Effects of preparation method on the properties of cobalt supported β-zeolite catalysts for Fischer-Tropsch synthesis

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ABSTRACT

The effect of preparation method on the properties of Co supported β-zeolite catalysts was examined in this study. Co-supported β-zeolite catalysts (20 wt.% Co as Co_3O_4) were prepared by impregnation (IMP20), incipient wetness (IW20), physical mixing (PHY20) and precipitation (PCT20) methods and were characterized by various methods including N_2 adsorption (BET), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), H_2 thermal programmed reduction (H_2-TPR), and transmission electron microscopy (TEM). Fischer-Tropsch (FT) synthesis was carried out over these catalysts at 230 °C and 1 MPa in a fixed-bed flow-type reactor. XPS and H_2-TPR analyses suggest that the catalysts can be ranked in terms of metal-support interactions: PCT20 > IMP20 ≅ IW20 > PHY20. On the other hand, based on reducibility, the catalysts were ordered as follows: PHY20 > IMP20 ≅ IW20 > PCT20. The catalytic activity and product selectivity during FT synthesis were also found to depend on the catalyst preparation method. The catalyst prepared by the incipient wetness method exhibited the highest CO conversion with high liquid production, whereas the physically mixed catalyst showed the lowest CO conversion. All the catalysts produced gasoline-range liquid hydrocarbons (C_5–C_{11}) mainly and the selectivity towards i-paraffins was more than 60% in the case of the catalyst prepared by precipitation. Furthermore, the composition of liquid products produced over catalysts prepared by the impregnation and incipient wetness methods were similar to each other. Thus, the results of the study clearly show that the physico-chemical properties of the catalysts as well as catalytic activities and product selectivity during the FT reaction strongly depend on the catalyst preparation method.

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1. Introduction

The Fischer-Tropsch (FT) process is used for the production of liquid fuels and other hydrocarbons from synthesis gas, which consists of CO and H_2 [1,2]. Synthesis gas is prepared from various raw materials such as coal, heavy crude oil, natural gas, and biomass [2,3]. Since the products of the FT reaction are free from sulfur and nitrogen compounds [2,3], FT is useful for producing alternative and clean liquid fuels. However, the products of the FT process are governed primarily by the Anderson-Schulz-Flory (ASF) distribution, which is characterized by the chain growth probability parameter (α). Therefore, the products generally have a very broad carbon distribution. In order to produce desired hydrocar-bon products, such as gasoline, diesel, and kerosene, the products of FT synthesis are subjected to further chemical transformations such as hydrocracking, isomerization, and de-waxing treatments [4]. For example, gasoline contains a wide variety of i-paraffin- and aromatic compound-rich hydrocarbons with carbon number distribution from 5 to 11.

Fe, Co and Ru are effective as catalysts for the FT reaction; typically, Fe or Co are used as catalysts in industrial processes, based on economic considerations. The choice of Fe or Co also depends on the syngas ratio of the gas that is available. Under mild conditions such as low space velocity and low temperature, Co exhibits greater catalytic activity than Fe [5,6]. Additionally, Co catalysts have a distinct advantage, the lack of water gas shift activity [5]. Thus, Co is typically supported on a suitable support material, which plays an important role in improving the activity and stability of the catalyst. It is known that by combining acid catalysts such as zeolites with typical FT catalysts, the range of gasoline products can be increased [6–8]. Zeolites promote hydrocracking and

isomerization owing to their acidity and shape-selective features. Thus, zeolites such as ZSM-5, exhibit selectivity towards light and branched hydrocarbons [7–9]. Mordenite and β-zeolite also tend to produce middle-chain products [10,11].

β-zeolite has two types of 12-membered pores and a three-dimensional structure [12], and is therefore, classified as a large-pore zeolite. β-zeolite is known to exhibit high cracking activity and high selectivity towards middle-chain hydrocarbons. Many studies have been conducted on the cracking and isomerization capabilities of β-zeolite [13–16]. Corma et al. [13] compared the cracking activities of β-zeolite and Y zeolite, which are classified as large-pore zeolites, and found that β-zeolite is superior to Y zeolite in terms activity and stability.

Co/β-zeolite catalysts prepared by the impregnation or incipient wetness method have been employed for FT synthesis by Espinoza [11], Pereira [17] and Tang [10]. Specifically, Tang et al. [10] compared the catalytic activities of Co/zeolite using different types of zeolites, such as ZSM-5, mordenite, Y zeolite, β-zeolite and SBA-15, and reported that Co/β-zeolite catalyst exhibited low CO conversion with the highest selectivity of C_5-C_9 hydrocarbons (gasoline fuel fraction). Other interesting results on β-zeolite catalysts have also been reported. For example, Li et al. [18] synthesized an encapsulated catalyst with H-β-zeolite shell over Co/Al_2O_3 and found that the encapsulated catalyst tends to show higher i-paraffin selectivity. Martínez et al. [19] mixed the Co/SiO_2 catalyst with various zeolites such as ZSM-5, mordenite, β-zeolite and USY, and found that β-zeolite exhibited enhanced gasoline selectivity.

