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Benzyl Alcohol Oxidation Using In Situ Generated Hydrogen Peroxide from Hydrogen and Oxygen

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Abstract

This thesis sets out an introduction to catalysis, particularly heterogeneous gold catalysis, the development of direct synthesis of hydrogen peroxide and benzyl alcohol oxidation by supported bimetallic gold-palladium catalysts. In addition the possibility of combining those two processes together to carry out the benzyl alcohol oxidation using in situ generated hydrogen peroxide.

The experimental chapter shows the detailed operation of preparing and testing of catalysts in particular for the reactions studied (H_2O_2 formation, CO oxidation and benzyl alcohol oxidation).

In the results and discussion section, some basic knowledge of gold and palladium catalysis is reviewed including some popular preparation methods, the operation of the reactors, and testing in both direct synthesis of hydrogen peroxide and low-temperature CO oxidation. Afterwards, results of gold-palladium catalysis in the oxidation of benzyl alcohol using a mixture of hydrogen and oxygen are shown. In detail, some improvements for the reaction conditions, including temperature and duration, and catalysts, including gold and palladium ratios in alloys and the effect of preparation methods are discussed. In conclusion, higher reaction temperature (75 ^{o}C) and longer reaction time (2 hours) seemed to be beneficial to converting benzyl alcohol to benzaldehyde by in situ generated H_2O_2. Moreover, sol-immobilized 1 wt% Au-Pd/TiO_2 with gold palladium ratio of 1:1 achieved the highest benzyl alcohol conversion and benzaldehyde selectivity among all samples with different metal ratios by different preparation methods.

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Chapter 1 Introduction

1.1 Catalysis

Catalysis, which has been widely used in the whole range of chemical areas, is a kind of chemical process which can increase a reaction rate without any change in position of the chemical equilibrium of the reaction. In modern society, it is well known to be used everywhere in our human life. For human beings, life cannot exist without energy formation from the environment by catalysis. As well as the chemical industry, without catalysis, most processes would be running under more severe conditions, and chemicals could not be produced economically. Moreover, global pollution, which is a grave problem, will not be solved without catalysis. As early as thousands of years ago, catalysis function was exploited by the Chinese people to make wine with an enzyme, as a biocatalyst. The word catalysis was first published by Jons Jakob Berzalius in 1836[1], and was regarded as a power of decomposition of old compounds and re-composition of new compounds. He called that the catalytic power. The agent of catalysis process is called a catalyst. Generally, it is defined as a material which can increase the rate of a catalytic reaction without being consumed and without any chemical change in itself. In other words, during reactions, catalysts would be firstly the reactants in former part of reactions and the products in a latter part, so catalysts would not be changed after the process. For example, in the oxygen production from potassium chlorate, manganese dioxide is used as a catalyst. But it also plays a role in intermediate process (Equation 1.1-1.4). Besides metal oxides, many other materials, such as acids, bases and metal particles etc., can be used as catalysts for certain reactions.

$$\text{Total: } 2KClO_3 \rightarrow 2KCl + 3O_2 \uparrow \text{(Equation 1.1)}$$

$$\text{In progress: } 2KClO_3 + 2MnO_2 \rightarrow 2KMnO_4 + Cl_2 \uparrow + O_2 \uparrow \text{ (Equation 1.2)}$$

$$2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2 \uparrow \text{(Equation 1.3)}$$

$$K_2MnO_4 + Cl_2 \rightarrow 2KCl + MnO_2 + O_2 \uparrow \text{(Equation 1.4)}$$

1.1.1 Activation Energy

In a whole process, the function of a catalyst is to decrease the activation energy, so the target product(s) can be more easily achieved (Figure 1.1). For a reaction of A+B to C, two pathways, catalyzed and uncatalyzed reactions, both have the same total Gibbs free energy (ΔG), but have different varied activation energy from reactants A and B to the product C. The activation energy of catalyzed pathways (Ea) is lower than that of uncatalyzed pathway (Ea_0), and therefore can be more easily achieved. The performance of a catalyst can also be varied by presence of inhibitors, which reduce the catalyst activity, and promoters, which increase the activity.

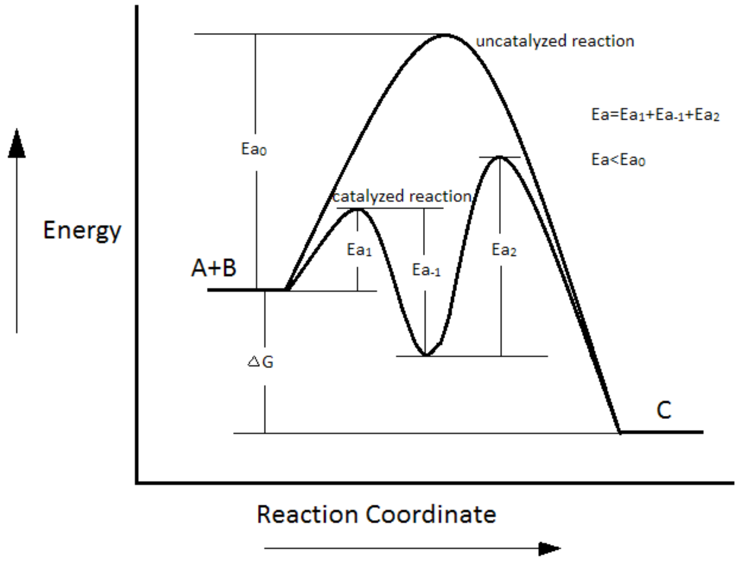


Fig. 1.1 Catalyzed and uncatalyzed pathways of A+B to C reaction (Ea: activation energy; ΔG: Gibbs free energy)

In the 20th century, catalysis began to develop rapidly. The Fischer-Tropsch Process, catalyzed by a cobalt or iron catalyst, which is for the synthesis of straight-chain hydrocarbons[2, 3], was invented by F. Fischer and H. Tropsch. It is widely used for making liquid fuels, mainly sulphur-free aromatic diesel currently. In 1908, Fritz Haber designed a high-pressure reactor for ammonia synthesis from mixture of hydrogen and nitrogen catalyzed by an iron based catalyst. In this process, high-pressure is required, and good yields of ammonia can be achieved. This is achieved using an Fe catalyst, and potassium cations (K^+)[4, 5] were also added as a promoter, which is beneficial for the activity of catalysts.

There are three main kinds of catalysis processes classified by phases and reactions: heterogeneous, homogeneous catalysis and biocatalysis. Heterogeneous catalysis, which is processed by a different phased catalyst with reagents and products, mainly solid catalyst with liquid or gas phase reactants, has been applied in a number of areas including environmental protection, food and chemical production[5]. However, homogeneous catalysis contains a catalyst in the same phase with the reaction system, mainly in a liquid phase. Biocatalysis uses enzymes as catalysts to produce certain functional proteins selectively. There are advantages and disadvantages for these three kinds of catalysis. Compared with conventional catalysis, biocatalysis by enzymes often does not need any protection. Moreover, it is efficient with low toxicity, and can be run in a more neutral pH condition. However it is not stable, and can only work in a certain environment. Because of insolubility of organic molecules in aqueous media, biocatalysis is often not possible. The advantages of homogeneous catalysis are numerous. Firstly, it has better control of chemo-, regio-, and stereoselectivity. It also allows a high catalytic potential with a soluble metal complex. But the main problem of homogeneous catalysis is the difficulty of removing catalysts and solvents from system because they are the same phase.

1.1.2 Heterogeneous Catalysis

Heterogeneous catalysis is the most widely used form of catalysis in the modern chemical industry because its products can be easily separated from the reaction system of other phases. The catalysts for heterogeneous catalysis are always solid with numerous pores on surface. The gas- or liquid-phase reagent system has an interaction with the surface of a catalyst. Heterogeneous catalysis involves seven steps: a. diffusion of reactant(s) on the outer surface of catalyst; b. diffusion of reactant(s) on the inner surface of catalyst (into pores); c. chemical adsorption of reactant(s) with the catalyst surface; d. chemical reaction proceeds; e. desorption of product(s) from the catalyst; f. inner diffusion of product(s) in catalyst pores; g. outer diffusion of product(s) on the catalyst surface. The first steps are called the physical adsorption powered by Van der Waals interaction. However, the most important step in heterogeneous catalysis is the chemical adsorption which forms strong bonds between reactants and catalyst surface for reaction. The difference between physisorption and chemisorption and their relationships are shown in Table 1.1 and Figure 1.2 respectively. When the reactant molecules get close to the catalyst surface, physisorption is firstly achieved spontaneously. Chemisorption occurs after getting even closer and activated by a relatively small energy, and each atom of reactants is bonded with the active sites on the catalyst surface.

	Physisorption	Chemisorption
Force	Van der Waals interaction	Bond energy
Enthalpy, ΔH	8-20 kJ mol^{-1}	40-800 kJ mol^{-1}
Activation energy, E_a	0	observable
Layers	Mono- and multi-layers	Only monolayer
Change of adsorbates	No	Yes

Table 1.1 Difference between physisorption and chemisorption

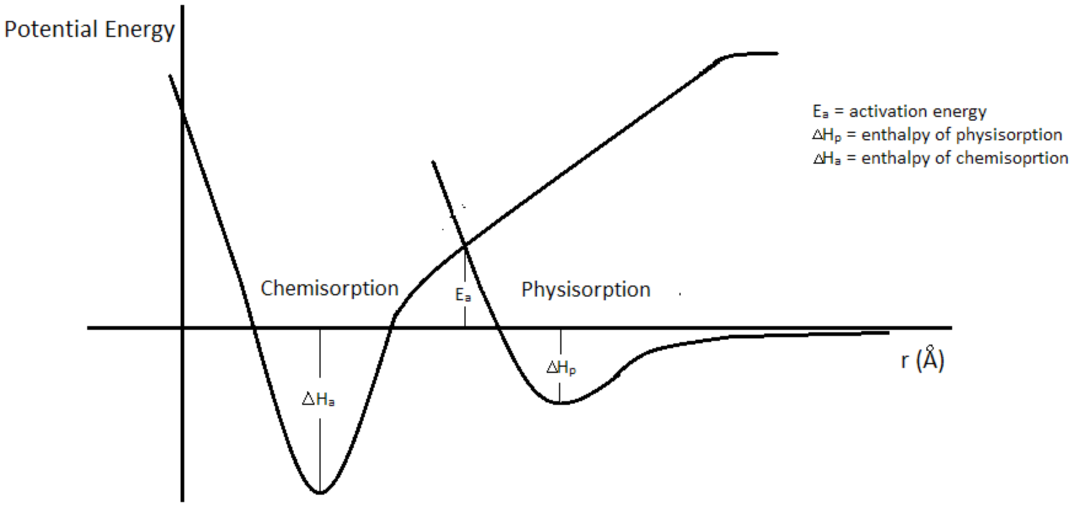


Fig. 1.2 Relationship between physisorption and chemisorption

1.1.3 Heterogeneous Solid Metallic Catalysts

Many metal particles can serve as catalyst materials, such as iron, nickel, cobalt, palladium, copper, silver and gold, etc. in modern industry. For example, iron (Fe^{3+}) based catalysts are used for the synthesis of ammonia from hydrogen and nitrogen in the Haber-Bosch process[7]. Moreover, the products of syngas reactions vary by different metal-based catalysts (Figure 1.3) because of the difference of adsorption power between CO and the metal surface. For hydrocarbons production, we need a neither too strong nor too weak binding. Binding that is too strong leads to the dissociation of CO, which is bad for the reaction and desorption. However, a too weak binding will lead the adsorption of molecule CO to catalyst surface, which means that C and O cannot be easily decomposed and re-composed. All the words above can be explained by the "volcano" principle (Figure 1.4).

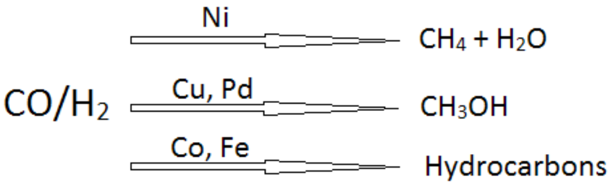


Fig. 1.3 various products from syngas by different metal catalysts

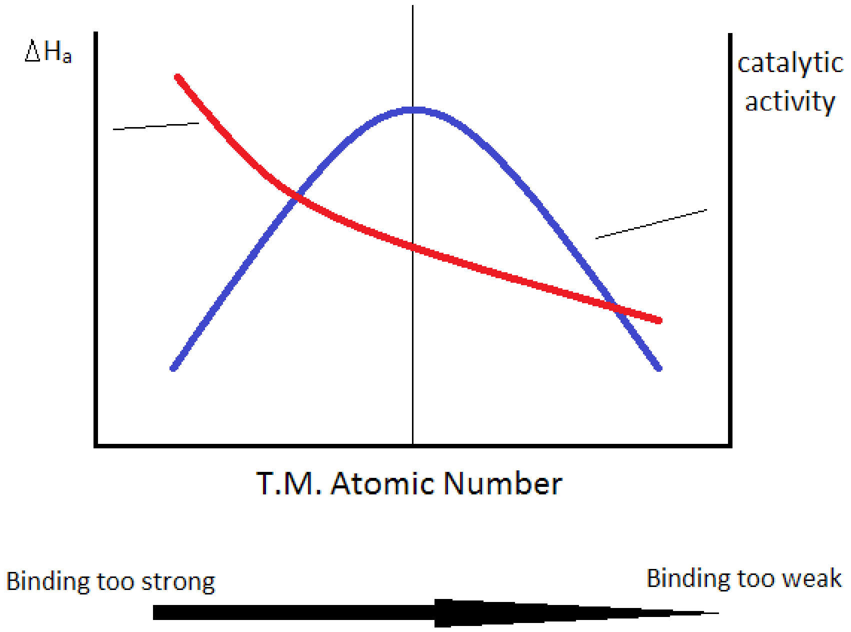


Fig. 1.4 “volcano” principle of catalytic activity versus metal sequence

Some heterogeneous catalysts, particularly for metallic ones, need supports. The catalytic metal particles are dispersed on the surface of another material, which means that catalyst particles are adsorbed on the outer-surface and pores of the large surface area support. This would obviously be beneficial to efficiency and economical consideration. Firstly, because reactions often occur on the active sites of catalyst surface, we have no need for large quantities of the precious metal. Instead, a much cheaper support with larger surface area can make small metal particles well-dispersed only on the surface. Also, a suitable support can prevent the sintering of the catalyst particles. Some supports may have strong interaction with the catalyst, which can improve the activity of catalyst. Overall, the choice of supports is very important for the preparation of highly active heterogeneous metal catalysts.

1.1.4 Gold Catalysis

Among the heterogeneous metal catalysts, some noble and precious metals, such as gold, were considered as not reactive and not catalytically active for a very long time.

However from 1980s, gold was found to be a superior active catalyst metal by two research groups, Haruta and Hutchings. Haruta and co-workers found that gold was very active in the low-temperature CO oxidation[8], as low as -76 ^{o}C. Hutchings successfully processed the hydrochlorination of ethyne to vinyl chloride with gold catalysis[9]. Bond's research group also made a great contribution to the use of gold catalysis in hydrogenation[10]. As gold catalysis has been developed rapidly in the 21st century, gold has become a hot topic in chemistry, and is equally effective as a heterogeneous or homogeneous catalyst because of its properties of high coordination and organometallic chemistry[11]. Recently, gold catalysis has been widely regarded as the best catalyst in many areas[12] such as the selective hydrogenation of N-Obonds[13], the selective oxidation of alcohols to acids[14] or aldehydes[15], and the direct synthesis of hydrogen peroxide[16]. Also, gold catalysis is beneficial to green chemistry[17] including the solution to waste, chemical hazard, potential of accidents and danger of organic solvents.

1.2 Low-temperature CO Oxidation

As known, CO is a harmful gas to human bodies. In daily life, CO is often required to be removed from the ambient environment. Moreover, CO is either reactant or product in water gas shift and stream reforming reactions, which leads to the blocking of active sites of the catalyst by excess CO[18]. An effective way to remove CO without oxidizing hydrogen is required for fuel cell applications. The high activity of supported gold catalysts was firstly found by Haruta's research group in 1980s[8]. The TiO_2, α-Fe_2O_3 and Co_3O_4 supported gold catalysts prepared by deposition-precipitation were shown to be very active in low-temperature CO oxidtion[19] even at below 0 ^{o}C. They also found that the performance of those catalysts were gold particle size dependent. 2-3 nm gold nanoparticles could rapidly increase the conversion of CO. Because small particles provided more active sites on the catalyst surface, not only CO molecules, but also more oxygen could be adsorbed. In Figure 1.5, comparing the two preparation methods for Au/Fe_2O_3, we can clearly see the difference of the effect of preparation method on the particle size. By the coprecipitated Au/Fe_2O_3, the CO conversion can reach a very high level even below 0 °C, but the other one was only active at above 0 °C.

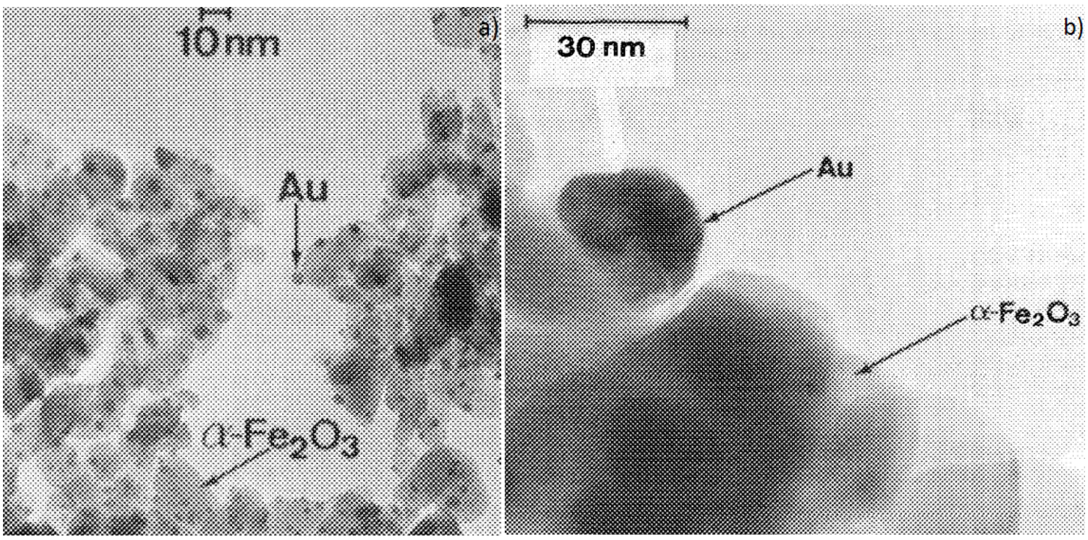


Fig. 1.5 TEM photographs of Au/α-Fe_2O_3 by coprecipitation (a) and conventional impregnation (b)[19]

Besides the gold particle size and preparation methods, other factors including supports and gold dispersion can influence the CO conversion in the low-temperature CO oxidation[20]. For the supports, there was a trend of activity: TiO2 <α-Fe_2O_3<Co_3O_4(Figure 1.6). Actually, oxides of transition series elements (Group 4-12) can be used as the supports of active catalysts[21].

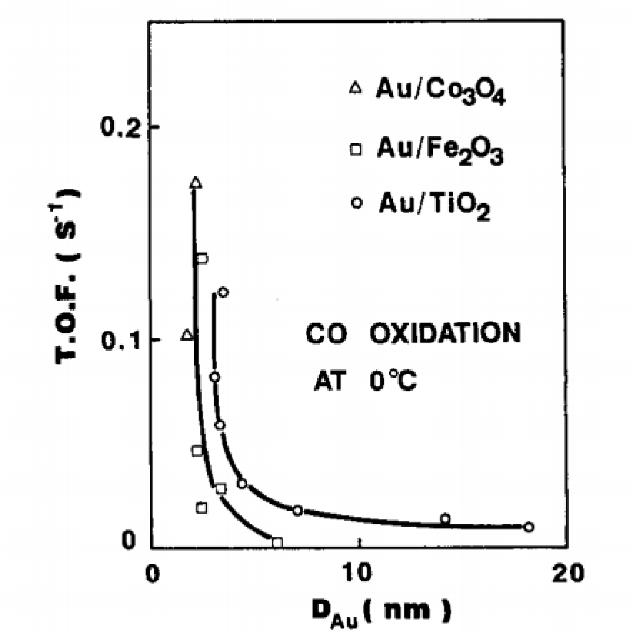


Fig. 1.6 Turnover frequencies of △, Au/Co_3O_4; □, Au/Fe_2O_3; ○, Au/TiO_2 in CO oxidation at 0 ^oC[20]

After that, a lot of developments have been made for gold catalyst in low-temperature CO oxidation. Au/TiO_2 was most used in the research of reaction mechanism and catalyst treatments[22]. Whether metallic Au^0 or oxidized Au^{3+} is indispensable for this reaction, researchers considered that the adsorption of CO on oxidised Au was not responsible for the catalyst activity[23]. Also, CO adsorption to cationic Au suffers nhibition by water[24]. The interaction between Au and titania is another factor which varies the activity. Haruta[25] found that a stronger interaction by high-temperature (673K) calcinations of the catalysts leads to higher CO conversion, although there was metal sintering during heat treatment (Table 1.2).

Catalyst [a]	Au diameter (nm)	$T_{1/2}$[b](K)	Rate (mol s^{-1} g^{-1})
473K treated	5.1 ± 1.3	479	$5.9 * 10^{-10}$
673K treated	7.5 ± 2.2	303	$2.1 * 10^{-7}$
873K treated	12.0 ± 2.5	278	$7.3 * 10^{-7}$

[a]. Au/TiO_2 prepared by the mixing of colloidal gold and titania powder

[b]. Temperature for 50% CO conversion

Table. 1.2 Gold particle size, temperature for 50% CO conversion and reaction rate by different heat-treated 3.3 wt% Au/TiO_2[25]

Bond and co-workers who investigated the mechanism of the CO oxidation by gold catalysis[26], proposed a possible process of reaction:

$$\mathrm{Au^0 + CO \rightarrow Au^0 \ldots CO}\ (1)$$

$$\mathrm{Au^{III} + OH_s^- \rightarrow Au^{II} \ldots OH}(2)$$

$$\mathrm{Au^0 \ldots CO + Au^{II} \ldots OH \rightarrow Au^{II} \ldots COOH + Au^0}(3)$$

$$\mathrm{O_2} + \blacksquare_s^- \rightarrow \mathrm{O_2^-} \ldots \blacksquare_s\ (4)$$

$$\mathrm{Au^{II} \ldots COOH + O_2^-} \ldots \blacksquare_s \rightarrow \mathrm{Au^{II} + CO_2 + HO_2^-} \ldots \blacksquare_s\ (5)$$

$$\mathrm{Au^{II} \ldots COOH + HO_2^-} \ldots \blacksquare_s \rightarrow \mathrm{Au^{II} + CO_2 + 2OH_s^-} + \blacksquare_s\ (6)$$

$$\mathrm{Au^{II}} + \blacksquare_s \rightarrow \mathrm{Au^{III}} + \blacksquare_s^-\ (7)$$

Based on known evidences, they supposed that both metallic Au^0 and Au^{x+} are responsible to the CO oxidation, as well as the interaction between gold and support.

1.3 Synthesis of Hydrogen Peroxide

Hydrogen peroxide, with the formula of H_2O_2, is another kind of hydrogen oxide which has a property of being a strong oxidizing agent. It was first found by Louis Jacques Thénard in 1818[27] as an intermediate product before discomposing to water. Hydrogen peroxide is now widely used in human life as a disinfectant and bleaching agent. In industrial areas, because of its strong oxidizing and environmental-friendly advantage with the only by-product being water, hydrogen peroxide has been applied in many oxidation processes of organic and inorganic aqueous chemicals. For safety consideration, hydrogen peroxide is always present in certain aqueous solution.

The world production of hydrogen peroxide in 1994 was only 1.9 million tons, and increased hugely to 2.2 million in 2006[28]. The produced hydrogen peroxide is used as a safe oxidizing agent in many areas such as industry and medical applications[29] (Figure 1.7). Among those, most hydrogen peroxide (over 60 %) is used in pulp and paper bleaching[28]. Also, in textile and detergent industry, hydrogen peroxide based agents have the advantage of color-safe, and have replaced many products successfully. All of these uses of bleaching are based on a high concentration of hydrogen peroxide aqueous solution. On the other hand, a low concentration solution (3-5 vol%) is safely used as housework disinfectants and hair dyes. In modern “green” chemistry, hydrogen peroxide as oxidant has also attracted much attention in chemical oxidation processes because of its higher oxygen activation than many other oxidants[29] and environmental-friendly advantage, such as epoxidation of propylene, removing of waste gases after adsorption in aqueous scrubbing liquors[30], and so on. A further new industrial approach of using hydrogen peroxide is the treatment of wastewater. Because of its highly oxidizing property, the hydrogen sulfide in wastewater can be oxidized to elemental sulfur liberating water.

