

Synthesis of High Surface Area Carbon Xerogel by using Pyrolysis of Resorcinol-Formaldehyde and Urea-Formaldehyde Precursors

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Abstract—In the present work, high surface area carbon xerogels were prepared using urea-formaldehyde and resorcinol-formaldehyde precursors. Sol-gel polycondensation of resorcinol with formaldehyde in slightly alkaline solution was done in presence of catalyst (Na_2CO_3) followed by drying and pyrolysis at 900°C ; while for the preparation of carbon xerogel from urea-formaldehyde, hydrolysis and acidification of the precursor was done followed by pyrolysis at 900 and 1000°C . The effects of stirring time, gelation time, precursor catalyst ratio and precursor ratio on the structure of prepared carbon xerogels were studied.

1. INTRODUCTION

During the last years, electrode material for electrochemical capacitors have been extensively developed due to increasing demand for a new type of accumulators of electrical energy with high specific power of more than 10kW/kg and a long durability (over 10^6 cycles). These devices have the ability of a high dynamic of charge propagation that may prove useful in hybrid power sources for electrical vehicles, digital communication systems, UPS for computers and pulse laser technique. The typical electrochemical accumulators are unable to fulfil these needs due to the physicochemical processes and electrode polarisation accompanying the conversion of chemical to electrical energy [1].

Electrochemical double-layer capacitors (EDLC) or supercapacitors (SC) are drawing the interest of researchers as a promising technology to fulfil the above mentioned demands. These are electrochemical capacitors based on carbon nano technology with high capacitance and high energy density in comparison to conventional capacitors and higher power densities compared to the batteries. Various porous carbon materials such as activated carbon, CNT, carbon aerogels, carbon fibres and carbide derived carbons have been studied as suitable materials for EDLC/ SC electrodes. Carbon aerogel and xerogels, in particular, are considered as promising alternative because of their

tridimensional porous structure, high specific surface areas and good electrical conductivity [2,3]. Extensive work has been done to synthesize carbon aerogel for supercapacitors using Resorcinol-formaldehyde (RF) [3], phenol-furfural [4], etc. The first results on carbon xerogels as electrodes in double layer capacitors were published by Pekala et al., in 1998 [5], wherein the capacities were reported to be 26F/cm^3 and initial circuit current densities as 4A/cm^2 . Then after numerous works were done to synthesize the carbon xerogel by pyrolysis of organic precursors, e.g., resorcinol-formaldehyde [6-8] and resorcinol-furfural [9]. The substitution of the expensive complex supercritical drying process (used to obtain aerogels) with an ambient drying method (used in case of xerogels) has proved to be a cheaper and more feasible method to synthesize porous carbon structures. However, the presence of capillary pressure inside the pores during the subcritical drying step may cause changes in the micro structural properties of the xerogels [3]. Thus there is a need to investigate the influence of the synthesis parameters such as the precursor ratio, the catalyst concentration etc.

Hence the present work focusses on the preparation of carbon xerogel using resorcinol-formaldehyde and urea-formaldehyde precursors. The synthesis parameters i.e. the precursor ratio, precursor to catalyst ratio, solvent, pyrolyzing time and temperature were optimized to achieve high surface area carbon xerogels.

2. MATERIAL AND METHODS

The carbon xerogel was prepared by polycondensation of resorcinol with formaldehyde (1:2 molar), adapting the procedure introduced by Pekala [5] and described elsewhere [10,11]. Accordingly, 9.3 gm of resorcinol was dissolved in 37ml of double distilled water using a magnetic stirrer. A solution of 1.8 gm Na_2CO_3 (catalyst) in 12ml of formaldehyde was prepared. Both the solutions were mixed to obtain a

homogeneous solution of RF Continuous stirring was employed until till an increase in viscosity was observed. When the color changes from golden brown to dark brown, stirring was stopped. The precursor to catalyst ratio was varied and also the solvent used as diluting agent and thus 13 different samples were formed. The list of the prepared samples has been listed in table 1. After the gelation was complete the sample was cut into small pieces and then dried up to 13 hours. After complete drying, a hard dark brown color resin was formed. The hard polymer formed after complete drying, is pyrolysed at 900°C for 2 hours under inert atmosphere. Finally a black graphitized form of carbon called xerogel was formed. The reaction involved is [12]:

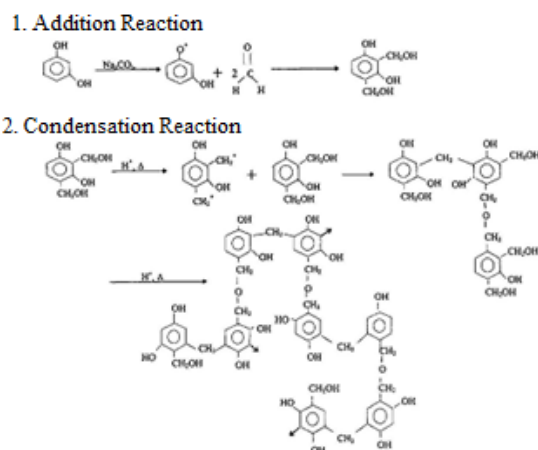


Fig. 1: Reaction mechanism of sol-gel polymerization of resorcinol with formaldehyde.[5]

