

# PHYSICOCHEMICAL CHARACTERIZATION OF CATALYTIC PALLADIUM SUPPORTED ON CHITOSAN HOLLOW FIBER AND DIFFUSION PROPERTIES

*Francisco Peirano Blondet*<sup>(1)</sup>, *Thierry Vincent*<sup>(1)</sup>, *Pierre Gaudon*<sup>(2)</sup>,  
*Jean Marie Taulemesse*<sup>(2)</sup>, *Eric Guibal*<sup>(1)</sup>

(1) Ecole des Mines d'Alès, Laboratoire de Génie de l'Environnement Industriel,

(2) Ecole des Mines d'Alès, Centre de Matériaux de Grande Diffusion  
6 avenue de Clavières, F-30319 Alès CEDEX, France

## Abstract

Palladium nanoparticles immobilized on chitosan have been used for hydrogenation reactions. Chitosan has been selected as a support due to its high sorption capacity. The catalytic fibers were prepared by immobilizing palladium on glutaraldehyde cross-linked chitosan fibers followed by an *in-situ* chemical reduction. The present study focuses on screening the parameters for catalytic hollow fiber preparation. Several parameters related to catalytic hollow fiber (CHF) manufacturing have been carried out in this study. Catalytic fibers were characterized by various amounts of palladium. Different techniques were used to characterize these catalytic membranes in terms of: (a) diffusion properties (diffusion of vitamin B12, cyanocobalamin, a non reactive molecule); and (b) physical and physico-chemical properties (scanning electron microscopy, transmission electron microscopy, X ray diffraction and X-ray photoelectron spectroscopy). Microscope observations coupled to X-ray diffraction show the size of palladium nanoparticles and their distribution in the fiber. With a high palladium content the distribution of the catalytic metal was almost homogeneous through the fiber section while with a low Pd loading the metal was mainly located on the internal wall of the hollow fiber. The amount of palladium also influences the size of nanoparticles. Palladium distribution is a key parameter since it may affect the accessibility of the substrate to palladium crystals, but also the diffusion of hydrogen from the outer compartment to the inner part of the hollow fiber where the substrate solution is flowing.

Key words: Chitosan hollow fibers, palladium nanoparticles, catalyst, hydrogenation, microscopy, diffusion properties

## Introduction

Chitosan hollow fibers have been carried out for the catalytic hydrogenation of nitrophenol in water using palladium as the catalytic metal, after chitosan had been tested in the form of flakes [1]. The metal is immobilized in/on the fiber; the solution to be treated is flowed through the lumen of the fiber while the hydrogenation reagent (sodium formate, hydrogen gas) is maintained in the outer compartment of the system. Though these preliminary results showed interesting perspectives, the transfer of the process in solvent systems for the hydrogenation of nitrotoluene has shown a great variability in the conversion performances with small changes in the aging of the fiber and experimental parameters.

## Material and Methods

### Preparation of chitosan hollow fibers

Chitosan hollow fibers have been prepared using a previously described procedure [2] derived from Agbo and Quin [3] and Modrzejewska and Kaminski [4]. Chitosan was dissolved in acetic acid solution (5 % w/w) at the concentration of 7 % (w/w). The solution was filtered to remove non-dissolved material and the viscous solution was de-bubbled under vacuum. The solution was then extruded into an alkaline coagulation bath, the external part of the fiber was first neutralized and the inner part of the extruded material was not coagulated. The core of the fiber was removed using air flow, followed by alkaline treatment. The fiber was finally rinsed and was stored in NaOH.

