



Cobalt aluminate-modified alumina as a carrier for cobalt in Fischer–Tropsch synthesis



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ABSTRACT

Modified alumina carriers were obtained by pre-coating cobalt aluminate on the surface of common alumina. Next, supported cobalt catalysts were obtained by incipient wetness impregnation, and their FTS performances were evaluated in a fixed-bed reactor. In situ XRD results suggested that HCP Co was obtained after reducing the aluminate-modified alumina-supported cobalt catalysts, as opposed to FCC Co, which was supported on common alumina. H₂-TPR results demonstrated that the modified catalysts possessed lower reduction temperatures. CO-TPD and in situ CO-FTIR characterizations indicated that bridged rather than linear CO adsorption occurred on the modified catalysts. The evaluation results indicated that the aluminate-modified catalysts possessed higher CO conversion rates, higher C₅⁺ selectivity, higher cobalt specific activity, higher C₅⁺ space-time yields (STYs), and lower methane selectivity than conventional catalysts in the FTS process.

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1. Introduction

Fischer–Tropsch synthesis (FTS) has received considerable attention as a practical route for the synthesis of chemicals and the derivation of clean fuel from coal, natural gas and biomass. Cobalt catalysts have been widely used in the FTS process because of their advantages of low selectivity in the water–gas shift reaction and high selectivity of long-chain paraffins [1,2].

Cobalt-based FTS mainly involves heterogeneous catalysis. The catalytic properties of the supported cobalt catalysts are collectively determined by the individual performance of the carriers, the performance of the modifiers, and the intrinsic catalytic performance of cobalt [3,4]. The carriers can improve the dispersion of cobalt metal; increase the surface area of the active ingredient, thereby reducing the cost of the catalyst; stabilize the dispersed cobalt metal after reduction; prevent degradation of the surface of the active phase; maintain the mechanical strength of the catalysts; and promote mass and heat transfer during the reaction process [2,5]. Hence, the dispersion and reduction of cobalt, the internal and external diffusion of the reaction, and the selectivity of the product can be affected and adjusted by the physical structures and chemical properties of the carriers [6,7].

Meanwhile, the catalytic properties of supported cobalt catalysts are also affected by chemical interactions between the carriers and the cobalt metal [8–10]. Weak interactions reduce the dispersion of cobalt metal, while strong interactions make reduction of the cobalt species difficult. Therefore, a balance in the interactions between the carriers and cobalt is crucial for FTS cobalt-based catalysis [9,11,12]. Additionally, the electronic state of the active cobalt metal can be affected by the electronic environment of the carrier, which affects the catalytic FTS performance [12,13]. In addition, the cobalt particle size and distribution can be affected significantly by the pore structure of the carrier, which remarkably affects the dispersion and reduction of cobalt particles and the corresponding catalytic performance [14–16].

Therefore, a better understanding of the relationship between the characteristics of the carrier and the catalytic performance of the supported cobalt catalyst is important for designing an improved supported cobalt-based FTS catalyst. The type and nature of the carrier greatly influence the catalytic activity, selectivity and stability. Traditional oxides, including silica, alumina, zirconia, and titanium, are often used as carriers for cobalt-based catalysts [2,10,17]. In recent years, to prepare catalysts with more efficient catalytic performance or with some special function, mesoporous molecular sieves, composite carriers, new carbon materials, etc. have been used as cobalt-based catalyst carriers [18–21].

Alumina, which has a regular pore structure and good thermal conductivity, can strengthen the diffusion and transfer of materials and reaction heat to prevent the coking and overheating of

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catalysts, and thus is widely used as a carrier for cobalt-based catalysts. However, cobalt species strongly interact with the carrier alumina, which may result in the formation of stoichiometric or non-stoichiometric cobalt aluminate [9,22], which arises from the diffusion of Co ions into lattice sites of alumina during calcination. The percentage of cobalt ions interacting with the carrier increases as the metal loading is decreased or the calcination temperature is increased [23,24], and the interaction between alumina and cobalt also depends largely on the chemical and physical properties of the alumina carrier [9,25,26].

The generated cobalt aluminate prevents the reduction and dispersion of cobalt and effectively reduces the active cobalt species, thereby reducing the FTS catalytic performance and exhibiting low activity [9], high methane production [27,28], and high deactivation rates [29]. Modification of the carrier surface may suppress the interaction and generation of cobalt aluminate, which can be improved to a certain extent by adding metal promoters such as Zr [30] Mg [31], Pt [32], and Re [33].

Alternatively, cobalt aluminate is hydrophobic and has low surface acidity, high thermal stability, high mechanical stability, and high pH stability, making it well suited to perform under harsh FTS conditions. Could cobalt aluminate be pre-coated on alumina to prohibit the production of new cobalt aluminate or to optimize the interaction between cobalt and alumina? Enger et al. [8] prepared alumina modified by magnesium aluminate, zinc aluminate and nickel aluminate and found that magnesium and zinc aluminate had a negative effect on both the activity and selectivity due to a likely chemical/site effect, while nickel aluminate improved the reaction rate and C_5^+ selectivity. However, there are few reports on cobalt aluminate-modified alumina-supported cobalt catalysts for FTS.

In this report, common alumina is coated with a layer of cobalt aluminate to obtain cobalt aluminate-modified alumina. The physical structure, chemical properties, and FTS performance of the prepared cobalt catalysts supported on cobalt aluminate-modified alumina are studied in great detail.

