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# **Palladium-tin catalysts for the direct synthesis of H<sub>2</sub>O<sub>2</sub> with high selectivity**

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## **Abstract**

The direct synthesis of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) from  $\text{H}_2$  and  $\text{O}_2$  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  $\text{H}_2\text{O}_2$ . 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  $\text{H}_2\text{O}_2$  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<sub>2</sub> and SiO<sub>2</sub> supports that can achieve > 95% selectivity toward direct H<sub>2</sub>O<sub>2</sub> 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<sub>2</sub>O<sub>2</sub> 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<sub>2</sub> catalyst as well as its monometallic analogs (8, 10). A synergistic effect toward the direct synthesis of H<sub>2</sub>O<sub>2</sub> 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<sub>2</sub> catalyst (62 mol kg<sup>-1</sup> h<sup>-1</sup>) is similar to that of a 2.5wt% Pd - 2.5wt% Au / TiO<sub>2</sub> catalyst (8) (*i.e.* 64 mol kg<sup>-1</sup> h<sup>-1</sup>). 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<sub>2</sub>, that exhibited an H<sub>2</sub>O<sub>2</sub> productivity of 68 mol kg<sup>-1</sup> h<sup>-1</sup> (Table 1, entry 1). By comparison, the H<sub>2</sub>O<sub>2</sub> degradation activity of the optimized Sn-Pd catalyst was very low compared to that reported for Au-Pd systems (65 mol kg<sup>-1</sup> h<sup>-1</sup> for 3wt% Pd - 2 wt% Sn / TiO<sub>2</sub> versus 235 mol kg<sup>-1</sup> h<sup>-1</sup> for 2.5wt% Pd - 2.5wt% Au / TiO<sub>2</sub>) which indicated that Sn is also playing a beneficial role in preventing the over hydrogenation/decomposition of H<sub>2</sub>O<sub>2</sub>. 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<sub>2</sub> catalyst after calcination by X-ray photoelectron spectroscopy (XPS) was carried out and showed the majority of the surface Pd was present as Pd<sup>2+</sup> while the Sn Auger parameter showed that SnO<sub>2</sub> 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 field imaging (STEM-HAADF) and electron

energy loss spectroscopy (EELS) revealed that the SnO<sub>x</sub> was present as a thin (< 2 nm thick) amorphous film coating the TiO<sub>2</sub> 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<sub>x</sub> thin films, and because these species were much less numerous in a 5wt% Sn-only / TiO<sub>2</sub> sample (Figure S4) (14), they were primarily associated with the PdO<sub>x</sub> component in the bimetallic catalyst.

A limiting factor in achieving high selectivity towards H<sub>2</sub>O<sub>2</sub> with Au-Pd / TiO<sub>2</sub> 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<sub>2</sub>O<sub>2</sub> 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<sub>x</sub> films. We postulated that it might be possible to further decrease the H<sub>2</sub>O<sub>2</sub> degradation activity of the catalyst by inducing encapsulation of the ultra-small Pd-rich NPs by this SnO<sub>x</sub> film. We therefore used subsequent thermal treatments in an attempt to induce a strong-metal-support-interaction (SMSI) between the Pd and SnO<sub>x</sub> layer (16-21). We first added a low-temperature reduction step (200 °C, 2 h, 5% H<sub>2</sub> in Ar), which made the catalysts stable to multiple reaction cycles (Table 1, entry 2). However, the H<sub>2</sub>O<sub>2</sub> degradation activity increased markedly from 65 to 300 mol kg<sup>-1</sup> h<sup>-1</sup>, which was associated with the reduction of Pd<sup>2+</sup> to metallic Pd, as shown by XPS, (Table S3, Figure S1) (14). Metallic Pd is known to be a more effective H<sub>2</sub>O<sub>2</sub> 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<sub>x</sub> 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<sup>2+</sup> 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 H<sub>2</sub>O<sub>2</sub> synthesis productivity, but markedly decreased the H<sub>2</sub>O<sub>2</sub> degradation activity (Fig. 2A). After a 4 h re-oxidation treatment, the catalyst showed no activity toward H<sub>2</sub>O<sub>2</sub> degradation and could produce H<sub>2</sub>O<sub>2</sub> with an H<sub>2</sub> 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 / TiO<sub>2</sub> catalyst was subjected to further H<sub>2</sub>O<sub>2</sub> testing including multiple sequential H<sub>2</sub>O<sub>2</sub> synthesis tests (Fig. 2B). After running the reaction consecutively 5 times, the H<sub>2</sub>O<sub>2</sub> concentration increased linearly to 0.53wt%, retaining both the high H<sub>2</sub>O<sub>2</sub> synthesis and zero H<sub>2</sub>O<sub>2</sub> degradation rates. This result implies that no subsequent decomposition or hydrogenation reactions of H<sub>2</sub>O<sub>2</sub> took place with this catalyst. The re-oxidized 3wt% Pd - 2wt% Sn / TiO<sub>2</sub> catalyst was also tested for H<sub>2</sub>O<sub>2</sub> degradation with varying concentrations of H<sub>2</sub>O<sub>2</sub> under a pressure of 5% H<sub>2</sub> / CO<sub>2</sub> (Fig. 2C) and showed no degradation of H<sub>2</sub>O<sub>2</sub> in solutions of up to 8 wt%, whereas the corresponding Au-Pd / TiO<sub>2</sub> catalyst showed substantially higher H<sub>2</sub>O<sub>2</sub> 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 SnO<sub>x</sub> films on the TiO<sub>2</sub> 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 SnO<sub>x</sub> 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 / TiO<sub>2</sub> 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 SnO<sub>x</sub> 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 H<sub>2</sub>O<sub>2</sub> degradation activity of the catalyst is limited (Fig. 3A). The larger uncovered Pd-Sn alloy NPs are then mainly responsible for the H<sub>2</sub>O<sub>2</sub> production and are inherently less prone to cause subsequent H<sub>2</sub>O<sub>2</sub> degradation than Pd-Au NPs. The monometallic Pd / TiO<sub>2</sub> 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 TiO<sub>2</sub> based.

