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## TECHNICAL NOTE

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# THE EFFECTS OF POTASSIUM PROMOTER ON THE SYNGAS CONVERSION OF COBALT CATALYSTS

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**Abstract** The effects of potassium promoter for production of heavy hydrocarbons from syngas with silica- supported cobalt catalysts has been studied. After preparing the catalysts in accordance with the sol-gel method, they were subjected to various tests by using a small steady micro-reactor and capable of operating in diversified situations, such as stable temperature range, flow rate, space velocity, etc. Thorough observations revealed that the conducive situations can be achieved by the ratio of  $H_2/CO=2$  with a temperature of 220 °C, whereas the flow rate of CO and  $N_2$  components must be equal about 35 ml/min.

**Key words** Fischer-Tropsch-Synthesis, Olefin, Synthesis gas, Cobalt catalyst, Promoter

**چکیده** در این پژوهش اثرات کاتالیست کبالت/ سیلیکا/ پتاسیم در تولید هیدروکربنهای سنگین از گاز سنتز مورد توجه قرار گرفته است. کاتالیست مربوطه با درصدهای مختلفی از پتاسیم تهیه شده و برای آزمایش استفاده شده است. این کاتالیست به روش سول ژل تهیه گردیده و در یک میکرواکتور از جنس فولاد ضد زنگ در شرایط دمایی، دبی حجمی، سرعت فضایی مورد آزمایش قرار گرفت. مشاهده شد که بهترین شرایط عملیاتی برای تولید هیدروکربنهای سنگین عبارتند از: نسبت  $H_2/CO=2$ ، دمای  $220^\circ C$  و دبی هر یک از مولفه های نیتروژن و مونوکسید کربن برابر با  $ml\ min^{-1}$

35

## 1. INTRODUCTION

Cobalt catalysts have been investigated intensively for their higher selectivity to heavy hydrocarbons in Fischer-Tropsch- Synthesis (FTS) process.

Recent developments in Fischer- Tropsch process incorporates modifications to produce suitable heavy hydrocarbons.

Cobalt catalysts with a suitable promoter such as potassium can be properly included in these modifications. It has been shown that cobalt

catalysts, in general , are superior to similarly prepared iron catalysts with respect to especially catalyst life [1,2]. Regarding the effects of this kind of promoter, only a few reports can be found in the literature.

Catalysts based on cobalt, have less activities with respect to water-gas-shift (WGS)reaction [3] . 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[4,5]. Also we proposed a system with most and high level metal dispersion, which relates to the method of catalysts preparation.

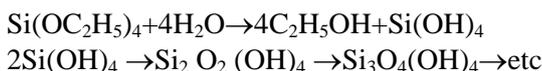
The aims of this research were evaluation of reaction temperature, H<sub>2</sub>/CO ratio, flow rate, space velocity and other parameters in selectivity for different kinds of heavy hydrocarbons, and also trying to minimize the reactions such as cracking, isomerization and hydrocracking, on basic support.

## 2. EXPERIMENTAL

### 2.1. Catalysts preparation

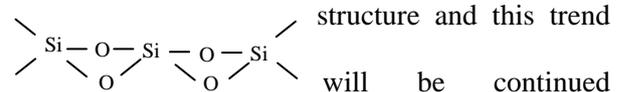
-jK catalysts which had 10% by weight cobalt and 90% by weight (remaining) SiO<sub>2</sub> and K<sub>2</sub>O, were made through sol-gel method [6] and KOCl<sub>2</sub> or potassium oxy-chloride was used to provide potassium ions. Potassium has also been supplied by the use of precursors such as KCl and KNO<sub>3</sub>. But the resulted catalysts appeared to be less active, that it is due to the impurities of existing KCl and KNO<sub>3</sub>. The precursor, KOCl<sub>2</sub>.4H<sub>2</sub>O, has been available with a high purity in our laboratory and the catalysts made by that has been considerably active and its functioning has been chosen for the sake of this paper. In this method, KOCl<sub>2</sub>, cobalt nitrate, oxalic acid and Si(C<sub>2</sub>H<sub>5</sub>O)<sub>4</sub> or (TS) were solved separately in pure ethanol and then we increased their temperature up to 75 °C. Then solutions of cobalt nitrate and TS were mixed with the promoter and after that they were entered into the container involving oxalic acid that severely was being stirred.

