A comparative study of supercritical petroleum ether and carbon dioxide drying in the preparation of carbon aerogels

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Abstract   Organic and carbon aerogels were synthesized from sol-gel polymerization of phenolic resole and methylolated melamine followed by supercritical drying and pyrolysis. Supercritical petroleum ether 30 ℃-60 ℃ drying SPD and supercritical carbon dioxide drying SCD were employed and compared for the preparation of organic and carbon aerogels. It was found that SPD which was carried out at 240 ℃ and 6.0 MPa for 1 h produced organic aerogels with lower BET surface areas and mesopore volumes than SCD which was carried out at 60 ℃ and 10.0 MPa for 7 d. However the porous structure of SPD organic aerogels is more stable during pyrolysis than that of SCD organic aerogels and as a result BET surface areas and mesopore volumes of SPD carbon aerogels are all larger than those of SCD carbon aerogels indicating that SPD whose drying process is substantially shorter than with SCD can be used as an alternative method for the preparation of carbon aerogels.

Keywords   Organic aerogels Carbon aerogels Porosity Supercritical drying

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1   Introduction

In recent years there are increasing interests in synthesis of sol-gel derived porous carbon carbon aerogels xerogels and cryogels [1-6] because of virtues of sol-gel process which allows microstructure control at the nanometer scale [7][8] and of their superior properties to inorganic counterparts in electrical conductivity biocompatibility and anticorrosion by acid or base etc [9][10]. Among the three forms of sol-gel derived porous carbons carbon aerogel is the best one because it is derived from supercritically dried organic aerogel whose microstructure is retained to a maximum possible extent as in the wet gel since no force is imposed on pore-wall of wet gel in supercritical drying process. However supercritical drying of organic gels with the most commonly used solvent carbon dioxide is especially long and tedious due to the low diffuse coefficient of solvent to carbon dioxide at low temperature. Although acetone with high critical temperature was used as supercritical solvent in one case [11] however no detailed information about microstructures of carbon aerogels was provided and especially organic gels could partly dissolve in supercritical acetone. In this paper an easy-available organic mixture petroleum ether 30 ℃-60 ℃ with the similar crit-

ical temperature as acetone is used as supercritical solvent to dry organic gels from sol-gel polymerization of phenolic resole and methylolated melamine. Possibility of dissolution of network in supercritical petroleum ether is excluded. Moreover due to high critical temperature and low critical pressure of petroleum ether which is estimated to be 220 ℃ and 4.5 MPa respectively and that organic solvent in the gels that need expelling is near its critical state at this condition drying process is substantially shortened. We compared further the microstructure of organic and carbon aerogels from supercritical petroleum ether drying SPD with that from supercritical carbon dioxide drying SCD . Applicability of petroleum ether as an alternative method for carbon dioxide is discussed.

2   Experimental

2.1   Materials and synthesis

As an example 2.5 g melamine and 6 mL 6 mole folds of melamine formaldehyde 37.5 w/% methanol stabilized was mixed with 5 mL 0.1 mol/L sodium carbonate and distilled water to form 50 mL solution which was heated to 70 ℃ with agitating for 10 min. Then 1 mL cresol mixture with 90 w/% m-cresol and 1 mL

formaldehyde were added with consecutive heating and agitating until drops of cresol were completely immersed into the solution. Finally 15 g of phenolic resole with solid content of 50 $w/\%$ was poured into the solution and distilled water was added until final volume of the solution reached 100 mL. The solution was decanted to glass ampoules which were sealed and placed in water bath at 85 ℃ ± 1 ℃ for 16 h. The solution formed transparent red gel in 5 h. After 11 h additional heating in the water bath the wet gels were then soaked in acetone bath at 45 ℃ for 3 d with fresh acetone replaced everyday. The SPD of gels were carried out in an autoclave which was filled up with petroleum ether boiling range 30 ℃-60 ℃ and the autoclave was heated to 250 ℃ with a heating rate of 2 ℃/min while the pressure was kept at 6.0 MPa by a modulating valve. The autoclave was isothermally depressurized to atmospheric pressure at 0.1 MPa/min after the organic gels were soaked at

250 ℃ 6.0 MPa for 1 h. The organic aerogels obtained are named as O-SPD . The cylindrical organic aerogels were pyrolyzed at 800 ℃ for 2 h under protection of nitrogen with oxygen and water less than $1 \times 10^{-4}\%$ and $5 \times 10^{-4}\%$ respectively. The carbon aerogels obtained are named as C-SPD. The SCD of wet gels was carried out in exactly same procedure and conditions as described by Pekala et al [12] and organic and carbon aerogel labeled as O-SCD and C-SCD respectively are obtained. Some organic aerogels O-SCD were heat-treated with the same temperature profile as used in the SPD yielding heat-treated organic aerogels O-SCD-250 ℃. In this study the concentration of phenolic resole PR ratios of m-cresol/phenolic resole m-C/PR and melamine/phenolic resole M/PR were varied under identical ratios of Na_2CO_3/phenolic resole S/PR formaldehyde/m-cresol F/m-C and formaldehyde/melamine F/M . Detailed formulations were shown in Table 1.

