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Direct synthesis of H$_2$O$_2$ in AuPd coated micro channels: An in-situ X-Ray absorption spectroscopic study

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Keywords: Direct synthesis; Hydrogen peroxide; Au-Pd catalysts; X-Ray absorption spectroscopy; In-situ/operando EXAFS; Bimetallic catalysts

1. Introduction

Hydrogen peroxide (H$_2$O$_2$) is an important commodity chemical with applications in paper and pulp industry as a bleaching agent, in wastewater treatment and in the synthesis of fine and bulk chemicals [1–4]. In addition, it is also a green oxidant releasing only water as the oxidation product [5]. The commercial production of H$_2$O$_2$, on the other hand, cannot be classified as a green technology. H$_2$O$_2$ is currently produced by the anthraquinone auto-reduction (AO) process, which involves complex processing steps, leads to excessive waste generation and is only economically viable when produced at a large scale. In this context, the direct synthesis of H$_2$O$_2$ from H$_2$ and O$_2$ at small scale is an attractive alternative [6–8]. Nevertheless, the process still suffers from low selectivity as undesired Pd catalyzed pathways lead to water formation, as shown in Scheme 1. Moreover, H$_2$O$_2$ is highly unstable and requires the use of liquid solvents like methanol to easily desorb it from the catalyst surface, as well as stabilizing agents like acids and halide promoters [7,9,10]. Finally, an important challenge in the direct synthesis of H$_2$O$_2$ lies in the use of H$_2$/O$_2$ mixtures, which are potentially explosive in the concentration range of 4–94% of H$_2$ in O$_2$, thus limiting the maximum H$_2$O$_2$ yield that can be achieved even on highly active catalysts.

There have been numerous studies on catalyst development and novel reactor approaches to overcome the challenges faced in the direct synthesis of H$_2$O$_2$. Hutchings et al. [7,11–13] was the first to show that the addition of small amounts of Au to Pd, leads to significant enhancement in performance, especially in terms of H$_2$O$_2$ selectivity. Other groups have also reported similar observations [14–16]. This Au-Pd synergism may originate from geometric and/electronic effects. Addition of Au to Pd may “dilute” the surface (i.e., geometric effects), thereby reducing the rate of decomposition [21,22]. Besides the role of Au in enhancing catalytic activity, the oxidation state of Pd is also under debate. Some reports have suggested that metallic Pd is the
active component [24,25], while other studies have claimed the importance of PdO in determining catalytic activity [26–28]. It has been shown that the use of different co-solvents can also tune catalytic activity and selectivity [24]. Aprotic solvents (e.g., acetonitrile, DMSO) at optimized concentrations may interact with the catalyst, as evidenced by IR studies, and lead to enhanced H₂O₂ selectivity [29]. These strategies have led to better performing catalytic systems but the underlying reasons were not explored in reaction conditions (in-situ/operando studies). To the best of our knowledge, no in-situ study has been performed so far on the bimetallic AuPd system during the synthesis of H₂O₂. Recent investigations on Pd catalysts [30,31] have provided a valuable insight on the Pd structure when used in a monometallic form. However, the corresponding catalytic activity of these systems is either not reported [30] or considerably low [31]. Besides, the influence of Au and its correlation with the catalytic activity under relevant reaction conditions remain unanswered.

A valid approach to enhance catalytic performance is by using concentrated reactant mixtures. It has been shown that the direct synthesis of H₂O₂ can be carried out safely using conventionally explosive reactant mixtures in wall-coated micro(channel) reactors [32]. The intrinsic safety of these microreactor systems is attributed to their distinctively small dimensions (i.e., 320 μm ID) and to their excellence in terms of flow distribution (i.e., Taylor flow), catalyst wetting and heat management [32–36]. Interestingly, not only the production of H₂O₂ was remarkably increased due to the use of concentrated H₂O₂ mixtures (i.e., an eight-fold increase) compared to dilute mixtures, but also a marked increase in selectivity was observed (i.e., from 25% in dilute systems to 65% using concentrated mixture). It was proposed that a higher surface coverage, which results from the increase in reactive partial pressure, leads to the blocking of the sites which would otherwise catalyze water formation reactions [32,36]. In our recent study we have used this concept and a novel synthesis technique to obtain exceptionally active Au, Pd and AuPd catalysts for the direct synthesis of H₂O₂ [37]. The bimetallic AuPd catalyst was superior in performance to the monometallic ones, in agreement with studies referred to above.

