

On Porosity of Carbon Aerogels from Sol-Gel Polymerization of Phenolic Novolak and Furfural

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Abstract. Carbon aerogels were prepared by sol-gel polymerization of phenolic novolak and furfural followed by supercritical drying and pyrolysis. The porosity and morphologies of carbon aerogels were characterized by nitrogen adsorption, apparent density, He- pycnometer method, and transmission electronic microscopy (TEM). Effect of ratios of phenolic novolak to furfural (Ra) and total concentration of reactants (C) in sol-gel step on porosity and morphologies of carbon aerogels was investigated. The carbon aerogels synthesized are rich in meso- and macropores. The Ra determines the cross-linking density of polymers, thereby the compatibility of the polymers, and ultimately the shrinkage of gels in the drying and pyrolysis. The network sizes and the porosity of organic and carbon aerogels are mainly determined by Ra. The C has no effect on volume shrinkage of gels in drying and pyrolysis and has only dilute effect in determining bulk density of organic and carbon aerogels, and ultimately the porosity of carbon aerogels. Conversion of mesopores to micro- and macropores is observed, which is related to combination of C and Ra, and determines the partition of micro-, meso- and macropores.

Keywords: carbon aerogels, organic aerogels, crosslinking, pyrolysis, porosity

1. Introduction

In recent years, there are increasing interests in synthesis of mesoporous carbon via sol-gel routine [1–4] owing to virtues of sol-gel process that allow microstructure control at the nanometer scale [5] and superior properties of sol-gel derived porous carbon (carbon aerogels, xerogels, and cryogels) to inorganic counterparts in electrical conductivity, biocompatibility and anticorrosion by acid or base, etc. [6–8]. A number of applications have been identified for them, including electrodes for double-layer supercapacitors and fuel cells, separators for heavy metals and ions, gas adsorption devices, catalyst support, filters, and chromatographic packing [9, 10].

Meso- and macro-porosity are the most important structure features related to the applications of carbon gels in the fields mentioned above, and are in the focus of the state-of-the-arts synthesis. There are four steps in the preparation of carbon aerogels, namely sol-gel, solvent exchange, supercritical drying and pyrolysis process, all of which affect porosity and morphologies of carbon aerogels. The sol-gel process is the most important one among the four because the physical and chemical structure of polymer gels, from which carbon aerogels are produced, are formed in this step. In this step alone, choice of precursors, molecular architecture, composition, molecular size, catalyst and solvent all affect porosity and morphologies of wet gels and ultimately carbon aerogels. Numerous studies have been devoted to understanding how the synthesis conditions in the sol-gel process affect the porous structure of

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organic and carbon aerogels. Pekala et al. investigated effects of ratios of resorcinol to catalyst, and ratios of resorcinol to water on porosity and morphologies of organic aerogels using small angle X-ray scattering [11]. Tamon et al. found mesoporosity of carbon aerogels from resorcinol-formaldehyde was correlated to ratios of resorcinol to water, and ratios of resorcinol to catalyst [12]. However, all of these investigations were carried out under the same ratio of reactants to separate the effect of polymer architectures from that of colloidal related issues. It is well known that molecular architecture of polymers can be altered by ratios of chemically distinct reactants, and plays an important role in the evolution of phase morphologies in polymer-polymer phase behavior by influencing polymer mobility [13]. The role of molecular architecture of polymers in carbon aerogel preparation might be much more complicated because solvent is included in sol-gel step, nonequilibrium phase phenomena are pronounced in drying and pyrolysis, and chemical reactions at high temperature in pyrolysis lead to a weight loss up to 50% and substantial microstructure changes. How molecular architectures of polymers affect the structure and morphologies of wet gels in the sol-gel step and the structure and porosity evolution in the drying and pyrolysis step is a complex and unanswered question. However, little effort has been made on this issue as far as authors know.

In this paper, phenolic novolak and furfural were selected as precursors of carbon aerogels for the sakes of cheap raw materials and short synthetic routine [14]. In order to alter molecular architecture of polymers that form wet gels, the ratios of phenolic novolak to furfural (Ra) were changed in the sol-gel step at different total concentration of reactants (C) under otherwise identical conditions. The objectives of the current research are to gain a fundamental understanding of how molecular architectures of polymers affect evolution of porous structure from wet gels to carbon aerogels, and to develop meso- and macroporous structure control strategies in the preparation of carbon aerogels.

2. Experimental

2.1. Materials

Phenolic novolak is low molecular weight polymer derived from the hydrochloride-catalyzed reaction of a molar excess of phenol with formaldehyde under 95°C for 45 minutes followed by water-washing and vacuum

drying. The soft point of phenolic novolak prepared under this condition is 76°C. Anhydrous hydrochloride, which was used as catalyst in this study, was prepared by slowly pouring acetylchloride into ice-bathed anhydrous methanol. All other reagents used are analytic grade.

2.2. Synthesis

In this study, Ra was varied at different C under otherwise identical conditions as described in what follows, yielding a series of samples, C/Ra. For an example, sample 5/0.5 is prepared under total concentration of reactants, C, being 5 g/100 ml and the ratio of phenolic novolak to furfural, Ra, being 0.5 wt/wt.

Phenolic novolak, furfural and 1-propanol defined by C/Ra with catalyst at concentration of 8 mmol HCl/100 ml for sixteen experiments, were mixed to form transparent solutions. The solutions were ultra-filtered and poured into glass ampoules (8 cm length $\times$ 2 cm internal diameter, each filled with 20 ml solution). The ampoules were sealed by gas torch, and cured in water bath at 85°C for seven days. Then, the necks of ampoules were broken, and sixteen cylindrical gels nested within the ampoule to prevent floating in fluid were put into an autoclave with internal dimension of $\Phi 70 \times 400$ (1500 ml), where supercritical drying was carried out to obtain organic aerogels. In the supercritical drying process, the autoclave was completely filled with petroleum ether (30–60°C) whose critical temperature and pressure were estimated to be 217°C and 5.2 MPa [15]. When the autoclave was being heated to 250°C at 2°C/min, pressure was maintained at 7 MPa by adjusting the relief valve. After one hour holding at 250°C, the autoclave was depressurized to atmospheric pressure at a rate of 0.1 MPa/min, and subsequently evacuated to 0.06 MPa to expel residue solvent when temperature decreased to 150°C under its own thermal mass. Finally, the carbon aerogels were formed by pyrolysis of the organic aerogels in a horizontal tube-furnace at 800°C for 3 hours under protection of nitrogen with oxygen ≤ 2 ppm and water ≤ 5 ppm. The heating rate was 5°C/min and cooling rate was set by thermal mass of the furnace.

