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Applied Catalysis A: General



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

Preparation of carbon aerogel supported platinum catalysts for the selective hydrogenation of cinnamaldehyde

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ARTICLE INFO

Article history: Received 4 November 2011 Received in revised form 27 February 2012 Accepted 6 March 2012 Available online 15 March 2012

Keywords: Carbon aerogel Surface chemistry Platinum Selective hydrogenation Cinnamaldehyde

ABSTRACT

The selective hydrogenation of cinnamaldehyde is investigated using platinum catalysts supported on carbon aerogels with different textural and chemical properties. Despite the large amount of oxygenated surface groups introduced after the oxidation step, the original porosity of the carbon aerogels is maintained. The oxidation treatments performed on the materials are found to strongly influence the surface chemistry which in turn affects the Pt dispersion, yielding larger metal particles after the chemical modifications and the H₂ pre-treatment. The presence of mesopores and the increase of the acidic character in the carbon aerogels lead to a higher catalytic activity and selectivity towards cinnamyl alcohol when compared with that obtained for the untreated materials. A thermal treatment at 973 K is found to favor the hydrogenation of the olefinic bond when using carbon aerogels, due to the remaining oxygenated surface groups, at variance with other previously reported carbon supports (xerogels and nanotubes).

1. Introduction

Following the first synthesis of carbon aerogels reported by Pekala [1] other types of carbon gels have been reported based on the use of different solvent removal steps in the synthetic route [2]: (i) aerogels, when supercritical CO_2 is used, (ii) xerogels, when the removal takes place under ambient temperature and pressure conditions, and (iii) cryogels, in the case of using a freeze-drying method. Carbon aerogels usually have surface areas between 400 and 1000 m² g⁻¹ and are promising materials for applications such as adsorbents, catalysts or capacitors [3–8]. Their potential is based on their unique properties: purity, homogeneity and above all, controllable porosity. Different precursors and methods have been developed over the years to produce highly porous carbon aerogels. The porous texture of carbon aerogels, and consequently their applications, depend strongly on several experimental conditions. The most important is the polymerization step, since it defines the

** Corresponding author at: Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Granada, Campus Fuentenueva s/n, 18071 Granada, Spain. Tel.: +34 958 243 235: fax: +34 958 248 526. structure and consequently the porous texture of the organic aerogels. In this context, meso- or macroporous carbon aerogels can be developed by simply modifying the polymerization catalyst, while maintaining constant the other synthesis parameters [9].

Because the support plays an important role in catalyst design, in order to optimize the dichotomy between metal and support, the use of a material whose properties can be finely tuned is highly desirable. Furthermore, due to the importance of the oxygenated surface groups in the design of efficient catalysts it is advantageous to have the possibility of easily modifying the surface chemistry of the support materials to incorporate those groups [10,11]. Thus, polymer-based carbon materials are an important category of materials suitable to produce noble metal supported catalysts [5]. This type of catalyst is extremely useful in heterogeneously catalyzed reactions, namely for fuel cell applications [12,13] and selective hydrogenation of α , β -unsaturated aldehydes (acrolein, crotonaldehyde, cinnamaldehyde, etc.) [14-17]. The latter is a key process for the production of important intermediates in the preparation of fine chemicals for fragrance, pharmaceutical and agrochemical industries [18,19]. Unfortunately, there are some thermodynamic and kinetic constrictions that limit the selectivity towards the unsaturated alcohol formation [20], commonly the most valuable intermediate compound. In spite of these drawbacks, the selectivity to unsaturated alcohols using heterogeneous catalysts can be improved by careful design of the catalyst. Several

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⁰⁹²⁶⁻⁸⁶⁰X/\$ - see front matter © 2012 Elsevier B.V. All rights reserved. doi:10.1016/j.apcata.2012.03.016