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Effect of different alumina supports on performance of cobalt Fischer-Tropsch catalysts

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ABSTRACT

Four identically-prepared 20 wt% cobalt/0.15 wt% ruthenium Fischer-Tropsch catalysts, supported on different aluminas, were synthesized by incipient wetness impregnation, characterized, and compared based on their performance under standard Fischer-Tropsch synthesis conditions. Three alumina supports were obtained from commercial sources (Sasol, St. Gobain, and Alfa Aesar), while the fourth was made using a published technique that included 5 wt% silica. The silica-stabilized alumina catalyst produced superior Fischer-Tropsch rates of 49 mmol CO/g_{cat} h, compared to the other catalysts on the commercial supports with rates of 26–39 mmol CO/g_{cat} h. The improved performance of the silica-stabilized alumina support compared to the commercially available aluminas is ascribed to a bimodal pore structure with larger average diameters and enhanced thermal stability. The support can be thermally treated to higher temperatures (e.g., 1100 °C) without transformation into α-alumina, allowing dehydroxylation of the surface prior to impregnation to stabilize a nearly ideal dispersion of cobalt crystallites.

1. Introduction

Large natural gas deposits globally have attracted interest in gas to liquid processes. Fischer-Tropsch Synthesis (FTS) is the key step for using syngas produced from natural gas resources to form liquid hydrocarbons. Unlike petroleum based fuels, FTS products do not contain sulfur or nitrogen impurities, making them a possible cleaner alternative than petroleum based fuels [1].

Cobalt and iron are two conventionally used catalysts for the FT reaction. Despite its higher cost, cobalt is preferred over iron for its higher activity; better resistance to deactivation, including deactivation due to byproduct water production; and lower selectivity to the water gas shift reaction [2,3]. Cobalt FT catalysts are supported to improve dispersion and resistance to loss in active surface area (sintering). Support characteristics, including morphology, pore properties (i.e., surface area, pore volume, and pore size distribution), and chemical properties, affect the catalyst activity, stability, and selectivity [2–4]. Variation in supports can result in either stronger or weaker interaction with cobalt, which will lead to different Co dispersions and in turn lead to different cobalt crystallite sizes and degrees of reducibility [2,5–7].

Alumina (Al_2O_3) and silica (SiO_2) have been thoroughly studied and used as supports for FT cobalt catalyst. Cobalt supported on alumina can result in small Co crystallites, which are more difficult to reduce [8–11]. To overcome this problem, noble metals, especially Ru and Pt, have been used as promoters to enhance the reducibility of cobalt oxides [3,12–14]. Water formation at high conversions during FTS can lead to formation of Co/aluminate spinels that are only reducible at very high temperatures and are inactive for FT [10,15–18]. However, adding a thin layer of silica can prevent cobalt from forming inactive Co/aluminates species [19] and consequently prevents deactivation. In addition, the pore properties of the supports, especially average pore size and pore size distribution, also affect the final Co FT catalyst properties. For instance, Shimura et al. [20] found that increasing the pore size results in higher active phase dispersion. They observed that activity of Co/Al_2O_3 catalysts are highly dependent on the pore structure instead of the alumina phase. In addition, they observed that C_{5+} selectivity decreases with increasing alumina surface area.

On the other hand, using silica instead of alumina as a support during Co FTS catalyst preparation often results in formation of larger Co crystallites (lower dispersions) that are easier to reduce [10,21]. Numerous studies have been performed on the effect of silica structure as a support for cobalt catalysts. For example, Ernst et al. [22] investigated the FT performance of silica supported

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cobalt prepared by the sol-gel method in both acid and basic medias. They found that catalyst activity is directly correlated with the support surface area and that the lowest methane selectivity is produced by catalysts supported with silica that have average pore diameters less than 4 nm. Saib et al.'s [23] study on Co/SiO_2 indicated that the best activity and long chain hydrocarbon selectivity resulted from supports with average pore diameters of 10 nm. Similarly, Li et al. [24] also found that an average silica pore diameter of 10.1 nm resulted in the best activity and C_{5+} selectivity.

The pore size distributions of conventionally-prepared silica or alumina supports are monomodal. Diffusional restrictions play a major role in supports with small pore sizes, especially in multiphase reactors. Bimodal supports, which have two distinct peaks in their pore size distribution, contain both large and small pores. Supports with bimodal pore size distributions increase the active metal dispersion and also facilitate the access of reactants to the active sites [2,17,25–27].

Although various alumina-silica supports are being used in different industrial applications [6,17,28–32], alumina-silica supports have not been thoroughly studied thus far for cobalt FT catalysts. Recently, we have developed a new alumina-silica support that has successfully been used to prepare iron FT catalysts [30,33]. Mixing alumina with small amount of silica (up to 6 wt%) can result in a support that has a higher surface area, a bimodal pore size distribution, improved porosity, higher thermal stability, and optimal acid site concentration [30,34].

