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# **Solid Acid Additives as Recoverable Promoters for the Direct Synthesis of Hydrogen Peroxide**

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**Abstract.**

The effectiveness of Cs-exchanged phosphotungstic acid as a recoverable solid acid additive for the direct synthesis of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) using an Au-Pd /  $\text{TiO}_2$  catalyst is investigated and compared to the promotion effect of common oxides and non-halo acids. A clear improvement in catalytic activity towards  $\text{H}_2\text{O}_2$  synthesis is reported when utilising Cs-containing heteropolyacids in addition to a standard  $\text{H}_2\text{O}_2$  synthesising catalyst. The effect of Cs content on the promotion of  $\text{H}_2\text{O}_2$  formation is investigated and the feasibility of a reusable heterogeneous additive has been explored revealing that the presence of the acid additive not only stabilises the  $\text{H}_2\text{O}_2$  that is produced but also increases the  $\text{H}_2\text{O}_2$  synthesis rate.

## Introduction

The catalytic direct synthesis of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) from molecular hydrogen and oxygen would represent an atom efficient process and would allow production to be decentralised<sup>1, 2</sup>. For over 100 years the reaction has been studied using catalysts based on Pd and more recently bimetallic and trimetallic nanoparticles containing Pd<sup>3, 4</sup>. A major limitation of the direct synthesis process is being able to control the subsequent unselective hydrogenation and decomposition reactions of  $\text{H}_2\text{O}_2$ , which limit reaction selectivity. Advances have been made in catalyst design demonstrating that it is possible switch off these subsequent reactions using both AuPd<sup>5</sup> and SnPd<sup>6</sup> bimetallic catalysts however many studies still use the addition of promoters such as acids and halides to suppress these reactions<sup>7-9</sup>.

The addition of acids to the reaction medium has been extensively studied as a means of suppressing the base catalysed decomposition of hydrogen peroxide using Pd and AuPd catalysts and stabilising the synthesised  $\text{H}_2\text{O}_2$ . Decreasing the pH of the reaction by addition of nitric, sulphuric, phosphoric and hydrochloric acids<sup>10</sup> has shown to be essential in achieving high yields of  $\text{H}_2\text{O}_2$  when using monometallic Pd catalysts and the presence of coordinating counter ions such as chloride and bromide can act as further promoters, suppressing the sequential over hydrogenation of hydrogen peroxide<sup>11, 12</sup>. This has been suggested to occur through poisoning of reactive Pd sites by the halide anions preventing O-O bond cleavage, which leads to water formation<sup>13</sup>. Despite these enhancements in hydrogen peroxide yield the removal of acid and halide ions from solutions of hydrogen peroxide increases the costs associated with the direct synthesis process. Recently it has been reported that the addition of organobromides such as bromobenzene to a reaction using a Pd catalyst supported on acidic resin showed similar performance to the addition of HBr as an ionic source of bromine<sup>14</sup>. This study reported that no free bromide was present in the reaction solution when using bromobenzene as promoter suggesting that organic additives could be attractive alternatives to halides in reaction solutions.

A recoverable acid promoter would be beneficial to the direct synthesis process, as it would remove the need to neutralise strong acidic solutions of  $\text{H}_2\text{O}_2$  before application, shipping or storage. We have recently reported catalysts for the direct synthesis of hydrogen peroxide based on solid acids such as caesium substituted phosphotungstic acid (HPA) supported Pd and AuPd nanoparticles<sup>15, 16</sup>. These catalysts show very high hydrogen peroxide productivity, especially under challenging aqueous reaction conditions. Despite the high productivities these materials also showed high  $\text{H}_2\text{O}_2$  degradation when metals are supported on them. In these cases it is not possible to carry out heat treatments that are usually used in catalyst preparation, as they will result in the decomposition of the parent support material<sup>17</sup>. In this study we investigate the addition of solid acid materials to the direct synthesis reaction using a well-studied 2.5 wt. % Au - 2.5 wt. % Pd /  $\text{TiO}_2$  catalyst as this allows the catalyst material to be prepared independently of the solid acid materials.

## Experimental

### Catalyst Preparation.

Bi-metallic gold-palladium catalysts were prepared by wet co-impregnation of TiO<sub>2</sub> with solutions of HAuCl<sub>4</sub> and PdCl<sub>2</sub>, using an excess of solvent (in this case water). The catalysts were prepared to have a nominal metal content of 5 wt. %. A typical catalyst preparation procedure (1.0 g 2.5 wt. % Au- 2.5 wt. % Pd / TiO<sub>2</sub>) was carried out according to the following procedure which has been previously reported in the literature<sup>(18)</sup>. PdCl<sub>2</sub> (0.042 g) was added to HAuCl<sub>4</sub> (2.04 ml, 12.25 g Au / 1000 ml) and heated to 80 °C with stirring and left until the PdCl<sub>2</sub> had completely dissolved. TiO<sub>2</sub> (0.095 g, Degussa, P25) support was then added to the solution and the water allowed to evaporate until the mixture formed a paste like consistency. The samples were dried (110 °C, 16 h) and then calcined in static air (400 °C, 3 h with a ramp rate of 20 °C min<sup>-1</sup>).

The degree of Cs-incorporation into the structure of H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> was varied by varying the mass of CsNO<sub>3</sub> added to an aqueous solution of H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>. A typical preparation procedure of Cs<sub>2.5</sub>H<sub>0.5</sub>PW<sub>12</sub>O<sub>40</sub> (1.0 g) was carried out according to the following procedure, which has been previously reported in the literature<sup>(15, 16)</sup>. CsNO<sub>3</sub> (0.151 g) dissolved in deionised water (5.0 ml) was added drop-wise to an aqueous solution of H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> (0.892 g) while stirring. The resulting solution was continuously stirred while heating (80 °C). The water was allowed to evaporate until the mixture formed a paste like consistency. The samples were dried (110 °C, 16 h) and then calcined in static air (300 °C, 2 h with a ramp rate of 20 °C min<sup>-1</sup>).

