



Impact of organic-ligand shell on catalytic performance of colloidal Pd nanoparticles for alkyne gas-phase hydrogenation



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ABSTRACT

Monodispersed Pd nanoparticles (NPs) have been prepared by colloidal technique and deposited on a structured support consisting of carbon nanofibers (CNF) grown on sintered metal fibres (SMF). The surface properties of Pd NPs have been fine-tuned by (i) changing the nature of stabilizing agent (electrostatic vs. steric), (ii) controlling Pd NPs size (2–10 nm) and (iii) grafting N-containing ligands onto the CNF/SMF surface. In the *semi*-hydrogenation of acetylene ($T = 393\text{ K}$; $P = 1\text{ bar}$) catalytic response was insensitive to the nature of the reducing agent where equivalent activity/selectivity were obtained over Pd NPs with similar dispersion, prepared with the same stabilizer.

A similar product distribution was recorded over Pd NPs with *similar crystal size* irrespective of the colloidal stabilizer (electrostatic vs. steric). In contrast, a stronger inhibiting effect on hydrogenation rate has been found with electrostatic stabilizer (sodium di-2-ethylhexylsulfosuccinate) as compared to the steric ones (polyvinylpyrrolidone or polyvinylalcohol) and assigned to geometric and electronic effects. Decrease (from 8 → 2 nm) in Pd NPs size results in a concomitant decrease in activity (antipathetic size-sensitivity), but higher selectivity to target ethylene product. Grafting of nitrogen-containing modifiers (polyvinylpyridine or polyethylenimine) on the CNF/SMF support results in a significant increase in olefin selectivity (up to 93%) where the catalyst shows remarkable stability during 120 h on-stream. This is explained by the electronic modifications promoted by interactions between the Pd NPs and the grafted ligands as confirmed by XPS analysis. In comparison, stabilizer-free Pd/CNF/SMF has low selectivity to ethylene (65%). In summary, controlled size Pd (core) nanoparticles with organic ligands (shell) demonstrated increased selectivity and remarkable stability in catalytic gas-phase alkyne *semi*-hydrogenation opening new tools for rational catalyst design.

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1. Introduction

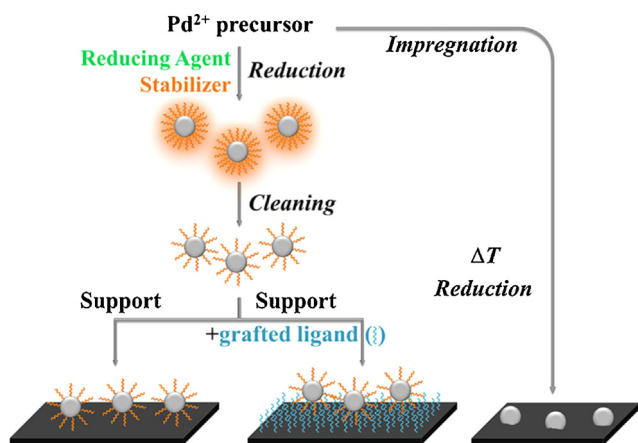
The conventional preparation methods for heterogeneous catalysts based on impregnation/deposition of metal precursors followed by drying, calcination and activation steps [1] present difficulties in terms of controlling metal nanoparticle (NP) size and shape, known to be of fundamental importance for catalysis. Colloidal techniques have emerged as a valuable alternative for tailoring metal NP morphology [2,3]. A control in metal crystallite size allows optimizing the surface to volume ratio, maximizing the use of noble metals and allowing to control catalytic performance [4]. Organic surfactants are typically employed during the synthesis of metal nanocolloids in order to prevent undesired agglomeration. Nonetheless, the presence of these compounds,

even in trace amounts, on the NP surface can have an impact on catalytic response. Up to date, the influence of metal NP size and the nature of organic shell on hydrogenations, *ca.* 20% of the reactions in the manufacture of pharmaceuticals and fine chemicals [5], has been mainly studied for liquid phase reactions [6] since ligands are more flexible in solutions (due to adsorption equilibrium) allowing the activation of adducts. For example, polymer-stabilized Pt and Pd NPs were shown to be active and highly selective in different liquid-phase reactions including hydrogenations [7].

However, these results cannot be easily extrapolated to gas-phase hydrogenations where the organic shells are believed to block the active sites with detrimental effect on catalytic activity. Borchert et al. for the first time showed that supported colloidal Pt NPs can be used in gas-phase catalysis without prior ligand removal [8] offering new prospective for the design of supported catalysts. Not only small molecules, like CO, can penetrate the ligand shell, but also the adsorption of sterically more demanding molecules, like benzene [9], has been reported. However, systematic studies

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Scheme 1. Schematic representation of the method used for the preparation of supported Pd-nanoparticles: conventional impregnation versus colloidal technique.

about the fate of organic shell under gas-phase reaction conditions are very rare. On the other hand, electronic and/or steric influences due to the partial coverage of metal NPs by ligands may cause a change in selectivity as compared to shell-free metal surface. Recently published reports [10,11] demonstrated the influence of organic ligands on catalytic properties. However, systematic studies about a beneficial effect of different ligand shells on the identical metal core (e.g. metal NPs size) during gas-phase hydrogenations are still warranted.

The method of the colloidal NPs preparation and their deposition onto support is schematically depicted in Scheme 1. Two main variables can be identified, namely: reducing and stabilizing agents [12]. The reducing agent promotes the $M^{x+} \rightarrow M^0$ reduction step and its effect on catalytic response has been flagged elsewhere [13]. The nature of stabilizing agents can be identified as: steric, *i.e.* stabilization through polymeric layers [14], and electrostatic [15] (stabilization *via* surface charges resulting in repulsion between NPs). Preformed NPs usually undergo a cleaning step from an excess of organics with the subsequent deposition on a suitable solid support. Furthermore, the support itself can be modified by grafting of different ligands controlling the microenvironment of the metal NPs which, in turn, can impact on the catalytic response [16].