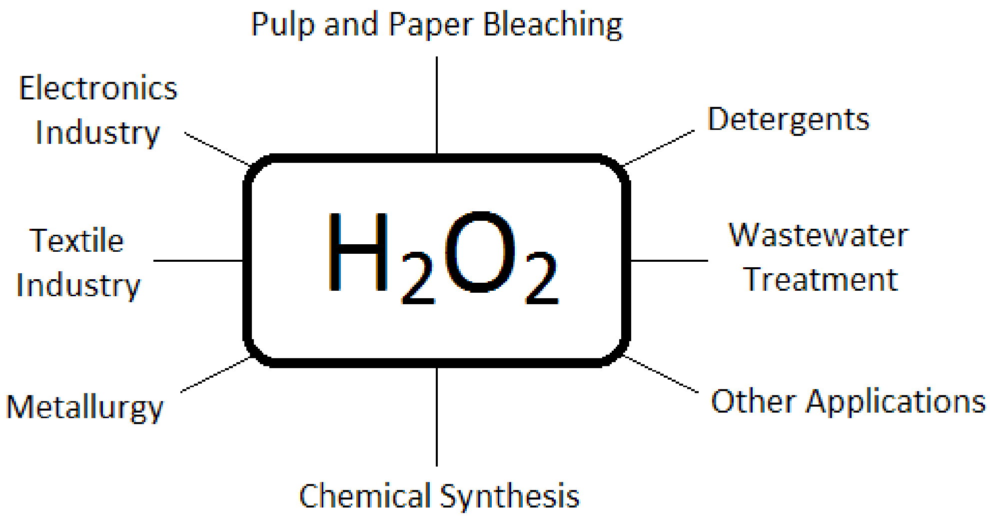
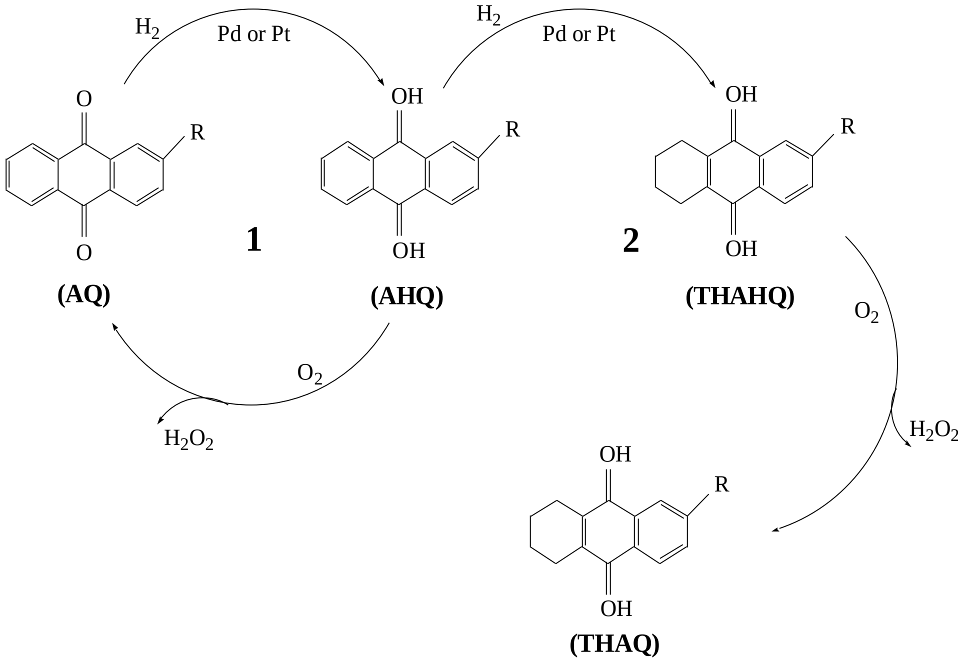


Fig. 1.7 Uses of hydrogen peroxide[29]

1.3.1 Anthraquinone (AQ) Autoxidation (AO) Process for Hydrogen Peroxide Production

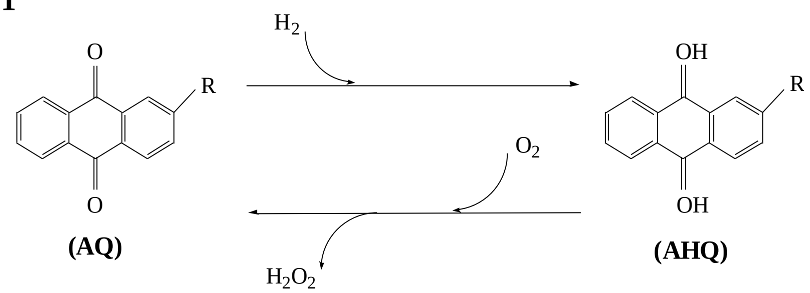
As the growth in demand of hydrogen peroxide, researchers have been focusing on the effective production of hydrogen peroxide for many decades. At present, a large-scale method is the continuous hydrogenation and oxidation of alkyl anthraquinone. This AO process is the most widely used method in industrial hydrogen peroxide production, although other ways such as electrolysis of $(NH_4)_2SO_4$ or H_2SO_4 and oxidation of secondary alcohols are also used. The original commercial AO process, Riedl-Pfleiderer process, was first operated by I.G. Farbenindustriein Germany in1939[31]. This AO process was developed from the work of the autoxidation of hydroquinone and hydrazobenzenes to peroxides under alkaline solutions[32].

In Scheme 1.1, the AQ process is clearly shown. An alkyl anthraquinone (AQ) is hydrogenated to alkyl anthraquinol (AHQ) by hydrogen catalyzed by a Pd or Pt catalyst. Then there are two pathways followed. The first is that AHQ is oxidized by oxygen back to the corresponding quinone (AQ) and H_2O_2. The second pathway is a further hydrogenation of AHQ to 5,6,7,8-tetrahydroanthrahydroquinone (THAHQ), finally oxidized to the THAQ and H_2O_2. In one word, both AHQ and THAHQ are active and can be oxidized to yield hydrogen peroxide and corresponding quinones. Among those two ways for hydrogen peroxide (Scheme 1.2 and 1.3), the first cycle is the alkyl anthraquinone hydrogenation and AQ reforming with H_2O_2 producing; but the second way occurs because of excess of AQ and AQ residence time, with the final product (THAQ) which has to be removed from the working solution.



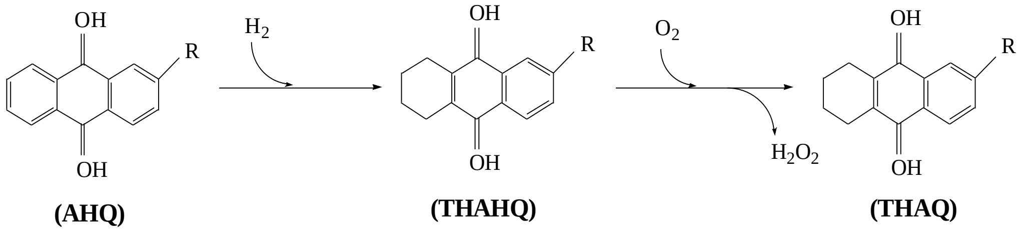
Scheme 1.1 Overall Anthraquinone autoxidation process for hydrogen peroxide production

Pathway 1



Scheme 1.2 AQ hydrogenation and reforming with H_2O_2 production

Pathway 2



Scheme 1.3 AHQ further hydrogenation and oxidation THAHQ with H_2O_2 production

The AO process has the advantage that firstly, hydrogen and oxygen are not directly contacted, so it avoids explosion in the gas mixtures. Secondly, it is very effective for hydrogen peroxide production because there are two pathways to the target molecule. However, some obvious drawbacks[11] also exist. For example, for some applications, it is not economical because the cost of working solvent system and the large scale operation is expensive. Moreover, periodical replacement of the reactants because of the by-product (THAQ) from further hydrogenation of AQ, toxic solvent system and high energy requirement, are significant disadvantages. As well as transportation and storage, because AO process operates at a very large scale system, large amounts of concentrated hydrogen peroxide are made and there may be unsafe and uneconomical during transportation and storage.

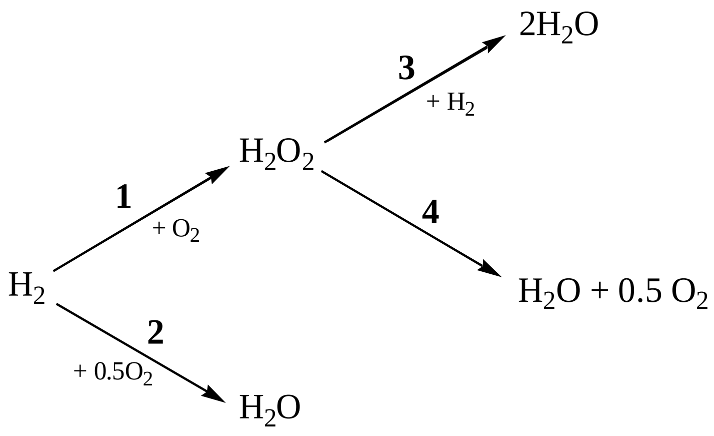
In summary, the anthraquinone autoxidation process is only efficient for the demand of large amounts of highly concentrated hydrogen peroxide. But usually, in daily life and small-scale fine chemical production, there is no need for such a high concentration. However, lower cost of transportation and storage would be an advantage. So, more new, efficient and small-scale processes for manufacturing of hydrogen peroxide to meet smaller demand at any time it is needed are required.

1.3.2 Direct Synthesis of Hydrogen Peroxide

The synthesis of hydrogen peroxide from hydrogen and oxygen (Scheme 1.4) directly has been regarded as an issue for over a hundred years. In 1914[33], Henkel and Weber first published this method but it was not researched for a long time. Many researchers were suffering difficulties of forming hydrogen peroxide with hydrogen/oxygen. The first problem of all is the control of the side reactions (Scheme 1.5)[34]. In detail, non-selective formation of water by combustion (Scheme 1.5 pathway 2) is the first technical problem associated to the synthesis. Secondly, as known, H_2O_2 is an unstable compound which should be carefully stored. So the formed H_2O_2 can be hydrogenated and decomposed (Scheme 1.5 pathway 3 and 4) to water and water with oxygen, respectively. Those more thermodynamically favorable side reactions need to be controlled. For example, lower reaction temperature can decrease the decomposition rate of H_2O_2; and shorter contacting time with catalyst can shut down the further reaction from produced H_2O_2 to H_2O_2 via hydrogenation. Some chemical additives were also added to raise the selectivity to H_2O_2 rather than combustion to water. Most importantly, a well-designed catalyst plays a key role in the synthesis reaction for both high yield and selectivity of hydrogen peroxide.

$$H_2 + O_2 \rightarrow H_2O_2$$

Scheme 1.4 Hydrogen peroxide formation directly from hydrogen and oxygen



1. Synthesis

$$H_2 + O_2 \rightarrow H_2O_2; \Delta H_{298K} = -135.9 \text{ kJ mol}^{-1}, \Delta G_{298K} = -120 \text{ kJ mol}^{-1}$$

2. Combustion

$$H_2 + 0.5\ O_2 \rightarrow H_2O; \Delta H_{298K} = -241.6 \text{ kJ mol}^{-1}, \Delta G_{298K} = -237.2 \text{ kJ mol}^{-1}$$

3. Hydrogenation

$$H_2O_2 + H_2 \rightarrow 2H_2O; \Delta H_{298K} = -211.5 \text{ kJ mol}^{-1}, \Delta G_{298K} = -354.0 \text{ kJ mol}^{-1}$$

4. Decomposition

$$H_2O_2 \rightarrow H_2O + 0.5O_2; \Delta H_{298K} = -105.8 \text{ kJ mol}^{-1}, \Delta G_{298K} = -116.8 \text{ kJ mol}^{-1}$$

Scheme 1.5 Pathways included in the synthesis reaction

Another problem in this direct synthesis is the hazard of explosion of hydrogen/oxygen mixture under high pressure[35]because of the wide explosion limits for H_2 in O_2 (From 4 vol% to 94 vol% at 25 °C under 1 atmospheric pressure). So the hydrogen concentration below 4 vol% in oxygen is necessary, which however, leads to a much lower yield of H_2O_2. The other gases mixed with H_2 and O_2 which have been introduced include nitrogen, carbon dioxide and argon. Because of the low yields of hydrogen peroxide, there are still no successfully commercialized plants in industry although Degussa–Headwaters[36]announced one.

1.3.2.1 Direct Synthesis Using Palladium Based Catalysts

In fact, the previous research by Henkel and Weber[33] was based on a palladium catalyst. Untill now, most research concerning the combination of hydrogen and oxygen for hydrogen peroxide formation are processed by palladium catalysts which have been used in numerous hydrogenation and oxidation reactions. Considering the direct synthesis, some of the early studies were concentrated on the mixing of H_2 and $O_2$with a palladium catalyst under high pressure in the explosive region, which could achieve over 35 wt% H_2O_2 solution[37]. However, because of the flammability of hydrogen in oxygen, such processes were dangerous in operation. Hutchings and co-workers mixed CO_2 into H_2 and O_2 to prevent such explosive mixture[16, 38].

As palladium supported catalysts were found to be active in the direct synthesis of hydrogen peroxide, investigations of the active states of palladium catalysts were also carried out by many research groups. Commonly, they proposed that the metallic palladium (Pd^0) is more active in the direct synthesis of hydrogen peroxide, but less selective than those oxidized palladium (Pd^{x+}) in the Pd catalyst[39]. Choudhary et al. claimed that a PdO catalyst has more selectivity in this synthesis than Pd^0 catalyst because there was less H_2O_2 decomposition and hydrogenation[40, 41]. They compared the productivity of hydrogen peroxide by using different reactant gases. A reduction of Pd catalyst with more H_2 in hydrogen/oxygen as reactant led to a decrease of H_2O_2 selectivity compared with that treated with more O_2 in the mixture gas. In summary, an oxidized treatment to Pd catalyst can cause the oxidation of surface or sub-surface of Pd catalyst from Pd^0 to PdO, and made a increase of H_2O_2 yield. Other oxidizing agents such as perchloric acid, hydrogen peroxide and nitrous acid also resulted in the same beneficial trend.

1.3.2.2 Additives to Pd Catalyzed Process

In order to reduce the decomposition and hydrogenation of the produced hydrogen peroxide in process, some additives including acids and halides were introduced to both Pd catalysts and the synthesis reaction. As early as 1961, Pospelova and co-workers[42-44]documented that an inorganic acid, such as HCl or HCN, inhibited the decomposition of H_2O_2 with presence of a Pd catalyst. Moreover, H_2O_2 is unstable and more easily decomposed inalkaline solution than in acidic medium, and H_2O_2 is the most stable at the pH 3.5 and 4.5[45]. Compared with those liquid acids, solid acids can be used to avoid the corrosion of reactor materials and the leaching of catalyst metal[40]. Halide ions also have a strong influence on H_2O_2 decomposition[46], especially Br^- and Cl^- ions. Among F^-, Cl^-, Br^-, I^-, the addition of I^- was proven to be most effective for high H_2O_2 selectivity and yield, whereas F^- has very little benefit. Moreover, halide together with H^+, which is in form of the halide acids (HCl, HBr or HI), will not only reduce the decomposition of produced hydrogen peroxide, but also decrease the combustion of hydrogen to water[46]. However, there is a problem which limits the use of halide-acid promoter. The halide ions with H^+ may cause substantial corrosion of the reactor, and the effect increases with increasing pressure. Generally, promoters such as halides (Br^-) and acids (phosphoric acid) are added to stabilize the hydrogen peroxide in the aqueous solution and solve the problem of non-selective by-reactions.

1.3.2.3 Addition of Gold to Palladium Catalysts

The Hutchings research group were the first to investigate the direct synthesis of hydrogen peroxide by gold catalysis[16]. In that paper, Au/Al_2O_3 was found to be active in this reaction (Table 1.3). The gold supported on SiO_2[47], Al_2O_3[16, 48], Fe_2O_3[49], TiO_2[50, 51], H-ZSM-5or H-Y zeolite[52-54], SiO_2-Al_2O_3[54], TS-1[54], activated carbon[55], and MCM-41[55] have been tested for the direct synthesis reaction.

Catalyst	Solvent	Temperature /^oC	Pressure /MPa	O_2/H_2 mole ratio	H_2O_2 /mmol $g_{cat}^{-1}h^{-1}$
Au/Al_2O_3	Methanol	2	3.7	1.2	1530
(1:1) Au:Pd $/Al_2O_3$	Methanol	2	3.7	1.2	4460
Pd/Al_2O_3	Methanol	2	3.7	1.2	370

Table 1.3 H_2O_2 formation by alumina supported gold and palladium catalysts[16]

However, gold or palladium only catalysts were found to be less active for the reaction compared with those with adding of palladium to the gold catalysts[16, 38]. Also, the catalysts prepared by impregnation method were more active than the corresponding ones prepared by co-precipitation and deposition-precipitation method (Table 1.4).

Catalyst	Preparation	Pre-treatment	Productivity /molH_2O_2 kg_{cat}^{-1} h^{-1}	H_2O_2 /wt%
5% Au/α-Fe_2O_3[a]	Co-precipitation	Air, 25 °C	0.126	0.001
5% Au/α-Fe_2O_3[a]	Co-precipitation	Air, 400 °C	0.207	0.002
5% Au/α-Fe_2O_3[a]	Co-precipitation	Air, 600 °C	0.366	0.004
5% Au/α-Fe_2O_3[a]	Impregnation	Air, 400 °C	0.54	0.005
2.5% Au–2.5% Pd/α-Fe_2O_3[a]	Impregnation	Air, 400 °C	16	0.161
5% Pd/α-Fe_2O_3[a]	Impregnation	Air, 400 °C	3.6	0.036
5% Au/Al_2O_3[b]	Impregnation	Air, 400 °C	3.1	0.006
2.5% Au–2.5% Pd/Al_2O_3[b]	Impregnation	Air, 400 °C	18	0.036
5% Pd/Al_2O_3[b]	Impregnation	Air, 400 °C	12	0.024
5% Au/TiO_2[a]	DP	Air, 25 °C	0.229	0.002

5% Au/TiO_2[a]	Deposition-precipitation	Air, 120 °C	0.482	0.005
5% Au/TiO_2[a]	Deposition-precipitation	Air, 400 °C	0.388	0.004
5% Au/TiO_2[a]	Impregnation	Air, 400 °C	7.1	0.014
4% Au/1% Pd/TiO_2[b]	Impregnation	Air, 400 °C	28	0.057
2.5% Au/2.5% Pd/TiO_2[b]	Impregnation	Air, 400 °C	64	0.128
5% Pd/TiO_2[b]	Impregnation	Air, 400 °C	31	0.061

[a] 50 mg mass of catalyst; [b] 10 mg mass of catalyst

Table 1.4 Performance of gold, palladium, and gold-palladium catalysts in direct synthesis of hydrogen peroxide (conditions: Methanol/water 66:34, 2 °C)[49, 50]

Choudhary and co-workers[56] also added Au to Pd, and obtained the same results that Au-Pd catalysts performed better than the Pd only catalysts. Hutchings and co-workers also investigated numerous Au, Pd and Au-Pd catalysts supported on different metal oxides, such as Al_2O_3[48], Fe_2O_3[49], SiO_2[57] activated carbon and TiO_2[50], and made a comparison (Table 1.5). In this paper[58], except the re-proving of superior performance of Au-Pd bimetallic catalysts compared to those gold or palladium only catalysts, they also investigated that, compared with those four metal oxides as supports, carbon supported 2.5 wt% Au-2.5 wt%Pd achieved the highest rate of hydrogen peroxide formation (carbon$\approx$ SiO_2> TiO_2>Al_2O_3). This demonstrates that the support for Au-Pd catalyst plays an important role in this catalytic process.

Catalyst[a]	H_2O_2 Formation ($molH_2O_2\ kg_{cat}^{-1}\ h^{-1}$)	Hydrogen Selectivity (%)[b]
5 wt% Au/SiO_2	1	nd
2.5 wt%Au-2.5 wt%Pd/SiO_2	108	80
5 wt% Pd/SiO_2	80	80
5 wt% Au/carbon	1	nd
2.5 wt%Au-2.5 wt%Pd/carbon	110	80
5 wt% Pd/carbon	55	34
5 wt% Au/Al_2O_3	2.6	nd
2.5 wt% Au-2.5 wt%Pd/Al_2O_3	15	14
5 wt% Pd/Al_2O_3	9	nd
5 wt% Au/TiO_2	7	nd
2.5wt%Au-2.5wt% Pd/TiO_2	64	70
5 wt% Pd/TiO_2	30	21

[a] All catalysts were clacined at 400 °C; [b] nd: not determined as too low yield

Table 1.5 Hydrogen peroxide formation using Au, Au/Pd, and Pd supported catalysts[58] (conditions: 5% H_2/CO_2 and25% O_2/CO_2, 1:2 H_2/O_2 at 3.7 MPa, 5.6 g MeOH, 2.9 g H_2O, 0.01 g catalyst and 1200 rpm)

Another key observation of Hutchings co-workers is that the heating pre-treatment of the catalyst has a significant effect on catalyst activity[58]. They have worked out the activity of uncalcined 2.5 wt% Au-2.5 wt% Pd/TiO_2(dried at 25 °C) is quite high (H_2O_2 forming rate of 202 $molH_2O_2h^{-1}\ kg_{cat}^{-1}$, H_2 conversionof 46% and H_2O_2 selectivity of 89%). However, in table 1.6, compared with the uncalcined and calcined 2.5 wt% Au-2.5 wt% Pd/TiO_2, we can observe that the uncalcined sample showed low stability after use leaching most of the metals. With the increasing heat-treatment temperature, the catalysts become more stable with less metal leaching, and finally without any metal loss after three uses after a 400 °C heating pre-treatment of the samples. The same phenomenon appeared when using other oxides supported Au-Pd catalysts. For example, the activated carbon supported sample was also getting more stable after treating at 400 °C (Figure 1.8).

Pre-treatment	Metal loading		Use	TOF /h^{-1}
	Au /wt%	Pd /wt%		
Dried 25 °C	2.5	2.5	1	564
Dried 25 °C	0.5	0.25	2	2298
Dried 25 °C	0.2	0.125	3	2966
Dried 200 °C	2.5	2.5	1	330
Dried 200 °C	2.22	2.5	2	216
Dried 200 °C	2.18	2.5	3	158
Dried 400 °C	2.5	2.5	1	176
Dried 400 °C	2.5	2.5	2	176
Dried 400 °C	2.5	2.5	3	176

Table 1.6 Effect of heating pre-treatment of 2.5 wt% Au-2.5 wt% Pd/TiO_2 catalyst[34] (conditions:5% H_2/CO_2 and25% O_2/CO_2, 1:2 H_2/O_2 at 3.7 MPa, 5.6 g MeOH, 2.9 g H_2O, 0.01 g catalyst, and 1200 rpm)

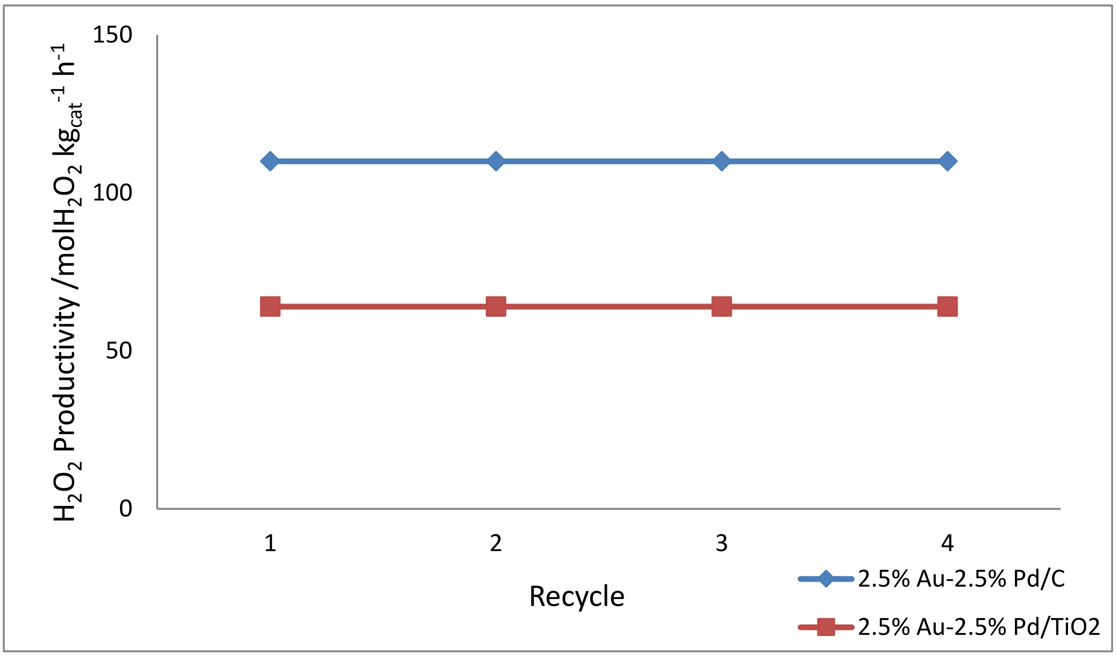


Figure 1.8 Effect of re-uses for 400 °C calcined 2.5 wt% Au-2.5 wt% Pd/C and 2.5 wt% Au-2.5 wt% Pd/TiO_2[58] (conditions: 5% H_2/CO_2 and25% O_2/CO_2, 1:2 H_2/O_2 at 3.7 MPa, 5.6 g MeOH, 2.9 g H_2O, 0.01 g catalyst, and 1200 rpm)

The effect of calcination temperature can be investigated by Scanning Transmission Electron Microscopy (STEM)[59]. Figure 1.9 shows the high angle annular dark field (HAADF) images of Au-Pd/Al_2O_3 with different heating pre-treatment. As we can see, with the increase of temperature, the structure of bimetallic Au-Pd changes from a homogeneous form to a core-shell structure with a gold-rich core surrounded by a palladium-rich shell. Although the uncalcined catalyst with homogeneous alloys could achieve higher activity, this kind of structure was considered to be less stable compared with those high-temperature calcined ones. For the oxides supported Au-Pd catalysts, calcination will lead the alloys to gold-rich core and palladium-rich shell structure which was proven to be more stable after several uses. They proposed that the Au present in the core acts as the electronic promoter for the palladium-rich shell of the Au-Pd alloy system[49-51]. However, the carbon supported Au-Pd catalyst still remained as a homogeneous structure after the 400 °C calcination (Figure 1.10). Interestingly, this homogeneous-structured carbon supported sample showed the highest (Table 1.5) and most stable activity with 110 mol$H_2O_2$$kg_{cat}^{-1}$ $h^{-1}$$H_2O_2$formation rate (Figure 1.8).

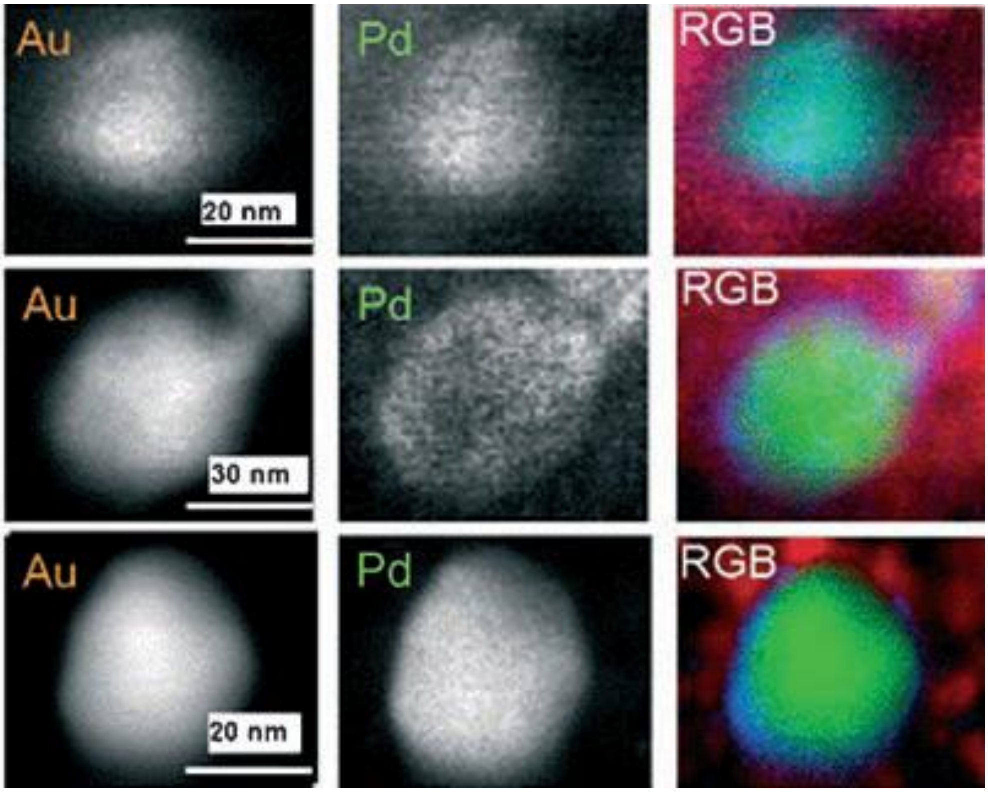


Fig. 1.9 High angle annular dark field (HAADF) images of 2.5 wt% Au-2.5 wt% Pd /Al_2O_3structure changes with increasing of calcination temperature[59] (first row: dried at 120 °C; second row: calcined at 200 °C; third row: calcined at 400 °C). The individual Au and Pd combined in red/green/blue images: red Al_2O_3, green Au, and blue Pd.

