HETEROGENEOUS GOLD AND PALLADIUM BASED CATALYSTS FOR SOLVENT-FREE OXIDATION OF TOLUENE

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In The Name of God Almighty, the Most Merciful, Most Compassionate

For The Blessing and Strength

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Abstract

Catalyzed oxidation of aromatic hydrocarbons with molecular oxygen has been studied for several decades. For example, toluene can be converted into oxidation products such as benzyl alcohol, benzaldehyde, benzoic acid and benzyl benzoate. At present, the principal industrial production of benzoic acid via the oxidation of toluene involves the use of homogeneous cobalt catalysts in an air pressurized aqueous acetic acid mixture in the presence of Mn ions. However, the use of solvent causes difficulties in the separation of catalysts and products, equipment corrosion, and due to the environmental hazards associated with the use of liquid acids as solvent. Developing solvent free toluene oxidation having great activity has attracted special attention as a promising environmentally friendly reaction. Recently, gold based supported catalyst have been found to be highly effective oxidation catalyst where a number of important discoveries have been made such as in hydrogen peroxide synthesis and selective oxidation of alcohols to aldehydes.

As a proof of concept for the following studies, oxidation of toluene and other aromatic hydrocarbons were carried out in round bottom flask with TBHP as oxidant. At mild condition (80 ºC), it was evident that Au-Pd supported catalyst is capable of oxidising aromatics C-H bonds on toluene and derivatives and TBHP as oxidant also have been discovered well in this thesis.

The catalyst preparation method was shown to be very important in the formation of active site catalysts. The sol-immobilisation catalyst with a narrow distribution of small particles, was more active than Au-Pd alloy having Au-core palladium shell with PdO dominance on the surface via impregnation catalyst. In addition to that, the choice of support is crucial and this study discovered carbon as a preferred support give enhance on performance activity of toluene. At the same time, the distribution of products can be

altered with the choice of preparation methods and support. The synergistic effect of Au and Pd was confirmed by superior catalytic activity compared to monometallic catalyst.

Investigations of reaction conditions such as reaction time, reusability, pre-treatment conditions, metal ratio, and mass of catalyst were fully investigated. It was found that the activity and selectivity of the catalyst was highly dependent on these variables.

Reaction mechanism was proposed and it was based on catalytic evaluation data. Even though, the proposed mechanism was contradicted by the EPR data study, it was believed that the reactive oxygen species (ROS) was involved in the surface of catalyst and give effect of the catalytic activity.

Overall, the oxidation of toluene was successfully studied by using Au-Pd supported catalyst and can not be denied that the importance of TBHP as oxidant involve in this process has been proven.

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CHAPTER 1

INTRODUCTION

1.1 Catalyst

1.1.1 Definition of catalysis

Most of the chemical reactions involved in industries and biology is based on catalytic/enzymatic processes known as catalysis/enzymatic processes. Catalysts play an essential role in the manufacture of a wide range of products, from gasoline and plastics to drugs and herbicides, which would otherwise be unobtainable or prohibitively expensive. Apart from manufacturing process, catalysis is finding other important and ever-increasing uses; for example, successful application of catalysis in the control of pollution and its use in environmental control are certain to increase in the future.

A catalyst is by definition a substance that increases the rate to attain equilibrium in a chemical reaction without being consumed in the reaction[1]. A catalyst also is a substance that when added in the balance of a chemical reaction, accelerates the achievement of the chemical equilibrium between reactants and products without influencing the thermodynamic equilibrium of the process. Usually catalysts are not consumed during the reaction and could be found unchanged after the reaction completes. In reality, catalysts are submitted to a slow transformation with use, causing a general decrease of the activity and/or selectivity. The first main distinction between catalysts depends on catalyst nature in relation to the reactants.

1.1.2 Properties of an industrial catalyst

The properties of an industrial catalyst which determine its choice are the following:

i. The activity, which can be expressed either in terms of rate (moles of product per volume of catalyst per hour), or of turnover number (moles of product per mole of catalyst or of active site), or of conversion (moles of transformed reactant per mole of inlet reactant). The higher the activity, the higher the productivity, and/or the lower the volume of the reactor and the milder the reaction conditions that can be used.

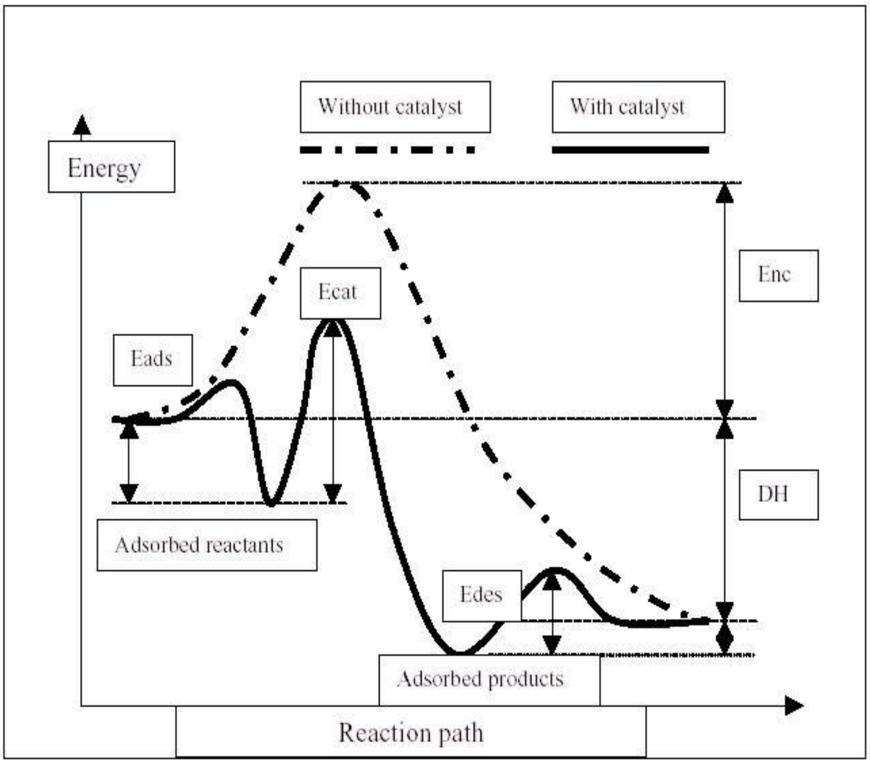
ii. The selectivity, (chemical, stereo or regio), expressed as moles of desired product per moles of converted reactant. The higher the selectivity, the lower the costs of separation, purification and waste treatments and the lower the amount of reagents necessary.

iii. The lifetime, expressed in years of use before catalyst unloading or, better, in terms of amount of chemical produced per amount of catalyst. The higher the lifetime, the lower the down time costs (loss of production due to exhaust catalyst substitution), and the lower the re-catalyzing costs.

iv. The ease of regeneration of spent catalysts (in order to increase the life time and to reduce the problems related to spent catalyst disposal).

v. The toxicity, the ease and safety in handling, and the disposal of spent catalysts.

vi. The price.



Activation energies
Eads-for adsorption
Ecat-for surface reaction
Edes-for desorption
Enc-for activation energy without catalyst
DH-total heat of reaction

Figure 1.1: Reaction profile for a chemical reaction with and without catalyst[2].

The main effect of a catalyst is to provide an alternative reaction path that permits to decrease the activation energies of the different reaction steps, reaching therefore the equilibrium in an easier and faster way. The two different reaction paths (without and with catalyst) are represented in Figure 1.1. In Figure 1.1, Enc is the activation energy that is necessary for the reaction without the use of catalyst, Eads is the adsorption energy of reactants on the catalyst surface, Ecat is the energy related to the activation of the chemical reaction between reactants on the catalyst surface, Edes is the desorption energy of the products of reaction. The process of reactants adsorption is considered as an exothermic process, while the products desorption is considered as endothermic. Finally DH is the total heat of reaction[2].

1.2 Types of catalyst

Industrial catalyst can be divided into two broad types of heterogeneous and homogeneous.

1.2.1 Homogeneous catalyst

When the catalyst, reactants and products are in the same phase, usually the liquid phase, this catalyst is called homogeneous. The catalysts are soluble acids, bases, salts or organometallic compounds. The catalyst is dissolved in a solvent which can also be the reactant or the product itself. The advantages of homogeneous catalysis can be summarized as follows:

i. The utilization of almost all the molecules of the catalyst in the catalytic act.
ii. The higher selectivity obtained in some reactions, especially in the synthesis of optically active compounds.
iii. The easier control of the temperature for highly exothermic reactions
iv. The higher selectivity achieved due to the fact that it is possible to operate at milder conditions (for instance, in oxidation reactions)

Homogeneous catalyst also has the following disadvantages:

i. Expensive procedures of separation and of catalyst recovery.
ii. Serious problems of corrosion (when acid catalyst or solvents are employed).
iii. Expensive treatments of toxic liquid wastes obtained after the separation, regeneration, and recycling of the catalyst.
iv. The possibility of contamination of the products by the catalyst.

v. The existence of gas-liquid-mass-transfer limitations in cases where one of the reactants is a gas (hydrogen, oxygen).

1.2.2 Heterogeneous catalyst

The catalyst and reactant are in different phases. Usually the catalyst is a solid, and the reactants and the products are in the liquid or vapor phase. The catalysts are either inorganic solids, such as metal oxides, sulfides or chlorides, or organic solids such as modified polymers. The catalyst can be used (i) as a powder, in slurry reactors in the presence of a liquid phase; (ii) in the form of pellets, in the presence of liquid phase in trickle-bed reactors; (iii) as pellets in the presence of gaseous reactants in fixed-bed reactors; and (iv) in small-sized particles in fluid or transport-bed rectors. The advantages of heterogeneous catalysis are follows:

i. The easier separation of catalysts from reactant and products.
ii. The elimination of corrosion problems and of liquid waste treatments.

The disadvantages are as follows:

i. The difficulty in the control of temperature for very exothermic reactions.
ii. The mass transfer limitations of reactants and products, both intraphase (inside the pores of the catalyst).
iii. The requirement of high mechanical and erosion resistance for the catalyst.

1.3 Selective oxidation

Selective oxidation of hydrocarbon is a very important industrial process that uses catalysts commonly based on transition metal oxides. There are two types of selective oxidation reaction[3].

1.3.1 Dehydrogenation and Oxygen Insertion Reactions

Oxygen is needed as oxidant both for incorporation into the hydrocarbon molecules and in the formation of water in the dehydrogenation steps. The general features of these reactions are that C-H bonds are broken and C-O bonds are formed. Exceptions to these are the catalytic process of an ammoxidation of propene, in which C-N bonds are formed. In some cases, such as oxidation of benzene to maleic anhydride, the carbon skeleton is broken. In others, the carbon skeletons remain intact. The selectivity is determined in part by the ability of oxide to catalyze the formation of C-O bonds without breaking (or breaking only desired number) of C-C bonds.

In selective oxidation reactions, gaseous oxygen is consumed in formation of oxygenates and water. The reaction pathway of oxygen is as follows. Gaseous oxygen is oxidatively adsorbed on the oxide as O^-, O_2^-, or incorporated as lattice O^{2-} species. The solid is oxidized in the step, and the electrons acquired by the adsorbed oxygen could be from reduced surface cations and anions vacancies with trapped electrons. When an oxygen atom is incorporated into a product molecule which is then desorbed, the electrons are returned to the solid. Therefore, in one catalytic cycle, electrons are removed from and then returned to the solid. In other words, the solid has undergone an oxidation-reduction cycle. If the oxygen species that is incorporated into the molecule is a lattice oxygen atom, the sites for adsorption of oxygen and for oxygen incorporation into the molecule may be different, and migration of oxide ions in the solid between the two sites would occur.

1.4 Toluene oxidation

1.4.1 Chemical and physical properties of toluene

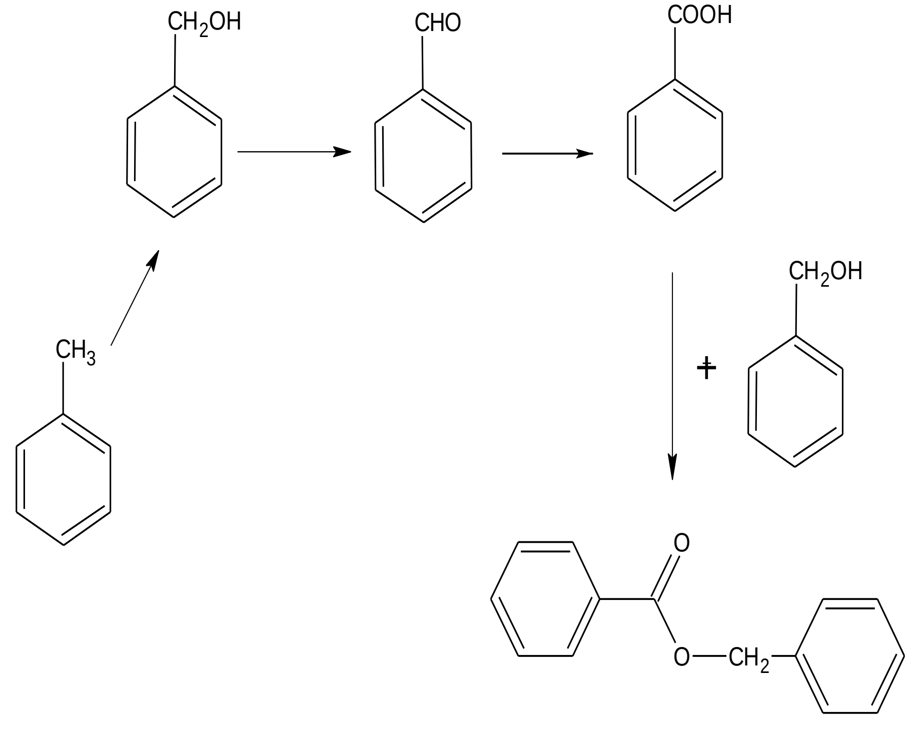
Selective oxidation of aromatic hydrocarbons to industrially important chemicals still remains a major challenge for industry [4-8]. In recent years academia has focused on the research of developing catalysts capable of oxidising hydrocarbons to the desired products. Toluene is one of the substrates in which there is current interest. Toluene, formerly known as toluol, is a clear, water-insoluble liquid with the typical smell of paint thinners. It is a mono-substituted benzene derivative, i.e., one in which a single hydrogen atom from the benzene molecule has been replaced by a univalent group, in this case CH_3[9]. Toluene is also a representative of aromatic hydrocarbons categorized as hazardous material[10]. Thus development of methods for the oxidation of aromatics such as toluene is also important for environmental reasons.

Table 1.1: Chemical properties of toluene[9].

Chemical Properties	
Molecular formula	C_7H_8 or $C_6H_5CH_3$
Molar Mass	92.14 g/mol
Appearances	Colorless liquid
Density	0.8669 g/mL (20 ºC)
Melting points	-93 ºC, 180 K
Boiling Points	110.6 ºC, 383.8 K
Solubility in water	0.47 g/L (20-25 ºC)

1.4.2 Uses

Toluene can be converted to oxygenated products such as benzyl alcohol, benzaldehyde, benzoic acid and benzyl benzoate (scheme 1.1). Benzyl alcohol is used as a general solvent for inks, paints, lacquers, and epoxy resin coatings. It is also a precursor to a variety of esters, used in the soap, perfume, and flavor industries. Benzaldehyde is used as synthetic flavouring material and as a versatile chemical intermediate in the manufacture of pharmaceuticals, dyes, perfumes and flavouring chemicals. Benzoic acid is an intermediate in the productions of chemicals, plasticizers, dyestuffs, preservatives and retardants. Finally, benzyl benzoate is used in chemical industry as flavour, placticizer and solvent.



Scheme 1.1: Reaction pathways for toluene oxidation.

1.4.3 Manufacture

In this study, the products of interest were benzaldehyde and benzoic acid due the high demand in the current industrial practice. Currently, benzaldehyde is produced by the hydrolysis of benzyl chloride or by the partial oxidation of toluene in liquid phase. Its production by chlorination of toluene followed by hydrolysis, which can not be used as the raw material for the production of medicines, food and flavours. In addition, The process involving Cl_2 causes environmental pollution and equipment corruption. On the other hand, the process of liquid phase selective oxidation of toluene usually produces benzoic acid as the main product and benzaldehyde is only a by-product (about 2-3%). Since benzaldehyde is more costly than benzoic acid [11], higher selectivity to benzaldehdye is desired. In the process of gas phase oxidation of toluene, the contact time might be decreased and thus the further oxidation of benzaldehdye might be reduced so that high selectivity to benzaldehdye might be achieved [12, 13]. However, no commercial plants are currently available for the production of benzaldehyde from the oxidation of toluene by air in gas phase, due to the low activity and/or selectivity. Studies are still ongoing to obtain the proper catalysts for the improved catalytic behavior[14].

Benzoic acid can be produced from toluene in various ways. Industrially, the oxidation of toluene to benzoic acid with molecular oxygen is a key step for phenol synthesis in the Dow phenol process and for ε-caprolactum formation in Snia-Viscosia Process[15, 16]. In 1995, the manufacturing capacity for benzoic acid in the USA, Western Europe, and Japan was about 107000, 162000 and 11000 tonnes per year respectively. Production numbers for benzoic acid in USA is given in a table 1.2 as shown as below:

Table 1.2: Benzoic acid production (in 1000 tonnes)[16]

	1995	1997	2000
USA	55	58	81

Furthermore, the commercial production of benzoic acid via the catalytic oxidation of toluene is achieved by heating a solution of the substrate, cobalt acetate and bromide promoter in acetic acid to 250 ºC with molecular oxygen at high pressure. Although complete conversion is achieved, however, the use of acidic solvents and bromide promoter results in difficult separation of products and catalyst along with the large volume of toxic waste and equipments corrosion. The system requires very expensive, specialized equipment, fitted with extensive safety features. Operating under such extreme conditions consumes large amount of energy. Therefore, attempts are being made to make this oxidation more environmentally benign by performing the reaction in the vapor phase using a variety of solid catalysts [17, 18].

In addition, liquid phase oxidation is easy to operate and can achieve high selectivity under relatively mild reaction conditions. Many efforts have been made to improve the efficiency of toluene oxidation in the liquid phase, however, most investigations still focus on homogeneous systems using volatile organic solvents but the conversion must be limited to avoid over oxidation to CO_2 and other byproducts[19]. Attempts to overcome these problems have prompted investigation of the use of supercritical CO_2 and ionic liquids, but this unfortunately resulted in low conversions[20, 21]. Employing heterogeneous catalysts in liquid phase oxidation of toluene without solvent would make the process more environmentally friendly. Besides that, heterogeneous catalysts are preferred over homogeneous catalysts because these materials can be readily separated from the reaction mixture. Heterogeneous catalysts can also be easily used in flow reactors, facilitating the efficient productions of materials using continuous processes.

Bastock *et al*. have reported the oxidation of toluene to benzoic acid in solvent free conditions using a commercial heterogeneous catalyst Envirocat EPAC in the presence of catalytic amount of carboxylic acid as promoter at atmospheric pressure[22]. The reaction was performed at 110-150 ºC, with oxygen flow rate of 400 mL/min. The isolated yield of benzoic acid was 85% in 22h. Subrahmanyan *et al.* have performed toluene oxidation in solvent free conditions using vanadium substituted aluminophosphate or aluminosilicate as catalyst[23]. Benzaldehyde and benzoic acid were the main products when *tert*-butyl hydroperoxide was used as the oxidizing agent while cresol was formed when H_2O_2 was used as oxidizing agent. Raja *et al.* have also reported the solvent free oxidation of toluene using zeolite encapsulated metal complexes as catalyst. Air was used as oxidant (3.5 MPa)[24, 25]. The highest conversion (45%) was achieved with manganese substituted aluminium phosphate with high benzoic acid selectivity (ca.83%) at 150 ºC in 16 h. Li *et al.* have also reported manganese oxide and copper manganese oxide to be active catalyst for toluene oxidation to benzoic acid in solvent free conditions with molecular oxygen (1.0 MPa) at 190-195 ºC[26, 27]. Further, a literature summary of oxidation of toluene is shown in Table 1.3

Table 1.3. Comparison of catalytic activity for the oxidation of toluene using molecular oxygen and TBHP as oxidant.

Catalyst	T/P	Oxidant	Conversion (%)	Selectivity (%)				TON	References
				Benzyl alcohol	Benzaldehyde	Benzoic acid	Benzyl benzoate		
Cu-Mn (1/1)	190 °C 1MPa	O_2	21.6	1.6	9.2	73.7	13.6	8	[28]
Cu-Fe/γ-Al_2O_3	190 °C 1MPa	O_2	25.4	1.0	27.4	71.6	*n.d.*	74	[29]
$MnCO_3$	190 °C 1MPa	O_2	25.0	5.3	9.7	80.8	*n.d.*	50	[30]
CoSBA-15	80 °C 1 atm	TBHP	8.0	*n.d.*	64.0	*n.d.*	*n.d.*	103	[31]
Cr/Silicalite	80 °C 1 atm	TBHP	18.4	5.2	23.3	25.7	*n.d.*	n.d.	[32]

n.d. =not determine

Recently, Kesavan *et al* have reported that using AuPd support catalyst with molecular oxygen as an oxidant can be used in toluene oxidation[33]. In addition, this reaction was operated at much lower reaction temperature, 120-160 ºC instead of 190 ºC whereas it was discovered by Kesavan *et. al* that the effect of homogeneous reaction is much less significant at that temperature[28-30].

1.5 Catalysis by gold

1.5.1 Physical and chemical properties of gold

Gold is an element with the symbol Au (from Latin: *aurum* "gold") and an atomic number of 79. Gold is a dense, soft, shiny, malleable and ductile metal. Pure gold has a bright yellow color and luster traditionally considered attractive, which it maintains without oxidizing in air or water. Chemically, gold is a transition metal and a group 11 element. Gold readily creates alloys with many other metals. These alloys can be produced to modify the hardness and other metallurgical properties, to control melting point or to create exotic colors. Gold is a good conductor of heat and electricity and reflects infrared radiation strongly. Chemically, it is unaffected by air, moisture and most corrosive reagents, and is therefore well suited for use in coins and jewelry and as a protective coating on other, more reactive, metals. However, it is not chemically inert. Common oxidation states of gold include +1 (gold (I) or aurous compounds) and +3 (gold (III) or auric compounds). Gold ions in solution are readily reduced and precipitated out as gold metal by adding any other metal as the reducing agent. The added metal is oxidized and dissolves allowing the gold to be displaced from solution and be recovered as a solid precipitate.[34]

Table 1.4. General and physical properties of gold

Element category	Transition metal
Group,period, block	11, 6, d
phase	solid
Molecular weight	79
Density (near room temperature)	19.30 g/cm3
Melting point	1337.33K , 1064.18 ºC
Boiling point	3129 K, 2856 ºC
Oxidation state	-1, 1, 2, 3, 4, 5 (amphoteric oxide)

1.5.2 History of catalysis by gold

Gold as a catalyst was discovered a long time ago but it was found to be relatively inactive. However, early and scattered reports on the use of gold as a catalyst existed, but none of these gold catalysts demonstrated to be superior to other catalysts. This changed in 1973 when Bond *et al*. reported the hydrogenation of olefins over supported gold catalysts. Unfortunately, gold was left and viewed not as viable alternative and not shown to be more effective than well dispersed palladium or platinum that was already well established at that time period[35]. After a decade later, in the early to mid 1980s, Haruta and Hutchings simultaneously and independently prognosticated gold to be an extraordinary gold catalyst and subsequently demonstrated it experimentally[36]: Haruta *et al.* investigated the low-temperature oxidation of CO[37] and Hutchings the hydrochlorination of ethyne to vinyl chloride[38], both heterogeneous reactions. For the first time these studies showed gold to be the best catalyst for these reactions, in stark contrast to previous reports on the poor activity of gold.

Since the mid 1990s, there has been a dramatic increase in research attention focused on the use of supported gold catalysts for redox reactions. However, as noted in the literature by Hashmi really interesting gold catalysis did not materialize until late 1990s, i.e. not until over a decade after the initial discoveries, but after the late 1990s the publications and patents concerning gold catalysis have grown exponentially even when normalized against the general growth in all scientific publications[39]. In the last few years, the number of publications appearing on gold catalysis involving both homogeneous and heterogeneous catalyzed reactions has risen exponentially, and these publication statistics have recently been published by World Gold Council (WGC) organisation[40](see Figure 1.2).

