

Preparation and Characterization of Petroleum-Pitch-Based Carbon Aerogels

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ABSTRACT: Carbon aerogels were prepared by the sol-gel polymerization of petroleum pitches followed by ambient-pressure drying and then carbonization. Furfural and sulfuric acid were found to be the best crosslinking agent and best catalyst for the reaction system, respectively. It was necessary to add acetic acid as a cosolvent, and the volume ratio of toluene to acetic acid played an important

role in the mass densities of the samples. The average diameters of the nanonetwork particles of the typical carbon aerogels thus obtained were about 30–40 nm, and their surface areas were over 360 m²/g. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 309–314, 2009

Key words: crosslinking; density; microstructure

INTRODUCTION

Aerogels are unique porous materials with a continuous three-dimensional framework whose composition, structure, and properties can be controlled on the nanometer scale. The related carbon aerogels (CAs), which have unique microstructures consisting of carbon nanoparticles and nanopores, are gaining considerable attention as promising materials for electric double-layer capacitors, chromatographic packing, adsorbents, and catalyst supports.^{1,2} With the traditional preparation method, CAs are typically prepared through the sol-gel polymerization of resorcinol with formaldehyde in an aqueous solution, which is followed by supercritical drying with liquid CO₂ and carbonization at elevated temperatures under an N₂ atmosphere.¹ This multistep procedure can be a time-consuming and high-cost process. Because of this, the preparation of CAs with a competitive price-to-performance ratio is currently an active research area. Many efforts have been made to simplify the preparation process^{3–8} and to exploit cheap raw materials.^{6,9–12}

Petroleum pitches constitute a huge number of products from petroleum production. Besides their abundance, cheapness, high carbon content, fluidity, and ease of graphitization, petroleum pitches have high reactivity, which has been neglected for a long

time. Therefore, it is necessary to develop products in high-tech fields from petroleum pitches with high reactivity. In the work presented here, our goal was to use petroleum pitches as cheap raw materials for the fabrication of CAs with a faster, easier, and cheaper process in comparison with traditional techniques. First of all, the sol-gel polymerization conditions were explored through changes in the types and amounts of crosslinking agents, catalysts, and solvents. Subsequently, the nanostructures of the as-prepared petroleum-pitch-based organic aerogels and CAs were characterized with transmission electron microscopy (TEM), scanning electron microscopy (SEM), and nitrogen adsorption and desorption.

EXPERIMENTAL

Sample preparation

Predetermined amounts of AH-90 petroleum pitches (Sinopec Corp., Guangzhou, China; softening point = 51°C; elemental contents: 85.56 wt % C, 10.42 wt % H, 0.76 wt % N, and 1.14 wt % S), crosslinking agents, and catalysts were mixed in appropriate amounts of solvents at room temperature according to predetermined recipes. The mixture was transferred into a vial. The vial was sealed and then put into an oil bath at 70°C to cure for 7 days. After curing, the gels were directly dried in air at room temperature for 1 day at first, then further dried under an infrared lamp with an irradiation temperature of about 60°C for 5 h, and finally dried in an oven at

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100°C under ambient pressure for 5 h. Subsequently, the resultant aerogels were heated to 900°C at a heating rate of 5°C/min and kept at this carbonization temperature for 3 h in flowing N₂ (800 mL/min). These resultant aerogels and related CAs are called AG-*xx* and CA-*xx*, respectively, where *xx* denotes the test number.

Measurements

The samples were mounted on a sample holder and coated with Au. The morphology images of the samples were recorded with SEM. Some powders were scraped from the bulk CA samples and dispersed with ethanol onto a copper grid for microscopic examination. The structures of the CA samples were observed by TEM. Approximately 0.1-g samples were heated to 150°C for the organic aerogels or to 250°C for the CAs to remove all the adsorbed species. Nitrogen adsorption and desorption isotherms were then taken with a surface area analyzer. The Brunauer–Emmett–Teller surface area, external surface area, micropore surface area, micropore volume, and mesopore volume of the samples were analyzed with the Brunauer–Emmett–Teller theory, t-plot theory, Horvath–Kawazoe theory, and Barrett–Joyner–Halenda theory, respectively. In addition, the pore size distribution was also analyzed by density functional theory.

