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Article

Aqueous-phase Fischer-Tropsch synthesis catalyzed by cobalt nanoparticles

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ABSTRACT

Converting syngas to hydrocarbons at much lower temperature with high efficiencies, namely aqueous-phase Fischer-Tropsch synthesis, has great potentials. In this article, we synthesized aqueous-stable cobalt nanoparticles for the reaction. The catalyst has an activity of $7.4 \times 10^{-7} \text{ mol}_{\text{CO}} \text{ g}_{\text{Co}}^{-1} \text{ s}^{-1}$ and C_{5+} selectivity of 40%, which is the best result in cobalt-catalyzed aqueous-phase Fischer-Tropsch synthesis. The catalyst is recyclable after reaction. We also characterized the catalyst by transmission electron microscopy, X-ray diffraction, and in-situ infrared observation to study the catalyst reconstruction process and boron contamination.

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1. Introduction

The Fischer-Tropsch synthesis, a collection of chemical reactions which convert a mixture of carbon monoxide and hydrogen into liquid hydrocarbons, plays an important role in the indirect syngas liquefaction process and can convert coals, nature gas, biomass, and other energy sources into fuels and valuable chemicals [1–5]. In the past 80 years, supported and non-supported metal catalysts were studied extensively and found that some transition metals such as iron, cobalt, and ruthenium show good catalytic activity for Fischer-Tropsch synthesis [6–10]. Cobalt-based catalysts give the optimal choice for Fischer-Tropsch synthesis due to their good stability, high heavy hydrocarbon selectivity, and relatively low cost [8–10]. There are not only a number of industrialized examples on cobalt-based catalysts but also many laboratory researches on catalysts, supporters, reaction conditions, and other variables [10–12]. Noble metal promoters such as Pt, Ru, and Pd for Co-based catalysts are becoming attractive [13]. Moreover,

people successfully adjusted the selectivity of reactions by optimizing the reactors and coupling multi-step reactions [14].

Because Fischer-Tropsch synthesis is highly exothermic, the reaction happening at relatively low temperatures would be more thermodynamically favorable, cleaner, and more environmental benign [15]. In our previous research, we achieved efficient aqueous-phase Fischer-Tropsch synthesis at a low temperature of 150 °C (200 °C or above for traditional processes) by using 2.0 nm of Ru nanoparticles as catalyst, which was dispersed in water [16]. The catalyst showed a high stability in a flow system even after 240 h [17]. Quek et al. [18] later found that over 70% of oxygen-containing products could be obtained using surface-oxidized Ru nanoparticles. We also revealed that aqueous-phase Fischer-Tropsch synthesis was able to provide a platform for studying anionic additives as promoters [19]. All above examples exhibit significant advantages of aqueous-phase Fischer-Tropsch synthesis. Nevertheless, due to the high cost and scarce of Ru, aqueous-phase Fischer-Tropsch synthesis using Fe- and Co-based catalysts is more

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practical. Although FeC_x as active species of Fe are too unstable in water to catalyze the synthesis, our group and Li's group individually realized Fe nanoparticles catalyzed poly(ethylene glycol)-phase Fischer-Tropsch synthesis [20,21]. Co-based catalysts are more stable in water than Fe ones, which increases the possibility of successful Co-catalyzed aqueous-phase Fischer-Tropsch synthesis. There are only a handful of reports on Co-catalyzed liquid-phase Fischer-Tropsch synthesis so far. For examples, Silva et al. [22] achieved the catalytic activity of $1.9 \times 10^{-7} \text{ mol}_{\text{CO}} \text{ g}_{\text{Co}}^{-1} \text{ s}^{-1}$ by dispersing Co-based catalyst in [Bmim][NTf₂] at 210 °C. Our group achieved the catalytic activity of $6.1 \times 10^{-6} \text{ mol}_{\text{CO}} \text{ g}_{\text{Co}}^{-1} \text{ s}^{-1}$ by dispersing Co nanoparticles in squalane at 200 °C [23]. However, it is rare to report exclusively Co nanoparticles-catalyzed aqueous-phase Fischer-Tropsch synthesis with high activity.

In this work, aqueous-phase stable Co nanoparticles by using LiBEt_3H as reducing agent were prepared and employed it in aqueous-phase Fischer-Tropsch synthesis at 150 °C. The Co nanoparticles prepared by other reducing agents just showed poor catalytic activity. We also compared the properties of various catalysts, especially for the catalysts reduced by LiBEt_3H and NaBH_4 .

2. Experimental

2.1. Catalyst preparation

For the preparation of Co nanoparticles reduced by LiBEt_3H , 30 mL THF dissolved 0.26 g CoCl_2 and 0.50 g SB3-12 (*n*-dodecyl-*N,N*-dimethyl-3-ammonio-1-propanesulfonate, as a protective agent), then 5 mL LiBEt_3H in THF solution (1 mol/L) was slowly injected by syringe with well stirring. The mixed solution quickly turned to black from blue, which indicated the reduction of cobalt. The reaction was quenched by 10 mL of ethanol after 10 min, followed by separation of nanoparticles with a permanent magnet. After washing twice with ethanol and then twice with water, nanoparticles were dispersed in water, which contained 2.20 g of PVP (polyvinylpyrrolidone, as nanoparticle aqueous phase protective agent) and then was ready for using. It was referenced as Co- LiBEt_3H .

For the preparation of Co nanoparticles reduced by NaBH_4 , 30 mL water dissolved 0.50 g $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ and 2.20 g PVP, then 0.40 g of NaBH_4 was added with well stirring. The mixed solution quickly turned to black from red, which indicated the reduction of cobalt. The nanoparticles were separated by a permanent magnet. After washing twice with water, nanoparticles were dispersed in water, which contained 2.20 g of PVP and then was ready for use. It was referenced as Co- NaBH_4 .

The preparation of Co nanoparticles by thermal reduction with N_2H_4 , $\text{LiAl}(\text{O}-t\text{Bu})_3\text{H}$, KH or ethylene glycol and thermal decomposition of $\text{Co}_2(\text{CO})_8$ are followed in literatures [24–27].

All above synthetic processes were operated under the protection of N_2 .

2.2. Characterization of catalysts

Transmission electron microscopy (TEM) of nanoparticles

was performed using a Tecnai F-30 electron microscope with working voltage of 300 kV. To prepare the testing sample, nanoparticles were first diluted in deionized water under the ultrasonication for 5 min, and then a drop of solution was placed on an ultrathin carbon film coated copper grid. The statistical quantity of particle size distribution of each sample was over 200 particles.