Structure-activity correlations can be explored using time resolved studies in reaction conditions to obtain insight on the pertinent questions in direct synthesis like the role of Au, the oxidation state of Pd (and Au) and the role of co-solvent. These studies generally require that the structure of the catalyst be probed simultaneously and at the same location to draw correlation between the catalytic performance and structural changes taking place in the catalyst [37]. To meet these requirements specially designed spectroscopic cells are used to facilitate high quality data acquisition while working in reaction/in-situ conditions [38,39]. Although ideal for obtaining clean spectroscopic data, these cells may be dominated by mass transfer effects leading to misinterpretation of the measured data. These mass transfer effects become more dominant when using solid/liquid reaction system like the direct synthesis of H₂O₂. The influence of mass transfer effects due to cell design was shown by Grundwaldt et al. [39]. It was found that the reduction of a PdO/ZrO₂ catalyst by benzyl alcohol took 45 min in a cell with pressed pellet while the same catalyst was reduced in only 2 min when used as a powder. A potential solution for avoiding these effects is by employing microreactors and in particular wall coated micro channel, as spectroscopic cells.

In this paper we report an in-situ XAS study at the Au L₃ and Pd K edges during the direct synthesis of H₂O₂ on silica supported Pd, Au and AuPd wall-coated capillary microreactors operated in the Taylor flow regime. This flow pattern provides excellent heat and mass transport properties, ensures efficient catalyst wetting and presents ideal flow distribution (i.e., no back mixing), contributing to the inherent safety of this microreactor system. In this study, the microreactor acts both as the reactor as well as the spectroscopic cell, thus allowing the XAS measurements to be exempt of reactor effects, and importantly, they are recorded in the exact same configuration and conditions as our reference lab experiments. Therefore, the XAS data presented in this study fully represent our working catalysts under realistic reaction conditions.

2. Experimental

2.1. Catalyst synthesis

Synthesis of the wall-coated catalytic micro channels/capillaries was carried out based on our previous study using the concept of Polyelectrolyte multilayers (PEMs) [37]. Fused silica, 320 μm ID capillaries of 1–1.5 m length with a silica pre-coat layer (CP-silicaPLOT, Agilent), were first pretreated by flushing with ammonium nitrate solution (1 M), followed by drying at 120 °C for 12 h and calcination at 300 °C for 2 h, in a static air oven. PEMs were built on the silica pre-coat layers using polyacrylic acid (PAA) and polyethylene imine (PEI). PAA (35 wt% in H₂O, Sigma-Aldrich) was prepared as a 10 mg/ml solution and PEI (50 wt% in H₂O, Sigma-Aldrich) as a 2 mg/ml solution with deionized water. Both solutions were treated by hydrochloric acid (0.1 M) and sodium hydroxide (0.1 M) to adjust the pH to 4 and 9 for PAA and PEI, respectively. Each fluid was fed through the capillary at 4 ml/hr for 20 min using a syringe pump, with an intermittent rinse with DI water. One layer of PAA followed by one layer of PEI constituted one bi-layer. After formation of two such bi-layers, metal deposition was carried out using precursors, HAuCl₄ (Aldrich, 30 wt% in HCl) and K₂PdCl₄ (Sigma, 99.99%). For AuPd deposition, a solution was prepared using these precursors in DI water, according to the desired loading of 5 wt% total metal (Au: Pd = 1:2 M ratio), based on the amount of silica pre-coat in the capillary and the empty volume. Thereafter, the capillary was completely filled with this solution and kept undisturbed for about 10 min, after which the excess solution was flushed using N₂. Reduction of the metal(s) was carried out by flushing ~1 mg/ml NaBH₄ solution through the capillaries followed by rinsing with DI water. The monometalllic capillaries were prepared in a similar manner with a target loading of 5 wt%. Finally, the capillaries were at dried at 120 °C for 12 h and calcined at 380 °C for 4 h. Three different capillaries were thus obtained: Au, Pd and AuPd.

2.2. In-situ XAS measurements

X-Ray absorption spectroscopy measurements were carried out at SAMBA Beamline in Soleil Synchrotron, Paris. A schematic representation of the experimental setup is shown in Scheme 2. The gases were supplied using mass flow controllers. The liquid phase consisting of H₂SO₄ (0.05 M) and 20 vol% methanol in DI water, was supplied to the system by a syringe pump. To maintain a constant pressure in the system, a back-pressure regulator (BPR) was put downstream after the gas-liquid separation unit. All experiments were carried out at 20 bar pressure and at room temperature. Table 1 shows the different experimental conditions in
which XAS data were recorded for three different catalysts – Pd, Au and AuPd.

