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Fischer-Tropsch Synthesis on Co/SiO_2 Catalysts with Potassium Promoter

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The effects of potassium-promoted Co/SiO_2 Fischer-Tropsch synthesis catalysts were investigated. After preparing the catalysts in accordance with the sol-gel method, they were subjected to various tests by using a small steely micro-reactor and finally, catalyst testing was performed under specific conditions [t = 220 °C, P = 7 atm, $H_2/CO = 2$, 6E-4 GHSV]. Catalysts were characterized by X-ray diffraction. The addition of potassium oxychloride (0-10 wt % of K) to silica-supported cobalt catalysts has been studied and some of the results are as follows: decrease in BET surface area of the resulted catalysts and in methane selectivity, increase in CO conversion, reaction rate, C_{5+}, C_{10+} and C_{22+} selectivity, decrease in the formation of activation energy of the heavy hydrocarbons in comparison with methane and change of product distribution towards the heavier hydrocarbons. Reactions such as cracking, isomerizing and hydrocracking can also be minimized on base construction of catalyst.

Key Words: Fischer-Tropsch, Cobalt catalyst, Potassium promoter, Synthesis gas, Silica supported, Hydrocarbon.

INTRODUCTION

The Fischer-Tropsch synthesis (FTS) is a classical heterogeneous reaction which produces mixture of linear gaseous, liquid and solid hydrocarbons from synthesis gas (H_2 and CO)[1-4]. In this reaction, CO and H_2 molecules react on the surface of an active metal as catalyst (Co, Fe, Ru, Ni)[5-7]. The main reaction involved in this process can be schematically written as:

$$nCO + 2nH_2 \rightarrow -(CH_2)_n- + nH_2O \quad \Delta H_R = -165 \text{ kJ/mol}$$

Cobalt catalysts have been intensively investigated for their higher selectivity to heavy hydrocarbons in FTS[8-10]. Various refractory supports have also been used to prepare Co F-T catalysts. Alumina, silica and titania[11,12] supports have been the most widely studied and patented during the past two decades. Recent developments in F-T process incorporate modifications to produce suitable heavy hydrocarbons.

Cobalt catalysts with a suitable promoter[13-16] such as potassium can be properly included in these modifications. Catalysts based on cobalt, have less activities with respect to water-gas shift (WGS) reaction[17-19].

Previous examinations and studies about Fischer-Tropsch reaction on supported commercial cobalt which is mainly oxidized like cerium oxide had some apparent advantages with regard to such supported catalysts[20]. We have also proposed a system with most and high level metal dispersion, which relates to the catalyst preparation method.

The aim of the present studies is to evaluate reaction temperature, H_2/CO ratio, flow rate, space velocity and other parameters which related to the selectivity of different kinds of heavy hydrocarbons and also trying to minimize as cracking, isomerizing and hydrocracking, on base construction of catalyst.

EXPERIMENTAL

Catalyst preparation: -jK catalysts which had 10 % by weight cobalt and 90 % by weight (remaining) SiO_2 and K_2O, were made through sol-gel method[21] and potassium oxychloride was used to provide potassium ions. In this method, potassium oxychloride, cobalt nitrate, oxalic acid and tetraethoxysilane (TS) were solved separately in pure ethanol and then their temperature was increased up to 75 ºC. Then cobalt nitrate and TS solutions were mixed with the promoter and after that they were entered into the container including oxalic acid that was severely being stirred.

Evaporation continues at constant 75 ºC while the solution is mixing, so viscosity of solution increases and finally gel is made.

The catalyst area depended on the amount of consumed ethanol, the time factor of evaporation, temperature range control and the mixing rate. The ideal amount of alcohol was 450 mL, while the evaporation time read 7 h. As far as all catalysts are concerned, drying process was carried out at100 ºC for 24 h. Calcinations were performed at 550 ºC for 5 h under atmospheric conditions.

