PREPARATION AND CHARACTERIZATION OF ORGANIC AEROGELS FROM A LIGNIN - RESORCINOL - FORMALDEHYDE COPOLYMER

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Lignin can be used as a cheap natural raw material to prepare organic aerogels based upon gelation and supercritical drying in ethanol. The aerogels were prepared from a mixture of the raw materials with lignin (L), resorcinol (R), and formaldehyde (F), followed by a reaction catalyzed by NaOH(C). The effect of the preparation conditions, such as the LRF concentration, the mass ratio of LR to NaOH (LR/C), the mole ratio of LR to F (LR/F), and the gelation temperature, on the gelation ability and the bulk density were studied. The results showed that the density of LRF aerogels increased with increasing reactant concentration and catalyst content. The microstructure of the porous carbon aerogels was investigated by SEM and TEM. The specific surface area and pore size distribution of LRF and RF aerogels were studied by nitrogen adsorption-desorption analysis. The pore width of LRF aerogels ranged from 1 nm to 100 nm. Most of the pores were about 50 nm wide, as is typical for mesoporous materials.

Keywords: Lignin; Resorcinol; Organic aerogel; Porous structure

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INTRODUCTION

In recent years aerogels have been presented as a new macrostructural material. Aerogels consist of highly porous organic or inorganic material having a three-dimensional polymeric network made up of primary particles in the size range 10 to 30 nm. Certain aerogels can exhibit some unique properties, such as a high specific surface area, a pronounced mesoporosity (Suh et al. 1996, 2000), a structure composed of uniform-sized nanoparticles, a fine dispersion in composites, and an excellent thermal stability (Jinsoon et al. 2007). These intrinsic characteristics have attracted interest in the use of aerogels as thermo-insulators, catalysts, adsorbents, dielectrics, and sensors. Aerogels are manufactured by the sol–gel technique with polymerization and polycondensation. After formation of a three-dimensional network of colloidal particles, the gel has to be dried without shrinkage in order to avoid its destruction by capillary forces. Drying is either done super-critically or under ambient conditions, provided the gel has been stabilized by suitable measures against the action of the capillary stresses.

The past few years have witnessed substantial research investigating the unique properties and applications of organic aerogels. Furthermore, many efforts have been made to simplify the processing (Fu et al. 2003; Albert et al. 2001; Pekala et al. 2000) and to exploit cheap raw materials (Li et al. 2000, 2001, 2002). Pekala and Kong (1989) developed a method to synthesize organic aerogels by polymerization of resorcinol (R) and formaldehyde (F), catalyzed by sodium carbonate. These aerogels were manufactured by supercritical drying. In 1995 Mayer et al. were the first to manufacture RF-aerogels by subcritical drying in air after substitution of the gel liquid by acetone. Thanks to the development of the sol–gel method and subcritical or supercritical drying with CO_2, remarkable progress has been made in lowering the cost of aerogel preparation. However, it is regrettable that one of the raw materials, resorcinol, is relatively expensive. In order to further decrease the cost of organic aerogels and to improve the utilization of biological resources as raw materials, in our experiments lignin is employed to poly-condense with resorcinol-formaldehyde for preparing organic aerogels.

EXPERIMENTAL

Materials

Resorcinol [$C_6H_4(OH)_2$, 98%(w/w%)] (R), formaldehyde [(HCHO), 37%(w/v%) solution] (F), sodium hydroxide [NaOH, 99.5%(w/w%)] (C), acetone [Fisher Scientific, reagent grade], peracetic acid[(CH_3COOH), 5%(w/v) solution], enzymatically isolated lignin (Purchased in ZhaoDong Ethanol Factory) (L), and deionized water (Purchased in HarBin ZhongYuan chemical company) (W) were used in the experiments.

