

Fischer-Tropsch Synthesis Over Titania-supported Cobalt Catalyst: Optimum Pressure for C₅₊ Hydrocarbons Production

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Abstract—Fischer-Tropsch (FT) runs were performed using a titania-supported cobalt catalyst at total operating pressures of 1, 10 and 20 bar respectively, to determine the optimal pressure for C₅₊ hydrocarbons production. The reaction temperature and feed flowrates were kept constant as 220°C and 20 Nml/g_{cat}/min respectively. Lower methane and higher C₅₊ hydrocarbons selectivities were measured at higher pressure. However the highest rate of C₅₊ hydrocarbons production was measured at an optimum pressure of 10 bar.

Index Terms— C₅₊ production rate, Fischer-Tropsch, Operating pressure

I. INTRODUCTION

THE central process in gas/coal/biomass to liquid technologies is Fischer-Tropsch (FT) synthesis.

Through this process, gas-, coal- or biomass-derived synthesis gas (a mixture containing H₂ and CO) is converted to hydrocarbons. This process yields a broad product spectrum with different carbon chain length. The main products formed include paraffins, olefins and some side products such as oxygenates (alcohols, aldehydes, ketones and carboxylic acids) and branched compounds [1]. A significant amount of water is also produced during an FT reaction. For industrial production, it is of economic interest to maximize the formation of liquid products (C₅₊). The product distribution can be influenced by operating conditions (temperature, pressure, etc.), the type of reactor and the catalyst used [1].

This study aims at determining the optimal operating pressure that maximizes the yield of liquid hydrocarbons (C₅₊) for an FT reaction over a Co/TiO₂ catalyst at 220°C and a feed gas flowrate of 10 Nml/min.

II. EXPERIMENTAL DETAILS

P25 Degussa TiO₂ powder was first mixed with deionized water, dried and calcined in air to make the catalyst support. The latter was subsequently impregnated with a solution of cobalt nitrate, dried and calcined in air in order to obtain a fresh catalyst with ca. 10 wt.% cobalt loading. The details on conditions used in each of the catalyst preparation steps are summarized in fig. 1

0.5g of fresh catalyst was loaded and maintained at the middle of a fixed-bed reactor (internal diameter: 16 mm, length: 260 mm) by two layers of quartz wool (one on top and the other at the bottom of the catalyst bed). The rest of the reactor was filled with stainless steel balls to improve heat transfer. The catalyst was reduced around atmospheric pressure using a gas mixture (30 Nml/min) containing 5%

H₂ in Ar at 350°C for 14 hours. After cooling the reactor below 100°C, pre-mixed synthesis gas containing ca. 10% N₂, 30% CO with an H₂ balance was introduced in the reactor at a flow of 10 Nml/min using an Aalborg mass flow controller. The FT reaction was first performed at 1 bar and 220°C and the pressure was further increased to 10 and 20 bar respectively while all other operating conditions (temperature, feed flow rate and feed gas composition) were kept unchanged. The catalyst stabilized within 10 hours after changing the pressure. The gas pressure in the reactor was built by using a back pressure regulator mounted downstream the reactor after two product knock-out pots used to collect condensed products. A portion of gas products was introduced through a six-port Valco sampling valve into a Dani Master gas chromatograph (GC) for on-line analysis. H₂, N₂, CO, CH₄ and CO₂ were separated using a 60/80 Carboxen 1000 column connected to a thermal conductivity detector (TCD) and organic products (light hydrocarbons up to C₈) were separated in a Supel-Q Plot fused silica capillary column connected to a flame ionization detector (FID). The GC was calibrated on a daily basis using a calibration mixture with the molar composition reported in table I.

TABLE I
MOLAR COMPOSITION FOR GC CALIBRATION MIXTURE

Component	Mol. %
C ₂ H ₄	0.98
C ₂ H ₆	0.98
CH ₄	5.2
CO ₂	4.8
N ₂	10.4
CO	24
H ₂	53.64

III. RESULTS AND DISCUSSION

The effect of operating pressure on CO conversion and CH₄ selectivity is summarized in fig. 2. CO conversion of ca. 22% was measured at 1 bar. This value increased to ca. 28% at 10 bar and decreased to ca. 19% upon further increase of the operating pressure to 20 bar.

