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# Silver Palladium catalysts for the direct synthesis of hydrogen peroxide

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### Summary

A series of bimetallic silver-palladium catalysts supported on titania were prepared by wet impregnation and assessed for the direct synthesis of hydrogen peroxide, and its subsequent side reactions. The addition of silver to a palladium catalyst was found to significantly decrease hydrogen peroxide productivity and hydrogenation, but crucially increase the rate of decomposition. The decomposition product; that is predominantly hydroxyl radicals can be used to decrease bacterial colonies. The interaction between silver and palladium were characterised using SEM, XRD, XPS and TPR. The results of the TPR and XPS indicated the formation of a silver-palladium alloy. The optimal 1% Ag-4% Pd/TiO<sub>2</sub> bimetallic catalyst was able to produce ~200ppm of H<sub>2</sub>O<sub>2</sub> in 30 minutes. The findings demonstrate that AgPd/TiO<sub>2</sub> catalysts are active for the synthesis of hydrogen peroxide and its subsequent decomposition to reactive oxygen species. The catalysts are promising for use in wastewater treatment as they combine both the disinfectant properties of silver, hydrogen peroxide production, and subsequent decomposition.

## Introduction

Currently around 2.2million metric tonnes of  $H_2O_2$  are produced by an indirect process in which  $H_2$  and  $O_2$  are reacted separately and safely with anthraquinone as a molecular vector<sup>1</sup>. The anthraquinone is sequentially hydrogenated and oxidised to yield  $H_2O_2$  and provides concentrated  $H_2O_2$  (70 wt.%) after extraction. This process is economic only on a large scale, and is not 100% C or  $H_2$  efficient<sup>2,3</sup>, and most oxidation processes that utilise  $H_2O_2$  downstream require much lower concentrations. The catalytically driven direct synthesis (DS) of  $H_2O_2$  from  $H_2$  and  $O_2$  was first postulated as an alternative over 100 years ago<sup>4,5</sup> and presents an attractive solution. Synthesis of  $H_2O_2$  on site at the required concentration (2-8wt%) is particularly desirable as this would completely eliminate transportation, concentration/extraction and storage costs. The key requirements for  $H_2O_2$  formed using a direct synthesis methodology is a hydrogen peroxide selectivity of >90% based on  $H_2$  and that the  $H_2O_2$  produced should be free from acid and halides additives. These are typically added to the reaction medium when utilising catalysts based on Pd to inhibit non selective reactions such as combustion and hydrogenation<sup>6,7</sup> (Scheme 1).

Hutchings *et al.* were the first to show that gold based catalysts were active for the direct synthesis of  $H_2O_2$ . In their initial studies on gold,  $Pd/Al_2O_3$ ,  $Au/Al_2O_3$  and Au:Pd (1:1)/ $Al_2O_3$  catalysts containing 5 wt.% metal were prepared and evaluated for the synthesis of  $H_2O_2$ . The rate of  $H_2O_2$  formation on the supported Au catalyst was observed to be more than 4 times higher than that of the supported Pd catalyst. The bimetallic AuPd/Al\_2O\_3 catalysts showed a significantly higher rate of  $H_2O_2$  formation than both the monometallic Au and Pd catalysts. This indicated a synergistic effect between Au and Pd.<sup>8,9</sup> Subsequently, Haruta *et al.* reported that Au/SiO<sub>2</sub> catalysts were effective at catalysing the direct

synthesis of H<sub>2</sub>O<sub>2</sub>. <sup>10</sup> Further work by Hutchings *et al.* investigated the synergistic effect between Au and Pd for the direct synthesis of H<sub>2</sub>O<sub>2</sub> on a series of oxide supports (Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, SiO<sub>2</sub> and carbon). Once again the addition of Pd to Au significantly enhanced the rate of H<sub>2</sub>O<sub>2</sub> synthesis, as well as the H<sub>2</sub>O<sub>2</sub> selectivity and yield. The AuPd alloy on the supports were found to be of a core shell nature, with a Pd rich shell surrounding an Au rich core. Careful manipulation of the catalyst preparation results in materials where the H<sub>2</sub>O<sub>2</sub> selectivity based upon H<sub>2</sub> is in excess of 95%<sup>11,12</sup>.

