



Preparation of Pd/C catalysts for hydrogenation reactions: a step by step of the impregnation and reduction processes monitored by EXAFS, UV-Vis and Raman spectroscopies

Experiment number:
CH-2350

Beamline: BM26 DUBBLE	Date of experiment: from: 01/12/2006 to: 07/12/2006	Date of report: 06/08/2010
Shifts: 18	Local contact(s): Sergey Nikitenko	<i>Received at ESRF:</i>

Names and affiliations of applicants (* indicates experimentalists):

C. Lamberti,* G. Agostini, E. Groppo, S. Bordiga, S. Bertarione, F. Rotunno, R. Pellegrini, G. Leofanti, G. Ricchiardi and B. Weckhuysen

Dipartimento di Chimica Inorganica, Fisica e dei Materiali, Università di Torino via P. Giuria, 7 I-10125 Torino, Italy

Chimet SpA - Catalyst Division, Via Pesciola 74, Viciomaggio Arezzo, I-52040 Italy

Department of Inorganic Chemistry, Utrecht University, Debye Institute, Sorbonnelaan 16, NL-3505 TB Utrecht, The Netherlands

Report:

During this experiments three different systems of Pd nanoparticles have been studied by XENES and EXAFS spectroscopy in order to investigate the local structure.

The first system investigated is constituted of Pd nanoparticles supported on $\text{SiO}_2\text{-Al}_2\text{O}_3$ in order to understand the effects of the activation temperature and activation atmosphere (air or H_2) on the particle size distribution, the fraction, and the type of exposed surface sites of Pd supported nanoparticles. The EXAFS allowed to followed the $\text{Pd}^{2+} \rightarrow \text{Pd}^0$ reduction by thermal decomposition and upon treatment in H_2 . The particle dimension extracted from the coordination number of the first shell mathed pretty well with the particle size distrition obtained by TEM. This agreement is very important because EXAFS measuremts provide for the low static of the TEM particle size distribution.[1]

Extremely small Pd nanoparticles, obtained from reduction of $\text{Pd}(\text{OAc})_2$ precursor inside two highly cross-linked polymers, namely a poly(ethylstyrene) and a poly(4- vinylpyridine), have been analyzed. The structural properties of the Pd/polymer composites have been followed during all the synthetic steps. These measurements (combined with TEM, FT-IR and, UV-vis) demonstrated that the nature of the polymericmatrix has a strong influence on the formation of the Pd nanoparticles and affect their final properties, in terms of particle size, electronic properties, and type and fraction of accessible surface sites.[2]

Finally, deep study was performed on the the preparation of Pd catalysts, supported on $\gamma\text{-Al}_2\text{O}_3$ and on active carbons from wood (Cw) and peat (Cp). This work consists of four successive parts: the investigation of (i) the solid precipitated phase (in the absence of substrate), (ii) the precipitated Pd^{2+} -phase on the supports as a function of Pd loading from 0.5 to 5.0 wt%, (iii) the Pd^0 -phase formed upon reduction with with chemical agents from liquid (HCOONa , NaBH_4 and H_2) and, (iv) gas phases in H_2 .