Organic Aerogel Preparation

RF hydrogels were synthesized by the polycondensation of resorcinol [$C_6H_4(OH)_2$] (R) with formaldehyde [HCHO] (F) according to the method proposed by Pekala and coworkers (1989, 1993). RF solutions were prepared by mixing the required amount of (R), (F), and sodium carbonate (C) with distilled water (W) under vigorous stirring for 45 minutes. The molar ratio of R to F (R/F) and R/W were kept constant, but the ratio of R to C (R/C) was varied. The following detailed procedure was used to prepare organic aerogels. According to the predetermined formulations, the polymerization reaction of reactants were lignin (L), resorcinol (R), formaldehyde (F), deionized water (W), and catalyst (NaOH), which were mixed with a magnetic stirrer at room temperature and then further mixed by the ultrasonic cleaning machine at 20 ^{o}C. The mixture was then transferred into a glass vial. The vial was sealed and then immediately put into a water bath (85 ^{o}C). After gelation, the aging agent (5% peracetic acid solution) was placed directly into the vial for the aging period. Subsequently, the resulting organic gels were transferred into a pressure vessel and dried under supercritical ethanol drying conditions (250 ^{o}C, 10 MPa). Finally, the aerogels were obtained.

Characterization of the Organic Aerogel

The organic aerogel was denoted as LRF. The densities were calculated by measuring the volume and weight of organic aerogels synthesized in this work. Transmission electron micrographs (TEM) and scanning electron micrographs (SEM) of the specimens were obtained with HITACHI-H7650 and QUANTA200 instruments. Nitrogen adsorption and desorption isotherms were then taken using an ASAP2020 Surface Area and Porosity Analyzer (Micromeritics Instrument Corporation). According to the IUPAC classification, the nano-pores of organic and carbon aerogels can be classified into three types: micropores (less than 2 nm in width), mesopores (between 2 nm and 50 nm in width), and macropores (more than 50 nm in width) (Gregg et al. 1982). The BET surface area (S_{BET}), the micropore size distribution, the micropore surface area (S_{mic}) and volume (V_{mic}), the mesopore surface area (S_{mes}), volume (V_{mes}), and the size distribution were analyzed by BET (Brunauer-Emmett-Teller) theory, HK (Horvath-Kawazoe) theory, *t* -plot theory, and BJH (Barrett-Johner-Halendar) theory.

RESULTS AND DISCUSSION

As is well known, lignin is a polymer, the molecular structure of which contains a large number of phenol units. Owing to the lower electron densities in the 2,4,6 ring positions, lignin has a much lower reactivity toward formaldehyde as compared with resorcinol. Therefore, it is important to determine whether lignin can also be employed to poly-condense with formaldehyde, leading to the formation of a gel nano-network. An overview of all samples prepared and a few of their properties are given in Tables 1. In order to find out the contrast between the RF and LRF aerogel catalyzed by sodium hydroxide, we also prepared some RF aerogels in the laboratory under constant conditions. The surface of the aerogels catalyzed with sodium hydroxide appeared glossy. The color ranged from ochre to dark brown. As mentioned above, the gelation time and temperature were kept constant. For this reason, various preparation conditions listed in Table 1 were investigated by changing the content of LR and formaldehyde (LRF concentration), the ratio of lignin and resorcinol (the concentration of lignin), and the mass ratio of NaOH to LR (LR/C), but the mass ratio of LR to formaldehyde (LR/F) remained unchanged. As can be seen from Table 1, the sol-gel polymerization of LR and

Table 1. Effect of Preparation Conditions on the Gelation Ability, the Drying Shrinkage and the Bulk Density of Organic Aerogels

Test No	LR/F (w/w)	LR/C (w/w)	Lconcent (wt%)	LRF concent (wt%)	Gel.temp (℃)	Gel.time (min)	Shrinkage (%)	Density (g/cm^3)
A1	1:2	25	50	5	85	150	63.6	0.244
A2	1:2	25	50	10	85	120	39.9	0.368
A3	1:2	25	50	15	85	100	26.1	0.488
A4	1:2	25	50	20	85	80	21.2	0.378
A5	1:2	25	50	30	85	50	19.1	0.439
B1	1:2	75	100	15	85	———	———	———
B2	1:2	75	90	15	85	———	———	———
B3	1:2	75	50	15	85	150	35.1	0.408
B4	1:2	75	10	15	85	120	30.1	0.368
B5	1:2	75	0	15	85	100	26.8	0.259