Evaporation continues through mixing at constant 75°C so that viscosity of solution can be increased and finally, gel can be made. Since 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. Hydrolysis and aggregation reactions include[7]:



Therefore, base construction is formed after alcohol evaporation [6].

If the two above reactions are widely rearranged, it can be deduced that because of the higher rate of the first reaction to that of the second one, enough Si(OH)<sub>4</sub> will be always available for the second reaction, and because of the second reaction, at first, the two Si(OH)<sub>4</sub> cause the structure and then, this structure with another Si(OH)<sub>4</sub> create the

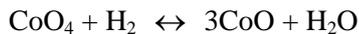


similarly.

Potassium and cobalt are deposited on the base construction (silica) in the form of cobalt oxalate and potassium oxalate. So base and catalyst are formed simultaneously. The advantage of this method is to gain a great deal of aggregate form catalyst in one phase and with uniform distribution. The single catalyst area depended on the amount of ethanol consumed or 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 seven hours. As for as all catalysts are concerned, drying process was carried out at 100 °C for 24 hours. Calcination was performed at 550 °C for 5 hours under atmospheric conditions.

Whilst filling the reactor with catalysts, the heat of reaction should have a uniform diffusion and the presence of hot spots and so, the coagulation of the catalysts should be prevented. Also to be sure about the existence of plug flow behavior of gas, the volume of reaction portion should be vast enough, about 3 cm<sup>3</sup>. Because of this, 1 gram of powdered catalyst and about 5 grams of silicon carbide(Si C), which was an inert material, were completely mixed together and then this solid mixture was put between two layers of glass wool, which was a refractory holder, in the middle of the reactor and in touch with thermocouple. Having performed these operations, we should make sure that the system has been completely sealed up. Thus, the system was filled with an inert gas such as N<sub>2</sub> with a pressure at will and for several hours. Then all of the valves were closed and the pressure of the system was controlled. If the pressure should drop, the unsealed must be realized and be sealed up, so that the obtained results and the mass balance calculations would be precise and so the results confirm the existing facts.

After sealing up the system, the catalysts were reduced to which these reactions are referred [8,9]:



So, on the contrary to most catalysts, here, if there is a complete reduction, cobalt itself 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  $\text{N}_2$  which merely plays a role in the  $\text{H}_2$  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 totally took 7 hours for reducing and pre-treating of each catalyst. The gas mixture for reduction, is a combination of 10 and 90% by volume, from  $\text{H}_2$  and  $\text{N}_2$  respectively. The temperature programming listed below was applied by total flow rate of 50 ml/min:

- Up to 180 °C with the slope of 1 °C/min and retention time of zero,

- 180-250 °C with the slope of 2 °C/min and retention time of 1 hour,

- 250-400 °C with the slope of 2 °C/min and retention time of 1 hour,

Then the  $\text{N}_2$  valve was closed and the reduction operation was continued by increasing the flow rate of pure hydrogen (20 ml/min) for 5 hours at 400 °C. This was the process of catalysts pre-treatment and reduction.

## 2.2. Catalysts characterization

In this research BET characterization was done with regard to measure the specific surface of catalysts, which the results are shown in table (5).

As other researchers [6] show and also according to the XRD tests done in our laboratory, finally this conclusion was acquired that adding potassium and other promoters such as Zr, Pd, ..., using the sol-gel provision method, have such a homogeneous distribution that no obvious peak was appeared in this visualization process. In other words, the structure of the catalysts by usage of this method was amorphous and the amount of noises in these images were too high (figure (2)).

For testing the catalysts, it necessarily took 10 hours to stabilize the system and to create the repeatable results in regard to some parameters such as selectivity and space velocity. The process

