Synthesis of Pd-Al/biomorphic carbon catalysts using cellulose as carbon precursor

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ABSTRACT

This work presents the results obtained with novel Pd and Pd-Al catalysts supported on carbon, which have been prepared using a biomorphic mineralization technique. The catalyst synthesis procedure includes a stage of thermal decomposition under reductive atmosphere of cellulose previously impregnated with the metallic precursors. We have studied the influence of the temperature and time of decomposition, and of the Al precursor addition, on the textural and catalytic properties. The characterisation results indicate that the preparation method used leads to the formation of carbonaceous supports with a high microporosity (up to 97% micropore volume) and values of the BET surface up to 470 m^2/g while maintaining the original external structure. The use of low temperatures (ca. 600 °C) during the decomposition step allows the preparation of highly dispersed catalysts with narrow Pd particle size distributions. However, the thermal decomposition at elevated temperatures (ca. 800 °C) increases the Pd particle size due to the sintering of the metallic phase. This phenomenon is augmented with the decomposition time and is not affected by the presence of Al. Consequently, the catalytic activity of these materials in cyclohexene hydrogenation is strongly affected by the operational conditions used during the thermal decomposition step. Unexpectedly, the more sintered catalysts, i.e. those prepared at 800 °C, show the highest activity. According to the characterization results, this fact can be explained considering that the smaller Pd particles obtained after preparation at e.g. 600 °C are quite inactive because they are confined in the internal structure of the micropores of the support and/or embedded inside the carbon matrix. In contrast, after decomposition at 800 °C, the larger Pd particles formed are placed at the external surface of the catalyst, being accessible to the reactants. In addition, for the specific conditions under which the Pd is accessible, the presence of Al favours the cyclohexene conversion due to the enhancement of the adsorption on the Pd surface as a consequence of a charge transfer phenomenon. These results can serve as a guideline for the preparation of these catalysts based on raw lignocellulosic materials in order to maximize their catalytic performance.

1. Introduction

Biomorphic carbon materials produced by controlled carbonization of lignocellulosic biomass wastes, or of various other biological resources, are promising materials for many practical applications. In most cases, biomorphic carbon materials have been investigated as electrodes in energy accumulator systems, due to their large and electrochemically stable surface and high electrical conductivity. In addition, their interconnected porous structure with controllable pore sizes make these materials very suitable for the transport of electrolyte ions and reacting molecules [1,2]. Because of these properties, this type of carbon is also widely used as filtration membranes and as adsorbents for air and water purification. Other fields of research include electrochemical hydrogen storage [3], or the development of thermal insulating materials [4]. Of course, the above-mentioned properties related to the chemical stability and controllable porous structure make biomorphic carbons excellent potential supports for catalysts in liquid or gas phase reactions [5–7].

Usually, this type of carbon is prepared by mineralization of the raw material. This technology allows the synthesis of inorganic materials using biological structures as templates [8,9]. This technique can be used to prepare materials whose production is very difficult using other

methods such as the "top-down" or "self-assembly" processes [10].

Some materials of natural origin, as for example vegetable tissues, have complex structures [8,11,12,13–15,16] that when reproduced with inorganic materials can be used in a wide range of applications such as catalysis, photonics, filters, drug delivery, molecular electronics, etc [15]. Plant constituents have high stiffness and elasticity at the micro and at the macro-scale, excellent resistance at low density and an anisotropic porous morphology [17,18]. All the above features make these materials very attractive for use in the development of new structured systems such as structured catalytic rectors, membranes, etc. [19].

Biomorphic materials are generally prepared by reactive or by molding techniques. Reactive techniques involve the pyrolysis of a bio-organic template into biomorphic material, in an inert or reducing atmosphere. In addition, before the pyrolysis, the raw material can be impregnated with catalytic precursors (e.g. Ni, Cu, Pd, Au, Si, Al, etc). In this case, after the thermal decomposition step, the solid obtained is made up of a biomorphic carbonaceous support containing highly dispersed metallic nanoparticles. Using this technique, supported metallic catalysts can be easily synthesized with a structure replicating original bio-organic material. The main limitation of this technique is that the use of high temperatures can destroy a large part of the original nanostructure with the result that the replication is only achieved at the microstructure but not at the nanostructure level [15]. On the other hand, the technique known as *chemical templating* allows the developing of materials in which the nanostructure of original materials is replicated perfectly. This technique is considerably more complex and involves a process in which the plant cells suffer chemical modifications (e.g. acid treatments), followed by the infiltration of precursor sols. Silica or iron oxide replicas of the cell wall structure can be developed with this technique [20,21].

In this work, a series of Pd and Pd-Al supported biomorphic carbon catalysts has been developed through reactive techniques because this is easier and cheaper than using the chemical templating protocols. In order to know how the thermal decomposition temperature and the addition of Al affect the physicochemical properties of these catalysts, the synthesized samples were characterized by thermogravimetric analyses in air (TGA-Air), nitrogen adsorption isotherm, Raman spectroscopy, X-Ray diffraction (XRD), X-Ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The activity of the prepared catalysts was measured in the liquid phase cyclohexene hydrogenation reaction, because this does not present any problem of selectivity and stability under the reaction conditions. The results obtained were compared with a typical catalyst of Pd/SiO_2, in order to know if the biomorphic carbons are suitable for use as catalytic supports in liquid phase reactions.

