Tuning of pore texture of carbon xerogels synthesized using resorcinol and paraformaldehyde as precursors

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Mesoporous carbon xerogels were synthesised using paraformaldehyde and resorcinol as precursors. Organic gel was obtained by sol-gel processing of the precursors. The wet gel was dried and then carbonized under nitrogen flow to obtain carbon xerogel. A series of carbon xerogels was synthesised by varying pH of sol-gel processing in the range of 5.5 to 6.3. One carbon xerogel was activated by nitric acid and subsequently heated at elevated temperatures (200 to 300°C) under vacuum to obtain another series of carbon xerogels. All the carbon xerogels were characterised by nitrogen adsorption-desorption isotherm measurement. The carbon xerogels were found to be significantly mesoporous. Pore texture was found to be tuned by the precursor sol-gel processing pH as well as by the post synthesis treatment by means of nitric acid activation-evacuation at elevated temperature.

Keywords: Carbon xerogel, texture tuning, mesoporous, sol-gel, catalyst support.

Introduction

Carbon materials are widely used in the fields such as catalysis, adsorption, fuel cell, etc.[1–9]. The carbon materials exhibit higher stability in acidic and basic media. Hence, they present advantages over conventional inorganic materials, especially for liquid phase applications; and thus carbon based catalysts are very common in liquid phase organic transformation[5–9]. Carbon xerogels can be produced with macroporous and mesoporous texture along with large pore volume. These characteristics are adequate for liquid phase applications to overcome diffusion limitation easily[2,5,10]. Carbon xerogels also possess high porosity, controllable pore size, high surface area, open pore network; and they can be synthesised in the desired form (powder, granule, thin film or monolith)[2,5,8]. Carbon xerogels have advantage over activated carbons in terms of composition, also. The composition of carbon xerogels is controllable and fully reproducible, which is not the case for activated carbons. The composition of the carbon is likely to play important roles in processes involving surface like adsorption, impregnation (for catalysts synthesis) or surface reaction, etc. Also, carbon materials as catalytic supports have advantage over inorganic oxide supports in terms of recovery of spent precious metals from used

catalysts. Burning-off of used catalyst and recovery of valuable metals from comparatively concentrated ash is easier.

Maximum availability of active sites in a supported catalyst is a prime issue. Activity of a supported catalyst is directly related to dispersion of active phase; a well dispersed active sites leads to higher activity. In a supported catalyst, dispersion of active phase is actively controlled by the surface chemical and textural characteristics of the support. Open pore networks along with mesoporous/macroporous texture are beneficial for higher dispersion of active phase. In this context, carbon xerogels are more suitable since their texture can be tuned by applying appropriate methodologies. In addition, carbon xerogels, containing appropriate surface groups, itself may be used as active catalyst for organic transformation. Two series of mesoporous carbon xerogels were synthesised using paraformaldehyde and resorcinol as precursors and characterised in the present study.

Experimental

Mesoporous carbon xerogels were synthesised by sol-gel condensation of paraformaldehyde with resorcinol followed by carbonisation of the dried gel[5]. In a typical synthesis 22.02 g (200 mmol) resorcinol was dissolved in 40 mL

deionised water under magnetic stirring. The pH of the solution was 3.23. The pH was increased to 5.4 by adding drops of 2 (*N*) NaOH solution. 12.012 g (400 mmol) paraformaldehyde, dissolved in 50 mL methanol, was added to the resorcinol solution with continuous stirring. The pH was adjusted to 5.5 by adding drops of 0.5 (*N*) NaOH solution. Stirring was continued for 15 min, then it was stopped, the magnetic bar was taken out, and the solution was left at 50°C. Slowly the gel was formed. The temperature was then increased slowly to 80°C, and the gel was cured at that temperature for 30 h. Subsequently, the hard gel was ground (0.2–2.0 mm) and washed with 1 (*N*) acetic acid for several times (to remove NaOH) followed by deionised water (to remove acetic acid). The gel was then dried overnight at 110°C. A portion of dried organic gel was examined by thermogravimetric analysis. The bulk of dried gel was then taken in a quartz tubular reactor, nitrogen gas flow (40 mL min^{-1}) was established, temperature was increased to 700°C at a ramp of 5°C min^{-1}, and carbonised for 3 h. Finally, the temperature of the reactor was brought down to room temperature slowly and the carbon xerogel was recovered. Fig. 1A shows a simplified schematic presentation and Fig. 1B shows the photographs of cured organic gel, dried ground organic gel and carbon xerogel. A series of carbon xerogels was synthesised by varying the pH of sol-gel processing in the range of 5.5 to 6.3. Another series of samples was obtained by means of treatment of a carbon xerogel with nitric acid under reflux condition and subsequently heat treated at elevated temperature under vacuum. In details, the carbon xerogel was refluxed with 6 (*N*) HNO$_3$ for 3 h, washed thoroughly with deionised water and then dried at 105°C for 10 h. Subsequently, the material was heated at temperature in the range of 200 to
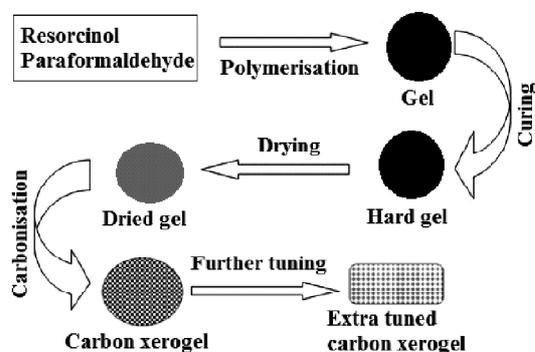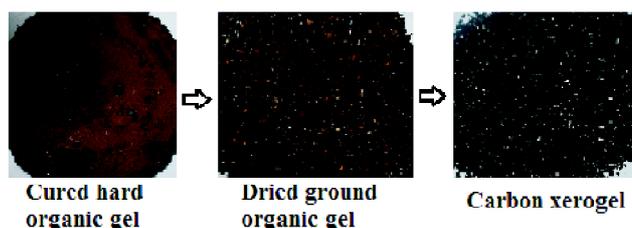

