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Study of Ni-Cu/Al_2O_3 Catalyst for Hydrodeoxygenation of Karanja Oil

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Bio-oil is considered as a potential alternative for conventional fossils fuel. The aim of the present study is the preparation and characterization of Ni-Cu/Al_2O_3 using impregnation methods for the hydrodeoxygenation of karanja oils. It can be catalytically converted to bio-fuels by hydrodeoxygenation process. There is a need to develop a low cost catalyst, which can reduce the operating condition for hydrodeoxygenation process. The Ni-Cu catalyst over alumina is developed and characterized for application in the reaction of karanja oil at low temperature and pressure. The catalyst Ni-Cu 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 and structural morphology and there potential application for the hydrodeoxygenation process at low temperature and pressure.

Keywords: Renewable and cleaner energy, Ni-Cu catalyst, Hydrodeoxygenation, Catalyst.

INTRODUCTION

A lot of work has been done on bio-based fuel production from rapeseed oil, palm oil, soybean oil, karanja oil, waste cooking oil *etc.* [1]. Bio-oil is a viscous, acidic and polar liquid with a low heating value. In most of the cases, bio-oil used directly in engine as a fuel is not suitable and inefficient. It is not suitable for direct engine use and are associated with its high level of water content (10-30 wt %) and also because of oxygen containing compound (30-40 wt% O_2) in the oil [2]. The bio-fuel properties are greatly influenced by the oxygen content of the bio based fuel. The high oxygen content resulted in low heating value, chemical instabilities, thermal degradation, insolubility with fossils fuel and higher tendencies for polymerization [3]. The quality of bio-oil has been improved by the development of a range of catalytic reforming method. The two most common used catalytic reforming methods are atmospheric pressure catalytic cracking and high pressure hydrodeoxygenation. Atmospheric pressure catalytic cracking over zeolite yields low result and the oxygen contained is high along with the formation of aromatic compound. On the other hand hydrodeoxygenation is the process of removing oxygenated compound basically in the form of water molecule using hydrogen in the presence of catalyst such as nickel-molybdenum, which is supported on alumina and zeolite [4]. The hydrodeoxygenation process reduces the oxygen content of oil with a corresponding increase in the heating value of the fuel. Thus the hydrodeoxygenation process can produce high quality bio-fuel than the catalytic cracking process and is a promising process in the production of bio based transportation fuel [5]. Bio-fuel can be produced by treating bio-oil with hydrogen at an elevated pressure of upto 200 bar and high temperature in the range of 200 to 400 °C. This process result in the conversion of oxygen compound into water and free fatty acid is converted into hydrocarbon chain, which is equivalent to crude oil. The hydrocarbon product can be easily separated from unconverted bio-oil by gravity settling method as the density of hydrocarbon compound is less than the bio-oil [6]. The major drawback of hydrodeoxygenation process is harsh operating condition like high pressure and high temperature. This make the process cost intensive [7,8]. So one of the challenges is to discover the catalyst, which is having high activity, high thermal stability, relatively inexpensive and can make the deoxygenation reaction to occur at low operating pressure and temperature [9,10]. In view of the aforementioned challenges, we had prepared a Ni-Cu catalyst, which can be used for hydrodeoxygenation of karanja oil, a bio-oil. 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 oxy-compound. The prepared catalyst was characterized using FTIR, SEM and XRD to study their structural morphology so as to analyze their suitability for their usage in hydrodeoxygenation reaction at low temperature and pressure. The surface area of the prepared catalyst was determined by using BET method.

EXPERIMENTAL

Analytical grade nickel nitrate, cupric nitrate, aluminum oxide (active), methanol are procured from Mayhem (Mumbai, India). Deionized water from organo laboratories (New Delhi, India). Hydrogen and nitrogen was obtained from Vadilal Chemical Ltd. (Baroda, India).

Catalyst preparation: The catalysts was prepared by wet impregnation method, by using a mixture of nickel and copper each of 5 g and is thoroughly mixed with 20 mL of deionized water in magnetic stirrer at 80 °C and is kept for 3 h. The resulting mixture is washed with deionized and is dried at 160 °C for 4 h in oven. The dried mixture is then calcined at 220 °C for 3 h. The catalyst prepared in these ways is crushed to a powder as it is thick, compact, lumped mass particle.

Catalyst casting on support: The aluminum oxide (Al_2O_3) of 9.80 g is dissolved in 20 mL of methanol. The 0.2 g of powdered catalyst is then mixed with the resulting methanol alumina solution and is stirred in magnetic stirrer at 80 °C for 30 min. The resulting mixture is then dried at 160 °C in oven for 4 h, followed by calcinations at 220 °C for 3 h. In this way the catalyst is loaded on alumina support [11] and represented as Ni-Cu/Al_2O_3.

