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Effect of Recycle Gas on Activity and Selectivity of Co-Ru/Al_2O_3 Catalyst in Fischer-Tropsch Synthesis

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Abstract—In industrial scale of Gas to Liquid (GTL) process in Fischer-Tropsch (FT) synthesis, a part of reactor outlet gases such as CO_2 and CH_4 as side reaction products, is usually recycled. In this study, the influence of CO_2 and CH_4 on the performance and selectivity of Co-Ru/Al_2O_3 catalyst is investigated by injection of these gases (0-20 vol. % of feed) to the feed stream. The effect of temperature and feed flow rate, are also inspected. The results show that low amounts of CO_2 in the feed stream, doesn`t change the catalyst activity significantly but increasing the amount of $CO_2$ (more than 10 vol. %) cause the CO conversion to decrease and the selectivity of heavy components to increase. Methane acts as an inert gas and doesn`t affect the catalyst performance. Increasing feed flow rate has negative effect on both CO conversion and heavy component selectivity. By raising the temperature, CO conversion will increase but there are more volatile components in the product. The effect of CO2 on the catalyst deactivation is also investigated carefully and a mechanism is suggested to explain the negative influence of CO_2 on catalyst deactivation.

Keyword—Alumina, Carbon dioxide, Cobalt catalyst, Conversion, Fischer Tropsch, Selectivity

I. Introduction

IN the twenty-first century, natural gas is expected to become an increasingly important raw material for manufacturing clean fuels and chemicals [1]–[3]. Fischer–Tropsch (FT) synthesis is a major part of gas-to-liquids (GTL) technology, which converts Syngas gas (H_2 and CO) into liquid fuels with very low sulfur and aromatic content [1]–[4]. Production of Syngas from methane, coal, and biomass followed by subsequent conversion of Syngas to a wide range of fuels and chemicals, is of particular interest as the worldwide reserves of crude oil are being depleted.

Supported cobalt catalysts have been particularly attractive for the conversion of synthesis gas to valuable long-chained hydrocarbons, because of their high activity, high stability, relatively low cost, high selectivity for long chain paraffins and low water–gas shift (WGS) reaction [5]–[7].

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The economical value of the process is related to the value of the products. Thus the product selectivity and the overall efficiency of the process are the main parameters of any gas converting design. In industrial scale, the gas products are separated from the desired products and after the condensation of water vapor, a part of this gas is recycled to the reactor in order to increase the efficiency of the process. This recycle gas includes: H_2 and CO (as unconverted feed), CO_2 and CH_4 (as side products) and other volatile hydrocarbons. Each of these gases has a different effect on the catalyst activity, product selectivity and deactivation of the catalyst. Many experiments have been performed to investigate the effect of olefins on the activity and selectivity of several catalysts by adding the olefin to the feed stream directly [8]–[11]; but there is little research about the influence of CO_2 and CH_4, which contribute to a significant part of the recycle gas, in the literature [12].

In this study, the effect of CO_2 and CH_4 on the product selectivity and the performance of the Co-Ru /Al_2O_3 catalyst were investigated by adding these gases to the feed stream (0-20 vol. % of the feed). On the other hand, Cobalt catalyst is more expensive than Iron based catalysts, so the deactivation rate of this catalyst is an important parameter [13]–[17]. In the other part of this study, the effect of CO_2 on the deactivation rate of Co-Ru /Al_2O_3 catalyst was inspected. The reaction was carried out in a fixed bed synthesis reactor operating at atmospheric pressure. The effects of feed flow rate and temperature were also investigated.

II. Experimental

A. Catalyst preparation

The catalyst used in this study, was made by the wet impregnation method. At first, Lanthanum was impregnated on Al_2O_3 using the Lanthanum Nitrate solution. After filtration, the sample was heated for 1 hour to reach 120˚C in an oven and was kept at this temperature for 2.5 hours. Calcination was done at 450˚C in a furnace. After the sample cooled down, Cobalt and Ruthenium were impregnated using the aqueous solution of Cobalt Nitrate and Ruthenium Nitrosyl Nitrate at the same time in one stage. The Cobalt weight loading was fixed at 15 wt. % and Lanthanum and Ruthenium were both fixed at 1 wt. % of the total weight of the catalyst.

B. Catalyst characterization

The catalyst elements were determined by XRF method and the quantity of each element was obtained by Atomic Absorption method. UOP303 standard was used to measure the amount of Cobalt and UOP873 for the promoters. In all cases 95-100% of the predicted amount of the elements was impregnated on the Alumina. The powder X-ray diffraction (XRD) patterns were obtained with a Philips diffractometer using Cu–Kα radiation.

