Some Studies on the Synthesis and Characterization of Carbon Aerogel

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Porous carbon aerogels were synthesized from resorcinol-formaldehyde monomers using acetic acid, sodium carbonate and sodium hydroxide catalysts. The synthesized aerogels were characterized by XRD, TGA, SEM, BET and FTIR. The carbon aerogel developed by acetic acid catalyst produced a very high surface area (619.26 m^2.g^{-1}). All the different catalysts resulted in different surface morphology of the aerogels. The synthesized carbon aerogels contained significant amount of hydroxyl, carboxyl groups and different types of C-C linkages. These aerogels exhibited potential as adsorbents for removal of toxic materials and heavy metals.

[Keywords : Carbon aerogels, Resorcinol-formaldehyde, Catalyst, Surface area]

Introduction

Generally, organic aerogels are produced by poly-condensation of two monomers using sol-gel technique. These monomers form functionalized clusters, which produce gels by covalent cross-linking process. After processing these gels under supercritical conditions organic aerogels are produced.

There has been a growing interest in the synthesis and characterization of organic aerogels due to the fact that their pyrolysis in inert atmosphere leads to a novel porous carbon material known as carbon aerogels, which can be used for a variety of applications. Basically carbon aerogels have a network structure of interconnected nano-sized primary particles. Carbon aerogels can be obtained in the form of monoliths, beads, powder and thin film. These materials find applications as membrane, adsorbent, carriers for metal catalysts, in high energy physics and acoustic technology and as thermal insulators due to their low thermal conductivity. Carbon aerogels are also promising materials due to their electrically conducting network. Basically carbon aerogels have a network structure of interconnected nanosized primary particles. The micropores of carbon aerogels are related to the intra-particle structure, whereas mesopores and macropores are produced by the inter-particle structure. The three dimensional structure of carbon aerogels has been modelled as random close packed structure of slightly overlapping spheres.[1] Due to the structure and texture of carbon aerogels, which can be designed and controlled at the nanometer scale, these materials have recently been classified as nano-structured carbons.[2]

A large number of researches have been going on worldwide on the synthesis and characterization of carbon aerogels to modify/improve their properties suitable for diversified applications. Some of the important works in this regard are mentioned here.

Saliger *et al.*[3] derived carbon aerogel via the pyrolysis of resorcinol-formaldehyde aerogels and observed that thermal and chemical activation of such aerogels could increase their accessible surface and double layer capacities. Moreno-Castilla and Maldonado-Hodar[4] described the preparation of metal doped carbon aerogels, their physicochemical surface properties and their applications as catalysts in various chemical reactions in a nice overview. Berthon-Fabry *et al.*[5] synthesized carbon aerogel by resorcinol-formaldehyde sol-gel reactions in acetone in a single step base catalysis and also in a double step base catalysis followed by supercritical drying and pyrolysis at 1050ºC under nitrogen flow. Carbon aerogels produced by both the methods exhibited narrow sized micropores in the structure and for single step base catalysis nanoporous aerogel with high surface area could be obtained. Fu *et al.*[6] prepared carbon aerogels by gelation and supercritical drying in isopropanol and observed that the aerogel sample exhibited a very narrow micropore distribution at about 0.5 nm. Stolarski *et al.*[7] studied the influence of process parameters on porous structure of monolithic and spherical resorcinol formaldehyde (RF) carbon aerogels, prepared by supercritical acetone and carbon dioxide drying of aerogels followed by condensation. They observed that low temperature supercritical drying of RF aerogels gave carbon materials of more advantageous texture parameters in comparison to carbon aerogels obtained in high temperature supercritical drying. Li *et al.*[8] synthesized carbon aerogels from cresol, resorcinol and formaldehyde as an alternative route to chemical resorcinol-formaldehyde (RF) synthesis. It was observed that the porous structure of mixed carbon aerogel was similar to that of RF carbon aerogel. The mesopore distribution of the gel was observed to be widened and the average pore

