Porous Carbon Nanomaterial from Corncob as Hydrogen Storage material

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Abstract

The corncob, one form of carbon source, is an excellent precursor for the synthesis of high specific surface area porous carbon nanomaterial. The research activity in the field of hydrogen storage has increased substantially over the last decade due to the practical need of hydrogen fuel for fuel cell automobiles and other hydrogen IC engines. In the search for new materials, carbon adsorbents are identified as a storage material due to their low cost and large surface areas. Activated carbon has attracted much attention for adsorption applications due to its lightweight, extensive internal pore structure and large surface area. In the present investigation, the porous carbon nanomaterial is prepared from corncob by impregnation with 70% H₃PO₄ followed by calcination at 500°C in the presence of N₂. H₃PO₄ treatment helps to get the dense porous structure, with higher surface area of 1600 m²/g, confirmed by microscope images. The hydrogen adsorption studies on the porous carbon nanomaterial are investigated using a Sieverts apparatus which gives a room temperature hydrogen adsorption capacity of about 2 wt% at 4 MPa hydrogen equilibrium pressure.

Key words: Hydrogen, storage, carbon, nanomaterial, porosity, surface area

INTRODUCTION

The research activity in the field of hydrogen storage has increased substantially over the last decade due to the practical need of hydrogen for fuel cell automobiles and other hydrogen transport technology. The interest in hydrogen storage is to develop new materials with large storage capacity of hydrogen. However, the storage of hydrogen at ambient conditions becomes the bottleneck for the hydrogen storage research field. After many studies, researchers concluded that the solid-state storage in materials is the potential solution for storage of hydrogen [1, 2]. A suitable hydrogen solid-state material requires different physical and chemical properties. The most important properties are those related to the hydrogen gas sorption behavior; high hydrogen storage capacity at moderate hydrogen equilibrium temperature, low hydrogen desorbing pressure for hydrogen desorption, reversibility of the process, low hysteresis loss during charging and discharging of hydrogen cycle process, rapid kinetics of sorption, reasonable stability against oxygen and moisture for achieving long cycle life and low cost (Vajo, 2011). Many carbon-based materials show promising results due to their physisorption and chemisorptions characteristics. Among different solid-state materials, carbon materials such as activated carbon, one-dimensional carbon nanotubes (CNTs), two-dimensional graphene and carbon nanofibers have been investigated for hydrogen storage (Dillon, Jones, Bekkedahl, Kiang, Bethune and Heben, 1997). At present, different applications of activated carbon are of interest due to the low cost factor. Activated carbon is used in many applications like food processing, pharmaceuticals, gas and liquid adsorptions, automobile etc (Hynek, 1997). These applications are much necessitated with regard to the surface chemistry, surface characteristics and morphology of the adsorbent carbons. Activated carbon has also been tried for
hydrogen storage due to its distinguished properties like light weight, good pore structure, high surface area (Jaybhaye, Sharon, Sharon and Singh (2006). However, high porosity and surface area are depending upon both the precursor and method of activation. Generally, activated carbons are synthesised by the decomposition of precursors like synthetic polymers such as PAN, or phenolics and then followed by activation. However, a cost effective feasible way of preparing the material is preferred, by choosing a material, which is inexpensive with high density, high yields and sufficient volatiles (Sharon, Soga, Afre, Sathiyamoorthy, Dasgupta, Bhardwaj, Sharon and Jaybhaye, 2007). Recently activated carbons are obtained from agricultural wastes. A primary reason for the lack of commercialization of the higher surface area activated carbons is the increased complexity and costs of their synthesis. In particular, high surface areas often have low yields. Heschel and Klose (1995) have presented a brief review on the synthesis of activated carbon selectively from the agricultural wastes. The preparation of activated carbon can be done in two ways viz., physical and chemical activation methods. Chemical activation is considered as prominent method over physical because in one single heat treatment, both decomposition and activation of the carbon take place. Many acidic and alkaline chemicals like H₂SO₄, ZnCl₂, KOH, NaOH, H₃PO₄ have been used to prepare activated carbon (Shah, 2007). It has been observed that orthophosphoric acid (H₃PO₄) activation is advantageous over thermal activation and chemical activation with other chemicals due to their low activation temperature and the carbon yield. For example, the temperature required for the synthesis of activated carbon will be ≤ 500°C using H₃PO₄ with a yield of 30-40% carbon while a KOH treated sample requires a high temperature of 750°C. Many studies have been done on carbon materials and alloy by various research groups for their hydrogen storage capacity and reported a value of 0.2 to 10 wt% depending on the temperature of operation (Louis, Ranjeet and Paul, 2007; Lasseigne-Jackson, Mishra and Olson, 2007; Varin and Czujko, 2002; Min, Haiping, Chunfeng, Shanshan and Wei, 2012; Aurora, Mancini, Mirabile, Montone, Pilloni, Todini and Vittori, 2009).

