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Comparison of supports for the direct synthesis of hydrogen peroxide from H_2 and O_2 using Au–Pd catalysts

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Abstract

The direct synthesis of hydrogen peroxide from H_2 and O_2 using a range of supported Au–Pd alloy catalysts is compared for different supports using conditions previously identified as being optimal for hydrogen peroxide synthesis, i.e. low temperature (2 °C) using a water–methanol solvent mixture and short reaction time. Five supports are compared and contrasted, namely Al_2O_3, α-Fe_2O_3, TiO_2, SiO_2 and carbon. For all catalysts the addition of Pd to the Au only catalyst increases the rate of hydrogen peroxide synthesis as well as the concentration of hydrogen peroxide formed. Of the materials evaluated, the carbon-supported Au–Pd alloy catalysts give the highest reactivity. The results show that the support can have an important influence on the synthesis of hydrogen peroxide from the direct reaction. The effect of the methanol–water solvent is studied in detail for the 2.5 wt% Au–2.5 wt% Pd/TiO_2 catalyst and the ratio of methanol to water is found to have a major effect on the rate of hydrogen peroxide synthesis. The optimum mixture for this solvent system is 80 vol.% methanol with 20 vol.% water. However, the use of water alone is still effective albeit at a decreased rate. The effect of catalyst mass was therefore also investigated for the water and water–methanol solvents and the observed effect on the hydrogen peroxide productivity using water as a solvent is not considered to be due to mass transfer limitations. These results are of importance with respect to the industrial application of these Au–Pd catalysts.

Keywords: Gold–palladium alloys; Hydrogen peroxide

1. Introduction

Hydrogen peroxide is a key commodity chemical produced on a large scale for use as a bleach and oxidant. It is often considered as a green oxidant as the sole by-product is water, and only the use of molecular oxygen is preferred as an oxidant. These days, increasing attention is being placed on green chemical reactions and this has the effect of focussing increasing interest in the design of processes that are atom efficient. This is particularly true in the fine chemicals industry, where many processes are operated with low atom efficiency. In this respect oxidation reactions exhibit significant problems as stoichiometric, i.e. non-catalytic, processes are often employed using a range of oxygen donors [1]. Although molecular oxygen is preferred [2], there are remarkably few processes operating with this oxidant, particularly under the mild reaction conditions required by many fine chemicals syntheses, and hence attention is being given to using hydrogen peroxide as an oxidant.

Hydrogen peroxide is produced commercially by an indirect process in which an alkyl anthraquinone is sequentially hydrogenated with hydrogen and oxidised with molecular oxygen [3]. A direct route would provide a preferable alternative for the manufacture of hydrogen peroxide, and there has been significant interest in this reaction in industrial laboratories using supported Pd catalysts for over 90 years [4–21]. Recently, we have shown that addition of Au to Pd dramatically enhances the yield of hydrogen peroxide in the direct synthesis using mild non-explosive reaction conditions. In the earlier work we have shown that Al_2O_3, α-Fe_2O_3 and TiO_2 are effective supports and we have reported detailed characterisation of these catalysts [22–26]. In this paper we compare these materials with carbon and SiO_2 as supports, and show that the support is indeed important and that much higher activities can be obtained using carbon and silica as supports when compared with Al_2O_3, α-Fe_2O_3 and TiO_2. In addition, in

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previous studies we have used a single solvent system (*ca.* methanol 70.9 vol.%–water 29.1 vol.%) and we now present the results for a full range of methanol–water solvent mixtures, and, in particular, we discuss the possibilities of using water alone as the solvent for this reaction.

