间苯二酚-甲醛树脂凝胶对Co/SiO₂催化剂费-托性能的影响

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摘要: 采用共沉淀法制备了高 Co 含量的 Co/SiO₂ 费托合成催化剂, 并向其中添加一定含量的间苯二酚-甲醛树脂凝胶。结果表明, 催化剂在 393 K 干燥时, 树脂会发生分解, 因而仅有少量的含碳凝胶残留在催化剂中。然而, 少量碳凝胶的存在显著增加了催化剂的还原度和金属钴的分散度, 致使催化剂表面产生更多的活性金属 Co, 同时, 催化剂的孔径也有所增大, 因此 Co/SiO₂ 催化剂具有更高的反应活性及高碳烃选择性。其中 80%Co/SiO₂-C 催化剂活性及高碳烃的选择性与我们前期报道的一种高活性的 80%Co-8%ZrO₂/SiO₂ 催化剂相近。

关键词: 高负载钴; 二氧化硅; 间苯二酚-甲醛树脂; 费-托合成; 微量吸附量热; 活性位数目

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Effect of Resorcinol Formaldehyde Resin Gel on the Preparation of Co/SiO₂ Catalysts for Fischer-Tropsch Synthesis

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Abstract: Highly loaded Co/SiO₂ catalysts were prepared by the co-precipitation method with resorcinol formaldehyde resin gel (RFG). Most RFG was decomposed during the drying process at 393 K, and little carbon was remained in the catalysts. However, the presence of RFG during the precipitation played the important roles in increasing the pore sizes of catalysts and the reducibility and dispersion of supported cobalt, leading to the more surface active cobalt sites and large pores of the catalysts and therefore the higher activity for the Fischer-Tropsch reactions to produce heavy hydrocarbons. The catalyst 80%Co/SiO₂-C thus prepared was as active and selective as the 80%Co-8%ZrO₂/SiO₂ (an excellent catalyst reported previously) for the synthesis of heavy hydrocarbons from syngas.

Key words: highly loaded cobalt; silica; resorcinol-formaldehyde resin gel; Fischer-Tropsch synthesis; microcalorimetric adsorption; number of active sites

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Co-based catalysts were found to be effective for producing high quality linear heavy hydrocarbons from syngas via the Fischer-Tropsch synthesis (FTS) [1–3]. Previous studies [4,5] showed that the reducibility and dispersion of supported cobalt were the important factors determining the activity and selectivity for heavy hydrocarbons, and the

activity and C₅₊ selectivity were related to the number of surface metallic cobalt particles (larger than 7–8 nm). Hence, many attempts were made to increase the reducibility and dispersion of supported Co. Promoters such as Pt, Ru, and Zr were found to be effective for improving the reducibility or dispersion of supported Co [6–8]. On the

other hand, the addition of some organic compounds (such as sucrose and mannitol) in the solution of cobalt nitrate was found to be favorable for the preparation of highly dispersed cobalt catalysts [6,9]. In addition, aqueous solutions of chelated cobalt complexes were employed for the preparation of supported cobalt catalysts for FTS. The results suggested that a steep increase in viscosity during the evaporation of solvent inhibited the redistribution of impregnated cobalt species on support, and thus increased the dispersion of supported Co [10]. Many other parameters such as cobalt precursor and solvent were also investigated for the increase of reducibility and dispersion of cobalt [11,12].

Supported cobalt catalysts were usually prepared by the incipient wetness impregnation method with porous materials such as SiO_2 , Al_2O_3 , and TiO_2 [13–15]. However, the strong interactions between the dispersed metal and supports might lead to the formation of compounds such as cobalt silicates and aluminates that were difficult to reduce, resulting in the low FTS activity [16]. Previously, we prepared the highly loaded Co/ SiO_2 (80%) catalysts by co-precipitation with an *n*-butanol drying process and found that the catalyst thus prepared was highly active and selective for FTS [17].

In this work, the preparation of highly loaded Co/ SiO_2 catalysts was modified with the addition of resorcinol formaldehyde resin gel (RFG) during the precipitation, so that the reducibility and dispersion of supported cobalt were significantly enhanced. Thus, the activity and selective for C_{5+} were increased for the FTS reactions. Techniques such as X-ray diffraction (XRD), transmission electron microscopy (TEM), and microcalorimetric adsorption were used to characterize the catalysts.