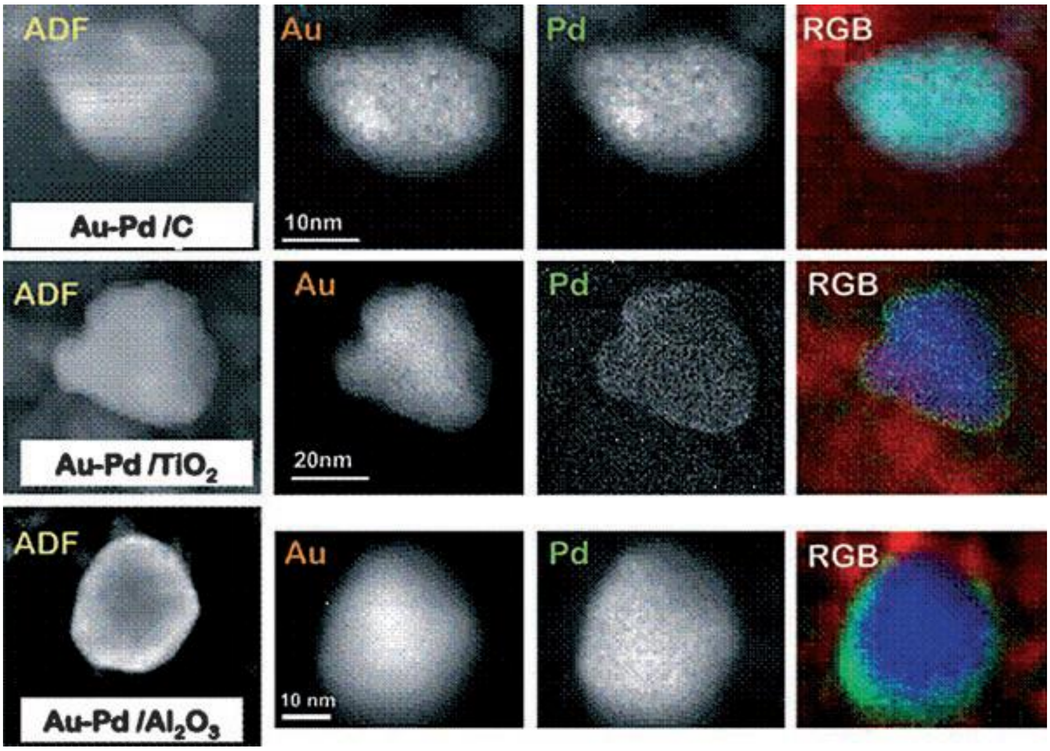


Fig. 1.10 High angle annular dark field (HAADF) images of first row: calcined Au-Pd/C, second row: calcined Au-Pd/TiO_2, third row: calcined Au-Pd/Al_2O_3 with combination of individual images of Au and Pd (red supports, green Au, blue Pd).

1.3.2.4 Effects of Reaction Parameters on the Direct Synthesis of Hydrogen Peroxide

As for the reaction mediums for the direct synthesis, a solvent with high gas solubility, low viscosity and low surface tension is required[39]. In the early studies, water was considered to be available because it has unlimited solubility of H_2O_2, and may stabilize the produced hydrogen peroxide in the reaction. Water alone was not suitable because of its low solubility of H_2 and O_2 compared with some primary alcohols. However, the problem of using alcohols only as reaction media was that a further hydrogenation of the produced hydrogen peroxide occurred because of excess soluble H_2 in the system. A water/methanol system was introduced by the Hutchings' research group[16] and proven to be effective in this reaction.

The choice of diluents for H_2 and O_2 is essential for the reaction. $CO_2$was added because it forms carbonic acid in situ, which acts as a stabilizer for hydrogen peroxide, and shuts down the further hydrogenation[34]. When using Ar or He instead of CO_2, there was a obvious decrease of hydrogen peroxide productivity from 110 to 10 mol kg_{cat}^{-1} h^{-1} by 2.5 wt% Au-2.5 wt% Pd/carbon[58]. So CO_2 as a diluent for H_2 and O_2 could not only reduce the explosive hazard of H_2 and O_2, but also improve the formation of H_2O_2. Moreover, there was no requirement for other additives, such as halides and acids, to achieve high productivity in this reaction.

Other reaction conditions, such as the reaction temperature, total pressure and H_2/O_2 ratio for the direct synthesis were also investigated by Hutchings and co-workers[60]. In Figure 1.11, we can see that the productivity was decreasing with increasing temperature (from 2 ^{o}C). When the temperature increased to over 10 ^{o}C, the productivity decreased rapidly, possibly due to more hydrogenation and decomposition happening. The pressure of the reaction gases was also investigated, and a linear trend was observed (Figure 1.12). The increasing productivity with higher pressure may be due to the larger solubility of H_2 and O_2[61] in reaction media and more activation of reactants on the catalyst surface[61]. In addition, as for the H_2/O_2 ratio, they supposed a “volcano” principle which means that the 1:1 of H_2/O_2 would be the optimum ratio[60] (Figure 1.13). There will be more hydrogenation of hydrogen peroxide with excess hydrogen and more combustion of hydrogen to water with excess oxygen.

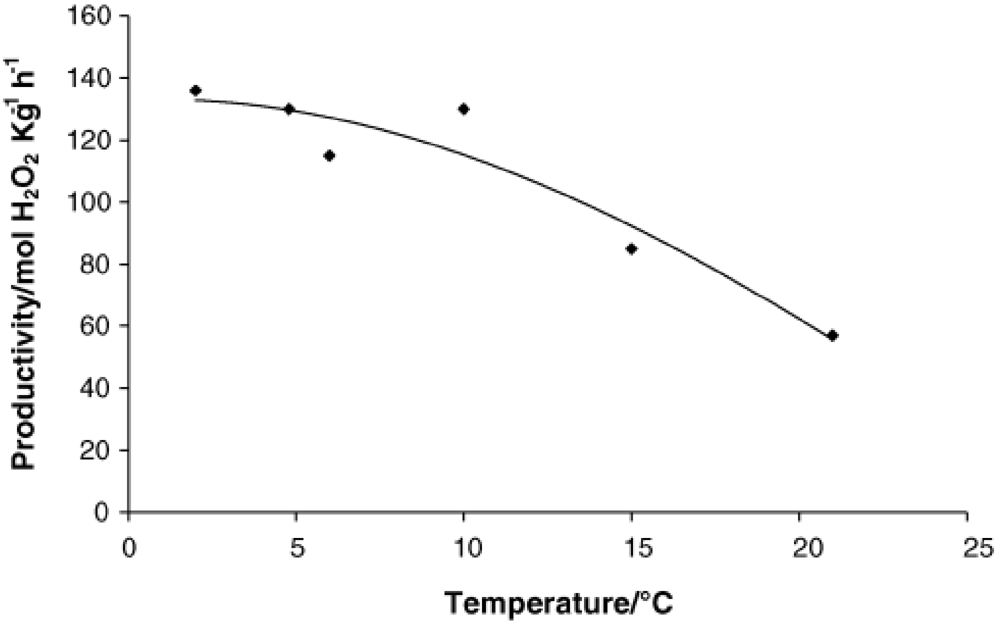


Fig. 1.11 H_2O_2 productivity with changing of reaction temperature[60] (conditions: 0.01 g catalyst, total pressure580 psi, $H_2/O_2 = 0.525$, 1200 rpm, 30 min, 5.6 gCH_3OH, 2.9 g H_2O)

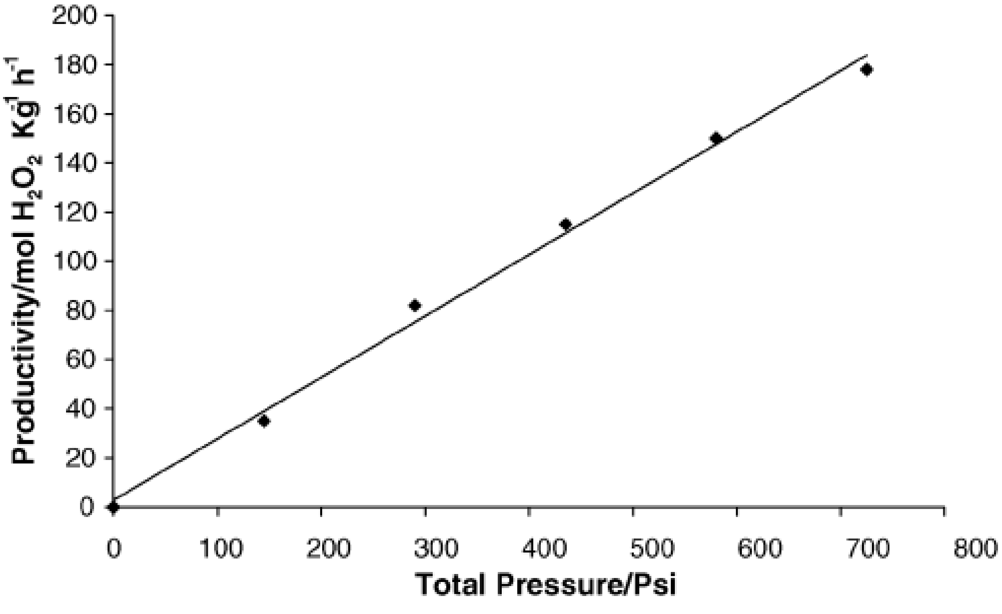


Fig. 1.12 H_2O_2 productivity with changing of total pressure[60] (conditions: 0.01 g catalyst, 2 °C, $H_2/O_2 = 0.525$, 1200 rpm, 30 min, 5.6 gCH_3OH, 2.9 g H_2O)

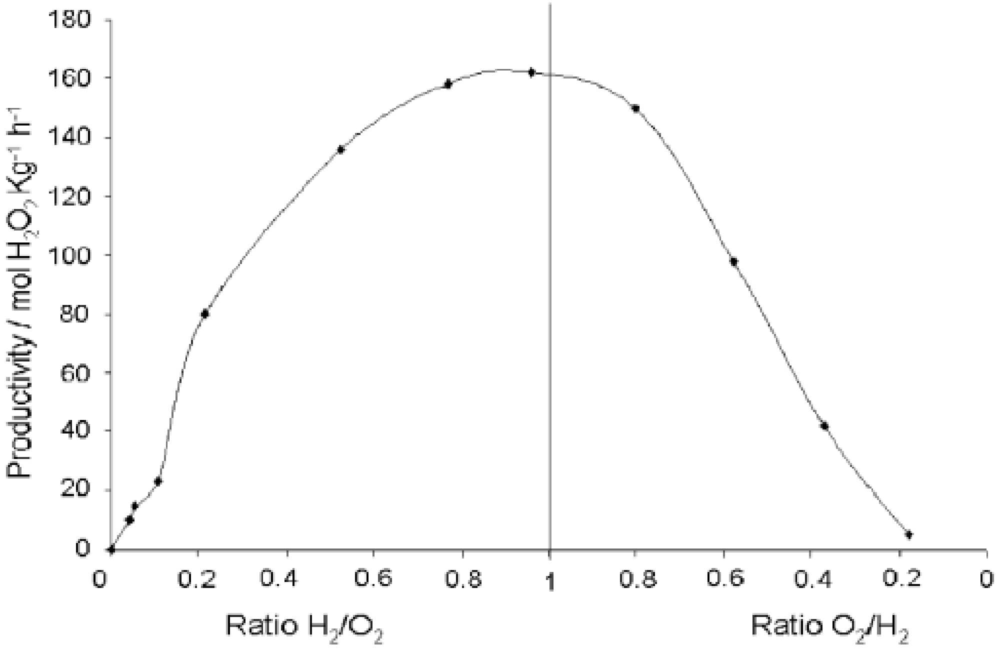


Figure 1.13 H_2O_2 productivity with changing of H_2/O_2 ratio[60] (conditions: 0.01 g catalyst, total pressure580 psi, 1200 rpm, 30 min, 5.6 gCH_3OH, 2.9 g H_2O, 2 ^{o}C)

1.3.2.5 Improvement of Preparation Method

Recent studies have been focused on the other preparation methods for Au-Pd catalysts in the direct synthesis of hydrogen peroxide. Lopez-Sanchezet al.[62] used a sol-immobilization for Au-Pd catalysts preparation, and got an enhanced activity for the reaction. Moreover, a modified impregnation method[63]which enables better control of the particle morphology, particle size distribution and nanoparticle composition showed the best performance among those three preparation methods (wet impregnation, sol-immobilization and modified impregnation) (Figure 1.14). This method was as high as four times more effective than wet impregnated or sol-immobilized Au-Pd catalyst. Moreover, after heating pre-treatment, the modified impregnated catalyst was stable after three uses and still maintained a high activity.

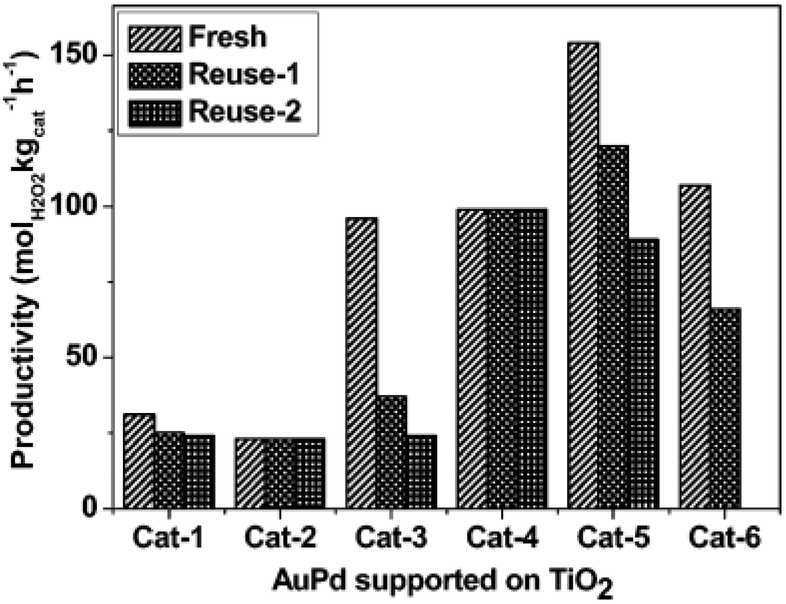


Fig. 1.14 H_2O_2 productivity and reusability of three kinds of prepared 0.5 %Au-0.5 %Pd/TiO_2[63] (Cat-1: sol-immobilization; Cat-2: wet impregnation; Cat-3: dried only modified impregnation; Cat-4: modified impregnation reduced in 5 %H_2/Ar at 400 °C/4h; Cat-5: modified impregnation reduced in 5 %H_2/Ar at 400 °C/4h with 0.58 M excess NaCl; Cat-6: modified impregnation reduced in 5 %H_2/Ar at 400 °C/4h with 2 M HCl) (conditions: 0.01 g catalyst, total pressure580 psi, H_2/O_2 = 0.525, 1200 rpm, 30 min, 5.6 gCH_3OH, 2.9 g H_2O)

1.3.2.6 Proposed Mechanisms for Direct Synthesis of Hydrogen Peroxide

Voloshin et al.[64] investigated the kinetics mechanism of the direct synthesis, and proposed that the reaction on catalyst surface might be the rate-determining step because the rate is independent of the reactant concentration, as it increases with more reactants, and then decreases slowly with gradual equilibrium of adsorption steps. Four possible mechanisms have been published as shown below.

Mechanism 1.

$$H_2 + 2^* \rightarrow 2H^* \ (1)$$

$$H^* + O_2 \rightarrow {}^* HO_2 \ (2)$$

$$\mathrm{H}^{*}+{}^{*}\mathrm{HO_2} \rightarrow \mathrm{H_2O_2} + 2^{*} \ (3)$$

Mechanism 2.

$$\mathrm{H_2}+{}^{**}\rightarrow \mathrm{H}^{**}\mathrm{H} \ (4)$$

$$\mathrm{O_2}+{}^{*}\rightarrow{}^{*} \mathrm{O_2} \ (5)$$

$$\mathrm{H}^{**}\mathrm{H}+{}^{*}\mathrm{O_2} \rightarrow \mathrm{H}^{**}\mathrm{HO_2}+{}^{*} \ (6)$$

$$\mathrm{H}^{**}\mathrm{HO_2} \rightarrow \mathrm{H_2O_2}+{}^{**} \ (7)$$

Mechanism 3.

$$\mathrm{H_2}+{}^{**}\rightarrow \mathrm{H}^{**}\mathrm{H} \ (8)$$

$$\mathrm{O_2}+{}^{**}\rightarrow{}^{**} \mathrm{O_2} \ (9)$$

$$\mathrm{H}^{**}\mathrm{H}+{}^{**}\mathrm{O_2} \rightarrow \mathrm{H}^{**}\mathrm{HO_2}+{}^{**} \ (10)$$

$$\mathrm{H}^{**}\mathrm{HO_2} \rightarrow \mathrm{H_2O_2}+{}^{**} \ (11)$$

Mechanism 4.

$$\mathrm{H_2}+{}^{*}\rightarrow{}^{*} \mathrm{H_2} \ (12)$$

$$\mathrm{O_2}+{}^{*}\rightarrow{}^{*} \mathrm{O_2} \ (13)$$

$${}^{*}\mathrm{H_2}+{}^{*}\mathrm{O_2}\rightarrow \mathrm{H}^{**}\mathrm{HO_2} \ (14)$$

$$\mathrm{H}^{**}\mathrm{HO_2} \rightarrow \mathrm{H_2O_2}+{}^{**} \ (15)$$

Scheme 1.6 Four possible kinetic mechanisms of direct synthesis of hydrogen peroxide

Mechanism 1, 2 and 3 were proposed by Pospelva and co-workers[65], and Mechanism 4 was published by Zhou and Lee[66]. Mechanism 4 was considered to be most reasonable because it has the highest R^2 value ($R^2 \approx 1$) for the Arrhenius plot.

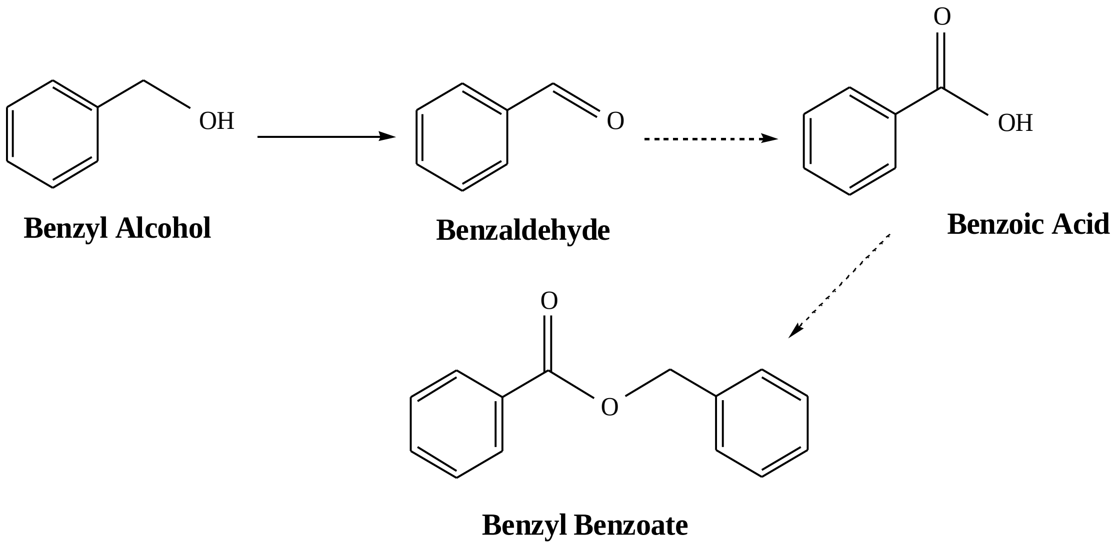
1.4 Selective Oxidation of Benzyl Alcohol to Benzaldehyde by Gold-Palladium Catalysts

It has been known that supported gold-palladium nanoparticles when used as heterogeneous catalysts are highly active for the selective oxidation of primary and secondary alcohols to their corresponding aldehydes[67]. The aldehydes are important and valuable intermediate for perfume industry[68]. But there is a limitation that the reagents are expensive and toxic[69].

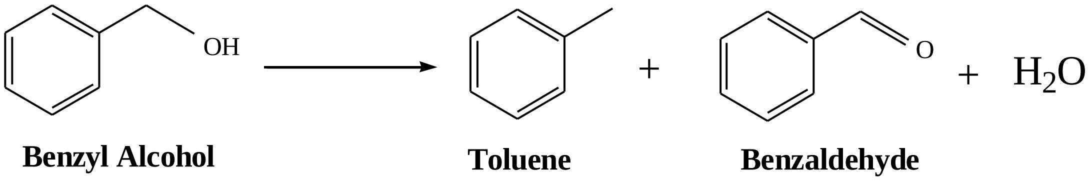
Hutchings' research group has concentrated on one of those model oxidation reactions, the oxidation of benzyl alcohol, for over one decade by using supported gold-palladium nanoparticle catalysts[67, 70]. Also, they used dioxygen as the oxygen donor which is considered to be effective in the oxidation. Previously, the presence of base, usually NaOH, was found to be necessary[71], but recently, gold catalysis without base condition was shown to be highly active in the alcohols oxidation[72].

1.4.1 Mechanism of Benzyl Alcohol Oxidation and Side Reactions

During the oxidation of benzyl alcohol, several reactions have been reported, which are firstly, direction oxidation of benzyl alcohol to benzaldehyde, benzoic acid and benzyl benzoate[73], secondly, self-disproportionation of two molecules of benzyl alcohol to form benzaldehyde, toluene and water[74], thirdly, dehydration to form dibenzylether[75], fourthly, self-condensation (benzylation) to form anthracene and stilbene[76]. However, some of side reactions only occur under particular conditions. For example, the self-condensation is active at higher temperature in the vapour phase[76]. The main process which is required is the selective oxidation of benzyl alcohol to benzaldehyde (Scheme 1.7), and the main side reaction is the self-disproportionation to form benzaldehyde and toluene (Scheme 1.8). Under the given conditions used by Hutchings and co-workers[67, 70, 73, 74], the other major product, toluene is generated from the self-disproportionation reaction, must be reduced for higher selectivity and yield of benzaldehyde to be achieved



Scheme 1.7 Selective oxidation of benzul alocohol to benzaldehyde and its further oxidation



Scheme 1.8 Self-disproportionation of benzyl alcohol to toluene and benzaldehyde

1.4.2 Solvent-free Oxidation of Benzyl Alcohol Using Gold-Palladium Catalysts

In 2006, Hutchings and co-workers[70] found that in a system without any reaction medium and solvents, the gold-palladium bimetallic catalysts showed higher activity, especially the superior selectivity (Figure 1.15). Compared with either the gold only or palladium only titania supported catalyst, the Au-Pd/TiO_2 reached very high selectivity, maintained this high level for 12 hours. But the monometallic samples both showed a decreasing trend of selectivity with longer reaction time. Although Pd/TiO_2 showed quite high benzyl alcohol conversion initially, there were numerous by-products, such as toluene and benzene, which largely decreased the selectivity of catalyst.

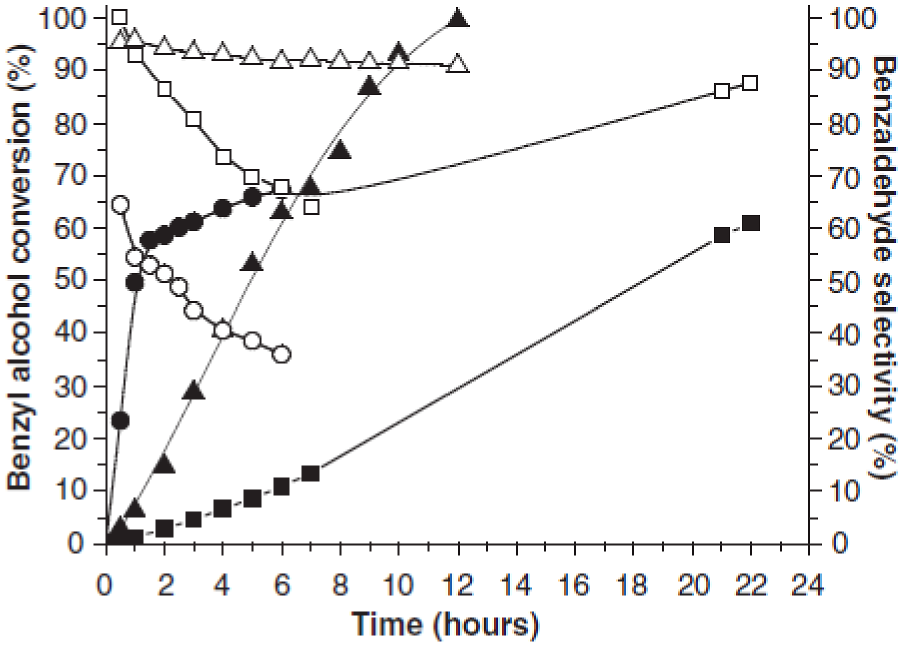


Fig. 1.15 Benzyl alcohol conversion and benzaldehyde selectivity with reaction duration by different catalysts. Squares: Au/TiO_2; circles: Pd/TiO_2; triangles: Au-Pd/TiO_2. Solid: conversion of benzyl alcohol; open: selectivity of benzaldehyde[70]. (Conditions: 373 K, 1 bar pO_2)

Also, other supports, Al_2O_3 and Fe_2O_3, which are active supports for Au-Pd catalysts, were investigated for catalyst preparation, and these catalysts performed slightly poorer than that TiO_2 supported sample (Table 1.7). It means that more acidic supports led to more by-products produced.