### Conditioning of chitosan hollow fibers

Chitosan being soluble in hydrochloric acid solutions (the solution to be used for palladium immobilization) it is necessary to reinforce the stability of chitosan fibers using a cross-linking treatment. A glutaraldehyde solution has been used for the cross-linking of hollow fibers. A Schiff base reaction takes place between amine groups of the polymer and the aldehyde functions of the cross-linking agent. The cross-linking ratio (herein defined by the ratio between amine groups and aldehyde in the batch mixture) strongly affects the mechanical properties of the polymer when it is conditioned in the form of gels. Indeed, additional bonds between polymer chains make the material more easily breakable. The breakability of the fibers strongly depends on the cross-linking treatment. The fibers were cross-linked by flowing at high velocity (flow rate: 1.5 ml min<sup>-1</sup>; flow velocity: 3.5 10<sup>3</sup> m h<sup>-1</sup>) 50 mL of diluted glutaraldehyde solution (0.25 %) through the lumen of the fibers. The high flow velocity is supposed to facilitate the reaction of the cross-linking agent with the amine groups on the entire length of the fiber and to prevent the cross-linking not being homogeneous along the fiber.

### Palladium immobilization and palladium reduction

Palladium chloride solutions were prepared in HCl solutions controlling the pH to 2, which was the optimum pH for metal sorption due to favorable electrostatic balance between protonated amine groups of chitosan and anionic chloropalladate species [5]. The palladium solution was flowed through the fiber (under recirculation) at high speed (to facilitate identical yields of Pd sorption along the entire length of the fiber). The amount of metal used (compared to the number of amine groups) was varied to investigate the influence of Pd loading on catalytic efficiency and more specifically to evaluate how this parameter can control the rationale use of Pd (measuring the turnover frequency).

The content of Pd on the fibers was evaluated by the mass balance equation (considering the initial and final concentrations of Pd solutions flowing through the fiber) during metal sorption step and compared to mineralized fibers (fibers loaded with Pd after metal reduction were reacted by concentrated HNO<sub>3</sub> and analyzed for Pd content using ICP-AES analysis). The difference in Pd content between the two methods did not exceed 5 %.

The reduction treatment consisted in passing through the fiber hydrogen gas that was produced by reaction of 250 ml of sulfuric acid solution (0.5 N) with 100 mg of zinc as a fine powder.

### Fibers Characterization

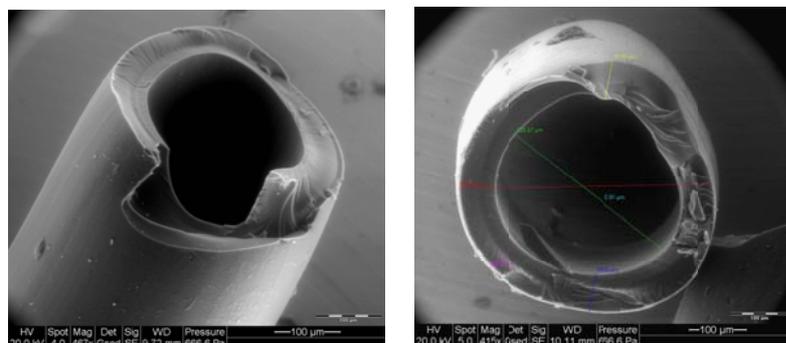
Catalytic hollow fibers were characterized by Environmental Scanning Electron Microscopy Quanta 200 FEG, (FEI company) equipped with an OXFORD Inca 350 Energy Dispersive X-ray microanalysis (EDX) system. Transmission Electron Microscopy was carried out with a JEOL 1200 EX (120 KV). X ray diffraction with a D8 Bruker diffractometer ( $\theta$ - $\theta$ , copper tube,  $\lambda = 1.54 \text{ \AA}$ , scintillator detector) and X-ray photoelectron spectroscopy XPS measurements were carried out with a Physical Electronics spectrometer Dual Anode X-rays Source.

## Results and Discussion

### 1.-Fiber dimensions

The internal diameter of wet fibers was  $400 \pm 20 \text{ }\mu\text{m}$  and the thickness of fiber walls was  $80 \pm 5 \text{ }\mu\text{m}$ . After drying, the internal diameter of the fibers decreased to  $200 \pm 15 \text{ }\mu\text{m}$  and the thickness of fiber walls was  $25 \pm 4 \text{ }\mu\text{m}$ .