Note: Gel.time: The time consumed for the reactants state from the initial stage(liquid) to the beginning gelatinous stage.

formaldehyde could not be induced to occur when the concentration of lignin was relatively high, such as 100% and 90%. These results indicated that the less lignin concentration to the total mass of the solution, the lower the density of the gel. With the reduction of LRF concentration, the gel time became longer.

Table 1 shows the effect of various preparation conditions on the bulk density of the organic material that was obtained. First of all, it can be seen that the ethanol supercritical drying method was quite successful for the fabrication of monolithic lignin-resorcinol-formaldehyde aerogels with some drying shrinkage. Then the bulk density of LRF organic aerogels increased with the LRF concentration ranging from 5% to 15%. Further investigations showed that in the case of the same LRF concentration, at a constant molar ratio LR/F and LR/C, the density of organic aerogels increased slightly upon drying. Table 1 shows shrinkage upon drying under ambient conditions for LRF aerogels with different LRF concentration and lignin concentration. It is shown that the shrinkage of LRF aerogels decreased from 63.6% to 19.1% as the LRF concentration increased from 5% to 30%. The shrinkage of LRF aerogel decreased from 35.1% to 26.8% as the lignin concentration decreased from 50% to 0 when the molar ratio LR/C was 75.

Shrinkage of the gel during drying is basically caused by capillary pressure (Shen et al. 2005), e.g, $P_c = -2\gamma/(r_p - t)$, where γ is the surface tension of the pore liquid, r_p is the pore radius, and t is the thickness of a surface adsorbed layer. In this work, the water in the pores is replaced with ethanol, and so the surface tension decreases from 72.1 dyn/cm to 24.0 dyn/cm. The smaller surface tension of the pore liquid and the larger pore radius decrease the capillary pressure during the drying process. The increase of particle size and the strong necks between the particles improves the mechanical properties of the skeleton. The gel could be dried under ambient conditions successfully pursuant to these changes. When other preparation conditions were kept constant, an increase in the LRF concentration helped to increase the initiating reaction system and thus accelerated the sol-gel polycondensation rate, eventually leading to an increase of the gelation ability of the L-R-F system and the formation of pores of relatively small radius. When other preparation conditions were kept unchanged, with the reduction of lignin concentration, the shrinkage of gel was minor. The reason may be that the higher resorcinol reactivity allowed easier formation of the gel in comparison with lignin. The experimental results showed that the bulk density of LRF organic aerogels could be easily tailored by the most important factors, i.e. the LRF concentration, the lignin concentration, the molar ratio LR/C, and so on.

The Morphology of LRF Organic Aerogels

Scanning electron microscopy with a magnification of 5,000 and 10,000 was employed to investigate the microstructure of the materials. Figure 1 shows images of the LRF aerogels (A3). The LRF aerogels were observed to have an open cell structure with continuous porosity and homogeneous spherical particles analogous to that of the representative RF aerogels prepared by Petricevic et al. (2001) and Shen et al. (2005).