One of the key areas where a direct synthesis process could couple directly with an application where dilute concentrations of  $H_2O_2$  are required is in greywater remediation. The average person in the UK flushes a toilet with 45L of clean, potable water per day-twice the volume indicated by UNICEF and the WHO as the minimum amount required to maintain a basic hygiene standard. Water consumption in the UK is increasing year on year, and whilst the situation is alleviated somewhat by the inclement climate, this is insufficient in densely populated areas like the South East which is constantly under water stress. One way of mitigating this demand on water resource is the development of household grey water remediation systems, where waste water containing no fecal or urinal contamination (45-55% of total domestic water used) can be quickly and cleanly recycled and used for applications where potable water is not required (WC, irrigation) If the DS process were to be applied in such a unit, a new series of catalysts would need to be developed, capable of producing  $H_2O_2$  and decomposing to OH radicals which are known to be effective at eradicating coliforms present in greywater such as E.coli. Silver is commonly utilised in wastewater and medical treatments due to its low toxicity to humans, and Ag ions are known to have one of the highest levels of antimicrobial activity of all metals.<sup>13</sup> In terms of water disinfection related applications, Ag is commonly used in filters to inhibit microbial growth or added as a secondary disinfectant. It is thought that Ag inhibits bacterial growth by binding to thiol groups found in the proteins of microbial cell walls.<sup>14</sup> A study by Chang et al. investigated the catalytic inactivation of E.coli in water using 4 wt.% Ag/Al<sub>2</sub>O<sub>3</sub> and AgCl/Al<sub>2</sub>O<sub>3</sub> catalysts<sup>15</sup>. Their study showed that dissolved oxygen could be catalysed at room temperature to generate reactive oxygen species (ROS), such as  $H_2O_2$  and hydroxyl radicals. Their study demonstrated that the synergistic interaction between ROS and Ag<sup>+</sup> can efficiently destroy 6x10<sup>7</sup> CFU/mL. Another study by Pedahzur et al. also showed that the combination of H<sub>2</sub>O<sub>2</sub> and Ag<sup>+</sup> causes significant inactivation of *E.coli* at concentrations that do not pose any health risks. A combination of 30 ppb of Ag and 30 ppm of H<sub>2</sub>O<sub>2</sub> was shown to cause a 5 log reduction in of E.coli concentration.<sup>16</sup>

To date, there are few studies reported on the direct synthesis of  $H_2O_2$  using Ag-Pd bimetallic catalysts. Initial studies by Abate *et al.* demonstrated that Ag-Pd bimetallic catalysts over ceramic membranes can considerably enhance the activity of  $H_2O_2$  formation by limiting the formation of  $\beta$ -PdH.<sup>17</sup> A study by Gu *et al.* reported that the addition of Ag to a Pd catalyst causes a significant enhancement in  $H_2O_2$  selectivity. For a 0.6 wt.% Ag-0.4 wt.% Pd/C catalyst, a  $H_2O_2$  productivity of 7022 mol. kg<sub>Pd<sup>-1</sup></sub> h<sup>-1</sup> and a  $H_2O_2$  selectivity of 70.9 % were obtained, which were superior to those of the pure 1 wt.% Pd/C catalyst. Moreover, the addition of Ag to Pd was shown to substantially decrease  $H_2$  conversion, decomposition and hydrogenation activity<sup>18</sup>.

The aim of this study is to prepare and evaluate Ag-Pd bimetallic catalyst for  $H_2O_2$  synthesis, which is then able to activate the  $H_2O_2$  produced to form water through  $H_2O_2$  decomposition. Decomposition of  $H_2O_2$  has been shown to generate hydroxyl and hydroperoxy radicals by transition metals. These radicals are known to be very powerful, non-selective oxidants in wastewater treatment.<sup>19</sup> A study by Ronen *et al.* have shown that around 125 ppm of stabilised  $H_2O_2$  kills around 99% of fecal coliforms in greywater solutions.<sup>20</sup> Therefore, a Ag-Pd bimetallic composition is needed that generates around 200 ppm of  $H_2O_2$  to investigate for *in-situ* application in treatment of wastewater.