Figure 1 shows Environmental Scanning Electron Microscopy (ESEM) photos of catalytic hollow fibers. This ESEM allows samples to be analyzed at pressures and humidity which approach normal laboratory conditions and avoids experimental artifact. Environmental mode and Pelletier system allow working in real humidity conditions.

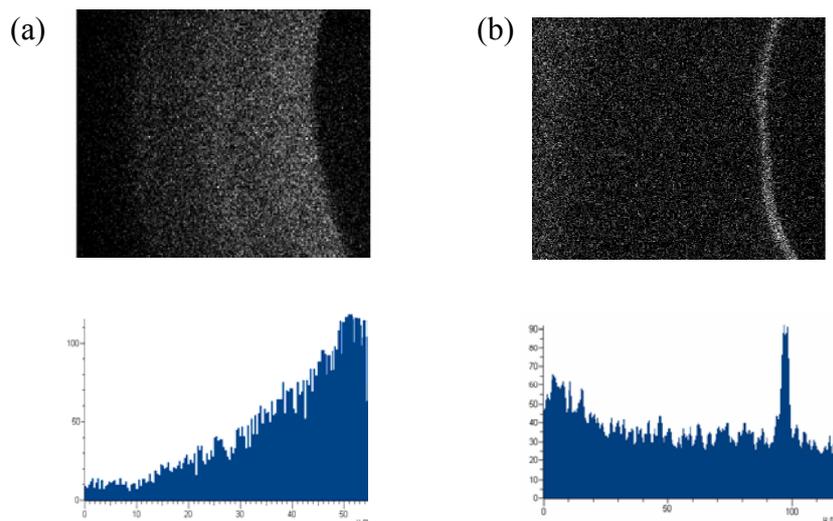


**Figure 1 :** SEM environmental Catalytic hollow fiber photos

### 2.- Pd distribution

Palladium distribution in the fiber was investigated by Transmission Electronic Microscopy (TEM) and electronic Environmental Scanning Electron Microscopy (ESEM). The EDX system can be used to acquire qualitative or quantitative spot analyses and qualitative or quantitative X-ray elemental maps and line scans.

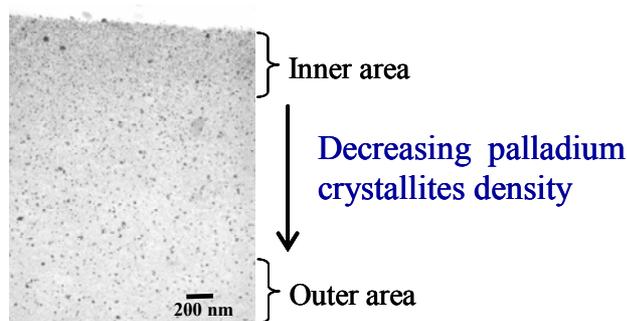
Figure 2 shows a micrograph of the fiber and the distribution of Pd along a section of the fiber for two different Pd loadings.



**Figure 2 :** Palladium distribution determined by EDX and palladium distribution scan lines. (a) High palladium content fiber; (b) Low palladium content fiber.

With high Pd loading the distribution of the catalytic metal was almost homogeneous along fiber section, while at low Pd loading the metal was mainly located at the internal wall of the hollow fiber. This is due to the impregnation procedure used for metal immobilization: the impregnation solution was circulated at high flow rate through the lumen of the fiber. As a consequence, the contact time was not large enough to let the metal diffuse into the whole thickness of the fiber and the metal was accumulated at the inner part of the fiber (clear-tone areas on the microphotographs).

Figure 3 shows a microphotograph by electronic transmission microscopy (TEM). The higher distribution at the internal part than external part of the fiber is clearly observed. Palladium density was obviously higher at the core side than at the periphery side shell.



