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Hydride phase formation in carbon supported palladium hydride nanoparticles by *in situ* EXAFS and XRD

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Abstract. In the current work we present a detailed analysis of the hydride phase formation in industrial Pd/C nanocatalysts by means of combined *in situ* X-ray absorption spectroscopy (EXAFS), X-ray diffraction (XRD) and volumetric measurements for the temperatures from -10 to 50 ℃ in the hydrogen pressure range from 0 to 1000 mbar. α- and β- hydride phases are clearly distinguished in XRD. For the first time, H/Pd atomic ratio were obtained by theoretical fitting of the near-edge region of the absorption spectra (XANES) and compared with volumetric measurements.

1. Introduction

Palladium-based nanomaterials play an important role in various fields such as medicine, chemistry, biology and catalysis [1]. In a number of industrial application, supported palladium nanoparticles catalyse hydrogenation reactions (e.g. hydrogenation of alkenes). In the presence of hydrogen, Pd catalyst may undergo one of its hydride phases which nature affects its catalytic performance [2]. Determination of the hydride phase in the palladium Pd nanoparticles is an important step in order to investigate the active phase of the nanocatalyst. Being element specific, EXAFS technique reflects Pd-Pd interatomic distance increase which is proportional to the number of hydrogen absorbed in the nanoparticle and is not affected by the molecular hydrogen adsorbed on the support surface. At the same time, phase specific XRD allows to discriminate between α- and β- hydride phases even in the mixed phase region [3], while EXAFS is able to detect the increase of the average Pd-Pd distance upon H intercalation [4]. In the current work we present a detailed investigation by means of *in situ* EXAFS and XRD of the hydride phase formation in industrial catalysts (Chimet S.p.A.) consisting of palladium deposited on an amorphous carbon support. The X-ray data is complemented by volumetric measurements.

2. Materials and methods

5 wt.% Pd on carbon catalyst were supplied by Chimet S.p.A. and it has been prepared by deposition-precipitation method on a wood-based activated carbon (surface area = 980 m^2g^{-1}; pore volume = 0.62 cm^3g^{-1}). Transmission electron microscopy measurements indicated the averaged size of the nanoparticles to be in the range of 3 – 4 nm. Pd black powder was used as a reference sample.
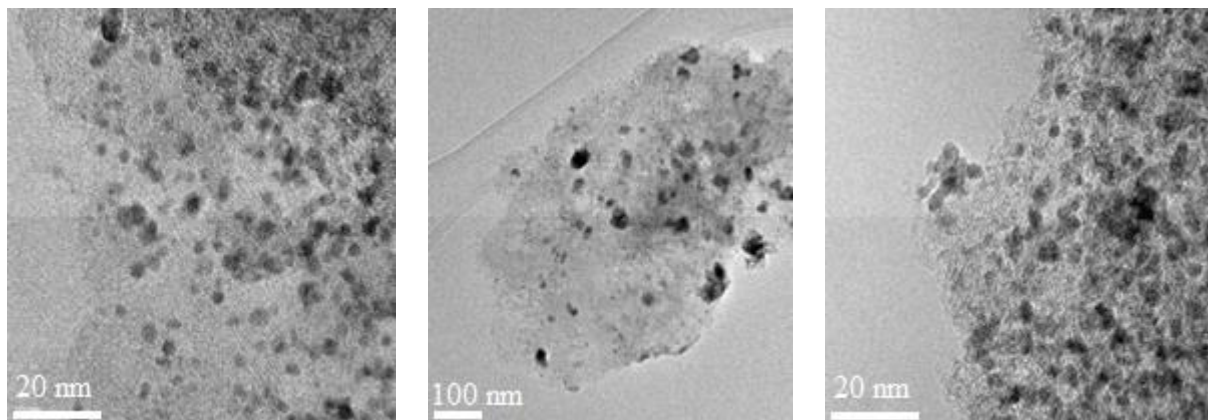
**Figure 1.** TEM images of the Pd/C nanocatalyst.

