 30%. Furthermore, the undesirable CH₄ selectivity of Co@C-M reaches 24.3%.

The catalytic performance of the catalyst is the result of the specific nanostructure of which. For the Co@C material derived from a carbon-based precursor, its detail texture was intricate due to the unordered reconstruction of carbon and metal species during pyrolysis process. Therefore, the correlation of structure and performance for Co@C catalysts must be discussed carefully. During the pyrolysis process of MOFs, the organic metal skeleton was destroyed, and metal ions were reduced to form particles synchronously. The unpredictable pyrolysis process may result in a wide distribution of particle size, many nanoclusters or even single atomic particles which are difficult to be found by conventional TEM measurement may exist in catalysts.²¹ Fu et al. suggested that smaller Co particles were more active in the promotion of direct carbon nanotubes methanation during a H₂ temperature-programmed reduction process.²² Then the Co@C-M sample was characterized with H₂-TPR. As shown in Figure S3, temperature of carbon methanation for Co@C-M was quite lower than Co@C Published on 15 December 2020. Downloaded on 12/16/2020 1:23:00 AM

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catalyst prepared by melting method (488 $^\circ C$ vs. 534 $^\circ C$). It indicated that the plentiful small Co particles were well distributed in the Co@C-M. Many researchers suggest that the catalytic performance of CO hydrogenation was dependent of cobalt particle size for catalysts with sizes less than 6 nm, CH₄ selectivity increased with the decreased of Co size.²³ We believed that the small Co particles (< 6 nm) undetected by TEM could be responsible for the higher CH₄ selectivity of Co@C-M. The TOF value of the catalyst is calculated based on the H₂ chemisorption data (Table S4). It can be seen that the TOF value increases with the Co loading. Based on the abovementioned discussion, the size distribution of Co particle in Co@C is broad due to the uncontrolled structural evolution during the pyrolysis process. Thus, it is expected that there is a larger number of small Co^0 particles (<6 nm) present in the catalyst with lower Co loading. This, would lower the TOF of the catalyst as a whole.

|--|

Catalysta	CO Conv. (%)	CTY ^c	CO ₂ Sel.	Hydrocarbon selectivity (%)		
Catalysis			(%)	CH_4	C ₂ - C ₄	C_5^+
20-Co@C	19.1	1.38	2.0	14.1	12.5	73.4
35-Co@C	26.6	1.38	1.6	15.9	14.6	69.5
50-Co@C	25.3	0.90	1.6	16.2	14.3	69.5
65-Co@C	32.5	1.10	1.4	16.0	18.3	65.7
35-Co@C-Al	64.5		5.8	36.0	18.2	45.8
35-Co@C-Ala	25.4		1.4	20.8	16.0	62.2
35-Co@C-Ti	50.8		3.3	26.2	17.9	55.9
35-Co@C-550	< 0.5					
35-Co@C-650	< 1					
Co@C-M ^b	30.7	1.76	1.8	24.3	10.6	65.1

Reduction conditions: in pure hydrogen at 450 °C, 1 bar and 3 SL·g⁻¹·h⁻¹ for 10 h. Reaction condition: H₂/CO = 2, 240 °C, 1.0 MPa and 4 SL·g⁻¹·h⁻¹. CO steady state conversion and hydrocarbon selectivity are collected at 15–40 h.

a: Reaction temperature was 220 °C.

b: Reaction temperature was 230 °C.

c: Cobalt time yield (CTY) = mol of CO converted to hydrocarbons (excluding CO₂) per time (s) per weight of Co, expressed as $10^{-5} \text{ mol}_{CO}g_{Co}^{-1}\text{s}^{-1}$.



Figure 6. SEM image of 35-Co@C catalyst.