X-ray powder diffraction (XRD) measurements were performed using a Rigaku D/MAX-2400 X-ray diffractometer with Cu anode, K_α radiation ($\lambda = 0.154 \text{ nm}$), voltage of 30 kV, current of 100 mA, 2θ scan range of 30° – 70° , scan rate of $2^\circ/\text{min}$, and step size of 0.02° . Before processing to test, nanoparticles were separated by magnets, washed with water twice, and then dried under vacuum.

The amounts of Co and B in samples were determined by inductively coupled plasma atomic emission spectrometry (ICP, Perkin Elmer Optima 2000 DV). The samples were dissolved in HNO_3 and HCl.

The Fourier-transformed infrared spectroscopy (FTIR) of CO absorption of catalysts was performed at 150 °C and 3 MPa. The spectra were collected by a Bruker TENSOR 27 infrared spectrometer with resolution of 2 cm^{-1} and acquisition times of 64.

2.3. Evaluation of catalysts

The performance of Co nanoparticles for Fischer-Tropsch synthesis was examined in a closed stirred reactor. Co nanoparticles was dispersed in 40 mL of water and then transferred into the stainless steel reactor. After purging the reactor by N_2 three times, 3.0 MPa of syngas ($\text{CO}:\text{H}_2:\text{Ar} = 32:64:4$) was re-filled. Fischer-Tropsch synthesis performance was measured at designated temperatures under stirring (800 r/min) until the total pressure decreased to 2.0–2.5 MPa (corresponding to a CO conversion of about 20%–30%). Except for the cases of very slow reaction rates, the reaction time required was in the range of 24–48 h.

As the reaction temperature returned to normal, the reactor was connected to a gas chromatograph (GC) to analyzed gas products. Then to the reactor 20.0 mg of decalin as internal standard and 10 mL of cyclohexane as extraction agent were injected. After stirring at 150 °C for 2 h, the reactor was cooled to room temperature and the cyclohexane layer was analyzed by GC to determine the liquid products.

In the recycle experiments, the Co nanoparticles were separated by magnet and then washed with deionized water twice before dispersed in the water containing 2.20 g of PVP and transferred to the stainless steel reactor for next round of reaction. The entire process was under the protection of nitrogen.

3. Results and discussion

3.1. Particle size distributions of Co nanoparticles

The TEM results of various Co catalysts are shown in Figs. 1–3. In Fig. 1 the TEM images and size distribution of Co- LiBEt_3H catalyst before and after use for Fischer-Tropsch

Fig. 1. TEM images and size distribution for Co-LiBEt₃H nanoparticles. (a) Before reaction; (b) After 1st reaction; (c) After 2nd reaction.

synthesis are shown. It's found that the average particle size of as-prepared Co nanoparticles before reaction is 8.3 nm (see Fig. 1(a)). After 1st reaction, there are a certain physical aggregations due to the wrap of products. The average particle size is 5.9 nm, which means a reconstruction of nanoparticles under the reaction condition. But the average particle size of nanoparticles almost remains unchanged after repeated reactions. The average particle size is 5.7 nm after 2nd recycle reaction, which exhibited a good stability of Co nanoparticles.

As for Co-NaBH₄ nanoparticles, shown in Fig. 2, there is a significant change before and after reaction. The average particle size is 14 nm with a broad distribution before reactions (Fig. 2(a)), which changes to only be 3.1 nm after reactions (Fig. 2(b)). In addition, Co-NaBH₄ nanoparticles lose their magnetism after reaction so that they fail to be recycled by magnets.

The TEM images of Co nanoparticles reduced by N₂H₄, LiAl(O-*t*Bu)₃H, and KH are shown in Fig. 3. Because reduced

nanoparticles seriously aggregate to too large pellet structure to be dispersed well, a flocculent form exists after preparation so that it is unsuitable to serve as catalysts for Fischer-Tropsch synthesis. As for the Co catalysts prepared by thermal reduction of ethylene glycol or thermal decomposition of Co₂(CO)₈ (Fig. 4), overlarge particle sizes, 340 and 31 nm, respectively, are obtained due to the employment of the low-protective stabilizer (SB3-12) and high synthesis temperature, which are not suitable for Fischer-Tropsch synthesis.

3.2. Catalytic performance of catalysts for Fischer-Tropsch synthesis

The catalytic performance of various Co nanoparticle catalysts for Fischer-Tropsch synthesis is listed in Table 1. Co-LiBEt₃H shows a high catalytic activity, i.e. at 130 °C the activity is significant; at 150 °C the activity is 7.4 × 10⁻⁷ mol_{Co} g_{Co}⁻¹ s⁻¹, which is similar to the activity of Co/Al₂O₃ at 190 °C

Fig. 2. TEM images and size distribution for Co-NaBH₄ nanoparticles. (a) Before reaction; (b) After reaction.

Fig. 3. TEM images of Co nanoparticles reduced by N_2H_4 (a), $\text{LiAl}(\text{O}-t\text{Bu})_3\text{H}$ (b), and KH (c).

Fig. 4. TEM images and size distribution of Co nanoparticles prepared by thermal reduction of ethylene glycol (a) and thermal decomposition of $\text{Co}_2(\text{CO})_8$ (b).

reported by Bechara et al. [28]; the activity increases to $1.3 \times 10^{-6} \text{ mol}_{\text{CO}} \text{ g}_{\text{Co}}^{-1} \text{ s}^{-1}$ at 170°C . We tested the activity of the catalyst at 150°C under the five times recycles (entries 4–8). The activity in the first repeated cycle ($6.7 \times 10^{-7} \text{ mol}_{\text{CO}} \text{ g}_{\text{Co}}^{-1} \text{ s}^{-1}$) and second repeated cycle ($5.9 \times 10^{-7} \text{ mol}_{\text{CO}} \text{ g}_{\text{Co}}^{-1} \text{ s}^{-1}$) decreases slightly, while keeps stable in the following recycles. The recy-

Table 1

Catalytic performance of various Co nanoparticle catalysts.