EXAFS and XRD data were collected at the BM01B (Swiss-Norwegian Beamline) of the European Synchrotron Radiation Facility (ESRF), Grenoble, France. Sample was loaded inside 1 mm glass capillary connected to a remotely controlled gas rig enabling to control the hydrogen pressure during the experiment. Nitrogen blower positioned above the sample was used to control the temperature. EXAFS spectra were collected in the transmission mode in the energy range around the Pd K-edge from 24.1 to 25.4 keV. Pd foil was measured simultaneously for energy calibration. Analysis of EXAFS spectra was performed with the Demeter software [5]. XRD patterns were measured using a λ = 0.50544 Å radiation and collected by a 2D Image Plate detector. Rietveld analysis of the diffraction profiles was performed by means of Jana2006 code [6].

Synchrotron measurements was complemented with volumetric adsorption isothermal data measured on a Micromeritics ASAP 2020 sorption analyser connected to a H2 cylinder (99.9999vol% purity, Rivoira) in the NIS centre of the University of Turin.

3. Results and discussion

3.1. EXAFS analysis

Palladium K-edge absorption spectra and diffraction patterns were collected during the formation of the palladium hydride induced by stepwise increasing of the hydrogen pressure from 0 to 1000 mbar. The evolution of absorption and diffraction data are shown in Figure 2 (left and righ part, respectively). The increase of Pd-Pd interatomic distances leads to the shift of the EXAFS oscillations