### Catalyst Characterisation and Testing.

Catalytic activity towards the direct synthesis of H<sub>2</sub>O<sub>2</sub> from H<sub>2</sub> and O<sub>2</sub> was determined using a Parr Instruments stainless-steel autoclave (equipped with overhead stirrer and temperature/pressure sensors) with a nominal volume of 100 ml and maximum working pressure of 14 MPa. During a standard synthesis reaction the autoclave was charged with MeOH (5.6 g), HPLC standard H<sub>2</sub>O (2.9 g) and catalyst (0.01 g). The autoclave was pressurised with 2.9 MPa 5 % H<sub>2</sub> / CO<sub>2</sub> and 1.1 MPa 25 % O<sub>2</sub> / CO<sub>2</sub> to give a total reaction pressure of 4 MPa. After cooling the autoclave to 2 °C the reaction mixture is stirred at 1200 rpm for 0.5 h. After the reaction was completed a gaseous sample was collected and analysed by gas chromatography when necessary. Aliquots of the solvent were titrated against a Ce(SO<sub>4</sub>)<sub>2</sub> solution acidified with 2% H<sub>2</sub>SO<sub>4</sub> using ferroin as an indicator. The concentration of the Cs(SO<sub>4</sub>)<sub>2</sub> solution was standardised by titration of a known amount of (NH<sub>4</sub>)<sub>2</sub>Fe(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O, using ferroin as an indicator.

The degradation activity of a catalyst towards H<sub>2</sub>O<sub>2</sub> was determined in a manner similar to the direct synthesis activity of a catalyst. The autoclave was charged with MeOH (5.6 g), H<sub>2</sub>O<sub>2</sub> (50 wt. % 0.69 g) HPLC standard H<sub>2</sub>O (2.21 g) and catalyst (0.01 g), with the solvent composition equivalent to a 4

wt. % H<sub>2</sub>O<sub>2</sub> solution. From the solution 2 aliquots of 0.05g were removed and titrated with acidified Ce(SO<sub>4</sub>)<sub>2</sub> solution using ferroin as an indicator to determine an accurate concentration of H<sub>2</sub>O<sub>2</sub> at the start of the reaction. The autoclave was pressurised with 2.9 MPa 5 % H<sub>2</sub> / CO<sub>2</sub> and cooled to 2 °C and the reaction mixture was stirred at 1200 rpm for 0.5 h. After the reaction was complete (0.5 h) the catalyst was immediately removed from the reaction solvents and as previously two aliquots of 0.05 g were titrated against the acidified Ce(SO<sub>4</sub>)<sub>2</sub> solution using ferroin as an indicator.

Investigation of the bulk structure of the materials was carried out using powder X-ray diffraction (XRD) on a (θ– θ) PANalytical X'pert Pro powder diffractometer using a Cu Kα radiation source operating at 40 keV and 40 mA. Standard analysis was performed using a 40 min scan between 2θ values of 10–80° with the samples supported on an amorphous silicon wafer. Diffraction patterns of phases were identified using the ICDD data base.

Surface area analysis was determined using a Micromeritics Gemini 2360 analyser. A known amount of sample, 100–200 mg was placed in a straight walled tube and degassed for 1 h at 120 °C under a flow of N<sub>2</sub>. The surface area was analysed using a single point analysis typically taking 5 points between P/P<sup>0</sup>= 0.05–0.1.

Metal leaching was quantified using microwave plasma - atomic emission spectroscopy (MP-AES). Post reaction solutions were filtered to remove the solid catalyst, after which the liquid phase was analysed using an Agilent 4100 MP-AES.

## Results and Discussion

In this study the previously reported 2.5 wt. % Au - 2.5 wt.% Pd / TiO<sub>2</sub> catalyst was used for all direct synthesis reactions<sup>18</sup>. This catalyst has been shown to be stable to multiple reaction cycles after calcination in static air at 400 °C, it consists of Au-Pd core shell nanoparticles with sizes ranging from 3- 30 nm and under our standard reaction conditions outlined in the experimental procedures this catalyst has a productivity of 64 mol<sub>H<sub>2</sub>O<sub>2</sub></sub>kg<sub>cat</sub><sup>-1</sup>h<sup>-1</sup><sup>18</sup>. Firstly, the pH of the reaction solution prior to reaction was altered using HNO<sub>3</sub> to confirm that an enhancement could be achieved on decreasing the pH of the reaction solution (excluding the effect of dissolved CO<sub>2</sub> forming carbonic acid as an *in-situ* acid promoter). Figure 1 shows that the measured productivity of the catalyst after 30 min reaction increased from 64 to 110 mol<sub>H<sub>2</sub>O<sub>2</sub></sub>kg<sub>cat</sub><sup>-1</sup>h<sup>-1</sup> when the pH of the solution was decreased from 6 to 1.5 in line with previous studies<sup>19</sup> on the effect of acid addition to the direct synthesis reaction.

Following this an investigation was carried out to evaluate if heterogeneous additives could also affect the productivity of the direct synthesis reaction in a positive way. We added 10 mg of common oxides and catalyst supports to the reaction mixture containing 10 mg of AuPd / TiO<sub>2</sub> catalyst. All the additives were screened for activity towards the direct synthesis of H<sub>2</sub>O<sub>2</sub> (Table S1) and all showed no activity

towards the synthesis of H<sub>2</sub>O<sub>2</sub>. However additives showed varying levels of H<sub>2</sub>O<sub>2</sub> degradation as has been previously reported<sup>20</sup>. Basic support materials such as MgO showed high levels (206 mol<sub>H<sub>2</sub>O<sub>2</sub></sub>kg<sub>cat</sub><sup>-1</sup>h<sup>-1</sup>) of H<sub>2</sub>O<sub>2</sub> degradation (Table S1) where as more acidic support materials such as Nb<sub>2</sub>O<sub>5</sub> showed lower levels of H<sub>2</sub>O<sub>2</sub> degradation (83 mol<sub>H<sub>2</sub>O<sub>2</sub></sub>kg<sub>cat</sub><sup>-1</sup>h<sup>-1</sup>). Figure 2 shows that on addition of bare additives to the direct synthesis reactions containing the AuPd catalyst a small enhancement in productivity was observed for acidic materials such as ZrO<sub>2</sub> and Nb<sub>2</sub>O<sub>5</sub> while basic materials such as MgO showed a negative impact through enhanced degradation of H<sub>2</sub>O<sub>2</sub>.