RESULTS AND DISCUSSION

Sol-gel polymerization conditions of petroleum pitches

Selection of the crosslinking agents

Petroleum pitches are black or dun dopes and are complex mixtures of polycyclic aromatic hydrocarbons and their heterocyclic analogues. In this study, the copolymerization of the petroleum pitches and crosslinking agents was a nucleophilic addition reaction. During the reaction, crosslinking agents formed carbonium ions, which were attacked by pitch monomer, being nucleophiles; then, the crosslinking reaction finished, and the base body was formed. It was necessary to select suitable crosslinking agents with one or more aldehyde groups or at least two hydroxymethyl or halomethyl groups in this reaction. Thus, we explored the feasibility of the polymerization of the petroleum pitches with divinylbenzene, 4,4'-bis(chloromethyl)-1,1'-biphenyl, benzaldehyde, formaldehyde, furfural, or trioxymethylene under the following conditions: a mass ratio of pitches to crosslinking agents of 0.5, a ratio of pitches to toluene (P/T) of 0.1 g/mL, a ratio of pitches to catalyst (P/C) of 5 g/mL, and gelling at 70°C for 7 days. We found that a black precipitate was formed with 4,4'-bis(chloromethyl)-1,1'-biphenyl, benzaldehyde, or trioxymethylene as a crosslinking agent; no precipitate or gel occurred with

divinylbenzene or formaldehyde. Fortunately, a good organic gel was achieved with furfural as a crosslinking agent. Therefore, we used furfural as the crosslinking agent in the following studies.

Selection of the catalysts

Generally, both Lewis acid catalysts and proton acid catalysts can be used to carry out a crosslinking reaction.¹³ Suitable catalysts are to be selected according to the types of raw materials and crosslinking agents and the adopted reaction conditions. In our initial experimental stage, we tried to use anhydrous stannic chloride as a catalyst for the polymerization of pitches and furfural in toluene. Unfortunately, we found that anhydrous stannic chloride failed to induce gelation under a variety of conditions. Because of this, we chose to use a proton acid such as sulfuric acid and *p*-toluenesulfonic acid as the catalyst for the synthesis of gels in toluene under similar reaction conditions discussed in the last section. Surprisingly, black organic gels could be formed after 1 h with sulfuric acid or after 48 h with *p*-toluenesulfonic acid. This meant that the sol-gel polymerization rate using sulfuric acid was much faster than that using *p*-toluenesulfonic acid. After these gels were dried under the ambient pressure, the *p*-toluenesulfonic acid catalyzed organic gels underwent serious shrinkage (radial drying shrinkage = 49.0%), but the drying shrinkage of the sulfuric acid catalyzed gels was 2.6%; this indicated that sulfuric acid was an appropriate catalyst under these gentle conditions.

Selection of the solvents

In our first exploration, the gelation of petroleum pitches with furfural was carried out with toluene as

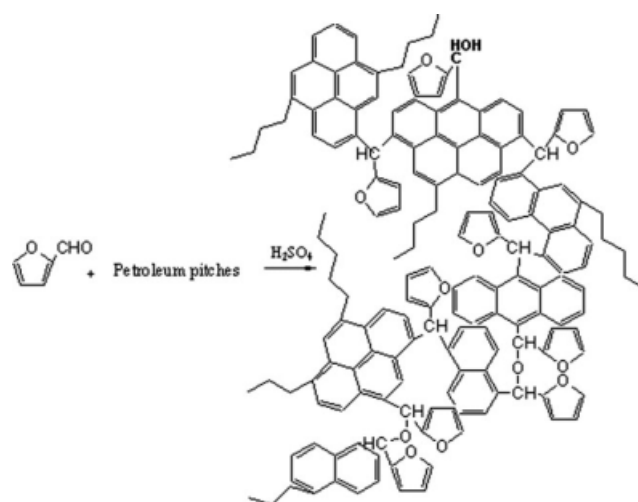


Figure 1 Schematic diagram of the reaction of furfural and pitches catalyzed by sulfuric acid.