For the monometallic Pd and Au catalysts, experiments were performed at the Pd K edge and Au L$_3$ edge respectively, while for the AuPd catalyst spectra were recorded on both these edges in separate set of experiments. All measurements were made in the fluorescence mode for 30–40 min in each experiment, which was enough to reach steady state condition (verified by monitoring the evolution of the spectra). The acquisition time for each spectrum was ca. 2 min. Reference spectra were collected in the transmission mode using Au and Pd foils and PdO powder.

EXAFS data were processed with the Athena/Artemis software package [40]. Data processing included normalization of the absorption edge and background subtraction and fitting of the structural parameters (EXAFS). Scattering paths were calculated with FEFF6 from relevant crystal structures obtained from the ICSD database. Fitted parameters were the energy shift ($\Delta E_0$), coordination number (CN), change in bond distance ($\Delta R$), and the relative mean square displacement ($r^2$). Amplitude reduction factors were determined from metal foils to be 0.85 and 0.89 for the Au L$_3$ edge and Pd K edge fits, respectively. The Au L$_3$ edge spectra were fitted in the range $\Delta k = 2–9$ Å$^{-1}$ and $\Delta R = 1.5–3.5$ Å and the Pd K edge spectra were fitted in the range $\Delta k = 2–11$ Å$^{-1}$ and $\Delta R = 1–3$ Å ($1–4$ in case spectra were fitted with Pd oxide scattering paths). Plotted spectra have a k-weight of 2 and are not phase corrected.

2.3. Catalytic tests

Simultaneously with the recording of XAS data under reaction conditions (Table 1, run 5), liquid samples were collected and titrated with standard cerium sulphate (0.1 N). With all the catalyst tested, the presence of H$_2$O$_2$ in the reactor outlet ensured that the XAS measurements were made on a working catalyst. A full analysis of the catalytic activity of these capillary microreactors was completed ex-situ at our lab facilities, where these samples were tested for the direct synthesis of H$_2$O$_2$ in the same conditions as used at the synchrotron. Here, besides analyzing the liquid samples by titration with standard solution of cerium (IV) sulfate to determine the H$_2$O$_2$ concentration (which showed comparable values to those measured at the synchrotron facility), gas samples were analyzed with an online GC (column: Molsieve plot 5 m 0.32 mm) equipped with TCD detector to determine H$_2$ conversion.

The schematic representation of the experimental set up can be found in the Supporting Information (Fig. S1).

2.4. Additional ex-situ characterization

Metal particle size was examined using a FEI Tecnai G2 Sphera transmission electron microscope (TEM). For this analysis, the wall-coated capillaries were entirely crushed and suspended in drops of ethanol. To determine the real loadings of Au and Pd present in the coated catalysts, inductively coupled plasma (ICP) was performed using a Spectra Cirosc$^{\text{CCD}}$ system. The samples were prepared by crushing the capillaries and dissolving them in aqua regia (HCl:HNO$_3 = 3:1$). The solutions were stirred at 80 °C for about 1 hr. After cooling, diluted HF (1:19) was added to each sample and finally, diluted with ultra-pure water to the required amount. The calibration line was obtained using standard gold (Sigma-Aldrich, 999 mg/L ± 2 mg/L Au) and palladium (Sigma-Aldrich, 999 mg/L ± 2 mg/L Au) solutions.

3. Results

3.1. Ex-situ characterization

Fig. 1 shows the representative TEM images of the Pd, AuPd and Au particles formed in the respective capillary microreactors. The particles are well distributed throughout the support in all the samples and particle size analysis revealed an average particle size ranging from about 1.5–3 nm. In case of the Au catalyst, some bigger particles (>10 nm) were also seen along with the smaller ones that were more abundant (Fig. 1(c)). ICP-OES revealed the metal content of the Pd, AuPd and Au particles as 4.3 wt%, 2.1 wt% and 3.0 wt%, respectively.

