

CARBON AEROGELS WITH METALLIC NANOSIZED PARTICLES AS CATALYSTS IN ORGANIC REACTIONS

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Aerogels form a new class of low density highly porous solids that show a wide range of applications. Until now, we have focused on using silica as a substrate for nanoparticles, but it is well known the important effect of the substrate in catalysis.¹ Carbon aerogels are promising candidates to be used as electrode materials in supercapacitors, rechargeable batteries, adsorbent materials and advanced catalysts supports in heterogeneous catalysis. Recently, considerable attention has been given to the possibility of nanocomposing metal species into carbon aerogels to expand their applications. Metal nanocomposed carbon aerogels were prepared through sol-gel polymerization of formaldehyde with the potassium salt of 2,4-dihydroxybenzoic acid, immersion of the obtained wet gel into several metal salts in aqueous solutions, dried with supercritical CO₂ and pyrolyzed at 1050 °C under N₂ atmosphere.² We have prepared Pd, Ni and Eu-nanocomposed carbon aerogels from Pd(OAc)₂, Ni(NO₃)₂·6H₂O and Ni(OAc)₂·4H₂O, and Eu(OTf)₃, respectively. No reduction step is required to obtain metallic particles of Ni(0) and Pd(0).

The obtained materials were characterized by nitrogen adsorption, transmission electron microscopy, X-ray diffraction and elemental analysis. The carbon aerogels with metallic nanosized particles exhibit high surface area, pore diameter in the micro- and mesopore region and electrical conductivity. The metal particles are formed by reduction of the M²⁺ ions during pyrolysis of the organic aerogels. In the case of Ni-nanocomposed carbon aerogels, TEM showed the presence of nanoparticles and the corresponding X-ray diffraction pattern was characteristic of metallic fcc-Ni; only a small amount of the fcc-NiO phase was detected with the materials obtained from Ni(NO₃)₂·6H₂O, and only traces of the fcc-NiO phase were present in the materials obtained from Ni(OAc)₂·4H₂O.

On the other hand, the micrograph of the precarbonized Pd-organic aerogel and the Pd-gel, showed particles with diameters between 6-10 nm and 3-5 nm, respectively. Using electron diffraction, we observed diffraction rings in the Pd-organic aerogel which can be ascribed to the (111), (200), (220), and (311) Pd spacings, and in the Pd-gel it can only be seen the rings corresponding to the (111) and (200) planes, because of the small dimension of the crystal nanoparticles (Fig. 1 and Fig. 2).³

The resulting Eu-doped material contained 12.0 wt%, 14 wt% and 27 wt% of Eu, for the Eu-gel, Eu-organic and Eu-carbon, respectively. In the three types of material, nanoparticles can be distinguished from the amorphous matrix in the TEM images. Powder X-ray presented rather amorphous patterns for the Eu-gel and Eu-organic samples indicating poor crystallinity of the particles. In contrast sharp peaks are evidenced for the Eu-carbon sample. During the process of the gel conversion into organic aerogel and finally into carbon aerogel a phase evolution took place, converting Eu(OTf)₃ into a mixture of europium oxides, sulfides and fluorides.⁴

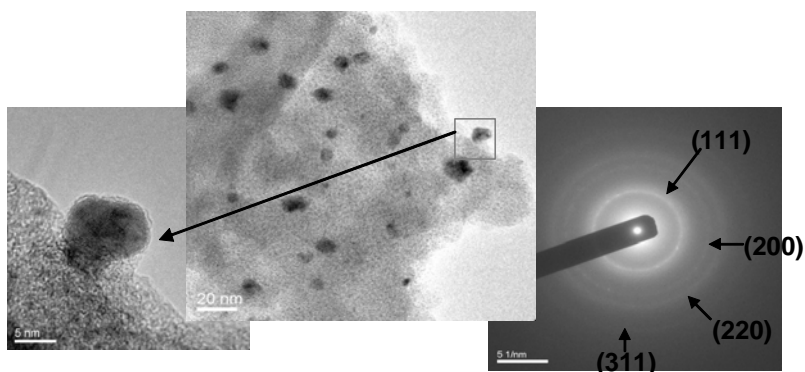


Figure 1. Pd-organic aerogel (TEM and EDX).

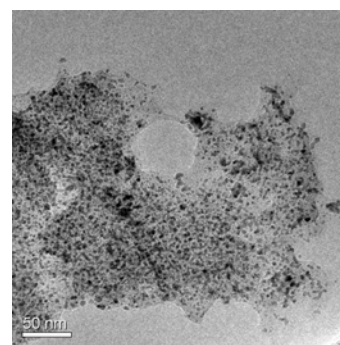


Figure 2. Pd-gel (TEM).

We are mainly interested in the application of heterogeneous catalysts in organic reactions. We have tested selected Pd(0)-doped materials as catalysts in the Mizoroki-Heck coupling reactions,³ hydrocarbonylation of aryl iodides and Sonogashira cross-couplings,⁵ giving rise to good activities. The catalysts could be easily recovered and reused several times. Ni(0)-doped materials were inert as catalysts.

In *Michael* additions,⁴ we have tested Eu-doped materials. The Eu-gels were active as catalysts and recoverable. A slight decrease in activity was observed with the Eu-organic aerogel and the Eu-carbon aerogel did not catalyze this type of reaction. It is known that *Michael* additions are catalyzed by *Lewis* acids as rare-earth metal chlorides and triflates, whereas the corresponding metal oxides are inert.

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Acknowledgements

This research was financed by “Ministerio de Educación y Ciencia” (Projects CTQ2005-04968-C02-01, MAT2006-13572-C02-01 and Consolider Ingenio 2010 (CSD2007-00006)) and “Generalitat de Catalunya” (Projects SGR 2005-00452 and SGR 2005-00305). L.M. wants to thank the MEC for a predoctoral scholarship and L.L-O. also wants to thank the European Marie Curie project “Green chemistry in supercritical fluids” (MRTN-CT2004504005). MATGAS is also acknowledged for the supercritical facilities and Raul Solanas for his technical assistance.