Despite these extensive investigations, the effect of various preparation methods on the performance of the catalysts during FT synthesis has not adequately been compared so far. FT synthesis is known to be sensitive to the structure of the catalyst. For example, small Co particles with average diameters below 3.5–10 nm increase methane selectivity and decrease the liquid product selectivity [20–24]. Additionally, the particle size of Co also affects the activity of the catalyst. Furthermore, the turn-over-frequency (TOF) decreases when the Co particles are below 6–8 nm in size [20–22,24]. The catalyst preparation method may lead to some differences in the structure of the catalyst, and it may be possible to change the catalyst properties by altering the preparation method. Therefore, the purpose of this study is to investigate the effect of preparation method of supported β-zeolite catalysts on their catalytic activity and selectivity during FT synthesis. Co supported β-zeolite catalysts were prepared by four different methods, namely impregnation, incipient wetness, precipitation and physical mixing. FT synthesis was conducted using these catalysts in a fixed-bed flow-type reactor and their catalytic activity towards CO conversion and product selectivity were investigated.

2. Experimental

2.1. Catalyst preparation

β-zeolite (SiO_2/Al_2O_3 = 17.5) was purchased from Tosoh Inc. Co. Ltd. The as received β-zeolite was first calcined at 540 °C for 6 h and subjected to an ion exchange procedure using 0.5 M NH_4Cl aqueous (Wako chemicals) for 3 h, at 40 °C. This procedure was repeated twice. After the ion-exchange process, the zeolite was washed using deionized water and dried at 110 °C for 16 h.

Co-supported β-zeolite catalysts were prepared using four methods, namely (1) impregnation, (2) incipient wetness, (3) physical mixing, and (4) precipitation. Cobalt nitrate (Co(NO_3)$_2$·6H_2O, Wako chemicals) was used as the precursor in all the methods and the catalyst was loaded with 20 wt.% Co_3O_4. The particle diameter of the catalyst was 450–600 μm. In all four preparation methods, the catalyst was dried at 110 °C for 16 h and calcined at 500 °C for

1 h. Except for β-zeolite, all the other chemicals were used without any purification. The four catalyst preparation procedures are described below.

In the impregnation method, 1.00 g of β-zeolite (450–600 μm) was added to the required amount of cobalt nitrate dissolved in 2 mL of deionized water. Subsequently, the catalyst was impregnated for 1 h at room temperature, after which the water was removed by a vacuum rotary evaporator. After drying and calcination, Co-supported β-zeolite catalysts were obtained. The catalyst prepared by this method was designated as IMP20.

In the incipient wetness method, the required amount of cobalt nitrate was dissolved in 0.29 mL (equivalent to pore volume of 1.00 g of β-zeolite, 0.29 cm^3/g) deionized water. The cobalt nitrate solution was then added to 1.00 g of β-zeolite (450–600 μm). After 15 min of degassing, it was dried and calcined, and Co-supported β-zeolite was obtained. The catalyst prepared in this method was denoted as IW20.

In the physical mixing method, Co_3O_4 powder, which was prepared by precipitation using cobalt nitrate and KOH (Wako chemicals) as the metal source and precipitating agent, was physically mixed with β-zeolite. The required amount of Co_3O_4 powder was ground to obtain a fine powder with average diameter below 300 μm and then mixed with a fixed amount of β-zeolite powder (7 μm) in a mixer at 100 rpm for 1 h. After that, the Co_3O_4/β-zeolite mixture was well mixed using an agate mortar. The Co_3O_4/β-zeolite mixture was then pressed into pellets using a hydraulic press. Finally, the Co_3O_4-β-zeolite pellets were crushed and sieved to obtain 450–600 μm size granules. The catalyst prepared by the physical mixing method is denoted as PHY20.

In the precipitation method, the 7.25 g of cobalt nitrate was dissolved in 84 mL of deionized water to prepare a 5 wt.% cobalt nitrate aqueous solution. 8.00 g of β-zeolite powder (7 μm) was then added to the cobalt nitrate aqueous solution. A 200% excess of NH_3 solution was added to 5 wt.% cobalt nitrate solution quickly with stirring, to which a sufficient amount of deionized water was added. An aqueous solution of NH_3 (5 wt.%), was prepared as the precipitating agent by dissolving 10.18 g of aqueous solution ammonia (25–27 wt.%, Wako chemicals) in 41 mL of deionized water. Subsequently, the solution was decanted several times with deionized water until the pH reached a value of 7. The solid obtained was filtered and washed with deionized water, and then dried and calcined. The powder was then pressed into pellets, crushed, and sieved to obtain the Co-supported β-zeolite catalyst with a granular size of 450–600 μm. This catalyst is denoted as PCT20.

2.2. Catalyst characterization

The specific surface area and pore size distribution of the catalysts were measured using a N_2-adsorption analyzer (Gemini 2375, Shimadzu) at liquid nitrogen temperature (−196 °C). Before the measurements, the samples were outgassed for 3 h at 350 °C using the degassing port of the adsorption apparatus.

The X-ray diffraction (XRD) patterns were recorded on a RIGAKU RINT2100 type diffractometer with Cu Kα radiation (1.5418 Å) at 40 kV and 40 mA. The average Co_3O_4 crystallite diameters were calculated from the full-width at half-maximum (FWHM) of the most intense Co_3O_4 peak at 2θ = 36.9° using the Scherrer equation. The Scherrer constant used was 0.94.

Temperature programmed reduction (TPR) experiments were conducted using a thermo-gravimetric analyzer TGA-40S (Shimadzu) to study the reduction behavior of the catalyst. Prior to the measurements, the samples were degassed at 350 °C for 3 h. In a typical experiment, 116 mg of the sample was placed in a platinum basket and dried at 110 °C for 1 h. Subsequently, a mixture of H_2 (20 vol% in N_2) was flowed at a rate of 200 cc-STP/min into the TGA chamber and the sample was heated at a rate of 7 °C/min up