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Effects of Ag promotion and preparation method on cobalt Fischer-Tropsch catalysts supported on silica-modified alumina

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ABSTRACT

A series of silver-promoted, 20 wt% cobalt Fischer-Tropsch synthesis (FTS) catalysts supported on an alumina modified with 5 wt% silica were prepared using two methods: traditional incipient wetness impregnation (IWI) and a new solvent deficient precipitation (SDP) technique. Catalysts containing silver promoter concentrations of 0.3, 0.6, 1.2, and 2.5 wt% were prepared using each of the two methods. Silver improved the reducibility of the cobalt significantly, lowering reduction temperatures by up to 100 °C, and increasing the extent of reduction by up to 35%. Further, in both preparation methods, changing the silver loading altered the cobalt dispersion. The smallest Co crystallite size was achieved with 1.2 wt% Ag loading, which produced average cobalt crystallite sizes of about 7 nm. The Fischer-Tropsch CO consumption rate increased with decreasing crystallite size and thus was highest for 1.2 wt% Ag. Intrinsic CO consumption rates per Co site (CO turnover frequency) were also measured for each catalyst. A clear increase in the intrinsic turnover frequency (TOF) was observed as Ag loading was increased from 0.6% to 1.2 wt% for both preparation methods. Both 1.2 wt% Ag catalysts produced TOF's of ~0.050 s^{-1} (equivalent to a CO consumption rate of ~65 mmol g_{cat}^{-1} h^{-1}), which are 20–30% higher than the catalysts containing 0.3, 0.6, and 2.5 wt% Ag and are comparable to reported rates for commercial FTS catalysts. Higher loadings of Ag (2.5 wt%) resulted in higher extents of reduction, but led to lower TOFs and larger Co crystallite diameters, which is assumed to be due to blockage of active sites and changes in the Ag-Ag and Ag-Co coordination ratio. Thus, silver promotion appears to improve catalytic performance by enhancing cobalt reduction, dispersion, and electronic properties. The SDP and IWI methods produced catalysts with essentially the same properties, but the SDP method is a simpler, one-pot technique that offers many potential advantages.

1. Introduction

Fischer-Tropsch Synthesis (FTS) is a commercially proven method for producing long chain hydrocarbon fuels from less valuable biomass, natural gas, or coal. Although FTS has been a research topic of both scientific and practical significance for almost 100 years, substantial improvements in catalyst, reactor, and process technologies are needed to realize greater commercial success [1]. To improve catalyst technologies, better catalyst activity, product selectivity, and stability are needed [1–3].

Iron (Fe) and cobalt (Co) are the two most commonly-used metals for FTS catalysts. Relatively inexpensive Fe catalysts may be preferred for the processing of hydrogen (H_2) deficient synthesis gas feeds obtained from biomass and coal-to-liquids processes. Co catalysts find application in gas-to-liquids processes because they are more active and productive for long-chain hydrocarbons and are less susceptible to deactivation [1,4].

Noble metal (NM) promoters have been widely used for Co catalysts to improve reducibility, mass-based catalytic activity, and C_{5+} selectivity. The noble metal also enables a high degree of reduction at lower temperatures, e.g. 300–450 °C, compared to the reduction temperature of unpromoted cobalt catalysts, e.g. 500–600 °C, which can lead to sintering of the active metal [5,6]. Reduction at such high temperatures may also require expensive steel alloys for the reduction vessel and may make in situ reduction impossible.

During the reduction of a Co catalyst, there are two stages of reduction that result in two peaks in the temperature programmed reduction (TPR) profile:

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$$Co_3O_4 + H_2 \rightarrow 3CoO + H_2O \quad (R1)$$

$$CoO + H_2 \rightarrow Co + H_2O \quad (R2)$$

In a typical commercially-relevant noble metal (NM)-promoted cobalt catalyst (containing 20–25 wt% cobalt, 0.05–0.5 wt% of NM), the first reduction reaction (R1) occurs at temperatures around 220–360 °C, while the second (R2) occurs at 350–450 °C.

Noble metals are typically classified as second and third row Group VIII metals, which include Ru, Rh, Pd, Ag, Re, Os, Ir, Pt, and Au; Cu is sometimes included in the less restrictive list of noble metals. All of these noble metals, except for Os, are known to aid in the reduction of Co oxides. Ru, Pd, Re, and Pt are used as commercial cobalt catalyst reduction promoters and are claimed in patents. Xu et al. [7] found that Pt, Pd, and Ru promotors increase the reducibility of the Co precursor and enhance CO adsorption on the catalyst. Cook et al. [5,8] investigated Pt, Re, and Ru addition to Co, finding Pt to be the most effective reduction promoter, with the first TPR peak at 230 °C compared to 330–355 °C for Re and 300–310 °C for Ru. Also, Pt has been used to promote Co at a level of 0.02 wt% in the Sasol Oryx catalyst. [9] Experiments performed by Pirola et al. [10] show that both Pt and Ru promoters triple the yield of C_5+ products for FTS. However, because Pt and other NM are quite expensive, the search continues for cheaper, alternative promoters. Thus, Cu and Ag have been investigated as promoters for cobalt catalysts [6,11–15].

