



Fischer–Tropsch synthesis: Attempt to tune FTS and WGS by alkali promoting of iron catalysts

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ARTICLE INFO

Article history:

Received 8 June 2010
Received in revised form
16 September 2010
Accepted 17 September 2010
Available online 25 September 2010

Keywords:

Fischer–Tropsch synthesis
Iron catalysts
Alkali
Water effect
Lithium
Potassium
Rubidium

ABSTRACT

The effect of water on the performance of alkali-promoted, precipitated Fe catalysts was investigated during Fischer–Tropsch (FT) synthesis in a continuously stirred tank reactor. In these studies, the added water (5–25 mol%) replaced an equivalent amount of inert gas so that all other reaction conditions remained the same before, during and after water addition. The externally added water had a positive effect on the CO conversion for all the alkali-promoted, precipitated iron catalysts. The impact of the added water is to increase the rate of the water-gas shift (WGS) reaction with up to 10–15 mol% added water, and then leveling off for further increases in the amount of water added to the feed gas. Increasing the water amount in the feed gas caused the fraction of CO converted into hydrocarbons to decrease and both the WGS activity and the oxygenate selectivity to increase. Common for all the alkali promoted iron catalysts was a decrease in C₅₊ selectivity and an increase in the methane selectivity with increasing amounts of water up to 10–15 mol%; with further increases of water, the C₅₊ selectivity increases and methane selectivity decreases. Methane selectivity is directly correlated to the CO conversion and H₂/CO ratio inside the reactor.

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1. Introduction

The indirect liquefaction of coal (i.e., coal-to-liquids or CTL), biomass-to liquids (BTL), and the gas-to-liquids (GTL) processes to produce synthetic liquid fuels and chemicals rely ultimately on the catalytic Fischer–Tropsch (FT) synthesis reaction [1,2]. As with any polymerization reaction, the resulting hydrocarbon product distribution is governed by chain growth kinetics, which are in turn influenced by reactor conditions (e.g., temperature, pressure, and feed ratio), as well as the structural-property relationships of the working FT catalyst.

One drawback in converting coal- or biomass-derived syngas produced from gasification to hydrocarbon products is that syngas produced from these sources tends to have a low H₂/CO ratio; some gasifiers do produce H₂:CO with ~2:1 ratio by forming CO₂ in the gasifier. Therefore, to achieve the needed stoichiometric feed ratio for converting the syngas to hydrocarbon products, the water–gas shift (WGS) reaction is employed, which reacts CO with H₂O to boost the H₂ content, rejecting CO₂ in the process.

Often, low cost iron-based catalysts are used to convert coal-derived syngas with a low H₂/CO ratio because of their intrinsic ability to concurrently carry out FT synthesis and WGS reactions. These catalysts are therefore good candidates for converting biomass-derived syngas, due to the low H₂/CO ratio typically involved [3]. At the other extreme, natural-gas derived syngas often has a high H₂/CO ratio. In that case, a more expensive cobalt catalyst is often preferred, because conventional cobalt catalysts possess low intrinsic WGS activity. Thus, little CO is sacrificed as CO₂ product from the FT reactor; rather, in this case hydrogen is rejected as water.

Against this backdrop, research into improved FT synthesis catalyst formulations is a prudent step. There are two main target areas of research regarding the addition of chemical promoters such as group I alkali metals to Fe-based FT synthesis catalysts. First, it is highly desirable to be able to fine tune and control the intrinsic catalytic WGS activity. Such a breakthrough in catalyst design would allow the operator discretion in selecting an appropriate catalyst formulation based on the syngas ratio generated by a particular gasifier, reformer, or combination of sources, in order to minimize CO₂ emissions and maximize hydrocarbon product selectivity. For example, if the WGS activity for a particular catalyst is too high, a fraction of the expensive CO generated in the gasifier would be converted to CO₂ instead of the desired hydrocarbon target. The thrust of the research in this particular contribution is to achieve

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this level of control by balancing the relative rates of FT synthesis and WGS through the incorporation of alkali promoters into a well-developed iron catalyst formulation. Yet research is still needed into defining the mechanisms by which the promoters such as alkali metals operate on or influence the catalytically active surface to control the relative rates of the different reaction pathways.

Secondly, the hydrocarbon product distribution is defined by the chain growth probability factor, which is in turn controlled by the operating conditions (pressure, temperature, and syngas feed ratio) as well as the structure-function properties of the working FT catalyst. It is becoming important for FT technologists to consider not only improving the activity of today's FT processes and catalysts, but also to responsibly optimize these factors in order to limit the emissions of not only CO₂, but even more detrimental greenhouse gases like methane. That is, by optimizing carbon efficiency, and with the advent of improved energetically efficient technologies and energy conservation approaches, FT synthesis could certainly play a vital role in providing energy security.