Phosphotungstic acid (H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>) is a soluble heteropolyacid in proton form with the Keggin structure<sup>21</sup>. The almost super-acidic nature of heteropolyacids (HPAs) such as phosphotungstic acid (H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>) has been well studied and the ability to produce insoluble salts of these solid acids through the incorporation of cations such as Cs<sup>+</sup>, Rb<sup>+</sup> and K<sup>+</sup> has led to their investigation as acidic supports in the direct synthesis of H<sub>2</sub>O<sub>2</sub><sup>22</sup>. The acidity, surface area and solubility of these structures can be tuned by proton exchange with alkali metal. Park *et.al.*<sup>23</sup> have studied Pd-exchanged heteropolyacids with varying Cs-content and shown that the catalyst (Pd<sub>0.15</sub>Cs<sub>2.5</sub>H<sub>0.5</sub>PW<sub>12</sub>O<sub>40</sub>) was active towards the synthesis of H<sub>2</sub>O<sub>2</sub>. Sun *et.al.*<sup>24</sup> have reported that Pd based catalysts utilising a heteropolyacid support shows greater productivity and selectivity towards H<sub>2</sub>O<sub>2</sub> when compared to more conventional supports. We investigated the use of Cs<sub>2.5</sub>H<sub>0.5</sub>PW<sub>12</sub>O<sub>40</sub> as a solid acid additive to the direct synthesis reaction, the productivity of the reaction using this additive increased from 64 to 99 mol<sub>H<sub>2</sub>O<sub>2</sub></sub>kg<sub>cat</sub><sup>-1</sup>h<sup>-1</sup>, a promotion of 55% in activity using the same catalyst material.

The ability to tune the acidic properties of this additive by alkali metal doping led us to investigate a range of materials (Cs<sub>x</sub>H<sub>3-x</sub>PW<sub>12</sub>O<sub>40</sub>) with differing Cs contents (x = 0-3). The additives were synthesized and were shown by XRD to have the characteristic diffraction patterns associated with the cubic structure of H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> (ICDD number 00-050-0657) (Figure S1). Upon incorporation of Cs<sup>+</sup> the reflections broaden and decrease in intensity indicating a loss in crystallinity. BET surface area analysis (Table 1) from N<sub>2</sub> physisorption shows that increasing the amount of Cs in the structure results in a higher surface area materials consistent with the loss in crystallinity observed by XRD. Table 1 shows the results of the material screening for H<sub>2</sub>O<sub>2</sub> synthesis, no heteropolyacid materials showed activity towards H<sub>2</sub>O<sub>2</sub> synthesis. Degradation activity was observed which increased linearly with the surface area of the material and decreasing acidity as more Cs was substituted in the HPA structure. This suggests that the degradation activity is affected by the acidic nature of the material and coupled with the fact that no H<sub>2</sub>O<sub>2</sub> was synthesised means that the degradation reaction is likely to be decomposition and the heteropolyacids are not able to activate H<sub>2</sub> leading to over hydrogenation. On addition of catalyst to the various Cs containing heteropolyacid additives a significant improvement in H<sub>2</sub>O<sub>2</sub> productivity was observed compared to the catalyst alone. When 10 mg of the soluble H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> was added the observed productivity increased by approximately 2.5 times from 64 to 157 mol<sub>H<sub>2</sub>O<sub>2</sub></sub>kg<sub>cat</sub><sup>-1</sup>h<sup>-1</sup>. As the amount of Cs substitution increased generating materials with larger surface areas and lower degrees of

acidity the extent of the promotional effect decreases until at full substitution ( $\text{Cs}_3\text{PW}_{12}\text{O}_{40}$ ) a negative effect was observed on addition of an additive. The degradation activity of the catalyst and additive reactions systems remains generally in line with the sum of the degradation of the catalyst and heteropolyacid suggesting that the addition of heteropolyacid does not results in a synergistic effect towards the over hydrogenation or decomposition of  $\text{H}_2\text{O}_2$  but could enhance the rate of  $\text{H}_2\text{O}_2$  synthesis.

The effect of adding increasing amounts of heteropolyacid was studied for all additives with varying Cs contents and the results are shown in Figure 3. The most acidic materials ( $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$   $x = 0 - 1$ ) showed increasing observed  $\text{H}_2\text{O}_2$  productivity with increasing additive amounts at all masses from 10 – 50 mg. At 50 mg addition of  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  the productivity of the reaction increased from 64 to 301  $\text{mol}_{\text{H}_2\text{O}_2}\text{kg}_{\text{cat}}^{-1}\text{h}^{-1}$  representing a near 5 fold increase. Apart from the fully exchanged Cs additive, which showed decreased activity over all mass loadings, all other materials showed a plateau of activity after an initial increase in activity with when increasing the amount of additive in the reaction. The exchange of Cs into the heteropolyacid materials also determines the solubility of the materials as previously reported by Misono *et. al.*<sup>24</sup> To investigate if leached materials could be responsible for the promotional effect MP-AES was carried out on the reaction solutions post reaction and the results are shown in Table 2. When using the more acidic and soluble heteropolyacid additives up to 9 ppm of Pd was detected in the reaction solution (corresponding to 10% of the total Pd in the reaction) this value decreased to 1 ppm (3% of the total Pd in the reaction) as the Cs exchange of the material was increased, reducing the acidity of the reaction solution. In all cases no Au leaching was observed but even in the case of the full exchanged material, Cs and W leaching was observed in the reaction media suggesting a low level of solubility or incomplete exchange. Tungsten leaching decreased with increasing exchange of Cs into the material over the range of materials studied whereas Cs leaching exhibited a maximum at  $x = 2$  and then decreased as more complete exchange was achieved. To investigate if the Pd present in the solutions was responsible for the activity, possibly in the form of colloidal or homogeneous Pd, which has been extensively reported by Lunsford and co-workers<sup>26, 27</sup>. Reactions were carried out using the solutions after the catalyst had been removed by filtration. Table 2 demonstrates that minimal  $\text{H}_2\text{O}_2$  synthesis activity was observed in these reactions suggesting that the leaching of metal from the catalyst or the presence of Cs or W in the solutions was not responsible for the enhanced activity. In addition a sample of the catalyst was washed with a  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  solution at concentrations and times to simulate a reaction. After washing and drying, the catalyst showed no enhancement towards the synthesis of  $\text{H}_2\text{O}_2$  compared to the fresh catalyst material suggesting that low amounts of physisorbed species were not responsible for the promotion.

