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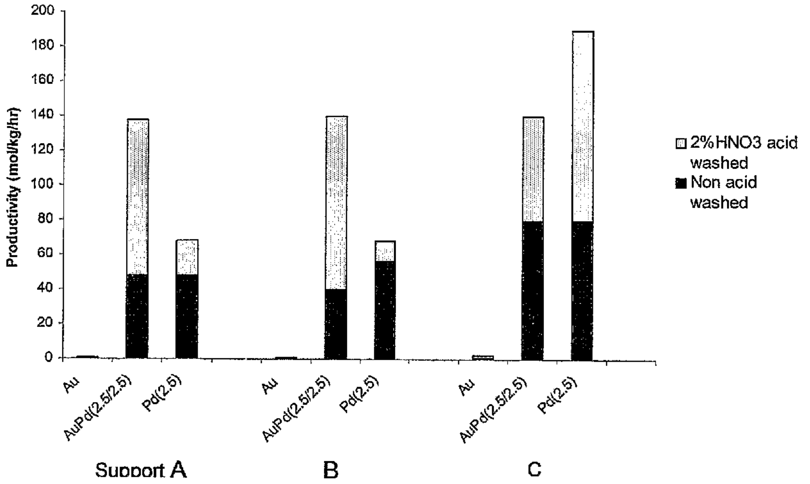

(57) Abstract: A catalyst effective for the direct reaction of hydrogen and oxygen to form hydrogen peroxide comprises particles of gold, palladium or, preferably, gold and palladium deposited upon an acid- washed support. Surprisingly high selectivity to and production of hydrogen peroxide is observed, with low hydrogen peroxide decomposition. The catalysts have extended lifespan.

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IMPROVEMENTS IN CATALYSTS

The present invention concerns improvements in catalysts especially for hydrogen peroxide production; more especially it concerns the catalytic production of hydrogen peroxide by direct reaction of hydrogen and oxygen.

The standard large scale production method for hydrogen peroxide involves the use of anthraquinone as an intermediate. This process is energy-intensive. There has been considerable study over the last 10 to 15 years of alternative processes for direct oxidation of hydrogen by oxygen, but these have not, to our knowledge, been successfully commercialised. There are understandable concerns over the danger of operating with explosive mixtures of hydrogen and oxygen. As examples of recent publications in this field, we mention in particular USP 5,135,731, in which gases containing hydrogen and oxygen are reacted in the presence of an aqueous reaction medium, an acid, a promoter, a multifunctional phosphonate and a catalyst, for example Pd and/or Pt which may be on a support such as carbon, alumina, silica, ion exchange resins and other conventional supports. USP 4,832,938 is another concept which involves reacting hydrogen with oxygen in an aqueous reaction medium having no, or less than 2%, organic content, a source of protons and chlorine or bromine ions and a combined Pt/Pd catalyst. The catalyst may be supported on carbon, silica or alumina. USP 4,009,252 also describes an aqueous medium system using a platinum group metal catalyst.

More recently, Landon et al have published a paper in Phys. Chem. Chem. Phys. 5 (2003) 917 studying a variety of Au and Pd catalysts, and disclosing that a gold alloy catalyst, specifically 5 wt% Au-Pd (1:1 wt%) supported on alumina is an active catalyst for H_2O_2 formation. Trials were carried out using a reaction medium including supercritical CO_2, but overall yields were low because of H_2O_2 decomposition. Although this academic work is interesting, it seems that high selectivities to H_2O_2 of 80-90% can be achieved at low temperatures of the order of 1-2 °C but only with low overall yields. Such low temperatures result in an energy-intensive process.

Two other patent documents are USP 5,449,655 and EP 0 049 810. USP 5,449,655 discloses that activated carbon catalyst supports may be acid-washed to reduce the ash content, and that a further treatment is desirable to improve the catalytic performance for hydrogenation of organic molecules after deposition of a platinum group metal on the supports. The further treatment suitably involves treatment with an oxidising agent such as hydrogen peroxide. This document does not have any relevance to the formation of catalysts for hydrogen peroxide formation by direct reaction of hydrogen and oxygen. EP 0 049 810 is concerned with an improvement in hydrogen peroxide production, using a palladium or palladium-gold catalyst supported catalyst, by selecting catalysts that show decreased hydrogen peroxide decomposition. The improved catalyst is prepared by pre-treatment of the catalyst with an aldehyde or a ketone and/or hydrochloric acid. The present invention relates not to the pre-treatment of the catalyst before use in the hydrogen peroxide process, but in the pre-treatment of the support, before formation of the catalyst.