## Experimental

**Catalyst** preparation

The monometallic and bimetallic silver-palladium catalysts were prepared by wet impregnation of TiO<sub>2</sub> (P25, Degussa) in aqueous solutions of PdCl<sub>2</sub> and/or AgNO<sub>3</sub>. All the catalysts prepared contained a total metal loading of 5 wt.%. The detailed procedure for the preparation of 2.5 wt.% Ag-2.5 wt.% Pd/TiO<sub>2</sub> (1g) was as follows: an aqueous solution of PdCl<sub>2</sub> (2.50 mL of a 10 mg mL<sup>-1</sup> solution) was added to an aqueous solution of AgNO<sub>3</sub> (2.50 mL of a 10 mg mL<sup>-1</sup> solution) in a glass vial fitted with a magnetic stirrer bar. The solution was heated to 80 °C with constant stirring. At 80 °C, 0.95 g of TiO<sub>2</sub> was added slowly to the solution over a period 8-10 min and the resultant slurry was stirred until a thick paste was formed. The paste formed was then dried in an oven at 110 °C for 16 h. After this, the catalyst was ground and calcined in static air at 500 °C for 3 h with a ramp rate of 20 °C min<sup>-1</sup>. Monometallic Ag and Pd catalysts were synthesised using the same protocol with appropriate amounts of PdCl<sub>2</sub> or AgNO<sub>3</sub> solution.

#### **Catalyst testing**

#### H<sub>2</sub>O<sub>2</sub> synthesis, decomposition and hydrogenation

 $H_2O_2$  synthesis, hydrogenation and decomposition experiments were evaluated using a Parr Instruments stainless steel autoclave with a volume of either 100 ml or 50 ml and a maximum working pressure of 14 MPa. To evaluate  $H_2O_2$  synthesis the following reaction conditions were used. The autoclave was charged with catalyst (0.010 g) and solvent (2.9g HPLC grade  $H_2O$  and 5.6g HPLC grade methanol, Fischer Scientific) and sealed. The autoclave was then purged three times with 5%  $H_2/CO_2$ before filling with 5%  $H_2/CO_2$  to a pressure of 2.9 MPa (420 psi) followed by the addition of a further 1.1MPa (160 psi) 25%  $O_2/CO_2$  (both BOC speciality gasses). The reaction mixture was stirred at 1200 rpm at systematically varied reaction times and temperatures.  $H_2O_2$  yield was determined by titrating aliquots of the filtered post-reaction solution with acidified Ce(SO<sub>4</sub>)<sub>2</sub> solution (c.a. 0.01 M, Sigma Aldrich) in the presence of Ferroin indicator (c.a. 0.1 ml, Sigma Aldrich).

 $H_2O_2$  hydrogenation and decomposition experiments were carried out with a similar procedure to that of  $H_2O_2$  synthesis experiments but only 420 psi (2.9 MPa) 5%  $H_2/CO_2$  or 420 psi (2.9 MPa) 25%  $O_2/CO_2$  were added to the reactor, respectively. Furthermore, a reaction solvent containing 4 wt%  $H_2O_2$ , prepared by the addition of  $H_2O_2$  solution (50 wt%, 0.68 g, Sigma Aldrich) to  $H_2O$  (7.82 g), was used. The concentration of  $H_2O_2$  in the reaction solution was accurately determined before and after the reaction by titrating aliquots of the reaction solution with acidified  $Ce(SO_4)_2$  in the presence of Ferroin indicator. When a hydrogenation experiment is performed, the measured degree of  $H_2O_2$ degradation represents the sum of both hydrogenation and decomposition processes; thus net hydrogenation can be determined by subtracting the measured decomposition value from the measured total hydrogenation/degradation value, assuming that the reactions happen independently of each other.

#### Catalyst characterisation

#### Powder X-ray Diffraction (XRD)

Catalysts were characterised using an X'PERT PANalytical diffractometer using a Cu K $\alpha$  radiation source operating at 40 keV and 40 mA. Standard analysis was performed using a 40 minute scan between 2 $\theta$  values of 10-80° with a back filled sample. Diffraction pattern of phases were identified using the International Centre for Diffraction Database (ICDD).