C. The fixed bed reactor system

The micro reactor used in this study, is a fixed bed column with 6 mm internal diameter and 50 cm length. Reactants are fed to the reactor whit the ratio of $H_2/CO = 2$ using two mass controllers. Feed gases are mixed by a mixer and enter to the top of the reactor. Some crushed Quartz with the particle sizes greater than the catalyst particles, is located at the top and the bottom of the reactor to avoid the flow of catalyst in the reactor. An agitated bath of melted salt is used to release the heat of the reaction and the temperature is controlled by a PID controller.

The gas product is sent to a GC (Varian-3800) equipped with a Flame Ionization Detector (FID) and a Thermal Conductivity Detector (TCD). The volumetric flow rate of these gases is determined before the GC system. In order to prevent the condensation of the gas products, the temperature of the exit line is kept at 20˚C more than the previous parts. The outlet line and the gas sampling loop of the GC are also washed by Nitrogen before each injection to avoid the condensation of gases and the agglomerate of heavy hydrocarbons. The inlet line is connected to the GC by a bypass stream in order to analyze the feed.

The mass controllers are calibrated by the Brooks Vol-U-Meter Calibrator (220 VAC) and the thermometers and temperature controllers are calibrated by the Hermitzet B 4001 Simens by the comparison method.

D. Activity and selectivity tests

For all experiments, 1 gram of catalyst with 30 to 100 μm particle sizes was loaded into the micro reactor. The reduction of catalyst was done by Hydrogen with 30 ml/min volumetric flow rate. The reactor temperature was increased to 400˚C and was kept at this temperature for 12 hours. After the reduction process, the temperature was reduced from 400˚C to the desired reaction temperature in 2 hours.

To determine the effect of temperature on the catalyst activity and selectivity, the reaction was performed at 200, 210 and 220˚C at atmospheric pressure. The feed flow rate was 45 ml/min. The influence of the feed rate was investigated at 220˚C and atmospheric pressure at 30, 45 and 90 ml/min flow rates. To investigate the effect of CO_2 on the catalyst activity and selectivity, the reaction was carried out at atmospheric pressure and at 220 and 240˚C. To investigate the effect of CO_2 on the deactivation of catalyst, the reaction was carried out at 260˚C. The volumetric flow rate was 60 ml/min and CO_2 was injected to the feed stream from a storage tank (0-20 vol. % of feed). For all runs, the total pressure of the tank was 12 bars. In order to have a constant feed flow rate, nitrogen was used in all runs. The influence of CH_4 was examined in the same situation, as CO_2, but only at 220˚C.

For all experiments, the mole fraction of each component in the outlet of the reactor was determined and the feed conversion and rate of hydrocarbon production per unit mass of the catalyst was subsequently calculated. Product selectivity was estimated from the rate of production of each component and the total amount of the consumed CO.

III. Results And Discution

A. Physicochemical properties of Co-Ru/Al_2O_3

The catalyst elements were determined by XRF method and the XRF patterns are shown in Fig.1 in which, the Aluminum, Cobalt and Ruthenium peaks can be seen clearly.

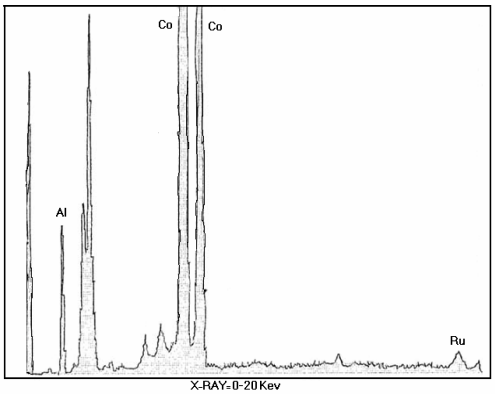

Fig.1 the XRF pattern of Co-Ru/Al_2o_3

Quantitative analysis of the catalyst elements was done by Atomic Absorption method and the result is shown in Table I. In all cases, 95-100% of the predicted amount of the element was impregnated on the Alumina.

TABLE I
RESULT OF ATOMINC ABSORPTION TEST

Component	Co	Ru	La
Approximated fraction	15	1	1
Ultimate fraction	14.7	1	1

Fig. 2 shows the XRD pattern of the Co-Ru/γ-Al_2O_3 catalyst. The Al_2O_3 exhibits reflection peaks at $2\theta = 46.1^\circ$ and 66.5°. The other peaks show the different crystalline types of Co_3O_4. The sharpest peak is observed at $2\theta = 36.8^\circ$.