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size increased as the mass density of the sample decreased. Balcic *et al.*[9] synthesized resorcinol-formaldehyde cryogels by sol-gel polycondensation of resorcinol with formaldehyde and carried out freeze drying with t-butanol. They observed a very promising specific capacitance value for this material operating in an acidic solution at room temperature. Kong *et al.*[10] synthesized carbon aerogels via aqueous polycondensation of resorcinol with formaldehyde followed by supercritical drying and subsequent pyrolysis at 1050ºC and observed that the permeability of aerogels was governed by a simple universal flow equation. Peikolainen *et al.*[11] observed that for aerogel preparation 5,methylresorcinol and its technical mixture Honeyol[TM] were very competitive precursors beside well studied resorcinol to control the gel structure easily. Haji and Erkey[12] studied the applications of carbon aerogels as adsorbents for the desulfurization of liquid hydrocarbon fuel used for fuel cell applications. It was observed that the carbon aerogel selectively adsorbed dibenzothiophene over naphthalene when both were present in solution. Zhang *et al.*[13] observed that microwave absorbing properties of carbon aerogels were influenced by its microstructure and density and with increasing thickness the peak value of the reflection coefficient moved to lower frequency. Jimenez *et al.*[14] observed that CO_2 activation of the carbon aerogel prepared with p-toluene-sulfonic acid as catalyst increased and widened the microporosity and had virtually no effect on the mesoporosity. Pekalar *et al.*[15] examined carbon aerogels as electrode for double layer capacitors, pseudo capacitors and capacitive deionization units. In another work Fu *et al.*[16] fabricated activated carbon fiber (ACF)/carbon aerogel (CA) composites by gelling a mixture of ACF and resorcinol and furfural, followed by supercritical drying of the mixture in isopropanol. It was observed that the mesopore volumes and the related diameters and mesopore size distributions of the ACF/CA composites were mainly affected by the mass density of the composites.

In spite of many attempts, a systematic investigation and comparison studies on the influence of different commonly available catalysts on the properties of carbon aerogel are not available. In this work, therefore, carbon aerogels have been synthesized from resorcinol-formaldehyde monomers in presence of three common catalysts, viz. acetic acid, sodium carbonate and sodium hydroxide. The formed aerogels have been characterized thoroughly to investigate the influence of the catalysts on their structural aspects.

Experimental

To synthesize carbon aerogels, resorcinol and formaldehyde were taken as the starting materials. Water was used as solvent and sodium carbonate, sodium hydroxide and acetic acid were used as the catalysts for the synthesis process. All the materials were taken in the form of AnalR grade. Resorcinol, water and the catalyst

were mixed and stirred in a beaker until the mixture became a homogeneous solution. The formaldehyde was then added and the solution was stirred for 1 h. The molar ratios of the reactants were maintained like the following : resorcinol/formaldehyde = 0.5, resorcinol/water = 0.125 and resorcinol/catalyst = 400. At the first stage, resorcinol-formaldehyde (RF) hydrogel was prepared by curing process at 85º±3ºC in an oven for a period of 7 days. The RF hydrogels were kept immersed in acetone for 3 days and the acetone was then extracted by supercritical drying with CO_2 using the supercritical fluid extraction (SFE) unit. In this third step the RF aerogels were carbonized under nitrogen flow (30 mL.min^{-1}) in a fixed bed activation unit (FBAU) to produce the carbon aerogels.

The crystallinity of the aerogels was analyzed by XRD analyses using a CuK$_\alpha$ radiation source (model: Bruker A&S D8 Advanced Diffractometer). The surface morphology of the samples was characterized by scanning electron microscopic (SEM) analyses (model: LEO 1430 VP, Oxford). BET surface areas of the samples were measured by nitrogen adsorption using Micrometrics ASAP 2000 gas analyzer. Thermogravimetric analyses of the samples were carried out under nitrogen atmosphere with gas flow rate of 20±1 mL.min^{-1} at a heating rate of 20ºC.min^{-1} using a thermogravimetric analyzer (model: Pyris 1). Fourier transform infrared (FTIR) spectroscopy was used to detect the vibration frequency changes for each of the functional groups present in the aerogels before and after the adsorption process with FTIR spectrometer (model: 8400S Shimadzu).