Entry	Catalyst	Temperature ($^\circ\text{C}$)	Activity ^a ($10^{-7} \text{ mol}_{\text{CO}} \text{ g}_{\text{Co}}^{-1} \text{ s}^{-1}$)
1	Co-LiBEt ₃ H	130	2.8
2	Co-LiBEt ₃ H	150	7.4
3	Co-LiBEt ₃ H	170	13
4	Co-LiBEt ₃ H	150 ^b	6.7
5	Co-LiBEt ₃ H	150 ^c	5.9
6	Co-LiBEt ₃ H	150 ^d	5.4
7	Co-LiBEt ₃ H	150 ^e	5.6
8	Co-LiBEt ₃ H	150 ^f	5.2
9	Co-NaBH ₄	130	1.2
10	Co-NaBH ₄	150	3.3
11	Co-NaBH ₄	170	4.7
12	Co-NaBH ₄	150 ^b	~0
13	Co-N ₂ H ₄	150	0.5
14	Co-LiAl(O- <i>t</i> Bu) ₃ H	150	0
15	Co-KH	150	0
16	Co-EG	150	0
17	Co-Co ₂ (CO) ₈	150	0
18	blank	150	0

^a Calculated based on CO conversion and steam transferred CO₂ was removed. ^b 1st recycle. ^c 2nd recycle. ^d 3rd recycle. ^e 4th recycle. ^f 5th recycle.

Reaction conditions: 150°C , $\text{CO}:\text{H}_2:\text{Ar} = 32:64:4$ (initial pressure 3.0 MPa).

cle experiments show the good long-time activity of Co-LiBEt₃H, also indicate that 5.9 nm of Co nanoparticles is stable after reconstruction from 8.3 nm of particles so that the catalytic activity can be remained.

As for Co-NaBH₄, its catalytic activity is lower than that of Co-LiBEt₃H at $130\text{--}170^\circ\text{C}$. If plotting the logarithm of the activity of catalysts and $1/T$, shown in Fig. 5, we can see that the activation energy fitting curve of Co-LiBEt₃H is always above the curve of Co-NaBH₄ and the former is relatively largely affected by temperature with activation energy of 57 kJ/mol, while the latter has activation energy of 45 kJ/mol. In addition, Co-NaBH₄ loses its activity after one time of reaction at 150°C (Table 1, entry 12), which means that the activity of 3.1 nm-particles decreases after reconstructed from initial parti-

Fig. 5. Activation energy fitting curves of Co-LiBEt₃H (1) and Co-NaBH₄ (2) catalysts.

Table 2
Product selectivities of Co-LiBEt₃H and Co-NaBH₄ catalysts.

Entry	Catalyst	Temperature (°C)	Selectivity (wt%)			
			CH ₄	CO ₂	C ₂₋₄	C ₅₊
1	Co-LiBEt ₃ H	150	26	9	26	39
2	Co-LiBEt ₃ H	170	29	8	28	35
3	Co-NaBH ₄	150	33	5	41	21
4	Co-NaBH ₄	170	40	7	36	17
5	Co-NaBH ₄	150 ^a	56	3	35	6

^a Using methanization condition of CO:H₂ = 1:10.

cles. The activities of Co nanoparticles reduced by other methods are not observed in Fischer-Tropsch synthesis (Table 1, entries 13–17).

The selectivity of Co-LiBEt₃H and Co-NaBH₄ are shown in Table 2 and Fig. 6. At 150 °C, the products from Co-LiBEt₃H-catalyzed Fischer-Tropsch synthesis contain 26% of methane, 26% of C₂₋₄, and nearly 40% of C₅₊ products; at 170 °C, the amount of methane increases and C₅₊ products decrease. As shown in Fig. 6(a), a half amount of C₂₊ products is olefin (43% of C₂₋₄, 37% of C₅₋₁₂, 37% of C₁₃₊), which is the typical result of reactions happening at low temperature. At 150 °C, the products over Co-NaBH₄ contain 33% of methane, over 40% of C₂₋₄ and only 20% of C₅₊ products, and the distribution of olefin is similar to that of Co-LiBEt₃H; at 170 °C, the amount of C₅₊ products further decreases. If the mixed gas of CO:H₂ = 1:10 is employed, the amount of methane will be 56% with only 6% of C₅₊ products at 150 °C. This shows that chain growth of Co-LiBEt₃H is much better than that of Co-NaBH₄. In Fig. 6(b), the products of the two catalysts match Schulz-Flory distribution, and the former chain growth factor of Co-LiBEt₃H (0.70) is higher than Co-NaBH₄ (0.62).

The results above demonstrate that the catalytic activity, recycling ability and heavy hydrocarbon selectivity of Co-LiBEt₃H catalyst are higher than those of Co-NaBH₄ catalyst. One possible reason is the difference of particle sizes of the two catalysts. Bezemer et al. [29] employed carbon fiber-supported Co catalysts in Fischer-Tropsch synthesis and found that particle size of Co catalysts should be about 6 nm in order to achieve the best activity, and the activity decreased observably if particle size is lower than 6 nm, which decreases the trend of desorption of CO from the surface of Co as well as the formation of B₅CO dissociation active center on nanoparticles. The average

Fig. 6. Hydrocarbon selectivities (a) and Anderson-Schulz-Flory distribution (b) of products for Co-LiBEt₃H (1) and Co-NaBH₄ (2) catalysts.

Fig. 7. XRD patterns of Co-LiBEt₃H (1, 2) and Co-NaBH₄ (3, 4) catalysts: before (2, 4) and after (1, 3) reaction.

size of Co-LiBEt₃H nanoparticles is 5.9 nm, which is around the optimal particle size. While the average size of Co-NaBH₄ nanoparticles is 3 nm, which is too small to be conducive to synthesis. This is consistent with the results reported by Bezemer et al. [29].

3.3. Research on B-doping of Co catalysts

Except the effect of particle size, one of the other reasons for the different reactivity between Co-LiBEt₃H and Co-NaBH₄ catalysts is their different structure. Different reduction methods usually determine the composition, structure, and stability of nanoparticles. Many results indicate that B-doping is general in the nanoparticles reduced by LiBEt₃H and NaBH₄, which allows metals to exist in the form of borate and thus affects the reactivity [30]. There are also a lot of research on the effects of B-doping to Co-based catalysts for Fischer-Tropsch synthesis. Li et al. [31] studied the effect of B on Co/TiO₂ catalyst and found that B could decrease the reduction degree of Co and excess B could noticeably reduce the activity and selectivity of Fischer-Tropsch synthesis. Figure 7 shows the XRD patterns of fresh and used catalysts. As for fresh Co-NaBH₄, even though the average particle size is only 14 nm, the peak signal of Co(111) or Co(0001) is unobvious, which represents a bad

crystalline degree of Co and a major amorphous state of Co, while a strong peak signal of CoB_x indicates that B-Co alloy is the major form of Co. There is no obvious peak signal of used Co-NaBH₄ catalyst due to too small particle size. After calcined the catalyst at 400 °C for 2 h with N₂ purging, many CoO and a small amount of Co(111) diffraction peak signals can be observed. As for fresh Co-LiBEt₃H, the diffraction peak signal of Co(111) are obvious, which accompanied with diffraction peak signal of Co(0001). However, the signal of CoB_x is covered by those of Co(111) and Co(0001), which means that the structure of CoB_x is rare. The peak signal of used Co-LiBEt₃H catalyst is still in the major of Co(111) with a little of signal of CoO. These XRD results indicate that the heavy B-doping in Co-NaBH₄ causes a mainly structural presence of B-Co alloy in the catalyst which allows Co to form crystalline phase hardly. In the process of reaction, the reconstruction of CoB_x under effects of water and syngas will form CoO; at the same time, Co is shattered to 3 nm of ultrafine nanoparticles in the reconstruction due to the presence of metastable amorphous Co.