Catalyst	BA Conversion (%)		Bezaldehyde Selectivity (%)		Bezaldehyde Productivity (mol h^{-1} kg_{cat}^{-1})	H_2O_2 Productivity (mol h^{-1} kg_{cat}^{-1})
	0.5 h	8 h	0.5 h	8 h	8 h	
Au-Pd/TiO_2	3.7	74.5	95.2	91.6	165	64
Au-Pd/SiO_2	3.6	35.7	97.3	88.0	76	80
Au-Pd/Fe_2O_3	3.6	63.4	74.9	66.4	102	16
Au-Pd/Al_2O_3	2.6	83.3	90.5	86.6	174	23
Au-Pd/C	2.9	69.2	53.9	46.4	78	30
Au/TiO_2	0.6	15.3	96.7	63.9	24	<2
Pd/TiO_2	13.4	60.1	51.3	54.4	79	24

Table 1.7 Benzayl alcohol oxidation data obtained after 0.5 hour and 8 hours, and hydrogen peroxide formation data obtained after 0.5 hour[70]. (Conditions of BA oxidation: 373 K, 2 bar pO_2, 1500 rpm; conditions of H_2O_2 formation: 0.01 g catalyst, 2 ^oC, $H_2/O_2 = 0.525$, 1200 rpm, 30 min, 5.6 gCH_3OH, 2.9 g H_2O)

1.4.3 Improvement of Catalyst Preparation Methods

Based on the active catalyst of the supported Au-Pd bimetallic materials, another preparation method, sol-immobilization, has been worked out, and showed a superior activity especially in the oxidation of benzyl alcohol[62, 73, 77]. Previously, the sol-immobilization has been used for preparing titania and activated carbon supported gold only catalysts for the benzyl alcohol oxidation[78] (Table 1.8), and showed significant results. The introduction of a second metal, palladium, into gold catalysts significantly enhanced the activity and yield of benzaldehyde (Table 1.9)[62]. Compared on the basis of the same metal content, the sol-immobilized catalysts generally performed better than those prepared by conventional impregnation in the benzyl alcohol oxidation to benzaldehyde. After that, the sol-immobilized bimetallic Au-Pd supported on titania was also investigated. When a sol-immobilized 1 wt% Au-Pd/TiO_2 was used for the solvent-free oxidation of benzyl alcohol, the conversion reached over 70% (Figure 1.16)[67]. The major product was benzaldehyde (over 75%), which was always maintained at a high level. The by-products were toluene (23-24 %) and a small amount of benzoic acid. All of these indicate that the main by-product was toluene produced from the self-disproportionation, and benzaldehyde was produced from both the direct oxidation and self-disproportionation of benzyl alcohol. In order to increase the selectivity of benzaldehyde, switching off the toluene formation is necessary.

Catalyst	BA Conversion (%)	Yield (%)		
		Toluene	Benzaldehyde	Benzoic Acid
Au/TiO_2	55	3.1	40.5	8.3
Au/C	48	2.8	30.8	10.9

Table 1.8 Benzyl alcohol oxidation by 1 wt% gold catalysts prepared by sol-immobilization[78] (conditions: 40 ml benzyl alcohol, 0.1 g catalyst, T = 160 °C, pO_2 = 10 bar, 4 h, 1500 rpm)

Catalyst	BA Conversion (%)	Yield (%)		
		Toluene	Benzaldehyde	Benzoic Acid
Au-Pd/C_{SIm}[a]	82	25.4	39.4	14.8
Au/C_{SI}[a]	48	2.8	30.8	10.9
Pd/C_{SI}[a]	56	10.9	34.2	13.3
Au-Pd/C_{SIw}[b]	81.1	33.17	44.61	1.05
Au-Pd/C_{SIw}[b] (400 °C treated)	6.7	0.16	5.27	0.24
Au-Pd/C_{Im}[a]	44.6	3.2	27.6	8.7
Au-Pd/C_{Im}[a] (400 °C treated)	72.1	17.3	40.8	11.3
Au-Pd/C_{Iw}[a]	74.3	10.0	37.2	23.3
Au-Pd/C_{Iw}[a] (400 °C treated)	47.8	9.1	35.3	1.5

Table 1.9 Benzyl alcohol oxidation by 1 wt% catalysts prepared by sol-immobilization and impregnation[62]. SIm: mole ratio 1:1 of Au/Pd prepared by sol-immobilization; SIw: weight ration 1:1 of Au/Pd prepared by sol-immobilization; Im: mole ratio 1:1 of Au/Pd prepared by impregnation; Iw: weight ratio 1:1 of Au/Pd prepared by impregnation. ([a] conditions: 40 ml benzyl alcohol, 0.1 g catalyst, T = 160

°C, pO_2 = 10 bar, 4 h, 1500 rpm; ^{b} conditions: 40 ml benzyl alcohol, 0.1 g catalyst, T = 120 °C, pO_2 = 150 psi, 2 h, 1500 rpm)

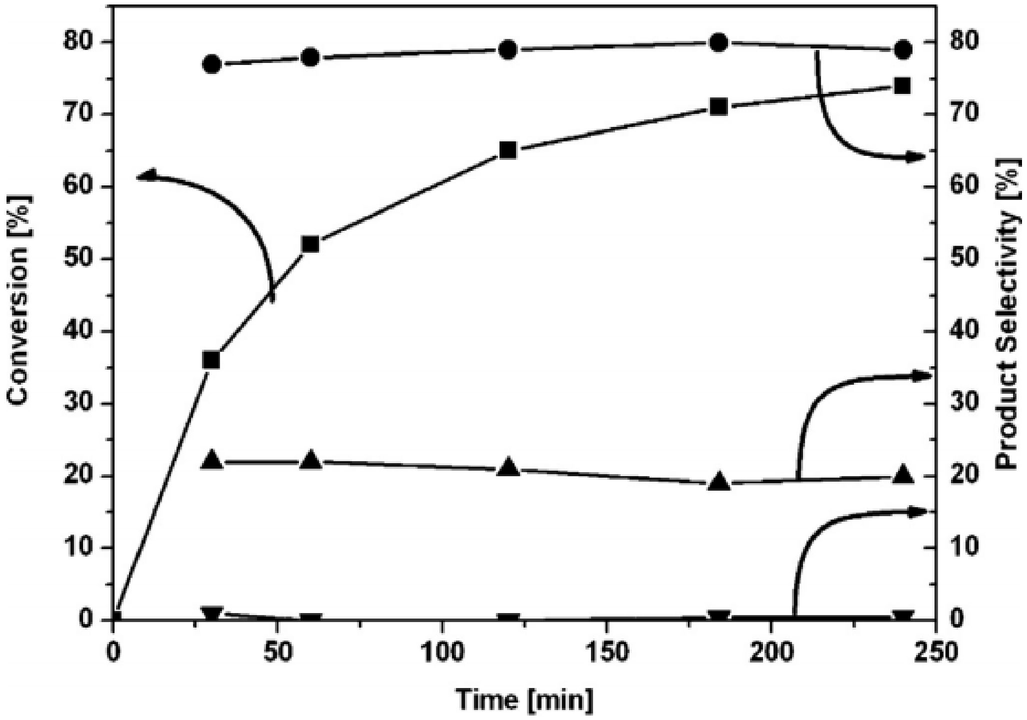


Fig. 1.16 Benzyl alcohol oxidation using sol-immobilized 1 % Au-Pd/TiO_2[67] ■: benzyl alcohol conversion; ●: benzaldehyde selectivity; ▲: toluene selectivity; ▼: benzoic acid selectivity.(conditions: 18.5 mmol benzyl alcohol, 1 bar O_2, 393 K, and substrate to metal molar ratio: 14000)

1.4.4 Switching Off the Formation of Toluene

To quantify the two reactions, direct oxidation and disproportionation, the turnover number of both should be measured. The disproportionation turnover number (TON_d) can be measured as the production of toluene, so the mole of consumed benzyl alcohol is two times the mole of produced toluene. As benzaldehyde is formed from both reactions, and the moles of benzaldehyde formed by disproportionation is equal to moles of toluene formed, then the amount of benzaldehyde formed form the oxidation reaction can be calculated by oxidation turnover number (TON_o) in Scheme 1.9[67].

$$\mathrm{TON_d} = \frac{2 \times \mathrm{mol_{toluene}}}{\mathrm{mol_{metal}}}$$

$$\mathrm{TON_o} = \frac{(\mathrm{mol_{BCHO}} - \mathrm{mol_{toluene}})}{\mathrm{mol_{metal}}}$$

Scheme 1.9 Equations of turnover numbers calculation of both disproportionation and oxidation.

The formation of toluene can be controlled by using a different support for the Au-Pd catalyst[67]. As reported, change of supports affected the difference of benzyl alcohol conversion. Among those samples, activated carbon, titania and Nb_2O_5 supported catalysts showed superior activity but has low selectivity of benzaldehyde. This can be explained by the calculation of TON_d and TON_o (Figure 1.17 and 1.18). As shown, those three highly active catalysts have both high TON_d and TON_o, but the ZnO or MgO supported catalysts, which have lower activity and higher selectivity, have no TON_d at all. Hence, the choice of supports for Au-Pd catalysts can switch off the non-selective disproportionation pathway in the benzyl alcohol oxidation.

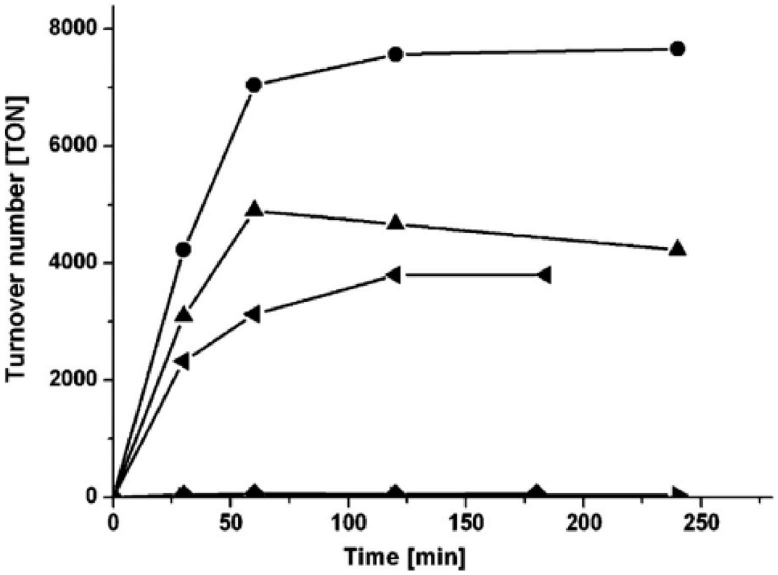


Fig. 1.17 TON_d with time on line by using different support for Au-Pd catalysts[67] (conditions: 18.5 mmol benzyl alcohol, 1 bar O_2, 393 K, and substrate to metal molar ratio: 14000) ●: 1 % Au-Pd/C; ▲: 1 % Au-Pd/TiO_2;◣: 1 % Au-Pd/Nb_2O_5; ◆:1 % Au-Pd/ZnO; ◢: 1% Au-Pd/MgO.

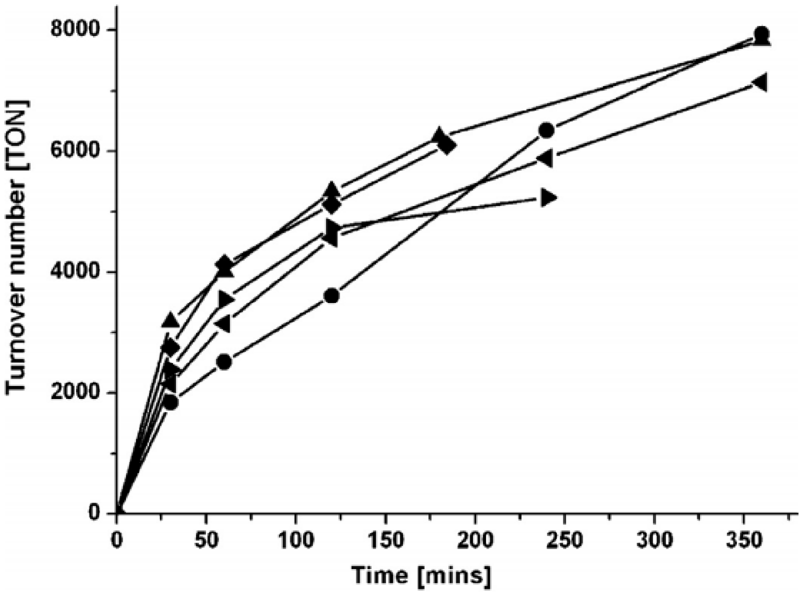


Fig. 1.18 TON_o with time on line by using different support for Au-Pd catalysts[67] (conditions: 18.5 mmol benzyl alcohol, 1 bar O_2, 393 K, and substrate to metal molar ratio: 14000) ●: 1 % Au-Pd/C; ▲: 1 % Au-Pd/TiO_2;◣: 1 % Au-Pd/Nb_2O_5; ◆:1 % Au-Pd/ZnO; ◢: 1% Au-Pd/MgO.

Moreover, the introduction of a third metal can also control the toluene formation[79]. A trimetallic Au-Pd-Pt supported on activated carbon was prepared by sol-immobilization, and found to be very active and selective in the solvent-free aerobic oxidation of benzyl alcohol. In table 1.10, it shows that the addition of Pt to Au-Pd promotes the selectivity of benzaldehyde while reducing the toluene formation. For example, the 0.45 Au-0.45 Pd-0.1 Pt/C performed a considerably high conversion of benzyl alcohol (53.9 %) and selectivity of benzaldehyde (80.2 %) with only a small amount of toluene being formed (0.1 %). The HAADF images showed the structure of Au-Pd-Pt with different alloy diameters (Figure 1.19). As the particle diameter increased, there were more palladium-rich alloys found, which is responsible to the non-desired disproportionation. The particles with over 10 nm diameter had the most palladium in the images.

Catalyst	BA conversion (%)	Selectvity (%)			
		Benzaldehyde	Toluene	B. Acid	B. Benzoate
0.65Au-0.35Pd	71.1	69.8	4.0	19.9	6.3
0.5Au-0.5Pd	80.7	67.0	3.4	23.1	6.5
0.3Au-0.4Pd-0.3Pt	35.4	83.3	0.9	7.9	7.9
0.4Au-0.4Pd-0.2Pt	36.7	81.7	0.6	8.0	9.7
0.45Au-0.45Pd-0.1Pt	53.9	80.2	0.1	13.1	6.6
1Au-1Pt*	11.8	79.9	2.0	8.4	9.7
0.5Au-0.5Pt	9.7	84.9	1.1	3.1	10.9
0.5Pd-0.5Pt	14.8	84.7	0.7	5.7	8.9
1Pt	2.8	90.7	0.0	0.7	8.6
1Pd	59.3	74.7	6.8	10.4	8.1

*total metal loading 2 wt% with 1 wt% Au and 1wt% Pd

Table 1.10 Benzyl alcohol oxidation with 1 wt% activated carbon supported catalysts by sol-immobilization[79] (conditions: benzyl alcohol, 0.05 g catalyst, 120 °C, pO_2= 150 psi, 1500 rpm stirring rate)

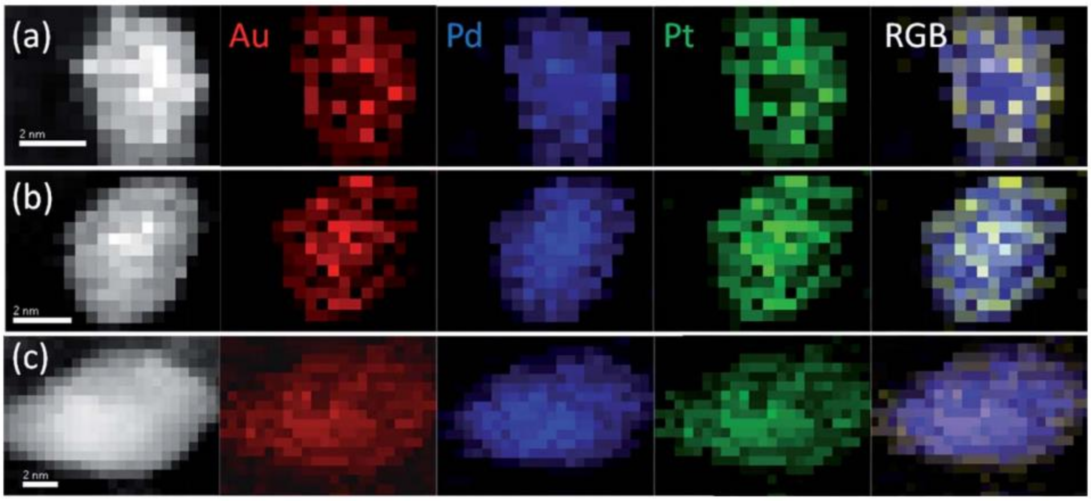


Fig. 1.19 HAADF images of (a) ~3 nm, (b) ~5 nm and (c) ~ 10 nm 1 wt% 0.3 Au-0.4 Pd-0.3 Pt/C, and the corresponding Au, Pd, Pt content in alloy[79] (red: Au, blue: Pd, green: Pt).

1.4.5 Benzyl Alcohol Oxidized by In Situ Generated Hydrogen Peroxide

Hydrogen peroxide, which is considered to be a potential green oxidant with only product being water, has been investigated in various selective oxidation reactions[80-82]. A new topic of selective oxidation by generating the active hydroperoxy species (-OOH) has become popular[83]. In previous research, the synthesis of hydrogen peroxide was processed at low temperature, typically subambient[16]. However, the temperature required for the oxidation of benzyl alcohol is around 120 °C[71]. Moreno et al.[84] claimed that combining the two reactions together at low temperature, which is beneficial to the former process, should be better for the benzyl alcohol oxidation by in situ generated hydrogen peroxide. They used bimetallic Au-Pd supported on titanium silicate materials, and achieved high selectivity of benzaldehyde. Santonastaso and co-workers[85] investigated the possibility of combining the two reactions. They considered that the alcohols can be processed at lower temperature (no higher than 50 °C) compared with that in previous research (120 °C), because oxygen can be activated in H_2O_2 synthesis with the presence of Au-Pd catalysts, and the generated hydroperoxy species are responsible for the oxidation of benzyl alcohol.

Santonastaso et al. showed that some of the reaction conditions, such as reaction temperature, solvent system, reaction duration and catalyst support were also important. To investigate the optimum temperature for combining the two processes, 2 ^{o}C, which is optimum for direct synthesis of hydrogen peroxide, room temperature and 50 ^{o}C were tried (Figure 1.20). Although the result at 2 ^{o}C showed a high selectivity of benzaldehyde, there was little benzyl alcohol converted. When the temperature was increased to 50 ^{o}C, both higher benzyl alcohol conversion and benzaldehyde selectivity were achieved. Water/methanol solvent system is considered to be best for the synthesis of hydrogen peroxide. In fact, in the pure methanol system, there is more hydrogen peroxide produced than that in the water/methanol, but the H_2O_2 is more unstable in methanol. So there was less H_2O_2 detected after reaction. However, because of the stability of H_2O_2 in water/methanol system, it is not easy to process the following oxidation. Instead, the methanol only performed better with higher conversion for this benzyl alcohol oxidation by in situ generated hydrogen peroxide shown in Figure 1.21. Figure 1.22 and 1.23 show the effect of the reaction time on the reaction. The conversion of benzyl alcohol reached a peak at 30 min, and then began to decrease slightly. The selectivity of benzaldehyde gave the maximum when reacting between 15 and 30 min. Moreover, the choice of support for Au-Pd catalyst plays an important role for this oxidation reaction. TiO_2 supported catalysts showed 5.9 % benzyl alcohol conversion and over 85 % benzaldehyde selectivity. In a previous report, MgO when used as a support could achieve high selectivity as well but low conversion in the solvent-free oxidation by gas phase dioxygen. In this process, a similar situation which reached such a very high selectivity, is observed but with only 2 % conversion after 30 min reaction (Figure 1.24). Interestingly, catalysts supported on ceria achieved superior activity than the other catalysts. However, it was observed that over 90 % of the metal loading on CeO_2 was leached during the raction[86], which means ceria as support is not suitable because of the low stability in such an acidic system.

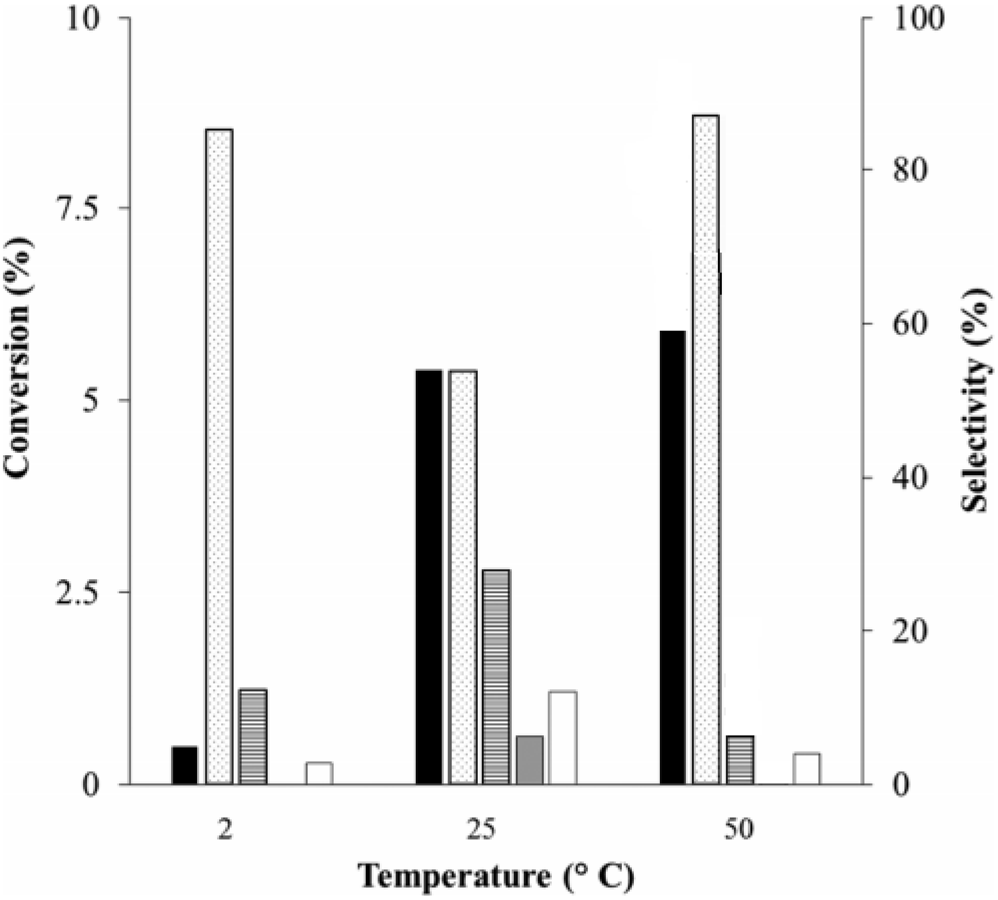


Fig. 1.20 Benzyl alcohol conversion and selectivities of some major products at 2 °C, 25 °C and 50 °C[85]. (Black bars: conversion; spotted bars: benzaldehyde selectivity; striped bars: toluene selectivity; gray bars: benzyl benzoate selectivity; white bars: benzoic acid)

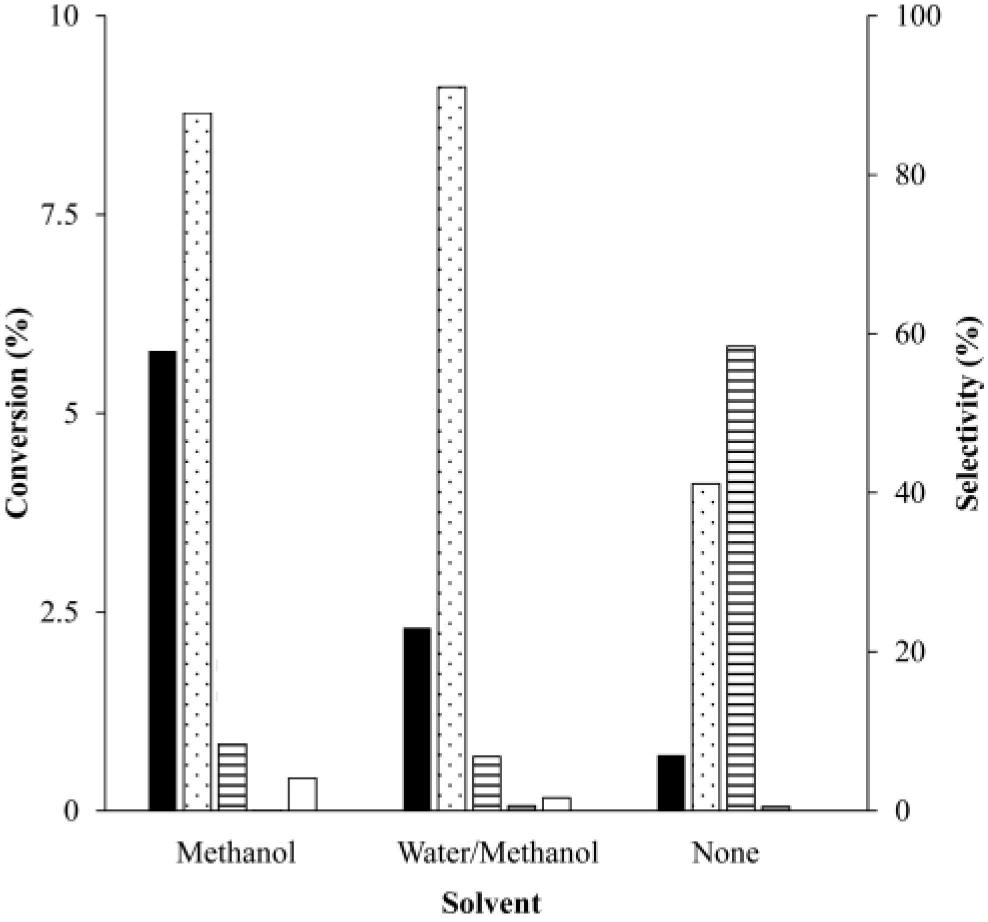


Fig. 1.21 Benzyl alcohol conversion and selectivities of some major products with solvent systems of 100 % methanol, 34 % water/66 % methanol and solvent free[85]. Black bars: conversion; spotted bars: benzaldehyde selectivity; striped bars: toluene selectivity; gray bars: benzyl benzoate selectivity; white bars: benzoic acid. (conditions: 0.01 g catalyst, 1 ml benzyl alcohol and 9 ml methanol, 420psi 5%H_2/CO_2 and 160psi 25%O_2/CO_2, 50 °C, 30 min)