2. Experimental

2.1. Catalyst preparation

Five weight percentage Au and 2.5 wt% Au–2.5 wt% Pd-supported catalysts were prepared using incipient wetness as described previously [22–26] using aqueous solutions of $PdCl_2$ (Johnson Matthey) and/or $HAuCl_4\cdot3H_2O$ (Johnson Matthey). As an example, for the 2.5% Au–2.5% Pd/Al_2O_3 catalyst the detailed procedure was as follows. An aqueous solution of $HAuCl_4\cdot3H_2O$ (10 ml, 5 g in 250 ml of water) and $PdCl_2$ solution (4.15 ml, 1 g in 25 ml of water) were simultaneously added to γ-Al_2O_3 (Condea SCF-140, 3.8 g). The paste formed was ground and dried at 80 °C for 16 h and finally calcined in static air at 400 °C for 3 h. Further series of catalysts were prepared by impregnation using TiO_2 (Degussa P25), carbon (Aldrich G60, Waterlink Sutcliffe Carbons Activated Carbon Grade: 207A, Mesh: 12 × 20), silica (Johnson Matthey) and α-Fe_2O_3 as supports. α-Fe_2O_3 was prepared by the precipitation of an aqueous solution of $Fe(NO_3)_3\cdot xH_2O$ at pH 8.2, by drop-wise addition of an aqueous solution of Na_2CO_3 (0.25 M). After filtration, the iron oxide was dried at 120 °C for 16 h before impregnation with Au or Au–Pd.

Three additional sets of catalysts containing 5 wt% Au using ZnO, TiO_2 and α-Fe_2O_3 as supports were prepared by co-precipitation (ZnO and α-Fe_2O_3) or deposition precipitation (TiO_2). Aqueous solutions of $PdCl_2$, $HAuCl_4\cdot3H_2O$ and a suitable salt of the support material, e.g. nitrate, were mixed in the required proportions and stirred at 80 °C. Na_2CO_3 was then added with stirring until pH 8.2–9.0 was achieved and the mixture was stirred for a further 30 min. The catalysts prepared by impregnation or precipitation were pretreated under a variety of conditions based on drying at 120 °C in air, calcination in static air at 200 °C for 3 h, calcination in static air at 400 °C for 3 h and reduction in flowing H_2 (5 wt% H_2 in Ar) at 500 °C.

Catalysts were characterised by powder X-ray diffraction using an Enraf Nonius PSD120 diffractometer with a monochromatic Cu $K\alpha_1$ source operated at 40 keV and 30 mA. Phases were identified by matching experimental patterns to the JCPDS powder diffraction file.

2.2. Catalyst testing

Hydrogen peroxide synthesis was carried out using a Parr Instruments stainless steel autoclave with a nominal volume of 50 ml and a maximum working pressure of 14 MPa. The autoclave was equipped with an overhead stirrer (0–2000 rpm) and provision for measurement of temperature and pressure. Typically, the autoclave was charged with catalyst (0.01 g unless otherwise stated), solvent (the standard solvent mixture being 5.6 g MeOH and 2.9 g H_2O) purged three times with CO_2 (3 MPa) and then filled with 5% H_2/CO_2 and 25% O_2/CO_2 to give a hydrogen to oxygen ratio of 1:2, at a total pressure of 3.7 MPa at 20 °C. Stirring (1200 rpm unless otherwise stated) was started on reaching the desired temperature, and experiments were run for 30 min unless otherwise stated. Gas analysis for H_2 and O_2, was performed by gas chromatography using a thermal conductivity detector and a CP, Carboplot P7 column (25 m, 0.53 mm i.d.). Conversion of H_2 was calculated by gas analysis before and after reaction. H_2O_2 yield was determined by titration of aliquots of the final filtered solution with acidified $Ce(SO_4)_2$ (7×10^{-3} mol/l). $Ce(SO_4)_2$ solutions were standardised against $(NH_4)_2Fe(SO_4)_2\cdot6H_2O$ using ferroin as indicator.

3. Results and discussion

3.1. Comparison of supports

The initial experiments were conducted using 5 wt% Au catalysts supported on ZnO, α-Fe_2O_3 or TiO_2 prepared by precipitation methods. These catalysts contain small Au nanocrystals typically in the range 2–5 nm [27] and we have previously shown that the catalysts are all active for CO oxidation [27]. These three materials were evaluated as catalysts for the synthesis of hydrogen peroxide and it is clear that they gave similar poor activities for this reaction (Table 1), which were not particularly affected by the calcination temperature, although drying at 120 °C did enhance the activity of these catalysts. In contrast, supported Au and Au–Pd catalysts prepared using impregnation methodology and calcined at 400 °C are much more active (Table 2).

