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Fischer–Tropsch synthesis on impregnated cobalt-based catalysts: New insights into the effect of impregnation solutions and pH value

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ABSTRACT

The Co-based catalysts were prepared with different cobalt acetate solutions. Effects of pH value were studied deeply on Fischer–Tropsch synthesis (FTS) through a semi-batch reactor. Among all impregnation solutions (water, butanol, amyl alcohol, acetic acid, nitric acid and ammonium nitrate), the catalyst prepared by NH_4NO_3 solution showed the highest catalytic activity due to its small particle size and high reduction degree. However, the catalyst with the smallest particle size derived from water as impregnation solution exhibited low activity as well as high methane selectivity since it was difficult to be reduced and inactive in FTS. According to FT-IR spectra results, the low intensity of absorbed CO on the catalyst prepared from water solution resulted in low FTS activity. Whereas, the high activity of catalysts prepared from NH_4NO_3 solution could be explained by the high intensity of absorbed CO on the catalysts. The cobalt species on the catalysts prepared under lower pH conditions exhibited smaller particle size distribution as well as lower CO conversion than those prepared at higher pH value.

1. Introduction

Fischer–Tropsch synthesis (FTS) is a promising route to produce clean fuels from syngas for substituting the petroleum fuel, and waxy hydrocarbons. Cobalt-based catalysts are the most promising candidate drivers for FTS [1–5]. However, the improvement of the catalyst activity still remains challenges under a mild reaction conditions.

Generally, the activity of Co-based catalysts depends on the number of active sites and dispersion on the surface of support [6,7]. The initial formation of small CoO and Co_3O_4 crystallites is required for high metal dispersion of FTS catalysts, however, such small oxide clusters result in the strong interaction with support, leading to a decreased reduction degree [8–10]. There are many cobalt compounds as feedstock used to prepare cobalt-based FTS catalysts, such as cobalt nitrate, cobalt acetate, cobalt chloride [11–13]. Employing cobalt nitrate as feedstock could produce CoO_x particles which were easily to be reduced, but had low dispersion. In contrast, cobalt acetate exhibited the small CoO_x particles with very high dispersion. However, in turn these small particles could be reduced completely only at very high temperature (above 800 K), resulting in low activity of Co-based catalysts [14].

Besides the effect of cobalt precursors, the impregnation solution used to dissolve the cobalt compounds also concerns the FTS activity. It was reported that using various organic solutions to dissolve cobalt nitrate improved the reduction degree [15]. Sun et al. have concluded that the Co-based catalyst prepared using dehydrated ethanol as cobalt nitrate impregnation solution exhibited high activity and very low methane selectivity [16]. Based on these literatures, using the different impregnation solutions to prepare catalysts will play an important role on metal dispersion, reduction behavior and catalytic activity. However, to the best of our knowledge, there is less information on the solution and pH value effects for the catalyst prepared from cobalt acetate. In the present study, the solution effect on reduction behavior and activity of cobalt–silica catalysts prepared from cobalt acetate were investigated.

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Table 1. Nomenclature of catalysts.

Catalyst	Solution
Co–H_2O	Water
Co–C_4OH	Butanol
Co–C_5OH	Amyl alcohol
Co–Acetic	Acetic acid
Co–7.8HNO_3	7.8 M nitric acid
Co–2NH_4NO_3	2 M ammonium nitrate

2. Experimental

2.1. Catalyst preparation

The catalysts were prepared by the incipient-wetness impregnation (IWI) method. In detail, a solution of cobalt (II) acetate precursor dissolved in various solutions was impregnated on a commercial available silica gel (ID gel, Fuji Davison, surface area 270 m^2/g and average pore diameter 8.7 nm). Subsequently, the catalysts were dried at 393 K for 12 h and calcined at 673 K for 2 h in air. Then, the calcined catalysts were activated by H_2 at 673 K for 10 h, subsequently the catalysts were passivated by 1% O_2 diluted in N_2. The catalyst nomenclatures were listed in Table 1. For example, Co–H_2O means the catalyst prepared using water as a cobalt impregnation solution. The Co content was 10 wt% for all catalysts. To compare the different pH value effects, two series of catalysts with varied concentrations of HNO_3 or NH_4NO_3 as solutions were also prepared by the same method.

2.2. Catalyst characterization

H_2 temperature-programed reduction (TPR) was measured by a flow-type quartz reactor. Briefly, 5% of H_2 diluted in N_2 was selected as reducing gas. The produced water in the effluent during the reduction gas was removed by a 3 A molecular sieve trap at the exit of reactor. The effluent gas was analyzed by a gas chromatography with TCD, where N_2 was used as a reference gas. The calcined catalyst samples with 0.2 g were initially flushed with He at 323 K for 30 min, then the reducing gas was introduced into the reactor and the temperature was linearly raised to 1073 K with a heating rate of 7 K/min.