2.2 Synthesis using urea-formaldehyde precursor

10 gm of urea was dissolved in 12.5 ml of formaldehyde and the pH was adjusted at 8 by using 5% of NaOH solution. The solution was stirred for about 15 minutes to dissolve the urea. After the dissolution, it was again stirred for about 45 minutes to complete mono, di and tri methylol urea formation. After hydrolysis 10% formic solution was added to adjust the pH to 4.3. Stirring was carried out till the formation of resin.

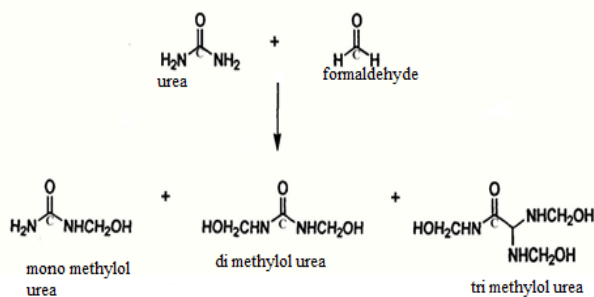


Fig. 2: Reaction mechanism of sol-gel polymerization of Urea with formaldehyde [5]

The sample was then cured for 2-3 days for hardening of the resin. Then the prepared polymer sample was pyrolysed under inert atmosphere for graphitization in muffle furnace at 900-1000°C. Four different samples were by varying the urea to formaldehyde ratio from 1.1:1 to 1.5:1 and the pyrolysis temperature as 900 and 1000°C. the reaction taking place is:

2.3 Characterization of the prepared sample

The Brunauer-Emmett-Tekker surface area (S_{BET}) of synthesized carbon xerogels was determined by MICROMERITICS –ASAP 2020 surface area and porosity analyzer instrument. XRD analysis was carried out to know the nature of the prepared samples using RIGAKU, ULTIMA-IV diffractometer.

3. RESULTS AND DISCUSSION

Table 1 and 2 show the BET surface area, the pore volume and the average hydraulic pore radius.

3.1 Effect of catalyst ratio

It can be observed from table 1 that as the catalyst ratio increases, higher BET surface areas are obtained (RF-9 to RF-13). The reason being that the gelation process occurs more rapidly with low R/C ratios. Thus the time of gelation is quite less (up to 1-3 hrs), which disrupts the cross linking of carbon molecules and gel microstructure so that proper condensation polymerization does not occur. Increase in R/C ratio results in an equivalent effect of increasing the concentration of solids in sol and results in better surface area. Maximum BET surface area was observed in case of R/C = 200.

3.2 Effect of solvent

The surface areas of the xerogels was improved when the solvent methanol/ethanol were mixed to water. The surface area was increased due to the attachment of hydroxyl functional group (OH^-), which increases the tendency of crosslinking of carbon atoms. Best results were obtained when 10% methanol was added to water:

Table 1: Resorcinol and Formaldehyde

Sr. No	xerogels	R/C	Solvent used	Surface area (m ² /g)	Pore volume (cm ³ /g)	Average pore hydraulic radius (Å)
1.	RF-1	5.0	water	26	0.018	2.67
2.	RF-2	2.0	water	25	0.016	2.85
3.	RF-3	4.0	water	37	0.021	2.95
4.	RF-4	5.0	water	44	0.022	3.01
5.	RF-5	10	water	66	0.022	3.17
6.	RF-6	1.0	water	52	0.021	3.18
7.	RF-7	2.5	water	42	0.02	3.47
8.	RF-8	3.0	water			3.33

9.	RF-9	100	Water+ 10% methanol	194	0.10	3.09
10.	RF-10	50	Water+ 15% methanol	245	0.13	3.53
11.	RF-11	200	Water+1 0% methanol	463	0.25	3.29
12.	RF-12	200	Water+1 0% ethanol	407	0.23	3.41
13.	RF-13	100	Water+ 15% methanol	42	0.07	3.31

Table 2 Urea and Formaldehyde

Sr. No	xerogels	Pyrolyzing temp.	U/F ratio	Surface area (m ² /g)	Pore volume (cm ³ /g)	Average pore hydraulic radius(Å)
1.	UF-1	900°C	1.1:1	366	0.18	3.21
2.	UF-2	900°C	1.5:1	322	0.17	3.31
3.	UF-3	1000°C	1.1:1	1026	0.6	4.59
4.	UF-4	1000°C	1.5:1	746	0.41	3.9027

3.3 Effect of precursor ratio

The effect of precursor ratio was studied for the xerogels prepared from urea-formaldehyde precursor and it was observed that the surface area was more when the ratio was 1.1:1.