2.3. Characterization

The volume evolution of gels from the wet to the carbon was traced simply by volume measurement. Volume shrinkage of gels from drying and pyrolysis steps was

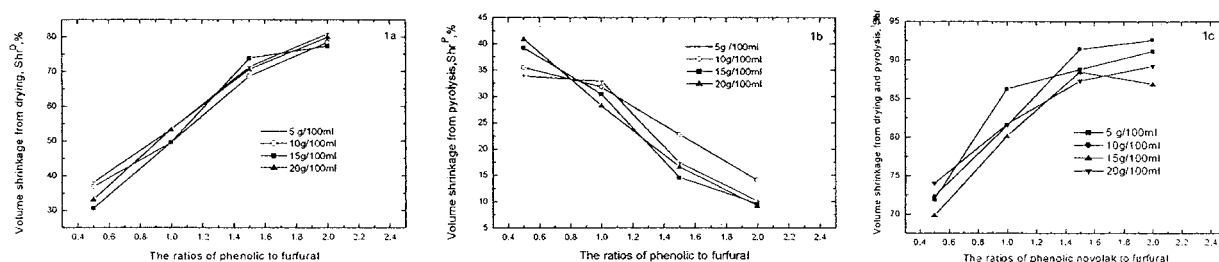


Figure 1. Volume shrinkage of gels from drying and pyrolysis versus the ratios of phenolic novolak to furfural R_a and the total concentration of reactants C .

defined based on the volume of original solution that forms the gels.

The bulk density ρ_c of monolithic cylindrical carbon aerogels were obtained from weight and volume of the cylindrical aerogels. The apparent density ρ_{ac} of aerogels was measured by a helium-pycnometer method. The total accessible pore volume V_T was calculated from the bulk density ρ_c and apparent density ρ_{ac} by the equation, $V_T = 1/\rho_c - 1/\rho_{ac}$.

Adsorption and desorption isotherms of nitrogen were measured at 77 K using a Sorptomatic 1990 (CE instrument). The BET surface area, S_{BET} of the aerogels were determined from the adsorption isotherm of nitrogen. The mesopore size distribution and mesopore volume V_{meso} were estimated for pore diameter $D_p = 2\text{--}50$ nm by applying the Dollimore-Heal [16] method to the desorption isotherm of nitrogen. The micropore volume, V_{micro} , and external surface area, S_{EXT} , were evaluated from adsorption isotherm of nitrogen by α_s -plot with reference to the standard nitrogen adsorption data for a nonporous carbon by Carrott et al. [17]. Some carbon aerogels are too fragile for Hg porosimetry, so there is no direct information available on the macropore volume. In this paper, the macropore volume V_{macro} was estimated by the formula $V_{macro} = V_T - V_{meso} - V_{micro}$ [18].

Finally, transmission electron micrographs were obtained with a Hitachi H-6000 transmission electron microscope (TEM).

3. Results

3.1. Volume Evolution of Gels

Polymerization of phenolic novolak and furfural led to opaque black gels for all sixteen samples. The volume of the wet gels is 1–5% less than that of the original solution due to syneresis. After 1-propanol in the wet gels was replaced by petroleum ether, slight

swelling of the gels occurred due to the interaction of hydrophobic furan group with petroleum ether, but the volume of petroleum ether-containing gels didn't exceed the volume of original solution. After being dried in supercritical petroleum ether, however, the gels suffered apparent shrinking. As indicated in Fig. 1(a), the volume shrinkage of the gels by the drying, $Shr^D\%$ is almost independent of C , and increases linearly with R_a , which can be fitted by the equation, $Shr^D\% = 20.87 + 30.60 R_a$ ($R = 0.98$). The bulk density of organic aerogels versus R_a and C are shown in Fig. 2(c) and 2(d) and they can be fitted by the equation, $\rho_0/C = 0.00295 + 0.01831 R_a$ ($R = 0.97$) as shown in Fig. 2(f), where ρ_0 is bulk density of organic aerogels in g/cm^3 , and R is correlation coefficient. Upon pyrolysis, organic aerogels also suffered apparent shrinking. As indicated in Fig. 1(b), the volume shrinkage of the gels from pyrolysis, $Shr^P\%$ is also independent of C , but decreases linearly with R_a , which can be fitted by the equation, $Shr^P\% = 47.40 - 18.56 R_a$ ($R = 0.96$). The total volume shrinkage of gels in drying and pyrolysis, $Shr^T\%$, which is the summation of $Shr^D\%$ and $Shr^P\%$ should increase linearly with increase R_a and is also independent on C . As indicated in Fig. 1(c), however, $Shr^T\%$ exhibits a slow increase at high R_a . The bulk density of carbon aerogels versus R_a and C are shown in Fig. 2(a) and (b) and similarly they can be formulated by the equation, $\rho_c/C = 0.00484 + 0.0235 R_a$ ($R = 0.95$) as shown in Fig. 2(e), where ρ_c is bulk density of carbon aerogels in g/cm^3 . The proportional dependence of ρ_c on C is in accordance with the independence of total volume shrinkage on C in drying and pyrolysis process.

3.2. Adsorption-Desorption Isotherm and Pore Size Distribution

Adsorption-desorption isotherms of carbon aerogels formed at different C and the same R_a 0.5 are shown