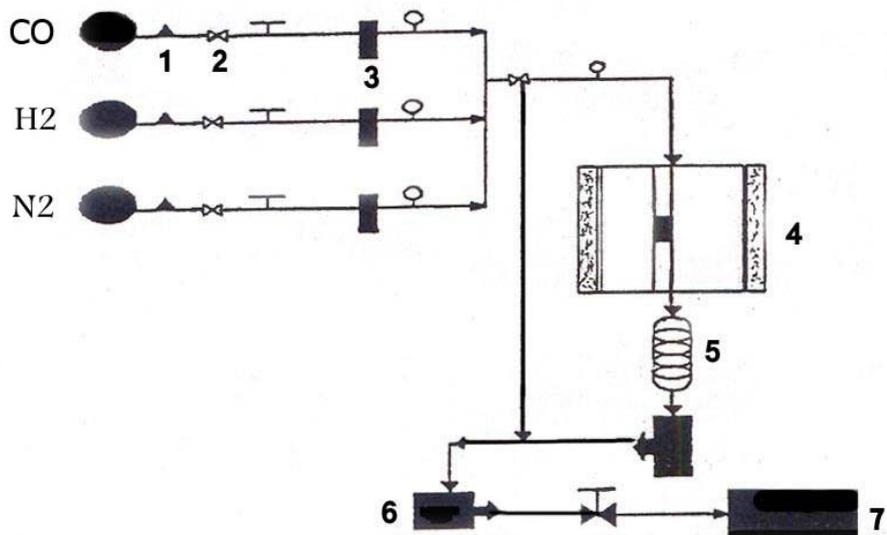
was performed under specific conditions, so that the optimum temperature, pressure, space-velocity and  $\text{H}_2/\text{CO}$  ratio were 220 °C, 7 atmospheres,  $6\text{E}-4$  GHSV and 2, respectively. These conditions were achieved by trial and error and were related to some issues like the rate and selectivity of desired reactions, the efficient life span of catalysts, also catalyst efficiencies regarding the production of the desired heavy hydrocarbons, the exothermicity of the existing reactions, etc. According to the figure(1), the reactor system was connected on-line to the set of GC-MS rig, so that, on account of this type of connection, the final conclusions were more easily obtainable. There was a products sampling period of half an hour until before the system stability was acquired (10 hours). It is important to notice that if GC-MS test rig was not available, it was possible to store the products into the sample bags at any desired time and to inject them off-line into the GC-MS set. But this procedure could be time consuming and may reduce the accuracy of the calculations and the results simultaneously.

## 3. RESULTS

Figure(1) shows the above mentioned micro reactor and its belongings. The results, relating to pure cobalt catalysts comprising reaction situation, production rate, output, selectivity, chain growth parameter ( $\alpha$ ), and the extent of conversion, have been presented in table (1). The data of the table were obtained as a result of constant conditions including the temperature ranging between 200 to 240 °C for a time period of 10 hours with a pressure of 7 atmospheres. The value deduction for the chain-growth probability or  $\alpha$  was obtained from ASF distribution [4].

The effects of changing operational conditions on this catalyst were also studied. For example, the effects of the temperature changes can be seen in table (2). Table (2) reveals the effects of temperature variation on CO conversion,  $\alpha$ , product distribution at a pressure 7 atmospheres and gas hours space velocity  $6\text{E}-4$  GHSV. The other task for this project is to investigate the effect of potassium promoter on catalyst activity. Potassium oxy-chloride between zero to ten

percents by weight were tested and the results are different promoters were used for Co/SiO<sub>2</sub> catalyst,



shown in table(3) .It is necessary to say that not only they increased highly the selectivity and  
1. Regulator, 2. Valve, 3. Flow meter, 4. Furnace, micro reactor, 5. Condenser, 6. Trap, 7. GC – MS

