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Factors influencing the activity of Co/Ca/TiO_2 catalyst for Fischer–Tropsch synthesis

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A series of Co/Ca/TiO_2 catalysts with different reduction degree of Co and dispersion of Co metal were prepared by varying the temperature of hydrogen reduction pretreatment, the types of Co precursor and TiO_2 support, and the Co-loading method. The activity of Co/Ca/TiO_2 catalysts for Fischer–Tropsch (FT) synthesis largely depended on the crystal phase of TiO_2 support, the reduction degree of Co and the surface area of Co metal. Rutile TiO_2 was more effective than anatase TiO_2 as the support TiO_2 material. The optimum reduction degree of Co was around 60% and the excess reduction decreased the activity. The reaction rate for FT synthesis linearly increased with increasing the surface area of Co metal. The highest activity was obtained over the catalyst prepared from rutile TiO_2 and $Co(NO_3)_2{\cdot}6H_2O$ by the impregnation method, followed by the hydrogen reduction at 300 °C. The space time yield (STY) of C_{5+} products over the best Co/Ca/TiO_2 catalyst was 1.3 and 3.5 times higher than those over Co/γ-Al_2O_3 and Co/SiO_2, respectively, as the representative catalysts for FT synthesis.

1. Introduction

Fischer–Tropsch (FT) synthesis, which can convert various carbon sources (e.g. coal, natural gas and biomass) into long chain hydrocarbons via syngas, is a promising way to produce an environmentally benign fuels with no sulfur and nitrogen compounds [1,2]. The current drastic increase in the price of crude oil and the demand for the clean alternative fuel have focused renewed attention on FT synthesis in both academia and industry. Certain transition metals such as Co, Fe, Ni and Ru have been frequently applied as the catalyst for FT synthesis [3,4]. Among them, cobalt is considered as the preferred catalyst due to its high selectivity for long-chain liner paraffins, high resistance toward deactivation by water and low activity for the competitive water-gas shift reaction. Several studies indicated that the activity of Co catalysts depended on the number of the exposed Co metal sites [5,6]. Therefore, Co is normally deposited on the high surface area support such as SiO_2 [7–22], Al_2O_3 [23–27], TiO_2 [28–31] and carbon materials [16,20,32,33], in order to increase the dispersion of active Co metal species.

Supported Co catalysts are usually prepared by impregnation, drying, calcination and reduction. Although this technique is very simple, structures of supported Co (e.g. the reduction degree, the dispersion and the particle size distribution) largely varied with the types of Co precursor [7–9,23,24,28,29] and solvent [10], the pH of the impregnation solution [11,25], the use of templates [12,13,32], and the conditions of drying [14], calcination [15–17,26] and reduction [18,30]. For example, effect of Co precursors was examined by various researchers. It is generally accepted that impregnation of cobalt nitrate on SiO_2 gives Co species with high reducibility and low dispersion, but impregnation of cobalt acetate and other organic precursors on SiO_2 gives Co species with low reducibility but high dispersion [7–9]. Tsubaki et al. reported that the dispersion of Co metal on Co/SiO_2 was enhanced by using dehydrated ethanol instead of water as the impregnation solvent [10]. Ming and Barker investigated the influence of solution pH upon the preparation of Co/SiO_2 catalyst [11]. They found that impregnation at pH ≥ 5 formed various cobalt silicates or hydrosilicates to decrease the Co reducibility. Yamada et al. found that Co/SiO_2 with high Co dispersion and reducibility could be prepared by impregnation method using Co nitrate and some chelating agents (e.g. nitrilotriacetic acid) [12,13]. Jong et al. reported that Co/SiO_2 catalyst with a narrow Co particle size distribution (4.6 ± 0.8 nm) could be prepared by impregnation, drying and calcination in NO/He [16]. On the other hand, other methods (e.g. precipitation [19], homogeneous precipitation [20], sol–gel [21,31], microemulsion [33], solvothermal [27] and surface impregnation combustion [22]) were also examined for the preparation of supported Co catalysts. Structures of Co metal such as the particle size, the reducibility and the morphology largely depended on the kinds of preparation methods. Therefore, we must systematically examine the effect of Co-loading method in

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order to develop highly active Co catalysts for FT synthesis. Furthermore, most of the previous studies for the preparation of supported Co catalysts were limited to Co/SiO_2 and Co/Al_2O_3 catalysts. Since the kinds of support materials largely influence the strength of Co-support interaction, the optimum preparation method and condition should vary with the kinds of support materials.

Our research group focused on TiO_2 as the support material of Co catalyst. TiO_2 is suitable for the practical application due to the low cost, the safety and the chemical stability. Techniques to control the morphology and the crystal phase of TiO_2 are well-established [34]. Furthermore, it was reported that the strength of Co-support interaction on Co/TiO_2 was in the middle of those on Co/SiO_2 and Co/Al_2O_3 [35]. This indicates that Co particles with high reducibility and dispersion would be obtained on TiO_2. These facts motivated us to use TiO_2 as the support material. In the previous study [36], we examined the loading effect of metal ions on the TiO_2 support and found that Ca additives most effectively enhanced the activity of Co/TiO_2 catalyst among the examined metal ions. Results of H_2-TPR, H_2 chemisorption and TEM-EDS revealed that loading small amount of Ca ions strengthened the Co-support interaction and suppressed the aggregation of Co particles during the thermal pretreatment. In other words, Ca additives greatly increased the Co dispersion and thereby increased the activity of the Co/TiO_2 catalyst. In the present study, we prepared various $Co/Ca/TiO_2$ catalysts by varying the temperature of hydrogen reduction pretreatment, the types of Co precursor and TiO_2 support, and the Co-loading method. The activities of the prepared $Co/Ca/TiO_2$ catalysts for FT synthesis were evaluated with the continuously stirred tank reactor. We systematically examined the relationships between the structure of supported Co and the catalytic activity in order to obtain the catalyst design concept.