Results and Discussion

The XRD diagram of the samples synthesized using three different catalysts are shown in Fig. 1. It is apparent from the figure that all the synthesized carbon aerogels were mostly amorphous in character. XRD peaks of the samples were observed at 23º and 43º 2θ and it is in agreement with the literature data.[17] From the diffractogram it can be seen that the carbon aerogel prepared using acetic acid catalyst is the most amorphous in nature among the samples as it did not exhibit any peak at all. Between the other two samples amorphous character was slightly more in the sample prepared with Na_2CO_3 catalyst.

From the thermogravimetric curve for carbon aerogels prepared using three different catalysts (Fig. 2) it is apparent that up to 90ºC the weight loss is not substantial for acetic acid catalysed sample. For this sample, the weight loss was about 7% up to 600ºC. For both the sodium carbonate and sodium hydroxide catalyzed carbon aerogels, there were slight weight losses within 100ºC. This weight loss can be related to the desorption of physical moisture from the aerogel structure. Further heating in the temperature range of 500º-900ºC resulted in about 92% weight loss for acetic acid catalyzed aerogel, whereas for both the sodium carbonate and sodium hydroxide catalyzed aerogels the loss was only about 12% at this temperature range. This weight loss can be
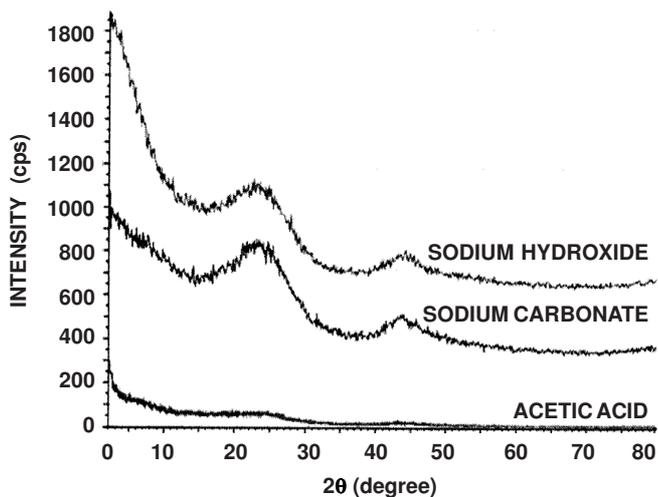
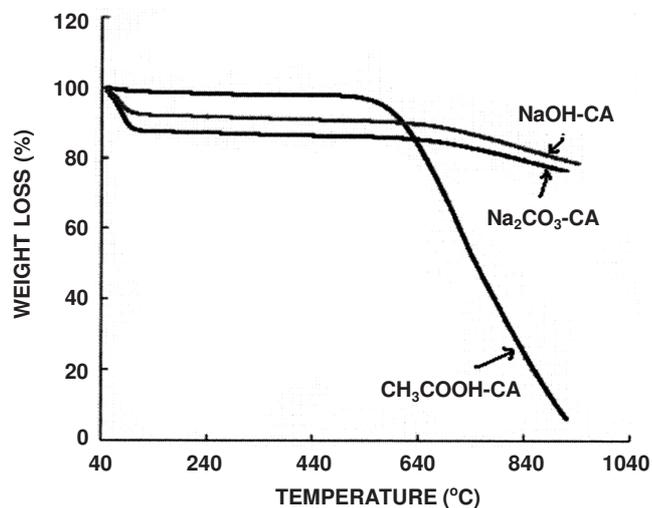Fig. 1 – XRD pattern for CAs prepared using acetic acid, sodium carbonate and sodium hydroxide

Fig. 2 – Thermogravimetric results for prepared CAs

Fig. 3 – CAs prepared using (a) acetic acid, (b) sodium carbonate and (c) sodium hydroxide

attributed to the loss of volatiles and consequent carbonization reaction in the organic aerogel and it was the highest in acetic acid catalyzed aerogel.

