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COMMUNICATION

Ionic liquid templated preparation of carbon aerogels based on resorcinol–formaldehyde: properties and catalytic performance

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A series of carbon aerogels were prepared with or without using ionic liquids as templates. By varying the structures and contents of ionic liquids, carbon aerogels with different pore size distributions could be obtained. The effect of the ionic liquids on the properties of the final carbon aerogels was explored and the catalytic performance of the carbon aerogels in the selective oxidation of tetralin was studied.

Introduction

Carbon aerogels have attracted extensive attention due to their specific properties, such as low mass densities, high surface areas, biocompatibility, energy storage performance, and so on.[1] Commonly, carbon aerogels are prepared through the sol–gel polymerization of resorcinol with formaldehyde in aqueous solution, drying of the organic gels and subsequent high temperature pyrolysis in an inert atmosphere.[2] Due to the specific physicochemical properties of carbon aerogels, they are expected to be used commercially as gas adsorption devices, separators for heavy metals, electrochemical capacitors, catalysts or catalyst supports, and many other promising applications.[3] Thus, since the first work reported by Pekala and co-workers through sol–gel polycondensation of resorcinol and formaldehyde,[2a,4] numerous articles have appeared concerned with the synthesis of carbon aerogels and how these affect the final structure of these materials.[5] As is well accepted, the unusual properties of carbon aerogels are derived from its unique structure. Thus, in order to develop carbon aerogels with potential applications, clean and economic preparation of carbon aerogels with controllable morphologies should be developed.

The development of ionic liquid chemistry offers potential choice in many fields.[6] Typically, it was reported that ionic liquids act as a versatile solvents in a number of polymerization reactions.[7] Moreover, ionic liquids have been used widely as template agents or carbon source in the fabrication of nano-structured organic materials.[8] Recently, del Monte *et al.*[9] explored the utilization of ionic liquids as deep eutectic solvents (DESs) for the polycondensation of phenol and aldehydes. In this process, ionic liquids acted as the solvent of starting materials and as the promoter for the formation of high molecular weight phenol polymers, which offers a method for the targeted synthesis of carbon aerogel.

Herein, we'd like to present our new results in carbon aerogel preparation using ionic liquids as templates. In this process, one of the key operations in the preparation of carbon aerogels, *i.e.* the freezing or supercritical drying of the organic gels before pyrolysis,[5d,5e,10] is avoided. Moreover, carbon aerogels with a wide range of pore sizes could be obtained by controlling the contents and structures of ionic liquids. These ionic liquid-oriented carbon aerogels can be directly used as catalysts in the selective oxidation of tetralin under mild conditions.

Experimental

Preparation of carbon aerogels

The carbon aerogels were prepared through a sol–gel polymerization of resorcinol and formaldehyde with Na_2CO_3 as a catalyst and ionic liquids as templating agents. Typically, resorcinol (R, 2.20 g, 20 mmol), formaldehyde (F, 3.25 g, 40 mmol, 36.5% in water, methanol stabilized) and 9 mL distilled water were added into a 100 mL polytetrafluoroethylene autoclave. Subsequently, 22.1 mg Na_2CO_3 (1 mol% to resorcinol) and a suitable amount of ionic liquid were added into the mixture. After vigorous stirring for 1 h, the autoclave was sealed and held at 80 °C for one day. Then, the autoclave was cooled to room temperature. The wet gels were put into a round-bottom flask and vacuum dried at 130 °C for 3 h. After being pyrolyzed at 800 °C for 5 h in nitrogen flow (20 mL min^{-1}), about 3.2 g black solid was obtained. Several carbon aerogels were prepared with or without ionic liquids as templates with the same procedure and denoted as RF-no IL, RF-5%BMImCl (B = butyl, M = methyl, Im = imidazole), RF-10%BMImCl, RF-20%BMImCl, RF-2.5%$BMImBF_4$, RF-10%$BMImBF_4$, RF-15%$BMImBF_4$, 20% $BMImBF_4$, RF-10%$EMImBF_4$ (E = ethyl), RF-10%$OMImBF_4$ (O = octyl), RF-10%$BMImPF_6$ and RF-10%$BMImN(CN)_2$. The numbers in the name of carbon aerogel samples represent the mass ratio of ionic liquids to resorcinol.

