Gas phase stabiliser-free production of hydrogen peroxide using supported gold–palladium catalysts†

Adeeba Akram,a Simon J. Freakley,a Christian Reece,a Marco Piccinini,a Greg Shaw,a Jennifer K. Edwards,b Frédérique Desmedt,b Pierre Miquel,b Eero Seuna,b David. J. Willock,a Jacob A. Moulijnab and Graham J. Hutchings*aa

Hydrogen peroxide synthesis from hydrogen and oxygen in the gas phase is postulated to be a key reaction step in the gas phase epoxidation of propene using gold–titanium silicate catalysts. During this process H2O2 is consumed in a secondary step to oxidise an organic molecule so is typically not observed as a reaction product. We demonstrate that using AuPd nanoparticles, which are known to have high H2O2 synthesis rates in the liquid phase, it is possible to not only oxidise organic molecules in the gas phase but to detect H2O2 for the first time as a reaction product in both a fixed bed reactor and a pulsed Temporal Analysis of Products (TAP) reactor without stabilisers present in the gas feed. This observation opens up possibility of synthesising H2O2 directly using a gas phase reaction.

Introduction

The direct synthesis of hydrogen peroxide (H2O2) from molecular H2 and O2 in the liquid phase is an active area of research in the field of heterogeneous catalysts.1 Catalysts based on Pd and Au–Pd nanoparticles supported on carbon and oxide materials as well as homogeneous gold/palladium systems show interesting properties and have been widely studied in many solvent systems.2–7 The direct combination of H2 and O2 to form H2O2 is carried out with a view to both synthesising viable concentrations of H2O2 and utilising synthesised H2O2 to carry out in situ oxidation reactions, including the epoxidation of propene.

One of the major problems associated with the vapour phase oxidation of propene to propene oxide (PO) using molecular oxygen is low reaction selectivity. The formation of the epoxide requires the electrophilic addition of an oxygen intermediate to the carbon–carbon double bond, however, propene can also be easily activated via the formation of allylic species which leads to non-selective oxidation. The addition of H2 to O2 streams as a sacrificial reductant, to synthesise H2O2 or peroxy species in situ, permits the activation of di-oxygen at temperatures that are typically much lower than required to activate oxygen alone. Haruta and co-workers were the first to demonstrate that highly dispersed Au/TiO2 catalysts show an extraordinary selectivity in the oxidation of propene to the corresponding epoxide (>99%), using a combination of H2 and O2 as oxidant.8–10 H2 was added as a sacrificial reductant which permits the activation of di-oxygen at relatively low temperatures (303–393 K) therefore allowing selective oxidation of propene to propene oxide.

Since TS-1 has been shown to be a selective material for the epoxidation of propene with H2O2 as the oxidising species the majority of the early studies used this as a catalyst support. Haruta and co-workers found that Au supported on TS-1 gave high selectivity to propanal above 100 °C however below 100 °C over 90% selectivity to PO could be achieved.11 In addition Moulijn12 and others13 demonstrated that Au/TS-1 catalysts were very stable and could be very selective to the formation of propene oxide. Mechanistic studies showed the important role of the gold nanoparticles in establishing a bidentate proxypoxy species as an intermediate.14 It is postulated in many mechanistic studies that H2O2 is formed on the Au nanoparticle, rather than a bound peroxy species, which is then capable of either desorbing/adsorbing or migrating on the surface to the tetrahedral Ti site in order to carry out the selective oxidation. In many studies H2O2 itself is not observed or analysed for in the reaction mixtures.

Examples in the patent literature report the direct combination of H2 and O2 in the gas phase at elevated pressures and temperature,15 however, these studies include the presence of acid and halides in the gas phase as stabilisers. In this study we aim to utilise catalysts comprising supported AuPd nanoparticles, which have been extensively shown to have a higher H2O2 synthesis rate than monometallic Au, to investigate if H2O2 can be formed and is able to desorb from the catalyst in the gas phase at atmospheric pressure, without adding stabilisers. Designing catalysts for the synthesis of H2O2 as part of...
Experimental

Supported bimetallic catalysts were prepared by a previously reported wet impregnation of the appropriate catalyst support with solutions of PdCl₂ and HAuCl₄. A typical preparation for 1 g of 2.5% Pd/2.5% Au/TiO₂ was carried out as follows: PdCl₂ (0.0416 g) was added to an aqueous solution of HAuCl₄ (2.04 ml, 12.25 g Au/1000 ml) and heated to 80 °C with stirring and left until the PdCl₂ had completely dissolved. TiO₂ (0.95 g Degussa P25) was then added to the solution and the water allowed to evaporate until the mixture formed a paste. The samples were dried at 110 °C for 16 h and then calcined in static air at 400 °C for 3 h with a ramp rate of 20 °C min⁻¹.