To further investigate the origin of the promotional effect and determine if it is purely an effect of acid stabilisation of the synthesised hydrogen peroxide, reactions were carried out with addition of the constituents of the heteropolyacid ( $\text{Cs}(\text{NO}_3)$ ,  $\text{H}_2\text{WO}_4$ ) and also the effect of changing the pH with various additives was investigated. Firstly the addition of  $\text{Cs}(\text{NO}_3)$  in amounts that correspond do the



Cs content in the HPA additives did not result in a promotion in  $\text{H}_2\text{O}_2$  productivity (Table S2). This confirmed that in the case of HPA additives the Cs solubilised from the additives was not responsible for the promotion in activity and also in the case of nitric acid addition the nitrate anion played no part in the promotion of  $\text{H}_2\text{O}_2$  activity. As reported in Figure 1 the addition of  $\text{HNO}_3$  in order to lower the reaction pH and stabilise the  $\text{H}_2\text{O}_2$  resulted in an improvement in the observed  $\text{H}_2\text{O}_2$  productivity during the reaction. When the pH of the solution was decreased using  $\text{H}_2\text{WO}_4$ , which contains the tungstate ions present in the HPA additives, a similar profile to the addition of  $\text{HNO}_3$  was observed suggesting that this promotion was similar in nature to  $\text{HNO}_3$  addition and the tungstate ions alone were not responsible for the improvement. When plotted together (Figure 4) the data from  $\text{HNO}_3$ ,  $\text{H}_2\text{WO}_4$  and oxide support addition show a similar trend in terms of observed  $\text{H}_2\text{O}_2$  activity with pH of the solution. In the case of addition of the full heteropolyacids, soluble or exchanged ( $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ ), this trend is broken by all of the compositions studied. The observed improvements are substantially higher using heteropolyacid additives at similar pH to that observed with the conventional acid addition or the addition of any constituent additives. The different behaviour with heteropolyacid additives with various amounts of Cs suggests an additional affect in increasing the amount of  $\text{H}_2\text{O}_2$  observed, in addition to the acid stabilisation for the synthesised  $\text{H}_2\text{O}_2$ , where the heteropolyacid structure is required. For example at a pH of 1.6 the promotion effect of  $\text{HNO}_3$  is an enhancement in the rate of  $\text{H}_2\text{O}_2$  synthesis of  $45 \text{ mol}_{\text{H}_2\text{O}_2}\text{kg}_{\text{cat}}^{-1}\text{h}^{-1}$ . However, using  $\text{Cs}_2\text{HPW}_{12}\text{O}_{40}$  as an additive for the 2.5 wt.% Au – 2.5 wt.% Pd /  $\text{TiO}_2$  catalyst the enhancement in the rate of  $\text{H}_2\text{O}_2$  formation is much greater at  $113 \text{ mol}_{\text{H}_2\text{O}_2}\text{kg}_{\text{cat}}^{-1}\text{h}^{-1}$  despite a less acidic pH of the reaction solution. Comparison of the  $\text{H}_2$  conversion and  $\text{H}_2\text{O}_2$  selectivity (Table 3) of reactions containing heteropolyacid additives reveal that reactions containing the heteropolyacid additives have increased  $\text{H}_2$  conversion compared to the catalyst alone.

The observation that the heteropolyacids alone are not able to synthesise  $\text{H}_2\text{O}_2$  and show no synergistic effect for  $\text{H}_2\text{O}_2$  degradation when used in combination with the catalyst suggests that the enhanced  $\text{H}_2$  conversion is not resulting from the hydrogenation of  $\text{H}_2\text{O}_2$  and that in fact the less acidic ( $x = 1-2.5$ ) materials have similar  $\text{H}_2\text{O}_2$  selectivity to the catalyst alone. It can be observed that the selectivity towards  $\text{H}_2\text{O}_2$  of the reactions decreases with the acidity of the acid, suggesting that acid stabilisation is a factor but not the only reason for the higher observed concentrations of  $\text{H}_2\text{O}_2$  produced. What is observed is that in the presence of heteropolyacid,  $\text{H}_2$  conversion of the AuPd catalyst increases resulting in greater formation of  $\text{H}_2\text{O}_2$  suggesting that the heteropolyacid is promoting the ability of the catalyst to selectively activate  $\text{H}_2$  to produce  $\text{H}_2\text{O}_2$  and not over hydrogenation.