Table 1 Formulation and properties of organic and carbon aerogels

Sample No.	PR ρ/g 100 mL^{-1}	M/PR ζ/m_M m_{PR}^{-1}	m-C/PR ζ/m_{m-C} m_{PR}^{-1}	S_{BET}/m² g^{-1}	υ_{mic}/cm³ g^{-1}	υ_{mes}/cm³ g^{-1}	D_p/nm
a-O-SPD				465.5	N.D.	0.78	7.3
a-C-SPD	7.5	1/3	0/7.5	618.3	0.10	0.45	5.4
a-O-SCD				590.4	N.D.	0.90	6.9
a-C-SCD				567.8	0.12	0.34	4.5
b-O-SPD				585.4	N.D.	1.19	6.5
b-C-SPD				765.0	0.12	0.68	4.8
b-O-SCD	7.5	1/3	1/7.5	721.0	N.D.	1.36	6.1
b-C-SCD				691.0	0.11	0.51	4.0
b-O-SCD-250 ℃				695.0	N.D.	1.27	6.2
c-O-SPD				521.2	N.D.	0.94	7.5
c-C-SPD	7.5	1/3	2/7.5	691.1	0.11	0.54	5.5
c-O-SCD				681.7	N.D.	1.21	7.1
c-C-SCD				651.3	0.14	0.45	4.7
d-O-SPD				461.2	N.D.	0.62	5.6
d-C-SPD	7.5	1/5	1/7.5	612.7	0.10	0.36	4.0
d-O-SCD				598.0	N.D.	0.80	5.2
d-C-SCD				571.1	0.12	0.30	3.5
e-O-SPD				454.0	N.D.	0.72	6.5
e-C-SPD	7.5	2/5	1/7.5	603.3	0.10	0.41	4.8
e-O-SCD				580.2	N.D.	0.85	6.0
e-C-SCD				553.1	0.11	0.33	4.0

N.D. not detected. D_p is the average mesopore diameter of organic aerogels when cylindrical pore geometry is assumed.

Other components Ratios of formaldehyde/melamine F/M   formaldehyde/m-cresol F/m-C and Na_2CO_3/phenolic resole S/PR are 1.35

mole ratio   6 mole ratio and 0.001 mol/1.5 g respectively.

2.2 Characterization

Nitrogen adsorption-desorption of orignic and carbon aerogels was carried out at 77 K with a Sorptomatic 1990 instrument. The mesopore size distributions and mesopore volumes υ_{mes} of organic and carbon aerogels were estimated for pore diameter D_p = 2 nm-50 nm by applying the Dollimore-Heal method [13] to the desorption isotherms of nitrogen. The micropore volumes υ_{mic} of
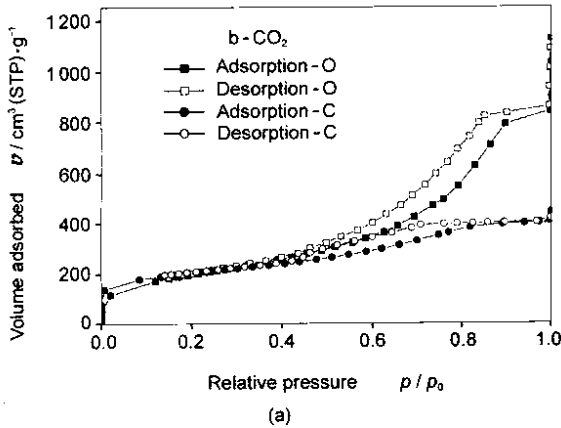
organic and carbon aerogels were evaluated by α_s-plot [14] with reference to the standard nitrogen adsorption data for nonporous carbon by de Boer and coworkers [15].

3 Results and discussion

Polymerization of phenolic resole and methylolated melamine led to transparent red organic gels in all formulations used. The mass of all organic aerogels by

either methods equal to the mass of reactants that form organic gels within experimental errors   indicating that polymerization proceeds completely and that there is no mass loss during SCD or SPD   excluding possibility of dissolution of organic gels in either supercritical fluid used.