There remains a need for a commercially viable catalyst and commercially viable direct reaction process for the production of H_2O_2.

Accordingly, the present invention provides an H_2O_2 formation catalyst comprising particles of gold, palladium or, preferably, gold and palladium, deposited on a support which has been acid washed prior to metal deposition. Preferably the particles are of gold and palladium, which may, on certain supports, have a gold-rich core and a palladium-rich shell.

The support is preferably an inorganic support material, preferably SiO_2, TiO_2, Al_2O_3 or Fe_2O_3, or may be an activated carbon. Acid washing is suitably carried using a mineral acid such as hydrochloric acid or nitric acid. Preferably the acid is dilute nitric acid, and supports are treated for example for 3 hours at ambient temperature. Experimental procedures involved washing supports in various concentrations of acid (see Fig1 below). It may be desirable to use a zeolite support, and synthetic zeolites such as beta zeolite or ZSM-5 are indicated, while tests indicate that zeolite Y tends to collapse.

deposited on its surface metal nanoparticles where there has been migration of gold towards the core of the nanoparticles and palladium towards the surface of the nanoparticles. Thus a palladium-rich shell surrounds a gold-rich core. Conveniently, the core contains 50 at% or more of gold, and the shell contains 50 at% or more of palladium.

In initial tests, the alloyed catalysts had a 2.5Au-2.5Pd wt% loading, with comparative Au and Pd monometallic catalysts having 2.5wt% and 5wt% loadings. Other metal loadings may be considered, especially during catalyst development directed to precious metal "thrifting".

The present invention further provides a method of manufacture of such a catalyst according to the invention, comprising acid washing a catalyst support, depositing gold and/or palladium, conveniently gold and palladium simultaneously, onto the washed support to form a catalyst precursor, and subsequently heat-treating, preferably at a temperature of 400 °C or above, the catalyst precursor to form a catalyst comprising the gold, palladium or gold and palladium particles.

The present invention also provides a process for the production of H_2O_2, comprising reacting hydrogen with oxygen in the presence of a reaction medium, preferably an aqueous reaction medium, and in the presence of a catalyst according to the invention.

The reaction medium is conveniently a water/organic solvent mix, where the organic solvent is water miscible. Solvents such as methanol, ethanol, isopropyl alcohol and acetone are suitable. In certain tests an acetone/water mix has been found to increase the activity of the bi-metallic catalyst (see Table 1 below). However, studies into different solvents (isopropyl alcohol, ethanol) showed no promotion of the catalyst activity. Studies into solvent effects have to be carried out with due care due to the possible formation of organic peroxy species, but studies by ^1H NMR and ^{13}C NMR with acetone and methanol have shown conclusively that under the conditions as stated in Table 1 there is no formation of such species.

Table 1

Catalyst	Solvent	Temperature / °C	Productivity $Mol/kg_{cat}/hr$	H_2O_2 decomposition [a] %
2.5-2.5%Au-Pd/HZSM-5	Water+Methanol	2	52	nd
2.5-2.5%Au-Pd/HZSM-5 10%HNO 3	Water+Methanol	2	87	Nd
2.5-2.5%Au-Pd/TiO_2	Water+Methanol	2	64	30
2.5-2.5%Au-Pd/TiO_2	Water+Methanol	20	25	70
2.5-2.5%Au-Pd/TiO_2 2%HNO_3	Water+Methanol	2	80	ca 5
2.5-2.5%Au-Pd/TiO_2 2%HNO_3	Water+Methanol	20	100	35
2.5-2.5%Au-Pd/TiO_2 2%HNO_3	Water+Acetone	2	95	13
2.5-2.5%Au-Pd/TiO_2 2%HNO_3	Water+Acetone	20	125	Nd
2.5-2.5%Au-Pd/TiO_2 2%HNO_3	Water+Acetone	40	64	Nd

Table 1 Effect of solvent and temperature on H_2O_2 synthesis – all catalysts calcined in air 400°C 3 hours. Note water is 2.9g in all cases-solvent 5.6g
Note a – H_2O_2 decomposition experiments; 0.5 wt% H_2O_2 added at start, no O_2

Using the nitric acid washed TiO_2 catalyst results in activity in temperatures 2°C – 40°C (table 1) without suffering a major loss in activity, in comparison to the non acid washed catalyst.

Other aspects of the present invention are disclosed in the Examples below.