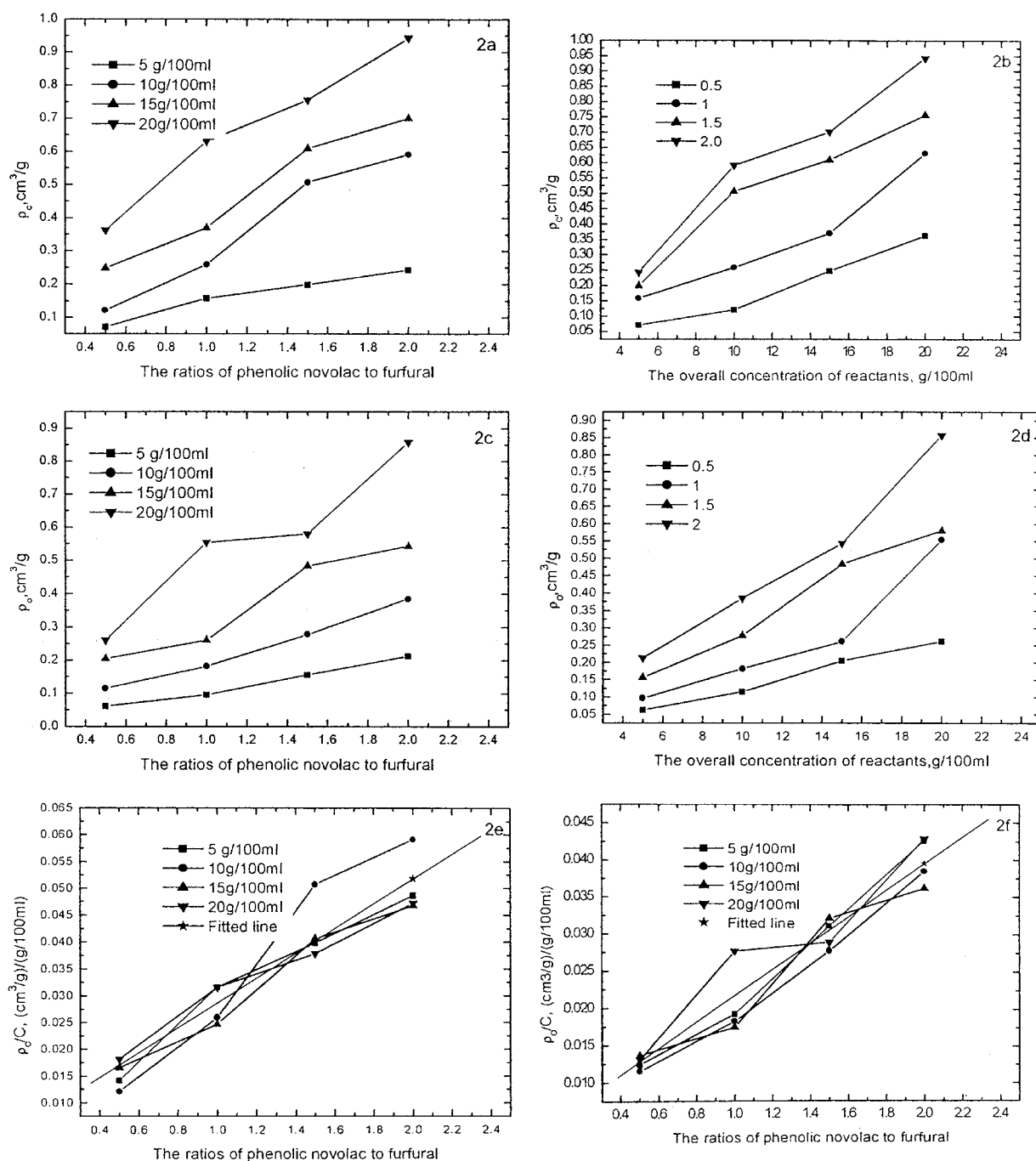


Figure 2. Bulk density of organic and carbon aerogels versus the ratios of phenolic novolac to furfural R_a and the total concentration of reactants, C .

in Fig. 3(a)–(d). Hysteresis loops of isotherms are usually attributed to capillary condensation occurring in mesopores and opening of hysteresis loops near unity relative pressure indicates coexistence of meso- and

macro-pores. Non-vanishing of volume adsorbed near zero relative pressure shown in adsorption isotherm in Fig. 3(a)–(d) indicate that there are small amount of micropores in carbon aerogels. The pore size distributions

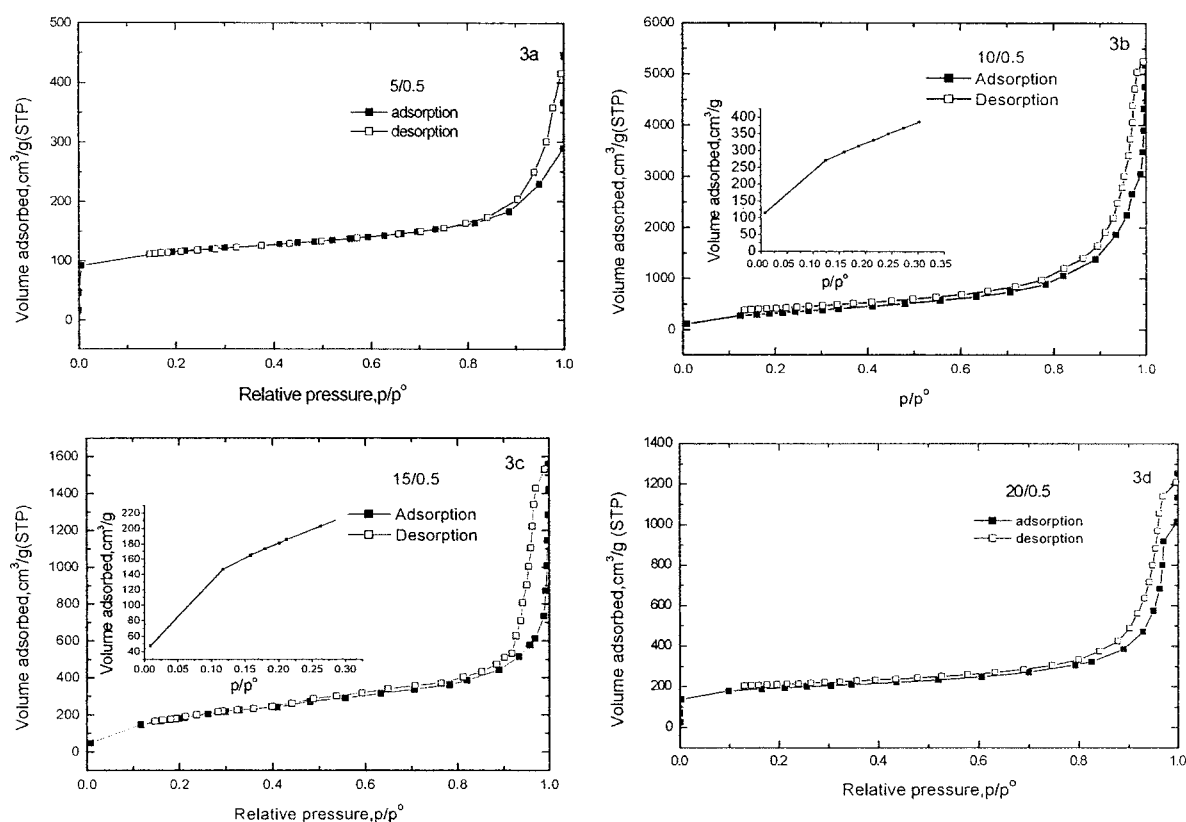


Figure 3. Nitrogen adsorption and desorption isotherms of carbon aerogels at Ra of 0.5 under different C.

