Controlled Preparation of $\text{Co}_3\text{O}_4@\text{porous-SiO}_2$ Nanocomposites for Fischer–Tropsch Synthesis

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Abstract Monodispersible Co_3O_4 nanoparticles were prepared via a facile solvothermal route using polyvinylpyrrolidone (PVP) as capping agent and the porous silica shell was then coated by means of the Stöber process to fabricate $\text{Co}_3\text{O}_4@\text{porous-SiO}_2$ ($\text{Co}_3\text{O}_4@p\text{-SiO}_2$) nanocomposites. The particle size of Co_3O_4 and porous silica shell thickness of $\text{Co}_3\text{O}_4@p\text{-SiO}_2$ nanocomposites could be easily controlled through changing the amount of PVP and tetraethoxysilane, respectively. The high resolution transmission electron microscopy results, together with the X-ray diffraction results, indicated that monodispersible Co_3O_4 nanoparticles were successfully prepared and uniformly encapsulated by porous silica. During the growth of silica shell, the PVP was trapped and dispersed in the silica shell. As a result, the porous silica shell was obtained after burning off the PVP and a positive correlation existed between the Brunauer–Emmett–Teller surface area of the porous silica shell and quantity of PVP in the original Co_3O_4 nanoparticles. Compared with the Co/SiO_2 reference catalyst, CO conversion of the $\text{Co}@p\text{-SiO}_2$ model catalyst was more stable and higher in a period of 240 h, and hydrocarbon selectivity towards $\text{C}_5\text{--C}_{18}$ fraction was also higher than that of the Co/SiO_2 catalyst. The results of analysis for the $\text{Co}@p\text{-SiO}_2$ catalyst showed that

core@shell structure could maintain high dispersion of Co particles so as to provide higher number of Co active sites, and enhance selectivity towards $\text{C}_5\text{--C}_{18}$ fraction due to confined structure of porous channel in the silica shell.

Keywords Fischer–Tropsch · Cobalt catalysts · Core@shell · Nanocomposites · Confined structure

1 Introduction

Fischer–Tropsch (F–T) synthesis has attracted much research attention nowadays because of the severe oil crisis and the tight fuel specifications [1, 2]. One of the goals of modern F–T synthesis research is to design a catalyst capable of highest selectivity to the desired product without sacrificing activity and lifetime [3]. Cobalt F–T synthesis catalysts are preferred due to their low activity for the water–gas shift reaction, slow deactivation rates and highly selective to linear paraffin than iron catalysts [4]. Since cobalt is ~1,000 times more expensive than iron, therefore optimal design of a cobalt catalyst is essential for its utilization. Decreasing the Co particle size to increase the exposed surface areas per unit mass of the Co [5] and hindering Co particles from agglomerating during reaction would be reasonable pathway to achieve this goal. Although up to now, many methods were designed to prepare cobalt-based catalysts with different Co particle size, and morphologies as well. It had been difficult to translate these advances into successful application in F–T synthesis as to be the drawback of easily agglomeration and sintering of the Co particles under harsh catalytic reaction conditions. In order to prevent Co particles from agglomerating and decrease the deactivation rates of the cobalt catalysts, a novel cobalt catalyst with core@shell

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structure was preferable to be adopted, where a porous shell played dual roles as: permitting syngas molecules to pass through the channel freely and preventing Co cores from coming into direct contact each other and thus hindering Co cores from agglomerating. This confined structure enabled cobalt catalyst showing special catalytic performances and product distribution in F–T synthesis. For example, Tsubaki co workers [6–9] had prepared core@shell cobalt catalysts by coating H-ZSM-5 zeolite membranes on the Co/SiO_2 catalysts, which showed an excellent selectivity to the $\text{C}_5\text{--C}_{11}$ isoparaffins (gasoline distillates) benefiting from the confined reaction conditions constructed by H-ZSM-5 membranes. Moreover, the article of Trépanier et al. [10] has also showed that carbon nanotubes, when used as a cobalt catalyst support, allowed a better Co dispersion and minimized the Co metal phase interaction with the support. The Co particles located inside the tubes were more active than the ones on the outer surface of the CNT owing to confined effect. Thus, how to synthesize cobalt catalysts with confined structure via a facile method became a big challenge.