The goal of this work is to study the influence of organic shell over nanocrystal core of colloidal pre-prepared Pd⁰ NPs regarding their catalytic response in selective $C\equiv C \rightarrow C=C$ hydrogenation by identifying the best stabilizer, reducing agent and the ligand grafted onto the support. The *semi*-hydrogenation of acetylene, as an important process for the removal of alkyne impurities from ethylene effluents obtained by cracking of heavy hydrocarbons [17], has been selected as a probe reaction. Palladium, known to be the best in terms of combined activity/selectivity for $C\equiv C$ bond partial hydrogenation, [2] is the metal of choice. The Pd-NPs were prepared using both electrostatic (sodium di-2-ethylhexylsulfosuccinate (AOT)) and steric (polyvinylalcohol (PVA) and polyvinyl pyrrolidone (PVP)) stabilizers.

In order to clearly demonstrate the beneficial or detrimental effect of the organic shell on the catalytic properties of palladium, the identical Pd⁰ NPs bearing the same size with and without ligands have been compared. The catalyst prepared *via* conventional impregnation of the same support has been used as a reference.

2. Experimental

2.1. Materials and analytical methods

Palladium (II) chloride (Aldrich), sodium chloride ($\geq 99.5\%$, Fluka), hydrazine monohydrate (HH, $\geq 99.0\%$, Fluka), L-ascorbic

acid (AA, 99.0%, Sigma–Aldrich), n-butanol (But, 99.5%, Acros organics), ethanol (Et, $\geq 99.0\%$, Acros organics), methanol (Met, $\geq 99.8\%$, Sigma–Aldrich), isooctane (2,2,4-trimethylpentane, $\geq 99.5\%$, Sigma–Aldrich, extra-dry), polyvinylpyrrolidone (PVP, Aldrich), polyvinylalcohol (PVA, Fluka), polyvinylpyridine (PVPy, Aldrich), polyethylenimine (PEI, Aldrich), palladium (II) acetate (98%, Aldrich) and acetonitrile (ACN, $\geq 99.5\%$, Sigma–Aldrich) were used as received without further purification. Sodium di-2-ethylhexylsulfosuccinate (AOT, 98%, Aldrich) was firstly vacuum-dried for 24 h at 333 K prior use. Hydrogen was produced *on-site* with a hydrogen generator (NMH₂ 500, Schmidlin-DBS AG) while the rest of the gases (acetylene and Ar) were of high purity ($>99.7\%$, Carbagas).

The composition of the gas mixture was analyzed using a HP 6890 gas chromatograph equipped with an extraction valve (periodical sampling every 10 min), a programmed split/splitless injector, and two (flame ionization (FID) and thermal conductivity (TCD)) detectors employing a Carboxen 1010 (Supelco, Fluka Holding AG, Switzerland) capillary column. The concentrations of the reactant/product species were determined from the total mass balance in the reaction mixture. Hydrogenation activity is expressed in terms of the conversion of acetylene under a steady state ($X_{C_2H_2}$):

$$X_{C_2H_2}(\%) = \frac{n_{C_2H_2, in} - n_{C_2H_2, out}}{n_{C_2H_2, in}} \times 100 \quad (1)$$

where $n_{C_2H_2}$ represents the number of moles of acetylene; the subscripts “in” and “out” refer to the inlet and outlet streams. Catalyst activity is also quantified in terms of quasi-steady-state specific (per m² of surface Pd) reaction rate and calculated as:

$$r(\text{mol}_{C_2H_2} \text{ m}_{Pd}^{-2} \text{ h}^{-1}) = \frac{F_{C_2H_2, in} \times X_{C_2H_2} \times \rho_{Pd} \times d}{6} \quad (2)$$

where $F_{C_2H_2, in}$ is the inlet molar flow of acetylene (mol s⁻¹), ρ_{Pd} the Pd density (g m⁻³) and d – the NPs mean diameter obtained from TEM/STEM analyses. The selectivity, *e.g.* of ethylene ($S_{C_2H_4}$) as the target product is given by:

$$S_{C_2H_4}(\%) = \frac{n_{C_2H_4, out}}{n_{C_2H_2, in} - n_{C_2H_2, out}} \times 100 \quad (3)$$

while the selectivity to green oil ($S_{\text{green oil}}$) was obtained from a mass balance: [18]

$$S_{\text{green oil}}(\%) = 100 - (S_{C_2H_4} + S_{C_2H_6}) \quad (4)$$

2.2. Catalyst preparation

The Pd NPs were synthesized *via* colloidal technique using a series of reducing (HH, AA, Et, Met, and But) and stabilizing (AOT, PVP, and PVA) agents. The supported catalysts were prepared by deposition of colloidal dispersions containing the monodispersed Pd NPs were deposited *via* impregnation on a structured support consisting in carbon nanofibers (CNF) grown on sintered metal fibers (SMF) prepared following the method as described in detail elsewhere [19]. For the ligand-grafted supports, the incorporation of the co-modifiers (PVPy or PEI) was carried out by impregnation of the CNF/SMF support, followed by deposition of the Pd NPs dispersions as described above. The catalytic systems without and with co-modifier employed in this study are denoted as Pd(*d*)_{R/S} and Pd(*d*)_{R/S/M}, respectively, where “R”, “S” and “M” refer to the reducing, stabilizing and co-modifying agents while “*d*” is the mean Pd NPs diameter obtained from scanning transmission electron microscopy (STEM) analyses (see Section 2.3). More detailed information on the synthesis conditions for each individual catalyst is summarized in Table 1.

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