To investigate if this effect was unique to the 2wt% Sn - 3wt%Pd / TiO<sub>2</sub> catalyst, similar heat treatment protocols were applied to the analogous 2.5wt% Au -2.5wt% Pd / TiO<sub>2</sub> system. The catalytic results (Table 1, entries 4-6) show that the same suppression of H<sub>2</sub>O<sub>2</sub> degradation was also not observed for a corresponding oxidized-reduced-oxidized Au-Pd / TiO<sub>2</sub> 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 TiO<sub>2</sub>-only supported catalyst systems (22). To demonstrate the proposed SMSI effect with SnO<sub>2</sub>, a 'model' 5wt% Pd / SnO<sub>2</sub> catalyst was also prepared and studied by electron microscopy. In the oxidized state, EELS mapping showed the PdO<sub>x</sub> 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 an SnO<sub>x</sub> overlayer (Fig. 3C, and Figs. S14, S15 (14)).

Further evidence that the suppression of the H<sub>2</sub>O<sub>2</sub> degradation does not originate from encapsulation of small Pd particles by TiO<sub>2</sub> but is an SMSI effect arising from the secondary SnO<sub>x</sub> component was obtained by using a non-reducible SiO<sub>2</sub> support in place of the TiO<sub>2</sub>. When the ratio of Sn : Pd on SiO<sub>2</sub> 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 / SiO<sub>2</sub> catalyst produced H<sub>2</sub>O<sub>2</sub> at a rate of 50 mol kg<sup>-1</sup> h<sup>-1</sup> (Table 1, entry 9) and showed no activity toward subsequent H<sub>2</sub>O<sub>2</sub> degradation. This 1wt% Pd – 4wt% Sn / SiO<sub>2</sub> catalyst showed no propensity to decompose or hydrogenate H<sub>2</sub>O<sub>2</sub> even in



solutions containing up to 12wt% H<sub>2</sub>O<sub>2</sub> (Figure S16) (14). Furthermore, the catalytic performance of the 1wt% Pd – 4wt% Sn / SiO<sub>2</sub> 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<sub>2</sub> catalyst showed analogous compositional and structural features (*i.e.* (i) amorphous SnO<sub>x</sub> films and associated ultra-small Pd-rich NPs and (ii) larger Pd-Sn alloy particles) as its 3wt% Pd - 2wt% Sn / TiO<sub>2</sub> 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<sub>2</sub>/SiO<sub>2</sub>) support system (i) shows no decomposition activity towards H<sub>2</sub>O<sub>2</sub> 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 using a nominal composition of 0.5wt% Pd - 4.5wt% M / TiO<sub>2</sub> 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<sub>2</sub>O<sub>2</sub> synthesis (between 30-64% of that displayed by the Sn-Pd catalyst) and no activity for H<sub>2</sub>O<sub>2</sub> 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<sub>2</sub>O<sub>2</sub>.