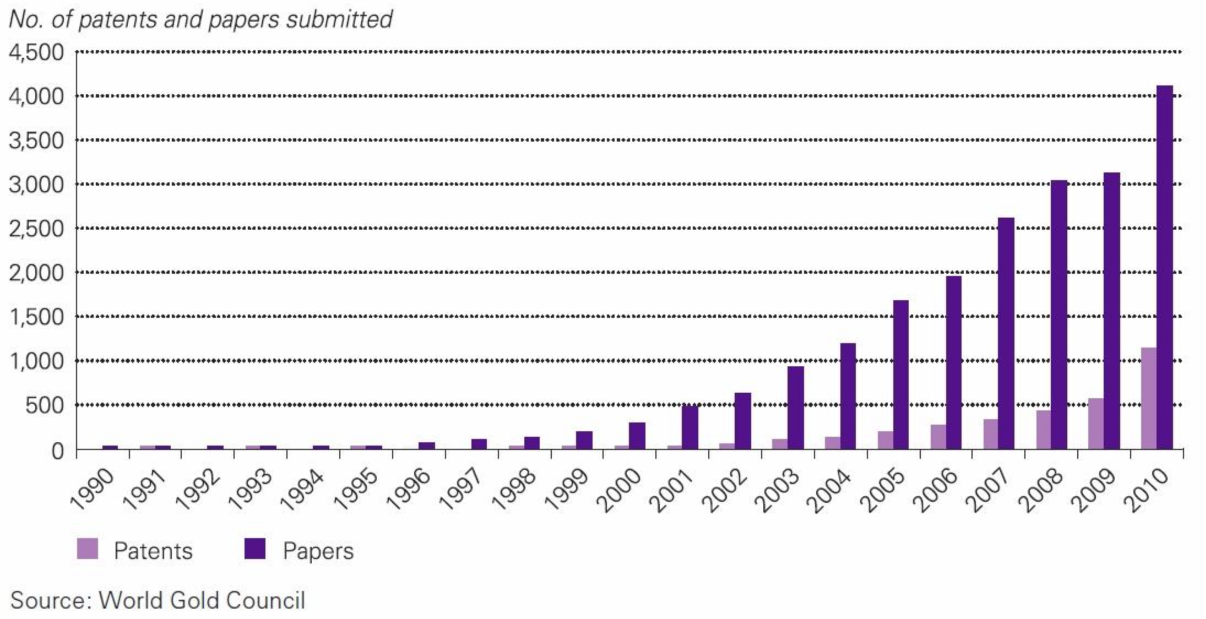


Figure 1.2: The increment of number of patents and papers submitted for publication using nanoparticles gold catalyst[40].

1.5.3 Importance and applications of gold catalysis for selective oxidation.

Au nanocrystals have been shown to be highly effective for the oxidation of alcohols with O_2 in an aqueous base, in particular diols and triols; but under these conditions, the product is the corresponding monoacid, not the aldehyde [41-44]. Gold catalysts have, however, been found to be effective for the gas–phase oxidation of volatile alcohols to the corresponding aldehydes and ketones [45].

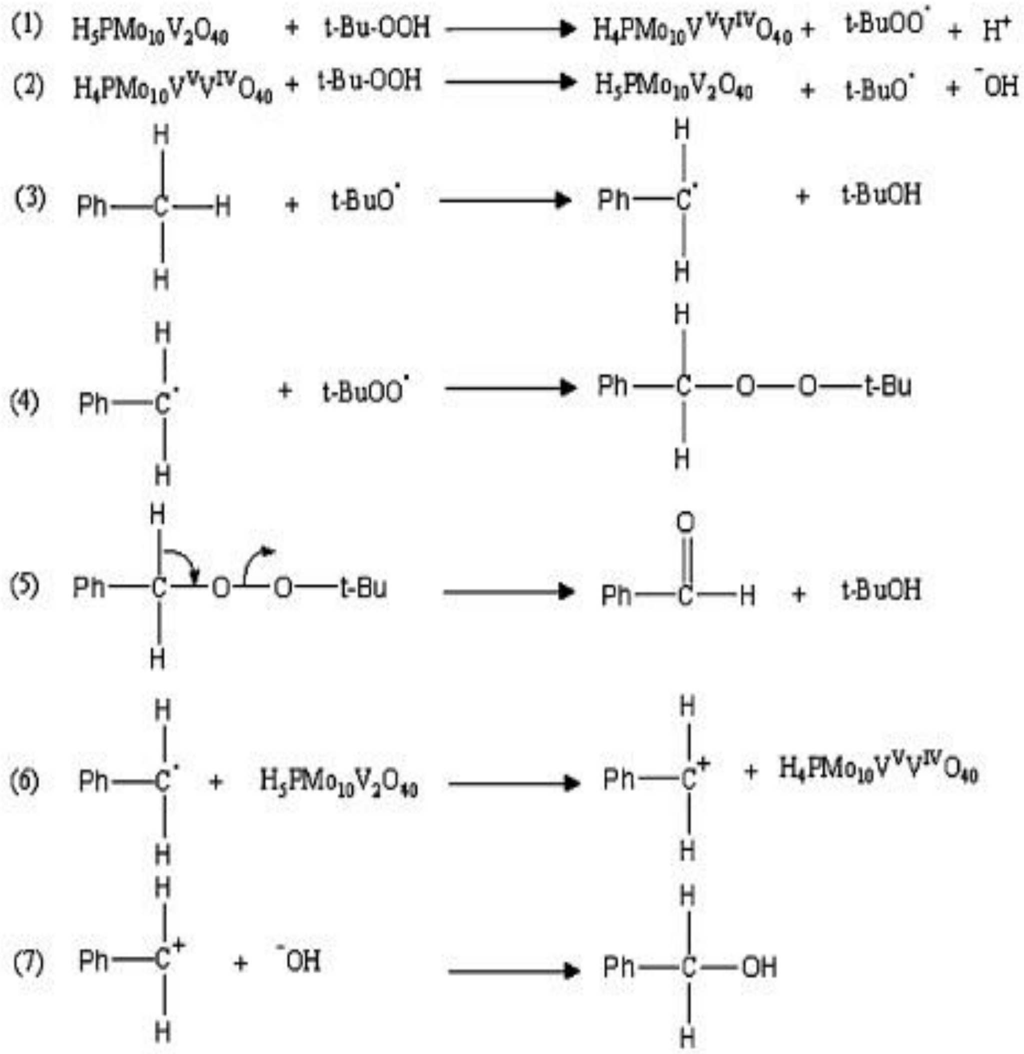
Subsequently, two studies have shown that supported metal nanoparticles can be very effective catalysts for the oxidation of alcohols to aldehydes using O_2 under relative mild conditions. Kaneda and co-workers found that hydroxyapatite-supported Pd nanoclusters (Pd/HAP) give very high turnover frequencies (TOFs) for the oxidation of 1-phenylethanol and benzyl alcohol but show limited activity for the oxidation of primary alkyl alcohols (such as octan-1-ol oxidation) [46]. Corma and co-workers have shown that the addition of Au nanocrystals to CeO_2 converts the oxide from a stoichiometric oxidant to a catalytic system[47] with TOFs similar to those obtained by Kaneda and co-workers[46]. Here the nanocrystalline nature of the support was crucial for the catalysis observed, and Corma and co-workers have shown that this catalyst is very effective for CO oxidation as well[48, 49]. Besides that, Hutchings *et al*. have shown that supported Au-Pd alloys are efficient catalysts for the direct synthesis of H_2O_2 from H_2 oxidation by O_2 at low temperature. In particular, Au-Pd/TiO_2 catalysts were very selective for H_2O_2 synthesis[45, 50-52]. Hydroperoxy species are considered to be involved in this H_2O_2 formation process, and because hydroperoxy species are key reagents/ intermediates in the oxidation of alcohols [53], Hutching and co-workers reasoned that these catalysts should also be effective for the oxidation of alcohols. In previous studies, Au-Pd/TiO_2 or Au/TiO_2 has shown significantly enhanced activity and selectivity for alcohol oxidation using a green chemistry approach with O_2 under mild, solvent-free conditions [54]. In particular, this 2.5 wt% Au-2.5% wt% Pd/TiO_2 catalyst was over 25 times more active for the selective oxidation of phenylethanol when compared with the Au/CeO_2 [47] or Pd/hydroxyapatite [46] catalyst under the same reaction conditions [54]. Extended studies were carried out by Dimitratos *et al*. using sol-immobilisation and impregnation methods for the preparation of Au, Pd and bimetallic Au-Pd supported metal catalyst onto TiO_2 and carbon respectively[55]. Strong synergistic effects were observed on Au-Pd bimetallic supported catalyst especially with TiO_2 as support prepared via impregnation method which is believed to be due to formation of core shell structure compared to homogeneous alloy on carbon. The smaller and narrower particle size distribution on analogue sol-immobilised catalyst produced better activity than the impregnated catalyst counterpart. The data showed that the choice of supports and the surface composition of Au nanoparticles are crucial in obtaining high activity and selectivity to glycerol carbonate. Interestingly, the catalyst was stable up to 10 catalytic cycles even in the presence of urea and temperature at 150 ºC. The presence of Au is crucial especially in controlling the glycerol carbonate selectivity which is believed to be involved in the second part of the reaction involving transformation of glycerol urethane. This is the first demonstration of using Au metal catalyst in this type of reaction[56]. Further studies on bimetallic Au-Pd supported nanoparticles catalysts on benzyl alcohol oxidation were carried by Dimitratos and co-workers [57-58]. In this case, the Au-Pd catalyst either supported on TiO_2 or carbon were synthesized via sol-immobilisation method and the results clearly displayed higher activity when compared with analogue catalysts synthesised via impregnation method. The better catalytic activities of sol-immobilisation samples were due to the similar reasons discussed above for glycerol oxidation reactions.

1.5.4 TBHP as an oxidant

There are only few reports on the selective oxidation of toluene carried out at low temperature using different oxidants like *tert*-butyl hydrogen peroxide (TBHP). Peroxides are very attractive, relatively cheap and waste-avoiding oxidants, but only when used in a controlled manner without organic solvents and other toxic compounds[59]. Brutchey *et al.*

have reported the toluene oxidation on Co-SBA-15 catalyst by using TBHP as an oxidant[31].

This catalyst system showed maximum toluene conversion of 8% with 64% benzaldehyde selectivity at 80 ºC in 24h. Ruthenium-based catalysts are extensively studied for oxidation reaction with TBHP [60-62]. However, these catalysts are expensive. Rao *et al.* have also reported selective oxidation toluene over vanadium substituted polyoxometalate catalysts using TBHP[63]. The selective formation of benzaldehyde over these vanadium containing polyoxometallic catalyst might be due to the plausible mechanism with TBHP. In this paper, it was proposed that when the polyoxometalate $[PMo_{10}V_2O_{40})^{5-}$ reacts with TBHP, the mechanism invariably proceeds with initial formation of *tert*-butyl peroxy (*t*- BuOO$^{\bullet}$) and *tert*-butyloxy radicals (*t*-BuO$^{\bullet}$)[64]. The *tert*-butyloxy radical reacts with toluene to form the benzyl radical. The benzyl radical combines with *tert*-butyl peroxy radical to yield benzaldehyde.The formation of benzyl alcohol proceeds via the formation of benzyl cations by the transfer of electron from benzyl radical to the catalyst. The benzyl cation reacts with hydroxyl anion to yield benzyl alcohol. The reduced catalyst is reoxidized by TBHP (see scheme 1.2).

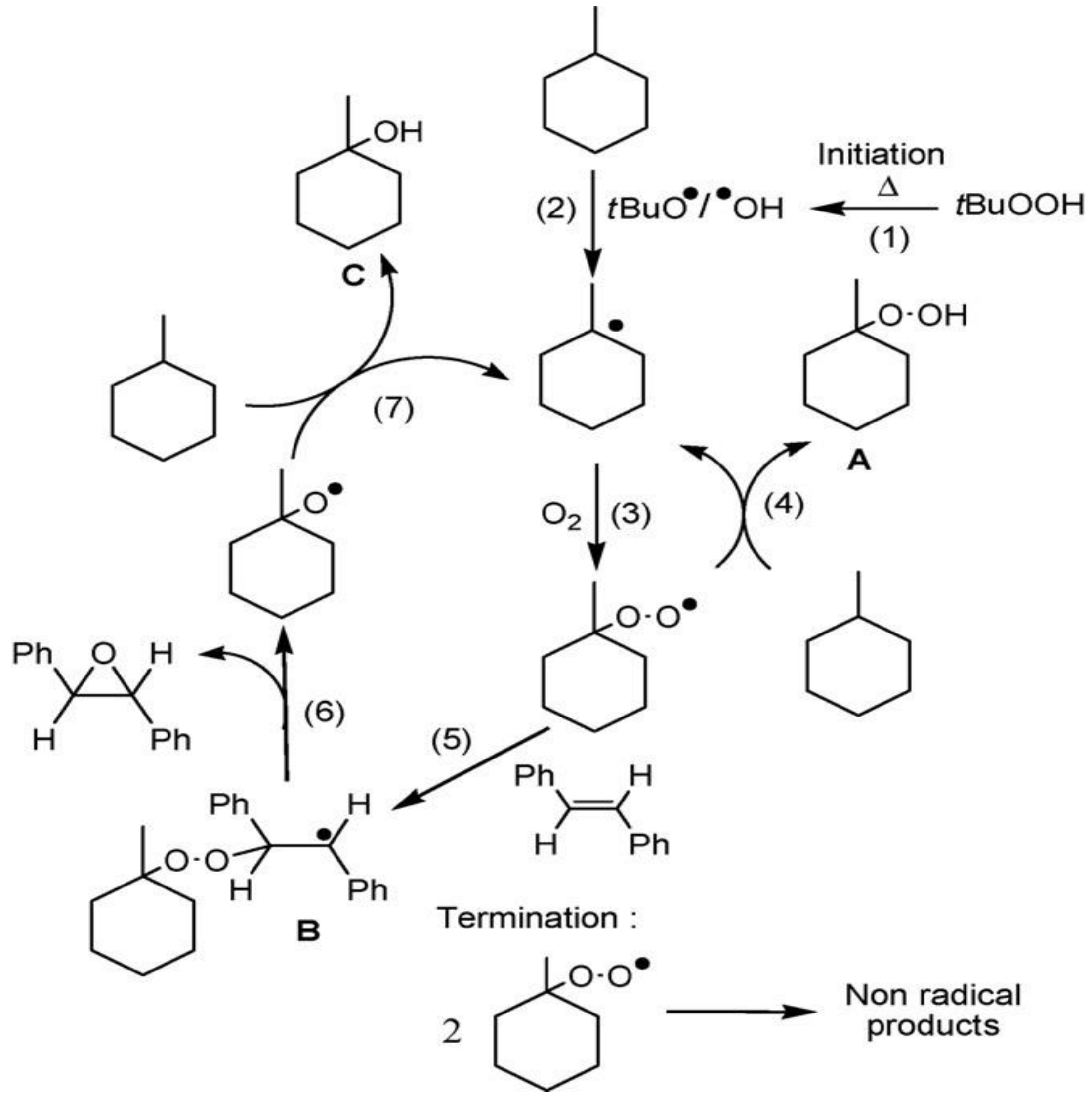


Scheme 1.2: Plausible reaction mechanism for the formation of benzyl alcohol and benzladehdye[63]

Furthermore, the oxidation of benzyl alcohol to benzaldehdye was fully studied by Choudhary *et al* using TBHP as an oxidant. A series of catalyst using transition metal containing layered double hydroxide and/or mixed hdroxides,[65] nano-size gold particles on MgO,[66] nanogold supported on TiO_2 and other transition metal oxide or rare-earth oxide,[67-68], was discovered at mild temperature conditions (94±1 ºC). All of these studies give a good selectivity of benzaldehdye. The catalytic performance of a particular supported nano-gold catalyst was thus found to depend on the reaction catalysed by them[67]. Moreover, it is strongly influenced by a number of catalyst parameters, such as the metal oxide support, the method of gold deposition on the support, the gold loading and also on the catalyst calcination temperature. Nano gold particles support interaction seems to play an important role in controlling the deposition of gold (amount of gold deposited, size and morphology of gold particles), formation of different surface gold species (Au^0, Au^{1+}, Au^{3+}) and electronic properties of gold particles consequently control the catalytic performance (both the activity and selectivity) of the supported nano-gold catalysts in the reactions[67] .

Choudhary *et al*. and subsequently Yin *et al*. have shown that gold nanoparticles supported on a range of oxides are active for the epoxidation of styrene using TBHP in greater than stoichiometry amounts[69-73-74]. Selectivities to sytrene oxide of ca. 50% are readily achieved using this approach. Salem *et al*. showed that during the oxidation of cyclooctene using mild solvent-free conditions, selectivities of over 80% to the epoxide could be achieved[75]. Further, it indicated that the peroxy initiator was not required to achieve selective oxidation but that lower selectivities to the epoxides were observed in their absence. In addition, it was suggested that when the peroxy initiator was present in the absence of catalyst,or in the presence of the graphite support some reactivity of the alkene was observed, but that it was not selective to the epoxide. This effect is presumably due to molecular oxygen being a di-radical in its ground state and so can participate in radical reaction without the need for activation at the catalyst surface. Subsequently, Lignier *et al*. have studied this experimental approach in detail for the oxidation of stilbene, for which it has been proposed a radical mechanism[76-77]. The involvement of co-oxidation of methylcyclohexane (MCH as a solvent) and the epoxidation of trans-stilbene have been suggested in this paper. In the proposed mechanism (Scheme 1.3), the initiation step consists of thermolysis of TBHP (1) and production of the methylcyclohexyl radical (2). The propagation step (3) consists of production of the methylcycohexyl peroxy radical. It can then add to trans-stilbene (5) or, to a lesser extent [78], carry out hydrogen abstraction from methylcyclohexane (4) to generate the methylcyclohexyl radical and form methylcyclohexyl hydrogen peroxide (compound A). Addition to (as compared to hydrogen abstraction from) trans-stilbene is favored since it has no allylic hydrogen that could be abstracted [79]. Species B is consistent with the results obtained in the Au/C-catalyzed oxidation of cis-stilbene, which yield exclusively trans-stilbene oxide. This implies the presence of an imtermediate which allow rotation around the C-C bond. Addition can be followed by unimolecular decomposition (6) to form the epoxide and a methylcyclohexoyl radical. This spesies will then abstract the tertiary hydrogen from methycylohexane (MCH) to produce methylcyclohexan-1-ol (compound C) and regenerate the methylcyclohexyl radical. Termination probably occured via recombination of the peroxo radicals[80-81]. This mechanism is consistent with the initial observation that catalyst amounts of a peroxy species were required to observe selective epoxidation.[82]

From the brief literature mentioned above, the TBHP as an oxidant was discovered and nanoparticle gold as a catalyst gave important value for the selective oxidation of reactions. Therefore, further studies were taken to perform the oxidation of toluene with Au-Pd as catalyst and TBHP as oxidant. One of the aims of this thesis is to perform this reaction at mild conditions (~80 ºC).



Scheme1.3: Proposed mechanism for the epoxidation of trans-stilbene in methylcyclohexane, in the presence of TBHP (5 mol%) and gold-based catalyst.[77]

1.6 Aims of the study

As described in the literature review, selective oxidation of toluene will be studied using supported gold catalyst and different parameters will be discussed.

The main objectives have been:

1) Study the effect of TBHP as oxidant on toluene oxidation under mild reaction condition.
2) Exploit the effect of support and TBHP as oxidant on oxidation of toluene
3) Systematic study into the effect of reaction parameters on the catalytic activity and selectivity.
4) Study the effect of the mechanism of the TBHP on the catalyst and oxidation of toluene.
5) Study the effect of mono and bimetallic catalyst system namely gold-palladium on the oxidation of toluene and observe the effect of metallic ratio on the reactions activity and selectivity.
6) Study the effect of the preparation of catalyst on the oxidation of other subsituted toluene compounds with TBHP as oxidant.

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CHAPTER 2

EXPERIMENTAL DETAILS

This chapter consists of three sections:

(i) Preparation of catalysts

(ii) Materials and Methods

(iii) Characterisation techniques

2.1 Preparation of catalysts

2.1.1 Impregnation method

A range of catalysts based on Pd-only, Au-only and Au-Pd bimetallic catalysts were prepared by impregnation of carbon (Darco G60, Aldrich) and TiO_2 (Degussa, P25), SiO_2 Aerocat (Degussa AG), CeO_2, nanopowder (Aldrich), CeO_2, nanopowder (degussa AG), γ-Al_2O_3, (Alfa Aesar), ZnO_2 (Aldrich), Graphite (Johnson Matthey), *via* an impregnation method using aqueous solutions of $PdCl_2$ (Johnson Matthey) and/ or $HAuCl_4.3H_2O$ (Johnson Matthey). For the 2.5%wtAu-2.5%wtPd/TiO_2 catalyst, the detailed preparation procedure employed is described below:-

An aqueous solution of $HAuCl_4.3H_2O$ (2 ml, 5g dissolved in water (250 ml)) and an aqueous solution of $PdCl_2$ (0.83 ml, 1 g in water (25 ml)) were simultaneously added to TiO_2 (1.9 g). The paste formed was ground and dried at 110°C for 16 h and then calcined (500mg, 3 inch glass boat) in static air, typically at 400°C for 3 h. The same procedure was also repeated using same weight percent using variable support materials. For monometallic catalysts the metal loading required (2.5 and 5% wt total metal) was adjusted as required by changing the volume of aqueous metal precursor and the procedure was repeated as above.

2.1.2 Sol-immobilisation method

Au, Pd and Au-Pd catalysts supported on carbon or TiO_2 were prepared using a sol-immobilisation method. An aqueous solution of $PdCl_2$ (Johnson Matthey) and $HAuCl_4.3H_2O$ of the desired concentration was prepared. To this solution polyvinylalcohol (PVA) (1 wt % solution, Aldrich, weight average molecular weight M_W = 9,000-10,000 g/mol, 80% hydrolysed) was added (PVA/metal (wt/wt) = 1.2). Subsequently, 0.1 M freshly prepared solution of $NaBH_4$ (>96%, Aldrich, $NaBH_4$/Au (mol/mol) = 5) was then added to form a dark-brown sol. After 30 min of sol generation, the colloid was immobilised by adding the supported material (activated carbon, titania) (acidified to pH 1-3 by sulfuric acid) under vigorous stirring conditions. The amount of support material required was calculated so as to have a total final metal loading of 1% wt. After 2 h the slurry was filtered, the catalyst washed thoroughly with 2L of distilled water and dried at 120 °C overnight.

2.2 Catalytic Testing

2.2.1 Glass reactor studies

All reactions were performed in a stirred glass round bottom flask (100 ml) fitted with a reflux condenser and heated in an oil bath. Typically, hydrocarbon (e.g. toluene, Acros organics) (10 ml) and the desired amount of catalyst was suspended in the solution. Then the tert-butyl hydroperoxide (TBHP, Aldrich) was added as the oxidant and the mixture was stirred at the desired temperature in an air atmosphere for 0.5 to 4 hours. Reaction time was extended up to 96 hours for some reactions. As a comparison, the O_2 gas and H_2O_2 solution will be used rather than TBHP in this reaction. By the way, precaution or safety awareness need to take when O_2 and H_2O_2 was performed due to the easier to explosive conditions.

Most of the reaction carried out in the open system at atmosphere pressure conditions. In section 4.2.3, the reaction was set and performed in helium condition. The condenser was attached with the balloon that full of helium gas and make sure all connector were closed properly. Before start the reaction, the helium gas was purge in the system before it shut to closed system and He environmentally

Aliquots of the reaction mixture were removed and filtered at desired time points for analysis. These were kept under cold conditions (on ice or in the refrigerator) until analysis was performed.

2.3. Analysis of reaction products

2.3.1 Gas Chromatography (GC)

The reactions products were analysed using a Varian Star 3400CX equipped with flame ionisation detector (FID) and a Varian CP Wax 52CB column (25m, 0.53mm i.d,2.0 micron capillary). He gas was used as a carrier in the column and injector and detector was set to 250°C. After reaction, an internal standard (500µL of 2-propanol) was added to the reaction products. The internal standard did not react with the reaction products (determined from other investigations) and eluted from the column at a different reaction time. Direct injections of 0.3µL of the reaction mixtures were then analysed by gas chromatography. Catalytic data for reactions were calculated using an internal calibration curve and internal standard (2-propanol). Internal standard also was used to determine the carbon balance of the reaction. Detailed calibration factors (CF) and calculation for both standards are shown in appendix A.1 (a, b, c, d).

The GC oven conditions are shown in table 2.1.

Table 2.1: GC column method

	Temp (°C)	Rate (°C min^{-1})	Hold (min)	Total time (min)
Initial	60	20	0	0
Final	250	20	3.5	13

The standard retention time of the internal standard including all of the compounds is shown in Table 2.2. The standard solutions of proposed reaction products were injected on a regular basis to ensure reliability. Compounds with low hydrogen bond interaction with the column (e.g. benzyl alcohol) and high boiling points (e.g. benzyl benzoate) eluted with longer retentions time as shown in Table 2.2.

Table 2.2: Order of elution and retention for each product for toluene reaction in liquid phase GC.

