

IMPREGNATION AND ACTIVATION OF CARBON AEROGELS MADE FROM 5-METHYLRESORCINOL AND FORMALDEHYDE.

F. Pérez-Caballero*, M. Koel.

Institute of Chemistry, Tallinn University of Technology. Akadeemia tee 15, Tallinn 12618, Estonia.

fernancelora@hotmail.com ; Fax: +372 620-2828

Carbon aerogels are good supports for catalysts for several catalytic applications to perform reactions in gaseous and liquid phases. Carbon aerogels can be further treated to increase the surface area and decrease the pore size by so called activation. Specific surfaces areas increase by 2-3-fold in a quick process whilst the porosity can be tailored according to the catalytic requirements from meso- to microporosity.

5-methylresorcinol-formaldehyde based aerogels were studied as support for metal catalyst, prepared by impregnation of aerogels with precursor in supercritical CO₂ and further reduction of it into its metal state. Thus, nano-particles of metal were formed on the surface and in the pores of carbon aerogel. By supercritical impregnation and reduction, the nanoparticles of metal are distributed very homogeneously in the structure of the carbon aerogel.

INTRODUCTION

Aerogels are materials characterized by their low densities and very high specific surface areas. Their structures consist of a solid network with open, branched mesopores. Aerogels can be obtained as monoliths, granulates, films or powders. Pekala et al. have synthesized organic hydrogels by sol-gel polycondensation of resorcinol (1,3-dihydroxybenzene) with formaldehyde and prepared resorcinol-formaldehyde (RF) aerogels by drying with supercritical carbon dioxide. They have pyrolyzed the aerogels in inert atmosphere at 1323K obtaining carbon aerogels. RF carbon aerogels have high porosity (>80%) and high surface areas (400-900 m²g⁻¹). [¹, ², ³]. The stoichiometry of the reactants in the solution determines the microstructures of RF aerogels and their pyrolyzed derivatives.

A high accessible surface area of the material is needed for applications in supercapacitors and fuel cells; indeed, a large micropore volume is a prerequisite.

The microporosity in carbon aerogels can be tailored by the pyrolysis conditions. Through N₂-adsorption basis, information for the accessible surface area and the overall porosity is generally obtained. The porosity that is not accessible for N₂ at 77 K can be considered as a surface area reservoir that can be made accessible via activation. The carbon burn-off is an indicator for the micropore volume and surface area obtained during activation. Via CO₂-activation of C-aerogels the BET surface area can be increased from 500 m²/g to well over 2 000 m²/g with a carbon burn-off of only 50%. It has been reported that the increase in the micropore volume detected by N₂-adsorption in more than 1 cm³/g is due to an opening of initially inaccessible micropores plus the creation of new voids. [⁴].

Moreover, the coexistence of micropores and mesopores can extend their potential for applications. [⁵, ⁶, ⁷]. Activation has been proven to be very effective in order to enhance the porosity and specific

surface area of carbon aerogels. Studies on activation using H₂O instead of CO₂ have been reported with interesting results as well [8].

The Supercritical Fluid (SCF) medium allows an easy penetration and wetting of pores compared to normal solvents, as well as avoiding pore collapses that occur when an aerogel is dried by leaving the sample to dry under ambient conditions. Amongst commonly used SCFs, scCO₂ has particularly accessible supercritical parameters (T_c = 31.1°C; P_c = 7.38 MPa), is non flammable, non-toxic, environmentally friendly, inexpensive and leaves no residues in the treated medium [9].

To impregnate the carbon network with metal nanoparticles, several methods have been developed, most beginning with an oxidised salt or metal complex followed by reduction and decompression [10, 11, 12]. A number of methods for reduction of the metal have been employed including thermal decomposition in an inert atmosphere and chemical conversion with hydrogen or air after depressurisation, chemical reduction in the (SCF) with a reducing agent such as hydrogen or an alcohol and thermal reduction in the SCF [13].

In this work, organic aerogels were synthesized by sol-gel polycondensation of 5-Methylresorcinol and Formaldehyde, and MR-F aerogels were prepared by drying using CO₂ in its supercritical state. [14]. Then carbon aerogels were obtained by pyrolysing MR-F aerogels in inert N₂ atmosphere. A further activation was then performed in a flow of CO₂ in order to enhance the nanopores properties.

