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The formation of Co_2C species in activated carbon supported cobalt-based catalysts and its impact on Fischer–Tropsch reaction

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The cobalt carbide (Co_2C) species was formed in some activated carbon supported cobalt-based (Co/AC) catalysts during the activation of catalysts. It was found that the activity of Fischer–Tropsch reaction over Co-based catalysts decreased due to the formation of cobalt carbide species. Some promoters and pretreatment of activated carbon with steam could restrain the formation of cobalt carbide.

KEY WORDS: cobalt carbide species; Fischer–Tropsch synthesis; cobalt-based catalysts; activated carbon.

1. Introduction

Fischer–Tropsch synthesis (FTS) is a most important way to synthesize clean, high quality oil fraction without sulphur from coal or natural gas and it is boomed by energy crisis and environment protection [1,2]. Cobalt-based catalyst is considered to be good catalysts for FTS because of its high activity, high stability, relatively low cost and low water shift reaction [3,4]. To enhance the activity of cobalt catalysts the active compound precursors were dispersed on porous carriers with SiO_2, Al_2O_3 and TiO_2 being the most frequently used. The interaction between cobalt and the supports leads to the formation of Co-support compounds including Co_2SiO_4, $COAl_2O_4$ and $CoTiO_3$ compounds, which can be only reduced or decomposed at elevated temperatures (>1000 K), and declines the activity of catalysts in FTS [5–9].

There are a few studies worked on the cobalt-based catalysts supported on activated carbon for FTS [10–13], but few research figures out whether there is Co-support compound existing in activated carbon supported cobalt-based catalysts and points out its impacts on the performance of F–T reaction. We studied the property of activated carbon supported cobalt-based (Co/AC) catalysts in FTS previously, and found that the catalyst had restricted chain producibility, the products of FTS major in naphtha and diesel distillates [14,15]. Our previous studies indicated that the doping of ZrO_2 could increase CO conversion, detract the formation of methane and enhance the selectivity of long chain products over the Co/AC catalysts [16,17].

This paper presents the performance of potassium, manganese, chromium-promoted Co/AC catalysts and a catalyst made from steam-pretreated activated carbon at high temperature. The aim of this paper will investigate the formation of the Co_2C species in some Co/AC catalyst and its impacts on the catalytic behaviors of CO hydrogenation over Co-based catalysts.

2. Experimental

2.1. Catalysts preparation

The activated carbon used in this study was made from almond materials. Steam pretreatment of the activated carbon was conducted with steam for 3 h at 1123 K. $Co(NO_3)_2\cdot 6H_2O$ (AR) used as the precursor of cobalt, KNO_3 (AR), $Mn(NO_3)_2$ (50% solution) and $Cr(NO_3)_3\cdot 9H_2O$ (AR) used as the precursors of promoters, respectively. The catalysts were prepared by aqueous incipient wetness co-impregnation of activated carbon with aqueous solutions of cobalt nitrate and with or without the solution of promoter precursor, with the amount of cobalt to be 15% by weight. The wet samples were dried at room temperature for several days, then baked at 363 K for 2 h in air and finally at 473 K for 8 h under pure N_2. The catalysts with and without co-impregnated promoters were denoted as 15CoXM/AC (X: the amount of promoter by weight, M = K, Mn, Cr) and 15Co/AC, respectively. The catalyst made from the steam-pretreated activated carbon was denoted as 15Co/AC-S.

2.2. Fischer–Tropsch reaction

The testing apparatus consisted of a fixed bed tubular reactor with an external heating system. The reactor was made of stainless steel with 350 mm length, 10 mm inner diameter. The catalysts were *in situ* activated in a flow of

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H_2 at 623 K for 19 h before CO hydrogenation. Then the syngas ($H_2/CO = 2$) was fed into the catalyst bed under conditions of 503 K, 2.5 MPa and GHSV = 500 h^{-1}. The effluent passed through a high-pressure gas–liquid separator that inserted in an ice–water bath. After 25 h stabilization, the liquid products for another 50 h were off-line analysed by HP-6890 GC with an HP-5 (cross linked 5% PH ME siloxane) capillary column and FID detector. The tail gas was on-line analyzed by HP-6890 GC with a Porapack-Q column and TCD detector.