Catalyst reduction: Whilst filling the reactor with catalysts, the heat of reaction should have a uniform diffusion at the presence of hot spots and so, catalyst coagulation should be prevented. Also to be sure about the existence of plug flow behaviour of gas, the volume of reaction portion should be vast enough, about 3 cm^3. Because of this, 1 g of powered catalyst and about 5 g of silicon carbide (SiC), which was an inert material, were completely mixed together and then this solid mixture was put between two layers of glass wool, which was refractory holder, in the middle of the reactor and in touch with thermocouple. After performing these operations, we should make sure that the system has been completely sealed up. Then, the system was filled with an inert gas such as N_2 with a favoured pressure for several hours.

Then all valves were closed and the pressure of the system was controlled. If the pressure drops, the unsealed parts must be recognized and sealed up. After sealing up the system, the catalysts were reduced. So that unlike most other catalysts, here, if there is a complete reduction, cobalt is eventually active. Both reactions are exothermic and it is necessary to perform the operations of heat transfer and the required steam transport by the application of N_2, which merely plays a role in the H_2 dilution. Also, the temperature increase should be done slowly and along with a gentle slope, so that any damage to catalysts is warded off. In these experiments, it took 7 h for reducing and pre-treating of each catalyst. The gas mixture for reduction is a combination of 10 and 90 % by volume, from H_2 and N_2, respectively. The temperature programming listed below was applied by total flow rate of 50 mL/min:

- Up to 180 ºC with the slope of 1 ºC/min and retention time of zero.
- 180-400 ºC with the slope of 2 ºC/min and retention time of 1 h.

Then the nitrogen valve was closed and the reduction operation continued by increasing the flow rate of pure hydrogen (20 mL/min) for 5 h at 400 ºC. This was the process of catalyst pre-treatment and reduction.

Catalyst characterization: In this research, BET characterization was done to measure the specific surface of catalysts, which its results are shown in Table-1 and also according to the X-ray diffraction (XRD) tests done in our laboratory.

TABLE-1
SPECIFIC SURFACES OF ACQUIRED CATALYSTS (BET MEASUREMENTS)

Catalysts	Specific surface, $10^{-6} \times (cm^2/g)$
-Co	4.81
-5K	3.43
-10K	3.29
-15K	3.11
-20K	2.97

Finally this conclusion was acquired that adding potassium and other promoters such as Zr, Pd, *etc.* using the sol-gel provision method, has such a homogeneous distribution that no obvious peak was appeared in this visualization process. In other words, the structure of the catalysts in this method was amorphous and the amount of noises in these images was too high (Fig. 1).