Catalytic reactions were carried out in a custom laboratory scale fixed bed reactor with 1/2 inch diameter PTFE tube. The catalyst bed, typically 50 mg unless stated, was suspended vertically in an oven by glass wool above and below. A low catalyst bed length/reactor diameter was used to help prevent back pressure issues. Reaction temperature (40–100 °C) was stabilised before a flow of 2% H₂ in synthetic air was introduced (50–200 ml min⁻¹). Reactions were typically carried out for 16 h using dreschel bottles in an ice bath to condense liquid products from the gas phase. After reaction the presence of H₂O₂ was determined by titrating aliquots of reaction solution with acidified Ce(SO₄)₂ solution in the presence of ferroin as an indicator. The Ce(SO₄)₂ solution was standardised against (NH₄)₂Fe(SO₄)₂·6H₂O using ferroin as an indicator. H₂O₂ decomposition was measured by comparing the difference in H₂O₂ concentration before and after the reaction using the same titration method outlined above. Oxidation experiments were carried out by bubbling gases through a solution of 2-propanol (99.5% as purchased) which once passed over the catalyst was condensed in an ice bath. NMR analysis of the reaction mixtures was then carried out to identify the presence of oxidation products.

The TAP experiments were performed using a TAP-2 system. A gas mixture containing 2% H₂ in air was pulsed over the catalyst from a reservoir at a pressure of 0.6 bar. The reactor was packed with 0.045 g of powdered catalyst held in place with SiC inert packing. The gas exiting the reactor bed was detected via quadrupole mass spectrometer. The response for mass 34 (H₂O₂) and mass 2 (H₂) was monitored over a time of 2 s for each pulse, giving a curve of intensity against time. The experiment was carried out at 60 °C, with a train of 20 pulses averaged per experiment.

Results

Initial experiments were carried out with the laboratory scale reactor to ensure that any H₂O₂ produced could pass through the reactor system without significant decomposition occurring. A H₂O₂ vapourisation calibration curve was established by flowing synthetic air through a 50 wt% H₂O₂ solution and measuring the moles of H₂O₂ carried in the vapour phase at various flow rates by condensing the gas phase mixture after the reactor (Fig. 1). The amounts of H₂O₂ in the gas phase suggest that the gas is not saturated with H₂O₂ due to the high flow rate used and the low vapour pressure of H₂O₂ at ambient temperature. Following this reactor tubes made of stainless steel and PTFE were trialled, stainless steel decomposed over 90% of the H₂O₂ vapourised in the gas phase. When a PTFE tube was used the number of moles of H₂O₂ carried through the tube in the gas phase matched the calibration curve in both synthetic air and 2% H₂ in air as shown in Fig. 1. All further experiments were carried out with a PTFE reaction tube.

Support materials that had been previously used to support AuPd nanoparticles for H₂O₂ synthesis were screened for H₂O₂ decomposition activity in the gas phase reactor (50 wt% H₂O₂ 145 ml min⁻¹ gas flow corresponding to 2.17 mol min⁻¹ from calibration in Fig. 1). Table 1 shows that all supports tested showed significant H₂O₂ decomposition, which is in contrast to the observed decomposition activity in the liquid phase.⁶⁻¹⁹

This can be attributed to the high surface concentrations of H₂O₂ passing over the catalyst without the protection of solvation that is available in the liquid phase. Despite these high observed decomposition rates we focused this study on a 2.5% Au 2.5% Pd/TiO₂ catalyst to investigate whether oxidative species could be generated from H₂ and O₂ mixtures on AuPd nanoparticles in the gas phase and if H₂O₂ could be synthesised and detected despite the high decomposition rates of the catalyst support materials.

The oxidation of 2-propanol to acetone was used to probe the presence of oxidative species formed by the catalyst. The gas phase oxidation of 2-propanol using Au catalysts and oxygen
has been previously studied by Rossi et al.\textsuperscript{20} who showed that oxidation occurred at 393 K with over 80% selectivity to carbonyl derivatives. Other studies have shown that Au/TiO\textsubscript{2} is also active for the reaction using oxygen with light-off curves beginning at 350–400 K.\textsuperscript{21} To avoid any reaction with oxygen alone we conducted gas phase oxidation reactions at 60 °C. Gases were bubbled through a solution of 2-propanol (99.5%), lines exiting the catalyst bed were passed through an ice bath so that remaining 2-propanol and liquid products could be condensed for analysis. NMR analysis of the resulting reaction mixtures was then carried out to identify qualitatively the presence of oxidation products.