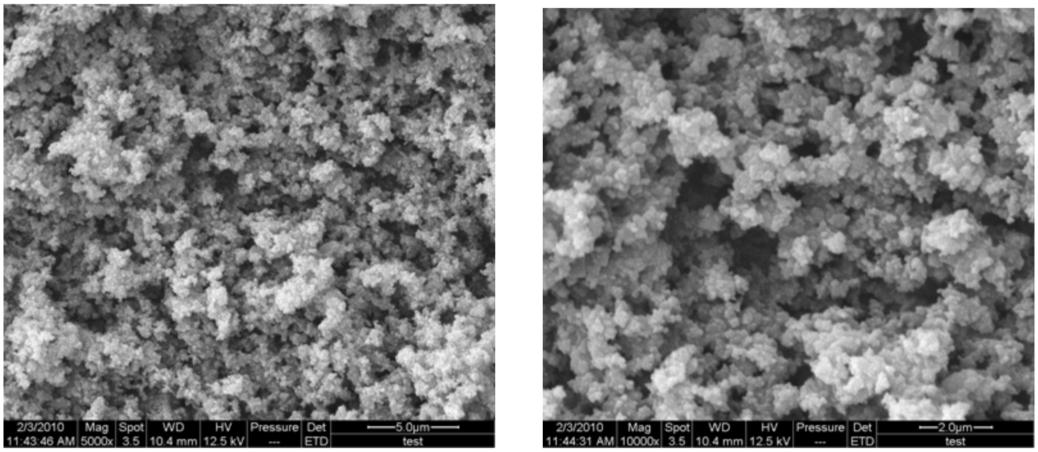


Fig. 1. Scanning electron micrographs (SEM) of the LRF aerogel (A3)

Figure 2 shows typical TEM photographs of the aerogels obtained. TEM observations indicated that the organic aerogels had a three-dimensional nano-network. The solid phase was composed of interconnected nano-particles with an average diameter of about 20 nm. The nano-particles were irregular in shape and were very similar to those prepared using the resorcinol as a raw material (Wu et al. 2004). There were abundant meso-pores with diameters less than 50 nm among the interconnected nano-particles. The micrographs show the lignin molecules dispersed in the LRF aerogel matrix, contributing to the network structure.

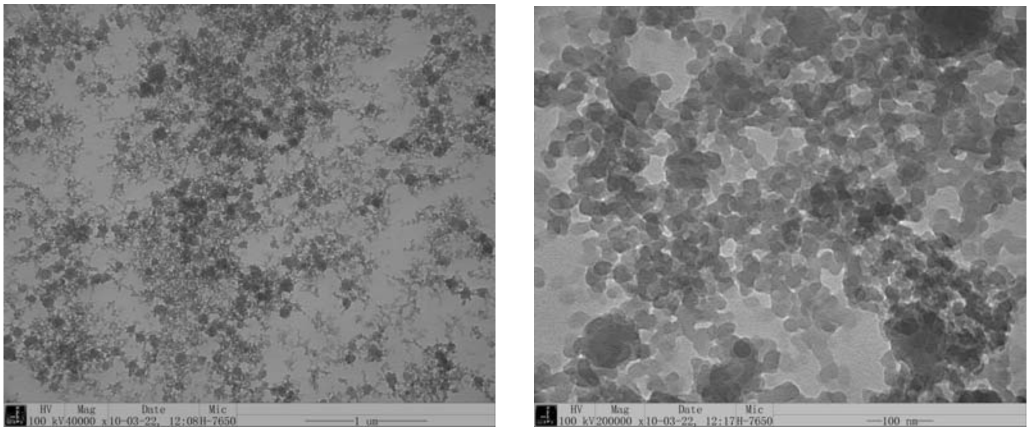


Fig. 2. Transmission electron micrographs(TEM) of the LRF aerogel (B3)

