

Effect of Temperature on CO Rate and Product Distribution during Fischer-Tropsch Reaction over Co/TiO₂ Catalyst

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Abstract—A 10%Co/TiO₂ catalyst has been synthesized by incipient wetness impregnation method and tested in a fixed-bed reactor at 20 bar and various temperatures to assess the effect of operating temperature on Fischer-Tropsch (FT) reaction. Increasing the operating temperature (from 200°C - 220°C) led to an increase in methane and light product selectivity but increased the CO conversion rate and the net C₅₊ production rate. Apparent activation energy for CO conversion and light alkanes (up to C₄) formation has also been estimated using Arrhenius plot.

Index Terms—Co/TiO₂, Effect of temperature, Fischer-Tropsch

I. INTRODUCTION

THE world's energy demand has significantly increased in the last decade and is expected to increase as more countries are being industrialized and the world population is increasing. A significant portion of energy demand is from the transportation sector which mainly uses crude oil-derived petrol/diesel. Unfortunately, the reserves of crude oils are dwindling and strategies for alternative fuels production have become the focus of many research activities around the world. Fischer-Tropsch (FT) synthesis is one of many alternative processes for producing fuels. It converts synthesis gas (a mixture of H₂ and CO) derived from various sources such as coal, natural gas or biomass into liquid fuels. The technology has been used at industrial scale mainly by SASOL in South Africa and SHELL in Malaysia. The most recently completed commercial FT projects include the Oryx GTL in Qatar by Sasol with Qatar Petroleum in 2007 [1] and the Pearl GTL by Shell and the government of the Qatar State in 2012 [2]. More projects are currently in various development stages and indicate an increased interest in FT processes than ever before. While all big projects completed to date use either coal- or natural gas-derived synthesis gas, research on using biomass-derived synthesis gas has also significantly developed. A catalyst is always required for the FT reaction to occur. Cobalt and iron-based catalysts are the most used for industrial application [3]. The performance of these catalysts depends on a number of factors such as operating pressure, temperature, gas composition and flowrates. A

better understanding of these factors can unfold opportunities for modeling FT processes more accurately and improve the development of new technologies.

The present study aims at evaluating the effect of operating temperature on the CO conversion rate and product selectivity during FT reaction using a titania-supported cobalt catalyst. In addition, the apparent activation energy for CO conversion and light hydrocarbons formation has been estimated.

II. EXPERIMENTAL DETAILS

The catalyst was prepared by incipient wetness impregnation method to achieve ca. 10 wt.% of Co on TiO₂ support. Prior to the FT reaction, the catalyst was first activated around atmospheric pressure using a gas mixture containing 5% H₂ in Ar at 350°C for 14 hours in a fixed-bed reactor. The FT reaction was performed at 20 bar and 200, 210 and 220°C respectively. The reaction feed was maintained at 10 Nml/min using an Aalborg mass flow controller and contained around 10% N₂, 30% CO with an H₂ balance. 0.5 g of catalyst was used for the reaction and loaded between two layers of quartz wool in the middle of the reactor. The rest of the reactor was filled with stainless balls of 3 mm in diameter to improve heat transfer. Two knock-out pots were mounted downstream the reactor for product collection and the outlet gas products were analyzed on-line using a Dani Master GC equipped with a thermal conductivity detector (TCD) and flame ionization detector (FID). A 60/80 Carboxen 1000 column was connected to the TCD and was able to separate H₂, N₂, CO, CH₄ and CO₂ while the analysis of organic products was performed on a Supel-Q Plot fused silica capillary column connected to the FID.

III. RESULTS AND DISCUSSION

The effect of operating temperature on CO conversion and methane selectivity is shown in fig. 1. Both the CO conversion and methane selectivity increased with an increase in temperature. CO conversion levels of ca. 13.2, 15.0 and 19.4% were measured at temperatures of 200, 210 and 220°C respectively. The methane selectivity followed a similar trend with values of ca. 6.1, 10.1 and 19.4% at 200, 210 and 220°C respectively.

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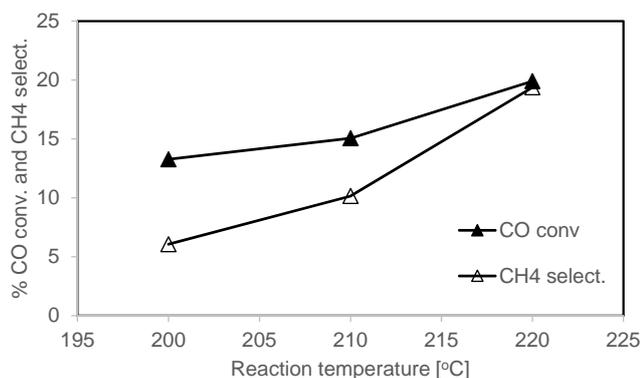


Fig. 1 Effect of operating temperature on CO conversion and methane selectivity

The selectivity to C_2 - C_4 and C_{5+} hydrocarbons was also significantly influenced by the operating temperature as shown in fig. 2. The selectivity to C_2 - C_4 increased from ca. 3.4% to 8.3 and 13.5% when the operating temperature was increased from 200 to 210 and 220°C respectively. The selectivity to C_{5+} decreased from ca. 90.5% to 81.6 and 67.1% upon increasing the reaction temperature from 200°C to 210 and 220°C respectively.