shown in Fig. 4(a)–(d) reveal that the carbon aerogels are rich in meso- and macropores and that under low C value, the sizes of pores extend to ultra macropore regime, which is outside the range for N_2 adsorption measurement. Large deviation of average pore size by porosity measurement from that by nitrogen adsorption measurement at low C shown in Fig. 5 is another evidence to confirm that the sizes of pores of carbon aerogels formed under low C value extend beyond nitrogen adsorption measurement.

3.3. Microporosity of Carbon Aerogels

Micropore volume of carbon aerogels and their portion in total pore volume with varying Ra and C is shown in Fig. 6(a)–(d). The micropore portions of carbon aerogels in total pore volume are all less than 28%. In addition, negative micropore volumes are found for samples 10/0.5 and 15/0.5 as shown in Fig. 6(a) and (b). Although the negative micropore volume takes only 2.97 and 1.35% in total pore volume for samples 10/0.5 and 15/0.5 respectively, it causes substantial over estimate

of external surface area (see Section 3.5) because contribution of micropores to surface area is large. There are no identical changing patterns for micropore volume either with increasing Ra at different C or with increasing C at different Ra (see Fig. 6(a) and (b)). So are the micropore portions of carbon aerogels in total pore volume (see Fig. 6(c) and (d)). After the micropore portions are divided by the total concentration of reactants, C, the linear correlation, although poor, is found as shown in Fig. 7(a) and (b) and can be fitted by the formula, $V_{\text{micro}}/V_T * 100/C = -0.113 + 0.555 * Ra$ ($R = 0.72$), indicating that the micropore portions of carbon aerogels in total pore volume are proportional to C and increase linearly with Ra. The large deviation from the linear line together with negative value of the micropore volume will be discussed in Section 4.

3.4. Meso- and Macroporosity of Carbon Aerogels

The mesopore volume obtained by nitrogen adsorption-desorption measurement and macropore volume estimated by the formula $V_{\text{macro}} = V_T - V_{\text{meso}} - V_{\text{micro}}$

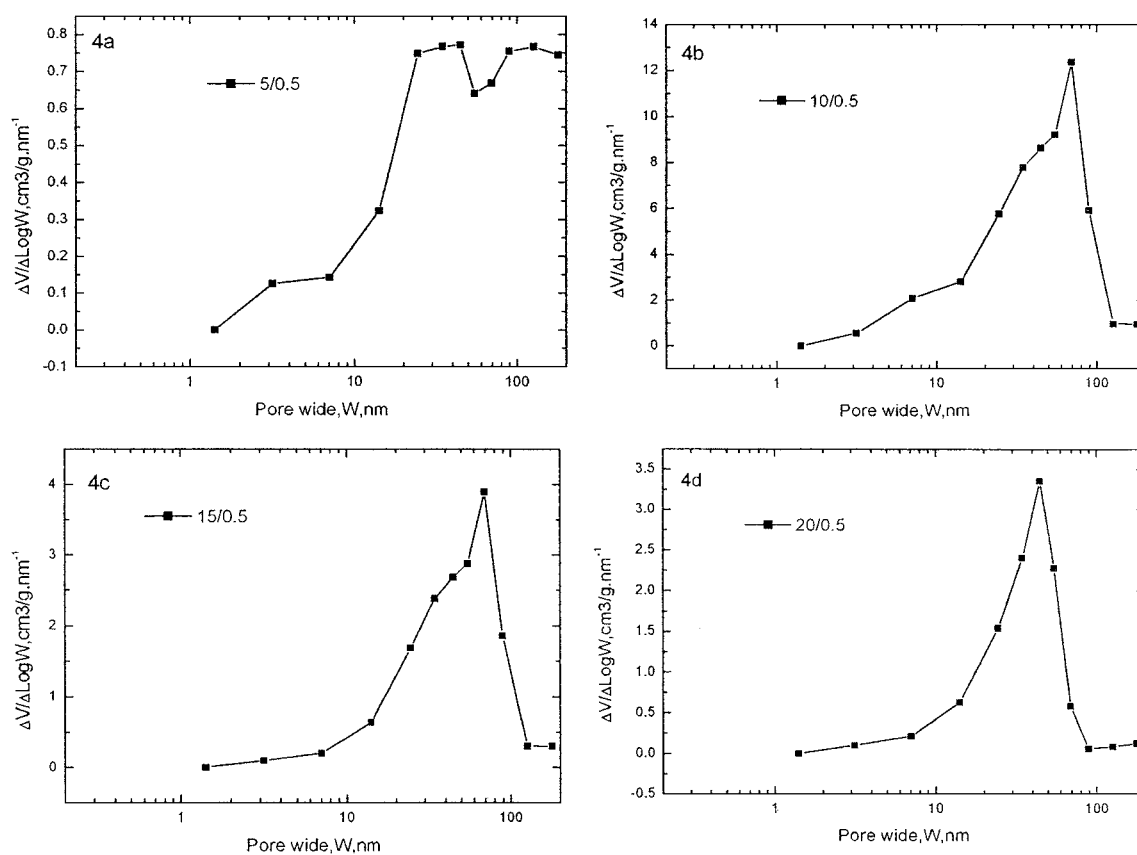


Figure 4. Mesopore size distribution of carbon aerogels at different total concentration of reactants.