**Figure 3 :** Palladium distribution determined by TEM

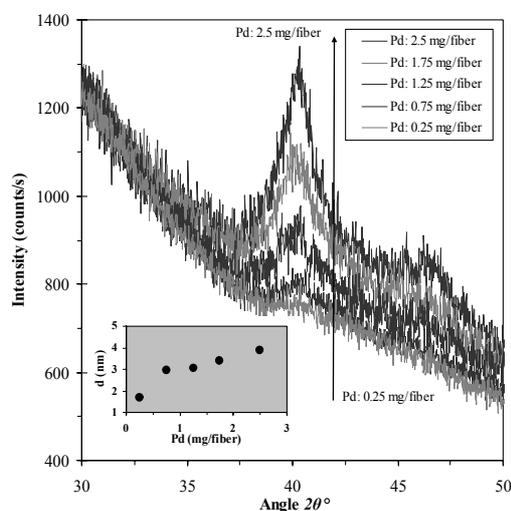
The distribution of Pd is a key parameter since it may affect (a) the accessibility of Pd crystals for the substrate, but also (b) the diffusion of hydrogen from the outer compartment of the fiber to the inner part of the hollow fiber where the substrate solution is flowing. A homogeneous distribution could favor hydrogen transfer, enhancing  $H_2$  jumps between Pd crystals; on the other hand, the Pd immobilized on the outer layers of the fiber may be difficultly accessible for diffusing substrate: in the case of non-accessible (or poorly accessible) Pd crystals, the TOF (turn over frequency), which is a criterion for the evaluation of the effectiveness of Pd use for the hydrogenation reaction, may be significantly affected.

### 3.- Size of Pd nanoparticles

Another important criterion that was pointed out by several studies is the influence of metal content on the size of the crystals: it is frequently cited that increasing the metal content can contribute to increase the size of Pd crystals. High loadings may also cause the formation of aggregates, which are usually less reactive than single nano-size crystals. TEM observations coupled to Wide Angle X-ray Diffraction (WAXD) show the size of palladium nanoparticles. The fibers prepared with different loadings of Pd have been characterized by X-ray diffraction analysis. The full width at half maximum of the band at the identification peak ( $\theta = 20.075$ ) allows determining the size of crystallites using the Scherrer equation. Wide angle X-ray scattering analysis (WAXS) is also frequently used: the Scherrer equation allows calculating the crystal diameter ( $d$ , nm) in function of the X-ray wavelength (nm), the full width at half maximum ( $\beta(\theta)$ , rad) of the identification peak, the diffraction angle and ( $\theta$ , rad) and  $k$  a constant typical of the equipment:

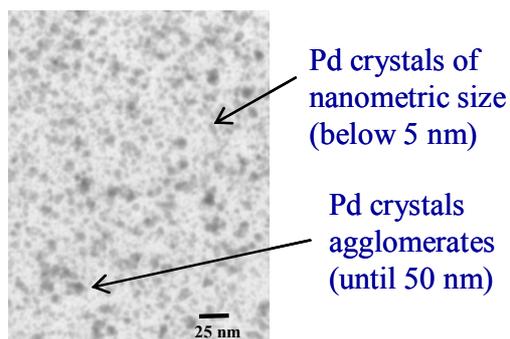
$$d = \frac{k\lambda}{\beta(\theta) \cos \theta} \quad (\text{Eq. 1})$$

This method is efficient for medium size nanoparticles; however, in the case of very small crystals (below 3 nm) the analytical procedure loses in precision. The poorly resolved peaks do not allow an accurate determination of crystal size. Figure 4 shows an example of X-ray diffraction patterns obtained with Pd-deposited on chitosan hollow fibers. The size of crystallites, deduced from the Scherrer equation, increases with Pd loading on the fiber.