MATERIALS AND METHODS

Anhydrous 5-methylresorcinol with a reported purity of 99.58% was obtained from CarboshaleAS, Estonia. It was used as received. Anhydrous sodium carbonate with a purity of 99.8%, Riedel-de-Haen, Germany was used as received. Water used was purified using a Milli-Q Water system. Formaldehyde (37% w/w solution in water), Sigma-Aldrich, was used as received. Palladium(II) hexafluoroacetylacetonate [Pd(C₅HF₆O₂)₂] was obtained from Aldrich and was used as received.

5-methylresorcinol and formaldehyde aerogels were synthesized using a doubly-catalysed polycondensation. Sodium carbonate (C) was used as a base. The aerogels were obtained by curing the solutions at room temperature for 48 hours. The moulds used were test tubes characterized by an approximate diameter of 1 cm and a length of 10 cm, in which 80% of the total volume was occupied by the gel. After that, the gel was placed in an acetic acid solution (pH ≈ 4) and left there for another 48 hours, changing the acetic acid every 24 hours. The MR-F aerogels prepared have structures filled with water. Being poorly soluble in CO₂, water was replaced by acetone over 4 days renewing the latter every 24 hours before the extraction. [15].

Drying with CO₂ was performed in three steps. First, the gel was left in contact with CO₂ at a pressure of 20 MPa and room temperature for 20 minutes. Then, the pressure was lower until 12 MPa and liquid CO₂ flowed for 150 minutes. Finally, the temperature was raised up to 50°C and this step was run for 120 minutes keeping the pressure at 12MPa.

The pyrolysis of the dried aerogel was performed in inert atmosphere (N₂) in a tubular furnace, with a working temperature of up to 1053 K, and controlled by a Nabertherm Program Controller S19 (Germany). The temperature program of the furnace is described in Figure 1. The furnace was cooled to a room temperature under its own thermal mass when the pyrolysis time was achieved.

Activation was carried out after pyrolysis by leaving the gel in the tubular furnace and rising the temperature up to 1173K for a time described in Table I in a flow of CO₂.

The composition and morphology of the carbon aerogels were analysed by an EDAX JEOL 6042 analyser and a Leo Supra 35 Scanning Electron Microscope (SEM). For nitrogen adsorption analyses, a Sorptometer KELVIN 1042 built by Costech International was used. The gas volume (N₂) adsorbed

on the surface of materials at liquid nitrogen temperature was measured. The precision of the measurements data of the adsorbed gas volume was $\leq 3\%$. Helium was used as a carrier gas with nitrogen as an adsorptive gas. The BET specific surface area (S_{BET}) was calculated according to the Brunauer-Emmet-Teller (BET) theory. The specific micropore volume (V_{mic}) was determined via the t-plot and the pore size distributions were analyzed using the Barrett-Johner-Halendar (BJH) theory. For the calculation of specific surface areas the range of P/P_0 was 0.05 – 0.25; for the determination of the micropore volumes P/P_0 was from 0.0005 -0.4.

DISCUSSION

The process of pyrolysis was performed by placing the gels in a tubular furnace in a flow of Nitrogen following the program described in Figure 1. The final temperature chosen was 1053K, which was shown to be optimum after having observed the fact that, above this temperature, the mass loss of the samples is very small as well as the change in the porosity and specific surface are not noticeable.

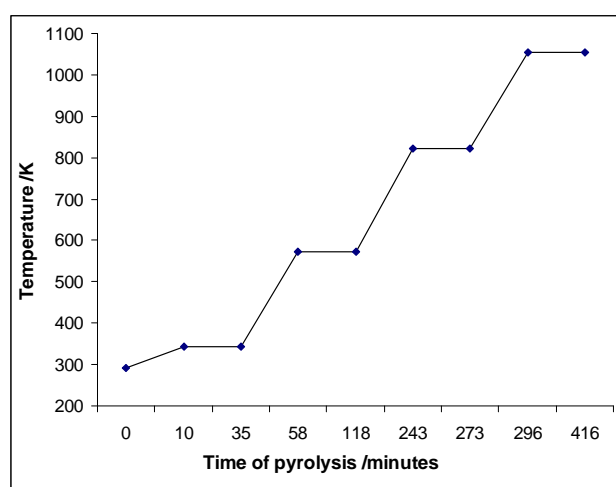


Figure 1. Pyrolysis program for aerogels.