#### X-ray Photoelectron Spectroscopy (XPS)

XPS was performed on a Thermo Fisher Scientific K-alpha+ spectrometer. Samples were analysed using a monochromatic Al X-ray source. Data was recorded at pass energies of 150 eV for survey scans and 40 eV for high resolution scans. Charge neutralisation of the sample was achieved using a combination of both low energy electrons and argon ions (less than 1 eV). All data were analysed using CasaXPS (v2.3.17 PR1.1) using Scofield sensitivity factors and an energy exponent of -0.6.

#### **Temperature Programmed Reduction (TPR)**

TPR experiments were carried out using a ChemBET TPR/TPD chemisorption analyser connected to a TCD. 0.05 g of sample was packed into a sample tube between Quartz wool. The sample was then heated from room temperature to 900°C at a heating rate of 15°C min<sup>-1</sup> under a flow of 10%  $H_2/Ar$ .

## **Results and Discussion**

A series of AgPd bimetallic catalysts supported on  $TiO_2$  were prepared, containing a total metal loading of 5 wt.% with varying amounts of Ag and Pd. The  $H_2O_2$  synthesis activity of the AgPd/TiO<sub>2</sub> catalysts were evaluated and compared with the activities of monometallic 5 wt.% Pd/TiO<sub>2</sub> and 5 wt.% Ag/TiO<sub>2</sub> catalysts. Wet impregnation method was used to prepare the catalysts as it is known to give rise to a very broad range of particle sizes, enabling access to a wide range of catalytically active structures<sup>21</sup>. The  $H_2O_2$  synthesis, decomposition and hydrogenation results for the monometallic and bimetallic AgPd catalysts are shown in Table 1.

It is apparent that the monometallic 5 % Ag/TiO<sub>2</sub> and bimetallic 4% Ag-1% Pd/TiO<sub>2</sub> catalysts have a very low activity for the direct synthesis of H<sub>2</sub>O<sub>2</sub>, whereas the monometallic 5 % Pd/TiO<sub>2</sub> has a very high activity for H<sub>2</sub>O<sub>2</sub> synthesis. The monometallic 5% Pd/TiO<sub>2</sub> catalyst had an activity of 106 mol. kg<sub>cat</sub>-<sup>1</sup> h<sup>-1</sup> which is significantly higher than the productivity reported in literature by Edwards *et al.* for a 5 % Pd/TiO<sub>2</sub> catalyst calcined at 400 °C (34 mol. kg<sub>cat</sub> h<sup>-1</sup>).<sup>21</sup> This is possibly due to the higher calcination temperature (500 °C) required to see a synergistic effect in the AgPd system, as observed by Abate<sup>17</sup>. Calcination at increasing temperature is likely to increase the concentrations of Pd<sup>2+</sup> (PdO) on the catalyst surface which has been shown to be beneficial for H<sub>2</sub>O<sub>2</sub> synthesis as the non selective side reactions are supressed<sup>22,23</sup>. Moreover, the results in Table 1 show that the addition of small amounts of Ag to a Pd catalyst substantially decreases H<sub>2</sub>O<sub>2</sub> productivity. This indicates that there is no synergistic effect between Ag and Pd for the synthesis of H<sub>2</sub>O<sub>2</sub>. In addition, as the loading of Ag is increased in the AgPd bimetallic catalysts, the H<sub>2</sub>O<sub>2</sub> productivity decreases. This shows that the addition of Ag is detrimental to the H<sub>2</sub>O<sub>2</sub> synthesis activity of a Pd/TiO<sub>2</sub> catalyst.