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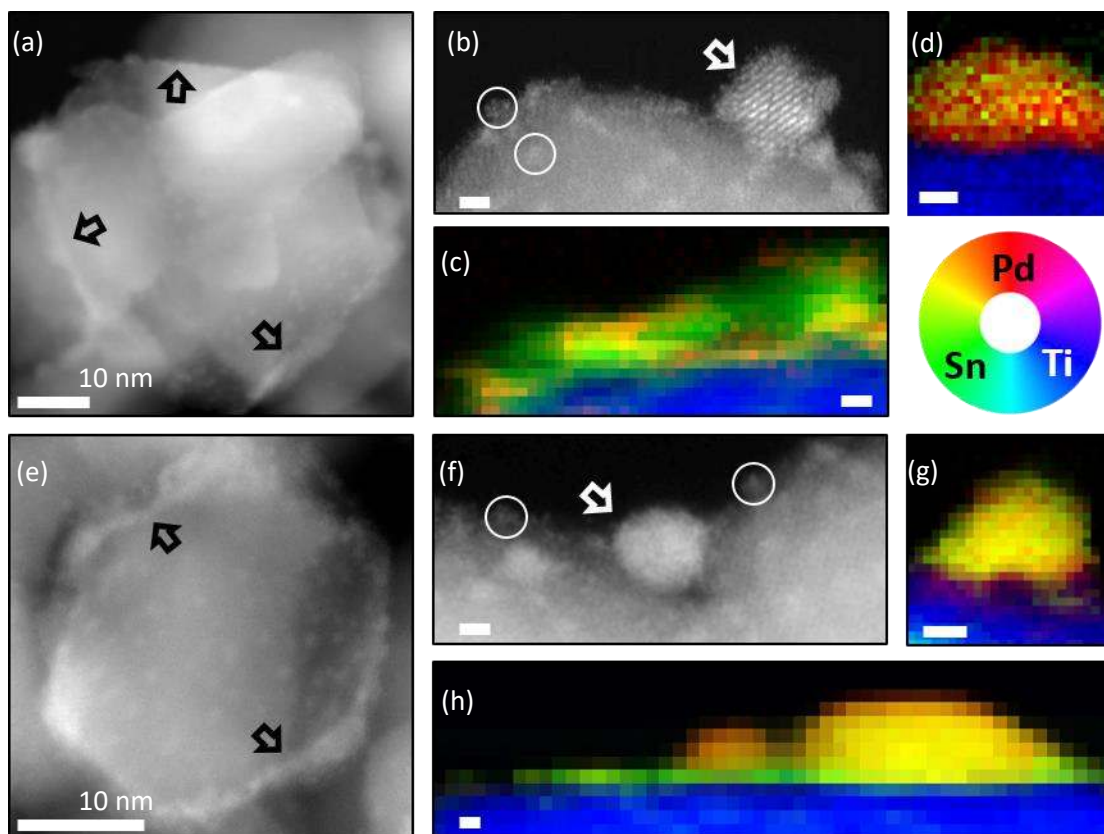
**Table 1. Direct H<sub>2</sub>O<sub>2</sub> synthesis kinetics.** Catalytic testing results of the optimized 3wt% Pd – 2wt% Sn / TiO<sub>2</sub> and 2.5wt% Pd - 2.5wt% Au / TiO<sub>2</sub> catalysts after being subjected to various heat treatment regimens.

Entry	Catalyst	H <sub>2</sub> O <sub>2</sub>	H <sub>2</sub> O <sub>2</sub>	H <sub>2</sub>	H <sub>2</sub> O <sub>2</sub>
		Productivity <sup>a</sup> (+ 2 <sup>nd</sup> use value in brackets) mol kg <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>	Degradation <sup>b</sup> mol kg <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>	Conversion %	Selectivity %
<b>3% Pd - 2% Sn / TiO<sub>2</sub></b>					
1	500 °C / 3 h / air	68 (14)	65	n.d.	n.d.
2	+ Reduced 200 °C / 2 h	60 (60)	300	20	46
3	+ 400 °C / 4 h / air	61 (60)	0	9	96
<b>2.5% Pd - 2.5% Au / TiO<sub>2</sub></b>					
4	400 °C / 3 h / air	64 (64)	235	22	66
5	+ Reduced 200 °C / 2 h	135	396	n.d.	n.d.
6	+ 400 °C / 4 h / air	82	277	n.d.	n.d.
<b>1% Pd - 4% Sn / SiO<sub>2</sub></b>					
7	400 °C / 3 h / air	66 (22)	62	n.d.	n.d.
8	+ Reduced 200 °C / 2 h	76 (76)	340	13	70
9	+ 400 °C / 3 h / air	50 (50)	0	8	95

