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Catalytic performance and characterization of cobalt-nickel nano catalysts for CO hydrogenation

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Abstract−A series of Co-Ni nano catalysts were prepared by co-precipitation method. We investigated the effect of Co/Ni molar ratios precipitate and calcination conditions on the catalytic performance of cobalt nickel catalysts for Fisher-Tropsch synthesis (FTS). The catalyst containing 90%Co/10%Ni was found to be optimal for the conversion of synthesis gas to light olefins. The activity and selectivity of the optimal catalyst were studied in different operational conditions. The results show that the best operational conditions are the H_2/CO=2/1 molar feed ratio at 310 °C and GHSV=1,200 h^{-1} under 5 bar of pressure. The prepared catalysts were characterized by powder X-ray diffraction (XRD), N_2 adsorption-desorption measurements such as BET and BJH methods, transmission electron microscopy (TEM) and thermal gravimetric analysis (TGA).

Keywords: Nano Catalysts, Co-precipitation, Light Olefins, Operational Conditions

INTRODUCTION

In the Fischer-Tropsch synthesis (FTS) process, hydrocarbons are produced from CO and H_2 [1-3]. Recently, FTS has received more attention than ever since it is considered an effective process to produce a wide-range of liquid hydrocarbon fuels and high-value added chemicals from relatively abundant resources, such as natural gas, coal and biomass, via synthetic gas [4]. Cobalt-based catalysts are widely used in the FTS. The goal of this reaction is to form linear aliphatic hydrocarbons with a broad molecular weight distribution [5,6]. The catalyst preparation method and the pretreatment conditions used for these catalysts are known to have great influence on the surface states of cobalt and cobalt oxide species formed. A number of studies have reported on the effect of pretreatment conditions on catalysts containing cobalt [7-11]. The FTS hydrocarbons products are mostly n-paraffins or n-olefins. There is a considerable increase in the demand for light olefins such as ethylene, propylene and isobutylene because of the growing interest in their applications for the manufacture of highly desirable products such as polyethylene, polypropylene, methyl tertiary butyl ether (MTBE) and ethyl tertiary butyl ether (ETBE) [15]. Group VIII metals, such as Fe, Co, Ni and Ru are the most popular FTS catalysts for hydrocarbon production [16,17]. Some researchers have argued that using bimetallic catalysts obtained from metal alloys may have some special advantages in CO hydrogenation [18-21]. Cobalt and iron are two reasonable choices for catalysts for FTS, but the iron-based catalysts have a high water gas shift (WGS) activity, whereas cobalt-based catalysts are effective in FTS and do not show significant WGS activity. Mixed oxide catalysts are important commercially in conversion of synthesis gas to desired products [22-25]. The preparation method plays an important role in the physical properties and performance of catalysts [25]. Due to the thermodynamic and kinetic limitations of the reaction, few catalysts are able to amplify the C_2-C_4 hydrocarbon fraction. Recent studies show that iron and cobalt particles are essential to achieve high FTS activity and products selectivity [26-29]. While Co/MnO was found to exhibit high selectivity to olefins in the C_2-C_4 range, the total yield of hydrocarbons was low. Addition of nickel to cobalt gave a stable catalyst having improved hydrocarbon yields while still retaining good olefin selectivity [30].

Our aim was to investigate the effect of preparation conditions, including the Co/Ni ratio of the precipitation solution and calcination conditions for C_2-C_4 olefin production. Further results are also reported concerning the effects of operational conditions such as H_2/CO molar feed ratio, a range of reaction temperature and total pressure on the catalytic performance of cobalt nickel catalyst. Characterization of catalysts was carried out using XRD, TEM, TGA and N_2 adsorption-desorption measurements.

EXPERIMENTAL

1. Catalyst Preparation

The cobalt nickel nano catalysts were prepared by the co-precipitation method in water-in-oil micro emulsion. Aqueous solution of $Co(NO_3)_2 \cdot 6H_2O$ (5.0 M) and $Ni(NO_3)_2 \cdot 6H_2O$ (1.0 M) with different molar ratios was pre-mixed in a round-bottomed flask containing 1-butanol and chloroform with respective ratio of 60 to 40%v/v and sodium dodecyl sulfate (SDS) as surfactant. A transparent mixture was aged for 2 h, with continuous stirring. Aqueous micro emulsion containing NH_4OH (20%) was added dropwise to the transparent mixture, and was continuously stirred while the temperature was maintained isothermally in 50 °C. Then, the mixture was set aside to decant overnight at room temperature. The solid phase was obtained by centrifuging and washing thoroughly with distilled water and ethanol. The samples were then dried at 120 °CC for 10 h to