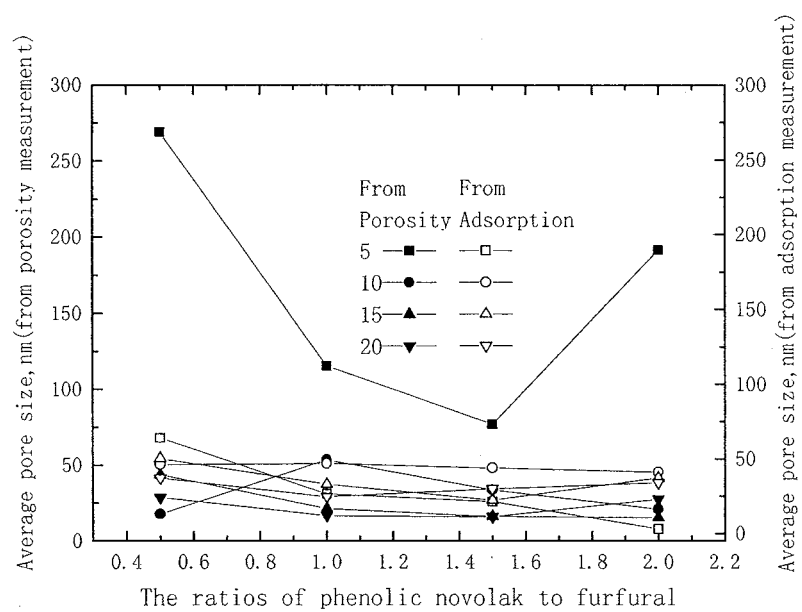


Figure 5. Comparison of average pore size determined from porosity and adsorption measurement.

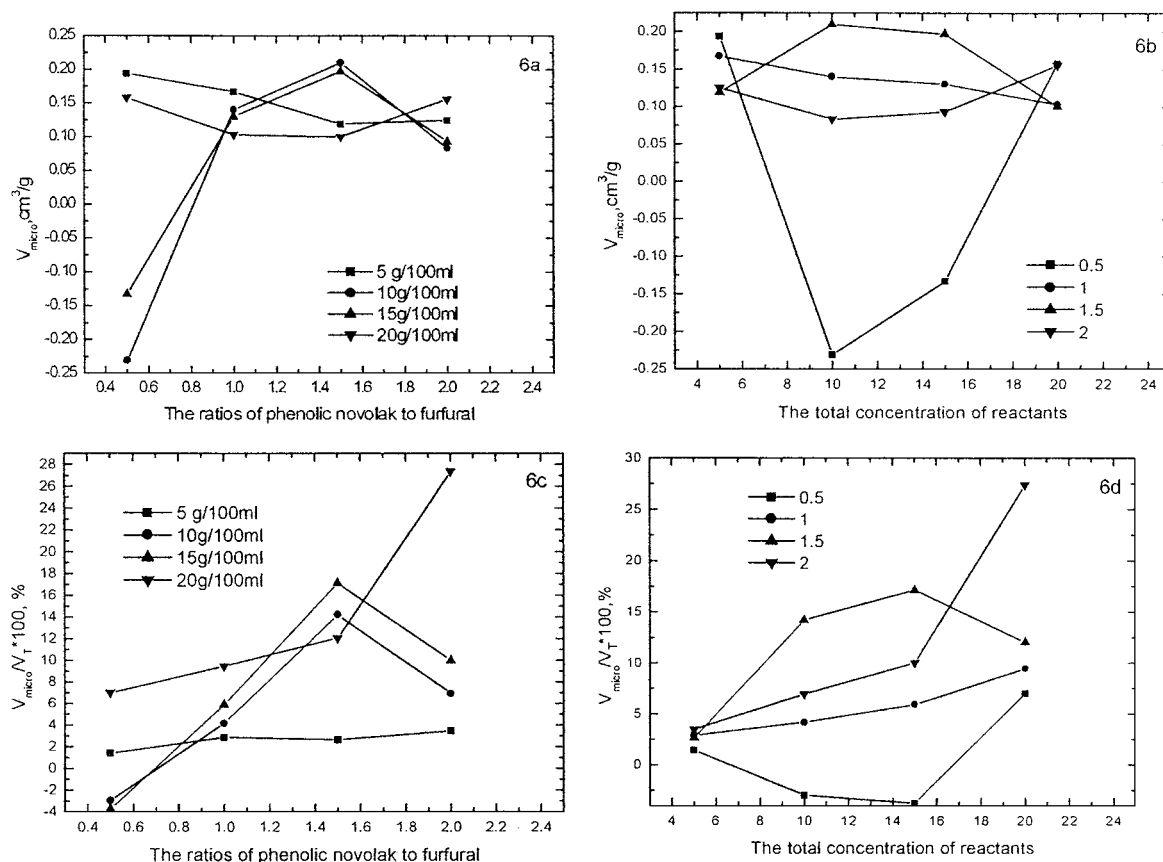


Figure 6. Micropore volume of carbon aerogels and their portion in total pore volume versus the ratios of phenolic novolak to furfural and total concentration of reactants.

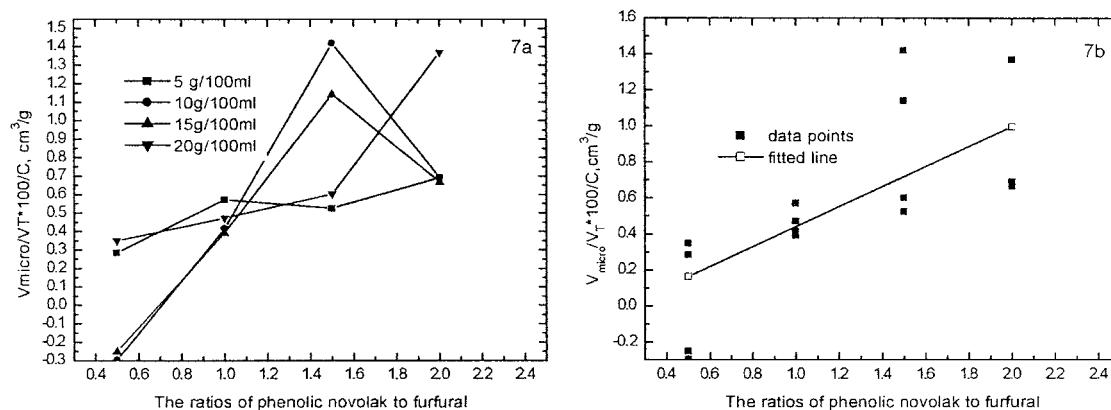


Figure 7. Micropore portion of carbon aerogels in total pore volume after divided by C and their linear relation to the ratios of phenolic novolak.