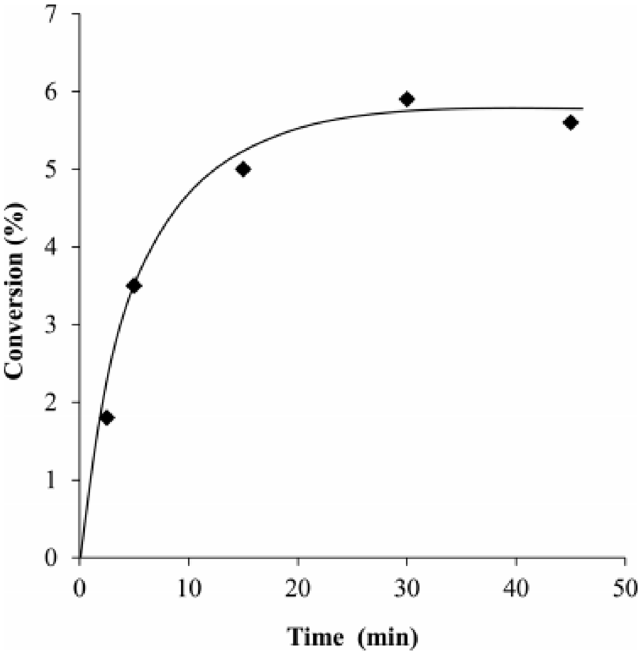


Fig. 1.22 Benzyl alcohol conversion with change of reaction time[85]. (conditions: 0.01 g catalyst, 1 ml benzyl alcohol and 9 ml methanol, 420psi 5%H_2/CO_2 and 160psi 25%O_2/CO_2, 50 °C, 30 min)

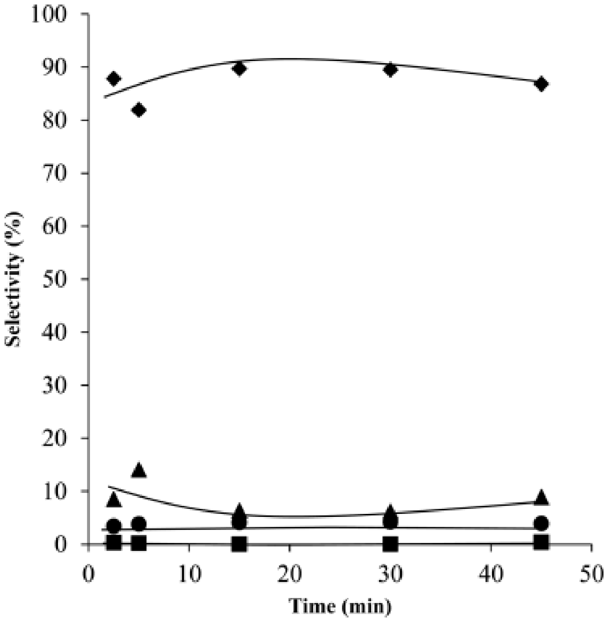


Fig. 1.23 Selectivity of major products with change of reaction time[85]. Diamonds: benzaldehyde; triangles: toluene; squares: benzyl benzoate; circles: benzoic acid. (conditions: 0.01 g catalyst, 1 ml benzyl alcohol and 9 ml methanol, 420psi 5%H_2/CO_2 and 160psi 25%O_2/CO_2, 50 °C, 30 min)

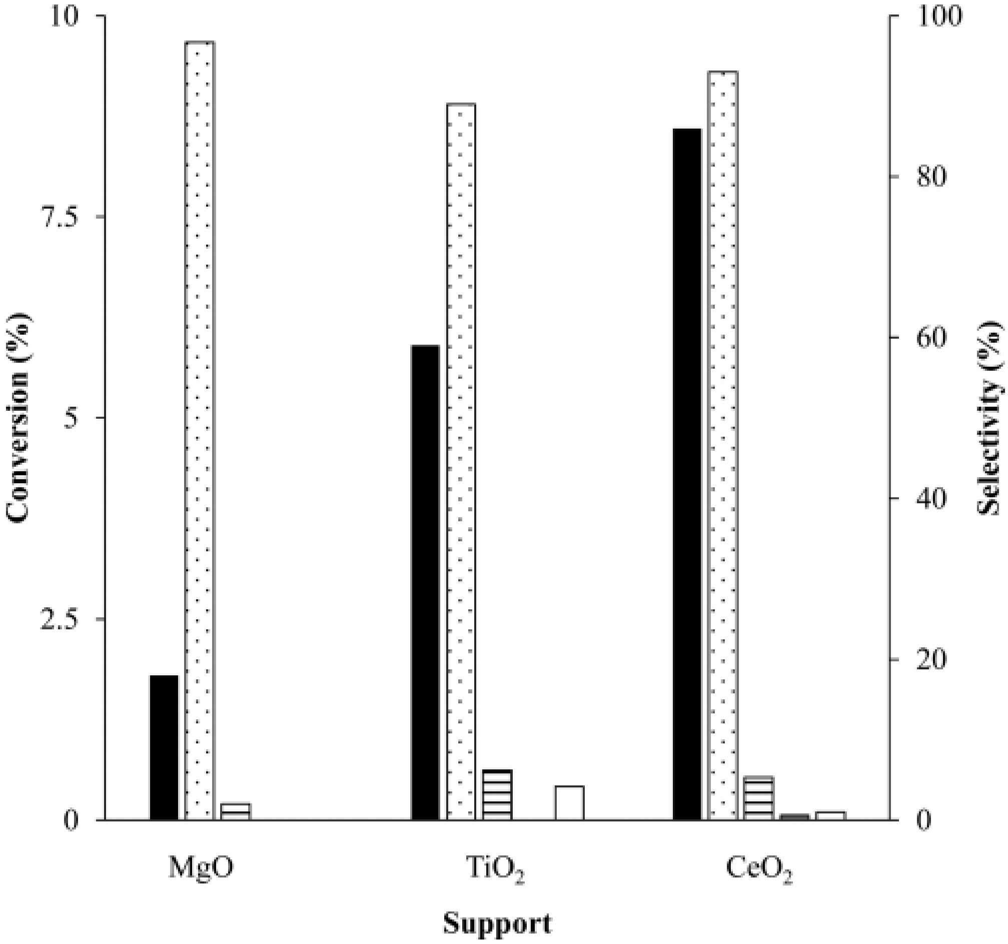


Fig. 1.24 Benzyl alcohol conversion and selectivities of some major products by using Au-Pd loading on different supports[85]. Black bars: conversion; spotted bars: benzaldehyde selectivity; striped bars: toluene selectivity; gray bars: benzyl benzoate selectivity; white bars: benzoic acid. (conditions: 0.01 g catalyst, 1 ml benzyl alcohol and 9 ml methanol, 420psi 5%H_2/CO_2 and 160psi 25%O_2/CO_2, 50 °C, 30 min)

1.5 Project Aims

Based on all the background knowledge reviewed in this chapter, we can find that there are still many problems present when using in situ generated H_2O_2 for the oxidation of benzyl alcohol. For example, some reaction conditions and possible improvements for catalysts can be further investigated.

Higher temperature, which is beneficial for the benzyl oxidation and produces unstable hydrogen peroxide, will be investigated in this reaction in this thesis. Moreover, the effect of longer reaction durations will also be studied. As for the catalysts, the effects of other metal ratios of gold and palladium, and different preparation methods, which have been used for both direct synthesis of hydrogen peroxide and benzyl alcohol oxidation by molecular oxygen, will also be studied.

In this thesis, the improvement in the reactants of benzyl alcohol obtained for both reaction conditions and catalysts for the benzyl alcohol oxidation with in situ generated hydrogen peroxide will be the main part of the investigations. Experimental and results will be shown in following chapters in detail.

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Chapter 2. Experimental Methods

2.1 Introduction

All the experiments have been done in laboratories 0.90, 0.86 and 0.88 in Main Building of Cardiff Catalysis Institute, school of chemistry, Cardiff University. There are three main parts of experimental, which are carbon monoxide oxidation, direct synthesis of hydrogen peroxide, and benzyl alcohol oxidation by generated hydrogen peroxide.

2.2 Materials and Instruments

Details about materials for catalysts, and reactants, gases and solvents for the catalyst tests and analysis are introduced in this part.

2.2.1 Catalyst Metals Precursors

Chloroauric acid ($HAuCl_4 \cdot 3H_2O$, Johnson Matthey) was used as the gold precursor; palladium chloride ($PdCl_2$, 99.99% trace metals basis for purity, Sigma Aldrich) was used as the palladium precursor.

2.2.2 Catalyst Supports

Titania (TiO_2, P-25, Degussa) and activated carbon (G-60, Darco) were used for the catalyst supports.

2.2.3 Gases

Carbon monoxide (5000ppm in synthetic air), 5%H_2/CO_2 (99.99%), 25%O_2/CO_2 (99.99%), 5%H_2/Ar (99.95%), N_2 (99.95%) and air, were all suppliedby BOC Gases or Air Products Ltd.

2.2.4 Liquids (for tests, solvents and titration)

Deionized water (HPLC grade, Sigma Aldrich), Methanol (HPLC grade, Sigma Aldrich), $(NH_4)_2Fe(SO_4)_2\cdot 6H_2O$ (98 %, Sigma Aldrich), benzyl alcohol (99.0 %, ACS reagent, Sigma Aldrich), mesitylene (99 %, ACROCS Organics), benzaldehyde (99.5%, Sigma Aldrich), toluene (99.8 %, Sigma Aldrich).

2.2.5 Instruments for Catalyst Tests

For CO oxidation, tests were processed in CO oxidation system in a U-shaped quartz tube reactor (5mm diameter), with a room temperature water bath.

Both hydrogen peroxide production and benzyl alcohol oxidationwere carried out in a Parr stainless steel autoclave (Figure 2.1) with a reactor filled to the maximum volume of 50ml and pressure of 14 MPa. An overhead stirrer, a heating/cooling controlling system and a pressure monitor were equipped with the autoclave.

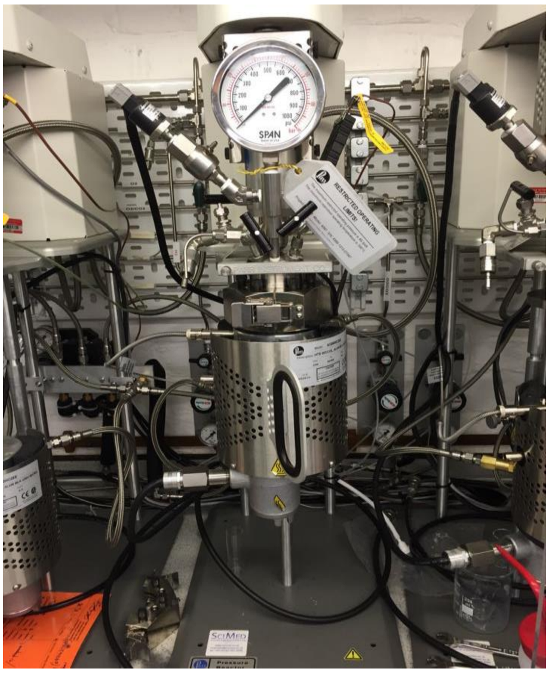


Fig. 2.1 Parr stainless steel autoclave for direct synthesis of hydrogen peroxide and benzyl alcohol oxidation

2.3 Catalyst Preparation

Many kinds of titania or activated carbon supported monometallic gold or palladium and bimetallic gold-palladium catalysts were prepared using impregnation, deposition-precipitation and sol-immobilization. The catalysts were evaluated for CO oxidation, the direct synthesis of hydrogen peroxide and benzyl alcohol oxidation by in situ generated hydrogen peroxide.

2.3.1 Conventional Wet Impregnation (CIm) (Figure 2.2)

Catalyst (2 g) for each batch was prepared by this method. For 2.5wt%Au-2.5wt%Pd/TiO_2 or carbon, 0.083g $PdCl_2$ powder was dissolved into 4.08ml $HAuCl_4$ solution with 12.25g Au in 1000ml water, kept stirring and heated to 80°C until all the $PdCl_2$ dissolved. Then 1.9g support (titania or activated carbon) was added into the solution with stiring at 80°C until a paste of mixture formed. The mixture was then dried (110°C, 16 h), and finally calcined (400°C, 3 h, heating rate is 20°C per min). The monometallic Au or Pd and different ratios of Au and Pd bimetallic catalysts, were prepared with same procedure.

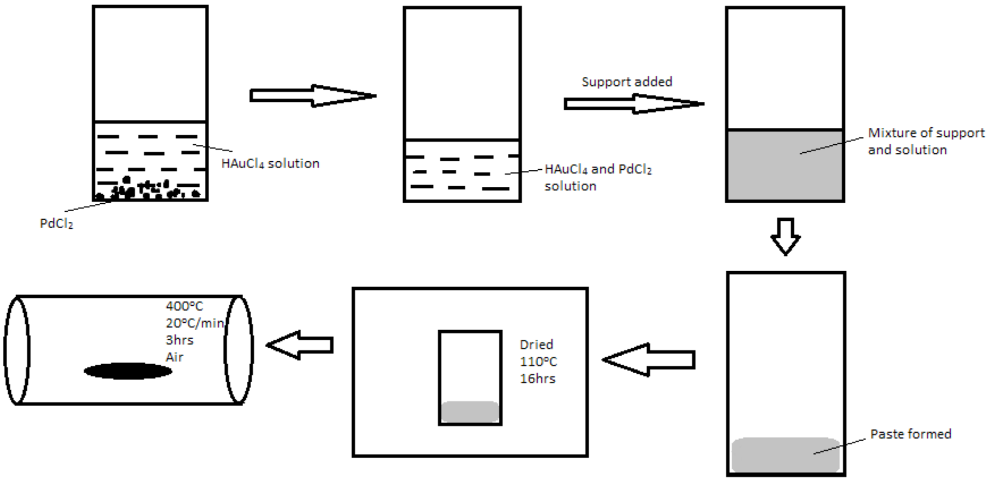


Fig. 2.2 Procedure of conventional wet impregnation for supported gold-palladium catalyst

2.3.2 Modified Impregnation (MIm)

1wt%AuPd/TiO_2 (different mole ratios), 1wt%Au/TiO_2 and 1wt%Pd/TiO_2 prepared by this method are described as follows: A certain amount of $HAuCl_4$ (12.5g/L) and $PdCl_2$ (8.6g/L) solutions with 0.58M HCl were mixed. Deionized water was used to adjust the suitable volume of solution. This solution was heated at a temperature of 60^{o}C for 10min with stirring (1000 rpm). The support was added gradually over 10-15 min into the solution until a homogeneous mixture was formed. The temperature was raised to 95 ^{o}C with stirring 16 h, and a dried solid was produced. This was then ground with a mortar and finally heat-treated. There were two kinds of heat-treatments for the samples. One is to calcine it in the air, which is the same as that in conventional wet impregnation procedure (Figure 2.3), and the other is to reduce the sample in the 5% H_2/Ar at 400 ^{o}C for 4 h with a rate of 10 ^{o}C/min (Figure 2.4).

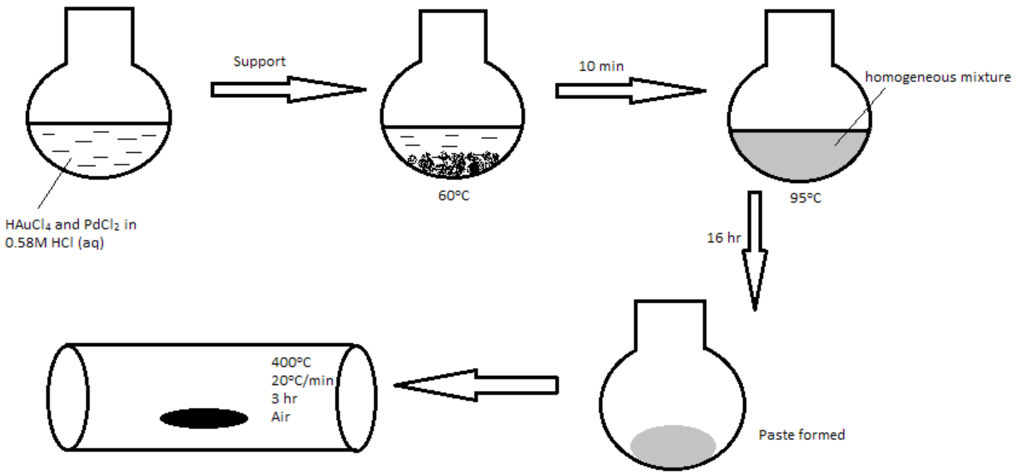


Fig. 2.3 Procedure of modified impregnation with reduction (MIm) for supported gold-palladium catalyst

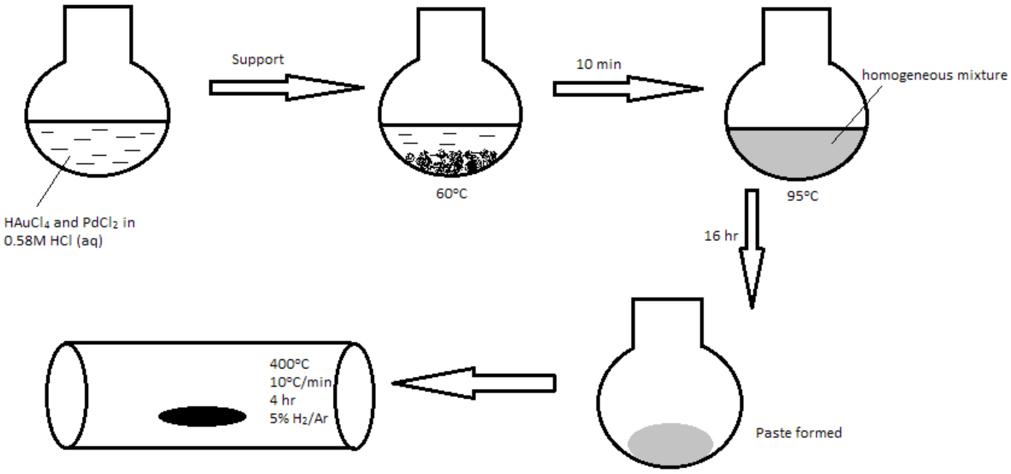


Fig. 2.4 Procedure of modified impregnation with calcination (MIm.cal) for supported gold-palladium catalyst

2.3.3 Deposition-Precipitation (DP)

A mixture of titania in water (pH = 3) was heated with stirring to 60 ^{o}C, then adjust dropwise the pH value was adjusted to 8.0 with 1M sodium carbonate. Gold solution (12.25 mg Au/L) was added into the mixture meanwhile keeping the pH at 8. The slurry was maintained at pH 8 and stirred at 60^{o}C for 1.5h.Then deionized water (2 L) was used to wash the catalyst by filtration for several times until pH value of the filterate to neutral (Figure 2.5). The solid obtained was treated in three different ways: drying at room temperature, drying at 110^{o}Cfor 16h in an oven and calcined it at 400 ^{o}C for 3h after drying at 110^{o}C.

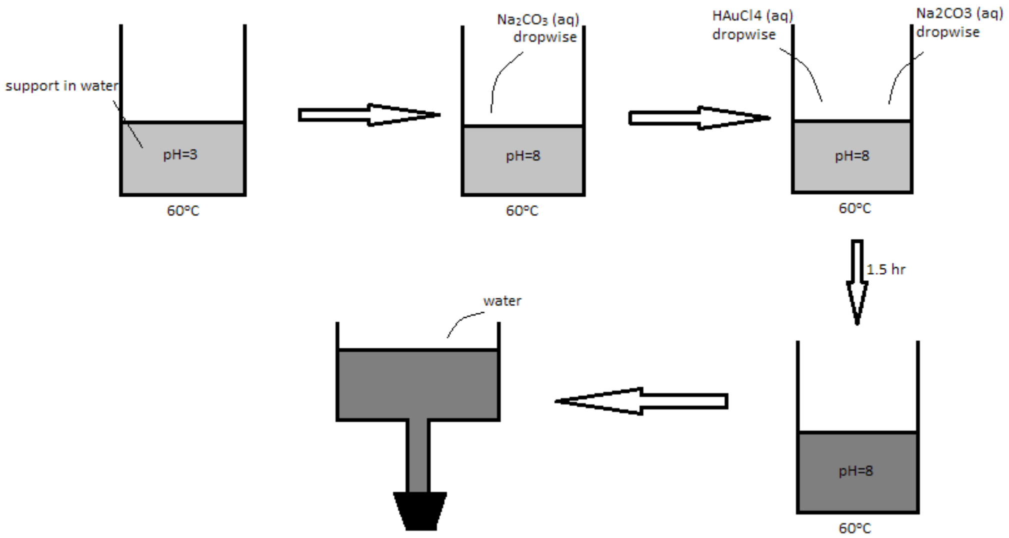


Fig. 2.5 Procedure of deposition-precipitation for supported gold catalyst

2.3.4 Sol-immobilization (SIm)

For bimetallic gold-palladium supported catalysts (Figure 2.6), gold and palladium precursor solutions were mixed and then a protecting agent, 1% polyvinyl alcohol (PVA), was added which prevented particle aggregation. Sodium borohydride (0.1 M $NaBH_4$), which was used as the reducing agent, and this was added to form the metal sol. After 30 min, the support was added and the metal sol was deposited onto the support at pH = 1-2, and the pH adjustment was carried out using H_2SO_4. Filtration was required for washing to remove the protecting agent, PVA. Finally, the solid was dried in an oven at 110 ^oC for 16 h in static air.

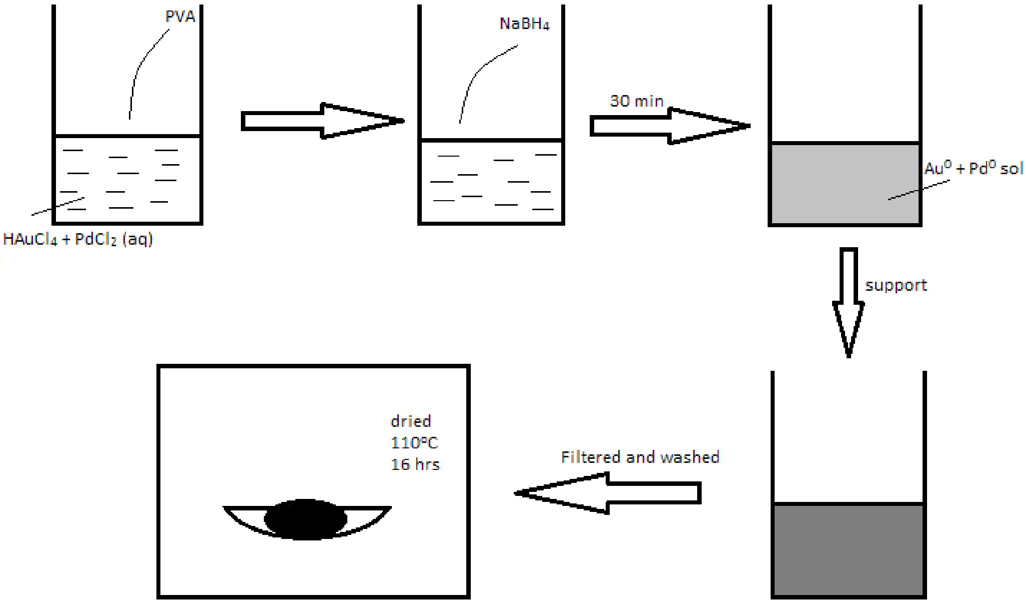


Fig. 2.6 Procedure of sol-immobilization for supported gold-palladium catalyst

2.4 Catalyst Testing

2.4.1 CO Oxidation

The CO oxidation was carried out at room temperature and catalyzed by 5 wt% Au/TiO_2. The main process is shown in Figure 2.7. Catalyst (50 mg) was loaded at one inlet of the U-shaped reactor by glass wool. The reactor was setup in the 25 °C water bath and connected to the m-line GC machine. CO (5000ppm in synthetic air) with a controlled the flow rate of 21 ml/min was used for all experiments. In each catalyst test, it was necessary to run 20 to 30 times to get a line graph to see both the stability and activity of one catalyst. The CO conversion data was obtained by Gas Chromatography and determined according to Equation 2.1.

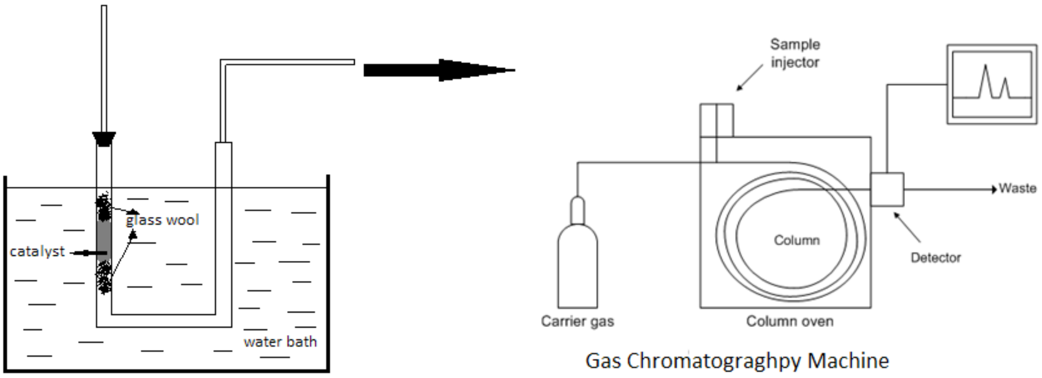


Fig. 2.7 Device of CO oxidation and GC analysis

$$\text{CO conversion }(\%) = \frac{\text{Counts}_{\text{CO2}}}{\text{Counts}_{\text{standard}}} \times 100\%$$

(Equation 2.1)

2.4.2 Standard Hydrogen Peroxide Synthesis

The direct synthesis of hydrogen peroxide was carried out in a Parr stainless steel autoclave. For the standard reaction conditions, water (2.9 g HPLC grade) and methanol (5.6 g) were added into the reactor (8.5 g solvent in total). Then catalyst (10 mg) was added. 5% H_2/CO_2 (3 Mpa) was added into the reactor for three times, which was for removing any air in the reactor, then 5% H_2/CO_2 (2.9 MPa) and 25% O_2/CO_2 (1.1 MPa) (below the explosion concentration) was charged to the reactor. Then the reaction was started after cooling down to 2 ^{o}C at 1200 rpm stirring speed. After 30 min reaction duration, the pressure was let down, and the liquid produced was recovered after filtration to remove the catalyst. We measured 1 to 2 g of product solution with adding of several drops of sulfuric acid to stabilize the produced hydrogen peroxide. The productivity and weight percent of hydrogen peroxide were identified by titration of acidified $Ce(SO_4)_2$ standard solution. The color change of ferroin indicator ($(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ solution) was used to determine the adding amount of titration solution (Equation 2.2).

$2Ce^{4+} + H_2O_2 = 2Ce^{3+} + 2H^+ + O_2$ (Equation 2.2)

$$\text{titrated volume of } Ce^{4+} \text{ for whole (ml)} = \frac{\text{titrated volume of } Ce^{4+} \text{ for part of product (ml)} \times 8.5\ (g)}{\text{Mass of part of product (g)}}$$

(Equation 2.3)

$$\text{Moles of } H_2O_2 = \frac{\text{Moles of } Ce^{4+}}{2} = \frac{\text{titrated volume } Ce^{4+} \text{ of for whole (ml)} \times [Ce^{4+}](\text{mol} \cdot L^{-1})}{2 \times 1000}$$

(Equation 2.4)

$$\text{Weight percent of } H_2O_2 = \frac{\text{Moles of } H_2O_2 \times MH_2O_2\ (34.04\ g \cdot ml^{-1})}{8.5\ (g)} \times 100\%$$

(Equation 2.5)

$$\text{Productivity of } H_2O_2\left(\text{mol}_{H_2O_2} \cdot kg^{-1}_{\text{cat.}} \cdot h^{-1}\right) = \frac{\text{moles of } H_2O_2}{10 \times 10^{-6}(kg) \times 0.5hr}$$

(Equation 2.6)

The blank tests with no catalyst, which used the same procedure as described above, were also processed to see if the reactor was clean or not. If a blank reaction was observed, then the reactor was washed with hot water several times.

