

THE USE OF PHOSPHOROUS COMPOUNDS AS POLYMERIZATION CATALYSTS IN THE SYNTHESIS PROCESS OF CARBON AEROGELS

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Introduction

Carbon aerogels are frequently obtained by the polycondensation of resorcinol and formaldehyde according to the synthesis process described by Pekala[1]; there are three major steps in this process: the first one includes the polymerization and condensation of the organic monomers in the presence of a catalyst (sol-gel process); in the second step, the organic gel obtained is dried with CO₂ in supercritical conditions and then, in the final step, the organic aerogel is pyrolyzed under inert atmosphere between 600 y 1100°C. Each stage influences the material morphology and porosity, however, the first stage is the one that exerts the main effect; the textural characteristics could be designed and controlled by adjusting the R/F, R/C and R/W ratios, the kind of catalyst used, the curing temperature and the mixture initial pH [2]. The polymerization catalyst and its R/C ratio influence the material surface area, density, mechanical properties and the meso-porosity ; its function is to promote the formation of the resorcinol anion and to enhance the addition of formaldehyde to the benzenic ring, producing hydroxymethyl derivatives. Once the derivatives had been formed, the process is followed by the condensation to form a highly cross-linked polymer [3].

Experimental

Carbon aerogels were prepared from resorcinol (R), and formaldehyde (F) in water (W), the R/F and R/W ratios were fixed in 0.5 and 0.13 respectively. The polymerization catalyst was potassium carbonate (A series), sodium dibasicphosphate (P series) or sodium glicerophosphate (GP series), the R/C ratio was set between 50 to 1200; for the samples nomenclature the R/C ratio used precedes the letter for each series. The mixture was poured into glass tubes (40 cm length x 0.5 cm i.d.). Glass tubes were sealed and the mixture were cured as described elsewhere [4].

After curing cycle, gel rods were cut into 5 mm pellets and place in acetone to exchange the solvent and then dried supercritically with CO₂ to obtain the corresponding organic aerogels. Pyrolysis of these organic aerogels was carried out in N₂ flow at 100 cm³ min⁻¹ and heated to 750 °C at a heating rate of 2 °C min⁻¹ and a soaking time of 4 h.

Carbon aerogels were characterized by the measure of N₂ adsorption isotherm at -196 °C in a Micromeritics Gemini 2375 adsorption apparatus. The isotherm data were processed to obtain the BET surface area, t-method mesoporous surface area and micropore volume, and DR micropore volume. The

oxygen surface groups for GP samples were characterized by meaning of temperature programmed desorption (TPD) of CO and CO₂, the analysis was carried out by heating the samples to 1100°C at 10 °C min⁻¹ and determining the CO and CO₂ evolved with the aid of a gas chromatograph equipped with a TCD detector, and a HP plotQ column; the injector and detector temperature were 250 °C and the column temperature was 30 °C.

Results and Discussion

All the samples of carbon aerogels have a high content of carbon and a low content of hydrogen as shown in table 1; the oxygen content varies from samples in each series, but the samples that use a phosphorous compound as catalyst trend to have greater contents of oxygen, especially at low charge of catalyst.

Table 1. Ultimate Analysis and Burn Off of Carbon Aerogels

Sample	%C	%H	%O	% Burn-off
200A	96.89	1.11	1.69	44.60
800A	97.80	1.18	0.95	47.93
1200A	96.38	1.15	2.42	42.02
50P	93.69	1.12	3.41	53.28
200P	97.00	1.13	1.43	50.41
800P	97.04	1.14	1.72	50.74
1200P	97.58	1.15	1.21	45.07
50GP	94.56	1.15	2.60	51.23
200GP	95.48	1.09	3.04	49.36
800GP	96.88	1.05	1.97	47.69

The burn off of all the samples is high and around the 50% for the carbon aerogels prepared with a phosphorous compound catalyst. These material losses are a little higher to those observed for carbon aerogels obtained with alkaline carbonates, being a disadvantage for the use these compounds as catalyst.

In table 2 are shown the textural characteristics of samples obtained by the BET, t-method and DR analysis of nitrogen adsorption isotherms. For the organic aerogels (OA) a significant diminution of the surface area when the R/C ratio increase from 800 to 1200 is observed due the strong acidity condition in the initial mixture of the 1200 samples. The organic aerogels have a relative well developed surface area; however after the carbonization process the surface area of carbon aerogels obtained is significant higher for those prepared using a phosphorous compound catalyst.

