



Direct assessment from cyclic voltammetry of size effect on the hydrogen sorption properties of Pd nanoparticle/carbon hybrids



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ABSTRACT

The hydrogen sorption properties of palladium particles synthesized with different sizes (2, 6 and 18 nm) dispersed on high surface area graphite powders are studied by both solid/gas and electrochemical methods. We demonstrate that we can directly evaluate by cyclic voltammetry the influence of the particle size on Pd hydride phase formation despite the ohmic losses and capacitive currents associated with powder electrodes. The size-dependent Pd hydride compositions calculated from electrochemical signals and pressure-composition-isotherms under ambient conditions are in good agreement and show the same trend: as the Pd particle size is reduced, the hydrogen content increases in the α phase and decreases in the β phase. Changes in electrochemical signals during cycling are observed when the potential domain covers the Pd oxide region, corresponding to an increase of the mean size of the smallest particles from 2 to \sim 12 nm (as confirmed by *ex situ* X-ray diffraction) whereas no modification occurs if it is restricted to the hydrogen region. This highlights that voltammograms can be used to readily detect *in situ* size modifications of Pd nanomaterials.

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1. Introduction

Nano-metals dispersed within carbon supports or matrices constitute an important class of materials that can find application in various fields like energy storage, energy conversion or catalysis. Among others, Pd/carbon hybrids have been used for a number of years as catalysts in organic chemistry (e.g. de/hydrogenation [1], Suzuki coupling [2]), fuel cells [3–8] and as model systems to study the effect of nanosizing on hydrogen storage properties [9]. Pd particles are particularly suited for this purpose because they can be synthesized in carbon matrices with controlled size and stabilized against agglomeration [9]. Nanosizing of Pd drastically changes the interaction with hydrogen. It shrinks the miscibility gap in the Pd–H phase diagram and reduces the hydrogen storage capacity at a given pressure. For example, hydrogen storage for 1 nm particles under 0.1 MPa and 300 K reaches half the bulk capacity (0.4 vs. 0.7 H/Pd respectively) according to Nützenadel et al. [10]. Nanosizing also increases the proportion of surface atoms leading to extremely developed surface area and hence strongly enhanced surface reaction kinetics, especially for solid/gas reactions. Finally, reaction paths involving atomic diffusion within the particles are reduced and allow very fast reaction rates.

Hence, downsizing Pd particles gives the possibility to tailor both hydrogen sorption thermodynamic and kinetics properties [11]. For Pd/carbon hybrids, these effects have been mainly investigated by solid/gas methods [12,13]. Establishing Pressure–Composition Isotherms (PCI) is the classical technique to characterize the different phase compositions and the formation of Pd hydride at nanoscale.

It is also possible to employ electrochemistry to study the hydrogen sorption in limited volume Pd electrodes by reduction of water or protons. Electrochemical studies have highlighted the effects of layer thickness and the presence of subsurface traps for ultra-thin layers of Pd deposited on various substrates (Au [14–20]; Pt [21]; reticulated vitreous carbon [22,23]; carbon nanotubes [24]). Regarding particles, pellets of Pd clusters with a narrow size distribution (i.e. pressed with a Cu powder) have been used as electrodes for electrochemical characterization [10]. For clusters of 2.6 and 3.7 nm size, hydrogen uptake of 0.57 and 0.51 H/Pd were measured respectively, compared to 0.7 for bulk Pd (RT, 0.1 MPa). The electrochemical properties of Pd particles/carbon hybrids have been reported in several studies [25–28]. However, only Takashu et al. and Tateishi et al. have attempted to characterize by electrochemistry the specific effect of particle size in a systematic manner, with particles deposited on a flat glassy carbon surface [29,30]. They also found reduced hydrogen storage capacity in nanosized Pd compared to bulk Pd.

This type of study has not yet been undertaken for Pd particles embedded in high surface area carbon powders. This is probably

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related to the difficulties associated with the electrochemistry of powder materials, in particular ohmic losses (low conductivity of electrodes made by mixing the powder with an insulating binder such as Teflon; limited diffusion of the electrolyte in the carbon matrix) and large capacitive currents (high surface area). In addition, hydrogen evolution results in an additional anodic current (HER wall) and a cathodic peak corresponding to its oxidation since it diffuses only slowly out of the carbon matrix. Altogether, distorted and complex voltammograms are often obtained which makes it difficult to resolve the electrochemical signals related to the different sorption processes.

The present paper demonstrates that despite these drawbacks, electrochemical measurements are suitable to account for size effects in hydrogen sorption properties of Pd particles embedded in the nanopores of a high surface area graphite powder. Cyclic voltammograms are established for three different particle sizes (2, 6 and 18 nm) over the hydrogen and Pd oxide potential domains and the hydride phase compositions deduced from electrochemical signals are compared to pressure-composition-isotherms recorded by solid/gas techniques.

2. Experimental

High surface area carbon powder HSAG500 from TIMCAL (hereafter designated as C_G) has been used for the synthesis of Pd/ C_G hybrid materials via a chemical wetting procedure. The synthetic method is described in details elsewhere [13]. The C_G powder was impregnated with a tetrachloropalladous acid (H_2PdCl_4) solution and subsequently reduced by heating in an Ar/ H_2 flow at 573 K for 3 h. For further control/growth of the Pd particle size, two heat treatments have been used at 773 and 1023 K for 1 h. Therefore, Pd/ C_G hybrids were synthesized with three different Pd sizes, as function of heat treatment at 573, 773 and 1023 K, respectively.

