

280. Hydrotalcite Based Cobalt Catalyst for Synthesis of Hydrocarbons from Syngas

Muhammad Faizan Sharif, Muhammad Arslan, Naseem Iqbal*

US Pakistan Centre for Advanced Studies in Energy (USPCAS-E), National University of Sciences and Technology, Islamabad
44000, Pakistan

*E-mail address: naseem@casen.nust.edu.pk

Abstract

The potential of using hydrotalcite based cobalt catalyst for Fischer Tropsch Synthesis application was studied in this paper. The hydrotalcite based cobalt (HT-Co) catalysts were prepared by using two different methods, co-precipitation and hydrothermal method. The main focus of the study is to see the effect of method of preparation on the activity and selectivity of catalyst. The catalysts were characterized by using various techniques like X- ray diffraction, scanning electron microscope, Brunauer-Emmett-Teller analysis, thermal gravimetric analysis, and Fourier-transform infrared spectroscopy. The difference between the properties and behavior of the two catalysts are shown in this study.

© 2016 "Muhammad Faizan Sharif, Muhammad Arslan, Naseem Iqbal" Selection and/or peer-review under responsibility of Energy and Environmental Engineering Research Group (EEREG), Mehran University of Engineering and Technology, Jamshoro, Pakistan.

Keywords: "Cobalt Catalyst; Hydrotalcite; Coprecipitation Method; Hydrothermal Method"

1. Introduction

Fischer Tropsch synthesis is a commercial technology that was first developed during second world war . The main purpose of this technology is to generate liquid fuels from various sources. As the world is moving towards the depletion of the oil resources and on the other hand the demand for the liquid fuel is increasing which have moved the researchers towards finding new sources that are either plenty and environmental friendly[1] . The Fischer Tropsch is one of such technology and is used for producing liquid fuels from various different sources like coal, methane gas, methane hydrates and biomass. These material are passed through gasification or steam reforming process to produce syngas which is the input material for FTS process. The FTS process used a catalyst to convert syngas into a series of hydrocarbons that can further be used as fuels[2]. Iron and Cobalt are two main active components of the catalyst used in FTS. The cobalt based catalyst usually produces lighter olefins and heavier paraffin whereas iron based catalyst produces oxygenates and branched hydrocarbons [3]. Iron is chosen while using syngas having low H₂/CO ratio whereas if that ratio is relatively high cobalt catalyst is favored [4]. Cobalt is favored because of its high activity for FTS, more stability and high selectivity for C₅+ [5].

The active component of the catalyst is usually incorporated on the surface of a supporting material and changing that support material can largely affect the properties of the catalyst. There are several compounds like activated carbon, Al₂O₃, TiO₂, SiO₂ and MgO which have been commonly used as supports for cobalt catalysts. Recently attempts were made to use hydrotalcite material as a support material for catalyst. Hydrotalcites are double or sometimes triple layered hydroxides and are generally used as a support material for catalysts used for carbon monoxide methanation[6], auto thermal reforming [7], , CO Hydrogenation[8] etc. The active component of hydrotalcite supported catalysts is implanted in the core structure of catalyst instead of surface adsorbing [9].

Attempts were made to use hydrotalcite based catalyst in FTS reactions. Those studies suggest that the high reducibility and high surface areas of hydrotalcite based cobalt catalyst renders them highly active

[8]. Apart from that, certain studies also varied the Al/Mg molar ratio in hydrotalcite structure and proposed that lower Mg/Al leads to better distribution of cobalt in the crystal [10]. Recent studies also suggest that hydrothermal method can considerably boost the catalyst activity and selectivity [11].

This study aims towards synthesis of hydrotalcite based cobalt catalyst for FT synthesis by using hydrothermal method and co-precipitation method. Potassium is used as precipitating agent because it increases C₅+ selectivity, decreases methanation, increase CO conversion and promotes water gas shift reaction. Apart from that it also helps in increasing the activity of cobalt in the FTS and prevents rapid catalyst deactivation [12]. The prepared catalysts were characterized and difference in their properties was studied.