EXAMPLE 1 (COMPARATIVE)

2.5 wt% Au-2.5 wt% Pd catalysts were prepared by impregnation of suitable support materials: carbon (commercially available G60), silica and TiO_2 (mainly anatase). An incipient wetness method using aqueous solutions of $PdCl_2$ (Johnson Matthey) and $HAuCl_4.3H_2O$ (Johnson Matthey) was employed. The paste formed was ground and dried at 80°C for 16h and calcined in static air, typically at 400°C for 3 h.

10 mg of the supported 2.5 wt% Au-2.5 wt% Pd catalyst were charged in an autoclave containing solvent (5.6 g MeOH and 2.9 g H_2O), which was 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) was started on reaching the desired temperature (2°C), and experiments were carried out for 30 min. Gas analysis for H_2 and O_2, was performed by gas chromatography using a thermal conductivity detector. 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 $(NH_4)_2Fe(SO_4)_2.6H_2O$ using ferroin as indicator. The following results were obtained:

Catalyst	Productivity Mol/kg_{cat}-h
2.5%Au2.5%Pd/TiO_2	64
2.5%Au2.5%Pd/Al_2O_3	15
2.5%Au2.5%Pd/G60	110
2.5%Au2.5%Pd/SiO_2	108

EXAMPLE 2

The supports were acid-treated (3h, 100 ml) prior to impregnation of Au and Pd (as described in Example 1) and hydrogen peroxide synthesis measured as described in Example 1. A reference sample washed for 3 h in pure water was also tested. The following results were obtained:

Catalyst	Pre-treatment	Selectivity %	Productivity Mol/kg$_{cat}$-h
2.5%Au-2.5%Pd/G60	None	80	110
2.5%Au-2.5%Pd/G60	Water	80	112
2.5%Au-2.5%Pd/G60	2%HNO_3	>98	160
2.5%Au-2.5%Pd/G60	2%H_3PO_4	30	120
2.5%Au-2.5%Pd/G60	2%HCl	15	130
2.5%Au-2.5%Pd/G60	2%NH_4OH	24	70
2.5%Au-2.5%Pd/G60	2%CH_3COOH	>98	175
2.5%Au-2.5%Pd/G60	1N HCl[*]	20	30
2.5%Au-2.5%Pd/G60	1N HNO_3[*]	80	110
2.5%Au-2.5%Pd/TiO_2	None	61	64
2.5%Au-2.5%Pd/TiO_2	Water	95	80
2.5%Au-2.5%Pd/SiO_2	None	80	108
2.5%Au-2.5%Pd/SiO_2	Water	73	185

[*] Catalyst was prepared on untreated carbon with 1N HCl or HNO_3 present during impregnation.

EXAMPLE 3

The solvent and solvent/water composition was varied and hydrogen peroxide synthesis measured (as in Example 1) for the catalysts formed from the G60 acid-treated and water treated supports. All catalysts were calcined in static air 400°C 3hrs. The results were as follows:

Catalyst	Pre-treatment	Solvent	Productivity Mol/kg$_{cat}$-h
2.5-2.5%Au-Pd/TiO_2	Water	Methanol/Water	64
2.5-2.5%Au-Pd/TiO_2	2%HNO_3	Methanol/Water	80
2.5-2.5%Au-Pd/TiO_2	2%HNO_3	Acetone/water	95
2.5%Au2.5%Pd/G60	Water	Methanol/Water[*]	118
2.5%Au2.5%Pd/G60	2%HNO_3	Methanol/ Water[*]	160
2.5%Au2.5%Pd/G60	Water	Ethanol/Water[*]	100
2.5%Au2.5%Pd/G60	2%HNO_3	Ethanol/Water[*]	200
2.5%Au2.5%Pd/G60	2%HNO_3	Ethanol/ Water[**]	60
2.5%Au2.5%Pd/G60	Water	Water	31
2.5%Au2.5%Pd/G60	2%HNO_3	Water	33
2.5%Au2.5%Pd/TiO_2	Water	Water	30
2.5%Au2.5%Pd/TiO_2	2%HNO_3	Water	32

[*] 74% alcohol by weight, Methanol/Water, Ethanol/Water same molar ratio

[**] 5% alcohol by weight

EXAMPLE 4

Examples of the supports and impregnated catalysts were tested for hydrogen peroxide decomposition. All catalysts were calcined in static air 400°C 3hr . The following results were obtained:

Support	Pre-treatment	H_2O_2Productivity (mol/Kg_{cat}-h)	Decomposition (%) * catalyst	Decomposition (%) * support
AC[1]	None	110	20	40^a, 38^b
AC[1]	Water	112	21	39
AC[1]	2%HNO_3	160	1.8	15^a, 0^b
TiO_2[2]	None	64	30	20^a
TiO_2[2]	Water	64	32	20^a, 19^b
TiO_2[2]	2%HNO_3	95	5	0^a,0^b

[*] Hydrogen peroxide decomposition over 2.5wt%Au-2.5wt%Pd catalyst or the support: H_2O_2 (0.4 wt.%) in a methanol/water solution (CH_3OH, 5.6 g; H_2O 2.9 g) reacted with 420psi H_2 for 30 min at 2 °C.

[1] 2.5%Au2.5%Pd/G60 activated carbon (Aldrich)

[2] TiO_2 (P25) ex Degussa

[a] Decomposition over fresh support

[b] Decomposition over once-used support

[a] Decomposition over fresh support

[b] Decomposition over used support

EXAMPLE 5

The catalyst supports detailed in Example 1 were treated with nitrate salts (sodium, potassium and ammonium) before impregnation with Au and Pd and tested for hydrogen peroxide synthesis (as described in Example 1). All catalysts were calcined in static air 400°C 3hr. The following results were obtained:

Catalyst	Pre-treatment	Productivity Mol/kg$_{cat}$-h
2.5%Au2.5%Pd/G60	None	118
2.5%Au2.5%Pd/G60	2%HNO_3	160
2.5%Au2.5%Pd/G60	2%$NaNO_3$	122
2.5%Au2.5%Pd/G60	2%KNO_3	120
2.5%Au2.5%Pd/G60	2% NH_4NO_3	115

EXAMPLE 6

Hydrogen peroxide synthesis was carried out with a 2.5 wt% Au-2.5 wt% Pd catalyst supported on G60 acid-treated and water treated carbon calcined in air 400^{O}C 3hrs air. The autoclave was vented at 30 minute intervals, the hydrogen peroxide concentration measured, and the gas mixture refilled and the synthesis allowed to continue. The results obtained are shown in Figure 4.

EXAMPLE 7

Hydrogen peroxide synthesis was measured as in Example 1, at various reaction temperatures for a 2.5 wt% Au-2.5 wt% Pd catalyst supported on TiO_2 - acid-treated and water treated – followed by calcinations in air at 400^{O}C for 3hrs. The following results were obtained:

Catalyst	Pre-treatment of support	Solvent	Temperature / °C	Productivity Mol/kg$_{cat}$-h
2.5-2.5%Au-Pd/TiO_2	Water	Water+Methanol	2	64
2.5-2.5%Au-Pd/TiO_2	Water	Water+Methanol	20	25
2.5-2.5%Au-Pd/TiO_2	Water	Water+Methanol	40	10
2.5-2.5%Au-Pd/TiO_2	2% HNO_3	Water+Methanol	2	80
2.5-2.5%Au-Pd/TiO_2	2% HNO_3	Water+Methanol	20	100
2.5-2.5%Au-Pd/TiO_2	2% HNO_3	Water+Methanol	40	60
2.5-2.5%Au-Pd/TiO_2	2% HNO_3	Water+Acetone	2	95

2.5-2.5%Au-Pd/TiO_2	2% HNO_3	Water+Acetone	20	125
2.5-2.5%Au-Pd/TiO_2	2% HNO_3	Water+Acetone	40	64

Catalyst testing was performed 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 (5.6 g MeOH/Acetone 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 2°C. Stirring (1200 rpm unless otherwise stated) was started on reaching the desired temperature, and experiments were run for 30 min unless otherwise stated. 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 $(NH_4)_2Fe(SO_4)_2.6H_2O$ using ferroin as indicator.

The reaction medium may comprise other components which contribute to a desired result or avoid an undesired result. For example, hydrogen bromide may be added to reduce the tendency for H_2O formation at higher temperatures, causing an increase in yield due to decreased decomposition (thus stabilisation) of the H_2O_2. Addition of HCl and HNO_3 will induce the same stabilisation. However, the presence of halides, and the effect of acid on stainless steel reaction vessels are not desirable in industry. Accordingly, it is assessed by the present inventors that a method of pre-treating a catalyst to induce the same stabilising effect without addition of these corrosive/toxic compounds would be highly desirable.

