Palladium-tin catalysts for the direct synthesis of H₂O₂ with high selectivity

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Abstract

The direct synthesis of hydrogen peroxide (H₂O₂) from H₂ and O₂ represents a potentially atom efficient alternative to the current industrial indirect process. We show that the addition of tin to palladium catalysts coupled with an appropriate heat treatment cycle switches-off the sequential hydrogenation and decomposition reactions, enabling selectivities of >95% towards H₂O₂. This effect arises from a tin oxide surface layer that encapsulates small Pd-rich particles while leaving larger Pd-Sn alloy particles exposed. We show this effect is a general feature for oxide supported Pd catalysts containing an appropriate second metal oxide component and we set out the design principles for producing high selectivity Pd-based catalysts for direct H₂O₂ production that do not contain Au.
Currently, the demand for \( \text{H}_2\text{O}_2 \) is met by an indirect process, which produces \( \text{H}_2\text{O}_2 \) through the sequential hydrogenation and oxidation of a substituted anthraquinone \((1)\). For economic reasons, the process is operated at large scale and produces concentrated \( \text{H}_2\text{O}_2 \). In reality, many applications, such as disinfection and water purification, require only dilute \( \text{H}_2\text{O}_2 \) which means that concentrated \( \text{H}_2\text{O}_2 \) has to be diluted at the point of use. Research into the direct synthesis of \( \text{H}_2\text{O}_2 \) from \( \text{H}_2 \) and \( \text{O}_2 \) as a more suitable solution to small-scale, on-site \( \text{H}_2\text{O}_2 \) production has focused on palladium (Pd)-based catalysts \((2-4)\). However, \( \text{H}_2\text{O}_2 \) is itself highly reactive and the presence of \( \text{H}_2 \) favors hydrogenation and decomposition reactions that form water. The addition of strong acids and halides into the reaction medium can suppress the sequential hydrogenation and degradation in supported Pd catalysts \((5)\); but can also promote metal leaching and requires further purification of the \( \text{H}_2\text{O}_2 \) before use.

Bimetallic Au-Pd alloy catalysts have been extensively studied as catalysts for the direct \( \text{H}_2\text{O}_2 \) synthesis reaction on a number of support materials including \( \text{TiO}_2 \), \( \text{SiO}_2 \) and activated carbon \((6-9)\). Comparable yields to monometallic Pd catalysts can be achieved without the need for acid and halide additives in the reaction mixture, and 95% selectivity to \( \text{H}_2\text{O}_2 \) could be achieved with Au-Pd alloy nanoparticles (NPs) dispersed on an acid pre-treated activated carbon support material \((10)\). Hydrogen peroxide hydrogenation could be decoupled from \( \text{H}_2\text{O}_2 \) synthesis with an acid pre-treatment that blocked sites on the carbon support material responsible for \( \text{H}_2\text{O}_2 \) degradation. Although this approach was very successful on an activated carbon support material, the same blocking effect could not be fully achieved on other commercial support materials such as \( \text{SiO}_2 \) and \( \text{TiO}_2 \).

As \( \text{O}_2 \) dissociation is undesirable in the direct synthesis of \( \text{H}_2\text{O}_2 \), the reaction can be treated as a selective hydrogenation of \( \text{O}_2 \). We explored other Pd-metal combinations that are used for selective hydrogenation reactions as potential catalysts for \( \text{H}_2\text{O}_2 \) synthesis, focusing on non-precious metal to lower costs. Tin has been used to modify hydrogenation catalysts in reactions such as the selective hydrogenation of 1-3 butadiene \((11)\). Further examples have been reported for the liquid phase hydrogenation of hexa-1-3-diene and hexa-1-5-diene \((12)\), as well as the hydrogenation of unsaturated alcohols \((13)\). The addition of Sn to Pd or Pt can alter the behavior of the catalyst during hydrogenation reactions and, in particular, may have an effect on subsequent reactions of the products with the catalyst.
We report the development of tin-containing palladium catalysts on commercially available TiO$_2$ and SiO$_2$ supports that can achieve > 95% selectivity toward direct H$_2$O$_2$ synthesis. These catalysts, after being subjected to an appropriate heat treatment regimen, obviate the need for pre-treating the support with acids, and contain far less precious metal than Au-Pd catalysts. Furthermore, we present the general principles whereby high selectivity catalysts can be obtained with other Pd-metal combinations.