Products	Retention time (min)
Internal standard (2-propanol)	1.07
Toluene	1.48
TBHP	2.70
Benzaldehdye	4.32
Benzyl alcohol	6.15
Benzoic acid	8.80
Benzyl benzoate	9.87

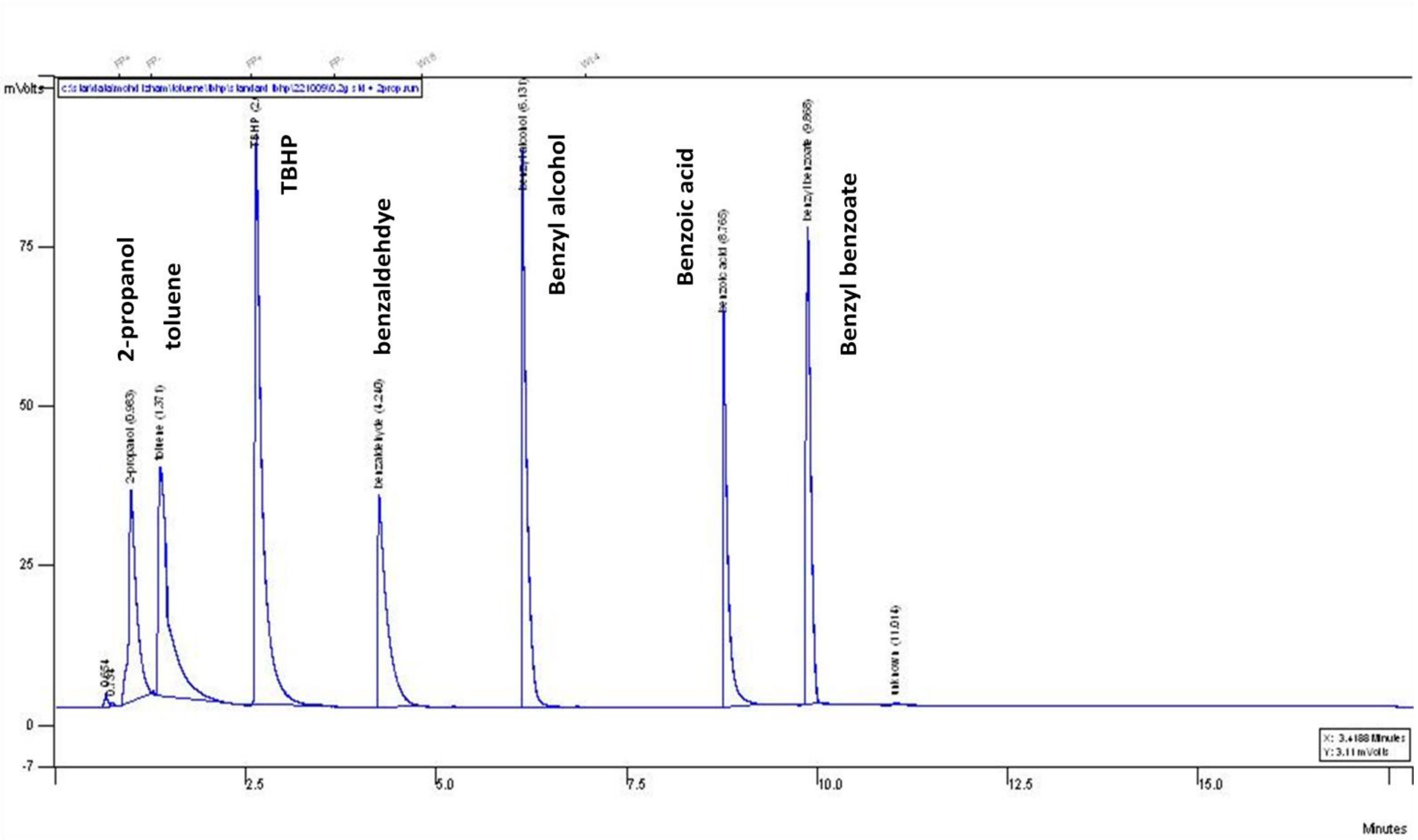

Figure 2.1: GC spectrum for standard toluene and TBHP with 2-propanol as an internal standard.

2.3.2 Gas Chromatography Mass Spectrometery (GC-MS)

For further identification and unambiguous confirmation of reaction products, Gas Chromatography- Mass Spectrometry methods were employed. After the reaction, 100µL of filtered reaction mixture was diluted with 1mL acetonitrile as a solvent. The analysis was performed on a Waters GCT Premier orthogonal acceleration time-of-flight mass spectrometer containing an Agilent 6890 oven fitted with an Agilent HP-5MS column (30m, 0.25 mm i.d.,0.25 µm film of (5%-Phenyl)-methylpolysiloxane)). Products were identified by fitting the MS fragmentation patterns of the main peaks from the experiment by matching to standards in the MS searchable library that was provided by the instrument. For further confirmation, the series of standard of the compounds was run using GC-MS to ensure accurate assignment.

Table 2.3: GC-MS Column Method

	Temp (°C)	Rate (°C min^{-1})	Hold (min)	Total time (min)
Initial	40	-	5.0	5.0
Final	280	8.0	5.0	40

2.4 Materials

The chemicals used in this study are as follows:

i) Toluene, 99+%, extra pure, Acros Organics

ii) Benzyl alcohol, 99+%, Aldrich

iii) Benzaldehyde, 99%, Aldrich

iv) Benzoic acid,99.5% A.C.S. Reagent, Aldrich

v) Benzyl benzoate, ≥99.0%, Sigma-Aldrich

vi) Tert-butyl hydroperoxide solution,70 wt % in H_2O, Aldrich

vii) 3-methoxytoluene, 99%, Aldrich

viii) 3-methoxybenzyl alcohol, 98%, Aldrich

ix) 3-methoxybenzaldehyde, Aldrich

x) 3-methoxybenzoic acid, 99%, Aldrich

xi) 2-methoxytoluene, 99%, SAFC

xii) 2-methoxybenzyl alcohol, 99%, Aldrich

xiii) 2-methoxybenzaldehyde, 98%, Aldrich

xiv) 2-methoxybenzoic acid, 99%, Aldrich

xv) 4-methoxytoluene, 99%, Aldrich

xvi) 4-methoxybenzyl alcohol,98%, Aldrich

xvii) 4-methoxybenzaldehdye,98%, Aldrich

xviii) 4-methoxybenzoic acid, 99%, Aldrich

xix) 2-nitrotoluene, 99+%, Aldrich

xx) 2-nitrobenzyl alcohol, 97%, Acros Organics

xxi) 2-nitrobenzaldehyde, 98%, Aldrich

xxii) 2-nitrobenzoic acid purum, ≥97% (HPLC), Fluka Analytical

xxiii) 3-nitrotoluene, Fluka Chemika.

xxiv) 3-nitrobenzyl alcohol, 98%, Aldrich

xxv) 3-nitrobenzoic acid, 99%, Aldrich

xxvi) 4-nitrotoluene, Aldrich

xxvii) 4-nitrobenzaldehyde purum, ≥97% (HPLC), Fluka Analytical

xxviii) 4-nitrobenzyl alcohol, 99%, Acros Organics

xxix) 4-nitrobenzoic acid purum, ≥98.0% (HPLC), Fluka Analytical

xxx) Ethylbenzene, anhydrous, 99.8%, Sigma-Aldrich

xxxi) 1-phenylethanol, 98%, Aldrich

xxxii) 2-phenylethanol, 99%, Aldrich

xxxiii) Phenylacetaldehyde, ≥90%, Aldrich

xxxiv) Acetophenone, 99%, Aldrich

xxxv) Phenylacetic acid,99%, Aldrich

xxxvi) 4-tertbutyltoluene, 95%, Aldrich

xxxvii) 4-tertbutylbenzaldehdye, 97%, Aldrich

xxxviii) 4-tertbutylbenzoic acid, 99%, Aldrich

xxxix) Dibenzyl ether purum, ≥98.0% (GC), Fluka Analytical

xl) Cumene hydroperoxide (Luperox®CU90),88%, Aldrich

xli) Ditert-butyl peroxide, 99%, AcrosOrganics

xlii) Acetonitrile reagen plus™, 99%, Aldrich

xliii) 2-propanol, Fisher Scientific.

2.5 Catalyst Characterisations

2.5.1 X-Ray Diffraction Analysis (XRD)

2.5.1.1 Backgrounds

X-Ray Diffraction is one of the most useful techniques to identify bulk phases, to monitor the kinetics of bulk transformations and to estimate particles sizes. In X-Ray Diffraction (XRD) a collimated beam of X-rays, with wavelength ($\lambda \sim 0.5 - 2$ Å), is incident on a powder specimen and is diffracted by the crystalline phases in the specimen according to Bragg's law ($\lambda = 2d \sin \theta$, where d is the lattice spacing between atomic of the crystalline phase and θ is the diffraction angle). The intensity of the diffracted X-rays is measured as a function of the diffraction angle 2θ and the specimen’s orientation. This diffraction pattern is used to identify the specimen's crystalline phases and to measure its structural properties.

XRD data may be used more efficiently for quantitative analysis of the crystalline phases in a mixture and also for the determination of the structural parameters as summarised in Table 2.4.

Table 2.4 Typical Applications of X-ray Diffraction Methods[1]

Determination of crystallographic parameters

Unit cell dimensions and lattice symmetry
Atomic coordinates and thermal parameters
Isomorphous substitution in lattice sites
Infra-lattice porosity (zeolites, microporous materials)

Determination of physical/morphological features

Crystallite size
Crystallinity
Lattice strain (stacking faults, dislocations, microtwinning)
Preferred orientation of the crystallites (texture)

Identification and quantisation of crystalline phases

2.5.1.2 Experimental

X-ray Diffraction (XRD) analysis was carried out using a PANanalytical Xpert PRO MPD Diffractometer to determine the phase compositions of catalysts at ambient temperature and under normal atmospheric conditions. Diffraction patterns were produced by employing CuK_α radiation (λ= 0.154098 nm) at 40 kV and 40 mA generated by a diffraction X-ray tube on the samples that were mounted on samples holder and the basal spacing was determined via powder technique. The samples were scanned at the range 2θ, started from θ =10 - 80°. The values of the d-spacing, intensity and full width at half maximum (FWHM) were calculated using X'Pert HighScore Plus software. Crystallite size calculations were determined using the Scherrer equation (equation 1)[2].

$$\text{Crystallite size} = \frac{(K * \lambda)}{(FWHM * \cos\theta)} \qquad \text{(Equation 1)}$$

Where, K	is the Scherrer constant
λ	is the wavelength of X-ray
FWHM	is the full peak width at half maximum
θ	is the angle of diffraction

2.5.2 BET Specific Surface Area Measurements

2.5.2.1 Background

The BET surface area was calculated and total pore volume was determined by the estimation from the nitrogen uptake at $p/p_o \rightarrow 1$, where p_0 is the saturation vapour pressure of the adsorptive and p is the pressure of the vapour.

In spite of the oversimplification of the model on which the theory is based, this is the most widely used standard procedure for the determination of surface area of finely divided and porous material. The BET equation applicable at low p/p_o range is customarily written in linear form as[3]:

$$\frac{p}{n^a(p_o - p)} = \frac{1}{n_m{}^a C} + \left[\frac{C-1}{n_m{}^a C}\right]\frac{p}{p_o} \qquad \text{(Equation 2)}$$

where n^a is the amount of the gas adsorbed at the relative pressure p/p_o, $n_m{}^a$ is the monolayer capacity and C is the so-called BET constant which, according to the BET theory, is related to the enthalpy of adsorption in the first adsorbed layer and gives information about the magnitude of adsorbent-adsorbate interaction energy[4].

2.5.2.2 Experimental

Total surface areas of Au-Pd catalyst were obtained from the adsorption-desorption isotherm of nitrogen at 77 K by using Micrometics Gemini 2360 surface analyzer instrument. Typically, 1.0 – 2.0 g of pure catalyst was used each time. The BET surface area was calculated and total pore volume was determined by estimation from the nitrogen uptake at $p/p_o \rightarrow 1$. Adsorption isotherms are obtained by plotting the volume of nitrogen adsorbed (ccg^{-1} at STP) against the equilibrium relative pressure (p/p_o) where p is the actual gas pressure and p_o is the vapour pressure of the adsorbing gas, N_2, at the temperature at which the test is conducted. The plots reveal much about the porous texture of the adsorbent catalyst simply from their shapes.

2.5.3 X-Ray photoelectron spectra (XPS)

2.5.3.1 Background

XPS is one of important technique in catalysis. This is a surface analysis technique that can gives information about elemental composition and the oxidation state of the elements. Based on the photoelectric effect, the sample surface was irradiated with X-Rays and the emitted photo electrons are measured[5]. When atom absorbs a photon of energy hν, a core or valence electron with binding energy E_b is ejected with kinetic energy E_k :

$$E_k = h\nu - E_b - \varphi \qquad \text{(Equation 3)}$$

Where, E_k is the kinetic energy of the photoelectron

h is Planck's constant

v is the frequency of the exciting radiation

E_b is the binding energy of the photoelectron with respect to the Fermi level of the sample

φ is the work function of the spectrometer

The XPS spectrum is usually a plot of the intensity of photoelectrons versus binding energy. Since the electrons whose energies are analyzed in XPS arise from a depth of no greater than about 5nm, the technique is highly surface specific[6]. A set of binding energies is characteristic for an element and hence XPS can be used to analyze the composition of samples, considering the area of the peaks and cross sections for photoemission. Binding energy is not only element specific but contains chemical information like oxidation state, because the energy levels of core electrons depend slightly on the chemical state of the atom. Chemical shifts are typically in the range of 0-3 eV. The most commonly employed are the Mg-Kα (1253.6 eV) and the Al-Kα (1486.6 eV), which are produced form a standard X-ray tube and the peaks detected in XPS spectra correspond to the bound core-level electron of the sample. The intensity of each peak is proportional to the abundance of the emitting atoms in the near-surface region, while the precise binding energy of each peak depends on the chemical oxidation state and local environment of the emitting atoms. Furthermore, XPS can provide information about the oxidation state and chemical environment of a given element due to shifts in the binding energies[7]

2.5.3.2 Experimental

X-ray photoelectron spectra were recorded on a Kratos Axis Ultra DLD spectrometer employing a monochromatic Al K_α X-ray source (75-150W) and analyser pass energies of 160 eV (for survey scans) or 40 eV (for detailed scans). Samples were mounted using double-sided adhesive tape and binding energies referenced to the C(1s) binding energy of adventitious carbon contamination which was taken to be 284.7eV.

2.5.4 Electron Paramagnetic Resonance Spectroscopy (EPR)

2.5.4.1 Background

The development of the theory of electron paramagnetic resonance is generally attributed to the work of Vleck[8], conducted in Harvard during the 1930’s. Following the Second World War, microwave generators developed for use in radar became widely available, leading to the development of the first spectrometers. Some of the earliest experimental advances were made by Gorter[9], but the first spectrum was not recorded until 1945 by the Russian experimentalist Zavoisky[10]. By the early 1960’s, commercial spectrometers were being built, and EPR technique became a common analytical tool in many research laboratories.

EPR spectroscopy is used to detect unpaired electron spin, i.e., paramagnetic centre and is most commonly applied to the detection of species in the solid and liquid phases. The lower detection limit for most commercial spectrometers usually approaches 10^{-6} to 10^{-7} moles of unpaired spin, though this figure very much depends on the dynamics of the system under study. In term of its experimental operation, EPR is in many ways analogous to nuclear magnetic resonance spectroscopy (NMR), which is used to detect nuclear spins. Both spectroscopic techniques are resonance techniques in which the interaction of odd spins with applied magnetic and electromagnetic fields form the basis of the experiment. However, EPR is less widely applicable than NMR due to the intrinsic instability and short life-time of many paramagnetic species. The main experimental parameter obtained from EPR measurement are the ***g*** value of the paramagnetic species, and hyperfine splitting arising from interactions with non-zero spin nuclei or asymmetric crystal field (giving rise to multiple line spectra). The g value is a constant associated with an electron in a given environment, and can be considered as being analogous to the chemical shift in NMR. Hyperfine splitting gives data regarding the structure of the radical of paramagnetic centre, e.g., the number and type of interacting nuclei, or vicinal lattice ion distribution.

Because of the ubiquitous nature of the free radicals throughout chemistry, EPR has been applied to the study of wide variety of problems in chemistry, physics, biology, and medicine. The data obtained from the EPR experiments provides valuable information regarding the structure, chemical environment (physical location) and amount of paramagnetic species in a sample.

The detection of paramagnetic centre or free radical by EPR is made by direct measurement when the species are sufficiently long-lived. In the case of short-lived moieties, certain refinements can be made to the technique. It is possible to maintain a steady state concentration of some short lived species by simultaneous UV irradiation during the EPR experiment, and this does not usually lead to a significant perturbation of order to accumulate a sufficient concentration for observation. Because the dynamics of non-zero spin systems vary with temperature, such experiments may also provide valuable information about the radical structure (EPR data have been collected typically in the temperature range of 4 to 1000K)[11]. In organic systems (which often contain very short-lived radical intermediates) diamagnetic radical scavengers can be added (termed spin traps), which react with short-lived radicals to produce stable secondary paramagnetic species (spin adducts). The spins adduct spectra often give useful clues to the identity of the trapped radical and can be used in comparative quantitative analyses.

2.5.4.2 Experimental

For EPR measurements, the samples (*ca.* 10-15 mg) were loaded into high purity quartz (Suprasil) EPR tubes. The samples were then placed onto a vacuum manifold and evacuated for 30 minutes to a residual base pressure of 1 x 10^{-3} Torr (to remove excess molecular oxygen which will considerably broaden any surface paramagnetic signals). The spectra were subsequently recorded at room temperature (298K) or low temperature (140K) on the as received samples. All measurements were performed on a Bruker EMX CW EPR spectrometer operating at X-band frequencies (9.8 GHz), 10mW power, 100 kHz field modulation in a Bruker high sensitivity cavity (ER 4119HS). The spectra were recorded at variable mW powers.

2.5.5 Temperature Programmed Desorption analysis (TPD)

2.5.5.1 Background

Temperature programmed methods for thermal analyses are also defined as transient response methods because they can be used for the investigation of kinetics of heterogeneous catalytic reactions. Instead of the reaction system being driven to a steady state, the system perturbed in a controlled way using a temperature programme. Among the thermo analytical techniques, temperature-programmed desorption (TPD), Temperature-programmed reduction (TPR) and temperature-programmed oxidation (TPO) are the most commonly used tools for heterogeneous catalyst characterisation[12, 13]. In this study, TPD with flow gas probe molecule such as NH_3 have been used in order to determine acid and basic sites respectively on different support materials.

Temperature programmed desorption was first described by Amenomiya and Cvetanovic in 1963[12]. In TPD studies a sample material previously equilibrated with an adsorbate under well-defined conditions (preferably immediately prior to TPR analysis) is submitted to a programmed temperature increase. Increasing thermal energy overcomes the adsorption energies of the previously adsorbed species in order of increasing adsorption energy. As the molecules desorbs from the surface they are swept by a carrier gas, such as helium, argon or nitrogen, to a thermal conductivity detector where they are quantified. The change in thermal conductivity of the gas mixture before and after reaction is measured. These results in a plot of the amount of adsorbates desorbed, *i.e.* change in thermal conductivity, versus the temperature of the surface to produce the TPD spectrum.

2.5.5.2 Experimental

Analysis was performed using a Thermal TPDRO 1100. The machine is designed to perform several experiments including pulse chemisorptions, temperature programmed reduction, desorption and oxidation.

The sample (100mg) was suspended in a plug of silica wool in a straight wall sample tube. The sample tube is loaded into the furnace. The sample is degassed in He for pretreatment by heating it to 308 K(20 cc/min), holding it under that stream at 308 K for 1 h, before cooling it to ambient. This pre-treatment procedure is carried out to remove residual H_2O and other volatile impurities. The flow was then switched to ammonia, NH_3 and the temperature was raised (20 cc/min) to 308 K for 10-15 minutes and flowed for 10 minutes. After that, the sample is degassed in He for analysis (5 K/min, rate 45 °C/min) and heated from ambient temperature to 1273K and held for 10 min before cool down to 313 K. This analysis takes about 4 hours to complete. The TPDRO machine is controlled by a PC, which is loaded with reaction conditions that operate during analysis. TPD profile is then plotted as the amount of ammonia desorbed from a catalyst versus time (which will is also converted to a function of temperature).

2.6 References

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CHAPTER 3

CHARACTERISATION OF THE CATALYST MATERIAL

3.1 Introduction

In this chapter, the catalyst was characterized in detail using bulk and surface-specific techniques, in order to establish how the nature of the Au-Pd catalyst affects reaction performance. Two major techniques were used, namely X-ray diffraction analysis (XRD) and X-ray photoelectron spectroscopy (XPS). In addition to this, the catalysts were subjected to BET surface area measurements to obtain the catalysts surface area. The characterisation data obtained in this study were then corroborated and combined with the related published data available on this type of catalyst.

3.2. X-Ray Diffraction (XRD) analysis

3.2.1 Uncalcined and calcined 2.5%wtAu-2.5%wtPd/TiO_{2I} catalyst by impregnation

X-Ray diffraction was conducted on the sample, using the techniques and equipment described in detail in chapter 2. The purpose of the characterization was to determine the crystal structure and the mean crystallite size of the involved metals as well as their oxidation state. Figure 3.1 shows the XRD pattern for uncalcined and calcined 2.5wt%Au-2.5%Pd/TiO_{2I} catalyst prepared by impregnation. The calcination process was done in furnace in static air and the catalyst was heated to 400°C for 3 hours. For uncalcined sample, the catalyst was only heated at 110 °C in oven for only drying process. The XRD pattern of the uncalcined sample indicated the presence of a characteristic peak of Au at $2\theta = 38.2^o$ (111) which became more intense after the calcination process. New peaks of Au were observed for calcined catalyst at 2θ= 44.3^o and 64.5^o which are assigned to the (200), (311) planes respectively. These particular reflections were obtained by referring to the JCPDS file no. 03-065-2870. In this results, the observation Pd peak was not detected due to the attribution smaller crystallite size which is lower than detectability limit of XRD (<5 nm) or due to the high metal dispersion on the TiO_2 support[1]. .XRD diffraction patterns for Au-Pd bimetallic catalysts evidently indicated the presence of Au or Au-Pd alloy peaks, whereas the Pd species were not detected probably due to the reason mentioned above (see Figure 3.2).

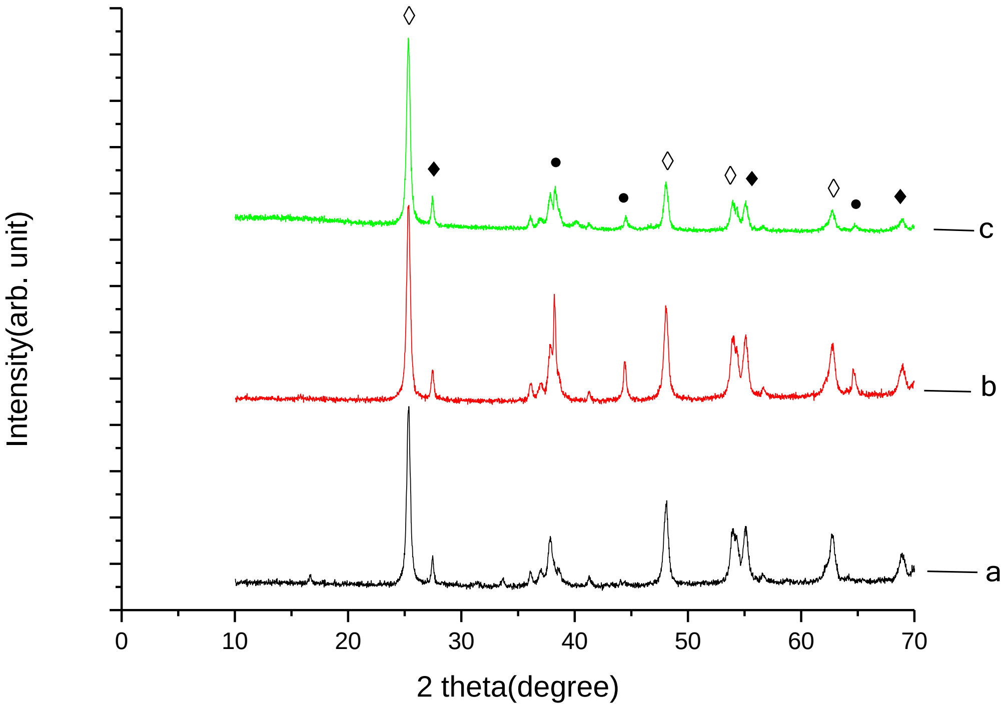

Figure 3.1: X-Ray diffractogram for 2.5%wtAu-2.5%wtPd/TiO_{2I} catalyst by impregnation method. Key: (a) uncalcined, (b) calcined at 400°C for 4 hours,(c)) reduced in 5% hydrogen in argon at 400 ^oC for 3 hours, Symbol: (●) Au/Au-Pd alloy, (◊) TiO_2 anatase phase and (♦) TiO_2 rutile phase

The diffraction lines corresponding to the TiO_2 (P25) support were clearly observed at 2θ = 25.3^o, 48.0^o, 53.9^o, and 62.7^o for anatase phase (JCPDS file no: 01-078-2486) whereas diffraction peaks corresponds to rutile phase TiO_2 could be detected by characteristic peaks at 27.4°, 56.5° and 68.7° (JCPDS file no: 01-072-4812). The ratio between anatase and rutile phase calculated in this study (77% anatase and 23% rutile) was comparable with the expected value (75% anatase and 25% rutile) for P25 type TiO_2 (Degussa) support material.

For 2.5wt%Au2.5wt%Pd/TiO_{2I} calcined sample, a slight shift of the Au peaks to the right (slightly higher of 2θ value) in figure 3.2 was observed indicating the formation of Au-Pd alloy as reported in literature[2-4].

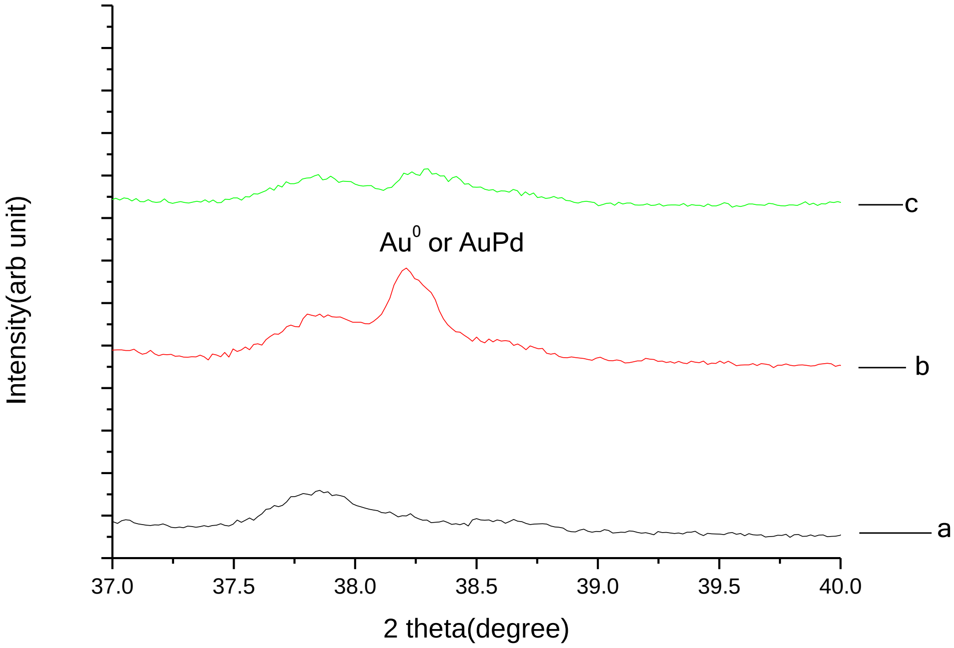

Figure 3.2: XRD Diffractogram for (a) 2.5%wtAu-2.5%wtPd/TiO_{2I} catalyst dried at 110°C(16h) ,(b) calcined at 400°C(3h) and (c) reduced in 5% hydrogen in argon at 400 °C for 3 hours.

