Supplementary Material (ESI) for *PCCP*

# Supporting Information:

# A UV-Vis Micro-spectroscopic Study to Rationalize the Influence of $Cl^-$ (aq) on the Formation of Different Pd Macro-Distributions on $\gamma$-$Al_2O_3$ Catalyst Bodies

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## 1. UV-Vi spectra of $PdCl_{4-x}(H_2O)_x^{(x-2)}$ in solution

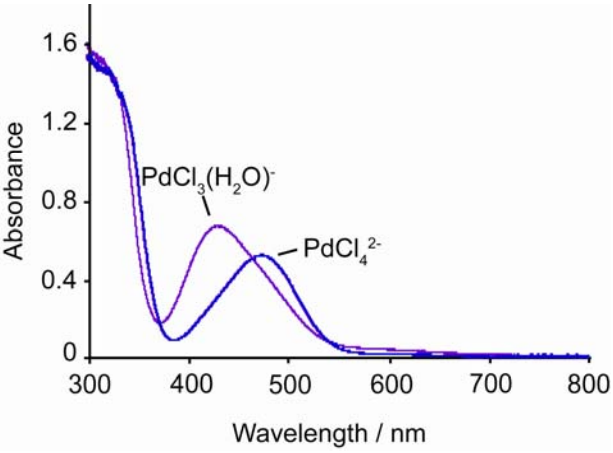


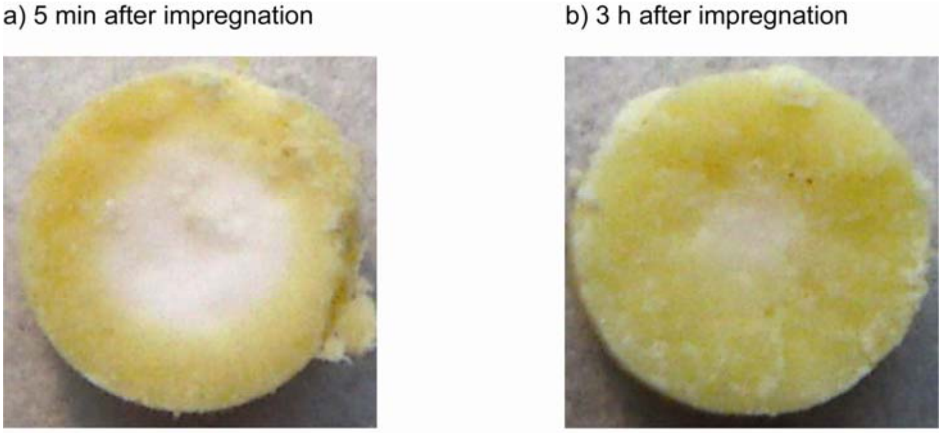
**Figure A**. UV-Vis spectra of the pure components $PdCl_4^{2-}$ (Solution A6) and $PdCl_3(H_2O)^-$ (solution B0).

Figure A illustrates the UV-Vis spectra between 300 and 800 nm obtained for the impregnation solutions A6 (blue spectrum) and B0 (pink spectrum). The spectra show a band between 400 and 550 nm assigned to a $Pd^{II}$ d-d spin-forbidden band, a very intense band below 400 nm is also observed, which maximum cannot be determined due to saturation of the detector. These UV-Vis spectra have been assigned to $PdCl_4^{2-}$ (maximum absorption at 474 nm) and $PdCl_3(H_2O)^-$ (maximum absorption at 431 nm), respectively. Thus, the rest of the impregnation solutions show a very similar pattern with the maximum absorption in between 431 and 474 nm.

As the figure indicates the band of these two species is very irregular in shape and very broad.

