Catalysis Today 142 (2009) 85–89

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

The solvent effects during preparation of Fischer–Tropsch synthesis catalysts: Improvement of reducibility, dispersion of supported cobalt and stability of catalyst

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ARTICLE INFO

Article history:
Available online 18 February 2009

Keywords:
Solvent
Cobalt catalyst
Fischer–Tropsch synthesis
Syngas

ABSTRACT

The different solvents were applied, such as acetic acid or ethanol, during preparation of Fischer–Tropsch synthesis (FTS) catalysts, to modify the surface properties of silica supports or as a solvent of cobalt precursors. The modification of silica supports by acetic acid or ethanol improves the reduction degree and dispersion of supported cobalt simultaneously, realizing higher catalytic activity, and the catalysts prepared from ethanol solution of cobalt precursor exhibit significant stability and activity in slurry phase FTS reaction during 100 h. The obtained catalysts were characterized by XRD, TPR, in situ DRIFT and H_2 chemisorption.

1. Introduction

The Fischer–Tropsch synthesis (FTS), which produces hydrocarbons from syngas, is considered an effective solution to the problem of finding suitable substitutes for liquid fossil fuel. On the other hand, directly converting coal gasifier gas or natural gas into higher hydrocarbons by FTS, has attracted great attentions because of the increase of demands for environmentally friendly liquid fuels. The FTS activity of cobalt catalyst depends solely on the number of active sites located on the surface of crystalline metal formed by reduction. The number of active sites was determined by the Co particle size dispersions, loading amount, and reduction degree [1,2]. Besides cobalt, some supports such as SiO_2 and Al_2O_3 are indispensable. The chemical and texture properties of the support influence the catalytic activity and product selectivity of Co catalysts, via their modifications on the reducibility and dispersion of cobalt or the formation of well-fined phases. Synthesis of highly dispersed Co catalysts requires strong interaction between the support and the Co precursor, but in turn, such strong interactions generally lower reducibility of such precursors [3].

Preparing impregnated catalyst is actually a complex process, in which many individual steps might influence the final performance of the catalyst, i.e., metal precursor, solvent, carrier, aging time, drying time/temperature, and calcination temperature. Failure to control these parameters might lead to irreproducible catalyst preparation. It is considered that the solvents, which applied to dissolve Co precursors or pretreat the supports, remarkably influence the interaction between the cobalt and silica supports, meanwhile, the groups from solvents, formed on the surface of supports, prohibit the sintering of supported cobalt [4–6]. On the other hand, the concentration, distribution, and nature of hydroxyl groups (silanols) on the silica surface also play important role in the dispersion of supported metal on the silica [5]. Ming and Baker [7] reported that the catalytic performance of a cobalt–silica gel FTS catalyst was strongly affected by preparation condition such as pH value of solution containing precursor, because the pH value of impregnation solution changed the interaction of cobalt and silica support, resulting in different dispersion and reducibility of supported cobalt.

In present work, acetic acid with different concentration and ethanol were applied to pretreat the silica support, before impregnation of cobalt precursors. The different acetic acid and ethanol should modify the properties of silica surface, such as nature of hydroxyl groups or oxyl groups, resulting in forming different catalytic property of relative catalyst. Meanwhile, ethanol was also used as solvent of cobalt precursors to form a stable FTS catalyst. The obtained catalysts were tested in slurry phase FTS reaction and characterized by XRD, TPR, in situ diffuse reflectance infrared Fourier transform (DRIFT) and H_2 chemisorption.

2. Experimental

Commercially available silica gel (ID gel, Fuji Silisya, specific surface area: 270 m^2 g, pore volume: 1.22 cm^3 g, average pore

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doi:10.1016/j.cattod.2009.01.014

diameter: 8.7 nm, pellet size: 20–40 mesh) was used as support in this study. The silica gel was treated with ethanol (99 wt.%) or different acetic acid, such as 20 wt.%, 60 wt.% and 95 wt.% acetic acid, for 1 h at room temperature by incipient-wetness impregnation method. And then, the samples were dried in air at 373 K for 12 h.