For the calcined catalysts made by impregnation, the Au only catalysts all generate H_2O_2 but at low rates. However, for all the supports the rate is higher than that observed for Au only catalysts prepared by precipitation, although the enhancement is less marked for α-Fe_2O_3. The best results for the Au only catalyst are obtained using TiO_2 as a support and this is significantly higher than the other supports evaluated to date, including silica which Okumura et al. [28] previously reported as the best support for Au only catalysts for the direct synthesis reaction.

Addition of Pd to gold demonstrates a synergistic effect [22–26], the rate of hydrogen peroxide synthesis is dramatically

Table 1
Hydrogen peroxide synthesis using catalysts prepared by precipitation[a]

Catalyst	Pretreatment	Productivity (mol H_2O_2/(h kg_{cat}))	H_2O_2 (wt%)
5% Au/TiO_2	Air, 25 °C	0.229	0.002
5% Au/TiO_2	Air, 120 °C	0.482	0.005
5% Au/TiO_2	Air, 400 °C	0.388	0.004
5% AuZnO	Air, 120 °C	0.224	0.002
5% Au/ZnO	Air, 400 °C	0.373	0.004
5% Au/α-Fe_2O_3	Air, 25 °C	0.126	0.001
5% Au/α-Fe_2O_3	Air, 400 °C	0.207	0.002
5% Au/α-Fe_2O_3	Air, 600 °C	0.366	0.004

[a] Standard reaction conditions using catalyst (50 mg).

Table 2
Hydrogen peroxide synthesis using catalysts prepared by impregnation[a]

Catalyst	Productivity (mol H_2O_2/(h kg_{cat}))
5% Au/TiO_2[b]	7.1
2.5% Au/2.5% Pd/TiO_2[b]	64
5% Pd/TiO_2[b]	21
5% Au/Al_2O_3[c]	3.1
2.5% Au/2.5% Pd/Al_2O_3[c]	18
5% Pd/Al_2O_3[c]	12
5% Au/α-Fe_2O_3[d]	0.54
2.5% Au/2.5% Pd/α-Fe_2O_3[d]	16
5% Pd/α-Fe_2O_3[d]	3.6
2.5% Au/C[e]	2
2.5% Au/2.5% Pd/C[e]	110
2.5% Pd/C[e]	42
2.5% Au/C[f]	0.4
2.5% Au/2.5% Pd/C[f]	34
2.5% Pd/C[f]	24
2.5% Au/SiO_2[g]	0.5
2.5% Au/2.5% Pd/SiO_2[g]	48

[a] All catalysts calcined at 400 °C, catalyst (10 mg), 2 °C, all catalysts are inactive for CO oxidation.
[b] Degussa P25.
[c] Condea SCF-140.
[d] Prepared by precipitation, catalyst (50 mg).
[e] Aldrich G60.
[f] Waterlink Sutcliffe Carbons Activated Carbon Grade: 207A, Mesh: 12 × 20.
[g] Johnson Matthey.

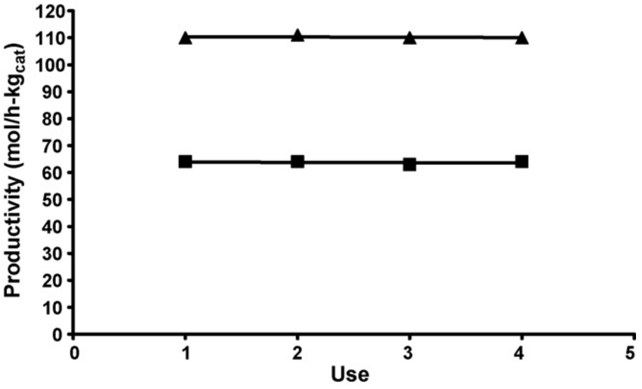

Fig. 1. Productivity of hydrogen peroxide with the number of uses for catalysts calcined in air at 400 °C. TiO_2 (■), Aldrich G60 carbon (▲).

