Research Article

Development of Hydrotalcite Based Cobalt Catalyst by Hydrothermal and Co-precipitation Method for Fischer-Tropsch Synthesis

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Abstract

This paper presents the effect of a synthesis method for cobalt catalyst supported on hydrotalcite material for Fischer-Tropsch synthesis. The hydrotalcite supported cobalt (HT-Co) catalysts were synthesized by co-precipitation and hydrothermal method. The prepared catalysts were characterized by using various techniques like BET (Brunauer-Emmett-Teller), SEM (Scanning Electron Microscopy), TGA (Thermal Gravimetric Analysis), XRD (X-ray diffraction spectroscopy), and FTIR (Fourier Transform Infrared Spectroscopy). Fixed bed micro reactor was used to test the catalytic activity of prepared catalysts. The catalytic testing results demonstrated the performance of hydrotalcite based cobalt catalyst in Fischer-Tropsch synthesis with high selectivity for liquid products. The effect of synthesis method on the activity and selectivity of catalyst was also discussed. Copyright © 2017 BCREC Group. All rights reserved

Keywords: Fischer-Tropsch synthesis; Cobalt catalyst; Hydrotalcite; Co-precipitation; Hydrothermal

1. Introduction

The rising awareness about using clean fuels and increasing inclination of masses towards green economies is influencing the oil industry to a great extent. There is more effort in play to minimize the environmental impacts of fuel in use. Work is being done to find a sustainable option that can both meet ever rising energy de-mand as well as reduces environmental impacts of fuel. Fischer-Tropsch synthesis is one of the cleaner production techniques and is used for generation of liquid products that are comparatively less hazardous to the environment as compared to their precursor [1]. Fischer-Tropsch synthesis (FTS) is a commercial polymerization process used for conversion of hydrogen and carbon monoxide into a variety of sulfur and aromatics-free hydrocarbons having wide range of chain length and functionality [2]. Syngas, which is a mixture of hydrogen and carbon monoxide, can be prepared by the gasification of coal

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or biomass and steam reforming of methane [3,4].

The FTS process usually employs a catalyst to carry out the reaction. Apart from others, iron and cobalt are the most commonly used active component of the catalysts used for FTS [5]. Heavy paraffin and light olefins are the characteristic product of cobalt catalysts whereas iron catalysts are inclined towards producing oxygenated compounds and branched hydrocarbons [6]. Iron catalysts can operate at a wide range of pressure, temperature, and H_2/CO ratio on the other hand cobalt catalysts can operate at limited temperatures, H_2/CO ratios and pressures [7]. Cobalt catalyst is more stable, more active, and has high selectivity towards straight chain hydrocarbons that is why cobalt is preferred in case of the higher H_2/CO ratio of syngas.

There are several types of support materials which can be used in Fischer-Tropsch catalysis. The choice of support material has an enormous effect on the activity and efficiency of catalyst [6]. Hydrotalcites are hydroxides having manifold layered structure and have the potential to be utilized as support material for catalyst in Fischer-Tropsch synthesis, and are widely used as a support material for cobalt catalysts used for auto-thermal reforming [8], carbon monoxide methanation [9] and CO hydrogenation [2], etc.

Literature studies showed several synthesis methods for hydrotalcite based catalyst. The mostly used method is the co-precipitation [10] at different pH and temperatures. A hydrothermal method at high temperature is also reported as another technique of synthesis of hydrotalcite [11]. The reported reaction time for this method is too long from 7-42 days. Another alternative method for the synthesis of hydrotalcite is the urea method based on the precipitation by hydrolysis of urea [12]. Recently, the HTs, like Ni and Co-Ni, were synthesized by co-precipitation method [13,14].

Attempts were made to use hydrotalcites as support material for catalysts used in FTS reactions. Those studies suggest that the hydrotalcite based cobalt catalyst showed higher activity for Fisher-Tropsch synthesis applications due to the higher relative surface areas and higher reducibility [2]. Beside this, some studies also focused on the effect of change of aluminium and magnesium molar ratio in hydrotalcite and suggested that lower Mg/Al leads to improved dispersion of cobalt in the crystal [15]. Recent studies showed that hydrothermal process could significantly enhance the catalyst FTS activity and C_{5+} selectivity [16].

The main focus of this study is to synthesize hydrotalcite supported cobalt catalyst for FTS by using two different synthesis methods. Co-precipitation and hydrothermal are two main techniques used for the synthesis of the catalyst. The prepared catalysts were characterized using various techniques and then tested for FTS in a fixed bed micro reactor.

