Carbon aerogel supported platinum catalysts for selective hydrogenation of cinnamaldehyde

B.F. Machado[1], S. Morales-Torres[2], H.T. Gomes[1,3], A.F. Pérez-Cadenas[2], F.J. Maldonado-Hódar[2], F. Carrasco-Marín[2], J.L. Figueiredo[1], J.L. Faria[1*]

[1] Laboratório de Catálise e Materiais (LCM), Laboratório Associado LSRE/LCM, Departamento de Engenharia Química, Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias s/n, 4200-465 Porto, Portugal

[2] Grupo de Investigación en Materiales de Carbón, Facultad de Ciencias, Universidad de Granada, Avda. Fuentenueva s/n, 18071 Granada, España

[3] Departamento de Tecnologia Química e Biológica, Escola Superior de Tecnologia e de Gestão, Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-857 Bragança, Portugal

Abstract

This paper describes the preparation and characterization of 1% wt. Pt catalysts supported in carbon aerogels for the application in the liquid-phase selective hydrogenation of cinnamaldehyde. Carbon aerogel supports with different textures were activated with hydrogen peroxide and ammonium peroxydisulfate leading to large amounts of surface groups but keeping unchanged their textural properties. After introducing Pt, the surface chemistry and morphology of the catalysts was characterized by analytical techniques like SEM, TPD, N_2 adsorption isotherms, mercury porosimetry and H_2 chemisorption. Catalysts prepared with activated aerogels exhibited good selectivity towards the desired product, cinnamyl alcohol. A high temperature post-treatment of the catalysts failed to enhance their selectivity, mainly leading to hydrocinnamaldehyde production.

1. Introduction

The synthesis of carbon aerogels was first reported by Pekala (1990). Depending on the solvent removal step, these materials are referred to as: (i) aerogels if supercritical CO_2 is used; (ii) xerogels when the removal takes place under ambient temperature and pressure conditions; and (iii) cryogels: if a freeze-drying method is used. Carbon aerogels are one of the most promising new carbon forms for many applications such as adsorbents, catalysts or capacitors (Moreno-Castilla, 2005; Maldonado-Hodar, 2007). Their potential is based on their unique properties: purity, homogeneity and above all, controllable porosity. Between the different precursors and methods developed during the last years, the sol-gel polymerization of resorcinol (R) and formaldehyde (F) is the most common. The porous texture of carbon aerogels, and consequently their applications, strongly depends on several experimental conditions. The most important is the polymerization step, since it defines the structure and consequently the porous texture of the organic aerogels.

Polymer-based (Moreno-Castilla, 2005; Samant, 2004) and other carbon materials like nanofibers, nanotubes or fullerenes (Serp, 2003) are an important class of materials to produce noble metal supported catalysts. This type of catalysts is extremely useful in the liquid phase heterogeneous selective hydrogenation of unsaturated aldehydes to the corresponding unsaturated alcohols. This is a key process for the production of important intermediates in the preparation of fine chemicals for fragrance, pharmaceutical and

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[*]Corresponding author. Tel + 351-225 081 645. E-mail: jlfaria@fe.up.pt

agrochemical industries. Unfortunately, there are some constrictions, both thermodynamic and kinetic, that limit the selectivity towards the unsaturated alcohol formation. In spite of these drawbacks, the selectivity to unsaturated aldehydes using heterogeneous catalysts can be improved by careful design of the catalysts, controlling the type and surface chemistry of the support, the nature of the active metal, and the addition of a promoter, among others.

In this work, we prepared several carbon aerogel supported Pt catalysts, using materials with different textures and surface chemistries, seeking to establish appropriate structure/activity relationships, which are useful for smart catalyst design.

2. Experimental

2.1 Catalyst preparation

Organic aerogels were synthesized by polymerization of resorcinol with formaldehyde in aqueous solution, according to the methodology developed originally by Pekala et al. (1990) using alkali carbonates (M_2CO_3; M = Li or Cs) as polymerization catalysts. This process yields organic RF-aerogels which were carbonized in N_2 flow at 900ºC. Carbon aerogels will be here referred as Li900 and Cs900 indicating the metal alkali and the carbonization temperature used in their synthesis.