to the lower energies. At the same time, indicative features of hydride phase are observed in the near-edge (XANES) region, which is in agreement with our previous results [7, 8]. Single-shell analysis of EXAFS indicates Pd-Pd distance increase from 2.74 to 2.82. The obtained coordination number N = 9.3 is consistent with the particle size of about 3 nm [9]. Debye-Waller parameter increase from 0.005 to 0.008 is caused by the coexistence of α- and β- phases with slightly different interatomic parameters. As determined from XRD, the difference $R_\beta - R_\alpha$ is about 0.05 Å: this difference is beyond the limit of standard EXAFS resolution of local structure distortion [10] with relatively short Δk interval (up to 12 Å $^{-1}$).
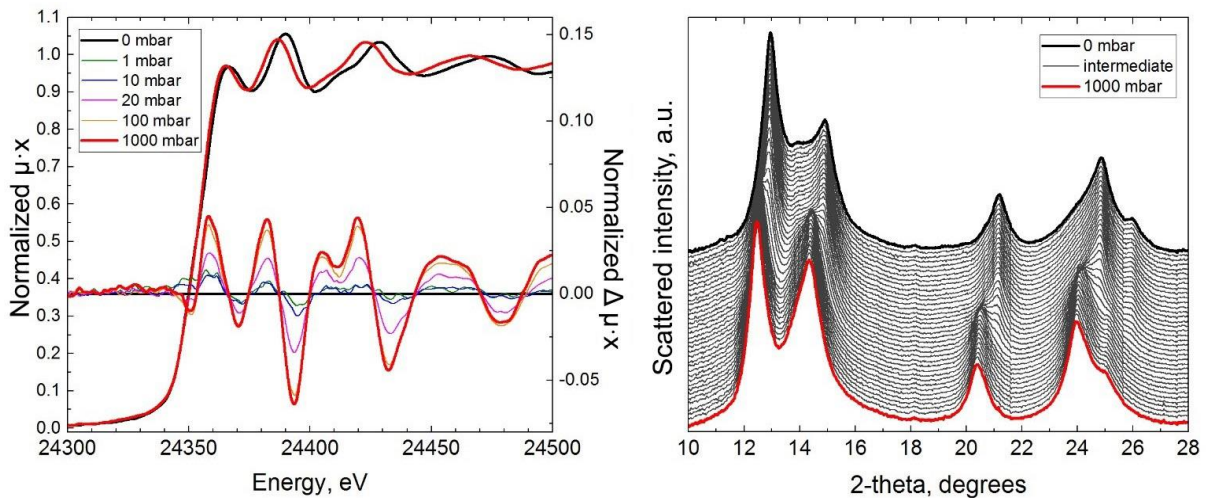
Figure 2. (left) Pd K-edge XANES and difference XANES taken at 20 °C. Black and red lines correspond to bare and hydride (final) palladium nanoparticles respectively, coloured lines represent intermediate states. (b) X-ray powder diffraction patterns from bare (black) to hydride (red) palladium nanoparticles taken at 20 °C. For better visualization, the patterns are shifted in vertical direction.
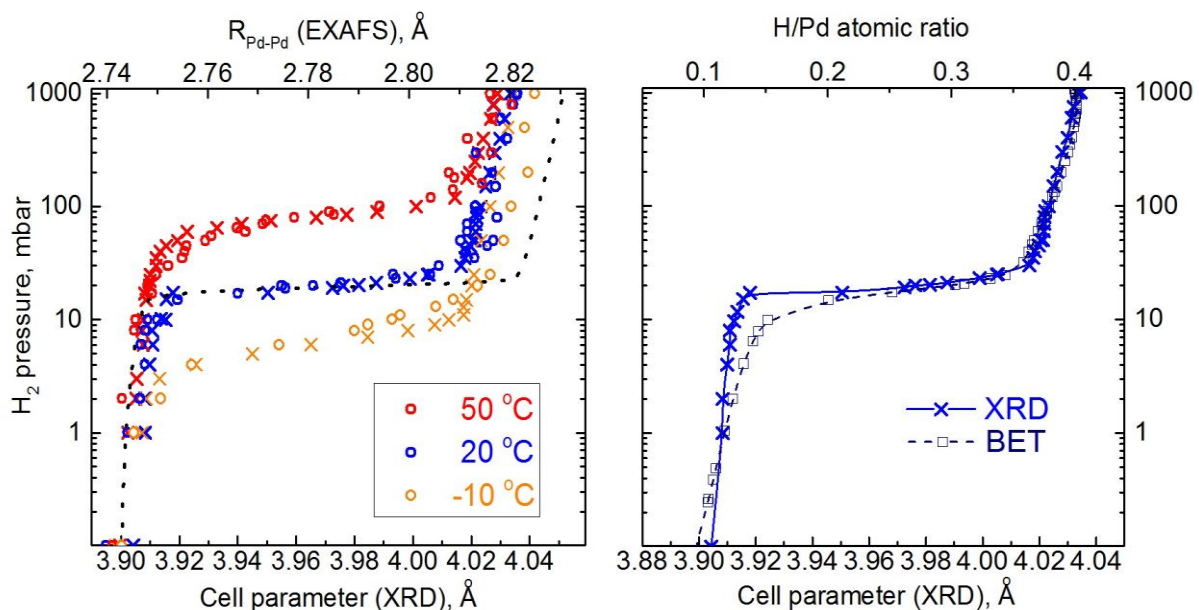
Figure 3. (left) Comparison of Pd-Pd interatomic distances obtained from EXAFS (circles) with cell parameter determined by XRD (crosses). Black dashed curved corresponds to the Pd black isotherm. (right) XRD measurements (crosses, blue line) vs volumetric data (squares. dashed navy line).