1 Experimental

1.1 Preparation of catalysts

The Co/ SiO_2 catalysts containing about 60% and 80% cobalt (mass percent) were prepared by the co-precipitation method. Specifically, a desired amount of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 100 ml distilled water to form a solution (I). Another solution (II) was obtained by dissolving desired amounts of Na_2CO_3 and $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ in 100 ml distilled water. The two solutions of (I) and (II) were simultaneously added dropwise into a beaker containing 250 ml distilled water at 353 K under vigorous stirring. RFG was added for the preparation of Co/ SiO_2 -C catalysts because FRG would be converted into carbon in the catalysts upon the reduction at high temperatures. In this case, desired amounts of 1,3-dihydroxybenzene and formaldehyde (with the molar ratio of 1/2) were dissolved in 250 ml distilled water in the

presence of Na_2CO_3 as a catalyst to form a solution (III), followed by heat treatment at 353 K for 4 h [18]. Then, the two solutions of (I) and (II) were simultaneously added dropwise into solution (III) at 353 K under vigorous stirring. The precipitates formed were filtered and washed thoroughly with water until the pH of the filtrates was 7. Then, the precipitates were added into 200 ml *n*-butanol and heated at 353 K overnight, during which water and *n*-butanol were evaporated. The samples were further dried in an oven at 393 K for 12 h. The powder samples thus obtained were pressed, crashed, and sieved to 20 and 40 meshes for further uses. All the chemicals used for the preparation of these catalysts were AR grade. The catalysts prepared without RFG were donated 60%Co/ SiO_2 and 80%Co/ SiO_2 , while those with RFG were donated 60%Co/ SiO_2 -C and 80%Co/ SiO_2 -C, respectively. The amount of RFG added was calculated by supposing that 10% carbon would be remained in the catalysts if all the carbon atoms would be deposited upon the heat treatments.

1.2 Characterization of catalysts

The nitrogen adsorption/desorption isotherms were determined at 77 K using a Micromeritics Gemini V 2380 autosorption analyzer. The used catalysts were washed several times with acetone to remove wax remained in pores and out-gassed in flowing nitrogen at 573 K for 3 h prior to the measurements. The specific surface areas were calculated using the Brunauer-Emmett-Teller (BET) method, and the pore size distributions were obtained by the Barrett-Joyner-Halenda (BJH) method according to the desorption branches.

XRD patterns were collected at ambient atmosphere by an X-ray diffractometer (Shimadzu XRD-6000) with Cu K_α radiation ($\lambda = 0.15408$ nm) generated at 40 kV and 30 mA. Diffraction intensities were recorded from $2\theta = 10^\circ$ to 80° at the rate of $2.0^\circ/\text{min}$ with a sampling width of 0.02° .

Temperature-programmed reduction (TPR) measurements were performed by using a quartz U-tube reactor loaded with about 50 mg of a dried sample in 5.03% H_2/N_2 (V/V) at a flow rate of 40 ml/min. The hydrogen consumption was monitored by a thermal conductivity detector (TCD). The reducing gas first passed through the reference arm of the TCD before entering the reactor. The exiting gas passed through a trap filled with a soda lime to remove water and possibly CO_2 and then reached the second arm of the TCD.

The infrared (IR) spectra were recorded on a Bruker VERTEX 70 spectrometer using KBr pellet in the range of $400\text{--}4000\text{ cm}^{-1}$. Thermogravimetric analysis (TGA) experiments of the catalysts were carried out using a thermogravimetric analyzer (Netzsch TG 449C, Germany). The

samples were exposed in the flow of air at a heating rate of 10 K/min.

Microcalorimetric adsorption measurements were performed using a Tian-Calvet type C-80 microcalorimeter (Setaram, France), which was connected to a glass vacuum-dosing system, equipped with a Baratron capacitance manometer (USA) for the pressure measurements and gas handling. About 0.1 g of a catalyst was loaded, reduced at 773 K for 2.5 h in flowing H₂, and then evacuated at 773 K for 1 h prior to a measurement. Then, the microcalorimetric adsorption of NH₃, CO₂, CO, and H₂ was carried out separately.

