Preparation of Co/Al$_2$O$_3$ catalyst for Fischer–Tropsch synthesis: Combination of impregnation method and homogeneous precipitation method

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ABSTRACT

Co(20 wt.%)/γ-Al$_2$O$_3$ catalysts were prepared by four methods, i.e., impregnation method (Imp), two kinds of precipitation methods using aqueous solution of ammonia (P_a) or ammonium oxalate (P_{ao}) as the precipitant and homogenous precipitation method (HP). The prepared Co/Al$_2$O$_3$ catalysts were characterized by XRD, H$_2$-TPR, H$_2$ chemisorption and TEM-EDS, and the catalytic activity for Fischer–Tropsch (FT) synthesis was evaluated with the continuously stirred tank reactor. For the Co/Al$_2$O$_3$ catalysts prepared by the Imp and P_a methods, the reducibility of Co and the surface area of Co metal were low, but the intrinsic activity per active Co metal species (TOF) was high. On the other hand, for the Co/Al$_2$O$_3$ catalysts prepared by the P_{ao} and HP methods, the reducibility of Co and the surface area of Co metal were high, but the TOF was low. Thus, the overall reaction rate increased in the following order: P_{ao} < HP < P_a < Imp. Combination of the Imp and HP methods was also examined for the preparation of Co/Al$_2$O$_3$ catalysts; that is to say, part of Co was loaded by the HP method, followed by loading with the rest of Co by the Imp method. Co/Al$_2$O$_3$ catalysts prepared by this two-step procedure (Co(x, Imp)/Co(y, HP)/Al$_2$O$_3$, $x+y=20$) showed higher activity than those prepared by either the Imp method (Co(20, Imp)/Al$_2$O$_3$) or the HP method (Co(20, HP)/Al$_2$O$_3$), and the Co(15, Imp)/Co(5, HP)/Al$_2$O$_3$ catalyst showed the best performance. The high activity of the Co(x, Imp)/Co(y, HP)/Al$_2$O$_3$ catalyst is originated from the coexistence of two different kinds of Co species, i.e., easily reducible Co species derived from the HP method and highly active Co species derived from the Imp method. These two kinds of Co species cooperatively promoted the reduction and the dispersion of Co metal to enhance the overall catalytic activity.

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1. Introduction

Fischer–Tropsch (FT) synthesis is an excellent way to convert various carbon sources (e.g. coal, natural gas and biomass) into liquid fuels and chemicals via syngas [1,2]. Much attention is currently focused on FT synthesis in both academia and industry due to the drastic increase in the price of crude oil and the demand for the clean alternative fuels. So far, various heterogeneous transition metal catalysts such as Fe, Co, Ni and Ru have been developed for this reaction [3,4]. Among them, Co-based catalysts are advantageous for the practical application due to the high activity and selectivity to long-chain liner hydrocarbons, high resistance toward deactivation, low activity for the competitive water-gas shift reaction and lower price than Ru. It is generally accepted that the activity of Co catalysts for FT synthesis depends on the number of Co metal atoms on the surface [5,6]. Therefore, Co is generally

deposited on the supports with high surface area (e.g., SiO$_2$, Al$_2$O$_3$, TiO$_2$ and carbon materials) in order to increase the number of active Co metal species [1–4].

Due to the high resistance to attrition and the ability to stabilize small clusters, alumina is one of the attractive support materials for Co-based FT catalyst. However, the strong interaction between Co and Al$_2$O$_3$ support often makes the reduction of Co oxide difficult, suppresses the formation of active Co metal species and thereby limits the activity of Co/Al$_2$O$_3$ catalyst. Thus, various attempts have been done in order to enhance the reducibility and dispersion of active Co metal species. For instance, many research groups reported that the addition of small amount of noble metal (e.g. Pt [7–9], Re [7,8,10], Ru [7,8,11], Pd [8] and others [12,13]) could promote the reduction of Co oxide species and increase the number of active Co metal sites, presumably by hydrogen dissociation and spillover from the promoter surface. Loading small amount of metal ions (e.g. Zr [14–16], alkali earth elements [17–20], rare earth elements [21,22] and others [23–26]) on Al$_2$O$_3$ support was also reported to be effective for the enhancement of reducibility and dispersion of active Co metal species, since addition of these