are shown in Fig. 8(a)–(f) (In case of negative micropore volume, zero volume of V_{micro} is arbitrarily set). From Fig. 8(c) and (e), it can be seen that both mesopore volume and macropore volume of carbon aerogels

decrease with Ra under all the C investigated, indicating that decreasing of Ra is favorable for meso- and macropore formation. Fig. 8(d) shows that the mesopore volume of carbon aerogels, however, experiences

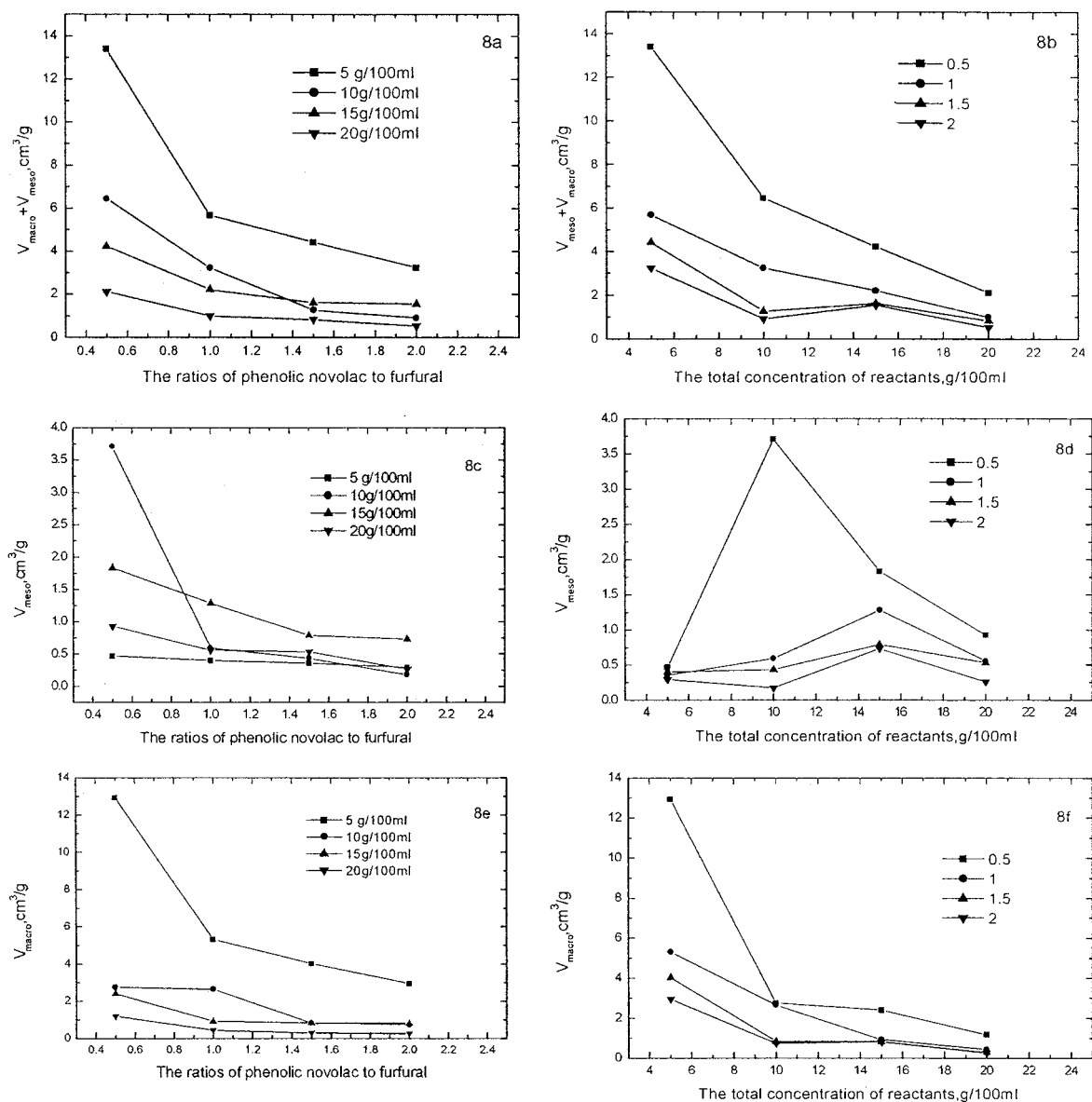


Figure 8. Meso-, and macropore volume of carbon aerogels versus the ratios of phenolic novolac to furfural and total concentration of reactants.

a maximum with increasing C under the same Ra, which is inconsistent with that of macropore volume or summation of macro and mesopore volume shown in Fig. 8(f) and (b).

3.5. BET and External Surface Area of Carbon Aerogels

Figure 9(a)–(d) show BET and external surface area of carbon aerogels with increasing Ra and C respec-

tively. It is found in Fig. 9(a) and (b) that BET surface area of carbon aerogels decrease with increasing Ra at all C, but exhibit no consistent patterns with increasing C at different Ra. The external surface area, however, exhibits almost the same patterns as mesopore volume does with increasing Ra at different C or with increasing C at different Ra (see Figs. 8(c), (d), 9(c), and (d)). This is because the contribution to external surface area from mesopores is much larger than from macropores. Besides, the external surface area of sample 10/0.5 and 15/0.5 are larger than BET surface area.