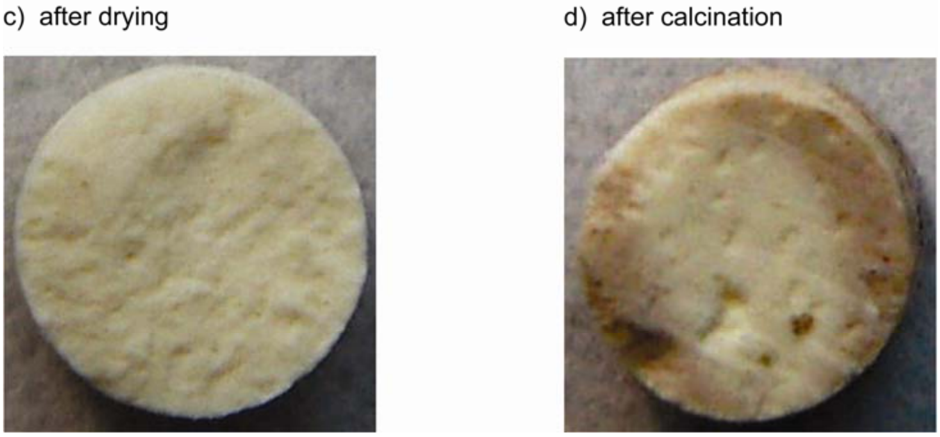
## 2. Digital Photographs of Bisected Pellets (1 wt%Pd/$\gamma$-$Al_2O_3$)

**Figure B.** Digital photographs of pellets prepared from solution 1wt%Pd-A1: (a) 5 min after impregnation; (b) 3 h after impregnation; (d) after drying; and (e) after calcination.



a) 5 min after impregnation

b) 3 h after impregnation



c) after drying

d) after calcination

**Figure C.** Digital photographs of pellets prepared from solution 1wt%Pd-B4: (a) 5 min after impregnation; (b) 3 h after impregnation; (d) after drying; and (e) after calcination.

As illustrated in Figures A and B, there is a clear difference in the Pd macro-distribution depending on the solution pH and concentration of $Cl^-$. After calcination, the pellets impregnated with solution 1wt%Pd-A1 show an egg-white profile with Pd present in a structure similar to $PdCl_2(O\text{-}Al)_2^{2-}$, as deduced from UV-

Vis micro-spectroscopy; whilst the pellets prepared from the solution 1wt%Pd-B4 yielded an almost uniform profile with Pd present also as $PdCl_2(O\text{-}Al)_2^{2-}$.

## 3. Curve Analysis of the Spectra Presented in Figures 6, 7 and 8

As observed in the following figures, all the spectra contain a band at around 260-280 nm which real maximum is difficult to estimate due to the closeness to the detection limit of the equipment.

Moreover, the bands assigned as background contribution on the Gaussian analysis are related to several facts. The background comes from the roughness of the surface after bisection, which is dependent of the specific point being measured and how well the bisection was performed. In some occasions this background might also include real contributions to the Pd d-d transition band coming from the presence of more chlorinated Pd species.