Characterization of the carbon materials

Nitrogen adsorption–desorption isotherms were recorded with an ASAP2010 and ASAP2020 adsorption analyzer at 77 K. The powder X-ray diffraction (XRD) patterns of the samples were recorded with a Stoe STADI P automated transmission diffractometer equipped

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with an incident beam curved germanium monochromator using Cu Kα_1 radiation. Scanning electron microscopy (SEM) investigations were carried out with a JSM-6701F instrument. Transmission electron microscopy (TEM) measurements were performed with a JEM 2010 microscope. XPS measurements were conducted on a VG ESCALAB 210 instrument provided with a dual Mg/Al anode X-ray source, a hemispherical capacitor analyser and a 5 keV Ar$^+$ ion-gun. The spectra were recorded using non-monochromatic Mg Kα (1253.6 eV) radiation.

Catalytic activity measurement

The catalytic activity was tested by the selective oxidation of tetralin. Typically, 2.6 g (20 mmol) tetralin and 50 mg catalyst were put into a 100 mL glass reactor equipped with magnetic stirrer. The reaction was carried out at 80 °C for 10 h under 1 atm oxygen. After reaction, the reaction mixture was cooled to room temperature and tested by GC-FID (Agilent 7890A) using hexadecane as an internal standard.

Results and discussion

First, by applying BMImBF$_4$ as template, the effect of the amount of ionic liquid on the structure of the targeted carbon aerogels was explored. Clearly, the variation of the amounts of ionic liquid affected the structure of the carbon aerogels remarkably.

According to the nitrogen adsorption–desorption isotherms, Fig. 1(a), there is no regular structure formation without the addition of ionic liquid as template. Therefore, the curve of the pore size distribution was not available by the BJH model. A micro-porous carbon aerogel was obtained if 2.5 wt% BMImBF$_4$ was added, Fig. 1(b). By raising the amount of BMImBF$_4$ to 10 wt%, we found the formation of meso-porous carbon aerogel. The pore size of the carbon aerogel is about 7 nm, Fig. 1(c). However, it turned to micro-porous carbon aerogel again if more BMImBF$_4$, *i.e.* 15 wt%, was added, Fig. 1(d). Subsequently, the structure of RF-10%BMImBF$_4$ before carbonization was studied by removing the ionic liquid under acetone refluxing. Clearly, it was composed of pores with diameters of 3.6 and 6.9 nm, Fig. 1(e). The results suggested that the porous structure was relatively stable after the formation of the gel. In other words, the mesopores were maintained during carbonization but reconstruction occurred.

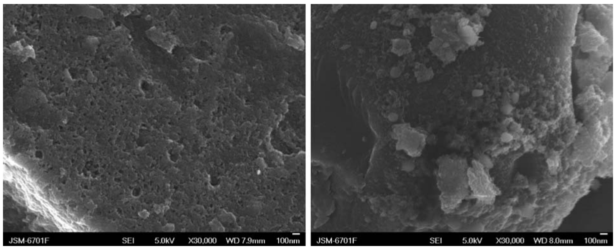


Fig. 2 SEM pictures of RF-no IL (left) and RF-10%BMImBF$_4$ (right).

SEM characterization suggested that the addition of BMImBF$_4$ does not influence the morphology of the carbon aerogels significantly. Two typical SEM pictures of RF-no IL and RF-10% BMImBF$_4$ were given in Fig. 2.

Further on, the influence of the structures of ionic liquids on the formation of carbon aerogels was explored. As we know from above, the addition of 10 wt% BMImBF$_4$ as template produced meso-porous carbon aerogels, so the same amount was chosen for the study