The present work developed a procedure that permitted the preparation of the $\text{Co}_3\text{O}_4@p\text{-SiO}_2$ ($\text{Co}_3\text{O}_4@p\text{-SiO}_2$) nanocomposites with different particle sizes of Co_3O_4 core and thickness of porous silica shell via solvo-thermal route using polyvinylpyrrolidone (PVP) as capping agent. Compared with the conventional Co/SiO_2 catalyst prepared via precipitation method, the $\text{Co}@p\text{-SiO}_2$ catalyst, together with high dispersion of Co particles due to confined structure, could exhibit higher and more stable CO conversion and higher selectivity towards $\text{C}_5\text{--C}_{18}$ fraction in F–T synthesis.

2 Experimental Section

2.1 Nanocomposites Preparation

2.1.1 Preparation of the $\text{Co}_3\text{O}_4@p\text{-SiO}_2$ Nanocomposites

The synthesis procedure for the $\text{Co}_3\text{O}_4@p\text{-SiO}_2$ nanocomposites was illustrated in Scheme 1. In a typical

synthesis, 7.09 g $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 3.54 g PVP were dissolved in 800 mL ethanol solution under magnetic stirring at room temperature. The concentrations of the solution were calculated in order to obtain 20 % cobalt loadings in the final catalysts. After the solution turned clear, it was transferred into a Teflon-lined stainless autoclave with the total volume of 1,000 mL, which afterwards was loaded in an oven at 453 K for 4 h and then naturally cooled to room temperature. The suspension was again transferred to the beaker. 2,076 mL ethanol was added into the suspension. After that, 1,656 mL distilled water and 144 mL 25 % ammonia were subsequently added into the suspension. After magnetic stirring for 2 h, 20 mL tetraethoxysilane (TEOS) was added dropwise into the suspension during 12 h. Magnetic stirring was continued for 48 h. The solid products were collected by filtration, washed thoroughly with distilled water and ethanol, and dried in an oven at 333 K. The template was removed by calcination at 773 K for 6 h in flowing air. The prepared nanocomposites were denoted as $\text{Co}_3\text{O}_4@p\text{-SiO}_2$, which were selected as model catalysts for the subsequent F–T synthesis. Meanwhile, by controlling Co/PVP mass ratio, $\text{Co}_3\text{O}_4@p\text{-SiO}_2$ nanocomposites with different core sizes and thickness of silica shell were also prepared using same method.

2.1.2 Preparation of the $\text{Co}_3\text{O}_4/\text{SiO}_2$ Nanocomposites

The $\text{Co}_3\text{O}_4/\text{SiO}_2$ nanocomposites (cobalt content 20 %) were prepared as follows: Firstly, 60 mL distilled water and 60 mL $\text{NH}_3 \cdot \text{H}_2\text{O}$ were dissolved in 648 mL ethanol solution in sequence with magnetic stirring at room temperature. After that, 31.8 mL TEOS was added dropwise into above solution. Magnetic stirring was continued for 2 h. The spherical SiO_2 support were collected by filtration, washed thoroughly with distilled water and ethanol, and dried in an oven at 333 K. Secondly, the Co_3O_4 nanoparticles were precipitated on the as-made SiO_2 support by adding a highly concentrated $\text{NH}_3 \cdot \text{H}_2\text{O}$ solution to a dilute cobalt nitrate solution. After aging for 2 h, the precipitate was separated from the suspension by filtration, washed thoroughly with distilled water and ethanol. Finally, the

Scheme 1 Schematic diagram of the procedure for synthesizing $\text{Co}_3\text{O}_4@p\text{-SiO}_2$ nanocomposites

products were dried at 333 K and calcined at 773 K for 6 h. The as-made nanocomposites were denoted as $\text{Co}_3\text{O}_4/\text{SiO}_2$, which were used as reference catalysts.

