

Effect of Total Pressure on CO Conversion and CH₄ Selectivity during Fischer-Tropsch Reaction over Gold-promoted Cobalt Catalyst

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Abstract—Au-promoted cobalt catalyst was prepared by two-step precipitation-deposition of cobalt and gold on a gamma alumina support. The prepared catalyst was characterized by XRD and BET, and used in a laboratory fixed-bed reactor to evaluate the effect of Fischer-Tropsch (FT) reaction total pressure on carbon monoxide conversion and methane selectivity. Carbon monoxide conversion was found to increase with an increase in system pressure and passed through a maximum at a pressure around 5 bar. The methane selectivity was very low and unexpectedly increased at high operating pressure.

Index Terms—Au/Co catalyst, Fischer-Tropsch, Total pressure.

I. INTRODUCTION

CURRENT Fischer-Tropsch processes are still confronted with a number of challenges that need to be constantly addressed by the research community. These include undesirable methane selectivity, broader product spectrum, water gas shift activity, metal-support compounds formation causing the loss of useful metals in inactive forms for FT reaction, catalyst deactivation, etc. These challenges are usually addressed by new catalyst synthesis methodology or by selecting optimum process conditions. Operating conditions that constantly need to be optimized to address the above-mentioned challenges include reaction temperature, pressure, space velocity, reactants partial pressures, type of reactor, etc.

In this study, we aim at evaluating the effect of system total pressure on carbon monoxide conversion and

methane selectivity during an FT reaction using a cobalt catalyst promoted by gold.

I. EXPERIMENTAL DETAILS

A. Catalyst preparation

Al₂O₃ support was first prepared by mixing 60 grams of alumina powder (from Sigma Aldrich) with ca. 45 grams distilled water to form a paste. The resulting paste was then dried in a drying oven set at a temperature of 100°C for more than 12 hours. This was followed by calcination in air at a temperature of 500°C for 10 hours. Particles between 100 and 150µm for use in the catalyst preparation.

Cobalt and gold were added to the support by two-step precipitation deposition method. In the first step, the support was mixed with a solution of Co (NO₃)₂ · 6H₂O in a calculated proportion to produce a catalyst containing ca. 10 wt.% Co. Cobalt was precipitated and deposited on the support by adding an ammonia solution (4-5M) drop wise to the mixture with stirring until a pH of ca. 8.5 was reached. After aging for 1 hour, the mixture was filtered, washed several times with distilled water to remove some residual ammonia and dried at 120°C for 17 hours before calcination at 500°C in air for 10 hours. In the second step, the calcined cobalt-containing catalyst was mixed with an aqueous solution of HAuCl₄·6H₂O followed by precipitation-deposition of gold using an ammonia solution (4-5M), similarly to the above-described procedure for cobalt precipitation-deposition. The target was to deposit ca. 1% of Au on the catalyst. After Au deposition and ageing for 1 hour, the sample was filtered and washed several times with distilled water to remove chlorides and dried in air at 120°C for 17 hours. The dried sample was calcined at 500°C for 10 hours to obtain the final catalyst sample.

B. Catalyst characterization

The prepared catalyst was characterized by X-ray diffraction (XRD) analysis to study the catalyst structure and the Brunauer-Emmett-Teller (BET) analysis to determine the surface area and pore distribution for the catalyst. XRD analysis was performed using a Rigaku Ultima IV X-ray powder diffractometer which used PDXL analysis software to process the data. The radiation source was Cu-Kα ($\lambda = 1.54 \text{ \AA}$), the current and voltage were set at 30 mA and 40 KV respectively. The

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step width was $2\theta = 0.01^\circ$. BET analysis was performed
by N_2