Although initial trials have been carried out in an autoclave, it is contemplated that it can operate in continuous, or semi-continuous mode. It is envisaged that the process of the invention may be optimised and scaled-up to industrial scale.

The catalysts according to the invention exhibit surprisingly long life and recyclability. The acid washed bi-metallic TiO_2 catalyst has been reused three times and has shown no decrease in activity (See Table 2 below, using 2.5-2.5%Au-Pd catalyst based on acid-washed TiO_2 support)

Table 2

Experiment	Productivity – Mol/kg$_{cat}$/hr
Initial	110
1st reuse	107
2nd reuse	108
3rd reuse	105

Further initial tests have been undertaken using acid-washed activated carbon supports, after depositing 2.5 wt% Au and 2.5 wt% Pd and heat treating at 400 °C for three hours in air. An untreated carbon support was compared for H_2O_2 productivity (mol/kg$_{cat}$/hr) with the same carbon washed with varying concentrations of nitric acid. The results are shown in Figure 1.

The influence of support source, and of the composition of metal particles deposited thereon was assessed, by measuring H_2O_2 productivity for three different silica supports, for Au-only catalysts, Pd-only catalysts and an AuPd catalyst, both without acid washing and after a pre-treatment with 2% nitric acid. The results are shown in Figure 2. The beneficial effects of acid washing are clear for all supports, and an increase of activity is observed for all catalysts, whether Au only, Pd only or Au and Pd.

Figure 3 is a comparative test showing that the optimum wt% Au/Pd for non-acid-washed alumina supported catalysts is 4.2%Au: 0.8%Pd, or approximately 5.25:1. It is expected that the same proportion will apply in the case of acid-washed supports.

The process according to the invention has, in preliminary trials, demonstrated high yields and/or high selectivity to H_2O_2. Preliminary results for operating the process at or around room temperature indicate that selectivities of greater than 90% can be achieved, and production rates of around 500 mol/kg$_{cat}$/hr can be achieved when operating under preferred conditions.

CLAIMS:

1. An H_2O_2 formation catalyst comprising particles of gold, palladium or gold and palladium, deposited on a support which has been acid washed prior to metal deposition.

2. A catalyst according to claim 1, wherein the particles are of gold and palladium.

3. A catalyst according to claim 1 or 2, wherein the support is silica, titania, alumina, Fe_2O_3, a zeolite stable under catalyst formation conditions or an activated carbon.

4. A catalyst according to claim 1, 2 or 3, wherein the support has been washed with a dilute nitric acid.

5. A catalyst according to claim 2 or any claim dependent thereon, wherein the weight ratio of gold and palladium in the catalyst is approximately 5.25:1.

6. A method of manufacturing a catalyst according to any one of the preceding claims, comprising acid washing a catalyst support, depositing gold and/or palladium precursors onto the washed support to form a catalyst precursor and subsequently calcining, preferably at a temperature of at least 400 °C, the catalyst precursor to form a catalyst comprising particles of gold, palladium or gold and palladium.

7. A process for the formation of H_2O_2 by direct reaction of oxygen and hydrogen in the presence of a reaction medium, comprising the use of a catalyst according to any one of claims 1 to 6.

8. A process according to claim 11, wherein the reaction medium is a mixture of water and a water-miscible organic solvent.

9. A process according to claim 12, wherein the reaction medium is aqueous methanol.

10. A process according to any one of claims 11 to 13, comprising the use of a reaction temperature in the range from 2 to 40 °C.