2. Experimentation

2.1 Catalyst preparation

Two different techniques, co-precipitation method, and hydrothermal method were used for the synthesis of catalyst.

2.1.1 Co-precipitation method (HT-Co-CPPT)

HT-Co-CPPT catalyst was prepared with 40 wt% cobalt metal loading. Metal nitrate solutions were prepared by adding magnesium nitrate hexahydrate ($Mg(NO_3)_2.6H_2O$ = 8.01 g), aluminium nitrate nonahydrate ($Al(NO_3)_3.9H_2O$ = 7.03 g), and cobalt nitrate ($Co(NO_3)_2.6H_2O$ = 7.27 g) in 100 mL deionizes water. Ten hundred mL solutions of sodium carbonate (Na_2CO_3) (1.49 g) and sodium hydroxide (NaOH) (8.99 g) were used as the precipitating agent. The metal solutions and precipitating agents were mixed at a rate of 60-70 drops per minute along with constant stirring. The pH of the solution around 8-9 was maintained by the addition of concentrated nitric acid (HNO_3) The solution was then heated at 80 °C for 18 hours with constant stirring to complete the precipitation followed by filtration, washing, and drying overnight at 85 °C and calcinations at 600 °C for 7 h.

2.1.2 Hydrothermal method (HT-Co-HT)

HT-Co-HT catalyst with 40 wt% Co metal loading was prepared by hydrothermal method. The precipitating agent and metal nitrate solutions were prepared as described in the above section. After mixing and pH adjustment, the solution was heated around 100 °C in a hydrothermal autoclave for 8 h. The precipitates were then separated, extensively washed with deionized water, dried at 80 °C overnight in an oven and calcined at 600 °C for 7 h.

2.2 Catalyst characterization

The surface morphology and elemental composition of the prepared samples were determined by Scanning Electron Microscope (SEM modal JEOL, JED 2300 equipped with EDX Thermal Gravimetric Analysis (TGA) with

Mettler TGA/SDTA 851eX-ray diffraction spectroscopy (XRD) with Bruker D8 System operating at 40 kV and 30 mA, step size 0.01, scan angle 10° to 80° and 0.2 sec per scan, and Fourier Transform Infrared Spectroscopy (FTIR) with Perkin Elmer Spectrum 100 Spectrometer.

2.3 Catalyst testing

The testing unit for Fischer-Tropsch synthesis is shown in Figure 1. Fischer-Tropsch catalytic activity was tested in a fixed bed microreactor having a length of 10 cm with a diameter of 3.3 cm. One g of freshly prepared catalyst was loaded into the reactor along with 5 g of ceramic balls as diluting material [17,18]. The inert ceramic balls having no effect on the activity and selectivity of the catalyst; were used for increasing the surface area of the catalyst. The loaded catalyst was initially reduced at 400 °C for 16 h using hydrogen gas at a flow rate of 50 sccm. The reaction was carried out at 250 °C with hydrogen to carbon monoxide ratio of 2:1 [18,19]. Flow rates were maintained at 50 sccm of hydrogen, 25 sccm of carbon monoxide and 10 sccm of nitrogen. The pressure of the reactor was maintained at 20 bars (0.20 MPa). The product was collected in the separator 1 (Hot Trap) at 150 °C and Separator 2 (Cold Trap) at room temperature. The 'Shimadzu QP2010 Ultra' system is used for GC-MS analysis of product obtained from both separators. Injection temperature was set at 120 °C. Helium was used as carrier gas at a pressure of 89.3 KPa and column flow rate of 1.44 mL/min. The total flow was 158.9 mL/min and total time of the process is 25 mins. The peak area in GCMS results is used to calculate the product selectivity.