2. Experimental

2.1. Catalyst Synthesis

First we prepared hydrotalcite based cobalt catalyst by co-precipitation method (HTCo-Cppt). The metal nitrate solution was prepared by mixing aluminium nitrate (7.03g) magnesium nitrate (8.01g) and cobalt nitrate (7.27 g) in 100 ml deionized water to get a purplish red hue. For preparing precipitating agent solution, potassium carbonate (1.94g) and potassium hydroxide (8.40g) were dissolved in 100ml deionized water to get clear solution. The metal nitrate solution was added to the later solution by drop-wise addition and provided with constant stirring. After complete mixing the pH of the solution was brought down to 8-9 by adding concentrated nitric acid. Then the solution was heated at 80°C for 16 h while constantly stirring to mature precipitates. After that the solution was filtered followed by precipitates washing with distilled water. After washing the precipitates were subjected to oven drying at 80°C overnight to get purple colored solid. The sample was then calcined at 600°C for 7 h in an airtight furnace.

Second we prepare hydrotalcite based cobalt catalyst by hydrothermal method (HTCo-Ht) using the same concentrations of solutions as mentioned in the above method. The only difference between two methods is the process used for maturation of precipitates. The solution was added to a hydrothermal autoclave and heated at 80°C for 16 h. In hydrothermal autoclave we are providing temperature along with pressure whereas coprecipitation process only uses temperature for maturation of precipitates. The precipitates were filtered and washed thoroughly with distilled water and then oven dried at 80°C overnight. After drying, purple colored solid was calcined at 600°C for 7 h in an airtight furnace.

2.2. Catalyst characterization

The prepared samples were characterized by using various characterization techniques like X-Ray diffraction spectroscopy (XRD), Scanning Electron Microscopy (SEM), Brunauer–Emmett–Teller (BET), Thermal Gravimetric Analysis (TGA) and Fourier Transform Infrared (FTIR). XRD is performed using STOE Powder Diffraction System and SEM and EDS were done with a JEOL, JED 2300 Analysis Station. FT-IR spectra of the prepared samples were recorded at room temperature using PerkinElmer Spectrum 100 Spectrometers. Brunauer–Emmett–Teller (BET) was performed using Tristar II 3020 apparatus whereas nitrogen was used as adsorbate.

3. Results and Discussion

3.1. Scanning Electron Microscope

SEM images of HTCo-Cppt are shown in Figure 1a. It is quite evident from the figure that the particles are of irregular shape and sizes however when viewed at larger resolution they show relatively plain particle symmetry. It can also be observed that average particle size of samples prepared by coprecipitation method is large as compared to hydrothermal method.

3.2. Energy Dispersive Spectroscopy

Elemental analysis of the samples is given in Table 1. HTCo-Cppt have approximately 1.02% potassium and HTCo-Ht have around 1.90% potassium. This small percentage may boast a little the activity of catalyst HTCo-Ht. However the cobalt percentage of HTCo-Ht is less than other counterpart. The HTCo-Cppt have less potassium but at the same time its cobalt loading percentage is way more than HTCo-Ht.

In other words the EDS suggest that catalyst prepared by coprecipitation method may have more catalytic ability than hydrothermal method.