In the present work activated carbon is prepared from corncobs, which is an abundant cheap renewable resource with the potential for use as hydrogen storage material. Corn cobs are the preferred feedstock from woody resources, contain a low amount of minerals, and produce carbons with high densities. Corncobs show very little ash contents compared to other agricultural residues and suitable for heating applications. Many research studies have been carried out on corncob for different applications (Rivas, Dominguez, Dominguez, Parajo (2002); Cao, Xie, Bao, Shen (2004); Narges and Jalal, 2011). Tsai, Chang and Lee, 1998; Aggarwal and Dollimore, 1997, have reported the preparation of activated carbons using the precursor corncobs. These activated carbons from corncobs have different applications for the cleaning the industrial wastewaters (Aggarwal and Dollimore, 1997) and for liquid adsorbents (Tsai, Chang and Lee, 1998). Recently Yong and Paul (2010), studied H₂ adsorbing property of chemically activated corncobs, for a two-step prepared KOH sample treated at 800°C. They reported a hydrogen storage capacity of 2 wt% at 77 K at 1 atm pressure and 0.44 wt% at 298 K at 5 MPa. In the present work, a single step activation procedure has been followed using phosphoric acid at 500°C. The samples give a higher surface area of 200 - 1600 m²/g depending on the loading of orthophosphoric acid. The hydrogen storage capacity is five times higher than that reported at room temperature with 4 MPa pressure. The reasons for the increase in hydrogen adsorbing capacity are discussed in detail.

**Experimental**

Generally the corn samples were separated in to various sections depending on the physical texture, heated and dried. The samples were treated with phosphoric acid for creating the high surface area as well pore structure capable of absorbing hydrogen. There are nine variable parameters involved in the synthesis of activated carbon fiber viz., pretreatment of corn cob with acid, pyrolysis temperature, duration of pyrolysis, atmosphere during the pyrolysis, flow rate, post-treatment of carbon, thermal treatment, duration of thermal treatment etc. Based on our previous experiments, we fixed certain critical 5 parameters viz., duration of pyrolysis, acid concentration, gases used during the pyrolysis (Ar), flow rate (10 ml/min) and the procedure is given below. As received corn cob carbon is made free from seeds and dried in a microwave oven at 1200W power for approximately 5 min to make corn cobs completely free from moisture. After removal of the dried husk, the dried portion of the soft central pith is removed from the inner core. The remaining hard wooden shell of the corncob is utilized to prepare the carbon material. This hard wooden shell of corn cobs is treated with 30-70% diluted orthophosphoric acid (GR 99%, Merck chemicals) at 80°C for 2 h. After the acid treatment, the solid material is filtered from the solution and dried at 150°C until all the liquid is evaporated. Further, the dried material is heated in N₂ atmosphere at 500°C for 1h and then washed, filtered. The sample is then dried in an oven at 80°C and labeled as C30, C40, C50, C60 and C70 depending on the loading of acid content, which varies from 30 to 70%.

The prepared samples are characterized using BET, SEM and TGA measurements. A 30kV Hitachi SU1500 SEM facility with EDX attachment is used to study the morphological studies on the porous carbon material.
Table 1. The main components of raw corncob and their weight percent (Min, Haiping, Chunfeng, Shanshan and Wei, 2012).

<table>
<thead>
<tr>
<th>Compositions</th>
<th>Contents</th>
<th>Element of corncob</th>
<th>Contents (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose</td>
<td>36.3</td>
<td>C</td>
<td>43.4</td>
</tr>
<tr>
<td>Hemicellulose</td>
<td>42.8</td>
<td>H</td>
<td>5.8</td>
</tr>
<tr>
<td>Lignin</td>
<td>9.3</td>
<td>N</td>
<td>0.6</td>
</tr>
<tr>
<td>Ash</td>
<td>0.2</td>
<td>O</td>
<td>50.2</td>
</tr>
</tbody>
</table>

Figure 1: Cross section of corncob

Thermogravimetric measurements are conducted to measure the thermal stability of the material in air atmosphere. Temperature range is maintained between 35-1000°C at a heating rate 10K/min using Netzsch Thermal analyzer facility STA 449 F1 model. Specific surface area of the samples are obtained from the N₂ adsorption–desorption at 77 K using ASAP 2020 from Micromeritics. The BET surface area is determined by keeping the relative pressures in the range 0.05 to 0.26. The Hydrogen adsorption studies are carried out using a home built Sieverts apparatus in the temperatures range RT to 100°C under different pressure ranging from 0.5-4 MPa and the hydrogen storage capacity is calculated and plotted.