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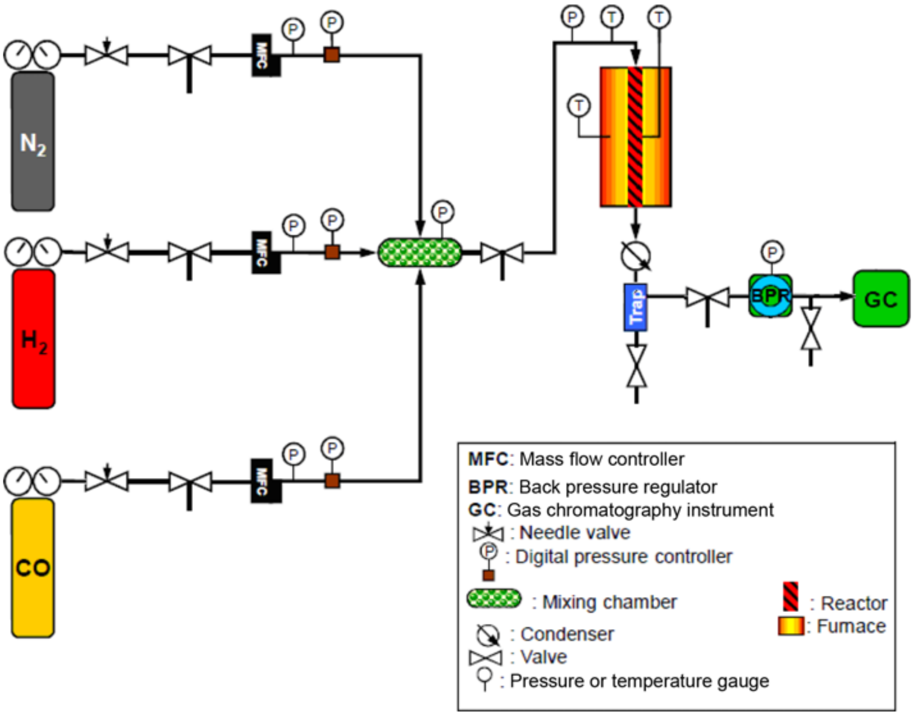

Fig. 1. Schematic representation of the catalyst performance system.

give a material denoted as the catalyst precursor, which was subsequently calcined in static air in a furnace.

Catalyst tests were conducted in a fixed bed stainless steel reactor at different operation conditions (Fig. 1). All catalysts were activated (reduced) for 8 h period on line in pure hydrogen (1 bar) at 400 °C and gas hourly space velocity (GHSV) of 1,200 h^{-1}. Meshed catalyst (1.0 g) diluted with similar granulometry of quartz beads (1.0 g), was held in the middle of the reactor (30 cm length and internal diameter is 7 mm). Reactant and stream products were analyzed on-line using a Varian gas chromatograph (Star 3600CX) equipped with a thermal conductivity detector (TCD) and a chromosorb column. The heavy hydrocarbon products were off-line 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 based on the fraction of CO forming carbon-containing products was according to the equation below:

$$\text{CO conversion } (\%) = \frac{\sum n_i M_i}{M_{CO}} \times 100 \qquad (1)$$

where n$_i$ is the number of carbon atoms in product i, M$_i$ is the percentage of product i and M_{CO} is the percentage of 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:

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

2. Catalyst Characterization

2-1. N$_2$ Adsorption-desorption Measurements

The specific surface area (using BET and BJH methods), total pore volume and the mean pore diameter were measured with a N$_2$ adsorption-desorption isotherm at liquid nitrogen temperature (−196 °C), using a NOVA 2200 instrument (Quantachrome, USA). Prior to the adsorption-desorption measurements, all the samples were degassed at 110 °C in a N$_2$ flow for 3 h to remove the moisture and other adsorbates.

2-2. X-ray Diffraction (XRD)

The XRD patterns of the precursor and calcined samples were recorded on a Philips X' Pert (40 kV, 30 mA) X-ray diffractometer. Scans were taken with a 2θ and step size of 0.02 from 2 to 60° and a counting time of 1.0 s using a Cu Kα radiation source (λ=1.542 Å) and a nickel filter.

2-3. Thermal Gravimetric Analysis (TGA)

The TGA was performed by using simultaneous thermal analyzer (Perkin Elmer) under a flow of dry air with a flow rate of 50 ml min^{-1}. The temperature was raised from 20 to 600 °C using a linear programmer at a heating rate of 4 °C min^{-1}.

