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## Hydrogen absorption properties of carbon supported Pd–Ni nanoalloys

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### ABSTRACT

Carbon supported Pd–Ni nanoalloys with well controlled composition and particle size distribution were synthesized by incipient wetness impregnation method. The Pd-rich nanoalloys (10 and 20 Ni at.%) form a hydride phase at atmospheric pressure and ambient temperature whereas, no hydride formation is observed for higher Ni content (30 at%), as determined by Pressure-Composition-Isotherms and *in situ* X-ray diffraction. Significant thermodynamic changes for hydride forming Pd–Ni nanoalloys are noticed as compared to pure Pd, in agreement with the bulk counterparts: the enthalpy of the hydride formation of Pd–Ni nanoalloys decreases by increasing the Ni content. These thermodynamic changes are not related to downsizing of particles but rather to an alloying effect. The sole effects of particle downsizing are the sloping and the shortening of the plateau observed in the PCI curves.

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### Introduction

The nanostructuring is shown to be an interesting approach for tailoring specific properties of materials in many research topics, such as catalysis, batteries [1] and hydrogen storage [2]. It has been reported that the downsizing of metals/alloys to the nanometric range size, induces thermodynamic changes and enhances the kinetics during their interaction with hydrogen [3–5].

For this purpose, nanosized palladium has been intensively investigated and its interaction with hydrogen is among the most well known [6–9]. Consequently, Pd-based nanoalloys provide excellent systems to explore the combined effect of alloying and nanosizing on hydrogen storage and on

the thermodynamic properties of these materials. Among the most studied candidates as alloying element, Ni and Co are proposed, because both Pd–Ni and Pd–Co are completely miscible bulk systems and form fcc solid solutions in the entire binary phase diagram. However, very few reports have been focused on hydrogen absorption by Pd–Ni and Pd–Co nanoalloys. Only one previous paper has reported the hydrogen sorption properties of carbon supported Pd–Ni nanoalloy (Pd<sub>60</sub>Ni<sub>40</sub>) [10]. The combined effect of alloying and nanosizing on the hydrogen sorption properties of Pd–Co alloys has been already investigated by our group [11,12].

Contrary to nanoscaled materials, bulk Pd–Ni alloys and their interaction with hydrogen are very well documented. Hara et al. reported that by assuming the Fermi energy of

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Pd–Ni to be the arithmetic means of the Fermi energies of pure Pd and Ni, a linear relation between the heat of the hydride formation and the Fermi energies was found [13]. The Fermi energies of Pd–Ni alloys raise by increasing Ni content, thereby, it was concluded that the enthalpy of the hydride formation decreases with increasing Ni content. Similarly, Fukai claimed a correlation between the heat of formation and the electronic energy of alloys, which can be related to the Fermi energies [14].

In order to highlight the effect of downsizing on hydrogen sorption and thermodynamic properties of Pd–Ni nanoalloys, the present work reports the synthesis and characterization of carbon supported Pd–Ni nanoalloys using the incipient wetness impregnation method. The physicochemical properties of Pd–Ni nanoalloys with maximum Ni content of 30 at % were characterized by X-ray diffraction and transmission electron microscopy. The thermodynamic changes of the hydride formation were also determined by volumetric hydrogen sorption method and *in situ* X-ray diffraction.

## Materials and methods

### Synthesis

Pd–Ni nanoalloys were synthesized by the incipient wetness impregnation method. Firstly, the mesoporous carbon host was prepared by soft template route as described elsewhere [15], then it was impregnated with an aqueous solution of the metallic precursors ( $\text{H}_2\text{PdCl}_4$  and  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  with the desired Pd/Ni at.% ratio) under magnetic stirring followed by drying at 60 °C until the total evaporation of the solvent. The metal ions have been reduced at 500 °C under a continuous  $\text{Ar}/\text{H}_2$  flow (0.5 mL/min) for 1 h. Three different composites containing Pd–Ni nanoparticles with the compositions  $\text{Pd}_{90}\text{Ni}_{10}$ ,  $\text{Pd}_{80}\text{Ni}_{20}$  and  $\text{Pd}_{70}\text{Ni}_{30}$  dispersed on the carbon support have been prepared. The total weight of Pd–Ni is 10 wt.% with respect to the total composite mass. For sake of comparison, pure Pd and Ni were also synthesized in the same conditions.