metal ions would improve the interaction between Co and Al_2O_3 support. Physicochemical properties of Al_2O_3 support such as pore size [27,28], acid-base property [29,30], crystal phase [31–34] and morphology [35,36] are another important factors to determine the structure of Co and the activity of Co/Al_2O_3 catalyst. For instance, Sun et al. examined the effect of acid-base property of Al_2O_3 support on the catalytic activity [29,30]. They found that Al_2O_3 support with low acidity promoted the reduction of Co oxide species and thereby increased the activity for FT synthesis. Holmen et al. examined the effect of crystal phase and pore size of Al_2O_3 support in detail [31,32]. They clearly showed that Co/Al_2O_3 catalyst prepared from α-Al_2O_3 with medium pore size showed the highest selectivity of C_{5+} products. On the other hand, Co-loading method also influences the structure of Co and the activity of Co/Al_2O_3 catalyst. Generally, Co/Al_2O_3 catalyst is prepared by an impregnation method, followed by drying, calcination and reduction. Although this technique is very simple, structure of Co particles largely varied with the kind of Co precursor [37–39] and solvent [39], the pH of the impregnation solution [39,40], the conditions of calcination and reduction [41,42]. Of course, other methods (e.g. precipitation method [43] and solvothermal method [44]) were also examined in order to prepare Co/Al_2O_3 catalysts with high dispersion and reducibility of Co. Therefore, it is concluded that precise control of the Co reducibility and dispersion should be very important subject to develop highly active Co/Al_2O_3 catalysts for FT synthesis.

In the present study, we examined the preparation method of Co/Al_2O_3 catalysts in order to enhance the catalytic activity for FT synthesis. Co/Al_2O_3 catalysts were prepared by four methods (impregnation method, two kinds of precipitation methods using aqueous solution of NH_3 or $(NH_4)_2C_2O_4$ as the precipitant, and homogenous precipitation method) and the catalytic activity for FT synthesis was evaluated with the continuously stirred tank reactor. We also examined the two-step synthesis of Co/Al_2O_3 catalysts and found that the combination of the impregnation method and the homogeneous precipitation method could improve the activity of Co/Al_2O_3 catalyst. We systematically examined the relationship between the structure of Co and the activity of Co/Al_2O_3 catalysts in order to obtain the catalyst design concept.

2. Experimental

2.1. Catalyst preparation

Co-loaded Al_2O_3 (named Co/Al_2O_3) catalysts were prepared by four methods, i.e., impregnation method (Imp), two kinds of precipitation methods using aqueous solution of ammonia (P_a) or ammonium oxalate (P_{ao}) as the precipitant and homogeneous precipitation method (HP). Typically, $Co(NO_3)_2 \cdot 6H_2O$ and γ-Al_2O_3 (Soekawa Chemical, $90 \, m^2 \, g^{-1}$) were employed as the Co precursor and the support material, respectively. Total loading amount of Co was 20 wt.% for all samples. In the Imp method, Al_2O_3 powder (8.0 g) was dispersed into an aqueous solution (100 mL) of Co nitrate and stirred for 0.5 h, followed by evaporation to dryness at 90 °C. Then, the obtained powder was dried at 100 °C for 12 h and calcined in air at 400 °C for 3 h. In the P_a and P_{ao} methods, Al_2O_3 powder (8.0 g) was dispersed into an aqueous solution (300 mL) of $Co(NO_3)_2 \cdot 6H_2O$ and stirred for 1 h, followed by adding an aqueous solution of NH_3 or $(NH_4)_2C_2O_4$ at one time. Co was deposited as Co hydroxide in the P_a method and Co oxalate in the P_{ao} method, respectively. The suspension was filtered off with suction, washed with distilled water, and dried at 100 °C in an oven overnight. The obtained powders were then calcined in air at 400 °C for 3 h. In the HP method, $Co(NO_3)_2 \cdot 6H_2O$ (9.9 g), Al_2O_3 (8.0 g), $(COOH)_2$ (5.0 g) and urea (20.4 g) were added to distilled water (400 mL), followed by heating at 90 °C until the supernatant solution turned

