Catalysis Communications 58 (2015) 64–69

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short Communication

Development of carbon xerogels as alternative Pt-supports for the selective hydrogenation of citral

Esther Bailón-García, Francisco Carrasco-Marín, Agustín F. Pérez-Cadenas, Francisco J. Maldonado-Hódar *

Group of Research in Carbon Materials, Dpt. of Inorganic Chemistry, Faculty of Sciences, University of Granada, Avda. Fuentenueva s/n. 18071, Granada, Spain

ARTICLE INFO

Article history:
Received 5 May 2014
Received in revised form 28 August 2014
Accepted 1 September 2014
Available online 15 September 2014

Keywords:
Citral hydrogenation
Selective catalysts
Pt-catalysts
Activated carbons
Carbon xerogels

ABSTRACT

The role of activated carbons and carbon xerogels as Pt-supports for the selective citral hydrogenation is compared. The influence of porosity and inorganic matter impurities in activated carbons determines the performance of their derivative catalysts. The presence of Pt-particles inside mesopores and acid mineral matter favors secondary reactions decreasing the unsaturated alcohols (UA) yield. Highly active and selective monometallic Pt-catalysts were obtained using pure carbon xerogels structured in microspheres as support.

1. Introduction

The selective hydrogenation of carbonyl groups of α,β-unsaturated aldehydes is a challenging process, either from a scientific and economic point of view [1]. Among them, citral is a cheap raw material obtained from different natural sources being their derivative unsaturated-alcohols (UA), nerol and geraniol, highly demanded by pharmaceutical and chemical industries. The design and development of catalysts for the selective citral hydrogenation are influenced by several factors determining the catalysts performance: the active metal phase and support nature [2], metal particle size [3], bimetallic catalysts [1,4] and factors related with the preparation method and metal–support interactions [5,6]. All these factors and the evolution of the designed catalysts were recently reviewed [7].

Carbon materials are very interesting catalyst supports due to their ability to fit their chemical and textural properties. Doing a bibliography review [8], it can be seen that three types of carbon materials have been used in the selective hydrogenation of citral: activated carbons [9,10], graphite [10,11], carbon nanotubes (CNT) or nanofibers (CNF) [11–13], being the best selectivity achieved around 65% at 30% conversion obtained with monometallic Pt- supported on electron-donor graphite [14].

It is noteworthy that no reference has been found in which carbon aerogels or xerogels were used as support, in spite of the benefits that these kinds of materials show in very different catalyzed reactions [15]. In this manuscript we have prepared two nanostructured carbon xerogels and their performance as Pt-support was compared to activated carbons on the basis of the different textural properties and purity.

2. Experimental

Two carbon xerogels (A1, A8) were prepared by polycondensation of resorcinol (R) with formaldehyde (F) in aqueous (W) media, using Cs_2CO_3 as polymerization catalyst (C). Briefly, the appropriate amounts of resorcinol (24.7 g) and Cs_2CO_3 (0.72 or 0.09 g) were dissolved in deionized water (670 mL) using a three-neck glass reactor (2 L) provided of reflux, controlled temperature and stirring. The temperature of this solution was fitted to 85 °C under stirring (250 rpm) and then, 36.3 g of formaldehyde solution (Sigma, 37 wt.%) was added dropwise. Thus, the composition of the mixture (molar ratio) was R/F = 1/2, R/W = 3/500 for both samples and R/C was 100 and 800, for A1 and A8 respectively. The gel formed was aged at 85 °C for 24 h, filtered and placed in acetone for 3 days, in order to reduce the porosity collapse during the subsequent drying process by microwave [16]. The gel was dried by microwave heating using a Saivod MS-287 W microwave oven under nitrogen atmosphere in periods of 1 min at 384 W until constant weight. Pyrolysis of organic xerogels was carried out at 900 °C for 2 h in N_2 flow (300 cm^3 min^{-1}). An activated carbon (EG) was also prepared in our laboratories by chemical activation of olive stones with KOH following the experimental procedure previously published [17]. Olive stones were milled and sieved to 1.0–2.0 mm, treated with sulphuric acid (1 N) to remove the rest of pulp and washed until all sulfates had been removed. An initial carbonization was carried out by heating at 10 °C min^{-1} to 400 °C and a soak time of 2 h under a