Simple impregnation of gold and palladium metal salts onto many catalyst supports has been shown to generate highly active catalysts for direct H$_2$O$_2$ synthesis. In addition, high-temperature calcination or reduction treatments are known to be crucial to improve the stability of the catalyst. As a starting point, we used this simple catalyst preparation methodology to prepare a 2.5wt% Pd-2.5wt% Sn / TiO$_2$ catalyst as well as its monometallic analogs (8, 10). A synergistic effect toward the direct synthesis of H$_2$O$_2$ was observed when both metals were present compared to the analogous monometallic catalysts after calcination in static air at 500 °C for 3 h (Table S1) (14). The activity of this 2.5wt% Pd - 2.5wt% Sn / TiO$_2$ catalyst (62 mol kg$^{-1}$ h$^{-1}$) is similar to that of a 2.5wt% Pd - 2.5wt% Au / TiO$_2$ catalyst (i.e. 64 mol kg$^{-1}$ h$^{-1}$). We then optimized the ratio of Sn-to-Pd while maintaining a total metal content of 5wt% (Table S2) (14), and found an optimum nominal composition, 3wt% Pd - 2 wt% Sn / TiO$_2$, that exhibited an H$_2$O$_2$ productivity of 68 mol kg$^{-1}$ h$^{-1}$ (Table 1, entry 1). By comparison, the H$_2$O$_2$ degradation activity of the optimized Sn-Pd catalyst was very low compared to that reported for Au-Pd systems (65 mol kg$^{-1}$ h$^{-1}$ for 3wt% Pd - 2 wt% Sn / TiO$_2$ versus 235 mol kg$^{-1}$ h$^{-1}$ for 2.5wt% Pd - 2.5wt% Au / TiO$_2$) which indicated that Sn is also playing a beneficial role in preventing the over hydrogenation/decomposition of H$_2$O$_2$. However, the Sn-Pd catalysts calcined at 500 °C for 3 h under static air were unstable to multiple reaction cycles (Table 1, entry 1).

The nature of the catalyst surface and in particular the oxidation states of the active metal are crucial to obtaining high selectivity. Therefore characterization of this 3wt% Pd - 2 wt% Sn / TiO$_2$ catalyst after calcination by X-ray photoelectron spectroscopy (XPS) was carried out and showed the majority of the surface Pd was present as Pd$^{2+}$ while the Sn Auger parameter showed that SnO$_2$ was present in the calcined catalyst (Figure S1, Table S3) (14). Analysis of the nanostructure of this catalyst using scanning transmission electron microscopy – high angle annular dark filed imaging (STEM-HAADF) and electron
energy loss spectroscopy (EELS) revealed that the SnO$_x$ was present as a thin (< 2 nm thick) amorphous film coating the TiO$_2$ support particles (Fig. 1, A to D, and Fig. S2 (14)). A population of 5 - 10 nm NPs were also present in the sample that contained a homogeneous mixture of both Pd and Sn (Figures 1(a)-(d) and S3 (14)). Lattice fringe fitting of these particles strongly suggests a metallic Pd-Sn alloy structure rather than segregated or mixed oxides meaning that only the surface of the particles is oxidised. Many sub-2 nm Pd-rich NPs were also observed and were often associated with the SnO$_x$ thin films, and because these species were much less numerous in a 5wt% Sn-only / TiO$_2$ sample (Figure S4) (14), they were primarily associated with the PdO$_x$ component in the bimetallic catalyst.