The adsorption of H₂ and O₂ was carried out in a home-made volumetric apparatus. The catalysts were reduced in H₂ at 773 K for 4 h and evacuated at 773 K for 1 h before the measurements. The adsorption of H₂ was performed at 423 K. After the adsorption of H₂, the sample was heated to 673 K and evacuated at the temperature for 1 h. The adsorption of O₂ was then performed at 673 K. The uptakes of H₂ and O₂ were obtained by extrapolating the coverage of corresponding isotherms to $p = 0$. The degree of reduction (reducibility), dispersion, and average particle size of supported cobalt were calculated based on the amounts of H₂ and O₂ adsorbed and loading of cobalt. The detailed calculation formulas could be found in the literature [19].

1.3 Catalytic tests

FTS reactions were carried out in a fixed-bed reactor. The reactor consisted of a stainless steel tube with an internal diameter of 10 mm heated by an electronic oven. Syngas was regulated with a mass flow controller. The reaction pressure was maintained by a backpressure regulator. Typically, 1 g catalyst mixed with quartz sands was loaded into the reactor. Prior to the reaction, the catalyst was reduced at 773 K in flowing H₂ (30 ml/min) for 4 h under atmospheric pressure. After the reactor was cooled down to 373 K, syngas (H₂:CO:N₂ = 64:32:4, molar ratio) was introduced, and the reactor was heated to the desired reaction temperatures. N₂ was added as an internal standard for the analysis of CO and products by a gas chromatograph (GC).

A hot trap at 423 K and a cold trap at 273 K were used to collect wax and liquid products, respectively. The FTS reactions reached the steady state on the catalysts after 12 h, and the effluent gases from the traps were analyzed on-line by a GC. A TDX-01 column was used with a TCD for the analysis of gaseous products CO, N₂, CO₂, and CH₄, while a Porapak-Qs column with a flame ionization detector (FID) was employed for the analysis of light hydrocarbons (C₁–C₄). Wax and liquid products were not analyzed, but weighed. The conversion of CO and selectivity for different products

were calculated according to the following equations:

$$\text{Conversion of CO} = \frac{n_{\text{CO, inlet}} - n_{\text{CO, outlet}}}{n_{\text{CO, inlet}}} \times 100\%$$

$$\text{Selectivity for CO}_2 = \frac{n_{\text{CO}_2, \text{produced}}}{n_{\text{CO, inlet}} - n_{\text{CO, outlet}}} \times 100\%$$

$$\text{Selectivity for CH}_4 = \frac{n_{\text{CH}_4, \text{produced}}}{n_{\text{CO, inlet}} - n_{\text{CO, outlet}} - n_{\text{CO}_2, \text{produced}}} \times 100\%$$

$$\text{Selectivity for C}_2\text{--C}_4 = \frac{n_{\text{C}_2\text{--C}_4, \text{produced}}}{n_{\text{CO, inlet}} - n_{\text{CO, outlet}} - n_{\text{CO}_2, \text{produced}}} \times 100\%$$

$$\text{Selectivity for C}_{5+} = 1 - S_{\text{CH}_4} - S_{\text{C}_2} - S_{\text{C}_3} - S_{\text{C}_4}$$

2 Results and discussion

2.1 Carbon content

Because RFG was added during the precipitation for the preparation of Co/SiO₂-C samples and its contents would change during the subsequent heat treatments, TGA experiments were performed to determine the change of RFG content in the catalysts dried at 393 K. Figure 1 shows the results. It is seen that when the catalysts were heated to 800 K, similar mass losses (about 15%) occurred for the 60%Co/SiO₂ and 60%Co/SiO₂-C due to the desorption of water and decomposition of cobalt and silica hydroxides. The mass losses were about 10% for the 80%Co/SiO₂ and 80%Co/SiO₂-C at the same experimental conditions. The similar mass losses in the Co/SiO₂ and Co/SiO₂-C implied that there were little RFG remained in the Co/SiO₂-C samples dried at 393 K. In another word, most RFG was decomposed in the samples during the drying at 393 K. In fact, the elemental analysis showed that the 60%Co/SiO₂-C and 80%Co/SiO₂-C contained only 1.1 wt% and 1.5 wt% carbon, respectively, after drying at 393 K.

Fig. 1. TGA curves recorded during thermal treatment of catalysts in air flow.