**Figure 4 :** X-ray diffraction patterns

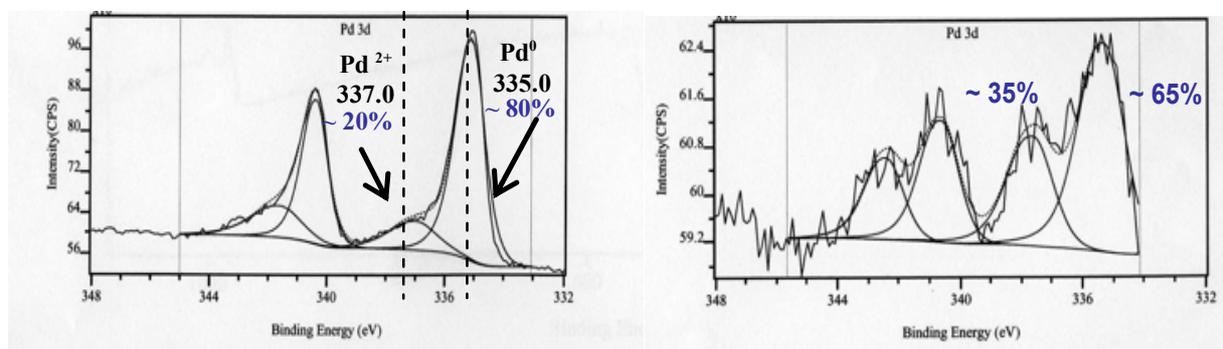
Figure 4 shows that when increasing the amount of Pd loaded on the fiber the size of crystals progressively increases. At low Pd loading, the size of crystals sharply increases from 1.7 to 2.9 nm when increasing Pd loading from 0.25 mg to 0.75 mg of Pd per fiber (i.e. from 11 to 33 mg Pd g<sup>-1</sup> fiber). Above a 0.75 mg/fiber loading the size of Pd crystals slightly increases up to 3.9 nm with a linear trend. Figure 5 shows that increasing metal concentration on the support may cause the aggregation of nanoparticles with significant impact on the catalytic properties.



**Figure 5 :** Palladium nanocrystals and palladium agglomerates by TEM

#### 4.- Pd oxydation form

Palladium oxidation form in the fiber was investigated by X-ray Photoelectron Spectroscopy analysis (XPS). Figure 6 shows the two characteristic peaks of palladium (Pd(0) and Pd (II)). XPS analyses show that palladium is only partially reduced and that a gradient in reduction efficiency may exist between outer and inner sides of the fiber: a significant difference in the percentage of Pd(0) is detected when comparing the XPS spectra of (a) raw and (b) grinded fibers. The effect of electron beam on palladium reduction makes difficult the exact determination of the percentage of metal reduction but the trends observed on a series of fiber loaded with different amounts of Pd confirm that the reduction process is a key step in the design of these catalytic hollow fibers.



**Figure 6 :** Palladium XPS spectrum of (a) raw and (b) grinded fibers.

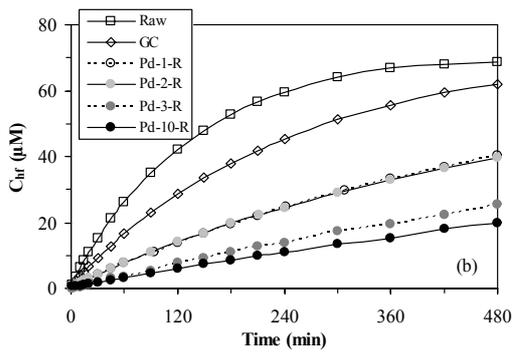
#### 5.- Diffusion properties and pore size