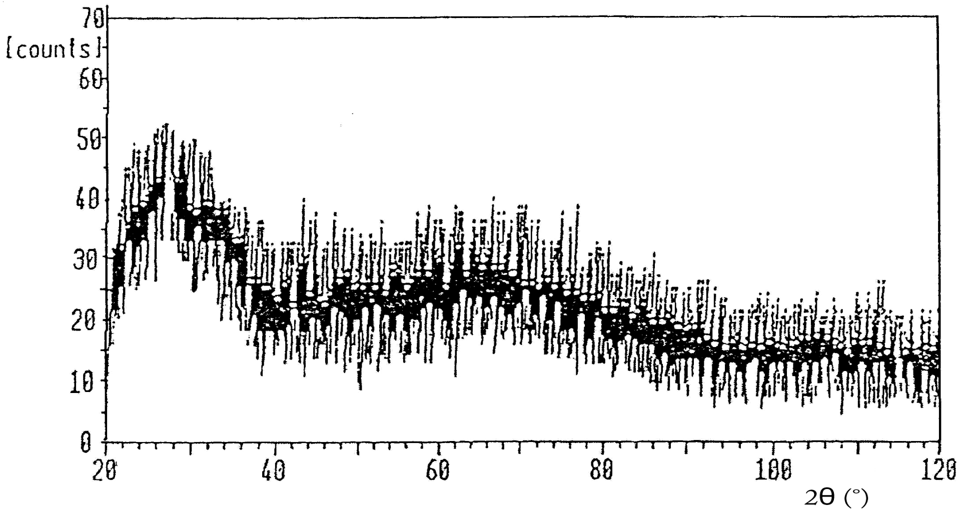


Fig. 1. X-Ray diffraction for -10 K catalyst prepared by sol-gel method

Catalyst testing: For testing the catalyst, it necessarily took 10 h to stabilize the system and to create the repeatable results regarding some parameters such as selectivity and space velocity. The process was performed under specific conditions, so that the optimum temperature, pressure, space-velocity and H_2/CO ratio were 220 °C, 7 atmospheres, 6E-4 GHSV (Gas hourly space velocity, m^3/(kgcat. s)) and 2, respectively. These conditions were achieved by trial and error and were related to some issues like the rate and selectivity of desired reactions, the efficient life span of catalysts, catalyst efficiencies regarding the production of the desired heavy hydrocarbons and the exothermicity of the existing reactions. According to the Fig. 2, the reactor system was connected on-line to the set of GC-MS rig. In this type of connection, the final conclusions were more easily obtainable. There was a product sampling period of 0.5 h after the system stability was acquired (10 h). It is important to note that if GC-MS test rig was not available, it was possible to store the products in sample bags and to inject them off-line into the GC-MS set at any desired time. But this procedure could be time consuming and may reduce the accuracy of the calculations and the results simultaneously.

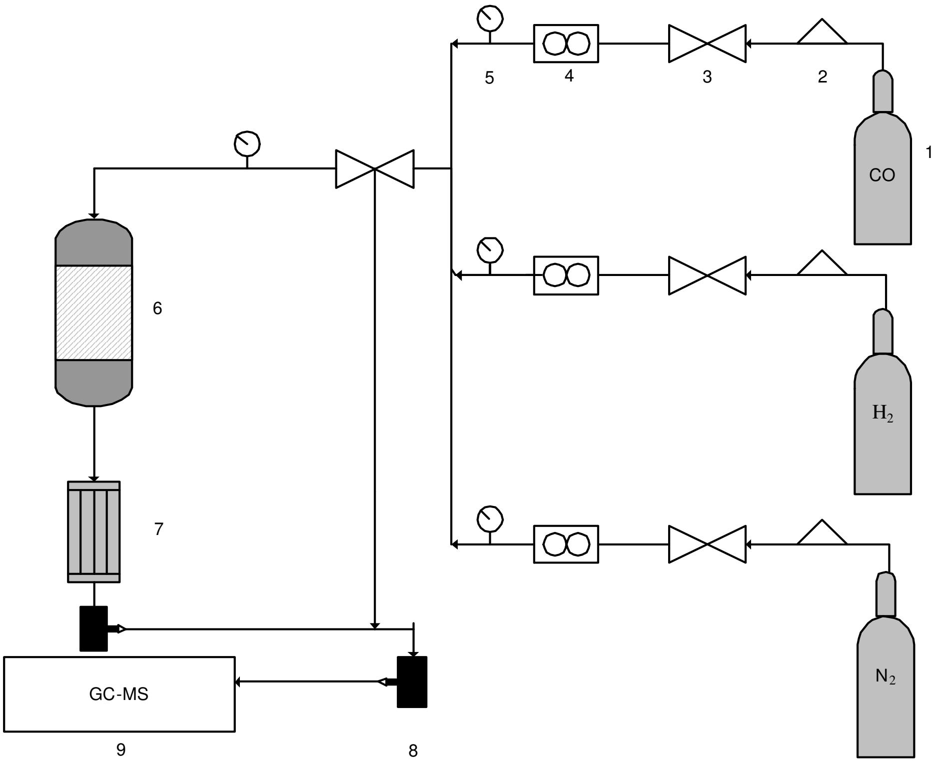


Fig. 2. Schematic representation of the reactor used: (1) gas cylinders, (2) pressure regulators, (3) valves, (4) Flow meter, (5) monometers, (6) micro reactor, (7) condenser, (8) trap (9) GC-MS

RESULTS AND DISCUSSION

The addition of potassium oxychloride (0-10 wt % of K) to silica supported cobalt catalysts has been studied and some of the results are as follows: decrease in BET surface area of the resulted catalysts and in methane selectivity, increase in CO conversion, reaction rate, C_{5+}, C_{10+} and C_{22+} selectivity, decrease in the formation activation energy of the heavy hydrocarbons in comparison with methane and change of product distribution towards the heavier hydrocarbons. Meanwhile, the probability of chain growth (α) increases which indicates increase in C_{10+} selectivity in promoted catalysts with potassium.