2-4. Transmission Electron Microscopy

TEM investigations were done by using a Hitachi H-7500 (120 kV). The sample for TEM study was prepared by ultrasonic dispersion of the catalyst in ethanol. The suspension was dropped onto a carbon-coated copper grid.

RESULTS AND DISCUSSION

1. Effect of Co/Ni Molar Ratio

Cobalt nickel catalysts were prepared by co-precipitation with a range of Co/Ni solution ratios varying from 100%Co to 100%Ni based on molar ratio. After calcination of these materials (400 °C, 6 h), the catalytic performance of each catalyst for light olefins production with same operation conditions (H$_2$/CO=2/1 at 300 °C, p=1 bar and GHSV=1,200 h^{-1}) was investigated. The CO conversion and

Table 1. Effect of different Co/Ni molar ratios on catalytic performance

	Co/Ni										
	1/0	9/1	8/2	7/3	6/4	5/5	4/6	3/7	2/8	1/9	0/1
CO conversion (%)	43.8	47.9	45.8	42.5	39.2	37.4	35.4	34.9	32.6	30.9	30.1
Product selectivity (%)											
CH_4	24.3	19.1	21.8	24.6	25.5	25.9	26.4	28.2	29.8	32.1	56.7
C_2-C_4 olefins	42.1	47.4	44.7	40.3	37.8	34.6	30.3	25.6	23.2	17.8	8.9
C_2-C_4 alkane	18.6	16.3	17.8	18.9	20.4	23.5	24.5	24.5	25.2	28.4	13.8
C_5-C_6	8.2	9.6	10.3	12.5	11.1	12.8	12.9	13.4	14.1	14.1	14.6
CO_2	3.6	2.1	2.1	2.0	1.8	1.8	1.6	1.6	1.6	1.5	1.3
C_{6+}	2.2	5.5	3.2	1.2	3.4	1.4	4.4	5.7	6.1	6.1	4.7

Reaction conditions: $H_2/CO=2/1$, GHSV=1,200 h^{-1}, P=1 bar at 300 °C

products selectivity percent present at steady state (the time required to attain steady state condition was about 10 h) and catalytic performance for cobalt nickel catalysts with different Co/Ni molar ratios are shown in Table 1. According to the obtained results, the CO conversion and also product selectivity percent changes with changing in the Co/Ni ratios and the activity slowly decreased steadily as the cobalt/nickel molar ratios decreased from Co/Ni=9/1-1/9. According to the obtained results, the catalyst containing Co/Ni=9/1 showed the best catalytic performance for FTS products especially C_2-C_4 olefins; therefore, the catalyst containing 90%Co/10%Ni was chosen as the optimal catalyst. Characterization studies were done using XRD technique for precursors prepared from different cobalt/nickel molar ratios. The precursors prepared from different Co/Ni molar ratios were largely found to be amorphous by XRD. The presence of amorphous phase in the XRD patterns of these precursors makes the other phases undetectable (Fig. 2). The calcined catalyst prepared from nickel nitrate solution with no cobalt component was composed of NiO (cubic and rhombohedral) phases; this catalyst showed the low selectivity with respect to light olefins and had highest selectivity to CH_4 (56.7%) in comparison with the other catalysts (Table 1). Co precipitation of cobalt component with nickel resulted in changes in CO hydrogenation. The activity increased steadily as the cobalt/nickel ratio decreased from 9/1-8/2 and then CO hydrogenation decreased. In addition, methane formation by using Co-Ni catalyst was suppressed. Similar phases were identified by using XRD for prepared catalysts with molar ratios from Co/Ni=9/1-1/9; these phases were Co_3O_4 (cubic), NiO (cubic) and Co_2NiO_4 (cubic), although the relative diffracted intensities of these phases for all catalysts were different (Fig. 3). However, the calcined catalyst synthesized from liquor containing only cobalt nitrate was found to be high selective to methane and CO_2 and low selective to C_2-C_4 olefins and alkans, the identified phases for this catalyst containing Co_3O_4 (cubic) phase. Comparing the obtained results in Table 1 leads to the conclusion that the catalyst containing 90%Co/10%Ni showed the best catalytic performance than the other prepared catalysts. Taking these results into consideration, this catalyst appears to be the optimum modified catalyst for the conversion of synthesis gas to C_2-C_4 light olefins and other FTS products. The actual phases identified in this catalyst under the specified preparation conditions were Co_3O_4 (cubic), NiO (cubic) and Co_2NiO_4 (cubic). To identify the phase changes of this catalyst during the reactions, the catalyst after reaction was characterized using powder XRD. The XRD phases of the tested catalyst were found to be in form of CoC_x (cubic), CoO (cubic),