* Corresponding author. Tel.: +34 958240444.
E-mail address: fjmaldon@ugr.es (F.J. Maldonado-Hódar).

http://dx.doi.org/10.1016/j.catcom.2014.09.001
1566-7367/

Table 1
Textural characteristics of carbon supports and derivatives Pt-catalysts.

Sample	N_2-adsorption					CO_2-adsorption			Mercury porosimetry	
	S_{BET}	W_0	L_0	V_{meso}	$V_{0.95}$	W_0	S_{mic}	L_0	V_2	V_3
	$m^2\ g^{-1}$	$cm^3\ g^{-1}$	nm	$cm^3\ g^{-1}$	$cm^3\ g^{-1}$	$cm^3\ g^{-1}$	$m^2\ g^{-1}$	nm	$cm^3\ g^{-1}$	$cm^3\ g^{-1}$
S	1284	0.53	1.57	0.12	0.66	0.39	888	0.87	0.014	0.481
SPt3-9	535	0.22	1.69	0.08	0.29	0.11	179	1.28	–	–
EG	2219	1.05	1.59	1.22	2.17	0.38	704	1.09	1.141	7.732
EGPt3-9	2065	0.843	1.37	1.53	2.16	0.422	696	1.21	–	–
A1	526	0.20	0.86	0.24	0.40	0.19	611	0.62	0.038	0.834
A1Pt3-8	503	0.20	0.87	0.12	0.29	0.21	781	0.55	–	–
A8	614	0.25	0.78	0.00	0.31	0.29	952	0.60	0.002	3.914
A8Pt3-8	531	0.21	0.62	0.00	0.22	0.28	960	0.58	–	–

SBET = BET surface area, W_0 = micropore volume, L_0 = micropore wide, V_{meso} = BJH mesopore volume, $V_{0.95}$ = total pore volume, S_{mic} = microporous surface, and V_2, V_3 = meso and macropore volume.

nitrogen flow of 300 $cm^3\ min^{-1}$ using a tubular furnace (from Heraeus). Chemical activation was carried out using a mixture of this carbonized material and KOH in a 1:7 mass ratio. This mixture was treated under nitrogen flow for two hours at 350 °C followed by three hours at 850 °C. Cooling to ambient temperature was performed by keeping the sample under nitrogen atmosphere. Additionally, a commercial activated carbon from Norit (Sorbo, S) was also used as reference material. Platinum-catalysts were prepared by impregnation of supports at 3 wt.% Pt-loading, using an aqueous solution of $[Pt(NH_3)_6]Cl_2$. Catalysts were pre-treated at 400 °C for 6 h in helium flow and referred indicating support, Pt-loading and Pt-particle size determined by H_2-chemisorption. For example, A8Pt3-8 was prepared with 3% of Pt using A8 carbon xerogel as support and after pre-treatment a Pt-particle size of 8 nm is obtained.

The sample morphology was studied by scanning electron microscopy (SEM) using a LEO (Carl Zeiss) GEMINI-1530 microscope. Textural characterization was carried out by N_2 and CO_2 adsorption at −196 °C and 0 °C, respectively, using a Quantachrome Autosorb-1 equipment. The BET and Dubinin–Radushkevich equations were applied to determine the apparent surface area (S_{BET}) and the micropore volume (W_0), the mean micropore width (L_0) and the microporous surface (S_{mic}), respectively. The total pore volume was considered as the volume of N_2-adsorbed at $P/P_0 = 0.95$ and the BJH method was used to calculate the mesopore volume of the samples (V_{meso}) [18–21]. The macropore volume (V_3) and a fraction (pores larger than 6.5 nm) of the mesopore volume (V_2) of the samples were determined by mercury porosimetry.