Conversion percentage regarding potassium oxychloride had significant increase up to 10 wt % of potassium but it decreases in higher percentages. In other words, the augmenting trend of production of heavy hydrocarbons will not keep on as steady as before as 10 % of consumed promoter. The possible reason may be due to some new interactions among existing components.

Potassium is a selective promoter; therefore, it has different influences on the rate and produced quantity of each special material in such a way that potassium promoter will further decrease the formation activation energy (E) of the heavy hydrocarbons in comparison with methane.

Potassium has also been supplied by the use of precursors such as KCl and KNO_3 but the resulted catalysts appeared to be less active, that is due to the impurities of existing KCl and KNO_3. The precursor, $KOCl_2 \cdot 4H_2O$, has been available with a high purity in our laboratory and the catalyst made by this precursor has been considerably active and cheap and abundance are the other advantages.

Fig. 2 shows micro reactor and its components. The relating results, to pure cobalt catalysts comprising reaction situation, production rate, output, selectivity, chain growth probability parameter (α) and the extent of conversion have been presented in Table-2. The data of the table were obtained as the result of constant conditions including the temperature ranging between 200 and 240 °C for a time period of 10 h within a pressure of 7 atmospheres. The value for the chain-growth probability was obtained from Anderson-Schulz-Flory (ASF) distribution[22].

TABLE-2
RESULTS RELATED TO PURE Co CATALYST

Catalyst	Temp. (ºC)	Press. (atm)	Weight (g)	Flow rate [mL/min]	Conversion (%)	α	C Balance (%)
-Co	220	7	1	35	11.1	0.8	102
Component	Methane	Ethylene	Ethane	Propylene	Propane	C_4	C_{5+}
Selectivity (wt %)	16.4	2.5	1.2	2.5	2.7	5.3	68.7
Cut	Methane	Ethylene	5-9	10	11-13	14-21	C_{25+}
Selectivity (wt %)	16.4	2.5	22.1	17.5	17.5	15.6	86

The effects of changing operational conditions on this catalyst were also studied. The effects of the temperature changes can be seen in Table-3. Table-3 reveals the effects of temperature variation on CO conversion, α, product distribution at the pressure of 7 atmospheres and 6E-4 GHSV.

TABLE-3
EFFECT OF TEMPERATURE VARIATIONS ON THE PRODUCT DISTRIBUTIONS

Temp. (ºC)	220	230	240	250
CO conversion (%)	8.2	11.5	18	26
α	0.95	0.93	0.88	0.85
Cut		Selectivity (wt%)		
Methane	12.2	16.1	24.1	26
Ethylene	1.1	1.8	1.2	1.8
Ethane	1.3	2.1	3.1	3.3
Propylene	3.7	2.9	3.2	4.1
Propane	2.4	2.2	3.4	3.9
C_4	6.9	7.6	9.1	7.8
C_{5+}	78	70.7	59.1	53

Increase in temperature may result in undesired processes such as increase in conversion rate and the produced methane (which is an undesirable substance in FTS), decrease in heavier products of C_{5+}, decrease in α and increase in olefin contents. Therefore, it is better to use lower temperatures to increase C_{5+} products. In the case of the stable temperature range, the selectivity of products with a temperature ranging between 200 and 240 °C tends to produce the desired products (heavier hydrocarbons) and repeatable results are obtained in this temperature range. It should be noted that the rate of desired reactions and their selectivity will be reduced below 200 °C.

Moreover, the existing catalysts are demolished quickly and are useless above 240 °C and their efficiencies of heavy hydrocarbon production will be decreased. So, stable temperature range was chosen between 200 and 240 °C, while the existing system was a flow one and most of the reactions were exothermic. 220 °C was chosen as the best temperature to test the catalysts containing potassium and to compare them due to the importance of conversion rate.