3.2.2 Mono and bimetallic 5%wtAu-Pd/TiO_{2I} catalyst by impregnation

Figure 3.3 shows that the peaks of Au were clearly observed as was mentioned earlier. Unfortunately, the diffraction pattern of 2.5wt%Pd/TiO_{2I} did not show any clear peaks assigned to either metallic Pd or PdO. The diffraction peaks for Pd in metallic state are expected at 2θ = 40.4°, 46.9° and 68.6° (JCPDS file 01-087-0645) whereas the formation of PdO (Pd^{2+}) would be identified by main peaks at 2θ = 33.6°, 33.9° and 54.8° (JCPDS file 00-006-0515) corresponding to (002), (101) and (112) reflections, respectively. An observed Pd peak could be attributed to the smaller crystallite size which is lower than the detectability limit of XRD (<5 nm) or due to the high metal dispersion on the TiO_2 support[1]. XRD diffraction patterns of Au-Pd bimetallic catalysts evidently indicated the presence of Au or Au-Pd alloy peaks, whereas the Pd species were not detected probably due to the reason mentioned above.

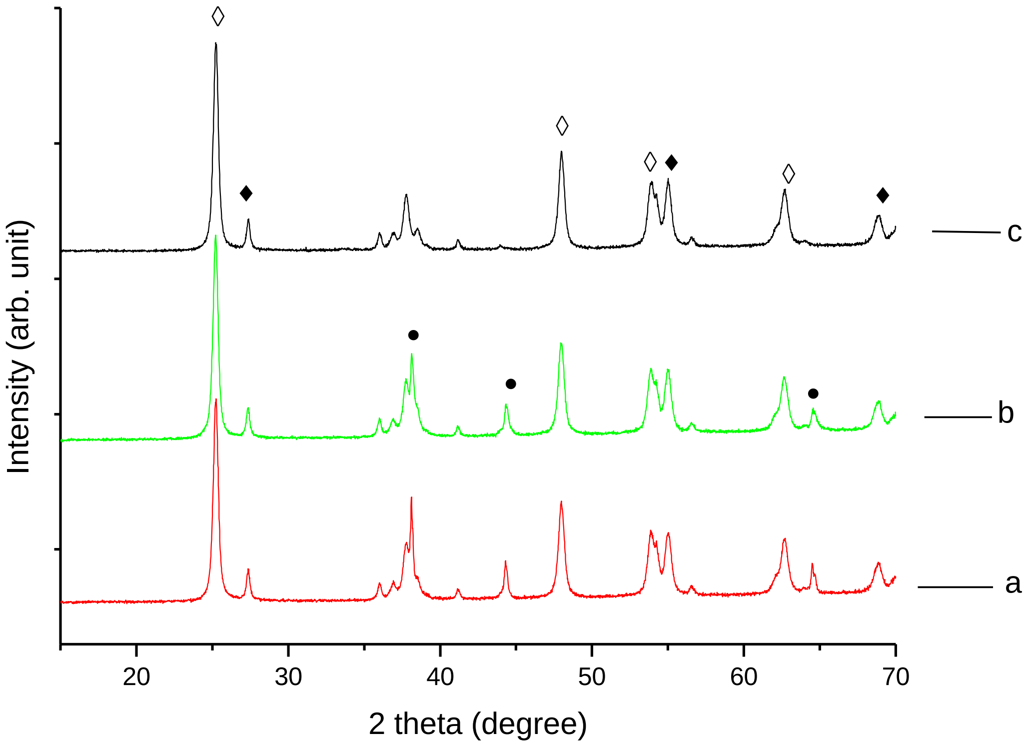

Figure 3.3: X-ray diffraction patterns of mono and bimetallic 2.5%wtAu/2.5%wtPd-TiO_{2I} catalyst calcined in air 400°C. Key: (a) 2.5wt%Au, (b) 5wt%Au-Pd/TiO_{2I}, (c) 2.5wt%Pd, Symbol: (•) Au/Au-pd alloy, (◊) TiO_2 anatase phase and (♦) TiO_2 rutile phase

To get clear picture of Au peaks, Figure 3.3 was expanded between 2θ =37.0 and 39.5 and it was observed the peak for Au was detected at 2θ = 38.2° which was assigned to the (111) planes (JCPDS file no. 03-065-2870)(see Figure 3.4). For bimetallic catalyst, it was observed the peak was shifted to the right to give conformation that Au-Pd alloy was observed at that level. Figure 3.4 also clearly shows that no Pd metal or PdO was detected from XRD pattern by mono Pd supported titania. The explanation regarding this condition was already explained in detail as above.

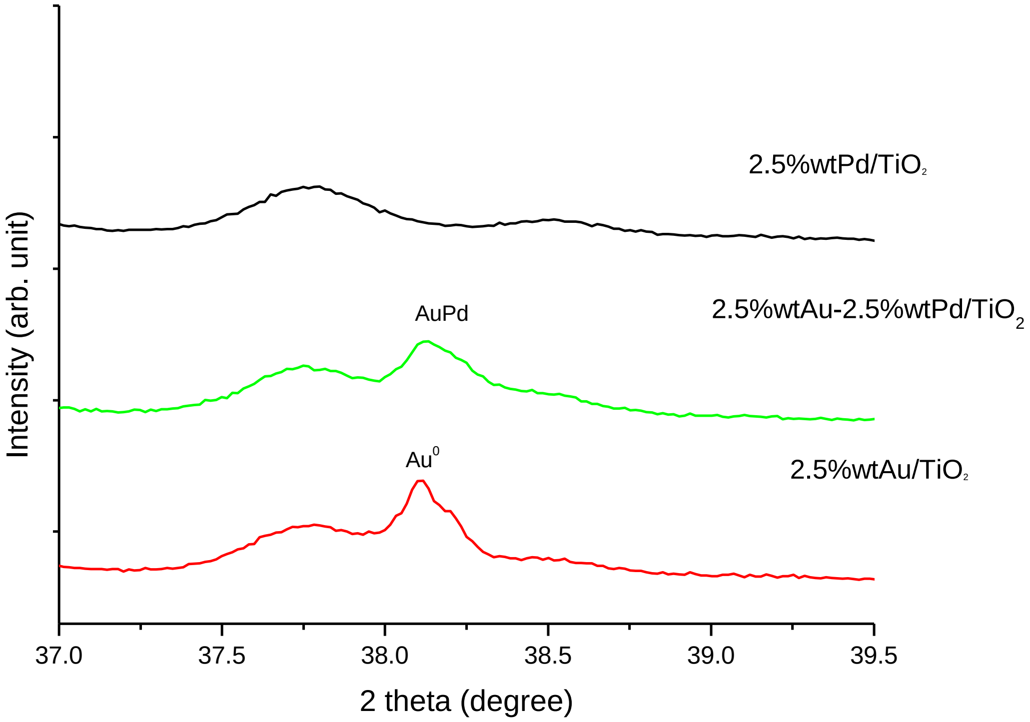

Figure 3.4: X-ray Diffraction patterns showed that Au metallic and Au-Pd alloy peaks.

In order to calculate the mean crystallite size of the Au or Au-Pd metal in all catalysts, the Scherer equation was used. [5] The diffraction peak at 44.3^o, corresponding to (200) reflection, was chosen instead of the (111) reflection based on the fact that the peak at 38.2^o was not fully resolved due to the overlapping with TiO_2 peak. Table 3.1 showed that the average crystallite size of Au on 2.5wt%Au/TiO_{2I} monometallic catalyst was bigger (34.4 nm) compared to the one calculated in bimetallic catalyst. The bigger crystallite size could be explained by the metal loading alone and a theoretically lower metal dispersion as well as presence of chloride species on the surface of catalyst.[1] Both factors could induce the agglomeration of Au particles during heat treatment and consequently generate larger metal crystallite sizes. In addition, it was claimed in the literature that the pure metal particles are generally bigger than alloyed particles[6].

The 2.5wt%Au2.5wt%Pd/TiO_{2I} catalyst calcined at 400 °C displayed the biggest Au-Pd crystallite size (23.6 nm) compared to the uncalcined dried catalyst (16 nm) as well as to catalysts with other type of pretreatment. The bigger crystallite size compared to the dried catalyst was explained by the sintering effect of metal particles during the calcination process at higher temperature. Further treatment with 5% H/Ar was used to study the reducing effect, which lead to a decrease in the crystallite size[7, 8]. Pretreatment in flowing gas could enhance the removal of chloride species and consequently suppress the metal agglomeration (see Table 3.1).

Table 3.1: Crystallite size of mono Au and bimetallic Au/Pd-TiO_2 catalysts with different treatment. All catalysts were synthesised using impregnation method.

Catalysts	Au, Au-Pd, FWHM (200) (2θ; 44.3°)	Au, Au-Pd, FWHM (200) Crystallite size[a] (nm)
2.5wt%Au-2.5%wtPd/TiO_2, dried in air, 110°C	0.535	16.0
2.5wt%Au-2.5%wtPd/TiO_2,static air, 400 °C	0.3631	23.6
2.5wt%Au-2.5%wtPd/TiO_2, 5%H_2/Ar, 400 °C,	0.389	22.1
2.5wt%Au, static air, 400 °C	0.2495	34.4

[a]Crystallite size by means of the Scherer equation: $\frac{0.9 * \lambda}{\beta_{hkl} * \cos\theta}$

3.2.3 Bimetallic 2.5%wt Au/ 2.5%wt Pd/TiO_{2I} catalyst with different support.

The following figures (figure 3.5 and 3.7) display the XRD diffractograms of 2.5wt%Au2.5wt%Pd supported on different materials (γ-Al_2O_3, SiO_2, ZrO_2, graphite (from Aldrich and Johnson Matthey), CeO_2, nano ceria, Carbon (G-60), TiO_2 respectively. The peaks corresponding to each support materials were compared to each JCPDS reference file. In terms of metal, peaks corresponding to Au-Pd alloy were clearly observed at 38.6^o (figure 3.6), 38.4º (figure 3.8) and 44.3^o. A gold peak was present at 38.2º which is assigned to the (111) plane. The peaks indicating the presence of metallic Pd were not observed as all the catalysts were subjected to calcinations in static air at 400 ^{o}C for 3 hours (figure 3.6 and 3.8).

Switching the type of support from TiO_2 to γ-Al_2O_3, carbon and SiO_2 respectively gave comparable Au-Pd crystallite size (table 3.2). Nano ceria and ZrO_2 showed slightly high crystallite size followed by CeO_2. The clear difference was only observed with graphite from Aldrich as support material, where an average crystallite size of 7.2 nm was observed.

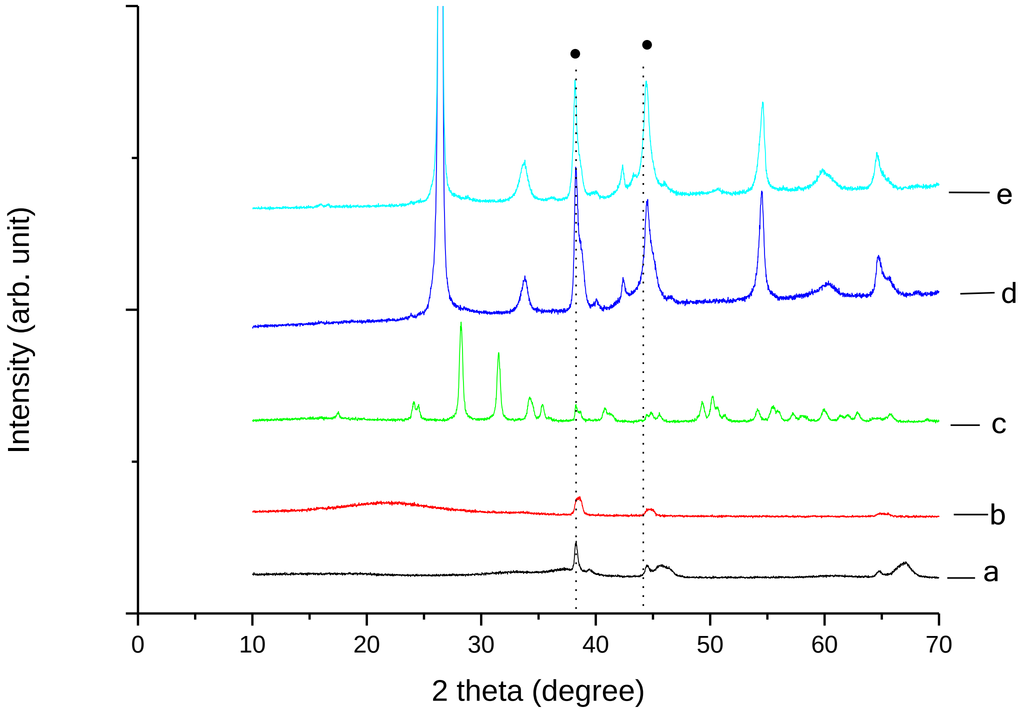

Figure 3.5: X-ray diffractogram of 2.5 wt% Au-2.5%wt Pd with different support catalyst and calcined in static air at 400°C for 3 hours. Key: (a) γ-Al_2O_3, (b) SiO_2, (c) ZrO_2, (d) graphite (from Aldrich), (e) graphite (from Johnson Matthey), Symbol: (●) Au or Au-Pd alloy. Other peaks corresponded to reflections for each respective support.

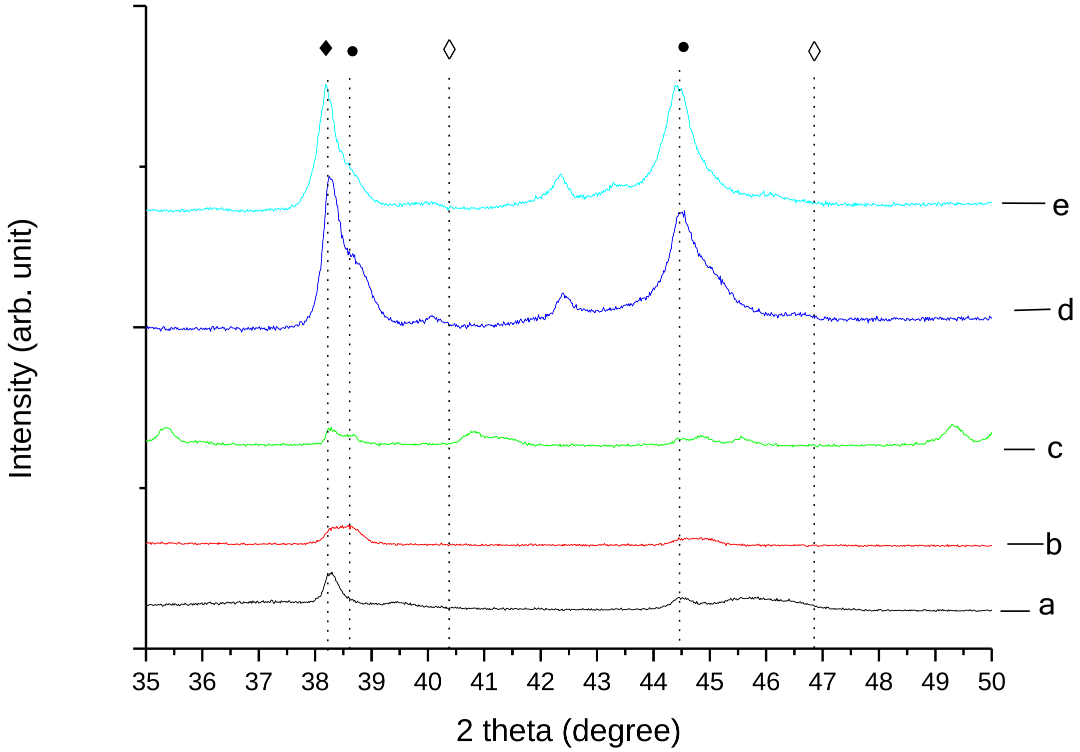

Figure 3.6: X-ray diffractogram of 2.5wt% Au-2.5%wt Pd with different support catalyst and calcined in static air at 400°C for 3 hours. Key: (a) γ-Al_2O_3, (b) SiO_2, (c) ZrO_2, (d) graphite (from Aldrich), (e) graphite (from Johnson Matthey), Symbol: (♦) Au, (●) Au or Au-Pd alloy and (◊) metallic Pd. Other peaks corresponded to reflections for each respective support.

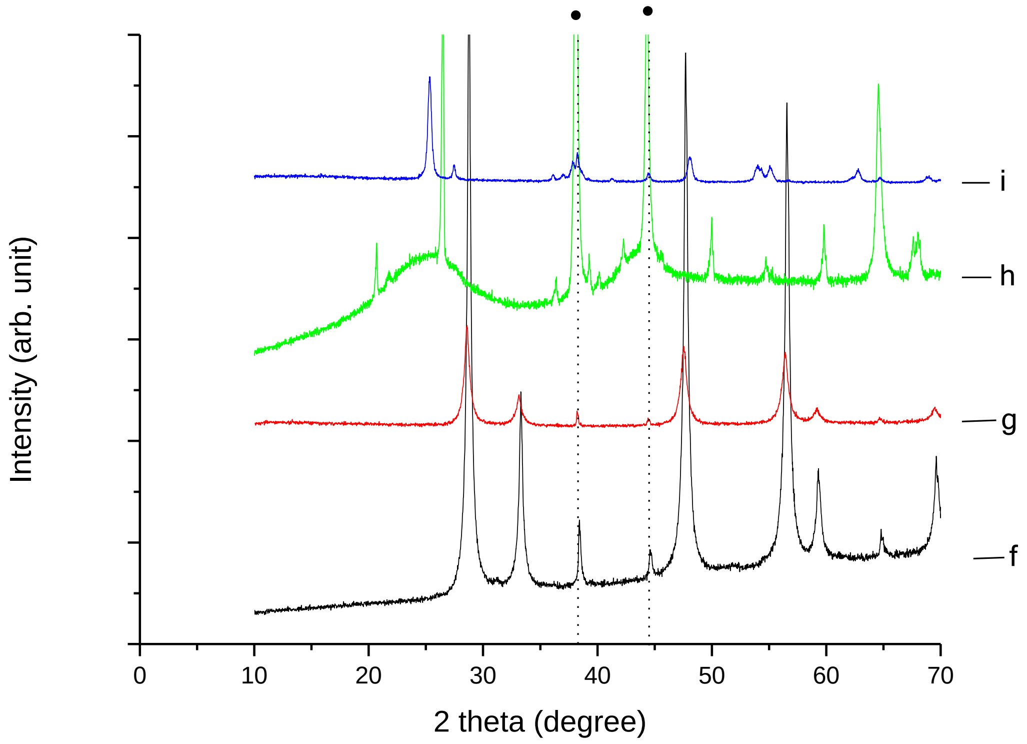

Figure 3.7: X-ray diffractogram of 2.5 5wt% Au-2.5%wt Pd with different support catalyst and calcined in static air at 400°C for 3 hours. Key: (f) CeO_2, (g) nano ceria, (h) Carbon (G-60), (i) TiO_2, Symbol: (●) Au or Au-Pd alloy. Other peaks corresponded to reflections for each respective support.

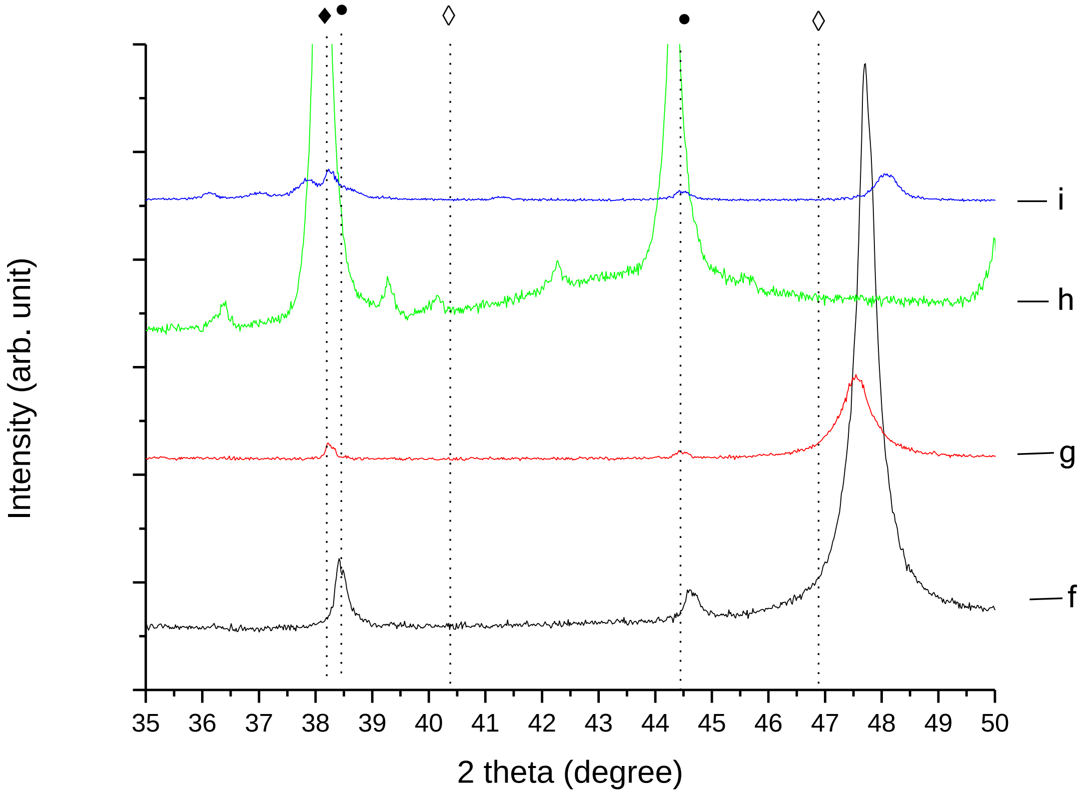

Figure 3.8: X-ray diffractogram of 2.5wt% Au-2.5%wt Pd with different support catalyst and calcined in static air at 400^{o}C for 3 hours. Key: (f) CeO_2, (g) nano ceria, (h) Carbon (G-60), (i) TiO_2, Symbol: (♦) Au, (●) Au or Au-Pd alloy and (◊) metallic Pd. Other peaks corresponded to reflections for each respective support.

Table 3.2: Crystallite size of 2.5wt%Au-2.5%wt Pd nanoparticles catalyst supported on different materials. All catalysts were synthesised using impregnation method and calcined in static air at 400 ^{o}C for 3 hours.

Supports	Au-Pd, FWHM (200) (2θ; 44.3^{o})	Au-Pd, FWHM (200) Crystallite size[a] (nm)
γ-Al_2O_3	0.3459	24.8
SiO_2	0.3316	25.8
ZrO_2	0.1844	46.5
Graphite (from Aldrich)	1.1984	7.2
Graphite (from Johnson Matthey)	1.1511	19.8
CeO_2	0.2515	34.1
Nano ceria	0.1777	48.3
Carbon (G-60)	0.2887	29.7
TiO_2	0.2844	23.6

[a]Crystallite size by means of Scherer's formula:

$$\frac{0.9*\lambda}{\beta_{hkl}*\cos\theta}$$

3.2.4 1%wtAu-Pd/TiO_2 catalyst prepared by sol-immobilisation catalyst

A small average crystallite size for Au-Pd/TiO_2 synthesised using the sol-immobilisation technique was determined by the lack of diffraction peaks corresponding to the deposited metals (Au, Pd) in the XRD spectra of 1.0wt%Au-Pd/TiO_{2SI} sample (figure 3.9 and 3.10). This is likely due to the detectability limit of XRD instrument as detailed above. It was reported in literature that transmission electron microscopy analysis (TEM) of a 1%Au-Pd/TiO_2 catalyst prepared through sol-immobilisation technique produced metal catalyst with mean particle size around 4 nm.[9] In addition, the lower total metal loading could also contribute to this observation. The XRD diffractogram for both impregnated and sol-immobilized samples look identical with diffractogram of bulk TiO_2 (figure 3.3(b)) sample.

