



Fischer-Tropsch synthesis: Effect of pretreatment conditions of cobalt on activity and selectivity for hydrogenation of carbon dioxide



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ABSTRACT

The effect of pretreatment conditions of cobalt on activity and product selectivity for the hydrogenation of carbon dioxide was studied over a 1%Na/20%Co–SiO₂ catalyst using a fixed-bed catalytic reactor operated at 220 °C and 1.89 MPa. The metallic form of cobalt was obtained from the reduction of cobalt oxide (Co₃O₄) by H₂ at 350 °C and produced primarily methane and lower hydrocarbons (C₂–C₄) from CO₂. Pretreatments with pure H₂ or syngas (H₂:CO) at 250 °C yield a fraction of partially reduced cobalt (CoO), which tends to suppress the hydrogenation activity of cobalt somewhat, reducing methane selectivity to a limited degree. After CO activation, partially reduced cobalt oxide (CoO) and cobalt carbide phases formed and produced significantly less methane (i.e., selectivity of 15.3%), and surprisingly, the selectivity for alcohols increased to 73.2%. In the absence of sodium, direct methanation is still a preferred reaction for CO₂ for CO pretreated cobalt; the XRD results of used catalysts revealed that the cobalt carbide phase converted to metallic cobalt. The results indicate that Na doping and carbide are important for low methane and high oxygenate selectivities. However, further work is needed to determine whether the role of Na is merely to stabilize the cobalt carbide phase, or whether Na is involved in promoting the catalytic cycle.

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1. Introduction

The Fischer-Tropsch synthesis (FTS) reaction converts syngas (H₂ + CO) derived from coal, biomass or natural gas into liquid fuels and chemicals [1–3]. However, production of syngas from these carbon sources involves generation of a significant quantity of CO₂. Therefore, the present hydrocarbon synthesis processes adopt separation of CO₂ from the reformer using solvents such as Rectisol [4]. However, CO₂ hydrogenation might be employed to convert CO₂ in syngas to more valuable products [5–7].

Iron- and cobalt-based catalysts are used by industry to convert syngas into liquid hydrocarbons. Iron-based catalysts possess intrinsic water–gas shift (WGS) activity, such that reverse water–gas shift (RWGS) can be used to convert a fraction of CO₂ into carbon monoxide, which further takes part in FTS. Under FTS conditions, cobalt has very low WGS activity and acts primarily as a methanation catalyst when CO₂ is used instead of CO [6,7]. This difference between iron and cobalt catalysts is mainly due

to the nature of the phases present during FTS and the intrinsic hydrogenation activity of each catalyst for CO and CO₂. Iron exists in part as iron carbide which is proposed to be active for FTS, whereas metallic cobalt is the active form of cobalt. The hydrogenation activity of cobalt in the metallic form is so high that methane is the dominant product formed from CO₂ [8]. It is highly desirable to lower the hydrogenation activity of cobalt such that CO₂ can be converted into higher hydrocarbons either by first forming CO or partially hydrogenated CO intermediates. So far, most studies on the hydrogenation of CO₂ have focused on iron-based catalysts [9–12]. In contrast, reports on the catalytic conversion of CO₂ to higher hydrocarbons and alcohols by cobalt-based catalysts are scarce [5,7,8]. Recently, Owen et al. [13] showed that cobalt has the ability to hydrogenate CO₂ at atmospheric pressure, and the authors claimed that the addition of alkali promoters like Na and K enhanced C₅⁺ selectivity. However, no further reports have been published regarding the state and nature of the active phase of cobalt that is responsible for the observed increase in C₅⁺ hydrocarbons. In the current study, three different activation conditions (H₂, syngas, and CO) were employed to control the chemical nature of cobalt phases present. Activity and selectivity for hydrogenation of CO₂ were evaluated using a fixed-bed reactor operating at 220 °C and 1.89 MPa and H₂/CO₂ ratio of 3.0. TPR and hydrogen

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chemisorption/pulse reoxidation were applied to H₂-reduced catalysts to characterize dispersion and reducibility. Fresh and used catalysts, pretreated by H₂, syngas, or CO, were characterized by XRD and HRTEM techniques.

2. Experimental

2.1. Catalyst preparation

For this study, the composition of the sodium-doped cobalt catalyst was 1%Na–20%Co/SiO₂, and PQ-silica CS-2133 (*S*_{BET}: 351 m²/g) served as the catalyst support. Cobalt nitrate hexahydrate [Co(NO₃)₂·6H₂O] and anhydrous sodium carbonate Na₂CO₃, purchased from Sigma–Aldrich, 99.5% were used as sources of cobalt and sodium, respectively. The SiO₂-containing 20 wt.% Co catalyst was prepared by following a two-step slurry phase impregnation method using an aqueous solution of cobalt nitrate. In this method, which follows a Sasol patent [14], the ratio of the volume of solution used to the weight of alumina was 1:1, such that the volume of loading solution was approximately 2.5 times the pore volume of the catalyst. After impregnation of the aqueous solution of cobalt nitrate, excess water was removed by vacuum evaporation at 80 °C. Afterwards, 1.0 wt% Na was introduced to the dried catalyst by following the same slurry phase impregnation technique using an aqueous solution of sodium carbonate. Finally, the catalyst was dried overnight at 120 °C and calcined in a muffle furnace at 350 °C for 4 h. For the purpose of comparison, cobalt catalyst without sodium (20%Co/SiO₂) was prepared in the same manner as described above (with the exception of the inclusion of a sodium addition step).

