



Feature Article

A long term study of the gas phase of low pressure Fischer-Tropsch products when reducing an iron catalyst with three different reducing gases



Joshua Gorimbo^{a,b,*}, Xiaojun Lu^a, Xinying Liu^a, Diane Hildebrandt^a, David Glasser^a

^a Materials and Process Synthesis (MaPS), University of South Africa (UNISA), Florida Campus, Private Bag X6, Johannesburg 1710, South Africa

^b Department of Chemical and Metallurgical Engineering, University of the Witwatersrand, Private Bag 3, Wits 2050, South Africa

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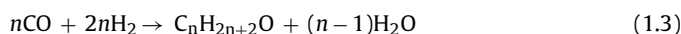
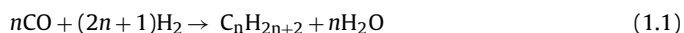
ABSTRACT

Low pressure Fischer-Tropsch synthesis was tested using iron catalysts reduced by three different reducing gases. In this regards, three reactors were set up in parallel and each of them loaded with the same quantity of the iron catalyst (FeCuKSiO₂). After loading, the catalysis in the first reactor was reduced with synthesis gas (a combination of carbon monoxide and hydrogen). The catalyst in the second reactor was reduced using hydrogen (H₂) gas, and while that in the third reactor was reduced with carbon monoxide (CO) gas. In this study only the gas-phase products leaving the reactors were analysed and compared under the same operating conditions such as flow rate, pressure and temperature for 1000 h TOS. The results obtained indicate that the initial use of different reducing agents does not have a large impact on the long term catalyst activity but does have an impact on long term selectivity. The three reactors stabilize to about the same overall CO conversion of 14.5% which corresponds to a consumption rate of 2.64×10^{-4} mol/min.gcat (reactivity) after about 150 h while the selectivities in the three reactors are not the same. Methane selectivity showed the trend: Carbon monoxide reduced > Syngas reduced > Hydrogen reduced. Furthermore, reducing with CO gives much more olefins than reducing with syngas and H₂. The paraffin production rates did not follow a consistent trend.

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1. Introduction

In the Fischer Tropsch synthesis (FTS) process, a mixture of predominantly CO and H₂ (synthesis gas/syngas) is catalytically converted to hydrocarbons. The syngas can be produced by gasification, reforming or partial oxidation of almost any carbon containing feedstock, such as coal, methane or biomass. The Fischer Tropsch (FT) process yields a wide spectrum of products, the most desirable being paraffins, olefins and oxygenates [1–4]. According to researchers, the FT process is best run with a syngas with a H₂/CO ratio close to 2:1 [5–8]. The syngas is mainly converted into a range of hydrocarbons of various molecular weights according to the following reactions:



The dependency of the FT product distribution on operating conditions has been studied by many researchers [9,10]. The process conditions are reported to have an effect on the overall product selectivity of FT [11]. It is reported that total pressure has a positive effect on the FTS reaction rate [12]. Research done by Dinse et al. [11], showed that increasing pressure results in a decrease in methane production, and an increase in the C₅₊ selectivity for a Mn promoted Co/SiO₂ catalyst. However, studies on an iron catalyst have shown that pressure has a negligible effect on FTS selectivity [13,14].

Generally, in the case of an FT process, the catalyst is reduced in situ with hydrogen, CO or syngas to yield an active catalyst. Several studies have been done to ascertain the effect of pressure during reduction. For example, Hao et al. [15] observed that the catalyst activity of their iron catalyst decreased with an increase in reduction pressure, and this was attributed to the decrease in the iron carbide content as activation pressure increased. After the catalyst has been reduced, it is introduced to the new environment where

* Corresponding author at: Materials and Process Synthesis (MaPS), University of South Africa (UNISA), Florida Campus, Private Bag X6, Johannesburg 1710, South Africa.

E-mail address: joshuagorimbo@gmail.com (J. Gorimbo).

syngas is added and it undergoes further speciation. The complexity of iron catalyst speciation during the FT catalyst reduction process has been investigated by many authors using spectroscopic studies [16–23]. Nevertheless, the literature on low pressure FT synthesis is scarce. However, based on Hao et al. [15], reduction of an iron catalyst with syngas at low pressure may increase the catalyst life span.

The safety issues and complexity of processes increases at high pressures. For example, current commercial FT processes operate at 20–40 bar and this makes the process highly complex and expensive to run [28,29]. The possibility of lowering the reaction pressure might simplify the process, especially in small to medium scale processes as might be used in Biomass to Liquid (BTL). The kinetics of low pressure operation predict lower CO conversion, and hence lower yields, and this may not be a viable design from an industrial point of view [29]. However if the catalyst can be reduced and operated at low pressure (close to ambient), then the mechanical design of the process and the safety issues are reduced, making this a possible option for small scale processes (1 ton per day or less of feed).