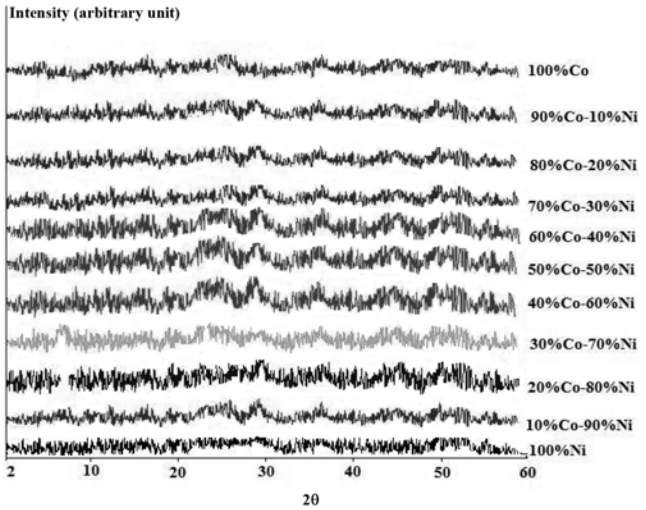

Fig. 2. XRD patterns for different Co/Ni molar ratios of catalyst precursor.

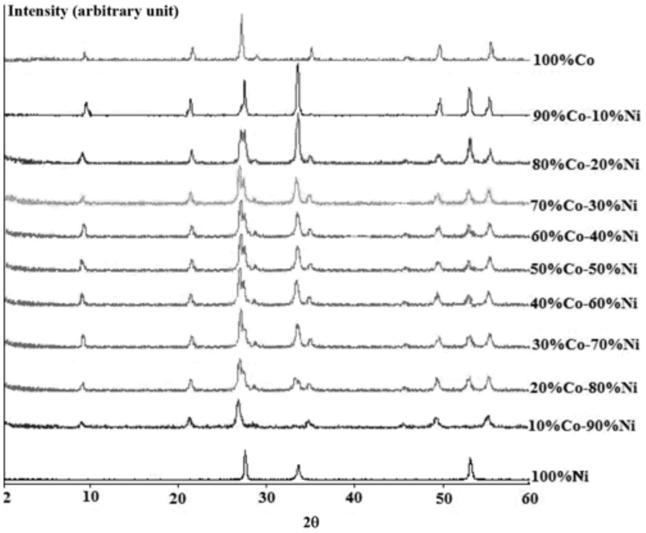

Fig. 3. XRD patterns for different Co/Ni molar ratios of calcined catalysts.

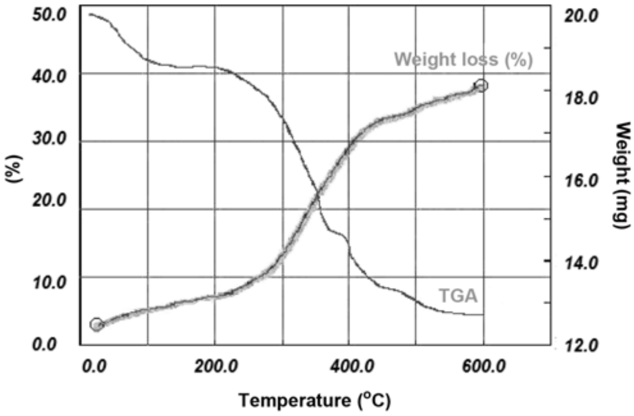

Fig. 4. TGA and weight loss curves for 90%Co/10%Ni catalyst precursor.

Table 3. N_2 physisorption results for the calcined catalysts with different Co/Ni molar ratio

Co/Ni	Specific surface area (m^2g^{-1})	Pore volume (cm^3g^{-1})
1/0	91.2	0.24
9/1	169.5	0.52
8/2	174.1	0.49
7/3	183.4	0.45
6/4	158.3	0.41
5/5	155.3	0.39
4/6	152.2	0.37
3/7	147.3	0.35
2/8	144.1	0.33
1/9	139.7	0.24
0/1	123.4	0.19

NiO (cubic) and Co_2NiO_4 (cubic). Oxidic phases are highly selective for the preparation of olefins, and carbide phases are active in the hydrogenation of CO [31-33].

