

# Hydrogen storage properties of Pd nanoparticles / carbon template composite.

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## Introduction

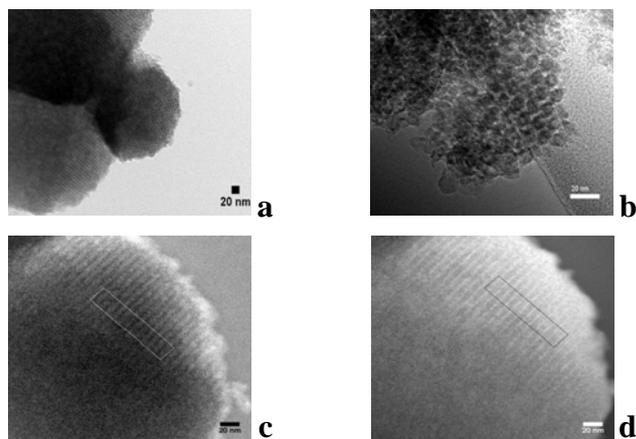
Theoretical studies predict outstanding hydrogenation properties for hybrid carbon/metal compounds [1,2]. In such compounds, we will take advantage of both adsorption and absorption reactions and of the fact that a nanosized metal is formed. Indeed, theoretical calculations have shown that decreasing the size of metallic clusters can dramatically change their thermodynamic properties toward hydrogen absorption [3,4]. The aim of this work is to design new materials with improved hydrogen storage performance in a wide range of temperature and pressure. We prepared a composite material made of a template ordered porous Carbon Template (CT) and nano-size hydride forming metal (e.g. Pd) which was formed inside the CT porosity, and we studied the hydrogenation properties.

## Experimental

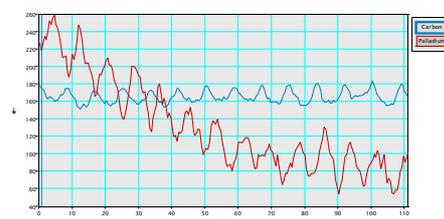
The carbon template has been prepared by a replica technique using SBA-15 as silica template and propylene as carbon precursor. The carbon replica was obtained by CVD of propylene at 750 °C and later removing the Silica by the mean of HF, as widely described elsewhere [5-7]. In order to disperse Pd nanoparticles in the carbon porosity, the CT was impregnated with a solution of acid tetrachloropalladic in acetone to get 10 wt% Pd content. Next, the impregnated carbon template was reduced by heating in an Ar/H<sub>2</sub> flow at 573K for 8 hours. The CT-Pd composite has been characterized by transmission electron microscopy (TEM) and its hydrogen storage properties have been investigated by Pressure-Composition-Isotherms (PCI) and Thermal Desorption Spectroscopy (TDS) measurements [8]. For the PCI measurements, between each cycle, hydrogen was desorbed from the samples by heating overnight at 150°C under primary vacuum.

## Results and discussion

Energy filtered bright field images (EFTEM) of the Pd-free CT show the arrangement of the carbon porosity (Figs. 1a and 1b). Bright fringes correspond to carbon channels lying perpendicular to the incident beam, whereas honeycomb pore structures are observed for the carbon channels aligned parallel to the incident beam (Fig. 1a). Fig. 1b shows a magnification of the hexagonal structure of the carbon channels.



**Fig.1 (a,b) EFTEM images of Pd-free Carbon Template. (c,d) EFTEM cartography images of CT-10 wt% Pd composite (c)C\_K map, (d) Pd\_M4,5 map**

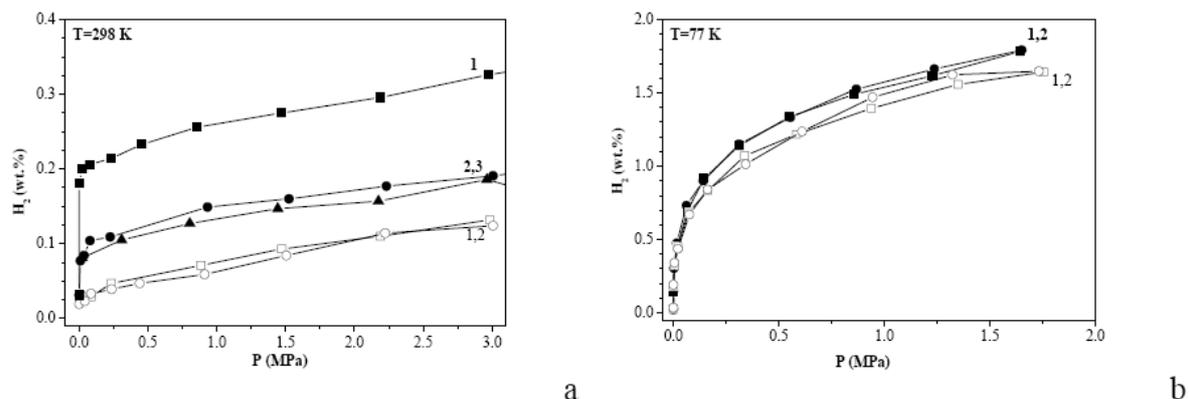


**Fig. 2 C and Pd (transmitted electron) intensity as a function of distance inside the insets of Fig. 1c and 1d**

Palladium dispersion into the CT channels in CT-10 wt% Pd composite has been confirmed by the EFTEM. Elemental maps of carbon and palladium have been recorded using respectively the C K and the Pd M4,5 edges respectively, and the three window method.