3.2. Catalytic activity

The activity of each catalyst for the direct synthesis of H$_2$O$_2$ is shown in Table 2. We see that under the (dilute) reaction conditions tested in this study, these catalysts form a remarkable
amount of \( \text{H}_2\text{O}_2 \) with a maximum productivity of 28.5 mol/kg cat/h, which is an order of magnitude higher than that reported in a recent in-situ study on Pd catalyst [31]. Hence this group of catalysts form a reliable system to study the structure activity correlation. We also observe that the AuPd catalyst is much superior to its monometallic counterparts both in terms of selectivity and productivity of \( \text{H}_2\text{O}_2 \). Selectivities lower than 100% are explained by the undesired oxidation of \( \text{H}_2 \) and/or \( \text{H}_2\text{O}_2 \) decomposition. Nevertheless, due to the difficulties in quantifying the formation of water (note that water will be collected in the aqueous liquid phase at these temperatures and pressures), the selectivity is calculated based on \( \text{H}_2 \) converted. The catalytic trends are in accordance with literature, thus ensuring the suitability of this set of catalysts for studying the influence of bimetallic interaction in enhancing the overall catalytic activity.

3.3. In-situ XANES

Fig. 2 shows the XANES spectra recorded on the Pd-K edge for the Pd and AuPd catalysts at different conditions. The spectra for standard samples of PdO and Pd foil are also shown for comparison. The Pd catalyst (measured in He flow) consists of a mixture of metallic Pd and PdO as shown in Fig. 2 (a). Upon introduction of \( \text{H}_2 \), the XANES spectra resembled that of Pd foil, indicating reduction of the PdO phase to Pd\( ^0 \). Interestingly, further exposure to \( \text{O}_2 \) and \( \text{H}_2\text{O}_2 \) mixtures did not result in re-oxidation of Pd. When the capillary is introduced to reaction conditions, the Pd remains metallic. The oxidation state remains unchanged even when the catalyst is exposed to a flow of 2 wt% \( \text{H}_2\text{O}_2 \) in the final experiment. Similar trends in Pd oxidation state is also exhibited by the AuPd catalyst (Fig. 2 (b)). We also observe that the oscillations shift to lower energies in certain conditions and this is more pronounced for the Pd catalyst. This is due to an increase in Pd-Pd interatomic distance and will be discussed in more detail in the EXAFS section.

The XANES spectra recorded on the Au L\( _3 \) edge for the Au and AuPd catalysts at different conditions are shown in Fig. 3. Both the fresh catalysts contain purely metallic Au which does not change when subjected to reaction (or other) conditions.

3.4. In-situ EXAFS

Fig. 4 shows the Fourier transform of the EXAFS spectra of the Pd catalyst on Pd K edge, along with Pd foil reference sample. The fitting parameters are summarized in Table 3. The fitting parameters are obtained by considering three paths of PdO--Pd-O, two Pd-Pd paths, named as Pd-Pd\(_1\) and Pd-Pd\(_2\), in addition to a Pd-Pd path for metallic Pd (fit shown in Fig S2). The fitted values obtained for these parameters are well in agreement with those reported for Pd\( ^0 \) and PdO in literature [41]. On passing \( \text{H}_2 \), the EXAFS Fourier transform resembles that of Pd foil, indicating the conversion of the PdO phase to metallic Pd. Furthermore, the Pd-Pd distance is found to be 2.766 Å, which is slightly higher than the Pd-Pd distance of metallic Pd (\( \approx \)2.74 Å). We speculate that this is due to the presence of Pd-hydride (PdH) which is formed after the reduction of Pd, as shown in Fig. 4 (b). The formation of PdH has been widely reported in Pd catalysts when subjected to \( \text{H}_2 \) atmosphere [42–46]. The increase in Pd-Pd distance is accompanied by an increase in the Debye-Waller factor (\( \sigma^2 \)), which is
indicative of disordering in the Pd structure induced by H₂ absorption [45]. The hydride formation was found to be completely reversible, as it was observed that on passing O₂ the Pd-Pd distance reduced to 2.742 Å, with a simultaneous decrease in σ². Introduction of the reactant gases (H₂ + O₂/He) again led to an increase in Pd-Pd distance and finally in reaction condition this distance increased furthermore to 2.822 Å, which is associated with β-PdH formation[47]. Finally, it was found that the presence of H₂O₂ did not re-oxidize the Pd, suggesting that the product formed most likely does not change the co-ordination environment of Pd.

Fig. 2. Pd K edge XANES spectra measured on (a) Pd and (b) AuPd catalysts recorded at indicated gas and/or liquid flow conditions starting with He. Pd foil and PdO spectra are also shown for reference.

