Full Length Article

Influence of sucrose addition and acid treatment of silica-supported Co-Ru catalysts for Fischer-Tropsch synthesis

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ABSTRACT

This article highlights the formulation and evaluation of Co-Ru catalysts on silica used in Fischer-Tropsch synthesis. An acid treatment of the support associated with the addition of sucrose as a chelating agent was employed. The six formulated catalytic systems were characterized (TG, XRD, N_2 adsorption, H_2-TPR, H_2 chemisorption) and evaluated in a fixed bed tubular reactor (H_2/CO:2:1, 2 MPa, space velocity 4.5×10^{-2} LN.$g_{cat}^{-1} \cdot h^{-1}$) at five different temperatures (185 °C, 200 °C, 215 °C, 230 °C, 260 °C). The combination of both methods enhanced the cobalt dispersion, which is accompanied by an increase in C_{5+} hydrocarbon productivity. However, an optimum acid treatment is required to avoid large cobalt particle formation that leads to low CO conversion.

1. Introduction

The Fischer-Tropsch (FT) synthesis is an alternative route to produce oil derivatives, especially diesel, from synthesis gas (syngas; CO, H_2) into hydrocarbons. This intermediary has outstanding participation in three main processes involving the production of liquid fuels and fuels, namely coal-to-liquid (CTL), gas-to-liquid (GTL) and biomass-to-liquid (BTL) [1–3]. The diesel produced by FT synthesis has a high cetane number and low contaminant content, while the same fraction obtained from refineries presents high levels of sulfur compounds and other contaminants [4]. However, FT synthesis is a catalytic process and thus requires efficient catalysts with high activity and selectivity for the economic feasibility of the process.

The active components of FT synthesis are transition metals such as cobalt (Co), iron (Fe) and ruthenium (Ru). Ru systems have the best performance, however, their high cost is a major obstacle to their application in this process. Low cost Fe catalysts, operating at elevated temperatures, exhibit less activity for the FT reaction while promoting the water-gas-shift side reaction. Alternatively, Co-based catalysts are often used to activate FT synthesis to produce diesel. As advantages, they are more resistant to deactivation, have high activity for FTS and high selectivity for linear hydrocarbons [4,5].

The reaction rate of FT synthesis depends strongly on the particle size of cobalt and its reducibility and stability [6–10]. Thus, since these characteristics depend on the preparation procedures of the catalysts, attention should be given to the various steps involved, such as modification and stabilization of the catalyst support, deposition of cobalt and promoters on the support and decomposition of the cobalt precursor before activation [11].

Several cobalt supports have been used such as Al_2O_3, TiO_2 and SiO_2 [12]. Among the most commonly employed for FT synthesis, alumina provides greater stability for Co clusters, increasing the life of the catalyst. However, important Co-Al_2O_3 interactions can occur, impairing the reduction of Co oxide [13]. This is attributed to the greater stability of the small metal clusters formed during the reduction process and to the formation of aluminates which are difficult to reduce [14]. On the other hand, the use of other support such as TiO_2, still allows interaction with Co greater than the Co-SiO_2 interaction [12]. Thus, catalysts using silica support, an almost inert oxide, although subjected to low stability due to the easy sintering of cobalt, should provide good metal reducibility.

The cobalt-silica weak interaction favors the reduction of cobalt particles, but promotes particles agglomerations reducing the number of active sites [15]. In addition, the cobalt crystal size depends on pore

size of silica support [16,17]: large pore size leads to larger crystal sizes with higher reduction degree. However, a solid-state reaction between cobalt oxide and silica could result in cobalt silicate species, which are not active in FTS and difficult to reduce [18]. Therefore, most studies for Co/SiO_2 type catalyst preparation are focused on minimizing the concentration of cobalt silicate species and maximize the cobalt dispersion [15].

The dispersion of active phase can be controlled by different parameters during the catalyst synthesis such as catalyst precursors [18,19], drying conditions [20] and calcination temperature [21]. Depending on the exothermicity of the cobalt precursor decomposition, supported cobalt ions either agglomerate into Co_3O_4 crystallites or react with silica, yielding amorphous cobalt silicate [18,19]. Modification of impregnating solution with chelating agents is an effective way for varying the cobalt precursor deposition. These chelating agents could tune the electrostatic adsorption of cobalt complex on support surface and accordingly modulate the active phase-support interactions [22]. The cobalt/chelating agent complexes formed during the drying step are moderately stable toward the heat treatment during calcination [23]. Moreover, the activity improvement due to the chelating agent incorporation depends on the affinity of the chelating agent for complexes formation with cobalt ions, being more active when the affinity is more important [23,24]. The use of chelating compounds, such as sucrose and polyols, during catalyst preparation leads to a decrease in cluster formation promoting significantly the active phase dispersion [25–17]. Mauldin [25] observed that sorbitol and mannitol, added during metal impregnation of the catalytic supports, increased about twice the metallic oxide crystals dispersion. On the other hand, the addition of sorbitol in different molar ratios during the preparation of a silica-supported Co-based catalyst has been also investigated [26]. The authors concluded that an optimal chelating compound amount was required. At increasing sorbitol content, the catalytic activity passed through a maximum before decreasing again, due to changes in catalyst reducibility.

Another approach used to improve the properties and performance of a catalyst is the application of an acid pre-treatment on the support. For this purpose, the most commonly used acids are HNO_3 and citric acid. The occurrence of Co with smaller particle size was observed in the synthesis of the catalyst due to the acid pre-treatment of the support. Such effects may have been the cause of increased catalytic activity in terms of long-chain hydrocarbon conversion and selectivity [28,29]. The reducibility and number of active sites observed in other formulated catalysts may also have been affected by acid treatment [30,31].