SEM images of the surface morphology of carbon aerogels are shown in Fig. 3. It is obvious that the three types of aerogels exhibit porous surfaces, but the surface textures are different. At micrometer scale, the surface morphology of acetic acid catalyzed sample is different from those of sodium carbonate and sodium hydroxide catalyzed samples. Sodium carbonate and sodium hydroxide catalyzed samples show a very open porous structure with large interconnected network of pores, whereas acetic acid catalyzed sample show a relatively smoother surface, which is formed by fused small particles.

In the FTIR spectra of carbon aerogel prepared using acetic acid (Fig. 4) the broad and intense peaks in the region of 3578.19, 3520.81, 3235.85, 3177.99, 3000.5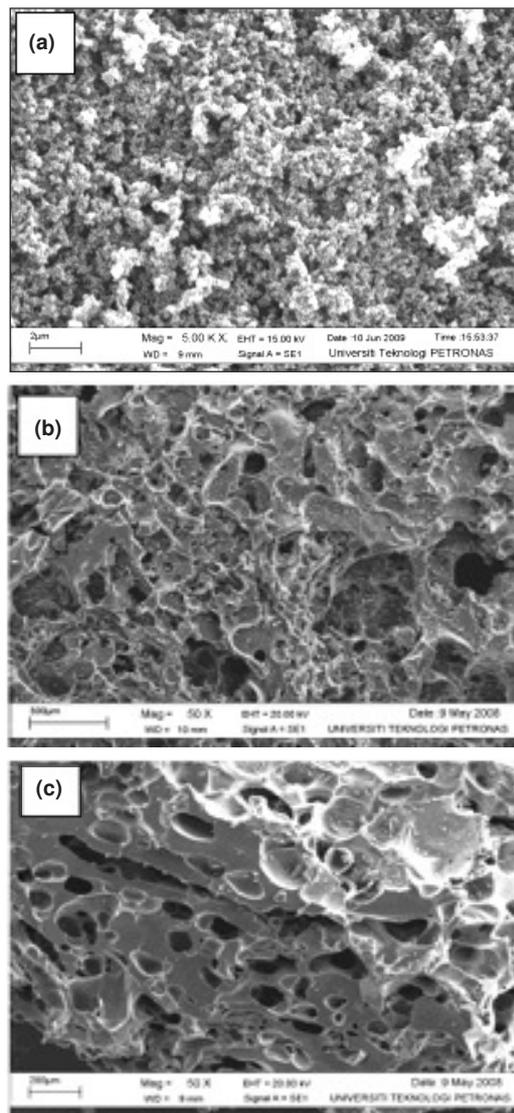5, 2837.09, 2745.96 and 2700.16 cm^{-1} are due to the O-H stretching vibrations of free hydroxyl groups and bonded O-H bands of carboxylic acids.[18, 19] The stretching frequencies of the carboxyl group are observed in the range 3235.85, 3177.99, 3000.55, 2837.09, 2745.96 and 2700.16 cm^{-1}.[18, 19] The sharp peak at 2040.06 cm^{-1} is an evidence of carbonyl group.[20] This group may be from the quinone group which may be formed at the broken C-O-C linkages in the presence of oxygen.[21] The range of 690-900 cm^{-1} is an evidence of C-H stretching vibration.[19] Because of heating, some of the CH_2-O-CH_2 linkages may have broken to form $-CH_2OH$ and $=CH_2$ groups attached to different resorcinol molecules.[20] This is further supported by the sharp intense peaks observed at around 660 cm^{-1} due to the $-C=CH_2$ group.[20] The peaks observed in 400-625 cm^{-1} region confirm the presence of C=C ring bend vibration.[18]