2.4.3 Benzyl Alcohol Oxidation Using In Situ Generated H_2O_2 from Hydrogen and Oxygen

The oxidation of benzyl alcohol using hydrogen and oxygen to form H_2O_2 in situ was also carried out in a Parr Instruments stainless steel autoclave. Catalyst (10 mg) was added into the reactor together with benzyl alcohol (1 ml as reagent) and methanol (9 ml as solvent).The autoclave was purged three times with 5% H_2/CO_2 (100psi) before introducing 5% H_2/CO_2(420psi) and 25% O_2/CO_2(160psi). For the reaction conditions, there were some variables which have been investigated (Table 2.1). The reaction was started before adjusting to required temperature. The stirrer was activated to 1200 rpm to run the reaction for required reaction time length. After the reaction, the product was filtered to remove the catalyst. Finally, the GC analysis was used to calculate the benzyl alcohol conversion and the selectivity of the target product, benzaldehyde. The preparation of the GC sample is shown as follows: product (0.5 ml) was mixed with a standard liquid, mesitylene (0.5 ml), in a vial. Standing the sample for some time to make sure the solution was mixed completely. To calculate the GC results, a series of standard mixture for each material, which had been made before, were used. The process of making standard samples is shown below (table 2.2 and Figure 2.8). The slopes of lines showed the factors in calculations.

Variables	Conditions
Reaction Temperature	25 ^oC, 50 ^oC, 75 ^oC
Reaction duration time	0.5 h, 2 h

Table 2.1 condition variables for benzyl alcohol oxidation by generated hydrogen peroxide

Standard solutions	Material contents (wt%)		
	Benzyl alcohol	Benzaldehyde	Toluene
1	90	5	5
2	5	90	5
3	5	5	90
4	50	25	25
5	25	50	25
6	25	25	50

Table 2.2 Standard solutions and their contents

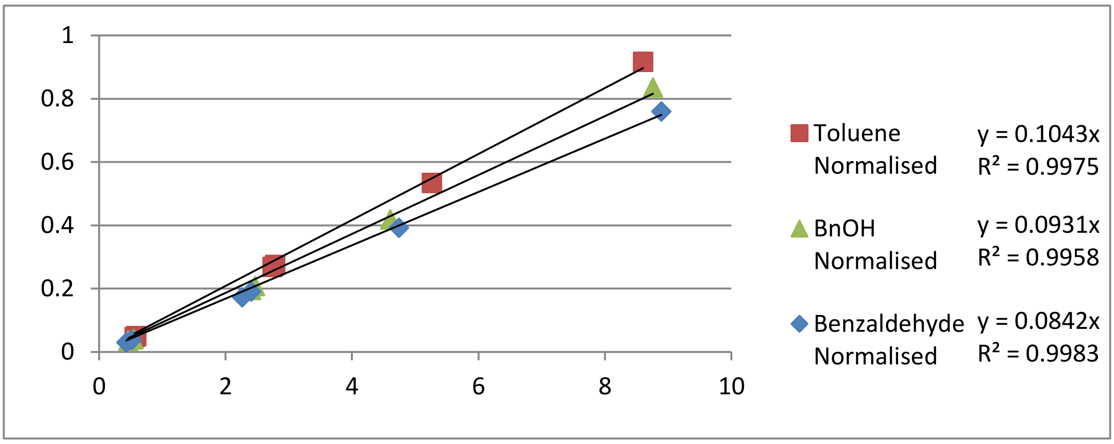


Fig. 2.8 Standard analysis for three main materials in product solution and their slopes (Slope$_{\text{benzyl alcohol}}$: 0.093; Slope$_{\text{benzaldehyde}}$: 0.084; Slope$_{\text{toluene}}$: 0.104)

Blank tests, in which nitrogen was used instead of 5 % H_2/CO_2, were also processed in the same way of standard reaction conditions. The purposes for the blank tests are to investigate the reactivity of oxygen only and influence of the hydrogen addition. In detail, from the results of blank tests, we can observe if there is any benzyl alcohol converted. Moreover, based on the difference of results between standard tests and blank tests, we can determine how much the reaction activity increases or decreases, so the role of hydrogen can be investigated.

Chapter 3. Standard Direct Synthesis of Hydrogen Peroxide and CO oxidation by Gold-Palladium Catalysis

3.1 Introduction

Hydrogen peroxide production and CO oxidation using prepared Au-Pd bimetallic catalysts was used as training for the experimental basis of benzyl alcohol oxidation by in situ generated hydrogen peroxide. In detail, the prepared impregnated Au-Pd catalysts was proven to be catalytically active for hydrogen peroxide synthesis; and the carbon monoxide oxidation at room temperature can be reactively catalyzed by gold catalysts.

3.2 The Standard Direct Synthesis of Hydrogen Peroxide by Conventional Impregnated Gold-Palladium Bimetallic Catalysts

The productivities of hydrogen peroxide by 2.5 wt% Au-2.5 wt% Pd supported by titania and activated carbon are known to be 64 mol • kg^{-1} • h^{-1} and 110 mol • kg^{-1} • h^{-1} respectively[1] when tested under the standard reaction conditions. Some batches of the catalysts were prepared for repeat experiments.

3.2.1 Productivity of Hydrogen Peroxide by 2.5 wt% Au-2.5 wt% Pd/TiO_2 by Conventional Impregnation

Batch number of 2.5 wt% Au-2.5 wt% Pd/TiO_2	Productivity of H_2O_2($mol_{H2O2} kg_{cat}^{-1} h^{-1}$)
1	95
1	114

Table 3.1 Productivities of hydrogen peroxide by Batch No.1 of 2.5 wt% Au-2.5 wt% Pd/TiO_2 (conditions: 5.6 g methanol, 2.9 g water, 0.01 g catalyst, 2.9 MPa 5% H_2/CO_2 and 1.1 MPa 25% O_2/CO_2, 2°C, 1200 rpm, 30 min)

The productivities at the beginning were higher than the published standard result (64mol_{H2O2} $kg_{cat}^{-1}h^{-1}$).

Batch number of 2.5 wt% Au-2.5 wt% Pd/TiO_2	Productivity of H_2O_2($mol_{H2O2} kg_{cat}^{-1} h^{-1}$)
2	66
2	82
2	93
2	68
2	88
2	95
2	90
2	95

Table 3.2 Productivities of hydrogen peroxide by Batch No.2 of 2.5 wt% Au-2.5 wt% Pd/TiO_2 (conditions: 5.6 g methanol, 2.9 g water, 0.01 g catalyst, 2.9 MPa 5% H_2/CO_2 and 1.1 MPa 25% O_2/CO_2, 2°C, 1200 rpm, 30 min)

The results obtained of batch 2 which were closer to the standard productivity. During the reaction with Batch No.2 catalyst, it was found that the cleaning of reactor was important. Leached metal particles might stay on the wall of a dirty reactor, which could cause the change of results. So a rewash by hot water was required to keep the reactor and liner clean before the next running of the reaction.

Batch number of 2.5 wt% Au-2.5 wt% Pd/TiO_2	Productivity of H_2O_2($mol_{H2O2}kg_{cat}^{-1}h^{-1}$)
3	99
3	97
3	97

Table 3.3 Productivities of hydrogen peroxide by Batch No.3 of 2.5 wt% Au-2.5 wt% Pd/TiO_2 (conditions: 5.6 g methanol, 2.9 g water, 0.01 g catalyst, 2.9 MPa 5% H_2/CO_2 and 1.1 MPa 25% O_2/CO_2, 2^{o}C, 1200 rpm, 30 min)

Batch number of 2.5 wt% Au-2.5 wt% Pd/TiO_2	Productivity of H_2O_2($mol_{H2O2}kg_{cat}^{-1}h^{-1}$)
4	86
4	92
4	88

Table 3.4 Productivities of hydrogen peroxide by Batch No.4 of 2.5 wt% Au-2.5 wt% Pd/TiO_2 (conditions: 5.6 g methanol, 2.9 g water, 0.01 g catalyst, 2.9 MPa 5% H_2/CO_2 and 1.1 MPa 25% O_2/CO_2, 2^{o}C, 1200 rpm, 30 min)

Batch number of 2.5 wt% Au-2.5 wt% Pd/TiO_2	Productivity of H_2O_2($mol_{H2O2}kg_{cat}^{-1}h^{-1}$)
5	83
5	82

Table 3.5 Productivities of hydrogen peroxide by Batch No.5 of 2.5 wt% Au-2.5 wt% Pd/TiO_2 (conditions: 5.6 g methanol, 2.9 g water, 0.01 g catalyst, 2.9 MPa 5% H_2/CO_2 and 1.1 MPa 25% O_2/CO_2, 2^{o}C, 1200 rpm, 30 min)

As more batches of catalysts were prepared, results were obtained that were more consistent and close to the published data of the catalysts.

3.2.2 Productivity of Hydrogen Peroxide by 2.5 wt% Au-2.5 wt% Pd/Carbon by Conventional Impregnation

Activated carbon (G-60) was also used as a support to prepare the bimetallic catalysts for this reaction (Table 3.6). The productivity of hydrogen peroxide (112-113 $mol_{H2O2}kg_{cat}^{-1}h^{-1}$) was close to that on papers (110 $mol_{H2O2}kg_{cat}^{-1}h^{-1}$)[1].

Batch number of 2.5 wt% Au-2.5 wt% Pd/TiO_2	Productivity of H_2O_2($mol_{H2O2}kg_{cat}^{-1}h^{-1}$)
1	113
1	112

Table 3.6 Productivities of hydrogen peroxide by Batch No.1 of 2.5 wt% Au-2.5 wt% Pd/Carbon (conditions: 5.6 g methanol, 2.9 g water, 0.01 g catalyst, 2.9 MPa 5% H_2/CO_2 and 1.1 MPa 25% O_2/CO_2, 2°C, 1200 rpm, 30 min)

3.2.3 Conclusion and Discussion

The bimetallic Au-Pd catalysts are active for the direct synthesis of hydrogen peroxide. But for the titania supported catalysts, there might be some metal leaching during the reaction, which caused the results obtained to be higher than the expected value, and larger productivities of next run because of the contaminated reactor. Compared with titania, activated carbon gave a better interaction with metals, and caused less leaching. So the standard results could be easily repeated. According to the leaching of metal particles, a second washing process was required after one run. A completely clean reactor helped in getting the accurate results.

3.3 Carbon Monoxide Oxidation by Gold Catalysis

The low-temperature CO oxidation processed by traditional deposition-precipitation 5 wt% Au/TiO_2 with three heat treatments: dried at 25 °C for 16 h, dried at 110 °C for 16 h and calcined at 400 °C for 3 h in the air after 16 h drying at 110 °C (Figure 3.1).

For comparison, 1 wt% Au/TiO_2, 0.1 wt% Au/TiO_2 and TiO_2 (Figure 3.2) only were also investigated in this reaction. In Figure 3.1 c), we can observe that there was no obvious difference between my result (42 %) and that according to the published data (40 %)[2] by using 5 wt% calcined gold loading titania catalyst.

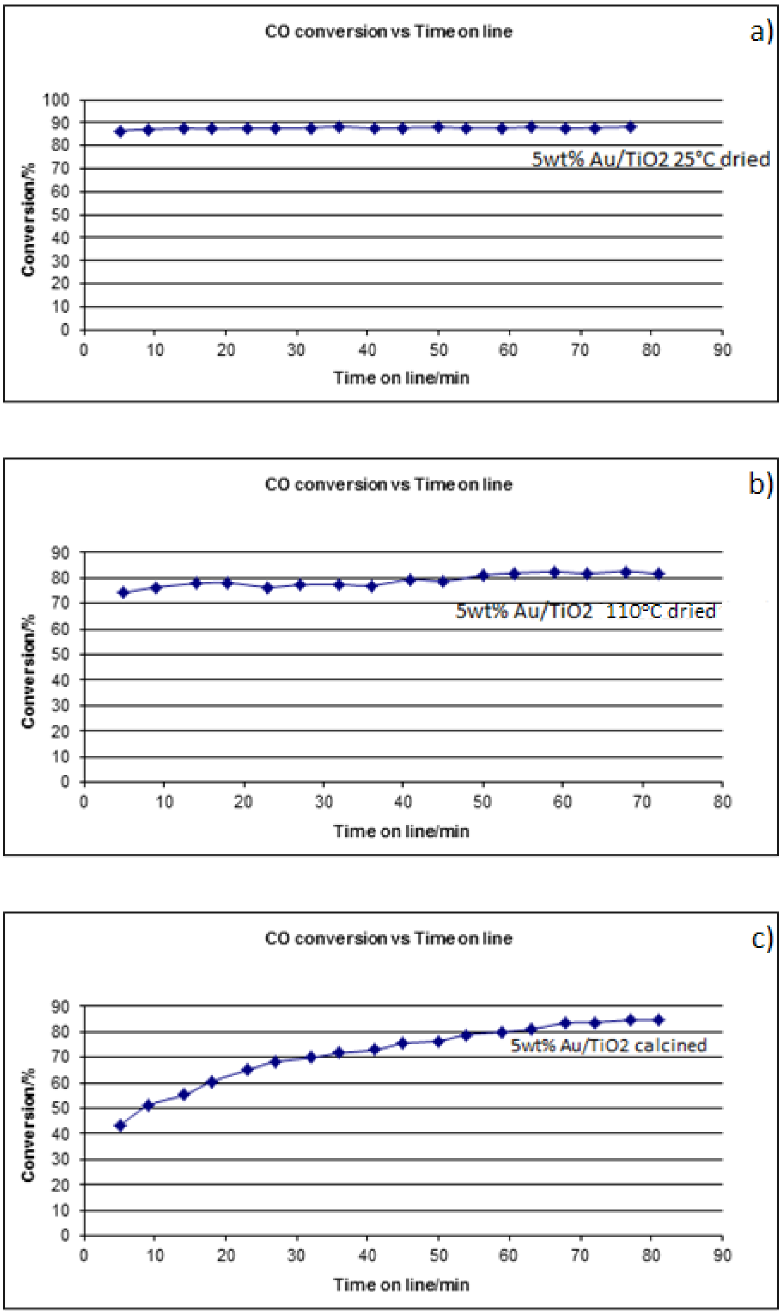
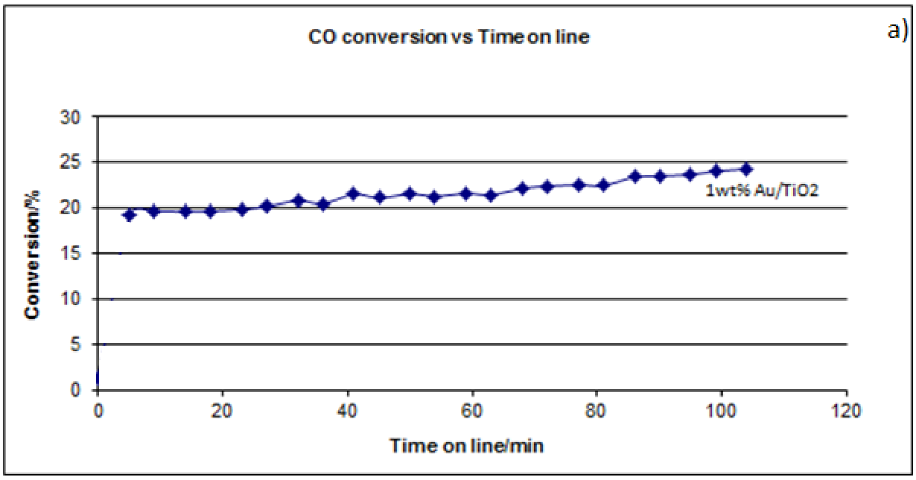
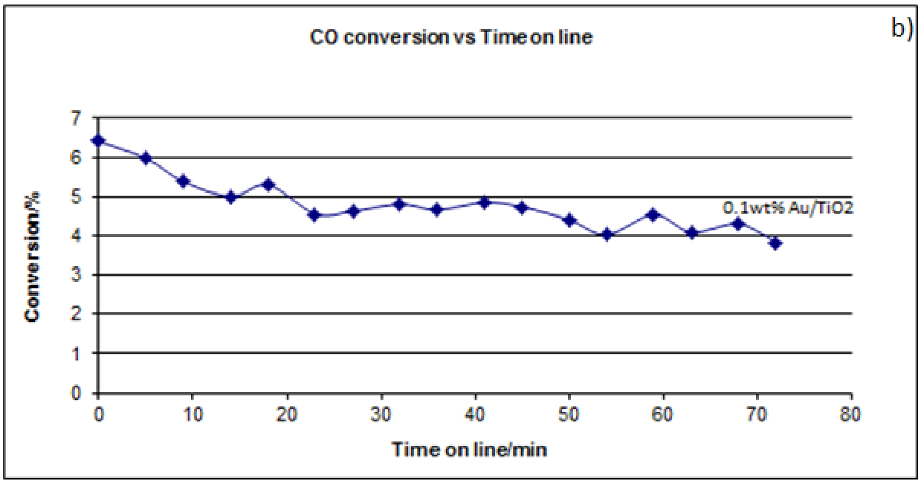


Fig. 3.1 CO conversion (to CO_2) versus Time on line by DP 5 wt% Au/TiO_2 with a) drying at 25 °C, b) drying at 110 °C and c) calcined after drying at 110 °C (conditions: 25 °C, 4 min, 21 ml/min)





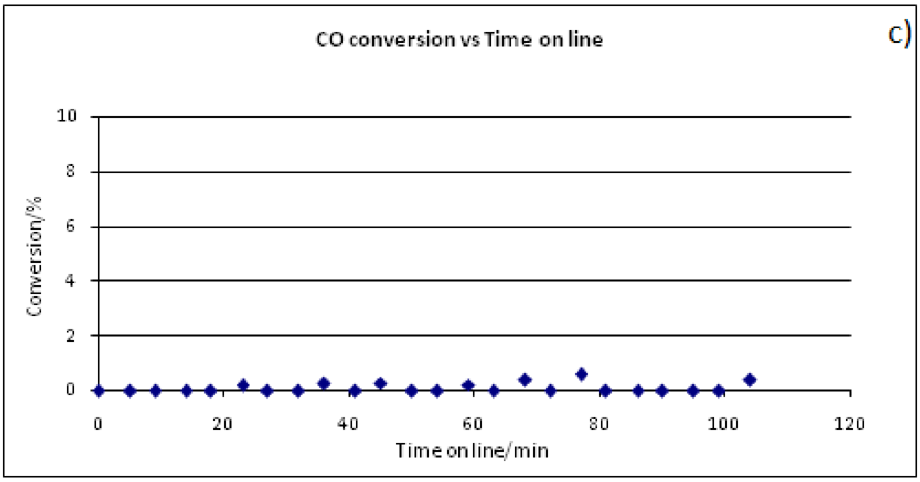


Fig. 3.2 CO conversion (to CO_2) versus Time on line by a) calcined 1 wt% Au/TiO_2, b) calcined 0.1 wt% Au/TiO_2 and c) calcined TiO_2 only (conditions: 25 °C, 4 min, 21 ml/min)

3.3.1 CO Oxidation Processed by DP Catalysts with Different Gold Loadings

The CO conversion at room temperature of 25 ^{o}C using dried 5wt%Au/TiO_2 could be stabilized at nearly 90% for the whole period of the reaction. A similar situation arose for those catalysts dried at 110 ^{o}C, the CO conversions were always as high as 80 %. However, the CO conversion of the calcined 5wt%Au/TiO_2 could reach over 80% after several cycles of reaction with only 42 % CO at the first run. Different metal loadings could be a major factor which can control the CO conversion (Figure 3.3). There was a very huge decrease with the less metal loading of the catalysts.

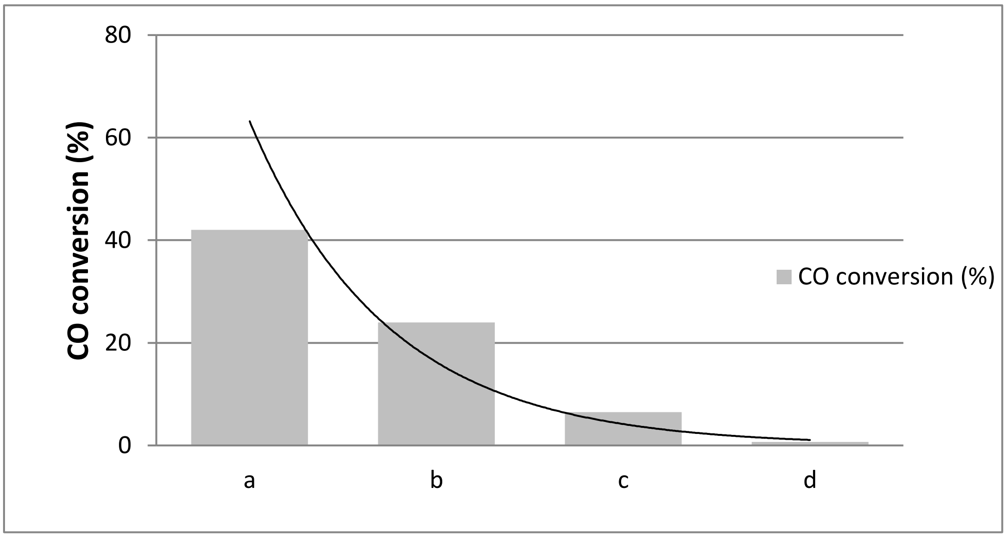


Fig. 3.3 Comparison of CO conversions (to CO_2) by different metal loadings of catalysts: a) calcined 5 wt% Au/TiO_2, b) calcined 1 wt% Au/TiO_2, c) calcined 0.1 wt% Au/TiO_2 and c) calcined TiO_2 only (conditions: 25 ^{o}C, 4 min, 21 ml/min)

3.3.2 Conclusion

The room-temperature CO oxidation can be catalyzed by gold catalysts, but different gold loadings of those DP titania supported catalysts with same treatments lead to various CO conversions to CO_2. A higher gold loading results in higher conversion, that is 5 wt% Au/TiO_2 could convert over 80 % of CO, whereas TiO_2 only with no metal showed the lowest activity. As for the 5 wt% Au/TiO_2, heat-treatments have little influence on the results, with all three catalysts by different heat treatments showing high CO conversion and stability after cycles of reaction.

Reference

1. J. K. Edwards, A. F. Carley, A. A. Herzing, C. J. Kiely, G. J. Hutchings, Faraday Discuss., 2008, 138, 225-239.
2. J. K. Edwards, B. E. Solsona, P. Landon, A. F. Carley, A. Herzing, C. J. Kiely, G. J. Hutchings, Journal of Catalysis, 2005, 236, 69-79.

Chapter 4. In-situ Oxidation of Benzyl Alcohol by In Situ Generated Hydrogen Peroxide

4.1 Introduction

As shown in Chapter 3, the catalytic activity of gold-palladium catalysts has been successfully demonstrated in both hydrogen peroxide synthesis and room-temperature CO oxidation. The further research is to oxidize a commonly used organic chemical, benzyl alcohol, by a mixture of hydrogen and oxygen in one step.

Both 5 wt% Au/TiO_2 prepared by DP, which was tested in CO oxidation, and the bimetallic 1 wt% AuPd/TiO_2 prepared by conventional wet impregnation, which is active for production of H_2O_2, were tested initially. Afterwards, the variables of reaction conditions and improvements of catalyst preparation method were investigated to get higher benzyl alcohol conversion and selectivity of the target product, benzaldehyde.

The main drawback of this reaction was to determine how to shut down the side reactions, and in the meantime, keep considerable conversion of benzyl alcohol. In another word, we want as higher benzaldehyde yield as possible. Since the combination of the generation of H_2O_2 and its utilization in the oxidation of benzyl alcohol is complicated, it is not possible to deduce the most beneficial reaction conditions and catalysts, hence they need to be tried at the beginning of the investigation based on the previous reports of benzyl alcohol oxidation by pure oxygen and direct synthesis of hydrogen peroxide.

4.2 DP Prepared Gold Catalysts for Benzyl Alcohol Oxidation

The 5 wt% Au/TiO_2, which had a good performance in room-temperature CO oxidation, seemed not as active as expected for benzyl alcohol oxidation (Table 4.1). Although both batches of this DP catalyst showed considerable selectivity of benzaldehyde, there was little benzyl alcohol converted during the reaction.

Batch No. of 5 wt% Au/TiO_2 (DP)	Conversion (%)	Selectivity (%)	
	Benzyl Alcohol	Benzaldehyde	Toluene
1	1.6	82	15
2	1.4	95	3

Table 4.1 BA conversion and selectivity of main products by DP 5 wt% Au/TiO_2 (conditions: 0.01 g catalyst, 1 ml BA and 9 ml methanol, 420psi 5%H_2/CO_2 and 160psi 25%O_2/CO_2, 50 ^oC, 30 min reaction duration)

4.3 TiO_2 Supported Au-Pd Catalysts Prepared by Conventional Wet Impregnation (CIm) for Benzyl Alcohol Oxidation

4.3.1 Advantages of Impregnated Bimetallic Catalysts

Compared with the DP prepared catalysts, the titania supported Au-Pd bimetallic catalyst performed much better under the same reaction conditions (Table 4.2), even though the Au-Pd catalyst had a lower metal loading of only 1 wt%.

Catalysts	Conversion (%)	Selectivity (%)		Yield (%)
	Benzyl Alcohol	Benzaldehyde	Toluene	Benzaldehyde
5 wt% Au/TiO_2[a]	1.6	82	15	1.3
1 wt% AuPd/TiO_2[b]	3.5	98	1	3.4

[a], Catalyst prepared by deposition-precipitation (DP)

[b], Catalyst prepared by wet impregnation (CIm)

Table 4.2 Comparison of BA conversion and selectivity of main products by DP 5 wt% Au/TiO_2 and CIm 1 wt% AuPd/TiO_2 (conditions: 0.01 g catalyst, 1 ml BA and 9 ml methanol, 420psi 5%H_2/CO_2 and 160psi 25%O_2/CO_2, 50 °C, 30 min reaction duration)

4.3.2 Investigation of the Reaction Conditions

4.3.2.1 Reaction Duration Effect

To detect the best yields of benzaldehyde for the benzyl alcohol (BA) oxidation using in situ generated hydrogen peroxide, the effect of reaction time was firstly investigated at 25°C, 50°C and 75°C with CIm 1 wt% Au-Pd/TiO_2 as the catalyst. The reactions were carried out for two different periods of time, 0.5 h and 2 h, to investigate how this factor influenced the results (Table 4.3, 4.4 and 4.5, Figure 4.1, 4.2 and 4.3). At all these three temperatures (25°C, 50°C and 75°C), similar trends were found, which are that the longer reaction time leads to an increase in benzyl alcohol conversion and benzaldehyde selectivity without obvious differences in the benzaldehyde selectivity.