All adsorption and desorption isotherms of organic and carbon aerogels obtained under different formulations are similar. As an example   Fig.1 shows adsorption and desorption isotherms of organic and carbon aerogels from different drying methods for formulation b. All organic and carbon aerogels have type IV isotherms with H2 hysteresis. Slight increase in micropore volume and sharp decrease in mesopore volumes are observed when organic aerogels are converted to carbon aerogels by pyrolysis.
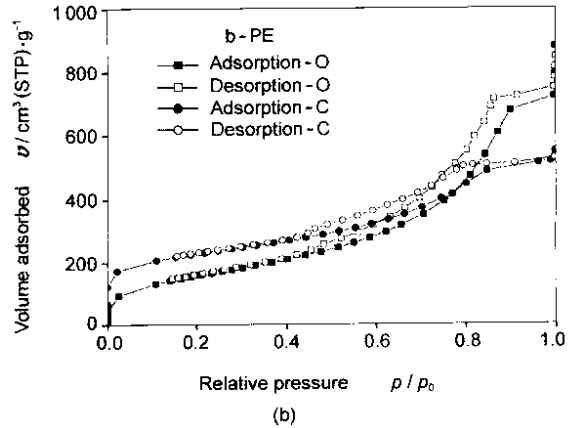

Fig.1   Adsorption and desorption isotherms of organic and carbon aerogels from different drying methods   formulation b

From Table 1   it is found that both S_{BET} and υ_{mes} of all SCD organic aerogels are larger than those of relevant SPD organic aerogels   and that average pore diameters of all SCD organic aerogels are smaller than those of relevant SPD organic aerogels. However   after pyrolysis   the S_{BET} and υ_{mes} of SCD carbon aerogels are all smaller than those of relevant SPD carbon aerogels   and that average pore diameters of SCD carbon aerogels are smaller than those of relevant SPD carbon aerogels. All organic aerogels have negligible micropores not detectable within experimental errors. All carbon aerogels have small amount of micropores   which could be developed in the pyrolysis process and might be path for evolving volatile components. Due to small and comparable micropore volumes of the two types of carbon aerogels and larger υ_{mes} of SPD carbon aerogels than SCD carbon aerogels   it could be concluded that it is the mesopores that are responsible for the larger S_{BET} of SPD carbon aerogels than SCD carbon aerogels. When the SCD organic aerogel was heat-treated by the same temperature profile in SPD   the S_{BET} and υ_{mes} of heat-treated sample are still larger than that of relevant SPD organic aerogel. From mesopore size distributions shown in Fig.2   it is found that mesopore sizes of SPD organic and carbon aerogel are larger and broader than that of SCD organic and carbon aerogels. All these imply that   gels were subjected to physical and chemical changes in SPD where temperature is high. From the experimental evidences   it could be concluded that restructuring of gel network that broadens pore sizes and stabilizes the network upon high temperature occur in the SPD   which is responsible for higher S_{BET} and υ_{mes} of SPD carbon aerogels. The high efficiency of SPD could be attributed to the enhanced diffusion of acetone because acetone is also in critical state under SPD process.
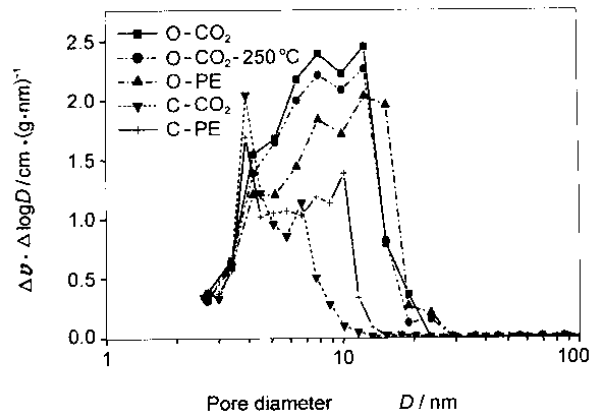

Fig.2   Mesopore size distributions of organic and carbon aerogels from different dying method   formulation b

4   Conclusions

SPD is an effective way to dry organic gels from sol-gel polymerization of phenolic resole and methylolated melamine. Although SPD is unfavorable for production of organic aerogels   it is favorable for production of carbon aerogels with high BET surface areas and high

mesopore volumes.

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                 2.   030001
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                    240 ℃ 6.0 MPa   1 h   60 ℃ 10.0 MPa   7 d

        BET

                                        BET