

## KCl Promoted Cobalt-iron Nanocatalysts Supported on Silica: Catalytic Performance and Characterization in Fischer-Tropsch Synthesis

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The SiO<sub>2</sub> supported cobalt-iron nano catalysts were prepared by the sol-gel method. This research investigated the effects of (Co/Fe) wt%, different Co/Fe ratios at different temperatures and loading of KCl wt% for Fischer-Tropsch synthesis (FTS). The results showed that the catalyst containing 50 wt% (Co/Fe)/SiO<sub>2</sub> (Co/Fe ratio is 70/30) promoted with 0.6 wt% KCl is an optimal nano catalyst for conversion CO + H<sub>2</sub> to a range of hydrocarbons especially light olefins. The results also indicated that optimal operating conditions for optimal nano catalyst are 250 °C, and H<sub>2</sub>/CO molar ratio 2/1 under 1 bar of pressure. Characterization of catalyst precursors and calcined catalysts were performed by different methods such as: powder X-ray diffraction (XRD), transmission electron microscopy (TEM), N<sub>2</sub> physisorption and thermal analysis methods such as thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC).

**Keywords:** Fischer-Tropsch synthesis, Syngas, Co/Fe nano catalyst, Sol-gel method

### INTRODUCTION

Undoubtedly, the main goal of the Fischer-Tropsch process is not only introduction of cheap, efficient and selective catalysts for production of fuels and heavier hydrocarbons from lighter hydrocarbons, but also is to produce the products with high quality. The Fischer-Tropsch synthesis (FTS) [1-3] can be carried out either in high (> 350 °C, HTFT) or in low (< 250 °C, LTFT) temperatures [4,5]. The HTFT process is carried out at slurry reactor, and produces light olefins, while the LTFT process could be carried out at both slurry and fixed-bed reactors and produce mainly paraffinic heavy hydrocarbons. Due to the thermodynamic and kinetic limitations of the reaction, few catalysts are able to amplify the heavier fraction of hydrocarbons. Among them, Ru-based catalysts show higher activity, however, they are very expensive [6-9]. Nickel-based catalysts could be employed but their

efficiencies in hydrogenation process which compete with FTS, and produce CH<sub>4</sub> as an undesirable byproduct [10,11]. Both Fe- and Co-based catalysts individually have advantages and disadvantages [12-19]. Therefore, effort to couple them in the hope to bring forth a more efficient catalyst having parents' advantages is of great importance. These bimetal catalysts should be inserted into a highly porous support to increase the surface area and mechanical stability of the catalysts and prohibition of the catalyst sintering. In addition to porosity, shape and size of the pores are critical secondary factors. The best supports are those that are simply manipulated to produce optimum texture properties. Silica [20,21] and  $\gamma$ -alumina [22,23] are good in this regard particularly in the Sol-Gel preparation method [24]. The purpose of this paper is to investigate the influence of catalyst composition and operational conditions on the FTS performance and product selectivity. Characterization of all catalysts were carried out by powder X-ray diffraction (XRD), transmission electron microscopy (TEM), N<sub>2</sub> physisorption and thermal analysis methods such

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as thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC).

## EXPERIMENT

### Typical Procedure for Preparation of Catalysts

A series of Co-Fe/SiO<sub>2</sub> catalysts with different loadings of Fe and Co was prepared. An appropriate amount of starting materials including cobalt nitrate [Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O] and iron nitrate [Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O] were dissolved in ethanol at 60 °C, separately and mixed well with each other. The required amounts of TEOS [Si(C<sub>2</sub>H<sub>5</sub>O)<sub>4</sub>] as silica source were dissolved in ethanol at 60 °C and then gradually added to the cobalt-iron containing solution to produce 30, 40, 50, 60, 70 and 80 wt% of Co/Fe = 1/1 (based on SiO<sub>2</sub> wt%) mixture solutions, respectively. An ethanol solution of oxalic acid (C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O, appropriate amount for TEOS hydrolysis) was added to a mixed solution under constant stirring to obtain a gel form. The gel was dried in an oven (120 °C, 12 h) to give a material denoted as the catalyst precursor. The promoted catalysts were then prepared by the incipient wetness impregnation method by adding different loadings (0.2-1.2 wt%) of KCl to cobalt-iron precursor. The obtained precursors was then dried at 110 °C for 12 h and calcined at 400 °C for 6 h.

### Characterization of Catalysts

The XRD patterns were obtained using a Bruker axS D8 Advance diffractometer. Scans were taken with a 2θ step size of 0.02 from 4 to 70° and a counting time of 1.0 s using Cu K<sub>α</sub> radiation source generated at 40 kV and 30 mA. N<sub>2</sub> physisorption was performed using a NOVA 2000 BET instrument. Prior to the measurements, all catalyst samples were slowly degassed at 150 °C for 4 h under inert N<sub>2</sub> atmosphere. Then, the samples were transferred to the adsorption unit to determine the textural properties. The TGA and DSC were carried out using simultaneous thermal analyzer STA 1500+ under a flow of dry air. The temperature was gradually raised from 25 °C to 650 °C using a linear programmer at a heating rate of 5 °C min<sup>-1</sup>. TEM image was carried out using a Hitachi H-7500 (120 kV). The sample for TEM image was prepared by ultrasonic radiation of the catalyst in ethanol solvent. The obtained

suspension was dropped on to a carbon-coated copper grid.