Hydrogenation and decomposition are known to be the main pathways for loss of selectivity and yield in the direct synthesis of  $H_2O_2$ . In order to investigate the behaviour of the bimetallic catalysts in these side reactions,  $H_2O_2$  hydrogenation and decomposition activity of the catalysts were evaluated. Hydrogenation experiments are carried out in the absence of  $O_2$  and the presence of  $H_2$  and  $H_2O_2$  in the water/methanol solvent system. The results show that the addition of small amounts of Ag to a Pd/TiO<sub>2</sub> catalyst results in a significantly lower hydrogenation activity of the catalyst. Irrespective of the Ag : Pd ratio, all the AgPd bimetallic catalysts are less active for  $H_2O_2$  hydrogenation than the corresponding Pd monometallic catalyst. Moreover, the monometallic 5% Ag/TiO<sub>2</sub> catalyst had the lowest hydrogenation activity, whereas the monometallic 5% Pd/TiO<sub>2</sub> catalyst had the highest hydrogenation activity. This is unsurprising given the  $H_2O_2$  synthesis data; in order to form  $H_2O_2$ ,  $H_2$ needs to be activated on the surface, if the catalyst is unable to convert  $H_2$  to form  $H_2O_2$  it is unlikely to further activate  $H_2$  a second time to over hydrogenate the  $H_2O_2$  present to form water.

The final column in Table 1 compares the decomposition activity of the monometallic Ag and Pd catalysts to the AgPd bimetallic catalysts. Here the amount of  $H_2O_2$  destroyed in the presence of the catalyst and  $O_2$  is measured over a 30 minute period. The results show that the monometallic 5% Ag/TiO<sub>2</sub> has the highest decomposition activity, whereas the bimetallic 1% Ag-4 % Pd/TiO<sub>2</sub> catalyst has the lowest decomposition activity. In general, as the amount of Ag in the bimetallic AgPd catalysts increased, the decomposition activity increased. What is extremely interesting is that the rates of  $H_2O_2$ 

decomposition are much higher than the rates of  $H_2O_2$  hydrogenation in catalysts containing Ag. In the hydrogenation experiment both hydrogenation and decomposition activities are measured, as it is impossible to separate the two. One explanation is that the presence of  $H_2$  in the hydrogenation experiment suppresses Ag<sup>+</sup> formation, thus minimising the decomposition activity (the major  $H_2O_2$  depletion pathway)

The AgPd/TiO<sub>2</sub> bimetallic catalysts are not particularly active for the synthesis of  $H_2O_2$ , however they are able to synthesis  $H_2O_2$  at greywater relevant levels (~200ppm  $H_2O_2$  for 2% Ag-3% Pd/TiO<sub>2</sub>), and with higher  $H_2O_2$  decomposition activities than the Pd catalyst, with much less Pd present. As such they are possible candidates for a greywater remediation system.

#### **Catalyst Characterisation**

#### TPR

H<sub>2</sub>-TPR measurements were carried out to investigate the reducibility of the catalysts to investigate the nature of the alloy in the PdAg system. Figure 1 shows the TPR profiles of the Ag and Pd monometallic catalysts supported on TiO<sub>2</sub>. For the 5% Ag/TiO<sub>2</sub> catalyst, there were three distinct reduction peaks observed at very low intensities. The individual maxima's observed can be attributed to the various forms of silver oxide and intermediate species formed during reduction<sup>24</sup> The low temperature peak at 106°C with a hard shoulder at 150°C is thought to be due to bulk reduction of AgO and Ag<sub>2</sub>O, respectively. The second peak at 360°C is due to reduction of well dispersed or small Ag<sub>2</sub>O clusters and the broad peak at around 540°C is due to reduction of Ag (I). In contrast, the 5% Pd/TiO<sub>2</sub> catalyst displayed a negative reduction peak at 90°C, which corresponded to H<sub>2</sub> evolution. This negative reduction peak was attributed to the decomposition of Pd  $\beta$ -hydride. The monometallic Pd catalyst also showed small reduction peaks between 370 and 550°C which were due to strongly bound PdO particles

A negative reduction peak is a common feature of Pd-based catalysts<sup>25</sup>. The adsorption of hydrogen is thought to take place on the surface of Pd-based catalysts at sub-ambient temperatures and is released in the form of  $H_2$  when the temperature is raised above 90°C, as illustrated by equation below.

