Journal of Molecular Catalysis A: Chemical 394 (2014) 22–32

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

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

Fischer–Tropsch synthesis over alumina supported cobalt catalyst: Effect of crystal phase and pore structure of alumina support

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ARTICLE INFO

Article history:
Received 28 April 2014
Received in revised form 24 June 2014
Accepted 27 June 2014
Available online 4 July 2014

Keywords:
Fischer–Tropsch synthesis
Cobalt
Alumina
Crystal phase
Pore structure

ABSTRACT

Effect of crystal phase and pore structure of Al_2O_3 support was examined in order to improve the activity of Co/Al_2O_3 catalysts for FT synthesis. Total 18 kinds of Al_2O_3 supports having different crystal phase and pore structures were prepared by the calcination of commercial boehmite and gibbsite under various conditions. Cobalt was loaded on these Al_2O_3 supports by the impregnation, drying and calcination. Activity of Co/Al_2O_3 catalyst for FT synthesis was evaluated with a continuously stirred tank reactor. Structure of Co particles and activity of Co/Al_2O_3 catalysts strongly depended on the pore structure (i.e. surface area and pore size) of Al_2O_3 support rather than the crystal phase. Among the examined samples, the highest activity was obtained over the catalyst, which was prepared from θ-Al_2O_3 having the moderate surface area ($84\ m^2\ g^{-1}$). When Al_2O_3 supports having the moderate surface area were used, the formation of Co particles having high dispersion and relatively uniform size was promoted by pores of suitable size and led to the enhancement of overall catalytic activity.

1. Introduction

It is highly desired to establish practical methods of producing clean alternative fuels in the near future due to the growing concern of environmental and energy problems. Fischer–Tropsch (FT) synthesis, which can synthesize hydrocarbon mixtures from syngas, is an excellent way to produce liquid fuel, since various carbon sources (e.g. coal, natural gas and biomass) can be used as feedstock [1,2]. Furthermore, liquid fuels produced by FT synthesis do not contain any sulfur, nitrogen and aromatic compounds. Therefore, FT synthesis has attracted renewed attentions as one of the production methods of liquid fuels. So far, various attempts such as development of catalysts and reactors have been made in both academia and industry to enhance the efficiency of this reaction system. Catalysts employed for FT synthesis are some heterogeneous transition metal ones such as Fe, Co, Ni and Ru. Among them, Co-based catalysts are advantageous to the practical application due to the relatively 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 [3,4]. Since activity of supported Co catalysts generally depends on the number of exposed Co metal atoms [5–7], Co is usually deposited on supports having high surface area (e.g. SiO_2, Al_2O_3, TiO_2 and carbon materials) in order to improve the dispersion of active Co metal species [1–4].

Alumina is one of the most employed supports for Co-based FT catalysts due to the high thermal stability and the strong resistance to attrition. Al_2O_3 support may also contribute to a stable catalytic activity for a long time, since the great ability of Al_2O_3 support to stabilize small metal clusters would suppress the aggregation of Co metal particles during the catalytic reaction. However, the strong interaction between Co particles and Al_2O_3 support often makes the reduction of Co oxide difficult and reduces the number of active Co metal species, resulting in the suppression of the activity of Co/Al_2O_3 catalyst. Thus, small amount of noble metal (e.g. Pt [8–10], Re [8,9,11], Ru [8,9,12], Pd [9,13], Ir [14], Au [15,16] and Ag [15,17]) is often added to Co/Al_2O_3 catalysts, since noble metal additives can 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. However, noble metals are not suitable to the industrial application due to their high cost. Therefore, various examinations are currently carried out, such as the development of more inexpensive promoters (e.g. Zr, alkali earth elements and rare earth elements) and the improvement in the preparation method of Co/Al_2O_3 catalysts and so on [1–4].

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http://dx.doi.org/10.1016/j.molcata.2014.06.034
1381-1169/

The physicochemical properties of Al_2O_3 support such as pore size [18–20], crystal phase [21–25], morphology [26–30] and acid–base property [31,32] also influenced the structure of Co particles and the activity of Co/Al_2O_3 catalyst. For example, it is generally accepted that Co particle size depends on the pore size of Al_2O_3 support and large Co particles tend to be formed on the Al_2O_3 support having large pore size [18–20]. Holmen et al. compared four kinds of Co/Al_2O_3 catalysts, which were prepared from Al_2O_3 supports having different crystal phase (α, γ, δ and θ). They found that Co/Al_2O_3 catalyst prepared from α-Al_2O_3 showed the highest selectivity of C_{5+} products [21–23]. Panpranot et al. reported that Co/Al_2O_3 prepared from χ-Al_2O_3 showed better catalytic performance than that prepared from γ-Al_2O_3 [24,25]. Martínez et al. applied the nanofibrous γ-Al_2O_3 as the support material along with several commercial Al_2O_3 [28]. They found that activity of CoRu/Al_2O_3 catalysts depended on the support surface area rather than the pore size and CoRu/Al_2O_3 catalyst prepared from nanofibrous γ-Al_2O_3 showed the highest activity. Sun et al. examined the impact of acid–base property of Al_2O_3 support on the catalytic activity [31,32]. They found that Al_2O_3 support with low acidity showed high catalytic activity due to having the high reduction degree of Co. Although the catalytic activity strongly depended on the structure of Al_2O_3 support as described above, influence of the structure of Al_2O_3 support on the activity of Co/Al_2O_3 catalyst for FT synthesis is not fully understood yet.

