

## Effects of Process Conditions on Production of Olefins from Synthesis Gas over a Cobalt Nanocatalyst

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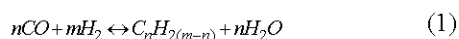
**Abstract:** An investigation of the synthesis gas (CO+H<sub>2</sub>) conversion to light olefins over Cobalt nanocatalysts promoted cerium has been carried out in a plug microreactor. The addition of cerium to cobalt nanocatalyst was found to improve the CO conversion and the olefin selectivity was slightly increased by the presence of cerium. The catalyst prepared by coprecipitation method in various ageing times (the time that precipitated remains in contact with the precipitating medium) resulted in a change in CO conversion and olefin selectivity. Catalysts were prepared in a 0 and 100 minute ageing time. These catalysts were tested at various temperatures and pressures in a stainless steel micro reactor. It was found that a catalyst with 100 minute ageing time was highly receptive to ethylene and methane.

**Key words:** Nanocatalyst • Cobalt catalyst • Synthesis gas • Fischer Tropsch • Olefins production

### INTRODUCTION

The depletion of fossil energy reserves, make the Fischer Tropsch synthesis very attractive. Fischer Tropsch synthesis, FTS, is expected as a production method of liquid fuels instead of petroleum fuels [1-2].

In (FTS), syngas (H<sub>2</sub>+CO) is converted to hydrocarbons mainly over Co-or Fe-based catalysts according to reaction (1).

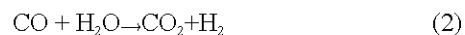


The synthesis gas feed can come from coal or residual oil gasification, methane reforming, or from biological wastes. There has been renewed interest in recent years in FT synthesis, especially for the selective production of petrochemical feedstocks such as ethylene, propylene and butylenes [3-4].

The mechanism for the FTS resembles a polymerization reaction where a monomeric unit is added to a growing hydrocarbon chain [5-7].

It is unnecessary to emphasize the importance of the catalysts in Fischer Tropsch synthesis. F-T catalysts have, as their basic constituents, the group VIII metals of the periodic table, especially iron, cobalt, nickel and ruthenium. Iron and cobalt are readily available. One special property of Fe catalysts is that they possess much higher water-gas shift (WGS) activities

(reaction 2) than Co catalysts and this may be advantageous in the case of syngas with H<sub>2</sub>/CO ratios lower than the FT usage ratio of 2.1, since some of the CO may be shifted to H<sub>2</sub> [8].



The FT reaction with cobalt-based catalysts has been studied by many investigators [9-12] and it has been shown that cobalt based catalysts, in general, are superior to similarly prepared iron-based catalysts with respect to especially catalyst life.

As reported by X. Dai and C. Yu (2008) and Q. Li (2001), CeO<sub>2</sub> promoted Co/SiO<sub>2</sub> catalyst for F-T synthesis had high activity (CO conversion higher than 85%), low yield of CH<sub>4</sub>, high selectivity for C<sub>5</sub>+ (about 80%), high stability and chain growth possibility [13-14].

The aim of this work was to investigate the effect of different process conditions such as temperature, pressure and gas space velocity on olefins selectivity and also the effects of ageing time in product selectivity. The ageing time is a parameter of crucial importance in the preparation of active oxide catalysts for hydrogenation of CO.

The parameter of ageing time has been investigated in other works reported by Varma *et al.* (1990), Stull *et al.* (1969), Rabo *et al.* (1978) and the similar result has also been reported [15-17].

## Experimental

**Catalyst Preparation:** The nanocatalysts precursors were prepared using the coprecipitation method. Aqueous solution of cobalt nitrate (0.25mol/lit) was inserted in the mixer. The cerium nitrate was added to the medium and premixed and the resulting solution was heated to 80°C. Aqueous sodium carbonate (0.25mol/lit) was added to the mixed nitrate solution, which was continuously stirred at 150 rpm, whilst the temperature was maintained at 80°C until pH between 8 and 8.3 was achieved. This procedure took approximately 10 to 15 minutes to complete. The resulting precipitate was then filtered and washed several times with hot and cold distilled water until the observed sodium content by atomic absorption was less than approximately 150 ppm. The precipitate was dried at 120°C for 16 hrs to give a material denoted as the catalyst precursor, which was then calcined (550°C, 6 hrs) to give the final catalyst. Specific surface area (345 m<sup>2</sup>/g) from BET analysis can be attributed to the porous structure of catalyst supported by its SEM images. The FE-STEM image indicated that the catalyst particle size is <85 nm.