The overall activity of Co@C catalyst was also highly dependent on the unique microstructure of which. Although the Co loading mass of as-synthesized Co@C was high, its catalytic activity was pale by comparison. To clarify the structure of our Co@C catalyst further, the surface morphology of the catalyst was detected by scanning electron microscope (SEM). Figure S4 and Figure 6 were the typical SEM of 35-Co@C sample. It can be seen that morphology of the catalyst was bulk like without a specific shape. After magnification the image it could be found that lots of cobalt particles distributed 106439thec carded framework. Furthermore, carbon nanotubes can be seen clearly on the parts of Co particles. To provide an insight into the formation mechanism of the as-prepared materials, we have attained the XRD, N2-adsorption, and Raman data of the catalysts prepared at different pyrolysis temperatures to track the evolution process of 35-Co@C. As shown in Figure 7, it can be clearly seen there are dramatic changes in the component and specific surface area of the catalyst with the increase in pyrolysis temperature. Co⁰ only appears as the pyrolysis temperature rises to 550 $^{\circ}$ C. When the pyrolysis temperature increases from 550 $^\circ\!\! C$ to 750 $^\circ\!\! C$, the diffraction peak that belongs to Co⁰ become sharper, and the diffraction peak at 26.5° that belongs to graphite also appears. Besides, the specific surface area increases sharply from 12 m²/g to 284.5 m²/g, and the intensity ratio of D band to G band increases from 0.95 to 1.35, simultaneously. This result implies that after the appearance of Co⁰, there is a dramatic change in the construction of the catalyst. The self-reduction behavior during the pyrolysis process, i.e., calcination, is well documented for Co-based catalyst that uses carbon material as the supporter. It is expected that Co⁰ particles are achieved via the reduction of precursor by the surrounding carbon species at high temperature. On the other hand, Co⁰ is known to be an effective catalyst for the growth of carbon nanotubes over a wide range of temperatures,²⁴ i.e., the texture properties of catalyst are highly dependent on the catalytic effect of Co⁰. The graphitic carbon that is formed near the Co⁰ particles extrudes the free carbon that is relatively far away from Co⁰, which results in the formation of disordered pore structure. However, this process is difficult to regulate precisely, and therefore, this would result in Co particles exhibiting a heterogeneous surface structure and a wide distribution of Co particles. Thus, based on these data, we have illustrated the entire formation process of the material with a schematic diagram(Figure 7 d).



Figure 7. a: XRD patterns, b: Raman spectrum, c: N_2 adsorption-desorption isotherms of 35-Co@C catalyst with different pyrolysis temperature; d : schematic diagram of the evolution of material during the heating process.

Subsequently, we tested the catalytic performance of 35-Co@C prepared at different pyrolysis temperatures, and the results are listed in Table 2. It can be seen that although the

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characteristic diffraction peak that belongs to Co⁰ is obvious for 35-Co@C-650 and 35-Co@C-550 samples, the CO conversions for both samples are negligible. This result indicates that the syngas is unable to approach the active sites of the catalyst. The N₂-adsorption data reveals that the as-prepared 35-Co@C-550 possesses a relatively low specific surface area. On the other hand, the specific surface area of 35-Co@C-650 is relatively high, with a low pore volume. The Co⁰ particles in 35-Co@C-650 and 35-Co@C-550 samples are likely to be blocked by the compact carbon matrix. When the pyrolysis temperature is set to 750 °C, the specific surface area of the catalyst increases from 12 m²/g to 284.5 m²/g. This result suggests a looser carbon structure, which facilitates the diffusion of syngas to the surface of the active site.



Figure 8. a, c and e: three typical HRTEM images of 35-Co@C catalyst; b, d and f: the corresponding surface diagram.

HRTEM was used to observe the subtle surface structure of the particles. The results show that the surface of Co@C material is not exactly the same. Three typical particle surface states were observed and their HRTEM images and corresponding schematic diagrams were lied in Figure 8. The morphology first typical particles were presented in Figure 8a, it can be seen that the particle was covered with more than ten layers of graphitic layer (Figure 8 a and b). It was expected that these particles were inactive. In the second case, several junctions between graphite flakes and Co were visible on the surface of particles (Figure 8 c and d). In the third case, it can be seen that the surface structure of the particles is more complex and varied. Parts of Co surface were covered by graphitic carbon with different layer while parts were fully exposed (Figure 8 e and f).