In order to see the change of RFG during the drying process, IR was carried out for the 80%Co/SiO₂-C dried at 353 and 393 K, respectively. The IR spectra were shown in Fig. 2. A broad band in the range of 1300–1700 cm⁻¹ was observed for the 80%Co/SiO₂-C dried at 353 K, which could be assigned to the vibrations of aromatic ring and CH₂ in RFG [18,20]. This band was almost completely disappeared for the 80%Co/SiO₂-C dried at 393 K, indicating that most RFG was decomposed upon the drying at 393 K. In addition, two IR bands appeared at 570 and 670 cm⁻¹, which could be attributed to the vibrations of Co₃O₄ [21,22]. Thus, the loadings of cobalt in the Co/SiO₂ and Co/SiO₂-C after drying at 393 K were quite close since only little carbon remained in the Co/SiO₂-C.

Fig. 2. IR spectra for the 80%Co/SiO₂-C dried at 353 and 393 K, respectively.

2.2 Textural and structural properties of catalysts

Table 1 summarizes the surface areas and pore parameters of the catalysts before reduction and after the FTS reactions. The addition of RFG during the precipitation decreased the surface area, increased the pore size, and maintained the pore volume, which was very obvious for the catalysts after the FTS reactions. Specifically, the surface area decreased from 118 to 89 m²/g while the average pore size increased from 5.6 to 12.2 nm for the 60%Co/SiO₂ catalysts. Similarly, the surface area was decreased from 73 to 41 m²/g while the average pore size increased from 12.4 to 24.1 nm for the 80%Co/SiO₂ catalysts. Figure 3 shows the pore size distributions for the catalysts after the FTS

Fig. 3. Pore size distributions derived from the desorption isotherms of N₂ for the 60%Co/SiO₂ (1), 60%Co/SiO₂-C (2), 80%Co/SiO₂ (3), and 80%Co/SiO₂-C (4) after the FTS reactions.

reactions. It was clearly shown that the addition of RFG significantly increased the pore sizes. It has been reported that cobalt oxides located in mesopores were easier to reduce [23,24], and large pores favored the diffusion of heavy hydrocarbons formed as well as the diffusion of CO and H₂ in pores filled with liquid products [25–28]. Thus, the increase of pore sizes upon the addition of RFG would favor the hydrogenation of CO to heavy hydrocarbons during FTS.

The pores of the catalysts were usually filled with liquid products during the FTS reactions, and thus the reduced cobalt species were more or less protected from the oxidation when they were exposed to air. Figure 4 shows the XRD patterns for the catalysts after FTS reactions. A diffraction peak at $2\theta = 44.4^\circ$ for metallic Co was observed for all the catalysts. The width of this diffraction peak was used to estimate the average sizes of supported cobalt particles according to the Scherrer equation (see Table 2). The cobalt crystal sizes in the 60%Co/SiO₂ and 80%Co/SiO₂ were found to be about 13 and 16 nm, respectively, while they were decreased to about 11 and 13 nm, respectively, upon the addition of RFG. Thus, the presence of RFG during the precipitation decreased the cobalt particles sizes and improved the dispersion of Co on SiO₂. In addition, two diffraction peaks at $2\theta = 21.3^\circ$ and 23.7° were clearly seen for wax in the pores of used catalysts.

Table 1 Textural and structural properties of the Co/SiO₂ and Co/SiO₂-C catalysts before reduction and after the FTS reactions

Catalyst	C content ^a (wt%)	BET area (m ² /g)		Pore volume (cm ³ /g)		Average pore diameter (nm)	
		Fresh	After reaction	Fresh	After reaction	Fresh	After reaction
60%Co/SiO ₂	—	437	118	0.7	0.4	4.7	5.6
60%Co/SiO ₂ -C	1.5	362	89	0.9	0.5	9.2	12.2
80%Co/SiO ₂	—	231	73	0.7	0.3	8.9	12.4
80%Co/SiO ₂ -C	1.1	213	41	0.7	0.3	11.1	24.1

^aObtained by elemental analysis for the catalysts dried at 393 K.

Fig. 4. XRD patterns of the 60%Co/SiO₂ (1), 60%Co/SiO₂-C (2), 80%Co/SiO₂ (3), and 80%Co/SiO₂-C (4) after the FTS reactions.