TABLE I
Effects of the Synthesis Conditions on the Bulk Density of Aerogels and CAs

No.	T/A (mL/mL)	P/F (g/mL)	P/C (g/mL)	P/(T + A) (g/mL)	Density of aerogel (g/cm ³)		Density of CA (g/cm ³)	Carbonization yield (wt %)
					Theoretical	Experimental		
A1	4	0.5	5	0.1	0.27	1.11	—	—
A2	2.33	0.5	5	0.1	0.27	0.73	—	—
A3	1.25	0.5	5	0.1	0.27	0.36	0.32	44.3
A4	1	0.5	5	0.1	0.27	0.33	0.30	44.1
B1	1	1	5	0.1	0.19	0.30	—	—
B2	1	0.67	5	0.1	0.23	0.30	0.21	34.9
B3	1	0.5	5	0.1	0.27	0.33	0.30	44.1
B4	1	0.33	5	0.1	0.34	0.41	0.33	44.5
C1	1	0.5	1	0.1	0.25	0.65	—	—
C2	1	0.5	2.5	0.1	0.27	0.38	0.30	33.0
C3	1	0.5	5	0.1	0.27	0.33	0.30	44.1
C4	1	0.5	10	0.1	0.27	0.27	0.21	44.3
D1	1	0.5	5	0.05	0.15	0.43	—	—
D2	1	0.5	5	0.1	0.27	0.33	0.30	44.1
D3	1	0.5	5	0.15	0.38	0.42	0.40	45.5
D4	1	0.5	5	0.2	0.47	0.50	0.45	45.6

a solvent. Unfortunately, the resulting gels underwent uneven shrinkage during subsequent drying, most likely because of the dispersive asymmetry of sulfuric acid in the reaction system. To modify the catalyst dispersion, acetic acid was added to the reaction solution as a cosolvent, and as a result, we successfully obtained homogeneous samples.

Otani et al.¹⁴ disclosed that a raw material containing one or more condensed polynuclear aromatic compounds with at least two condensed benzene rings could react with a crosslinking agent with one or more aldehyde groups catalyzed by acid. Petroleum pitches are mixtures of various compounds including mainly condensed polynuclear aromatic hydrocarbons with three to five condensed benzene rings. Therefore, it seemed quite credible that pitches reacted with furfural through a reaction mechanism similar to the reaction of petroleum pitches and terephthalic aldehyde, which is described in detail in ref. 15. Like terephthalic aldehyde, furfural may have reacted with pitches with sulfuric acid as a catalyst to form mixtures of addition and condensation compounds, which could have reacted further to form a crosslink-

ing network. The principal reactions involved could have included (1) the formation of α -furfurylhydroxymethyl derivatives of pitches, (2) the condensation of the α -furfurylhydroxymethyl derivatives to form α -furfurylmethylene ether bridged compounds, and (3) the disproportionation of the α -furfurylmethylene and α -furfurylmethylene ether bridges to form α -furfurylmethylene bridges plus furfural as a byproduct. Figure 1 shows a schematic diagram of the fundamental reaction of pitches with furfural catalyzed by sulfuric acid. For simplicity, we omitted the secondary reactions of pitches and furfural. For example, furan ring scission and a reaction with another pitch nucleus may have occurred; this would be similar to the furfural-phenol reaction.¹⁶

Effect of the preparation conditions on the aerogel density

In the past, when general sol-gels were dried under the ambient pressure, their bulk density obviously increased because of the collapse of their nanoparticle network arising from the large capillary