### Fischer-Tropsch Reaction

Catalytic performance test was carried out in a fixed bed stainless steel reactor at different operation conditions (Fig. 1). All catalysts were activated (reduced) for 16 h period on line in pure hydrogen (1 bar) at a temperature of 400 °C at flow rate of 30 ml min<sup>-1</sup>. Meshed catalyst (1.0 g) was loaded in the reactor (30 cm length and internal diameter is 7 mm). Feed and products were analyzed on-line using a Varian gas chromatograph (Star 3600CX) whose detector for gas analysis is thermal conductivity detector (TCD) and a chromosorb column. The liquid hydrocarbon products were analyzed using a Varian CP 3800 with a Petrocol Tm DH100 fused silica capillary column and a flame ionization detector (FID). The conversion percentage of CO is calculated based on the CO fraction forming carbon-containing products, according to Eq. (1)

$$\text{CO conversion (\%)} = \frac{C_{\text{CO}_m} - C_{\text{CO}_{out}}}{C_{\text{CO}_m}} \times 100 \quad (1)$$

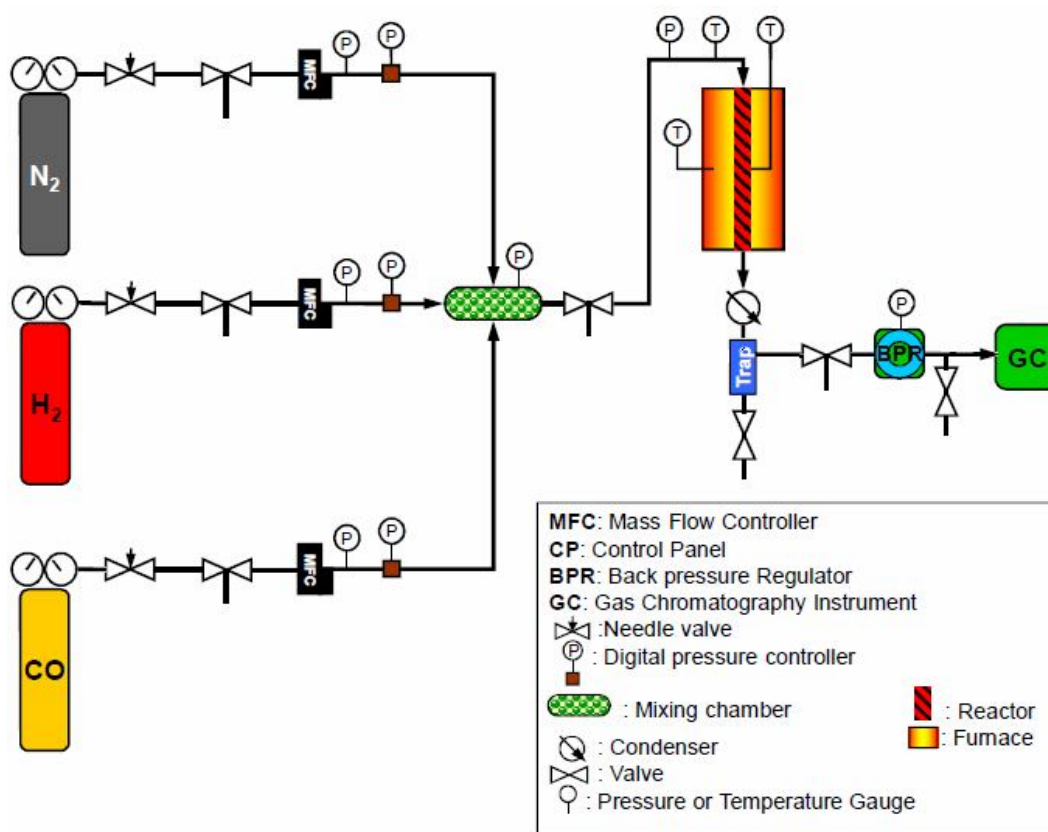
where,  $n_i$  is the number of carbon atoms in product  $i$ ,  $M_i$  is the percentage of product  $i$ , and  $M_{\text{CO}}$  is the CO % in the syngas feed. The selectivity ( $S$ ) of product  $i$ , is based on the total number of carbon atoms in the product and therefore is defined as:

$$S_i (\%) = \frac{n_i M_i}{\sum n_i M_i} \times 100 \quad (2)$$

## RESULTS AND DISCUSSION

### Effect of Cobalt-iron Weight Percentage

As a starting point of our investigation, the effect of different wt% of cobalt/iron (based on the SiO<sub>2</sub> weight) under the same reaction conditions (H<sub>2</sub>/CO = 2/1, GHSV = 1200 h<sup>-1</sup>, P = 1 bar and T = 220 °C) was investigated. As Table 1 shows, the catalyst activity based on CO conversion increases linearly with decreasing wt% of (Co/Fe) while the selectivity toward undesirable methane and CO<sub>2</sub> decreases till 50 wt% of Co/Fe and then increases markedly. According to the obtained results, the catalyst containing 50



**Fig. 1.** Schematic representation of the testing system for the catalyst and used reactor.

**Table 1.** Effect of Different wt% of (Co/Fe) on FTS Performance and Product Selectivity

	wt%( Co/Fe)					
	30	40	50	60	70	80
CO conversion (%)	41.5	40.9	40.0	37.0	36.4	34.5
CH <sub>4</sub>	28.8	27.1	25.6	27.6	28.1	29.7
C <sub>2</sub> -C <sub>3</sub> paraffin	13.3	14.0	15.1	14.3	14.1	13.7
C <sub>2</sub> -C <sub>3</sub> olefin	17.8	18.1	19.6	17.8	17.4	15.4
C <sub>4</sub> -C <sub>5</sub> paraffin	9.2	9.1	9.5	9.1	8.5	8.5
C <sub>4</sub> -C <sub>5</sub> olefin	10.5	10.7	12.0	9.3	8.6	8.3
C <sub>6</sub> <sup>+</sup>	12.0	13.3	12.9	13.7	14.0	14.0
CO <sub>2</sub>	8.4	7.7	5.3	8.2	9.3	10.4

Reaction conditions: H<sub>2</sub>/CO = 2/1, GHSV = 1200 h<sup>-1</sup>, P = 1 bar and 220 °C.