 $PdO + H_2 \rightarrow Pd \beta-hydride \rightarrow Pd + H_2$ 

Moreover, all the AgPd bimetallic catalysts displayed a negative reduction peak at around 90°C, except the 4% Ag-1% Pd/TiO<sub>2</sub> catalyst which displayed two positive reduction peaks, as shown in Figure 2 The negative reduction peak was attributed to the decomposition of Pd  $\beta$ -hydride. In addition for the AgPd bimetallic catalysts, an increase in Ag content was shown to decrease the intensity of the H<sub>2</sub> desorption peaks and shift the desorption peaks towards a higher temperature. Both of these observations suggest that the addition of Ag to a Pd catalyst inhibits the formation of Pd  $\beta$ -hydride and indicates that the Pd is present in a different form possibly an alloy. It also indicates that in the bimetallic catalysts more Pd species are present in the form of Pd<sup>0</sup>.

The shift in Pd  $\beta$ -hydride decomposition temperature indicates an interaction between Ag and Pd. The decrease in intensity of the H<sub>2</sub> desorption peaks supports the H<sub>2</sub>O<sub>2</sub> hydrogenation results, which showed that an increase in Ag content decreases the H<sub>2</sub>O<sub>2</sub> hydrogenation activity of the bimetallic catalysts. From these observations, it could be said that the presence of Ag prevents the formation of Pd  $\beta$ -hydride, which is a feature required for H<sub>2</sub> activation. In addition, the TPR results showed that the Pd  $\beta$ -hydride was more stable when the Pd was present as a bimetallic, as it decomposed at a higher temperature than the hydride of pure Pd.

Furthermore, the 4% Ag-1% Pd/TiO<sub>2</sub> catalyst showed two over-lapping low temperature reduction peaks at 72 and 90°C. This indicated that a high Ag content supressed the formation of Pd  $\beta$ -hydride and as a result the disappearance of the Pd  $\beta$ -hydride peak was accompanied by the formation of two reduction peaks. These two reduction peaks could be due to the simultaneous reduction of palladium and silver oxide species or the presence of two mixed phases such as PdO, AgO or Ag<sub>2</sub>O.

#### Powder XRD

The metal crystallite phases of the catalysts were characterised using XRD. Figure 3 shows the X-ray diffraction patterns of AgPd monometallic and bimetallic catalysts supported on  $TiO_2$  after calcination at 500°C for 3h in static air.

All the catalysts showed intense reflections corresponding to TiO<sub>2</sub> (P25). A mixture of anatase and rutile phases were observed and both of these phases remained stable in all the catalysts investigated. For the 5% Ag/TiO<sub>2</sub> catalyst there were no characteristic Ag reflections observed; potentially as the particle size of Ag are too small to be detected by XRD. In contrast, the monometallic 5% Pd/TiO<sub>2</sub> and all the AgPd bimetallic catalysts, except the 4% Ag-1% Pd/TiO<sub>2</sub> catalyst, exhibited a characteristic PdO reflection at 33.8°. The intensity of the PdO reflection decreased with increasing Ag content in the bimetallic catalysts. Interestingly, the intensity of the PdO reflection in the 5% Pd/TiO<sub>2</sub> catalyst was very weak compared to the AgPd bimetallic catalysts. This suggests that the bimetallic catalysts contained larger PdO particles.

Moreover, all the bimetallic catalysts displayed three reflections corresponding to AgCl and AgO, except the 1% Ag-4% Pd/TiO<sub>2</sub> catalyst which displayed one reflection characteristic of AgO. The AgCl reflections were displayed at Bragg angles 27.8 and 46.3° and can be indexed as the [111] and [220] planes of a cubic structure, respectively. The AgO reflection was displayed at Bragg angle 32.3° and indexed as the [-111] plane of a monoclinic structure. The intensity of the AgCl and AgO reflections were found to increase with increasing Ag content.

#### XPS

The elemental and chemical compositions of the catalysts were analysed by XPS to determine the oxidation states of the active metal components. Figure 4 shows the Ag(3d) core-level spectra of the catalysts. For all Ag containing catalysts, the Ag  $3d_{5/2}$  peak of all samples showed binding energies between 367.3 - 367.8 eV, characteristic of oxidised Ag. This indicated that the Ag on TiO<sub>2</sub> was mainly in the form of Ag<sub>2</sub>O and AgO, which is consistent with the TPR data. From XPS, the changes in binding energy of the Ag( $3d_{5/2}$ ) component is not direct evidence a change in oxidation state for silver based materials and the so-called Auger parameter is best used<sup>26</sup> however the overlapping Auger signals of the Ti(LMM) and Ag(MNN) peaks preclude such analysis, and the shifts in energy noted here in are attributed to particle size effects.