The carbon dark field and palladium bright field map (Fig. 1c,d) are completely congruent. Fig 2 shows the intensity variations of carbon and palladium signals along the insets of Figs. 1c and 1d. Each maximum of the carbon intensity corresponds a minimum of Pd one and vice versa.

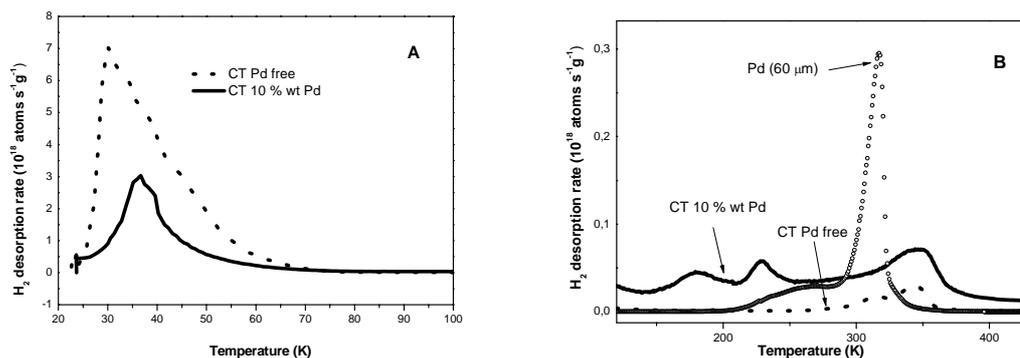
The hydrogen uptake was studied at 298 K and 77 K for both CT and CT-10 wt% Pd composite samples (Fig. 3). At 298 K (Fig. 3a), filling of CT with 10wt% nanocrystalline Pd leads to an increase of the hydrogen uptake (0.32 wt% maximum value), respect to the Pd-free CT (0.13 wt% maximum value), of 0.19 wt% for the first hydrogenation cycle. For the second and following cycles the increase is equal to 0,054 wt. %. At 77 K (Fig. 3b), the hydrogen storage capacity of the Pd/CT composite (1.6 wt% at 1.6 MPa) is slightly lower than that of the Pd-free CT (1.8 wt% at 1.6 MPa).



**Fig. 3** PCI sorption curves of the Pd-free carbon template (open symbols) and CT-10 wt% Pd composite (Full symbols) at 298 K (a) and 77 K (b). Squares, circles and triangles stand for first, second and third Hydrogenation cycle respectively. Cycle numbers are also given directly in the plot.

After cooling under H<sub>2</sub> pressure of 0.075 MPa to 20 K, the hydrogen desorption properties of the CT-10wt% Pd composite and Pd free-CT sample have been investigated by TDS from 20 K to 470 K with a heating rate of 0.1 K/s. Fig. 4a shows the TDS spectra of CT-Pd free and CT-10wt% Pd composite in the range 20-100 K. Both samples exhibit a single desorption peak which are characteristic for physisorbed H<sub>2</sub>. The difference in their relative intensities could be attributed to a lower accessible surface area for CT-10wt% Pd composite with respect to that of CT-Pd free. Fig 4b shows the TDS spectra of both composites in the range 100-400 K. For comparison purposes, the TDS spectrum from microcrystalline Pd-hydride powder of 60μm in particle size is also given. The TDS spectrum of Pd-hydride powder exhibits a double peak structure related to hydrogen desorption from β-hydride (low-temperature peak at 260K) and from α+β phase transformation (high temperature peak at 310K) [9]. It can be noted that the TDS spectrum of CT-10wt% Pd composite shows two peaks between 160 and 260 K and one between 270 and 370 K while the Pd free-CT composite presents only the peak between 270 and 370 K.

The two-peak structure (at 160 and 260 K) for the CT-10 wt% Pd composite is attributed to H-desorption from Pd nanoparticles since no peak is observed with the CT Pd-free sample. This confirms that the hydrogenation reaction takes place with the nanosized Palladium present in the CT porosity. The shift to lower temperature as compared to microcrystalline Pd (260 and 310 K) could be related to the smaller size of the Pd particles dispersed in the Carbon Template with respect to palladium powder. However, we can not exclude some influence of the interaction between CT and Pd nanoparticles on the hydrogen desorption from CT-10wt% Pd composite. The peaks observed around 350K for the CT samples with and without Pd may be attributed to some water desorbed from the carbon sample and/or the TDS chamber walls which decomposition in the mass spectrometer leads to the formation of hydrogen.



**Fig. 4** TDS desorption curves of the Pd-free carbon template (dash line) and CT-10 wt.% Pd composite (continuous line) from 20 to 100 K (a) and from 100 to 400 K (b). The TDS spectrum of Pd-hydride powder (60  $\mu\text{m}$ ) is also given in (b) as a open circles

### Conclusions

Pd nanoparticles have been deposited by chemical impregnation into the channels of a Carbon Template leading to an enhancement of the hydrogen storage capacity at RT. The reversible hydrogen capacity decreases for subsequent hydrogenation cycle but it is still higher than that of the Pd-free carbon template. In contrast, the CT-10 wt% Pd composite shows a lower hydrogen storage capacity compared to that of the Pd-free carbon template at 77 K, the origin of that slightly difference in the hydrogen uptake can be explained in term of a smaller specific surface area. These results have been confirmed by TDS measurements which have also shown that Pd nanoparticles desorb hydrogen at lower temperatures than microcrystalline Pd powder.

### Acknowledgements

The present work has received funding from the European Community's Sixth Framework Program trough a Marie Curie Research Training Network (MRTN-CT-2004-512443)

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