Activation differs from pyrolysis in the temperature program and in the carrier gas. CO_2 flowed through the reactor, which was heated from room temperature until 1173K at a rate of 10^0 /minute. Then, when the final activation temperature was reached, the gel was left for a certain time, as it is described in table I, where the data obtained from applying Nitrogen Adsorption to the activated carbon aerogels obtained are too shown.

Sample	Activat. Time /h	V mic /mm ³ /g	Total pore V /mm ³ /g	Mic Area /m ² /g	Non-Mic /m ² /g	S. BET /m ² /g	% Mic	Density /g/cm ³	Mass Loss (%)
Aerogel	Not pyrolysed	0	NA	0	295,5	295,5	0	0,206	--
CA	Not activated	82,92	NA	235,3	240,2	475,5	49,5	0,303	--
ACT 1	0,5	263,2	812,9	747,0	281,3	1028,3	72,6	0,245	27,33
ACT 2	1	290,7	NA	825,1	NA	NA	85,1	0,217	33,40
ACT 3	1,5	472,5	NA	1341,0	248,9	1589,9	84,3	0,178	42,72
ACT 4	2	261,2	1253,3	741,2	914,6	1656,0	44,8	0,158	66,92

Table I. Characteristics of samples studied. V_{mic} is the volume occupied by microporous. Total Pore V. and Mic. Area are the total pore volume and the microporous area of the activated carbon aerogels. Non-Mic. is the specific surface area of non-microporous standards. S. BET is the Brunauer-Emmet-Teller Specific surface area and % Mic is the percentage of microporosity in the samples. Mass Loss is the lose in mass of the sample in the activation process. NA = not available.

It can be observed that the increase of the activation time in samples produces an increase in the total pore Volume of the samples reaching a value of over 1200 mm³/g after two hours of activation. Equally; there is an increase in the BET surface area running from below 300 m²/g of samples non-activated or just activated less than half an hour, up to values well over 1 500m²/g for samples activated over 1 hour as it appears in Figure 2. According to the tendency of the values obtained, it seems unlikely to obtain much larger values of BET surfaces for activation times of over 2 hours.

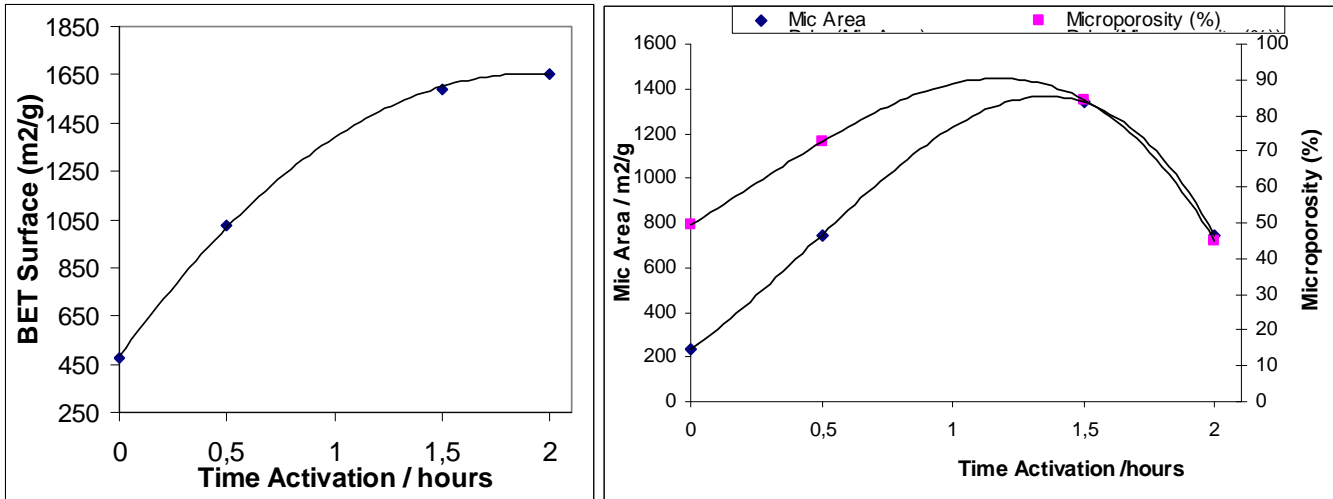


Figure 2: BET Surface area of samples studied.