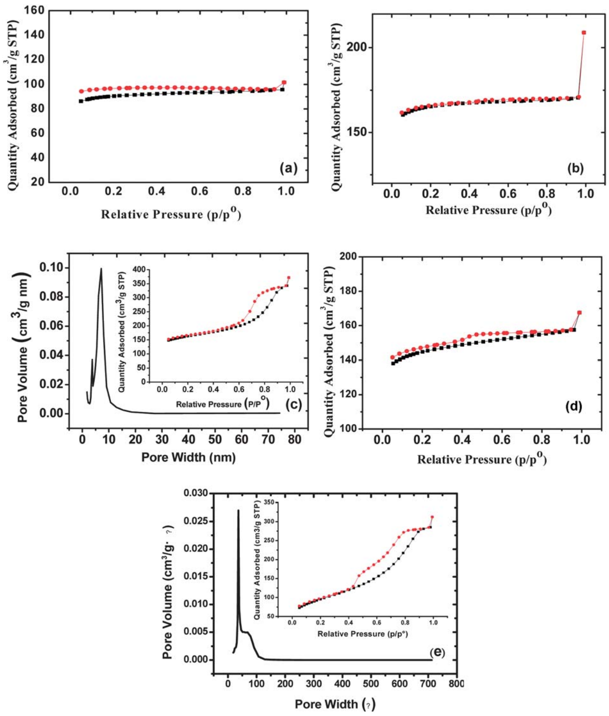


Fig. 1 N$_2$ adsorption–desorption isotherms of (a) RF-no IL, (b) RF-2.5%BMImBF$_4$, (c) RF-10%BMImBF$_4$, (d) RF-15%BMImBF$_4$ and (e) RF-10%BMImBF$_4$ (before carbonization but removing ionic liquid) and BJH pore distributions of (c) and (e).

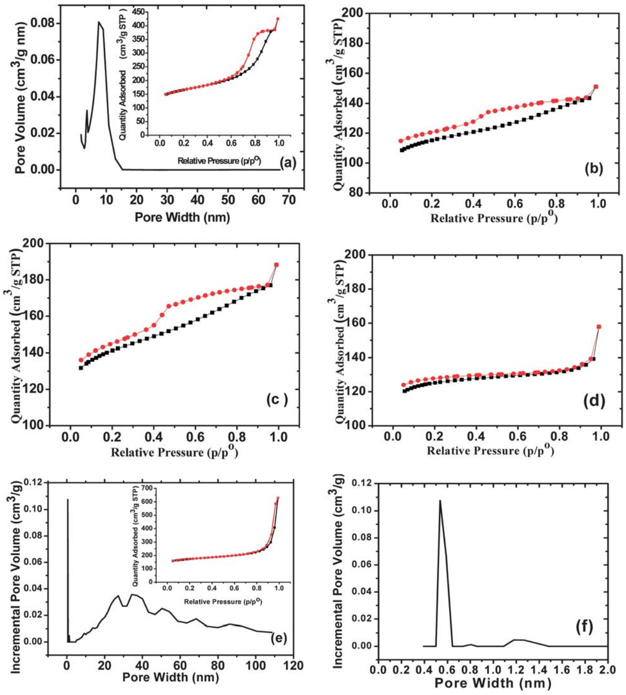


Fig. 3 N$_2$ adsorption–desorption isotherm of (a) RF-10%OMImBF$_4$, (b) RF-10%EMImBF$_4$, (c) RF-10%BMImPF$_6$, (d) RF-10%BMImN(CN)$_2$ and (e) RF-10%BMImCl; BJH pore distribution of (a) RF-10% OMImBF$_4$; DFT pore distribution of (e) RF-10%BMImCl and enlarged DFT pore distribution of (f) RF-10%BMImCl in the range of 0–2 nm.

Table 1 Physicochemical properties of carbon aerogels

Entry	Catalysts	S_{BET} ($m^2\ g^{-1}$)	Pore diam. (nm)	Pore volume ($cm^3\ g^{-1}$)	Density[a] ($g\ cm^{-3}$)
1	RF-2.5%BMImBF$_4$	386	—[b]	—[b]	0.19
2	RF-10%BMImBF$_4$	559	7.0	0.44	0.5
3	RF-15%BMImBF$_4$	490	—[b]	—[b]	0.75
4	RF-20%BMImBF$_4$	394	—[b]	—[b]	0.74
5	RF-10%EMImBF$_4$	391	—[b]	—[b]	0.67
6	RF-10%OMImBF$_4$	570	7.5	0.53	0.67
7	RF-10%BMImPF$_6$	481	—[b]	—[b]	0.77
8	RF-10%BMImN(CN)$_2$	422	—[b]	—[b]	0.36
9	RF-5%BMImCl	511	—[b]	—[b]	0.36
10	RF-10%BMImCl	590	0.6[c] 20–80[c]	—[b]	0.15
11	RF-20%BMImCl	20	—[b]	—[b]	0.16
12	RF-no IL	371	—[b]	—[b]	0.77