A limiting factor in achieving high selectivity towards H$_2$O$_2$ with Au-Pd / TiO$_2$ catalysts prepared by the wet impregnation method is that the catalysts exhibit a variation in composition with particle size, with the smallest particles being Pd-rich (9). These small Pd-rich NPs are likely to be highly active for H$_2$O$_2$ synthesis and also for its subsequent hydrogenation/decomposition, as has been shown when Au-Pd catalysts are prepared by colloidal techniques with particle sizes typically 2 to 4 nm(15). In the case of the Sn-Pd system, the small Pd-rich NPs are often associated with the amorphous SnO$_x$ films. We postulated that it might be possible to further decrease the H$_2$O$_2$ degradation activity of the catalyst by inducing encapsulation of the ultra-small Pd-rich NPs by this SnO$_x$ film. We therefore used subsequent thermal treatments in an attempt to induce a strong-metal-support-interaction (SMSI) between the Pd and SnO$_x$ layer (16-21). We first added a low-temperature reduction step (200 °C, 2 h, 5% H$_2$ in Ar), which made the catalysts stable to multiple reaction cycles (Table 1, entry 2). However, the H$_2$O$_2$ degradation activity increased markedly from 65 to 300 mol kg$^{-1}$ h$^{-1}$, which was associated with the reduction of Pd$^{2+}$ to metallic Pd, as shown by XPS, (Table S3, Figure S1) (14). Metallic Pd is known to be a more effective H$_2$O$_2$ hydrogenation catalyst (7).

Detailed STEM analysis of this reduced sample was carried out to investigate any structural changes in the sample on reduction (Figures S5 and S6) (14). Analysis identified the presence of thin SnO$_x$ films, sub-2 nm Pd NPs, and 5 to 10 nm NPs whose lattice fringe spacings and angles were consistent with Pd-Sn metallic alloy phases. We then re-oxidized, this reduced catalyst to restore Pd$^{2+}$ as the predominant surface species (as confirmed by XPS (Figure S1, Table S3)) (14) and complete an oxidation-reduction-
oxidation (O-R-O) cycle with the aim of encapsulating the small Pd species and re-generating the oxidised Pd-Sn surface on the larger NPs. Re-oxidizing the reduced catalyst for various time periods at 400 °C under static air had little effect on the H₂O₂ synthesis productivity, but markedly decreased the H₂O₂ degradation activity (Fig. 2A). After a 4 h re-oxidation treatment, the catalyst showed no activity toward H₂O₂ degradation and could produce H₂O₂ with an H₂ selectivity of > 95% (Table 1, entry 3). This catalyst was stable to multiple reaction cycles and showed negligible leaching of Sn (0 ppb) or Pd (2 ppb) during a 30 min reaction as measured by ICP-MS. This re-oxidized 3wt% Pd - 2wt% Sn / TiO₂ catalyst was subjected to further H₂O₂ testing including multiple sequential H₂O₂ synthesis tests (Fig. 2B). After running the reaction consecutively 5 times, the H₂O₂ concentration increased linearly to 0.53wt%, retaining both the high H₂O₂ synthesis and zero H₂O₂ degradation rates. This result implies that no subsequent decomposition or hydrogenation reactions of H₂O₂ took place with this catalyst. The re-oxidized 3wt% Pd - 2wt% Sn / TiO₂ catalyst was also tested for H₂O₂ degradation with varying concentrations of H₂O₂ under a pressure of 5% H₂ / CO₂ (Fig. 2C) and showed no degradation of H₂O₂ in solutions of up to 8 wt%, whereas the corresponding Au-Pd / TiO₂ catalyst showed substantially higher H₂O₂ degradation activity at all of the concentrations studied.