Fig. 1B. Sequential photographs of cured organic gel to carbon xerogel.

300°C under vacuum for 2 h. Table 1 summarises the designation of the carbon xerogels at a glance.

Table 1. Designation of the synthesised carbon xerogels

Precursor sol-gel processing pH ↓	Designation of resulted carbon xerogel
5.5	CX5.5
5.7	CX5.7
5.9	CX5.9
6.1	CX6.1
6.3	CX6.3
Nitric acid treatment of CX5.5 ↓	
Nil	CX5.5
Refluxed with 6 (*N*) HNO$_3$ for 3 h, washed, dried, heated at 200°C under vacuum for 2 h. Mass loss = 2.3%	CX5.5NA-200
Refluxed with 6 (*N*) HNO$_3$ for 3 h, washed, dried, heated at 250°C under vacuum for 2 h. Mass loss = 6.0%	CX5.5NA-250
Refluxed with 6 (*N*) HNO$_3$ for 3 h, washed, dried, heated at 300°C under vacuum for 2 h. Mass loss = 8.4%	CX5.5NA-300

Textural properties of the carbon xerogels were determined by means of analysis of nitrogen adsorption-desorption isotherms measured at –196°C in fully automated Nova Touch LX4 adsorption apparatus, operated using Quantachrome TouchWin^{TM} software (Quantachrome Instruments). Total surface area (S_{BET}) was determined using Brunauer-Emmett–Teller (BET) equation. Mesopore area (S_{meso}) and micropore volume (V_M) were calculated using t-plot. Total pore volume was determined from adsorption data at relative pressure of 0.995. Pore size distribution was obtained applying Barrett-Joyner-Halenda (BJH) method on the desorption branch of the isotherms[5,11].

Fig. 1A. Schematic presentation of synthesis of carbon xerogel.

Results and discussion

The dried organic gel was examined by thermogravimetric analysis (TGA). A typical TGA profile is shown in Fig. 2. The first slope at 100 to 160°C indicates the removal of moisture that is trapped inside the gel framework. Whereas, the steeper slope at 510 to 660°C indicates the carbonisation of the organic gel. It is clear from the TGA profile that the organic gel can be carbonised successfully at above 660°C within an acceptable period of time. Hence, carbonisation of the dried organic gel was performed at 700°C for a period of 3 h[12].
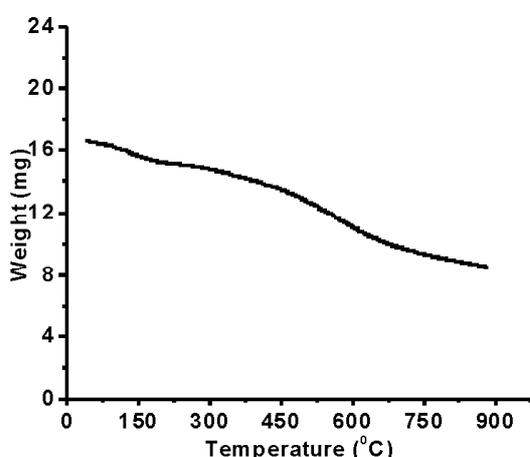

Fig. 2. Thermogravimetric analysis (TGA) profile of organic RF xerogel.