Such diverse structures of particles are derived from the uncontrollable pyrolysis process. It has been reported that the confined space between graphite and metal could promote CO reaction,²⁵ while thicker graphite layer on surface would masking the active site completely. Large number of coveredactive sites could responsible to the lower activity of our Co@C. To improve the catalytic performance of the Co@C catalyst, we have added AI and Ti precursor during the melting process to enhance this material. The detailed catalytic performance data are listed in the Table 2. It can be observed that when the catalyst is enhanced with Al and Ti, the catalytic activity is significantly improved, even though the CH₄ selectivity increases concurrently. We have also tested the catalytic performance of 35-Co@C-Al at 220 °C , whereby a CO conversion of 25.4% is recorded. This result is almost similar to the CO conversion recorded for 35-Co@C at 240 $\,^\circ\!\mathrm{C}$, which suggests that AI could improve the catalytic performance of 35-Co@C significantly. However, further improvements in the structure of the catalyst and the reduction in methane selectivity are needed. We have also tested the catalytic property of 35-Co@C without reduction. It can be seen that the CO conversion is 20.5% at 240 $^{\circ}$ C, and the CH₄ selectivity is up to 38.5%. The overall performance of the catalyst without reduction is inferior to that of the reduced catalyst. The surface compositions of the reduced 35-Co@C are analyzed and compared to those of the fresh catalyst. After the reduction process, the Co/O ratio increases from 0.27 to 0.31, while the C content decreases from 92.4% to 77.5% (Table S2). This result implies that more Co⁰ is accessible to the syngas. Besides, the TPR-MS result reveals that a proper reduction process can remove some of the free carbon from the Co@C, which would facilitate the exposure of more active phases. Thus, based on



the results, we propose that an appropriate reduction process is necessary to enhance the performance of Co@C catalyst.

Figure 9. CO conversion vs. time for the as-synthesized Co@C catalysts in the steam.

Preventing and limiting catalyst deactivation is one of the most important topics in the development of the next generation of industrial catalysts. Thus, in this work, the stability of the assynthesized Co@C is also investigated. As shown in Figure 9, all Co@C samples present excellent stability at 240 $^{\circ}$ C for 120 h. To examine the catalytic stability of Co@C under a harsh

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condition, we raise the reaction temperature further to 260 $^\circ\!\mathrm{C}$. Detail performance data listed in Table S3. The CO conversion of 65-Co@C is stable at 58% at 260 $^\circ\!\mathrm{C}$ for 50 h, and the rest of the samples also shown good stability at similar reaction condition.

For a typical Co-based catalyst used in Fischer-Tropsch synthesis, deactivation of the catalyst typically originates from the decrease in the amount of accessible active surface area due to oxidation and sintering of Co particles.²⁶⁻²⁷ Thus, to investigate the stability of the as-synthesized catalysts, the phase compositions of all Co@C after 200 h in the stream are characterized using XRD. As shown in Figure 10, no phase transformation can be observed for all Co@C after 200 h in the stream. Water is one of the primary byproducts in FTS reaction, and the partial pressure of water increases with CO conversion. Small Co and Fe particles would be oxidized by the water, which easily leads to a decrease in the active sites. The stability of the active phase in the reaction process is also thanks to the special carbon environment around it. It should be noted that the diffraction peak assigned to graphite carbon were broadened obviously compared to fresh catalysts, indicating that the crystallinity of graphite carbon decreased after reaction. It suggested that the graphite structure was not stable in Fischer-Tropsch synthesis reaction. Raman spectroscopy was used to determine the carbon type, structural ordering degree, and the presence of defects in Co@C materials. It can be seen that all the catalysts presented typical D-band and G-band of carbon, indicating large number of defects distributed on graphite carbon (Figure S5). These defects could be an important reason for the instability of graphite layer during reaction process.



Figure 10. XRD spectra of 20-Co@C-U, 35-Co@C-U, 50-Co@C-U, and 65-Co@C-U, after 200 hours in the stream.

4. Conclusions

In this work, we have successfully developed a series of Co@C via a unique melting approach. The catalysts possess abundant porous structure that can facilitate the mass transfer process. Highly dispersed Co nanoparticles can improve the catalytic efficiency significant. Furthermore, the graphitic layers that are coated on the particles can render a unique chemical environment for the actives phase. This could prevent the particles from being oxidized by the water, which can help to improve the stability of the catalyst. While the multiple graphite

layers on surface of Co would cover the active sites, this should be taken into account when designing additional of the collective results, this approach opens another pathway towards the development of metal nanoparticles with both high stability and reactivity as highly efficient catalyst in the hydrogenation application.

Conflicts of interest

There are no conflicts to declare.

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