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Carbon Aerogels as Catalyst Supports

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Abstract

Influence of the process parameters on porous structure of monolithic and spherical resorcinol–formaldehyde (RF) carbon aerogels prepared by supercritical acetone and carbon dioxide drying of alcogels, followed by carbonization is presented. The prepared organic RF aerogels were carbonized at 600 °C to form carbon aerogels and their porous structure was characterized by nitrogen adsorption. It was stated that synthesis parameters of RF organic aerogels (catalyst type, gel curing time, R/C ratio, resorcinol concentration in water) and drying method (low- or high-temperature supercritical drying) strongly influence textural parameters of the final carbon aerogels. Application of KOH in RF aerogel preparation allows obtaining carbon aerogels of the most advantageous parameters irrespective of the used drying method. Elongation of curing time of RF gels results in an increase in specific surface area and total pore volume of the carbon aerogels obtained both in the course of low- and high-temperature drying. Low-temperature supercritical drying of RF aerogels gives carbon materials of more advantageous texture parameters in comparison to carbon aerogels obtained in high-temperature supercritical drying.

INTRODUCTION

Aerogels (organic and inorganic) are porous materials, produced by supercritical drying of sols or polymers to solvent removing and simultaneously to prevent shrink or collapse of the weak structure of the solid matrix. For the first time organic and carbon aerogels were prepared by Penkala *et al.* [1, 2] in 1987. The organic aerogels consist of cross-linked polymers and are thermosetting; they must be carbonized in an inert atmosphere to form carbon aerogels. The carbon aerogels prepared in the form of monoliths, powders or microspheres are characterized by high specific surface area and porosity, low thermal conductivity and electrical resistance and high capacitance [2–4]. Taking into account their unique properties, carbon aerogels are promising materials for numerous practical applications such as isolation materials, electrodes and especially as adsorbents and catalyst supports [3–6].

Organic resorcinol–formaldehyde (RF) aerogels are most frequently prepared in a multistage process which includes aqueous polycondensation of resorcinol with formaldehyde at a temperature of 70–95 °C mainly in the presence of Na_2CO_3 as a catalyst, exchanging of water from gel structure to acetone, exchanging of acetone to CO_2 before drying of the obtained gel and carbon dioxide supercritical drying of gels. The classic method of organic aerogel synthesis is time-consuming and gel drying operation lasts about two weeks, while the two finishing operations last four days.

RF aerogels are the precursors of carbon aerogels and their porous structure depends on the porous structure and other physicochemical properties of initial RF aerogels. Therefore, it is interesting to find a low-cost and time-saving preparation method of RF aerogels. One of the possibilities of shortening the RF aerogel preparation is the application of new catalyst [7] or drying of RF gels with supercritical acetone [8].

In this paper the results of studies on the influence of the catalyst type and molar ratio resorcinol to catalyst (R/C), concentration of resorcinol in water and curing time on porous structure of monolith carbon aerogels prepared by supercritical acetone and carbon dioxide drying are presented. In the further part the influence of the selected synthesis parameters (type of dispersing liquid) on grain size and porous structure of spherical carbon aerogels is presented and discussed.

EXPERIMENTAL

In the present work, RF monolithic aerogels were synthesized by aqueous polycondensation of resorcinol (R) with formaldehyde (F) in a molar ratio of 1 : 2. Sodium hydroxide, potassium hydroxide, calcium carbonate and sodium carbonate were used as catalysts (C). The applied shares of the individual reagents: resorcinol to catalyst molar ratio and resorcinol concentration in water as well as curing time are presented in the further parts of the paper in the respective Tables and Figures.

In the first step reagents were dissolved and the prepared solutions of reagents were divided into two parts. The A samples were submitted to gelation by placing in glass vials in water bath at a temperature of 70 °C. The gelation times attained values from 80 to 430 min, in dependence on reagent mixture compositions. In the next step the obtained gels were submitted to curing (cross-linking) at a temperature of 70 °C for 48, 72 and 120 h.

After finishing the determined cross-linking periods the obtained gels were taken off from the water bath and vials and were placed in polyethylene containers. In these containers water contained in gels was replaced by acetone. The replacement lasted for three days, two times per day while gel samples were totally submerged in liquid (acetone). After this operation, the A gels were dried at the acetone supercritical conditions (temperature 250 °C, pressure 10 MPa). The A aerogel series was called high temperature supercritical drying, HTSCD aerogels.

Samples B series were prepared using the same method. However, after exchanging of water for acetone samples B were being placed in autoclave that in the next step was filled with liquid carbon dioxide. These replacements of acetone for carbon dioxide lasted for three days two times per day. After this operation, the B gels were dried at carbon dioxide supercritical conditions (temperature 70 °C, pressure 15 MPa). The B series was called low temperature supercritical drying, LTSCD aerogels.