Catalyst characterization: The crystalline morphology of Ni-Cu/Al_2O_3 catalyst was analyzed using X-ray diffraction (XRD, Tam PANalytical Empyrean) in reflection mode using Cu-Co radiation of wavelength 1.598 Å at 35 kV and 40 am. Scanning electron microscope (Carl Zeiss Ultra plus analyzer) maintained at 15 kV acceleration voltage has been used to analyze the structural morphology of the Ni-Cu catalyst. To identify whether the Cu-Ni group is introduced to the alumina support or not, the FTIR spectra of the unloaded alumina support and loaded support are obtained using AGILENT technologies spectrometer in the range of 4000 to 500 cm^{-1}. The surface area per unit volume of a catalyst was obtained from Brunauer-Emmett-Teller (BET) method over the relative pressure range of 0.05-0.20 psi [12].

RESULTS AND DISCUSSION

X-ray diffraction: X-ray diffraction characterization peaks represent the crystalline structure of Ni-Cu/Al_2O_3. Lattice indices of the various picks at their respective 2θ values were calculated using Bragg's law. The lattice values of NiO are (001), (110) and (111) and the corresponding 2θ values are 19.601, 39.269 and 50.317, respectively. The analysis of the above values reveals it is a simple cuboids structure and the crystal system was monoclinic. For the CuO, lattice values are (010), (101) and (111) and corresponding 2θ values are 8.35, 10.59 and 13.50, respectively. By analyzing the CuO lattice and 2θ values, it is an orthorhombic structure and the crystal system is FCC [13]. The XRD pattern is shown in Fig. 1.

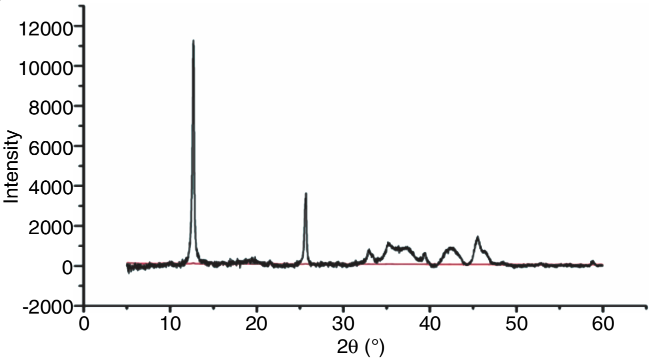

Fig. 1. XRD patterns of Ni-Cu/Al_2O_3 support

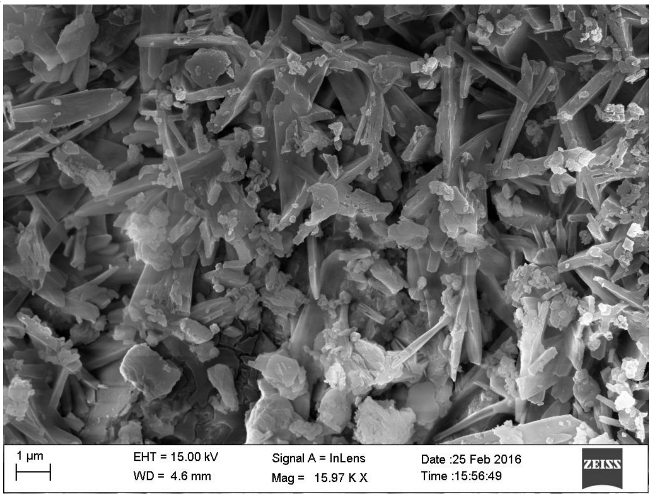

Fig. 2. SEM image of Ni-Cu/Al_2O_3

Scanning electron microscope: The SEM characteristic of the prepared Ni-Cu/Al_2O_3 catalyst at 10 kV acceleration voltages has been used to analyze change in structural morphology of the Ni-Cu 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 needle 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].

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 supports whereas Fig. 3(b), 3(c) and 3(d) indicate the FTIR spectrum of 10, 5 and 2 % Ni-Cu catalyst loaded on alumina, respectively.

Major's peaks could be observed at 530, 710, 1400, 1687, 2370 and 3450 cm^{-1}. The peak below 1000 cm^{-1} represents alumina support and metal oxides (NiO, Cu_3O_4) arising from inter-atomic vibration. The peaks 1400, 1649 and 3450 cm^{-1} are attributed to the adsorbed water molecules [15].

The notable peaks of 1687 cm^{-1} and 1565 cm^{-1} in the Fig. 3(b), 3(c) and 3(d) indicate the presence of C=O group and C=N groups, respectively. The presence of C=O and C=N functional group specify the presence of Ni-Cu complex on the surface of alumina support [16].