Characterization of the catalyst precursor containing 90%Co/10% Ni catalyst was also done to measure the loss of weight as the temperature of the sample was increased. The TGA curve for this catalyst precursor is shown in Fig. 4. The weight losses found from TGA measurements agree fairly well with those expected for the decomposition of hydroxide to oxides. For this catalyst precursor, the thermogravimetric curve seems to indicate three-stage decomposition. The first stage is considered to be due to the removal of adsorbed water (40-110 °C), and the second stage is due to the decomposition of hydroxyl bimetallic or nitrate precursor (205-380 °C). The peak around 390-540 °C is due to the decomposition of cobalt and nickel hydroxide to oxide phases. The weight loss curve is involved with a total overall weight loss of ca. 38 wt%. The specific surface area (BET method), pore volume (BJH method) of the precursors and calcined catalysts are given in Tables 2 and 3. According to the obtained results, the specific surface areas are dependent on the Co/Ni molar ratio. It can be clearly illustrated that for catalyst precursors, with the increasing molar ratio of Co/Ni, at first all these physical characteristics increased and then they decreased in excess of Co/Ni=7/3. The BET specific surface area measurements for calcined catalysts showed a higher surface area than their corresponding precursors. The specific surface areas (BET) results for different Co/Ni molar ratio catalysts are given in Table 3. Monometallic 100% Co is used as the basis for comparing the physical characteristics and CO hydrogenation performance and selectivity for the bimetallic Co-Ni catalysts (Tables 1, 3). As shown in Table 3, the BET surface areas for the catalysts prepared from different cobalt/nickel molar ratios are dependent on the Co/Ni ratios. However, the specific surface area of catalyst for each molar ratio was found to be different. Besides, the BET data for the catalysts containing Co/Ni=9/1 showed the high specific surface area (169.5 m^2g^{-1}) and pore volume (0.52 cm^3g^{-1}); this might be a reason why the Co/Ni catalyst showed a better catalytic performance than the other catalysts. XRD technique is commonly used to evaluate the particle size by using the Scherrer equation [34], and the results show that the catalyst containing Co/Ni=9/1 has tiny particle size in comparison with the other prepared catalyst. This phenomenon conforms to the BET results (Table 4). The particle sizes were calculated from the most intense line ($2\theta\approx27°$). The particle size results for the calcined catalysts are shown in Table 4. As shown in Tables 1 and 4, the CO conversion and product selectivity are dependent on the catalyst particle size. It can be seen that the catalyst particle size up to about 31 nm did not exert a major effect on the catalytic performance of the

Table 2. N_2 physisorption results for the precursors with different Co/Ni molar ratio

Co/Ni	Specific surface area (m^2g^{-1})	Pore volume (cm^3g^{-1})
1/0	82.4	0.21
9/1	121.5	0.37
8/2	124.8	0.28
7/3	132.8	0.26
6/4	124.1	0.30
5/5	116.3	0.32
4/6	112.6	0.26
3/7	106.2	0.29
2/8	108.4	0.23
1/9	99.4	0.20
0/1	84.3	0.18

Table 4. Particle size of Co-Ni catalysts with different Co/Ni molar ratio

Catalyst	$2\theta°$	Size (nm)
100%Co	27	35
90%Co/10%Ni	34	31
80%Co/20%Ni	34	32
70%Co/30%Ni	27	34
60%Co/40%Ni	27	36
50%Co/50%Ni	27	38
40%Co/60%Ni	27	39
30%Co/70%Ni	27	39
20%Co/80%Ni	27	42
10%Co/90%Ni	27	43
100%Ni	28	46

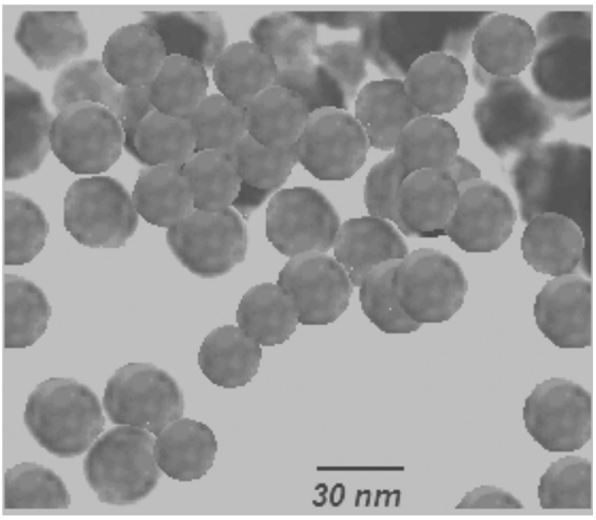

Fig. 5. TEM image of calcined catalyst containing 90%Co/10%Ni.