Fig. 3. Au L₃ edge XANES spectra measured on (a) Au and (b) AuPd catalysts recorded at indicated gas and/or liquid flow conditions. The spectra for Au foil is shown for reference.

Fig. 4. Magnitude of Fourier transform of Pd K edge EXAFS spectra for the Pd foil and Pd catalyst at (a) different conditions (b) in H₂ at different measurement times.
Table 3
EXAFS fitting parameters for the Pd catalyst at different conditions collected at Pd K edge. Uncertainties are reported in parenthesis.

<table>
<thead>
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<th>Condition</th>
<th>Shell</th>
<th>R (Å)</th>
<th>CN</th>
<th>σ² * 10², Å²</th>
<th>R² (%)</th>
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<td>He</td>
<td>Oxidic phase:</td>
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<td></td>
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<tr>
<td>Pd-O</td>
<td>2.021 (0.006)</td>
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<td>0.8 (0.8)</td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td>Pd-Pd₁</td>
<td>3.058 (0.005)</td>
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<td>Pd-Pd₂</td>
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<td>3.8 (0.4)</td>
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<td>H₂/He</td>
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<td>2.766 (0.003)</td>
<td>9.5 (0.5)</td>
<td>9.2 (0.4)</td>
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<td>O₂/He</td>
<td>Pd-Pd</td>
<td>2.742 (0.004)</td>
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<td>9.0 (0.5)</td>
<td>6.4 (0.4)</td>
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</table>

4. Discussion

In this study, XAS was performed for the first time on both Au and Pd edges during the direct synthesis of H₂O₂ from H₂ and O₂ on Au, Pd, and AuPd catalysts. XANES was used to reveal the oxidation state of both metals in a range of gas flow conditions as well as during reaction using a biphasic (gas-liquid) environment, while EXAFS gave further insight about the coordination environment of Au and Pd under these conditions. In addition, comparison among AuPd catalyst with the monometallic counterparts is used herein to elucidate the role of Au in the AuPd catalyst, often correlated with an increase in product selectivity.

4.1. Metal oxidation state

The XANES on Pd K edge revealed that both Pd and AuPd catalysts initially consisted of Pd/PdO phases and were reduced to Pd⁰ in reaction conditions. This is a strong indication that it is the metallic Pd which is the active phase in peroxide formation, a topic that has been highly debated in past studies. Earlier studies performed in our lab at different H₂/O₂ ratios using concentrated feed mixtures showed that the optimum ratio in terms of productivity is 1:1. When H₂/O₂ was decreased to <1, a fall in productivity was observed. It was also showed that this change was reversible, as catalyst activity could be restored after flowing pure H₂ [36]. This could be an indirect evidence of PdO (likely formed in H₂/O₂ < 1) being detrimental to H₂O₂ formation and Pd⁰ (formed when H₂ is passed) being responsible for regaining the initial activity. This is suggestive of Pd⁰ being the active species, and it is consistent with the in-situ XANES findings of this study. It may be argued that if this is the case, PdO should have been observed in the “only O₂ experiments” (Table 1, run 3), which is contrary to our observation. This can be attributed to the lower partial pressures of O₂...
Au was present in its metallic form in the working state of all the catalysts studied. We also evaluated the ability of the product of re-oxidizing Pd to PdO and hence effecting catalyst performance, but we can firmly conclude that the Pd (and Au) oxidation states remained unchanged in presence of H\textsubscript{2}O\textsubscript{2} for AuPd and Pd catalysts. Although it has been argued that the role of Au in the superior activity of AuPd catalysts lies in its ability to inhibit oxidation of Pd [52], our results do not support such argument. According to our observations, Au is not essential to prevent Pd re-oxidation. The governing factor most likely is the reaction conditions (in particular the H\textsubscript{2}:O\textsubscript{2} ratio) which can change the oxidation state of Pd and consequently the activity.

4.2. AuPd nanoparticle structure

EXAFS analysis on the AuPd capillary gave evidence of Au-Pd alloying and indicated that the particles may have a core-shell structure. The structure in the fresh catalyst consists of an Au rich core surrounded by a shell of PdO and metallic Pd domains. Upon reduction in H\textsubscript{2}, this structure is retained with a completely metallic Pd shell. PdH formation is seen in both AuPd and Pd catalysts, in presence of H\textsubscript{2} and H\textsubscript{2} + O\textsubscript{2} characterized by an increase in Pd-Pd distance. When subjected to reaction conditions (addition of a liquid phase), this increase disappears in case of the AuPd catalyst, indicating loss of PdH phase. Simplified structures showing these transformations for the AuPd catalyst are depicted in Scheme 3.