The addition of potassium oxy-chloride (0-10 wt % of K) to silica supported cobalt catalysts has been studied and the results are shown in Table-4. Table-4 suggests conversion percentages of CO, cobalt catalyst selectivity with silica base and potassium promoter at 220 °C, 7 atmospheres and 6E-4 GHSV. The table reveals some findings by increasing promoter content such as: increase in CO conversion and reaction rate, increase of C_{5+} selectivity, change of product distribution towards the heavier hydrocarbons and increase of α.

It is necessary to say that different promoters were used for Co/SiO_2 catalyst, although they highly increased the selectivity and rate of desired reactions, but had also a short life span. Therefore, potassium was used as the only promoter for

TABLE-4
RESULTS FOR $KOCl_2$ AS A PROMOTER OF Co CATALYST

Catalyst	CO conversion (%)	Selectivity (wt %)					α
		Methane	Ethane	Propane	C_4	C_{5+}	
-Co	9.3	16.4	3.4	4.5	5.2	65.2	0.7
-2K	17.2	14.3	2.8	2.4	5.8	70.3	0.76
-5K	21.6	12.7	3.6	2.2	2.9	74.1	0.74
-7K	23.7	11.3	2.4	3.3	5.2	72.4	0.77
-10K	24.1	9.6	3.7	2.8	2.6	76.6	0.75

continuing this research. Table-5 indicates the effects of potassium oxychloride on the catalysts with weight percentages ranging between 0 and 20 %, which were thoroughly examined. Since the medium is acidic, the hydrolysis time rate of TS is higher than aggregation rate of Si-OH groups and Si-O-Si is formed during evaporation[23]. Thereafter, with drying, calcinating and measuring their specific surface by BET tests, the resulted catalysts showed little quantities of specific surface without any special trend. After ample repetitions, it seemed that the shortage of the specific surface of the catalysts has been due to the lack of enough water to complete hydrolysis of TS, since according to the hydrolysis reaction, each mole of Si needs 4 moles of water for undergoing the hydrolysis, which can be supplied by water molecules along with the precursors of cobalt, potassium and also oxalic acid. According to this preparation method, water quantity along with the precursors cannot provide the required water to complete hydrolysis of TS. For example, in the case of the catalyst with the following formula [-20 K]:

$$10\ \%\ \text{Co}/(18\ \%\ K_2O\ \text{and}\ 72\ \%\ SiO_2)$$

TABLE-5
EFFECT OF $KOCl_2$ ON THE OPERATIONAL CONDITIONS

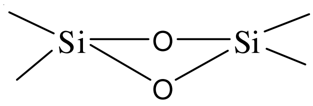
Catalyst	-Co	-5K	-10K	-15K	-20K
CO conversion (%)	9.9	21.1	24.2	19.8	20.1
α	0.8	0.84	0.85	0.85	0.78
Cut	Selectivity (wt%)				
1	16.4	12.3	9.9	10.0	11.5
1-4	17.1	10.8	10.5	9.5	6.6
5-9	21.4	20.3	17.7	14.6	11.7
10-13	17.1	20.8	21.2	22.5	23.1
14-21	14.9	21.3	24.5	26.2	28.4
C_{5+}	63.3	72.4	76.1	77.1	78.6
C_{10+}	41.2	52.9	57.2	62.1	66.9
C_{22+}	7.6	9.7	9.8	11.4	12.6
C balance (%)	102.7	95.1	96.9	97.1	101.1

The mole numbers of water with oxalic acid will be completely supplied when 5 wt % of excess acid is used for depositing of potassium and cobalt oxalates. After repeated experiments, we came to the conclusion that the lack of sufficient water caused the TS hydrolysis to be imperfect and subsequently, there may be decrease in specific surface and the random trend of catalysts. To solve this problem, the direct adding of the distilled water to the reaction medium was not efficient and this procedure did not provide a suitable specific surface, which was likely due to gradual evaporation of water. Excess acid was utilized to provide necessary water for hydrolysis reaction, when oxalic acid was used for catalyst preparation, at a rate which can compensate the difference between the quantity of essential water for TS hydrolysis and the water along the precursors. With modifications such as precise controlling of temperature, mixing rate and ethanol quantity (6.5-7.0 h as the evaporation time of alcohol for providing catalysts), catalysts with suitable and repeatable specific surfaces, regarding repeated provisions were acquired. Hydrolysis and aggregation reaction of TS include[24]:

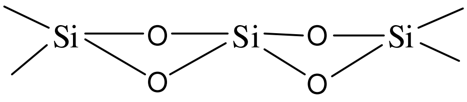
$$Si(OC_2H_5)_4 + 4H_2O \rightarrow 4C_2H_5OH + Si(OH)_4$$

$$2Si(OH)_4 \rightarrow Si_2O_2(OH)_4 \rightarrow Si_3O_4(OH)_4$$

Therefore, base construction is formed after alcohol evaporation. If the both above reactions are widely rearranged, it can be deduced that the rate of the first reaction is higher than the second one, therefore, enough $Si(OH)_4$ will be available for the second reaction and by the second reaction, at first, the two $Si(OH)_4$ causes the structure that is shown in **Scheme-I** and then, this structure with another $Si(OH)_4$ create the structure that is shown in **Scheme-II** and this trend will continue similarly.



Scheme-I: Structure of two $Si(OH)_4$



Scheme-II: Structure of three $Si(OH)_4$

It should be noted that oxalic acid was used as the catalyst of the process of hydrolysis and the producer of oxalate gels. Potassium and cobalt are deposited on the base construction (silica) in the form of cobalt oxalate and potassium oxalate. So, the base construction and catalyst are formed simultaneously. The advantage of this method is gaining a great deal of aggregate form catalyst in one phase and with uniform distribution.

After sealing up the system, the catalysts were reduced to which the following reactions are referred[24]:

$$CoO_4 + H_2 \rightarrow 3CoO + H_2O$$

$$CoO + H_2 \rightarrow Co + H_2O$$

In cobalt catalyst without promoters, conversion rate is reduced and methane production is enhanced with the increase of temperature. Also, production rate of C_{5+}, heavy products, α and olefins are increasing.

According to the Arrhenius' rule, there is a correlation between the activation energy and temperature: (k = A * exp (- E/RT))[25].

The created effects of the abnormally- high temperature would be justified based on the fact that the activation energy of methane production is higher than the other reactions[26]. Therefore, temperature increasing will have a greater effect on the quantitative production of methane and its selectivity. Following the increase of H_2/CO ratio some of the results are such as increasing CO conversion percentage, higher production ratio of saturated hydrocarbons to olefins, decreasing C_{5+} hydrocarbons and α parameter. Reactions such as cracking, isomerizing and hydrocracking can also be minimized on basic construction. Meanwhile, we observed them through high activity of reaction, regarding the production of light olefins.

Conclusion

In this research, the addition of potassium oxychloride (0-10 wt % of K) to silica-supported cobalt catalysts has been studied and some of the results are as follows: decrease in BET surface area of the resulted catalysts and in methane selectivity, increase in CO conversion, reaction rate, C_{5+}, C_{10+} and C_{22+} selectivity, decrease in the formation activation energy of the heavy hydrocarbons in comparison with methane and change of product distribution towards the heavier hydrocarbons. Reactions such as cracking, isomerizing and hydrocracking can also be minimized on base construction of catalyst.

Conversion percentage regarding potassium oxychloride had significant increase up to 10 wt % of potassium but it decreases in higher percentages. 220 °C was chosen as the best temperature to test the catalysts containing potassium.

Nomenclatures

GHSV = Gas hourly space velocity, $m^3/(Kg_{cat}\cdot s)$
GC-MS = Gas chromatogram coupled with mass spectroscopy apparatus.
α = Chain growth probability parameter
i+ = Hydrocarbons heavier than C_i
-jK = Catalyst containing 0.9j % of K_2O, 10 % cobalt and remaining SiO_2
-Co = Catalyst containing 10 % of cobalt and remaining SiO_2

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