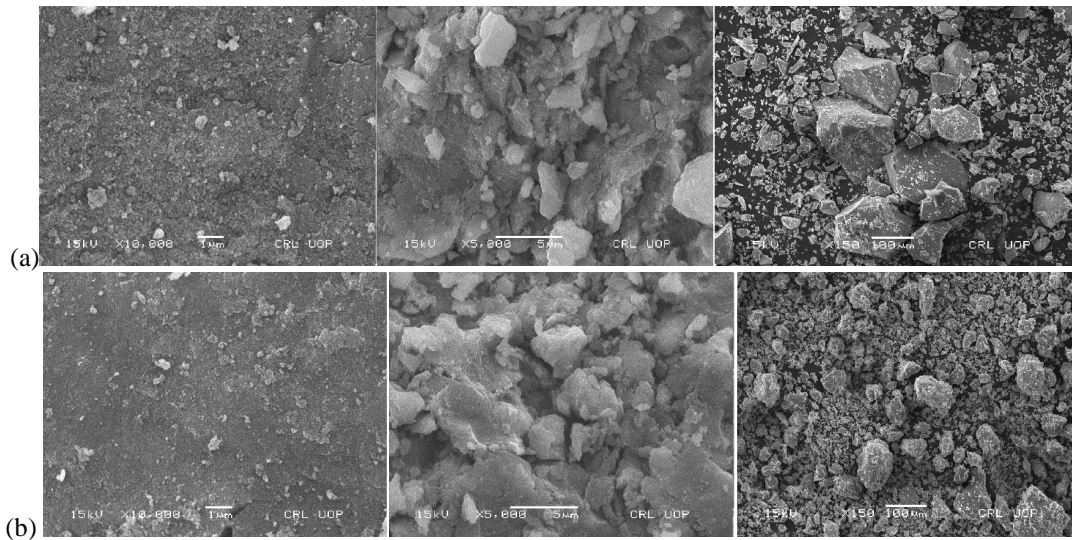


Fig. 1. SEM images of (a) HTCo-Cppt (b) HTCo-Ht.

Table 1. EDS of HTCo prepared by coprecipitation and hydrothermal method

Catalyst	O (%)	K (%)	Mg (%)	Al (%)	Co (%)
HTCo-Cppt	36.07	1.02	11.50	9.75	41.66
HTCo-Ht	38.97	1.90	12.13	10.48	36.52

3.3. X-Ray Diffraction Spectroscopy

XRD pattern of HTCo-Cppt and HTCo-Ht are shown in the Figure 2. There peaks around 31°, 37°, 44.8°, 65° which are the characteristics peaks for different planes of cobalt oxide[13]. Cobalt develops into hexagonal close packed structures (hcp) however at high pressure where the magnetism is effectively repressed, we expect a shift from hcp to fcc (face centered cubic structure) [14].

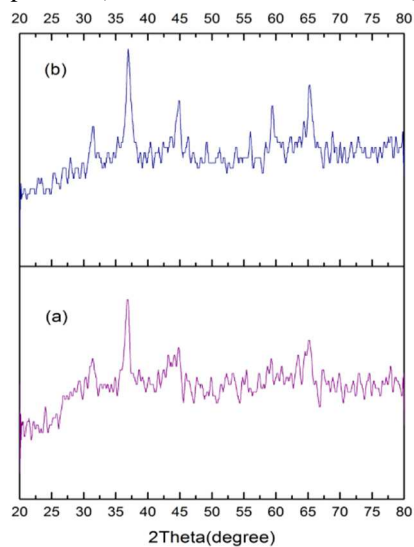


Fig. 2. XRD Patterns of (a) HTCo-Ht (b) HTCo-Cppt.

3.4. Thermal Gravimetric Analysis

TGA of the HTCo-Cppt sample is given in the Figure 3. The catalyst shows typical hydrotalcite behaviour and give two weight losses. The curve suggests that weight of sample starting to fall till 220 °C. This is due to the hydration water removal from the interlayer space of crystal. Between 220 to 410 °C another weight loss occurs which shows the removal of OH- group from inlayered water molecules [15]

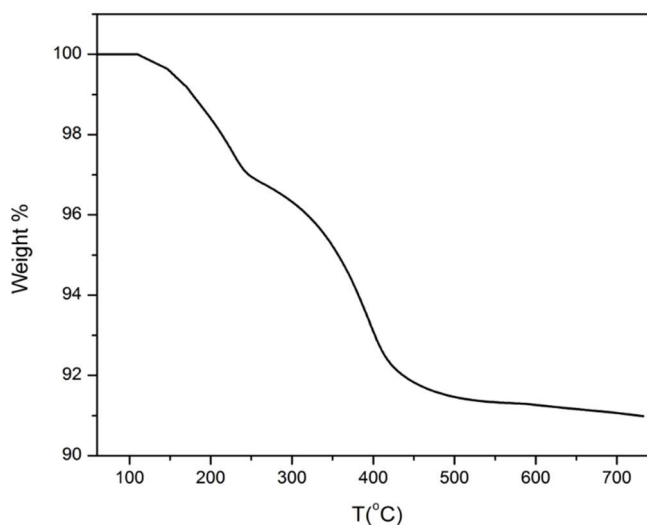


Fig. 3. TGA Graph of HTCo-CpPt.