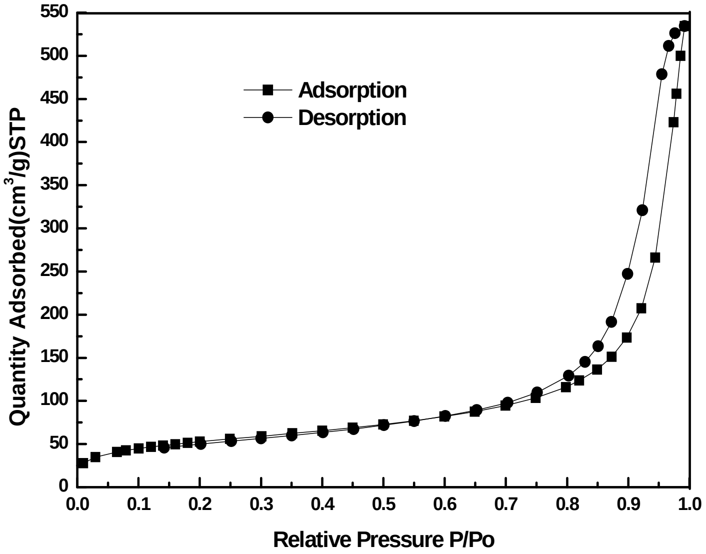
The Porous Structure of LRF Organic Aerogels

Figure 3 shows the adsorption-desorption isotherms of the typical LRF and RF organic aerogels. These isotherms could be classified as type-IIb with a H3 hysteresis loop (Rouquerol et al. 1999). According to the isotherms of the samples, the detailed, quantitative pore characteristics of the samples were calculated, and the results are shown in Table 2 and Fig. 4.

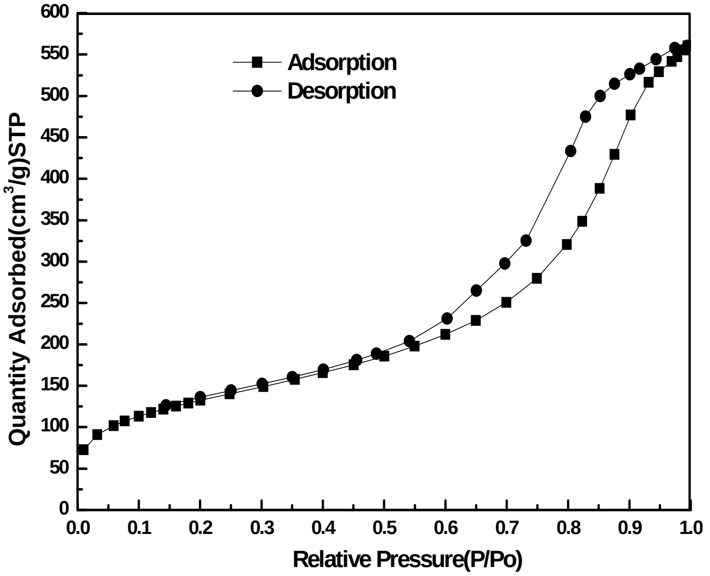
Table 2. Textural Characteristics of the Organic Aerogel Samples in the Study

Sample	S_{BET} (m^2/g)	S_{mic} (m^2/g)	S_{mes} (m^2/g)	V_{mes} (cm^3/g)	V_{mic} (cm^3/g)	D_{avg} (nm)
LRF-B3	191.426	17.473	179.216	0.834	0.005	13.673
LRF-B4	478.597	59.759	457.806	0.895	0.023	7.004
RF	552.385	74.974	529.095	0.875	0.028	5.895