In the FTIR spectra of carbon aerogel prepared using sodium carbonate (Fig. 5) the peaks at 3730.07, 3626.89,

3516.95, 3361.21 and 3297.08 cm^{-1} can be considered as an evidence of presence of hydroxyl groups,[18, 19] mainly due to the –OH groups bonded to the benzene ring,[19] and also may be due to –CH$_2$OH groups connected to the resorcinol molecule.[21] The peak at 2041.99 cm^{-1} is an evidence of carbonyl group.[20] C-H stretching vibration is represented by 2999.58, 2919.45, 2834.68, 2747.41 and 2685.21 cm^{-1}. Intensity of band at 2041.99 cm^{-1} is related to the carbonyl group.[20] The peaks at 1210.25, 1163.96, 1104.65 and 939.75 cm^{-1} region probably represent C-O-C linkage stretching between the two resorcinol molecules which is expected in the poly-condensation reaction between resorcinol and formaldehyde.[21] The peak at 711.68 cm^{-1} refers to C-H groups, which is a confirmation for the presence of hydroxyl group.[19] Because of heating, some of the CH$_2$-O-CH$_2$ linkages may have broken to form –CH$_2$OH and =CH$_2$ groups attached to different resorcinol molecules. This is further supported by the sharp intense

peaks observed at around 660 cm^{-1} due to –C=CH$_2$ group.[20] C=C stretching vibration was found at 1654.81 cm^{-1}.[19] The peaks observed in 400-625 cm^{-1} region (636.95, 588.25, 442.63 cm^{-1}) can be related to the C=C ring bend vibration.[18]

In the FTIR spectrum of the carbon aerogel prepared using sodium hydroxide (Fig. 6) the bands observed at 3569.03, 3517.92, 3351.09 and 3291.30 cm^{-1} are assigned to the stretching of hydroxyl groups (O–H)[18, 22] and to the inter- and intra-molecular hydrogen bonding of resorcinol.[18, 22] The peaks at 2015.96, 2065.62 and 2117.69 cm^{-1} are an evidence of the presence of carbonyl group[20] from the quinone group.[19] C-H stretching vibration is observed at 2998.62, 2927.26, 2746.93 and 2698.71 cm^{-1}.[18] The peaks at 2117.69, 2065.62, and 2015.96 cm^{-1} are attributed to the stretching of carbonyl group. The peaks at 1209.77 cm^{-1} region probably represent C-O-C linkage stretching between the two resorcinol molecules
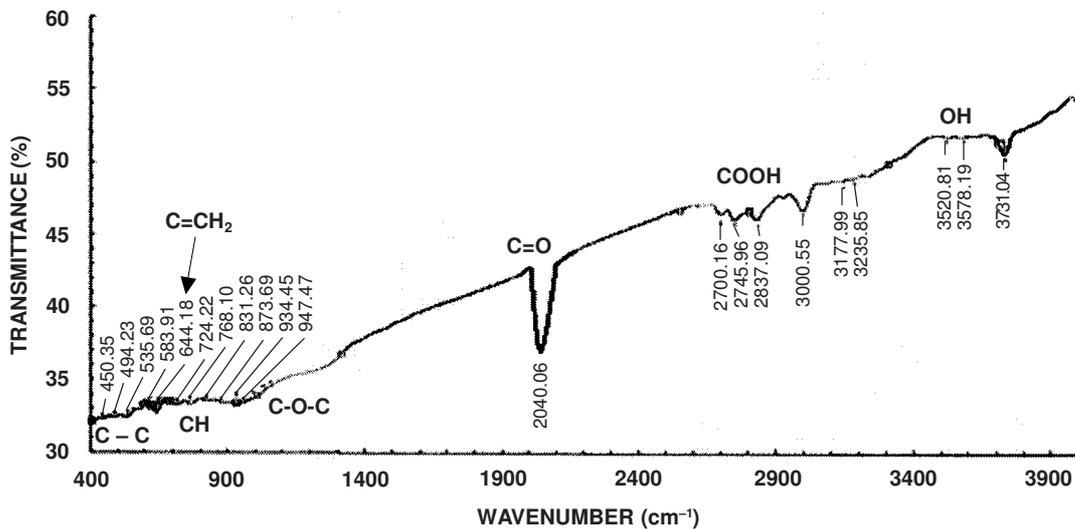