Figure 5 displays the TEM images of the catalysts after FTS reactions. It was found that the sizes of cobalt particles in the 60%Co/SiO₂ and 80%Co/SiO₂ were estimated to be about 17 and 34 nm, respectively, while they were decreased to about 13 and 24 nm, respectively, in the 60%Co/SiO₂-C and 80%Co/SiO₂-C. Thus, the addition of RFG during the precipitation decreased the sizes of cobalt particles, consistent with the result of XRD. On the other hand, the images showed that the sizes of cobalt particles became more even in the Co/SiO₂-C catalysts, especially those in 60%Co/SiO₂-C.

The number of surface cobalt sites could be titrated by the adsorption of H₂ at 423 K [15,29], according to which

Fig. 5. TEM images of 60%Co/SiO₂ (a), 60%Co/SiO₂-C (b), 80%Co/SiO₂ (c), and 80%Co/SiO₂-C (d) after the FTS reactions.

the average particle sizes of cobalt could also be estimated. The sizes of cobalt particles (Table 2) were estimated to be about 52 and 46 nm, respectively, in the 60%Co/SiO₂ and 80%Co/SiO₂, while they were estimated to be about 40 and 35 nm, respectively, in the 60%Co/SiO₂-C and 80%Co/SiO₂-C. Table 2 summarizes the sizes of cobalt particles determined by XRD, TEM, and H₂ adsorption. The inconsistent results seemed to indicate the limitations of different methods for the determination of particle sizes of Co [17,23]. However, the trend was the same, i. e., the addition of RFG during the precipitation decreased the sizes of cobalt particles on SiO₂.

2.3 Reducibility and dispersion of supported cobalt

Figure 6 shows the TPR profiles for the catalysts. No clear reduction peaks were observed in the TPR curve of 60%Co/SiO₂ up to 750 K (see Fig. 6(1)), indicating that the strong interactions between Co and SiO₂ inhibited the reduction of supported cobalt. Two reduction peaks were observed for the 60%Co/SiO₂-C in the range of 500–900 K (Fig. 6(2)), which could be attributed to the sequential reductions from Co₃O₄ to CoO and then to Co [30–33]. However, the presence of RFG did not seem to change the reduction sequence of cobalt species in the 80%Co/SiO₂, but the intensity of the low temperature peak seemed increased a little. Thus, the addition of RFG during the precipitation favored the reduction of supported cobalt species.

Fig. 6. TPR profiles of the 60%Co/SiO₂ (1), 60%Co/SiO₂-C (2), 80%Co/SiO₂ (3), and 80%Co/SiO₂-C (4) dried at 393 K.

Table 2 Results of chemisorption of H₂ and O₂ on the catalysts with the sizes of supported Co particles determined by different methods

Catalyst	Adsorption (mol/g)		Dispersion (%)	Reducibility (%)	Diameter of Co (nm)		
	H ₂	O ₂			XRD	H ₂ adsorption	TEM
60%Co/SiO ₂	49	3522	1.9	51.9	13	52	17
60%Co/SiO ₂ -C	71	3915	2.4	57.6	11	40	13
80%Co/SiO ₂	81	5184	2.1	57.3	16	46	34
80%Co/SiO ₂ -C	118	5830	2.7	64.4	13	35	24

The adsorption of H_2 and O_2 was carried out at 423 and 673 K, respectively, on the reduced catalysts and the dispersion and reducibility of supported cobalt were derived accordingly. Table 2 summarizes the information obtained by the adsorption of H_2 and O_2 . It was shown that the reducibility and dispersion of cobalt were about 51.9% and 1.9%, respectively, for the 60%Co/SiO₂, while they were increased to about 57.6% and 2.4%, respectively, for the 60%Co/SiO₂-C. Similarly, the reducibility and dispersion of cobalt were about 57.3% and 2.1%, respectively, for the 80%Co/SiO₂, and they were increased to about 64.4% and 2.7%, respectively, for the 80%Co/SiO₂-C. Thus, the addition of RFG during the precipitation promoted the reducibility and dispersion of supported cobalt, consistent with the results of XRD, TEM, and TPR.