In the present study, we examined the effect of crystal phase and pore structure of Al_2O_3 support on the activity of Co/Al_2O_3 catalyst for FT synthesis. Al_2O_3 supports having different crystal phase and pore structures were prepared by the calcination of commercial boehmite and gibbsite at various temperatures, and Co was loaded by an impregnation method using Co nitrate as the Co precursor. The activity of prepared Co/Al_2O_3 catalysts for FT synthesis was evaluated with a continuously stirred tank reactor. We systematically examined the relationship between the structure of Co particles and the activity of Co/Al_2O_3 catalysts in order to obtain the catalyst design concept.

2. Experimental

2.1. Catalyst preparation

Al_2O_3 supports having different crystal phase and pore structure were prepared by the calcination of commercial boehmite ($AlO(OH) \cdot nH_2O$, Wako) and gibbsite ($Al(OH)_3 \cdot nH_2O$, Merck) in air under various conditions (600–1050 °C, 3–10 h). Al_2O_3 supports prepared from boehmite and gibbsite were referred to as Al-B(calcination temperature, calcination time) and Al-G(calcination temperature, calcination time), respectively. One commercial γ-Al_2O_3 purchased from Soekawa chemical (named Al-S) was also used as comparison.

Co-loaded Al_2O_3 (named Co/Al_2O_3 or Co/Al) catalysts were prepared by an impregnation method using $Co(NO_3)_2 \cdot 6H_2O$ (99.5%, Wako) as Co precursor. Loading amount of Co was 20 wt% for all samples. In the impregnation 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.

2.2. Characterization

N_2 adsorption/desorption isotherms of the samples were measured at −196 °C using a BERSORP-miniII equipment (BEL Japan Inc.). Prior to the measurements, the samples (0.15 g) were outgassed at 105 °C for 6 h under vacuum. The specific surface area was obtained by applying the Brunauer–Emmett–Teller (BET) model [33] 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. The pore size distribution of the samples was determined by the BJH (Barrett–Joyner–Halenda) model [34] from the adsorption branches of the nitrogen isotherms. According to the IUPAC classification, all samples exhibited the type H3 shaped hysteresis loop [35]. This suggests that Al_2O_3 supports and Co/Al_2O_3 catalysts prepared in the present study have slit-type pores, which are associated with the interparticle voids generated in solids with plate or fiber-like morphology.

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 $2\theta = 36.9°$ with the Scherrer equation. The obtained particle size of Co_3O_4 could be used to calculate that of Co metal (d_{Co}) after hydrogen reduction pretreatment by the following formula (Eq. (1)) [10].

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

Temperature programmed reduction under H_2 (H_2-TPR) was carried out with BELCAT-B (BEL Japan Inc.). The calcined catalyst (0.10 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 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 400 °C for 6 h in a flow of 5% H_2/Ar (15 ml min^{-1}) and held at 400 °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. Corrected dispersion (D_{corr}, Eq. (2)) and surface area of Co metal were calculated according to the method reported in literature [36].

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

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).

The amount of sodium included in the Al-B(600, 3) and Al-G(600, 3) supports was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The samples were dissolved in nitric acid solution before analysis.

2.3. Typical procedures of catalytic reactions

FT synthesis was performed with a continuously stirred tank reactor in a similar way to the previous study [37]. Before reaction, catalyst (2.5 g) was in situ reduced in a flow of H_2 (40 ml min^{-1}) at 400 °C for 6 h. After the reactor was cooled down to room temperature and purged by N_2 gas, *n*-hexadecane (80 g) solvent was added. Then, the reaction was carried out at 230 °C and 1.0 MPa for 8 h in a flow of synthetic gas (100 ml min^{-1}). The syngas used for this reaction was obtained by the gasification of woody biomass, followed by the gas purification and the composition adjustment [38]. Composition of this biomass-derived syngas was confirmed by gas chromatography (GC) as follows: H_2 (59.9%), CO (29.8%), CH_4 (5.0%), N_2 (4.9%) and CO_2 (0.4%). The effluent gas after FT synthesis was analyzed by on-line GC. A thermal conductivity detector (TCD) with a Porapak-Q column was used to analyze inorganic gases (H_2, CO, CO_2, CH_4 and N_2). Light hydrocarbons (C_1–C_4) were analyzed by