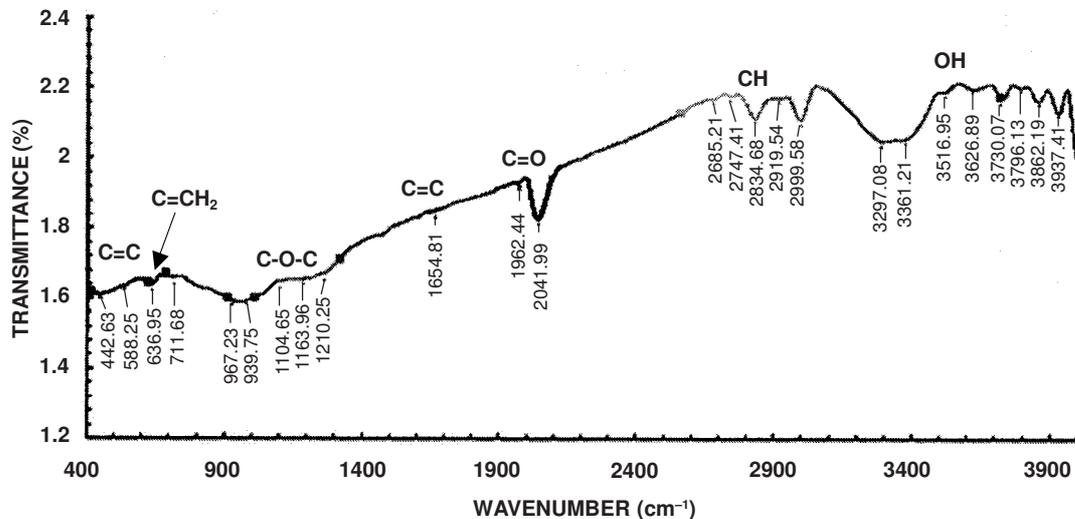**Fig. 4 – FTIR result for CA prepared using acetic acid**

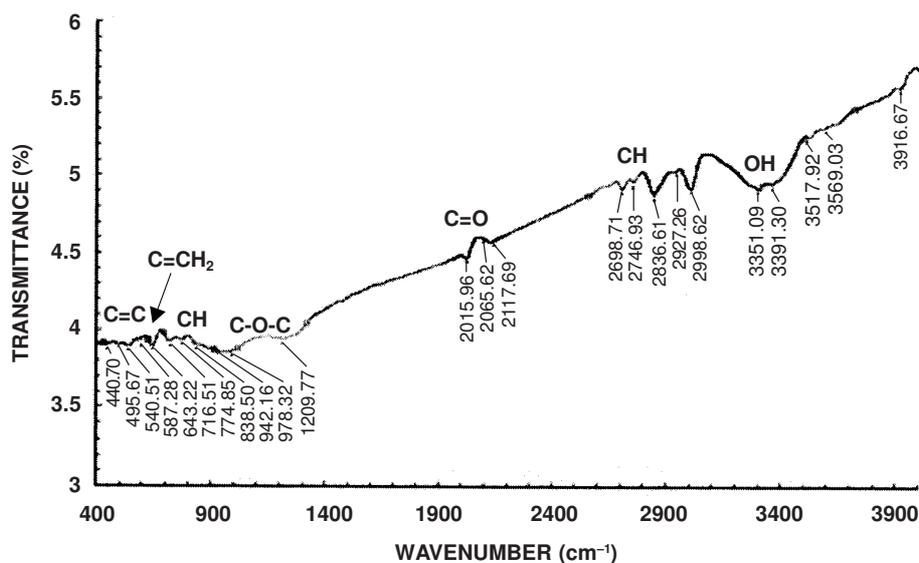**Fig. 5 – FTIR result for CA prepared using sodium carbonate**