The present work aimed to evaluate the influence of the procedures of preparation of cobalt and ruthenium catalysts for the Fischer-Tropsch (FT) synthesis involving an acid treatment on the silica support associated with the introduction of a chelating compound. The catalysts were analyzed by TGA, TPR, XRD and H_2 chemisorption providing characteristics related to the structures and forms due to the introduction of the chelating compound and by the application of different times and concentrations during acid treatment. The effects were evaluated by quantifying the catalytic activity for FT and the consequent selectivity of hydrocarbons.

2. Experimental procedure

2.1. Preparation of the catalysts

In this work, 6 different catalysts supported on SiO_2 (Kali Chemie AF125) were prepared, in which four of them included supports treated by HNO_3 with concentrations of 30 or 60 v/v% for 2 or 4 h. For each acid treatment, 5 g of amorphous silica was weighted and added to a round bottom flask with 400 mL of acidic solution. The flask was immersed in water at 80 °C during the referred acid treatment time (2 or 4 h). The generated steam was condensed to maintain acidic solution

concentration (30 and 60% vv). After the treatment, samples were decanted and the supernatant was removed. The silica treated was then washed until neutral pH was reached, followed by drying at 50 °C for 48 h. Similar methodology was used by other authors [28,30,31].

Catalysts with 20.0 w% Co and 0.5 w% Ru loading were prepared via two-step incipient wetness co-impregnation. An aqueous solution of $Co(NO_3)_2 \cdot 6H_2O$, ruthenium nitrate (II) and sucrose with molar ratio sucrose/Co of 0.1 (only one catalyst was prepared without sucrose) was added to the support. After each impregnation step, the mixture was dried at 120 °C for 6 h. Finally, the catalysts were calcined in air at 350 °C for 6 h.

The catalyst that did not undergo sucrose addition or acid treatment is denoted $Co-Ru/SiO_2$, and the other catalysts are denoted $Co-Ru/SiO_2$-S-t-C, where S indicates the presence of sucrose during catalyst preparation, t is the acid treatment time in hours and C is the concentration of the acid solution.

2.2. Catalysts characterization

The catalysts were characterized by thermogravimetric analysis, XRD, N_2-adsorption/desorption, H_2-TPR and H_2 chemisorption.

Thermogravimetric analysis (TGA) of precursors and catalysts were carried out using a DTA-TG Shimadzu Apparatus (model DTG-60H). In each measurement, the samples of 16.0×10^{-3} g were heated from room temperature to 600 °C at a heating rate of 10 °C/min under air flow of 50×10^{-6} m^3/min.

X-ray diffraction (XRD) analyses was performed on a Shimadzu diffractometer (model XRD 6000, Cu Kα radiation, 40 kV, 30 mA). The metallic mean crystal size of Co ($d_{Co}^0 = 0.75 d_{Co_3O_4}$) and its dispersion (D= $96/d_{Co}^0$) were estimated by the Scherrer equation [33], from the diffraction peak at 2θ 36.8°, which is the most intense for cobalt oxide [13,28,32]. $d_{Co_3O_4}$ is the mean crystal size of Co_3O_4.

The textural properties of carriers and catalysts were measured by adsorption-desorption of N_2 (Quantachrome Autosorb-iQ). Prior to analysis, 200 mg samples were degassed at 120 °C for 3 h.

The catalysts reduction pattern was investigated by the programmed reduction temperature method (H_2-TPR/TPD, SAMP3 chemosorption, Termolab Equipments Ltd, Brazil). The 40 mg samples were treated with a reducing gas mixture (1.50 v/v H_2/Ar, 10 °C/min, 30×10^{-6} m^3/min) in the range from room temperature to 700 °C.

Chemisorption and oxidation (H_2, O_2, Micromeritics ASAP 2020Cv) were used to determine the metallic surface area, mean crystal size and degrees of dispersion and reduction of metal. First, the samples were degassed at 120 °C to a vacuum of 2 μm Hg. Thereafter, the catalyst was reduced at 350 °C in a stream of pure H_2 for 10 h. The adsorption isotherm was obtained after the catalyst was subjected to vacuum and maintained at 100 °C. According to the criterion of Reuel and Bartholomew [34], only a single H_2 adsorption isotherm was recorded. After the H_2 chemisorption, the sample was purged with He at 100 °C, and evacuated at 5 μm Hg for 1 h. Then, it was heated to 400 °C in a He flow for 90 min under vacuum to eliminate physisorbed H_2 molecules. Finally, a pseudo-adsorption O_2 isotherm was obtained at 400 °C to measure the amount of oxygen needed to oxidize the reduced Co to Co_3O_4. The amounts of H_2 and O_2 measured in the adsorption and re-oxidation processes allowed the calculation of Co dispersion (D), reduction percentage (R), and the average size of the cobalt particles (Dp (Co_0)), as obtained from the expression Dp(Co_0) (nm) = 0.96R(%)/D (%).

2.3. FT synthesis catalytic tests

The FT processing was performed in a lab-scale tubular fixed-bed reactor (Fig. 1). The catalyst (1.25×10^{-3} g) was charged into reactor mixed with SiC (6.25×10^{-3} g) and activated with pure H_2 introduced at a flow rate of 4.5×10^{-2} NL/min at 0.2 MPa. The reactor temperature was increased (1 °C/min) from room temperature to 350 °C, and