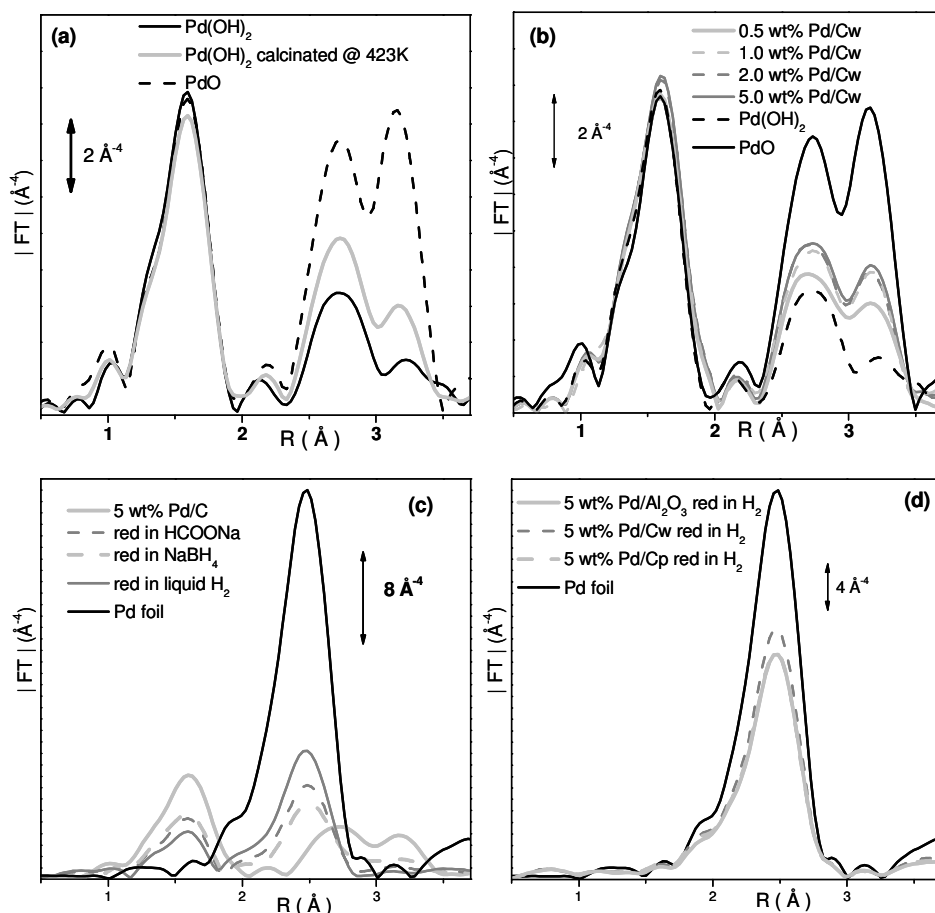
(i) The unsupported precipitated phase, $\text{Pd}(\text{OH})_2$, represents a model material for the active supported phase. Thermal treatments at increasing temperature of this phase cause

progressive water loss and resulted in a progressive increase in crystallinity typical of a defective PdO-like phase. The EXAFS spectrum of the final catalysts has been found to be intermediate between that of the unsupported amorphous Pd^{2+} -polynuclearhydroxo complexes and that of the $\text{Pd}(\text{OH})_2$, see part (a) of the figure.[3]

(ii) Independent of the support, EXAFS was not able to evidence any fraction of reduced metallic Pd, meaning that all Pd is in the 2^+ -oxidation state within the sensitivity of the technique. The Pd local environment of the as-precipitated samples changes slightly as a function of Pd loading from 0.5 to 2.0 wt %: at higher loadings, no further modification has been observed, see part (c) of the figure.[3]

(iii) The three different chemical agent in liquid phase are not able to reduce completely the Pd nanoparticles, the decrease of the features of the PdO phase and corresponding increasing of Pd-Pd contribution due to Pd⁰ phase has been observed. For the three supports the following reduction strength scale holds: $\text{NaBH}_4 < \text{HCOONa} < \text{H}_2$ from the liquid phase. In all cases this difference is well established, with the only exception of the Cw support, where NaBH_4 and HCOONa have the same effect, see part (c) of the figure.

(iv) After reduction in an H_2 atmosphere, no PdO phase has been detected and two trends have been observed: the Pd nanoparticles dimensions tends to decrease with increasing Pd concentration(less significantly on Al_2O_3 -supported samples and more significantly on carbon-supported ones) and, the Pd particle dimension depends on the carrier following the sequence $\text{Al}_2\text{O}_3 \cong \text{Cp} > \text{Cw}$ according to the increasing palladium-support interaction strength, see part (d) of the figure.[3]



[1] G. Agostini, A. Piovano, E. Groppo, C. Lamberti et al. *Langmuir*, **26** (2010) 11204.

[2] E. Groppo, G. Agostini, C. Lamberti et al. *Chem. Mater.*, **22** (2010) 2297.

[3] G. Agostini, E. Groppo, C. Lamberti et al. *J. Phys Chem. C*, **113** (2009) 10485.