According to Bock and collaborators [5], the structure of a carbon aerogel is made of primary particles like spheres; the microporosity is due to the intraparticular spaces and the mesoporosity to the interparticular spaces. For R/C ratios of 1200 the micropore volume and the mesopore surface area of the samples diminished due to the formation of a lot of aerogel

primary particles of great size; for R/C ratios of 50 the microporosity is favored.

Table 2. Textural Characteristics of Carbon Aerogels Synthesized

Sample	OA ¹		CA ²		
	S_{BET} (m^2g^{-1})	S_{BET} (m^2g^{-1})	S_{mes} (m^2g^{-1})	W_{0t} (cm^3g^{-1})	W_{0DR} (cm^3g^{-1})
200A	474.6	386.2	55.89	0.089	0.169
800A	336	631.4	38.50	0.219	0.258
1200A	9.62	22.63	5.59	0.00259	0.00928
50P	467.7	691.2	74.55	0.200	0.278
200P	402.1	623.3	39.29	0.214	0.258
800P	275.5	584.6	45.17	0.202	0.239
1200P	18.47	46.27	5.86	0.00586	0.0252
50GP	539.4	743.9	161.9	0.108	0.300
200GP	460.8	613.8	61.02	0.182	0.247
800GP	420.7	451.9	59.74	0.121	0.182

¹Organic aerogel

²Carbon aerogel

Table 3 shows the CO and CO₂ content evolved after the TPD analysis. GP50 sample have a higher content of CO₂ related to strong acidic oxygen groups and GP800 sample have a higher CO content related to weak acidic or basic oxygen groups. When R/C ratio is about 50 the distribution of oxygen surface groups is in a 1.4 ratio between basic and acidic groups, and increase to 1.9 when the R/C ratio increase to 200, and to 4.8 when the R/C ratio increase to 800.

Table 3. CO and CO₂ Evolved After TPD Analysis

Sample	CO	CO ₂	CO/CO ₂
	(μmol/g)		
GP50	39.98	29.05	1.38
GP200	32.32	17.38	1.86
GP800	83.78	17.60	4.76

Table 4. Ultimate Analysis and Burn Off of Carbon Aerogels

Sample	Carboxylic	Lactone	Anhydride	Phenol	Carbonyl-Quinone
	(μmol g ⁻¹)				
50GP	14.28	8.12	4.19	3.59	28.73
200GP	0.58	11.20	5.02	6.80	17.58
800GP	0.37	11.08	5.54	3.59	23.86

The oxygen surface groups content is shown in table 4, the data were obtained as described elsewhere [6]. The GP50 sample has a high content of carboxylic surfaces groups and a high content of carbonyl-quinone groups too. Samples GP200 and GP800 have a similar distribution of oxygen groups like carboxylic, lactone anhydride and phenol, but the carbonyl-quinone content is significantly higher for GP800 sample. The oxygen surface groups content depends of the initial pH

conditions of the mixture of precursor used, acidic conditions enhance the carboxylic groups content and basic conditions the carbonyl-quinone groups contents. For the use of sodium glicerophosphate low R/C ratios cause an acidic condition in the initial mixture of precursors and high R/C ratios cause basic conditions.

Conclusions

Phosphorous compounds are suitable catalysts for the synthesis process of carbon aerogels, its use propose a new way to obtain this kind of materials. The control of catalyst concentration is a key factor to design the textural characteristics of carbon aerogels, low concentrations produce materials with low surface area and microporosity, with the exception of materials obtained by the use of sodium glicerophosphate (GP series), these samples have a well developed porosity in all the interval of catalyst concentrations worked. The use of sodium glicerophosphate increases the oxygen content; with an R/C=50; the concentration of carboxylic oxygen groups is significant higher than the other R/C ratios worked. Also the use of sodium glicerophosphate produce higher textural characteristics than those obtained with the alkaline carbonates at a same R/C ratio.

Acknowledgments. Acknowledgments are made to the División de Investigaciones de la Sede Bogotá (DIB) at Universidad Nacional de Colombia, for the support to this research through the project 201010013227.

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