PREPARATION AND CHARACTERIZATION OF BIMETALLIC Fe-Co / Al_2O_3 FOR HYDROGENOLYSIS OF GLYCEROL

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Abstract

Production of value added chemical product from glycerol, used as a co-product in biodiesel, is essential in sustaining bio-diesel industry. The Fe-Co catalyst over alumina is developed and characterized for application in the hydrogenolysis of glycerol using in situ hydrogen, produced during dehydrogenation of glycerol to lactic acid. The catalyst Fe-Co was developed by wet impregnation method and was subsequently loaded on alumina. The loaded catalyst was characterized by FTIR, SEM and XRD to analyze their structure & structural morphology and their potential application for the hydrogenolysis reaction of glycerol is analyzed.

***Keywords:** Bimetallic, Characterization, Hydrogenolysis, and Glycerol Etc…*

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1. INTRODUCTION

As the concern about the greenhouse gas is increasing, more and more efforts are being made for the production of biodiesel and the significance of renewable energy is being realized owing to depleting fossils fuel and degrading environment. Global biodiesel production has tremendously increased for the past ten years and in US alone the production is predicted to grow to approximately 912 million gallons in 2015 [1].

The main by-product in biodiesel production is a polar, non-toxic, biodegradable, recyclable glycerol which is having promising physical and chemical properties [3]. However with each mole of triglycerides converted to biodiesel, one mole of glycerol is produced [2]. Due to biodiesel growth, glycerol is available to the market in abundant quantity and has made the market saturated which result in over supply and reduced cost [4]. Many value added chemical can be produced from Glycerol which will open a new market for glycerol application and can improve the sustainability of biodiesel production. It is a remarkable point to note that glycerol has been selected as one of the top 12 platform chemical from biomass and its conversion to useful chemical has been widely investigated in recent years [5].

One of the important glycerol application is the hydrogenolysis of glycerol to produce 1,2-propanediol (propylene glycol), traditionally derived from propylene oxide, and 1,3-propanediol, used as a monomer in the manufacturing of polyester fibers [6]. The process involves the reaction of glycerol with hydrogen in the presence of heterogeneous catalyst which involves two steps. The first steps is in the formation of intermediate acetol or 3-hydroxypropanol, followed by second steps of hydrogenation of acetol and 3-hydrooxypropanol to a final product of 1,2- propanediol or 1,3- propanediol respectively [7]. The glycerol hydrogenolysis reaction is carried out at high H_2 pressure of above 10MPa and it involves the breaking of C-O bond with the simultaneous addition of hydrogen. The external hydrogen is usually obtained from fossils feedstock's which involve additional purchase and handling costs. Hence this way, depending on the external hydrogen source, the developed propylene glycol (PG) process, which was supposed to be based on renewable resources, would become dependent on fossil fuels. It is important to note that during glycerol to PG conversion process, partly dehydrogenation of glycerol to lactic acid (LA) takes place which is associated with release of hydrogen gas, which could potentially allow in situ transformation of glycerol to PG by hydrogenation of intermediate lactic acid to desired propylene glycol [2]. Despite many research attempts, the requirement of external hydrogen presents one of the major drawbacks of the glycerol hydrogenolysis technology [8].

In view of the aforementioned challenges, we had prepared a bimetallic Fe-Co catalyst over alumina support which can be used for hydrogenolysis of glycerol derived from biodiesel. The catalyst was supported on Alumina (Al_2O_3) support, as Al_2O_3 has many active sites and provides a rich adsorption sites for hydroxyl compound. The prepared catalyst was characterized using FTIR, SEM, & XRD to study their structural morphology so as to analyze their suitability for their usage in Hydrogenolysis reaction of glycerol at optimum temperature and pressure. The surface area of the prepared catalyst was determined by using BET method.

2. EXPERIMENT

2.1 Materials

Analytical grade catalyst precursor salt cobalt (II) nitrate Hexahydrate and ferric Nitrate (non-Hydrate) are procured from LOBA Chemie Pvt Ltd. (Mumbai), Alumina oxide as an active support material was obtained from Molychem Pvt Ltd. (Mumbai, India). Deionised water was kindly purchased from organo laboratories (New Delhi, India).

2.2 Catalyst Preparation

Bi-metallic supported catalysts were prepared by the incipient wet impregnation method at some elevating temperatures. An aqueous solution of cobalt nitrate and ferric nitrate of equal weight proportion (5 grams each) was prepared in 20 ml of water. The resulting aqueous solution was stirred continuously for 3 hours on hot plate magnetic stirrer at 80° C and about 350 rpm. After stirring for 3 hours the precipitate formed was dried in vacuum oven for 4 hours at 120°. The dried precipitate was calcined at 350° C for 2 hours. The calcined solid obtained was thick, compact and lumped mass particle which is crushed to a powder form [10].