X-ray diffraction (XRD) patterns were measured using a Rigaku RINT 2400 equipped with CuK_α irradiation (40 KV, 200 mA) and a scan rate of 2.0 °/min. The metallic Co crystallite diameter of the passivated catalysts was calculated by Scherrer's equation.

The FT-IR spectra were recorded on a Nicolet Nexus 470 spectrometer with a diffuse reflectance attachment and a MCT detector. The catalyst sample of 15 mg was grounded and placed in an infrared cell with Zinc Selenide (ZnSe) windows. The catalysts were reduced at 673 K using H_2 at 50 mL/min for 1 h. After pretreatment, CO adsorption was performed at room temperature by a flow of CO/He (a ratio of 1/1) at 20 mL/min for 1 h. Then, the physically adsorbed CO was removed by flowing He at 20 mL/min for 2 h. Finally, the IR spectra of CO adsorbed on the catalysts were recorded by collecting 32 scans at 2 cm^{-1} resolution.

2.3. Catalytic activity test

The activity of the catalysts on FT synthesis was measured in a flow-type semi-batch reactor with an inner volume of 80 mL. A cooling trap was loaded between the reactor and pressure regulator to collect water and liquid hydrocarbons. The passivated catalyst (1 g, 20–40 mesh) was grounded in *n*-hexadecane of 20 mL as a reaction medium. It was activated by syngas at 513 K for 1 h before reaction and then the temperature was cooled down to 473 K and kept for 20 min. Subsequently, syngas was pressurized to 10 bar, accompanying by the increase of reaction temperature. The effluent gas from the reactor was cooled at a cooling trap, subsequently introduced and analyzed by two online gas chromatography equipped with TCD using an activated charcoal column for CO, CO_2, and CH_4, FID using a Porapak Q column for light hydrocarbons, respectively. The liquid hydrocarbon products collected in cooling trap were combined and analyzed by gas chromatography equipped with FID using a SE-30 column. Argon was used as an internal standard with a concentration of 3% in feed gas. The CO conversion and product yields were calculated as follows:

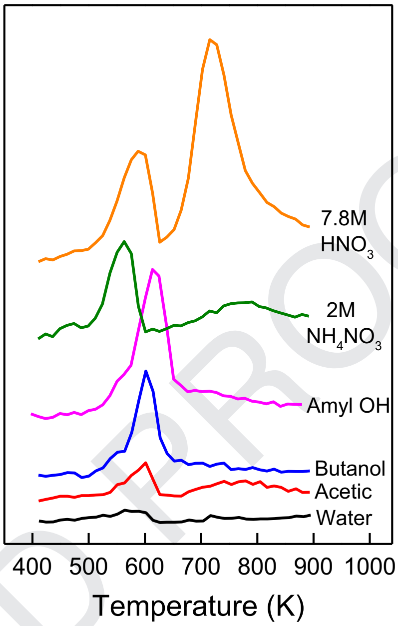

Fig. 1. TPR profiles of Co based catalysts prepared from different solutions.

$$\text{CO conversion}\ (\%) = \left[\frac{\frac{\text{CO}}{\text{Ar}}\,\text{in feed} - \frac{\text{CO}}{\text{Ar}}\,\text{in effluent}}{\frac{\text{CO}}{\text{Ar}}\,\text{in feed}}\right] \times 100\%$$

$$\text{Selectivity}\ (\text{C} - \text{mmol}) = \frac{100 \times C_n(\text{C} - \text{mmol})}{\sum C_i(\text{C} - \text{mmol})}$$

3. Results and discussion

3.1. Influence of impregnation solutions

The TPR profiles of the catalysts prepared from different solutions, are given in Fig. 1. The Co–H_2O catalyst exhibits two small peaks at 588 and 720 K, indicating that it was reduced quite difficultly at 673 K, leading to low catalytic activity. The Co–7.8 M HNO_3 also exhibits two peaks but the intensity is much higher. The high intensity of the first peak is also observed at 588 K. The high intensity of the second peak appears at much lower temperature, indicating that the catalyst is easy to be reduced. These two peaks are the conversion of Co_3O_4 to CoO($Co_3O_4+H_2\rightarrow3CoO+H_2O$) followed by Co^{2+} to Co ($CoO+H_2\rightarrow Co^0+H_2O$), which have been identified as the dual-reduction steps of Co_3O_4 [17]. The reduction processes of the other catalysts are also improved if compared to that of Co–H_2O as shown in the higher intensity of the first peak.

The IR spectra of adsorbed CO on the catalysts prepared from different solutions are shown in Fig. 2. It is clear that the CO absorption mode on the Co sites of the catalysts depended on the type of impregnation solutions. The bands above 2000 cm^{-1} are assigned to the linear CO geometry, and that below 2000 cm^{-1} is assigned to the bridged CO geometry adsorbed on the Co sites [18,19]. For Co–H_2O, the three peaks at 2060, 2038, and

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