The diffusion properties of the catalytic hollow fibers (at the different stages of the synthesis procedure) have been investigated using vitamin B12 as the tracer. The solute is recirculated in the fiber immersed in a closed water tank, the concentration of vitamin B12 is monitored on-line at the outlet of the fiber by UV-visible spectrophotometric analysis. The mass balance equation is used for the determination of the amount of solute that migrates through the fiber into the outer compartment of the fiber. The flux of vitamin B12 ( $F$ ,  $\mu\text{mol m}^{-2} \text{min}^{-1}$ ) is determined in function of the gradient of vitamin B12 concentration between the inner (lumen side,  $C_{\text{hf}}$ ,  $\mu\text{mol L}^{-1}$ ) and the outer (shell side,  $C_{\text{r}}$ ,  $\mu\text{mol L}^{-1}$ ) compartments. Taking into account the thickness of the fiber ( $l$ , here  $60 \mu\text{m} \pm 5 \mu\text{m}$ ) it is possible to approximate the diffusion

coefficient in the fiber ( $D$ ,  $\text{m}^2 \text{min}^{-1}$ ), neglecting the diffusion of the solute in the film on both sides of the membrane. Changing the flow rate (i.e. the superficial velocity and the turbulence in the fiber) and strongly agitating the solution in the tank confirms this hypothesis.

$$F = \frac{D}{l}(C_r - C_{hf}) \quad (\text{Eq. 2})$$

Figure 7 shows how diffusion properties are depreciated after every treatment step. The lower diffusivity is obtained at high palladium loading on cross-linked chitosan material after reduction.

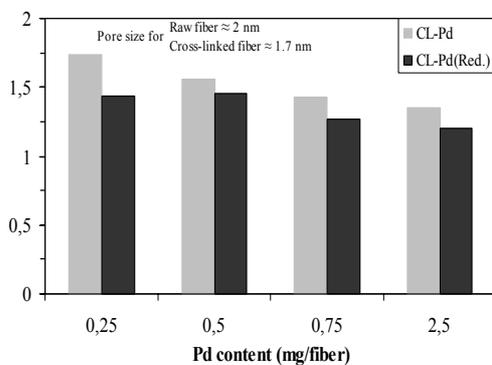


**Figure 7 :** Vitamine B12 diffusion compared for raw, glutaraldehyde cross-linked and Pd-loaded/reduced fibers

The Renkin equation is used for the evaluation of pore size ( $R_p$ , nm), based on the molecular diffusivity of vitamin B12 in water ( $D_{mol}$ ,  $2.274 \cdot 10^{-8} \text{m}^2 \text{min}^{-1}$ ) and the hydrodynamic radius of vitamin B12 ( $R_s$ , 0.85 nm)

$$\frac{D}{D_{mol}} = \left(1 - \frac{R_s}{R_p}\right) \left[1 - 2.104 \left(\frac{R_s}{R_p}\right) + 2.09 \left(\frac{R_s}{R_p}\right)^3 - 0.95 \left(\frac{R_s}{R_p}\right)^5\right] \quad (\text{Eq. 3})$$

Figure 8 shows the reduction in the pore size for fibers with different palladium loadings and after reduction process



**Figure 8 :** Pore size using the Renkin equation

The Renkin equation should be taken into account as indicative of the order of magnitude of the pore size, since the relation requires  $R_s/R_p$  to be greater than 0.5. These results show that the cross-linking treatment of the fiber decreases the porosity and that Pd binding also diminishes the mass transfer rate. The reduction in pore size is increased when increasing Pd content, especially above 0.5 mg Pd/fiber (i.e. above 22 mg Pd g<sup>-1</sup>). Palladium content in the fibers should be optimized taking into account its impact on diffusion properties and catalytic efficiency.

## Conclusions

The affinity of chitosan for palladium metal and Pd availability in the membrane make these chitosan fibers an efficient support for heterogeneous catalysis. Palladium distribution is a key parameter since it may affect the accessibility of the substrate to palladium crystals, but also the diffusion of hydrogen from the outer compartment to the inner part of the hollow fiber where the substrate solution is flowing.

At high palladium content the distribution of the catalytic metal was almost homogeneous along the fiber section while with a low Pd loading the metal was mainly located on the internal wall of the hollow fiber. Increasing the amount of palladium in the fiber reduces diffusion properties, decreases the pore size of the membranes and induces the formation of aggregates.

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