The aqueous solution of cobalt nitrate was impregnated onto the pretreated silica supports by incipient wetness method. The loading of cobalt was 10 wt.% for all catalysts. The catalysts were dried at 393 K for 12 h and calcined at 673 K for 2 h. Then, the calcined samples were reduced with H_2 at 673 K for 10 h followed by passivation with 1% O_2 in N_2 at room temperature, hereafter noted as Co–ethanol, Co–20Ac, Co–60Ac and Co–95Ac, respectively. Co–silica ID, which cobalt was supported on silica ID without pretreatment, was used as a reference. As a comparison of catalyst prepared from acetic acid pretreated silica, the nitric acid, which has the same pH value with the used 60 wt.% acetic acid, was employed to pretreat silica ID support, and the catalyst prepared by this kind of support was noted as Co–HNO_3.

The ethanol (99 wt.%) was also used to dissolve cobalt nitrate for impregnation of silica ID support, to prepare 10 wt.% cobalt silica catalyst with the same method mentioned above. This kind of catalyst was noted as Co–ethanol–S.

FTS reaction was carried out in a semi-batch slurry-phase reactor with the inner volume of 80 ml. The passivated catalyst of 1.0 g was loaded in the reactor with 20 ml liquid medium (n-hexadecane). Before the reaction, the passivated catalyst was reduced by syngas at reaction temperature for 1 h. The reaction conditions were P (total) = 1.0 MPa, T = 513 K, CO/H_2 = 1/2, W/F (CO + H_2 + Ar) = 10 g-cat. h/mol. The effluent gas from the reactor was analyzed by on-line gas chromatography (GC). A thermal conductivity detector (TCD) was used to analyze gaseous products (CO, CO_2 and CH_4). Light hydrocarbons (C_1–C_5) were on-line analyzed by another GC with flame ionization detector (FID) using a Porapak-Q column. The analyses of hydrocarbons dissolved in the solvent and cooled in the trap were carried out with GC-FID using silicone SE-30 column. The mass balance of various reactions were calculated, which were almost 95% based on carbon mole for all reactions.

Temperature-programmed reduction (TPR) experiments were carried out in a quartz tube reactor using 0.2 g calcined catalysts. The reducing gas, a mixture of 5.1% H_2 diluted by N_2, was fed via a mass flow controller at 50 ml/min and the temperature was increased at a rate of 8 K/min from 323 K until 1073 K. The effluent of reactor passed through a 5A molecular sieve trap to remove produced water, before reaching TCD.

Chemisorption experiments were carried out in a static volumetric glass high-vacuum system (Quantachrome Autosorb-1, Yuasa Ionics). Research grade gases (H_2: 99.9995%, CO: 99.99%, Takachiho Co.) were used without further purification. Before adsorption of H_2, the catalysts, which were previously reduced by H_2 and passivated, were treated in H_2 at 673 K for 1 h, followed by evacuation. H_2 adsorption isotherms were measured at 373 K. It was reported that H_2 chemisorption at 373 K was most reliable for silica-supported cobalt catalyst [8,9].

An X-ray diffractometer (XRD, Rigaku, RINT2000) was used to detect supported cobalt crystalline size of the passivated catalysts. The crystalline average size was calculated by $L = K\lambda/\Delta(2\theta)\cos\theta_0$, where L is the crystalline size, K is a constant (K = 0.9–1.1), λ is the wavelength of X-ray (CuK_α = 0.154 nm), and $\Delta(2\theta)$ is the width of the peak at half height.

The calculation methods were described elsewhere [10], such as CO conversion, selectivity and α value (chain growth probability) based on TCD or FID data, metallic cobalt surface area, dispersion, average crystalline diameter of supported cobalt, and TOF based on H_2 chemisorption or XRD data.

In situ diffuse reflectance infrared Fourier transform spectra were collected on a Nexus 470 FT-IR spectrometer equipped with a diffuse reflectance attachment and MCT detector. The dried pretreated-silica powder of 14 mg was contained in a diffuse reflectance infrared cell with a ZnSe window, which can work at high temperature and high pressure. In situ absorbance spectra were obtained using 32 scans at 2 cm^{-1} resolution. Before collection of spectra, the sample was treated in situ in a He stream flowing at 50 ml/min at 393 K for 2 h. The spectra were obtained at room temperature under the He stream. The spectra were referenced to those of dried nonpretreated silica.