Initially reactions were carried out with synthetic air and 2% H\textsubscript{2} in synthetic air without the presence of a catalyst, in both cases no oxidation products were detected by NMR (Table 2), similar results were observed when using bare TiO\textsubscript{2}. Also, when the catalyst was present with 2-propanol in synthetic air no oxidation products were detected. However, when 2% H\textsubscript{2} in air was used as reactant gas NMR analysis showed the presence of acetone in the reaction solutions condensed after passing over the catalyst. This confirms that, at 60 °C, the AuPd particles are able to activate oxygen in the presence of H\textsubscript{2} to oxidise organic molecules such as 2-propanol. This temperature is lower than reported for oxygen alone indicating that H\textsubscript{2} can initiate the oxidation at lower temperature, probably through the formation of a surface bound – hydroperoxy intermediate or through the formation of free H\textsubscript{2}O\textsubscript{2} which is further activated to carry out the oxidation.

### Table 1: Decomposition of concentrated H\textsubscript{2}O\textsubscript{2} in the gas phase over potential catalyst support materials

<table>
<thead>
<tr>
<th>Support</th>
<th>H\textsubscript{2}O\textsubscript{2} decomposed/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe\textsubscript{2}O\textsubscript{3}</td>
<td>91</td>
</tr>
<tr>
<td>Carbon</td>
<td>85</td>
</tr>
<tr>
<td>CeO\textsubscript{2}</td>
<td>77</td>
</tr>
<tr>
<td>MgO</td>
<td>68</td>
</tr>
<tr>
<td>TiO\textsubscript{2}</td>
<td>58</td>
</tr>
<tr>
<td>SiO\textsubscript{2}</td>
<td>53</td>
</tr>
<tr>
<td>Al\textsubscript{2}O\textsubscript{3}</td>
<td>47</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Reaction conditions: catalyst mass 10 mg, 25 °C, 145 ml min\textsuperscript{-1} gas flow.

### Table 2: Catalytic tests for the direct gas phase oxidation of propan-2-ol to acetone

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Gas mixture</th>
<th>Oxidation to acetone</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>None</td>
<td>Industrial grade air</td>
<td>No</td>
</tr>
<tr>
<td>2</td>
<td>None</td>
<td>2% H\textsubscript{2}/air</td>
<td>No</td>
</tr>
<tr>
<td>3</td>
<td>TiO\textsubscript{2}</td>
<td>Industrial grade air</td>
<td>No</td>
</tr>
<tr>
<td>4</td>
<td>TiO\textsubscript{2}</td>
<td>2% H\textsubscript{2}/air</td>
<td>No</td>
</tr>
<tr>
<td>5</td>
<td>5% AuPd/TiO\textsubscript{2}</td>
<td>Industrial grade air</td>
<td>No</td>
</tr>
<tr>
<td>6</td>
<td>5% AuPd/TiO\textsubscript{2}</td>
<td>2% H\textsubscript{2}/air</td>
<td>Yes</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Reaction conditions: catalyst mass 50 mg, 60 °C, 50 ml min\textsuperscript{-1} gas flow – reaction products qualitatively analysed by NMR.

Temporal analysis of products (TAP) reactor studies were carried out to investigate whether H\textsubscript{2}O\textsubscript{2} is formed and able to desorb from the catalyst surface. Reactions were carried out at 60 °C by pulsing 2% H\textsubscript{2}/air over the catalyst bed. Fig. 2 shows the accumulated signals observed for mass 34 (H\textsubscript{2}O\textsubscript{2}) and 2 (H\textsubscript{2}) during the pulses.

A large H\textsubscript{2} signal is detected at the beginning of each pulse along with a smaller signal at mass 34 corresponding to the mass of H\textsubscript{2}O\textsubscript{2}. This result shows that it is possible to generate H\textsubscript{2}O\textsubscript{2} in the gas phase and under the vacuum of the TAP reactor it is possible to desorb the H\textsubscript{2}O\textsubscript{2} from the surface of the catalyst and detect it as a reaction product.