B. Temperature effects

The temperature effect was inspected at atmospheric pressure with 45 ml/min feed flow rate at 200, 210 and 220˚C and $H_2/CO=2$. Fig.3 shows that both the CO conversion and the reaction rate increase with increasing reaction temperature.

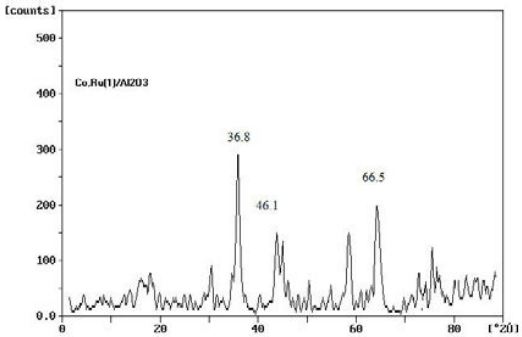

Fig.2 XRD pattern of Co-Ru/Al_2O_3

As shown in Fig.4, increasing the temperature causes a decrease in C_5+ selectivity and an increase in CH_4 and C_2-C_4 selectivity. This means that by increasing temperature, there are more volatile hydrocarbons in the products.

C. *Effects of feed flow rate*

Fig.5 shows the effect of feed flow rate on CO conversion at 220˚C, atmospheric pressure and H_2/CO=2. Increasing the feed flow rate resulted in a decrease in the conversion of CO due to lower residence times.

As shown in Fig.6, selectivity of volatile hydrocarbons increased with increasing feed flow rate as. By raising the flow rate, the residence time of olefins on the catalyst surface would decrease reducing the probability of olefin adsorption and regrowth thus increasing the selectivity for more volatile hydrocarbons in the products.

D. *CO_2 effect*

To investigate the effect of CO_2 on the catalyst activity and selectivity, the reaction was carried out at atmospheric pressure and at 220 and 240˚C with 60 ml/min feed flow rate and H_2/CO=2. Fig.7 shows the effect of CO_2 on CO conversion at 220˚C. Adding small amounts of CO_2 to the feed stream did not change the CO conversion significantly. By injection of about 10 vol. % and more, however, the CO conversion would decrease. The Lanthanum promoter which is a basic metal adsorbs CO_2 on the catalyst surface. By increasing the amount of CO_2 in the feed, the adsorption of this gas on the catalyst surface would increase the surface concentration of CO_2 and consequently decrease the surface concentration of H_2. Since the reaction rate is directly related to the surface H_2 concentration, the reaction rate would also decrease. As shown in the Fig.7, by adding 20 vol. % CO_2 to the feed stream, there will be 36.7% reduction in the CO conversion.