In this present study, we compare this newly developed alumina-silica (Al-Si) support with commercial supports for cobalt FT catalyst preparation. Other than the support material, each catalyst was prepared identically, with 20 wt% Co metal and 0.15 wt% Ru added to decrease reduction temperatures and to prevent cobalt crystals from sintering during reduction. The commercial supports used for comparison in this study are Puralox from Sasol and aluminum oxides from Alpha Aesar and Saint Gobain. The prepared materials and catalysts were characterized by a variety of techniques, including X-ray diffractions (XRD), nitrogen physisorption, transmission electron microscopy (TEM), temperature programmed reduction (TPR), temperature programmed oxidation (TPO), extent of reduction (EOR), hydroxyl group measurement, and H_2 chemisorption. Catalytic performance, including FTS rate and selectivity, was evaluated in the fixed bed reactor for each type of supported catalyst. Both characterization and kinetic results are discussed in detail in this paper.

2. Experimental

2.1. Catalyst preparation

A series of four catalysts were prepared with four different alumina supports: 5 wt% silica-stabilized alumina (Al-Si), Alfa Aesar (Al-AA), St. Gobain (Al-SG), and Sasol (Al-Sa). The Al-Si support was synthesized by an one-pot, solvent deficient method that includes combining a 5:1 ratio of water to aluminum isopropoxide (AIP, Alfa-Aesar, 98+%) followed by a 2:1 ratio of water to tetraethyl orthosilicate (TEOS, Sigma-Aldrich, 99%) (equivalent to 5 wt% silica), as described in detail elsewhere [30,34–36]. These precursors were mixed for 30 min with a Bosch Universal Mixer (model: MUM6N10UC) and followed by calcination in flowing air in a muffle oven at 1100 °C with a ramp rate of 4 °C/min prior to impregnation. The other three alumina supports were obtained commercially from their respective manufacturer and calcined at 700 °C for 2 h prior to impregnation.

The 20 wt% cobalt, 0.15 wt% Ru catalysts were prepared in two steps by incipient wetness co-impregnation of the supports using an aqueous solution containing the desired amount of cobalt nitrate hexahydrate (Alfa Aesar, 98+%) and ruthenium nitrosyl nitrate solution (Sigma-Aldrich, 99%). In each step, 10 wt% Co was dissolved in 20% excess water corresponding to the support mesopore volume obtained from nitrogen physisorption (BET) measurements. The excess water was added to compensate for the micro-pores not detected by the BET experiment. Then, the solution was added dropwise to the powdered support, with continuous stirring to achieve uniform Co dispersion. The catalysts were dried at room temperature for 4 h, followed by drying for 16 h at 100 °C to remove excess water, and then calcined in a direct flow quartz reactor with a ramp rate of 1 °C/min to a final temperature of 300 °C for 10 h. This process was repeated in order to add the remaining 10 wt% Co and 0.075 wt% Ru promoter. After the second calcination, the catalysts were reduced in 10% H_2/He with a ramp rate of 1 °C/min to a maximum temperature of 415 °C and further reduced for 4 h in 100% H_2 at 415 °C. Reduced catalyst samples were passivated by slowly exposing them to less than 1% O_2/He, while monitoring the temperature to ensure that the catalysts were not exposed to temperatures in excess of 60 °C or over-oxidized. The catalysts are named according to their corresponding support with a Co prefix, e.g., the Co catalyst supported on Al-Si is named Co-Al-Si.

All gases used in this study were obtained from Airgas with 99.9% purity or higher.

2.2. Nitrogen adsorption/desorption

Nitrogen adsorption measurements were carried out using a Micromeritics Tristar 3020 to determine surface properties at −196 °C. Samples were degassed under ambient pressure at 120 °C for 16 h in N_2 flow prior to measurements. The surface areas were calculated using the Brunauer Emmett-Teller (BET) method in the P/P_0 range from 0.05 to 0.20. Pore volumes were determined at a single point of P/P_0 equal to 0.990. Pore size distributions were calculated using an improved slit pore geometry (SPG) model for large pore sizes [37].

2.3. X-ray diffraction (XRD)

To estimate average crystallite size, powder XRD data were collected for each catalyst using a PANalytical X'Pert Pro diffractometer with a Cu source and a Ge monochromator tuned to the Cu $K_{\alpha 1}$ wavelength (k = 1.54 Å). Both calcined and reduced catalyst samples were scanned from 2θ 10–90° using a step size of 0.016 and a step time of 350 s. As described in Section 2.1, the reduced catalysts were passivated in air prior to XRD measurement. Diffraction patterns were compared to standard patterns in the International Centre for Diffraction Data (ICDD) database. Average Co crystallite size was calculated from the Scherrer equation using the Co peak located at 2θ = 44.3.

2.4. Temperature programmed reduction (TPR)

TPR experiments were performed in a Mettler Toledo TGA/DSC 1 equipped with an automated GC 200 gas controller to determine catalyst reduction temperature-time profiles. 10–25 mg samples were exposed to a reducing gas mixture of 10% H_2/He, while the temperature was increased at 3 °C/min from ambient to 800 °C. To correct the weight loss curves for the effect of strongly absorbed water, another set of TGA experiments was performed on the calcined catalysts using the same temperature profile with time, but under pure He flow. The weight loss due to water desorption was then subtracted from the total weight loss of the corresponding TPR.