The nanostructure of the catalyst after the oxidation-reduction-oxidation treatment was characterized to identify any structural changes that could be responsible for the observed high selectivity. Three structures were again revealed to be present in the catalyst–amorphous SnOₓ films on the TiO₂ particles, small Pd species associated with these films, and larger Pd-Sn NPs (Fig. 1, E to H, and Figures S7 and S8 (14)). Detailed EELS analysis of the thin film regions (Figure S9 (14)) after various heat treatments indicates the presence of SnOₓ films which can be either reduced or oxidised depending on the final heat treatment stage as indicated by the absence/presence of the O K edge in the EELS spectrum. In contrast to the thin films, EELS analysis of Sn-Pd nanoparticles (Figure S10 (14)) at different stages of the heat treatment cycle show no clear O K edge. This confirms these nanoparticles to be metallic Pd-Sn alloys, at least in the bulk, which is also consistent with the lattice fringe fitting. Some slight oxidation of the surface of these particles is possible as detected by our XPS measurements, but at such a level that is below the detectability limit of the EELS measurements. The 3wt% Pd – 2wt% Sn / TiO₂ catalyst after the oxidation-
reduction-oxidation cycle shows evidence that the small Pd-rich particles NPs responsible for high hydrogenation activity often appear to be encapsulated in the amorphous SnOₓ layer (Figure S11 (14)). We suggest that by generating strong metal-support interactions (SMSI) that can effectively ‘bury’ the population of smaller Pd-rich NPs, the H₂O₂ degradation activity of the catalyst is limited (Fig. 3A). The larger uncovered Pd-Sn alloy NPs are then mainly responsible for the H₂O₂ production and are inherently less prone to cause subsequent H₂O₂ degradation than Pd-Au NPs. The monometallic Pd / TiO₂ catalyst that was subjected to the optimized oxidation-reduction-oxidation cycle (Table S4, entries (1-2) (14)) did not induce this effect, confirming that the amorphous layer responsible for SMSI is not TiO₂ based.

To investigate if this effect was unique to the 2wt% Sn - 3wt% Pd / TiO₂ catalyst, similar heat treatment protocols were applied to the analogous 2.5wt% Au - 2.5wt% Pd / TiO₂ system. The catalytic results (Table 1, entries 4-6) show that the same suppression of H₂O₂ degradation was also not observed for a corresponding oxidized-reduced-oxidized Au-Pd / TiO₂ catalyst. Results obtained for monometallic Pd and bimetallic Sn-Pd catalysts (Table S4, entries 3-5) (14) also indicate that the reduction step is crucial, as three oxidative treatments fail to induce the effect. It should also be noted that the 200°C reduction temperature used in this study is much lower than that typically reported to induce SMSI effects in TiO₂ only supported catalyst systems (22). To demonstrate the proposed SMSI effect with SnO₂, a ‘model’ 5wt% Pd / SnO₂ catalyst was also prepared and studied by electron microscopy. In the oxidized state, EELS mapping showed the PdOₓ particles appear to be clean (Fig. 3B, Figs. S12, S13 (14)), whereas after the oxidation-reduction-oxidation treatment the Pd particles show clear evidence of a SnOₓ overlayer (Fig. 3C, and Figs. S14, S15 (14)).