![Scheme 3. Structure of AuPd nanoparticles in different conditions (a) fresh calcined (b) on H\textsubscript{2} introduction (c) prolonged H\textsubscript{2} flow/mixture of H\textsubscript{2} + O\textsubscript{2} and (d) during reaction; Yellow: Au atoms, brown: Pd atoms, red: PdO, blue: interstitial hydrogen. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)](image)

used in this study with respect to those in our previous work (2 bar vs. 10 bar).

Table 4

<table>
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<th>Condition</th>
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<th>R\textsuperscript{2} (%)</th>
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<td>5.6 (0.9)</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>Pd-Au</td>
<td>2.732 (0.011)</td>
<td>4.5 (0.4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Au-Au</td>
<td>n.d.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Au-Au</td>
<td>n.d.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H\textsubscript{2} + O\textsubscript{2}/He</td>
<td>Pd-Pd</td>
<td>2.820 (0.009)</td>
<td>7.5 (1.1)</td>
<td>7.3 (1.5)</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>Pd-Au</td>
<td>2.795 (0.025)</td>
<td>3.6 (0.9)</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>Au-Pd</td>
<td>4.2 (0.9)</td>
<td></td>
<td>12.3 (1.7)</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>Au-Au</td>
<td>9.0 (1.4)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reaction</td>
<td>Pd-Pd</td>
<td>2.748 (0.005)</td>
<td>7.5 (0.5)</td>
<td>6.0 (0.6)</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>Pd-Au</td>
<td>2.788 (0.013)</td>
<td>3.7 (0.4)</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>Au-Au</td>
<td>4.8 (1.0)</td>
<td></td>
<td>13.0 (1.9)</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>Au-Au</td>
<td>9.0 (1.1)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H\textsubscript{2}O\textsubscript{2}</td>
<td>Pd-Pd</td>
<td>2.759 (0.008)</td>
<td>7.3 (0.9)</td>
<td>5.0 (1.1)</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td>Pd-Au</td>
<td>2.817 (0.026)</td>
<td>3.3 (0.6)</td>
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<td></td>
<td>Au-Pd</td>
<td>n.d.</td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td>Au-Au</td>
<td>n.d.</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

n.d.: not determined as fitting for Au is done only at the most relevant conditions.

* Shared for Pd-Pd, Au-Pd and Pd-Au to fit the large number of parameters.

Table 5

<table>
<thead>
<tr>
<th>Condition</th>
<th>R (Au-Au), (Å)</th>
<th>CN (Au-Au)</th>
<th>σ\textsuperscript{2} (Au-Au) \times 10\textsuperscript{4}, Å\textsuperscript{2}</th>
<th>R\textsuperscript{2} (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He flow</td>
<td>2.871 (0.006)</td>
<td>11.0 (1.1)</td>
<td>7.8 (1.0)</td>
<td>1.2</td>
</tr>
<tr>
<td>H\textsubscript{2} + O\textsubscript{2}</td>
<td>2.862 (0.005)</td>
<td>11.0 (1.0)</td>
<td>7.5 (0.9)</td>
<td>1.0</td>
</tr>
<tr>
<td>Reaction</td>
<td>2.871 (0.008)</td>
<td>10.9 (1.4)</td>
<td>7.7 (1.4)</td>
<td>2.4</td>
</tr>
</tbody>
</table>

4.2. AuPd nanoparticle structure

EXAFS analysis on the AuPd capillary gave evidence of Au-Pd alloying and indicated that the particles may have a core-shell structure. The structure in the fresh catalyst consists of an Au rich core surrounded by a shell of PdO and metallic Pd domains. Upon reduction in H\textsubscript{2}, this structure is retained with a completely metallic Pd shell. PdH formation is seen in both AuPd and Pd catalysts, in presence of H\textsubscript{2} and H\textsubscript{2} + O\textsubscript{2} characterized by an increase in Pd-Pd distance. When subjected to reaction conditions (addition of a liquid phase), this increase disappears in case of the AuPd catalyst, indicating loss of PdH phase. Simplified structures showing these transformations for the AuPd catalyst are depicted in Scheme 3.