**Table 2.** Textural Properties of the Cobalt/Iron Precursors

wt% (Co/Fe)	Specific surface area (m <sup>2</sup> g <sup>-1</sup> )			Pore diameter (Å)		Pore volume (cm <sup>3</sup> g <sup>-1</sup> )	
	BET	BJH	DH	BJH	DH	BJH	DH
30	139.3	141.6	137.5	16.8	16.3	0.27	0.29
40	136.9	139.1	136.9	17.2	17.5	0.32	0.30
50	134.7	132.6	134.1	18.3	18.6	0.38	0.36
60	123.2	126.1	124.8	16.8	17.0	0.31	0.34
70	108.5	106.4	104.7	13.6	13.9	0.26	0.24
80	103.4	105.7	105.3	12.7	13.1	0.23	0.25

**Table 3.** Textural Properties of the Cobalt/Iron Catalysts

wt% (Co/Fe)	Specific surface area (m <sup>2</sup> g <sup>-1</sup> )			Pore diameter (Å)		Pore volume (cm <sup>3</sup> g <sup>-1</sup> )	
	BET	BJH	DH	BJH	DH	BJH	DH
30	156.8	155.3	151.5	17.4	16.8	0.60	0.56
40	149.3	153.4	154.1	15.9	18.3	0.64	0.63
50	147.8	150.1	148.3	16.6	17.4	0.64	0.68
60	138.2	139.6	137.7	12.2	13.1	0.56	0.59
70	132.6	130.4	131.3	11.3	10.7	0.47	0.45
80	124.7	126.2	125.9	10.4	11.7	0.41	0.46

**Table 4.** Textural Properties of the Cobalt/Iron Catalysts after the Test

wt% (Co/Fe)	Specific surface area (m <sup>2</sup> g <sup>-1</sup> )			Pore diameter (Å)		Pore volume (cm <sup>3</sup> g <sup>-1</sup> )	
	BET	BJH	DH	BJH	DH	BJH	DH
30	139.7	137.1	142.3	14.8	14.1	0.48	0.51
40	138.1	141.5	139.4	13.7	14.8	0.41	0.45
50	144.5	145.9	143.1	14.3	16.0	0.58	0.61
60	129.4	127.3	128.6	10.6	11.4	0.44	0.40
70	119.5	120.7	117.6	9.5	8.9	0.39	0.36
80	111.7	110.8	112.2	8.2	8.5	0.32	0.34

wt% of (Co/Fe) presents the best catalytic performance compared to the other tested catalysts at the mentioned operational conditions. This catalyst showed the highest selectivity towards olefinic products ( $C_2$ - $C_5$ ) and the low selectivity towards methane and  $CO_2$ . Thus, this catalyst was selected as the optimal catalyst. The specific surface area (BET, DH and BJH methods), pore volume and pore diameter of the precursors and calcined catalysts (before and after reaction) are given in Tables 2, 3 and 4, respectively. A relatively high surface area of the precursor is mainly due to solvent evaporation which makes a porous surface of high surface area. The surface area of the calcined catalysts is higher than the corresponding precursors which is mainly due to gas evolution from the solid during of calcination process. It can be seen that the increase of (Co/Fe) wt% results in a linear decrease in the catalyst surface area which is in conformity with catalyst activity based on CO conversion. On the other hand, the pore volume increases with increasing the cobalt/iron ratio to reach a maximum at 50 wt% of (Co/Fe), and then decreases with further increasing of cobalt/iron ratio which is in agreement with selectivity trend. The calcined catalysts were examined with powder X-ray diffraction to investigate the effect of loadings of cobalt/iron on the phase structure. Typical XRD patterns for the precursors and calcined forms of the catalysts are shown in Figs. 2 and 3, respectively. The precursors prepared from different cobalt-iron ratios were largely found to be amorphous and silicate phases (Fig. 2). These amorphous phases make the other phases such as iron hydroxide phases undetectable. In addition, the calcined catalysts contain the oxide phases of  $Co_3O_4$  (cubic),  $Fe_2O_3$  (cubic, tetragonal),  $CoFe_2O_4$  (cubic),  $Co_2SiO_4$  (orthorhombic), and  $Fe_2SiO_4$  (cubic), however, the relative diffracted intensities, especially for main phases, were different and noticeable (Fig. 3).

Taking into account that the optimum catalyst was the 50 wt% of (Co/Fe)/ $SiO_2$  catalyst, in order to identify the changes happened to this catalyst during the reactions, and also for detection of the phases formed, this catalyst after the test was characterized by XRD (Fig. 4). The phase of catalyst after the test ( $T = 220\text{ }^\circ\text{C}$ ) was found to be metallic iron in the form of cubic structure, and  $Fe_3O_4$  (cubic),  $Fe_2SiO_4$  (cubic),  $Co_3C$  (orthorhombic),  $Fe_3C$  (orthorhombic),  $CoO$  (cubic) phases. As shown, the tested catalyst has

oxidic and iron carbide phases, both of which have been generally accepted to be the most likely active phase for FTS performance [25-29]. One of the affecting parameters on catalytic performance was catalyst particle size. This parameter could be calculated by Scherrer-equation [30,31]. Table 5 summarizes the results obtained from XRD. It was found that the crystallite size of catalysts were decreased with increasing of  $SiO_2$  (decreasing wt% Co/Fe) content which clearly confirm the dispersion effect of  $SiO_2$  that is support of catalyst. From the results presented in Table 5, it is clear that the catalyst particle size was in nano dimension. It was found that cobalt particle size had a strong impact on cobalt catalyst selectivity; the olefin selectivity decrease with increasing the particle size of catalyst [32-35]. Our results are in agreement with these reports and lower olefins selectivity were obtained for higher cobalt loading contain higher particle size.