Experiments were also conducted in a continuous fixed bed reactor to test under practical conditions for H\textsubscript{2}O\textsubscript{2} synthesis at various temperatures between 40 and 80 °C using 2% H\textsubscript{2} in air at 60 °C. When no catalyst was present with air or 2% H\textsubscript{2} in air no condensate was seen after the reactor in the cold trap indicating that there was no detectable moisture in the gas feeds. In the presence of 50 mg of catalyst with the synthetic air mixture again no condensate was seen in the cold trap. When 2% H\textsubscript{2} in air was used as the reactant gas, liquid was observed in the cold trap indicating that at 60 °C the AuPd nanoparticles were capable of reacting H\textsubscript{2} and O\textsubscript{2} in the gas phase. On titration it was determined that the solution contained 53 ppm of H\textsubscript{2}O\textsubscript{2}. This result demonstrates that when using a 5% AuPd/TiO\textsubscript{2} catalyst, that is known to have high H\textsubscript{2}O\textsubscript{2} synthesis rates in the liquid phase at 2 °C, it is possible to produce H\textsubscript{2}O\textsubscript{2} in the gas phase reactor system where the residence time is of the order of seconds at ambient pressure. The result also demonstrates that it is possible for H\textsubscript{2}O\textsubscript{2} to desorb from the catalyst into the gas phase after it is formed.

Fig. 3a shows the effect of increasing the reaction temperature from 40–80 °C in the flow reactor. As the temperature is increased the amount of product condensed in the cold trap after 16 h remained constant, full conversion of the H\textsubscript{2} in the
agreement with the complete conversion of H2 passing over the catalyst bed. H2O2 synthesis rates over the catalyst were 5% AuPd/TiO2 (50 mg), 16 h. (b) Atmospheric pressure, various temperatures, 2% H2/air (50 ml min-1), 5% AuPd/TiO2 (50 mg), 16 h. (b) Atmospheric pressure; 60 °C, 2% H2/air, 5% AuPd/TiO2 (50 mg), 16 h.

Fig. 3 (a) Effect of reaction temperature on the synthesis of H2O2 in the gas phase (b) effect of gas flow on the synthesis of H2O2 in the gas phase. Both figures – ● mass product □ H2O2 concentration. (a) Atmospheric pressure, various temperatures, 2% H2/air (50 ml min-1), 5% AuPd/TiO2 (50 mg), 16 h. (b) Atmospheric pressure; 60 °C, 2% H2/air, 5% AuPd/TiO2 (50 mg), 16 h.

gas stream was observed across the whole temperature range, explaining why we see no increase in liquid reaction product with increasing temperature.

The amount of H2O2 present in the liquid reaction products formed increased from 23 ppm at 40 °C to 55 ppm at 60 °C before decreasing at temperatures above 60 °C. This indicates that there is a balance between the synthesis/desorption and stability of H2O2 through the catalyst bed. H2O2 synthesis rates over the duration of the experiments were approximately 1 × 10-3 mol kgcat−1 h−1, due to the high H2 conversion and extremely low selectivity leading to mainly H2O production. The observation that it is possible to detect H2O2 at all suggests that the water produced could be the result of a H2O2 decomposition pathway rather than combustion of hydrogen and oxygen without the intermediate production of H2O2. These rates are significantly lower than reported rates in the liquid phase at elevated pressure under optimum conditions (64 mol kgcat−1 h−1).

Fig. 3b shows the effect of varying the total gas flow through the catalyst bed over the 16 h reaction. With increasing gas flow, the amount of liquid product observed increased linearly, in agreement with the complete conversion of H2 passing over the catalyst. The concentration of H2O2 in the liquid phase increases over the range studied presumably because the faster gas flows can more effectively strip the H2O2 from the catalyst bed.

As no liquid condensate is seen from the gas phase without the presence of the catalyst we can conclude that the water formed is through the combination of H2 and O2 over the catalyst bed. Despite this, the results show that it is possible to produce and collect H2O2 in the gas phase although at low concentrations. Preventing the subsequent decomposition of H2O2 through the catalyst bed remains a challenge never the less this study shows that the concept of producing H2O2 in the gas phase is can be realised.

Conclusions

We demonstrate for the first time that the H2O2 synthesis rates of catalysts that are well studied in the liquid phase with high pressure gas phase reagents are, in fact, high enough to produce H2O2 in the gas phase at atmospheric pressure. Using TAP analysis we have shown that H2O2 can be synthesised and desorbed from the catalyst surface in the gas phase suggesting that gas phase direct synthesis of H2O2 could be feasible. This observation goes some way to explaining the increased reaction rates observed for propene epoxidation when H2 is added to the reactant gas stream. In this study H2 conversions were high and selectivity towards H2O2 was extremely low due to the nature of the packed bed however detectable amounts of H2O2 were synthesised. Through future reactor design and optimization of conditions, coupled with catalyst improvements a simpler process design might be feasible to produce H2O2; the results enable fundamental investigation of the reaction possible through operando surface sensitive spectroscopies.

Acknowledgements

We would like to acknowledge Solvay for financial support of A. A.

Notes and references