The main objective of this work was to experimentally explore the behaviour of low pressure reduction and operation of an iron catalyst for long term operation. In particular, three different reduction gases were used, namely syngas, CO and H₂. Currently, no FT studies investigating simultaneously the influence of three different reducing agents (syngas, H₂ and CO) on the long term catalyst activity and selectivity for both reduction and synthesis at close to ambient pressure have been reported. The current study performed FTS at 1 bar gauge, a value which is far below the normal FT runs at 20–40 bar in an attempt to achieve a simpler and less expensive process that might be suitable for small scale FTS processes.

2. Experimental

2.1. Catalyst and catalyst reduction

Three fixed bed reactors were each loaded with one gram of an iron based catalyst. A different reduction gas was used in each reactor, namely syngas for the catalyst reduction of reactor 1 (Reac-Syn), H₂ for reactor 2 (Reac-H₂) and CO for reactor 3 (Reac-CO) as shown in Fig. 1.

Before catalyst reduction, the catalyst in each reactor was dried under the flow of nitrogen at 60 mL(NTP)/min, at a temperature of 120 °C, and at atmospheric pressure, for 2 h, to get dry the catalyst.

The temperature was increased from 120 °C (drying temperature) to 250 °C (reduction temperature) at a heating rate of 1 °C/min while the pressure was maintained at atmospheric pressure. Once the temperature reached 250 °C, the temperature was kept constant and the reducing agent was introduced at a flowrate of 60 mL(NTP)/min for 48 h. Thereafter the reduction gas was switched off and syngas was introduced as described in the next section.

2.2. FT synthesis

After reduction, Reac-syn was maintained at the same temperature and flow rate but the pressure was increased from atmospheric to 1 bar gauge for FTS run. The temperature of Reac-H₂ and Reac-CO was reduced to 100 °C before introducing syngas feed so as to avoid any temperature runaways once the FTS reaction was initiated. Similarly, the pressure of Reac-H₂ and Reac-CO was increased from atmospheric to 1 bar gauge (1.85 bar absolute) and the temperature was raised gradually from 100 °C to 250 °C at a rate of 1 °C/min. The FTS experiments were carried out under these reaction conditions for 1000 h of time on stream (TOS) without changing

Table 1

Summary of experimental conditions for FTS for differently reduced iron based catalysts.

Reducing gas	Reac-Syn Syngas	Reac-H ₂ Hydrogen	Reac-CO Carbon monoxide
Catalyst weight (g)	1	1	1
Catalyst particle size (mm)	0.5–1.0	0.5–1.0	0.5–1.0
Temperature (°C)	250	250	250
Flowrate mL(NTP)/min	60	60	60
Pressure bar (abs)	1.85	1.85	1.85

the operating conditions for all three reactors. A summary of the operating conditions used during our FT experiments is shown in Table 1.

The data reported in this paper are from this first 1000 h TOS. Thereafter reaction conditions were changed to see the effect of this on the catalyst performance. The reactors were run for a further 12 000 h under varying reaction conditions until the activity of the catalyst had reduced considerably; thereafter we tried to reactivate the catalyst and ran the reactors for a further 2500 h TOS. These results are not presented in this paper as it is hard to compare the results as conditions were changing. Furthermore we could not characterise the catalyst at 1000 h TOS as we did not remove the catalyst from the reactors at this time.

3. Results

3.1. CO conversion and rate

The CO conversion and consumption rate of the FT reactions for the three differently reduced reactors (Reac-Syn, Reac-H₂ and Reac-CO) were measured against the TOS for 1000 h and the results were plotted in Fig. 2. The Reac-syn showed a sharp initial increase in the CO conversion, whereas the magnitude of this spike was not that pronounced in the Reac-H₂ and Reac-CO. The difference in the catalyst activity shown in Fig. 2 were only apparent at the initial stages of 150 h after the syngas was introduced to Reac-H₂ and Reac-CO, as opposed to Reac-syn where the syngas was kept flowing through the catalyst after the reduction process without reducing the temperature and only increasing the feed gas pressure. In all cases, a steady state was reached after about 150 h of TOS when all the reactors in the system had about the same reaction rate.

It is thus evident from Fig. 2a that the long term CO conversion for the differently reduced catalysts all attained a steady state conversion of about 14.5% for TOS greater than 300 h. The activity of all three catalysts was stable thereafter for up to 1000 h TOS. The Reac-Syn conversion may seem to be slightly higher but this difference is fairly small.

Reac-Syn displayed the highest initial increase in CO reaction rate at the beginning of the FT reaction, reaching a maximum CO consumption rate of 2.64×10^{-4} mol/(min.gcat) at around 75 h TOS. Thereafter the CO rate began decreasing reaching a steady state value after around 150 TOS. On the other hand, the Reac-H₂ and Reac-CO showed a smaller increase initially in the rate with the rate of Reac-CO being higher than Reac-H₂ followed by a gradual decrease. The shape is fairly typical of FTS and is usually attributed to the catalyst settling in, caused by changes to the catalyst surface. What is very interesting is that all three catalysts reached the same a steady state rate of CO consumption of around 1.17×10^{-4} mol/(min.gcat) after approximately 150 h and maintained this rate for the next 850 h TOS. This observed phenomenon signifies that, irrespective of the reducing agent used, effectively the same overall reaction rate is eventually achieved.

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