2. Experimental

2.1. Catalyst preparation

TiO_2 modified with Ca ion (named Ca/TiO_2) was prepared by the incipient wetness impregnation method using TiO_2 powder and an aqueous solution of $Ca(NO_3)_2{\cdot}4H_2O$. Three kinds of TiO_2 samples (JRC-TIO-4, 6 and 13, Catalysis Society of Japan) were used as the support materials. Ca-loading amount was fixed at 0.8 wt%. After impregnation, the obtained powders were dried at 100 °C for 12 h, followed by calcination in air at 500 °C for 3 h.

Co-loaded Ca/TiO_2 (named $Co/Ca/TiO_2$) catalysts were prepared by three methods, i.e., impregnation method (Imp), homogeneous precipitation method (HP) and precipitation method (P). The Co precursors employed were $Co(NO_3)_2{\cdot}6H_2O$ (CoN), $Co(CH_3COO)_2{\cdot}4H_2O$ (CoA) and a mixture of $Co(NO_3)_2{\cdot}6H_2O$ and $Co(CH_3COO)_2{\cdot}4H_2O$ (CoN + CoA). Loading amount of Co was 20 wt% for all samples. In the impregnation method, Ca/TiO_2 powder (8.0 g) was dispersed into an aqueous solution (100 mL) of Co precursor 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 homogeneous precipitation method, $Co(NO_3)_2{\cdot}6H_2O$ (9.9 g), Ca/TiO_2 (8.0 g) and urea (20.4 g) were added to distilled water (400 mL), followed by heating at 90 °C until pH of the solution reached to 7. 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. The obtained powders were then calcined in air at 400 °C for 3 h. In the precipitation method, Ca/TiO_2 powder (8.0 g) was dispersed into an aqueous solution (300 mL) of $Co(NO_3)_2{\cdot}6H_2O$ and stirred for 1.0 h, followed by adding an aqueous solution of NH_3, $(NH_4)_2C_2O_4$, Na_2CO_3 or NaOH. Precipitation methods using aqueous solutions of NH_3, $(NH_4)_2C_2O_4$, Na_2CO_3 and NaOH were referred to as P_A, P_{AO}, P_{SC} and P_{SH}, respectively. The suspension was filtered off with suction, washed with distilled water, and dried at 100 °C in an oven. The obtained powders were then calcined in air at 400 °C for 3 h. The prepared $Co/Ca/TiO_2$ catalysts were referred to as $Co/Ca/TiO_2$ (Co precursor or Co loading method) such as $Co/Ca/TiO_2$(CoN) and $Co/Ca/TiO_2$(HP). As the reference sample, Co (20 wt%)/SiO_2 and Co (20 wt%)/γ-Al_2O_3 were prepared from commercially available SiO_2 (Q-10, Fuji Silysia Chemical Ltd Co.), γ-Al_2O_3 (Soekawa chemical, 90 $m^2\ g^{-1}$) and $Co(NO_3)_2{\cdot}6H_2O$ by the impregnation method, followed by drying at 100 °C for 12 h and calcination in air at 400 °C for 3 h.

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 were calculated from the diffraction line at $2\theta = 31.2^\circ$ with the Scherrer equation. The obtained particle size of Co_3O_4 could be used to calculate that of Co metal after reduction by the following formula (Eq. (1)) [37].

$$d(Co^0) = 0.75d(Co_3O_4) \qquad (1)$$

The weight fraction of the rutile phase in the TiO_2 sample (W_R) was calculated from the XRD peak intensities using the following formula (Eq. (2)) [38],

$$W_R = \frac{1}{[1 + 0.884(A_{\text{anatase}}/A_{\text{rutile}})]} \qquad (2)$$

where A_{anatase} and A_{rutile} represent the X-ray integrated intensities of anatase (1 0 1) and rutile (1 1 0) diffraction peaks, respectively.

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 $cm^3\ min^{-1}$). The heating rate was 10 °C min^{-1}. The reduction degree of supported cobalt was calculated from the amount of H_2 consumption during hydrogen reduction pretreatment at 300–400 °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 300–400 °C for 6 h in a flow of 5% H_2/Ar (15 $cm^3\ min^{-1}$) and held at 300–400 °C for 1 h in a flow of Ar (30 $cm^3\ min^{-1}$) 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 dispersion and the surface area of Co metal were calculated according to the method reported in the literature [39].

Transmission electron microscopy (TEM) images of the reduced and passivated $Co/Ca/TiO_2$ catalysts were recorded by a JEOL electron microscope (JEM-3000F, 300 kV).

2.3. Typical procedures of catalytic reactions

FT synthesis was performed with the continuously stirred tank reactor in a similar way to the previous study [40]. Before reaction, the catalyst (2.5 g) was in situ reduced in a flow of H_2 (40 mL min^{-1}) at 300–400 °C for 6 h. After the reactor was cooled down to room