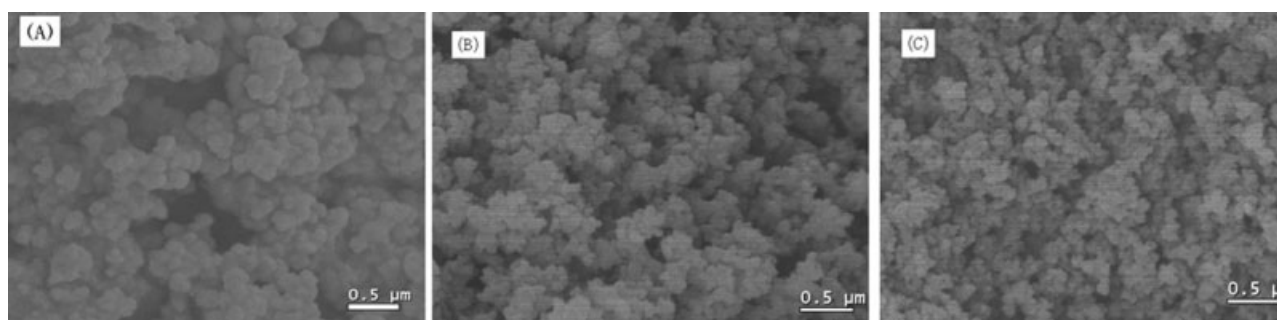


Figure 2 SEM photographs of aerogel samples. (A) AG-A4, (B) CA-A4, and (C) CA-A3.

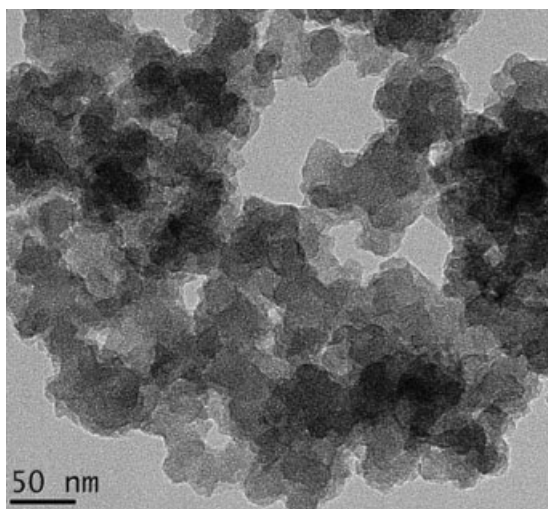


Figure 3 TEM photograph of CA-A3.

pressures during drying and the low stiffness of the network matrix. Therefore, in our research, the bulk density of sol-gels and related CAs was first studied, and the results are shown in Table I. It was concluded that the volume ratio of toluene to acetic acid (T/A) played an important role in the mass densities of organic aerogels and related CAs on the basis of the results of the tests (A1–A4) in Table I. When T/A was 4, the actual densities of the samples were much larger than their theoretical densities, and this indicated that structural collapse and shrinkage occurred during the ambient-pressure drying process. When the T/A ratio decreased (the acetic acid

content increased) to 1.25, the organic aerogels that were then obtained no longer collapsed and shrank after ambient-pressure drying, so their actual densities were close to the theoretical values. When the T/A ratio further decreased to 1, the actual density could decrease to 0.33 g/cm^3 . That is, we can prepare aerogel materials under ambient-pressure drying conditions as long as we control the acetic acid concentration suitably. It can also be seen from Table I that the densities of related CA samples (A1–A4) were slightly less than those of their organic aerogel precursors. The carbonization yield of the CAs was about 44%.

The experimental results of B1–B4 in Table I show that the ratio of pitches to furfural (P/F) did not affect the gelation and drying results when the P/F value was under 0.67. When the P/F ratio was 0.67, although the obtained organic aerogel had a value close to its theoretical density, the density of the related CAs obviously decreased in comparison with the density of the organic aerogel precursor; this most likely indicated that the organic aerogels thus obtained had a lower crosslinking density than those prepared with lower P/F ratios. Furthermore, when the P/F ratio was increased to 1.0, the concentration of furfural became too low for a strong polymeric network to form, and therefore only black precipitates, rather than sol-gels, were obtained.