Samples of Li900 carbon aerogel were further oxidized (1 g carbon/10 mL of solution) with concentrated hydrogen peroxide (HP, H_2O_2, 9.8 M) and with a saturated solution of ammonium peroxydisulfate (AP, $(NH)_4S_2O_8$) in sulfuric acid (H_2SO_4, 1M) during 48 h at ambient temperature (Moreno-Castilla, 1995). After oxidation, the samples were washed with distilled water and dried at 120ºC in an oven during 24 h. The samples oxidized with H_2O_2 and with $(NH)_4S_2O_8$ will be here referred as Li900H and Li900S, respectively.

Supported Pt (1 wt. %, $Pt(NH_3)_4(NO_3)_2$) catalysts were prepared by incipient wetness impregnation on the above described materials. Prior to reaction, the resulting catalysts (Li900Pt, Li900HPt, Li900SPt and Cs900Pt) were treated in N_2 for 4 hr and reduced in H_2 for 2 hr. A post-reduction treatment (2 hr, N_2) was performed at 700ºC to remove part of the surface groups (Li900Pt700, Li900HPt700, Li900SPt700 and Cs900Pt700).

2.2 Catalyst characterization

The surface morphology of the aerogels was studied by SEM (LEO, model Gemini-1530, equipped with EDX microanalysis). Textural characterization was carried out using mercury porosimetry (Quantachrome Autoscan 60) and N_2 adsorption at -196ºC (Quantachrome autosorb-1). Mercury porosimetry allowed the determination of pore volume (V_{MES}: 3.5 nm < dpore < 50 nm and V_{MAC}: dpore > 50 nm) and the external surface area (S_{EXT}: dpore > 3.7 nm). The BET equation (Brunauer, 1938) and Dubinin-Raduskevich and Stoeckli et al. (2002) relations were used for analysis of N_2 adsorption isotherms.

The surface chemistry of the carbon aerogels was characterized by temperature-programmed desorption (TPD). TPD experiments were carried out by heating the samples to 1000ºC in He flow (60 cm^3 min^{-1}) at a heating rate of 50ºC min^{-1}. The amount of evolved gases was recorded as a function of temperature using a quadrupole mass spectrometer (Balzers, model Thermocube), as described elsewhere (Alvarez-Merino, 2000). The oxygen content was calculated from the amounts of CO and CO_2 released during the TPD experiments.

Pt dispersion (D_{Pt}) and average particle size (d_{Pt}) were obtained by H_2 chemisorption measurements performed at 40 ºC. Assuming the formation of spherical particles and a H:Pt = 1:1 stoichiometry it was possible to determine the Pt particle size (d_{Pt} = 1.08/D_{Pt} (nm)). H_2 chemisorption isotherms were measured in conventional volumetric equipment made of Pyrex glass, free of mercury and grease, which reached a dynamic vacuum better than 10^{-6}

mbar at the sample location. Equilibrium pressure was measured with a Baratron transducer from MKS.

2.3 Catalytic hydrogenation

Hydrogenation of cinnamaldehyde was carried out in a 100 mL well-stirred stainless steel high pressure reactor at 90ºC and 10 bar (total pressure). The reaction mixture contained heptane (solvent), cinnamaldehyde, decane (internal standard for gas chromatography) and the catalyst. As the reaction proceeded samples were withdrawn to monitor product distribution. The analysis was performed in a DANI GC-1000 Gas Chromatograph, equipped with a WCOT Fused Silica column (length 30 m, 0.32 mm i.d., film thickness 1 μm). The results of the reaction runs were analyzed in terms of cinnamaldehyde conversion, turn-over frequency and product selectivity.

3. Results and discussion

3.1 Support characterization

The selection of the polymerization catalyst had a great influence over the porous texture of the aerogel: smaller cations like Li were found to produce materials with significant mesoporous volume, whereas larger Cs cations led to macroporous materials (Figure 1). The higher BET surface area (increase of about 150 m^2 g^{-1}) of the Li900 materials relatively to the macroporous material (Table 1) is explained in terms of smaller particle size.

The aerogel surface oxidation treatments resulted in the formation of different oxygen-containing groups like carboxylic acids, lactones and phenols. The introduction of these groups was achieved without any significant changes of the initial textural properties of the aerogels (a decrease of only *ca.* 4% was observed in the S_{BET} values). On the other hand, the surface acidity of the material was seriously affected by the oxidation procedure. The acidic character of the samples, determined by pH_{PZC} measurements, was found to increase in the following order: Li900S (3) > Li900H (5) > Li900 ≈ Cs900 (10). In addition, the amount of O_2 present at the surface was found to increase with decreasing pH_{PZC}, i.e.: Li900S (10 wt.%) > Li900H (3% wt.%) > Li900 ≈ Cs900 (1 wt.%).