Results and discussion

The chemical composition of the sample, and their weight percent are given in Table 1 (Lasseigne-Jackson, Mishra and Olson, 2007). Figure 1 shows the cross section of the corncob, which shows that there are three distinct regions namely, chaff, hard wooden shell and soft pith. The hard wooden shell has been used for the present study.

SEM analysis

The morphology of the porous carbon material was studied using scanning electron microscopy and is shown in Figure 2, revealing a good porous structure. Figure 3 shows the morphology of corn cob treated with different percentages (30-70%) of orthophosphoric acid. All the carbon samples show a porous structure with a honeycomb shape with irregular holes. The morphology of corncob carbon also shows that the material contains tubular like channel structure of 10-100 μm in diameter and 100 μm in length. The carbon samples C30, C40, C50, C60 and C70 retain a similar morphology. Each macropore again divides into sub macropores of 1-5 μm sizes. But with increase in the percent of phosphoric acid
treatment, the density of sub macropore structure is increasing to 30-70%.
The sub macropores facilitates the hydrogen adsorption process due to the very good pore development, especially for dense porous C70 material. It can be hypothesized that the creation of such pores may be responsible in aiding the adsorption of hydrogen. It is suggested that hydrogen can penetrate the surface through the micropores forming an intercalated layer of hydrogen. Fan et al, 1999) have proposed that hydrogen
condenses in the hollow pores of activated carbons to increase the hydrogen adsorption.

**Thermogravimetric analysis**

Thermogravimetric curves of corncob carbon activated with different loading of orthophosphoric acid chemical activator are shown in Figure 4. The thermogravimetry studies of corncob result into three decomposition regions in the temperature range studied. The first and second decomposition occur around 100 and 200°C, respectively; represent the elimination of hemicellulose, moisture, cellulose and lignin of the corncob material. The third stage occurs between 400-700°C, which corresponds to the complete decomposition of the corncob carbon. There is a residual mass of 18 wt% as shown in TGA plot which is due to the residual phosphates deposited on the sample. The third region where there is a major weight loss occurs around 500°C is due to H₃PO₄ activation and oxidation of carbon. From this analysis it is observed that with increase in the percentage of H₃PO₄ for C30, C40 and C50, the thermal stability of the material has increased. This shows that the increase in porosity has not affected the graphitic structure and the presence of oxygen functional groups in C30, C40 and C50 has shown improved thermal stability of the carbon. However, for samples with higher acid content viz., C60 and C70, the thermal stability has been reduced as can be seen from Figure 4. This shows that with increase in the porosity, there is an increase of disorder structure, which assists the oxidation of carbon at lower temperatures. This result also supports that, with the increase of percentage of phosphoric acid treatment, the porosity can be increased.

**Surface area analysis**

The surface area of the as prepared porous carbon materials, measured using the BET surface area analyzer is given in Table 2. Table 2 shows the single point, multiple point and Langmuir surface area of the materials. These results show that increasing the phosphoric acid increases the surface area of the carbon material. These results are in agreement with the SEM micrograph images where there is an increase in the sub-micron structure with increase in the phosphoric acid treatment. Jiacheng and Stefan (2012) studied the pore widening of activated carbons during KOH activation with increased concentration. They have also discussed that the textural properties and surface chemistry of KOH-activated carbons depend on not only the synthesis parameters, but also different carbon sources employed including fossil/biomass-derived materials, synthetic organic polymers, and various nanostructured carbons.
Table 2. BET and Langmuir surface areas of different carbon samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area</th>
<th>BET surface area</th>
<th>Langmuir surface area</th>
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<tbody>
<tr>
<td></td>
<td>single point</td>
<td>multiple point</td>
<td></td>
</tr>
<tr>
<td>30% acid treated carbon</td>
<td>0.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>50% acid treated carbon</td>
<td>1437</td>
<td>1481</td>
<td>2180</td>
</tr>
<tr>
<td>70% acid treated carbon</td>
<td>1668</td>
<td>1726</td>
<td>2552</td>
</tr>
</tbody>
</table>

Hydrogen absorption measurements

The hydrogen absorption studies have been carried out for sample C70 which showed a highly porous structure and high surface area. The hydrogen adsorption study was carried out using Sievert’s apparatus and Pressure was measured when hydrogen was introduced to the system containing known weight of carbon material (P1). Before carrying out the experiment, the system was checked for its leakage under both vacuum and at high pressure at 200°C for 24 hours. A hydrogen uptake study, without the sample, was also carried out at 80 bar and at RT. The study showed no hydrogen absorption within the limits of the lowest count of the instrument. The sample tube and the connecting tubes were evacuated and left under the vacuum for 8 hours. There was no change in the pressure. Finally the tube was filled with gas at 60 bar and left for 4 hours.