enhanced and the best results are obtained using the Aldrich G60 carbon as support (Table 2); the productivities are markedly higher than for TiO_2 which we have previously reported in a detailed study [26]. Indeed, the addition of Pd to Au on the Aldrich G60 carbon demonstrates the most significant synergistic effect we have observed to date. Interestingly, an alternative carbon (Waterlink Sutcliffe Carbons Activated Carbon Grade: 207A, Mesh: 12 × 20) gives much poorer performance, probably due to a function of the surface groups due to the different preparation methods. These effects and the detailed nature of the structure of the Au and the Au–Pd catalysts supported on carbon will be the subject of a detailed subsequent study.

One of the key factors that must be considered for heterogeneous catalysts operating in three phase systems, such as we have in the direct synthesis of hydrogen peroxide, is the possibility that active components can leach into the reaction mixture, thereby leading to catalyst deactivation or, in the worst case, leading to the formation of an active homogeneous catalyst. To demonstrate that the supported gold/palladium catalysts functioned as wholly heterogeneous catalysts, experiments were carried out with the Au and Au–Pd-supported catalysts calcined at 400 °C. These were tested and the yield of H_2O_2 was determined. Following reaction, the catalyst was removed by careful filtration using celite and the solution was used for a second experiment using O_2/H_2. In all cases when the catalyst was calcined at 400 °C no further H_2O_2 was formed. To confirm that no homogeneous reaction took place, the used catalyst was tested and the same productivity to hydrogen peroxide was obtained that the one with the fresh catalyst. Another experiment with the catalyst used twice was carried out and again the same amount of H_2O_2 was achieved. Chemical analysis by atomic absorption of fresh and used samples demonstrated that leaching of Au and Pd was negligible. In general, calcination of the Au–Pd catalysts led to the generation of stable reuseable catalysts [26].

If the catalysts are heat treated at temperatures less than 400 °C then they are unstable, although they can give much higher rates of hydrogen peroxide synthesis on first use. In view of this we always calcine the materials at 400 °C, following which the catalysts are stable for many uses as shown in Fig. 1 for the two most active catalysts used in this study. Indeed, we have successfully reused catalysts up to 10 times without loss of performance and without leaching of any Au or Pd from the catalyst. The calcination procedure aids the formation of Au–Pd alloy nanocrystals as revealed by powder X-ray diffraction studies (Figs. 2 and 3). Figs. 2 and 3 show the powder X-ray diffraction patterns for Au, Au–Pd and Pd on alumina and α-Fe_2O_3 catalysts calcined at 400 °C. For the Pd only catalysts the Pd is present as PdO as shown by a very broad (1 0 1) reflection. Au and Au/Pd catalysts showed metallic gold reflections, particularly an intense (1 1 1) reflection. However, for the Au–Pd catalysts the reflection corresponding to Au° shifts to higher angles in comparison with the Au only catalysts. This is more clearly shown in the figures [WHICH?] where the diffraction pattern from 37.5° to 39° is plotted, and the shift of the (1 1 1) reflection of metallic gold can be clearly observed, indicative of alloy formation [29]. The gradual shift is further emphasised in Fig. 4, where the X-ray diffraction patterns of a series of Au–Pd catalysts on alumina as a support are contrasted. The morphology of the gold–palladium alloys for the very active materials supported on active carbon is now the subject of a detailed study which will be reported subsequently.