Spherical RF aerogels were synthesized quite similarly. The obtained RF sols were transferred to glass flask containing paraffin oil or cyclohexane and non-ionic surface active agent (Rokwin 80). Resorcinol and formaldehyde polycondensation and RF gel cross-linking reactions were realized at a temperature of 45 °C for 24 h (mixing of flask liquid content, 500 rpm). After that RF gels were separated from dispersing agents by simple filtration. Similarly as in the case of monolithic gels water contained in gels was replaced by acetone and in the next step acetone was replaced by liquid carbon dioxide (three days). The obtained RF aerogels were dried using low temperature supercritical drying (LTSCD). All dried RF aerogels were carbonized in a gravimetric apparatus at 600 °C in argon atmosphere with heating rate increase 5 °C/min.

The porous structure of RF organic and carbon aerogels was determined by N_2 adsorption method at 77 K using an adsorption apparatus, Quantachrome Autosorb 1-C. Samples were evacuated at 50 °C in case of the RF aerogels or at 150 °C in the case of the carbon aerogels before adsorption measurements. The Brunauer–Emmett–Teller surface area (S_{BET}), micropore volume (V_{mic}) and mesopore volume (V_{mes}) of the samples were analyzed by Brunauer–Emmett–Teller theory, *t*-plot theory and Barret–Joyner–Halendar (BJH) theory, respectively.

RESULTS AND DISCUSSION

Influence of catalyst type

The obtained results indicated that the type of the used alkaline catalyst essentially influences both the effective gelation time of resorcinol–formaldehyde system as well as textural parameters of final RF carbon aerogels. The physicochemical properties of the carbon aerogels obtained in resorcinol–formaldehyde

TABLE 1

The used gelation catalysts and textural properties of the carbon aerogels (resorcinol content in water 12.5 mass %; R/F 0.5 mol/mol; R/C 150 mol/mol, curing time 48 h)

Sample	Catalyst	Gelation time, min	Textural parameters of carbon aerogels				
			S_{BET}, m^2/g	V_{tot}, cm^3/g	V_{mic}, cm^3/g	V_{mes}, cm^3/g	Average pore diameter, nm
			LTSCD*				
RF1b/C	NaOH	130	710	0.486	0.126	0.303	2.74
RF2b/C	KOH	150	726	0.542	0.160	0.367	2.99
RF3b/C	Na_2CO_3	80	312	0.209	0.023	0.037	2.68
RF4b/C	$CaCO_3$	175	730	0.656	0.153	0.464	3.60
			HTSCD**				
RF1a/C	NaOH	130	272	0.318	0.035	0.235	4.62
RF2a/C	KOH	150	669	0.664	0.077	0.470	4.45
RF3a/C	Na_2CO_3	80	777	0.837	0.112	0.663	4.31
RF4a/C	$CaCO_3$	175	853	1.827	0.157	1.635	8.57

*Low temperature supercritical drying method.

**High temperature supercritical drying method.

aqueous polycondensation reaction with using of various catalysts are presented in Table 1.

According to the obtained results, application of sodium carbonate as catalyst makes it possible to attain gelation point in the shortest time at a temperature of 70 °C while in the case of calcium carbonate (RF3b/C and RF4b/C samples) time of gelation is the longest one.

Irrespective of the type of catalyst used (excluding Na_2CO_3) the classic drying procedure of RF aerogels, *i.e.* under carbon dioxide supercritical conditions gives carbon aerogel materials of relatively high and almost the same specific surface areas (S_{BET} is 710–730 m^2/g).

On the other hand, high-temperature drying of alcogels allows obtaining materials with more differentiated specific surface areas, *i.e.* in the broad range 272–853 m^2/g. The highest surface was found for carbon aerogels prepared with $CaCO_3$ ($S_{BET} = 853$ m^2/g), and the lowest one with NaOH as catalyst ($S_{BET} = 272$ m^2/g).

It is very interesting to notice that the high total pore volume of aerogels (up to 1.827 cm^3/g), in the mesopore volume (1.635 cm^3/g) is obtained using high temperature RF alcogel drying (see Table 1), in the presence of $CaCO_3$ catalysts. In comparison to LTSCD aerogel series application of Na_2CO_3 catalyst gives aerogels of much better developed pore structure, larger specific surface area and pore volume, especially in the mesopore diameter range. Micropore volumes in all carbon aerogels are rather small, do not exceed 0.160 cm^3/g and as a rule they do not depend on the drying method used.