2.2 Nanocomposites Characterization

High resolution transmission electron microscopy (HRTEM) images were obtained on a Philips CM200FEG operating at 200 kV. The powder X-ray diffraction (XRD) patterns were recorded on a Bruker diffractometer using a $\text{CuK}\alpha$ radiation. The texture properties of nanocomposites were determined by N_2 adsorption/desorption isotherms at 77 K using a Micromeritics Tristar 3000 sorptometer. The pore size distribution and pore volume were determined by the BJH method. X-ray photoelectron spectroscopy spectra (XPS) were performed on a PerkinElmer PHI-5300 spectrometer. Hydrogen temperature programmed reduction (H_2 -TPR) was carried out in a quartz microreactor heated by an electrical furnace. The reactor was loaded with 25 mg of calcined sample and heated at a rate of 10 K/min to 1,233 K with a gas consisting of 5 % H_2 in N_2 . The gas flow rate was 60 mL/min. The mount of H_2 consumed by the sample was measured by analysis of the effluent gas with a thermal conductivity detector (TCD).

2.3 Catalysts Test

F–T synthesis was carried out at 2 Mpa, $1,000 \text{ h}^{-1}$ (the gas flow rate: 33.3 mL/min) and a H_2/CO ratio of 2 in a stainless-steel fixed-bed reactor (i.d. = 10 mm) with a catalyst loading of 2 mL. The catalyst was reduced in a flow of hydrogen at 673 K for 10 h and then naturally cooled to room temperature before switching to syngas. Data were taken at steady state after 24 h on-stream. Wax was collected with a hot trap and the liquid products were collected in a cold trap. The gas effluents were analyzed on-line by using Carbosieve-packed column with TCD. The gas hydrocarbons were analyzed on-line using Porapak-Q column with FID. Oil and wax were analyzed offline in OV-101 capillary columns. 5 % N_2 was added to syngas as an internal standard. The carbon balance and mass balance were $100 \pm 5 \%$.

3 Results and Discussion

3.1 Synthesis and Characterization of $\text{Co}_3\text{O}_4@p\text{-SiO}_2$ Nanocomposites

PVP is an amphiphilic polymer and usually employed as stabilizer for the preparation of various metal nanoparticles [11–15]. As reported previously, the Co_3O_4 nanoparticles with different particle size could be prepared via

solvothermal route using PVP as stabilizer [16]. The PVP was chosen as stabilizer for the following reasons. The hydroxyl groups located on the surface of prepared Co_3O_4 nanoparticles, the hydrogen bond could form between PVP and Co_3O_4 nanoparticles [18]. By adsorbing PVP onto the surface of Co_3O_4 nanoparticles, this PVP layer could help to stabilize Co_3O_4 nanoparticles and avoid aggregation. It has been known that the coating of the host materials by PVP was very effective for the subsequent silica shell formation [19]. Figure 1a showed the XRD pattern of the Co_3O_4 nanoparticles prepared via solvothermal methods. It was found that all the diffraction peaks matched Co_3O_4 well with standard JCPDS data (42–1,467). After coating with porous silica shell, the $\text{Co}_3\text{O}_4@p\text{-SiO}_2$ nanocomposites, as shown in Fig. 1b, exhibited similar diffraction peaks to that of the Co_3O_4 nanoparticles, suggesting that the Co_3O_4 phase was retained. However, it was found that the diffraction peaks of $\text{Co}_3\text{O}_4@p\text{-SiO}_2$ nanocomposites had relatively low intensity, because of the shielding effect of the porous silica shell to the detecting X-rays [17]. Moreover, the $\text{Co}_3\text{O}_4/\text{SiO}_2$ reference nanocomposites, as shown in Fig. 1c, also exhibited similar diffraction peaks to that of the Co_3O_4 nanoparticles, indicating that cobalt phase was also present in the form of Co_3O_4 spinel.