3.2. Effect of water/methanol ratio

In the preceding section, we have shown that 2.5 wt% Au/TiO_2 is a very effective catalyst for the direct synthesis of hydrogen peroxide. In these experiments we used a methanol–water mixture of a fixed composition (methanol 70.9 vol.%–water 29.1 vol.%). However, for a three phase reaction the

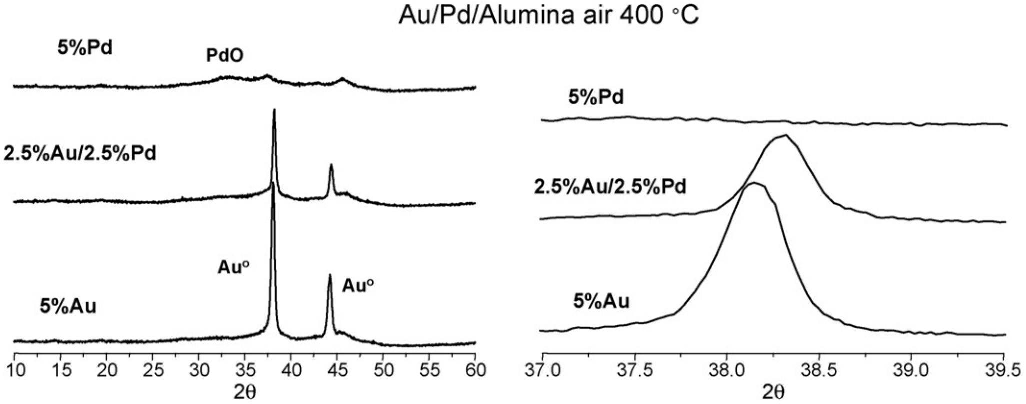

Fig. 2. XRD patterns of Au, Au–Pd and Pd/Al_2O_3 catalysts calcined in air at 400 °C.

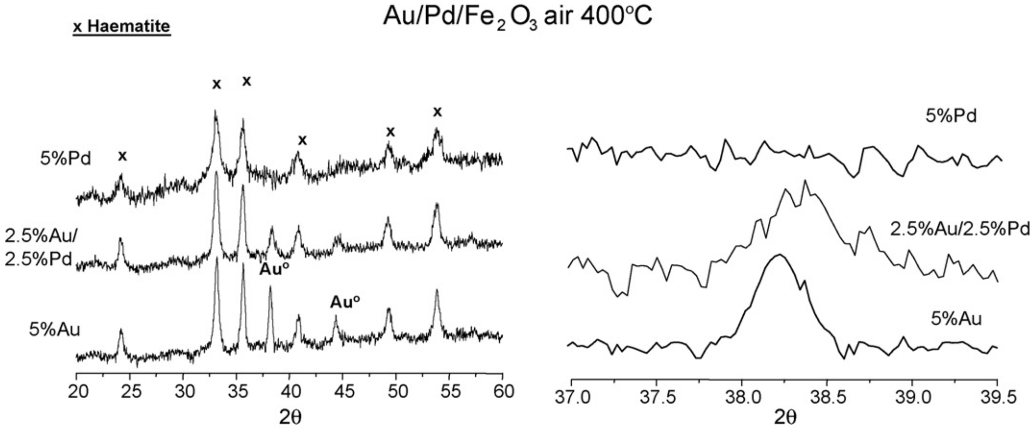

Fig. 3. XRD patterns of Au, Au–Pd and Pd/Fe_2O_3 catalysts calcined at 400 °C.

nature of the solvent can be very important and this has been studied. Hence, a series of experiments were carried using the 2.5 wt% Au–2.5 wt% Pd/TiO_2 catalyst in which the ratio of water and methanol were varied whilst maintaining the overall volume constant. These reactions were carried out for a standard reaction time of 0.5 h at 2 °C using a very small mass of catalyst (10 mg) under identical conditions and all experiments were carried out in duplicate. In addition regular blank reactions, i.e. in the absence of catalyst, were conducted to ensure that there was no contamination of the autoclave. The results, shown in Fig. 5 clearly show that the methanol–water ratio is indeed an important parameter and the optimal ratio is 80 vol.% methanol and 20 vol.% water. Although this is close to the ratio we have used in our previous detailed studies the rate of hydrogen peroxide synthesis appears to be very sensitive around this optimal point.