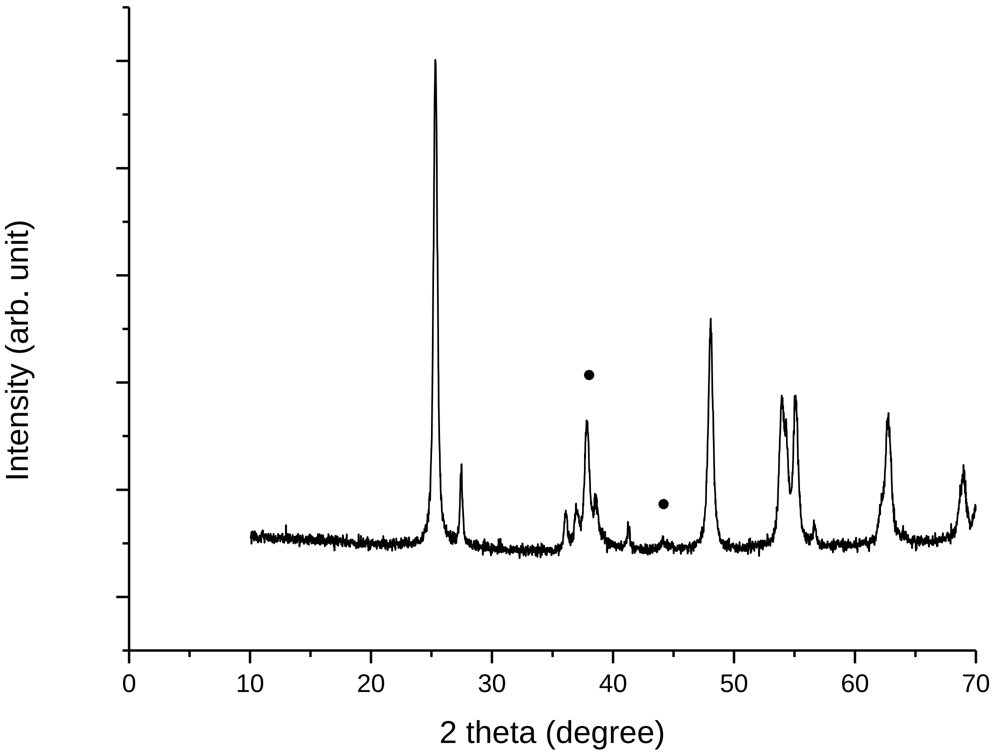

Figure 3.9: X-ray diffractogram of 1%wt Au-Pd/TiO_{2SI} prepared by sol-immobilisation method and dried 110°C for 3 hours. Symbol: (●) Au or Au-Pd alloy.

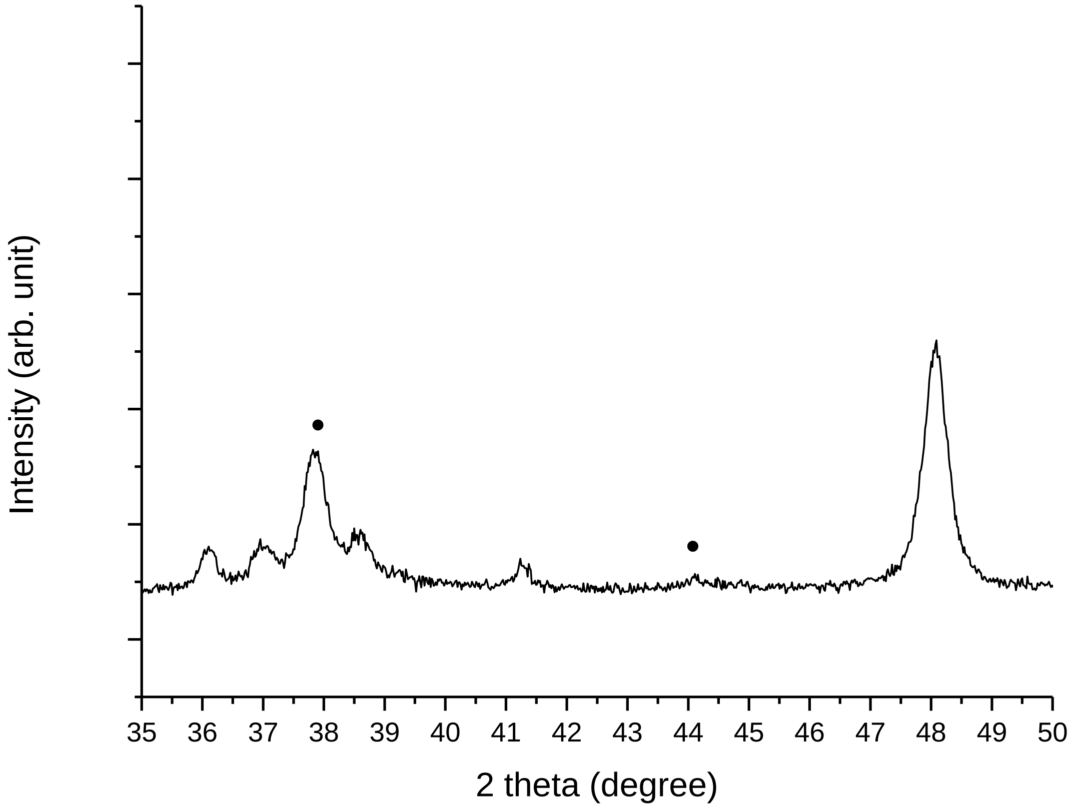

Figure 3.10: An enlargement of the X-ray diffractogram of 1%wt Au-Pd/TiO_{2SI} prepared by sol-immobilisation method and dried 110^oC for 3 hours. Symbol: (●) Au or Au-Pd alloy.

3.3 BET surface area measurement

The total surface area can often play an important role in determining the catalytic performance of a catalyst.[10] In the case of a metal supported catalyst, the area of metal (accessibility and dispersion) is one of the crucial factors in determining the efficiency of catalysis process and in the absence of support material, the metal would undergo sintering rapidly and would therefore lose activity. In this study, the surface areas of the synthesized catalysts were measured in order to know the effect of total surface area on catalytic reaction.

Depositing Au and Pd metal onto the TiO_2 support slightly decreased the surface area from 55.3 to 48.8 m^2/g (table 3.3). Lower surface area in metal supported catalyst could possibly be due to the blockage of the surface or pores of the TiO_2 by the metals, or by another compound such as chloride (Cl^-). Subjecting the 2.5wt%Au2.5wt%Pd/TiO_{2I} catalyst to different pretreatments did not alter the BET surface area, indicating the stability of TiO_2 support.

Table 3.3: BET analyses of 5wt%Au-Pd/TiO_2 catalyst synthesised using impregnation method followed by different pretreatment

Catalyst	Pretreatment	BET surface area (m^2/g)
TiO_2	Static air, 400 °C	55.3
2.5wt%Au2.5wt%Pd/TiO_2	Static air, 400 °C	48.8
2.5wt%Au2.5wt%Pd/TiO_2	5%H_2/Argon, 400 °C	48.7

However, different catalyst surface areas were obtained by using different supports material (table 3.4). As expected, Au-Pd metals catalysts supported on highly porous carbon displayed highest surface area (735.5 m^2/g) followed by SiO_2 and nano ceria, while Au-Pd supported on CeO_2 and Al_2O_3 show BET surface area comparable to TiO_2 as support. Further ZrO_2 displayed 20 m^2/g of surface area followed by graphite from Johnson Matthey (11.1 m^2/g). The lowest surface area was observed by graphite from Aldrich, which gave only 9.0 m^2/g. Therefore, it is believed that Au-Pd metals were highly dispersed on carbon, SiO_2 and nano ceria compared to TiO_2, CeO_2 and γ-Al_2O_3 supported catalysts, which later might contribute to the difference in catalytic performance. However, in this study, the total BET surface area was not considered as an important factor with respect to catalytic activity and selectivity obtained with toluene oxidation reaction using TBHP as oxidant. The statement was based on higher TOF productivity and selectivity observed with lower surface area catalyst (Au-Pd/ZrO_2 and AuPd/graphite (Aldrich).

Table 3.4: BET analyses of 5wt%Au-Pd with different supports prepared using impregnation technique and calcined in static air at 400 ^oC for 3 hours.

Catalysts	BET surface area (m^2/g)
2.5wt%Au2.5wt%Pd/TiO_2	48.8
2.5wt%Au2.5wt%Pd/CeO_2	58.3
2.5wt%Au2.5wt%Pd/SiO_2	256.8
2.5wt%Au2.5wt%Pd/γ-Al_2O_3	57.3
2.5wt%Au2.5wt%Pd/Carbon	735.5
2.5wt%Au2.5wt%Pd/Ceria (nano)	72.5
2.5wt%Au2.5wt%Pd/ZrO_2	20.6
2.5wt%Au2.5wt%Pd/graphite (Johnson Matthey)	11.1
2.5wt%Au2.5wt%Pd/graphite (Aldrich)	9.0

Table 3.5 shows that carbon was observed to have higher surface area compared to TiO_2 when sol-immobilisation technique was used. These data were similar to those for the impregnated catalyst, showing that the effect of the porosity of carbon is to enhance the surface area.

Table 3.5: BET analyses of 1%Au-Pd/TiO_2 synthesised via sol-immobilisation techniques

Catalyst	Preparation technique	BET surface area (m^2/g)
0.5wt%Au0.5wt%Pd/TiO_2	Sol-immobilisation, dried in air, 110 ^oC	57.8
0.5wt%Au0.5wt%Pd/C	Sol-immobilisation, dried in air, 110 ^oC	485.1

3.4 X-ray photoelectron spectroscopy (XPS) analysis

It is well reported in literature that not only the particle size of the supported Au-Pd metal is important, but also its oxidation state and surface composition could also affect catalytic performance.[1,11] For this reason, measurements using X-ray photoelectron spectroscopy have been carried out. XPS is an analytical technique with the ability to give information regarding which elements are present on the surface of the catalyst, and more detailed information on their oxidation state. In addition to qualitative analysis, quantitative information such as atomic percentages of each metal can also be determined using XPS analysis.[12] This information is important in order to examine the surface composition of each metal, especially in the sample with more than one metal involved. In this study, the 5wt%Au-Pd/TiO_{2IW} catalysts after different pretreatments were analyzed by XPS and the obtained Au (4d) and Pd (3d) combined spectra were plotted in figure 3.11.

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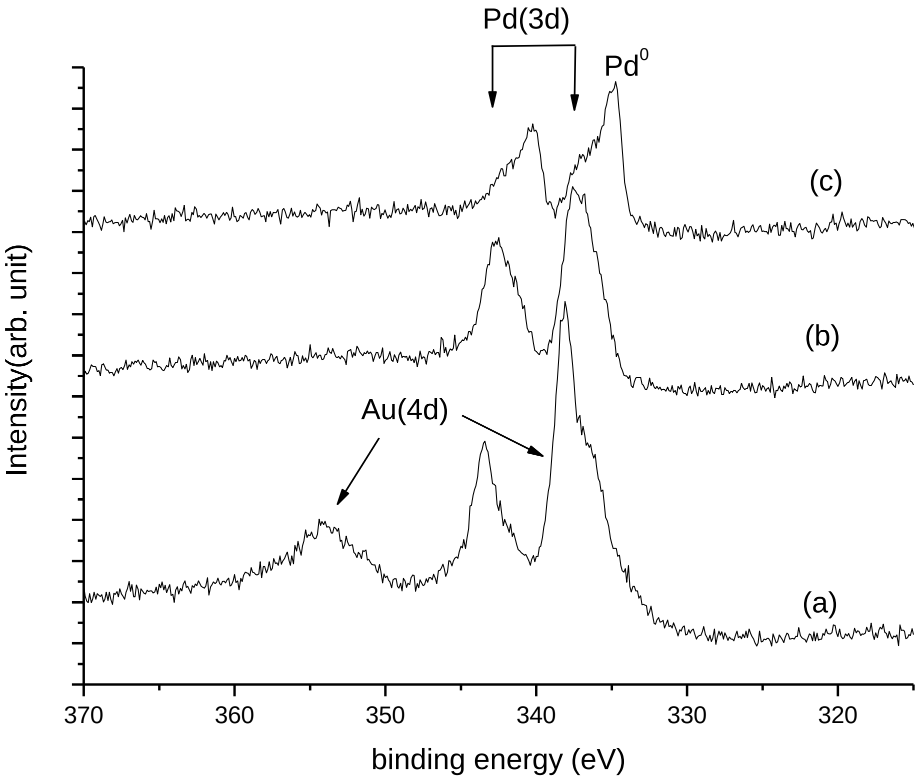

Figure 3.11: Pd (3d) and Au (4d) spectra of 2.5wt%Au-2.5%wt Pd/TiO_{2I} catalysts with different pretreatment (a) uncalcined, (b) 400 °C in static air, (c) 400 °C in 5%H_2/Ar flow

Figure 3.11 shows the combined Au 4d and Pd 3d spectra for 2.5%wtAu-2.5%wtPd/TiO_2 catalyst after different heat treatment. For the uncalcined sample, there were clear spectral contributions from both Au and Pd, leading to severe overlaps of peaks. After heat treatment at 400 ºC, the intensity of the Au 4d peaks feature below detection limits. To quantify the surface composition of the uncalcined catalyst, it had been necessary to deconstruct the spectral envelope into its respective Pd 3d and Au 4d components. This was best achieved by substracting out the Pd 3d contribution, using a suitably scaled and shifted reference spectrum. In all cases, the intensity of the Au ($4d_{3/2}$) feature at higher binding energy around 355-358 eV was below detection limits, and the signals corresponding to Pd species were clearly observed. The Pd ($3d_{5/2}$) feature has a binding energy around 334-337 eV, and the Pd ($3d_{3/2}$) feature has a characteristic binding energy around 5.4 eV higher than Pd ($3d_{5/2}$) signals.

The calcined 5wt%Au-Pd/TiO_{2I} catalyst with the shell structure enriched with PdO phase showed an XPS feature mainly corresponding to Pd^{2+} species (see figure 3.11 (b)), whereas the catalyst reduced in a hydrogen environment (see figure 3.11 (c)) displayed a mixture of Pd^{2+} (336.3-336.8 eV) and Pd^0 (334.7-334.8 eV). The presence of Pd^{2+} was confirmed by the observable shoulder peak signal around 336.3-337.0 eV.

In view of the fact that the oxidation state of Au cannot be observed and determined from the Au ($4d_{3/2}$) feature, the Au ($4f_{7/2}$) transition has instead been used in all cases. From this, it was found that Au was in the metallic state i.e. the oxidation state of Au is 0. It was claimed that metallic gold (Au^0) could be obtained under heating treatment in any gases because of the instability of Au_2O_3.[1]

In order to calculate and verify the overall surface composition of both Au and Pd metals, area integration of each XPS signal were carried out and the results were displayed in table 3.6. It was clear that the Pd:Au atomic ratios obtained for bimetallic 2.5wt%Au2.5wt%Pd/TiO_{2IW} catalyst calcined in static air is higher (5.15) than the expected value of 1.86 (by assuming a random solid solution) for the catalyst with Au and Pd present in 1:1 atomic ratio. This trend was expected and is in agreement with the available literature reporting the formation of Au core and Pd rich structure on 2.5wt%Au2.5wt%Pd/TiO_2 catalysts synthesized using an impregnation method and calcined in static air at higher temperature (> 200 ^oC).[13] The Pd/Au ratio calculated for hydrogen treatment catalysts were lower compared to calcined catalyst, although high enough in order to assume a core-shell structure.

Table 3.6: Surface elemental compositions derived from XPS for the 5wt%Au–Pd/TiO_{2IW} catalysts prepared by impregnation method followed by different pretreatment

Entry	Catalyst/treatment	Composition (atom %)		Atom ratio (Pd/Au)	
		Au/Ti	Pd/Ti	Measured	Theoritically expected[a]
1	Dried, 110 ^{o}C	0.0369	0.0537	1.46	1.86
2	Static air, 400 ^{o}C	0.0079	0.0407	5.15	1.86
3	Flow 5%H_2/Ar,400 ^{o}C	0.0049	0.0165	3.37	1.86

[a] Assuming a random solid solution

In another set of XPS analysis, the 1wt%Au-Pd/TiO_{2SI} catalyst synthesised via sol-immobilisation technique was subjected to XPS characterisation. The major difference observed in samples prepared by sol-immobilisation compared to an impregnation catalyst is in the electronic states of Pd, which is mostly in the metallic state for the sol-immobilised catalyst (figure 3.12). In addition to this, the signal for the Au (4d) feature is now observed, and the lower signal intensity was likely due to the low catalyst metal loading, though it could also be due to the presence of ligand (PVA), which covers the surface of the metals. In order to quantify the surface composition of the sample, the spectral envelope was deconstructed into its respective Pd (3d) and Au (4d) components. Following this, the contribution from Au (4d) was subtracted out. The surface Pd/Au atomic ratio (table 3.7) shows limited evidence of Pd enrichment and therefore indicates the presence of a homogeneous random Au-Pd alloy. Similar types of alloy have also been claimed for similar catalyst characterised in earlier studies.[14]

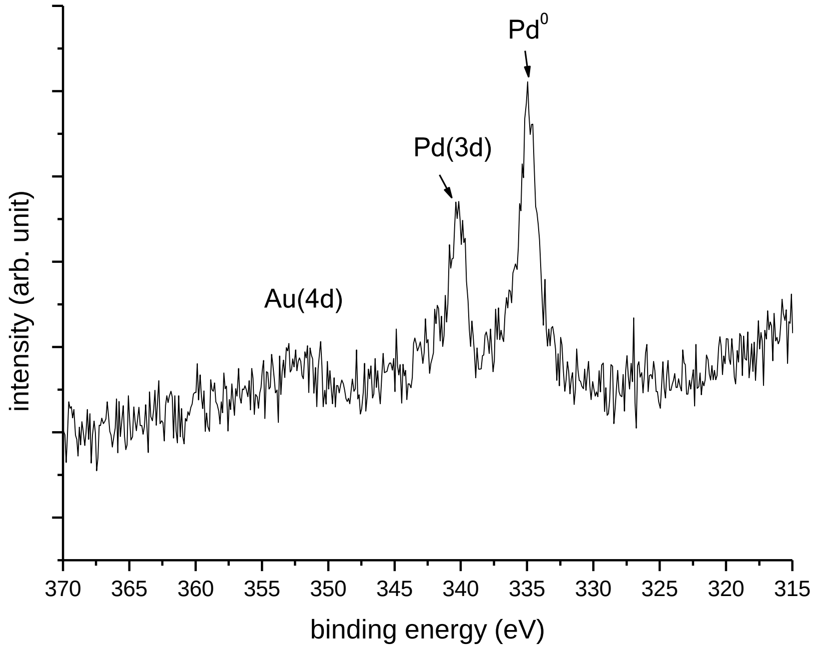

Figure 3.12: Pd (3d) and Au (4d) spectra of 0.5wt%Au-0.5%wt Pd/TiO_{2SI} prepared by sol-immobilisation catalyst.

Table 3.7: Surface elemental compositions derived from XPS for the Au–Pd/TiO_2 catalysts prepared by sol-immobilisation method.

Entry	Catalyst	Composition (atom %)		Atom ratio (Pd/Au)
		Au	Pd	
1	0.5wt%Au0.5wt%Pd/TiO_{2SI}	0.0079	0.0406	5.14

3.5 Temperature Programmed Desorption Analysis (TPD)

It was reported in the earlier studies by Enache *et al.* on benzyl alcohol oxidation using molecular oxygen as oxidant and gold catalysts that the formation of by-products (benzoic acid and benzyl benzoate) were associated with the presence of strong acid sites on the catalysts.[15] In general, the acidity of each support used in this study is weak. This statement is based on ammonia TPD analysis on Au on different supported materials reported in literature where TiO_2, CeO_2, carbon and SiO_2 only showed physisorbed ammonia indicating weaker acidity.[15] From the figure 3.13, it showed the stronger acidity in range 325-350 ºC for ZrO_2-supported catalyst. This is in agreement with strong acid increasing the formation of benzoic acid (Refer to table 4.6 in section 4.2.8). However, this statement contradicts by TiO_2 due to small peaks being observed at 350 ºC. No increment was detected for benzoic acid. The broad peaks for SiO_2 and Al_2O_3 apparently could be a reason for the higher conversion in toluene oxidation. Although CeO_2 support gives strong acidity in figure 3.13, it seems that the conversion was less amongst the other oxide support.

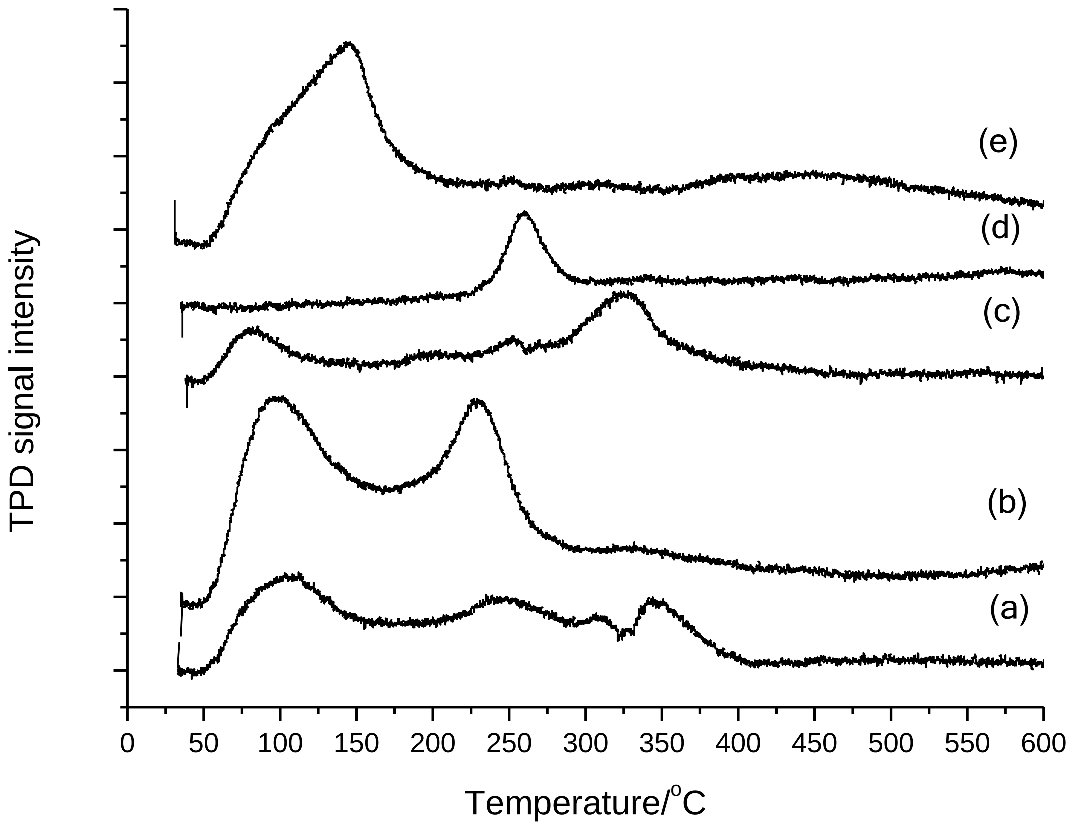

Figure 3.13: TPD-NH_3 chromatogram for Au-Pd different support. Key: (a) TiO_2, (b) Al_2O_3, (c) ZrO_2, (d) CeO_2, (e) SiO_2

3.6 Conclusions

In this chapter, the Au-Pd bimetallic catalyst prepared by impregnation and sol-immoblilisation was characterised using XRD, BET and XPS. The observations from XRD for impregnation catalyst indicate the characteristic peaks for Au or Au-Pd alloy. The XRD diffractogram for sol-immobilisation looks identical with the diffractogram of the impregnated catalyst. Further the crystallite size was calculated for bimetallic Au-Pd catalyst with different support from the Debye Scherer equation. From the BET measurement, the trend in surface area was: C > SiO_2 > ceria nano > CeO_2 > Al_2O_3 > TiO_2 > ZrO_2 > graphite (JM) > graphite (Aldrich). XPS data show that PdO (Pd^{2+}) was formed in the Au-Pd catalyst via impregnation, whereas Pd^0 was formed in the catalyst made by sol immobilization. The stronger acidity of the Au-Pd supported on oxides could be the reason for the higher formation of acid over these catalysts.

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CHAPTER 4

SOLVENT FREE OXIDATION OF TOLUENE

4.1 Introduction

In this chapter, the oxidation of toluene with supported Au-Pd based catalyst is described. Mainly tert-butyl hydroperoxide (TBHP) was used as oxidant. The heterogeneously developed catalyst system is compared with analogue homogeneous systems and further studies were carried out by varying reaction conditions i.e temperature, time, others oxidant, oxidant concentrations and catalyst screening. The section also highlights how the different techniques of preparation affect the conversion of reactant and can contribute a different product formation distributions and activities.

4.2 Use of bimetallic Au-Pd supported catalyst via impregnation method technique

4.2.1 Variation of oxidant

In this study, all reactions were performed and the temperature was set at 80 ºC for 4 hours of reaction. Initially, 5%wt Au-Pd/TiO_{2I} catalyst prepared by impregnation was used due that it was investigated previously and shown to be very active for H_2O_2 synthesis [1] and alcohol oxidation [2]. The blank reaction in the absence of catalyst was performed primarily in order to verify the contribution from homogeneous reactions which could possibly occur especially when using molecular O_2, TBHP and H_2O_2 as oxidant at mild temperature of reaction (~80 ºC). It is evident in Table 4.1 that blank reaction gave zero conversion after 4 hours reaction with O_2 as oxidant. The experiment was conducted by flowing the O_2 gas into the solution at 1 bar and rate of flow was 40 ml/min. This provides an indication that the reaction is not significant at this level of the temperature. Further, the investigation was carried out using TBHP and H_2O_2, the conversion was start to increase only 0.3 and 0.1%, respectively. This reaction gives evidence that TBHP is useful as oxidant at mild condition of temperature rather than O_2 and H_2O_2. In terms of selectivity in blank reaction, once the baseline reaction was established, the reaction was carried out with 5%wtAu-Pd/TiO_2 sythesised via an impregnation technique, TBHP as oxidant gave higher conversion (3.0%) compared to O_2 (0.2%) and H_2O_2 (0.2%). This proves that the catalyst gives enhancement of the activity of toluene as described in Table 4.1.