Seen from Fig. 2a–c, it could be clearly observed that the PVP-stabilized Co_3O_4 nanoparticles were monodisperse and uniform. By controlling the amount of PVP, the Co_3O_4 nanoparticles with different size could be prepared. Moreover, these PVP-stabilized Co_3O_4 nanoparticles favored uniform growth of silica shell owing to interaction between PVP and Si–OH groups. To fabricate $\text{Co}_3\text{O}_4@p\text{-SiO}_2$ nanocomposites, the stöber process would be applied to coat the silica onto the PVP-stabilized Co_3O_4 nanoparticles, which acted as seeds or nuclei for silica shell

Fig. 1 XRD patterns of *a* Co_3O_4 nanoparticles; *b* $\text{Co}_3\text{O}_4@p\text{-SiO}_2$ nanocomposites; *c* $\text{Co}_3\text{O}_4/\text{SiO}_2$ nanocomposites

Fig. 2 HRTEM photographs of **a–c** different particle sizes of Co_3O_4 nanoparticles [uniform $7.09 \text{ Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was provided under different PVP mass from **d** (PVP = 14.17 g), **e** (PVP = 7.09 g) to **f** (PVP = 3.54 g)]; **d–f** $\text{Co}_3\text{O}_4@p\text{-SiO}_2$ nanocomposites with different particle sizes of Co_3O_4 nanoparticles [uniform 20 mL TEOS was

provided under different PVP mass from **d** (PVP = 14.17 g), **e** (PVP = 7.09 g) to **f** (PVP = 1.77 g)]; **g–i** $\text{Co}_3\text{O}_4@p\text{-SiO}_2$ nanocomposites with different thicknesses of porous silica shell [uniform 3.54 g PVP was provided under different TEOS from **d** (TEOS = 20 mL), **e** (TEOS = 40 mL) to **f** (TEOS = 60 mL)]

formation. Furthermore, in order to ensure uniform coating and to avoid formation of individual silica particles, the reaction conditions had to be properly controlled. For example, a lower TEOS concentration was indispensable of preventing aggregation of the particles during the growth of the initial silica shell [20]. Furthermore, by varying the amount of PVP and TEOS, $\text{Co}_3\text{O}_4@p\text{-SiO}_2$ nanocomposites with different particle size of Co_3O_4 and silica shell thickness could also be prepared. Seen from Fig. 2d–i, monodispersible and uniform silica coating of $\text{Co}_3\text{O}_4@p\text{-SiO}_2$ nanocomposites could be clearly observed in HRTEM photographs. It was remarkable that nearly perfect

core@shell morphology was obtained, with rather uniform size distributions. Such results demonstrated the high efficiency of this procedure, despite its simplicity, as compared to other silica-coating techniques previously reported [21–25].

Since the major contribution of surface area and porous structures results from PVP, it is therefore necessary to correlate the quantity of PVP in the reacting system with final specific surface area of $\text{Co}_3\text{O}_4@p\text{-SiO}_2$ nanocomposites. Figure 3 showed the Brunauer–Emmett–Teller (BET) surface area of $\text{Co}_3\text{O}_4@p\text{-SiO}_2$ nanocomposites after calcinations at various PVP/Co mass ratios. It could

Fig. 3 The BET surface area of $\text{Co}_3\text{O}_4@p\text{-SiO}_2$ nanocomposites after calcinations at various PVP/Co mass ratios

be clearly observed that the BET surface area of the $\text{Co}_3\text{O}_4@p\text{-SiO}_2$ nanocomposites increased with increasing PVP/Co mass ratio from 0.25 to 2.0. This result indicated that a positive correlation existed between the BET surface area of the porous silica shell and quantity of PVP.

In addition, Fig. 4 also showed HRTEM images of the $\text{Co}_3\text{O}_4@p\text{-SiO}_2$ model catalysts and $\text{Co}_3\text{O}_4/\text{SiO}_2$ reference catalysts before and after reaction, respectively. Seen from Fig. 4a, the fresh $\text{Co}_3\text{O}_4@p\text{-SiO}_2$ catalysts showed nearly perfect core@shell morphology, Co_3O_4 nanoparticles were completely coated by porous silica. After F–T reaction, the HRTEM image of the spent $\text{Co}@p\text{-SiO}_2$ model catalysts (see Fig. 4b; Table 1) illustrated that the core@shell structure was perfectly preserved due to higher hydrothermal stability of porous silica shell. The coated Co particles did not agglomerate owing to protection of porous silica shell during the reaction. However, the HRTEM image of the fresh $\text{Co}_3\text{O}_4/\text{SiO}_2$ catalysts prepared via a controlled coprecipitation of cobalt nitrate with ammonia showed the fluffy Co_3O_4 nanoparticles were synthesized onto outer surface of spherical SiO_2 support (see Fig. 4c; Table 1). For the spent Co/SiO_2 catalysts, it was clear that serious aggregation of the Co particles were observed on the external surface of spherical SiO_2 support (see Fig. 4d),