Figure 1. Test rig flow diagram

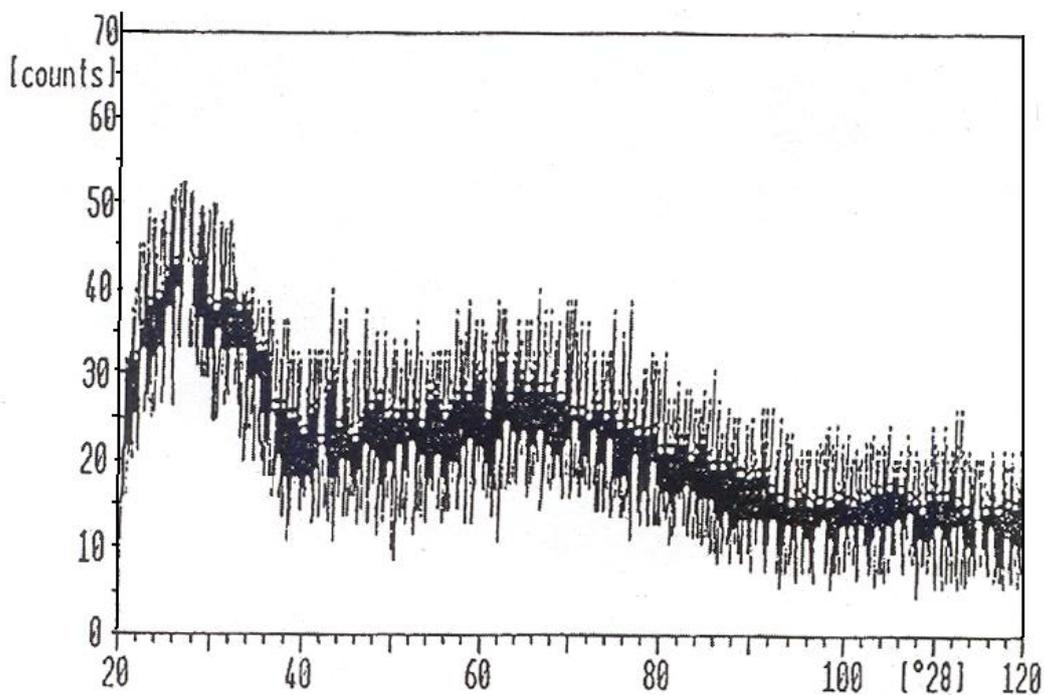


Figure 2. X-Ray diffraction for -10 K catalyst prepared by sol-gel method

**Table 1.** Results related to pure Co catalyst

C balance (%)	$\alpha$	Conversion (%)	Flow rate $\left(\frac{\text{ml}}{\text{min}}\right)$	Weight (gr)	Press. (atm)	Temp.(°C)	Catalyst
102	0.8	11.1	35	1	7	220	-Co
5 <sup>+</sup>	4	propane	propylene	ethane	ethylene	methane	Component
68.7	5.3	2.7	2.5	1.2	2.5	16.4	Selectivity (wt%)
25 <sup>+</sup>	14-21	11-13	10	5-9	ethylene	methane	Cut
86	15.6	17.5	17.5	22.1	2.5	16.4	Selectivity (wt%)

**Table 2.** The effect of temperature variations on the product distributions

250	240	230	220	Temp.(°C)
26	18	11.5	8.2	CO conversion(%)
0.85	0.88	0.93	0.95	$\alpha$
Selectivity (wt%)				Cut
26	24.1	16.1	12.2	methane
1.8	1.2	1.8	1.1	ethylene
3.3	3.1	2.1	1.3	ethane
4.1	3.2	2.9	3.7	propylene
3.9	3.4	2.2	2.4	propane
7.8	9.1	7.6	6.9	4
53	59.1	70.7	78	5 <sup>+</sup>

**Table 3.** Results for KOCl<sub>2</sub> as a promoter of Co catalyst

$\alpha$	Selectivity (wt%)					CO conversion (%)	Catalyst
	5 <sup>+</sup>	4	propane	ethane	methane		
0.7	65.2	5.2	4.5	3.4	16.4	9.3	-Co
0.76	70.3	5.8	2.4	2.8	14.3	17.2	-2K
0.74	74.1	2.9	2.2	3.6	12.7	21.6	-5K
0.77	72.4	5.2	3.3	2.4	11.3	23.7	-7K
0.75	76.6	2.6	2.8	3.7	9.6	24.1	-10K

rate of desired reactions, but had also a short life span. Therefore, potassium was used as only promoter for continuing this research. Table (4) indicates the effects of potassium oxy-chloride on the catalysts with weight percentages ranging between 0 and 20 percents of potassium, which were thoroughly examined.

#### 4. DISCUSSION

1. Temperature increasing may result in undesired processes such as increase in conversion rate and methane produced (which is an undesirable substance in Fischer-Tropsch-Synthesis), decrease in heavier products of 5<sup>+</sup>,

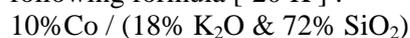
decrease of chain growth parameter ( $\alpha$ ) and increase of olefin contents. Therefore it is better to use lower temperatures to increase  $5^+$  products. Here the  $220^\circ\text{C}$  was chosen as the best temperature to test the catalysts containing potassium and for comparing them due to importance of conversion rate.

2. Table (3) suggests conversion percentages of CO,  $\alpha$ , selectivity for cobalt catalysts with silica base and potassium promoter at  $220^\circ\text{C}$ , 7 atmospheres and  $6\text{E-}4$  GHSV. The table reveals some conclusions by increasing promoter content such as: increase of CO conversion and reaction rate, increase of  $5^+$  selectivity, change of products distribution towards the production of heavier hydrocarbons and increase of  $\alpha$ .