The ability of heteropolyacids to selectively promote the direct synthesis of hydrogen peroxide could occur from a number of reasons previously suggested in the literature. Firstly it has been recently proposed that the direct synthesis occurs through a hydrogen oxidation/oxygen reduction reaction couple similar to electrochemical Oxygen Reduction Reactions where protic solvents are required and the activity depends on the concentration of protons in the solution<sup>28</sup>. Heteropolyacids are able to

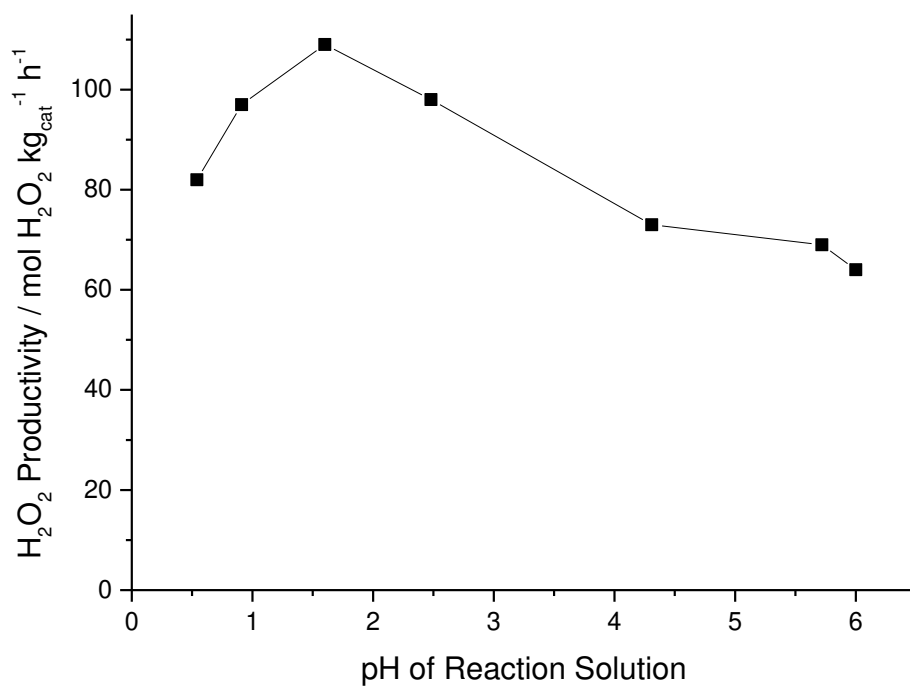
conduct protons effectively in aqueous solutions and therefore enhance proton mobility towards the catalyst surface if they were to be in proximity or form a coating on the catalyst. Heteropolyacids have been used as modifiers to surfaces to increase proton mobility<sup>29</sup> and also as electrolytes in the oxygen reduction reaction using Pt catalysts where it has been hypothesised that the Keggin ion is able to stabilise  $\text{H}_2\text{O}_5^+$  aquaions with strong proton activity resulting in promising performance<sup>30</sup>. It has also been reported that the presence of heteropolyanions can accelerate hydrogenation reactions including reductive carbonylation of nitrobenzene<sup>31</sup> and the hydrogenation of propargyl alcohol using homogeneous  $\text{PdCl}_2$  complexes<sup>32</sup>. In this study it was suggested that the redox properties of the heteropolyacid bound to Pd could maintain the Pd in an active state. Bronsted acidity has also been shown to have a positive promotional effect in the hydrogenation of aromatics using Pt catalysts where the proximity of acid sites to Pt leads to the Pt becoming electron deficient and increases activity<sup>33</sup>.

It is clear that in this case the presence of heteropolyacid additives increases the rate of hydrogen activation resulting in hydrogen peroxide synthesis and not the over hydrogenation of hydrogen peroxide, which could be suppressed by the acidity of the additives. Hydrogen activation and the turnover of the sites needed for hydrogen activation / oxidation could be promoted by the enhanced proton mobility of the HPA additives in the solution accelerating the consumption of protons from the solution and allowing turnover of the active sites as it has been shown that the rate of  $\text{H}_2\text{O}_2$  synthesis is dependent on the hydrogen partial pressure but not the oxygen partial pressure so an increase in  $\text{H}_2$  turnover would result in increased  $\text{H}_2\text{O}_2$  productivity<sup>34</sup>.

To investigate the stability of HPA additives as recoverable promoters, after reactions of the AuPd bimetallic catalyst with the 50 mg addition of  $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$   $x = 2$  and 2.5 the solids were recovered by centrifugation and dried before the mixture of catalyst and additive was re-tested with the results shown in Table 4. These additives were chosen as they showed minimal amounts of Pd leaching in the reactions. It was observed that the productivity of the catalyst and additive combination was maintained with no loss in activity observed for the  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$  additive which retained a near 3 fold increase on the baseline catalyst activity and only a small loss in activity was observed for the  $\text{Cs}_2\text{HPW}_{12}\text{O}_{40}$  additive, possibly due to the higher solubility of the additive.

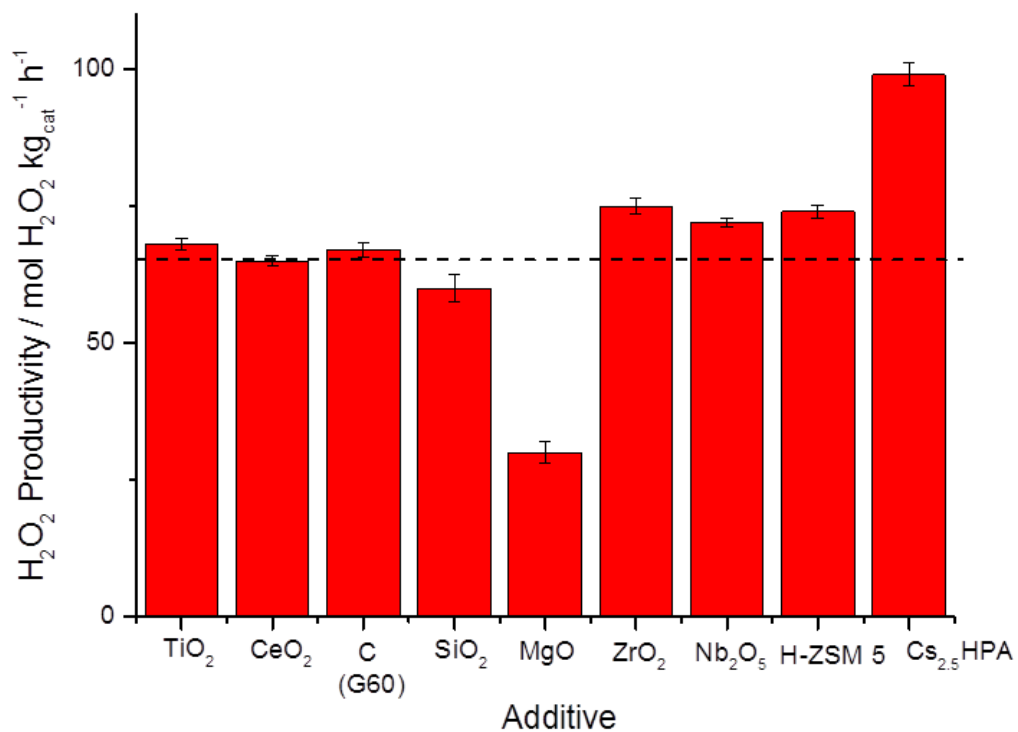
In conclusion we have demonstrated that it may be feasible to use a heterogeneous acid additive to promote the direct synthesis of hydrogen peroxide and have shown it could be reusable, although some leaching of the constituents Cs and W were observed. In addition it was observed that as well as stabilising the hydrogen peroxide that has been produced by decreasing the pH of the reaction solution a promotional effect on the catalytic activity towards  $\text{H}_2\text{O}_2$  synthesis is achieved through the use of these HPA additives the origin of this effect will be investigated in subsequent studies.

