Investigations into enhanced wax production with combustion synthesized Fischer–Tropsch catalysts

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ABSTRACT

Combustion synthesized (CS) cobalt catalysts deposited over two supports, alumina and silica doped alumina (SDA), were characterized and tested for its Fischer–Tropsch (FT) activity. The properties of CS catalysts were compared to catalysts synthesized by conventional impregnation method (IWI). The CS catalysts resulted in 40–70% increase in the yield of C_{6+} hydrocarbons compared to IWI catalysts. The FT activity for CS catalysts showed formation of long chain hydrocarbon waxes (C_{24+}) compared to the formation of middle distillates (C_{10}–C_{20}) for IWI synthesized catalysts, indicating higher hydrocarbon chain growth probability for CS catalysts. This is ascribed to the smaller crystallite sizes, increased degree of cobalt reduction and consequentially, a higher number of active metal sites exposed over the catalyst surface. Additionally, 12–13% increase in the overall C_{6+} hydrocarbon yield is realized for SDA-CS catalysts, compared to Al_2O_3-CS catalysts. The improved performance of CS-SDA catalysts is attributed to 48% increase in cobalt dispersion compared to Al_2O_3 supported CS catalysts, which is again caused by the decrease in the cobalt-support interaction for SDA supports. The metal support interactions were analyzed using XPS and H_2 TPR–TPD experiments. Combustion method produced catalysts with smaller crystallite size (17–18 nm), higher degree of reduction (~92%) and higher metal dispersion (16.1%) compared to the IWI method. Despite its enhanced properties, the CS catalysts require prominently higher reduction temperatures (~1100–1200 K). The hydrocarbon product analysis for Al_2O_3 supported catalyst showed higher paraffin wax concentrations compared to SDA supported catalysts, due to the lower surface basicity of Al_2O_3. This work reveals the impact of the CS catalysts and the nature of support on FT activity and hydrocarbon product spectrum.

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1. Introduction

Escalating energy demands due to depleting petroleum sources has renewed interests in Fischer–Tropsch (FT) process. FT synthesis reaction is at the core of gas to liquid (GTL) process and can be used to convert natural gas, coal or biomass to liquid transportation fuel [1]. Recently, biomass to liquid (BTL) process has attracted much attention for producing environment friendly, carbon neutral diesel from biomass [2]. In this process, biomass is subjected to gasification to generate syngas (mixture of CO and H_2), followed by conversion to higher hydrocarbons via the FT process [3,4]. The hydrocarbon products are cracked to produce high quality diesel that are characterized by high cetane number and are generally devoid of sulfur, nitrogen or aromatic compounds [5]. High quality diesel is obtained in large quantities (nearly 80 wt.% of the total products) using cobalt catalysts in the low temperature FT (LTFT) reaction. The LTFT reactors, operating in the temperature range of 463–513 K, predominantly yield waxes as a major products. The commercially operating FT reactors maximize the production of diesel by mild hydrocracking of waxes. The major advantage of this particular process is that the wax can be hydrocracked completely to diesel, yielding nearly 80% diesel fractions. Moreover, the diesel obtained by hydrocracking of waxes has higher degree of branching that gives it an advantageous lower pour point and also has nearly zero aromatic content, rendering it a high quality fuel [6]. Leckel [7] described a process scheme that maximizes this high quality diesel yield from an LTFT reactor, wherein nearly two-thirds of the final diesel is obtained from the wax hydrocracker while the remaining one-third is obtained from the fractionation of the hydrotreated LTFT condensation fraction. Overall, the FT products range from low molecular weight hydrocarbons to long chain waxes. The products obtained are a direct function of reaction conditions (temperature, pressure, space velocity) and catalytic properties.

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Catalyst synthesis procedure and choice of supports have a broad effect on FT activity and selectivity. Several supports like Al_2O_3, SiO_2, TiO_2, alumino-silicates and carbon nanofibers have been investigated for its effect on FT activity [8–11]. Though the fundamental operation of a support is just of physical nature, i.e. to increase the amount of surface area available for reactants, very often the dispersed metals show a strong affinity for the support, eventually altering the catalytic activity [12]. FT active metals, cobalt and iron, deposited over oxide supports show a distinct metal-support interaction and depending on the nature of this interaction FT activity is dynamically affected. Detailed work on the influence of choice of support on FT reaction has been given by Storsæter et al. [13]. The extent of metal reduction was shown to be the least for Al_2O_3 supported catalysts, and highest for SiO_2 supported catalysts, indicating a stronger metal support interaction for Al_2O_3 compared to SiO_2 supported catalysts. For cobalt–alumina system, the formation of cobalt aluminate species over Al_2O_3 supports further reduce the available active sites for FT synthesis [13]. Apart from the formation of bulk aluminates over Al_2O_3 supports, the degree of reduction and hence the metal dispersion reduces due to the formation of $Co_{2+}Co_{2-x}^{3+}Al_xO_4$ mixed spinels, additionally reducing the FT activity [14,15].