### *3.1. Curve Analysis of the Spectra in Figure 6*

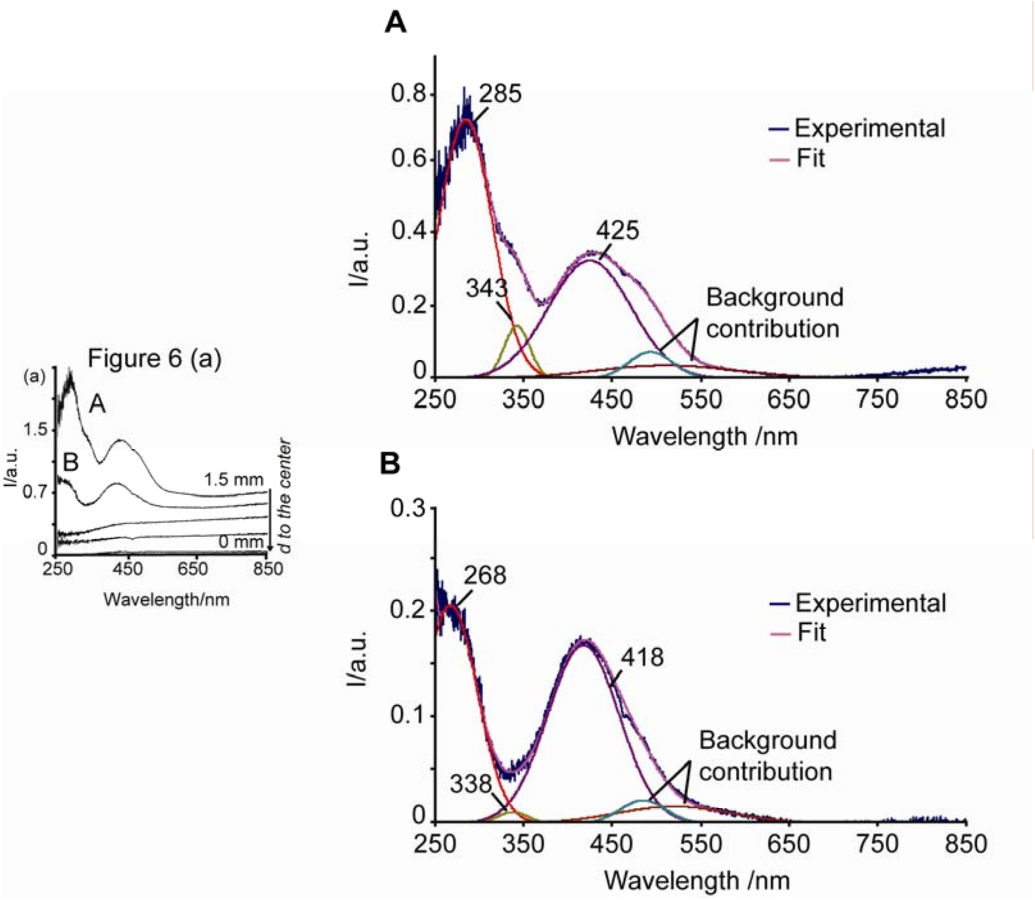


**Figure D.** Curve analysis of the UV-Vis spectra from Figure 6 (a): Space resolved UV-Vis spectra from the edge to the center of pellets 5 min after impregnation with solution 1wt%Pd-A1.

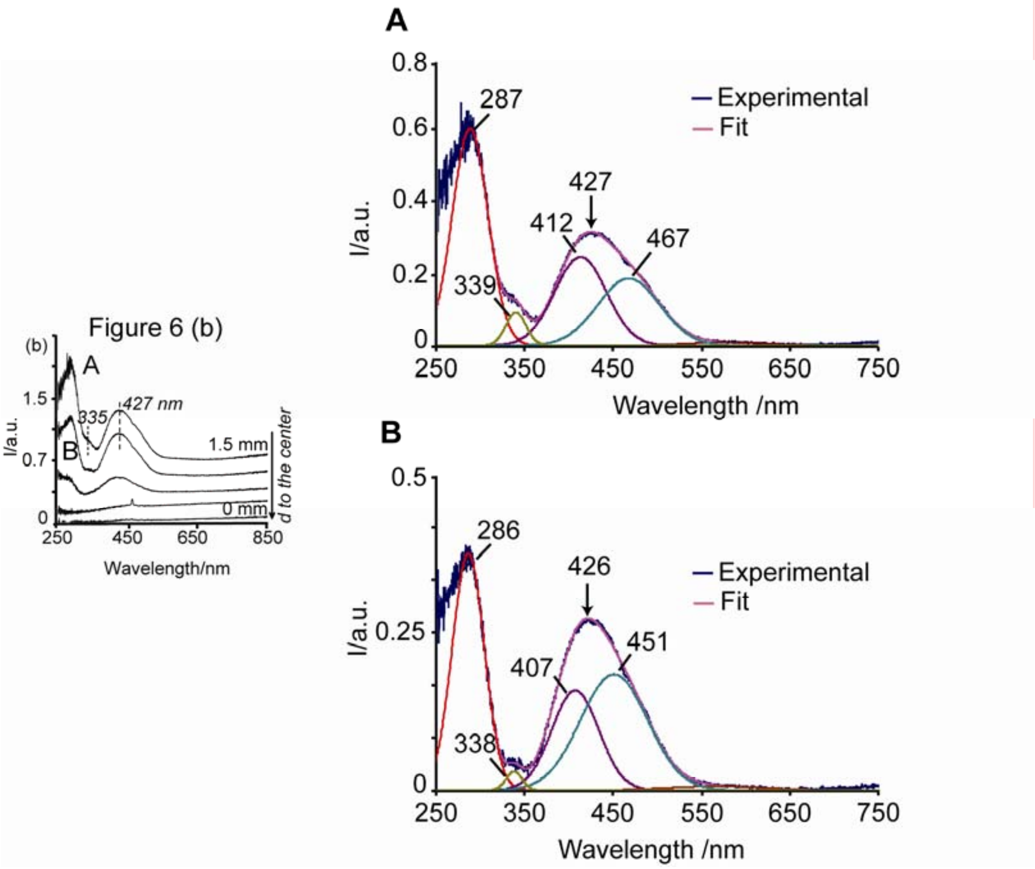


**Figure E.** Curve analysis of the UV-Vis spectra from Figure 6 (a): Space resolved UV-Vis spectra from the edge to the center of pellets 5 min after impregnation with solution 1wt%Pd-B4.