It was reported that cobalt silicate could be easily formed during the precipitation for the preparation of Co/SiO₂ catalysts, and they could be reduced only at the high temperatures [21,22,34]. Thus, the formation of cobalt silicate should be avoided so that more cobalt could be reduced to produce more cobalt sites for FTS reactions. In this work, IR was employed for the catalysts after the FTS reactions to detect cobalt silicate. Figure 7 shows the results. A strong and broad band around 1020 cm⁻¹ was seen for all the catalysts, which could be assigned to the stretching vibrations of Si–O–Co in cobalt silicate [21,34], indicating the presence of large amount of cobalt silicate in the used Co/SiO₂ catalysts. However, this band was weaker for the Co/SiO₂-C than for the Co/SiO₂, indicating that the addition of RFG during the precipitation inhibited the formation of cobalt silicate, and thus promoted the reduction of supported cobalt.

Fig. 7. IR spectra of the catalysts after the FTS reactions.

2.4 Surface acidity and basicity

Previous studies revealed that the surface acid-base properties significantly affected the activity and selectivity of

FTS reactions [35,36]. Microcalorimetric adsorptions of NH_3 and CO_2 were used to probe the surface acid-base properties of catalysts studied in this work. Figure 8(a) shows the results for the adsorption of ammonia at 423 K on the catalysts reduced and evacuated at 773 K. The initial heat and uptake were measured to be about 90 kJ/mol and 650 $\mu\text{mol/g}$, respectively, for the adsorption of NH_3 on the 60%Co/SiO₂, indicating that the catalyst possessed significant amount of surface acid sites, probably owing to the presence of cobalt silicate [22]. The initial heat and uptake were measured to be about 91 kJ/mol and 760 $\mu\text{mol/g}$, respectively, for the adsorption of NH_3 on the 60%Co/SiO₂-C, similar to those on the 60%Co/SiO₂. The initial heat and uptake were measured to be about 83 kJ/mol and 508 $\mu\text{mol/g}$, respectively, for the adsorption of NH_3 on the 80%Co/SiO₂, while the corresponding values were about 85 kJ/mol and 532 $\mu\text{mol/g}$, respectively, for the 80%Co/SiO₂-C. These results indicated that the addition of RFG during the precipitation did not affect the surface acidity. However, the surface acidity was stronger on 60%Co/SiO₂ than on 80%Co/SiO₂, probably owing to that more cobalt silicate was present in 60%Co/SiO₂ than in 80%Co/SiO₂ (Fig. 7).

Fig. 8. Differential heats versus coverage for the adsorption of NH_3 (a) and CO_2 (b) at 423 K over the catalysts reduced at 773 K.

The results of microcalorimetric adsorption of CO_2 at 423 K on the reduced catalysts are shown in Fig. 8(b). The uptakes were low and no heat was measured for the adsorption of CO_2 on the catalysts, indicating that the Co/SiO₂ and Co/SiO₂-C samples essentially did not possess any surface basicity. It was fortunate since surface basicity was unfavorable for the FTS reactions [37,38].

Thus, the addition of RFG during the precipitation did not affect the surface acidity and basicity, according to the re-

sults of microcalorimetric adsorption of NH₃ and CO₂, and the effect of surface acidity and basicity of the catalysts on the FTS reactions could be excluded.

2.5 Microcalorimetric adsorption of H₂ and CO

Apparently, the adsorptions of CO and H₂ on cobalt surfaces are important steps for FTS reactions. Thus, microcalorimetric adsorptions of H₂ and CO on the catalysts were performed. Figure 9(a) shows the results of microcalorimetric adsorption of H₂ at 423 K for the catalysts. The initial heat and uptake were measured to be about 70 kJ/mol and 63 μ mol/g, respectively, for the adsorption of H₂ on the 60%Co/SiO₂. The initial heat was almost not changed while the uptake was increased to about 82 μ mol/g for the adsorption of H₂ on the 60%Co/SiO₂-C. The initial heat and uptake were measured to be about 73 kJ/mol and 127 μ mol/g, respectively, for the adsorption of H₂ on the 80%Co/SiO₂, and the uptake increased to about 155 μ mol/g while the initial heat was not changed for the adsorption of H₂ on the 80%Co/SiO₂-C.

Fig. 9. Differential heats versus coverage for the adsorption of H₂ (a) and CO (b) over the catalysts at 423 and 303 K, respectively.

