

THERMAL ANALYSIS OF COBALT CATALYST SUPPORTED ON CARBON AEROGELS

Maria Helena Garcia, Nelson Oswaldo Briceño, Ariel Oswaldo Cadena, Yazmín Yaneth Agamez, José de Jesús Díaz.

Departamento de Química Universidad Nacional de Colombia, Bogotá D.C. 11321, Colombia

Introduction

Carbon aerogels are nanostructured carbonaceous materials, obtained throughout the pyrolysis of organic aerogels. They are widely used in many aspects of our lives, like thermal and acoustic insulators, electrical double layer capacitors, electrodes for fuel cells, adsorbents, catalyst and catalyst supports[1]. The carbon aerogels more widely know are the ones obtained throughout the polycondensation of resorcinol with formaldehyde in water and using a lightly basic catalyst to enhance the polymerization process by promoting the dehydrogenation of resorcinol and the subsequently formaldehyde anion addition to the benzenic ring to form the cross-linked net[2-3]. These materials should have some special features, to be able to be used in several application; these features includes mechanical resistance, high surface area and pore volume; and the possibility of to assume a tailor work by building the structure of the carbon aerogel; the advantage of use these carbonaceous materials over others, is basically the possibility of to control their micro and meso-porosity independently, and another important parameter is a high resistance to the thermal degradation process, this due to their use as thermal insulators or special component for space uses or to be used as catalyst or catalyst support in chemical reactions that involves high temperatures. Thermogravimetric Analysis is a thermal analysis technique used to measure weight changes as function of temperature and/or time. TGA analysis of carbon aerogels, leads to determinate the thermal stability of these materials and other compounds associated with these carbonaceous matrix.

Experimental

Organic aerogels were prepared by the polycondensation of resorcinol (R) with formaldehyde (F), in a lightly basic aqueous solution, using deionized water (W) as solvent and K_2CO_3 as polymerization catalyst (C); to promote the dehydrogenation of resorcinol[4]. The solution was stirred and formaldehyde was slowly added to the mixture. Resorcinol ($C_6H_6O_2$) molar ratio used respect to formaldehyde was 0.5 ($R/F = 1/2$) in all cases[5]. Molar ratio R/C (resorcinol/polymerization catalyst) used was varied from 50 to 200. After stirring, the solution was placed in glass cylindrical shape molds and aged in a temperature program from 30 to 80°C for given days; to enhance the polymerization process. The hydrogels were removed from the molds and then cut in small pieces. Solvent exchange was performed with acetone at ambient conditions during 3 days; acetone was replaced once a day. Organic gels dry was carried out by using CO_2 in

supercritical conditions (1500 PSI y 33°C). Carbon Aerogels were prepared by pyrolysis of the organic aerogels in inert atmosphere, using a temperature ramp from room temperature to 750°C, with a residence time at the maximum temperature of 2 hours, in constant nitrogen flow (226 mL/min), letting that furnace became at room temperature again. The carbon aerogels were then placed into a desiccator. Samples of the RF 50 y 200 carbon aerogels were impregnated with a cobalt (III) acetate solution in a concentration in cobalt content with respect to the whole catalyst bulk of the 2.5%, by using the incipient impregnation method. The impregnation process was carry out in vacuum conditions, assisted by ultrasonic technique. Samples where dried and grinded into powder.

Thermal stability analysis of the cobalt supported carbon aerogel catalysts with R/C=50 y 200 and carbon aerogel support with the same R/C molar ratio without cobalt charge, were analyzed by TGA/DSC (Thermogravimetric Analysis / Differential Scanning Calorimetry), using a Mettler-Toledo TGA/DSC 1. Where the samples were loaded in a platinum pan and heated from ambient temperature to 1100°C at a $10^\circ C \text{ min}^{-1}$ heating rate [6] under constant nitrogen UHP flow of 105 mL min^{-1} .

Results and Discussion

The thermal properties of Carbon Aerogels R/C 50 y 200 without Co charge and impregnated with Co 2.5%; were observed by TGA y DSC, as shown in Figures 1 y 2; 3 y 4 respectively. Fig. 1 shows that carbon aerogels R/C=50 without cobalt charge starts to decomposes at around 30°C until approximately 320°C; the weight was rapidly decreased between this temperature interval, followed for an apparent stability temperature interval with not considerable weight loss between 330°C and 760°C; after this point the material undergoes another weight loss until 1100°C. Carbon aerogels R/C=50 with Co 2.5% starts to decomposes almost at the same temperature that the uncharged one, although this process is more constant that the first one from 30°C to 1100°C. The carbon aerogels R/C=50 without cobalt charge presents a greater thermal stability that the impregnated one among the temperature interval studied.

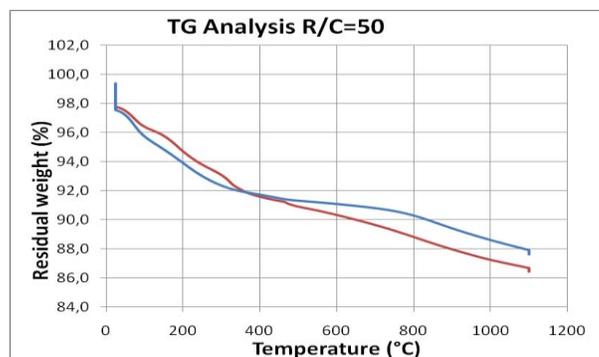


Fig. 1 TGA thermogram of carbon aerogels R/C = 50. Blue line R/C 200 without Co; red line R/C 200 with 2.5% cobalt supported.