cobalt-nickel catalysts, while the catalyst particle size in excess of 31 nm resulted in a significant decrease in the olefin product selectivity. The results show that the decrease in the particle size of the cobalt nickel catalyst leads to increase in the CO conversion. In contrast, it has also been reported that the catalytic performance of cobalt catalysts supported by nano fibers is much lower for cobalt metal particles smaller than 6-8 nm. In addition, it was found that cobalt particle size has a strong impact on cobalt catalyst selectivity. The results showed a decrease in the cobalt particle size, which induces high olefin selectivity and low C_5+ selectivity [35-37]. The catalyst containing Co/Ni=9/1 was characterized with TEM (Fig. 5). As shown in Fig. 5, the particle sizes are from 25-40 nm. This result conforms to the obtained results that were studied by using the Scherrer equation.

2. Effect of Calcination Temperature

In this part of the investigation, the effects of calcination temperature were examined. Four samples were prepared by co-precipitation method and aged for 2 h. The first sample containing Co/Ni=9/1 was calcined for 6 h at 400 °C, and the other samples containing Co/Ni=9/1 were calcined at 500, 600 and 700 °C for 6 h at heating rate of 2.0 °Cmin^{-1} in air atmosphere, respectively. Then, these samples were tested at the same reaction conditions (H_2/CO=1/1, p=1 bar, at 300 °C and GHSV=1,200 h^{-1}). The CO conversion and hydrocarbons and light olefins selectivity percent, under the above calcination condition, is shown in Table 5. It was found that the optimum calcination temperature was 500 °C and at this temperature, CO conversion was higher than the other calcination temperature; selectivity with respect to light olefins was higher and also low CH_4 and CO_2 selectivity was observed. The specific surface areas (BET) results for the catalysts at different calcination temperatures are given in Table 6. In accordance with the results of this table, the surface area value obtained for the all calcined catalysts for CO hydrogenation is different. As mentioned before, the catalyst calcined at 500 °C for 6 h showed a higher selectivity toward light olefins. So, one of the origins of the higher activity of catalyst calcined at 500 °C for 6 h may be due to its higher BET specific surface area.

Table 5. Effect of different calcination temperature on the catalytic performance of 90%Co/10%Ni catalyst

	Temperature (°C)			
	400	500	600	700
CO conversion (%) Product selectivity (%)	47.9	52.7	45.2	35.4
CH_4	27.1	17.6	19.1	28.2
C_2-C_4 olefins	37.5	49.3	47.4	31.6
C_2-C_4 alkane	17.9	18.2	16.3	16.8
C_5-C_6	8.7	8.6	9.6	10.9
CO_2	4.6	1.6	2.1	1.6
C_{6+}	5.2	3.2	5.5	1.1

Reaction conditions: H_2/CO=2/1, GHSV=1,200 h^{-1}, P=1 bar at 300 °C

Table 6. BET results for different calcination temperatures of 90%Co/10%Ni catalyst

	Temperature (°C)			
	400	500	600	700
Specific surface area (m^2/g)	172.4	189.5	183.4	167.8

3. Effect of Calcination Time

Optimal nano-catalyst containing Co/Ni=9/1 was calcined at different calcination times separately at 500 °C and heating rate of 2.0 °C min^{-1} in air atmosphere; four samples of precursor were calcined during 4, 5, 6 and 7 h. The CO conversion and C_2-C_4 light olefins selectivity for these calcined catalysts are shown in Table 7 (H_2/CO=2/1, p=1 bar, at 300 °C and GHSV=1,200 h^{-1}). A comparison of the results in Table 7 for the catalysts prepared at different calcinations time indicates that the catalyst calcined at 6 h had the highest CO conversion and highest selectivity with respect to C_2-C_4 light olefins. Therefore, in this study, the best calcination conditions were found to be air atmosphere at 500 °C for 6 h with a heating rate of 2 °Cmin^{-1}. The catalyst calcined at 6 h is more selective to C_2-C_4 olefins (49.3%) and for CO conversion was 52.7% when undesirable CH_4 was less than others (17.6%). It was obvious that the optimum calcination time was 6 h at 500 °C in air atmosphere and 2 °Cmin^{-1} heating rate.