Influence of curing time

One can state that application of KOH in RF aerogel preparation (low price, good solubility) or calcium carbonate makes it possible obtaining carbon materials of the most advantageous texture parameters irrespective of the used drying method of the alcogels. This observation is supported by the physicochemical properties of the carbon materials obtained by carbonization of selected RF alcogels presented in Table 2. These RF alcogels were synthesized by aqueous polycondensation of resorcinol and formaldehyde using different curing times (48, 72, 120 h) and two drying methods, low- and high-temperature supercritical drying. It is visible that elongation of curing time from 48 to 120 h influences developing of aerogel porous structure.

From Table 2 one can see that at the used preparation parameters the 48 h curing time is sufficiently long for obtaining carbon aerogels with well developed specific surface area of the applied drying method, low- or high-

TABLE 2

Influence of curing time on textural properties of the carbon aerogels (KOH as catalyst, resorcinol content in water 12.5 mass %; R/F 0.5 mol/mol; R/C 150 mol/mol)

Sample	Curing time, h	Textural parameters of carbon aerogels				
		S_{BET}, m^2/g	V_{tot}, cm^3/g	V_{mic}, cm^3/g	V_{mes}, cm^3/g	Average pore diameter, nm
			LTSCD			
RF2b/C	48	726	0.542	0.177	0.365	2.98
RF5b/C	72	745	0.617	0.199	0.418	3.33
RF6b/C	120	774	1.503	0.190	1.313	7.76
			HTSCD			
RF2a/C	48	427	0.307	0.138	0.169	3.32
RF5b/C	72	669	0.664	0.197	0.467	4.45
RF6a/C	120	703	0.934	0.190	0.744	5.98

temperature. However the further elongation of curing time gives essential further pore structure developing. In both drying series, elongation of curing time results in large (almost three times) increase in pore volumes (especially in mesopore diameter region) and considerable enlargement of specific surface areas of HTSCD aerogel series.

Alcogel drying under CO_2 supercritical conditions enables obtaining carbon materials of relatively high specific surface area (S_{BET} = 726–774 m^2/g), negligibly increasing with curing time in comparison to the alcogels dried at the high temperature supercritical drying (S_{BET} = 427–703 m^2/g). It is visible that LTSCD products are characterized by high total pore volume (0.542–1.503 cm^3/g), increasing with curing time. Increase in curing time, from 48 to 120 h results in pore diameter increasing as a result of increase in share of mesopore volume in total pore volume from 67 % for 48 h curing time up to 87 % (0.365–1.313 cm^3/g). Irrespective of drying method volume of micropores is rather small and does not exceed 0.2 cm^3/g.

In summary one can state that increase in curing time in both drying methods results in enlargement of specific surface area (better visible in HTSCD method) and almost three times higher total pore volume, mainly mesopores. It results in an increase in average pore diameter. Then curing time can be used as the main pore diameter controlling parameter.

TABLE 3

Influence of resorcinol concentration in water on textural properties of the carbon aerogels (KOH as catalyst, R/F 0.5 mol/mol; R/C 150 mol/mol, curing time 48 h)

Sample	Content of resorcinol in water, mass %	Gelation time, min	Textural parameters of carbon aerogels				
			S_{BET}, m^2/g	V_{tot}, cm^3/g	V_{mic}, cm^3/g	V_{mes}, cm^3/g	Average pore diameter, nm
			LTSCD				
RF7b/C	10	430	695	0.526	0.164	0.344	3.03
RF8b/C	20	160	867	1.836	0.161	1.673	8.47
RF9b/C	30	130	777	0.667	0.158	0.476	3.43
			HTSCD				
RF7a/C	10	430	554	0.444	0.102	0.317	3.70
RF8a/C	20	160	720	0.715	0.100	0.535	4.48
RF9a/C	30	130	696	0.594	0.099	0.418	3.31

TABLE 4

Influence of molar ratio R/C on textural properties of the carbon aerogels (KOH as catalyst, R/F 0.5 mol/mol; content of resorcinol 20 mass %, curing time 48 h)

Sample	Molar ratio R/C, mol/mol	Gelation time, min	Textural parameters of carbon aerogels RF				
			S_{BET}, m^2/g	V_{tot}, cm^3/g	V_{mic}, cm^3/g	V_{mes}, cm^3/g	Average pore diameter, nm
			LTSCD				
RF10b/C	100	95	679	0.429	0.071	0.180	2.90
RF8b/C	150	160	867	1.836	0.161	1.673	8.47
RF11b/C	200	205	737	0.667	0.165	0.515	3.86
			HTSCD				
RF10a/C	100	95	696	0.579	0.096	0.409	3.75
RF8a/C	150	160	720	0.715	0.100	0.535	4.48

Influence of resorcinol concentration

An increase in resorcinol concentration essentially influences both gelation time and pore structure of carbon aerogels (Table 3).

At the used synthesis parameters, the longest resorcinol and formaldehyde gelation time (430 min) was stated for RF alcogels obtained at 10 mass % of resorcinol in water and the shortest one for alcogels obtained at 30 mass % of resorcinol in water.