2.3 Catalyst Casting On Support

The aluminum Oxide (approximately) 9 g is dissolved in 20 ml of deionized water. The 1 gm of powdered catalyst is then mixed with the resulting aqueous alumina solution and is stirred in magnetic stirrer at 80° C for 30 minutes. The resulting mixture is then dried at 160° C in oven for 4 hrs, followed by calcinations at 320° C for 3 hrs. In this way the catalyst is loaded on alumina support [9].

2.4 Catalyst Characterization

The crystalline morphology of the prepared catalyst sample was determined by X-ray powder diffraction (XRD, Tam Panalytical Empyrean) technology using Cu-Kα radiation of wavelength 1.542 Å operating at 40 KV and 30 mA. The measurement was carried out over 2θ range of angle 10^0 to 65^0. The structural morphology of the Fe-Co catalyst was analyzed by scanning electron microscope (SEM, Carl Zeiss Ultra Plus Analyzer)

To identify the Fe-Co group introduced by the loading of catalyst on the support, the FTIR spectra of unloaded and loaded alumina are obtained using AGILENT technologies spectrometer in the range of 4000 to 500 cm^{-1} as shown in fig. The surface area per unit volume of a catalyst was obtained from Brunauer-Emmett-Teller (BET) method over the relative pressure range of 0.05-.020 psi [11].

3. RESULT AND DISCUSSION

3.1 X-Ray Diffraction (XRD)

XRD Characterization peaks represent the crystalline structure of Fe-Co/ Al_2O_3. Lattice indices of the various peaks at their respective 2theta values were calculated using Bragg’s law. The lattice value of Fe_2O_3 is (331) and the corresponding 2theta value is 36.7 The analysis of the above values reveals it is a simple cuboids structure and the crystal system is FCC. For the Co_3O_4, lattice values are (420) & (333) and corresponding 2theta values are 38.30 & 45.43 respectively. By analyzing the Co_3O_4 lattice and 2 theta values, it is simple cuboids with crustal system being FCC . For bimetallic catalyst along with characteristic peaks of Co_3O_4 & Fe_2O_3, diffraction peaks of $CoFe_4O_4$ also appeared at 2 theta values of 14.37, 28.07 & 48.98 and their respective lattice values are (111), (311) & (440). This appearance confirms the formation of complex oxide. The peak analyses reveals that the crystallinity is in increasing order of Fe_2O_3 < Co_3O_4 < $CoFe_4O_4$. The average particle size is calculated using Scherrer equation and the values lies between 10 to 40 nm [12-13]. The XRD pattern is shown in fig 1.

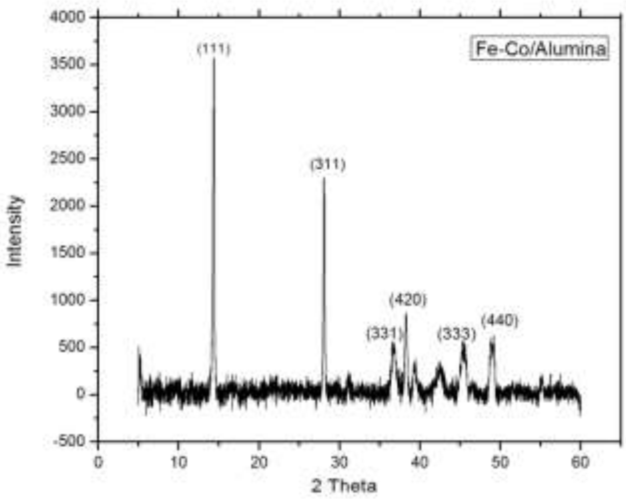


Fig. 1: XRD image

3.2 Scanning Electron Microscope

The SEM characteristic of the prepared catalyst at 10 KV acceleration voltages has been used to analyze change in structural morphology of the Fe-Co catalyst after loading on Alumina. The SEM picture of loaded catalyst is shown in fig 2. The powdered sample was kept under vacuum in a gold coated form so that it can conduct electrons effectively. The observed morphological structure of a catalyst is a result of a systematic alignment of aggregated nanoparticles and random self assembly of cubic like structure which consequently reduce high surface energy. Large abundant void space present due to specific structure which provides active sites for the adsorption of reactants on the catalyst surface [14].