The Pd(3d) component of the XPS spectra and the surface composition of the catalysts are shown in Figure 5 and Table 2.

The ratio of different Pd states was determined using peak-fitting. For the monometallic 5% Pd/TiO<sub>2</sub> catalyst, the XPS profile was dominated by a peak at 337.7 eV characteristic of Pd-Cl bonds, a peak characteristic of PdO was also evident at 336.1 eV. Quantificaiton of the Pd states on the surface of the Pd monometallic catalyst showed that around 60% of the Pd was present as Pd-Cl and 40% was PdO, there was no metallic Pd was detected on the surface of the catalyst. This could offer two possible explanations for the high H2O2 synthesis activity observed. Chlorine is known to selectively poisoning sites responsible for over hydrogenation of H<sub>2</sub>O<sub>2</sub><sup>28</sup>, and a PdO surface is known to promote H<sub>2</sub>O<sub>2</sub> synthesis activity.

For the AgPd bimetallic catalysts peaks characteristic of Pd-Cl bonds were not present, however, peaks due to both PdO and Pd<sup>0</sup> were observed. This fits with the observations of Choudhary who showed that the presence of metallic palladium is detrimental to H<sub>2</sub>O<sub>2</sub> synthesis activity<sup>27</sup>. Table 3 illustrates that in general as the content of Ag increases in the bimetallic catalysts there is an increase in the ratio of Pd<sup>0</sup> which is in agreement with the TPR results.

A shift of *ca*. 0.5 – 0.6 eV towards a higher binding energy for the Pd-O peak was observed in the bimetallic catalysts with respect to the monometallic Pd catalyst. Whereas, the Ag peak shifted *ca*. 0.01 – 0.5 eV towards a lower binding energy with respect to the monometallic Ag catalyst. This suggests the possibility of charge transfer between Ag and Pd, again suggesting some possible interaction between the two metals and the formation of an alloy.

## Conclusions

The results of the  $H_2O_2$  synthesis reactions showed that AgPd/TiO<sub>2</sub> bimetallic catalysts were active for the synthesis of  $H_2O_2$ . The  $H_2O_2$  synthesis, hydrogenation and decomposition activities were found to be highly dependent on the Ag : Pd ratio. In general, as the content of Ag was increased in the bimetallic catalysts, the rate of both  $H_2O_2$  synthesis and hydrogenation decreased, whereas the rate of decomposition increased.

The optimal 1% Ag-4% Pd/TiO<sub>2</sub> and 2% Ag-3% Pd/TiO<sub>2</sub> bimetallic catalysts were shown to give the highest productivities of 11 and 10 mol<sub>H2O2</sub> kg<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>, respectively. These catalysts yielded H<sub>2</sub>O<sub>2</sub> concentrations of 194 and 222 ppm, which is advantageous as this is sufficient to be used directly in a greywater remediation system. The bimetallic AgPd catalysts also show much higher decomposition activity than Pd only catalyst, indicating they would be good candidates in a greywater system as the generation of biocidal OH radicals is facilitated. Temperature programmed reduction experiments indicated an interaction between Ag and Pd as an increase in Ag content was found to suppress the formation of Pd  $\beta$ -hydride. This finding was also in agreement with the XPS results which showed an increase in the Pd<sup>0</sup> oxidation state in the bimetallic catalysts with increasing Ag content. The results of both XPS and TPR suggested the formation of an alloy and the possibility of charge transfer between Ag and Pd.

Combining the results of all the characterisation techniques, it could be said that the addition of Ag to a Pd catalyst results in the formation of an alloy and that the Ag modifies the electronic properties of Pd. The addition of Ag to a Pd catalyst didn't show an enhancement in  $H_2O_2$  productivity as previously reported for the Au bimetallic catalyst. Furthermore, it could be said that the AgPd bimetallic catalysts produce more  $H_2O_2$ , but the  $H_2O_2$  formed is rapidly decomposed as soon as it comes into contact with Ag. At present, it can be concluded that AgPd/TiO<sub>2</sub> catalysts are promising for *in-situ* production of  $H_2O_2$  for application as a greywater treatment process.