In pH=7, small particles with a large surface area were prepared. The calcined catalyst contained 11wt% cobalt. Catalysts were reduced in the reactor with hydrogen (99.99%) at 350°C, 1atm, 4hrs. The catalyst was prepared in two samples. Sample A with 0 and sample B with a 100 minute ageing time. Ageing of the precipitates obtained by co-precipitation method, leads to phase changes towards the forms which are more stable thermodynamically.

**Microreactor:** The reaction equipment used was a fixed bed microreactor, which allows for working up to 50 bar and 600°C. The microreactor is an isothermal fixed bed of 10 mm internal diameter, 300 mm length and a volume of catalyst up to 5 cm<sup>3</sup>. It is located on the inside of a stainless steel chamber, which is heated by an electric resistance. All gas lines to the reactor bed were made from stainless steel tubing. Three mass flow controllers (Brooks, Model 5850E) equipped with a four-channel control panel (Brooks 0154) were used to adjust automatically the flow rate of the inlet gases.

Glass wool supported the catalyst and prevented loss of the fine particles. After controlling temperature, pressure and flow rate, feed gas passes through the microreactor.

The experimental unit has been shown in Fig. 1 and consist of gas cylinders, valves, pressure regulators, flow meters, microreactor, furnace and gas chromatograph. In this work, a gas chromatographic system has been

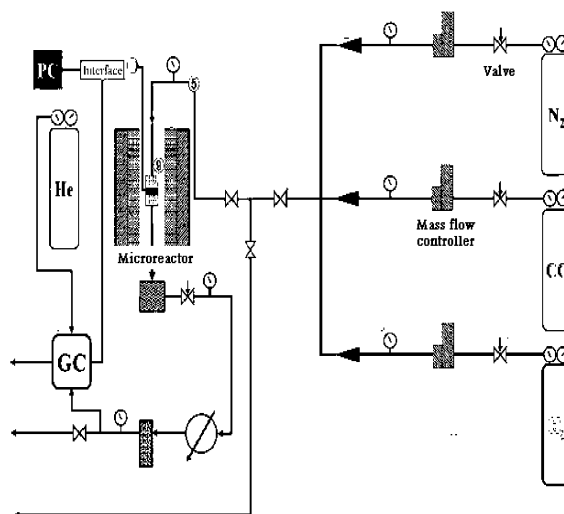


Fig. 1: Experimental unit for the test of catalysts

developed for the on-line analysis of Fischer-Tropsch products. The gas chromatograph model Varian 3400 with FID and TCD detectors has been used.

A packed Porapak-Q column and a porous-layer open-tubular column have been used for separation of the products. The capillary column separates the C<sub>1</sub>-C<sub>4</sub> hydrocarbons and permits a reasonable analysis of the hydrocarbons in the C<sub>5</sub>-C<sub>7</sub> range. The packed column is used for the separation of methane, carbon monoxide, carbon dioxide and water.

## RESULTS AND DISCUSSION

The performance of the catalysts in the screening microreactor at various temperatures, pressure and gas space velocity (GHSV) is summarized in Table 1.

The Conversion, selectivity and gas space velocity can be calculated by the following relations:

$$\%Conversion = \frac{CO_0 - CO}{CO_0} * 100 \quad GHSV = \frac{\left(\frac{ml}{min}\right)_{feed}}{ml_{Catalyst}}$$

$$\%Selectivity = \frac{C_p}{CO_0 - CO} * 100$$

In reactions lasting 24 and 48 hrs, the activity of this catalyst appeared to stabilize after 4 hrs on stream and showed very little change thereafter.