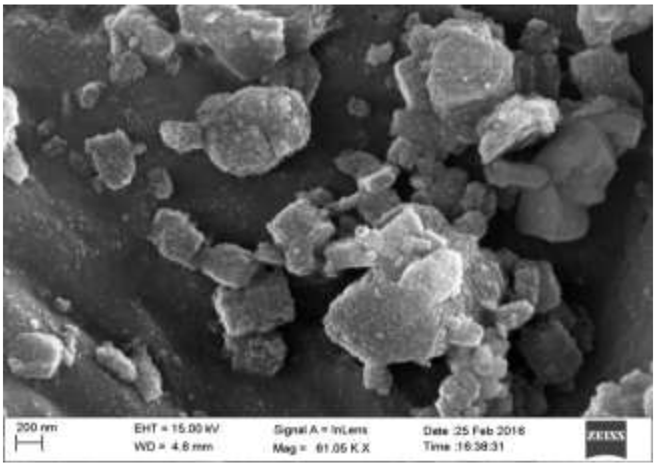


Fig. 2: SEM picture of loaded catlyst

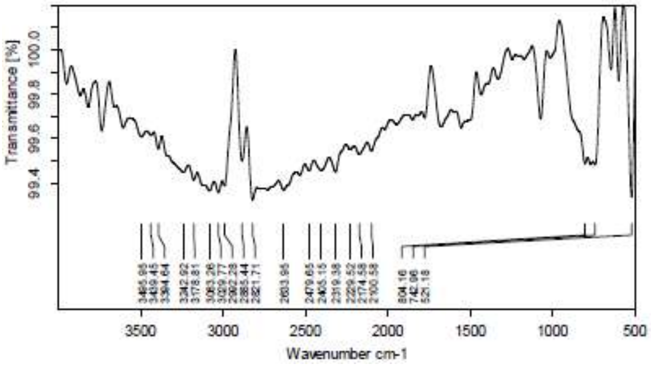
3.3 Fourier Transform Infrared Radiation

The FTIR analysis was performed on a Bruker vector 22 instrument in the wave number range of 4000-500 cm-1. For FTIR analysis, the sample was initially grinded with KBR pellets followed by pressing to 1 mm thick film. Fig. 3(a) shows the FTIR spectrum of unloaded alumina support whereas fig 3(b) indicate the FTIR spectrum of 10% Fe-Co catalyst loaded on alumina support.

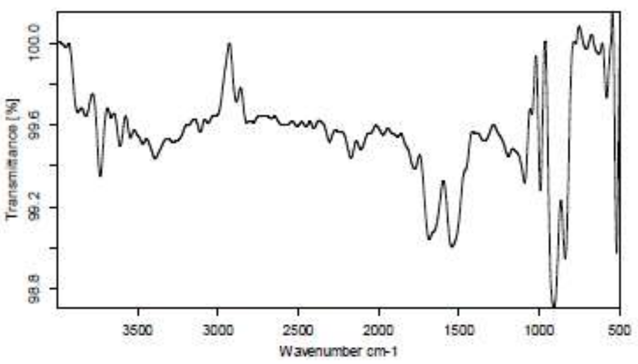
Major's peaks could be observed at 707 cm^{-1}, 838 cm^{-1}, 1545 cm^{-1}, 1776 cm^{-1}, 3469 cm^{-1} and 3824 cm^{-1}. The peak below 1000 cm-1 represent Alumina support and metal oxides (Fe_2O_3, Co_3O_4) arising from inter-atomic vibration. The peaks 3825 cm^{-1} indicate the presence of hydroxyl group whereas peaks 1776 cm^{-1} and 3469 cm^{-1} are attributed to the adsorbed water molecules [15].

The notable peaks of 1685 cm^{-1} and 1545 cm^{-1} in the figure 3(b) indicate the presence of C=0 group and C=N groups respectively. The presence of C=O and C=N functional group specify the presence of Fe-Co complex on the surface of alumina support [16].

On comparing the two spectra in the range of 1340 cm^{-1} and 1780 cm^{-1}, the absence of major peaks in the fig. 3(a) implies the absence of catalyst loading on the support whereas presence of peak in the same range of fig. 3(b) indicate that the catalyst has been successfully introduced on the support matrix.



(a)



(b)

Fig. 3: FTIR Spectra: (a) unloaded Alumina support; (b) loaded Catalyst on alumina

3.4 BET Analysis

The surface area per unit volume of a catalyst was calculated using Brunauer-Emmett-Teller (BET) method over the relative pressure range of 0.05-.020 psi. The average BET surface area of the 10% Fe-Co catalyst over alumina was 117.6 m^2/g and the average pore diameter was 7.1 nm.

4. CONCLUSION

The Fe-Co /Al_2O_3 was prepared by wet impregnation method and was characterized to study its structural morphology so as to facilitate it usage in hydrogenolysis reaction of glycerol. The characterization study reveals that the catalyst Fe-Co was successfully loaded on alumina support and is crystalline in structure as verified by sharps peaks from XRD. The binding energy between metal and oxygen in their oxides greatly affect the catalyst reducibility. As a consequence of reducibility , the amount of active sites and catalytic activity in Fe-Co/ Al_2O_3 greatly increased.

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