3.4 XRD analysis

XRD analysis of all the samples were carried out (Fig.3 and 4). The peaks for the xerogel was at 23° and 43° which is in agreement with the literature data.[10].The XRD patterns of all the samples were similar. The reflections correspond to graphitic phase of carbon (JCPD#322-1069). This indicates that carbon in the xerogel is crystalline material and has graphitic structure.

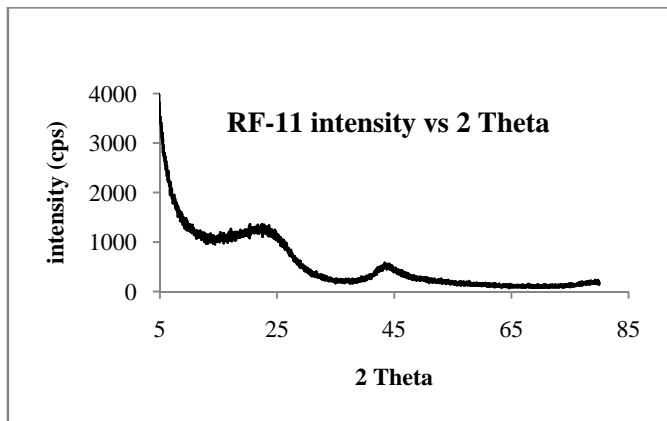


Fig. 3: XRD of RF-11 Solution

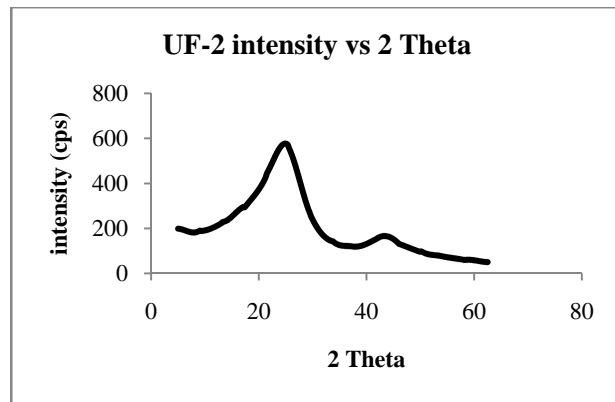


Fig. 4: XRD of UF-2 Solution

3.5 Thermo-Gravimetric analysis

Thermo-Gravimetric analysis of the samples were performed to estimate the mass lost during pyrolysis. The results are shown in fig 5. The total mass lost during pyrolyzing was 45.8% in RF-11 sample, this loss in mass was due to the removal; of oxygen and hydrogen from RF polymer sample.

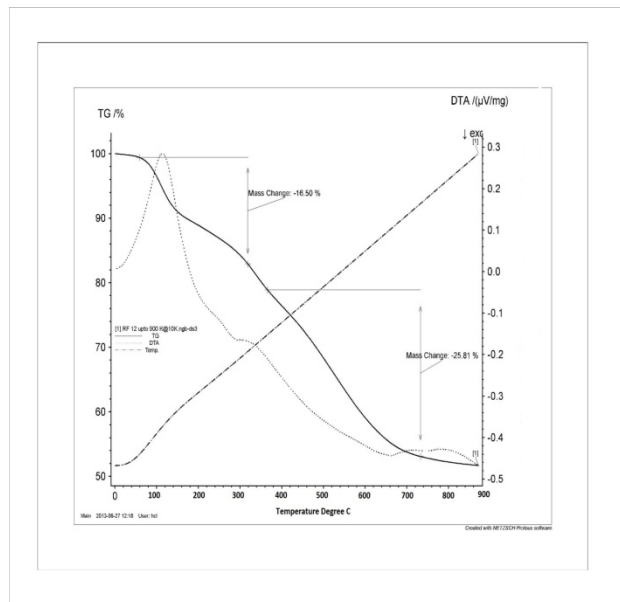


Fig. 5: Mass loss In RF-11 at 900°C BY TGA

4. CONCLUSIONS

Thus, it can be concluded that the surface area of the carbon xerogel obtained from urea formaldehyde preursors were greater in comparison to the carbon xerogel prepared from resorcinol-formaldehyde precursors. For RF xerogels the maximum BET surface area was obtained at maximum precursor/catalyst ratio and 10% methanol added to water, as

the solvent. Maximum surface area in case of UF xerogels was obtained at a precursor ratio of 1.1:1 and 1000°C pyrolyzing temperature.

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