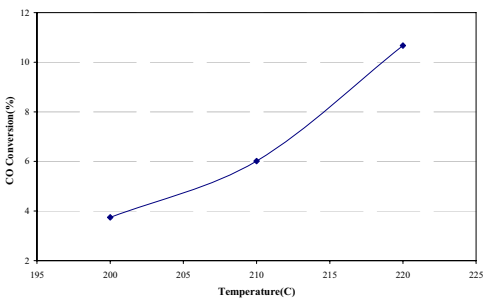

Fig. 3 temperature effect on CO conversion

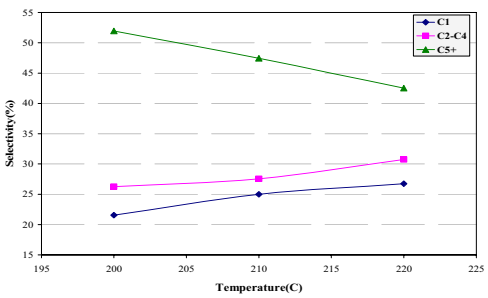

Fig. 4 temperature effect on product selectivity

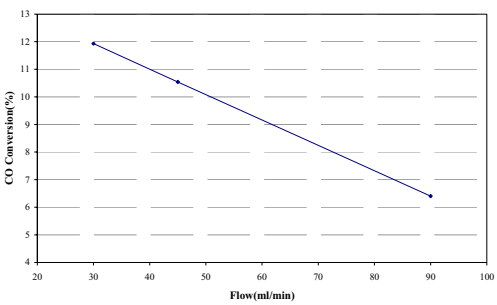

Fig. 5 effect of feed flow rate on CO conversion

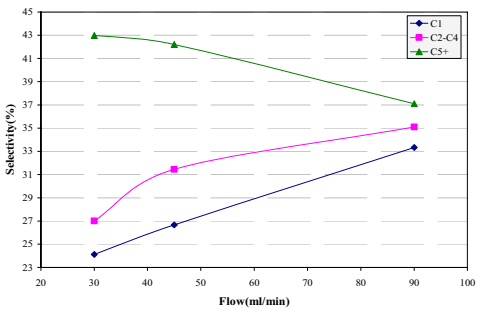

Fig. 6 effect of feed flow rate on product selectivity

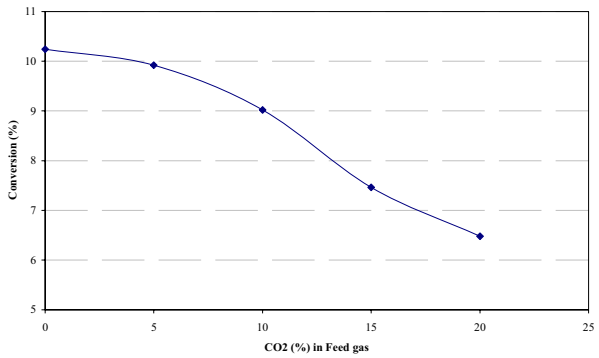

Fig. 7 effect of CO_2 on CO conversion at 220˚C

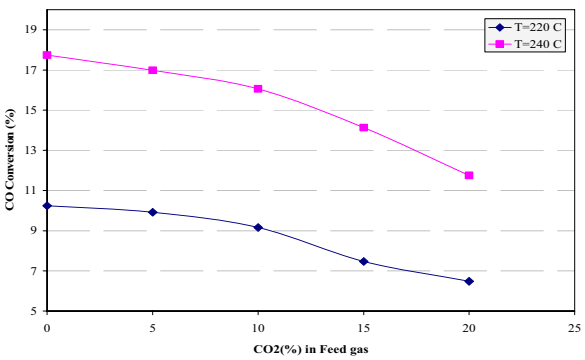

Fig. 9 the effect of CO_2 on CO conversion at 220˚C and 240˚C

The effect of CO_2 on the product selectivity is shown in Fig.8. It can be seen that adding small amounts of CO_2 (less than 10 vol. %) would not significantly affect the product selectivity. Further increases in the amount of CO_2 in the feed, however, would decrease the selectivity for CH_4 and other volatile hydrocarbons and increase those for the heavy components (C_5+). Increasing the amount of CO_2 in the feed and the consequent reduction of surface H_2 concentration, would suppress hydrogenation reactions and therefore the chain growth and the product selectivity for heavy components would increase. The production of saturated paraffin hydrocarbons would decrease due to lower rate of hydrogenation reactions leading to the presence of more olefins in the products [18], [19].

Increasing the amount of CO_2 in the feed would increase the product selectivity for heavy components and liquid hydrocarbons and decrease the overall reaction rate. Similar trends were observed at the higher temperature of 240˚C. The reduction in CO conversion, however, is more significant at the lower temperature. As shown in Fig.9 at 240˚C, addition of 20 vol. % of CO_2 to the feed stream would result in 33.8% reduction in the CO conversion. The effect of CO_2 on the product selectivity at 240˚C is shown in Fig.10. The C_5+ selectivity at this temperature are lower than those at 220˚C over the entire range of the amounts of CO_2 added to the feed.

To investigate the effect of CO_2 on catalyst deactivation, the reaction was carried out under conditions that both the reaction rate and the CO conversion were high; namely at 260˚C, atmospheric pressure, 60 ml/min feed flow rate and H_2/CO=2 for 30 hours. The results are shown in Fig.11 for different amounts of CO_2 added to the feed stream. The relative activity is defined as the ratio of CO conversion at a given time to the CO conversion at the start of the reaction. As illustrated in Fig.6, if there is no CO_2 in the feed, the relative activity of catalyst would decrease by 21.8% in the first 15 hours. With 20% CO_2 in the feed, however, the relative activity would decrease by 39.8% over the same time period. For all experiments, the reduction in activity was only significant over the first 15 hours after which the relative activity would remain relatively unchanged.

