Improved performance of carbon nanofiber-supported palladium particles in the selective 1,3-butadiene hydrogenation: Influence of carbon nanostructure, support functionalization treatment and metal precursor

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ABSTRACT

Two types of commercial carbon nanofibers with different graphitic structure, Pyrograph PR24-HHT (NF_{HHT}) and PR24-PS (NF_{PS}) were chemically modified to introduce oxygen groups or SO_3H-containing species on their surface. Incorporation of these surface groups was confirmed by temperature programed desorption (TPD) and X-ray photoelectron spectroscopy (XPS). Palladium catalysts using these modified supports and $PdCl_2$ as precursor were prepared, and subsequently tested in the partial hydrogenation of 1,3-butadiene under conditions of excess hydrogen. The effect of using a different Pd precursor ($PdSO_4$) was also studied. All the prepared catalysts were characterized by transmission electron microscopy to determine the Pd nanoparticle sizes and by X-ray photoelectron spectroscopy to obtain the surface composition and the oxidation state characteristics of the Pd surface species. The carbon nanofiber structure seems to determine the Pd particle size and morphology, probably due to different metal–support interaction. Selectivities to butenes higher than 95% were obtained with the catalysts prepared on SO_3H-modified supports or with the $PdSO_4$ precursor, while over-hydrogenation to butane took place over the Pd on oxidized supports. Catalytic activity–structure correlations have been derived and it is proposed that the catalytic behaviour depends on the type of sulfur species, functional group or adsorbed residual sulfur. Furthermore, variations in 1-butene selectivity and 2-butene *trans/cis* ratio between the two series of catalysts were also detected and ultimately related to the different nanostructure of the carbon nanofiber.

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1. Introduction

Palladium-based supported catalysts have been widely applied for hydrogenation reactions and in particular for selective partial hydrogenation of alkynes or diolefines that are technologically important processes [1]. It is known that the structure of Pd can undergo different modifications (changes) as the conditions to which the catalyst is exposed change, and, for example, hydrocarbonaceous deposits are formed on the palladium surface as soon as hydrogenation reaction starts. Besides, palladium carbide and palladium hydrides (α- and/or β-phase) can be also formed under reaction conditions. However, surface and subsurface properties of Pd seem to be the key factors that control the selectivity. Experimental and theoretical studies have mainly proposed that sub-surface Pd–carbon have a decisive positive role, while Pd–hydrogen species have a detrimental influence [2]. On the other hand, a general opinion that is getting acceptance is that improvements in partial hydrogenation selectivity are observed when a reduction in the stability of bulk palladium hydride and/or availability of subsurface hydrogen species occurs [3]. Furthermore, this reaction is structure-sensitive and studies on model catalysts have shown that Pd (1 1 0) exhibits a higher selectivity for butenes formation than Pd (1 1 1) [4,5]. Also, it has been seen that deactivation under reaction conditions and hydrogen stability [6,7] depend on the preferred exposed crystal planes.

Different approaches have been attempted in order to get Pd modifications, as the formation of bimetallics or alloys [8], the use of additives or modifiers as CO or diphenyl sulphide [9,10]. In this sense, addition of sulfur-containing compounds is known to poison the catalysts and cause deactivation problems, but in some cases can be used for the selective poisoning of active sites [11]. It was shown that the addition of low amounts of sulfur from thiophene promoted the selective hydrogenation of crotonaldehyde to crotyl alcohol with gold supported catalysts [12]. In this case, the Au sites are electronically promoted by sulfur. In the hydrogenation of alkynes and dienes, the influence of S has been attributed to both electronic and ensemble size effects and is difficult to discriminate among them [13].

Carbon materials have attracted a great interest as supports in heterogeneous catalysis due to their specific characteristics: inertness, the possibility to control porosity and to modify the surface chemistry introducing different functional groups that can facilitate the controlled synthesis of metal nanoparticles giving high dispersions. Amongst these materials, carbon nanostructures, nanotubes (CNTs) and nanofibers (CNFs) have been shown to possess extraordinary physical and chemical properties. These properties have allowed carbon nanostructures to be successfully applied in a wide variety of fields, including their use as a heterogeneous catalyst [14] support in, amongst others, hydrogenation catalytic reactions [15]. Furthermore, electronic effects derived from different carbon nanostructures and the peculiar metal–support interaction are reported to affect the catalytic behaviour on hydrogenation reactions [16–18]. In addition, this interaction could also induce a spreading of the metal on the support surface, and then, the metal crystallites adopt morphology very different to that usually existing on traditional support materials [19], i.e. flat-like morphology versus round-shaped one. However, very few studies of the application of catalysts supported on carbon materials to hydrogenation of olefins have been published. These studies have shown promising results in the hydrogenation of alkenes [20], alkynes [21] and dienes [17] with high yields and stability to deactivation. It has been suggested that the higher stability is due to the ability of the catalysts to regularly rearrange the accumulated species permitting its migration and facilitating the exposure of the reaction-selective phase PdC_x [22].