2. Experimental

2.1. Materials

The organic material used to prepare the biomorphic catalyst was cellulose provided by Sigma Aldrich. The metal precursors were Pd (II) nitrate hydrate supplied by Acros Organics (ref.: 10239293) and Al nitrate nonahydrate provided by Sigma Aldrich (ref.: 237973). Al oxide (98%) and silica gel (refs.: 11028 and 60741, respectively), used as catalyst model supports, were supplied by Sigma Aldrich. The solvent selected for the reaction was decalin (decahydronaphtalene) and the reactive was cyclohexene, both purchased from Sigma Aldrich (refs.: 294772 and 125431, respectively).

2.2. Catalysts preparation

The catalysts were prepared with 6% of Pd and variable contents of Al: 0%, 1.75% and 7%. These were named respectively as: Pd/BC, Pd-Al(1.75)/BC and Pd-Al(7)/BC and were prepared in the following

manner. The cellulose was dried at 100 °C overnight and then impregnated by incipient wetness with the appropriate amounts and concentrations of Pd and Al aqueous solutions. After impregnation, the solid was dried at 80 °C overnight and then thermally decomposed in a reducing atmosphere (15% H_2, 85% N_2). The temperature and time of the thermal decomposition stage was varied from 600 °C to 800 °C and from 30 to 120 min, respectively. In all cases, the decomposition temperature was reached at high heating rates (ca. 42 °C/min). Finally, the catalyst was milled and sieved to obtain a homogeneous particle size distribution ranging between 80 and 200 micrometres.

The comparison catalyst of Pd(1%)/SiO_2 was also prepared by the incipient wetness method. The support, SiO_2, was impregnated by a Pd aqueous solution, dried at 100 °C overnight, and finally calcined at 300 °C for 3 h in air. The final catalysts were milled to obtain a homogeneous particle size ranging between 80 and 140 micrometres.

2.3. Catalytic conversion of cyclohexene

The catalytic hydrogenation of cyclohexene was carried out in a high pressure reactor (Berhof BR-100) following a procedure similar to that described previously [6]. Briefly, 20 mg of the selected catalyst was added to a vessel containing 32.5 mL of decalin. With the aim of attaining high dispersion of the catalyst particles, the mixture was sonicated for 15 min at 25% amplitude in an Ultrasonic Processor 750 W, and then placed in the reactor. In order to avoid the presence of any re-oxidized layer of Pd at the surface of the exposed particles, the catalyst was reduced *in situ* at 100 °C and 20 bar pressure of hydrogen for 1 h. After that, a solution containing 3.8 mL of cyclohexene and 1.2 mL of decalin was added to the reactor. The temperature and hydrogen pressure were then kept at 100 °C and 20 bar, respectively, during the reaction. A stirring rate of 1400 rpm was selected after checking that under these operating conditions the external and internal mass-transfer limitations are negligible. After 1 h reaction time, the hydrogen was evacuated from the reactor and nitrogen was introduced to maintain an inert atmosphere during the cooling step. The reactor was cooled in an ice bath to room temperature. The reactor content was then filtered and the liquid phase analysed by a GC Agilent 7890A equipped with a J & W HP-5 capillary column and FID detector. The integration of the peaks, corresponding to cyclohexene, cyclohexane and decalin, displayed in the chromatogram was used to calculate the conversion of cyclohexene.

2.4. Catalyst characterization

The catalysts were characterized by several techniques in order to ascertain the textural and structural properties. The thermogravimetric analyses in air (TGA-Air) were carried out using a Mettler Toledo TGA/SDTA 851e. The air flux used during the TGA measurements was 50 mL/min. This technique was employed to calculate the amount of Pd and Al deposited on the biomorphic carbon support after the thermal decomposition of the cellulose. After the decomposition step in TGA-Air, the solid residue of the catalysts contained ashes, PdO and, in the case of the samples with Al, Al_2O_3. The percentage of ashes was calculated from metal-free biomorphic carbon prepared under the same experimental conditions as the catalysts. The Pd content was estimated as the difference between the Pd/BC residue and the ashes previously calculated. In the same way, the Al content was estimated subtracting the Pd content and the ashes from the Pd-Al/BC residue. In order to check the validity of this method, an Al(7%)/BC sample was also synthesised, and the concordance of the% of Al was excellent. The protocol was repeated three times with each sample, obtaining in all cases coefficients of variation less than 2%.

Specific area and porosity were obtained from nitrogen adsorption–desorption isotherms at 77 K using an ASAP 2020 (Micromeritics Instrument Corp.). BET specific surface areas were measured from the adsorption branches in the relative pressure range of 0.001–0.10.