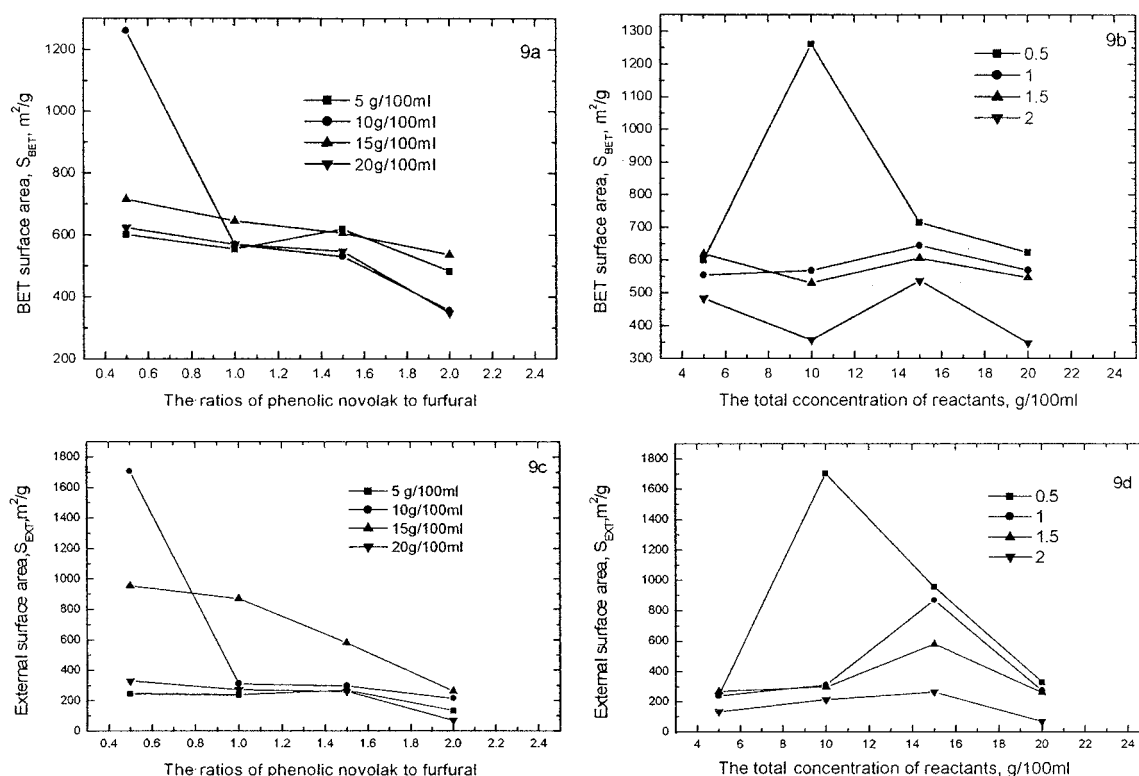


Figure 9. BET surface area and external surface area of carbon aerogels versus the ratios of phenolic novolak to furfural and total concentration of reactants.

This is in agreement with the negative micropore volume summarized in Section 3.3 and will be discussed in Section 4.

3.6. TEM Morphologies and Porosity

Figure 10(a)–(h) show TEM micrographs of organic and carbon aerogels formed under different C and Ra. Under the same C of 5 or 10 g/100 ml, the network size of both organic and carbon aerogels with low Ra of 0.5 (see Fig. 10(a), (c), (e), and (g)) is smaller than those with high Ra of 1.5 (see Fig. 10(b), (d), (f), and (h)). Apparent sintering in pyrolysis is found for organic aerogels synthesized at high Ra (see Fig. 10(f) and (h)). Under the same Ra of 0.5 or 1.5, the network sizes of both organic and carbon aerogels with low C of 5 g/100 ml (see Fig. 10(a), (e), (b), and (f)) is larger than that with high C of 10 g/100 ml (see Fig. 10(c), (g), (d), and (h)). Networks of both organic and carbon aerogels tend to be discrete at high Ra (see Fig. 10(b), (d), (f), and (h)), but is bicontinuous at low Ra (see Fig. 10(a), (c), (e), and (g)).

4. Discussion

The porosity of carbon aerogels, when all other conditions except Ra are identical, are determined by physical and chemical structure of polymers that form gels. At low Ra, which corresponds to an abundant cross-linking agent, the cross-linking density of polymers is high, and as a result, polymers are less compatible due to high energy cost for stretching and compressing chains from their preferred configuration when they are combined together. This profoundly affects structure evolution of gels from at the very beginning of gelation to when organic aerogels are formed by supercritical drying. This is because polymer gels are highly unstable [19], and are in constant evolution to a more stable state either in the gelation process in the wet state or in the supercritical drying process. Especially in supercritical drying, the instability of gels is increased due to elevated temperature and pressure and complete removal of solvent. The extent, to which the polymer gels can shrink in the gelation and supercritical drying process, depend on compatibility or cross-linking density