2.3. Catalysts characterization

All the used samples were washed with CS_2 solution before characterization in order to clean the produced liquid products in the catalysts. The catalyst of 15Co/AC without FTS reaction, which was activated under the same condition with the same procedures and then passivated in air, was denoted as 15Co/AC-P. The X-ray diffraction (XRD) patterns of catalysts were conducted in air on X′ Pert PRO diffractometer (PANalytical) using $CuK_{\alpha 1}$ radiation at 40 kV and 40 mA and were recorded from 35° to 60° at a scanning rate of 0.02°/s. The particle sizes of cobalt particles were calculated by the Scherer equation using cubic cobalt [111]: $d = B\lambda/\beta_{1/2}\cos\theta$ where λ is the X-ray wavelength, B is the particle shape factor, and $\beta_{1/2}$ is the full width at half-maximum (in radians) of the cobalt line.

X-ray photoelectron spectroscopy (XPS) measurement was performed using a VG ESCA LABMK II spectrometer. The instrument typically operated at pressure below 1.33×10^{-7} Pa and AlK_α line (1486.6 eV) was used. The binding energy of all spectra was calibrated with respect to the C_{1s} line at 284.6 eV.

3. Results and discussion

3.1. Performance of Fischer–Tropsch reaction

Table 1 shows the performance of Fischer–Tropsch reaction over various Co/AC catalysts. The FTS activity of 15Co/AC-S was the highest in all catalysts (ca. 62.2 mmol CO g Co^{-1} h^{-1}), and the selectivity of C_5^+ could reach ca. 73.2%. Comparing with data of 15Co/AC catalysts, it could be concluded that the pretreatment of activated carbon with steam at high temperature could greatly enhance CO hydrogenation activity of Co-based catalyst. However, the activity decreased from 28.4 to 10.6 mmol CO g Co^{-1} h^{-1} and the selectivity of CH_4 increased from 13.9% to 34.4% when 1.0 wt.% *K* was doped on 15Co/AC catalysts.

Table 1
The catalytic behavior of Fischer–Tropsch reaction over various Co/AC catalysts

Catalysts	Activity mmol g Co^{-1} h^{-1}	Selectivity, mol.%		
		Methane	C_2-C_4	C_5^+
15Co/AC	28.4	13.9	20.7	62.0
15Co/AC-S	62.2	14.8	11.9	73.2
15Co1K/AC	10.6	34.4	24.4	39.4
15Co1Mn/AC	20.2	5.9	14.0	80.0
15Co3Mr/AC	39.2	18.4	20.1	61.3
15Co5Mn/AC	50.9	27.3	19.7	52.9
15Co1Cr/AC	50.2	18.3	16.8	64.7
15Co3Cr/AC	58.6	20.9	16.3	62.7
15Co5Cr/AC	56.3	20.6	15.0	64.3
15Co7Cr/AC	54.5	27.8	14.8	55.8

Reaction conditions: $T = 503$ K, 2.5 MPa, $H_2/CO = 2$ and GHSV = 500 h^{-1}.

It is interesting to find that the activity of F–T reaction first decreased from 28.4 to 20.2 mmol CO g Co^{-1} h^{-1}, and the selectivity of CH_4 decreased from 13.9% to 5.9% when 1 wt.% Mn were added into Co/AC catalysts, then the activity increased surprisingly when more than 3 wt.% Mn was doped into Co/AC catalysts. For example, the activity of 15Co5Mn/AC catalysts increased up to 50.9 mmol CO g Co^1 h^{-1}, while the selectivity of CH_4 increased unfortunately up to 27.3%.

