



When the nature of surface functionalities on modified carbon dominates the dispersion of palladium hydrogenation catalysts

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ABSTRACT

Commercial carbon nanofibers with different graphitic structure and commercial multiwall carbon nanotubes (CNT) were chemically modified in order to introduce specific alkyl ligands on their surface. Palladium catalysts have been prepared using these modified supports and subsequently tested in the partial hydrogenation of 1,3-butadiene under conditions of excess hydrogen. Herein, we used thermogravimetry (TG), temperature programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM) and nitrogen adsorption at 77 K techniques in order to characterize both supports and catalysts. We focus on testing the effects of support surface functionalities either on morphology of supported palladium (Pd) nanoparticles (NPs) or on their catalytic performances. High selectivity to butenes was obtained with the catalysts prepared over supports containing alkyl chains, while over-hydrogenation to butane took place over oxygen-containing functional groups. Nicely the catalysts with modified supports minimize the secondary hydrogenation of butenes even at high conversions. Therefore, Pd NPs on modified nano-carbon catalysts may open up more opportunities to optimize the activity and the selectivity for partial hydrogenation reactions.

1. Introduction

Catalytic hydrogenations are among the most important processes in the chemical industry, in particular the selective partial hydrogenation of alkynes or diolefins is a group of technologically important processes [1]. Thus for instance, butene purification is performed by selective hydrogenation of butadiene. A good process will consequently work in such a way that the complete hydrogenation of butadiene into butenes takes place avoiding any butane formation. Besides, butadiene hydrogenation is an interesting reaction for model catalysis because it has four different products (1-butene, cis-2-butene, trans-2-butene, n-butane) and therefore allows the study of both activity and selectivity. The critical requirement for a catalyst applied in this process is to achieve high selectivity to butenes (1-butene is the most desirable product), especially at high conversions. Also, these catalysts have to achieve long durability against deactivation. So, carbonaceous deposit formation needs to be avoided.

Pd NPs are known to be the most active catalysts for these reactions, but because they lack selectivity to the desired n-butenes, promoters or modifiers are needed to enhance the yield of partially hydrogenated

products. Thus, monometallic catalyst has been modified by using either promoters (Ag, Au, Ga, or Cu) or additives (CO or sulfur) [2–6]. Studies on model catalysts have revealed that Pd (110) exhibits a higher selectivity for butenes formation in comparison with Pd (111) [7,8]. In many cases, it has been well established that catalytic properties of Pd NPs are size and geometry depending hence this group of reactions is structure-sensitive [9]. However different results were obtained by Silvestre et al. [10] who studied the correlation of the catalytic activity with the exact Pd particle surface structure. They reported that butadiene hydrogenation, in spite of being structure sensitive, is particle size independent for Pd NPs supported on Al₂O₃. A general observation was that the properties of Pd particles larger than 4 nm behave very similarly to Pd (111) single crystals whereas small Pd particles can deviate from those of Pd single crystal structures.

Kinetic studies have reported that palladium active centres are hindered because Pd undergoes dynamic changes and reaction-created intermediates continuously interact with the Pd and the support to form an active complex during reaction. For example, palladium carbide (PdCx), palladium hydrides (α - and/or β -phase) and deposited species like carbonaceous accumulations can be formed under reaction condi-

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tions [11]. Under these conditions, surface and subsurface chemistry (hydride and carbide formation) have an important role on the selective hydrogenation of unsaturated hydrocarbons [12]. Moreover metal-support interactions (SMSI effect) may affect reactions for Pd supported catalysts. In this way the interaction between the metal NPs and CNTs has been demonstrated to be critical, since it controls the mutual charge transfer and determines the stability of metal NPs at high temperature [13].

Detre Teschner et al. [14] studied the alkyne hydrogenation on palladium, where different subsurface species define which of the possible reaction paths dominates the overall reaction. They have explored why palladium can selectively hydrogenate alkynes to alkenes, when Pd itself is usually even more active in hydrogenating the corresponding alkene to the alkane. It has been proposed that an improvement in the partial hydrogenation selectivity is observed when a reduction in the stability of bulk palladium hydride and/or availability of subsurface hydrogen species occurs [11,15]. Then sub-surface Pd-carbon and surface hydrogen have a decisive positive role while Pd-hydrogen species or sub surface hydrogens have detrimental influence. In general, unselective hydrogenation is produced on hydrogen saturated β -hydride (favored on larger particles) and α -phase (formed on particles smaller than 2 nm) is less active and more selective.

The catalytic behaviour can depend on the structure or nature of the materials used as support [16]. In fact the support seems to induce different shapes and sizes of the metal NPs [17]. In this context, the use of carbon materials as supports of metal NPs is widely employed for preparing heterogeneous catalysts [18,19–21]. Among many reasons because as a consequence of the metal-graphite interaction new catalytic properties can be easily achieved. Moreover, carbon materials offer excellent properties as a high flexibility for the dispersion of the active phase since it is possible to modulate their specific surface area or easily functionalize chemically their surfaces by doping or grafting. Normally, to overcome the hydrophobic and inert character of these materials, modification of carbon surface with functionalities to effectively anchor metal NPs is needed [22]. Moreover, it is crucial to define the interaction between the surface functionality and the supported metal. These interactions could determine the activity and the selectivity in a catalytic reaction. Taking into account this, activity and selectivity control of these catalytic systems depends strongly on the surface functionalities.