4. Effect of H_2/CO on the Catalytic Performance

The influence of the H_2/CO (synthesis gas ratio) on the catalytic

Table 7. Effect of different calcination time on the catalytic performance of 90%Co/10%Ni catalyst

	Time (h)			
	4	5	6	7
CO conversion (%) Product selectivity (%)	47.9	52.7	53.9	45.2
CH_4	24.5	18.5	17.6	24.3
C_2-C_4 olefin	32.5	39.1	49.3	34.2
C_2-C_4 alkane	19.2	22.3	18.2	12.9
C_5-C_6	6.4	7.1	8.6	13.1
CO_2	6.5	3.8	1.6	5.4
C_{6+}	10.9	9.2	3.2	10.1

Reaction conditions: H_2/CO=2/1, GHSV=1,200 h^{-1}, P=1 bar at 300 °C

Table 8. Effect of H_2/CO on the catalytic performance of 90%Co/10%Ni catalyst

	H_2/CO			
	1/1	2/1	5/2	3/1
CO conversion (%)	52.7	53.9	50.1	43.9
Product selectivity (%)				
CH_4	19.6	17.6	18.9	23.1
C_2-C_4 olefins	41.4	49.3	41.4	30.8
C_2-C_4 alkane	14.1	18.2	19.2	22.2
C_5-C_6	7.8	8.6	12.4	15.5
CO_2	2.9	1.6	5.5	6.3
C_{6+}	14.2	3.2	2.6	2.1

Reaction conditions: GHSV=1,200 h^{-1}, P=1 bar at 300 °C

performance (Co/Ni=9/1 for the FTS at H_2/CO=1/1, p=1 bar, 300 °C and GHSV=1,200 h^{-1}) was investigated and catalyst performance is shown in Table 8, with the change of H_2/CO from 1/1 to 3/1. However, at H_2/CO ratio of 2/1 and T=300 °C (GHSV=1,200 h^{-1} and p=1 bar), the total selectivity of C_2-C_4 light olefins was higher than that at the other H_2/CO feed ratios, and the selectivity for methane and CO_2 was also lower than other H_2/CO ratios. Therefore, H_2/CO=2/1 at 300 °C was chosen as the optimum molar feed ratio for converting synthesis gas to C_2-C_4 light olefins. On one hand, higher H_2/CO shortens the residence time, which is unfavorable for chain growth. In this reaction, the effect of H_2/CO ratio is remarkable, and in turn the lower H_2/CO ratio in the reactor results in a higher C_6+ selectivity. From the results, we can also draw the conclusion that the higher H_2/CO ratio is preferential for chain termination to produce light hydrocarbons, while lower H_2/CO ratio is preferential for chain growth and the production of heavy hydrocarbons [38-40]. Therefore, the C_6+ selectivity decreased with increasing H_2/CO ratio.

5. Effect of Reaction Temperature

The effect of reaction temperature on the catalytic performance of the 90%Co/10%Ni catalyst was studied at a range of temperature between 250-340 °C and the results are presented in the Table 9 (P=1 bar, H_2/CO=2/1 and GHSV=1,200 h^{-1}). The results show that as the operating temperature is increased, the CO conversion is increased. In addition, for the reaction temperature of 310 °C, the total selectivity of light olefins products was higher than the other reaction temperatures under the same reaction conditions. In general, an increase in the reaction temperature leads to an increase in the catalytic performance; furthermore, it shows that the reaction temperature should not be too low [41]. At low reaction temperatures, the conversion percentage of CO is low and so it causes a low catalytic performance. The CO conversion increased linearly with increasing temperature, as shown in Table 9. Similar results were also obtained by Schulz and Claeys [42,43]. Both the CO conversion and CO_2 formation followed the same trends as the FTS reaction, and almost presented a linear correlation with increasing reaction temperature. Bukur et al. [44] investigated a precipitated iron catalyst in a fixed bed reactor under a variety of process conditions, and have also observed that light olefin selectivity was high at a reaction temperature of around 300 °C during FTS. Therefore, in this study, 310 °C is considered to be the optimum because it has a high CO conversion, total selectivity of light olefins products, low CH_4 and also a high light olefin/paraffin ratio (3.07). These results indicate that the operating temperature is a parameter of crucial importance in the catalytic performance of optimal catalyst for hydrogenation of CO.

