

# Direct synthesis of hydrogen peroxide in AuPd coated micro channels: an in-situ XAS study

**Citation for published version (APA):**

Kanungo, S., Neira d'Angelo, M. F., van Haandel, L., Ordonskiy, V., Hensen, E. J. M., & Schouten, J. C. (2017). Direct synthesis of hydrogen peroxide in AuPd coated micro channels: an in-situ XAS study. In *Proceedings of the EuropaCat 2017: A bridge to the future, August 2017, Florence, Italy*

**Document status and date:**

Published: 01/08/2017

**Document Version:**

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

**Please check the document version of this publication:**

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

**General rights**

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

[www.tue.nl/taverne](http://www.tue.nl/taverne)

**Take down policy**

If you believe that this document breaches copyright please contact us at:

[openaccess@tue.nl](mailto:openaccess@tue.nl)

providing details and we will investigate your claim.

## Direct synthesis of hydrogen peroxide in AuPd coated micro channels: An in-situ XAS study

**Shamayita Kanungo<sup>a\*</sup>, M. Fernanda Neira D'Angelo<sup>a</sup>, Lennart van Haandel<sup>b</sup>, Vitaly Ordonskiy<sup>c</sup>, Emiel J.M. Hensen<sup>b</sup> and Jaap C. Schouten<sup>a\*</sup>**

<sup>a</sup>Chemical Reactor Engineering, Eindhoven University of Technology, Eindhoven, 5600 MB, The Netherlands

<sup>b</sup>Inorganic Materials, Eindhoven University of Technology, Eindhoven, 5600 MB, The Netherlands

<sup>c</sup>Unité de catalyse et de chimie du solide, Université Lille, UMR 8181 CNRS, France

\*Corresponding author: s.kanungo@tue.nl, j.c.schouten@tue.nl

*In-situ X-Ray Absorption Spectroscopy (XAS) was conducted for the first time on both Au and Pd edges for the direct formation of H<sub>2</sub>O<sub>2</sub> in coated micro channels, in order to elucidate the oxidation state and coordination environment of Au and Pd in reaction conditions. The micro channels were prepared by depositing the active phase (Au, Pd and AuPd nanoparticles) on silica pre coated capillaries, by a novel polyelectrolyte multilayer technique. XAS spectra were recorded in reaction conditions – total pressure 20 bar, room temperature, 5 vol% each of H<sub>2</sub> and O<sub>2</sub> (total gas flow = 5 ml/min) and liquid (extraction phase with stabilizer) flow rate 0.1 ml/min. The presence of H<sub>2</sub>O<sub>2</sub> was verified by titration with cerium sulfate standard solution. It was found that the fresh capillaries predominantly contained PdO, which was reduced to Pd<sup>0</sup> in reaction conditions, while Au was found to be in metallic form. In the AuPd capillary, alloying of Au and Pd was also observed in the reduced samples.*

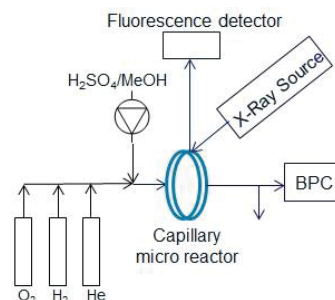
### 1. Scope

Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) is an environmentally friendly, versatile chemical which finds application in many industrial processes. The direct synthesis of H<sub>2</sub>O<sub>2</sub> from H<sub>2</sub> and O<sub>2</sub> using AuPd catalysts is a “greener” alternative to the traditional process of peroxide synthesis using anthraquinone. But the direct synthesis route offers many challenges like the explosive nature of the H<sub>2</sub>/O<sub>2</sub> mixture and the need for optimum catalysts with high activity and selectivity towards H<sub>2</sub>O<sub>2</sub><sup>1</sup>.

The most commonly used catalysts for this reaction are Pd based and it has been shown that alloying Pd with Au leads to higher H<sub>2</sub>O<sub>2</sub> selectivity and yield, but the reason behind this effect is not well understood yet. Moreover, the oxidation state (OS) of Pd during reaction is also under debate, with different groups reporting conflicting observations<sup>1</sup>. In this study, X-Ray Absorption Spectroscopy (XAS) was used at the Au-L<sub>3</sub> and Pd-K edges, to investigate the change in the OS of the metals (XANES) and their co-ordination environment (EXAFS) in reaction conditions. The reaction was carried out in 320µm ID capillaries, that were coated with (a) Au, (b) AuPd and (c) Pd nanoparticles, by a novel polyelectrolyte multilayer technique. The use of these micro-reactors ensures safe and continuous operation even at explosive conditions and also leads to better mass transfer<sup>2</sup>.