3. Results and Discussion

3.1 Catalyst characterization

3.1.1 Characterization by X-Ray Diffraction

The x-ray diffraction pattern of both catalysts prepared through co-precipitation and hydrothermal methods are shown in Figure 2. A hexagonal closed packed (hcp) ferromagnetic structure was observed for cobalt, whereas, at high pressures when the magnetism is adequately suppressed, we observe a transference from hexagonal closed packed (hcp) to cubic face centered structure (fcc) [20]. Figure 2 shows peaks at 31°, 37°, 44.8°, 65° represents a cubic crystalline form of cobalt oxide (Co_3O_4) [21,22]. The Co^{2+} ion has slightly larger ion radius than the Al^{3+} and Mg^{2+} (having ion radius of 60 pm and 65 pm, respectively) hence the insertion of big cobalt ions in the hydrotalcite structure renders the structure less crystalline [23].
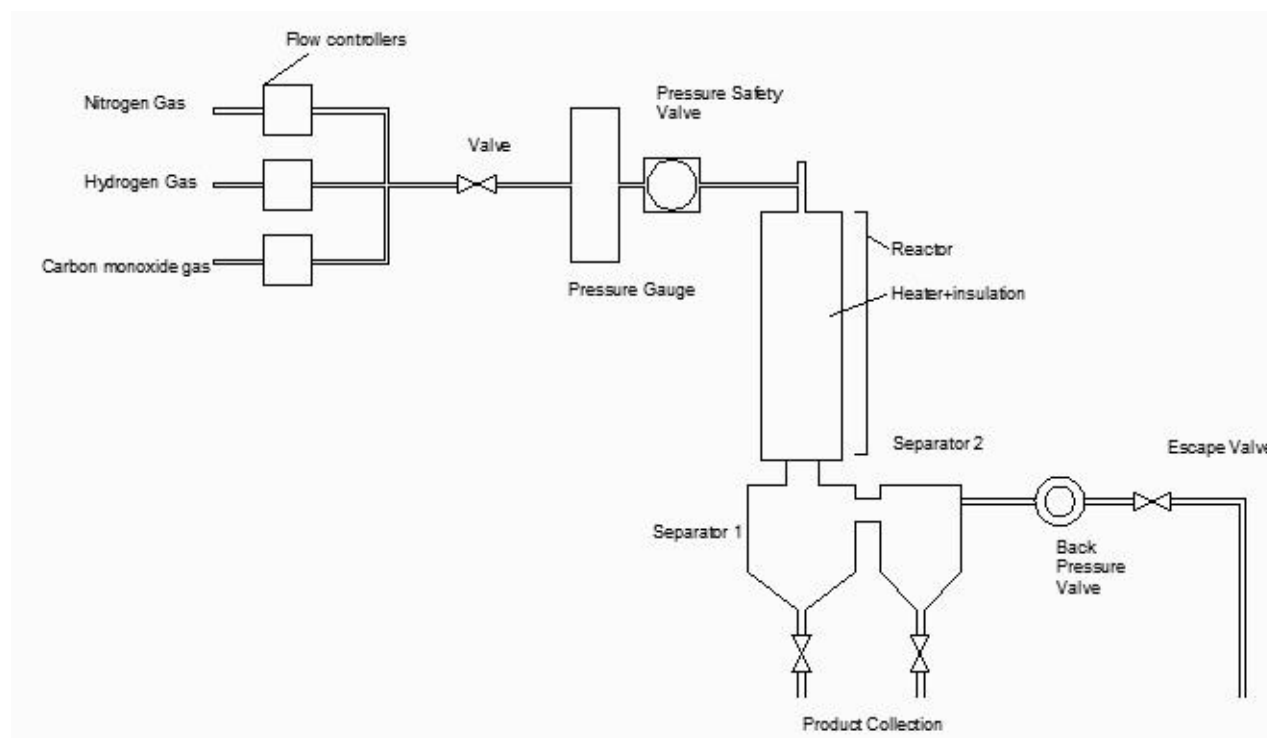

Figure 2. FTS plant diagram

3.1.2 Characterization by SEM

SEM micrographs of the calcined samples are shown in Figure 3. SEM images show the development of irregular shaped rock-like aggregates of diverse sizes with small platy particles. Most of the particles in the lattice have a size of few micrometers ranging from 1-10 µm. However, some aggregates have a size exceeding 10 µm. Elemental analysis of the catalysts prepared by both methods is shown in Table 1. 32 to 36 % cobalt loading was confirmed by EDX analysis. Samples prepared by co precipitation method showed less cobalt loading of 32 % while samples prepared by hydrothermal method showed higher cobalt loading of 36 %. The change in the oxygen percentage is a proof of other oxygenates formed in both of the synthesis methods.