The experimental results for C1–C4 and D1–D4 show that the P/C ratios and pitches to toluene plus acetic acid (P/(T + A)) ratios were also able to control the density and carbon yield and had a control

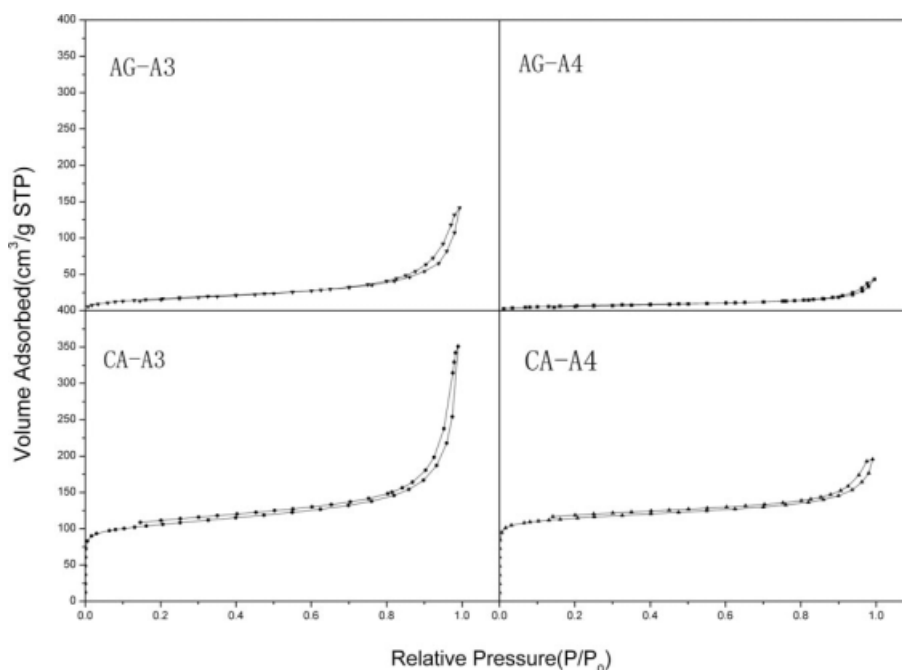


Figure 4 Nitrogen adsorption–desorption isotherms of representative aerogel samples at 77 K (P = pressure; P_0 = initial pressure). P/P_0 , the ratio of adsorption pressure (P) and the saturation of vapor pressure (P_0).

TABLE II
Textual Characteristics of the Samples

Sample	T/A (mL/mL)	S_{BET} (m^2/g)	S_{ext} (m^2/g)	S_{mic} (m^2/g)	V_{mic} (cm^3/g)	V_{meso} (cm^3/g)	D_{mic} (nm)
AG-A3	1.25	65	75	0	0	0.22	
CA-A3	1.25	360	125	235	0.11	0.44	1.10
AG-A4	1	25	30	0	0	0.07	
CA-A4	1	385	90	295	0.14	0.17	1.04

D_{mic} = micropore diameter; S_{BET} = Brunauer–Emmett–Teller surface area; S_{ext} = external surface area; S_{mic} = micropore surface area; V_{meso} = mesopore volume (Barrett–Joyner–Halenda desorption cumulative pore volume of pores between 1.7 and 300 nm in diameter); V_{mic} = micropore volume.

rule similar to that of B1–B4. When the P/C ratio was equal to 2.5, the actual densities were close to the theoretical values. However, the carbonization yield of the CAs was 33%, and this indicated that the crosslinking density of the network was low. When the P/(T + A) ratio was 0.05, the actual densities of the samples were much larger than their theoretical densities, and this indicated that structural collapse and shrinkage occurred during the ambient-pressure drying process.

Microstructure of petroleum-pitch-based organic aerogels and CAs

Figure 2 shows SEM photographs of the organic aerogels and related CAs that were prepared. Figure 3 presents a TEM image of a representative CA prepared with petroleum pitches and dried at the ambient pressure. A comparison of Figure 2(B,C) shows that the size of the carbon particles and pore diameter in the resultant aerogels obviously increased with a decrease in the T/A ratio. The CAs prepared in this work had nanonetwork structures typical of samples prepared with other raw materials and with a supercritical drying technique.^{8,9,17,18} Additionally, after carbonization, the size of the carbon particles decreased because of the emission of many non-carbon elements and some carbon-containing compounds during pyrolysis [see Fig. 2(A,B)]. According to SEM and TEM images, the average diameters of the carbon nanoparticles of the obtained CAs were about 30–40 nm. Many mesopores and macropores were found among the carbon nanoparticles, as observed with SEM and TEM.