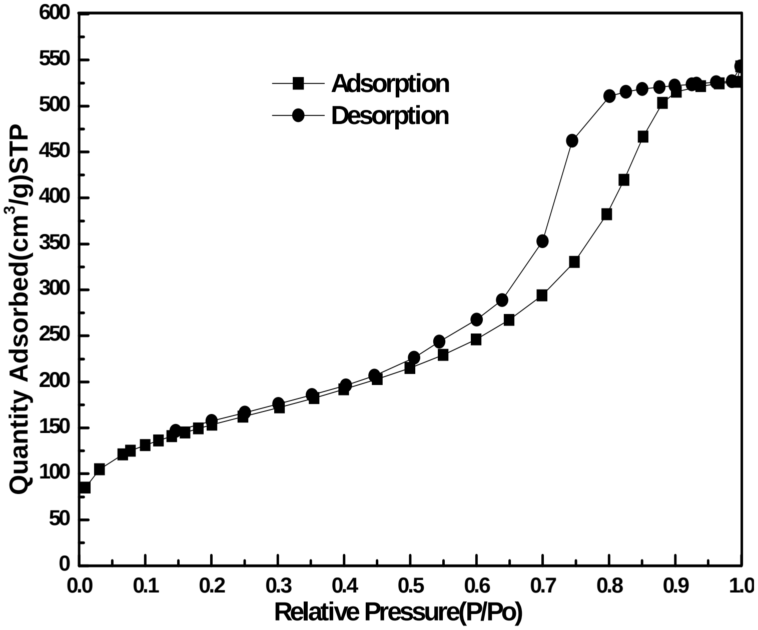
Note: S_{BET}: BET surface area; S_{mes}: BJH desorption cumulative surface area of pores between 1.7 and 300 nm diameter; S_{mic}: Micropore surface area; V_{mes}: BJH desorption cumulative pore volume of pores between 1.7 and 300 nm diameter; V_{mic}: Micropore volume; D_{avg}: Average pore width



(a-B3)



(b-B4)



(c-B5)

Fig. 3. Adsorption and desorption isotherms for LRF aerogel with RC ratio 75, LRF mass concentration 15%, lignin concentration 50% **(a-B3)**, lignin concentration 10% **(b-B4)**; RF aerogel with RC ratio 75 and RF mass concentration 15%.**(c-B5)**

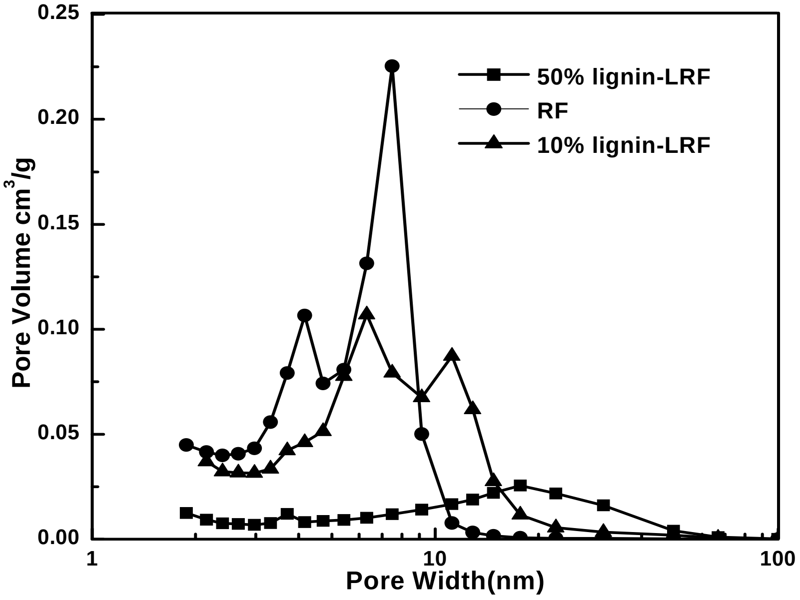


Fig. 4. Pore size distribution of RF, 50% lignin-LRF and 10% lignin-LRF with RC ratio 75 and LRF mass concentration 15%

The BET surface area was calculated using the BET theory. Micropore volume and micropore surface area were calculated using the *t*-plot theory. Mesopore volume and mesopore surface area were calculated using the BJH theory (Wu et al. 2005, 2006). In Table 2, the results reveal that RF and LRF organic aerogels exhibited high BET surface areas ranging from 191 to 552 m^2/g and large mesopore volumes ranging from 0.834 to 0.895 cm^3/g. In addition, organic aerogels had few micropores. The maximum micropore volume was only 0.028 cm^3/g. It also can be seen that BET surface area, micropore surface area, and micropore volume increased with decreasing lignin concentration. The mesopore volume, however, was maintained almost without change. Besides, the average pore width of the samples ranged from 5.89 to 13.67 nm. The trend is the more the lignin concentration, the larger the pore width.