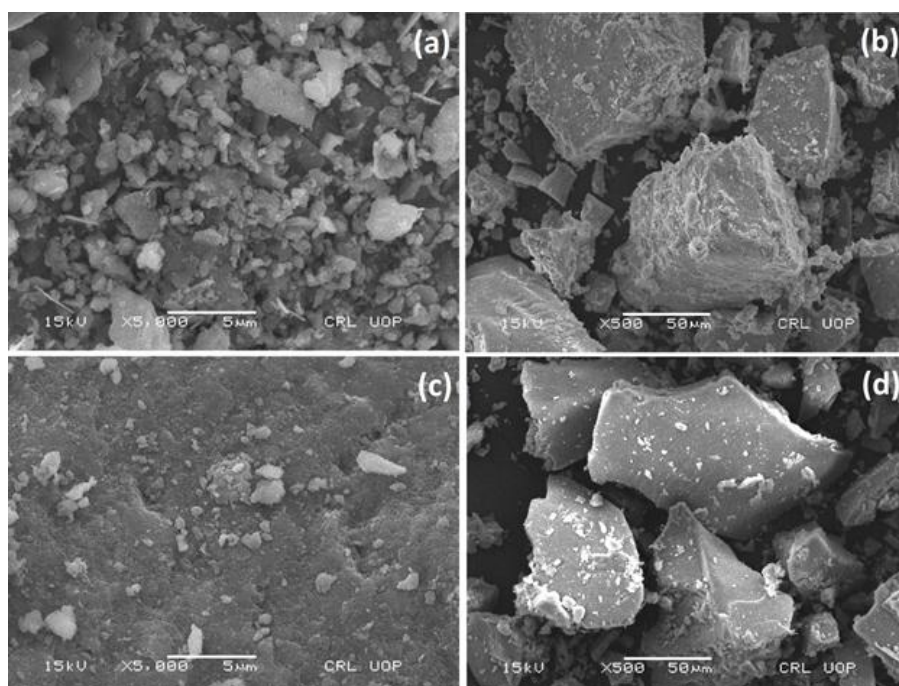### 3.1.3 Characterization by TGA

Thermal gravimetric analysis of calcined samples are performed in nitrogen atmosphere
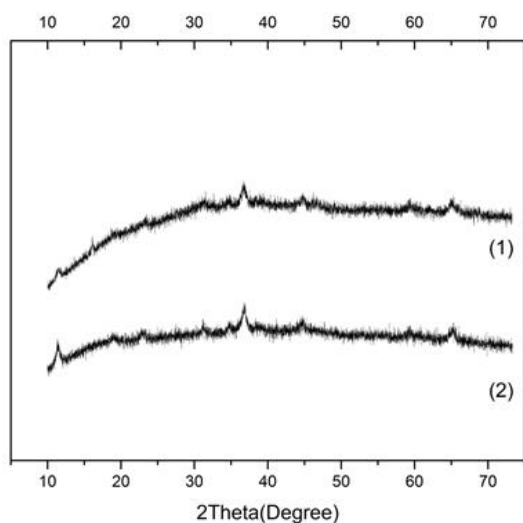
Figure 2. XRD patterns of calcined samples of (1) HT-Co-CPPT, (2) HT-Co-HT
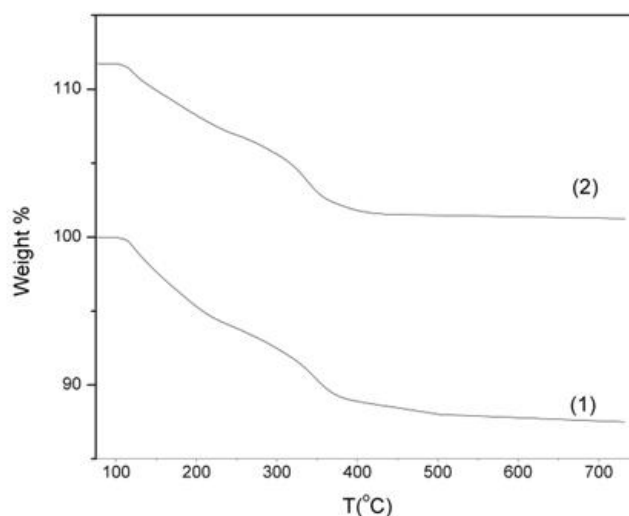
Figure 4. Thermal gravimetric analysis of (1) HT-Co-CPPT, (2) HT-Co-HT

Figure 3. SEM micrographs of HT-Co catalyst after calcination: (a) HT-Co-CPPT at X5000, (b) HT-Co-CPPT at X500, (c) HT-Co-HT at X5000, (d) HT-Co-HT at X500

are shown in Figure 4. The hydrotalcite material usually has two characteristic weight loss. The first weight loss occurs from 110 to 280 °C is due to the elimination of water of hydration from the interlayer space of the crystal. Another weight loss occurs around 280 to 370 °C. The second weight loss is mainly because of elimination of hydroxyl group (OH·) from inlaid water molecules [24,25].