3. Results and discussion

3.1. The effects of acetic acid pretreatment

To investigate the promotional role of acetic acid in pretreatment silica support, Co/SiO_2 catalysts prepared by pretreated silica supports were applied to slurry phase FTS reaction.

As shown in Table 1, Co–60Ac catalyst exhibited the highest CO conversion as 70.3% in slurry phase FTS reaction and lower selectivity of CH_4 in this study. Co–Silica ID catalyst showed lower CO conversion as 48.5% in this study. As a comparison of catalyst prepared from acetic acid pretreated silica, the nitric acid, which has the same pH value with the used 60 wt.% acetic acid, was employed to pretreat silica ID support, and this kind of catalyst showed lower CO conversion than that of Co–silica ID in Table 1, indicating that only lower pH value of the pretreated solution could not improve the catalytic activity of Co/SiO_2 catalyst in FTS reaction, as the lower pH value of solution was favorite to form large particle size of supported cobalt [7]. It was considered that the Co–silica ID catalyst formed large cobalt particle size, leading to lower cobalt surface area, resulting in lower catalytic activity. For the catalysts, prepared from acetic acid pretreated silica supports, the different surface properties of silica supports contributed to formation of the small supported cobalt particle, resulting in high dispersion of supported cobalt, while the high dispersion of supported cobalt would contribute to high catalytic activity of these catalysts in FTS reaction, if the reduction degree of cobalt particles was also high enough at the same time.

The activity of cobalt catalyst in FTS depends solely on the number of active sites located on the surface of crystalline metal formed by reduction. The number of active sites is determined by the Co particle size, loading amount, and reduction degree [11]. The supported cobalt particle size of various catalysts was determined by XRD and H_2 chemisorption. The XRD patterns of various passivated catalysts are shown in Fig. 1. The cobalt crystalline size of Co–HNO_3 catalyst was the largest, as shown in Table 2. On the other hand, the others catalysts, prepared by acetic acid pretreated silica supports, exhibited smaller cobalt particle size than Co–silica ID, according to H_2 chemisorption data, as compared in Table 2 as well. It was found that there

Table 1
The reaction performance of various acetic acid modified catalysts.

Catalyst	CO conversion (%)[a]	Sel. (%)		α
		CH_4	CO_2	
Co–silica ID	48.5	7.01	1.64	0.86
Co–20Ac	56.5	6.07	1.83	0.87
Co–60Ac	70.3	6.25	1.49	0.86
Co–95Ac	58.3	6.92	1.97	0.86
Co–HNO_3	40.2	7.10	2.01	0.86

Reaction conditions: 513 K, 1 MPa, W/F = 10 g-cat. h/mol, H_2/CO = 2, weight of catalyst = 1 g and Co loading = 10 wt.%.

[a] Steady state.

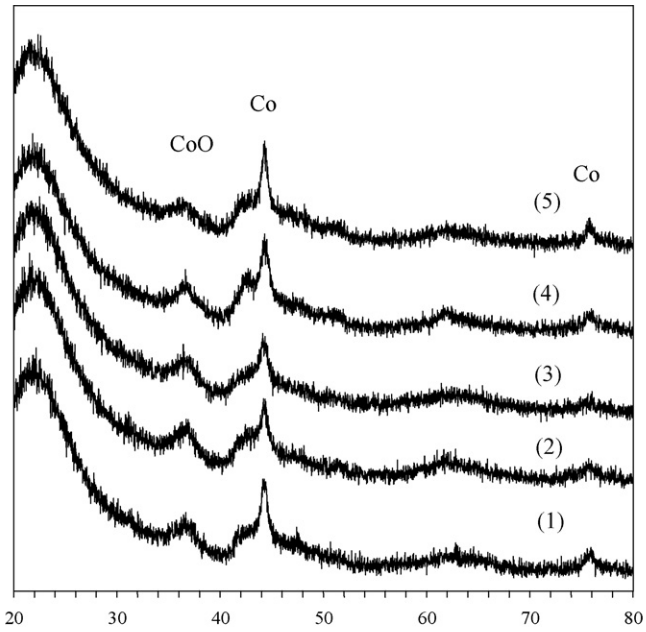

Fig. 1. The XRD profile of nonpreteated, acetic acid modified and nitric acid modified catalysts. (1) Co–silica ID; (2) Co–20Ac; (3) Co–60Ac; (4) Co–95Ac; (5) Co–HNO_3.