Fig. 6 – FTIR result for CA prepared using sodium hydroxide

which are expected in the poly-condensation reaction between resorcinol and formaldehyde.[19] Because of heating, some of the CH_2-O-CH_2 linkages may have broken to form –CH_2OH and =CH_2 groups attached to different resorcinol molecules. It is supported by the sharp intense peaks observed at around 660 cm^{-1} due to the $C=CH_2$ group.[19] C=C ring bend vibration was found in 400-625 cm^{-1} region.[22]

So from the FTIR spectrum analyses of the aerogel samples it is evident that all the aerogel samples contain significant amount of –C=O, –OH stretching and different types of C-C stretching at the surfaces. Therefore the aerogels have the potential as adsorbent for the removal of toxic heavy metal cations from solutions. The aerogel prepared with acetic acid catalyst exhibits sharp stretching vibration for the carbonyl group compared to the other two samples and it also contains stretching vibration for the –COOH group at the surface. This indicates that the surface activity towards the adsorption of cationic species would be relatively more for this aerogel sample compared to the other two samples.

The results of adsorption and desorption isotherms with N_2 at 77 K on the CAs are shown in Table I. The isotherms of the aerogels have been observed to be of Type II following the IUPAC classification. This type of isotherm is identified with unrestricted monolayer-multilayer adsorption, and is characteristic of macroporous adsorbents. The data in Table I reveals that the aerogels prepared using acetic acid have higher BET surface area (619.2625 m^{2}g^{-1}) and the aerogel prepared with Na_2CO_3 catalyst exhibits the minimum surface area (209 m^2.g^{-1}). Average pore diameter, total pore volume, micropore diameter and micropore volume have also been observed to be the maximum for the sample prepared using acetic acid catalyst and minimum for the sample prepared using Na_2CO_3 catalyst.

Conclusions

Three different varieties of porous carbon aerogels were synthesized from resorcinol-formaldehyde monomers using three different catalysts, viz. acetic acid, sodium carbonate and sodium hydroxide in a three-step process. In the first step resorcinol-formaldehyde hydrogel was prepared which was converted to aerogel by supercritical fluid extraction process. Finally the aerogel was converted to carbon aerogel by carbonization under controlled atmosphere. The weight loss and the carbonization process with the application of temperature was the maximum with aerogel prepared with acetic acid catalyst.

Table I : Adsorption isotherm results

Adsorbent	BET surface area (m^2.g^{-1})	Average pore diameter (Å)	Total pore volume	Micropore volume (cm^3.g^{-1})	Micropore area (m^2.g^{-1})
Acetic acid CA	619.2625	30.1404	0.466620	0.209409	527.8312
Sodium hydroxide CA	362.2702	17.0906	0.154785	0.140363	358.9642
Sodium carbonate CA	209	18.6248	0.097619	0.082826	212.8770

The FTIR analysis showed that the synthesized carbon aerogels were rich in hydroxyl and carbonyl groups as well as with different C-C linkages. The sample prepared with acetic acid catalyst exhibited the maximum surface activity towards adsorption of cationic species. Again, carbon aerogel prepared using acetic acid catalyst showed a smoother surface, whilst carbon aerogels prepared using sodium carbonate and sodium hydroxide showed an open structure with large interconnected network of pores. Sample prepared using acetic acid catalyst also exhibited the highest surface area, more pore volume and microporous area compared to the other samples.

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