Synthesis of Mesoporous Carbon Xerogel and Activation by Oxidative Treatment

Nihar Ranjan Mahato, Kamala Mandy Hansda, Ajit Das, Jayanta Banerjee, Sridhar Mondal and Nagendranath Mahata[*]

Center for Adsorption and Reaction Engineering on Surface (CARES), Department of Chemistry, Sidho-Kanho-Birsha University, Purulia-723104, India

*Corresponding author: E-mail: nagendranath_mahata.chem@skbu.ac.in

Synthesis of carbon xerogel and modification of its surface by various oxidative treatments are explored. Organic gel was synthesized by following the conventional sol-gel approach using formaldehyde and resorcinol. The wet gel was dried under subcritical condition and then carbonized, leading to carbon xerogel. Subsequently, the carbon xerogel was subjected to surface activation by means of oxidative treatment with nitric acid, sulphuric acid as well as aerial oxidation. Surface acid/base properties of the carbon xerogel have been strongly altered by treatments with nitric acid as well as with sulphuric acid. On the other hand, total surface area and pore volume have been significantly modified by air activation.

Keywords: Carbon xerogel, Oxidative activation, Surface acidity, Carbon catalysts.

INTRODUCTION

Carbon materials find versatile applications in the fields such as adsorption, catalysis, fuel cell, *etc*. [1-7]. Especially for liquid phase applications, they present advantages over conventional inorganic materials, such as higher stability in acidic and basic media. Recently, carbon xerogels have attracted a great deal of interest, since they can be produced with mesoporous and macroporous texture combined with large pore volume, which is more adequate for liquid phase applications [2-5,8,9]. Also, carbon xerogels possess excellent characteristics as catalyst supports, such as high surface area, high porosity, open pore network, controllable pore size and can be prepared in the desired form (granule, monolith, thin film or powder) [4-6]. Another important advantage of carbon xerogels is that the composition of the carbon is controllable and fully reproducible, which is not the case for activated carbons. The composition of the carbon may play a major role in processes like impregnation (for catalysts manufacture) or during reactions, adsorption, *etc*. Also, in terms of recovery of precious metals from spent catalysts, carbon materials as supports possess advantage. Burning-off of spent catalyst and recovery of precious metals from concentrated ash is easier [5].

A very important issue in supported catalysts is the maximum availability of the active phase. A well dispersed active phase is beneficial to obtain the maximum activity of a catalyst. The textural and surface chemical properties of a support play a crucial role in dispersing the active phase. Open pore networks and the presence of suitable anchoring sites for the precursor are beneficial in this regard. Carbon materials are superior in this context, since their texture and surface chemistry can be modified in a controlled way by appropriate methodologies [1,2,10]. In addition, surface activated carbon xerogel itself can be used as catalyst for organic transformation. Surface of carbon xerogel can be tuned to increase acidic sites by applying proper oxidative treatments; thereby acid catalyzed organic transformations can be successfully performed by applying carbon xerogel having highly acidic surface.

EXPERIMENTAL

Mesoporous carbon xerogel was prepared by sol-gel condensation of resorcinol and formaldehyde and subsequent carbonization of the dried gel. Sol-gel processing was performed with a formaldehyde/resorcinol ratio of 2.0 at pH 5.7 (adjusted by dilute NaOH solution). The organic gel was cured at 75 °C for 36 h. The hard gel was ground to preferred

size (0.2-2.0 mm) and washed several times with 2 N acetic acid (to remove sodium hydroxide) followed by distilled water (several times, to remove acetic acid). The organic gel was then dried at 120 °C in an air oven for 48 h and resorcinol-formaldehyde (RF) xerogel was obtained. Subsequently, the dried organic gel (RF xerogel) was taken in a tubular quartz reactor; the reactor was placed in a tubular furnace and nitrogen gas flow through the reactor was established. The material was heated to 700 °C at a ramp of 5 °C min^{-1} and carbonized for 4 h under nitrogen flow (40 mL min^{-1}). Finally, the reactor was cooled to room temperature slowly and the material was recovered. The carbon xerogel obtained thus was designated as CX-UA. A simplified schematic presentation of synthesis of carbon xerogel is shown in Fig. 1 [11].
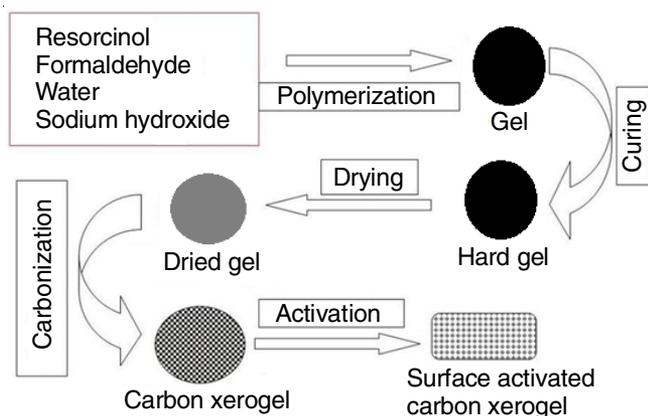