For the control of the relative FT and WGS rates by alkali promotion, it is important to highlight a number of approaches used in the past to examine the impact of water. Water is, of course, produced during FT synthesis and will always be present in varying quantities during the FT reaction. As noted previously, a fraction of the water, formed as a primary product by FT synthesis, is converted over an iron-based catalyst to CO₂ by the simultaneous occurrence of the WGS reaction. Not surprisingly, for iron catalysts, researchers have found that external addition (i.e., co-feeding) of water during FT synthesis changes the CO and H₂ partial pressures inside the reactor by increasing the WGS rate [4–6]. Other claims on product selectivity have also been made. For example, in 1950, Exxon researchers reported that addition of steam to a fluidized bed reactor containing an iron catalyst increased the amount of oxygenates formed [7], while researchers at Mobil indicated that subjecting an iron catalyst to steam induces selectivation, resulting in an increase in the liquid hydrocarbon selectivity relative to that of the catalyst prior to steam addition [8]. In the open literature, Karn et al. [5] found that 10–30% H₂O added to syngas with a 1:1 H₂/CO ratio, close to that used in the current investigation, had relatively little effect on CO conversion using a fixed bed reactor and a fused iron catalyst. A notable work by Satterfield et al. [6], where a slurry reactor was utilized, examined water co-feeding to iron FT synthesis catalysts employing two different H₂/CO syngas ratios – 0.96 and 0.52. In the former case, additional water accelerated the deactivation rate during FT synthesis; in the latter case addition of 20 mol% water to the feed exhibited little effect on the FT reaction rate. Finally, Reymond et al. [9] noted a three-fold drop in CH₄ and CO₂ rates; however, from a commercial standpoint the studies were carried out under less than ideal conditions – atmospheric pressure, differential conversion, and the addition of only 0.6% H₂O to syngas having a 9:1 H₂/CO ratio.

Variations among these studies could certainly be attributed to reactor type or catalyst used. In this contribution, the goal is to examine the influence of alkali promoters on the relative rates of FT synthesis and WGS under realistic FT conditions (i.e., using a slurry reactor under suitable total pressure, reactant partial pressures, and space velocities) and attempt to assess not only the impact of alkali promoter basicity (e.g., Li, K, and Rb were assessed) on WGS activity, but also whether or not increases in the rate of WGS (i.e., CO₂ production) come at the expense of FT hydrocarbon production.

2. Experimental

2.1. Catalyst preparation

Precipitated iron catalysts were prepared using a ferric nitrate solution obtained by dissolving iron (III) nitrate nonahydrate

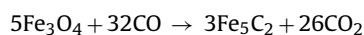
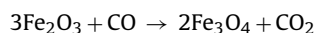
(1.17 M) in deionized water, and then tetraethylorthosilicate was added to provide the desired Fe:Si ratio. The mixture was stirred vigorously until the tetraethylorthosilicate had hydrolyzed. A flow of the tetraethylorthosilicate and iron nitrate mixture was added to a continuously stirred tank reactor (CSTR) precipitation vessel together with a stream of ammonium hydroxide (15.6 M) that was added at a rate to maintain a pH of 9.0. By maintaining the slurry pH at 9.0 and an average residence time of 6 min, a base catalyst material containing iron and silicon was obtained. The slurry from the CSTR was filtered with a vacuum drum filter and the solid was washed twice with deionized water. The final filter cake was dried for 24 h in an oven at 110 °C with flowing air. For this study, the Fe:Si catalyst base powder was then impregnated with the proper amount of aqueous alkali nitrate (e.g., LiNO₃, KNO₃, or RbNO₃) and Cu(NO₃)₂ solution to produce the desired composition of Fe:Si:alkali:Cu = 100:4.6:1.25:2.0 (atomic ratios). Catalysts were dried at 110 °C overnight followed by impregnation, drying, and calcination at 350 °C in an air flow for 4 h.

2.2. Characterization

The surface area, pore volume, and average pore radius of the base catalyst and promoted catalysts were measured by using a Micromeritics Tri-Star 3000 gas adsorption analyzer system. Nitrogen was used as the adsorption gas and sample analysis was performed at 77 K. Prior to the measurement, the samples were slowly ramped to 433 K and evacuated overnight to approximately 50 mTorr. The total pore volume was calculated from the amount of N₂ adsorbed at a relative pressure of 0.99. The pore size distribution was evaluated from the desorption branch of the isotherms using the Barrett–Joyner–Halenda (BJH) method. Characterizations of similar catalysts have been described in detail [10].

2.3. In situ activation of catalysts

In this study, the alkali promoted iron catalysts were pretreated with CO at 270 °C at 1.3 MPa for 24 h to carburize the iron. The reduction of Fe₂O₃ with CO occurs in at least two steps:



In practice, other iron carbide phases are formed in addition to Fe₅C₂ that is used for illustration in the above equation. However, for high surface area materials these two steps may merge into one step based upon the temperature increase rate.

2.4. Reactor system

The FT synthesis experiments were conducted using a 1 L CSTR equipped with a magnetically driven stirrer with a turbine impeller, a gas-inlet line, and a vapor outlet line with a stainless steel (SS) fritted filter (2 μm) placed external to the reactor. A tube fitted with a SS fritted filter (0.5 μm opening) extending below the liquid level of the reactor was used for withdrawing reactor wax (i.e., re wax, which is not volatile at the reactor temperature and is a solid at room temperature), thereby maintaining a relatively constant liquid level in the reactor. Separate mass flow controllers were used to control the flow of hydrogen and carbon monoxide to the reactor at the desired rate. The gases were premixed in a equalizing vessel before entering the reactor. Carbon monoxide passed through a vessel containing lead oxide on alumina to remove any traces of iron carbonyl. The mixed gases entered the CSTR below the stirrer, which was operated at 750 rpm. The reactor temperature was maintained constant (±1 °C) by a temperature controller. After the

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