clear and colorless. In the HP method, as the hydrolysis of urea proceeds, oxalate ions are gradually produced in the solution and react with Co^{2+} ions to form CoC_2O_4 as the precipitate. After cooling down to room temperature, the suspension was filtered off with suction, washed with distilled water and dried at 100 °C in an oven overnight. The obtained powders were then calcined in air at 400 °C for 3 h. The prepared Co/Al_2O_3 catalysts were referred to as Co(loading amount, loading method)/Al_2O_3 such as Co(20, Imp)/Al_2O_3.

Some Co/Al_2O_3 catalysts were prepared by two-step procedure. First, part of Co was loaded by the HP method, followed by filtration, washing with distilled water, drying at 100 °C and calcination in air at 400 °C for 1.5 h. Then, the rest of Co was loaded by the Imp method, followed by drying at 100 °C and calcination in air at 400 °C for 1.5 h. The catalysts prepared by two-step procedure are referred to as Co(x_2, M_2)/Co(x_1, M_1)/Al_2O_3, where x_1 and M_1 show the Co-loading amount and method in the first step, and x_2 and M_2 show the Co-loading amount and method in the second step, respectively.

2.2. Characterization

N_2 adsorption/desorption isotherms of the samples were measured at -196 °C using a BERSORP-MAX equipment (BEL Japan Inc.). Prior to the measurements, the samples (0.2 g) were out-gassed at 105 °C for 6 h under vacuum. The specific surface area was obtained by applying the Brunauer–Emmett–Teller (BET) model for absorption in a relative pressure range of 0.05–0.30. The total pore volume was calculated from the amount of N_2 vapor adsorbed at a relative pressure of 0.99.

Powder X-ray diffraction (XRD) pattern was recorded at room temperature on a Rigaku diffractometer RINT 2500 TTRIII using Cu Kα radiation (50 kV, 300 mA). The mean particle size of Co_3O_4 ($d_{Co_3O_4}$) was calculated from the diffraction line at $2\theta = 31.2°$ with the Scherrer equation. The obtained particle size of Co_3O_4 could be used to calculate that of Co metal (d_{Co}) after H_2 reduction pretreatment by the following formula (Eq. (1)) [9].

$$d_{Co} = 0.75 \times d_{Co_3O_4} \tag{1}$$

Temperature programmed reduction under H_2 (H_2-TPR) was carried out with BELCAT-B (BEL Japan Inc.). The calcined catalyst (0.1 g) was mounted in a quartz cell and heated up to 900 °C in a flow of 5% H_2/Ar (30 ml min^{-1}). The heating rate was 10 °C min^{-1}. The reduction degree of supported cobalt was calculated from the amount of H_2 consumption during H_2 reduction pretreatment at 300 °C for 6 h. The effluent gas was passed through a 5A molecular sieve trap to remove the produced water before reaching a thermal conductivity detector.

Hydrogen chemisorption experiments were performed on BELCAT-B. Before measurement, the samples were reduced at 300 °C for 6 h in a flow of 5% H_2/Ar (15 ml min^{-1}) and held at 300 °C for 1 h in a flow of Ar (30 ml min^{-1}) to desorb the residual chemisorbed hydrogen. After cooling the sample down to 100 °C in a flow of Ar, H_2 chemisorption measurements were started. The corrected dispersion (D_{corr}, Eq. (2)) and the surface area of Co metal were calculated according to the method reported in the literature [45].

$$D_{corr} = \frac{(\text{number of surface Co metal atoms})}{(\text{number of total Co atoms}) \times (\text{fraction reduced})} \times 100 \tag{2}$$

Transmission electron microscopy (TEM) images of the reduced and passivated Co/Al_2O_3 catalysts were recorded by a JEOL electron microscope (JEM-3000F, 300 kV) equipped with energy dispersive X-ray spectroscopy (EDS).