[a] The density was measured according to ISO 3953. [b] The BJH model is no longer valid for micro- and macro-porous materials characterization, thus the values are not given. [c] Porosity distribution obtained by original density functional theory (DFT).

of other ionic liquids as templates, Fig. 3. The physicochemical properties of different carbon aerogels were summarized in Table 1.

To our delight, meso-porous carbon aerogels were obtained with ionic liquids OMImBF$_4$ as templates too, Fig. 3(a). The pore size of this carbon aerogel is about 8.1 nm. If EMImBF$_4$ was used as template, a micro-porous carbon aerogel was obtained, Fig. 3(b). The changing of anions of ionic liquids influenced the structure of carbon aerogels significantly, too. A micro-porous carbon aerogel was obtained if using BMImPF$_6$ as template, Fig. 3(c). However, some meso-porous structures should be contained in RF-10%EMImBF$_4$, and RF-10%BMImPF$_6$ due to the formation of little hysteresis loops. If BMImN(CN)$_2$ was used to instead of BMImBF$_4$ or BMImPF$_6$, the meso-porous structure disappeared totally and a micro-porous carbon aerogel formed, Fig. 3(d). Interesting results were obtained with BMImCl as templating agent, which resulted in the formation of remarkable amounts of micro-, meso- and macro-pores, Fig. 3(e) and (f). This structure was only observed in the sample with BMImCl as template. Therefore, based on the results given in Table 1 and Fig. 3, it can be concluded that the structures of the anions and also the cations affected the porous structure of the final carbon aerogels remarkably.

Due to the interesting observation of micro-, meso- and macro-pore distributions of RF-10%BMImCl, Fig. 3(e) and (f), it was further characterized by SEM and TEM. As expected, a carbon aerogel with different morphology was formed. According to the SEM measurement, this carbon aerogel was composed of a small carbon particle of about 100 nm in size, Fig. 4(a). This structure was confirmed by the TEM characterization, Fig. 4(b), and it further suggested that the particle is composed of 20–30 nm particles with micro-pores, Fig. 4(c) and (d).

One of the features of our experiments is that the ionic liquid template is maintained in the wet gels without removing before pyrolysis. It makes the operation simple but possibly contaminates

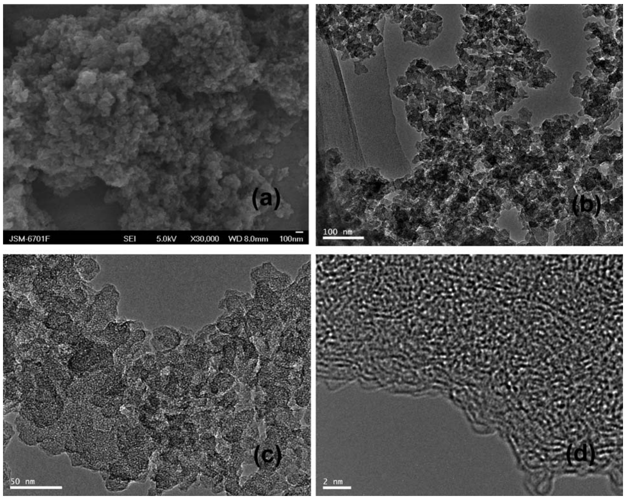


Fig. 4 SEM (a) and TEM (b–d) pictures of RF-10%BMImCl.