Fig. 4 HRTEM photographs of **a** fresh $\text{Co}_3\text{O}_4@p\text{-SiO}_2$ nanocomposites, **b** spent $\text{Co}@p\text{-SiO}_2$ model catalysts, **c** fresh $\text{Co}_3\text{O}_4/\text{SiO}_2$ nanocomposites, **d** spent Co/SiO_2 reference catalysts

Table 1 Textural properties of fresh and spent catalysts

Catalysts	Surface area (m^2/g)	Pore volume (cm^3/g)	Average pore size (nm)	Co_3O_4 crystallite size ^a (nm) XRD	Co_3O_4 particles size (nm) HRTEM	Co crystallite size (nm) ^b XRD	Co particles size (nm) ^b HRTEM	Reducibility ^c (%) <673.0 K
$\text{Co}_3\text{O}_4@p\text{-SiO}_2$	181.1	0.4	8.8	19.8	31.5	18.4	31.5	53.0
$\text{Co}_3\text{O}_4/\text{SiO}_2$	60.9	0.2	13.1	9.8	—	40.3	—	85.0

^a Calculated from the Scherrer equation according to the (311) diffraction peak of Co_3O_4

^b Crystallite size for spent catalysts

^c Calculated from H_2 -TPR

Fig. 5 XPS spectra of the *a* $\text{Co}_3\text{O}_4@p\text{-SiO}_2$ nanocomposites and *b* $\text{Co}_3\text{O}_4/\text{SiO}_2$ nanocomposites

indicating that small Co particles located on outer surface of the nonporous spherical SiO_2 support were easier to agglomerate into large Co clusters without protection.

In Fig. 5a, it was not found Co_{2p} or Co_{LMM} peaks in XPS spectra of $\text{Co}_3\text{O}_4@p\text{-SiO}_2$ nanocomposites, whereas XPS spectra was sensitive only to the Co ions localized at the surface and subsurface layer of the nanocomposites (depth of analysis ~ 6 nm) [26]. This result indicated that the Co_3O_4 nanoparticles did not located on the surface of porous silica shell and were completely coated by porous SiO_2 . Whereas, in the case of $\text{Co}_3\text{O}_4/\text{SiO}_2$ nanocomposites, Co_{2p} or Co_{LMM} peaks were presented in XPS spectra in Fig. 5b, suggesting that the Co_3O_4 nanoparticles located on the external surface of nonporous silica spheres.

3.2 Reducibility of the $\text{Co}_3\text{O}_4@p\text{-SiO}_2$ Nanocomposites

Hydrogen temperature programmed reduction is a very convenient technique for studying the reduction behaviors of catalysts qualitatively. In some case it is also possible to

Fig. 6 H_2 -TPR profiles of the $\text{Co}_3\text{O}_4@p\text{-SiO}_2$ and $\text{Co}_3\text{O}_4/\text{SiO}_2$ catalysts