**Figure 1** – Productivity of 2.5 wt.% - Au 2.5% wt. Pd / TiO<sub>2</sub> towards the direct synthesis of H<sub>2</sub>O<sub>2</sub> with addition of HNO<sub>3</sub> to the reaction mixture in order to vary reaction pH.



**Reaction conditions:** Catalyst (0.01 g), total pressure 4 MPa, H<sub>2</sub> /O<sub>2</sub> = 0.525, 1200 rpm, 5.6 g CH<sub>3</sub>OH + 2.9 g H<sub>2</sub>O (66 wt. % CH<sub>3</sub>OH), 0.5 h, 2 °C.

**Figure 2** – Hydrogen peroxide productivity with addition of various additives (10 mg) to a standard reaction with 2.5 wt.% - Au 2.5% wt. Pd / TiO<sub>2</sub> – dotted line is the activity of the catalyst alone.



**Reaction conditions:** Catalyst (0.01 g), total pressure 4 MPa, H<sub>2</sub> /O<sub>2</sub> = 0.525, 1200 rpm, 5.6 g CH<sub>3</sub>OH + 2.9 g H<sub>2</sub>O (66 wt. % CH<sub>3</sub>OH), 0.5 h, 2 °C.

**Table 1.** Catalytic activity of  $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$  towards  $\text{H}_2\text{O}_2$  synthesis and its subsequent degradation, when utilised alone and in combination with 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$ .

	BET	$\text{H}_2\text{O}_2$	$\text{H}_2\text{O}_2$	$\text{H}_2\text{O}_2$	$\text{H}_2\text{O}_2$
	Surface	Productivity <sup>[a]</sup> /	Degradation <sup>[a]</sup> /	Productivity <sup>[b]</sup> /	Degradation <sup>[b]</sup>
	Area	$\text{mol}_{\text{H}_2\text{O}_2} \text{kg}_{\text{cat}}^{-1} \text{h}^{-1}$	$\text{mol}_{\text{H}_2\text{O}_2} \text{kg}_{\text{cat}}^{-1} \text{h}^{-1}$	$\text{mol}_{\text{H}_2\text{O}_2} \text{kg}_{\text{cat}}^{-1} \text{h}^{-1}$	$\text{mol}_{\text{H}_2\text{O}_2} \text{kg}_{\text{cat}}^{-1} \text{h}^{-1}$
	$\text{m}^2 / \text{g}$				
	Additive Only			Additive + Catalyst	
No Additive	-	0	0	64	213
$\text{H}_3\text{PW}_{12}\text{O}_{40}$	<1	0	35	157	230
$\text{Cs}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$	<1	0	39	143	240
$\text{CsH}_2\text{PW}_{12}\text{O}_{40}$	4	0	63	153	260
$\text{Cs}_2\text{HPW}_{12}\text{O}_{40}$	50	0	88	105	309
$\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$	112	0	124	99	350
$\text{Cs}_3\text{PW}_{12}\text{O}_{40}$	121	0	187	29	429

<sup>[a]</sup>Rate of  $\text{H}_2\text{O}_2$  synthesis : Catalyst (0.01 g), total pressure 4 MPa,  $\text{H}_2 / \text{O}_2 = 0.525$ , 1200 rpm, 5.6 g  $\text{CH}_3\text{OH} + 2.9$  g  $\text{H}_2\text{O}$  (66 wt. %  $\text{CH}_3\text{OH}$ ), 0.5 h, 2 °C.