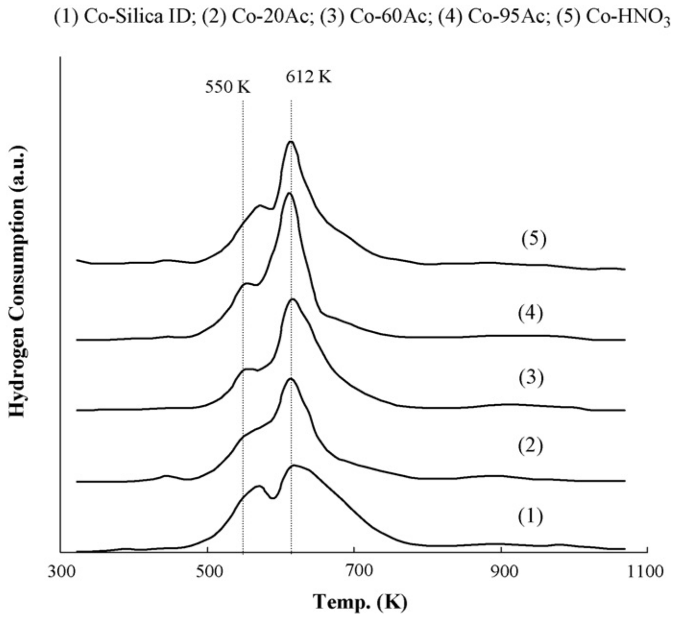

Fig. 2. The TPR profile of nonpreteated, acetic acid modified and nitric acid modified catalysts. (1) Co–silica ID; (2) Co–20Ac; (3) Co–60Ac; (4) Co–95Ac; (5) Co–HNO_3.

were two kinds of silanol groups on silica surface, H-bonded SiOH and isolated (non-H-bonded) SiOH [12,13]. It was reported that the supported metal species interacted with H-bonded SiOH resulting in large supported metal particle. However, those interacted with isolated SiOH leading to formation the smaller supported metal particle, and H-bonded SiOH was easier to be removed than isolated SiOH by calcination of silica support [14,15]. It was considered that the pretreatment of silica by acetic acid increased the isolated SiOH ratio on the silica surface or obstructed the reactivity of H-bonded SiOH with cobalt species, contributing to formation of smaller supported cobalt particle. On the other hand, because the pH of pretreatment solvents, which was different from isoelectric point of silica, could adjust the charge of silica surface [7,16], it was considered that a surplus of negative charge was present on the pretreated silica surface, contributing to increased cobalt dispersion. For the catalyst prepared from nitric acid pretreated silica support, lower pH value of pretreated solution increased the positive charge of silica support, forming large supported cobalt particle size [7]. For catalyst prepared by acetic acid pretreated silica support, the acetate or oxyl groups from acetic acid formed on the silica surface could also modified charge of silica surface, leading to formation of smaller supported cobalt particle also [10,17]. On the other hand, the cobalt particle size of Co–60Ac was smaller than that of Co–20Ac and Co–95Ac, which also indicates that both of the acetic acid promotional effects and pH value influence the dispersion of supported cobalt, because the 20 wt.% acetic acid has the lowest acetic acid concentration and 95 wt.% acetic acid is the strongest acid in three acetic acid solution. From these findings, it is proved that the pretreatment of silica support by acetic acid improved the dispersion of the supported cobalt, as compared in Table 2.

Table 2
The properties of various acetic acid modified catalysts.

Catalyst	Co particle size (nm)		Reduction degree[a] (%)	Co dispersion[b] (%)	TOF[c] (10^{-2} S^{-1})
	H_2 ad.[d]	XRD			
Co–silica ID	20.6	24	65.1	4.9	8.1
Co–20Ac	15.6	18	64.1	6.2	7.9
Co–60Ac	13.9	16	65.2	6.8	8.5
Co–95Ac	17.3	21	68.3	5.7	8.1
Co–HNO_3	23.6	28	70.2	4.1	7.7

[a] Determined by TPR from 323 K to 1073 K.
[b] Determined by H_2 chemisorption.
[c] Based on H_2 total uptake determined by H_2 chemisorption.
[d] Calculated from H_2 chemisorption at 373 K.