The optimal catalyst containing 50 wt% of (Co/Fe)/ $SiO_2$  was characterized with TEM (Fig. 5). As clearly seen in this figure, the size of particles is 35-50 nm, that is in agreement with what was obtained from the Scherrer equation. The precursor was subjected to thermal gravimetric analysis and differential scanning calorimetry. As shown in Fig. 6, the TGA/DSC curves of 50 wt% (Co/Fe)/ $SiO_2$  catalyst precursor exhibit a three-step weight loss. The first step at the temperature below  $150\text{ }^\circ\text{C}$  was attributed to the evaporation of residual moistures of the support and loss of physisorbed waters. The second step at the temperature, between  $150$  and  $280\text{ }^\circ\text{C}$ , was the decomposition of oxalate phases and removal of hydrate and bound waters. The third weight loss occurs above  $280\text{ }^\circ\text{C}$  corresponds to the full decomposition of all oxalate phases and the formation of stable cobalt and iron oxides.

### Effect of Cobalt/iron Weight Ratio

The influence of the cobalt/iron weight ratio at various reaction temperatures on the catalytic performance of cobalt/iron nano catalyst containing 50 wt% (Co/Fe)/ $SiO_2$  under atmospheric pressure,  $H_2/CO = 2/1$  and GHSV =  $1200\text{ h}^{-1}$  were studied (Tables 6-10). The results showed that variation of cobalt/iron ratio (90/10-20/80) at different temperatures ( $220$ - $260\text{ }^\circ\text{C}$ ) resulted in different products selectivity. However, for the catalyst containing 50 wt% (Co/Fe)/ $SiO_2$  with cobalt/iron = 70/30 at  $T = 250\text{ }^\circ\text{C}$ , the

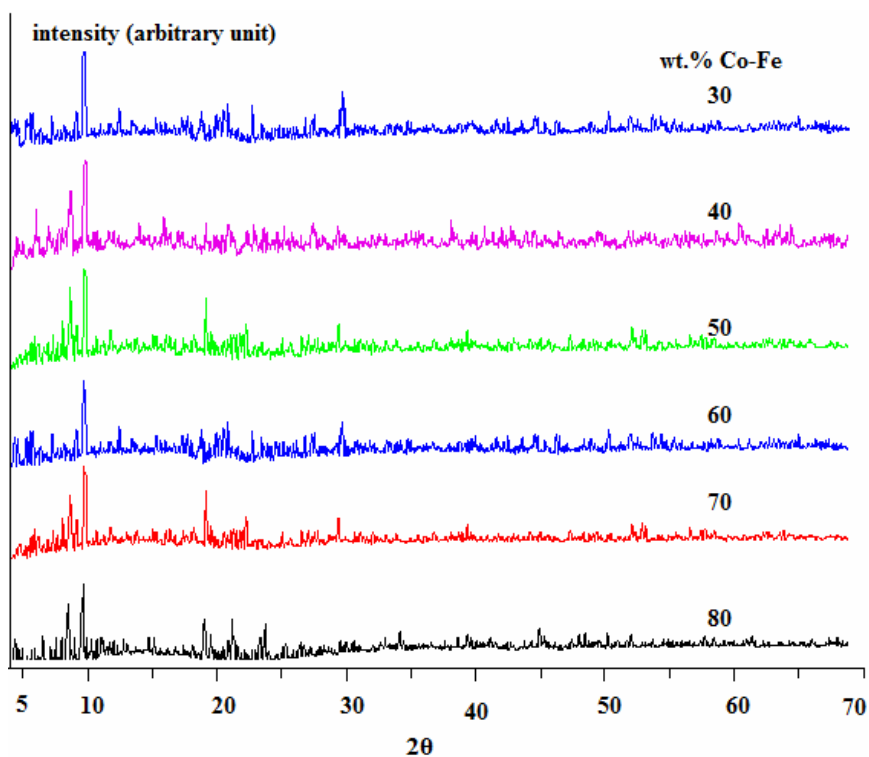


Fig. 2. XRD patterns of catalyst precursors with different wt% of (Co/Fe).