The low level of B doping in Co-LiBEt₃H allows B leaving the system as BEt₃ form when reduced by LiBEt₃H, which results in better purity and crystalline of Co catalyst. The diffraction peak signal of Co(111) and Co(0001) indicates the fcc and hcp structures existing at the same time and fcc Co is the majority. According to the literature, fcc Co is a major form when the particle size is less than 20 nm, which coincides with the observed signal of Co(111). There is no noticeable signal of CoB_x , which indicates effect of B-doping on structure is small. Although the signal of CoO increases slightly, which means a minor oxidation happened in the process, its signal is still much lower than that of pure Co. These results indicate that when 8.3 nm of Co reconstructs to the smaller 5.9 nm of pure Co nanoparticles, the mixed phase of two structures also changed to single fcc Co phase due to the stability of fcc. Co(fcc) also exhibits good catalytic performance for Fischer-Tropsch synthesis.

Table 3 shows the concentration of Co and B of two catalysts before and after the reaction, which is a more direct comparison of contents of Co and B in the system. Before the reaction, the concentration of Co and B in Co-NaBH₄ is 3.81 and 3.51 µg/mL, respectively, and the atom ratio of Co/B is 0.199. Much B exists in the catalyst and dopes into Co to form a lot of CoB_x in an alloy status. Co is difficult to form an order structure under the effect of B that the generation of active site of catalyst is blocked. The atom ratio of Co and B is 0.171, which is similar to the one before reaction. However, considering the tiny XRD signal of CoB_x , the B-Co alloy is tend to be amorphous before reaction. As for the Co-LiBEt₃H, the concentration of Co and B is 2.28 and 0.206 µg/mL, respectively, and the atom ratio of Co/B

is 2.03. B exists in the catalyst as small portion so the effect of B on Co is small. Although XRD results show that the content of B is half of Co, CoB_x alloy is not noticeable, and the system is in major of pure Co. This is the reason why Co-LiBEt₃H shows high catalytic activity and selectivity for Fischer-Tropsch synthesis. After reaction, the atom ratio of Co/B is 1.63, Co is still in majority, and no significant amount of CoB_x alloy is generated. ICP results also indicate that although Co nanoparticles reconstruct their structure and reduce their particle size during the Fischer-Tropsch synthesis, the content ratio of Co/B has no obvious change and B will not be removed from catalyst by reconstruction, which indicates the necessity to decrease the introduction of B at the preparation step.

3.4. FTIR research on reconstruction of catalysts

The characterization of particle size and catalytic activity of catalysts indicate that a reconstruction of Co nanoparticles happened in the reactions; the examination of XRD and ICP show a certain level of B-doping in Co nanoparticles. Conditions of reconstruction, whether B induces reconstruction and how reconstructions affect Fischer-Tropsch synthesis are to be studied. Therefore, we used CO as probe molecule and in-situ FTIR to study the reconstruction of Co-LiBEt₃H and Co-NaBH₄ in reactions.

Figure 8 shows the FTIR spectra of Co-LiBEt₃H and Co-NaBH₄. Comparing Fig. 8(a) and (b), under the condition (1), a weak bridge-like adsorption signal at 1849 cm⁻¹ appears for Co-LiBEt₃H catalyst after a pulse of CO, but no signal for Co-NaBH₄ catalyst. This suggests that Co-LiBEt₃H has a faster response and easier chemisorption to CO. Under the condition (2), there are end-like and bridge-like signals at 1976 and 1860 cm⁻¹, respectively, for Co-LiBEt₃H catalyst. There are similar signals at 1970 and 1840 cm⁻¹ for Co-NaBH₄, which shows a red shift comparing to the former. Tan et al. [33] reported that excessive B-doping would cause a red shift for IR signal. At the same time, the C–O bond is weakened and the adsorption of CO at the surface of metals is strong enough to inhibit subsequent reactions.

Under the conditions of (3), (4), and (5), as for Co-LiBEt₃H catalyst, the end-like and bridge-like IR adsorptions blue shift to 1985 and 1865 cm⁻¹ when the system reaches reaction temperature. After 1 h of reaction, the adsorptions further blue shift to 2009 and 1902 cm⁻¹ and then remain stable in subsequent reactions. These blue shifts should result from the decrease of particle size rather than the decrease of B in catalyst, which is due to the fact that the ratio of Co/B doesn't change before and after reactions so that B cannot be removed out from catalysts (Table 3). The particle size of Co-LiBEt₃H changes from 8.3 to 5.9 nm in the reaction because B takes part in the reconstruction of catalysts, which also changes the electronic properties of metals because of the changes of Co-B structure [33] so that the interaction of metals to C–O bond is changed. That is the reason why the changes of particle size can be monitored by FTIR. Reconstruction leads to the blue shift of IR absorption, which weakens the adsorption of metals to CO so that CO can remove from systems more easily. Actually, under the

Table 3
ICP data of Co-LiBEt₃H and Co-NaBH₄ catalysts.

Catalyst	Reaction	Co concentration (µg/mL)	B concentration (µg/mL)	Co/B (atom ratio)
Co-LiBEt ₃ H	before	2.28	0.206	2.03
	after	1.30	0.146	1.63
Co-NaBH ₄	before	3.81	3.51	0.199
	after	3.11	3.32	0.171

Fig. 8. In-situ FTIR spectra using CO as probe. (a) Co-LiBEt₃H; (b) Co-NaBH₄. (1) At room temperature, CO pulse testing under H₂ atmosphere; (2) At room temperature, the testing after refilling 3 MPa syngas and mixing for 1 h; (3) At 150 °C, the testing under the condition of 3 MPa of syngas; (4) The testing after 1 h of reaction; (5) The testing after 2 h of reaction.

condition (2), the difference of absorption peaks for Co-LiBEt₃H and Co-NaBH₄ may result from the difference of initial particle sizes.