Fig. 2 shows the thermal behavior of carbon aerogels R/C 200 without Co charge, the initial decomposition temperature is above the 25°C, with an appreciable weight loss until 350°C approximately. In the other hand, the carbon aerogel with a 2.5% Co charge had a more pronounced weight loss inside the temperature interval studied. In general terms, can be observed that carbon aerogels R/C=200 presents higher decomposition temperatures than the R/C=50 ones.

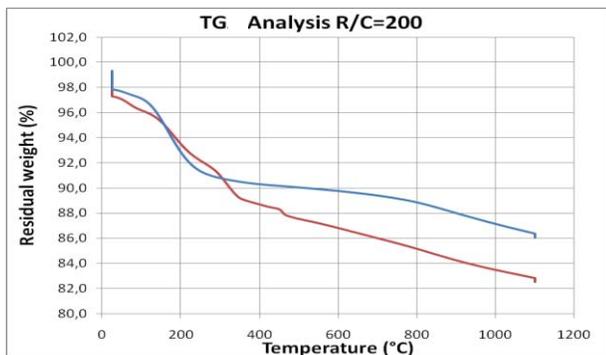


Fig.2 TGA thermogram of carbon aerogels R/C = 200. Blue line R/C 200 without Co; red line R/C 200 with 2.5% cobalt supported.

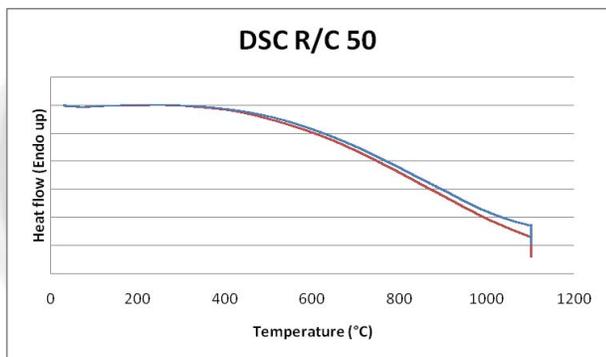


Fig.3 DSC thermogram of carbon aerogels R/C = 50. Blue line R/C 50 without Co; red line R/C 50 with 2.5% cobalt supported.

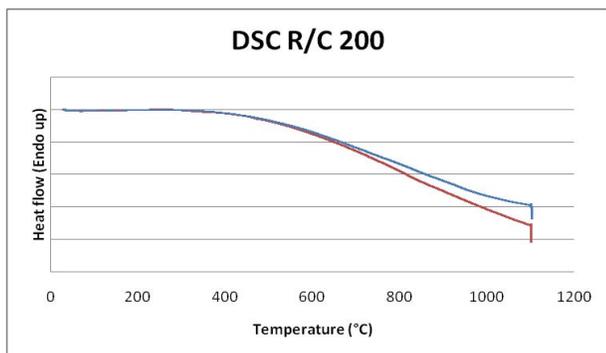


Fig.4 DSC thermogram of carbon aerogels R/C = 200. Blue line R/C 200 without Co; red line R/C 200 with 2.5% cobalt supported.

Fig. 3 and Fig. 4 present the DSC thermograms for carbon aerogels R/C=50 and R/C=200 respectively; for the carbon aerogels without Co charge and the impregnated with Co ones.

The plots show that the process is completely exothermal in both cases, showing the rearrange of the structure during the thermal treatment. The curves of the impregnated carbon aerogels presents more exothermal process that the uncharged ones for the carbon aerogels R/C 50 and 200; however, this plots do not present remarkable peaks pointing out to exothermal process ended between the temperature interval of work probably due to the carbonaceous matrix stability obtained during the pyrolysis process carried out before the thermal analysis.

Conclusions

Thermal analysis of carbon aerogels (TGA/DSC) don't show great differences for the results obtained by doing variations in the molar ratio R/C respect to the thermal stability of the samples; however some differences can be observed in the thermal analysis due to the impregnation of the carbon aerogels R/C=50 y 200 with cobalt, doing smaller the thermal resistance of the material accompanied with a more exothermal process to.

Acknowledgments. The authors want to express their acknowledgments to the research division of the Universidad Nacional de Colombia, research project code DBI.201010013227

References

1. Pierre, A.C. and G.M. Pajonk, *Chemistry of Aerogels and Their Applications*. Chemical Reviews, 2002. **102**(11): p. 4243-4266.
2. Pekala, R.W. and J. Fricke, *Organic Aerogels*, in *Encyclopedia of Materials: Science and Technology*, K.H.J. Buschow, et al., Editors. 2001, Elsevier: Oxford. p. 6502-6506.
3. Fairén-Jiménez, D., F. Carrasco-Marín, and C. Moreno-Castilla, *Porosity and surface area of monolithic carbon aerogels prepared using alkaline carbonates and organic acids as polymerization catalysts*. Carbon, 2006. **44**(11): p. 2301-2307.
4. Pekala, R.W., *Organic aerogels from the polycondensation of resorcinol with formaldehyde*. Journal of Materials Science, 1989: p. 3221-3227.
5. Moreno-Castilla, C. and F.J. Maldonado-Hódar, *Carbon aerogels for catalysis applications: An overview*. Carbon, 2005. **43**(3): p. 455-465.
6. Horikawa, T., J. Hayashi, and K. Muroyama, *Controllability of pore characteristics of resorcinol-formaldehyde carbon aerogel*. Carbon, 2004. **42**(8-9): p. 1625-1633.