Fig. 1. Synthesis of carbon xerogel

The carbon xerogel was subjected to three different activation procedures. In the first process the carbon xerogel was treated with 7 N HNO$_3$ under reflux condition for 3 h, washed several times with distilled water and then dried at 110 °C for 6 h. Similarly, in the second proces, the carbon xerogel was treated with 7 N H$_2$SO$_4$ under reflux condition for 3 h, washed several times with distilled water and then dried at 110 °C for 6 h. On the other hand, in the third procedure, the carbon material was activated under diluted air (20 %) flow (in nitrogen) at 415 °C for 10 h. The first two activation processes left the samples with almost unchanged mass, while the third one resulted in about 12 % mass loss. The % mass loss was termed as burn-off (B.O.). The activation processes and the designations of the activated samples are shown at a glance in Table-1.

TABLE-1
ACTIVATION OF CARBON XEROGEL AND
DESIGNATION OF RESULTING MATERIALS

Starting material	Type of activation	Resulting material
CX-UA	Unactivated	CX-UA
	Treated with 7 N HNO$_3$ under reflux for 3 h	CX-NA
	Treated with 7 N H$_2$SO$_4$ under reflux for 3 h	CX-SA
	Treated with 20 % Air (in N$_2$) flow at 415 °C for 10 h (burning off = 12 %)	CX-AR

Nitrogen adsorption-desorption isotherms were measured at -196 °C and the textural characterization of the samples was based on the analysis of the isotherms. BET surface area (S$_{BET}$), mesoporous surface area (S$_{meso}$) and total pore volume

(V$_P$) were calculated using BET equation and *t*-method [10]. Pore size distributions were obtained from the desorption branch of the isotherm using the Barrett, Joyner and Halenda (BJH) method [12].

Chemical nature of the surface was assessed by measuring surface acidity and basicity of the materials. In a typical acidity measurement, 0.300 g sample was suspended in 50 mL 0.2 N NaOH solution (exact concentration was predetermined) and the mixture was stirred on a mechanical shaker at the rate of 200 rpm for 6 h. The mixture was allowed to settle for 1 h. 5 mL aliquot of supernatant clear liquid was pipette out, titrated with standard oxalic acid and concentration of NaOH was determined. From the difference in concentration of NaOH (initial and final), amount of NaOH consumed by the surface was calculated. That was the acidity of the surface.

Similarly, in a typical basicity measurement, 0.300 g sample was suspended in 50 mL 0.2 N HCl solution (exact concentration was predetermined) and the mixture was stirred on a mechanical shaker at the rate of 200 rpm for 6 h. Then the mixture was allowed to settle for 1 h. 5 mL aliquot of supernatant clear liquid was pipette out, titrated with standard NaOH solution and concentration of HCl was determined. From the difference in concentration of HCl (initial and final), amount of HCl consumed by the surface was calculated. That was the basicity of the surface.

RESULTS AND DISCUSSION

Dried organic gel (RF xerogel) was subjected to thermogravimetric analysis (TGA) prior to carbonization. The TGA profile of RF xerogel is in Fig. 2. The first slope at 105 to 180 °C signifies the removal of moisture trapped inside the framework of the organic RF xerogel. On the other hand, slope at 500 to 690 °C signifies the carbonization of the organic gel. The TGA profile clearly indicates that RF xerogel can be successfully carbonized above 650 °C within a reasonably short period of time. Hence, carbonization of the organic RF xerogel was performed at 700 °C.

The textural properties of the surface activated carbon xerogels along with the pristine carbon xerogel are shown in
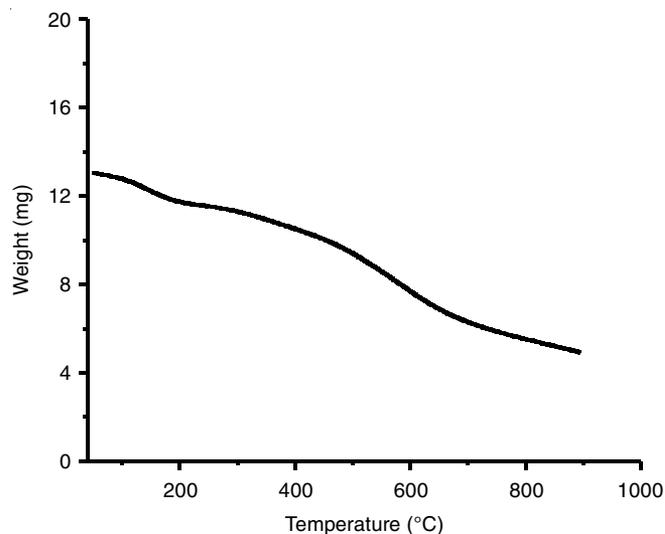