As for Co-NaBH₄ catalyst, the linear-like and bridge-like IR absorptions blue shift to 1994 and 1845 cm⁻¹ with weaker strength when the system reaches reaction temperature. At the same time, a new absorption at 2020 cm⁻¹ can be observed, which may represent a reconstructed nanoparticle with very small particle size. After 1 h reaction, the absorptions at 1994 and 1845 cm⁻¹ disappear, and a new absorption at 2030 cm⁻¹ is observed, which remains stable after 2 h. These observations indicate a process that larger 14 nm particles are gradually consumed and small 3.1 nm particles are generated under the reaction conditions. The small particles have no bridge-like adsorption, which is an important indicator of activity of the Fischer-Tropsch synthesis [34], so the catalytic activity of 3.1 nm Co nanoparticles is very low. The activity decreases after reconstructed to small particles. Actually, in the real reactions, an obvious pressure decrease is observed at the first several hours, and reaction rate decreases significantly at late stage of reaction. The case of no activity in recycling reaction also demonstrates that catalysts deactivate quickly.

The FTIR results show that Co-LiBEt₃H gradually finishes its reconstruction in 1 h and the reconstruction leads to the decrease of adsorption of CO by metals and easily removing of CO from surface, which are benefit to reactions. The reconstruction of Co-NaBH₄ generates small 3.1 nm of nanoparticles, which are hard to form a bridge-like adsorption and thus not conducive to Fischer-Tropsch synthesis. Because B induces the reconstructions of both catalysts, the electronic effect is significant enough to red shift the IR adsorptions to be observed conveniently.

4. Conclusions

We employed Co nanoparticles reduced by LiBEt₃H to catalyze aqueous-phase Fischer-Tropsch synthesis, which showed high catalytic activity and recycling ability at low temperature (150 °C). Co nanoparticles reduced by other methods were also

evaluated but exhibited poor performance. By comparing the distribution of particle size of Co-LiBEt₃H and Co-NaBH₄ catalysts before and after reaction, catalyst reconstruction occurs during the reaction catalyzed by these two catalysts. Analyzing the composition of nanoparticles and characterizing the structure showed that a certain amount of B-doping in both catalysts happened in the reaction and B-doping in Co-LiBEt₃H is much less than the other catalyst. In-situ FTIR results showed that a significant reconstruction happened in the reaction and thus caused noticeable adsorption shifts because of the introduction of B, which explained the variation of particle size.

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Graphical Abstract

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Aqueous-phase Fischer-Tropsch synthesis catalyzed by cobalt nanoparticles

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Cobalt nanoparticles prepared by LiBEt₃H reduction undergo a reconstruction process at 150 °C and 3 MPa syngas (CO:H₂ = 1:2) and give an activity of 7.4×10⁻⁷ mol_{CO} g_{Co}⁻¹ s⁻¹ with 40% C₅₊ products, which is the best result in cobalt-catalyzed aqueous-phase Fischer-Tropsch synthesis.

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钴纳米粒子催化水相费托合成

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摘要: 水相费托合成可以在远低于传统温度下实现, 其低温高效的特点使其具有重要的应用潜力. 本文制备了水相稳定且可循环利用的Co纳米粒子并应用于水相费托反应, 150 °C下活性为7.4×10⁻⁷ mol_{CO} g_{Co}⁻¹ s⁻¹, C₅₊选择性接近40%, 是目前纯钴水相费托合成的最好结果, 而其它方法合成的催化剂在150 °C时活性低下. 对催化剂进行了粒径、结构、成分测定和原位红外光谱检测, 研究了催化剂在反应中的重构过程和B掺杂效应.

关键词: 水相费托合成; 钴纳米粒子; 硼掺杂; 原位红外光谱

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1. 前言

费托合成,即CO在临氢条件下生成碳氢化合物的反应,在合成气的间接液化过程中扮演着重要的角色,可以将煤、天然气、生物质等能源转化为有价值的化学品及燃料^[1–5].在过去的80年里,人们系统研究了担载及非担载的金属催化剂,发现铁、钴、钌等过渡金属具有较好的费托合成活性^[6–10].钴基催化剂因其具有好的稳定性、高的重质烃类选择性及相对低的价格成为费托反应的较好选择^[8–10],不但有许多工业化的实例,也有许多实验室层面上的研究,诸如催化剂、载体、反应条件等多种变量^[10–12];Pt,Ru和Pd等贵金属助剂也是人们研究钴系费托合成的热点^[13];此外,人们还通过优化反应器以及多步反应偶合来实现选择性的调控^[14]等.

考虑到费托合成本身是强放热过程,将反应在相对较低的温度下进行热力学上更有利而且更加洁净、绿色^[15].在之前的工作中,本课题组实现了低温高效的水相费托合成:用2.0 nm的Ru纳米粒子作为催化剂均匀分散在水中,可以在低于传统费托合成温度50 °C的条件下实现高效转化^[16],而且催化剂在流动体系中运行240 h,其活性得到良好地保持^[17].随后,Quek等^[18]发现表面氧化的Ru纳米粒子上可以得到70%以上的含氧产物,我们的研究也发现水相费托可以提供研究阴离子助剂的平台^[19],这都说明了水相费托的巨大优势.由于Ru的价格过于昂贵而且是全球稀缺资源,Fe和Co系催化剂的水相费托合成往往更具有实际意义,也更值得我们研究.不过,Fe的活性物种 FeC_x 难以在水中稳定存在,使整个过程较难实现;退而求其次,我们与李永旺课题组分别实现了聚乙二醇相的铁纳米粒子液相费托^[20–21].而相比于Fe催化剂,Co可以在水中稳定存在,这使得钴基水相费托成为可能.目前已有一些钴基液相费托的报导,如Silva等^[22]将催化剂置于离子液体[Bmim][NTf₂]₂中在210 °C反应,活性为 $1.9 \times 10^{-7} \text{ mol}_{\text{CO}} \text{ g}_{\text{Co}}^{-1} \text{ s}^{-1}$;我们实验室将Co纳米粒子均匀分散在角鲨烷中,200 °C得到 $6.1 \times 10^{-6} \text{ mol}_{\text{CO}} \text{ g}_{\text{Co}}^{-1} \text{ s}^{-1}$ 的活性^[23].但到目前为止,仍然鲜有纯Co纳米粒子催化水相费托合成具有良好反应性能的报道.