Table 4.1. Liquid phase oxidation of toluene at 80 °C for bimetallic supported catalysts prepared by impregnation[a]. Reaction performed for 4 hours

			Selectivity (%)				
Catalyst	Oxidant	Conv. (%)	Benzyl alcohol	Benzaldehyde	Benzoic acid	Benzyl Benzoate	TOF (h^{-1})[d]
No catalyst	O_2	0.0	0.0	0.0	0.0	0.0	0.0
	TBHP	0.3	26.1	72.3	1.6	0.0	0.0
	H_2O_2	0.1	8.5	19.5	0.0	0.0	0.0
5%wtAu-Pd/TiO_{2I}	O_2[b]	0.2	0.5	8.5	91.1	0.0	0.4[c]
	TBHP	3.0	27.6	70.4	2.1	0.0	9.9[c]
	H_2O_2	0.2	32.2	31.8	31.0	0.0	0.5[c]

[a]Reaction conditions: toluene = 94.1mmol, catalyst = 0.2g, ratio amount of the reactant(mol): TBHP(mol) = 1:1, ratio toluene(mol) :H_2O_2(mol) = 1: 0.1, T = 80°C, 1 bar O_2, flow rate = 40ml/min., [b]T = 120°C, reaction time =7 hours, I: Impregnation method, [c]Substrate/metal = 1300, [d]TOF (h^{-1}) at 4 and 7 hours[b]. TOF numbers were calculated on the basis of total loading of metals

4.2.2 Effect of temperature of reaction

By increasing the temperature from 60 to 90 ºC, an increase in toluene conversion was observed for blank reaction without catalyst (Table 4.2). Adding the catalyst in this reaction, it was apparent that the conversion increased. This was suggested that the effect of catalyst is important to enhance the activity. Increasing the temperature to 90 ºC, it was observed that the conversion was slightly inferior due to the decomposition of TBHP to tert-butyl alcohol having started at this temperature level. In terms of selectivity, blank reactions and catalyst give more selectivity to benzaldehdye and initially overoxidation to benzoic acid at higher temperature condition (90ºC). Further the temperature was set to 80 ºC for next subsequent studies.

Table 4.2. Liquid phase oxidation of toluene at 80 °C for bimetallic supported catalysts prepared by impregnation[a]. Reaction performed for 4 hours

Catalyst	Temp (ºC)	Conv. (%)	Selectivity (%)				TOF (h^{-1})[d]
			Benzyl alcohol	Benzaldehyde	Benzoic acid	Benzyl Benzoate	
TBHP/no catalyst	60	0.14	27.3	66.8	5.8	0.0	0.0
	80	0.3	26.1	72.3	1.6	0.0	0.0
	90	0.59	18.0	63.6	18.3	0.0	0.0
5%wtAu-Pd/TiO_{2I}[b]	60	1.56	27.8	70.5	1.8	0.0	5.7[c]
	80	3.0	27.6	70.4	2.1	0.0	9.9[c]
	90	2.80	38.0	46.9	15.0	0.0	9.1[c]

[a]Reaction conditions:toluene = 94.1mmol, catalyst = 0.2g, ratio amount of the catalyst(mol): TBHP(mol) = 1:10,[b] ratio toluene(mol):TBHP(mol):1:1, I: Impregnation method, [c]Substrate/metal = 1300, [d]TOF (h^{-1}) at 4 hours. TOF numbers were calculated on the basis of total loading of metal.

4.2.3 Toluene oxidation in He conditions

The catalytic data in Table 4.3 show that air in atmosphere conditions give a small contribution for oxidation of toluene when using Au-Pd catalyst. It is clearly observed that catalyst and TBHP in He conditions was inferior than the conversion with air conditions. Nothing was converted when catalyst run in He conditions without TBHP as an oxidant.

Table 4.3. Liquid phase oxidation of toluene using TBHP as an oxidant at 80 °C for bimetallic supported catalysts prepared by impregnation[a]. Reaction performed for 4 hours.

Catalyst	Gas	Reaction Time/h	Conv. (%)	Selectivity (%)				TOF (h^{-1})[c]
				Benzyl alcohol	Benzaldehyde	Benzoic acid	Benzyl Benzoate	
5%wtAu-Pd/TiO_{2I}	TBHP + He	4	2.0	28.6	71.4	0	0	6.59 [b]
	He	4	0	0	0	0	0	0
	TBHP + air	4	3.0	27.6	70.4	2.1	0	9.86[b]

[a]Reaction conditions: toluene = 94.1mmol, catalyst = 0.2g, ratio toluene(mol): TBHP(mol) = 1:1, T = 80°C, I: Impregnation method, [b]Substrate/metal = 1300, [c]TOF (h^{-1}) at 4 hours. TOF numbers were calculated on the basis of total loading of metals

4.2.4 Effect of mono Au or Pd and bimetallic catalyst

The effect of mono Au or Pd only and bimetallic Au-Pd catalyst was studied in toluene oxidation using TBHP as an oxidant. It clearly showed when adding Au to a Pd/TiO_2, the conversion was increased (Figure 4.1). This is in agreement that synergistic effect will be give effect of the toluene reaction.[2] Initially, mono Au/TiO_2 observed has high initial conversion after 1 hour, further to end of the reaction, bimetallic catalyst give higher conversion (3.0) amongst the others. The Au-Pd/TiO_2 catalyst retained high selectivity to benzaldehyde at high conversion rates, a feature not observed with the supported pure Au and pure Pd catalyst. Formation of benzoic acid was observed for both mono catalysts, but it seems the bimetallic catalyst decreased selectivity to benzoic acid (see Table 4.4). One key factor that must be considered for heterogeneous catalyst operating in three phase system is the possibility that active components can leach into the reaction mixture, thereby leading the catalyst deactivation or in the worse case, to the formation of an active homogeneous catalyst. In this case, the catalysts were calcined at 400 ºC, it was stable and does not leach Au or Pd into solution, a feature that had previously studied by Edwards *et. al* on hydrogen peroxide synthesis.[4-5] With the Au-Pd/TiO_2 catalyst, initial TOF of 27/hour was obtained after half an hour of reaction. Under this condition, the mono Au and Pd catalyst gave TOFs of 19 and 20/hour, respectively. According to the available literature, this bimetallic catalyst form large “core-shell” particles on calcinations, with an Au core surrounded by a Pd shell, which is shown clearly by XPS and STEM.[1]

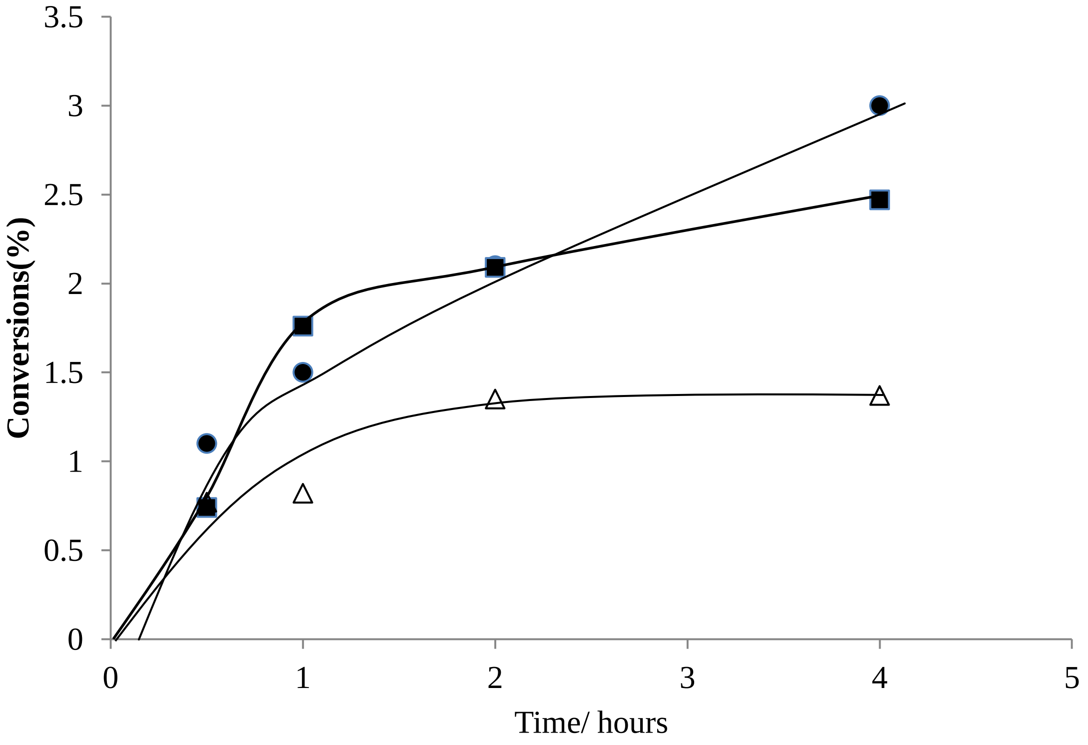


Figure 4.1: Selective oxidation of toluene in the presence of the mono and bimetallic catalysts. Reaction conditions: Toluene 10 mL, T= 80ºC, Ratio toluene (mol):TBHP(mol) = 1:1, Key: ● 5%wtAu-Pd/TiO_{2I} (%), ■ 5%wt Au/TiO_{2I}, Δ 5%wtPd/TiO_{2I}

Table 4.4. Liquid phase oxidation of toluene using TBHP as an oxidant for mono and bimetallic AuPd supported catalysts prepared by impregnation[a]. Reaction performed for 4 hours.

Catalyst	Reaction Time/h	Conv. (%)	Selectivity (%) Benzyl alcohol	Benzaldehyde	Benzoic acid	Benzyl Benzoate	TOF (h^{-1})[d]
5%wtAu-Pd/TiO_{2I}	0.5	1.1	28.1	71.9	0.0	0.0	27.41[b]
	1	1.5	28.4	70.7	0.9	0.0	20.15[b]
	2	2.1	28.0	70.6	1.4	0.0	13.5[b]
	4	3.0	27.6	70.4	2.1	0.0	9.9[b]
5%wtAu/TiO_{2I}	0.5	0.74	32.8	61.4	5.8	0.0	19.19[b]
	1	1.76	32.3	56.8	10.9	0.0	22.90[b]
	2	2.09	32.2	53.4	14.4	0.0	13.60[b]
	4	2.47	22.1	50.6	27.2	0.2	8.01[b]
5%wtPd/TiO_{2I}	0.5	0.77	29.9	64.3	5.8	0.0	20.05[b]
	1	0.82	28.7	64.2	7.2	0.0	10.6[b]
	2	1.35	27.5	63.3	9.2	0.0	8.75[b]
	4	1.37	23.7	62.1	14.1	0.1	4.45[b]

[a]Reaction conditions: toluene = 94.1mmol, catalyst = 0.15-0.3g, ratio amount of the reactant(mol): TBHP(mol) = 1:1, I: Impregnation method, [b]Substrate/metal = 1300, [d]TOF (h^{-1}) at 4 hours. TOF numbers were calculated on the basis of total loading of metals

4.2.5 Time on-line profile

Time on-line studies are crucial in determining the product distribution and to identify the reactions pathways involved in this particular reaction time. The effect of the reaction time on product formation was studied at 80 ºC and it is shown in Figure 4.2 and 4.3.

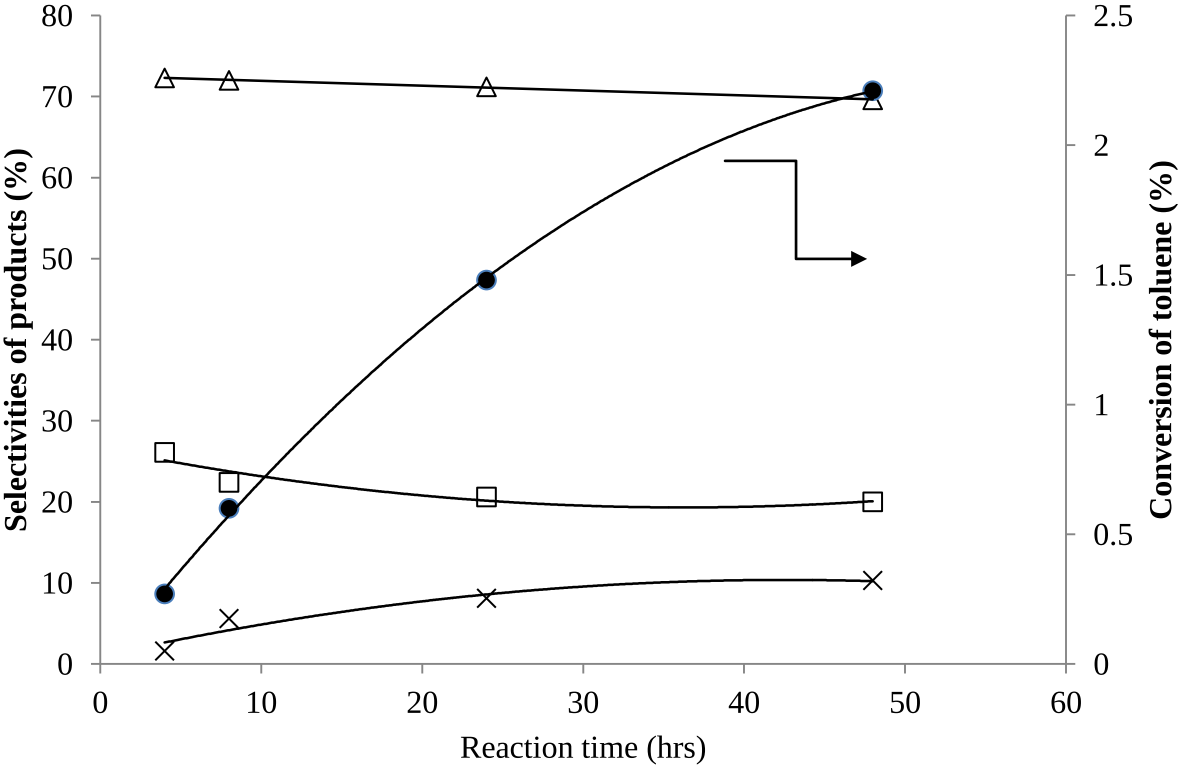


Figure 4.2: Time online plot of toluene oxidation for blank reaction (no catalyst). Reaction conditions: Toluene 10 mL, T= 80ºC, Ratio toluene (mol):TBHP(mol) = 1:1, Key: ● conversion of toluene (%), □ benzyl alcohol selectivity (%), Δ benzaldehdye selectivity (%), x benzoic acid selectivity (%).

Prolonging the reaction time from 4 to 48 hours with blank reaction without catalyst, it shows an enhancement of toluene conversion whereas further increase of reaction time lead to decrease in benzyl alcohol and benzaldehyde with significant increase of benzoic acid formation (Figure 4.2). Otherwise, the conversion only 2.2 %, it is enough to propose that probably the formation of radical TBHP was develop in this reaction and will be explain in detail in section 4.4.3.

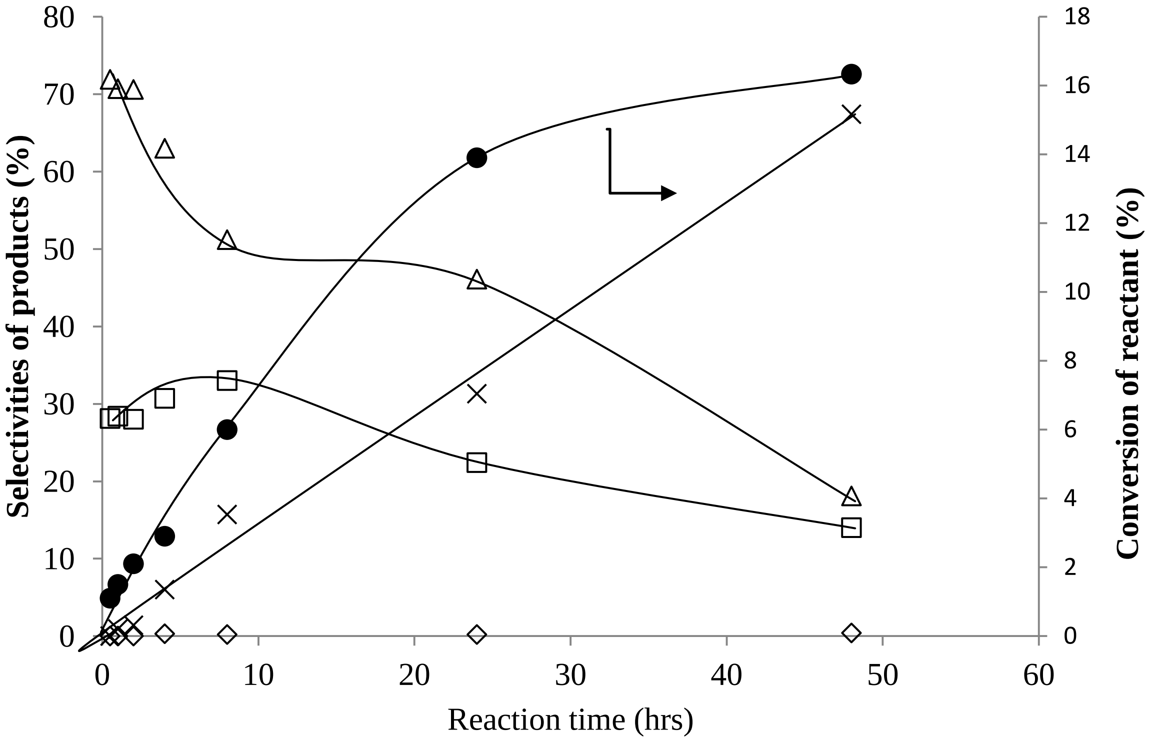


Figure 4.3: Time online plot of toluene oxidation in presence of 5%wtAu-Pd/TiO_2 catalyst. Reaction conditions: Toluene 10 mL, T= 80ºC, Ratio toluene (mol):TBHP(mol) = 1:1, Key: ● conversion of toluene (%), □ benzyl alcohol selectivity (%), Δ benzaldehdye selectivity (%), x benzoic acid selectivity (%), ◊ benzyl benzoate selectivity.

On adding Au-Pd/TiO_2 catalyst, the conversion of toluene increased compared to blank reaction. It was suggested that the catalyst plays an important role to activate and interact with TBHP to form radical. The radical such as *tert*-butyl peroxy (*t*- BuOO$^\bullet$) and *tert*-butyloxy radicals (*t*-BuO$^\bullet$) could be formed and interact with Au-Pd metal and probably *tert*-butyloxy radical reacts with toluene to form the benzyl radical. The benzyl radical combines with *tert*-butyl peroxy radical to yield benzaldehyde.[6] Further, benzaldehyde will react with OH$^\bullet$ to form benzoic acid. In term of selectivity, the consecutive formation of benzoic acid was increased due to longer hours of reaction. The selectivity of benzyl alcohol and benzaldehyde was decreased towards a time online reaction.

4.2.6 Catalyst pretreatment and its influence on toluene oxidation.

In view of the fact that the optimum composition of the Au-Pd supported on TiO_2 was determined to be an equal weight ratio (2.5wt%Au2.5wt%Pd) as described in section 4.2.4, further steps towards catalyst optimisation have been taken by pre-treating the catalyst. Either the dried catalyst was used, or the catalyst was calcined prior to use. It is reported in the literature that catalyst pretreatment will affect the catalyst properties and consequently their catalytic activity.[7] It was apparent that a reductive pretreatment, by flowing 5% hydrogen in argon over the catalyst, led to a increase in the productivity of the catalyst, as determined over 4 hours of reaction time (Figure 4.4). This trend was contrary to monometallic Au or Pd catalytic systems, where both samples showed lower activity compared to calcined counterparts.

Structural analysis of catalysts by means of X-ray diffraction (XRD) illustrates that a smaller crystallite size (22.1 nm) was observed for the reduced catalysts, as compared to 23.6 nm crystallite size obtained in the case of calcined sample (see section 3.2.2 of previous chapter). The XRD pattern also clearly shows the peak corresponding to Pd in metallic state based on the JCPDS reference file. Further analysis with XPS in section 3.4 confirmed the data obtained by XRD where a PdO (Pd^{2+}) signal dominated the calcined catalyst whereas the reduced catalysts had a mixture of Pd^0 and Pd^{2+}. In particular, the Au-Pd/TiO_{2IW} catalyst pre-treated in hydrogen environment have 50.3% Pd^0 and 49.7% Pd^{2+} phase.[8] The presence of Pd^0 seems to be beneficial towards toluene oxidation activity and this give selectivity to benzoic acid is higher compared to calcined catalyst in Table 4.4.

In general, at these particular conditions, toluene oxidation with TBHP added as oxidant, high catalytic activity requires Au-Pd catalyst with metal particle size probably more than 20 nm and the palladium should be in the reduced state.

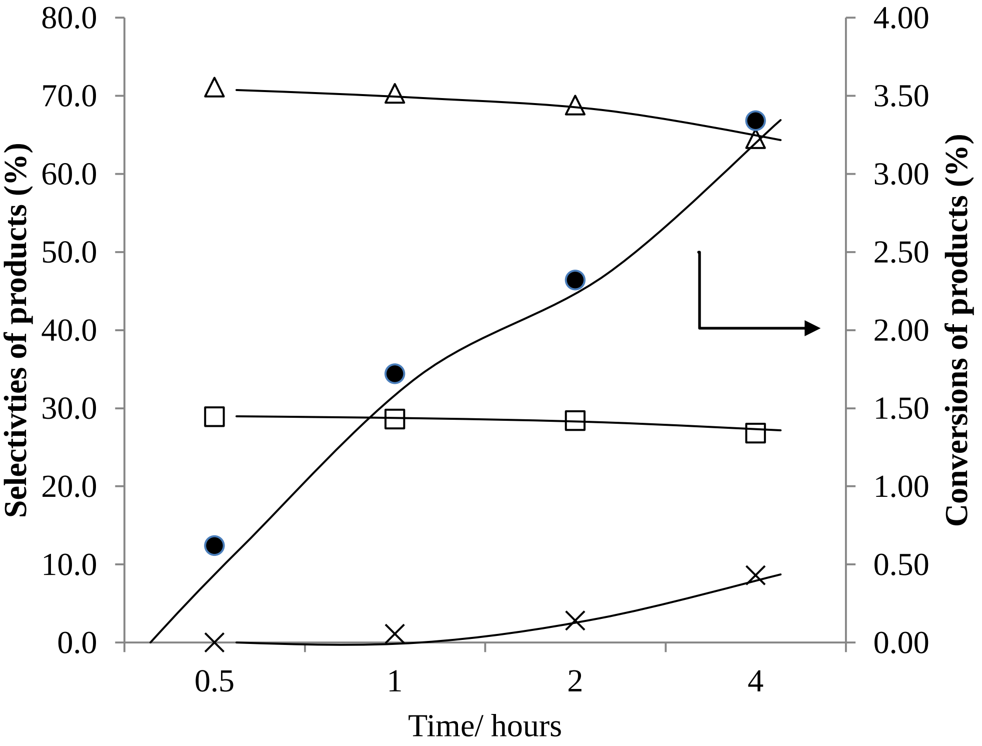


Figure 4.4: Time online plot of toluene oxidation in presence of 5%wtAu-Pd/TiO_2 catalyst with flowing 5% H_2/Ar heat treatment. Reaction conditions: Toluene 10 mL, T= 80ºC, Ratio toluene (mol):TBHP(mol) = 1:1, Key: ● conversion of toluene (%), □ benzyl alcohol selectivity (%), Δ benzaldehdye selectivity (%), x benzoic acid selectivity (%), ◊ benzyl benzoate selectivity.

4.2.7 Reused catalyst

Bimetallic gold catalyst was tested for the stability Au-Pd metal in the toluene oxidation reaction. This test was studied by using the same catalyst and the reaction was repeated 6 times. Each of series was run for 4 hours and the solution after reaction was filtered, run for GC and the data was shown as in Table 4.5. Au-Pd supported on TiO_2 was shows very stabile after 5 times reproducibility. The conversion was observed give not much different. The prediction maybe the formation of Au core-Pd shell type alloy structure with Pd^{2+} (PdO) dominance in the Au-Pd impregnation catalyst give an important role.

As mentioned earlier, the calcination of this catalyst at high temperature (400 ºC) in static air will be enhancing the stability of the catalyst.

Table 4.5. Liquid phase oxidation of toluene using TBHP as an oxidant at 80 °C for bimetallic supported catalysts prepared by impregnation method and sol-immobilisation[a]. Reaction performed for 4 hours

Catalyst	Conv. (%)	Selectivity (%)				TOF (h^{-1})[d]
		Benzyl alcohol	Benzaldehyde	Benzoic acid	Benzyl Benzoate	
5%wt Au-Pd/TiO_{2I}	2.52	29.4	53.2	17.2	0.2	8.19[b]
1st reused	2.07	30.8	53.6	15.4	0.2	*6.71*[b]
2nd reused	2.10	32.5	57.2	9.9	0.4	*6.83*[b]
3rd reused	1.90	32.2	57.2	10.5	0.1	*6.17*[b]
4th reused	2.00	29.6	60.7	9.6	0.2	*6.51*[b]
5th rused	1.94	26.2	51.1	22.3	0.4	*6.3*[b]
5%wtAu-Pd/C_I	6.47	24.9	38.1	36.8	0.2	21.04[b]
1st reused	4.12	24.3	36.6	39.0	0.2	*13.41*[b]
2nd reused	6.32	23.2	32.9	43.7	0.2	*20.54*[b]
3rd reused	4.56	24.8	51.2	23.8	0.3	*14.83*[b]
4th reused	3.80	27.0	43.3	29.4	0.3	*12.36*[b]

[a] Reaction conditions:Toluene = 94.1mmol, catalyst = 0.2g, ratio toluene(mol): TBHP(mol) = 1:1, T = 80 ºC, I: Impregnation method, [b] Substrate/metal = 1300, [c] TOF (h^{-1}) at 4h reaction. TOF numbers were calculated on the basis of total loading of metals.