As for the Cr-promoted catalysts, the addition of Cr could enhance the activity of Co/AC catalysts. It appears that the activity of 15Co3Cr/AC was the highest in Cr-promoted catalysts, which reached to 58.6 mmol CO g Co^{-1} h^{-1} that almost was equal to the level of 15Co/AC-S. Meanwhile, the selectivity of CH_4 also increased with the addition of Cr. Therefore, it could be concluded that the doping of various promoters and steam-pretreatment at high temperature could change the activity and the product distribution of Co/AC catalysts in FTS.

3.2. XRD measurement

Figures 1 and 2 demonstrate the XRD patterns of various used and passivated Co-based catalysts. The Co species existed in four kinds of compounds according to the XRD patterns, which included α-Co, cubic Co, Co_2C and Co_3O_4 (figure 1). There appeared [100] and [101] for α-Co species, [111] and [200] for cubic Co, [311] for Co_3O_4 and there were three peaks belonged to Co_2C species in the XRD patterns.

It is obvious that the apparent difference between 15Co/AC and 15Co/AC-S was whether there were the diffraction peaks of Co_2C species. There were some strong peaks that attributed to Co_2C species in the XRD pattern of 15Co/AC samples, while no Co_2C species could be detected except for the peaks that ascribed to cubic Co species in 15Co/AC-S (see figure 1b). The Co particle sizes of used Co-based catalysts, the relative intensity of Co_2C species to corresponding cubic Co species and the relative intensity of cubic Co to that in 15Co/AC are summarized in table 2. From the data shown in table 2, it was found that the Co metallic

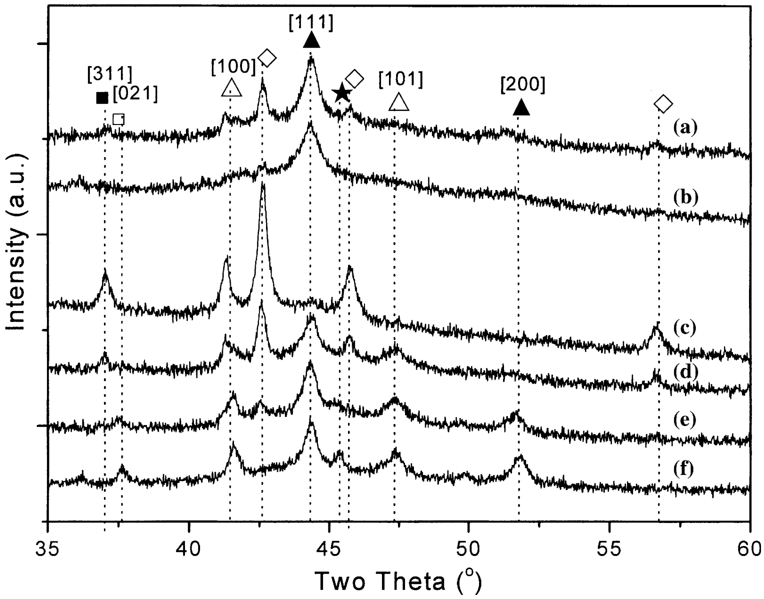

Figure 1. XRD patterns of used Co-based catalysts (a) 15Co/AC; (b) 15Co/AC-S; (c)15Co1K/AC; (d) 15Co1Mn/AC; (e) 15Co3Mn/AC; (f) 15Co5Mn/AC. ■: Co_3O_4; □: MnO; ▲: Cubic Co; △: α-Co; ★: Mn_5C_2; ♦: Co_2C.

particle size of 15Co/AC-S was bigger than that of 15Co/AC catalysts. Based on the results of CO hydrogenation and XRD measurements of 15Co/AC and 15Co/AC-S catalysts, it could be concluded that the increase of catalytic activity was mainly relative to whether existence of Co_2C species in Co-based catalysts. So it could be deduced that the formation of Co_2C species reduced the activity in FTS, which is due to the low density of metallic Co active sites and the decrease of accessible Co atoms available for F–T reaction [18].