The porous structures of the obtained CAs were further characterized by nitrogen adsorption and desorption, and the results are shown in Figure 4. The isotherms of the obtained CAs presented an H3 hysteresis loop and a sharp uptake at a relatively low pressure, which indicated the existence of mesopores and micropores, respectively.¹⁹ However, those of the precursor organic aerogels did not show sharp phenomena at a low relative pressure. On the basis of the isotherms of the samples, the surface area,

pore volume, and pore distribution of the samples were calculated, and the results are also listed in Table II and Figure 5. It can be seen from Figure 5 that the sample had many mesopore and macropore peaks as well as two micropore peaks. In addition, the mesopore distribution peaks spanned from approximately 4 nm to approximately 40 nm, and the biggest macropore peak was at approximately 54.4 nm; the two micropore peaks of the CAs were concentrated at approximately 0.73 and 1.18 nm, respectively. The data of Table II reveal that the organic aerogel precursors had very few micropores and lower Brunauer–Emmett–Teller surface areas than the related CAs. This indicated that the micropores in the CAs were mainly produced during carbonization. The CAs thus prepared had a close micropore diameter (ca. 1.10 nm) and a close micropore volume (0.10–0.15 cm^3/g). The mesopore volumes of the samples increased greatly after carbonization. The increase in the T/A ratio resulted in an increase in the mesopore volume. The reason was most likely that the reduction of the catalyst's effective concentration with the decrease in the amount of acetic acid led to inadequacy of gelation; this weakened the strength of the produced aerogel network and

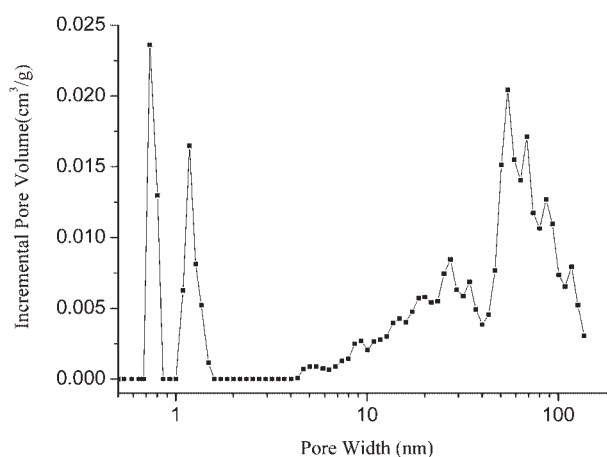


Figure 5 Pore size distribution of CA-A3 by the density functional theory method.

thus caused a lot of shrinkage of macropores into mesopores.

It could be concluded from these investigations that the addition of an appropriate amount of acetic acid could increase the carbon particle to a suitable size, thus enhancing the strength of the pitch-based aerogel network, and could simultaneously increase the pore diameter to a suitable size by changing the stacking of the carbon nanoparticles, thus reducing the capillary pressure. Therefore, we could fabricate petroleum-pitch-based organic aerogels and related CAs by synthesizing H₂SO₄-catalyzed petroleum pitch-furfural gels in a toluene-acetic acid solvent system and then drying them at the ambient pressure.

CONCLUSIONS

The significant conclusion to be drawn from this work is that petroleum pitches can be used in sol-gel polymerization and thus can be used as very cheap raw materials for the preparation of CAs. Furfural is a proper crosslinking agent and sulfuric acid is an appropriate catalyst in this gelation system. In addition, the T/A ratio plays an important role in forming a three-dimensional nanonetwork with uniform nanoparticles and affects the mass densities under ambient-pressure conditions. The addition of acetic acid can enhance the strength of the aerogel network and reduce the capillary pressure of the aerogel. Other synthesis conditions, such as the P/F ratio, the P/C ratio, and the P/(T + A) ratio, also affect the fabrication of low-density organic aerogels with the ambient-pressure drying technique. The nanoparticle structure of the as-prepared petroleum-pitch-based

CAs is similar to that of typical CAs prepared with other raw materials or with a supercritical drying technique. The sizes of the carbon particles of the representative CAs that were obtained were in the range of about 30–40 nm, and their surface areas were over 360 m²/g.

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