Further catalyst for supported carbon was studied and the results show uncertain conversion after 5 times of reproducibility. Carbon is very fine particles and formation of homogeneous alloy particles with bimetallic Au-Pd catalyst will be reason that the condition could be observed.

4.2.8 Effect of support on catalytic activity of Au-Pd bimetallic catalyst.

The catalytic properties of a supported catalyst are often affected by the nature of the support material. The choice of support is vital in sythesising the metal supported catalyst with different structure and particles size, and such a series of catalysts were prepared on other oxide supports. The most active Au-Pd catalyst (see Table 4.6) was prepared on activated carbon and the order of catalytic activity was the following: Carbon>Ceria(nano)>SiO_2>γ-Al_2O_3>ZrO_2>Graphite (Sigma Aldrich)>TiO_2>CeO_2(Sigma Aldrich)>Graphite (JM). Higher selectivity to benzaldehyde was observed with TiO_2, SiO_2 and Al_2O_3 Au-Pd supported catalysts, whereas with activated carbon and ZrO_2 significant level of benzoic acid was observed (20-30% selectivity to benzoic acid) at similar levels of conversion. In the majority of the cases the addition of gold and palladium resulted in an enhancement in terms of conversion. In terms of selectivity the deposition of gold and palladium seem to enhance in the majority of the cases the consecutive oxidation of benzyl alcohol to benzaldehyde and benzoic acid. High selectivity to benzaldehyde (63-74%) was observed with the use of oxide supported catalysts, especially with SiO_2, TiO_2 and CeO_2 supported gold-palladium catalysts. High selectivity of benzoic acid (21-33%) was detected with carbon and ZrO_2 catalyst. It was observed that adding the Au-Pd metal into the support could enhance the conversion by comparing only dried support blank reaction in Table 4.7.

All catalysts with different support materials were calcined in static air at high temperature *i.e.* 400 ^oC. It was expected from previous literature that Au-Pd with TiO_2, SiO_2 and CeO_2 to have Au core-Pd shell structure whereas with carbon as support material, formation of homogeneous alloy should occur. It seems the catalytic activity is strongly related to the structure of Au-Pd alloy evolved in catalyst. This statement was based on higher TOF values observed in AuPd/C_I compared to TOF of Au-Pd other support catalyst. Moreover, Au-Pd/CeO_{2I} having comparable activity to Au-Pd/TiO_{2I} catalyst. Another factor should be considered here is the particle size and distribution of metals on each supports. Detailed studies on particle size and metals distribution of Au/Pd on different supports synthesised using similar procedure as used in this study have been carried out in earlier works by Edwards *et.al.* by using STEM technique, all catalysts were shown to have bi-modal particle size.[4,9] In term of mean particle size, Au-Pd catalyst support on TiO_2, Al_2O_3, SiO_2 and carbon were calculated (based on XRD data, see section 3.2.3 of Chapter 3) to have almost similar average crystallite size (23-29 nm) whereas Au-Pd metal in CeO_2 as support shows around 34.1 nm in size. Since the nano ceria support catalyst displayed higher catalytic activity, as comparison it observed the crystallite size for this support is 48.3 nm and indicated second higher after carbon as a support.

Other than different structure of Au-Pd alloy, compared to TiO_2, carbon has higher surface area which provided superior metal dispersion and more important it may increase the availability of exposed corner/edges sites on metal nanoparticles with carbon as support. Higher metal exposition is due to the formation of spherical structure rather than hemisphere as observed on TiO_2 as support. In view of the fact that alloy type or particle size alone could not give a clear correlation to the demonstrated catalytic activity pattern, the origin of superior activity might be derived from the combination of several factors such as Au-Pd surface composition also the dispersion of metal on support.

Table 4.6 Liquid phase oxidation of toluene using TBHP as an oxidant at 80 °C for bimetallic supported catalysts prepared by impregnation method[a]. Reaction performed for 4 hours

Catalyst	Conv. (%)	Selectivity (%)				TOF (h^{-1})[c]
		Benzyl alcohol	Benzaldehyde	Benzoic acid	Benzyl Benzoate	
No TBHP/no catalyst	0.0	0.0	0.0	0.0	0.0	0.0
TBHP/no catalyst	0.3	26.1	72.3	1.6	0.0	0.3
5%wtAu-Pd/TiO_{2I}	2.9	30.7	63.0	6.0	0.3	9.3[b]
5%wtAu-Pd/C_{I}	8.3	23.2	44.3	32.1	0.4	26.9[b]
5%wtAu-Pd/$CeO_{2\,I}$	2.7	26.7	72.5	0.2	0.6	8.7[b]
5%wtAu-Pd/γ-$Al_2O_{3\,I}$	3.9	32.1	66.0	0.2	1.6	12.8[b]
5%wtAu-Pd/$SiO_{2\,I}$	4.6	25.2	72.6	0.9	1.3	15.0[b]
5%wtAu-Pd/$ZrO_{2\,I}$	3.6	20.2	56.5	21.4	1.9	11.7[b]
5%wtAu-Pd/$nanoceria_{I}$	6.7	29.4	54.9	8.5	7.3	21.7[b]
5%wtAu-Pd /$Graphite_{I}$ (Johnson Matthey)	2.1	33.8	64.4	1.5	0.2	6.7[b]
5%wtAu-Pd/ $Graphite_{I}$ (Aldrich)	3.1	32.0	61.6	6.2	0.2	10.0[b]

[a]Reaction conditions:Toluene = 94.1mmol, catalyst = 0.2g, ratio toluene(mol): TBHP(mol) = 1:1, T = 80 ºC, I: Impregnation method, [b]Substrate/metal = 1300, [c]TOF (h^{-1}) at 4h reaction. TOF numbers were calculated on the basis of total loading of metals.

Table 4.7. Liquid phase oxidation of toluene using TBHP as an oxidant at 80 °C for only supported catalysts[a]. Reaction performed for 4 hours

Catalyst	Conv. (%)	Selectivity (%)			
		Benzyl alcohol	Benzaldehyde	Benzoic acid	Benzyl Benzoate
TiO_{2DR}	0.5	16.9	80.4	2.6	0
$Carbon_{DR}$	2.70	29.9	45.5	24.4	0.2
CeO_{2DR}	1.4	22.9	75.7	1.4	0.0
γ-Al_2O_{3DR}	0.4	28.8	71.2	0.0	0.0
SiO_{2DR}	0.5	21.4	65.3	11.0	2.3
ZrO_{2DR}	0.8	24.2	73.3	2.5	0.0
Nano $Ceria_{DR}$	0.9	27.2	70.7	2.0	0.0
$Graphite_{DR}$ (Johnson Matthey)	1.4	24.0	71.5	3.6	0.9

[a]Reaction conditions: Toluene= 94.1mmol, support = 0.2g, ratio toluene(mol): TBHP(mol) = 1:1, T = 80 ºC, DR: dried at 110°C for 16h in oven,

4.3 Effect of different preparation technique on Au-Pd supported catalyst

4.3.1 Sol-immobilisation catalyst.

It is well-known in catalysis that different preparation techniques affect catalyst properties, such as the oxidation state of the deposited metal, the average particle size and structure, and therefore overall catalytic activity. There are several techniques that have been developed for synthesising metal supported catalysts, and in addition, even using the same technique, each additional parameter, such as heat treatments procedure is carefully manipulated and tuned to attain the target catalyst.[7] Generally, catalysts with higher surface areas and smaller metal particles are superior for catalytic oxidation reactions. Both factors can improve the accessibility of the substrate onto catalyst active site, and in some cases the electronic and geometric properties of the metal could be modified by having a small metal particle.[7] However, this is not always the rule. A unique catalyst property in many cases has to be developed for each substrate and reaction conditions.

In this section, attempts have been made to compare the catalytic activities of the catalysts based on preparation techniques such as impregnation and sol-immobilisation. The conventional impregnation technique has been chosen due to the fact that the preparation is relatively straightforward. Furthermore, the method is broadly used on synthesising commercial catalysts where the simplicity and cost are important. The Au-Pd/TiO_2 catalyst synthesised via impregnation method and calcined in static air at higher temperature (400 ^oC) resulted in the formation of metal particles with bimodal particle size distribution where the smaller particle distribution was between 2-10 nm, whereas most of the large particles were 35-80 nm in size.[9] The metal particle size distribution obtained on analogue Au-Pd/TiO_2 catalyst prepared by sol-immobilisation was found to be much narrower *i.e.* between 6-7 nm.[10-11] Catalysts synthesized via the sol-immobilisation method are therefore typically more active than impregnation counterparts for several reactions such as benzyl alcohol and hydrogen peroxide synthesis.[12]

As shown in literature, sol-immobilisation technique creates a different structure of bimetallic particles where it consist a homogeneous Au-Pd alloy with both Pd and Au in metallic state.[11-12] The presence of the ligand (polyvinyl alcohol (PVA)) which may cover the active metal as protecting agent and therefore possibly stabilize the accessibility of the metal. In view of this, the catalytic data give higher conversion and effect the catalytic acitivity. Sol-immobilisation method also includes the reduction of metal using sodium borohydride ($NaBH_4$), and therefore it possibility give enhancement. XPS data from chapter 3 explained that formation of Pd^0 was observed with sol-immobilisation catalyst whereas reduction Pd^{2+} to Pd^0 has already detected from pretreatment H_2/Ar with impregnation catalyst give slightly a little increment. Based on this observation, Pd^0 could be important role to the highest activity and conversion toluene using TBHP as oxidant. The observation from XPS data in chapter 3 suggested that Au core-Pd shell type alloy structure with Pd^{2+} (PdO) dominance the Au-Pd impregnation catalysts calcined at high temperature (i.e 400ºC).

Table 4.8. Liquid phase oxidation of toluene using TBHP as an oxidant for bimetallic supported catalysts prepared by impregnation and sol-immobilisation[a]. Reaction performed for 4 hours.

Catalyst	Reaction Time/h	Conv. (%)	Selectivity (%)				TOF (h^{-1})[d]
			Benzyl alcohol	Benzaldehyde	Benzoic acid	Benzyl Benzoate	
1%wt(Au-Pd) colloid/ no support	0.5	0.33	32.9	67.1	0.0	0.0	42.7[b]
	1	0.58	30.5	69.5	0.0	0.0	37.8[b]
	2	0.97	30.3	69.7	0.0	0.0	31.4[b]
	4	2.0	30.3	67.8	1.9	0.0	32.5[b]
1%wt Au-Pd/TiO_{2SI} (1:1 weight ratio)	0.5	1.72	26.3	53.2	20.5	0.0	223.1[b]
	1	2.63	19.4	42.9	37.7	0.0	171.14[b]
	2	4.17	14.8	29.6	55.6	0.0	135.44[b]
	4	6.43	10.2	20.0	69.8	0.0	104.5[b]
1%wtAu-Pd/C_{SI} (1:1 weight ratio)	0.5	2.4	33.4	44.5	22.1	0.0	314.7[b]
	1	3.7	26.3	34.9	38.8	0.0	240.2[b]
	2	4.9	18.0	23.5	58.5	0.0	157.3[b]
	4	12.0	10.1	21.3	68.6	0.0	195.2[b]
1%wtAu-Pd/TiO_{2I}	0.5	1.20	38.7	61.1	0.2	0.0	153.4[c]
	1	1.50	38.3	60.3	1.5	0.0	94.40[c]
	2	2.30	36.9	59.0	4.1	0.0	73.60[c]
	4	3.70	36.7	48.5	14.8	0.0	60.60[c]

[a]Reaction conditions: toluene = 94.1mmol, catalyst = 0.2g, ratio amount of the reactant(mol): TBHP(mol) = 1:1, I: Impregnation method, SI: Sol immobilization, [b]Substrate/metal = 6500, [b]Substrate/metal = 1300, [d]TOF (h^{-1}) at 4 hours. TON and TOF numbers were calculated on the basis of total loading of metals

In order to fairly compare the effect of preparation techniques on Au-Pd supported TiO_2 catalyst, similar loading of metal was prepared using an impregnation method and calcined in static air at 400 °C. This catalyst is expected to have bigger metal particle size with wider metal particle size distribution compared to sol-immobilised catalyst counterpart as well as difference in composition of metal oxidation state. By using similar mass of catalyst, it is apparent from table 4.8 that impregnated catalyst gave lower activity on TOF values at similar reaction time. In term of selectivity, the selectivity is more to benzoic acid for sol-immobilised catalyst whereas impregnation observed more to benzaldehyde. Comparison with carbon as support, it clearly showed that higher conversion and TOF can be increased and similar pattern for selectivity with TiO_2. This pattern is same as observed for the catalyst with impregnation catalyst that expected carbon give higher results. Since the support give important role towards the reactions, one experiment was run without support in homogeneous conditions. It clearly show that the Au-Pd colloid gives lower activity and conversion and prove the accessibility of support during reaction.

4.3.2 Effect of mono and bimetallic Au-Pd catalyst

As discussed earlier in section 4.2.4, the effect of synergistic of Au and Pd could be enhancing the conversion of toluene. This trend was observed in impregnation catalyst show that same pattern was also observed that mono gold give higher conversion compared to Pd only. Further, mono Au/TiO_2 give higher selectivity to benzoic acid and selectivity of more to benzaldehyde was observed to Pd mono catalyst (Table 4.9).

Table 4.9 Liquid phase oxidation of toluene using TBHP as an oxidant for mono and bimetallic AuPd supported TiO_2 catalysts prepared by sol-immobilisation[a]. Reaction performed for 4 hours.

Catalyst	Reaction Time/h	Conv. (%)	Selectivity (%)				TOF (h^{-1})[c]
			Benzyl alcohol	Benzaldehyde	Benzoic acid	Benzyl Benzoate	
1%wtAu-Pd/TiO_{2SI} (1:1 weight ratio)	0.5	1.72	26.3	53.2	20.5	0.0	223.1[b]
	1	2.63	19.4	42.9	37.7	0.0	171.14[b]
	2	4.17	14.8	29.6	55.6	0.0	135.44[b]
	4	6.43	10.2	20.0	69.8	0.0	104.5[b]
1%wtAu/TiO_{2SI}	0.5	2.04	24.8	47.8	27.4	0.0	265.56[b]
	1	3.09	21.1	37.3	41.5	0.0	200.64[b]
	2	4.97	15.6	27.4	57.0	0.0	161.46[b]
	4	5.78	10.2	20.0	69.8	0.1	94.02[b]
1%wtPd/TiO_{2SI}	0.5	0.61	48.9	47.4	3.7	0.0	79.66[b]
	1	0.90	47.7	46.3	6.0	0.0	58.39[b]
	2	1.44	47.3	46.3	6.4	0.0	46.79[b]
	4	1.98	43.7	46.2	9.6	0.5	32.11[b]

[a]Reaction conditions: toluene = 94.1mmol, catalyst = 0.15-0.3g, ratio amount of the reactant(mol): TBHP(mol) = 1:1, I: Impregnation method, SI: Sol immobilisation, [b]Substrate/metal = 6500, [c]TOF (h^{-1}) at 4 hours. TOF numbers were calculated on the basis of total loading of metals

This study also demonstrated that bimetallic Au-Pd catalyst supported with carbon show the higher TOF value 781 compared to mono Au or Pd only. In term of selectivity, mono and bimetallic catalyst shows consecutive selectivity to benzoic acid.

Table 4.10 Liquid phase oxidation of toluene using TBHP as an oxidant for mono and bimetallic AuPd supported carbon catalysts prepared by sol-immobilisation[a]. Reaction performed for 4 hours.

Catalyst	Reaction Time/h	Conv. (%)	Selectivity (%)				TOF (h^{-1})[c]
			Benzyl alcohol	Benzaldehyde	Benzoic acid	Benzyl Benzoate	
1%wtAu-Pd/C_{SI} (1:1 weight ratio)	0.5	2.4	33.4	44.5	22.1	0.0	157.3
	1	3.7	26.3	34.9	38.8	0.0	240.2
	2	4.9	18.0	23.5	58.5	0.0	314.5
	4	12.0	10.1	21.3	68.6	0.0	780.9
1%wtAu/C_{SI}	0.5	2.18	26.7	45.1	28.2	0.0	141.5
	1	2.98	23.8	33.1	43.0	0.0	193.7
	2	4.01	20.0	25.1	54.9	0	261.0
	4	6.94	13.2	13.6	73.2	0	451.2
1%wt Pd/C_{SI}	0.5	1.19	45.2	50.0	4.7	0.0	77.1
	2	2.41	34.2	47.6	18.2	0.0	157.0
	4	3.76	26.4	32.8	40.8	0.0	224.3

[a] Reaction conditions: toluene = 94.1mmol, catalyst = 0.15-0.3g, ratio amount of the reactant(mol): TBHP(mol) = 1:1, I: Impregnation method, SI: Sol immobilisation, [b] Substrate/metal = 6500, [c] TOF (h^{-1}) at 4 hours. TOF numbers were calculated on the basis of total loading of metals

4.3.3 Oxidation with different Au/Pd metal ratio supported on carbon

Following on from the work described in section 4.3.2, it is clear that carbon will be the best support for oxidation of toluene with TBHP as oxidant. A Series of Au-Pd bimetallic catalysts with different Au to Pd(wt% ratio) were prepared on this support using sol-immobilisation method, and their activity for toluene oxidation was evaluated after the catalyst had been dried at 110ºC for 3 hours. All catalysts have similar total metal loading equal to 1%. The results shown in table 4.11 illustrate that the catalysts are active towards toluene oxidation but with different catalytic performance.

Table 4.11. Liquid phase oxidation of toluene using TBHP as an oxidant for 1%wtAu-Pd supported carbon catalysts prepared by sol-immobilisation[a]. Reaction performed for 4 hours.

		Selectivity (%)				
Au/Pd molar	Conv. (%)	Benzyl alcohol	Benzaldehyde	Benzoic acid	Benzyl Benzoate	TOF (h^{-1})[d]
1:0	6.94	13.2	13.6	73.2	0	112.81[b]
7:1	8.4	7.8	9.9	80.6	1.7	149.0[c]
3:1	8.7	9.2	8.2	81.2	1.4	155.4[c]
2:1	8.8	9.5	11.7	78.1	0.8	156.8[c]
1:1	11.8	8.5	47.9	42.7	0.8	211.3[c]
1:2	8.6	11.5	19.5	69.0	0.0	154.2[c]
1:3	6.8	15.5	13.9	70.3	0.3	121.9[c]
1:7	5.7	25.7	24.3	50.0	0.0	101.3[c]
0:1	3.76	26.4	32.8	40.8	0.0	61.07[b]

[a]Reaction conditions: toluene = 94.1mmol, catalyst = 0.2g, ratio amount of the reactant(mol): TBHP(mol) = 1:1, SI: Sol immobilisation, , [b]Substrate/metal = 6500, [c]Substrate/metal = 7137, [d]TOF (h^{-1}) at 4 hours. TOF numbers were calculated on the basis of total loading of metals

Monometallic Au catalyst exhibits the lower activity towards reactions. The addition of Pd to Au significantly enhance the catalytic performance, with the optimum Au-Pd composition being 1 to 1 molar ratio, where a compromise between catalytic acitivity and conversion toward benzoic acid was achieved. A further increase in the Pd content resulted in a progressive decrease in catalytic activity. In the presence of gold, the selectivity of benzoic acid is increase but it is opposite with the Pd. Based on TEM micrographs that were studied by Pritchard *et al.* observed that the median particles sizes for the monometallic Au or Pd colloids were found to be 3.5 and 5.4 nm, respectively.[12] The median particles for all the Au_xPd_y alloys were in the 2.9 -4.6 nm range, the metal particles were found to be random homogeneous Au-Pd alloys.[12]

4.3.4 Effect of reaction time

As described in section 4.2.6, the conversion of toluene was increased throughout the reaction time. Comparing carbon and TiO_2 as a support in Figure 4.5 and 4.6, it showed the double of increment of conversion of toluene was observed after prolonged the reaction. Almost 100% selectivity of the benzoic acid was observed in time and led to a decrease in benzyl alcohol and benzaldehyde. A trace of benzyl benzoate also forms during the prolonged reaction time.

Further investigation was taken to see effect of decomposition of TBHP towards conversion of toluene. In figure 4.7, the carbon based catalyst goes to completion for decomposition of TBHP but the TiO_2 based catalyst does not after 48 hours of reaction. A tentative explanation could be the inhibition of the AuPd by the formed benzoic acid. In the carbon based catalyst only the AuPd would be inhibited and the carbon itself could carry the decomposition to completion. For the blank reaction without catalyst, only 17% conversion was observed. This is further strengthened by the observation that the Au-Pd catalyst can give important contribution to interact with TBHP to form radical and enhanced the activities of toluene oxidation.

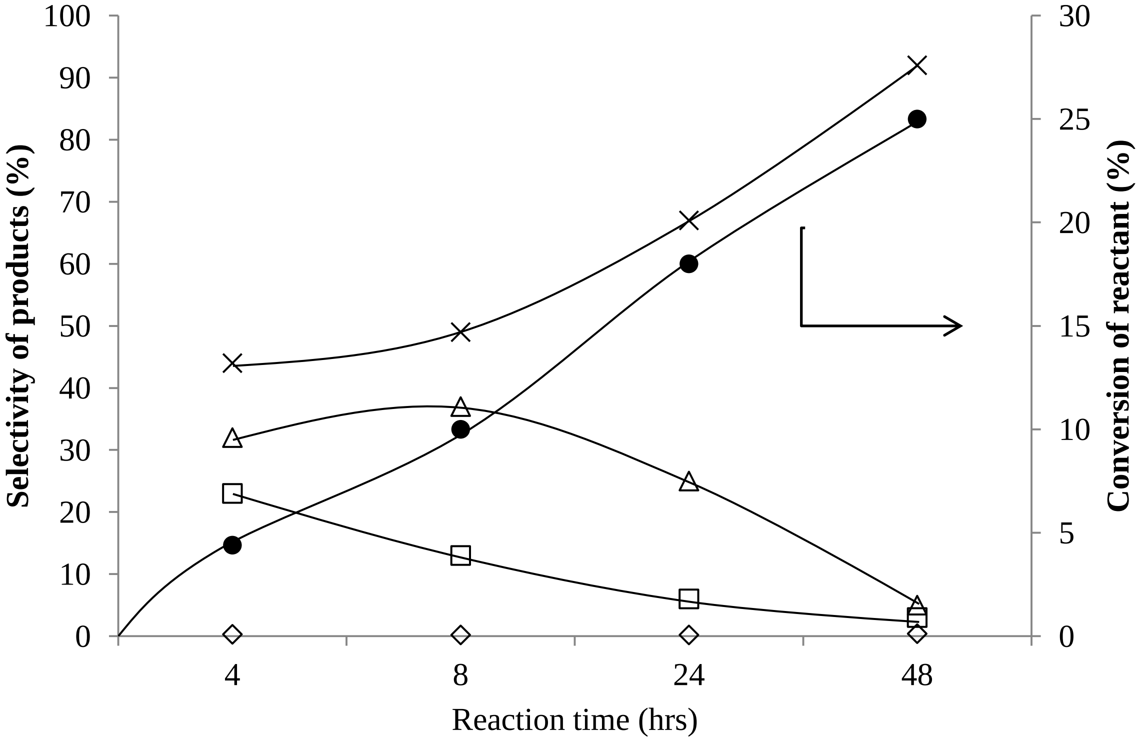


Figure 4.5: Time online plot of toluene oxidation in presence of 1%wtAu-Pd/TiO_2 prepared by sol-immoblisation catalyst. Reaction conditions: Toluene 10 mL, T= 80ºC, Ratio toluene (mol):TBHP(mol) = 1:1, Key: ● conversion of toluene (%), □ benzyl alcohol selectivity (%), Δ benzaldehdye selectivity (%), x benzoic acid selectivity (%), ◊ benzyl benzoate selectivity.

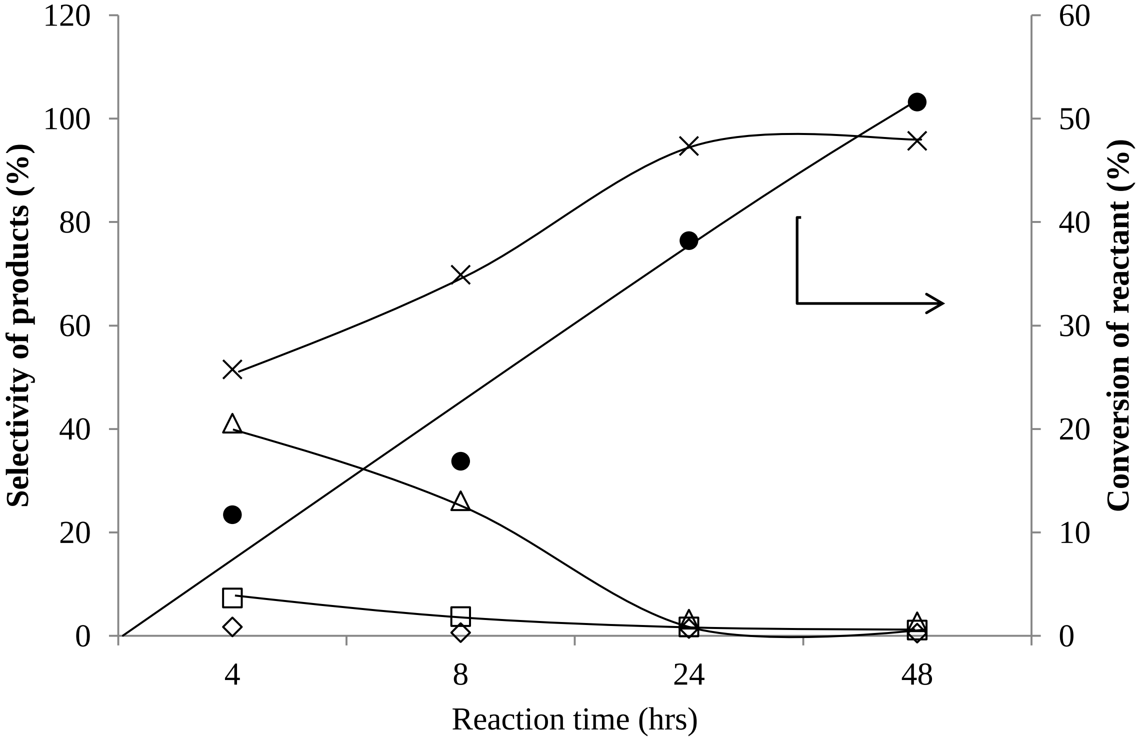


Figure 4.6: Time online plot of toluene oxidation in presence of 1%wtAu-Pd/C prepared by sol-immoblisation catalyst. Reaction conditions: Toluene 10 mL, T= 80ºC, Ratio toluene (mol):TBHP(mol) = 1:1, Key: ● conversion of toluene (%), □ benzyl alcohol selectivity (%), Δ benzaldehdye selectivity (%), x benzoic acid selectivity (%), ◊ benzyl benzoate selectivity (%).