The reduction performance of various catalysts was determined by temperature-programmed reduction. In TPR spectra of various catalysts, as shown in Fig. 2, two peaks exist for the Co–silica ID catalyst, which locate at 571 K and 612 K, respectively. The two peaks have been identified as conversion of Co^{3+} to Co^{2+} followed by the conversion of Co^{2+} to Co [18]. For Co–HNO_3 catalyst, the reduction performance was similar to that of Co–silica ID. However, for the acetic acid pretreated catalysts, the first peak located at 550 K, lower than that of Co–silica ID catalyst, and the other peak located at 612 K, which was sharper and rather stronger than that of Co–silica ID. Comparing the reduction degrees of various catalysts, which were calculated by TPR data from 353 K to 1073 K, the Co–silica ID and Co–60Ac catalyst showed the almost same reduction degree as 65.1% and 65.2%, respectively, as shown in Table 2, even though the cobalt particle size of Co–60Ac was significantly smaller than that of Co–silica ID. It was obvious that the large cobalt oxide particles formed from cobalt nitrate were easier to be reduced, which activated hydrogen after reduction, and the activated hydrogen reduced the small cobalt oxide particles formed from cobalt acetate by spill-over effect, contributing to the high reducibility of acetic acid pretreated catalyst, where cobalt nitrate and acetate might coexist [10]. Since the oxyl groups (RO–) on silica surface were stable under 673 K in air [17], it is considered that the oxyl groups from acetic acid formed on silica surface not only obstructed the sintering of cobalt, but also promoted activating hydrogen or accelerated the hydrogen spill-over effect under the reduction process, contributing to realizing higher dispersion and reduction degree of these catalysts simultaneously. The Co–HNO_3 catalyst has the highest reduction degree in this study, due to its largest supported cobalt particle, which was generally easy to be reduced than smaller supported cobalt particle.

To investigate the effects of OH groups on the catalyst properties, the modified SiOHs on the surface of pretreated silica ID support were determined by in situ DRFIT. The FTIR spectra of various pretreated silica were referenced to that of the dried unpretreated silica ID support. As reported, the bond around 3750 cm^{-1} is the non-H-bonded SiOH, and the broad band from 3700 cm^{-1} to 3200 cm^{-1} is the H-bonded SiOH [19]. As shown in Fig. 3, the OH groups, both of non-H-bonded and H-bonded OH groups, on the surface of 60 wt.% acetic acid pretreated silica significantly decreased, however, three C–H bands were detected from 2910 cm^{-1} to 2990 cm^{-1}. This observation strongly supported that acetic acid reacted with OHs during pretreatment of silica ID by 60 wt.% acetic acid [20], leading decreasing the coverage of OHs on silica surface and forming oxyls groups on surface of pretreated silica supports. Because the supported metal species interacting with H-bonded SiOH formed large supported metal particle, and those interacting with non-H-bonded SiOH favored the smaller supported metal particle [14], the lower coverage of H-bonded SiOHs of pretreated silica could contribute to forming smaller supported cobalt particle to realize high dispersion of supported cobalt. On the other hand, the newly formed oxyls groups from acetic acid on the pretreated silica supports should modify the charge of silica surface to increase negative charge on the pretreated silica surface, contributing to increased cobalt dispersion. For both 20 wt.% and 95 wt.% acetic acid pretreated silica ID supports, beside the C–H bands, the non-H-bonded OH groups decreased and the H-bonded OH groups increased simultaneously, indicating that oxyls groups and more H-bonded OH groups were formed on silica surface. Because the higher water content of 20 wt.% acetic acid and lower pH value of 95 wt.% acetic acid, the H-bonded OH groups was increased, leading to formation of relatively large cobalt particle size as shown in Table 2. Only 60 wt.% acetic acid has favorite balance of acetic acid concentration and pH value, contributing to form the best catalytic performance of catalyst prepared from it.