3. Table(4) suggests conversion percentage of CO,  $\alpha$  and selectivity percentages of hydrocarbons for catalysts containing 10 weight percents of cobalt (with promoter of  $\text{K}_2\text{O}$  produced from potassium oxy chloride with different weight percentages) at  $220^\circ\text{C}$ , 7 atmospheres and  $6\text{E-}4$  GHSV.

4. It should be noted that oxalic acid was used as the catalyst of the process of hydrolysis and the producer of oxalate gels. The complete hydrolysis of TS has been mentioned in the reference[7]. In an acidic medium, the hydrolysis rate of TS was more than the aggregation rate of Si-OH and Si-OR groups and the structure of Si-O-Si was formed

during the evaporation. 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 for 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 can not provide the required water for complete hydrolysis of TS. For example, in the case of the catalyst with the following formula [-20 K]:



the number of water moles with oxalic acid will be completely supplied when 5% by weight of excess acid to be used for depositing of potassium and cobalt oxalates. Having 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. For solving this problem, directly adding of the distilled water to the reaction medium was not efficient and this procedure did not provide a suitable specific surface, that was likely due to

**Table 4.** The effect of  $\text{KOC1}_2$  on the operational conditions

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

gradual evaporation of water. Excess acid was utilized to provide necessary water for hydrolysis reaction, when oxalic acid was used for preparing each catalyst, at a rate which can make up 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 ( the evaporation time of alcohol for providing catalysts has been 6.5 – 7 hours) catalysts with suitable and repeatable specific surfaces, regarding repeated provisions were acquired. The results of BET measurements for final catalysts are shown in table(5).

5. Some indications after increasing the promoter include: decrease in BET specific surface of the resulted catalysts and also decrease in methane selectivity (short of a special process) and in cuts 1-4, 5-9, as well as increase in CO conversion and reaction rate and in the selectivity of cuts having 10-13,14-21,5<sup>+</sup>,10<sup>+</sup>,22<sup>+</sup>(waxes) and also change of products distribution towards the production of heavier hydrocarbons. Meanwhile, the probability of chain growth ( $\alpha$ ) increases which is indicative of increasing in selectivity of 10<sup>+</sup> in promoted catalysts with potassium.

6. Potassium is a selective promoter, therefore, it has different influences on the rate and production quantity of each special material in such a way that this promoter will further decrease

the formation activation energy ( E ) of the heavy hydrocarbons in comparison with methane [10,11]. This is the reason why we chose it for this research. Cheapness, abundance and the high purity of potassium precursors are the other reasons why we made this choice.

Conversion percentage regarding potassium oxy chloride had remarkable increase to 10 weight percents 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 between existing components.

7. In the case of the stable temperature range, as mentioned in the text, according to our aims which were about the production of heavy hydrocarbons, having done ample experiments, it was shown that the selectivity of products with a temperature ranging from 200 – 240 °C tends to move toward the desired products or heavier hydrocarbons and the corresponding stability of the system ,in the case of results repeatability in these desired conditions , also occurs in this temperature range. It should be said that the rate of desired reactions and their selectivity will be reduced below 200 °C, and also the existing catalysts are demolished quickly and gone out of use above 240 °C, and their efficiencies of heavy hydrocarbons production will be decreased . Thus, stable temperature range was chosen in the range of 200-240 °C , as the existing system has been a flow one and most of the reactions have been exothermic.

8. In cobalt catalyst without promoters, conversion rate is reduced with the increase of temperature and methane production is enhanced. Also, production rate of 5<sup>+</sup>, heavy products ,  $\alpha$  and olefins increases. According to the Arrhenius' rule, there is a correlation between the activation energy and temperature :

( $k = k_0 \cdot \exp(- E / RT)$ ) [10] . The created effects of the abnormally- high temperature increase would be justified based on the fact that the activation energy of methane production, which is higher than the other reactions [10]. Therefore, temperature increase will have a greater effect on

**Table 5.** Specific Surfaces of acquired catalysts (BET measurements)

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

the quantitative production of methane and its selectivity .

9. Following the increase of H<sub>2</sub>/CO ratio some events include: increase of CO conversion percentage, higher production ratio of saturated hydrocarbons to olefins, decrease of 5<sup>+</sup> hydrocarbons and  $\alpha$  parameter.

10. Reactions such as cracking, isomerization and hydrocracking can also be minimized on basic support. Meanwhile we observed them through high activity of Boudouard reaction, regarding the production of light olefins.