本文采用 LiBEt_3H 作为还原剂制备了水相稳定的Co纳米粒子并用于水相费托合成,在150 °C下活性为 $7.4 \times 10^{-7} \text{ mol}_{\text{CO}} \text{ g}_{\text{Co}}^{-1} \text{ s}^{-1}$.而其他方法还原的Co纳米粒子的费托合成的活性则处于很低水平或无法观测.随后以 NaBH_4 还原的Co纳米粒子为比较,研究了两种催化剂的不同性质.

2. 实验部分

2.1. 催化剂的制备

LiBEt_3H 还原的Co纳米粒子:将0.26 g无水 CoCl_2 与0.50 g SB3-12 (3-磺丙基十二烷基二甲基甜菜碱内盐,作为保护剂)混合溶解于30 mL THF中,用注射器缓慢将5 mL 1 mol/L的 LiBEt_3H 的THF溶液滴加至溶液中,并伴随充分搅拌.混合溶液迅速从蓝色变黑,表示Co被还原.反应进行10 min后,用10 mL乙醇淬灭反应,随后将纳米粒子用一块永久磁铁分离,用乙醇洗两次、再用水洗两次.随后,纳米粒子分散在含有2.20 g PVP (聚乙烯吡咯烷酮,作为水相纳米粒子保护剂)的水中用于反应.记为Co- LiBEt_3H .

NaBH_4 还原的Co纳米粒子:将0.50 g $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ 与2.20 g PVP混合溶解于30 mL水中,加入0.40 g NaBH_4 固体,并伴随充分搅拌.混合溶液迅速从红色变黑,表示Co以纳米粒子的形式被还原出来.合成的纳米粒子被一块永久磁铁分离、水洗两次.随后,纳米粒子分散到含有2.20 g PVP的水中用于反应.记为Co- NaBH_4 .

其它方法还原的Co纳米粒子:对于 N_2H_4 , $\text{LiAl}(\text{O}-t\text{Bu})_3\text{H}$,KH,乙二醇热还原, $\text{Co}_2(\text{CO})_8$ 热分解法制备的Co纳米粒子,按照文献[24–27]所示方法合成.但在油相还原时采用SB3-12作为保护剂,随后转移到水中用PVP做保护剂.

以上合成纳米粒子的过程均在 N_2 保护下完成.

2.2. 催化剂的表征

纳米粒子的透射电镜(TEM)表征使用Tecnai F-30电镜,工作电压为300 kV.纳米粒子被去离子水稀释且在超声下分散5 min,之后滴在附有超薄碳膜的铜网上.每个样品的粒子粒径分布统计数量超过200个粒子.

样品的X射线衍射(XRD)测试在Rigaku D/MAX-2400型X射线衍射仪上进行,Cu K_α 辐射源, $\lambda = 0.154 \text{ nm}$,管电压30 kV,管电流100 mA,扫描范围 $2\theta = 30^\circ\text{--}70^\circ$,扫描速度 $2^\circ/\text{min}$,步长 0.02° .纳米粒子用磁铁分离、水洗两次,之后在真空下干燥,对粉末进行测定.

样品的Co和B含量测定是利用电感耦合等离子体发射光谱(ICP, Perkin Elmer Optima 2000 DV),用硝酸和盐酸来溶解样品.

催化剂的CO吸附原位红外光谱表征(FTIR)采用自制的原位红外装置,工作条件为150 °C,3 MPa.采集红外信息利用Bruker TENSOR 27型红外光谱仪,分辨率为 2 cm^{-1} ,采集次数为64次.

2.3. 催化剂的评价

Co纳米粒子的费托合成性能评价在封闭搅拌式反应釜中进行。将Co纳米粒子分散在40 mL水中, 转移到不锈钢反应釜, 置换3次N₂, 之后充入3.0 MPa合成气(CO:H₂:Ar = 32:64:4)。反应釜升到指定温度, 充分搅拌(600 r/min)进行反应; 当压力降到2.0–2.5 MPa时停止反应并进行检测。除速率过慢的反应外, 反应时间一般为24–48 h之间。

反应后恢复常温, 将反应釜连接到气相色谱以分析气体产物。随后在反应釜中注入20.0 mg十氢萘作为内标、10 mL环己烷作为萃取剂, 150 °C加热搅拌2 h, 恢复常温, 分离得到环己烷相, 进行气相色谱分析以确定液体产物。

对于循环实验, 待反应完成后, 将Co纳米粒子用磁铁吸下来, 去离子水洗2次后加入含有2.20 g PVP的水中分散, 转移到不锈钢反应釜中进行反应。过程在N₂保护下完成。

3. 结果与讨论

3.1. Co纳米粒子的粒径分布

利用不同还原方法得到的Co催化剂的电镜结果见图1–3。图1为Co-LiBEt₃H反应前后的TEM照片和粒径分布。可以看到, 新鲜的Co纳米粒子平均粒径为8.3 nm。进行一次费托合成后, 在产物的包裹下粒子有一定的物理聚集, 但仍较易区分, 其平均粒径为5.9 nm, 这说明在费托合成的条件下纳米粒子发生了重构, 粒径发生变化。反应后的纳米粒子在之后的多次反应后粒径基本保持不变, 如图1(c)所示, 循环一次后平均粒径为5.7 nm, 说明了5.9 nm的Co纳米粒子在反应中具有较好的稳定性。

对于图2的Co-NaBH₄纳米粒子, 其反应前后粒径有明显的变化: 反应前平均粒径为14 nm, 且分布很宽; 而反应后只有3.1 nm。此外, 该Co纳米粒子在反应后失去磁性, 无法用磁铁进行分离。

N₂H₄, LiAl(O-*i*Bu)₃H和KH还原的Co粒子如图3所示。由于还原的Co纳米粒子存在明显的聚积, 粘连成较大的片状结构而无法很好地分散, 呈絮状形式存在, 不适合用做费托合成的催化剂。

乙二醇热还原、Co₂(CO)₈热分解制备的Co催化剂如图4所示。由于采用与金属相互作用不强的SB3-12保护剂(相较于油酸保护剂), 而且制备温度较高, 得到的粒径分别为340和31 nm, 粒径过大, 同样不适合进行反应。