The catalysts prepared by pretreated supports realized the higher dispersion and reduction degree of supported cobalt, due to the modified SiOH and the formed acetate or oxyl groups on the silica surface, resulting in higher catalytic activity in liquid phase FTS. The TOF of various catalysts was calculated. All catalysts showed very similar TOF value, varying from 0.07 s^{-1} to 0.09 s^{-1} as shown in Table 2, indicating that the pretreatment of silica support by acetic acid did not promote the site activity of supported cobalt.

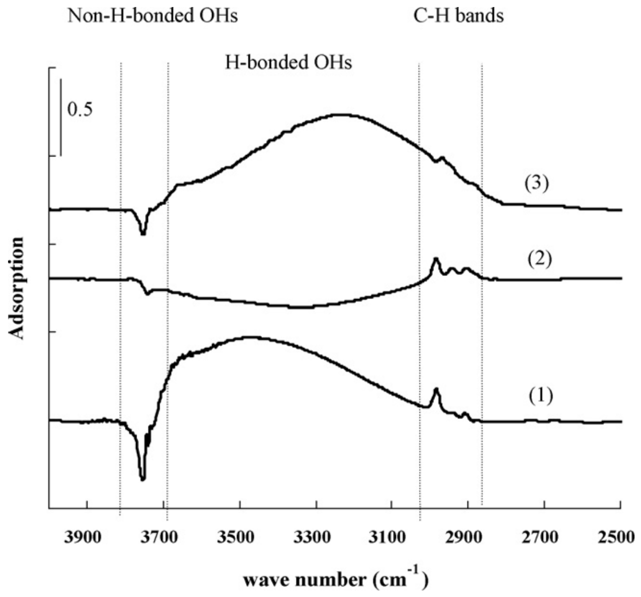

Fig. 3. In situ DRIFT spectra of various acetic acid modified silica support. (1) 20 wt.% acetic acid; (2) 60 wt.% acetic acid; (3) 95 wt.% acetic acid.

3.2. Promotional effects of ethanol

Ethanol was applied to modify the surface of silica ID support and dissolve cobalt nitrate precursor, respectively. The reaction performance of these kinds of catalysts in slurry phase FTS reaction was exhibited in Table 3. The Co–ethanol and Co–In–ethanol catalysts exhibited higher CO conversion than Co–silica ID catalyst, indicating that ethanol, as modification solvent or cobalt precursor solvent, could improve the catalytic activity of supported cobalt catalyst. For the Co–ethanol catalyst, the ethanol formed ethoxyl [21] and decreased coverage of the OHs groups on the surface of silica ID support, contributing to formation of smaller cobalt particle size. Because the newly formed ethoxyl on surface of support could promote the reduction degree of supported cobalt [5], this kind of catalyst realized higher reduction degree than Co–silica ID catalyst, even though the cobalt particle size was smaller than that of Co–silica ID catalyst, as compared in Table 4.

The Co–ethanol–S exhibited the highest CO conversion and the smallest cobalt particle size in Tables 3 and 4. It is known that, with silanol groups, water, as a solvent, formed a glassy layer of immobilized water due to the formation of hydrogen bond on the silica surface [22,23]. If solvents that are less able to form these hydrogen bonds, such as ethanol, are used, the silanol group can form these H-bonds directly with the original water ligands of the cobalt complex. This might promote the fixation of the precursor onto the silica surface and increase the cobalt dispersion. Furthermore, the solvent of cobalt precursors would modify the surface of silica support during the impregnation step, such as obstructing formation of more H-bonded OHs or lowering the reactivity of H-bonded OH groups, contributing to formation of smaller cobalt particles. On the other hand, the lower reduction degree of Co–ethanol–S, as shown in Table 4, was due to the fact that the decreased polarity of the solvent caused an increase in the interaction between the cobalt complex in ethanol and silica gel surface, forming more species that should be reduced at higher temperature. It was considered that as the solvent effects, the Co–ethanol–S catalyst realized the higher dispersion of supported

Table 3
The reaction performance of ethanol promoted catalysts in slurry phase FTS.

Catalyst	CO conversion (%)[a]	Selectivity (%)		α
		CH_4	CO_2	
Co–silica ID	48.5	7.0	1.6	0.86
Co–ethanol	58.6	8.0	1.5	0.85
Co–ethanol–S	66.5	5.1	1.2	0.87

Reaction conditions: 513 K, 1 MPa, W/F = 10 g-cat. h/mol, H_2/CO = 2, weight of catalyst = 1 g, Co loading = 10 wt.%.