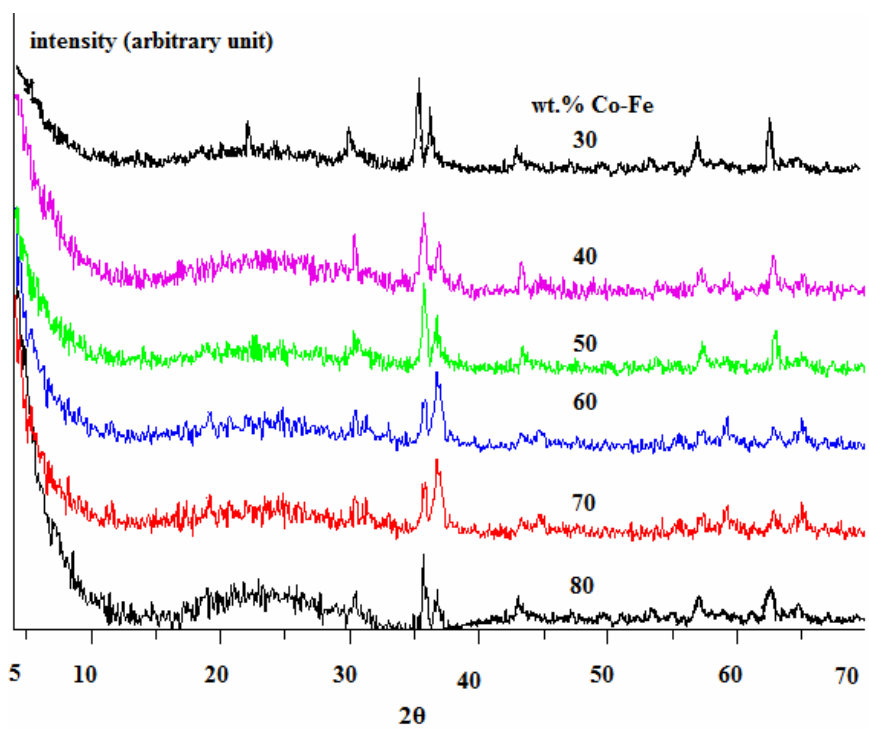
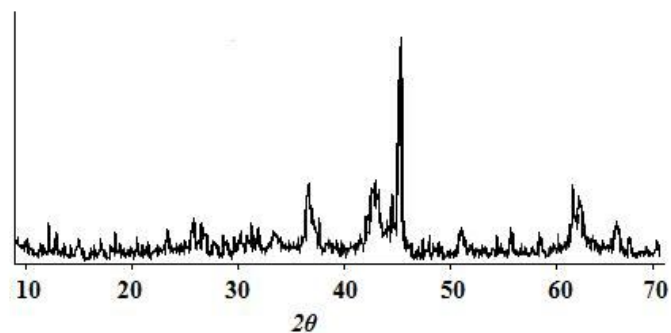


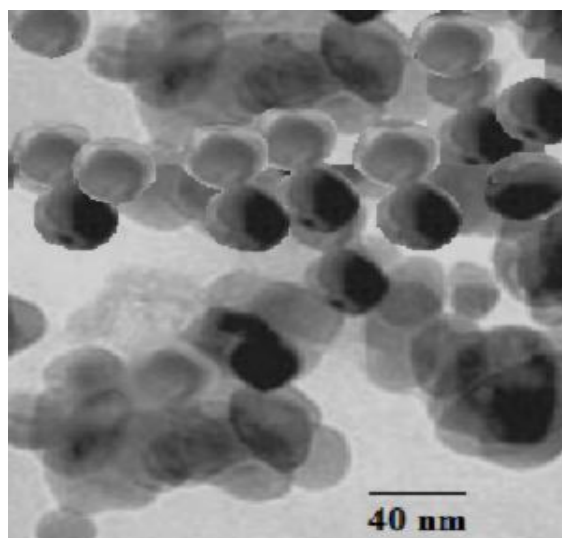
Fig. 3. XRD patterns of catalysts with different wt% of (Co/Fe).



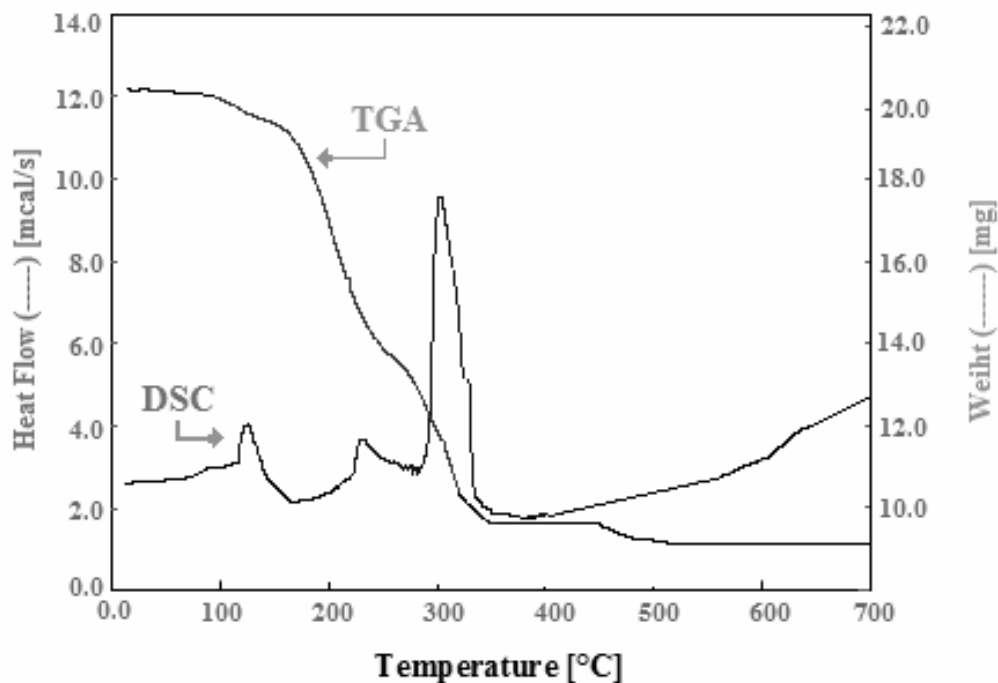
**Fig. 4.** XRD pattern of catalyst with 50 wt% (Co/Fe)/SiO<sub>2</sub> after the test.