obtain useful information about the degree of interaction of the supported phase with the support from the reduction profiles of supported oxides. Figure 6 showed the H_2 -TPR profiles for the $\text{Co}_3\text{O}_4@p\text{-SiO}_2$ and $\text{Co}_3\text{O}_4/\text{SiO}_2$ nanocomposites. For the $\text{Co}_3\text{O}_4@p\text{-SiO}_2$ nanocomposites (see Fig. 6a), the first peak was apparent and this was attributed to the reduction of Co_3O_4 to CoO . However, the first peak was significantly shifted to higher temperature than that of the $\text{Co}_3\text{O}_4/\text{SiO}_2$ nanocomposites. This result could be attributed to the protective effects of porous silica shell which inhibited H_2 to diffuse along the porous channels to access Co_3O_4 nanoparticles [27, 28]. Moreover, the second peak was also gradually shifted to higher temperatures and this was attributed to the reduction of CoO to metallic Co^0 . This result indicated that the reduction of CoO to metallic Co^0 was difficult owing to H_2 diffusion limitation in porous channels. A reduction pattern in the temperature range of about 820–1,015 K was observed for the $\text{Co}_3\text{O}_4@p\text{-SiO}_2$ nanocomposites. Such a high reduction temperature might be assigned to the reduction of cobalt silicate species formed during the H_2 -TPR experiment by reaction of CoO with Si-OH groups [26]. However, for the $\text{Co}_3\text{O}_4/\text{SiO}_2$

nanocomposites (see Fig. 6b), two peaks were apparent and these were attributed to the reduction of Co_3O_4 to CoO , which then reduced at lower temperature to metallic Co^0 . Significantly increasing area of the second peak indicated that the CoO particles were much easier to be reduced to active Co species. Thus first and second peaks were shifted to lower temperatures due to the lower interaction between CoO and Si-OH groups and higher contact area with H_2 . As to the reduction of cobalt silicate species, a small reduction peak in the temperature range of about 595–695 K was also observed for the $\text{Co}_3\text{O}_4/\text{SiO}_2$ nanocomposites. Thus, the reducibility of the $\text{Co}_3\text{O}_4/\text{SiO}_2$ nanocomposites was higher than that of the $\text{Co}_3\text{O}_4@p\text{-SiO}_2$ nanocomposites, as shown in Table 1.

3.3 FTS Performances

The performances of the $\text{Co}@p\text{-SiO}_2$ and Co/SiO_2 catalysts for F–T synthesis were evaluated in a fixed-bed reactor. Figure 7 depicted the variations of CO conversion with the time on-stream (TOS) under the same reaction temperature (503 K). CO conversion of the $\text{Co}@p\text{-SiO}_2$ catalyst was more stable and higher than that of Co/SiO_2 catalyst. In the case of the $\text{Co}@p\text{-SiO}_2$ catalyst, CO conversion decreased slightly from 71.6 to 56.1 % in a period of 240 h, whereas, the Co/SiO_2 catalyst showed a quick drop in CO conversion from 61.7 to 30.5 %. It is well known that dispersion and reducibility of the cobalt catalyst play an important role in catalytic activity. Although the $\text{Co}@p\text{-SiO}_2$ catalyst had the lower reduction degree than the Co/SiO_2 catalyst, it maintained a high dispersion of Co particles and number of active sites due to the protection of porous silica shell (see

Fig. 4b; Table 1), which inhibited the agglomeration of Co particles during the reaction process. Therefore, more Co active sites were available for the CO hydrogenation. However, Co particles of the Co/SiO_2 catalyst agglomerated easily among them during the reaction without the protection of porous silica shell (see Fig. 4d), thus decreasing the number of active sites and catalytic activity. To conclude, it is known that the CO conversion not only related to the reducibility of catalysts, but also to the dispersion of Co active sites. A high and stable CO conversion of the $\text{Co}@p\text{-SiO}_2$ catalyst could therefore be attributed to a combination of high Co dispersion and appropriate reducibility in comparison to that of the Co/SiO_2 catalyst.

