The effect of catalyst preparation method on the performance of supported Au-Pd catalysts for the direct synthesis of hydrogen peroxide

Supplementary Information

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Measurement of the uptake of Au and Pd compounds during impregnation using UV-vis spectroscopy

The uptake of Au and Pd precursor salts onto C and TiO₂ was assessed using ultraviolet-visible spectroscopy taking into consideration both metal concentration and stirring time. With the aid of a distilled water reference, the rate of metal uptake onto C was found to be unaffected by Au-Pd precursor concentration (Figures SOM 1, 2a). The UV-vis spectra recorded at intervals; 2, 5 and 10mins after stirring C with the Au-Pd precursor solution are identical to the water reference. This indicates that the Au and Pd have been rapidly adsorbed onto the C. After stirring is stopped a clear liquid phase is observed (Fig SOM 2b). In contrast, the spectra recorded for AuPd/TiO₂ catalysts show a characteristic Au plasmon absorbance band in the UV region centred around 300nm for all the times investigated (Figures SOM 3a, 4a) indicating that the uptake of Au and Pd onto TiO₂ proceeds significantly slower than for C. A UV-vis spectrum was recorded for the Au-Pd precursor solution only and indeed this is identical to spectra recorded at intervals after the addition of TiO₂. Even after 25 minutes stirring Au and Pd are still present in solution (28.5ml water) and it seems likely that removal of water to generate a paste is required to facilitate this uptake (akin to an incipient wetness technique). In addition, the absorbance profiles for AuPd/TiO₂ appear unaffected by the Au-Pd concentration.

There is a considerable difference in surface area between C (Aldrich G-60 = ~800m²/g) and TiO₂ (Degussa P-25 = 48m²/g) materials and therefore an additional experiment was performed to establish the role of surface area on Au-Pd uptake. This involved increasing the mass of TiO₂ used from 0.475 to 7.92g to give an exposed surface area equivalent to C and using additional water for effective stirring. The subsequent UV-vis spectrum (Fig SOM 5) showed only minor uptake of Au-Pd onto TiO₂ even after increasing the mass of support, confirming that the rapid uptake of metal onto C is not merely a surface area effect. We suggest that the iso-electric point (IEP) of each support (IEP C = pH 3.2, IEP TiO₂ = 6.4 ) could be a further factor concerning this observed behaviour.
**Fig SOM 1:** Plot of absorbance against wavelength for AuPd/C catalyst solution (water added = 2ml). Upon mixing Au-Pd precursors with C, sample extractions (0.5ml) were performed at intervals: (a) 2mins, (b) 5mins, (c) 10mins and referenced against the Au-Pd solution and distilled water (blank).
**Fig SOM 2a:** Plot of absorbance against wavelength for AuPd/C catalyst solution (water added = 28.5ml). Upon mixing Au-Pd precursors with C, sample extractions (0.5ml) were performed at intervals: (a) 2mins, (b) 5mins, (c) 10mins and referenced against the Au-Pd solution and distilled water (blank).

![Absorbance vs Wavelength Graph](image)

**Fig SOM 2b:** Complimentary Images of the Au-Pd precursor solution (water added = 28.5ml) mixed with C support (left) and after 30 seconds rest (right) showing near-instant uptake of metal onto C.
**Fig SOM 3a:** Plot of absorbance against wavelength for AuPd/TiO$_2$ catalyst solution (water added = 2ml). Upon mixing Au-Pd precursors with TiO$_2$, sample extractions (0.5ml) were performed at intervals: (a) 2mins, (b) 5mins, (c) 10mins and referenced against the Au-Pd precursor and distilled water (blank).

**Fig SOM 3b:** Complimentary images of the Au-Pd precursor solution (water added = 2ml) before addition of support (left) and after mixing with TiO$_2$/ reduced to a paste consistency (right).
Fig SOM 4a: Plot of absorbance against wavelength for AuPd/TiO$_2$ catalyst solution (water added = 28.5ml). Upon mixing Au-Pd precursors with TiO$_2$, sample extractions (0.5ml) were performed at intervals: (a) 2mins, (b) 5mins, (c) 10mins, (d) 15mins, (e) 25mins and referenced against the Au-Pd precursor and distilled water (blank).

Fig SOM 4b: Complimentary images of the Au-Pd precursor solution (water added = 28.5ml) before addition of support (left) and mixed with TiO$_2$ support (right).
**Fig SOM 5:** Plot of absorbance against wavelength for AuPd/TiO$_2$ catalyst* solution (water added = 100ml). Upon mixing the Au-Pd precursors with C, sample extractions (0.5ml) were performed at intervals: (a) 2mins, (b) 5mins, (c) 10mins and referenced against the Au-Pd solution and distilled water (blank).

* The mass of TiO$_2$ was increased from 0.475 to 7.92g to give an exposed surface area equivalent to C.

\[
S_{\text{BET}} \text{ Carbon (Aldrich G-60)} = \sim 800 \text{m}^2/\text{g} \\
S_{\text{BET}} \text{ Titania (Degussa P-25)} = 48 \text{m}^2/\text{g}
\]
Hydrogen peroxide decomposition studies

Hydrogen peroxide decomposition was evaluated using a Parr Instruments stainless steel autoclave with a nominal volume of 50 ml and a maximum working pressure of 14 MPa. To test each catalyst for H₂O₂ decomposition, the autoclave was charged with catalyst (0.01g) and a solution containing 4 wt% H₂O₂ (5.6 g MeOH, 2.22 g H₂O and 0.68 g H₂O₂ (50 %)). The charged autoclave was then purged three times with 25% O₂/CO₂ (0.7 MPa) before filling with 25% O₂/CO₂ to a pressure of 2.9 MPa at 20 °C. The temperature was allowed to decrease to 2°C followed by stirring (at 1200 rpm) of the reaction mixture for 30 mins. The above reaction parameters represent the optimum conditions we have established for the synthesis of H₂O₂. The only difference is the absence of H₂ and the addition of H₂O₂ in the reaction mixture. The wt% of H₂O₂ hydrogenated or decomposed was determined by titrating aliquots of the fresh solution and the solution after reaction with acidified Ce(SO₄)₂ (0.0288 M) in the presence of two drops of ferroin indicator. The data are shown in Table S1.

Table S1 Effect of the amount of water added during the impregnation step of catalyst preparation on the activity of TiO₂-supported catalysts for H₂O₂ decomposition (0.5 g preparation scale).a

<table>
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<tr>
<th>H₂O/ml</th>
<th>[Au] /mol l⁻¹b</th>
<th>[Pd] /mol dm³⁻</th>
<th>Decomposition activity /molH₂O₂/kg-cat/h⁻c</th>
</tr>
</thead>
<tbody>
<tr>
<td>2d</td>
<td>0.248</td>
<td>0.458</td>
<td>103</td>
</tr>
<tr>
<td>2</td>
<td>0.062</td>
<td>0.115</td>
<td>172</td>
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<tr>
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<td>0.0106</td>
<td>157</td>
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<tr>
<td>28.5</td>
<td>0.0021</td>
<td>0.0040</td>
<td>104</td>
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</table>

a5wt% AuPd/ TiO₂ catalyst (0.5 g preparation scale) with water added during the impregnation step prior to drying (110 °C, 48 h), b concentration of the metals prior to drying at 110 °C, c30 min decomposition of 4 mol% H₂O₂, d catalyst formed into a paste by stirring at 80 °C to remove 75% of the 2ml water present in the impregnation step.