**Table 5.** Average Size of the Particles of Studied Catalysts

wt% (Co/Fe)	$2\theta$	Size (nm)
30	37	36
40	37	38
50	37	40
60	37	44
70	37	51
80	37	54



**Fig. 5.** TEM image of calcined catalyst containing 50 wt% (Co/Fe)/SiO<sub>2</sub>.



**Fig. 6.** TGA/DSC curves for the 50 wt% (Co/Fe)/SiO<sub>2</sub> catalyst precursor.

**Table 6.** Effect of Different Co/Fe Ratios on the Catalytic Performance at 220 °C

	Co/Fe Ratio							
	(%)							
	90/10	80/20	70/30	60/40	50/50	40/60	30/70	20/80
CO conversion (%)	35.7	37.2	38.0	39.2	40.0	41.3	42.0	43.3
CH <sub>4</sub>	25.1	24.3	23.0	26.0	25.6	25.3	26.5	27.4
C <sub>2</sub> -C <sub>3</sub> paraffin	14.9	15.5	15.5	12.8	15.1	15.1	13.9	13.6
C <sub>2</sub> -C <sub>3</sub> olefin	17.0	19.4	20.9	21.0	19.6	17.3	20.5	19.7
C <sub>4</sub> -C <sub>5</sub> paraffin	10.0	9.2	9.0	8.1	9.5	11.0	10.4	9.2
C <sub>4</sub> -C <sub>5</sub> olefin	10.4	10.6	12.0	12.4	12.0	10.8	9.0	9.5
C <sub>6</sub> <sup>+</sup>	17.1	15.7	14.9	15.0	12.9	14.8	13.8	14.3
CO <sub>2</sub>	5.5	5.3	4.7	4.7	5.3	5.7	5.9	6.3

Reaction conditions: H<sub>2</sub>/CO = 2/1, GHSV = 1200 h<sup>-1</sup> and P = 1 bar.



**Table 7.** Effect of Different Co/Fe Ratios on the Catalytic Performance at 230 °C

	Co/Fe Ratio							
	(%)							
	90/10	80/20	70/30	60/40	50/50	40/60	30/70	20/80
CO conversion (%)	37	38.9	41.9	42.2	43.2	43.6	45.7	46.8
CH <sub>4</sub>	22.4	21.6	19.4	22.5	23.7	25.2	26.1	26.4
C <sub>2</sub> -C <sub>3</sub> paraffin	15	15.5	16.1	13.3	14.1	14.3	14.6	13.4
C <sub>2</sub> -C <sub>3</sub> olefin	17.5	18.9	21.2	22.2	20.6	20.5	20.4	21.5
C <sub>4</sub> -C <sub>5</sub> paraffin	10.6	10.1	9.8	8.8	9.6	9.3	8.7	9.4
C <sub>4</sub> -C <sub>5</sub> olefin	11.5	11.8	12.4	13.1	12.8	11.7	10.3	9.6
C <sub>6</sub> +	17.8	17.1	16.8	15.6	14.3	14.8	14.2	13.7
CO <sub>2</sub>	5.2	5	4.3	4.5	4.9	5.5	5.7	6

Reaction conditions: H<sub>2</sub>/CO = 2/1, GHSV = 1200 h<sup>-1</sup> and P = 1 bar.

**Table 8.** Effect of Different Co/Fe Ratios on the Catalytic Performance at 240 °C

	Co/Fe Ratio							
	(%)							
	90/10	80/20	70/30	60/40	50/50	40/60	30/70	20/80
CO conversion (%)	45.5	48.6	55	55.5	53.7	56.4	57	58.1
CH <sub>4</sub>	28.2	26.8	21.1	25.1	26.3	26.9	28.5	29.0
C <sub>2</sub> -C <sub>3</sub> paraffin	18.4	17.9	18.3	18.2	16.9	16.2	17.0	18.3
C <sub>2</sub> -C <sub>3</sub> olefin	16.2	19.3	21.5	19.1	19.0	18.2	16.3	17.4
C <sub>4</sub> -C <sub>5</sub> paraffin	8.5	7.9	9.8	9.3	9.1	8.2	9.2	7.2
C <sub>4</sub> -C <sub>5</sub> olefin	9.3	9.9	10.2	8.4	8.1	7.1	6.9	7.9
C <sub>6</sub> +	11.9	11.1	14.0	13.9	14.1	15.6	13.5	10.9
CO <sub>2</sub>	7.5	7.1	5.1	6.0	6.5	7.8	8.7	9.3

Reaction conditions: H<sub>2</sub>/CO = 2/1, GHSV = 1200 h<sup>-1</sup> and P = 1 bar.

**Table 9.** Effect of Different Co/Fe Ratios on the Catalytic Performance at 250 °C

	Co/Fe Ratio							
	(%)							
	90/10	80/20	70/30	60/40	50/50	40/60	30/70	20/80
CO conversion (%)	45.5	48.6	55	55.5	53.7	56.4	57	58.1
CH <sub>4</sub>	28.2	26.8	21.1	25.1	26.3	26.9	28.5	29.0
C <sub>2</sub> -C <sub>3</sub> paraffin	18.4	17.9	18.3	18.2	16.9	16.2	17.0	18.3
C <sub>2</sub> -C <sub>3</sub> olefin	16.2	19.3	21.5	19.1	19.0	18.2	16.3	17.4
C <sub>4</sub> -C <sub>5</sub> paraffin	8.5	7.9	9.8	9.3	9.1	8.2	9.2	7.2
C <sub>4</sub> -C <sub>5</sub> olefin	9.3	9.9	10.2	8.4	8.1	7.1	6.9	7.9
C <sub>6</sub> +	11.9	11.1	14.0	13.9	14.1	15.6	13.5	10.9
CO <sub>2</sub>	7.5	7.1	5.1	6.0	6.5	7.8	8.7	9.3

Reaction conditions: H<sub>2</sub>/CO = 2/1, GHSV = 1200 h<sup>-1</sup> and P = 1 bar.