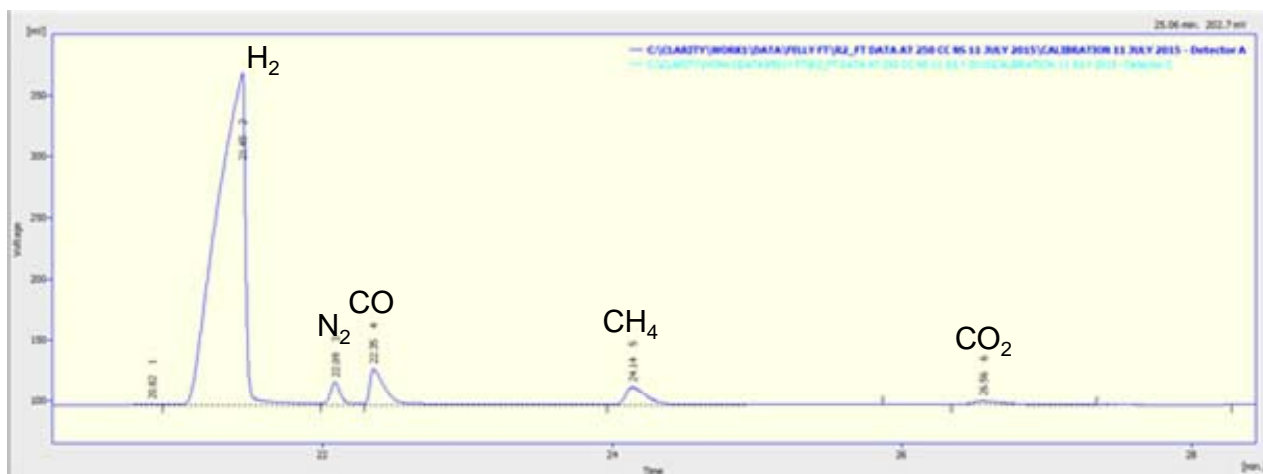


Fig. 1 Sample chromatogram for GC calibration mixture on TCD

sorption at 77 K using a Micromeritics Tristar 3000 apparatus.

C. Catalyst evaluation

The catalyst was tested in a fixed-bed reactor to evaluate the effect of total operating pressure on the performance of Au-promoted cobalt catalyst supported on alumina for FT reaction. The amount of catalyst used for FT testing was 0.5g. As the active form for FT reaction is metallic cobalt [1], the fresh catalyst was first activated by reduction in a flow of 5% H_2 in Ar (30 ml/min standard conditions) around atmospheric pressure at 350°C for 14 hours. The FT reaction was performed using a synthesis gas feed (10 ml/min standard conditions) with an H_2/CO ratio of 2 and containing ca. 10 N_2 used as internal standard for mass balance calculations. The operating temperature was 220°C and operating pressures of 1, 5, 10 and 20 bar were respectively used. Two products collecting pots were mounted downstream the reactor to collect condensed products and the outlet gas product was analysed on-line using a Dani Master gas chromatograph (GC). 60/80 Carboxen 1000 column was connected to a thermal conductivity detector (TCD) on the GC and was used for the analysis of inorganic gases, and methane. Organic compounds were analysed using Supel-Q Plot fused silica capillary column connected to a flame ionization detector (FID). The GC was calibrated on daily basis using a calibration mixture with the following certified molar composition: 0.98% C_2H_4 , 0.98% C_2H_6 , 5.2% CH_4 , 4.8% CO_2 , 10.4% N_2 , 24% CO , balance H_2 . An example of a TCD chromatogram for the calibration mixture is given in fig. 1.

II. RESULTS AND DISCUSSION

A. Catalyst characterization

XRD characterization data for the fresh catalyst are presented in fig. 2.

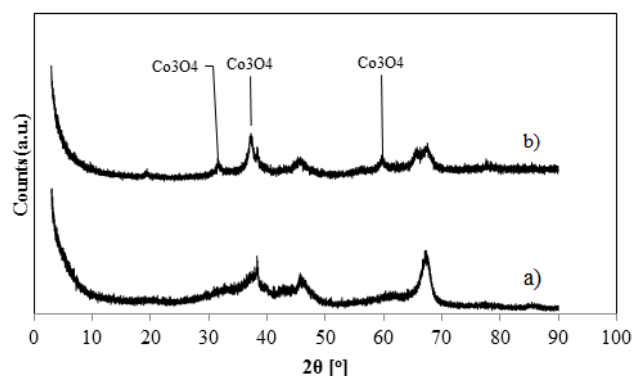


Fig 2. XRD data for a) blank calcined Al_2O_3 support and b) Au/Co/ Al_2O_3 catalyst

The blank calcined support (gamma alumina) had three major diffraction peaks at ca. 38°, 45.9° and 67.7° (fig 2a). For the calcined Co/ Al_2O_3 catalyst, in addition to the gamma alumina diffraction, new peaks were detected at ca. 31.3°, 37.1°, 59.2° and due to Co_3O_4 particles. The particle size of Co_3O_4 as determined by using the Williamson-Hall method was found to be ca. 5 nm. Au diffraction peaks were not visible possibly because the crystallite size were too small.

BET analysis data for the fresh catalyst Al_2O_3 are summarized in table 1.