The chemical characterization of supports and catalysts was carried out by elemental analysis, XPS, DRX and thermal programmed desorption (TPD). Determination of the pH_{zpc} values was performed according to the method proposed by Leon et al. [22]. Pt dispersion (D) and mean particle size (d) were obtained by H_2-chemisorption and the analysis of images from high-resolution transmission electron microscopy (HRTEM), obtained using a Phillips CM-20 microscope.

The citral hydrogenation was carried out in 100 mL heptane solution at a constant hydrogen pressure of 8.3 bar and 90 °C using a Parr reactor model 5500. The experimental conditions: citral concentration, catalyst weight and stirring speed were previously optimized in order to avoid mass transfer limitations (results not showed) and fixed in 0.05 M, 500 mg and 1500 rpm, respectively. A small volume of sample (1 mL) was periodically withdrawn and analyzed by chromatography using a Bruker 430-GC equipped with a FID detector and a Varian GC Capillary Column CP7485 (25 m × 0.32 mm × 0.45 μm). Both citral and any possible product were previously calibrated.

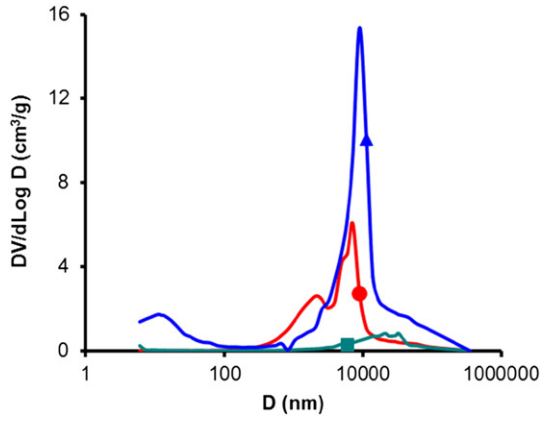

Fig. 1. Pore size distribution obtained by mercury porosimetry of supports A1 (■), A8 (●) and EG (▲).

3. Results and discussions

The textural characteristics of supports and their respective Pt-catalysts are summarized in Table 1. Only the support A8 is an exclusively microporous material; the rest of supports present a certain mesopore volume that increases in the sense S < A1 < EG. When V_2 and V_{meso} values (Table 1) were compared, it is observed that the large part of mesopores are smaller than 6.5 nm for both S and A1 support, while both parameters are quite similar in the case of EG, indicating a very opened mesoporosity as shown by mercury porosimetry (Fig. 1). In this case, large mesopores of around 10 nm in diameter, together with a wide distribution of macropores, were observed. Carbon xerogels, but specifically A8, present a narrower microporosity (L_0 values) than activated carbons. The A8 microporous carbon xerogel also exhibits a significant macropore volume (Fig. 1), probably located between primary particles [9,10]. All pretreated catalysts present smaller pore volumes and surface areas than their corresponding supports, denoting a certain pore blockage by the deposition of Pt-particles.

The chemical characteristics of carbon supports are summarized in Table 2. All samples behave as basic materials due to the very low oxygen contents, but the pH_{pzc} values increases from 7.3 to 11.0. In general, this parameter decreases with increasing the oxygen content, because in this sense the formation of acid oxygenated surface groups (OSG) is favored evolving as CO_2 (carboxylic acid, anhydrides, lactones, etc.) during TPD experiments, while those OSG that evolve as CO

Table 2
Chemical characteristics of carbon supports.

Sample	CO	CO_2	O_2	CO/CO_2	pHpzc	Elemental analysis		
	(μmol g^{-1})		%			C(%)	O(%)	H(%)
S	1080	447	3.2	2.4	11.0	89.7	9.8	0.3
EG	1156	148	2.3	7.8	7.3	–	–	–
A1	388	230	1.4	1.7	10.3	94.5	5.0	0.5
A8	303	81	0.8	3.7	9.4	95.1	4.3	0.5

CO and CO_2 evolved during TPD runs.