3.1.4 Surface Area Characterization by BET

Nitrogen physisorption measurements were performed using Tristar II 3020 apparatus. The samples were outgassed under vacuum at 300 °C for 5 hours. Table 2 shows the surface area, pore volume, pore size and particle size of prepared catalyst. Greater surface area of 87.84 m^2/g for the samples prepared by hydrothermal method as compared to 37.88 m^2/g in case of co-precipitation method confirm the advantage of hydrothermal method over co-precipitation method. The average particle size was calculated from BET analysis by BJH method. The hydrothermal method leads to supercritical conditions which result in small particle size and larger pore volume which give higher surface area as compared to co-precipitation method [26]. The smaller average particle size and larger pore volume of the samples prepared by hydrothermal method also confirm advantages of this process [27,28].

3.1.5 Characterization by FTIR

Figure 5 shows the FTIR spectra of the two samples. It is evident from the spectra that there exists a trough around 3400 cm^{-1} in case of HT-Co-CPPT and 3700 cm^{-1} in case of HT-Co-HT, correspond to the –OH stretching between 2500 cm^{-1} and 3900 cm^{-1} [29]. The absorption at 1650 cm^{-1} corresponds to H–OH bending vibration. The Co–O stretching for the characteristic absorption of Co_3O_4 spinal phase at 668 cm^{-1} is evident from the spectra [3]. The peak around 550 cm^{-1} represents the Al_2O_3 stretching [20]. The calcined material leads to the formation of wide bands attributed to the cobalt oxide phase. After calcination, the absorption band of the nitrate anion is very insignificant due to nitrate degradation.

3.2 Catalyst testing

Table 3 shows the catalytic activity for both of our prepared catalysts HT-Co-CPPT catalyst gave 68.45 % selectivity for lighter hydrocarbons ($<C_5$) and 31.54 % of C_{5+} hydrocarbons. Similarly HT-Co-HT showed selectivity of 62.52 % for lighter hydrocarbons and 37.47 % selectivity for C_{5+} hydrocarbons. Overall the catalyst prepared by hydrothermal method
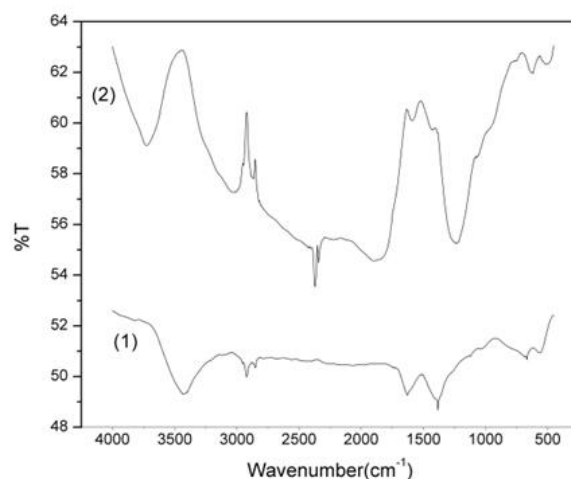

Figure 5. FTIR spectra of (1) HT-Co-CPPT, (2) HT-Co-HT

Table 1. EDS of HT-Co prepared by co-precipitation and hydrothermal method

Sample ID	Weight Percentage %				
	O	Na	Mg	Al	Co
HT-Co-CPPT	42.81	4.35	12.15	8.46	32.22
HT-Co-HT	39.64	3.75	12.34	8.39	35.89

Table 2. BET analysis of calcined catalyst prepared by co-precipitation and hydrothermal method

Sample	BET Surface Area (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)	Avg. particle size (nm)
HT-Co-CPPT	37.88	0.064	7.67	158.36
HT-Co-HT	87.84	0.142	6.61	68.3

Table 3. FTS Product analysis obtained with catalyst HT-Co-CPPT and catalyst HT-Co-HT

Catalyst	Reactor Pressure (bar)	H_2 to CO ratio	Selectivity (%)	
			$< C_5$	$\geq C_5$ to C_{27}
HT-Co-CPPT	20	2:1	68.45	31.54
HT-Co-HT	20	2:1	62.52	37.47

gave more selectivity towards C_{5+} as compared to co-precipitation method.

4. Conclusions

Hydrotalcite supported cobalt catalysts were synthesized using co-precipitation as well as hydrothermal techniques. The characterization reveals that HT-Co-HT has more cobalt metal loading and have more stable crystal structure as compared to HT-Co-CPPT. The hydrothermal method leads to a high surface area of catalyst as compared to co-precipitation method due to supercritical conditions. Catalyst testing for Fischer-Tropsch synthesis showed higher C_{5+} selectivity by catalyst prepared through hydrothermal as compared to other. Hence it is evident from the above results that hydrothermal method significantly improves crystal structure, reduction behavior, and surface area which in turns increase the catalyst activity and selectivity towards desired hydrocarbons.

Acknowledgement

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