Thus, to take advantage of the full potentiality of the carbon supported Pd materials, significant effort should be devoted to the synthesis of the catalysts, to the control of nanostructure morphologies and to their addressing for numerous catalyzed processes. However, the study of metal graphitic carbon catalysts is challenging because the stability of palladium NPs supported on carbon depends strongly on its surface properties including the added functional groups. In this communication we report the selective hydrogenation of 1,3-butadiene (Bd) in H_2 -rich streams over Pd based catalysts supported on three types of graphitic carbon nanomaterials with different nanostructures. The aim of the work was to develop catalytic activity-structure correlations and to investigate how surface groups can affect the catalytic performance. Alkyl-modified supports were used for designing high-performance Pd catalysts. With these materials we have been able to improve selectivity in hydrogenation reactions, besides the conventional methods of promotion-poisoning of Pd NPs. Characterization of the carbon materials and of the supported catalysts was performed using nitrogen adsorption isotherms (BET), transmission electron microscopy (TEM), thermogravimetric analysis (TGA), temperature programmed desorption (TPD) and X-ray photoelectron spectroscopy (XPS). The synthesis of catalysts, relative catalytic properties of the materials and some structure-property correlations are presented, focusing on the influence of the modified supports on the catalytic activity and selectivity as well as on the influence of the size of the Pd NPs.

2. Experimental

2.1. Preparation of carbon supports

Three types of commercial carbon materials were used in this study, two Pyrograph III carbon nanofibers (CNFs) PR24-HHT ($S_{BET} = 32 \text{ m}^2/\text{g}$) and PR24-PS ($S_{BET} = 36 \text{ m}^2/\text{g}$), both of which were provided by Applied Sciences Inc, and multiwall carbon nanotubes (3100 Series, 95% purity) obtained from NanocylTM. The PR24-HHT fibers (denoted as HHT) are originally treated at high temperature ($\sim 3300 \text{ K}$), possessing 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. The PR24-PS (denoted as PS) are pyrolytically stripped carbon fibers treated at 1373 K , and therefore, less graphitized than HHT. Finally, carbon nanotube sample (named CNT) possesses multiple walls with a hollow inner core and close both their ends. The PS support was functionalized on the surface by treatment with concentrated nitric acid at reflux during 3 h yielding PS_{OX} . The presence of carboxylic acids and others oxygen surface groups was detected in this material. In the case of HHTox and CNTox preparations, the treatment at reflux was extended for 8 h, considering the lower reactivity of the pristine HHT and CNT supports. To graft moieties terminated by long alkyl chains, PS_{OX} , HHT_{OX} and CNT_{OX} were further refluxed in a solution of thionyl chloride for 24 h at 343 K under argon, then the solvent was evaporated under vacuum and finally dried under vacuum for 24 h. These chlorinated samples were reacted with excess of hexadecylamine (HDA) in THF at 338 K for 24 h to produce the amide surface groups presenting a long alkyl chain. Finally, THF was evaporated and the resulting PS_{HDA} , HHT_{HDA} and CNT_{HDA} samples were washed with ethanol to remove excess amine, and dried at 373 K for 24 h under vacuum. To graft a short alkyl-chain, the chlorinated supports were treated with propylamine (PA) under the same conditions as those for HDA. However, chlorinated samples were reacted with excess of PA in THF but at ambient temperature due to the higher reactivity of this short alkyl amine. The resulting modified samples were labelled PS_{PA} , HHT_{PA} and CNT_{PA} .

2.2. Preparation of supported palladium catalysts

Catalysts were prepared by wetness impregnation. The samples were immersed in an acetone solution of $Pd(NO_3)_2$, under alternative stirring and ultrasonic treatment. After 2 h, the solvent was removed under vacuum. The catalysts were prepared with a 1 wt% Pd loading. The exact metal content was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) by a Perkin Elmer Optima 3300 DV. The obtained results were similar to the nominal loading.

2.3. Supports and catalysts characterization

The BET surface area of the supports was measured from the nitrogen adsorption isotherms determined on a Micromeritics ASAP 2020 instrument. All the samples were also characterized by X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), thermogravimetric analyses (TGA) and temperature programmed desorption (TPD). XPS analysis was performed with an ESCA-PROBE P (Omicron) spectrometer by using non monochromatized Mg-K radiation (1253.6 eV). The spectral data for each sample were analysed 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. TEM micrographs were performed on a JEOL JEM-2100F microscope at 200 kV . The samples were ground and ultrasonically suspended in ethanol before TEM images were generated. The mean diameter of the Pd NPs was calculated based on a minimum of 300 particles. Thermogravimetric analyses were conducted under helium in a TA instruments, model SDT Q600 TA System. The sample ($\sim 5 \text{ mg}$)

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