Further evidence that the suppression of the H₂O₂ degradation does not originate from encapsulation of small Pd particles by TiO₂ but is an SMSI effect arising from the secondary SnOₓ component was obtained by using a non-reducible SiO₂ support in place of the TiO₂. When the ratio of Sn : Pd on SiO₂ was optimized (Table S5) (14) and the same oxidation-reduction-oxidation heat treatment regimen was applied (Table 1, entries 7-9), the resulting 1wt% Pd – 4wt% Sn / SiO₂ catalyst produced H₂O₂ at a rate of 50 mol kg⁻¹ h⁻¹ (Table 1, entry 9) and showed no activity toward subsequent H₂O₂ degradation. This 1wt% Pd – 4wt% Sn / SiO₂ catalyst showed no propensity to decompose or hydrogenate H₂O₂ even in
solutions containing up to 12wt% H$_2$O$_2$ (Figure S16) (14). Furthermore, the catalytic performance of the 1wt% Pd – 4wt% Sn / SiO$_2$ material was stable through multiple uses (Table S5) (14). XPS analysis (Figure S1, Table S4) (14) and electron microscopy characterization (Figures S17 and S18) (14) of the 1wt% Pd – 4wt% Sn / SiO$_2$ catalyst showed analogous compositional and structural features (i.e. (i) amorphous SnO$_x$ films and associated ultra-small Pd-rich NPs and (ii) larger Pd-Sn alloy particles) as its 3wt% Pd - 2wt% Sn / TiO$_2$ counterpart.

Our approach of encapsulating small Pd-rich species generated by wet impregnation preparations with secondary oxides can be generalized if the second metal oxide added to the Pd/primary oxide (e.g. TiO$_2$/SiO$_2$) support system (i) shows no decomposition activity towards H$_2$O$_2$ when in oxide form, (ii) forms an alloy or mixed oxide phase with Pd, and (iii) can encapsulate small Pd-rich particles by SMSI. Based on these design rules and a using a nominal composition of 0.5wt% Pd - 4.5wt% M / TiO$_2$ that had been subjected to the optimised oxidation-reduction-oxidation treatment, we synthesized a series of bimetallic catalysts where M = Ni, Zn, Ga, In and Co. All of these catalysts showed activity for H$_2$O$_2$ synthesis (between 30-64% of that displayed by the Sn-Pd catalyst) and no activity for H$_2$O$_2$ degradation (Table S6) (14). Thus, our approach opens up the possibility of designing reusable catalysts with greatly reduced precious metal content while still retaining high selectivity to H$_2$O$_2$. 
References

14. Supporting information is available online (Experimental details, Tables S1–6, Figures S1–18, and references 23-25)

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Table 1. Direct H₂O₂ synthesis kinetics. Catalytic testing results of the optimized 3wt% Pd – 2wt% Sn / TiO₂ and 2.5wt% Pd - 2.5wt% Au / TiO₂ catalysts after being subjected to various heat treatment regimens.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>H₂O₂ Productivity* (+ 2nd use value in brackets) mol kg⁻¹ cat⁻¹ h⁻¹</th>
<th>H₂O₂ Degradationb mol kg⁻¹ cat⁻¹ h⁻¹</th>
<th>H₂ Conversion %</th>
<th>H₂O₂ Selectivity %</th>
</tr>
</thead>
<tbody>
<tr>
<td>3% Pd - 2% Sn / TiO₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>500 °C / 3 h / air</td>
<td>68 (14)</td>
<td>65</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>2</td>
<td>+ Reduced 200 °C / 2 h</td>
<td>60 (60)</td>
<td>300</td>
<td>20</td>
<td>46</td>
</tr>
<tr>
<td>3</td>
<td>+ 400 °C / 4 h / air</td>
<td>61 (60)</td>
<td>0</td>
<td>9</td>
<td>96</td>
</tr>
<tr>
<td>2.5% Pd - 2.5% Au / TiO₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>400 °C / 3 h / air</td>
<td>64 (64)</td>
<td>235</td>
<td>22</td>
<td>66</td>
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<td>5</td>
<td>+ Reduced 200 °C / 2 h</td>
<td>135</td>
<td>396</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>6</td>
<td>+ 400 °C / 4 h / air</td>
<td>82</td>
<td>277</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>1% Pd - 4% Sn / SiO₂</td>
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<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>7</td>
<td>400 °C / 3 h / air</td>
<td>66 (22)</td>
<td>62</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>8</td>
<td>+ Reduced 200 °C / 2 h</td>
<td>76 (76)</td>
<td>340</td>
<td>13</td>
<td>70</td>
</tr>
<tr>
<td>9</td>
<td>+ 400 °C / 3 h / air</td>
<td>50 (50)</td>
<td>0</td>
<td>8</td>
<td>95</td>
</tr>
</tbody>
</table>

a) Rate of H₂O₂ production determined after reaction using reaction conditions: 5% H₂/CO₂ (2.9 MPa) and 25% O₂/CO₂ (1.1 MPa), 8.5 g solvent (2.9 g HPLC water, 5.6 g MeOH) 0.01g catalyst, 2 °C, 1200 rpm, 30 mins.