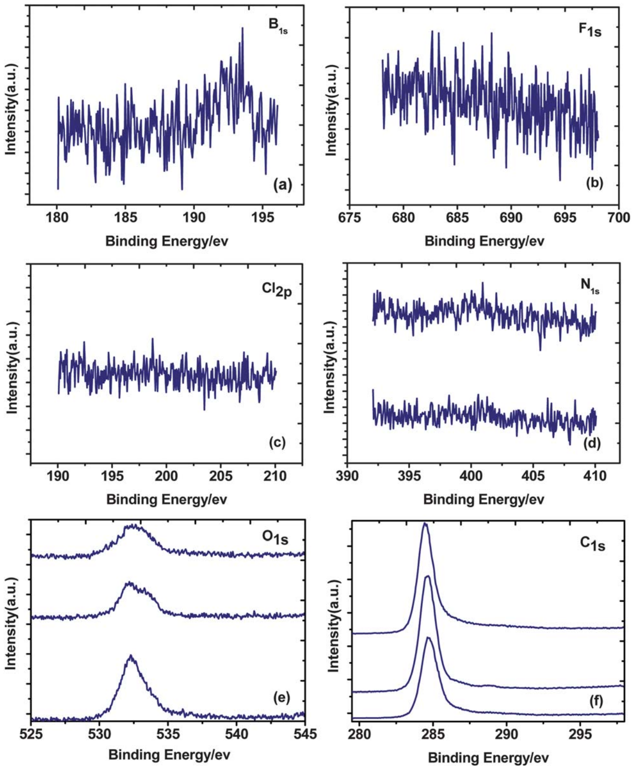


Fig. 5 XPS spectra of (a) B_{1s} of RF-10%BMImBF$_4$, (b) F_{1s} of RF-10% BMImBF$_4$, (c) Cl_{2p} of RF-10%BMImCl, (d) N_{1s} of RF-10%BMImBF$_4$ (top) and RF-10%BMImCl (bottom), (e) O_{1s} of RF-10%BMImBF$_4$ (top), RF-10%BMImCl (centre) and RF-no IL (bottom) and (f) C_{1s} of RF-10% BMImBF$_4$ (top), RF-10%BMImCl (centre) and RF-no IL (bottom).

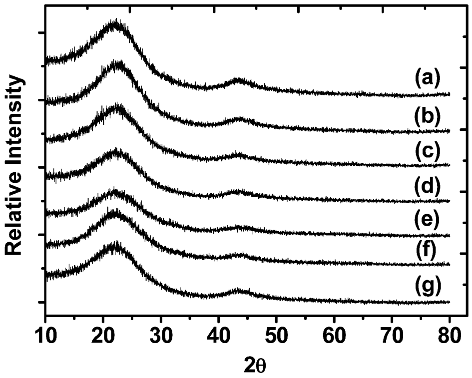


Fig. 6 XRD diffraction patterns of (a) RF-no IL, (b) RF-10%BMImBF$_4$, (c) RF-10%EMImBF$_4$, (d) RF-10%OMImBF$_4$, (e) RF-10%BMImCl, (f) RF-10%BMImPF$_6$ and (g) RF-10%BMImN(CN)$_2$.

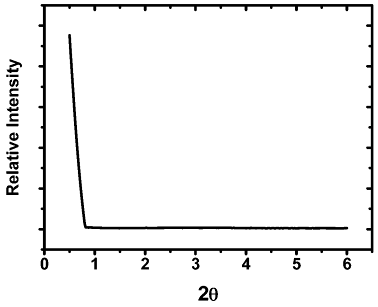


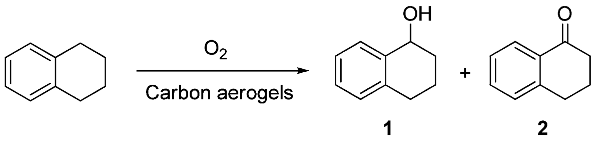
Fig. 7 The SAXRD diffraction patterns of the RF-10%BMImBF$_4$.