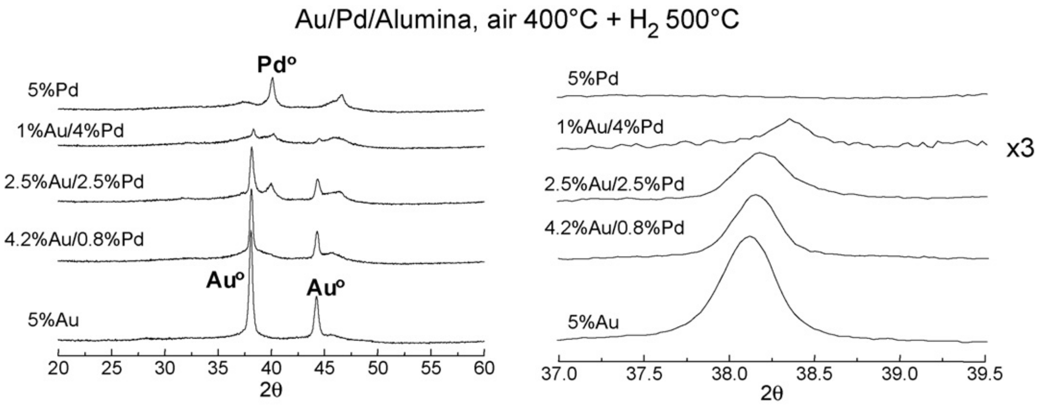

Fig. 4. XRD patterns of Au, Au–Pd and Pd/Al_2O_3 catalysts calcined in air at 400 °C and in H_2 at 500 °C.

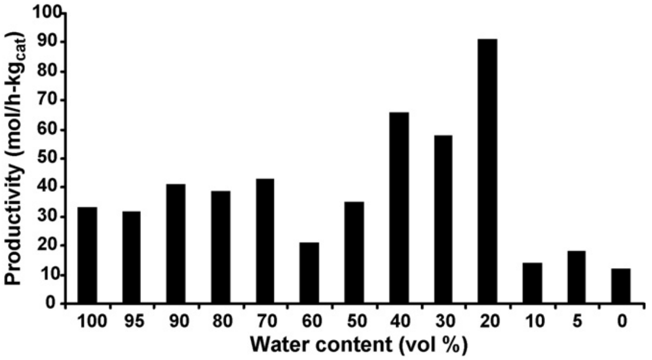

Fig. 5. Effect of water–methanol ratio on the rate of synthesis of hydrogen peroxide under standard reaction conditions at 2 °C.

There are three interesting features of these data. First, there is the sensitivity noted above, and in particular increasing the methanol concentration above the optimal value leads to a dramatic decrease in the rate of hydrogen peroxide synthesis. The second is that the total absence of water leads to very low rates being observed. Thirdly, the use of pure water still leads to an effective rate for the production of hydrogen peroxide. However, there are two possible causes for these effects, namely the reaction becomes mass transfer limited due to the change in the solvent mixture, and secondly, a related factor is that the solubility of hydrogen and oxygen will vary as a function of the composition of the solvent and this will therefore directly affect the rate of synthesis, even in the absence of diffusion limitations.