b) Rate of H₂O₂ degradation calculated from the loss of H₂O₂ using standard reaction conditions: 5%H₂/CO₂ (2.9 MPa), 8.5 g solvent (5.6 g MeOH, 2.22 g H₂O and 0.68 g 50% H₂O₂), 0.01 g catalyst, 2 °C, 1200 rpm, 30 mins.

n.d. = not determined
Figure 1. Microstructural analysis of 3wt% Pd – 2wt% Sn / TiO₂ - Representative STEM-HAADF grayscale images and STEM-EELS (RGB) maps of 3wt% Pd – 2wt% Sn / TiO₂ catalysts at (a-d) the oxidized and (e-h) the oxidized-reduced-oxidized stages. From the STEM-HAADF images, three distinct supported species are found in both these catalysts: namely (i) relatively large (i.e. 3-10 nm) nanoparticles (white arrows), (ii) smaller clusters on the nm or sub-nm scale (white circles), and (iii) continuous film covering the TiO₂ support surface. The qualitative elemental distribution of Pd, Sn and Ti are represented by red, green and blue respectively in the STEM-EELS maps. (d) and (h) show that the continuous film mainly contains Sn, which either supports or embeds the smaller Pd-rich species. (c) and (g) demonstrate that the larger particles are Pd-Sn alloys. Scale bars in the images and maps represent 1 nm unless noted otherwise.
**Figure 2.** $\text{H}_2\text{O}_2$ direct synthesis and degradation testing of 3wt% Pd - 2wt% Sn / TiO$_2$

Experimental conditions reported in Table 1 for figure 2 (a-c).

(a) Effect of re-oxidation time under static air at 400 °C on $\text{H}_2\text{O}_2$ synthesis and $\text{H}_2\text{O}_2$ degradation activity for oxidised-reduced 3wt% Pd - 2wt% Sn / TiO$_2$ catalyst.

(b) Sequential $\text{H}_2\text{O}_2$ synthesis reactions over the 3wt% Pd - 2wt% Sn / TiO$_2$ material after oxidation-reduction-oxidation treatment.

(c) Degradation activity of optimized oxidised-reduced-oxidised 3wt% Pd - 2wt% Sn / TiO$_2$ catalyst compared to 2.5wt% Au-2.5wt% Pd / TiO$_2$ (8).
Figure 3. Evolution of catalyst through oxidation-reduction-oxidation cycle (a) Proposed mechanism for switching-off $\text{H}_2\text{O}_2$ hydrogenation by small Pd-rich NPs through a strong metal support interaction (SMSI). The secondary metal must form both an alloy with Pd and oxidize to form a secondary support (i.e. SnO$_x$) that can encapsulate the relatively small, poorly alloyed, Pd-rich NPs after an oxidation-reduction-oxidation cycle. This step prevents these NPs from decomposing/hydrogenating the $\text{H}_2\text{O}_2$ product. STEM-EELS mapping of a 5wt% Pd / SnO$_2$ model catalyst at the (b) oxidized and (c) oxidized-reduced-oxidized stages, showing partial encapsulation of the Pd NP (red) by SnO$_x$ (green) after the oxidation-reduction-oxidation heat treatment cycle. The Sn intensities in the SnO$_2$ support area were deliberately saturated to show up any relatively weak signals in the particle region. The scale bars represent 1 nm.