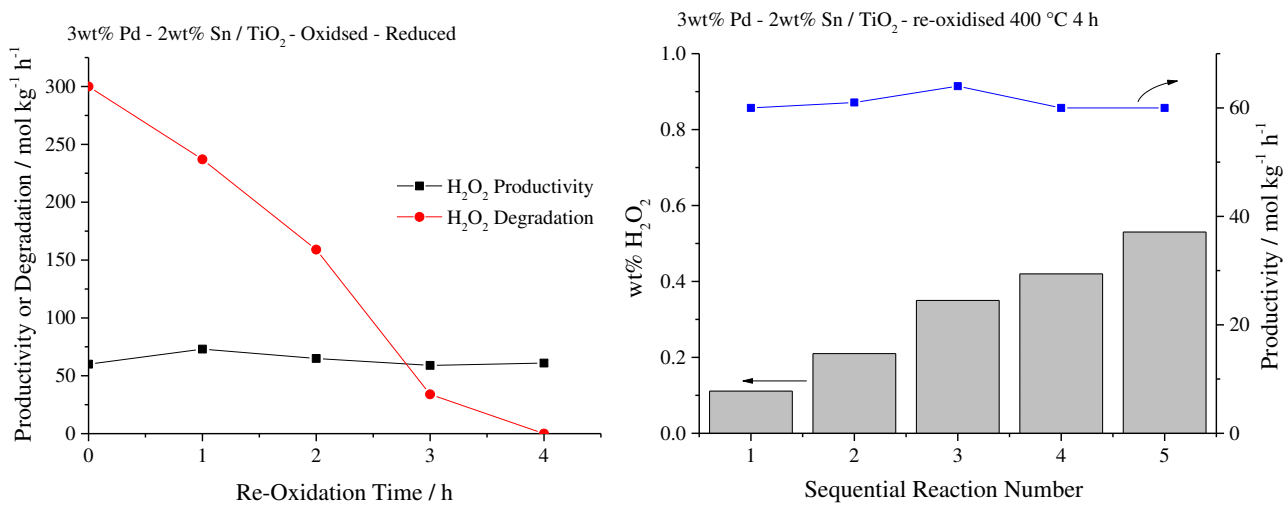
a) Rate of H<sub>2</sub>O<sub>2</sub> production determined after reaction using reaction conditions: 5% H<sub>2</sub>/CO<sub>2</sub> (2.9 MPa) and 25% O<sub>2</sub>/CO<sub>2</sub> (1.1 MPa), 8.5 g solvent (2.9 g HPLC water, 5.6 g MeOH) 0.01g catalyst, 2 °C , 1200 rpm, 30 mins.

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

n.d. = not determined

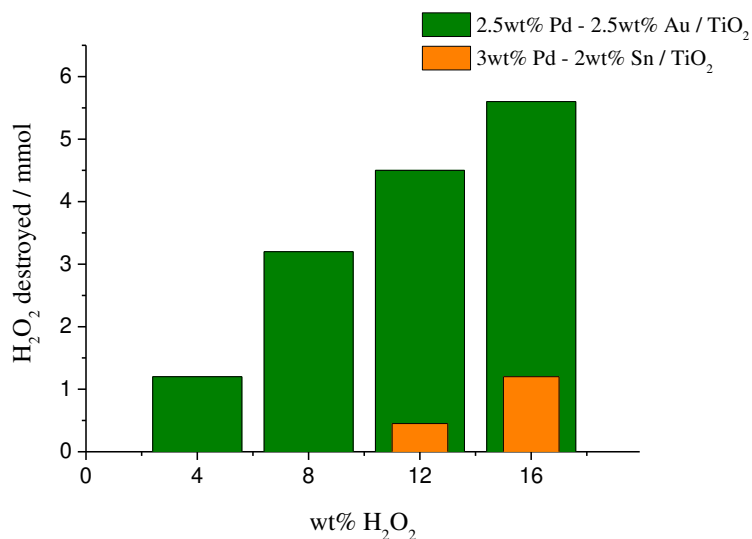


**Figure 1. Microstructural analysis of 3wt% Pd – 2wt% Sn / TiO<sub>2</sub>** - Representative STEM-HAADF grayscale images and STEM-EELS (RGB) maps of 3wt% Pd – 2wt% Sn / TiO<sub>2</sub> catalysts at (a-d) the oxidized and (e-h) the oxidized-reduced-oxidized stages. From the STEM-HAADF images, three 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 TiO<sub>2</sub> 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.