3.5. Brunauer–Emmett–Teller

BET of the HTCo-CpPt is shown in the Table 2. The table suggests that the average particle size of the sample is around 52.83 nm. The pore volume is very small so there is a very small chance of diffusion. However the pore size is large and there is a very little chance of blocking of pore mouth. The surface area value shows that the HTCo-CpPt have appropriately large surface area hence there is bigger playground for FTS reaction. The pore size of HTCo-CpPt is 6.33 nm so the majority of the pores fall under the category of mesopores (2nm < size < 50nm) [16].

Table 2. BET Analysis of HTCo-CpPt

Catalyst	BET Surface Area (m ² /g)	Pore volume (cm ³ /g)	Pore size (nm)	Avg. particle size (nm)
HTCo-CpPt	114.9709	0.1819	6.33	52.836

3.6. Fourier Transform Infrared

The FTIR spectra of the HTCo-CpPt shows that there exists a depression around 3400 cm⁻¹ which is due to the hydroxyl stretching [17]. The bending vibrations due to H and OH bond is creating a depression around 1650 cm⁻¹. There is another depression around 660cm⁻¹ which is due to cobalt oxide (Co-O stretching) [9]. The calcination of the sample results in the formation of huge bands due to the cobalt oxide phase. The depression around 550 cm⁻¹ is attributed to the Al₂O₃ stretching [15].

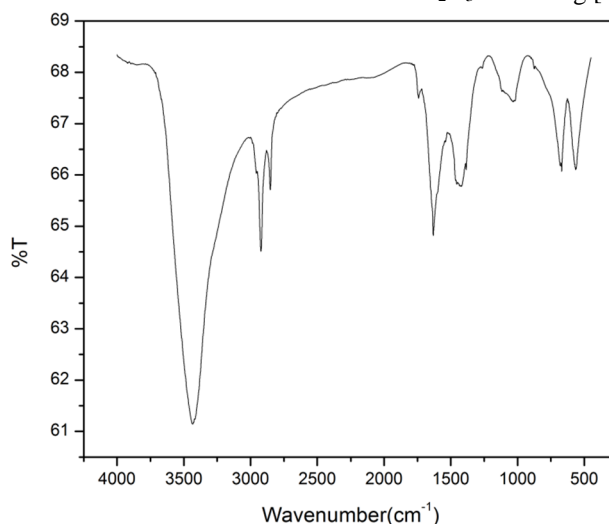


Fig. 4. FTIR Spectra of HTCo-CpPt.

4. Conclusion

The Hydrotalcite based cobalt catalysts were prepared using both hydrothermal and coprecipitation methods. The characterization suggests that HTCo-Cppt (Coprecipitation method) have the high cobalt loading and more stable crystal structure as compared to other counterpart. HTCo-Cppt has fairly large surface area which can increase reaction rate. These developed catalyst have potassium in their core structure which itself have the promoting ability for FTS. The overall crystal structure and the properties of catalyst suggests that using this catalyst (HTCo-Cppt) in FTS can increase the yield and selectivity towards desired hydrocarbons.

Acknowledgements

- Dr. Naseem Iqbal
- Dr. Nisar Ahmad
- Dr. Tayabba Noor
- Muhammad Arslan
- Saeed Iqbal
- Amin Durrani