The methane selectivity decreased from ca. 30% at 1 bar to ca. 21 and 19% when the operating pressure was increased to 10 and 20 bar respectively.

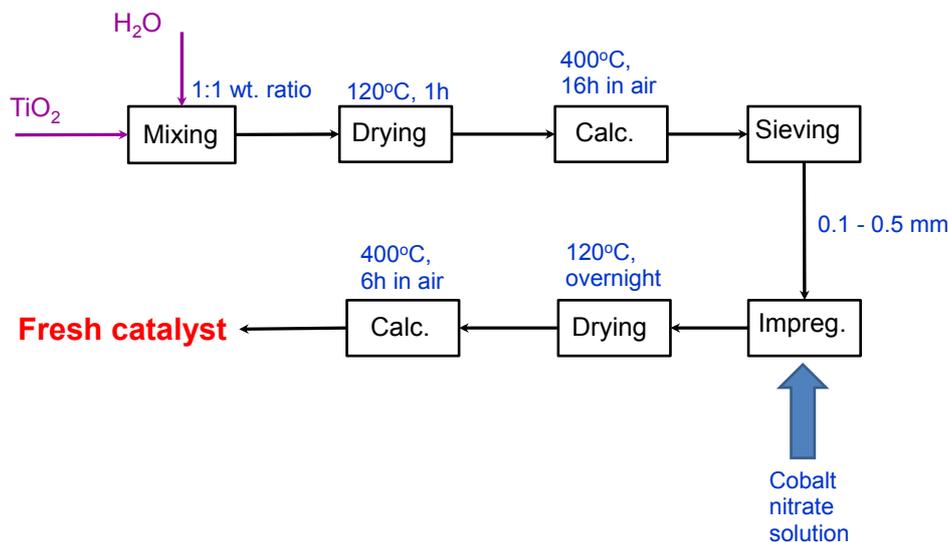


Fig. 1 Detailed catalyst preparation steps

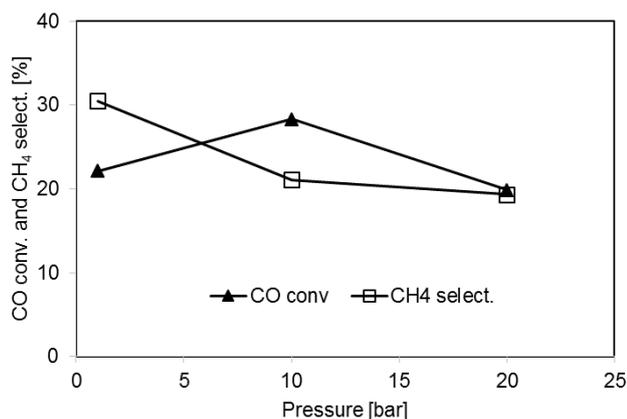


Fig.2 CO conversion and methane selectivity as function of the operating pressure

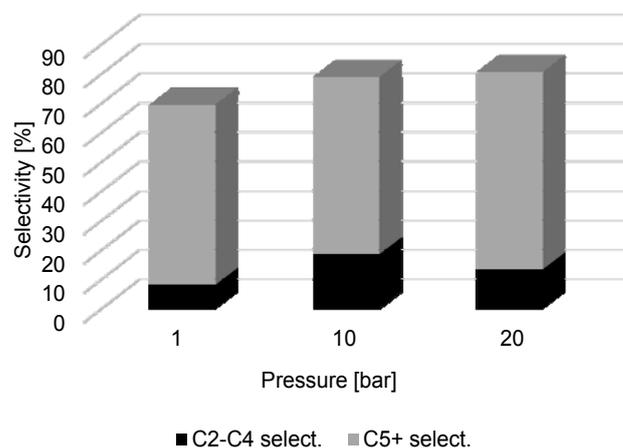


Fig. 3 C₂-C₄ and C₅₊ selectivity as function of pressure

C₂-C₄ and C₅₊ selectivities as function of the operating pressure are reported in fig. 3. The C₂-C₄ selectivity increased from ca. 8.3 % at 1 bar to ca. 18.6% at 10 bar and decreased to ca. 13.5 at 20 bar. The C₅₊ selectivity did not significantly change as it remained around 60% when the operating pressure was increased from 1 to 10 bar and increased to the highest value of ca. 67% when the pressure was further increased to 20 bar. These data and those in fig. 2 indicate that at higher operating pressure, for example 20 bar in this study, the methane selectivity is minimized and the selectivity to C₅₊ is high. However, when the rate of C₅₊ hydrocarbons formation is plotted as function of the operating pressure (fig. 4), an operating pressure of 10 bar yields the highest productivity.