Table 1. Textural properties of the carbon aerogels.

Support	S_{BET} (m^2 g^{-1})	V_{MIC}† (cm^3·g^{-1})	L_0† (nm)	S_{ext}* (m^2·g^{-1})	V_{MES}* (cm^3·g^{-1})	V_{MAC}* (cm^3·g^{-1})
Li900	902	0.37	1.0	191	1.06	0.00
Li900H	863	0.35	1.1	-	-	-
Li900S	861	0.35	1.1	-	-	-
Cs900	758	0.30	0.7	59	0.07	1.20

†Dubinin-Radushkevich and Stoecki equations applied to N_2 adsorption data.
*Determined by mercury porosimetry.
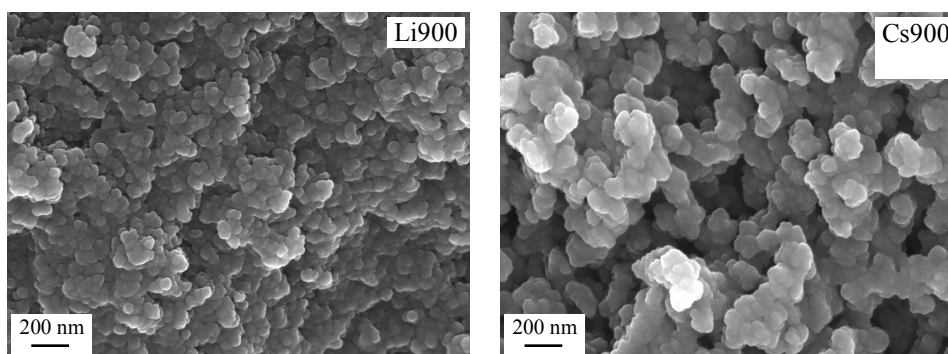
Figure 1. SEM images of Li900 and Cs900 aerogels.

3.2 Metal-phase characterization

Platinum dispersions and particle sizes of the carbon aerogel supported catalysts are given in Table 2. Excellent Pt dispersions over the untreated aerogels (Li900Pt and Cs900Pt) were observed, but somewhat lower values were detected when using the oxidized supports (Li900HPt and Li900SPt). There are two main factors that can affect the metal dispersion over a support: (i) the available surface area and (ii) the interaction between the surface and the precursor solution. The textural properties of the supports were not significantly changed by the oxidation treatments, as already showed, but the presence of oxygenated surface groups increased the hydrophilic character of the surface. Taking into consideration that the surface is negatively charged (pH_{PZC} < pH precursor solution) and the cationic nature of the precursor ($[Pt(NH_3)_4]^{+2}$) an improved metal dispersion was expected when using the oxidized supports, in comparison to the catalysts prepared using the untreated ones. However this is not the case, because the oxygen surface groups act as anchoring sites, which can retain the Pt-precursor molecules at the entrance of the pores preventing the Pt diffusion through the porous structure. On the other hand, during the reduction treatment, the less stable oxygen surface complexes will be removed, which can promote the mobility of the platinum particles favoring their agglomeration (Román-Martínez, 1994).

When a post-reduction treatment is carried out in N_2 at 700 ºC, the experimental conditions are severe enough to induce some sintering of the Pt particles. This seems to be related to the surface chemistry of the materials as the Pt particle size supported in untreated aerogels increases *ca.* 2.3 times while for the activated supports an increase of only 1.5-1.6 times is observed. Besides a sintering effect, the treatment at 700ºC is also able to purge the surface of many of the oxygenated surface groups.

Table 2. Pt dispersion and particle size for the aerogel supported catalysts.

Catalyst	D_{Pt} (%)	d_{Pt} (nm)
Li900Pt	74.1	1.5
Li900Pt700	31.3	3.4
Li900HPt	46.1	2.3
Li900HPt700	30.5	3.5
Li900SPt	44.4	2.4
Li900SPt700	28.7	3.8
Cs900Pt	87.3	1.2
Cs900Pt700	40.3	2.7