Fig. 2. Thermogravimetric analysis (TGA) profile of organic RF xerogel

Table-2. It is clear from the table that the oxidative treatment with nitric acid or sulphuric acid does not modify the textural properties significantly. On the other hand, activation by air considerably increases the BET surface area and the total pore volume. However, the mesoporous area remains more or less the same; only a little increase has been observed. Formation of new pores and opening of otherwise inaccessible pores during air activation results in the increase of BET surface area and pore volume [10,13]. This is reasonable as activation by diluted air was performed at comparatively higher temperature (415 °C). Mass loss (burn-off at the extent of 12 %) evidently indicates formation and/or opening of new pores. However, none of the activation processes significantly changes average pore size. Pore radii of all the samples are centred at 5.8 nm. Pore size distribution profiles of two representative samples, pristine (CX-UA) and air activated (CX-AR) carbon xerogels, are shown in Fig. 3. Pore size distribution profiles of nitric acid (CX-NA) and sulphuric acid activated (CX-SA) carbon xerogels are almost super imposable to that of the pristine (CX-UA) carbon xerogel. Fig. 3 clearly depicts that the counts of all pores increases evenly as a result of activation by air. This is again substantiated by the mass loss (burn-off) during the activation by air.

TABLE-2
TEXTURAL PROPERTIES OF THE PRISTINE AND SURFACE ACTIVATED CARBON XEROGELS

Sample	S_{BET} (m² g⁻¹)	S_{meso} (m² g⁻¹)	V_P (cm³ g⁻¹)	R_P (nm)
CX-UA	630	250	0.490	5.8
CX-NA	635	255	0.495	5.8
CX-SA	620	245	0.485	5.8
CX-AR	720	270	0.575	5.8

S_{BET} = Total surface area, S_{meso} = Mesoporous area, V_P = Total pore volume, R_P = Average pore radius.
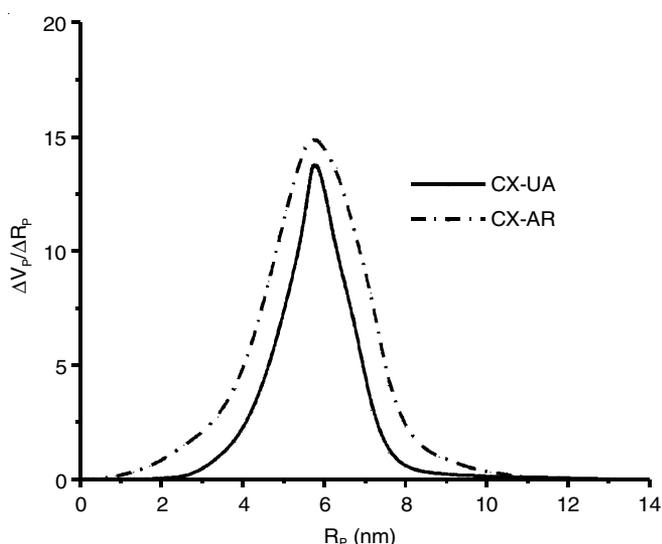

Fig. 3. Pore size distribution profiles of pristine (CX-UA) and air activated (CX-AR) carbon xerogels

Surface acid/base properties of the pristine carbon xerogel along with that of the surface activated carbon xerogels are shown in Table-3. Surface of pristine xerogel is mostly neutral. Concentrations of acid and/or basic sites are found to be very low; the surface is only marginally inclined to be basic. Treat-

TABLE-3
SURFACE ACID/BASE PROPERTIES OF THE PRISTINE AND ACTIVATED CARBON XEROGELS

Sample	Acidity (mmol g⁻¹)	Basicity (mmol g⁻¹)
CX-UA	0.4	0.9
CX-NA	8.9	–
CX-SA	9.7	–
CX-AR	3.9	0.5

ment of the pristine carbon xerogel with nitric acid or sulphuric acid leads to creation of highly acidic surfaces. Concentration of acidic sites increases to large extent. At the same time, basic sites are destroyed; no detectable basicity was observed on the surfaces of nitric acid (CX-NA) and sulphuric acid activated (CX-SA) carbon xerogels. On the other hand, activation by air moderately increases acidity of the surface; at the same time decreases basicity. Concentration of the acid sites is increased significantly and that of the basic sites is decreased marginally.