References

- [1] S. Mousavi, A. Zamaniyan, M. Irani, and M. Rashidzadeh, "Generalized kinetic model for iron and cobalt based Fischer–Tropsch synthesis catalysts: Review and model evaluation," *Applied Catalysis A: General*, vol. 506, pp. 57-66, 2015.
- [2] A. Tavasoli, R. M. M. Abbaslou, M. Trepanier, and A. K. Dalai, "Fischer–Tropsch synthesis over cobalt catalyst supported on carbon nanotubes in a slurry reactor," *Applied Catalysis A: General*, vol. 345, pp. 134-142, 2008.
- [3] E. Iglesia, "Design, synthesis, and use of cobalt-based Fischer-Tropsch synthesis catalysts," *Applied Catalysis A: General*, vol. 161, pp. 59-78, 1997.
- [4] A. Y. Khodakov, W. Chu, and P. Fongarland, "Advances in the development of novel cobalt Fischer-Tropsch catalysts for synthesis of long-chain hydrocarbons and clean fuels," *Chemical Reviews*, vol. 107, pp. 1692-1744, 2007.
- [5] G. Jacobs, C. Bertaux, V. R. R. Pendyala, W. D. Shafer, J.-S. Poirier, Q. Xiao, *et al.*, "Fischer-Tropsch synthesis: Cobalt catalysts on alumina having partially pre-filled pores exhibit higher C₅₊ and lower light gas selectivities," *Applied Catalysis A: General*, vol. 516, pp. 51-57, 2016.
- [6] L. He, Q. Lin, Y. Liu, and Y. Huang, "Unique catalysis of Ni-Al hydrotalcite derived catalyst in CO₂ methanation: cooperative effect between Ni nanoparticles and a basic support," *Journal of Energy Chemistry*, vol. 23, pp. 587-592, 2014.
- [7] K. Takehira, T. Shishido, P. Wang, T. Kosaka, and K. Takaki, "Autothermal reforming of CH₄ over supported Ni catalysts prepared from Mg–Al hydrotalcite-like anionic clay," *Journal of Catalysis*, vol. 221, pp. 43-54, 2004.
- [8] Y.-T. Tsai, X. Mo, A. Campos, J. G. Goodwin, and J. J. Spivey, "Hydrotalcite supported Co catalysts for CO hydrogenation," *Applied Catalysis A: General*, vol. 396, pp. 91-100, 2011.
- [9] A. Di Fronzo, C. Pirola, A. Comazzi, F. Galli, C. Bianchi, A. Di Michele, *et al.*, "Co-based hydrotalcites as new catalysts for the Fischer–Tropsch synthesis process," *Fuel*, vol. 119, pp. 62-69, 2014.
- [10] A. Forgionny, J. Fierro, F. Mondragón, and A. Moreno, "Effect of Mg/Al Ratio on Catalytic Behavior of Fischer–Tropsch Cobalt-Based Catalysts Obtained from Hydrotalcites Precursors," *Topics in Catalysis*, vol. 59, pp. 230-240, 2016.
- [11] J. Zhang, S. Lu, S. Fan, T. Zhao, and K. Zhang, "Hydrothermal preparation of Fe-Mn catalyst for light olefin synthesis from CO hydrogenation," *Nano Reports*, vol. 1, 2015.
- [12] H. Jahangiri, J. Bennett, P. Mahjoubi, K. Wilson, and S. Gu, "A review of advanced catalyst development for Fischer–Tropsch synthesis of hydrocarbons from biomass derived syn-gas," *Catalysis Science & Technology*, vol. 4, pp. 2210-2229, 2014.
- [13] M. Trépanier, A. K. Dalai, and N. Abatzoglou, "Synthesis of CNT-supported cobalt nanoparticle catalysts using a microemulsion technique: role of nanoparticle size on reducibility, activity and selectivity in Fischer–Tropsch reactions," *Applied Catalysis A: General*, vol. 374, pp. 79-86, 2010.

- [14] C.-S. Yoo, P. Söderlind, and H. Cynn, "The phase diagram of cobalt at high pressure and temperature: the stability of-cobalt and new-cobalt," *Journal of Physics: Condensed Matter*, vol. 10, p. L311, 1998.
- [15] J. Perez-Ramirez, G. Mul, F. Kapteijn, and J. Moulijn, "A spectroscopic study of the effect of the trivalent cation on the thermal decomposition behaviour of Co-based hydrotalcites," *Journal of Materials Chemistry*, vol. 11, pp. 2529-2536, 2001.
- [16] G. Leofanti, M. Padovan, G. Tozzola, and B. Venturelli, "Surface area and pore texture of catalysts," *Catalysis Today*, vol. 41, pp. 207-219, 1998.
- [17] J. T. Kloprogge and R. L. Frost, "Fourier transform infrared and Raman spectroscopic study of the local structure of Mg-, Ni-, and Co-hydrotalcites," *Journal of Solid State Chemistry*, vol. 146, pp. 506-515, 1999.