Duration	BA	Benzaldehyde	
		Selectivity (%) [a]	Yield (%) [a]
(h)	Conversion (%) [a]		
0.5	1.5	97.8	1.5
2	1.8	98.8	1.8

[a],Tested under room temperature (25 °C)

Table 4.3 BA conversion, benzaldehyde selectivity and yield under the condition of room temperature (conditions: 0.01 g CIm 1 wt% Au-Pd/TiO_2 catalyst, 1ml benzyl alcohol and 9ml methanol, 420psi 5%H_2/CO_2 and 160psi 25%O_2/CO_2, 25 °C)

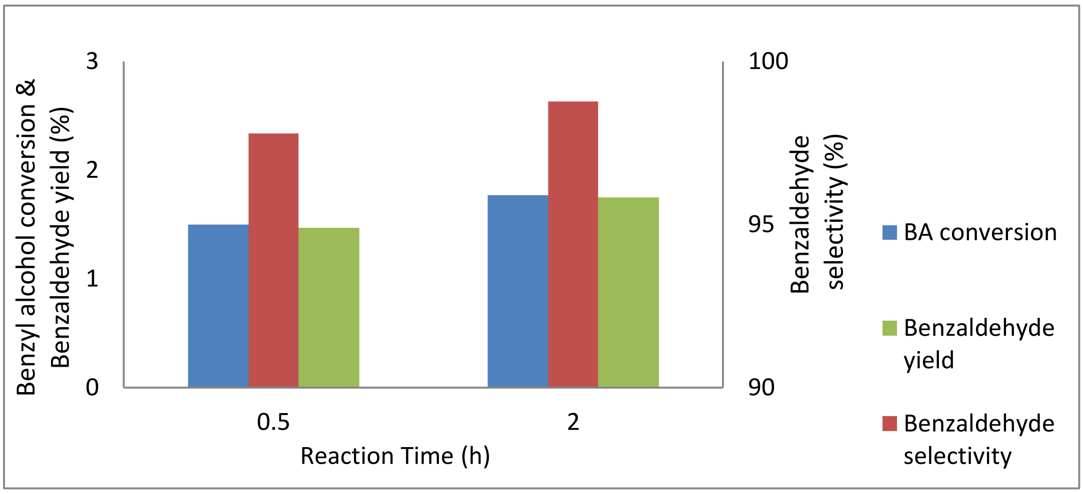


Fig. 4.1 Trend of BA conversion, benzaldehyde selectivity and yield versus reaction time under the condition of room temperature (conditions: 0.01 g CIm 1 wt% Au-Pd/TiO_2 catalyst, 1ml benzyl alcohol and 9ml methanol, 420psi 5%H_2/CO_2 and 160psi 25%O_2/CO_2, 25 °C)

Duration	BA	Benzaldehyde	
		Selectivity (%) [b]	Yield (%) [b]
(h)	Conversion (%) [b]		
0.5	3.5	98.5	3.5
2	4.0	98.7	4.0

[b],Tested under 50 °C

Table 4.4 BA conversion, benzaldehyde selectivity and yield under the condition of 50 °C (conditions: 0.01 g CIm 1 wt% Au-Pd/TiO_2 catalyst, 1ml benzyl alcohol and 9ml methanol, 420psi 5%H_2/CO_2 and 160psi 25%O_2/CO_2, 50 °C)

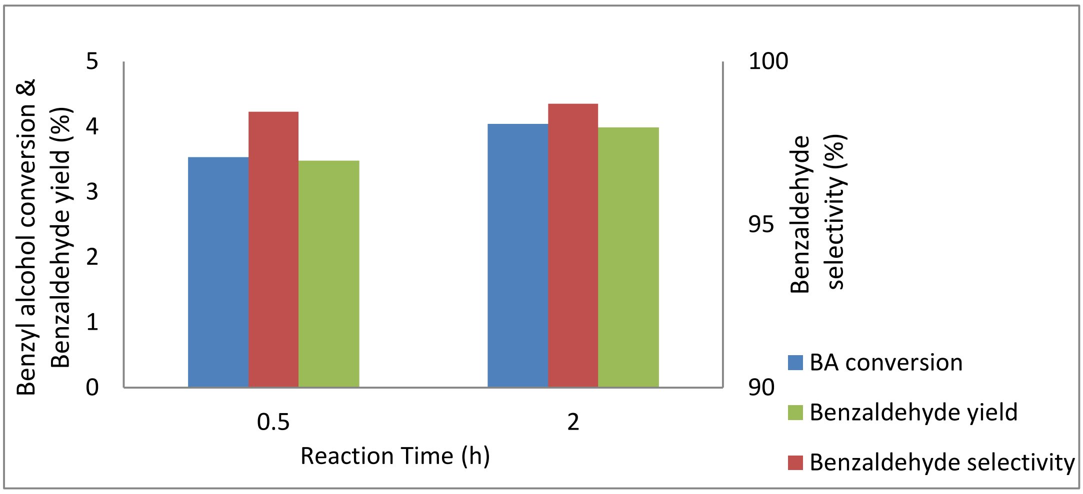


Fig. 4.2 Trend of BA conversion, benzaldehyde selectivity and yield versus reaction time under the condition of 50 °C (conditions: 0.01 g CIm 1 wt% Au-Pd/TiO_2 catalyst, 1ml benzyl alcohol and 9ml methanol, 420psi 5%H_2/CO_2 and 160psi 25%O_2/CO_2, 50 °C)

Duration	BA	Benzaldehyde	
		Selectivity (%) ^{c}	Yield (%) ^{c}
(h)	Conversion (%) ^{c}		
0.5	9.0	99.0	8.9
2	18.6	99.0	18.4

^{c},Tested under 75 °C

Table 4.5 BA conversion, benzaldehyde selectivity and yield under the condition of 75 °C (conditions: 0.01 g CIm 1 wt% Au-Pd/TiO_2 catalyst, 1ml benzyl alcohol and 9ml methanol, 420psi 5%H_2/CO_2 and 160psi 25%O_2/CO_2, 75 °C)

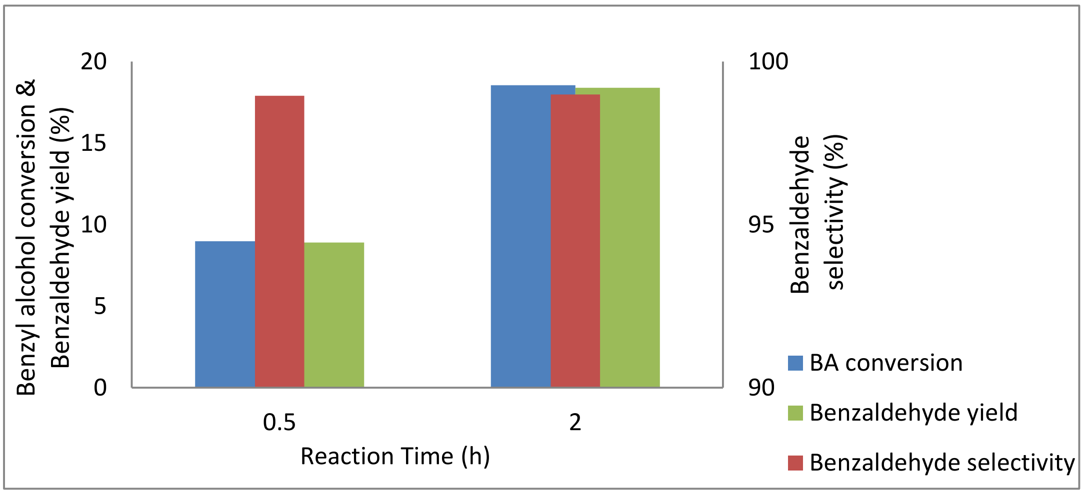


Fig. 4.3 Trend of BA conversion, benzaldehyde selectivity and yield versus reaction time under the condition of 75 °C (conditions: 0.01 g CIm 1 wt% Au-Pd/TiO_2 catalyst, 1ml benzyl alcohol and 9ml methanol, 420psi 5%H_2/CO_2 and 160psi 25%O_2/CO_2, 75 °C)

4.3.2.2 Effect of Reaction Temperature

Comparing the results at 25 °C, 50 °C and 75 °C, the effect of the reaction temperature was observed for both 0.5 h and 2 h (Table 4.6 and 4.7, Figure 4.4 and 4.5). A similar trend to that of a longer reaction time appeared, which was that high temperature led to more benzyl alcohol conversion and benzaldehyde yield.

Temperature (°C)	BA Conversion (%) [a]	Benzaldehyde	
		Selectivity (%) [a]	Yield (%) [a]
25	1.5	97.8	1.5
50	3.5	98.5	3.5
75	9.0	99.0	8.9

[a], tested for 0.5 h

Table 4.6 BA conversion, benzaldehyde selectivity and yield run for 0.5 h (conditions: 0.01 g CIm 1 wt% Au-Pd/TiO_2 catalyst, 1ml benzyl alcohol and 9ml methanol, 420psi 5%H_2/CO_2 and 160psi 25%O_2/CO_2, 0.5 h)

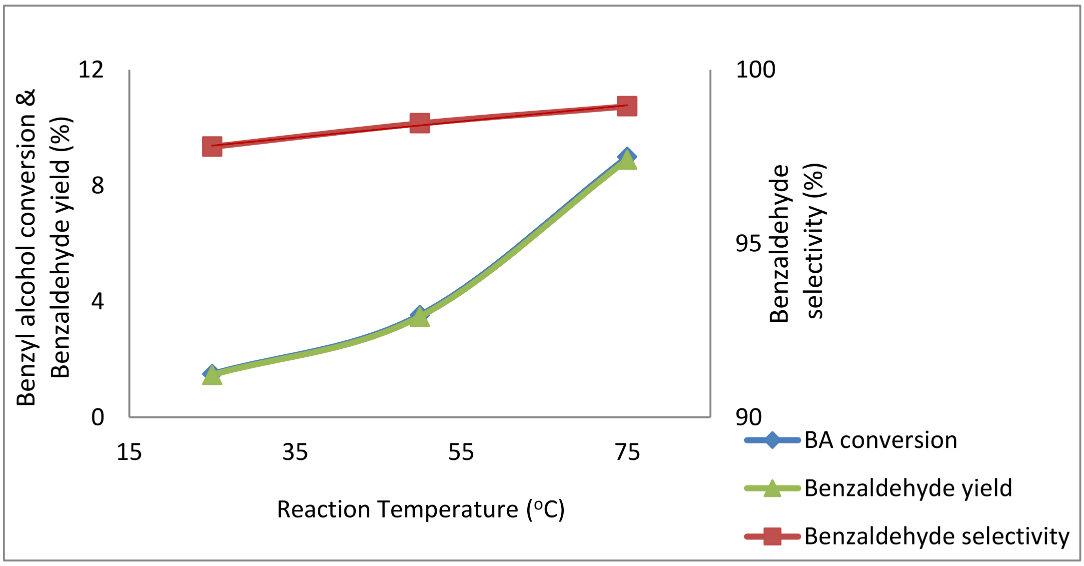


Fig. 4.4 Trend of BA conversion, benzaldehyde selectivity and yield versus reaction temperature run for 0.5 h (conditions: 0.01 g CIm 1 wt% Au-Pd/TiO_2 catalyst, 1ml benzyl alcohol and 9ml methanol, 420psi 5%H_2/CO_2 and 160psi 25%O_2/CO_2, 0.5 h)

Temperature (^oC)	BA Conversion (%) [b]	Benzaldehyde Selectivity (%) [b]	 Yield (%) [b]
25	1.8	98.8	1.8
50	4.0	98.7	4.0
75	18.6	99.0	18.4

[b], tested for 2 h

Table 4.7 BA conversion, benzaldehyde selectivity and yield run for 2 h (conditions: 0.01 g catalyst, 1ml benzyl alcohol and 9ml methanol, 420psi 5%H_2/CO_2 and 160psi 25%O_2/CO_2, 2 h)

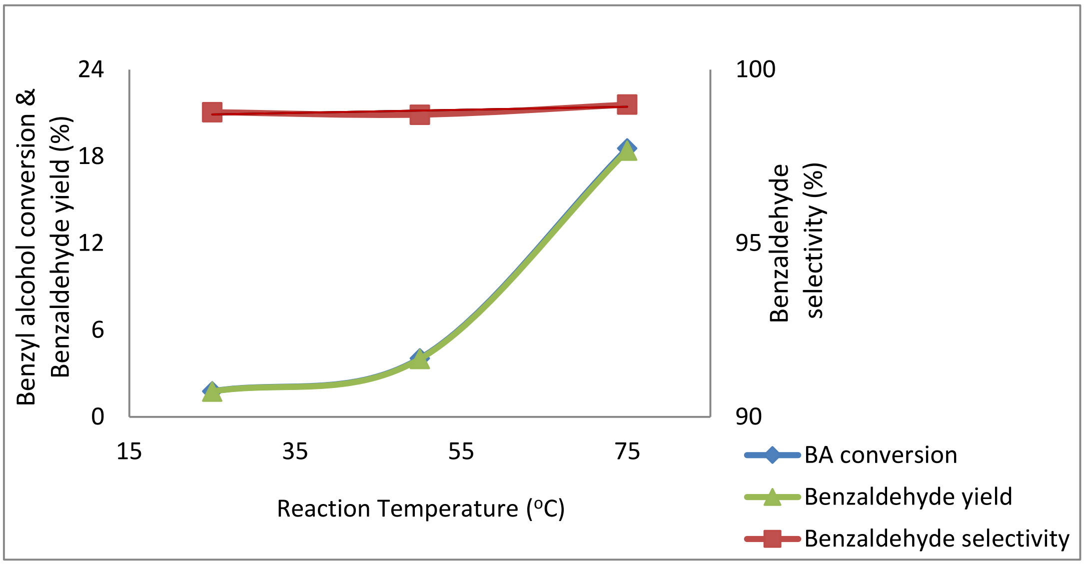


Fig. 4.5 Trend of BA conversion, benzaldehyde selectivity and yield versus reaction temperature run for 2 h (conditions: 0.01 g catalyst, 1ml benzyl alcohol and 9ml methanol, 420psi 5%H_2/CO_2 and 160psi 25%O_2/CO_2, 2 h)

4.3.2.3 Discussion

Reaction conditions such as reaction time and temperature obviously influence the results in a certain trend, which was that longer reaction time and higher temperature, as expected, largely increased the conversion of benzyl alcohol and the yield of benzaldehyde, whereas the benzaldehyde selectivity little changed. The best result was obtained under 75 ^{o}C running for 2 h.

However, oxygen itself can also be responsible for the benzyl alcohol conversion under these conditions. Hence the role of hydrogen addition in this oxidation needs to be investigated as well and this is discussed in the next section.

4.3.3 Blank Tests with Oxygen/Carbon Dioxide and Nitrogen

Blank tests with nitrogen, which had no effect in the reaction, in place of hydrogen and carbon dioxide were considered to be worth exploring. At 75 ^{o}C for 2 h using the catalyst of 1 wt% Au-Pd/TiO_2, where the best result was obtained for the condition where both O_2 and H_2 present, we can clearly see how adding of hydrogen affected the oxidation by comparing the benzaldehyde yields between with hydrogen and those without hydrogen. In the Figure 4.6a, we can see that the addition of hydrogen led to a significant increase in the benzaldehyde yield overall. According to the benzaldehyde yield observed without addition of hydrogen, more oxidation occurred with only oxygen added at the higher temperature. However most importantly, the difference of slopes between these two trend lines indicates that there was more development of benzaldehyde yield after adding of hydrogen with an increase in temperature. A similar observation for the longer reaction time as that with higher temperature appeared is shown in the Figure 4.6b.

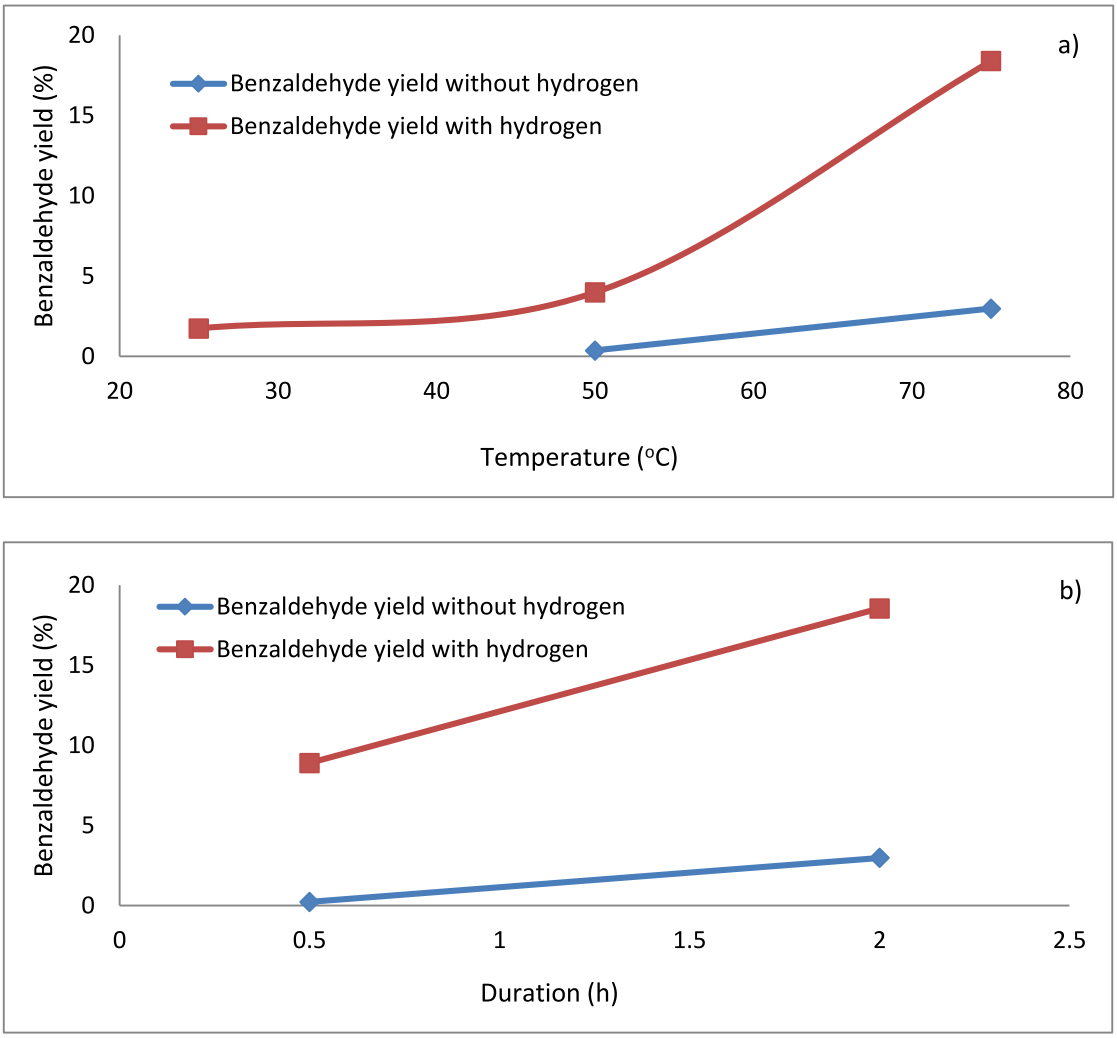


Figure 4.6 Comparison of benzaldehyde yields by adding of hydrogen and without hydrogen (a. conditions: 0.01 g catalyst, 1ml benzyl alcohol and 9ml methanol, 420psi 5%H_2/CO_2or N_2,and 160psi 25%O_2/CO_2, 2 h duration time; b. conditions: 0.01 g catalyst, 1ml benzyl alcohol and 9ml methanol, 420psi 5%H_2/CO_2 and 160psi 25%O_2/CO_2, 75 °C)

4.3.4 Conclusion

In summary, the conventional wet impregnated bimetallic Au-Pd catalyst performed much better than that DP prepared monometallic Au catalyst in the benzyl alcohol oxidation using in situ generated hydrogen peroxide. The choice of the reaction conditions is a very important factor which can lead to improved results. The activity was lowest at room temperature, and highest when temperature was 75 °C, the increase of either reaction duration or temperature could enhance the benzyl alcohol conversion and benzaldehyde yield without any obvious change of benzaldehyde selectivity. Although these two variables made a large contribution to the oxygen-oxidized process, more improvement in the total reactive activity can be made using in situ generated H_2O_2. In this research, the most suitable conditions for the process are considered to be: 75 ^{o}C for 2 h.

4.4 Optimization of the Catalysts

4.4.1 Introduction

Based on the findings of the studies of the effect of the reaction conditions, it was considered that more improvement of catalyst itself should be investigated. The catalyst used initially was a titania supported 1 wt% Au-Pd by conventional wet impregnation (CIm) with a 1:1 metal mole ratio of gold and palladium. Both metal ratios of Au:Pd and preparation methods have the potential to be developed. In this part of the thesis, the results of using a range of metal ratios (Au:Pd = 9:1, 3:1, 1:1, 1:3, 1:9, gold only and palladium only) and other catalyst preparation methods (modified impregnation (MIm), modified impregnation with calcination instead of reduction (MIm.cal) and sol-immobilization (SIm)) will be shown as a means of optimization of the catalyst for the benzyl alcohol oxidation using in situ generated H_2O_2.

4.4.2 Effect of Different Gold-Palladium Metal Ratios

The result of benzaldehyde yield catalyzed by CIm 1 wt% AuPd/TiO_2running at 25 ^{o}C has been shown to be very low. The same phenomenon appeared when using different gold-palladium metal ratios at 25 ^{o}C (Table 4.8). The research on the effect of metal ratios of the catalyst was focus on the higher reaction temperatures, i.e. 50 ^{o}C and 75 ^{o}C.

Metal ratios of Au:Pd	Benzyl alcohol Conversion (%)	Benzaldehyde	
		Selectivity (%)	Yield (%)
9:1 [a]	0.6	94.9	0.6
9:1 [b]	1.1	96.4	1.1
3:1 [a]	1.5	92.1	1.4
3:1 [b]	2.4	93.6	2.2
1:1 [a]	1.5	97.8	1.5
1:1 [b]	1.8	98.8	1.8
1:3 [a]	1.4	95.4	1.4
1:3 [b]	3.1	96.5	3.0
1:9 [a]	1.3	95.3	1.2
1:9 [b]	3.0	95.4	2.8

[a],duration: 0.5 h

[b],duration: 2 h

Table 4.8 Results of benzyl alcohol oxidation by different ratios of CIm 1 wt% Au-Pd/TiO_2 tested at 25 °C (conditions: 0.01 g catalyst, 1ml benzyl alcohol and 9ml methanol, 420psi 5%H_2/CO_2 and 160psi 25%O_2/CO_2)

From Table 4.9 and 4.10, we can see that the gold only catalyst always produced the lowest benzaldehyde at both 50 °C and 75 °C compared with those gold-palladium or palladium only catalysts, while the palladium only catalyst showed a surprisingly high BA conversion and benzaldehyde selectivity. All of which seems to tell us that palladium is necessary for this reaction whereas gold is not. At the most favorable condition (75 °C for 2h), the titania supported 0.5 Au-0.5 Pd catalyst still performed best among all the samples (Figure 4.7), so the addition of gold to palladium catalyst could significantly improve the activity of oxidation under certain conditions. As the benzyl alcohol conversion was increasing with higher temperature, we can also conclude that the CIm Au only catalyst that performed low activity at 50 °C and 75 °C should be even worse when at 25 °C. Also, as the observation from Table 4.8, 4.9 and

4.10, the Pd only catalyst also can be considered to be no better than those bimetallic Au-Pd catalysts at room temperature.

Metal ratios of Au:Pd	Benzyl alcohol Conversion (%)	Benzaldehyde	
		Selectivity (%)	Yield (%)
no Pd [a]	0.5	96.0	0.5
no Pd [b]	0.6	98.8	0.6
9:1 [a]	1.2	95.7	1.1
9:1 [b]	1.7	97.1	1.6
3:1 [a]	1.1	93.9	1.0
3:1 [b]	2.4	97.9	2.3
1:1 [a]	3.5	98.5	3.5
1:1 [b]	4.0	98.7	4.0
1:3 [a]	4.0	98.1	3.9
1:3 [b]	6.2	97.2	6.0
1:9 [a]	2.6	92.9	2.4
1:9 [b]	4.9	96.4	4.8
no Au [a]	5.7	97.4	5.6
no Au [b]	6.8	97.9	6.7

[a],duration: 0.5 h

[b],duration: 2 h

Table 4.9 Results of benzyl alcohol oxidation by different ratios of CIm 1 wt% Au-Pd/TiO_2 tested at 50 ^{o}C (conditions: 0.01 g catalyst, 1ml benzyl alcohol and 9ml methanol, 420psi 5%H_2/CO_2 and 160psi 25%O_2/CO_2)

Metal ratios of Au:Pd	Benzyl alcohol Conversion (%)	Benzaldehyde	
		Selectivity (%)	Yield (%)
no Pd [a]	1.0	98.4	1.0
no Pd [b]	0.2	98.8	0.2
9:1 [a]	2.9	97.9	2.8
9:1 [b]	3.8	97.4	3.7
3:1 [a]	4.1	97.2	4.0
3:1 [b]	9.8	98.6	9.6
1:1 [a]	9.0	99.0	8.9
1:1 [b]	18.6	99.0	18.4
1:3 [a]	8.2	98.3	8.1
1:3 [b]	8.5	98.4	8.3
1:9 [a]	9.7	95.7	9.3
1:9 [b]	8.4	96.7	8.2
no Au [a]	11.1	97.1	10.7
no Au [b]	16.3	97.2	15.9

[a],duration: 0.5 h

[b],duration: 2 h

Table 4.10 Results of benzyl alcohol oxidation by different ratios of CIm 1 wt% Au-Pd/TiO_2 tested at 75 ^{o}C (conditions: 0.01 g catalyst, 1ml benzyl alcohol and 9ml methanol, 420psi 5%H_2/CO_2 and 160psi 25%O_2/CO_2)

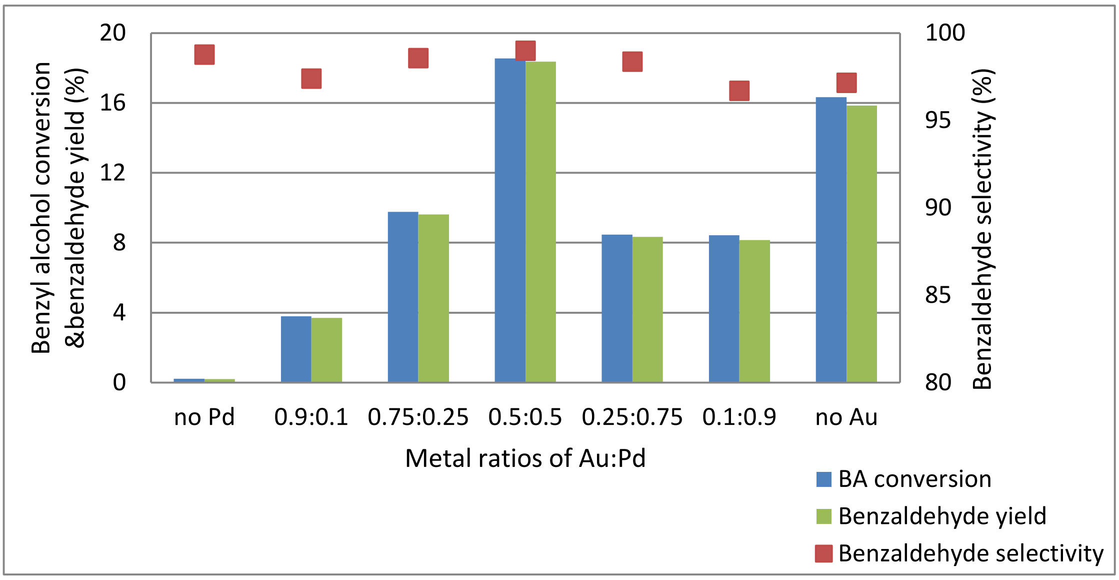


Fig. 4.7 Results of benzyl alcohol oxidation by different metal ratios of bimetallic gold- palladium catalysts with total 1 wt% loading (conditions: 0.01 g catalyst, 1ml benzyl alcohol and 9ml methanol, 420psi 5%H_2/CO_2 and 160psi 25%O_2/CO_2, 75 °C, 2 h)

4.4.3 Effect of Different Preparation Methods for Gold-Palladium Catalysts

4.4.3.1 Reactions with Hydrogen and Oxygen Present

Besides the conventional wet impregnation, other preparation methods, i.e. modified impregnation and sol-immobilization, were also tried for gold only, 0.5 Au 0.5Pd and palladium only catalysts. Unfortunately, the modified impregnated (MIm) catalysts, which were regarded to be more active for direct synthesis of hydrogen peroxide[1], did not make any improvement in benzaldehyde yield compared with those obtained for CIm (lines 1 and 2 of Table 4.11). Since the main difference between these two methods is the heat-treatment, we can consider that the calcination was better than the reduction treatment for the catalysts in this reaction. A modified impregnated sample with calcination (MIm.cal) was prepared, and this kind of sample performed slightly better than either MIm or CIm sample(lines 1, 2 and 4 of Table 4.11). Overall, a sol-immobilized (SIm) sample showed the highest advantage of benzaldehyde yield (Figure 4.8).