### *2.2. Curve Analysis of the Spectra in Figure 7*

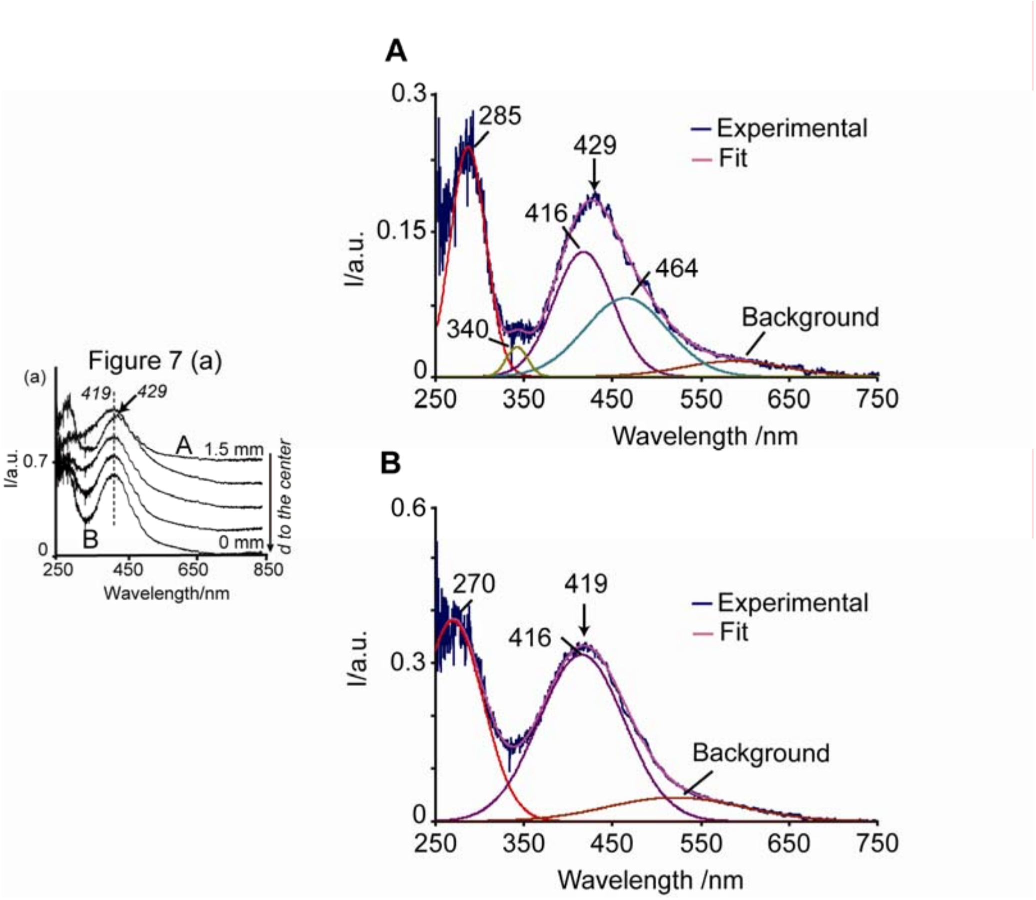


**Figure F.** Curve analysis of the UV-Vis spectra from Figure 7 (a): Space resolved UV-Vis spectra from the edge to the center of pellets 3 h after impregnation with solution 1wt%Pd-A1.