2. Experimental

2.1. Sample preparation

γ - Al_2O_3 with a surface area of $297\text{ m}^2/\text{g}$, pore volume of $0.89\text{ cm}^3/\text{g}$ and average pore diameter of 6.4 nm was prepared by precipitating aluminum nitrate and ammonium carbonate [34]. Preparation of the aluminate-modified γ - Al_2O_3 was carried out following the procedures below. First, a certain amount of $Co(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, and citric acid (CA) were dissolved in distilled water with Al^{3+}/Co^{2+} and CA/M ($M = Al^{3+} + Co^{2+}$) in molar ratios of 2:1 and 1:1, respectively. Then, the solution was stirred and evaporated to a desired volume, followed by the addition of the prepared γ - Al_2O_3 by incipient wetness impregnation. Finally, the samples were dried at 110°C for 12 h and calcined at 800°C for 10 h in air to obtain the cobalt aluminate (namely, $CoAl_2O_4$ or spinel)-modified γ - Al_2O_3 . The $CoAl_2O_4$ -modified alumina is designated AS-x, in which A represents alumina γ - Al_2O_3 , S represents spinel $CoAl_2O_4$, and x represents the molar ratio of $CoAl_2O_4$ to Al_2O_3 in the final carrier, namely, $x = 5, 10, 15, 20$ and 25 . Common alumina was calcined at 800°C for 10 h and is designated AS-0, as a blank comparison. $Co(NO_3)_2 \cdot 6H_2O$ dissolved in water was supported on the common and modified γ - Al_2O_3 by incipient wetness impregnation. The obtained samples were dried at 110°C for 12 h and calcined at 400°C for 4 h in air to obtain the final catalysts. The Co content in all samples was 15%, and the resultant catalysts are denoted ASC-x according to the corresponding designations of the carriers.

2.2. Characterization techniques

Ex situ X-ray diffraction (XRD) patterns were recorded in the 2θ range of 10 – 80° at a rate of $8^\circ/\text{min}$ on a PANalytical XPert3 powder diffractometer with $Cu\ K\alpha$ radiation ($\lambda = 1.54\text{ \AA}$).

In situ XRD patterns were recorded in the 2θ range of 5 – 40° at a rate of $1.8^\circ/\text{min}$ on the same apparatus as the ex situ XRD experiments with $Mo\ K\alpha$ radiation ($\lambda = 0.71\text{ \AA}$). The reactor cell is an Anton Paar HPC 900 equipped with a long fine-focus molybdenum tube that delivers X-rays and is connected to a solid-state X'Celerator detector. Samples were heated from 25 to 250°C (1°C min^{-1}), maintained at that temperature for 2 h, then heated from 250 to 400°C (1°C min^{-1}) and maintained at that temperature for 6 h.

X-ray photoelectron spectroscopy (XPS) was performed with an Axis Ultra DLD X-ray photoelectron spectrometer equipped with a monochromatized $Al\ K\alpha$ source (1486.6 eV). The $C\ 1s$ line (284.6 eV) was used as a reference in the calibration of the binding energy.

The nitrogen adsorption results were measured with a Micromeritics ASAP 2020 analyzer using nitrogen at -196°C . Prior to measurements, all catalysts were out gassed at 150°C under 1×10^{-5} Torr residual pressure.

Hydrogen temperature-programmed reduction (H_2 -TPR) was carried out on an Altamira AMI-300 HP automatic adsorption instrument. A 30 mg sample was reduced at a heating rate of $10^\circ\text{C min}^{-1}$ to 900°C under a flow of 5% H_2/N_2 . The effluent gas was detected by a thermal conductivity detector (TCD) after removing the produced water.

Hydrogen chemisorption measurements were carried out using a Micromeritics Autochem 2920 analyzer. Briefly, 100 mg of catalyst was reduced at 400°C for 10 h and then cooled to 50°C under hydrogen flow. Then, the hydrogen flow was switched to argon flow at the same temperature for approximately 30 min to remove physisorbed hydrogen. Afterwards, the temperature-programmed desorption (TPD) of the samples was obtained by increasing the temperature to 400°C under argon flow at a ramp rate of 10°C/min .

Carbon monoxide temperature-programmed desorption (CO-TPD) experiments were performed in the same apparatus as the TPR experiments. First, the catalysts were reduced at standard conditions (1°C/min to 400°C and maintained for 6 h). The reduced catalysts were cooled to 25°C under flowing hydrogen and flushed with Ar for 1.0 h, and then the catalysts were exposed to CO for 1.0 h at 25°C . The final signal acquisition of CO desorption involved heating at a rate of $10^\circ\text{C min}^{-1}$ to 800°C under flowing Ar.

In situ carbon monoxide Fourier transform infrared spectroscopy (CO-FTIR) was performed with a Thermo Scientific Nicolet iS10 spectrometer equipped with a PIKE Diffus IRTM reactor cell using a resolution of 8 cm^{-1} . First, the catalysts were pretreated in hydrogen for 6 h at 400°C . Then, the temperature of the samples was reduced to 25°C , and CO gas was adsorbed until saturation. Finally, the samples were purged with Ar until no carbon monoxide gas remained, and the FTIR spectra were collected.

2.3. Catalyst tests

The as-prepared catalysts were evaluated in a stainless-steel fixed-bed reactor (I.D. = 10 mm). First, the catalysts were heated from 25 to 250°C (1°C min^{-1}) and maintained at that temperature for 2 h, and then they were heated from 250 to 400°C (1°C min^{-1}) and maintained at that temperature for 6 h. The reduced catalysts were cooled to room temperature, and mixed H_2 -CO ($H_2/CO = 2.0$) gas was added (gas hourly space velocity, GHSV = 1000 h^{-1}) at an operating pressure of 2.0 MPa . Wax and liquid products were collected by hot and cold traps, respectively. The exhaust gases were analyzed using a Carbosieve-packed column with a TCD and a Porapack-Q column with a flame ionization detector (FID). Oil and

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