Figure 3: Microporous Area and percent of microporosity dependence with time of Activation.

Regarding the porosity of the samples studied, in figure 3, it can be observed that the activation plays a fundamental role in the final appearance of the gels. At activation times between 1 hour and 90 minutes, the microporosity achieved reached its maximum and samples with microporosity near to 90% were produced. However, when the activation time was still increased, the average pore size increases and samples with less than 50% of microporosity were produced. The same effect is observed in samples activated for 30 minutes or less.

Figure 4 shows the change in the densities of gels with the activation. Densities below 0.16 g/mL were achieved for gels activated for 2 hours. The mass loss of these gels was almost 70% and by observing the tendency of mass loss, it is expected that activation in this conditions, cannot be carried out for a much longer time than 2 hours.

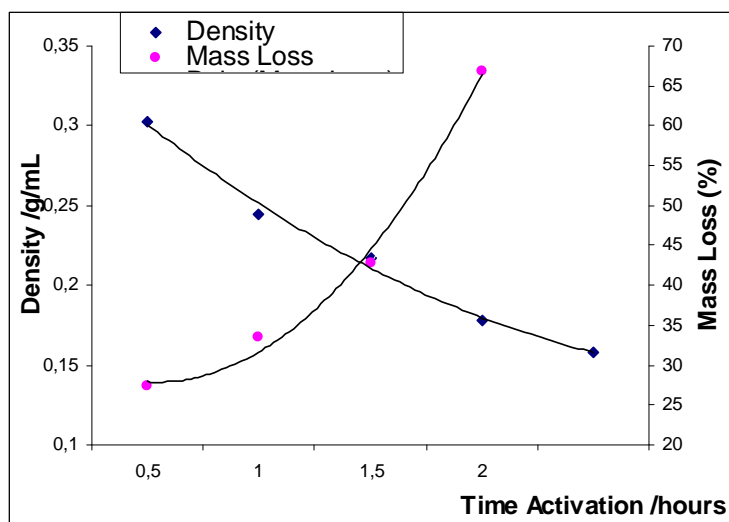


Figure 4: Densities and Mass Losses of gels after activation.

In order to carry out the impregnation process, a quantity of a carbon aerogel was weighed and placed in a high pressure reactor. Subsequently, $[\text{Pd}(\text{C}_5\text{HF}_6\text{O}_2)_2]$ was added together with a stirring bar and the reactor was then sealed and placed in a bath at 40°C . The amount of Pd complex weighed was in the range of 10-15 mass percent compared to the mass of carbon aerogel. CO_2 was then pumped in up to a pressure of 150 bars and the system was left for 2 hours in order to allow the palladium complex time to dissolve. Then, a mixture $\text{CO}_2:\text{H}_2$ (15:1) was pumped in until the final pressure in the reactor was 185 bars, then, the system was left reacting for 25 minutes before slow decompression. After opening the reactor, carbon decorated with palladium nanoparticles was obtained and analysed. Figure 5 shows how the carbon network of the aerogel was decorated with palladium nanoparticles after the reduction and decompression in the reactor. The catalyst was tested in the reduction of cis-cyclooctene into cyclooctane in SC-CO_2 with a basically total conversion in a quick reaction. Moreover, the impregnated piece of carbon aerogel was reused twice in the same reaction reaching the same level of conversion.