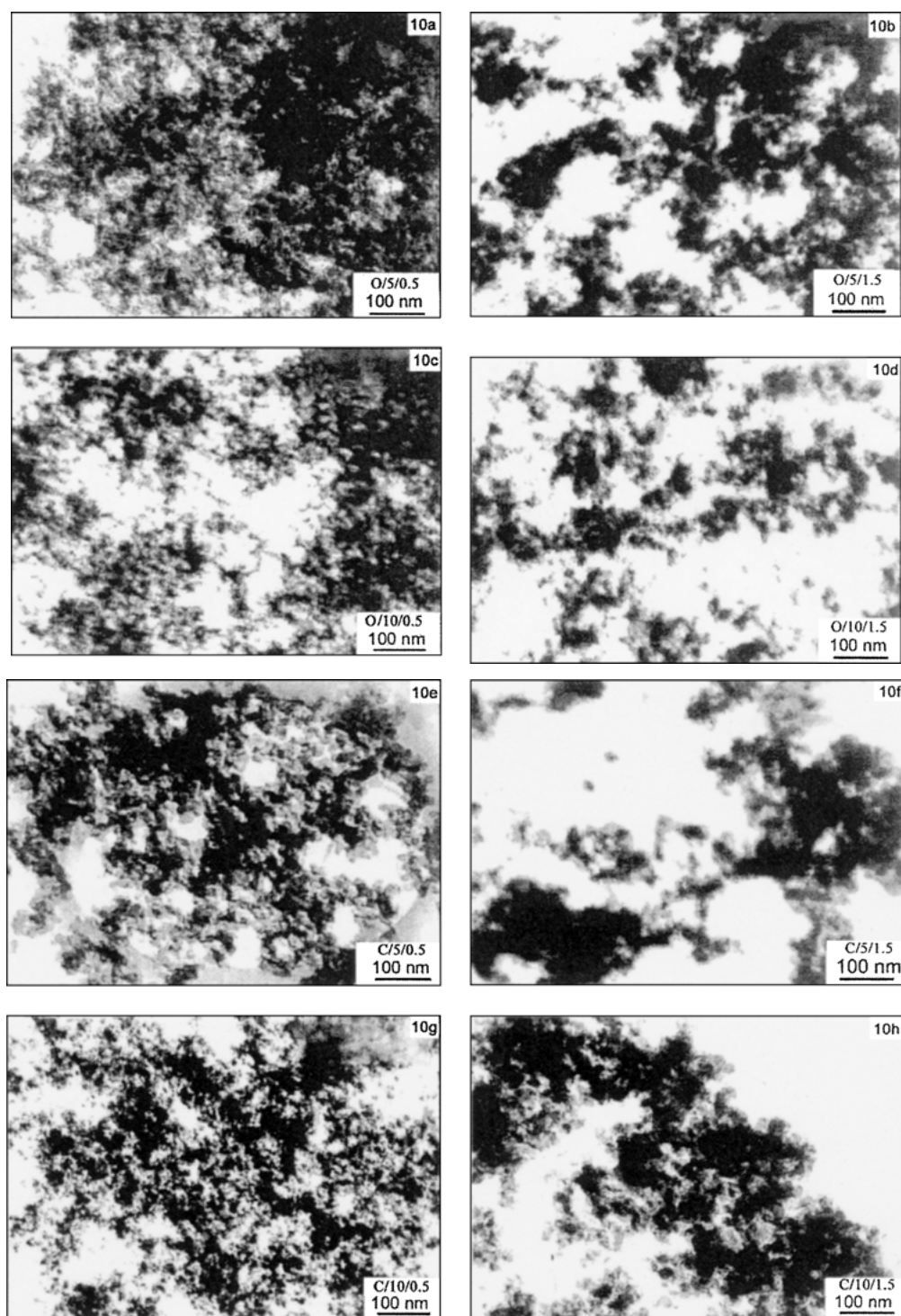


Figure 10. TEM micrographs of organic and carbon aerogels. The organic aerogels are labeled as O, and carbon aerogels as C. Samples with total concentration of reactants 5, 10 g/100 ml and ratios of phenolic novolak to furfural 0.5, 1.5 are imagined for both organic and carbon aerogels.

of polymers. The higher is R_a , the lower is the cross-linking density of polymers or the higher is the compatibility of polymers. As a result, the volume shrinkage of organic gels in the supercritical drying process increases linearly with increasing R_a irrespective of C as shown in Fig. 1(a) and the network size of organic aerogels at low R_a is smaller than that at high R_a as shown in Fig. 10(a)–(d). In pyrolysis, where temperature is high enough to break chemical bonding, intermolecular interaction is no longer dominant. The lower R_a , the less the polymer gels have shrunk in the supercritical drying step, and as a result, the higher are the energy state of the organic aerogels when intermolecular interaction is broken, and the higher are the shrinkage of the organic aerogels in pyrolysis step due to a higher thermodynamic driving force. This could account for the fact that the volume shrinkage of the organic aerogels from pyrolysis decreases linearly with increasing the R_a irrespective of C as shown in Fig. 1(b). Also apparent sintering is found in pyrolysis for organic aerogels formed at high R_a as shown in Fig. 10(b), (d), (f), and (h). This could account for the slow increase of total volume shrinkage at high R_a mentioned in 3.1. The compromising action of R_a with respect to volume shrinkage from supercritical drying and pyrolysis process determine bulk density, and hence the porosity of carbon aerogels. The independence of volume shrinkage from drying and pyrolysis on C and proportional dependence of bulk density of carbon aerogels on C imply that C has dilute effect only in determining bulk density or total porosity of carbon aerogels. However, with increasing C under the same R_a , the mesopore volume of carbon aerogels experiences a maximum as shown in Fig. 8(d). This could be explained in what follows. At low C , on the one hand, the density of gels is low and as a result, their ability to decrease interfacial area is larger than the gels formed at high C . Because surface curving of mesopore is much larger than macropore, mesopores suffer greater change than macropores, leading to a decrease in mesopore volume. On the other hand, a low C is favorable to formation of mesopores at the very beginning of gelation. So it is the two opposite factors that determine changing of mesopore volume with C . From the fact that the sum of meso- and macropore volume of carbon aerogels obey the result derived from compatibility of polymers that form gels and observation that network size of organic and carbon aerogels is larger at low C than at high C under the same R_a as shown in Fig. 10(a)–(h), it could be conjectured that conversion of mesopores to macro-

pores occur as a result of mesopore volume shrinking to decrease interface area at low C . The proportional dependence of micropore portion in total pore volume on C and linear increase of it with increasing R_a indicate that gelation and coarsening from the very beginning of gelation to the formation of carbon aerogels also convert mesopores to micropores. The ink-bottom micropores with their opening accessible to helium but inaccessible to nitrogen could be formed in the light that He- pycnometer gave the same apparent density of 2.03 g/cm³, but micropore volume at C value of 10 and 15 g/100 ml and R_a value of 2 by nitrogen tiling is significantly below the linear lines (see Fig. 7(a)).

Of particular interesting phenomena is that negative micropore volume is found for samples 10/0.5 and 15/0.5, which is in accord with the observations that external surface area is larger than BET surface area for the two samples and in contradiction to the presence of micropores for them as shown in Fig. 2(b) and (c). This could be the validity of α_s -plot that gives rise to the phenomena. The α_s -plot is empirical method based on the standard adsorption data of non-porous and finely divided carbon. In case of carbon aerogels whose micropores between contiguous particles are rich, these micropores could give enhanced adsorption in multi-layer range, and increase slope of α_s -plot below α_s value of 1, which overestimates the external surface area and underestimate micropore volume. For samples 10/0.5 and 15/0.5, small network sizes are expected as discussed above and percolation threshold has not been attained, which give much more rich micropores of this kind than other samples do and as a result, a larger deviations from α_s -plot. Similar phenomena have been found in contiguous range in single wall carbon nanotube assemblies in which case density of hydrogen or methane within interstitial space (contiguous range) is 1.5 times as much as that within internal space (within nanotubes) [20].

5. Conclusion

Carbon aerogels rich in meso- and macroporosity have been synthesized using phenolic novolak and furfural as precursors.

The study reveals how R_a and C affect meso- and macroporosity of carbon aerogels from phenolic novolak-furfural. The ratios of phenolic novolak to furfural, R_a determines the cross-linking density of polymers and hence, the compatibility of the polymers,

which, in turn, determines the shrinking behaviors of gels in the drying and pyrolysis, the network size of organic and carbon aerogels, and ultimately the porosity of carbon aerogels. The total concentration of reactants, C has no effect on volume shrinkage of gels in drying and pyrolysis and has only dilute effect in determining bulk density of organic and carbon aerogels, and ultimately the porosity of carbon aerogels. Conversion of mesostructure to macrostructure from the very beginning of gelation to carbon aerogel formation is much more pronounced under low C and high Ra than under the other cases. Conversion of mesopores to micropores also occurs.

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