**Table 10.** Effect of Different Co/Fe Ratios on the Catalytic Performance at 260 °C

	Co/Fe Ratio							
	(%)							
	90/10	80/20	70/30	60/40	50/50	40/60	30/70	20/80
CO conversion (%)	43.5	47.4	50.1	51.8	51.5	50	49.2	50.5
CH <sub>4</sub>	30.7	30.1	29.6	33.4	34.5	35.4	35.7	37.5
C <sub>2</sub> -C <sub>3</sub> paraffin	15.7	14.8	14.1	13.8	14.5	13.8	12.9	12.4
C <sub>2</sub> -C <sub>3</sub> olefin	17.3	18.7	20.1	17.3	15.7	15.8	16.0	14.2
C <sub>4</sub> -C <sub>5</sub> paraffin	12.0	13	10.9	10.6	10.1	9.8	9.2	6.9
C <sub>4</sub> -C <sub>5</sub> olefin	7.9	7.1	6.8	7.2	7.9	6.9	6.8	7.3
C <sub>6</sub> +	8.5	8.0	9.9	8.8	8.0	9.0	9.1	10.5
CO <sub>2</sub>	8.0	8.3	8.6	8.8	9.3	9.3	10.3	11.2

Reaction conditions: H<sub>2</sub>/CO = 2/1, GHSV = 1200 h<sup>-1</sup> and P = 1 bar.

catalyst activity (based on CO conversion to products) was higher than other tested catalyst at different temperatures, and also the selectivities toward undesired products of methane and CO<sub>2</sub> were lower. Therefore, cobalt/iron = 70/30 ratio at 250 °C was chosen as the optimum catalyst. This result is in agreement with previous reports that the reaction temperature should not be too low or high [36]. At low reaction temperatures, the conversion of CO is low and so it causes a low catalytic performance. On the other hand, increasing the reaction temperature leads to the formation of amounts of coke. The CO conversion increased linearly with increasing temperature, similar results were also obtained by Schulz and Claeys [37,38]. Both the CO conversion and CO<sub>2</sub> formation followed the same trends as the FTS reaction, and almost presented a linear correlation with increasing reaction temperature. Bukur *et al.* [39] investigated a precipitated iron catalyst in a fixed bed reactor under a variety of process conditions, and also observed that selectivity of light olefins was high at the reaction temperature of around 300 °C during FTS. The XRD technique was carried out to identify the changes in phases of catalyst which may occur during the reaction. The optimum catalyst after the test was characterized by XRD and its phases were found to be Fe<sub>3</sub>O<sub>4</sub> (cubic), FeC<sub>2</sub> (orthorhombic), CoO (cubic), Fe<sub>2</sub>SiO<sub>4</sub> (cubic), CoFe<sub>2</sub>O<sub>4</sub> (cubic), and Co<sub>2</sub>SiO<sub>4</sub> (orthorhombic). As shown, the tested catalyst has oxidic and iron carbide phases. In course the reaction, metallic iron phases converted to iron carbide, and then, the iron carbide may be oxidized to iron oxide. It is well known that the iron carbide phases are active for FTS, and oxidic species are responsible for production of olefins [40,41]. The selectivity toward CO<sub>2</sub> increases with increasing the loading of iron which is in agreement with literature about the efficacy of iron catalysts toward water-gas shift [42-44].

### Effect of Percentage of KCl

To study the effect of KCl impregnation on the catalytic performance, different KCl wt%, from 0.2-1.2 wt%, were considered and all tested under atmospheric pressure, H<sub>2</sub>/CO = 2/1, T = 250 °C and GHSV = 1200 h<sup>-1</sup>. Both potassium and chlorine were reported to have positive [45,46], negative [47,48], or no effect on the catalyst performance, depending on a number of different factors

such as the support material, loading amount of K and Cl, and reaction conditions. As shown in Table 11, the activity of catalyst containing 50 wt% (Co/Fe)/SiO<sub>2</sub> (Co/Fe ratio is 70/30) increases with increasing wt% of KCl and achieve a maximum activity of 70.9% for 0.6 wt% KCl, and then decreases with further increasing of KCl wt%. At these conditions, methane and CO<sub>2</sub> production decreases till 0.6 wt% KCl then increases markedly. In overall, impregnation with 0.6 wt% KCl was selected as optimal. The effect of chlorine on the Fischer-Tropsch synthesis over iron and cobalt catalysts was investigated by Barrault [49] who reported a significant increase in the selectivity to light olefins, a marked drop in methane production, and increase in activity of catalyst. They found that a weak poisoning of iron catalysts by halogen ions suppresses secondary hydrogenation of olefins, resulting in an increased olefin selectivity, in agreement with what has been obtained in this study. The BET surface areas, pore volumes and average pore diameters of the incorporated catalyst with KCl are listed in Table 12. The decreased pore volume and BET specific surface area are observed when the catalyst is loaded with different wt% of KCl, possibly due to pore filling and/ or pore blocking of mesopores during the impregnation step.

### Effects of Total Pressure

The effect of total pressure was considered for 50 wt% (Co/Fe)/SiO<sub>2</sub> (Co/Fe ratio is 70/30) promoted with 0.6 wt.% KCl nano catalyst. The catalyst performance shows two opposite trend with respect to pressure (Table 13). With increasing the pressure, the CO conversion decreases slowly while selectivity toward heavy hydrocarbons increases (at same operational conditions of H<sub>2</sub>/CO = 2/1, GHSV = 1200 h<sup>-1</sup> and 250 °C). This behavior indicates that many parameters including economical considerations should be involved in the pressure optimization. High total selectivity toward heavy hydrocarbons (C<sub>6</sub>+, C<sub>4</sub>-C<sub>5</sub> olefin and C<sub>4</sub>-C<sub>5</sub> paraffin) at higher pressures may be due to more condensation of hydrocarbons, which are normally in the gaseous state at atmospheric pressure [50]. However, lower CO conversions are probably due to increasing the importance of diffusion step and/or changes in the morphology of the catalyst. Therefore, in this study, p = 1 bar was considered to be the optimum total pressure because