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

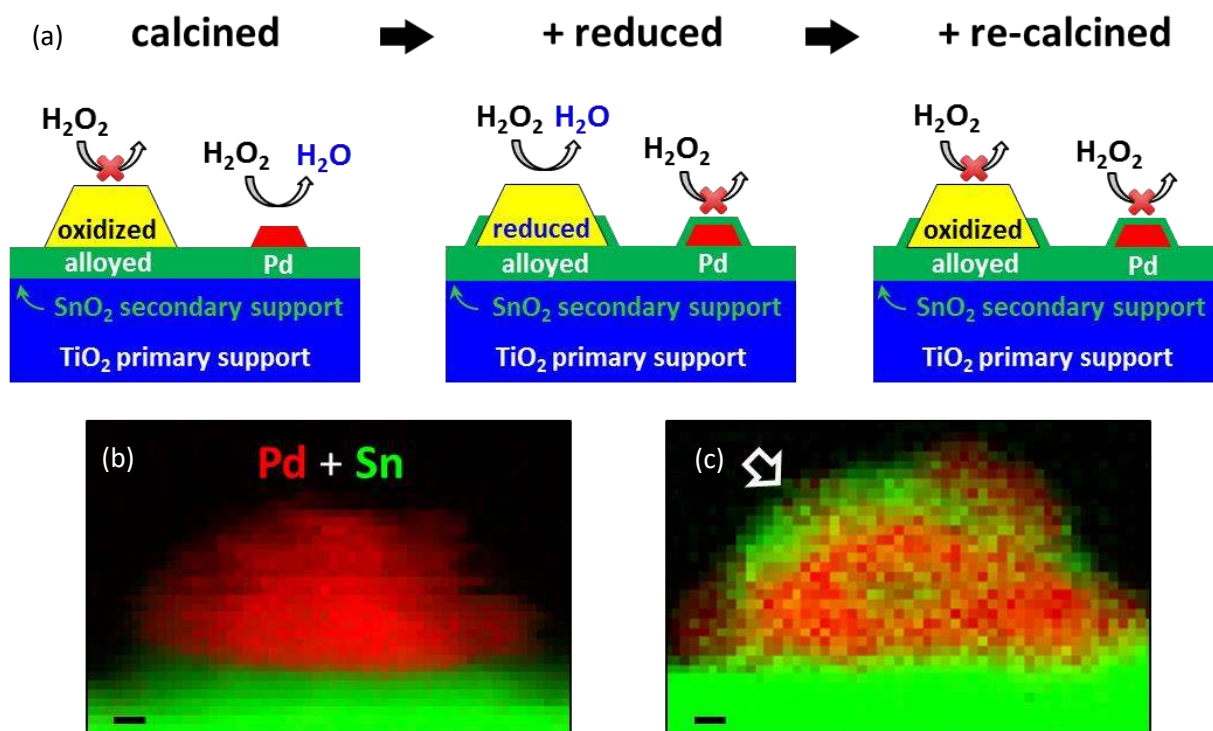
(b) Sequential H<sub>2</sub>O<sub>2</sub> synthesis reactions over the 3wt% Pd - 2wt% Sn / TiO<sub>2</sub> material after oxidation-reduction-oxidation treatment.



(c) Degradation activity of optimized oxidised-reduced-oxidised 3wt% Pd - 2 wt% Sn / TiO<sub>2</sub> catalyst compared to 2.5wt% Au-2.5wt% Pd / TiO<sub>2</sub> (8)

**Figure 2.** -H<sub>2</sub>O<sub>2</sub> direct synthesis and degradation testing of 3wt% Pd - 2wt% Sn / TiO<sub>2</sub>

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



**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.*  $\text{SnO}_x$ ) 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 /  $\text{SnO}_2$  model catalyst at the (b) oxidized and (c) oxidized-reduced-oxidized stages, showing partial encapsulation of the Pd NP (red) by  $\text{SnO}_x$  (green) after the oxidation-reduction-oxidation heat treatment cycle. The Sn intensities in the  $\text{SnO}_2$  support area were deliberately saturated to show up any relatively weak signals in the particle region. The scale bars represent 1 nm.