3.3 Hydrogenation of cinnamaldehyde

Some of the possible pathways for the selective hydrogenation of cinnamaldehyde (CAL) in a non alcohol solvent are shown in Figure 2. The thermodynamically preferred path goes through the hydrogenation of the C=C bond yielding the saturated aldehyde (hydrocinnamaldehyde, HCAL). Selective hydrogenation of the C=O bond gives the unsaturated alcohol (cinnamyl alcohol, COL). Both COL and HCAL can be further hydrogenated to produce the fully saturated alcohol (hydrocinnamyl alcohol, HCOL). In some experiments, a number of side-products involving the loss of the hydroxyl group (β-methylstyrene (MS) and 1-propylbenzene (PB)) were also detected in different amounts, indicating a strong adsorption over the metal sites and a possible poisoning effect.
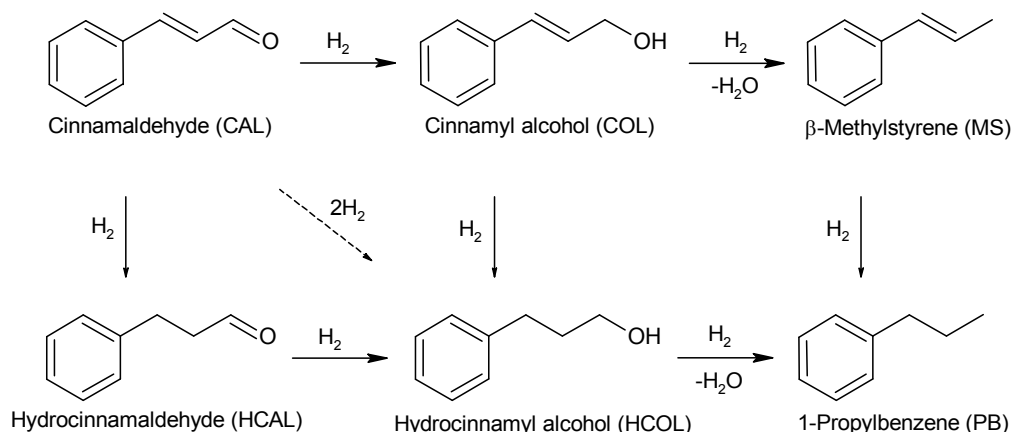
Figure 2. Reaction scheme for the selective hydrogenation of cinnamaldehyde.

The reaction results obtained at 90ºC and 10 bar (total pressure) are gathered in Table 3. Taking into account the average pore size diameter in both aerogels (12 and 48 nm) and the cinnamaldehyde molecule size (< 1 nm) we could expect the absence of internal mass transfer limitations during the reaction. This assumption was confirmed by the higher activity (TOF) exhibited by Li900Pt regarding the macroporous Cs900Pt catalyst.

Table 3. Initial turn over frequency and selectivities towards COL, HCAL and HCOL, measured at 50% conversion of CAL.

Catalyst	TOF (s^{-1})	S_{COL} (%)	S_{HCAL} (%)	S_{HCOL} (%)
Li900Pt	1.6	11	54	20
Li900Pt700	3.4	12	54	25
Li900HPt	1.6	53	18	20
Li900HPt700	3.5	21	41	28
Li900SPt	2.3	36	23	25
Li900SPt700	4.4	21	44	27
Cs900Pt	0.9	24	34	35
Cs900Pt700	2.8	12	54	19

Oxidation of the carbon materials had a marked effect over the selectivity towards cinnamyl alcohol. Selectivity increased by a factor of 4.8 for Li900HPt (53% at 50% conversion of cinnamaldehyde) and 3.3 for Li900SPt (36%) compared with the catalyst prepared using the non-treated support (11%).

In previous studies we used a high temperature treatment to enhance selectivity of the catalysts (Solhy, 2008). In the present study a thermal treatment at 700ºC in N_2 increased the TOF up to a factor of 3 and shifted selectivity to the C=C bond. The selectivity towards the carbonyl group appears to be related to the surface chemistry of the material, as a more acidic surface favors the interaction with the carbonyl group and a more basic surface favors the reduction of the olefinic bond.

4. Conclusions

Macro or mesoporous carbon aerogels were obtained depending on the type of polymerization catalyst used. Oxidation treatment with H_2O_2 and $(NH_4)_2S_2O_8$ allowed the porous structure to remain relatively unchanged while introducing significant amounts of oxygenated groups. The acidic character of most groups led to a strong decrease of the pH_{PZC} of the support surface. The Pt dispersion over the aerogels was strongly influenced by these chemical modifications, decreasing in all cases after oxidation treatments. The

increased acidity of the Li900HPt and Li900SPt supports leads to a higher selectivity towards cinnamyl alcohol when compared with that obtained with Li900Pt. A thermal treatment at 700ºC removed most of the support surface groups and shifted the selectivity back to the hydrogenation of the C=C bond.

Acknowledgements

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