### X-ray powder diffraction

The structural properties of supported Pd–Ni nanoalloys have been determined by X-ray powder diffraction (XRD) using a D8 advanced Bruker diffractometer (Cu  $K_\alpha$  radiation, Bragg-Brentano geometry, Anton Paar chamber TTK450 and Vântec Position Sensitive Detector). In order to characterize the crystallographic changes induced by hydrogen absorption, *in situ* XRD measurements were performed at different temperatures (22, 0, –10 and –20 °C) by stepwise increase of hydrogen pressure. The powder samples were placed in Plexiglas and copper sample holder for measurements at room and cryogenic temperatures, respectively. Prior to any experiment, the chamber was evacuated under primary vacuum and the samples were treated under hydrogen atmosphere to remove oxides layer at the surface [16]. Then, the hydrogen pressure was stepwise increased up to the maximum pressure of 1 bar at fixed temperature. The *in situ* XRD data were acquired with a step size of 0.05°. The XRD patterns have been refined by TOPAS software (Bruker AXS Topas 4.2) to determine the

lattice parameters and the phase evolution under  $\text{H}_2$  pressure using the fundamental parameters approach.

### Transmission electron microscopy

The microstructural observations were performed by Transmission Electron Microscopy (TEM) with a 200 kV FEG TEM (FEI Tecnai F20 equipped with a Gatan energy Imaging Filter, resolution 0.24 nm). The histograms of nanoparticle size distribution and average size have been determined by statistical analyses of several TEM images.

### Hydrogen absorption measurements

The hydrogen absorption properties have been determined by measuring Pressure-Composition-Isotherms (PCI) at different temperatures up to a maximum of 1 bar of hydrogen pressure using an automated volumetric device (Autosorb IQ Quantachrome). Prior to any sorption measurement, the samples were treated under hydrogen atmosphere at room temperature to reduce oxides at the surface of nanoparticles and subsequently degassed at 120 °C to remove water molecules formed during oxide reduction [16]. The PCI curves were measured twice (*i.e.* two full absorption–desorption cycles) with a good measurement repeatability. The hydrogen absorption/desorption is completely reversible for all samples. Hydrogen adsorption on the mesoporous carbon support is negligible under these conditions, therefore, the hydrogen uptake can be entirely attributed to the absorption in nanoalloys. Thus, we have expressed the PCI curves as equilibrium pressure (bar) versus hydrogen sorption capacity of nanoalloys (H/M), which excludes the mass of carbon support.

## Results

### Structure and microstructure

The XRD patterns and typical TEM images with the corresponding histograms of the particle size distribution of the supported Pd–Ni nanoalloys ( $\text{Pd}_{90}\text{Ni}_{10}$ ,  $\text{Pd}_{80}\text{Ni}_{20}$  and  $\text{Pd}_{70}\text{Ni}_{30}$ ) are shown in Fig. 1. For the sake of comparison, XRD patterns and TEM images of pure Pd and Ni nanoparticles synthesized under similar conditions are also shown.

The XRD patterns (Fig. 1a) confirm that all supported Pd–Ni nanoalloys adopt a fcc crystal structure ( $Fm\bar{3}m$ ) typical for both pure Pd and Ni bulk metals. The diffraction peaks of Pd–Ni nanoalloys are shifted to higher  $2\theta$  angles as compared to pure Pd, in agreement with bulk alloys [17]. This indicates the formation of Pd–Ni nanoalloys in our synthetic conditions.

The TEM images show that the nanoparticles are well dispersed on the carbon host, irrespective of composition. The average size of Pd–Ni nanoparticles (Table 1) does not show a clear trend with composition. Only pure Ni nanoparticles show a very large size distribution with an average size of ~8.0 nm, which is higher than pure Pd nanoparticles and Pd–Ni nanoalloys.

The lattice parameters for all Pd–Ni compositions are listed in Table 1 while their evolution as function of Ni

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