The influence of thermal treatment on the textural properties of Pd/ C_G hybrids has been determined by nitrogen adsorption isotherm at 77 K using an Autosorb IQ Quantachrome instrument. The specific surface area was obtained by the Brunauer–Emmett–Teller (BET) method and the mean pore size by the Barrett–Joyner–Halenda (BJH) method. The total porous volume was calculated at a relative pressure P/P_0 of 0.99. The textural properties of the pristine carbon and the three Pd/ C_G hybrids are listed in Table 1.

The amount of Pd contained in each samples was determined by Inductively Coupled Plasma–Optical Emission Spectrometry (ICP–OES) and is constant around 10% (cf. Table 1).

Structural characterizations were performed by X-ray diffraction (XRD) using a D8 advanced Bruker diffractometer (Cu $K\alpha$ radiation). The XRD patterns of Pd/ C_G hybrids have been analyzed by the TOPAS software (Bruker AXS Topas 4.2). The Pd lattice parameter has been obtained from the position of the diffraction peaks and the crystallite size by line-profile fitting using the fundamental parameters approach (TOPAS). Microstructural observations were performed by Transmission Electron Microscopy (TEM) with a 200 kV FEG TEM (FEI Technai F20 equipped with a Gatan energy

Imaging Filter, resolution 0.24 nm). The mean Pd particle size has been determined by statistical analyses of several TEM images.

Hydrogen excess sorption properties were determined by measuring the Pressure–Composition–Isotherm (PCI) at 300 K up to 0.1 MPa hydrogen pressure using an automated volumetric device (Autosorb IQ Quantachrome). Before any sorption measurements, the samples were outgassed under secondary vacuum at 423 K for 12 h. The PCI curves were measured twice (i.e. two full adsorption–desorption cycles) with a good measurement repeatability. The samples were degassed under secondary vacuum at 373 K between each hydrogen absorption/desorption cycles to ensure complete hydrogen desorption.

Electrochemical measurements were carried out with a classical 3-electrode cell using an Autolab PGSTAT 30 potentiostat. The reference and counter electrodes were a saturated calomel electrode with KCl (SCE) isolated from the solution by an electrolyte bridge and a platinum wire, respectively. For the sake of convenience, potential values are expressed with respect to the Standard Hydrogen Electrode (SHE), the redox potential of SCE being +0.244 V vs. SHE at 25 °C. The working electrodes were classical powder electrodes (PEs) prepared by pressing on a stainless steel grid (1 cm² in diameter) under 3 tons, ~10 mg of a film made of 90% Pd/ C_G powders and 10% Teflon. The grid was then fixed on an Au wire as current collector. The current intensities of the voltammograms are corrected from the slightly different Pd contents in each PE (mA/mg). H_2SO_4 solutions at 0.1 mol L⁻¹ were prepared from concentrated H_2SO_4 (95%, AnalaR Normapur, Prolabo) and ultra-pure water (18.2 MOhm cm). All the cyclic voltammograms (CVs) were recorded at 0.1 mV s⁻¹, under Ar bubbling and standard ambient conditions. Before starting the CV, the PEs were let to rest 4 h in the solution to insure full impregnation of the carbon matrix by the electrolyte. During this time, the electrodes were held at 0.24 V/SHE to prevent any Pd oxidation/dissolution that could occur at open circuit voltage (OCV). Indeed, Pd/ C_G hybrids usually assume OCVs in the Pd oxide region (i.e. ~0.64 V/SHE in our conditions) and we show in Section 3.4 that extending CVs to these anodic potentials affects the particle size. Polarization at 0.24 V/SHE also presents the advantage to reduce the Pd surface oxides that form when handling the samples in air after synthesis.

3. Results and discussion

3.1. Textural, structural and microstructural characterizations

The BET surface area and total porous volume of pristine C_G and Pd/ C_G hybrids are listed in Table 1. The mean pore size of C_G and Pd/ C_G hybrids is around 3.5–4 nm regardless of the reducing thermal treatment conditions. Compared to the pristine C_G powder, the textural properties (S_{BET} and total porous volume) are slightly decreased by Pd insertion. This can be explained by both the increase of the overall weight and the pore blocking by Pd nanoparticle insertion.

Fig. 1 shows the XRD patterns of the different hybrids. The pristine C_G has a graphitic structure that is not affected by the Pd particle insertion. Pd nanoparticles crystallize in a fcc structure

Table 1
Reducing temperature (T_R), Pd content (wt.%), BET surface area (S_{BET}), total porous volume ($V_{0.99}$), Pd lattice parameters (a) and mean Pd particle sizes of Pd/ C_G hybrids.

Sample	T_R (K)	Pd (wt.%)	S_{BET} (m ² /g) ± 10	$V_{0.99}$ (cm ³ /g)	a (Å)	Mean particle size (std deviation) (nm)	
						XRD	TEM
C_G	–	–	506	0.81	–	–	–
Pd _{2nm} / C_G	573	10.7	432	0.62	3.90 (0.07)	2 ± 1	2.4 (0.6)
Pd _{6nm} / C_G	773	10.7	464	0.77	3.88 (0.04)	6 ± 1	4.8 (1.4)
Pd _{18nm} / C_G	1023	10.2	461	0.78	3.89 (0.01)	18 ± 1	16.6 (7.7)

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