Tuning by varying pH of sol-gel processing of precursor organic gel:

Textural properties of final carbon xerogel likely depend on parent organic gel. pH of content during sol-gel processing is one among the important factors that governs the characteristics of the parent organic gel; thereby shape the texture of final carbon xerogel[11,13-15]. Sol-gel processing was done at five different pH values (in the range of 5.5 to 6.3) and thus five carbon xerogels were obtained. The carbon xerogels were examined by N_2 adsorption-desorption isotherm measurement study at −196°C, and the isotherms are shown in Fig. 3. The adsorption-desorption isotherms exhibit type IV nature with hysteresis loop characteristic of mesoporous materials. This indicates that the carbon xerogels are typically mesoporous. Also, the shape of the hysteresis loop indicates that the pores in the materials are cylindrical and open at both ends[16].
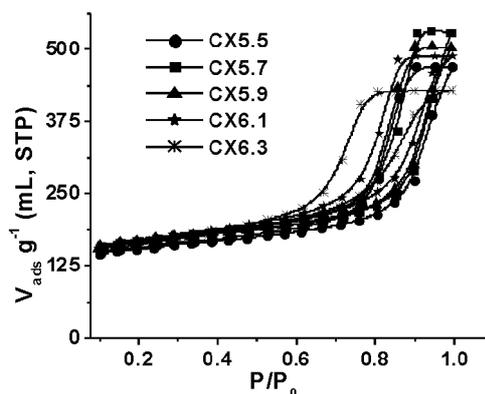

Fig. 3. N_2 adsorption-desorption isotherms exhibited by the carbon xerogels obtained by varying pH of sol-gel processing of the precursor organic gel.

The textural properties extracted from N_2 adsorption-desorption study are listed in Table 2. It is interesting to observe that the pH of sol-gel processing during the synthesis of the precursor organic gel significantly affects the pore radius, pore volume, and mesoporous area of the final carbon xerogel. However, no significant variation in BET area has been observed. Higher pH of sol-gel processing resulted in carbon xerogel with higher mesoporous area. Again, increase in pH of sol-gel processing from 5.5 to 5.7 resulted in increases in pore radius and pore volume. However, further increase in pH of sol-gel processing resulted in gradual decrease in pore radius and pore volume of the final carbon xerogel. Pore size distributions of the samples are shown in Fig. 4. It is interesting to note that sol-gel processing done at pH 6.3 resulted in carbon xerogel containing significantly narrow distribution of pore size. Almost all pores are concentrated with radius in the range of 2.7 to 5.0 nm, which could

Table 2. Textural properties of the carbon xerogels obtained by varying pH of sol-gel processing of the precursor organic gel

Carbon xerogel	S_{BET} $(m^2 g^{-1})$	S_{meso} $(m^2 g^{-1})$	V_T $(cm^3 g^{-1})$	V_{micro} $(cm^3 g^{-1})$	R_P (nm)
CX5.5	497	162	0.729	0.168	6.49
CX5.7	511	172	0.824	0.181	7.90
CX5.9	510	179	0.779	0.177	6.32
CX6.1	505	202	0.758	0.172	5.86
CX6.3	513	223	0.666	0.154	4.03

S_{BET} = Total surface area, S_{meso} = Mesoporous area, V_T = Total pore volume, V_{micro} = Micropore volume, R_P = Average pore radius.
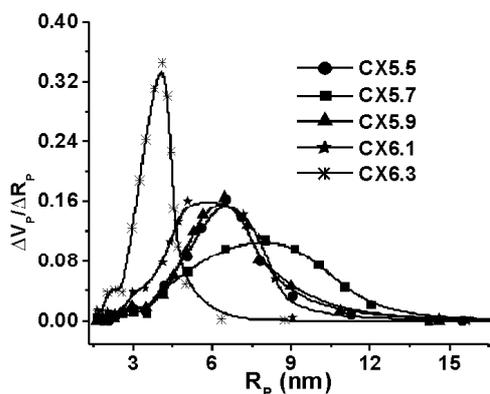
Fig. 4. Pore size distribution of the carbon xerogels obtained by varying pH of sol-gel processing of the precursor organic gel.

be suitable for selective use. On the other hand, the results also revealed that sol-gel processing performed at pH 5.7 resulted in the carbon xerogel containing large pores along with high pore volume; even though distribution of pore size was broad (pore radius: 4 to 12 nm). This type of sample would be beneficial in liquid phase applications to overcome diffusion limitation easily[2,5,10].

