



Carbon-supported Pd nanoparticles as catalysts for anthracene hydrogenation



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HIGHLIGHTS

- Catalysts based on carbon-supported Pd nanoparticles (NPs) were prepared.
- Catalysts activity was investigated in the hydrogenation of anthracene.
- High conversions and selectivities towards the hydrogenated products were achieved.
- No cracking or ring-opening products were obtained.
- Reaction pathway for anthracene hydrogenation is proposed.

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ABSTRACT

The catalytic activity of carbon-supported Pd nanoparticles (NPs) was investigated in the hydrogenation of anthracene at different temperatures and reaction times. These nanocatalysts were prepared by direct reduction of a palladium precursor impregnated on the carbon support. Small spherical and homogeneously dispersed Pd NPs were thus achieved. Nanocatalyst performance was evaluated as a function of surface properties, including porosity, defects and Pd NPs population. High conversions and selectivities towards the hydrogenated products without cracking or ring-opening products were achieved. The selectivity of the nanocatalysts to the production of hydrogenated species depended on temperature, reaching a maximum at 300 °C. At this temperature and short reaction time, the catalytic activity is thought to have been favored by the presence of a large amount of surface defects in the nanocatalysts that can promote hydrogen transfer to the anthracene molecule. On the other hand, at longer reaction times the porosity and density of Pd nanoparticles on the catalyst were the factors behind the deeper hydrogenation achieved. Finally, a plausible reaction pathway for anthracene hydrogenation in the presence of these Pd nanocatalysts was proposed.

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1. Introduction

The combustion of polyaromatic hydrocarbons contained in diesel is responsible for the emission of benzene, a proven human carcinogenic. Hydrogenation of these species plays a key role in oil upgrading, as polyaromatic hydrocarbon groups are found in asphaltene and other heavy fractions. Aromatics can be saturated via catalytic hydrogenation, a reaction widely studied using metal sulfides (CoMoS, NiMoS) and metals (Ni, Pt, Pd) as catalysts [1]. The

use of noble metals allows hydrogenation at lower temperatures thus avoiding thermodynamic limitations imposed by the exothermic nature of the hydrogenation reactions. However, they are easily poisoned by sulfur or nitrogen which are present in industrial feedstocks [2]. The use of a catalyst support and the presence of a second metal are known to increase the sulfur resistance [3,4]. Among catalyst supports, zeolites are one of the most important at industrial scale for aromatic hydrogenation, although their high acidity may promote an excessive cracking and further catalyst deactivation by coke [3]. Moreover, conventional zeolites cannot accomplish deep hydrogenation of the bulky aromatics present in diesel fuels due to pore size limitations [5]. These drawbacks can be partially circumvented by using non acidic catalyst supports in hydrogenation reactions.

In this context, Kotanigawa et al. have performed selective hydrogenation of polynuclear aromatics in the presence of Ru

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supported on mixed oxides [6]. The non acidic supports reduce the scission of C–C bonds of saturated carbons formed by hydrogenation, thus preventing the production of gaseous fragments. Therefore, deep hydrogenation and higher product yields can potentially be obtained provided that the catalytic cracking function is suppressed [7].

Carbon materials with neutral or slightly basic surface have been successfully applied as catalyst supports [8]. In comparison with other solid supports, these materials offer very interesting advantages such as relatively low cost, availability, high mechanical strength and chemical stability. Moreover, their pore structure and surface chemistry allow carbon materials to be modified by straight-forward procedures to improve both metal immobilization and reactant access to the active metal sites.

Carbon-supported metals catalysts have also been successfully tested in hydrotreating processes, showing higher activity than those prepared with acidic supports such as alumina [9]. Specifically, several examples can be found in the literature addressing the hydrogenation of polyaromatic structures such as naphthalene, anthracene or phenanthrene. These compounds are representative of the heavy molecules which are typically present in heavy oil fractions and coal derived products. For example, an activated carbon-supported Ni catalyst was tested in the hydrogenation of anthracene at 300 °C and 3 MPa of hydrogen pressure [10], leading to complete conversion into a mixture of di-hydro, tetra-hydro and octa-hydro anthracene. Activated carbon supported Pd catalyst was studied in the hydrogenation of 9,10-diphenyl anthracene [11] and in the nitrogen heteroatom removal of tetrahydrofuran/methanol insoluble fraction from bituminous coals under hydrogenation conditions [12]. More recently, carbon-supported Pd catalysts were used in microwave-assisted hydrogen transfer to anthracene and phenanthrene [13], reporting high selectivity to perhydro derivatives.

Hydrogenation of aromatic structures with three condensed rings has been generally studied using metal-supported catalysts, although the use of carbon materials as catalysts in hydrogenation has also been addressed in some studies. Activated carbons were observed to split molecular hydrogen into atomic form and catalyze monatomic hydrogen transfer to aromatic rings present in three-polycyclic arenes such as anthracene [14]. Hydrogenation of anthracene catalyzed by activated carbons has also been reported [15]. Although metal-free carbon materials were found to be effective in anthracene hydrogenation at 300 °C, the extent of hydrogenation was however limited to di-hydro and tetra-hydro derivatives. In these cases, complete anthracene conversion was only achieved after relatively long residence time.