On analyzing the above spectrum, we infer that in the range of 1687 and 1677 cm^{-1} of Fig. 1 there is no loading of catalyst, but when compared with Fig. 3(b), 3(c) and 3(d) in the same corresponding range, there is appreciable wideness

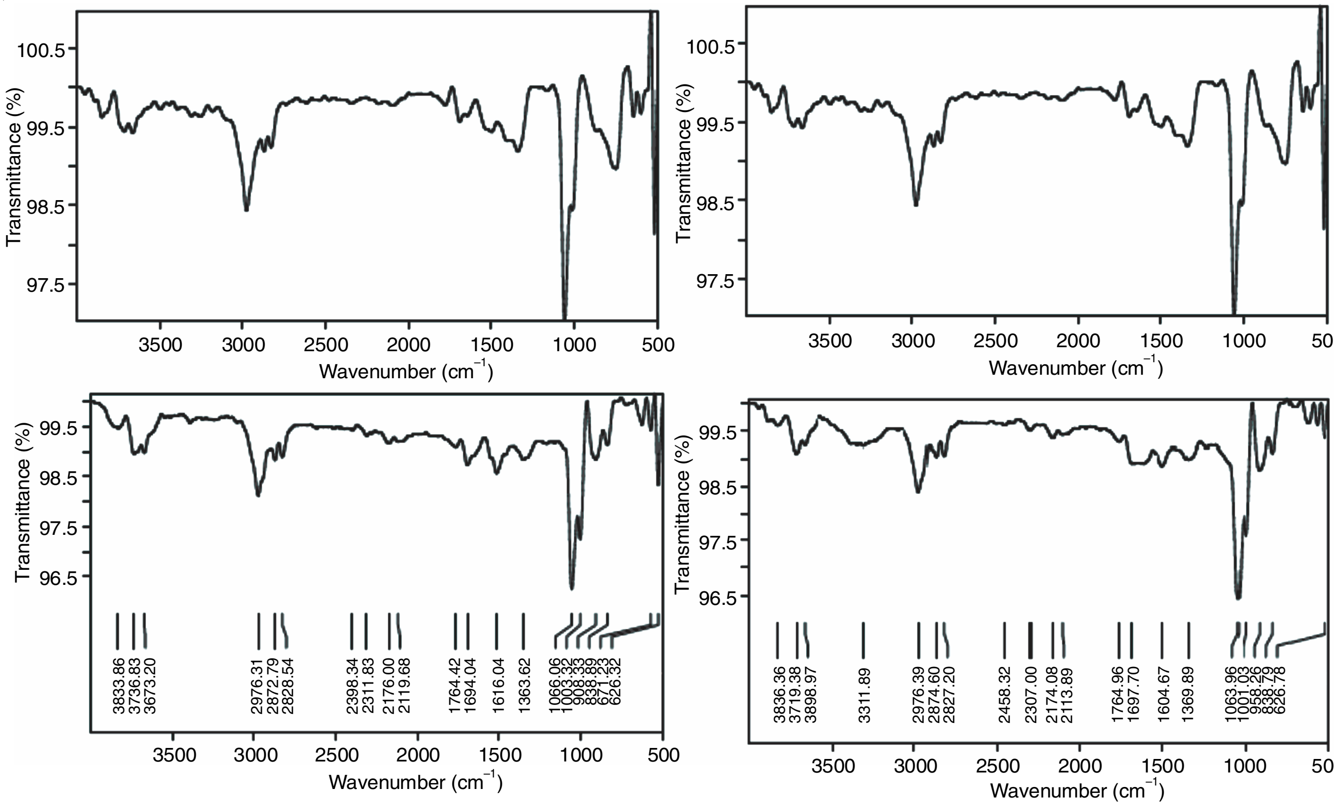

Fig. 3. FTIR spectra (a) Al_2O_3 support (b) 10% Ni-Cu/Al_2O_3 (c) 5% Ni-Cu/Al_2O_3 (d) 2% Ni-Cu/Al_2O_3

and remarkable change in area of the peak which shows that the catalyst Ni-Cu has been successfully loaded. The wideness in peak of Fig. 3(b), 3(c) is narrow and flat respectively whereas the peak in Fig. 3(d) is remarkable and appropriate which lead to the optimum loading of 2 % catalyst which could give the better results.

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 0.05-0.020 psi. The average BET surface area of the 2% Ni-Cu/Al_2O_3 catalyst was 190.2 m^2/g and the pore diameter was 7.1 nm.

Conclusion

The trend to use renewable and cleaner energy is increasing due to increasing crude oil price and environmental degradation because of use of fossil fuel. The conversion of bio-oil to bio-fuel can be done by hydrodeoxygenation process, the only drawback being high temperature and pressure. In view of aforementioned challenge, the developed Ni-Cu catalyst loaded on alumina was characterized and their result was carefully analyzed. The developed catalyst facilitates the hydrodeoxygenation process to be carried at low temperature and pressure. The characterization analysis shows the 2 % loading of Ni-Cu on alumina support give high surface area and better activity and selectivity over other catalyst.

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