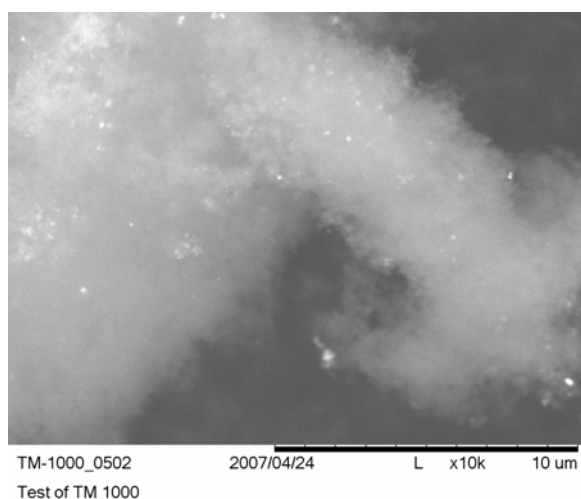


Figure 5: SEM image of a piece of carbon aerogel impregnated with black palladium.

CONCLUSION

The final properties of gels can be tailored as shown in this study. A deep study on the activation time is crucial in order to select the final size of pore and the specific surface area. Thus, a wide variety of samples have been produced by changing the activation time; samples with high microporosity and considerable BET surface were produced as well as samples with higher BET surface areas and characterized by being constituted by mesoporous mainly. Activation times of over 2 hours would lead to too high Mass Loss and consequently, a total burnt off of the samples.

Using Palladium salts soluble in CO₂, impregnation of carbon aerogels were successfully carried out by dissolving the salt in CO₂ and then allowing the oxidized Pd to enter the pores before a quick reduction with H₂. The rapid reaction lead to samples homogeneously decorated with black Palladium potentially interesting for heterogeneous catalytic reactions.

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REFERENCES

- (1) PEKALA, R.W.. *J. Mater. Sci.* 24, **1989**, 3221-7.
- (2) PEKALA, R W., ALVISO, C.T. *Mater. Res. Soc. Symp. Proc.* 270, **1992**. 3-14.
- (3) BRUNAUER, S., EMMETT P.H., and TELLER, E. *J. Am. Chem. Soc.* 60, **1938**: 309-19.
- (4) SALIGER, R., REICHENAUER G., and FRICKE J.. *Proceedings of the 5th International Symposium on the Characterization of Porous Solids (COPS-V)*, **2000**, 381.
- (5) HANZAWA, Y. and KANEKO, K.. *J. Surf. & Colloids.* 26. **2006**. 6167.
- (6) ISHII, C., MATSUMURA, Y., KANEKO, K. *J. Phys. Chem.*, 99, **1995**. 5473.
- (7) NAKAYAMA, A., SUZUKI, K., ENOKI, T., ISHII, C., KANEKO, K., ENDO, M., SHINDO, N. *Solid State Commun.*, 93. **1995**. 323.
- (8) ALAR J., KURIG, H., LUST, E.. *Carbon* 45, **2007**. 1226.
- (9) WOOD, C.D., TAN, B., ZHANG, H., COOPER, A. I. *Thermodynamics, Solubility and Environmental Issues.* **2007**. 383.
- (10) SAQUING, C.D., KANG, D., AINDOW, M., ERKEY, C. *Microp. & Mesop. Mat.* 80. **2005**. 11.
- (11) COTET, L.C., GICH, M., ROIG, A., POPESCU, I.C., COSOVEANU, V., MOLINS, E., DANCIU, V. *J. Non-Cryst. Sol.* 352, **2006**, 2772.
- (12) CACCHI, S., COTET, C. L., FABRIZI, G., FORTE, G., GOGGIAMANI, A., MARTÍN, L., MARTÍNEZ, S., MOLINS, E., MORENO-MAÑAS, M., PETRUCCI, F., ROIG, A., VALLRIBERA, A. *Tetrahedron* 63, **2007**, 2519.
- (13) ZHANG, Y., ERKEY, C. *J. Supercritical Fluids*, 38, **2006**, 252.
- (14) F. PÉREZ-CABALLERO, A-L. PEIKOLAINEN, M. UIBU, R. KUUSIK, O. VOLOBUJEVA, M. KOEL. *J. Microp. & mesop. Mat.* 108, **2008**. 230.
- (15) LI, W-C., LI A-H., CAI, S. *J. Colloid & Interf. Sc.* 254, **2002**, 153.