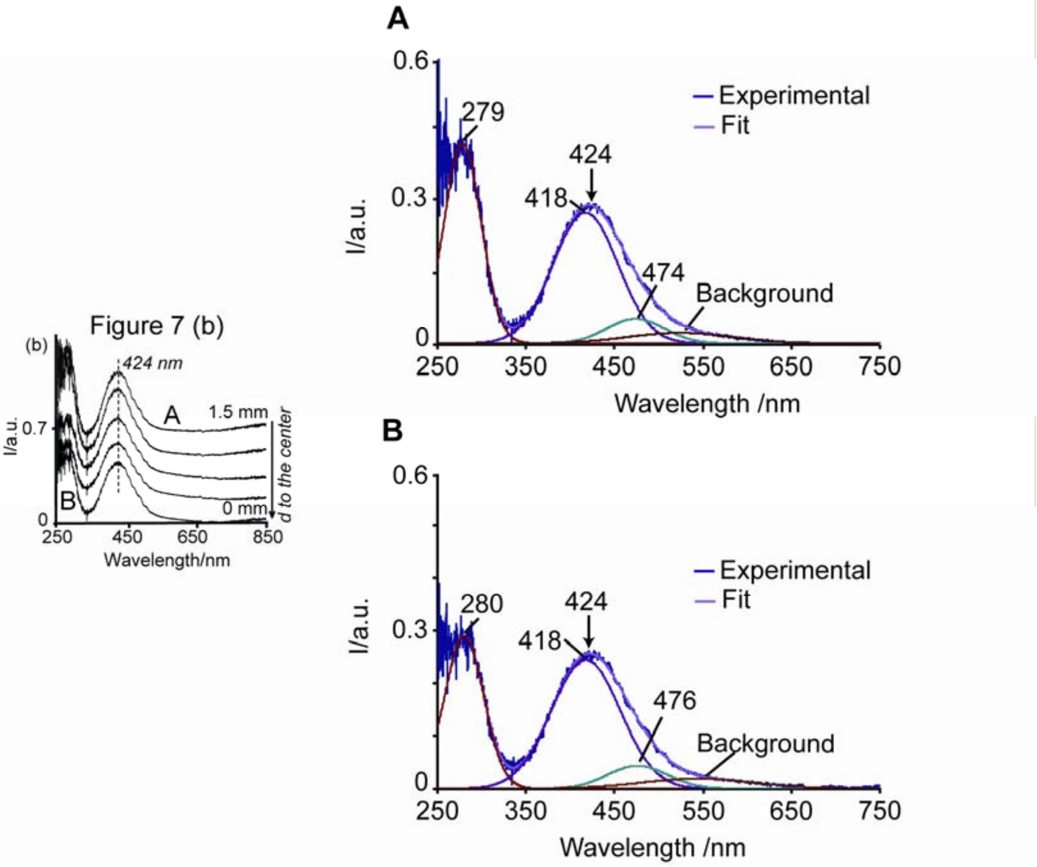


**Figure G.** Curve analysis of the UV-Vis spectra from Figure 7 (b): Space resolved UV-Vis spectra from the edge to the center of pellets 3 h after impregnation with solution 1wt%Pd-B4.