Figure 9(b) shows the results of microcalorimetric adsorption of CO at 303 K for the catalysts. Similar initial heats (about 90 kJ/mol) were generated for the adsorption of CO on the catalysts, indicating the similar electron densities of surface cobalt atoms in these catalysts [39]. However, the uptakes were increased for the adsorption of CO on Co/SiO₂-C as compared to that on Co/SiO₂, due to the increased surface cobalt sites. Thus, the addition of RFG during the precipitation did not change the chemical properties of surface Co in the Co/SiO₂ catalysts, but increased the numbers of Co active sites for the FTS reactions.

2.6 Catalytic performance

Table 3 summarizes the catalytic performance of the catalysts for FTS reactions. It was shown that the conversion of CO and selectivity for C₅₊ were about 22.6% and 81.6%, respectively, on the 60%Co/SiO₂ at 473 K. The corresponding values were increased to about 63.8% and 89.5%, respectively, on the 60%Co/SiO₂-C, indicating that the addition of RFG during the precipitation significantly enhanced the activity and selectivity for heavy hydrocarbons on the 60%Co/SiO₂. The conversion of CO and selectivity for C₅₊ were about 83.0% and 85.1%, respectively, on the 80%Co/SiO₂ at 473 K, and they were increased to about 87.1% and 91.1%, respectively, on the 80%Co/SiO₂-C at 463 K. Again, the addition of RFG during the precipitation increased the activity and selectivity for C₅₊ on the 80%Co/SiO₂.

ZrO₂ has been considered to be an effective promoter of Co catalysts for the production of heavy hydrocarbons from syngas [8,40]. Our previous study also showed that the activity and selectivity for C₅₊ were significantly enhanced on Co promoted by ZrO₂ [17]. In fact, excellent FTS performance was obtained on the 80%Co-8%ZrO₂/SiO₂ [17], and the corresponding data were adopted for comparison in Table 3. It is seen that the activity and selectivity for C₅₊ were similarly high on the 80%Co/SiO₂-C as on the 80%Co-8%ZrO₂/SiO₂. Thus, the addition of RFG during the precipitation might be an effective way in promoting the FTS performance of the Co/SiO₂ catalysts to produce heavy hy-

Table 3 Catalytic performance of Co/SiO₂ and Co/SiO₂-C catalysts for the FTS reactions

Catalyst	T/K	Conversion (%)	Selectivity (%)			
			CO ₂	CH ₄	C ₂ -C ₄	C ₅₊
60%Co/SiO ₂	473	22.6	0.0	12.4	6.0	81.6
60%Co/SiO ₂ -C	473	63.8	0.8	8.6	1.9	89.5
80%Co/SiO ₂	473	83.0	1.9	12.0	2.9	85.1
80%Co/SiO ₂ -C	463	87.1	1.0	7.3	1.6	91.1
	473	99.5	4.5	14.3	2.6	83.1
80%Co-8%ZrO ₂ /SiO ₂ [17]	463	71.4	2.2	8.2	1.3	90.5
	473	90.7	3.5	9.5	2.0	88.5

Reaction conditions: *p* = 2 MPa, GHSV = 2000 ml/(g·h).

drocarbons from syngas.

3 Conclusions

Addition of resorcinol formaldehyde resin gel (RFG) during the precipitation for the preparation of highly loaded Co/SiO₂ catalysts was found to be effective in promoting the reducibility and dispersion of supported cobalt, leading to the more surface active cobalt sites of the catalysts, and therefore higher activity for the Fischer-Tropsch reactions to produce heavy hydrocarbons. Although a large amount of RFG was added during the precipitation, little carbon was remained in the Co/SiO₂ catalysts after drying at 393 K owing to the decomposition of RFG during the drying process. However, the presence of RFG during the precipitation might reduce the contact of cobalt cations with silica, decreasing the formation of cobalt silicate that was difficult to reduce. In addition, the presence of RFG might result in the formation of mesopores in the catalysts that benefited the diffusion of reactants and products. No other effects were observed on the catalysts upon the addition of RFG for the preparation of Co/SiO₂ catalysts. The surface acidity and basicity were not affected, neither the electronic density of cobalt surfaces. The only positive effects brought about by the addition of RFG were the significantly increased surface cobalt active sites and pore sizes that were the two important factors in determining the FTS activity and selectivity. In fact, the 80%Co/SiO₂-C was as active and selective as the 80%Co-8%ZrO₂/SiO₂ (an excellent catalyst reported in Ref. [17]) for the synthesis of heavy hydrocarbons from syngas.

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