## 5. SUMMARY

In this research work, initially a short history of the developments in the F-T process, and its reformation for the production of heavier hydrocarbons were discussed. The aims and objectives of this research work, and the explanation of useful reactions as well as destructive reactions were also discussed. Similarly, the superiority of cobalt catalysts were also hinted on. Practically working, the manner of supplying cobalt catalysts with silica base, and the potassium promoter were thought over. The processes and reactions at the time of supplying catalysts were debated according to a new method called sol-gel. The benefits and privileges contained in this method, and the procedure of optimization of the acquired catalysts were properly discussed. A medium of calculation for assessing the consumed oxalic acid was explained. In the conclusions division, first the performance of pure cobalt catalyst, and the conditions of steady state, as well as the distribution of the acquired ASF were taken into consideration. Then the effects of the changes, in operational conditions, on these catalysts were pointed out. Later the destructive effects of high temperatures were referred to and then the selection of the optimum temperature was conducted. The catalysts bearing potassium promoter were then examined, and subjected to tests of different percentages while containing contents of promoter substance. The increase and decrease in parameters and light as well as heavy cuts were also taken into account. Afterwards, the weakness of catalysts having

dominating amounts over the promoter was expounded and the effects of the consequences brought about by relative increase in H<sub>2</sub>/CO were reviewed.

## 6. NOMENCLATURES

GHSV: Gas Hourly Space Velocity, m<sup>3</sup> / (Kg<sub>cat</sub> . s)  
GC-MS: Gas Chromatogram coupled with Mass Spectroscopy apparatus.

$\alpha$ : Chain growth probability parameter

i<sup>+</sup>: Hydrocarbons heavier than C<sub>i</sub>

i-j: Cut C<sub>i</sub>-C<sub>j</sub>

-jK: Catalyst containing 0.9j% of K<sub>2</sub>O, 10% cobalt and remaining SiO<sub>2</sub>

-Co: Catalyst containing 10% of cobalt and remaining SiO<sub>2</sub>

## 7. APPENDIX (A)

An example of quantitative calculation is shown below. In this calculation oxalic acid rate is 5% more than needed quantity.

So:

oxalic acid weight = (0.5\*potassium moles +cobalt moles)\* molecular weight of oxalic acid \*1.05

In regard to the above relationship, since oxalic acid and potassium have the valences of 2 and 1 respectively, the number of potassium moles was multiplied by 0.5 . The coefficient of 1.05, stands for 5% by weight of excess acid. This is to make sure that the complete precipitation of cobalt and potassium oxalates and TS complete hydrolysis are performed accordingly. For further clarification of the recent relationship, an example for catalyst preparation has been given in section (8) and to explain more about the details, the KCl precursor has been chosen for providing potassium.

## 8. APPENDIX (B)

To describe more details about the calculation relationship of required oxalic acid, here, an example of catalyst ingredients calculation is given. For example, to provide 7 grams of catalyst

including 10% by weight of cobalt and 20% by weight of  $K_2O$ , we used the following relationship in regard to describe the base combination :

$10\%Co / (18\% K_2O \& 72\% SiO_2)$

cobalt weight was 0.7 gram and the number of its moles were calculated as :

$$0.7 / 58.94 = 0.0118$$

this number of cobalt moles was acquired by cobalt nitrate  $Co(NO_3)_2 \cdot 6 H_2O$ , (Mw = 291). The weight of cobalt nitrate made equal to 3.457 grams ( $0.0118 * 291$ ), depending on the purity of cobalt nitrate. The entire weight of support includes 90% of catalyst weight, namely, 6.3 grams ( $7 * 0.9$ ) that 20% of it belongs to  $K_2O$  and 80% of it belongs to  $SiO_2$ . Therefore, 1.26 grams of  $K_2O$  and 5.04 grams of  $SiO_2$  were required for the number of potassium and silicon moles to be made equal to :

$$\text{moles of Si} = 5.04 / 60.06 = 0.084$$

$$\text{moles of K} = 1.26 / 94.192 = 0.0133$$

Since, Si has been acquired from TS (Mw = 208.3) and  $K_2O$  from one of the potassium precursors such as KCl (Mw = 54.5), therefore, the required TS weight is 4.57 grams ( $0.084 * 54.5$ ). Depending on the purity of above materials, the weight quantities were modified. The consumed oxalic acid quantity (Mw = 126.07) for the formation of the deposits of cobalt and potassium oxalates is :

$$\text{Acid weight} = (0.5 * 0.0133 + 0.0118) * 1.05 * 126.07 = 2.45 \text{ grams.}$$

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