3.2. 催化剂的费托合成反应性能

不同Co催化剂的费托合成活性如表1所示。Co-LiBEt₃H在130 °C即表现出了明显的活性, 在150 °C时为 $7.4 \times 10^{-7} \text{ mol}_{\text{CO}} \text{ g}_{\text{Co}}^{-1} \text{ s}^{-1}$, 与Bechara等^[28]在Co/Al₂O₃催化剂上190 °C的数据相当, 而升到170 °C时活性上升为 $1.3 \times 10^{-6} \text{ mol}_{\text{CO}} \text{ g}_{\text{Co}}^{-1} \text{ s}^{-1}$ 。将该催化剂在150 °C条件下进行五次循环(实验4–8), 活性依次为 6.7×10^{-7} , 5.9×10^{-7} , 5.4×10^{-7} 和 $5.2 \times 10^{-7} \text{ mol}_{\text{CO}} \text{ g}_{\text{Co}}^{-1} \text{ s}^{-1}$, 保持相对稳定。这说明催化剂在反应后可以较好地循环利用, 也表明在反应过程中, 8.3 nm的Co纳米粒子在重构为5.9 nm的Co纳米粒子后可以稳定存在, 进而使得催化活性得到了较好的保持。

对于Co-NaBH₄, 在130–170 °C时的活性都不及Co-LiBEt₃H。图5为催化剂活性的对数与1/T的关系图。可以看出, Co-LiBEt₃H均在Co-NaBH₄上方, 两者活化能分别为57和45 kJ/mol。此外, Co-NaBH₄在150 °C下进行一次反应即失去活性, 实验12的循环反应活性几乎为0, 这说明初始的Co纳米粒子在重构为3.1 nm之后催化性能明显下降。对于N₂H₄, LiAl(O-*i*Bu)₃H, KH还原, 乙二醇热还原及Co₂(CO)₈热分解得到的催化剂, 在150 °C下均未观测到费托合成活性(实验13–17)。

Co-LiBEt₃H与Co-NaBH₄催化剂的选择性如表2和图6所示。在150 °C时, Co-LiBEt₃H催化的费托合成产物中有26%甲烷, 26% C_{2–4}和近40%的C₅₊产物; 升温到170 °C时, 甲烷有所升高, C₅₊有所下降。从图6(a)的产物选择性图中可看到, C₂₊产物中烯烃占有产物的近一半(烯烃比例C_{2–4}为43%, C_{5–12}为37%, C₁₃₊为37%), 这也是低温反应的特有结果。对于Co-NaBH₄, 150 °C条件的产物中有33%甲烷, 40%以上C_{2–4}, C₅₊仅有20%, 烯烃分布与Co-LiBEt₃H相近; 在170 °C时C₅₊会进一步减少; 如果采用CO:H₂ = 1:10的气体, 在150 °C条件下甲烷可达56%, C₅₊仅有6%。这说明Co-LiBEt₃H的链增长能力明显优于Co-NaBH₄。从图6(b)可知, 两种催化剂的产物均符合Schulz-Flory分布, 前者的链增长因子为0.70, 高于后者的0.62。

以上数据表明, Co-LiBEt₃H的费托合成活性、循环性能以及重质烃类的选择性均优于Co-NaBH₄催化剂, 其原因之一是两种催化剂粒径的差异。Bezemer等^[29]在碳纤维上负载了不同粒径的Co催化剂用于费托合成, 发现Co催化剂的粒径需要在6 nm左右以达到最佳, 在低于6 nm时活性会显著下降。这是因为在Co纳米粒子粒径较低时, CO不易在Co表面上脱附从而导致后续反应难以进行, 而且纳米粒子上也不容易形成B₅ CO解离活性

中心, 导致活性和选择性降低. 本工作所合成的 Co-LiBEt₃H 在反应中重构得到的纳米粒子粒径约为 5.9 nm, 处于最佳粒径附近, 而 Co-NaBH₄ 重构后为 3 nm, 粒径过小因而不利于反应. 这与 Bezemer 等^[29]的结果相符.

3.3. Co 催化剂中 B 掺杂的研究

除粒径效应之外, Co-LiBEt₃H 与 Co-NaBH₄ 催化性能不同的另一个原因是其具有不同的结构. 不同的还原方法往往决定了纳米粒子的成分、结构和稳定性. 研究表明, B 掺杂在 NaBH₄ 及 LiBEt₃H 还原制备的纳米粒子中普遍存在, 使得金属以硼化物的非 0 价形式存在, 从而影响催化性能^[30]; B 掺杂对 Co 基费托合成的影响也有很多研究, 李金林等^[31]研究了 B 对 Co/TiO₂ 催化剂的影响, 发现 B 可以降低 Co 的还原度, 过量的 B 可以显著降低费托合成活性和选择性. 为此, 两种催化剂分别进行了反应前后的 XRD 实验, 结果如图 7 所示. 对于新鲜的 Co-NaBH₄, 虽然平均粒径有 14 nm, 但 Co(111) 或 Co(0001) 的信号都不明显, Co 的晶态程度很差, 多以无定形存在; 而 CoB_x 的信号较强, 表明 Co-NaBH₄ 的 Co 以 Co-B 合金为主. 反应后的 Co-NaBH₄ 由于粒径过小而没有明显 XRD 信号, 因此将样品在 400 °C N₂ 焙烧 2 h 后进行 XRD 实验, 得到如图 7(b) 所示的谱图, 出现了明显的 CoO 衍射峰以及较弱的 Co(111) 衍射峰. 对于新鲜的 Co-LiBEt₃H, 其 Co(111) 衍射峰很明显, 同时伴有 Co(0001) 的衍射峰, 而 CoB_x 信号淹没在 Co(111) 与 Co(0001) 中, 表明 CoB_x 结构并不明显; 反应后的样品出现少量的 CoO 衍射峰, 但仍以 Co(111) 为主. XRD 结果表明, 在 Co-NaBH₄ 中, B 的大量掺杂使得 Co 主要以 Co-B 合金结构存在, Co 并不是以 0 价存在于体系中, 而且难以形成晶相, 几乎看不到 Co(111) 的衍射峰. 在反应过程中, CoB_x 会在水、合成气的作用下进行重构, Co 脱离 B 而形成了 CoO; 同时因为 Co 以亚稳定的非晶态存在, 所以重构为 3 nm 的超细 Co 纳米粒子.

在 Co-LiBEt₃H 中, B 的掺杂程度明显较低, LiBEt₃H 还原时 B 多以 BEt₃ 的形式离开体系, 所以得到的 Co 相对较纯净, 同时晶化程度较好, Co(111) 和 Co(0001) 衍射峰表明 fcc 与 hcp 结构同时存在, 以 fcc Co 为主. 研究表明^[32], Co 在粒径小于 20 nm 时主要以 fcc 结构存在, 这与本实验中观测到的 Co(111) 信号吻合. 在反应后, 样品的 Co(0001) 信号几乎消失, Co 以 fcc 的 Co(111) 存在. 没有出现明显的 CoB_x 信号, 表明 B 掺杂对其结构影响很小; CoO 的衍射峰强度略有上升, 表明在反应过程中可能存在少量的氧化, 但这种氧化不占主导地位, CoO 衍射峰

强度比纯 Co 要低很多. 这说明在反应过程中, 8.3 nm 的 Co 会重构为 5.9 nm, 粒径变小, fcc 结构更加稳定, 从而由两种结构的混相转变为单一的 fcc Co 结构, 后者也具有良好的费托合成性能.