In the present study, the hydrogenation of 1,3-butadiene under conditions of excess hydrogen is described over Pd catalysts supported on two types of carbon nanofibers with different graphitic structure. The aim of the work was to derive catalytic activity–structure correlations and to investigate how sulfur modifiers can affect the catalytic performance. With this purpose, the CNFs were chemically modified to introduce O- or S-containing species on their surface. Furthermore, the effect of a S-derived Pd precursor was analyzed. The reaction was carried out in excess of hydrogen, which are challenging conditions to obtain good selectivities, but at the same time ideal to suppress coke formation and, in this case, to study the real effect of the support nanostructure and of the sulfur species.

2. Experimental

2.1. Preparation of carbon supports

Two types of commercial carbon nanofibers were used in this study: Pyrograph III PR24-HHT (S_{BET} = 32 m^2/g) and PR24-PS (S_{BET} = 36 m^2/g), both of them were provided by Applied Sciences Inc. The PR24-HHT fibres (denoted as NF_{HHT}) are originally treated at high temperature (∼3300 K), possess a stacked-cup morphology with a hollow core through the length of the fibre and also present a jagged outer surface with "round heads" or "loop" structures which connect several layers [16]. The PR24-PS (denoted as NF_{PS})

are pyrolitically stripped carbon fibres treated at 1100 °C, and therefore, less graphitized than NF_{HHT}.

NF_{PS} were functionalized on the surface with carboxylic acids and others acid groups by concentrated nitric acid at reflux during 8 h yielding NF_{PSox}. NF_{HHT} were functionalized according to reported procedures yielding NF_{HHTox} [23]. Briefly, parent NF_{HHT} were refluxed in 50% nitric acid (carbon/HNO$_3$ = 1 g/10 mL) at 100 °C for 48 h. NF_{HHT} and NF_{PS} were also functionalized with sulfanilic acid; a typical preparation is as follows: the nanofibers (1 g) were dispersed in DMF (50 mL), heated at reflux in inert atmosphere and reacted with 6 mmol of sulfanilic acid followed by 6 mL of isoamyl nitrite. The resulting mixture was stirred 24 h. Finally, the powder was washed with successive aliquots of DMF and isopropyl ether, and allowed to dry overnight at 100 °C. The modification was carried in situ as the diazonium cations are directly formed from the corresponding amine. The resulting modified samples were labelled NF_{HHT-DZ} and NF_{PS-DZ}.

NF_{HHT} and NF_{PS} were also subjected to a sulfonation treatment [24]. Aliquots of 3 g of fibres were immersed in 150 mL of fuming sulfuric acid (15 wt% SO$_3$) at 80 °C under a nitrogen gas atmosphere for 7 h. After the treatment, the suspension was washed with deionized water to remove any excess sulfuric acid in the carbon nanomaterial, filtered and dried at 120 °C. The respective resulting samples were denoted NF_{HHT-SO_3H} and NF_{PS-SO_3H}.

2.2. Preparation of supported palladium catalysts

The catalysts were prepared with a 1 wt% Pd loading. In the case of PdCl$_2$, the precursor was dissolved in concentrated HCl to generate dihydrogentetrachloropalladate (H$_2$PdCl$_4$), heated to eliminate chlorine, dissolved in distilled water, dried and again diluted in water until the final volume was reached. This solution was dropped to the carbon nanofibers. When PdSO$_4$ was used as precursor, the catalysts were prepared by incipient wetness impregnation using water solutions. The respective resulting catalysts were labelled Pd-NF$_{HHTox}$, Pd-NF$_{HHT-DZ}$, Pd-NF$_{HHT-SO_3H}$, Pd-NF$_{PSox}$, Pd-NF$_{PS-DZ}$, Pd-NF$_{PS-SO_3H}$, PdSO$_4$-NF$_{HHTox}$ and PdSO$_4$-NF$_{PSox}$. The exact metal content was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) in a Perkin Elmer Optima 3300 DV, after solubilization of an aliquot of each catalyst in strong acidic media. The obtained results are similar to the nominal loading as expected with the applied preparation method (incipient wetness impregnation).

2.3. Supports and catalysts characterization

Thermogravimetric analyses (TGA) of the supports were conducted under helium in a CI Electronics microbalance (MK2-MC5) apparatus. The sample was heated with a 10 °C min^{-1} ramp between room temperature and 850 °C. The chemical nature of the functional groups was evaluated by temperature programed desorption coupled with mass spectrometer (TPD–MS) experiments under vacuum in a conventional volumetric apparatus connected to a RGA-200 SRS mass spectrometer [25]. The sample was evacuated for 30 min at room temperature and then ramped to 850 °C at a 10 °C min^{-1} rate.

X-ray photoelectron spectra of the supports and catalysts were recorded with an ESCA-PROBE P (Omicron) spectrometer by using non-monochromatized Mg Kα radiation (1253.6 eV). Each sample was pressed into a small pellet of 15 mm diameter, placed in the sample holder and degassed in the chamber for 6–8 h to achieve a dynamic vacuum below 10^{-8} Pa before analysis. The spectral data for each sample was analyzed using CASA XPS software. The relative concentrations and atomic ratios were determined from the integrated intensities of photoelectron lines corrected for the corresponding atomic sensitivity factor.