**Table 11.** Effect of Different Contents of KCl on the Catalytic Performance

	wt% KCl						
	0.0	0.2	0.4	0.6	0.8	1.0	1.2
CO conversion (%)	55	57.1	60.6	70.9	64.2	52.3	45.5
CH <sub>4</sub>	21.1	20.6	19.4	13.3	18.1	18	19.5
C <sub>2</sub> -C <sub>3</sub> paraffin	18.3	20	20.8	21.8	21	20.7	22
C <sub>2</sub> -C <sub>3</sub> olefin	21.5	23.5	26.6	28.3	23.2	20	18.2
C <sub>4</sub> -C <sub>5</sub> paraffin	9.8	9.3	8.8	10.8	10.3	10.8	8.6
C <sub>4</sub> -C <sub>5</sub> olefin	10.2	9.9	10.1	11.2	9.3	9	8.3
C <sub>6</sub> +	14	11.8	10.1	11.7	12.3	14.2	14.2
CO <sub>2</sub>	5.1	4.9	4.2	2.9	5.8	7.3	9.2

Reaction conditions: H<sub>2</sub>/CO = 2/1, GHSV = 1200 h<sup>-1</sup>, P = 1 bar and 250 °C.

**Table 12.** The BET Surface Areas, Pore Volumes and Average Pore Diameters of the Catalysts Promoted with KCl

Wt% KCl	Specific surface area (m <sup>2</sup> g <sup>-1</sup> )			Pore diameter (Å)		Pore volume (cm <sup>3</sup> g <sup>-1</sup> )	
	BET	BJH	DH	BJH	DH	BJH	DH
0.0	147.8	150.1	148.3	16.6	17.4	0.64	0.68
0.2	143.6	141.7	140.5	15.3	17.1	0.67	0.55
0.4	145.8	147.3	134.5	14.8	15.5	0.61	0.58
0.6	144.9	141.9	142.5	16.9	16.4	0.58	0.54
0.8	140.8	142.6	143.8	14.2	15.8	0.53	0.57
1.0	142.1	144.3	141.7	13.9	14.5	0.61	0.55
1.2	138.5	141.8	143.5	15.7	16.4	0.60	0.61

of the high CO conversion (70.9%), total selectivity to C<sub>2</sub>-C<sub>5</sub> olefins (39.5%), low CO<sub>2</sub> (2.9%) and  $\sum \text{Olefin} / \sum \text{paraffin} = 1.21$ .

## CONCLUSIONS

Many variable factors are important such as Co/-Fe

**Table 13.** Effect of Different Total Pressures on Catalytic Performance of Optimal Nano Catalyst

	Pressure (bar)										
	1	3	5	7	9	11	13	15	17	20	25
CO conversion (%)	70.9	70.4	69.9	66.9	65.9	64.5	63.4	62.3	61.3	60.6	59.8
CH <sub>4</sub>	13.3	13	12.6	12.0	11.8	11.5	11.1	10.6	10.4	10.6	10.2
C <sub>2</sub> -C <sub>3</sub> paraffin	21.8	20.6	20.1	19.2	18.6	16.7	15.4	14.1	11.4	9.0	8.1
C <sub>2</sub> -C <sub>3</sub> olefin	28.3	25.5	23.4	20.5	19.2	17.4	15.4	12.0	9.7	7.1	5.7
C <sub>4</sub> -C <sub>5</sub> paraffin	10.8	11.9	12.6	13.4	14.1	14.6	15.3	16.1	16.4	16.6	17.2
C <sub>4</sub> -C <sub>5</sub> olefin	11.2	13.0	12.8	13.8	14.4	15.1	15.7	17.5	16.8	17.6	17.5
C <sub>6</sub> +	11.7	12.8	15	17.4	18.5	21.1	23.4	26.8	32.4	35.9	38
CO <sub>2</sub>	2.9	3.2	3.5	3.7	3.4	3.6	3.7	2.9	2.9	3.2	3.3
ΣOlefin/Σparaffin	1.21	1.18	1.11	1.06	1.03	1.04	1.01	0.98	0.95	0.97	0.92
Carbon balance (%)	97.6	97.1	96.8	97.5	96.1	96.3	95.1	96.6	94.9	96.4	97.1

Reaction conditions: H<sub>2</sub>/CO = 2/1, GHSV = 1200 h<sup>-1</sup> and 250 °C.

wt%, different Co/Fe ratios and KCl wt% in the preparation of the catalyst during catalyst preparation and FTS. The catalytic performances of optimal nano catalyst were investigated under different reaction conditions. The optimal reaction conditions for 50 wt% (Co/Fe)/SiO<sub>2</sub> (Co/Fe ratio is 70/30) nano catalyst promoted with 0.6 wt% KCl as optimal catalyst were: T = 250 °C with molar feed ratio of H<sub>2</sub>/CO = 2/1, GHSV = 1200 h<sup>-1</sup> under 1 bar of total pressure. The optimal catalyst was found to be superior to the other catalysts in terms of catalytic activity (based on CO conversion) probably due to the facile formation of iron carbide during FTS reaction that is essential for light olefin production. In addition, methane production by using the 50 wt% (Co/Fe)/SiO<sub>2</sub> (Co/Fe ratio is 70/30) nano catalyst promoted with 0.6 wt% KCl was suppressed, which caused decreasing of methane selectivity from 25.6% for non promoted catalyst (50 wt% (Co/Fe)/SiO<sub>2</sub>) to 13.3% for promoted catalyst.

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