Meanwhile, figure 1c shows that the Co species existed in the 15Co1K/AC catalyst majored in the format of Co_2C, α-Co and Co_3O_4. It is appears that the XRD intensity of Co_2C species greatly increased when K was doped in 15Co/AC samples. Therefore, it could be extrapolated from above findings that low CO conversion of FTS was obtained over 15Co1K/AC catalysts. The low CO conversion of 15Co1K/AC catalysts further proven an inversion impact of Co_2C species formation on the performance of Co-based catalysts in F–T reaction. This was also the reason why steam-pretreatment of activated carbon and doping of K had an opposite effect on the activity of 15Co/AC catalyst in FTS.

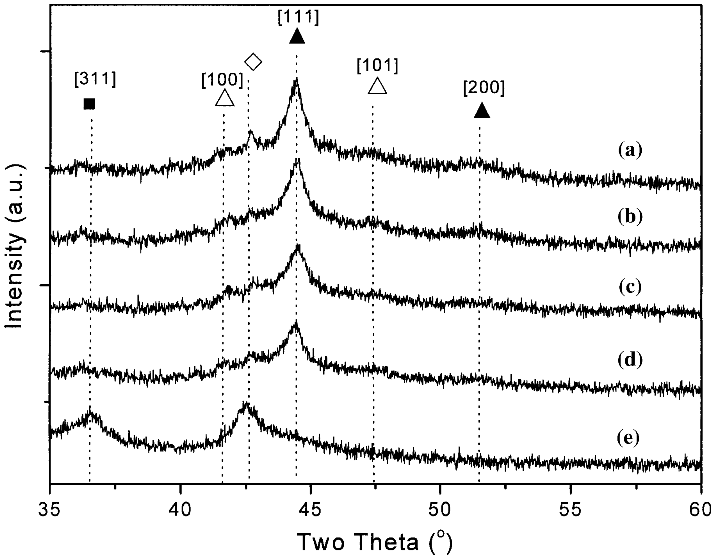

Figure 2. XRD patterns of used Cr-promoted catalysts and passivated catalyst (a) 15Co1Cr/AC; (b) 15Co3Cr/AC; (c) 15Co5Cr/AC; (d) 15Co7Cr/AC; (e) 15Co/AC-P. ■: Co_3O_4; △: α-Co; ▲: cubic Co; ♦: Co_2C.

For the XRD patterns of Mn-promoted catalysts, the relative intensity of the peaks belong to α-Co [100] and [101], cubic Co [111] and [200] which shown in figure 1d–f increased while those of the peaks ascribed to Co_2C decreased with the amount of Mn doping. It is obvious from the data shown in table 2 that the ratio of the intensity of Co_2C species at $2\theta = 42.5°$ to that of cubic Co [111] species at $2\theta = 44.3°$ in 15Co1Mn/AC sample was larger than that of 15Co/AC catalysts, which caused the decrease of catalyst in F–T reaction. However, the diffraction peaks of Co_2C species almost disappeared when 5 wt.% of Mn was doped into 15Co/AC samples, consequently, CO conversion of 15Co5Mn/AC catalysts was the highest one in all Mn-promoted catalysts. Therefore, the doping of Mn promoter could change the capability of Co_2C formation in Co/AC catalysts. In addition, it was found that the dispersion of Co particles in Co/AC catalysts decreased when Mn was doped into the Co-based catalysts.

Table 2
The Co particle sizes of catalysts and the ratio of the intensity of Co_2C/cubic Co and relative intensity of cubic Co species

Catalysts	Co particle size (nm)	Ratio of Co_2C/cubic Co[a]	Relative intensity of cubic Co[b]
15Co/AC	23.0	0.76	1
15Co/AC-S	63.4	–	0.87
15Co1K/AC	–	∞	–
15Co1Mn/AC	23.1	1.22	0.68
15Co3Mn/AC	42.2	0.34	0.77
15Co5Mn/AC	36.2	–	0.77
15Co1Cr/AC	42.2	0.31	0.99
15Co3Cr/AC	63.4	–	0.85
15Co5Cr/AC	42.2	–	0.61
15Co7Cr/AC	21.1	–	0.59

[a] The ratio of the intensity of Co_2C at $2\theta = 42.5°$ to that of the cubic Co [111] in the same catalyst.
[b] The ratio of the intensity of cubic Co [111] in Co-based catalysts and that in 15Co/AC catalysts.