It is evident that surface chemical properties of carbon xerogel can be tuned by applying oxidative treatments. And thus, oxidative treatments lead to potential for designing and tailoring synthetic carbon xerogels to fit specific application. Surface acidity/basicity of carbon xerogels are due to the presence of surface oxygen groups. Surface of pristine carbon xerogel hardly contains oxygen groups [14], which is reflected by the very low concentration of acidic/basic sites. Oxidative treatments by nitric acid (CX-NA), sulphuric acid (CX-SA) and air (CX-AR) are likely to increase the number of carboxylic anhydride, phenolic and carobonyl/quinone surface groups [1,2,10]. In addition, carboxylic acid group is introduced by the treatments with nitric acid (CX-NA) and sulphuric acid (CX-SA) [10]. As results, concentrations of acid sites over CX-NA and CX-SA are very high (Table-3). Surface activated carbon xerogels can be applied as support for molecular dispersion of catalytic active sites utilizing surface oxygen groups as anchoring sites for catalyst precursor. On the other hand, highly acidic surface can be applied as catalyst for acid catalyzed organic transformation.

Conclusion

Surface physico-chemical properties of carbon xerogels can be modified and tuned by oxidative treatments with nitric acid, sulphuric acid and by air. Activation by air creates new pores; thereby increases total surface area and pore volume. Highly acidic surface can be created by treatment with nitric acid or sulphuric acid.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. J.L. Figueiredo, M.F.R. Pereira, M.M.A. Freitas and J.J.M. Órfão, *Carbon*, **37**, 1379 (1999);
   https://doi.org/10.1016/S0008-6223(98)00333-9.

2. N. Mahata, A.R. Silva, M.F.R. Pereira, C. Freire, B. de Castro and J.L. Figueiredo, *J. Colloid Interface Sci.*, **311**, 152 (2007);
   https://doi.org/10.1016/j.jcis.2007.02.080.

3. S. Álvarez, R.S. Ribeiro, H.T. Gomes, J.L. Sotelo and J. García, *Chem. Eng. Res. Des.*, **95**, 229 (2015);
   https://doi.org/10.1016/j.cherd.2014.11.001.

4. J.C. Calderon, N. Mahata, M.F.R. Pereira, J.L. Figueiredo, V.R. Fernandes, C.M. Rangel, L. Calvillo, M.J. Lazaro and E. Pastor, *Int. J. Hydrogen Energy*, **37**, 7200 (2012);
   https://doi.org/10.1016/j.ijhydene.2011.12.029.

5. N. Mahata, F. Gonc¸alves, M.F.R. Pereira and J.L. Figueiredo, *J. Appl. Catal. A*, **339**, 159 (2008);
   https://doi.org/10.1016/j.apcata.2008.01.023.

6. Z. Zapata-Benabithe, F. Carrasco-Marín, J. de Vicente and C. Moreno-Castilla, *Langmuir*, **29**, 6166 (2013);
   https://doi.org/10.1021/la4007422.

7. N. Mahata, O.S.G.P. Soares, I. Rodríguez-Ramos, M.F.R. Pereira, J.J.M. Órfão and J.L. Figueiredo, *Appl. Catal. A Gen.*, **464-465**, 28 (2013);
   https://doi.org/10.1016/j.apcata.2013.05.018.

8. J.P.S. Sousa, M.F.R. Pereira and J.L. Figueiredo, *Catalysts*, **2**, 447 (2012);
   https://doi.org/10.3390/catal2040447.

9. F. Maia, N. Mahata, B. Jarrais, A.R. Silva, M.F.R. Pereira, C. Freire and J.L. Figueiredo, *J. Mol. Catal. A*, **305**, 135 (2009);
   https://doi.org/10.1016/j.molcata.2008.10.045.

10. N. Mahata, M.F.R. Pereira, F. Suarez-Garcia, A. Martinez-Alonso, J.M.D. Tascon and J.L. Figueiredo, *J. Colloid Interface Sci.*, **324**, 150 (2008);
    https://doi.org/10.1016/j.jcis.2008.05.006.

11. J.L. Figueiredo, *Bol. Grupo Espanol Carbon*, **26**, 12 (2012).

12. S.J. Gregg and K.S.W. Sing, Adsorption, Surface Area and Porosity, Academic Press: San Diego (1982).

13. P.V. Samant, F. Gonçalves, M.M.A. Freitas, M.F.R. Pereira and J.L. Figueiredo, *Carbon*, **42**, 1321 (2004);
    https://doi.org/10.1016/j.carbon.2004.01.034.

14. N. Job, R. Pirard, J. Marien and J.-P. Pirard, *Carbon*, **42**, 619 (2004);
    https://doi.org/10.1016/j.carbon.2003.12.072.