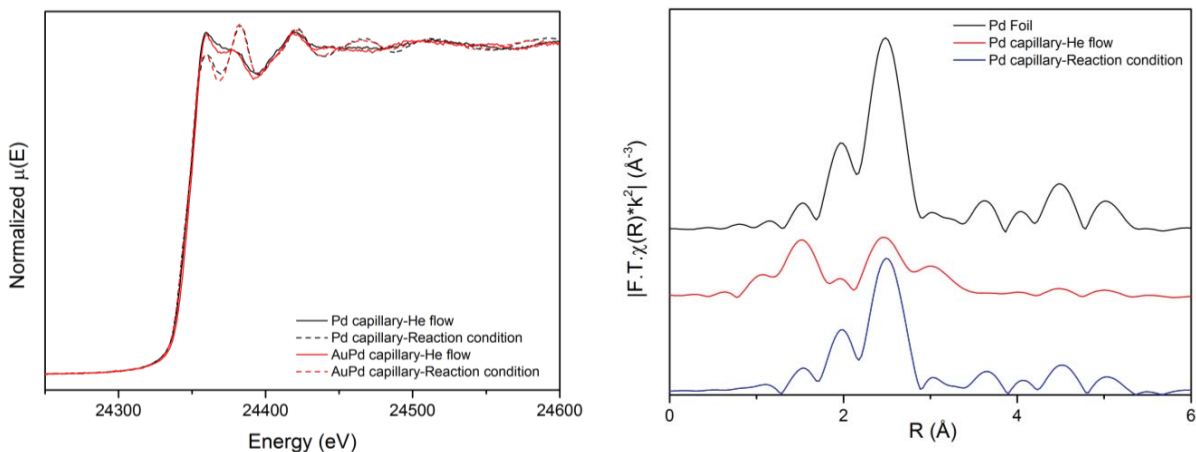
### 2. Results and discussion

The XAS data was recorded at the synchrotron in Soleil, Paris on the Au and Pd edges at different conditions – static, He flow, O<sub>2</sub> flow, H<sub>2</sub> flow, H<sub>2</sub> + O<sub>2</sub>, reaction condition and H<sub>2</sub>O<sub>2</sub> co-feeding. The reaction condition used was - 20 bar total pressure, room temperature, with 5 vol% each of H<sub>2</sub> and O<sub>2</sub> (total gas flow = 5 ml/min) and liquid (0.05M H<sub>2</sub>SO<sub>4</sub> + MeOH) flow rate 0.1 ml/min, as shown in Figure 1.



**Figure 1.** In-situ microreactor XAS experiment, Soleil (Paris)

From the XANES spectrum (Figure 2) we can see that in both the Pd and AuPd capillaries, Pd is present as PdO, which is reduced to Pd<sup>0</sup> in reaction condition. On the other hand, it is found that Au is present in its metallic state in all samples and does not show change in OS in reaction (or other) conditions. The change in OS of Pd and its co-ordination environment when subjected to reaction conditions is also observed from the EXAFS spectra, as shown in Figure 2 (b). In the AuPd capillary, alloying of Au and Pd was also observed in the reduced samples. It must be noted that all capillaries were found to produce H<sub>2</sub>O<sub>2</sub> in the reaction condition used. This was measured by the standard titration technique for quantifying peroxide, using cerium sulfate.



**Figure 2.** (a) XANES spectra at Pd-K edge for Au and AuPd capillaries at reaction and inert (He flow) conditions and (b) Magnitude of Fourier transform of Pd-K edge EXAFS spectra for Pd foil and Pd capillary at inert and reaction condition

### 3. Conclusions

The direct synthesis of hydrogen peroxide, made possible by AuPd catalysts, is a cleaner and greener route for obtaining this valuable chemical commodity. In order to make this alternate route commercially relevant, it becomes imperative to understand the mode of operation of the most active catalysts. This work sheds light on the much debated oxidation state of Pd involved in the mechanism of peroxide synthesis. We find that PdO readily converts to its metallic form in reaction conditions. It provides further insight on the role of Au, which retains its metallic form even during reaction and shows alloying with Pd. These findings will lead to smarter catalyst development for this coveted reaction.

### References

1. J.K. Edwards and G.J. Hutchings, *Angew. Chemie - Int. Ed.*, **2008**, 47, 9192.
2. V. Paunovic, V. Ordonsky, M. F. Neira D'Angelo, J. C. Schouten and T. A., Nijhuis, *J. Catal.*, **2014**, 309, 325-332.