Post synthesis tuning by nitric acid activation-heat treatment:

Post synthesis treatment of carbon xerogel with nitric acid followed by heating under vacuum was performed in order to further tune the porous texture. The samples were characterised by N_2 adsorption-desorption isotherm measurement. The isotherms are shown in Fig. 5, and the textural
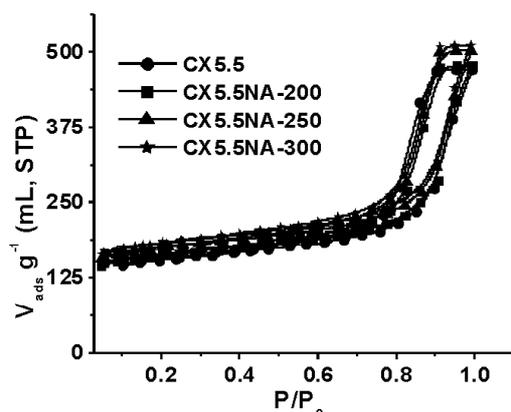

Fig. 5. N_2 adsorption-desorption isotherms exhibited by the pristine (CX5.5) and treated (by means of nitric acid activation-evacuation at elevated temperatures) carbon xerogels.

properties are listed in Table 3. Pore size distributions are shown in Fig. 6.

Table 3. Textural properties of the pristine (CX5.5) and treated (by means of nitric acid activation-evacuation at elevated temperatures) carbon xerogels

Carbon xerogel	S_{BET} $(m^2 g^{-1})$	S_{meso} $(m^2 g^{-1})$	V_T $(cm^3 g^{-1})$	V_{micro} $(cm^3 g^{-1})$	R_P (nm)
CX5.5	497	162	0.729	0.168	6.49
CX5.5NA-200	570	177	0.739	0.173	7.13
CX5.5NA-250	610	184	0.777	0.188	7.12
CX5.5NA-300	639	189	0.791	0.198	7.01

S_{BET} = Total surface area, S_{meso} = Mesoporous area, V_T = Total pore volume, V_{micro} = Micropore volume, R_P = Average pore radius.
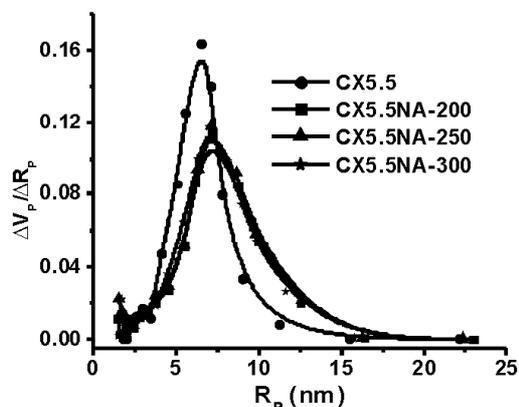

Fig. 6. Pore size distribution profiles of pristine (CX5.5) and treated (by means of nitric acid activation-evacuation at elevated temperatures) carbon xerogels.

Fig. 5 shows that the adsorption-desorption hysteresis loops presented by the samples are practically similar in shape; the hysteresis loops are characteristic of cylindrical (open at both ends) pores[16]. The observation clearly indicates that shape of pores remains unchanged upon the treatment by means of nitric acid activation-evacuation at elevated temperatures. However, extent of N_2 adsorption increased gradually with increase in temperature of treatment. More information on the outcome of this treatment is gathered in Table 3. BET area has increased to a large extent (15 to 29%) by this treatment. Mesopore area, total pore volume and micropore volume area have also been increased gradually. Average pore radius has increased significantly upon nitric acid activation followed by heating at 200°C under

vacuum. However, treatment at further higher temperatures (up to 300°C) did not change average pore radius. Enhancement in surface area, pore volume and pore radius can be explained as follows. Nitric acid activation created surface oxygen groups (carboxyl, carboxylic anhydride, lactones, etc.)[11,17]. These groups decompose severely during vacuum treatment at elevated temperature and evolved as CO_2, CO, and H_2O[11,17]. As result, porosity/surface area are increased; opening up of otherwise inaccessible pores are also plausible. Similar result with commercial activated carbon was reported by Szymanski *et al.*[17]. Pore size distribution showed in Fig. 6 confirmed that the number of pores of larger width increased by this treatment.

Conclusions

Mesoporous carbon xerogels with cylindrical pores, open at both ends, were prepared from paraformaldehyde and resorcinol precursors.

Pore texture of the carbon xerogels was tuned by the precursor sol-gel processing pH as well as by the post synthesis treatment by means of nitric acid activation-evacuation at elevated temperature.

The treatment, nitric acid activation-evacuation at elevated temperature, widens existing pores as well as likely opens up otherwise inaccessible pores.

Acknowledgements

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