### *2.3. Curve Analysis of the Spectra in Figure 8*

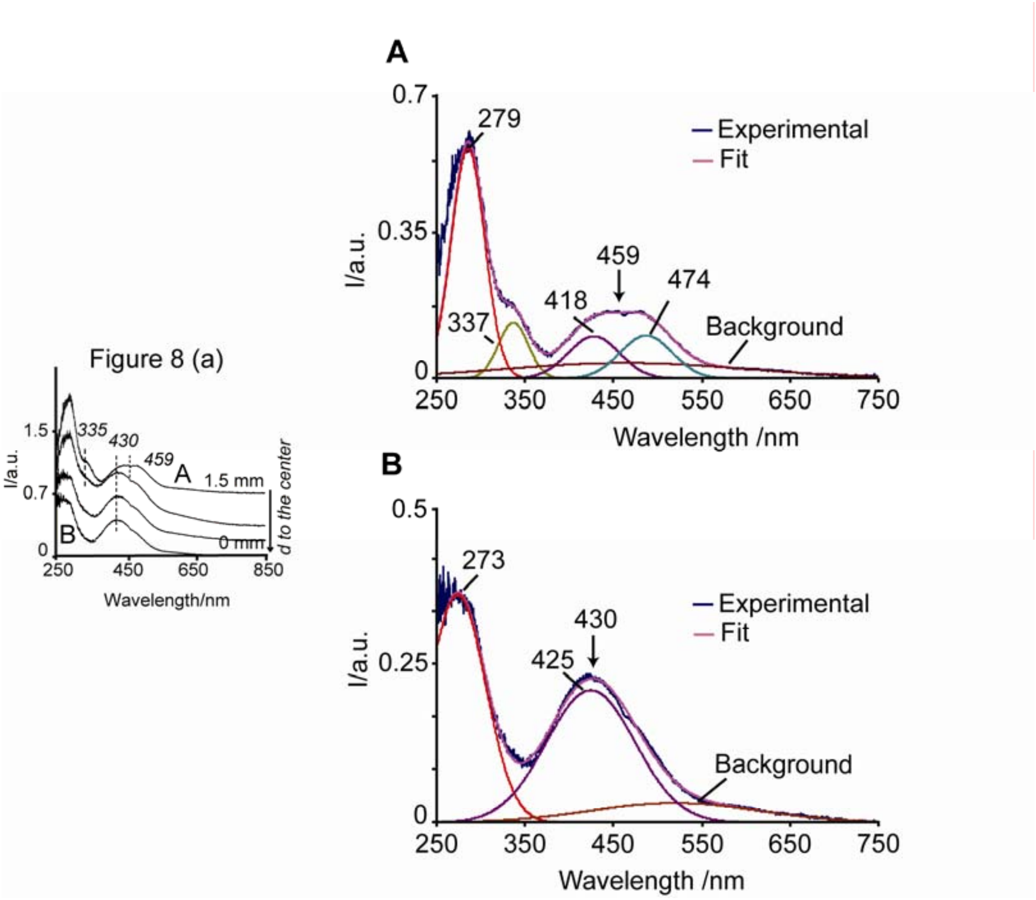


**Figure H.** Curve analysis of the UV-Vis spectra from Figure 8 (a): Space resolved UV-Vis spectra from the edge to the center of a pellet after impregnation and drying with solution 1wt%Pd-A1.

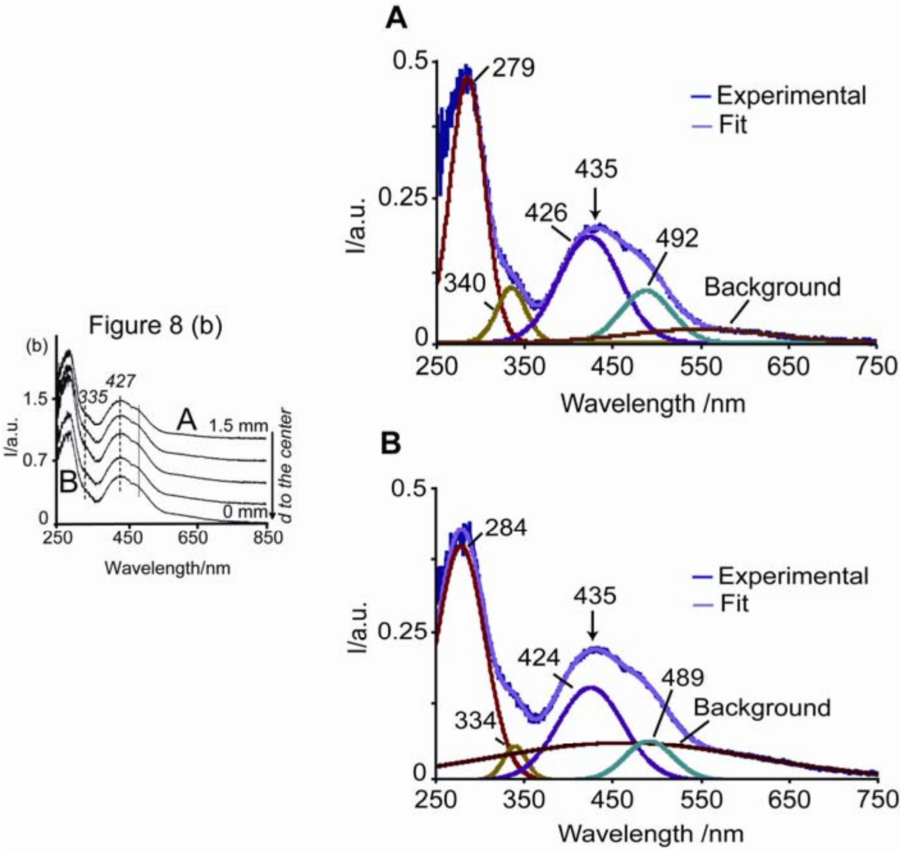


**Figure I.** Curve analysis of the UV-Vis spectra from Figure 8 (b): Space resolved UV-Vis spectra from the edge to the center of a pellet after impregnation and drying with solution 1wt%Pd-B4.