[a] Steady state.

Table 4
The characteristic of ethanol promoted catalysts.

Catalyst	Co particle size (nm)		Reduction degree[a] (%)	Co dispersion[b] (%)	TOF[c] (10^{-2} S^{-1})
	H_2 [d]	XRD			
Co–silica ID	20.6	24	65.1	4.9	8.1
Co–ethanol	19.0	22	68.1	5.1	8.5
Co–ethanol–S	16.4	18	54.2	6.1	10.2

[a] Determined by TPR from 323 K to 1073 K.

[b] Determined by H_2 chemisorption.

[c] Based on H_2 total uptake determined by H_2 chemisorption.

[d] Calculated from H_2 chemisorption at 373 K.

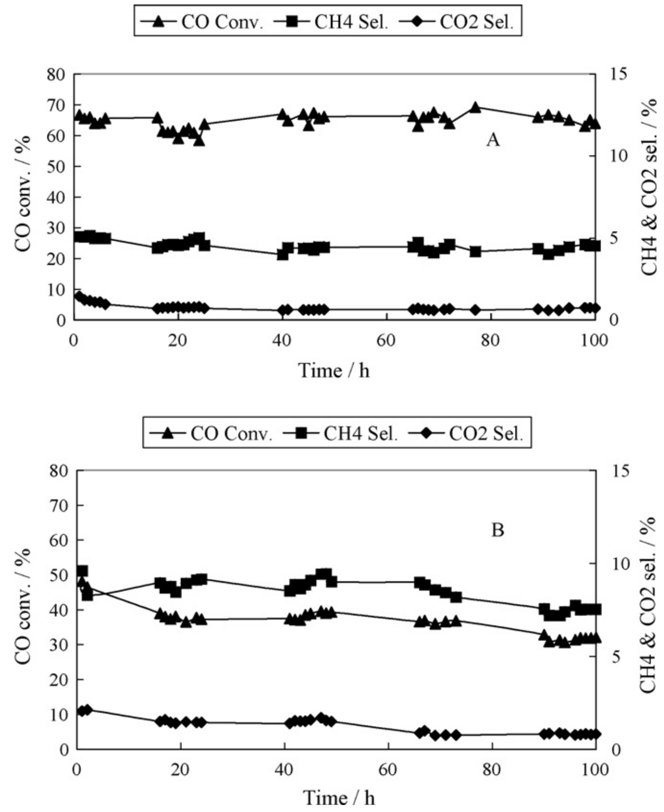

Fig. 4. Reaction performance of Co–ethanol–S and Co–silica ID catalyst in slurry phase FTS reaction during 100 h. (A) Co–ethanol–S; (B) Co–silica ID.

cobalt and kept relatively high reduction degree, resulting in higher catalytic activity. The TOF of Co–ethanol–S was slightly higher than that of Co–silica ID catalyst, as compared in Table 4. Co–ethanol–S was also very stable, which kept the highest activity and low methane as well as CO_2 selectivity for 100 h continuously. But Co–silica ID was not so stable. The activity with time on stream of both two kinds of catalysts was shown in Fig. 4. Based on these finding, for ethanol promoted catalyst, ethanol as solvent of cobalt precursor was advantageous to form smaller cobalt particle and realize more stable catalytic performance in FTS reaction.

4. Conclusion

The promotional effects of solvent during the preparation of FTS catalyst were investigated. The acetic acid modified the silanol groups and formed new oxyls on silica surface. The modified surface properties of silica support realized high dispersion and reduction degree of supported cobalt simultaneously, contributing to high catalytic activity of this kind of catalyst in slurry FTS reaction. Meanwhile, the ethanol as solvent of cobalt precursor promoted dispersion of supported cobalt and kept relatively high reduction degree, resulting in high activity and stability of this catalyst. It is found that dilemma of dispersion and reducibility of supported metal would be easily resolved via reconstructing the surface properties of supports by various solvent, such as acetic acid or ethanol, during preparation of catalyst. The simultaneously improved dispersion and reducibility of supported metal would contribute to forming more active site on catalysts, which is advantageous to any structure-insensitive reaction.

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