Nanoparticles (NPs) and hybrid nanomaterials have been used as catalysts for numerous chemical reactions showing high activity and selectivity as well as long lifetime [16–18]. In this work, anthracene hydrogenation reaction has been studied in a batch reactor at different temperatures and reaction times using Pd NPs supported on carbon materials displaying different textural and surface chemical properties. These nanocatalysts were designed and prepared by direct reduction of a Pd organometallic precursor impregnated on the solid carbon support, as previously reported [19,20]. The performance of the carbon-supported Pd NPs in anthracene hydrogenation is discussed on the basis of the nanocatalysts surface properties in terms of Pd NPs size and population, and porosity.

2. Experimental

2.1. Carbon supports and carbon-supported Pd nanocatalysts: preparation and characterization

A full description of the nanocatalyst preparation can be found in [18]. Briefly, mesoporous carbon beads (MB) of particle sizes in

the range of 0.5–1.0 mm with a spherical shape were used as the starting support. They are commercially available phenolic resin-based activated carbons with a bi-modal pore texture [21]. MB was heated at 2000 °C leading to a new material named MB-2000. Oxidation of both starting MB and MB-2000 was carried out with low temperature ashing (LTA) by oxygen plasma and the resulting oxidized materials were denoted MB-LTA and MB-2000-LTA. MB, MB-LTA and MB-2000-LTA carbon materials were further used as supports for the immobilization of Pd NPs. Details of the heating and oxidation treatments as well as the surface characterization of these carbon supports were also reported in [19]. The textural parameters (surface area and pore volume) are provided as Supporting Information (Table S1).

The Pd NPs were prepared using the Tris(dibenzylideneacetone)dipalladium (0) organometallic complex ($[\text{Pd}_2(\text{dba})_3]$) as metal source [22]. In a typical experiment, 2 g of the carbon material (MB, MB-LTA or MB-2000-LTA) were introduced in a Fischer–Porter reactor and then, 310.8 mg of $[\text{Pd}_2(\text{dba})_3]$ (0.34 mmol) dissolved in 20 ml of degassed toluene were added. The mixture was firstly stirred at 300 rpm, the solvent was then evaporated to dryness and the Fischer–Porter reactor pressurized with H_2 (3 bar) overnight to decompose the palladium complex and form the Pd NPs on the surface of the carbon support. Excess of H_2 was releases, after they were washed with toluene (3×20 ml) and dried under vacuum overnight. The nanocatalysts were denoted Pd/MB, Pd/MB-LTA or Pd/MB-2000-LTA.

The textural properties of the nanocatalysts were measured by N_2 adsorption at 77 K in a Micromeritics Tristar apparatus. The specific surface areas and pore volumes were calculated by applying the BET method to the respective N_2 adsorption isotherms (Fig. S1; Supporting Information).

Temperature-programmed oxidation (TPO) profiles of the carbon supports were obtained in a Perkin Elmer Pyris 1 Thermogravimetric Analyzer (TGA) carried out under air flow of $50 \text{ mL} \cdot \text{min}^{-1}$ using a heating rate of $10 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$.

Pd weight contents in the nanocatalysts were determined by Inductively Coupled Plasma–Mass Spectrometry (ICP–MS). The samples were dissolved in H_2O_2 , HNO_3 and HCl before analyses.

2.2. Anthracene hydrogenation

A microbomb reactor (MBR) consisting in a $\frac{1}{2}$ in. bored-through Swagelok union tee with two ends plugged and pressurized through the third was used for the hydrogenation of anthracene. The reactor is attached to a shaking mechanism and heated inside a Techne SBL-2D fluidized sand bath. This experimental setup has been described in detail elsewhere [23]. In a typical experiment, the MBR was loaded with 250 mg of anthracene and the nanocatalyst in a anthracene: catalyst ratio of 10:1 (w:w), purged with He to ensure an oxygen-free atmosphere, and subsequently charged with an initial H_2 pressure of 3 MPa. Hydrogenation reactions were carried out in the temperature interval of 250–350 °C at a reaction time (defined as the holding time once the reactor reaches the desired reaction temperature) ranging from 5 to 60 min. Under these conditions, anthracene changed to liquid phase. The reactor heat-up time was typically 3 min. Once the reaction time was reached, the reactor was quenched with water to stop the hydrogenation reactions.

The reaction products were recovered from the MBR using a chloroform–methanol mixture 4:1 v:v and the nanocatalysts were recovered by filtration. Reaction products were analyzed in a Perkin Elmer Clarus 500 gas chromatograph (GC) fitted with a flame ionisation detector (FID). The GC was equipped with a non-polar HT-5 (25 m \times 0.32 mm) column from SGE, UK. Identification of the reaction products was performed in a Varian Star 3400/Saturn 2000 GC–MS by comparison with data in the instrument library.

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