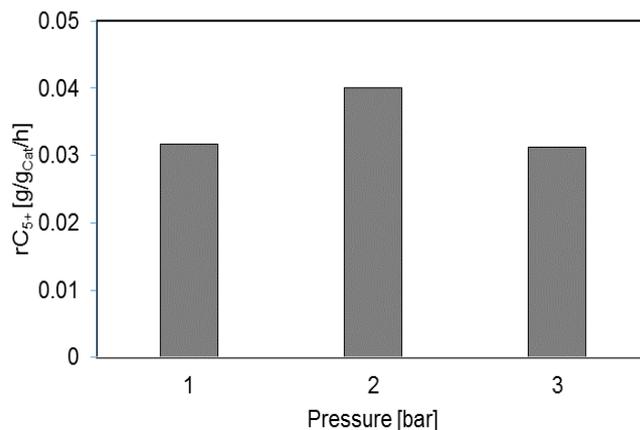


Fig. 4 C₅₊ production rate as function of operating pressure

0.032 g of C₅₊/gCat/h were produced at 1 bar, increased to ca. 0.040 g/gCat/h at 10 bar and decreased to ca. 0.031 g/gCat/h at 20 bar (fig. 4). Even though an operating pressure of 20 bar led to better CH₄ and C₅₊ selectivity, it had the lowest rate of C₅₊ production. This is due to a low CO conversion measured at 20 bar as shown in fig. 1.

Zennaro *et al.*[2] have conducted kinetics study on titania-supported cobalt catalyst under conditions where pore-diffusional mass transfer were avoided (3 - 5% CO conversion) and found that their data were best fitted by the following simple Langmuir-Hinshelwood rate equation:

$$-r_{CO} = \frac{aP_{H_2}^{0.74}P_{CO}}{(1+bP_{CO})^2} \quad (1)$$

Where $-r_{CO}$ is the CO turnover frequency [TOF], P_{H_2} the hydrogen partial pressure, P_{CO} the CO partial pressure and a, and b temperature-dependent constants.

This model was used in this study to compare the predicted and measured trends of CO rate as a function of the operating pressure. No CO TOF was determined in our study but since our experiments were all performed on a single catalyst sample at different pressures but same temperature, and space velocity, the CO TOF as function of the operating pressure should yield a similar trend as that for CO conversion. The predicted CO rates are summarized in table II.

TABLE II
PREDICTED CO RATE AS FUNCTION OF OPERATING PRESSURE

Total P [bar]	P_{CO} [bar]	P_{H_2} [bar]	a*	b*	-rCO [s ⁻¹]
			0.0011	0.04	
1	0.3	0.6			0.0002
10	3	6			0.0099
20	6	12			0.0270

* From [2]

The model predicts a significant increase in CO rate as the partial pressures of CO and H₂ (consequently the total operating pressure) are increased. This does not totally agree with the CO conversion trend measured in this study (fig 2). An increase in CO conversion was only observed when the pressure was increased from 1 to 10 bar and can be attributed to an increase in reactants (H₂ and CO) pressures in the reactor. The decrease in CO conversion as the pressure was further increased to 20 bar could be explained by significant mass transfer limitations in the catalyst resulting from the condensation of product in the catalyst pores. A similar trend was observed by Feyzi *et al.* [3] on a 40%Fe/60%Ni/40%Al₂O₃ where a significant decrease in CO conversion was observed when the total operating pressure was increase above 7 bar.

IV. CONCLUSION

The total operating pressure for an FT reaction over a Co/TiO₂ catalyst was found to have an effect on catalyst activity and product distribution. Increasing the operating pressure respectively from 1 to 10 and 20 bar decreased the methane selectivity and increased the selectivity to C₅₊ hydrocarbons. However the maximum C₅₊ hydrocarbons production rate was obtained at an optimal pressure of 10 bar. Further experiments are needed to determine whether this optimal pressure is also function of other parameters such space velocity, reaction temperature, catalyst type and pores distribution in the catalyst support.

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