A similar restraining effect of Cr on the formation of Co_2C species could also be observed in Cr-promoted Co/AC catalysts. The diffraction peaks of Co_2C at $2\theta = 42.5°$ species disappeared when the loading of Cr addition reached more than 3 wt.% (see figure 2b–d). From the data shown in table 2, it was found that the Co particle sizes of Cr-promoted Co/AC catalysts first increased from 23.0 up to 63.4 nm when the amount of Cr doping reached 3.0 wt.%, then decreased from 63.4 down to 21.1 nm when 7.0 wt.% of Cr was doped into Co/AC samples. Concurrently, the activity of CO hydrogenation first enhanced from 28.4 up to 58.6 mmol CO g Co^{-1} h^{-1} when 3.0 wt.% was added into Co/AC catalysts, then descended from 58.6 to 54.5 mmol CO g Co^{-1} h^{-1} with the continuous increase of Cr loading up to 7.0 wt.% (see table 1).

Co_2C species could also be found in the passivated 15Co/AC samples (figure 2e), which implied that the Co_2C species were formed during the reduction of catalysts at 623 K under hydrogen atmosphere. The temperature of 583–663 K was favorable to the formation of Co_2C species [19].

3.3. XPS measurement

Figure 3 shows the C_{1s} XPS spectra of used 15Co1K/AC and 15Co/AC-S samples. There were two peaks centered at 283.2 and 284.6 eV in the C_{1s} XPS spectra fitted using Gaussian method of 15Co1K/AC catalyst

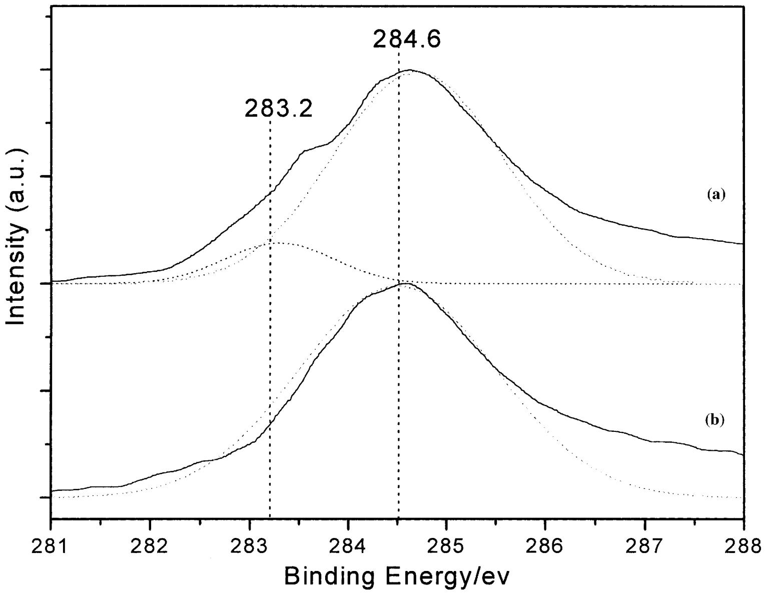

Figure 3. C_{1s} XPS spectra of used Co-based catalysts (a) 15ColK/AC; (b) 15Co/AC-S.

(figure 3a). The peak at 283.2 eV corresponded to the binding energy of C_{1s} in Co_2C species, the peak at 284.6 eV attributed to that of carbon–carbon bonds [20]. It is obvious that C_{1s} peak of Co_2C species at 283.2 eV could not be observed in the 15Co/AC-S samples which shown figure 3b.

In summary, the evidence for the presentation of Co_2C species formed during the reduction at 623 K in the Co/AC catalysts was obtained by XRD and XPS measurements, and the formation of Co_2C species reduced the activity of CO hydrogenation over the Co-based catalysts. The doping of promoters, such as Mn and Cr, and pretreatment of the activated carbon with steam could restrain the formation of Co_2C species, consequently, increase the activity of CO hydrogenation.

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