As mentioned by Snel, R. (1987), Friedel, R. A. and Anderson, R. B. (1950) and King *et al.* (1981) these catalysts showed high methane and high alkenes content in ethylene fractions [18-20]. The water gas shift reaction has low activity in cobalt catalysts, but the bodouard reaction ( $2CO + CO_2 + C$ ) has a high activity and leads to

Table 1: Result of 0 and 100 min age Co/CeO<sub>2</sub>

%Selectivity											
C <sub>4</sub> H <sub>10</sub>	C <sub>3</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	CH <sub>4</sub>	%Conv.	H <sub>2</sub> /CO	GHSV hr <sup>-1</sup>	P atm	T°C	Ageing time min	
-	-	0.1	-	-	40	1	3600	1	350	0	
-	0.1	0.6	-	0.1	31	1	3600	1	400		
-	1.6	4	-	4	21	1	3600	1	450		
0.3	1.9	4.5	-	3.5	19	1	7200	1	450		
-	0.6	0.9	0.3	4	30	1	7200	5	450		
-	-	0.5	-	1.3	50	1	3600	1	350	100	
-	0.7	1.8	-	1.5	38	1	3600	1	400		
0.1	0.7	44	-	48	17	1	3600	1	450		
-	0.5	2	0.3	4	40	2	3600	1	450		

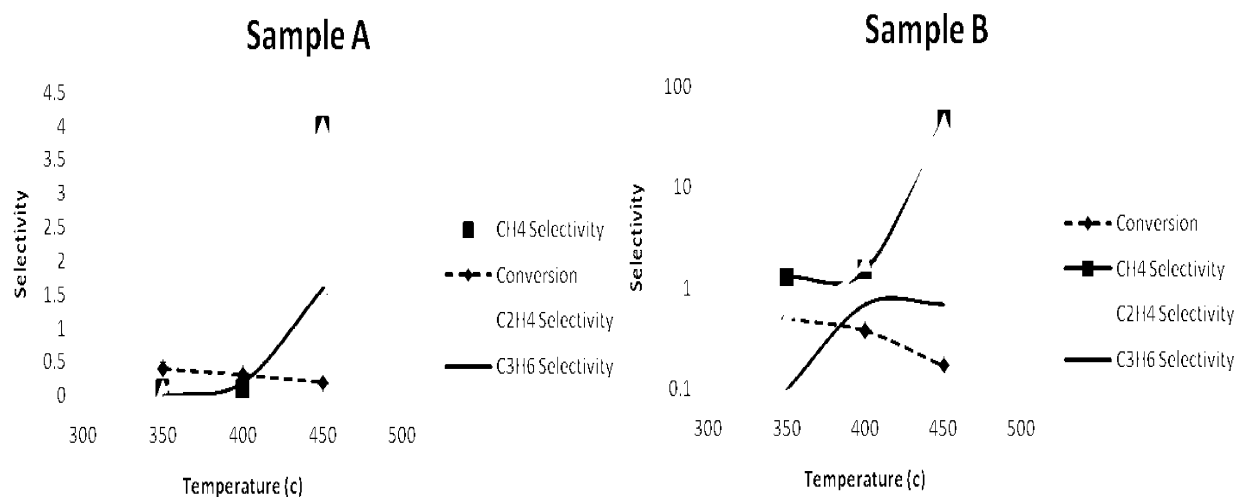


Fig. 2: Effect of temperature on selectivity

production and deposition of carbon bulk in the bed of the microreactor. Deposition of carbon may lead to excessive methane formation, catalyst deactivation and destruction of catalyst pellets. Carbon deposition via the bodouard reaction is favored over the formation of olefins.

**Effects of Space Velocity:** As space velocity increased, the effective conversion decreased and the olefin selectivity in the C<sub>2</sub> and C<sub>3</sub> fraction increased. In this case, the hydrogenation of primary products, olefins were somewhat inhibited and the selectivity of olefins increased. An increase in olefin selectivity with increasing space velocity was reported in a study by Dictor, R. A. and Bell, A. (1986) [21]. Increasing GHSV causes reduction in retention time and production of light component. It is obvious that increasing of GHSV causes faster deactivation of the catalyst.