It must be noted here that since structural inhomogeneties may
exist in the sample, the presence of other structures like random alloys cannot be completely discounted [53]. This can be better elucidated using advanced microscopic techniques with elemental mapping [13,54] but lies beyond the scope of the present work.

4.3. Role of Au in inhibiting hydride formation

Pd nanoparticles in H₂ can form PdH phases which may have an impact on the catalytic activity as shown in recent literature [55–57]. For example, Selinsek et. al. [31] very recently reported the formation of bulk PdH during the synthesis of H₂O₂ on monometallic Pd. According to their results, the concentration of hydrogen influenced the specific phase of PdH formed (i.e., αPdH in hydrogen lean, and βPdH in hydrogen rich conditions) as well as the final yield of H₂O₂, in agreement with our observations. The presence of PdH and its influence on catalytic activity has also been shown for other systems. In the hydrogenation of acetylene to ethene, PdH formation leads to excessive ethene formation by over-hydrogenation, thereby reducing selectivity [58]. The selectivity has been shown to be improved on AuPd nanoparticles where Pd being highly dispersed is unable to form PdH which is reflected in much lower ethene formation and hence enhanced ethene selectivity [55]. Similarly, in glycerol oxidation, AuPd nanoparticles provide a balance between hydride formation (beneficial for this reaction) and PdO formation, leading to superior activity compared to monometallic catalysts [56]. In our study, we see that both Pd and AuPd catalysts form PdH in the reactant gas mixture, but for AuPd the PdH phase is lost upon addition of the solvent (in reaction conditions). The introduction of the solvent has been shown to have interesting solvation [59] as well as chemical effects [29] that may change catalytic process. The loss of the PdH phase in the bimetallic system also indicates that the PdH formed in the AuPd catalyst is less stable. Hydride formation in Pd is greatly affected with particle size, with decreased H content in smaller particles [47,60,61]. Alloying with Au has a similar effect as it leads to higher Pd dispersion and hence a lower H content. In fact, temperature-programmed desorption with H₂ (TPD-H₂/TPR) has been used extensively to determine AuPd alloying and Pd dispersion in AuPd catalysts [15,16,62]. Neutron scattering and deuteron (D₂) dedication study on Au-Pd-D system showed that the nature of hydrides formed and site occupancy of D₂(H₂) was different for AuPd and Pd. D₂ was easily desorbed around 325 K for Au₀.2₅Pd₀.7₅, while pure Pd showed a shoulder at 325 K and a sharp peak at 380 K [63]. Hence, it can be inferred that, although PdH formation in AuPd catalysts is possible, it is less stable than in Pd-only catalysts. As a result, these species were not observed in reaction conditions in our XAS measurements. Therefore, we propose that the absence of PdH in AuPd catalysts can help to decrease the hydrogenation of the formed H₂O₂, thereby increasing product selectivity.

5. Conclusions

In-situ XAS using highly active Au, Pd and AuPd catalytic microchannel reactors was performed for probing the chemical environment of the metals during the direct synthesis of hydrogen peroxide. We successfully carried out these measurements in a complex gas-solid-liquid reaction system, operating at high pressures and using potentially flammable reactant mixtures. This demonstrates the prospect of using microreactors as an attractive spectroscopic tool for conducting in-situ studies where "true reaction conditions" can be achieved during measurements. From the XANES analysis, it was found that during reaction both metals are present in their metallic state. The addition of Au did not affect Pd reducibility. EXAFS analysis gave further insight on the Au and Pd co-ordination environment and particle morphology. The fresh catalyst consisted of an Au core and a Pd/PdO shell. During reaction, the Pd was completely reduced and the corresponding structure exhibited a core (Au)-shell (Pd) geometry. No significant restructuring was observed in the conditions studied. Finally, the Pd catalyst showed PdH formation during reaction indicated by an increase in the Pd-Pd distance, unlike the AuPd catalyst. PdH as observed in Pd catalysts may facilitate further hydrogenation of the product to water, thereby lowering selectivity. Thus, we propose that in the reaction conditions studied (presence of acid, absence of halide promoter, ambient reaction temperature and dilute O₂/H₂ mixture) one of the major reasons for enhanced performance observed in AuPd catalyst is the role of Au in inhibiting PdH formation, thereby increasing the selectivity to H₂O₂. The insights from this study can aid in smarter catalyst design and form a step towards understanding the factors that determine the true reaction mechanism.

Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcat.2018.12.017.

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