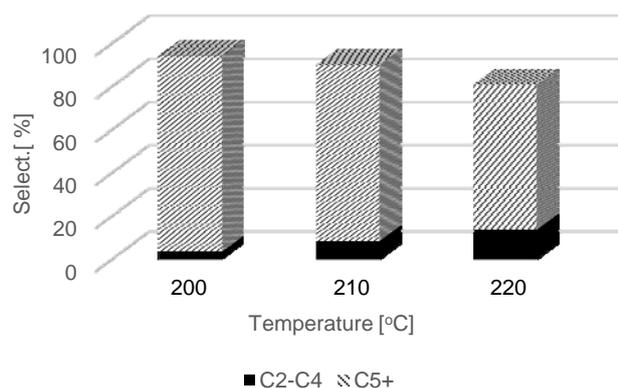


Fig. 2 Effect of operating temperature on C_2 - C_4 and C_{5+} selectivities

These results suggest that an increase in operating temperature for the FT reaction has a negative effect on the product selectivity as it increases the methane and light hydrocarbons selectivities. On the other hand, higher operating temperatures result in higher catalyst activity. In order to determine the optimum operating temperature, in addition to the CO conversion and product selectivity, one must also consider a number of factors such as the rate of liquid hydrocarbons production ($r_{C_{5+}}$) and catalyst deactivation profile. The rate of C_{5+} hydrocarbons production as well as the chain growth probability (α) as function of the operating temperature are reported in table 1. The α value did not change when the temperature was increased from 200 to 210°C but slightly decreased from 0.52 to 0.50 when the temperature was increased from 210 to 220°C. However, the productivity for C_{5+} hydrocarbons increased from 0.031 $g/g_{cat}/h$ to 0.035 and 0.047 $g/g_{cat}/h$ when the temperature was increased from 200 to 210 and 220°C respectively. Even though the highest temperature used in this study led to undesirable high selectivity to light products, it however also led to higher CO conversion rates

resulting in higher C_{5+} production rate. The effect of operating temperature on catalyst deactivation profile is part of a separate study and will be reported in future communications.

TABLE I
EFFECT OF OPERATING TEMPERATURE ON CHAIN GROWTH PROBABILITY AND C_{5+} HYDROCARBONS FORMATION RATE

Temp. [°C]	Alpha ^a	$r_{C_{5+}}$ [g/gCat/h]
200	0.52	0.031
210	0.52	0.035
220	0.50	0.047

^a: based on gas phase product excluding methane and C_2 , i.e. based on C_3 to uncondensed C_7

Olefin to paraffin (O/P) ratios are also useful parameters that give an indication on the catalyst hydrogenation properties. The results in fig. 3 show that an increase in reaction temperature leads to more olefins hydrogenation to paraffins as suggested by the decrease in O/P ratio. For example, an ethylene to ethane ratio of ca. 0.85 was measured at 200°C, decreased to ca. 0.45 at 210°C and ethylene almost disappeared when the temperature was increased to 220°C as its corresponding GC peak was below the detection threshold. Similar trends can be observed for C_3 and C_4 O/P ratios.

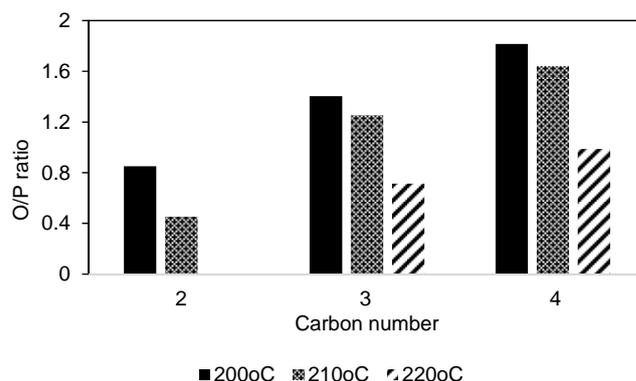


Fig. 3 Effect of operating temperature on light olefin-to-paraffin ratio

Arrhenius plots for CO conversion and light hydrocarbons formation have been generated to evaluate their apparent activation energies. The plot for CO conversion rate was fairly linear (fig. 4) with a calculated activation of ca. 39 kJ/mol. This value was significantly lower than values around 100 kJ/mol reported by other studies [4, 5] that also used cobalt-based catalyst probably due to the difference in operating conditions and type of catalyst used. For example Yan *et al.* [5] conducted their experiments at very low pressure (0.33 to 1 bar) and a H_2/CO ratio of 1 over a model Co/SiO_2 catalyst different from our conditions where the reaction was performed at 20 bar with a H_2/CO of 2.