Specifically, Eschemann et al. [11] showed the effectiveness of Ag as a reduction promoter for Co/TiO_2 supported catalysts. Gnanamani et al. [12] further investigated the effect of silver on cobalt catalysts supported on indium- and gallium-modified reducible ceria. However, the most closely related previous research on cobalt catalysts supported on alumina has been conducted at the Center for Applied Energy Research at the University of Kentucky [6,13–15]. Jacobs et al. [6,13] have investigated Cu, Ag, and Au promoters, which decrease the Co reduction temperature, although only at high loadings of NM (on order of 1 wt%). Although Cu is an excellent reduction promoter of cobalt oxide, i.e. it lowers the reduction temperature from 580 °C to about 350 °C, it poisons the Co surface and lowers FT activity of the catalyst [6,13]. Further, Cu, Pd, and Au induce higher selectivities towards lighter gaseous products [6]. Jacobs et al. [13] studied the effectiveness of the Ag promoter at different addition levels. They found that higher loadings of Ag led to less active catalysts, most likely because at higher loadings, the probability of Ag—Ag bond formation increases, which lessens the likelihood of Ag—Co bonds forming. In a later study, Jermwongratanachai et al. [14] performed a direct comparison of Pt and Ag promoted catalysts. Their results show that much like Pt, Ag forms Ag—Co bonds that enhance reducibility of cobalt oxides. However, measurements of extent of reduction (EOR) were essentially the same for all concentrations of Ag in their study, suggesting that Ag is not an effective reduction promoter [14]. In addition, the optimal loading of Ag was not determined.

Thus, while the previous work indicates that Ag is a potential candidate to replace expensive noble metals in Co FTS catalysts, these studies have not addressed (1) the effectiveness of Ag as a reducing agent for alumina based supports, (2) the optimal level of Ag in supported Co-Ag FTS catalysts, (3) the role of preparation chemistry on Ag promotion, and (4) the effectiveness of silver in altering the Co metal dispersion and turnover frequency (TOF).

In this study, the effectiveness of Ag as a promoter for Co FTS catalysts was studied using two different preparation methods: conventional incipient wetness impregnation (IWI) and a new one-pot solvent deficient precipitation (SDP) method. To optimize the Ag promotion effects, catalysts with 20 wt% Co and four different Ag loadings were prepared by each of the two preparation methods and characterized by transmission electron microscopy (TEM), nitrogen physisorption, X-ray diffraction (XRD), hydrogen temperature programmed reduction (H_2 TPR), and CO chemisorption. The eight catalysts were activated in situ and their catalytic performances were evaluated in a fixed bed reactor.

2. Experimental

2.1. Catalyst preparation

The silica-alumina support (referred to as AlSi and containing 5 wt% silica) [16] used for the catalysts in this study was prepared by a method reported by Huang et al. [17] and Mardkhe et al. [18] and calcined at 1100 °C. Prior to catalyst synthesis, the AlSi support was calcined again in flowing dry air (Airgas Grade D, at 2000 GHSV) for 10 h at 800 °C with a ramp rate of 2 °C/min to ensure dehydration and surface dehydroxylation.

Two methods were then used to prepare the catalysts in this study. The first was traditional aqueous incipient wetness impregnation (IWI) using a $Co(NO_3)_2$ precursor, with loadings of 0.3, 0.6, 1.2, and 2.5 wt% Ag to produce four IWI 20 wt% Co/AlSi Ag promoted catalysts. The second was solvent deficient precipitation (SDP) [19] to produce four additional catalysts with the same loadings of Co and Ag as the IWI catalysts. In previously reported SDP preparations of non-supported iron FT catalysts [20], no water was added because the iron catalyst precursor ($Fe(NO_3)_3{\cdot}9H_2O$) released sufficient waters of hydration to produce the required solvent. However, during the SDP preparation in this study, the cobalt precursor ($Co(NO_3)_2{\cdot}6H_2O$) has fewer waters of hydration and the dry mixing of the cobalt precursor with the support and ammonium bicarbonate (ABC) does not result in the release of water. Consequently, a small amount of water (1.6 times of the pore volume of the AlSi support) was added to dissolve stoichiometric amounts of cobalt (II) nitrate hexahydrate (Sigma Aldrich 98%) and silver nitrate (Allied Chemical 99.9%) promoter. The Co and Ag solution was then mixed with and absorbed by the porous AlSi support. Subsequently, ABC (Baker Analyzed, 21.30–21.73% as NH_3) was added to this mixture to facilitate the formation of the active phase. Upon addition of the ABC, CO_2 was released according to the reaction:

$$Co(NO_3)_2{\cdot}6H_2O + 2NH_4HCO_3 \rightarrow Co(OH)_2 + 2NH_4NO_3 + 2CO_2 + 6H_2O \quad (R3)$$

The mixture was stirred until all of the ABC reacted (until bubbles stopped forming) and became less viscous with more stirring.

After impregnation or SDP, each of the catalysts was calcined in a flow reactor in dry air (Grade D, a rate of 2000 GHSV). For careful and slow removal of nitrate precursors, the temperature was raised at a heating rate of 1 °C/min from 25 °C to an intermediate hold position (about 170 °C). This hold temperature was determined from prior temperature programmed oxidation (TPO) profiles obtained by thermal gravimetric analysis (TGA) (Mettler-Toledo TGA/DSC 1) and was about 10 °C below the temperature at which significant weight loss from intermediate decomposition was detected. Following this 2 h hold, the temperature was ramped to 300 °C at 0.5 °C/min to slowly decompose the remnant nitrates and then held at 300 °C for 10 h to ensure complete nitrate removal. The obtained catalysts were named according to the Ag content in wt% and the preparation method. For example, 0.3Ag-IWI represents the catalyst prepared using IWI with an Ag loading of 0.3 wt%.

2.2. Catalyst characterization

2.2.1. Nitrogen physisorption

Nitrogen (Airgas 99.998%) physisorption at −196 °C (Micromeritics TriStar 3020) was used to obtain surface area, pore