表 3 给出了两种催化剂在反应前后 Co 和 B 的浓度. 在反应前, Co-NaBH₄ 中的 Co 浓度为 3.81 μg/mL, B 浓度为 3.51 μg/mL, Co 与 B 的原子比为 0.199, B 在催化剂中大量存在, 而且会与 Co 掺杂形成大量的 CoB_x, 使得倾向于无序的 CoB_x 以合金形式存在; 同时在 B 的影响下 Co 难以很好地形成有序结构, 因而抑制了催化剂活性位的形成. 反应后的 Co/B 原子比为 0.171, 与反应前差别不大, 但结合 XRD 谱图上仅有的很小 CoB_x 衍射峰, 说明反应前 Co-NaBH₄ 的 Co-B 合金趋于无定形化. 对于 Co-LiBEt₃H, 其反应前 Co 浓度为 2.28 μg/mL, 而 B 浓度仅有 0.206 μg/mL, Co 与 B 的原子比为 2.03, B 在样品中并非大量存在, 对 Co 的影响很小; XRD 也表明体系中的 Co 物种以纯 Co 为主, 因而表现出较好的活性和选择性. 反应后, Co/B 原子比为 1.63, Co 仍占多数, 且样品中未形成可观的 CoB_x 合金. ICP 结果同时表明在费托合成前后, 虽然 Co 纳米粒子进行重构、粒径变小, 但 Co 与 B 的含量比例没有太大的变化, B 并不会因为重构而脱离催化剂, 所以必须在制备时降低 B 的引入.

3.4. FTIR 结果

综上, Co 纳米粒子在反应中存在重构现象和不同程度的 B 掺杂. 重构发生条件、B 是否会诱导重构、重构如何影响费托合成反应等有待研究. 为此, 我们以 CO 为探针分子利用原位 FTIR 来检测在实际反应中 Co-LiBEt₃H 与 Co-NaBH₄ 两种催化剂在反应中的重构行为. 图 8 所示为 Co-LiBEt₃H 和 Co-NaBH₄ 的原位红外光谱. 可以看出, 在 (1) 条件下, 体系中打入 CO 脉冲后, Co-LiBEt₃H 在 1849 cm⁻¹ 处出现了一个较弱的桥式吸附信号, 而 Co-NaBH₄ 没有出现任何信号. 这说明前者对 CO 响应更快, 更容易进行 CO 的化学吸附. 在 (2) 条件下, Co-LiBEt₃H 分别在 1976 和 1860 cm⁻¹ 处出现了端式和桥式吸附, Co-NaBH₄ 则分别位于 1970 和 1840 cm⁻¹ 处, 比前者有较明显的红移. 从 Tan 等^[33]的工作得知, 过多的 B 掺杂会导致红外信号红移, 同时 C-O 键被削弱、CO 在金属表面吸附过强因而会抑制后续反应.

在 (3), (4) 和 (5) 条件下, 对于 Co-LiBEt₃H, 当体系达到反应温度后, 端式与桥式 CO 的红外吸收峰蓝移至 1985 和 1865 cm⁻¹ 处; 反应约 1 h 后进一步蓝移到 2009 和 1902 cm⁻¹ 处, 随后基本没有太大的变化. 从表 3 得知, 反

应后Co/B原子比不会上升, B并不会从催化剂中脱离, 所以蓝移应该归于粒径的降低. Co-LiBEt₃H的粒径从反应前的8.3 nm到反应后的5.9 nm, 因为两种催化剂的重构都存在B的参与, 不仅会导致粒径的变化, 也会因Co-B结构改变使得金属的电子性质发生变化^[33], 从而使得金属对C-O键的作用发生变化, 所以粒径变化可以通过红外吸收峰的位移来观测到. 重构使得吸收峰蓝移, 金属对CO的吸附减弱, CO更加容易脱离体系, 从而使后续反应容易发生. 实际上, 对于(2)条件, 红外吸收峰位置的不同也有可能是Co-LiBEt₃H与Co-NaBH₄的初始粒径不同所致.

而对于Co-NaBH₄, 当体系达到反应温度后, 端式与桥式CO吸收峰蓝移至1994和1845 cm⁻¹处, 其强度有所减弱, 同时在2020 cm⁻¹处出现一新的吸收峰. 该吸收峰应对应于经重构后粒径很小的纳米粒子, 其费托合成活性较低; 在反应约1 h后, 1994和1845 cm⁻¹处的峰消失, 在2030 cm⁻¹处出现了一个新的吸收峰, 且反应2 h后基本没有变化. 这说明在反应条件下, 较大的14 nm粒子逐渐被消耗、形成粒径较小的3.1 nm粒子的过程. 较小的粒子上没有桥式吸附CO信号, 而桥式吸附是费托活性

的重要指标^[34], 因而费托活性很低, 以致很快失活.

原位FTIR结果表明, Co-LiBEt₃H在反应条件下会逐渐重构, 反应1 h后基本完成. 重构使得金属吸附CO的能力下降、导致CO更容易从表面脱除从而利于反应. 而Co-NaBH₄在反应过程中也存在重构, Co粒子重构成3.1 nm的较小粒子, 难以形成桥式吸附因而不利于费托合成. 由于两种催化剂都存在B掺杂, 重构在B诱导下进行, 电子效应比较明显, 红外吸收峰的位置有明显移动因而易于红外观测.

4. 结论

LiBEt₃H还原的Co纳米粒子催化剂催化水相费托合成, 在低温(150 °C)下具有良好的催化性能和循环能力. 其它方法还原的Co纳米粒子同样被用做水相费托的评价, 但效果均不佳. LiBEt₃H和NaBH₄还原得到的两种催化剂在反应过程中都存在重构行为及不同程度的B掺杂, 其中LiBEt₃H作为还原剂时B掺杂明显较少. 原位FTIR结果表明, Co纳米粒子在反应过程中重构现象明显, 这种重构因由B的引入而使得吸收峰位移明显, 从而很好地解释了粒径的变化规律.