We therefore investigated whether the reaction was mass transfer limited for water only and the standard methanol–water solvent mixture by varying the amount of catalyst, and the results are shown in Fig. 6. For the water-only experiments, although the rate of hydrogen peroxide synthesis is lower than when methanol is present, the concentration of hydrogen peroxide produced varies linearly with the catalyst mass in the range 10–40 mg. In addition, the rate of hydrogen peroxide production is reasonably constant as the catalyst mass is varied. The observations lead us to conclude that the lower rate of hydrogen peroxide observed with this catalyst using water as solvent under our reaction conditions is not due to mass transfer effects. For the standard solvent mixture the concentration of hydrogen peroxide is linearly dependent on the mass catalyst up to a mass of 20 mg. Above this the concentration of hydrogen peroxide is not greatly enhanced and the rate of production is decreased (Fig. 6). Although the rate of hydrogen peroxide synthesis is enhanced by the addition of methanol to the water, the water only reaction mixture can utilise higher catalyst masses and consequently can still achieve enhanced rates of reaction. Industrial application of the direct synthesis route is likely to favour the use of non-organic solvents. In particular, small scale synthesis for medical uses will necessitate the use of water as a solvent. Our study shows that the high activity catalysts based on supported gold–palladium alloys can be used with water as solvent. Furthermore, no additives such as bromide or acid, e.g. phosphoric acid are required, whereas these additives are essential for the Pd only catalysts to ensure the stability of the hydrogen peroxide in the presence of the Pd catalyst.

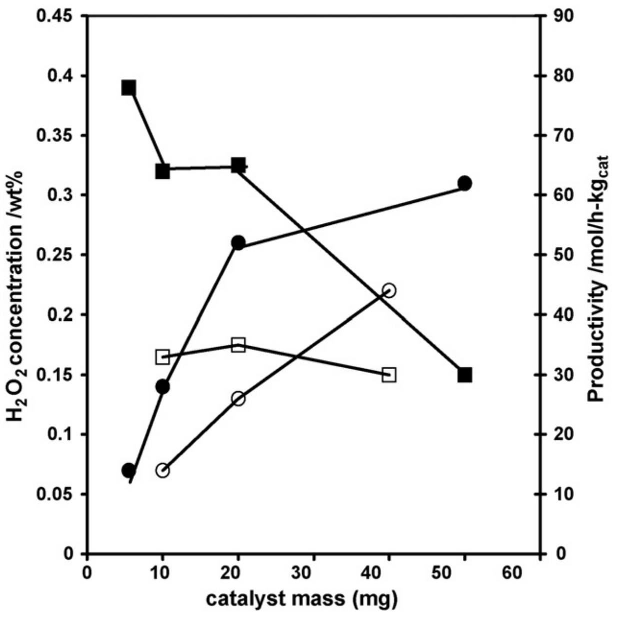

Fig. 6. Effect of catalyst mass on H_2O_2 concentration (circles) and activity (squares) for a 2.5 wt% Au–2.5 wt% Pd/TiO_2 calcined catalyst in 100 vol.% H_2O (open symbols) and 70.9 vol.% water:29.1 vol.% methanol system (closed symbols).

It is interesting to comment further on the variation in rate of hydrogen peroxide synthesis as the water–methanol ratio is changed (Fig. 5). As the data were collected using catalyst mass of 10 mg, these data do not result from mass transfer limitation. The increase in rate from pure water on addition of methanol is due to the enhanced solubility of hydrogen and oxygen in the solvent. However, this effect is not significant at low methanol ratios. As the gases are more soluble in methanol the rate with pure methanol should be higher than that of pure water, but this is not the case. This may indicate that water plays an essential role in the reaction mechanism, maybe through the provision of surface hydroxyls at the interface between the support and the alloy nanocrystals, and this possibility will be examined in subsequent studies.

4. Conclusions

Au–Pd catalysts prepared by impregnation have been shown as very active for the direct formation of hydrogen peroxide from molecular hydrogen and oxygen and the nature of the support is an important factor, with the order of reactivity being carbon > TiO_2 > SiO_2 > Al_2O_3 > Fe_2O_3. These catalysts prepared by impregnation are inactive for CO oxidation. In contrast, Au catalysts prepared by coprecipitation or deposition–precipitation gave a very low hydrogen peroxide rate although these are known to be very active in the CO oxidation at room temperature. Calcination in air is essential to obtain a stable catalyst, and these can be reused several times without loss of Au or Pd from the catalysts, and this aids the formation of a gold–palladium alloy which is considered to be the active phase. The methanol–water solvent mixture is also an important factor that affects the rate of hydrogen peroxide synthesis.

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