HYDROGEN ADSORPTION STUDY OF METAL NANOPARTICLE DECORATED CARBON NANOFIBER

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Abstract: In this study, synthesis of carbon nanofibers (CNFs) from natural cotton fibers have been discussed. The synthesized CNFs were activated by KOH solution and Ni nanoparticles were decorated on to the surface of CNFs by thermal reduction method. The as obtained carbon material is used for studying hydrogen adsorption capacity by static volumetric techniques using Sievert’s apparatus. Raman spectra and X-ray diffraction of carbon revealed the presence of combination of graphitic and amorphous nature. The CNF decorated with Ni nanoparticles have the higher Specific surface area (SSA) which is confirmed by the BET analysis. Due to the spillover effect, the Ni-CNFs exhibited the maximum hydrogen adsorption as 7.01%.

Index Terms – Carbon nano fibers, hydrogen adsorption, metal decoration Sievert’s apparatus.

I. INTRODUCTION

The decrease in fossil fuels has created a tremendous demand for renewable energies having higher energy efficiency. In addition, this has raised worldwide efforts to develop alternative fuels and technologies. (Schlapbach & Zuttel 2001) The pollution due to combustion of fossil fuels has added to the drastically changing climatic issues. Thus, the need of the hour is to develop eco-friendly clean fuels, which, unfortunately is very challenging. (Spyrou et al, 2013) Hydrogen storage technologies play an important role in the transition of carbon-based energy economy. (DOE-USA) Hydrogen is considered to be one of the promising energy fuels for automobiles and its use can be further extended to smaller portable device like laptops and mobile phones etc. (Dimitrakakis et al, 2008) Hydrogen is efficient, renewable and eco-friendly source and has great potential to replace non-renewable fossil fuels. The present energy consumption for mobility and transport applications accounts for one third of the fossil fuel being used and therefore use of hydrogen will cause reduced carbon dioxide production as combustion of hydrogen will produce water as the by-product. (Spyrou et al. 2013, Dimitrakakis et al. 2008 and Satyapal et al. 2007) While at the same time, low volumetric energy density of hydrogen hinders the development of safe storage system. (Zuttel, 2004) Several ways of hydrogen storage have been investigated such as high-pressure gas, liquid hydrogen, metal hydrides and adsorption on nano-materials. (Schlapbach & Zuttel 2001 and Spyrou et al, 2013) Among all the methods currently adopted for hydrogen adsorption, physisorption on carbon material is quite promising as there is no chemical bond between hydrogen and carbon surface, thus giving completely reversible hydrogen uptake and release. (Sircar et al. 1996, Rzepka et al. 1998 and Benard et al. 2007) It is believed that adsorption at ambient conditions on porous material with weak Van der Waals interaction can fulfill the value that have been set by the U.S. Department of Energy (DOE). (DOE, Sumida et al. 2013 and Salam et al. 2013) Numerous materials with sufficient adsorption capacities have been investigated in recent years for hydrogen storage via physisorption and chemisorption. (Sharon et al. 2007 and Tellez-Juarez et al. 2014)

Over the years, porous nano materials have gained considerable attention, as an adsorbent. For example, adsorbent materials like nano-structured carbaceous materials including carbon nanotube (CNT), graphite nanofibers, graphene and CNFs have been developed. (Tellez-Juarez et al. 2014, Schaefer et al. 2017 and Cheng et al. 2008) Carbon nanomaterials (CNM) due to their high SSA and porosity, in addition to its unique mechanical property, allow it to be an ideal substrate which can be modified through metal decoration for increasing hydrogen adsorption. (Wang et al. 2012, Rangel et al. 2014 and Gao et al. 2008) Sheng et al. has reported 2 % hydrogen adsorption on decorated CNT (Sheng et al, 2014). Magnesium and Copper decorated CNMs have shown considerable hydrogen adsorption (Pandyan et al. 2014 and Prakash et al. 2016). Among transition metal for enhancing hydrogen
storage capacity, nickel is promising because it is abundant, inexpensive compared to other metals and can enhance hydrogen adsorption properties.

In this study, nickel nanoparticles were decorated onto the CNFs by thermal reduction method. The nickel on the CNF surfaces enhanced the hydrogen adsorption capacity of CNFs by hydrogen spill-over effect.

II. EXPERIMENTAL

Synthesis of carbon nano-fibers
The natural cotton fibers procured from local market were first cleaned and used for synthesis of CNF. The synthesis was carried out by pyrolysis technique using Lindberg’s horizontal furnace at 600°C for 4 hours in presence of Argon. The as-obtained CNFs were then activated by 2M KOH solution. The activated CNFs were treated by two different method viz.

(1) as-obtained CNFs were annealed at 700°C for two hours in presence of CO₂ gas and named as K-CNF
(2) CNFs obtained were decorated with Ni nanoparticles during annealing period and named as Ni-CNF.