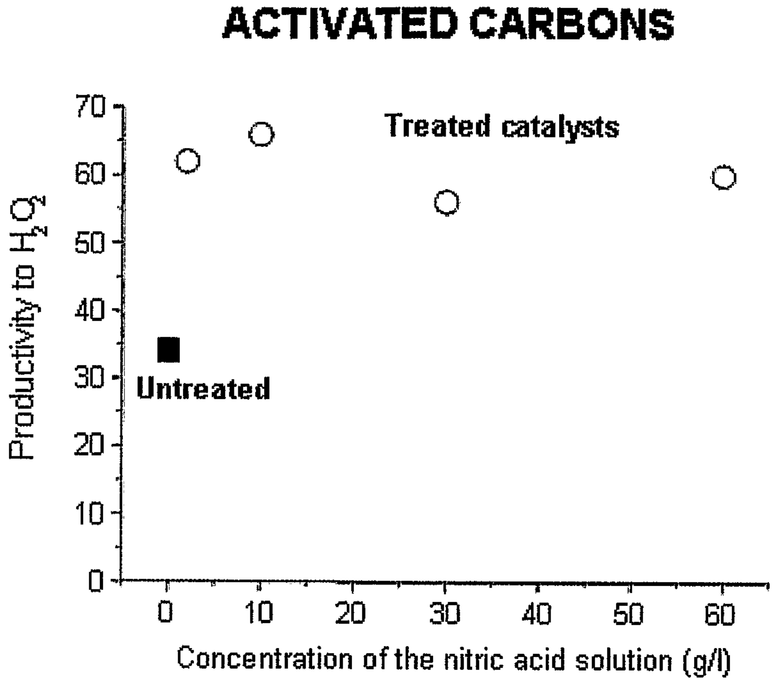

Figure 1

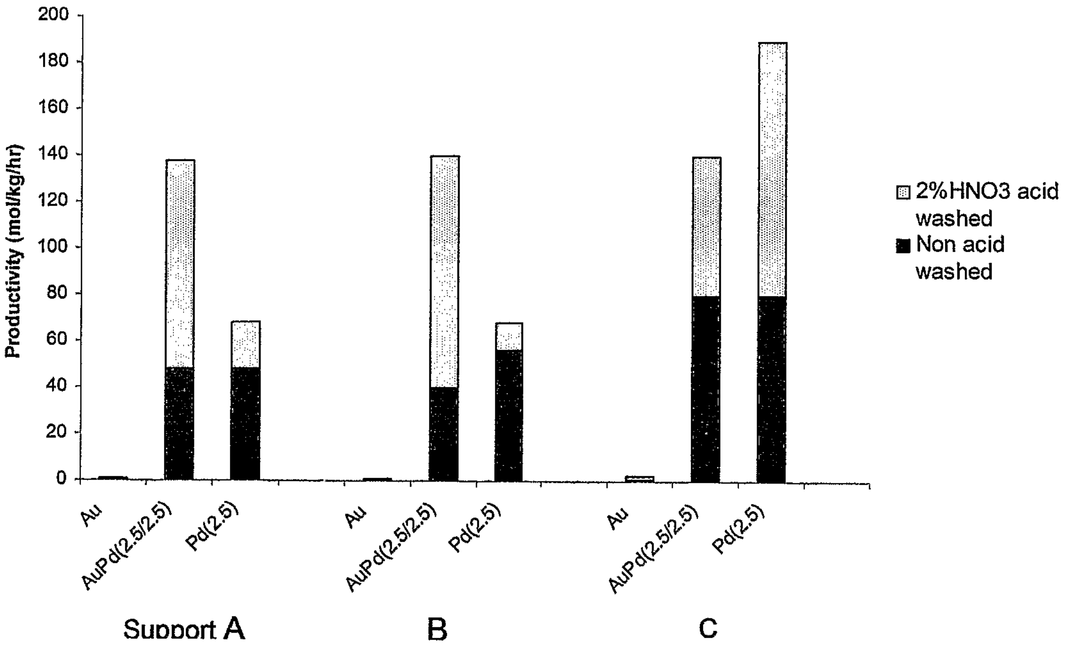

Figure 2

Figure 3

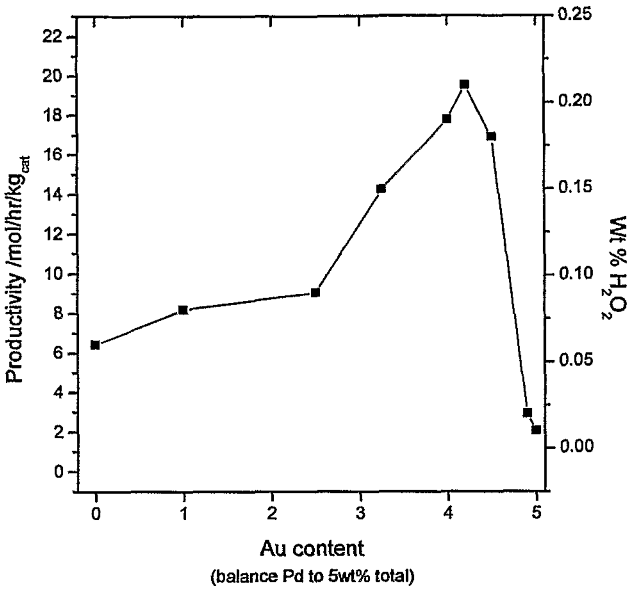

Figure 4