The calcined cobalt catalyst was pretreated at different conditions in order to obtain various forms of cobalt:

- (i) H₂ activation: two different pretreatment temperatures were examined in order to vary the relative fractions of cobalt metal and cobalt oxide (CoO). About 2.5 g of calcined cobalt catalyst (1%Na–20%Co/SiO₂) were pretreated under flowing H₂ (10 nL/h) at 350 °C for 15 h to obtain primarily metallic cobalt. On the other hand, partially reduced cobalt (i.e., having higher CoO content) was obtained by reducing supported cobalt oxide (i.e., Co₃O₄) under flowing H₂ (10 nL/h) at 250 °C for 15 h.
- (ii) Syngas activation: About 2.5 g of calcined cobalt catalyst (1%Na–20%Co/SiO₂) were pretreated under flowing syngas at a H₂:CO ratio of 1.0 (10 nL/h) at 250 °C for 15 h. Under these conditions, cobalt mainly forms cobalt oxide (CoO) and cobalt carbide (Co₂C).
- (iii) CO activation: About 2.5 g of calcined cobalt catalyst (20%Co/SiO₂ or 1%Na–20%Co/SiO₂) were pretreated under CO flow (10 nL/h) at 250 °C for 15 h to obtain a mixture of cobalt carbide (Co₂C), cobalt oxide (CoO), and carbon.

The presence of a small amount of metallic cobalt for the syngas and CO pretreatment methods was either detected or cannot be ruled out for the samples treated at 250 °C.

2.2. Catalyst characterization

The catalyst compositions of freshly activated and used catalysts after passivation were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) using a Varian 720-ES analyzer. The materials were dissolved in a perchloric/nitric acid mixture and the emission spectra of dissolved species (Co, alkali) were compared to those of a series of standard solutions of known concentrations. Carbon analyses were made using a Leco CHN 628

analyzer. The sample was combusted at 1223 K in oxygen and the carbon, as CO₂, was determined using an IR detector.

A Micromeritics Tri-Star system was used to determine surface area and porosity of the support and catalysts. Prior to the measurement, each sample was slowly ramped to 160 °C and evacuated for 24 h to approximately 50 mTorr. Hydrogen chemisorption/pulse reoxidation by hydrogen temperature programmed desorption (TPD) and pulse oxygen titration was measured using a Zeton Altamira AMI-200 unit. Details about the chemisorption method are described elsewhere [15]. The catalysts were activated at different temperatures (250 °C and 350 °C) prior to hydrogen chemisorption/O₂ titration measurements.

Temperature programmed reduction (TPR) profiles of catalysts were also recorded using the Zeton Altamira AMI-200 unit. Calcined fresh samples were first purged in flowing inert gas to remove traces of water. TPR was performed using a 10% H₂/Ar mixture referenced to Ar at a flowrate of 30 cm³/min. The sample was heated from 323 to 1273 K using a heating ramp of 10 K/min.

Powder X-ray diffractograms of activated and used cobalt FT catalysts were recorded after passivation (at room temperature (25 °C) under flowing 1%O₂ in N₂) using a Philips X'Pert diffractometer with monochromatic Cu Kα radiation (λ = 1.5418). XRD scans were taken over the range of 2θ from 10 to 90°. The scanning step was 0.01, the scan speed was 0.0025 s⁻¹, and the scan time was 4 s.

The morphology and in-depth analysis of individual cobalt particles were obtained using a field emission analytical transmission electron microscope (JEOL JEM-2010F) operated at an accelerating voltage of 200 kV. HRTEM images were recorded under optimal focus conditions at a typical magnification of 100–500 K. The electron beam had a point-to-point resolution of 0.5 nm. Gatan Digital Micrograph software was used for image processing.

2.3. Catalyst testing

The experiments were conducted using a fixed bed reactor (stainless steel having a length of 17 cm and an inside diameter of 1.6 cm). For the experiment, 2.5 g of calcined cobalt catalyst (60–100 μm) were diluted with 10 g of glass beads in the size range of 40–100 μm, and loaded onto a quartz wool plug in the reactor. The temperature of the catalyst bed was monitored by placing a K-type thermocouple in the middle of the catalyst bed. After activation, a gas mixture, containing 75% H₂ and 25% CO₂ at 3.0 nL/h/g catalyst, was fed to the reactor, which was maintained at a temperature of 220 °C and a pressure of 1.89 MPa. Brooks mass flow controllers were used to control the flow rates of H₂ and CO₂. The conversions of CO₂ and H₂ were obtained by gas-chromatography (GC) analysis (micro-GC equipped with thermal conductivity detector) of the reactor exit gas mixture. The reaction products were collected in two traps maintained at different temperatures – a hot trap (150 °C), and a cold trap (5 °C). The products were separated into different fractions for quantification. The liquid products condensed in the hot trap were analyzed using a HP 6890 GC with DB-5 capillary column, while the aqueous phase was analyzed using a HP 5790 GC with Porapak Q packed column. A 5973N MSD coupled to the 6890 GC from Agilent was employed for qualitative analysis of alcohols, which were further quantified using a flame ionization detector (FID). The conversion and selectivity reaction parameters are defined as:

$$\text{conversion} = 100 \times \frac{n_{\text{CO}_2\text{in}} - n_{\text{CO}_2\text{out}}}{n_{\text{CO}_2\text{in}}}$$

$$\text{selectivity} = 100 \times \frac{n_{\text{productout}} \cdot \text{carbon number}}{n_{\text{CO}_2\text{in}} - n_{\text{CO}_2\text{out}}}$$

where $n_{\text{CO}_2\text{in}}$ and $n_{\text{CO}_2\text{out}}$ are the numbers of moles of CO₂ fed and not-consumed, respectively. The selectivity is defined as the

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