the carbon aerogels. Therefore, the carbon aerogels were characterized by XPS to check the ionic liquid species. The extraneous species possibly derived from the ionic liquids are B, F, Cl and N, and the typical XPS spectra of these elements are given in Fig. 5. Clearly, they were all unobservable on the surface of carbon aerogels even though the ionic liquids were not removed before the pyrolysis. So, although we don't remove the ionic liquids before pyrolysis, it doesn't contaminate the final carbon aerogels. Moreover, based on the typical O$_{1s}$ and C$_{1s}$ spectra of carbon aerogels with or without the addition of BMImBF$_4$ and BMImCl, Fig. 5(e) and (f), similar O$_{1s}$ and C$_{1s}$ spectra were observed. These results indicated that the addition of ionic liquid only altered the porosity of the carbon aerogels without changing the chemical valence of carbon in the final materials. Moreover, the surface O/C ratios of RF-no IL, RF-10%BMImBF$_4$, RF-5%BMImCl, RF-10%BMImCl and RF-20%BMImCl were 0.26, 0.015, 0.06, 0.013 and 0.019, respectively. So it could be imagined that the addition of ionic liquids as templates reduced the quantity of surface oxygen.

In order to check the crystal structure of the obtained carbon aerogels, the typical samples were characterized by XRD. As shown in Fig. 6, typical diffraction patterns of amorphous carbon materials were observed with or without the addition of ionic liquids as templates. As a typical technique for meso-porous material characterization, small-angle X-ray diffraction (SAXRD) was applied in the characterization of RF-10%BMImBF$_4$, Fig. 7, and there is no observable diffraction pattern of typical crystallized meso-porous material.

Carbon materials have been used extensively in catalysis as supports or catalysts, and here, the selective oxidation of tetralin was used as the model reaction to check the possibility of the carbon aerogels to be used as catalysts directly, Table 2. The results suggested that these carbon aerogels exhibited good activity in the selective oxidation of tetralin with or without using ionic liquids as templates, entries 1–9. Commonly, the catalytic activity could be improved using ionic liquids as templates. By applying a typical carbon aerogel, *i.e.* RF-10%BMImCl, as catalyst, the conversion of tetralin to 1,2,3,4-tetrahydronaphthalen-1-ol and 3,4-dihydronaphthalen-1-one reached 30% with 78% selectivity. According to the characterization results given in Fig. 3 and 4 and Table 1, the high activity of RF-10%BMImCl might be derived from its specific structure, *i.e.* the highly dispersed nano-particles, the presence of abundant micro-, meso- and macro-pores and the low density.

Table 2 Selective oxidation of tetralin catalyzed by typical carbon aerogels[a]



Entry	Catalysts	Conversion[b]/%	Selectivity[c]/%	Yield[d]/%	**1** : **2**
1	RF-no IL	15.7	84	13.2	1 : 2.2
2	RF-10%BMImBF$_4$	18.9	68	12.5	1 : 3.2
3	RF-10%EMImBF$_4$	25	46	11.5	1 : 2.4
4	RF-10%OMImBF$_4$	17.8	75.6	13.4	1 : 2.4
5	RF-10%BMImPF$_6$	15.4	89	13.8	1 : 2.4
6	RF-10%BMImN(CN)$_2$	19.3	81.5	15.7	1 : 2.2
7	RF-5%BMImCl	17.5	75	13	1 : 1.9
8	RF-10%BMImCl[e]	30	78	23.9	1 : 2.2
9	RF-20%BMImCl	24	71	17	1 : 1.9
10	Activated carbon[f]	4.5	64	2.9	1 : 1.1
11	Activated carbon[g]	14.6	80	11.6	1 : 2.2

[a] *Reaction conditions*: 2.6 g (20 mmol) tetralin, 50 mg catalyst, 80 °C, 10 h, 1 atm O$_2$. [b] Tetralin converted. [c] The selectivities to **1** and **2**. [d] **1** and **2** produced. [e] Average result of reactions repeated three times. [f] $S_{BET} = 1000$ m^2 g^{-1}. [g] $S_{BET} = 200$ m^2 g^{-1}.

Conclusion

In summary, the influence of ionic liquid on the structure of carbon aerogels was explored with resorcinol and formaldehyde as starting agents. Carbon aerogels with micro- or meso-porous structures could be controllably synthesized by varying the side chain of imidazolium cation or the anions of ionic liquids. In this method, the ionic liquid template remained inside the wet gel without removing before pyrolysis. Catalytic activity measurement suggested these carbon aerogels are potential catalysts for selective oxidation reactions. This work offers a simple method for the controllable preparation of carbon aerogels with tunable structures.

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