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#### Data Accessibility

Readers can contact opendata@cardiff.ac.uk

#### **Competing Interests**

The authors have no competing financial interests.

#### **Authors Contributions**

Zainab Khan, Nicholas Dummer and Jennifer Edwards each provided substantial contributions to conception and design, or acquisition of data, or analysis and interpretation of data, drafting the article or revising it critically for important intellectual content and final approval of the version to be published.

#### Tables/figures



**Table 1** – Hydrogen peroxide synthesis, hydrogenation and decomposition activities for AgPd catalysts.

Catalyst	Productivity	$H_2O_2$	Hydrogenation	Decomposition
	(mol <sub>H2O2</sub> kg <sub>cat</sub> -1 h <sup>-1</sup> )	concentration (ppm)	(mol <sub>H2O2</sub> kg <sub>cat</sub> -1 h <sup>-1</sup> )	(mol <sub>H2O2</sub> kg <sub>cat</sub> -1 h <sup>-1</sup> )
5% Ag/TiO <sub>2</sub>	1	29	10	138
4% Ag-1% Pd/TiO <sub>2</sub>	1	29	26	65
3% Ag-2% Pd/TiO <sub>2</sub>	2	43	27	55
2.5% Ag-2.5% Pd/TiO <sub>2</sub>	3	56	32	43
2% Ag-3% Pd/TiO <sub>2</sub>	10	194	33	26
1% Ag-4% Pd/TiO <sub>2</sub>	11	222	58	21
5% Pd/TiO <sub>2</sub>	106	2124	186	38

Reaction conditions: 0.01 g catalyst, 8.5 g solvent (5.6 g MeOH and 2.9 g  $H_2O$ ), 5%  $H_2/CO_2$  (420 psi) and 25%  $O_2/CO_2$  (160 psi), 2°C, 1200 rpm, 30 mins. All catalysts were prepared by wet impregnation and calcined in static air at 500°C for 3h.

	Pd <sup>2+</sup> (%)			
Catalysts	Pd-O	Pd-Cl	Pd <sup>0</sup> (%)	
5% Pd/TiO <sub>2</sub>	40.4	59.6	-	
1% Ag-4% Pd/TiO <sub>2</sub>	87.5	-	12.5	
2% Ag-3% Pd/TiO <sub>2</sub>	72.8	-	27.2	
2.5% Ag-2.5% Pd/TiO <sub>2</sub>	66.3	-	33.7	
3% Ag-2% Pd/TiO <sub>2</sub>	76.7	-	23.3	
4% Ag-1% Pd/TiO <sub>2</sub>	75.8	-	24.4	

Table 2- Pd species present in AgPd catalysts determined by XPS

#### **Figure titles**

**Figure 1** – TPR profiles of Ag and Pd monometallic catalysts after calcination at 500°C for 3h in static air.

**Figure 2** – TPR profiles of Ag-Pd monometallic and bimetallic catalysts supported on  $TiO_2$  after calcination at 500°C for 3h in static air.

**Figure 3** – XRD patterns of (a)  $TiO_2 P25$  calcined at 500°C (b) 5% Pd/TiO<sub>2</sub> (c) 1% Ag-4% Pd/TiO<sub>2</sub> (d) 2% Ag-3% Pd/TiO<sub>2</sub> (e) 2.5 % Ag-2.5% Pd/TiO<sub>2</sub> (f) 3% Ag-2% Pd/TiO<sub>2</sub> (g) 4% Ag-1% Pd/TiO<sub>2</sub> (h) 5% Ag/TiO<sub>2</sub>.

**Figure 4** – Ag(3d) XPS spectra of the Ag monometallic and AgPd bimetallic catalysts supported on  $TiO_2$  after calcination at 500°C for 3h.

**Figure 5** - Pd(3d) XPS spectra of the Pd monometallic and AgPd bimetallic catalysts supported on  $TiO_2$  after calcination at 500°C for 3h.