6. Effects of Total Pressure

An increase in total pressure would generally result in condensation of hydrocarbons, which are normally in the gaseous state at atmospheric pressure. Higher pressures and higher carbon monoxide conversions would probably lead to saturation of catalyst pores by liquid reaction products [45]. A different composition of the liquid phase in catalyst pores at high syngas pressures could affect the rate of elementary steps and carbon monoxide and hydrogen concentrations. A series of experiments were carried out for the 90%Co/10%Ni catalyst to investigate on the performance of this catalyst in variation of total pressure in the range of 1-20 bar, at the optimal conditions of H_2/CO=2/1, GHSV=1,200 h^{-1} and 310 °C (Table 10). The results indicate that at the total pressure of 1 bar, the optimal catalyst showed a total selectivity (6.6%) to C_6+ products. It is also apparent that increasing in total pressure significantly increases the C_6+ selectivity and leads to an increase to 23.8% at the pressure of 20 bar. On the other hand, as it can be seen on Table 10, in the range of 1-5 bar total pressures, no significant decreasing on CO conversion was observed; however, the light olefin selectivity was increased and the results indicate that at the total pressure of 5 bar, the optimal catalyst containing 90%Co/10%Ni, showed the highest total selectivity of 53.6% with respect to C_2-C_4 light olefins and also led to

Table 9. Effect of reaction temperature on the catalytic performance of 90%Co/10%Ni catalyst

	Temperature (°C)									
	250	260	270	280	290	300	310	320	330	340
CO conversion (%)	24.6	27.9	34.8	47.5	50.1	53.9	60.2	68.8	72.6	76.3
Product selectivity (%)										
CH_4	15.5	15.7	16.2	16.2	17.1	17.6	20.6	25.2	28.0	33.1
C_2-C_4 olefins	38.9	39.7	42.7	47.9	48.3	49.3	47.7	42.6	40.2	32.8
C_2-C_4 alkane	24.8	22.6	20.5	18.9	19.2	18.2	15.5	14.5	13.2	12.4
C_5-C_6	13.3	12.4	12.7	12.5	10.2	8.6	10.2	12.0	13.1	12.6
CO_2	1.6	1.9	1.9	2.0	1.8	1.6	1.6	1.9	2.4	3.4
C_{6+}	5.9	6.7	5.6	1.2	3.4	3.2	4.4	3.7	3.1	2.7

Reaction conditions: H_2/CO=2/1, GHSV=1,200 h^{-1} and P=1 bar

Table 10. Effect of pressure on the catalytic performance of 90%Co/10%Ni catalyst

	Pressure (bar)								
	1	3	5	7	9	12	15	17	20
CO conversion (%)	57.8	57.1	56.8	54.6	52.1	50.3	49.8	48.2	47.7
Product selectivity (%)									
CH_4	17.1	16.5	16.2	16.0	16.0	15.1	15.0	14.1	14.1
C_2-C_4 olefin	52.6	53.1	53.6	50.3	47.5	43.5	39.5	34.7	26.4
C_2-C_4 alkane	16.3	14.4	13.7	12.4	10.0	9.1	8.2	7.4	7.1
C_5-C_6	6.3	7.2	7.4	8.5	9.8	12.3	14.1	18.1	20.0
CO_2	1.1	1.1	1.1	1.4	1.8	2.5	3.1	3.4	3.6
C_{6+}	6.6	7.7	8.0	11.4	14.9	17.5	20.1	22.3	28.8

Reaction conditions: H_2/CO=2/1, GHSV=1,200 h^{-1} and 310 °C

8.0% total of selectivity towards the C_6+ products. The results also indicate that the CO conversion and the total selectivity with respect to C_2-C_4 light olefins were decreased as the total pressures were increased from 7 bar to 20 bar. Hence, because of high CO conversion, low CH_4 selectivity at the total pressure of 5 bar, this pressure was chosen as the optimum pressure. It is also apparent that increasing the total pressure in the ranges of 7-20 bar significantly increases the C_6+ selectivity and leads to an increase to 28.8% at the pressure of 20 bar.

CONCLUSIONS

Co-Ni bimetallic catalysts were prepared by co-precipitation technique and calcined in different calcination conditions. The best calcination conditions were found to be air atmosphere at 500 °C for 6 h with a heating rate of 2 °C min^{-1}. The catalytic performance of optimal catalyst containing 90%Co/10%Ni was studied under different operational conditions including reaction temperatures, different H_2/CO, total pressures of reaction. The optimal operating conditions were found to be 310 °C with molar feed ratio of H_2/CO=2/1, GHSV=1,200 h^{-1} under the 5 bar pressure. The optimal catalyst was found to be superior to the other catalysts in terms of better C_2-C_4 selectivity in the FTS products and higher olefin/paraffin ratio (3.9) because of the facile formation of metallic carbide during FTS reaction. In addition, methane selectivity for 100%Ni catalyst (56.7%) was suppressed by using Co-Ni bimetallic catalyst, which caused a decreasing of methane selectivity from 56.7 to 16.2%.

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