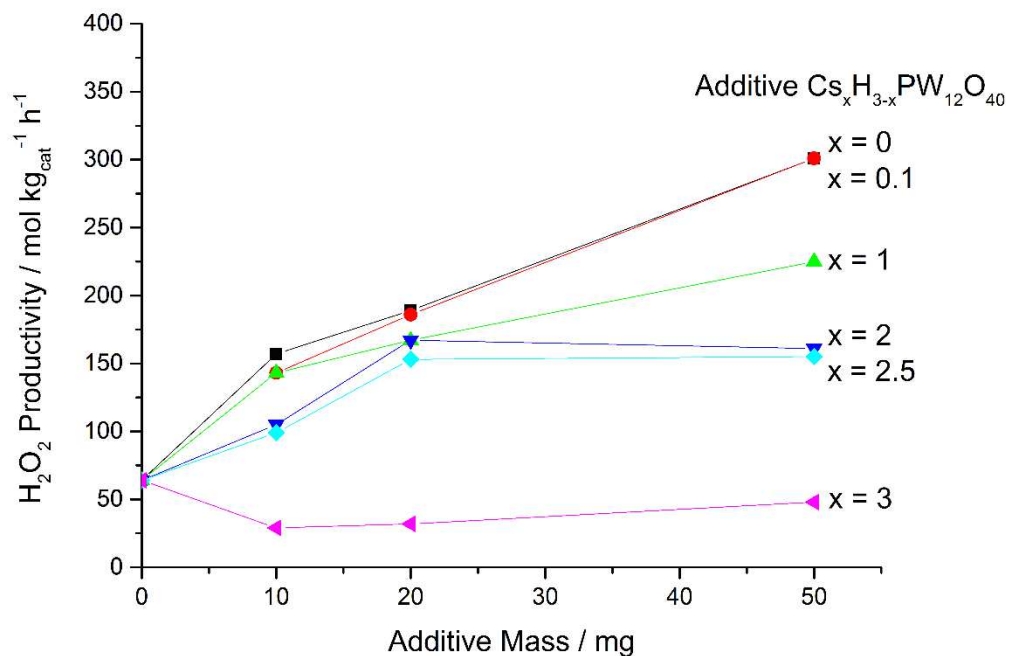
<sup>[b]</sup>  $\text{H}_2\text{O}_2$  degradation : Catalyst (0.01 g), 2.9 MPa,  $\text{H}_2 / \text{CO}_2$ , 1200 rpm,  $\text{H}_2\text{O}_2$  (0.68 g, 50 wt. %) 5.6 g  $\text{CH}_3\text{OH} + 2.21$  g  $\text{H}_2\text{O}$  (66 wt. %  $\text{CH}_3\text{OH}$ ), 0.5 h, 2 °C.

**Table 2.** Leaching during the direct synthesis of H<sub>2</sub>O<sub>2</sub> using 2.5 wt. % Au – 2.5 wt.% Pd/TiO<sub>2</sub> and Cs<sub>x</sub>H<sub>3-x</sub>PW<sub>12</sub>O<sub>40</sub> and the activity of leached metal towards subsequent H<sub>2</sub>O<sub>2</sub> synthesis.

Catalyst	Pd / ppm	Au / ppm	Cs / ppm	W / ppm	Productivity of reaction solution / mol <sub>H2O2</sub> kg <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>
No Cs <sub>x</sub> P <sub>3-x</sub> W <sub>12</sub> O <sub>40</sub>	0	0	0	0	0
H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>	9	0	0	1834	19
Cs <sub>0.1</sub> H <sub>2.9</sub> PW <sub>12</sub> O <sub>40</sub>	8	0	0.05	1723	17
CsH <sub>2</sub> PW <sub>12</sub> O <sub>40</sub>	5	0	0.6	1096	12
Cs <sub>2</sub> HPW <sub>12</sub> O <sub>40</sub>	2	0	183	564	3
Cs <sub>2.5</sub> H <sub>0.5</sub> PW <sub>12</sub> O <sub>40</sub>	1	0	150	359	3
Cs <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>	1	0	95	240	3

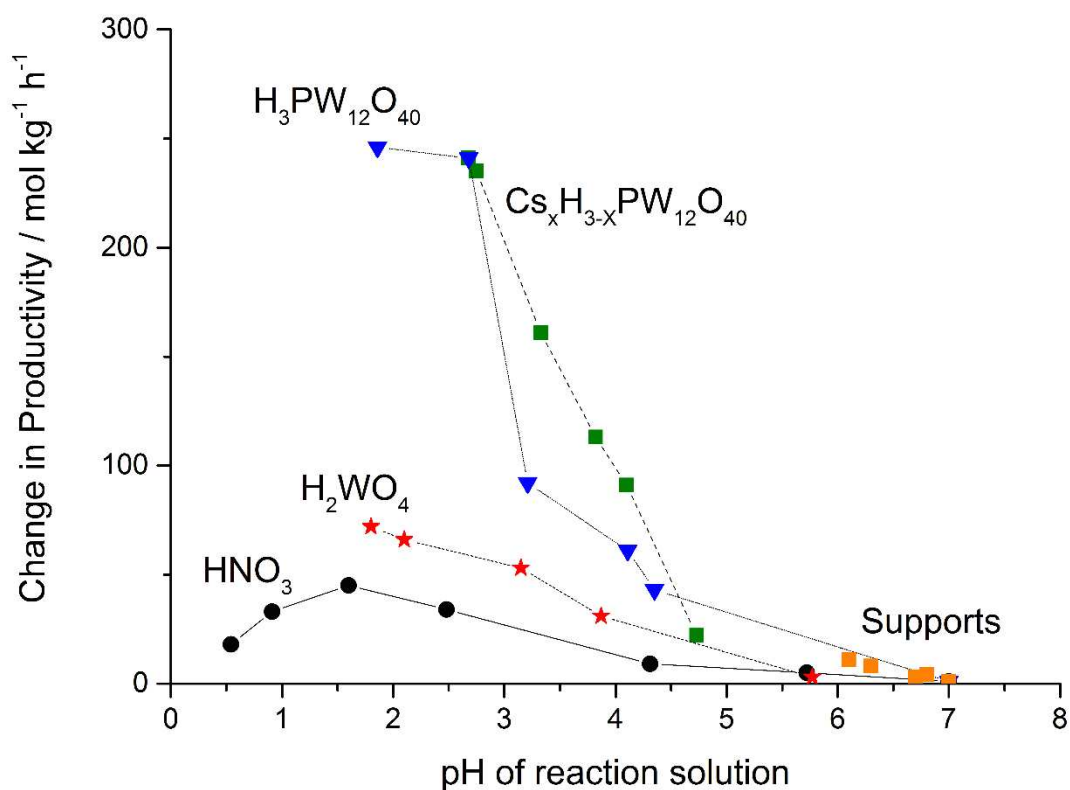
**Reaction Conditions:** Total pressure 4 MPa, H<sub>2</sub> /O<sub>2</sub> = 0.525, 1200 rpm, 5.6 g CH<sub>3</sub>OH + 2.9 g H<sub>2</sub>O (66 wt. % CH<sub>3</sub>OH), 0.5 h, 2 °C.