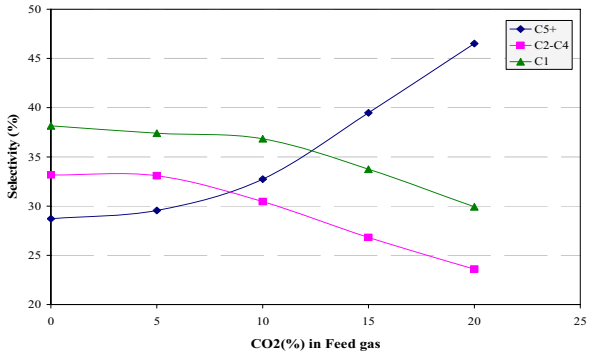

Fig.10 the effect of CO_2 on the product selectivity 240˚C

In FT synthesis and at high CO conversions, the adsorption of CO_2 on the catalyst surface by the Lanthanum promoter is high causing a decrease in catalyst activity. Furthermore, by increasing the CO_2 partial pressure, the hydrogen concentration on the catalyst surface is reduced resulting in the oxidation of surface Cobalt and the reaction of Cobalt and Alumina [20]. However, the deactivation of alumina supported cobalt catalyst due to increasing amount of CO_2 in the feed stream is mainly due to the water-gas shift reaction. In FT synthesis the water-gas shift reaction is a reversible reaction with CO_2 as one of the products:

$$H_2O+CO \leftrightarrow CO_2+H_2 \qquad K_p = (P_{CO2}*P_{H2}) / (P_{CO}*P_{H2O}) \qquad (1)$$

If the partial pressure of CO_2 increases, the reaction proceeds in the reverse direction producing water. The increase in water vapor partial pressure enhances the oxidation of cobalt as well as the interaction between cobalt and alumina. The produced cobalt aluminate reduces the catalyst activity [21], [22].

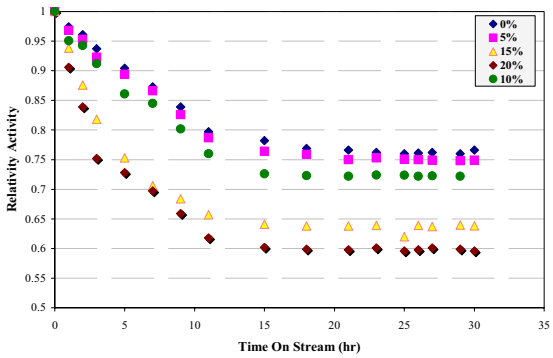

Fig.11 the effect of CO_2 on catalyst deactivation

E. CH_4 effect

To inspect the effect of CH_4 addition, the reaction was carried out at 220˚C and at atmospheric pressure with H_2/CO=2 and a feed flow rate of 60 ml/min. The results are presented in Table II. It can be seen that increasing the amount of CH_4 in the feed stream did not significantly change the CO conversion and the product selectivity and CH_4 merely acts as an inert gas.

IV. Conclusion

The experiments conducted in this study indicated that CO conversion and the reaction rate increase with increasing temperature. Increasing the reaction temperature also leads to a decrease in the C_5+ selectivity and an increase in the CH_4 and C_2-C_4 selectivity. Increasing the feed flow rate resulted in an increase in the selectivity for volatile hydrocarbons and a decrease in CO conversion.

Adding small amounts of CO_2 to the feed stream did not significantly change the CO conversion or the product selectivity. With addition of 10 vol. % CO_2 and more, however, the CO conversion would decrease while the selectivity for heavy components would increase. At 220 and 240˚C, addition of 20 vol. % of CO_2 to the feed stream resulted in 36.7% and 33.8% reduction in CO conversion, respectively. The C_5+ selectivity at 240˚C were higher than those at 220˚C.

If there was no CO_2 in the feed, the relative activity of the catalyst would decrease 21.8% in the first 15 hours but with 20% CO_2 in the feed, the reduction of the relative activity was 39.8% over the same time period. The reduction of activity was only significant in the first 15 hours. Addition of CH_4 to the feed stream did not significantly change the CO conversion or the product selectivity.

TABLE II
EFFECT OF CH_4 ON CO CONVERSION AND PRODUCT SELECTIVITY

CH_4 (%) in Feed gas	N_2 (%) in Feed gas	C_2-C_4 Sel. (%)	C_5^+ Sel. (%)	CO Conversion (%)
0	20	35.486	33.102	10.378
5	15	35.834	32.865	10.318
10	10	35.208	33.242	10.56
15	5	36.16	32.724	10.435
20	0	35.364	33.343	10.337

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