Hydrogen Uptake Measurements
10 grams of each of the CNFs viz. K-CNF and Ni-CNF were used independently for the hydrogen uptake measurement. The hydrogen adsorption isotherms were measured by static volumetric technique using Sievert’s apparatus at ambient temperature at 60 bars.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET m²g⁻¹</th>
<th>Pore Volume Cc/g</th>
<th>Adsorption wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>K-CNF</td>
<td>660.13</td>
<td>0.1842</td>
<td>3.81</td>
</tr>
<tr>
<td>Ni-CNF</td>
<td>1229.84</td>
<td>0.7521</td>
<td>7.01</td>
</tr>
</tbody>
</table>

III. RESULT AND DISCUSSION

Characterisation of Ni-CNF
The CNFs obtained by pyrolysis is analyzed by X-Ray Diffraction (XRD). XRD of CNFs shows broad peak at 2θ = 24.9° corresponding to (002) plane of graphitic oxide and sharp peaks at 2θ = 43.9°, 56°and 78° shows presence of nickel nano-particles [Fig. 2]. It is observed that peak 2θ = 24.9° low value which suggests sample was not crystalized well but is a mixture with amorphous carbon.

Morphology of Ni-CNF
The scanning electron microscopy (SEM) micrograph of CNFs shows that, the peculiar morphology of cotton fibers has been retained in the CNFs formed with fairly uniform distribution of nickel nano-particles [Fig. 1]. The CNFs were found to have thickness in the range of 20-30 nm.

Raman Spectroscopy Analysis of Ni-CNF
A Raman spectrum shows [Fig. 3] one peak at 1565 cm⁻¹ of G band and second at 1380 cm⁻¹ of D band which are the characteristic for graphitic material containing some disorder structure as well as presence of crystalline graphene. This confirms that the sample is a mixture of amorphous and graphitic carbon materials (Mukherjee et al. 2013 and Zacharia et al. 2005).

Fig 1. Scanning electron microscopy (SEM) micrograph of Ni-CNF
Hydrogen adsorption study of K-CNF and Ni-CNF

There were two samples of CNF used to study the hydrogen storage capacity. In the Table 1, the adsorption measurements of K-CNF and Ni-CNF mentioned are at ambient temperature. The hydrogen adsorption capacity of K-CNF and Ni-CNF were found to be 3.81 wt% and 7.01 wt% respectively at 60 bar pressure. The Brunauer-Emmett-Teller (BET) surface area of K-CNF and Ni-CNF are 660.13 m²g⁻¹ and 1229.84 m²g⁻¹ respectively. For the decoration of the CNF with metal nanoparticles, it is treated with metal ion solution. During the annealing of the metal ion treated CNF further chiseling effect on the carbon is observed resulting in increased SSA; this effect is not observed in untreated CNF. In addition, the pore volume of K-CNF and Ni-CNF are 0.1842 cc/g and 0.7521 cc/g respectively. Among K-CNF and Ni-CNF the adsorption is high in Ni-CNF. The hydrogen capacity of Nickel nanoparticle decorated CNM (Ni-CNF) is higher than that of untreated CNM i.e., K-CNF. This is due to the presence of nickel nanoparticles, which strongly enhances the hydrogen storage capacity of CNFs coupled with synergic effect of increased SSA. In general, hydrogen adsorption depends on specific surface area, pore volume and pore size of the adsorbent. In this case hydrogen adsorption is not consistent with the textural properties. Nickel nano particles act as hydrogen favorable site and play important role in hydrogen adsorption. In Nickel nanoparticles decorated material, charge transfer takes place between materials and nickel. A nickel nanoparticle carries a positive charge, polarizes the hydrogen molecules, and then binds the hydrogen atoms. The nickel nanoparticles of the adsorbents led to a spill-over effect of hydrogen molecules leading to physisorption. Nickel particles act as catalyst to hydrogen spill-over, causing enhancement in the hydrogen storage capacity (Ruse et al. 2016 and Geng et al. 2014). The metal particles dissociate hydrogen thus enhancing the hydrogen adsorption capacity. Thus, present work explains the enhancement of hydrogen storing capacity of sample Ni-CNF.

IV. CONCLUSION

In this investigation, Pyrolysis of cotton (utilizing Lindberg’s horizontal furnace at 600°C for 4 hours in presence of Argon) is carried out and hydrogen adsorption is determined for it. It has been tracked down that because of the Ni-CNF there is an upgrade in hydrogen adsorption capacity as compared to K-CNF at 60 bar pressure. Raman spectra unmistakably expresses the combination of graphitic and amorphous nature of carbon. Additionally, CNFs obtained with decorated Ni nanoparticles have higher surface area and pore volume than K-CNF which are upheld by the outcomes obtained from BET and SEM analysis.

V. ACKNOWLEDGEMENT

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VI. REFERENCE