**Figure 3.** H<sub>2</sub>O<sub>2</sub> Productivity for 2.5 wt. % Au – 2.5 wt. % Pd / TiO<sub>2</sub> and Cs<sub>x</sub>H<sub>3-x</sub>PW<sub>12</sub>O<sub>40</sub> as a function of additive loading.



**Reaction conditions:** Catalyst (0.01 g), total pressure 4 MPa, H<sub>2</sub> /O<sub>2</sub> = 0.525, 1200 rpm, 5.6 g CH<sub>3</sub>OH + 2.9 g H<sub>2</sub>O (66 wt. % CH<sub>3</sub>OH), 0.5 h, 2 °C.

**Figure 4.** The effect of Cs-exchanged HPAs, dilute  $\text{HNO}_3$  and  $\text{H}_2\text{WO}_4$  on promoting the direct synthesis of  $\text{H}_2\text{O}_2$ , utilising 2.5 wt.% - Au 2.5% wt. Pd /  $\text{TiO}_2$ .



**Reaction conditions:** Catalyst (0.01 g), total pressure 4 MPa,  $\text{H}_2/\text{O}_2 = 0.525$ , 1200 rpm, 5.6 g  $\text{CH}_3\text{OH} + 2.9 \text{ g H}_2\text{O}$  (66 wt. %  $\text{CH}_3\text{OH}$ ), 0.5 h, 2 °C.



**Table 3.** The effect of  $\text{Cs}_x\text{H}_{(3-x)}\text{PW}_{12}\text{O}_{40}$  addition on catalytic activity of 2.5 wt.% - Au 2.5% wt. Pd /  $\text{TiO}_2$  towards the direct synthesis of  $\text{H}_2\text{O}_2$ .

	$\text{H}_2\text{O}_2$ Productivity <sup>[a]</sup> /mol $\text{H}_2\text{O}_2\text{kg}_{\text{cat}}^{-1} \text{h}^{-1}$	$\text{H}_2$ Conversion / %	$\text{H}_2\text{O}_2$ Selectivity / % <sup>[b]</sup>
No Additive	64	21	61
$\text{H}_3\text{PW}_{12}\text{O}_{40}$	301	70	85
$\text{Cs}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$	299	69	86
$\text{CsH}_2\text{PW}_{12}\text{O}_{40}$	225	66	63
$\text{Cs}_2\text{HPW}_{12}\text{O}_{40}$	161	55	54
$\text{Cs}_3\text{PW}_{12}\text{O}_{40}$	48	17	22

**Reaction conditions:** Catalyst (0.01 g), total pressure 4 MPa,  $\text{H}_2 / \text{O}_2 = 0.525$ , 1200 rpm, 5.6 g  $\text{CH}_3\text{OH} + 2.9$  g  $\text{H}_2\text{O}$  (66 wt. %  $\text{CH}_3\text{OH}$ ), 0.5 h, 2 °C.

**Table 4.** Reusability of 2.5 wt. % - Au 2.5% wt. Pd / TiO<sub>2</sub> - Cs<sub>x</sub>H<sub>(3-x)</sub>PW<sub>12</sub>O<sub>40</sub> towards the direct synthesis of H<sub>2</sub>O<sub>2</sub>.

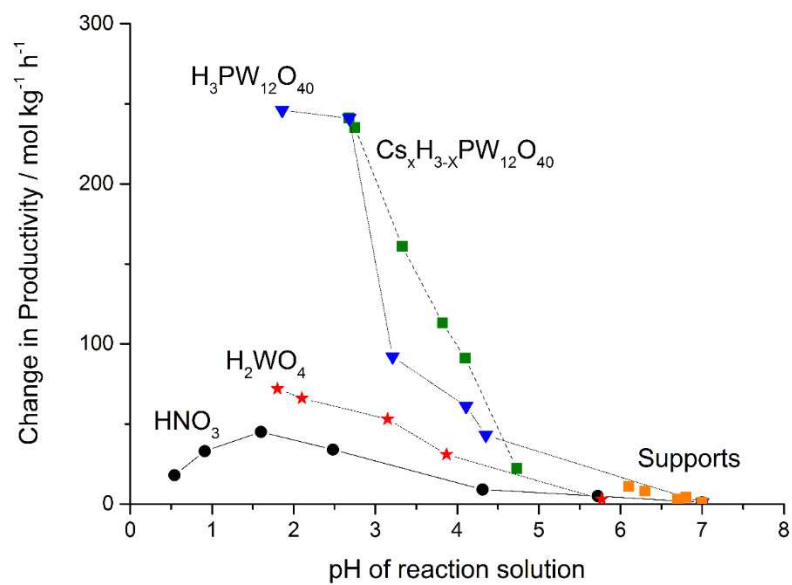
Catalyst system 2.5% Au – 2.5 % Pd / TiO <sub>2</sub> + additive	Productivity Fresh / mol <sub>H<sub>2</sub>O<sub>2</sub></sub> kg <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>	Productivity Used / mol <sub>H<sub>2</sub>O<sub>2</sub></sub> kg <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>
Cs <sub>2.5</sub> H <sub>0.5</sub> PW <sub>12</sub> O <sub>40</sub>	155	155
Cs <sub>2</sub> HPW <sub>12</sub> O <sub>40</sub>	161	130

**Reaction conditions:** Catalyst (0.01 g), total pressure 4 MPa, H<sub>2</sub> /O<sub>2</sub> = 0.525, 1200 rpm, 5.6 g CH<sub>3</sub>OH + 2.9 g H<sub>2</sub>O (66 wt. % CH<sub>3</sub>OH), 0.5 h, 2 °C.

## Supporting information.

Supporting information describes catalytic activity of common supports, as well as increasing concentrations of  $\text{CsNO}_3$ , towards the direct synthesis and degradation of  $\text{H}_2\text{O}_2$ .

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