According to the adsorption-desorption isotherms, the pore structure of the LRF organic aerogels was quite similar to that of RF aerogels. As the figures show, the LRF and RF aerogels exhibited the same type of adsorption isotherm. Both were of type II, indicating multilayer adsorption occurring on the surface of the organic aerogel. 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 (Zhang et al. 2003).

Non-vanishing of volume adsorbed near zero relative pressure is shown in the adsorption isotherm in Fig. 3. This result indicates that there was a small amount of micropores in the organic aerogels. At the front part of the isotherms, the adsorption volume increased slowly, and the increasing trend accelerated with decreasing lignin concentration. This indicated that decreasing of the lignin concentration in an RF aerogel is favorable to micropore formation, leading to higher micropore surface area and micropore volume of RF aerogel under the same condition, compared to the LRF aerogel. This is in agreement with the distribution for the BET surface area of the organic aerogel. With increasing relative pressure, the adsorption volume increases suddenly due to the capillary condensation (Lowell, et al. 2004). When the sorbent has pores smaller than 2 to 3 nm, the isotherms show this type of behavior, although multilayer adsorption and capillary condensation occur on the surface of the sorbent (Yan et al. 1986; Fu et al. 1990). However, the adsorption is not saturated, because of the widely distributed pore diameters. Compared to the LRF aerogel, the adsorption volume of RF aerogel was higher. This indicates that all the pores of the aerogel were completely filled with the adsorbent.

Figure 4 shows the pore size distributions calculated using the BJH method from desorption branches for RF, 50% lignin-LRF and 10% lignin-LRF with RC ratio 75 and LRF mass concentration 15%. The pore size distribution plot of RF aerogel showed two obvious peaks at about 4 nm and 8 nm, and the 10% lignin-LRF also showed two peaks at about 7 nm and 20 nm. However, the 50% lignin-LRF had a relatively broad distribution of the pore width, ranging from 2nm to 90nm, with no obvious peak. Compared to LRF aerogel, the RF aerogel had a more concentrated pore size and a larger micropore and mesopore volume, consistent with its larger specific surface area. In addition, the micropore and mesopore volume of LRF aerogel decreased with increasing lignin concentration.

CONCLUSIONS

1. Organic aerogels can be prepared by the gelation of a lignin-resorcinol-formaldehyde mixture using NaOH as a catalyst under specified experimental conditions, including LRF concentration, LR/F ratio, LR/C ratio, gelation temperature, and gelation time. The experimental results showed that the gelation ability of the L-R-F system could be enhanced by increasing the LRF concentration (and the LR/C ratio). The bulk density of the organic aerogels can be controlled by these above preparation conditions, especially the LRF concentration and the LR/C ratio. The lowest density of organic aerogel was 0.244 g/cm^3, which was reached under the conditions of LR/C 25, lignin concentration 50%, and LRF concentration 5%. In addition, if the lignin concentration is too high, organic LRF could not be obtained.
2. LRF and RF aerogels were comprised of a three-dimension nano-network, among which numerous mesopores and macropores existed. SEM and TEM micrographs showed that the LRF had an open cell structure with continuous porosity and homogeneous spherical particles. Furthermore, compared to the RF aerogel, the BET surface area, the micropore surface area, and the micropore volume of the LRF aerogel was relatively lower, but the average pore width of the LRF aerogel was larger than the RF aerogel. With increasing lignin concentration, The BET surface aera and the pore volume of the LRF also became lower, and the pore size distribution ranged widely, but the density became larger. When the lignin concentration is too high, it was too hard to form the LRF aerogel.
3. To a certain extent, lignin can replace resorcinol to prepare LRF organic aerogel, which not also reduced the cost of the organic content, but also improved the utilization of lignin. This may be a potentially high value-added application for lignin.

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