3.2. XRD analysis

In order to reduce the number of variables, Rietveld refinement was performed in several steps. At the first step, initial and final XRD profiles (palladium in the metallic and hydride form, respectively) were used to obtain profile shape, asymmetry and background. Then, cell parameters (for α- and β- phases), zero angle shift and phase concentrations were refined for each pattern. At the last step zero shift values were averaged and fixed, and only cell parameters of α- and β- phases and their concentrations were optimized.

For comparison with EXAFS averaged cell parameters were calculated. Palladium hydride isotherms obtained by single-shell Fourier analysis of EXAFS and Rietveld analysis of XRD data are shown in Figure 3 (left). To quantify the hydrogen present in the palladium at each pressure, volumetric measurements were performed. Assuming that the amount of hydrogen adsorbed in the carbon support is linearly proportional to the hydrogen pressure, this contribution was subtracted resulting in a similar isotherm as obtained from XRD and EXAFS (Figure 3 right).

3.3. Volumetric measurements
Volumetric data shown in figure 3 (right) provide quantitative information on the amount of hydrogen absorbed by palladium nanoparticles which allows to derive how interatomic distance depends on the hydrogen loading. However, several difficulties in conducting volumetric measurements exists in the case of the nanoparticles. First, the method is not element selective, and one has to perform separate measurement for the support itself, which is needed to be subtracted in order to obtain proper Pd-H isotherm. Second, experimental data reflects also adsorption of hydrogen on the surface of nanoparticles, and on the non-palladium species in the sample. This results in the non-zero H/Pd ratio for hydrogen pressures even less than 0.1 mbar. Third, the method cannot be applied in reaction conditions to estimate the H/Pd loading in the working nanocatalyst.
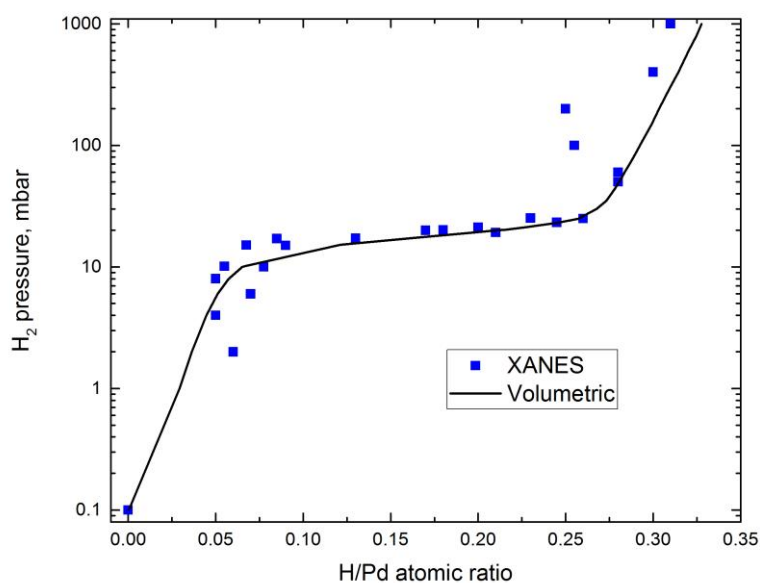
Figure 4. Comparison of H/Pd atomic ratio during hydrogen absorption by the palladium nanoparticles obtained by volumetric method (black line) and theoretical fitting of XANES (blue squares). Volumetric curve is shifted by 0.1 to lower H/Pd ratio.

3.4. XANES fitting
As was shown in figure 2 (left) the presence of hydrogen can be monitored by difference XANES. In order to obtain hydrogen concentration we used multidimensional interpolation approach of FitIt-3 [11]. Following the procedure described in our previous work [8] the hydrogen concentration were fitted to obtain the minimum of root-mean-square difference between experimental and theoretical [12] difference spectra. The interatomic distances were set as obtained from EXAFS, while hydrogen loading x in theoretical models of PdH_x clusters was changing from 0 to 0.5. The results of the fit are presented in Figure 4 together with volumetric data. In order to overcome the effect of non-zero hydrogen absorption in the low-pressure region, discussed in section 3.3, volumetric curve was shifted by 0.1 to lower H/Pd ratio.

4. Conclusions

We have performed a systematic study of hydride formation in the industrial palladium nanocatalysts by means of element-specific EXAFS and XANES, phase-specific XRD performed simultaneously on the same sample, measured under the same temperature and hydrogen pressure and independently complemented by volumetric measurements. The results obtained from these three techniques are in excellent agreement. We illustrate the advantage of diffraction measurements to get detailed information on the phase fractions which cannot be obtained from EXAFS.

We underline the importance of XANES analysis and show the indicative features of hydride formation region in the near edge region. Quantitative analysis of XANES using theoretically calculated spectra was shown to be in a good agreement with volumetric data. This shows for the first time, that XANES data can give quantitative information on H/Pd ratio in the conditions where volumetric measurements cannot be performed, highlighting the relevance of these method for in situ catalytic experiments.

The obtained pressure-composition isotherms provide deeper understanding of Pd-H phase transitions in the palladium nanoparticles and can be used as a reference for more complex catalytic experiments.

5. Acknowledgments

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