TABLE I
SUMMARY FOR BET ANALYSIS DATA

1%Au/10%Co/ Al_2O_3	
BET Surface area (m^2/g)	115.6
Total Pore volume (ml/g)	0.22
Average pore size (nm)	60.8

The surface area for the Al₂O₃fresh catalyst was 115.6 m²/g and the total pore volume and average pore size were 0.22 ml/g and ca. 60.8 nm. This average pore size is significantly broader than the average Co₃O₄ crystallite size of ca. 5 nm determined from XRD analysis and suggests that minimal pores obstruction by cobalt species can be expected.

B. Catalyst evaluation

CO conversion and CH₄ selectivity as function of total operating pressure are presented in fig 3.

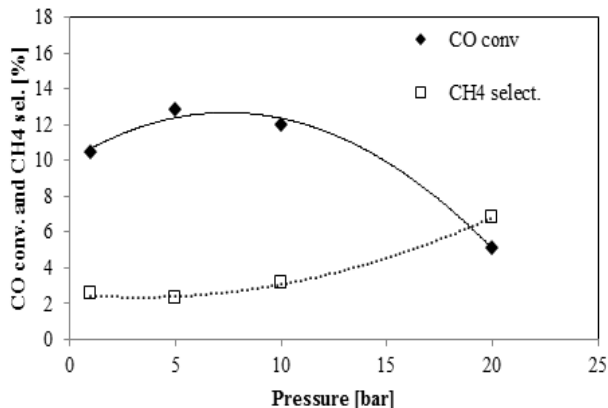


Fig 3. CO and CH₄ selectivity as function of total operating pressure

The CO conversion was observed to increase from ca. 10.5% at 1 bar to 13%. However, further increase of the total operating pressure to 10 and 20, resulted in a decrease in CO conversion to ca. 12 and 5% respectively. The increase in CO conversion with pressure (1 to 4) was expected and can be explained by an increase in reactants (CO and H₂) partial pressures. One of the explanations for the decrease in CO conversion with an increase in system pressure can be an increased mass transfer resistance in the catalyst due to more reaction products condensation at high pressure. The methane selectivity was very low, around 2.5 % at 1 and 5 bar. This could be due to the promoting effect of Au. It increased to ca. 3 and 7% when the pressure was further increased to 10 and 20 bar respectively. An increase in CH₄ selectivity, concomitant to a decrease in CO conversion is usually an indication of catalyst deactivation through surface cobalt oxidation. Higher methane selectivities on cobalt catalysts is usually attributed to oxidized cobalt species [2 - 4]. Cobalt oxides increase the local H₂/CO ratio near the cobalt metal sites through the water-gas-shift (WGS) reaction and hence increases the methane selectivity [6]. In our case, the agent that can potentially oxidize surface cobalt in the catalyst is reaction water if present in the reactor at higher partial pressures. In order to examine this possibility, the water partial pressure in the reactor has been calculated as function of the total pressure and CO conversion. The following expression was used:

$$P_{H_2O} = (\%CO)_{feed} \times P_T \times \%CO_{conv}. \quad (1)$$

Where (%CO)_{feed} is the molar % of CO in the feed gas and P_T the total system pressure. This expression was based on the assumption that for every mole of CO converted, one mole of water is formed. This is a reasonable assumption for cobalt catalysts since they have very low selectivity to oxygenates. The results are summarized in table 2.

TABLE II
CALCULATED WATER PRESSURE IN THE REACTOR AS
FUNCTION OF TOTAL SYSTEM PRESSURE

P _T [bar]	%CO conv.	P _{H₂O} [bar]
1	10.5	0.03
5	12.9	0.19
10	12.0	0.36
20	5.1	0.31

Higher water pressures were measured at conditions where the total system pressure was 10 and above. However these pressures are still low to lead to cobalt oxidation. One possible explanation for methane selectivity increase at high pressure could be Au-catalysed WGS reaction. Au has been reported to have some WGS activity under FT conditions [5-6]. Even if the water pressure at higher operating system pressure is low to lead to cobalt oxidation in this case, it could be enough to trigger some WGS reaction leading to an increase in CH₄ selectivity.

III. CONCLUSION

The effect of total operating pressure on CO conversion and CH₄ selectivity over Au/Co/Al₂O₃ catalyst has been evaluated. The CO conversion was found to initially increase with an increase in system pressure but passed through a maximum at a pressure around 5 bar. The increase in CO conversion was explained by increased reactants partial pressures and the decrease with an increase in system pressure by possible mass transfer resistance in the catalyst as a result of more reaction product condensation in the catalyst at high pressures. The methane selectivity was very low, around 3% at low pressure (1 to 5 bar) and increased to ca. 7% at high pressure. This was explained by some possible WGS activity over the Au species contained in the catalyst as the water pressure increased at high system pressures.

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