**Effect of Temperature:** The elevation of the reaction temperature increased the activities of the catalysts. Figure 2 showed the effect of temperature on ethylene and propylene selectivity for unages catalysts. Temperature increase would cause an increase in the concentration of hydrogen on the surface of catalyst due to an increase in hydrogen mobility, thus enhancing the rate of termination reactions leading to a decrease in the selectivity for heavier products.

In sample B, the bodouard reaction is very active and this tendency increases with increasing temperature. The results showed a marked decreased conversion% and increase of gas phase selectivity with increased temperature for both samples. At the conversion of 17% for sample B, selectivity of ethylene and methane were 44% and 48%, respectively. In this sample, with decreased temperature, %conversion reached 50% and ethylene selectivity reached 0.5%. Sample A showed that an increase in temperature leads to an increase in olefins

selectivity and a decrease in conversion percentage. An increase in olefin selectivity with increasing temperature was reported by Bukur *et al.* (1990), Manfred Muller and Ute Hubsch, Ulmann's (2002) and Steynbery *et al.* (1999)[22-24].

**Effect of Pressure:** Heavy hydrocarbon selectivity increases at high pressure, because the hydrogenation and cyclic reactions proceed at higher rates. When the reaction pressure was elevated from 1atm to 5 atm at a constant temperature, the conversion of CO rose from 21% to 40% and selectivity of ethylene decreased.

**Effect of H<sub>2</sub>/CO ratio:** For this catalyst, total olefins selectivity decreases with an increase in H<sub>2</sub>/CO because of the increase in the rate of olefins hydrogenation to heavy hydrocarbons. The increase of the CO amount in the synthesis gas ( $\frac{H_2}{CO} < 1$ ) lowered the activities of the catalysts. In fact the increasing feed H<sub>2</sub>/CO ratio increases hydrogen concentration at the surface of catalyst and together with a decrease in CO surface concentration would enhance termination reactions leading to a decrease in selectivity of heavier products.

**Effect of Ageing Time:** As expected, preparation of the catalysts in different ageing times led to notable ethylene selectivity. The unage catalyst showed low ethylene selectivity. The results show that the ageing of the precipitates leads to phase changes towards the forms which are more stable thermodynamically. These results show that there is considerable variation in the catalyst activity with respect to the ageing time and the sample aged for 100 min gave the highest ethylene selectivity in Fischer-Tropsch synthesis. Therefore, the ageing time is a parameter of crucial importance in the preparation of active cobalt/cerium oxide catalysts for hydrogenation of CO.

## CONCLUSIONS

The FT synthesis carried out in a microreactor provided important information useful for the design of the process unit. As was shown, several reactions may proceed simultaneously over the cobalt catalyst during the synthesis of hydrocarbons from synthesis gas. Water gas shift (wgs) and bodouard reactions are side reactions and produce carbon bulk and carbon dioxide in the catalyst bed of the reactor and must be inhibited by changing the process conditions.

In this paper, effective parameters such as ageing time, temperature, pressure of the reaction and space velocity were investigated. From the results presented in this study, it is clear that the catalyst ageing time has been found to be of most significance. The Co/CeO<sub>2</sub> catalyst in the 100 minute ageing time has been found to be selective for light alkenes production from synthesis gas.

Both samples (aged and unaged catalysts) have a high activity for the bodouard reaction. In high pressure and H<sub>2</sub>/CO>1, production of olefins is very low. In general, high temperature, low pressure and low H<sub>2</sub>/CO are effective for the production of light olefins with high selectivity. The increasing feed H<sub>2</sub>/CO ratio increases hydrogen concentration at the surface of catalyst and together with a decrease in CO surface concentration would enhance termination reactions leading to a decrease in selectivity of heavier products. Also Temperature increase would cause an increase in the concentration of hydrogen on the surface of catalyst due to an increase in hydrogen mobility, thus enhancing the rate of termination reactions leading to a increase in the selectivity for lower olefins.

## Nomenclature:

**C:** Concentration (mol/lit)

**CO<sub>0</sub>:** Initial concentration of carbon monoxide (mol/lit)

**C<sub>p</sub>:** Product concentration (mol/lit)

**GHSV:** Gas Space Velocity (min)<sup>-1</sup>

**P:** Pressure (atm)

**T:** Temperature (K)

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