After ascertaining zero leakage, the instrument was filled with known weight of carbon. The sample tube was evacuated and heated to 200°C for 24 hours. When no change in the pressure was observed, the main experiment started as mentioned above. The system was left for 24 hours to attain the equilibrium. After 24 hours the decrease in pressure was measured (P2). The amount of hydrogen adsorbed by carbon material was calculated from the pressure difference, i.e. from (P1–P2). As the volume of the system and weight of carbon were known, the amount of hydrogen in the unit of wt % was calculated. The quantity of hydrogen adsorbed was calculated using the general gas law as modified by Van der Waal’s (Van der Waal's gas law), using the following equation.

\[ P + \frac{n}{V_r} (V_r - nb) = nRT \]

The constants ‘a’ and ‘b’ have positive values and are characteristic of the individual gas. For hydrogen gas ‘a’ is 2.45 * 10^2 Pa.m^3 and ‘b’ is 26.61*10^-26 m^3/mol.

Hydrogen adsorption was measured by using hydrogen up to 80 bar pressure and all the experiments have been carried out a minimum of 3–5 times to ascertain the reproducibility.

The hydrogen storage measurements are conducted at 100, 75, 50 and 25°C at different hydrogen equilibrium pressures, using the pressure reduction method. The typical measurement is as follows:- 0.1 g of the sample was evacuated and heated at 300°C for 2 h for degassing. Hydrogen of 99.999% purity was allowed and the isotherm at room temperature was noted in the pressure range between 0.1 and 5 MPa. 15 to 20 cycles were measured for every sample. After evacuating the system, a new cycle was started. Hydrogen adsorption isotherms are shown in Figure 5.

It shows ~2 wt% uptake capacity at 4 MPa at ambient temperature, and 95% of which can be released during the release of pressure. The dependence of hydrogen uptake of the sample was measured by increasing the temperature to 100°C. It is found that the hydrogen intake capacity of the sample decreases with increase in temperature. A high number of investigations of KOH-activated carbons for H2 adsorption are found in the past several years and observed activated carbons with different porosities by KOH activation (Fierro, Szczurek, Zlotea, Mareche, Izquierdo, Albinjak, Latroche, Furdin and Celzard, 2010; Jorda-Beneyto, Suarez-Garcia, Lozano-Castello, Cazorla-Amor and Linares-Solano, 2007; Monteiro-de-Castro, Martinez-Escandell, Molina-
revealing that phosphoric acid treatment gives a higher activated using phosphoric acid showed a high hydrogen surface area and hydrogen storage capacity compared to raw materials like coffee bean waste, wood, and corn cobs showing a variable specific surface area of 780–3012 m²/g, activated using KOH showed ten H₂ absorption ranging from 0.4–0.8 wt% at 298–303 K and 20–120 bar (Yong and Paul, 2010; Akasaka, Takahata, Toda, Ono, Ohshio, Himeno, Kokubu and Saitoh, 2011; Bhat, Contescu, Gallego and Baker, 2010; Huang, Chen, Chen and Huang, 2010). Based on the analysis of the results obtained for all the synthetic and carbons derived from natural resources, the present sample corn cob activated using phosphoric acid showed a high hydrogen storage capacity of 2 Wt%, at RT and at 4 MPa, thereby revealing that phosphoric acid treatment gives a higher surface area and hydrogen storage capacity compared to KOH activation. It was also believed that the hydrogen adsorption capacity was suppressed when significantly increasing the amounts of surface acidic groups. These studies are in progress.

Conclusion

Porous carbon nanomaterials produced from corn cob by a single step H₃PO₄ acid activation show highly microporous materials with a BET specific surface area of 1600 m²/g. The hydrogen adsorption capacity of higher denser sample C70, prepared by treating corn cob with 70% diluted orthophosphoric acid, is ~2.0 wt% at ambient temperature and 4 MPa, which is higher than 0.44 wt% at 298 K and 5MPa reported for a similar sample treated with KOH. Desorption of 95% of adsorbed hydrogen can be achieved by releasing the hydrogen pressure. These studies indicate that the synthesis of activated carbon from corn cob with high specific surface area can be easily achieved with orthophosphoric acid treatment which has a high hydrogen storage capacity. Further modification of the surface of the porous carbon nanomaterial with selective nanoparticles may be a promising approach for the use of abundant agricultural waste as gas storage medium.

Acknowledgement

The authors would like to acknowledge Dr. G. Sundararajan, Director ARCI for supporting this work. The financial support of MNRE, Government of India is acknowledged.

References


NOTE