Regardless of the used drying method the carbon aerogels synthesized using 20 mass % resorcinol concentrations were characterized by the highest specific surface area (720 and 867 m^2/g) and the highest pore volume (1.673 and 0.535 cm^3/g). Similarly as in the previous aerogel series, the low-temperature drying of RF gels gives carbon materials of the higher specific surface areas in comparison to their homologues prepared using high-temperature drying (see Table 3). This statement refers also to aerogel pore volume. It seems that application of 20 mass % resorcinol concentration in water is the optimal value taking into account specific surface area, pore volume and average pore diameter. Irrespective of resorcinol concentration in water and RF gel drying method, volume of micropores is relatively small and does not exceed 0.2 cm^3/g.

Influence of R/C molar ratio

Table 4 presents results of the studies of the influence of R/C molar ratio on porous structure of RF carbon aerogels. It turned out that R/C ratio increase from 100 to 200, *i.e.* really decrease in catalyst mass in reaction mixture, results in elongation of gelation time. This observation is true regardless of the RF gel drying method used. On the basis of LTSCD aerogel series one can suggest that taking into account total porosity of the carbon aerogels the R/C = 150 ratio is the most advantageous one.

Preparation of spherical carbon aerogels

Table 5 characterizes porous structure of the spherical carbon aerogels obtained in our

TABLE 5

Influence of dispersion medium on textural parameters of the spherical carbon aerogels (KOH as catalyst, resorcinol content 30 mass %, R/C 150 mol/mol, R/F 0.5 mol/mol, V_{gel}/V_{med} = 0.1 %, V_{surf}/V_{med} = 0.03 %)

Sample	Dispersion medium	Textural parameters of carbon aerogels RF				
		S_{BET}, m^2/g	V_{tot}, cm^3/g	V_{mic}, cm^3/g	V_{mes}, cm^3/g	Average pore diameter, nm
RF12b/C	Cyclohexane with surface active agent	509	0.252	0.166	0.041	1.98
RF13b/C	Paraffin oil without surface active agent	749	0.990	0.136	0.016	5.28

Notes. 1. V_{surf}/V_{med} is content of surfactant in reaction mixture (including dispersion medium). 2. V_{gel}/V_{med} is alcogel content in reaction mixture (including dispersion medium).

TABLE 6

Comparison of porous structure of the prepared carbon aerogels and the commercial active carbon

Material type	S_{BET}, m^2/g	V_{tot}, cm^3/g	V_{mic}, cm^3/g	V_{mes}, cm^3/g
Active carbon SX Ultra Cat from Norit	1020	0.809	0.372	0.437
Carbon aerogel monolith	867	1.836	0.161	1.673
Carbon aerogel spheres	749	0.990	0.136	0.016

laboratory using two different dispersing agents, cyclohexane with surface active agent and paraffin oil without surface active agent.

Application of cyclohexane as dispersing agent (oil phase) and surfactant makes it possible to obtain carbon microspheres of 20–40 μm diameter. Replacement of cyclohexane by paraffin oil results in an increase in the diameter of carbon spherical aerogel grains up to 2–3 mm and creates better developed pore structure (see Table 5). The obtained investigation results indicate also that physicochemical properties, especially porous structure, are similar to the commercial active carbons considered as catalyst supports (Table 6). However, it is noteworthy that substantial part of spherical aerogel porosity is created by macropores.

SUMMARY

– Parameters of synthesis of RF organic aerogels (catalyst type, gels curing time, R/C ratio, resorcinol concentration in water) and drying method (low- and high-temperature supercritical drying) strongly influence textural parameters of the final carbon aerogels (specific surface area (S_{BET}), total and mesopore volume).

– Application of KOH or $CaCO_3$ in RF aerogel preparation allows obtaining carbon aerogels of the most advantageous parameters irrespective of the drying method used. Taking into account catalyst price and lower $CaCO_3$ solubility in water the more profitable catalyst for RF aerogel synthesis seems to be KOH.

– Elongation of curing time of RF gels results in increase in specific surface area and total pore volume of the carbon aerogels obtained both in the course of low- and high-temperature drying.

– Regardless of the applied RF aerogel drying method the highest surface area and total pore volume were found for carbon aerogels synthesized with 20 % resorcinol solution in water.

– Low-temperature supercritical drying of RF aerogels gives carbon materials of more advantageous texture parameters in comparison to carbon aerogels obtained in high-temperature supercritical drying.

– Regardless of RF aerogel drying method an increase in resorcinol to catalyst molar ratio (R/C) is accompanied by developing of porous structure of carbon aerogels at a charge of shortening of gelation time of resorcinol–formaldehyde system.

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