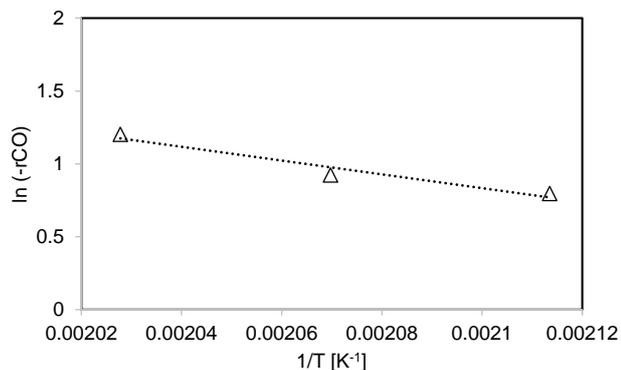


Fig. 4 Arrhenius plot for CO conversion

Arrhenius plots for light hydrocarbons are shown in fig 5. A linear trend line could not be properly fitted to light olefins (fig. 5a). However, satisfactory linear trends were obtained for light alkanes (fig. 5b) with their calculated apparent activation energies summarized in table 2. Methane had the lowest activation energy of ca. 106.8 kJ/mol and this can explain its higher selectivity compared to other light alkanes. The apparent activation energy for C₂ was the highest at ca. 183 kJ/mol. Thereafter, it decreased with an increase in carbon chain length.

TABLE II
APPARENT ACTIVATION ENERGY FOR LIGHT SATURATED
HYDROCARBONS FORMATION

	Apparent Ea [kJ/mol]
C1	106.8
C2	182.9
C3	168.2
C4	152.3

IV. CONCLUSION

The effect of operating temperature on FT reaction over a cobalt-based catalyst has been evaluated. The data show that increasing the temperature from 200°C to 210 and 220°C leads to an increase in methane and light product selectivity but increases the CO conversion rate and the net C₅₊ production rate. An apparent CO activation energy of ca. 39 kJ/mol was determined using Arrhenius plot. Apparent activation energies for light alkanes (up to C₄) have also been estimated and show the lowest value (ca. 106.8 kJ/mol) for methane and the highest (ca. 183 kJ/mol) for ethane. Arrhenius plots for light olefins did not give a satisfactory linear trend.

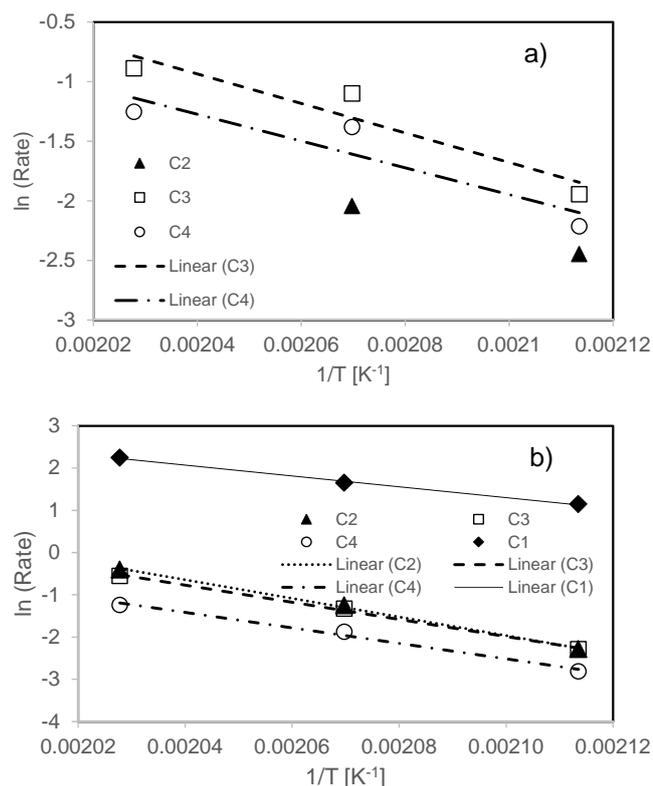


Fig. 5 Arrhenius plot for light hydrocarbons: a) olefins, b) alkanes

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