Preparation of 0.5Au-0.5Pd/TiO_2	Benzyl alcohol Conversion (%)	Benzaldehyde	
		Selectivity (%)	Yield (%)
Wet impregnation	18.6	99.0	18.4
Modified impregnation	15.6	99.6	15.5
Sol-immobilization	34.5	99.5	34.4
Modified impregnation. cal	21.9	99.4	21.8

Table 4.11 Results obtained under 75 °C running for 2 h (conditions: 0.01 g catalyst, 1ml benzyl alcohol and 9ml methanol, 420psi 5%H_2/CO_2 and 160psi 25%O_2/CO_2)

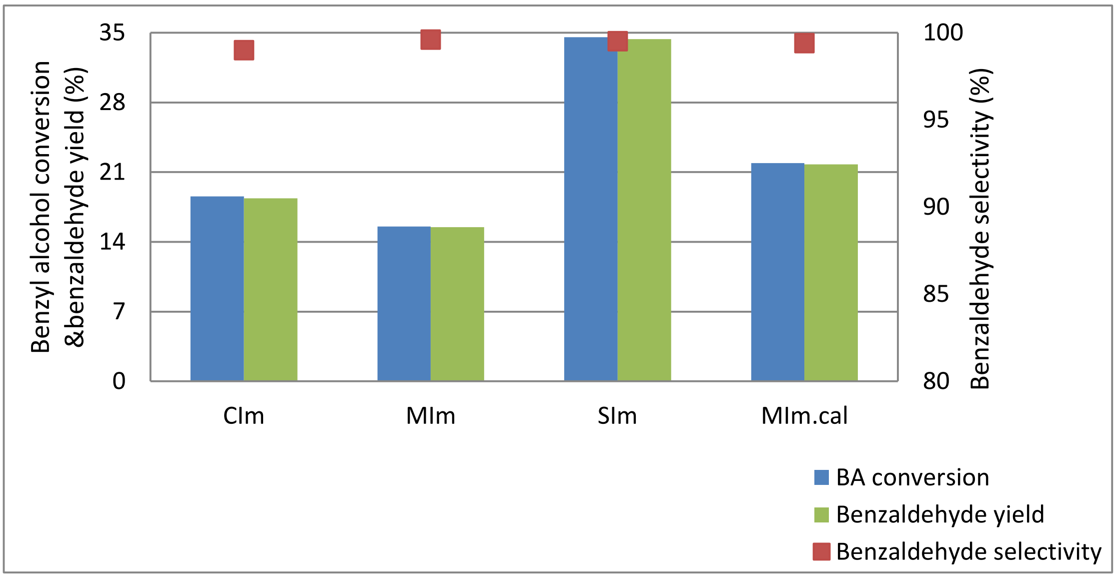


Fig. 4.8 Comparison of performance of 0.5 Au-0.5 Pd/$TiO_2$by different preparation methods (conditions: 0.01 g catalyst, 1ml benzyl alcohol and 9ml methanol, 420psi 5%H_2/CO_2 and 160psi 25%O_2/CO_2, 75 °C, 2 h)

To examine this phenomenon, further experiments were carried out 75 °C for 2h (Table 4.12 and 4.13, Figure 4.9 and 4.10). The SIm Au-Pd catalyst always performed best in any condition. Moreover, MIm.cal showed no obvious difference among those three impregnation-based methods.

Preparation of 0.5Au-0.5Pd/TiO_2	Benzyl alcohol Conversion (%)	Benzaldehyde	
		Selectivity (%)	Yield (%)
Wet impregnation	9.0	99.0	8.9
Modified impregnation	6.1	99.4	6.0
Sol-immobilization	11.2	99.5	11.1
Modified impregnation. cal	7.6	99.1	7.6

Table 4.12 Results obtained under 75 °C running for 0.5 h (conditions: 0.01 g catalyst, 1ml benzyl alcohol and 9ml methanol, 420psi 5%H_2/CO_2 and 160psi 25%O_2/CO_2)

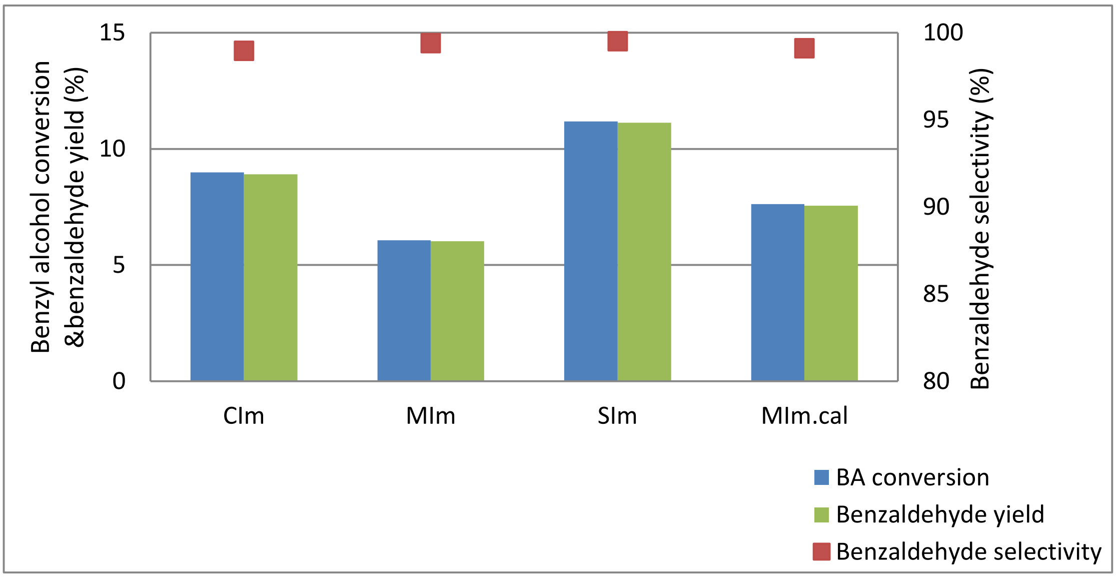


Fig. 4.9 Comparison of performance of 0.5 Au-0.5 Pd/$TiO_2$by different preparation methods (conditions: 0.01 g catalyst, 1ml benzyl alcohol and 9ml methanol, 420psi 5%H_2/CO_2 and 160psi 25%O_2/CO_2, 75 °C, 0.5 h)

Preparation of 0.5Au-0.5Pd/TiO_2	Benzyl alcohol Conversion (%)	Benzaldehyde	
		Selectivity (%)	Yield (%)
Wet impregnation	4.0	98.7	4.0
Modified impregnation	4.1	99.8	4.1
Sol-immobilization	8.6	99.7	8.5
Modified impregnation. cal	4.3	99.8	4.3

Table 4.13 Results obtained under 50 °C running for 2 h (conditions: 0.01 g catalyst, 1ml benzyl alcohol and 9ml methanol, 420psi 5%H_2/CO_2 and 160psi 25%O_2/CO_2)

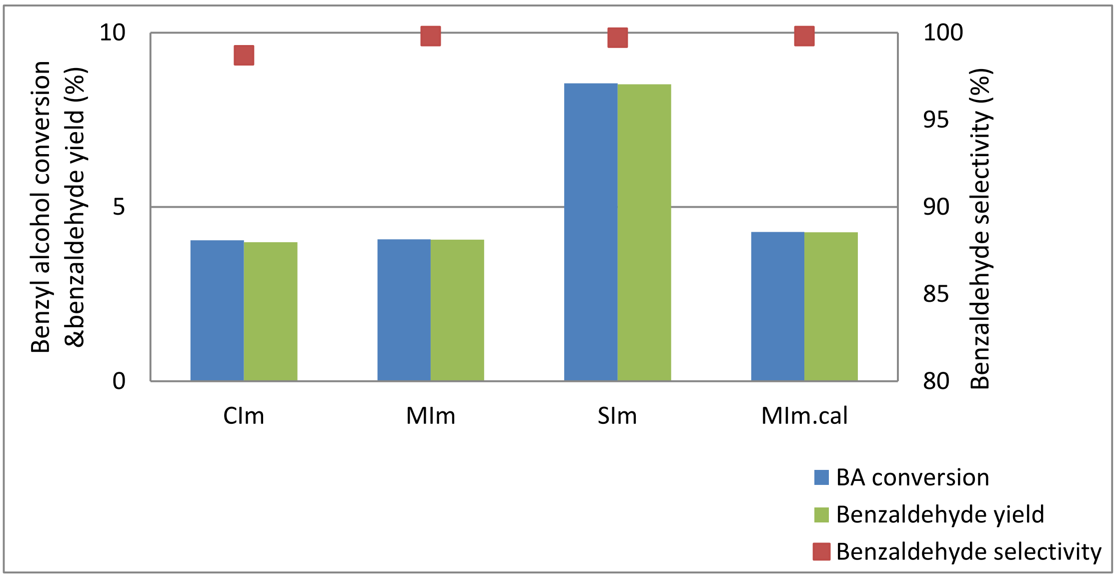


Fig. 4.10 Comparison of performance of 0.5 Au-0.5 Pd/$TiO_2$by different preparation methods (conditions: 0.01 g catalyst, 1ml benzyl alcohol and 9ml methanol, 420psi 5%H_2/CO_2 and 160psi 25%O_2/CO_2, 50 °C, 2 h)

4.4.3.2 Reactions in the Absence of Hydrogen

Blank tests with nitrogen instead of hydrogen/carbon dioxide were also carried out with the catalysts (CIm, SIm and MIm.cal) to investigate which one is the most oxygen-independent compared with their normal tests (Figure 4.11). At the condition of 75 °C for 2 h, SIm sample showed a very high benzaldehyde yield with oxygen only, whereas the MIm.cal catalyst had the best effect of the addition of hydrogen.

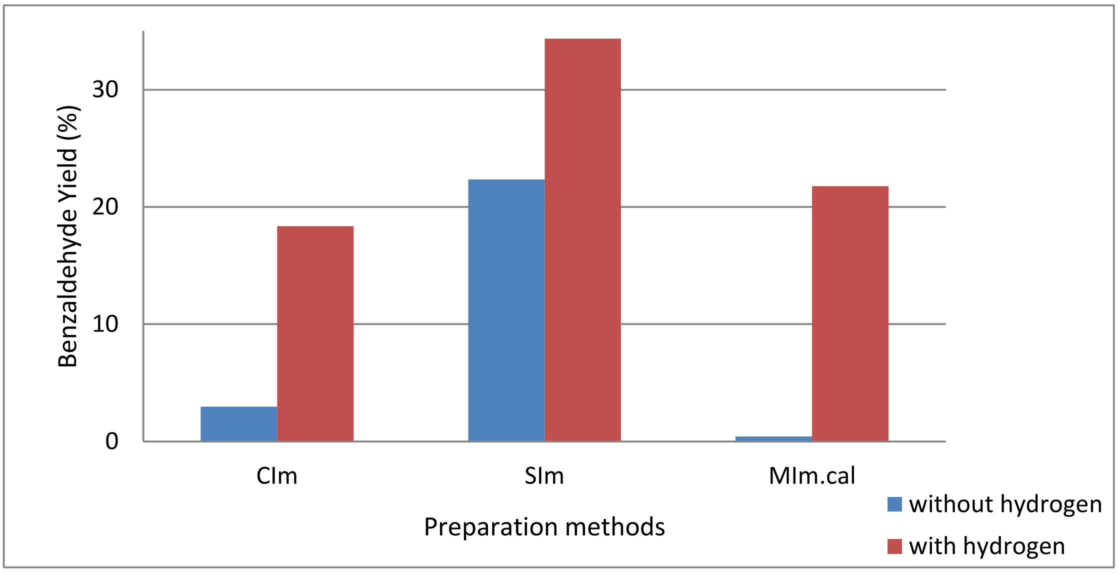


Fig. 4.11Benzaldehyde yields of blank tests by three preparation methods compared with their normal tests with hydrogen (conditions: 0.01 g catalyst, 1ml benzyl alcohol and 9ml methanol, 420psi 5%H_2/CO_2or N_2, and 160psi 25%O_2/CO_2, 75 ^{o}C, 2 h)

4.5 Discussion

4.5.1 Effect of Reaction Time

Among the three impregnation-based preparation methods (CIm, MIm and MIm.cal), the sample prepared by the modified impregnation method with calcination was observed to have the highest activity (21.9 % benzyl alcohol conversion and 21.8 % benzaldehyde yield at 75 ^{o}C for 2 h) and gave the most improvement with longer reaction times (Figure 4.12).

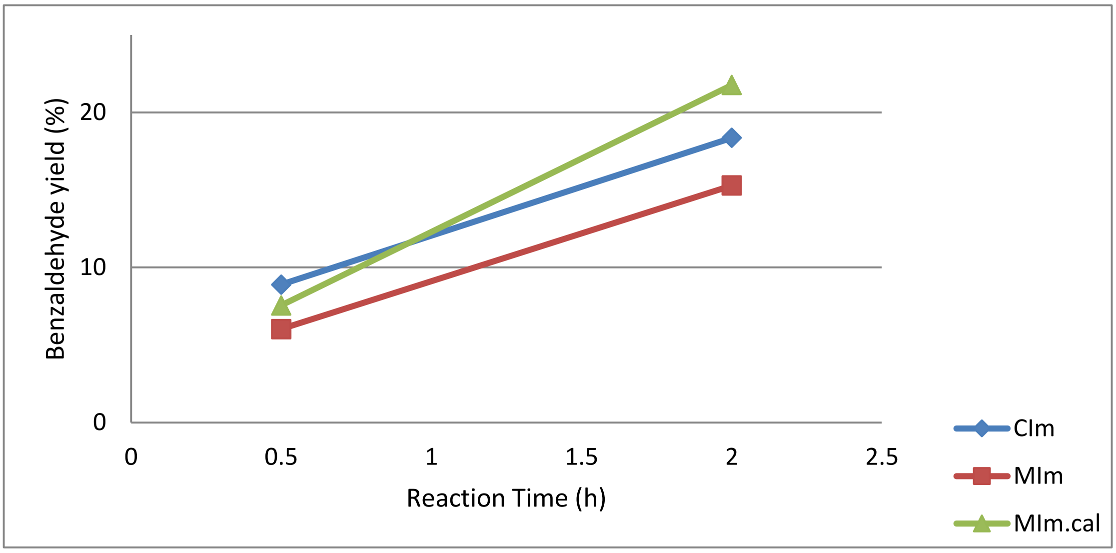


Fig 4.12 Benzaldehyde yields versus reaction duration by three kinds of prepared catalysts (conditions: 0.01 g catalyst, 1ml benzyl alcohol and 9ml methanol, 420psi 5%H_2/CO_2, and 160psi 25%O_2/CO_2, 75 ^oC)

The remaining question is whether we could get improved results with longer reaction time using the MIm.cal 1 wt% Au-Pd/TiO_2 catalyst. We can observe that with the increase in duration to 3 h, there was not much improvement of benzaldehyde yields by either CIm sample or MIm.cal sample (Figure 4.13). Considering the efficiency of time and economy, it is considered two hours reaction time might be the most suitable duration for this process.

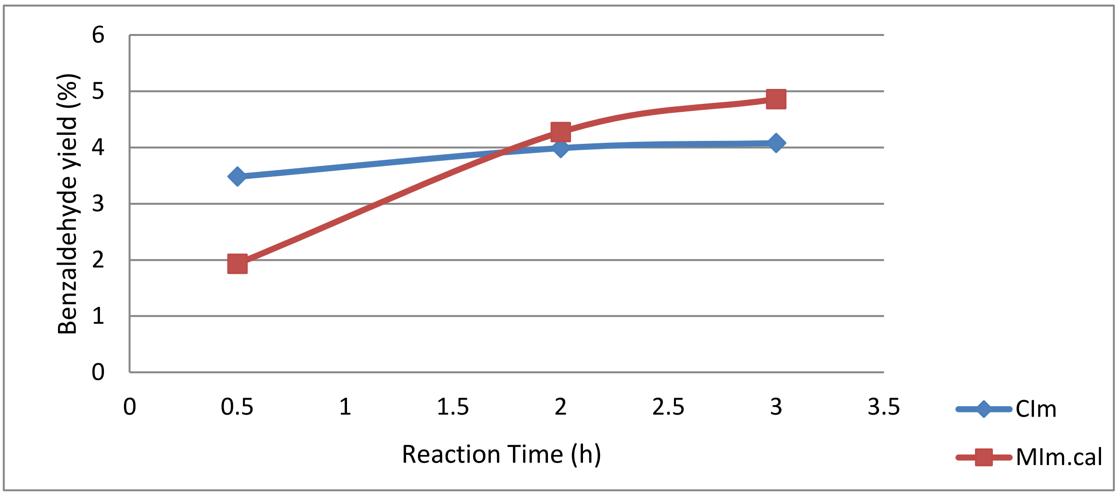


Fig. 4.13 Time on line results of benzaldehyde yield by CIm and MIm.cal 1 wt% Au-Pd/TiO_2 (conditions: 0.01 g catalyst, 1ml benzyl alcohol and 9ml methanol, 420psi 5%H_2/CO_2, and 160psi 25%O_2/CO_2, 50 ^oC)

4.5.2 Effect of Using Lower Temperature

From all the data present in the thesis, it can be concluded that the 1 wt% Au-Pd/TiO_2 prepared by sol-immobilization could produce both the highest benzyl alcohol conversion and benzaldehyde yield under any conditions evaluated, though it is apparent that oxygen played an important role in oxidation process. So we questioned that if we decreased the reaction temperature, would SIm sample still keep a high activity compared with other catalyst? Room-temperature reaction for SIm sample was carried out as well as its blank test (Figure 4.14). Much lower benzaldehyde yield (3.6 %) was obtained at 25 ^oC compared with those at higher temperatures. In order to get a reasonable high benzaldehyde yield, temperature as high as 75 ^oC should be necessary.

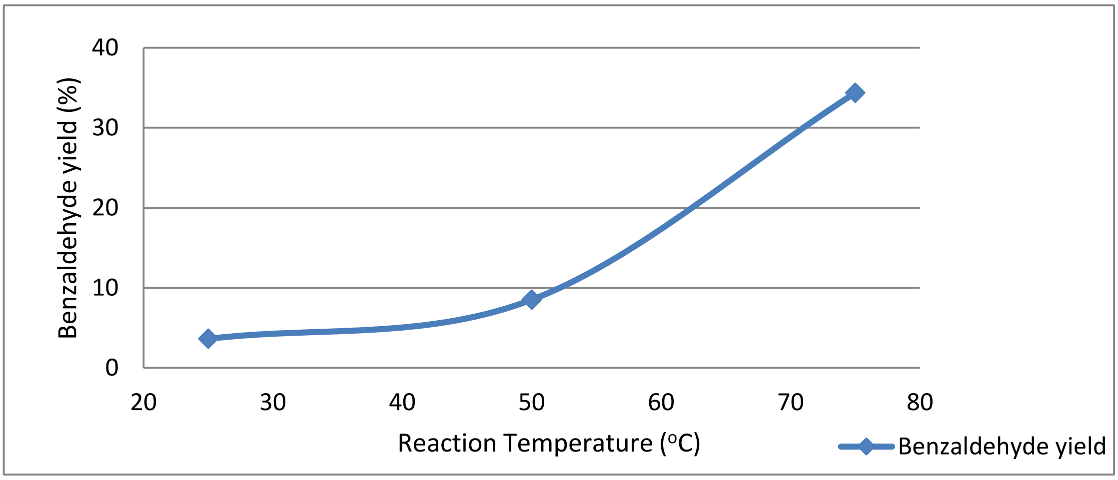


Fig. 4.14 Temperature on line results of benzaldehyde yield by SIm 1 wt% Au-Pd/TiO_2 (conditions: 0.01 g catalyst, 1ml benzyl alcohol and 9ml methanol, 420psi 5%H_2/CO_2, and 160psi 25%O_2/CO_2, 2 h)

4.5.3 Calculations in Ideal Conditions

The ideal moles of produced benzaldehyde and the conversion of hydrogen should be calculated to see how much was the reaction processed. At a particular condition (Table 4.14) for example, if all hydrogen was converted to hydrogen peroxide, the production of hydrogen peroxide could be come out by the ideal gas equation (Equation 4.1). Moreover, if all hydrogen peroxide was responsible to the oxidation in second step, the results of produced benzaldehyde could be obtained by Equation 4.2 and 4.3, because the excess oxygen itself also played a role in oxidation. In summary, at this the condition which hydrogen can be all converted to hydrogen peroxide, the cost of benzyl alcohol and productivity of benzaldehyde should both be 0.0081 mol totally. However, the benzyl alcohol we added as reactant was about 0.0096 mol, which means that not all the benzyl alcohol can be converted to benzaldehyde (84% in conversion).

But actually, as hydrogen can hardly be converted completely and the mechanism of the whole two-step reaction is complicated, we can hardly realize how to achieve the expected results. The following exploration we could do is to increase the benzyl alcohol conversion with high benzaldehyde selectivity and improve the catalysts.

	Temperature	Time	Catalyst	Hydrogen	Oxygen	Benzyl Alcohol
Ideal Conditions	75 ºC	2 hours	SIm 1 wt% AuPd/TiO$_2$	420 psi 5 % H$_2$/CO$_2$	160 psi 25 % O$_2$/CO$_2$	1 ml

Table 4.14 Discussion of assumptive reactive potential in perfect conditions

$$pV = nRT \text{ (Equation 4.1)}$$

$$H_2O_2 + C_6H_5CH_2OH \rightarrow C_6H_5CHO + 2H_2O \text{ (Equation 4.2)}$$

$$\frac{1}{2}O_2 + C_6H_5CH_2OH \rightarrow C_6H_5CHO + H_2O \text{ (Equation 4.3)}$$

Reference

1. G. J. Hutchings, C. J. Kiely, *Accounts of Chemical Research*, **46**,2013, 1759-1772.

Chapter 5 Conclusion and Future Work

5.1 Conclusion

First of all, the bimetallic gold-palladium supported catalysts were shown to be active in the reaction of benzyl alcohol oxidation by generated H_2O_2, and performed very impressiveselectivity of bezaldehyde in all tests (most over 95%).

In conclusion, higher reaction temperature and longer reaction time seemed to be beneficial to the benzyl alcohol conversion to benzaldehyde by in situ generated H_2O_2. When the reaction temperature and reaction duration was increased from 25 ^oC to 75 ^oC and 0.5 h to 2 h respectively, we can clearly observe the significant increase of both benzyl alcohol conversion and benzaldehyde yield, with little change of benzaldehyde selectivity.

Moreover, palladium is a necessary component of the catalyst. Compared with monometallic gold or palladium catalyst, 1:1 bimetallic gold-palladium performed better in this one-step oxidation of benzyl alcohol to benzaldehyde.Among all the preparation methods used for the 1 wt% Au-Pd/TiO_2,sol-immobilized sample had the highest benzyl alcohol conversion and benzaldehyde selectivity, although oxygen played an important role in the oxidation with these catalysts.The difference of activities of modified impregnated samples with two kinds of heat treatments demonstrates that oxidative heat treatment in the catalyst preparation showed a superior effect than a reduction treatment.

5.2 Future Work

As we know, besides the conditions which have been investigated, the total pressure of incoming gases is an important factor for the direct synthesis of hydrogen peroxide[1]. How this affects the new combined process would be an interesting topic. As expectation, higher total gas pressure may lead to the increase of reaction activity. If so, one more economical, safe and environmental-friendly consideration which is how to decrease the H_2 and O_2 mixture pressure and keep high benzyl alcohol oxidation activity in the meanwhile will come out in the future.

Some further improvements for catalysts can be considered as well. The supported bimetallic Au-Pd nanoparticles have been proven to be active, but how about other alternative metals or the addition of a third metal to the catalysts? Hutchings and co-workers have worked out that a third metal, platinum, added to the Au-Pd system, could bring a superior enhancement for selectivity of catalyst in the reaction of solvent-free benzyl alcohol oxidation[2]. For economical considerations, if some cheap non-noble alternative metals, such as nickel and copper, could be found effective, it would be a large development in modern industrial uses. Finally, other effective supports, such as titanium silicate (TS-1), which has been used in preparing heterogeneous catalysts for various oxidation reactions[3, 4], will be worth a trial in this in situ oxidation process.

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