The hydrocarbon selectivity of both $\text{Co}@p\text{-SiO}_2$ and Co/SiO_2 catalysts were summarized in Table 2 under the different reaction temperatures (503 and 513 K). The data showed that selectivity towards both CH_4 and $\text{C}_5\text{--C}_{18}$ fraction of the $\text{Co}@p\text{-SiO}_2$ catalyst was higher than that of the Co/SiO_2 catalysts. Whereas, the Co/SiO_2 catalyst was more selective towards C_{19+} fraction while its selectivity towards both CH_4 and $\text{C}_5\text{--C}_{18}$ fraction were lower. Reuel and Batholomew [29] reported that high CH_4 selectivity observed on the Co/SiO_2 catalyst with narrow pore was likely to be attributed to the presence of either unreduced cobalt species or the small cobalt particles which produced relatively high CH_4 fraction at the expenses of the C_{19+} fraction than large cobalt particles. In our case, a part of unreduced CoO in the $\text{Co}@p\text{-SiO}_2$ catalyst, which was discussed in $\text{H}_2\text{-TPR}$ session, resulted in high CH_4 selectivity. Moreover, it is known that large Co particles lead to more selective for long-chain hydrocarbons under the same cobalt loadings [30, 31]. Khodakov et al. [27] had shown that large Co particles were more active in F–T synthesis and produced higher selectivity towards long-chain hydrocarbons than small Co particles. In addition, confined effect of the porous channel could inhibit the growth of long-chain hydrocarbons, thus increasing the selectivity towards $\text{C}_5\text{--C}_{18}$ fraction in the $\text{Co}@p\text{-SiO}_2$ catalyst. The

Fig. 7 Change in CO conversion with TOS for the $\text{Co}@p\text{-SiO}_2$ and Co/SiO_2 catalysts (reaction conditions: $\text{H}_2/\text{CO} = 2$, $\text{GHSV} = 1,000 \text{ h}^{-1}$, $P = 2 \text{ MPa}$, $T = 503 \text{ K}$)

Table 2 Catalytic performances of catalysts for F–T synthesis

Catalysts	Reaction temperature (K)	CO conversion (%)	Hydrocarbon selectivity (wt%)			
			C_1	$\text{C}_2\text{--C}_4$	$\text{C}_5\text{--C}_{18}$	C_{19+}
$\text{Co}@p\text{-SiO}_2$	503.0	71.2	14.9	2.5	56.9	25.6
	513.0	77.3	16.2	2.4	59.4	22.0
Co/SiO_2	503.0	61.7	12.0	2.5	53.8	31.7
	513.0	64.3	12.4	2.6	54.3	30.7

Reaction conditions: $\text{H}_2/\text{CO} = 2.0$, $\text{GHSV} = 1,000.0 \text{ h}^{-1}$, $P = 2.0 \text{ MPa}$

results of product selectivity analysis for $\text{Co}@p\text{-SiO}_2$ catalysts showed that high CH_4 selectivity and low selectivity towards C_{19+} fraction of the $\text{Co}@p\text{-SiO}_2$ catalyst resulted from partly unreduced CoO species and the small Co particles. It was also reasonable to suggest that the confined structure of porous channel in the $\text{Co}@p\text{-SiO}_2$ catalyst could enhance product selectivity towards $\text{C}_5\text{--C}_{18}$ fraction. Whereas, high selectivity towards both CH_4 and C_{19+} fraction of the Co/SiO_2 catalyst could be ascribed to high reducibility and formation of the large Co clusters (see Fig. 4d), respectively. This result in turn led to decreasing of $\text{C}_5\text{--C}_{18}$ selectivity.

4 Conclusions

Our work showed that Co_3O_4 nanoparticles could be synthesized via a facile solvothermal route using PVP as capping agent. Novel core@shell $\text{Co}_3\text{O}_4@p\text{-SiO}_2$ nanocomposites with different Co_3O_4 particle sizes and silica shell thickness had been subsequently prepared via the Stöber process. CO conversion of the $\text{Co}@p\text{-SiO}_2$ model catalyst was more stable and higher than that of the Co/SiO_2 reference catalyst due to confined structure of porous silica shell, which could maintain high Co dispersion and number of active sites during harsh reaction condition. Selectivity towards both CH_4 and $\text{C}_5\text{--C}_{18}$ fraction of the $\text{Co}@p\text{-SiO}_2$ catalyst were higher than that of the Co/SiO_2 catalyst due to more unreduced CoO and confined effect of porous channels, respectively. Compared with the $\text{Co}@p\text{-SiO}_2$ catalyst, the large Co clusters formed during reaction owing to agglomeration among small Co particles was in favor of enhancing selectivity towards C_{19+} fraction for the Co/SiO_2 catalyst.

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