More recently, several researchers have investigated the properties of FT active metals supported over silica doped alumina (SDA). Catalysts characterized by Jean-Marie et al. [16], showed lower concentrations of cobalt aluminate compounds in SDA compared to alumina supported catalysts. The use of SDA support with composition of 5% SiO_2 and 95% Al_2O_3, significantly enhanced the cobalt reducibility, resulting in 18% increase in CO conversion [16]. The work by Daniell et al. [17] reported formation of Lewis and Bronsted acid sites by addition of SiO_2 to γ-Al_2O_3. Moreover, the quantity and the strength of these acid sites were highest for 40% SiO_2 weight fraction in the synthesized supports [17]. Consequently, the amount of acid sites has a direct influence on the FT product spectrum. Low acidity catalysts produce hydrocarbon products comprising mostly straight chain alkenes and alkanes. More acidic catalysts result in FT products comprising lighter and more branched hydrocarbons [18].

The catalyst synthesis conditions display pronounced effect on the FT activity, hydrocarbon selectivity and product distribution. Catalyst synthesis involves introduction of metal precursor into supports of high surface area and calcination of the deposited metal salt into its oxide form. For the FT reaction, the metal oxide is further reduced to its zero valent form by H_2 reduction step. Addition of metal salts into the catalyst carrier is achieved most commonly by incipient wetness impregnation (IWI) method and co-precipitation method. The combustion synthesis (CS) method of catalyst preparation has been used for synthesis of large number of metal oxides [19–29] and can be applied for synthesizing supported cobalt catalysts for FT reactions. The CS method, also referred to as self-propagating high temperature synthesis, is an efficient approach for developing metal oxides, wherein the heat required for the decomposition of the metal precursors to its corresponding metal oxides is generated by the exothermic redox reaction of a fuel and an oxidizer. The synthesis process includes impregnation of a mixture of fuel (urea, citric acid, hydrazine, etc.) and oxidizer (active-metal salts like cobalt nitrate) into the support extrudes and ignition of this mixture by an external heating source. The combustion of this mixture generates a high temperature reaction wave across the volume causing decomposition of the mixture precursors and resulting in the formation of metal oxides. The major limitation for CS process is the high heat release and the consequential high temperature rise rates ($\sim$200–300 K/min), resulting in the evolution of combustion products with uncontrolled explosion, eventually powdering the catalysts and

in most cases resulting in the loss of active components. Such vigorous behavior of CS reaction is distinctly evident for metal loading >8–10% [22]. The use of these powdered catalysts in a fixed bed reactor demands either re-pelletizing or re-molding which is considered very disadvantageous [30].

Shi et al. [31] synthesized SiO_2 supported Co catalysts by combustion synthesis and reported a CO conversion of 46.5% compared to 16.7% for IWI synthesized catalysts. The increased CO conversion was primarily attributed to reduced crystallite size, increased degree of reduction and higher metal dispersion for CS catalysts. In another work, FT active SiO_2 catalysts were synthesized by Shi et al. [32] in a single step without the need for further reduction. This was achieved by maintaining an equivalence ratio (the ratio of the actual fuel-to-oxidizer ratio to the stoichiometric fuel-to-oxidizer ratio) of 1.5 and a non-oxidizing environment during the combustion step. Though a remarkable method of synthesizing active catalyst, the authors in their work have not reported the crucial information indicating the effect on hydrocarbon product selectivity or product distribution. LeViness et al. [33], in their work reported the use of silica cobalt catalysts synthesized by the proprietary *organic matrix combustion process*, used in a microchannel reactor. The authors reported an average CO conversion of 70%, CH_4 selectivity of 7%, and a C_{5+} selectivity of 88%. The productive reaction performance was achieved by improved catalyst properties and efficient reactor performance.

In the present study, the combustion synthesis of 20 wt.% cobalt on alumina and, silica doped alumina support extrudes has been explored. The synthesized catalysts are characterized to understand the impact on metal support interaction as a consequence of the synthesis mechanism and its influence on the FT activity and product selectivity. Catalysts are characterized using DTA–TGA, FTIR, TPR–TPD, XRD, and XPS. The investigations conducted confirm the influence of support and the role combustion synthesis method on the hydrocarbon chain length formed. Properties of CS catalysts and its FT activity are compared with the catalysts synthesized by IWI method.

2. Experimental procedure

2.1. Catalyst synthesis

The redox mixture comprised of cobalt nitrate hexahydrate (Co $(NO_3)_2 \cdot 6H_2O$, Merck emplura) and hexamethylenetetramine ($C_6H_{12}N_4$, Alfa Aesar) as metal and fuel precursors respectively. The supports, γ-alumina and silica doped alumina (40 wt.% SiO_2/60 wt.% Al_2O_3) comprised of 1 mm spheres with a surface area of 158 m^2/g and 380 m^2/g respectively. The aqueous solution of metal and fuel precursors was impregnated in the supports by stirring in a rotary vacuum evaporator. Cobalt loading for CS catalysts was attained in multiple steps. IWI catalysts were synthesized by calcining the impregnated support in a furnace maintained at 823 K for a duration of 6 h.

The stoichiometry for the redox reaction was selected with the equivalence ratio of one, to achieve maximum heat release. As described by Eq. (1), the metal nitrate to fuel molar ratio is 3.86. The impregnated catalyst spheres were calcined in a muffle furnace, and the temperature increased to 673 K at 10 K/min. To measure the combustion reaction temperature, a known mass of the redox-mixture impregnated support is placed in a beaker and heated in a muffle furnace. An R-type (1 mm diameter) thermocouple is inserted into this beaker which contains the impregnated support. The reaction temperature is recorded using a P-Daq data acquisition system. Further, the redox mixture is heated by increasing the furnace temperature at the rate of 10 K/min using a PID controller. Once the reaction gets initiated, a reaction wave