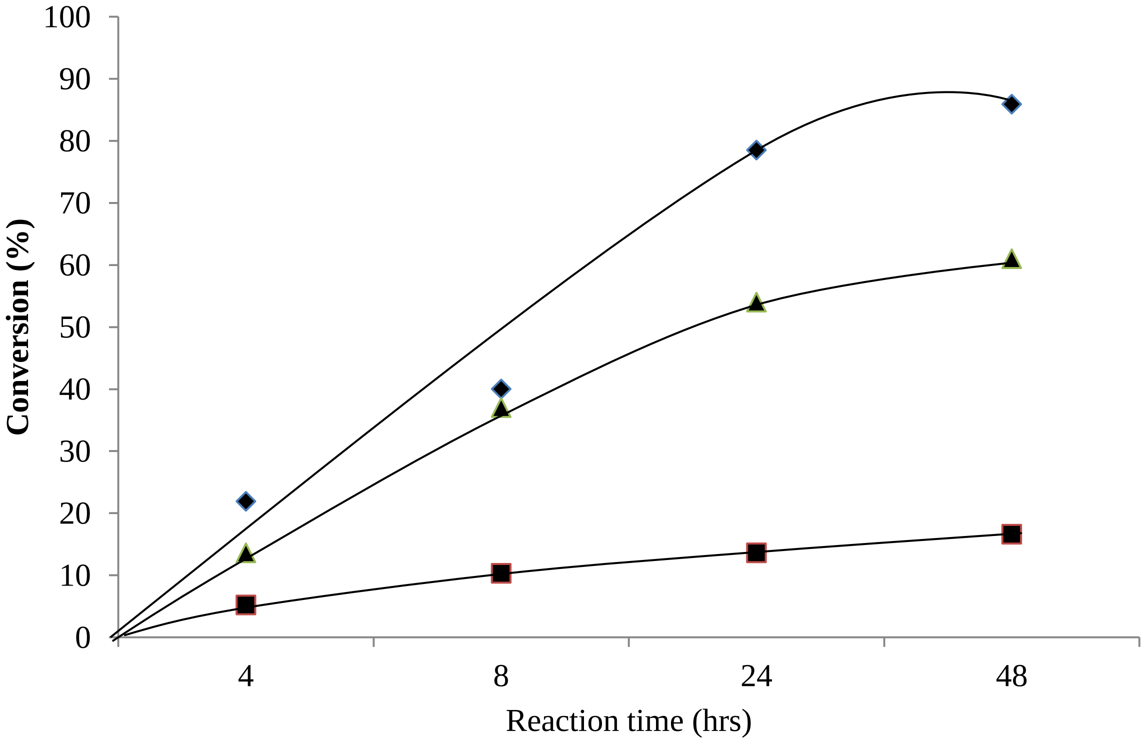


Figure 4.7: Time online plot of conversion of TBHP. Reaction conditions: Toluene 10 mL, T= 80ºC, Ratio toluene (mol):TBHP(mol) = 1:1, Key: ■ conversion of TBHP without catalyst (%), ▲ conversion of TBHP with 1%wtAuPd/TiO_2 (%), ♦ conversion of TBHP with 1%wtAuPd/C (%)

4.3.5 Effect of catalyst mass

The amount of catalyst used is an important variable in toluene oxidation since there are a number of competing processes that also lead to the decomposition of TBHP, which can significantly affect catalytic activity. The influence of increasing the amount of catalyst in the round bottom flask is shown in figure 4.8 for the 5wt%Au-Pd/TiO_{2IW} catalyst. The reactions were carried out at 4 hours of reaction. Between 0.05 – 0.8 g of catalyst, toluene conversion increased linearly. It seems that by increasing the mass of catalyst above 0.8 g, the decomposition of TBHP was accelerated, and this subsequently affected the amount of oxidant available during the reaction and therefore the rate of reaction.

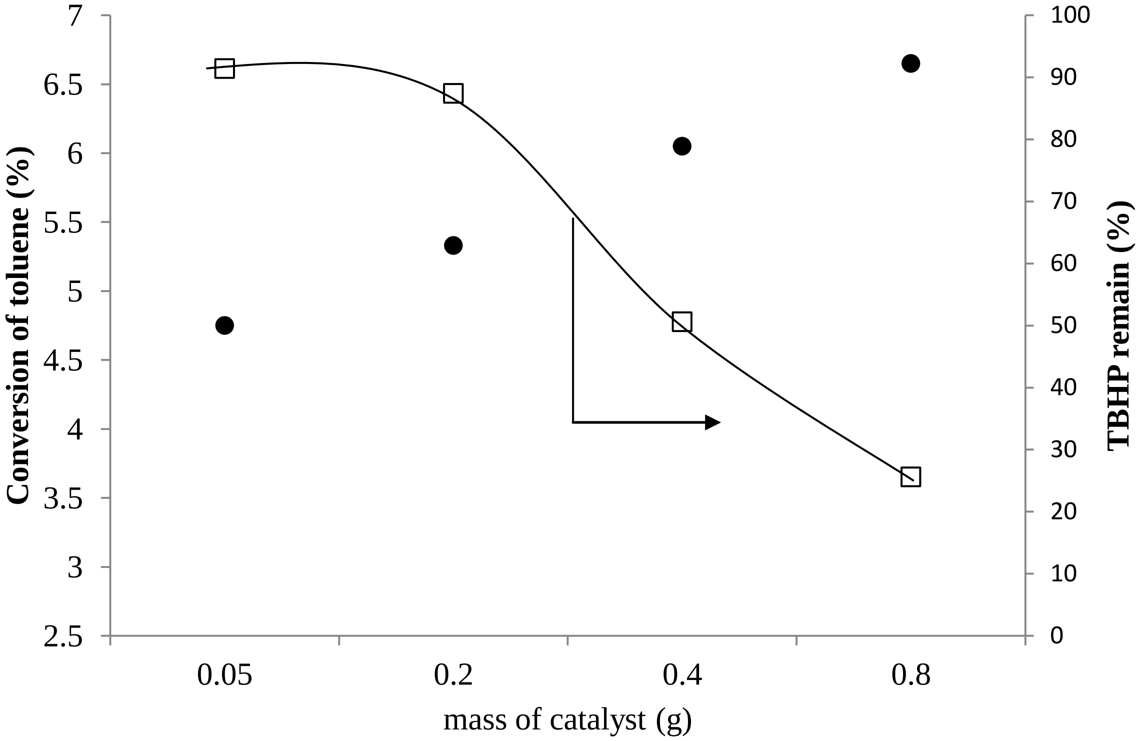


Figure 4.8: Effect of catalytic mass on catalytic performance of 1%Au-Pd/TiO$_{2SI}$ for selective toluene oxidation with TBHP. Key: ● conversion of toluene (%), □ TBHP remains after reaction (%). Reaction conditions: Toluene 10 mL, T= 80ºC, Ratio toluene (mol):TBHP(mol):1:1, Time = 4 hours.

As a result, the formation of benzoic acid increased linearly with decreasing the benzyl alcohol and benzaldehdye was observed over the range of 0.05 to 0.8 g of catalyst (Figure 4.9).

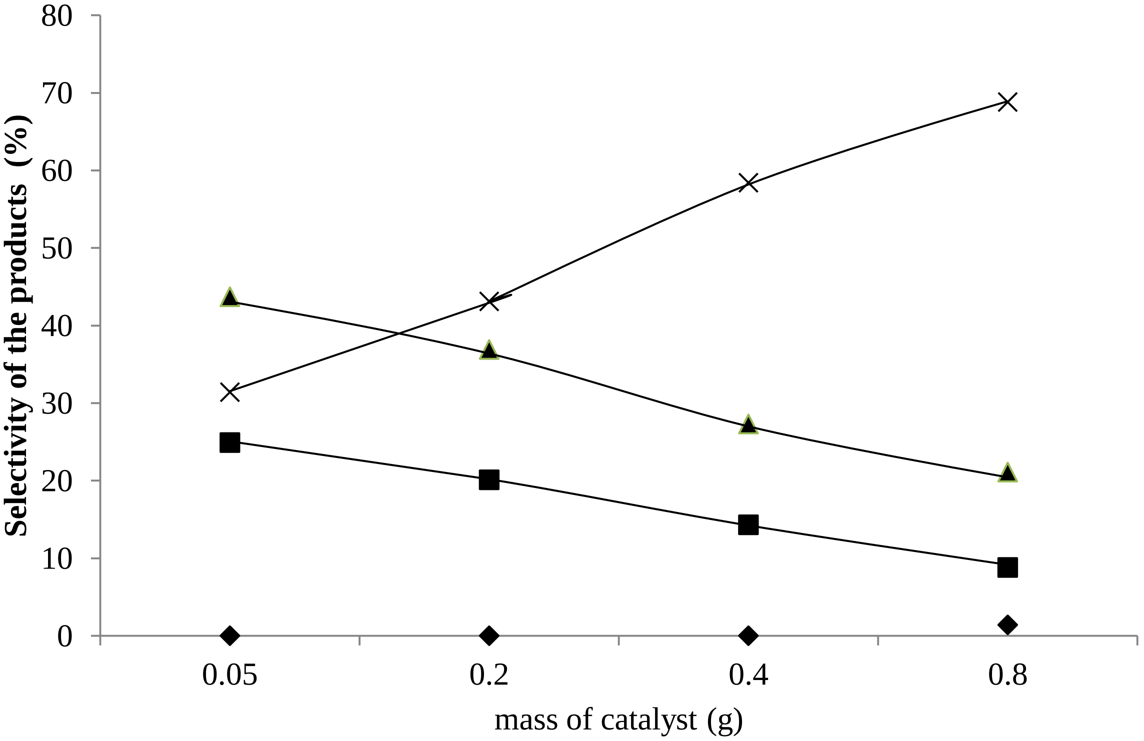


Figure 4.9: Effect of catalytic mass on catalytic performance of 1%Au-Pd/TiO_{2SI} for selective toluene oxidation with TBHP. Key: ■ benzyl alcohol (%), ▲ benzaldehdye (%), x benzoic acid (%), ♦ benzyl benzoate (%), Reaction conditions: Toluene 10 mL, T= 80ºC, Ratio toluene (mol):TBHP(mol):1:1, Time = 4 hours.

4.3.6 Effect of reused catalyst.

Table 4.12 shows that sol-immoblisation catalysts also have stability after being reused for 5 times. This is very important to industrial that this catalyst can use for longer time of reaction. It was evident from the experiment that reusability of the catalyst is strongly not affected by the changes in the morphology of the catalyst.

Table 4.12. Liquid phase oxidation of toluene using TBHP as an oxidant at 80 °C for bimetallic supported catalysts prepared by sol-immobilisation[a]. Reaction performed for 4 hours

Catalyst	Conv. (%)	Selectivity (%)				TOF (h^{-1})[d]
		Benzyl alcohol	Benzaldehyde	Benzoic acid	Benzyl Benzoate	
1%wtAu-Pd/TiO2$_{SI}$ (1:1 wt ratio)	4.40	23.2	32.3	44.4	0.1	72.2[b]
1st reused	4.00	18.0	34.7	47.3	0.0	*64.4*[b]
2nd reused	4.00	16.9	33.7	49.3	0.1	*64.3*[b]
3rd reused	3.80	14.7	37.1	48.1	0.0	*61.3*[b]
4th reused	4.20	15.9	27.9	56.1	0.1	67.6[b]
5th reused	4.00	15.0	36.3	48.7	0.0	65.8[b]

[a]Reaction conditions:Toluene = 94.1mmol, catalyst = 0.2g, ratio toluene(mol): TBHP(mol) = 1:1, T = 80 ºC, SI: Sol-immobilisation method, [b]Substrate/metal = 6502, [c]TOF (h^{-1}) at 4h reaction. TOF numbers were calculated on the basis of total loading of metals.

4.4 Mechanistic study of TBHP in toluene oxidation reactions

4.4.1 Introduction

It is well known that metal nanoparticles can efficiently decompose oxidants such as H_2O_2 and TBHP.[13] Recently, it has been reported that supported gold catalysts can produce extremely high rates of decomposition of peroxides to produce oxygenated radical species, for example hydrogen peroxide is decomposed to form $^{\bullet}OH$ and $^{\bullet}OOH$ radicals. In addition, the efficient conversion of alcohols using TBHP has been demonstrated.[14,15] Furthermore, decomposition of the organic peroxides can produce reactive oxygen species (ROS) , such as $^{\bullet}OH$ and $tBuO^{\bullet}$, in addition to decomposition products such as H_2O, O_2 and *t*-butyl alcohol. The activity of the surface bound (metal and/or support) ROS with the organic substrates has not previously been considered in any detail since it is generally accepted that the ROS work mainly in solution with the role of the surface merely being to increase the rate of their formation. However, it has been recently shown that surface species, derived from azobis-iso-butyronitrile (AIBN), can be formed on gold catalysts and these can promote oxygen activation *via* peroxo-radical species. [16-18]

4.4.2 Study of the decomposition of TBHP using Au-Pd bimetallic catalysts

To elucidate details of the reaction mechanism and especially the role of the supported metal nanoparticles on TBHP, a series of experiments was carried out (Table 4.13). In the first case (A), the oxidation of toluene over 7 h in the absence of catalyst but presence of TBHP showed low conversion (0.53%). In case (B), the oxidation of toluene in the presence of catalyst and TBHP showed high activity, highlighting the importance of the catalyst in significantly increasing the rate of reaction. Notably in the case of the full system (B) the product distribution differs to when the catalyst was removed in that the selectivity to benzoic acid is appreciably higher (49.4% versus 8.9%) than in (A). This clearly points to the role of the support Au-Pd particles in the selective formation of benzoic acid. It was possible here that combination of small metal particle size and higher metal dispersion as well as presence of Au and Pd in metallic state in sol-immobilised catalyst is more efficient in activating aromatic hydrocarbons and consequently increase the rate of reaction.

In case (C) TBHP was completely decomposed over the catalyst (monitored by GC analysis), followed by the addition of toluene and minimal conversion of 0.13% was observed. Even though the conversion was minimal the product distribution still differs from that of (A) at similar conversion levels (i.e. 1.5h point in A) as the benzoic acid selectivity is increased almost 8-fold when the catalyst was present. Again this supports the previous finding that the catalyst is crucial to the transformation of benzaldehyde to benzoic acid.

In case (D) TBHP was decomposed over the catalyst (1%wt(Au-Pd)/TiO_{2SI}); the solid catalyst was removed by filtration, dried overnight at room temperature and then reacted with toluene; whereas, in the case (E) the same procedure was followed with the exception that the catalyst was not dried and toluene was added after the decomposition of TBHP. In both these experiments (D, E) low levels of toluene conversion of 0.06% were observed. In cases (F, G) the complete decomposition of TBHP in the presence or absence of catalyst, and the subsequent addition of toluene, did not produce any products. The low levels of conversion observed using a ‘pre-TBHP-activated’ catalyst indicate that residual surface-stabilized ROS/organic surface radicals can lead to the conversion of toluene. Furthermore, after the complete decomposition of TBHP in the presence of catalyst, followed by filtration to remove the catalyst, addition of toluene to the remaining solution gave no appreciable conversion. This again highlights the importance of surface-based ROS/organic surface radicals, and demonstrates that the solution based ROS are truly short lived, and cannot induce toluene oxidation in the absence of a supply of TBHP. Thus it is proposed that the surface acts to provide a platform to stabilize the ROS, thereby extending their lifetime and facilitating oxidation and is also implicated in the transformation of primary to secondary products.

Table 4.13. The oxidation of toluene with TBHP for bimetallic supported catalysts prepared by the sol-immobilisation method.^{a}

			Selectivity [%]				
Reaction	Time [h]	Conv. [%]	Benzyl alcohol	Benzaldehyde	Benzoic acid	Benzyl Benzoate	TOF [h^{-1}]^d
A	1.5	0.17	18.9	77.8	3.2	0	
	3	0.33	15.9	77.3	6.8	0	
	7	0.53	14.9	76.2	8.9	0	
B	1	2.63	19.4	42.9	37.7	0.0	
	2	4.17	14.8	29.6	55.6	0.0	
	4	6.43	10.2	20.0	69.8	0.0	
	8	10.0	12.8	37.2	49.4	0.6	171^b
C	1.5	0.04	12.2	87.8	0.0	0	
	3	0.11	11.7	76.3	12.0	0	
	7	0.13	8.1	67.8	24.1	0	0.33^c
D	1.5	0.01	12.0	88.0	0	0	
	3	0.01	7.9	92.1	0	0	
	7	0.06	3.2	96.8	0	0	0.7^c
E	1.5	0.04	30.5	68.8	0.7	0	
	3	0.04	30.0	64.2	5.8	0	
	7	0.06	29.5	61.0	9.5	0	0.26^c
F	1.5	0	0	0	0	0	
	3	0	0	0	0	0	
	7	0	0	0	0	0	
G	1.5	0	0	0	0	0	
	3	0	0	0	0	0	
	7	0	0	0	0	0	0

^{a}Reaction conditions:toluene = 94.1mmol, catalyst = 0.2-1.0g, ratio toluene (mol): TBHP (mol) = 1:1, 80°C,

A: Solution of toluene and TBHP in the absence of catalyst;

B: Solution of toluene and TBHP in the presence of catalyst 0.5%Au-0.5%Pd/TiO$_2$;

C: The first step was the complete decomposition of TBHP in the presence of 0.5%Au-0.5%Pd/TiO$_2$ and addition of toluene in the reactor;

D: The first step was the complete decomposition of TBHP in the presence of 0.5%Au-0.5%Pd/TiO$_2$ followed by filtration of the solution, and drying and addition of toluene to the dried catalyst;

E: The first step was the complete decomposition of TBHP in the presence of 0.5%Au-0.5%Pd/TiO$_2$ followed by recovery of the catalyst by filtration and addition of toluene in the reactor in the presence of the catalyst;

F: The first step was the complete decomposition of TBHP in the presence of 0.5%Au-0.5%Pd/TiO$_2$ followed by filtration for removal of the catalyst and addition of toluene in the reactor in the absence of the catalyst;

G: The first step was the complete decomposition of TBHP in the absence of catalyst, followed by of toluene in the reactor.

^{b}Substrate/metal = 6500, ^{c}Substrate/metal = 1300, ^{d}TOF (h^{-1}) at 7 and 8 hours. TOF calculated on the basis of total loading of metals

For further support of the hypothesis and to confirm that the metal is associated with the surface radicals one experiment was carried out using half of metal percentage loading (i.e 0.5% wt (Au-Pd)/TiO_{2SI}) . The step D in Table 4.13 was repeated with the same condition of procedure and using the half metal loading catalyst as described as earlier. The data was shown in Table 4.14. If toluene conversion had remained constant, then it could be hypothesized that the radicals are probably associated with the TiO_2 surface. It was clearly shown that the conversion of toluene decreased as the total metal loading decreases (catalyst amount was kept constant). This observation shows that the surface radicals are probably associated with the metal particles.

Table 4.14. The oxidation of toluene with TBHP for bimetallic supported catalysts prepared by the sol-immobilisation method.[a]

Reaction	Reaction Time/h	Conv. (%)	Selectivity (%)				TOF (h^{-1})[c]
			Benzyl alcohol	Benzaldehyde	Benzoic acid	Benzyl Benzoate	
H	1.5	0.01	19.3	80.7	0	0	
	3	0.02	12.3	87.7	0	0	
	7	0.02	9.3	90.7	0	0	0.07[b]

[a]Reaction conditions: : toluene = 94.1mmol, catalyst = 1.0g, ratio toluene(mol): TBHP(mol) = 1:1, temp=80°C,

H: The first step was the complete decomposition of TBHP in the presence of 0.25%wtAu-0.25%wt Pd/TiO_{2SI} followed by filtration of the solution, and drying and addition of toluene to the dried catalyst;

[b]Substrate/metal = 2600, [d]TOF (h^{-1}) at 7 hours. TOF numbers were calculated on the basis of total loading of metals

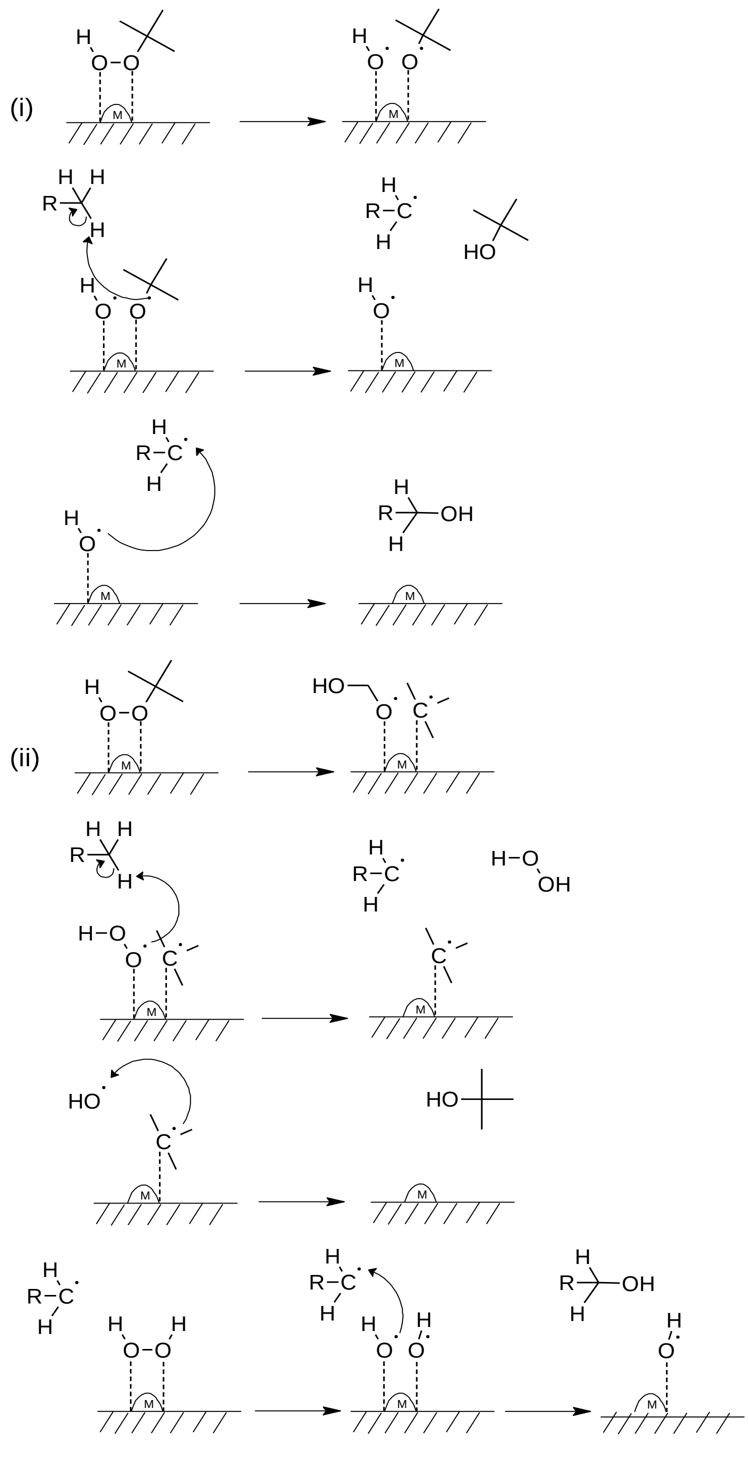
4.4.3 General proposal on plausible mechanistic pathways on toluene oxidation using Au-Pd based on supported nanoparticles catalyst and TBHP as an oxidant

Based on the experimental data, the following plausible reaction pathways can be proposed (Scheme 4.1): (i) TBHP can decompose on the metal surface to produce surface $tBuO^{\bullet}$ and $^{\bullet}OH$ radicals. $tBuO^{\bullet}$ can abstract $H^{\bullet}$ from toluene forming *tert*-butanol (which was detected experimentally) whilst the resulting toluene derived alkyl radical can react with $^{\bullet}OH$ to form benzyl alcohol; (ii) TBHP can decompose to $tBu^{\bullet}$ and $^{\bullet}OOH$ radicals at the surface of the gold-palladium particles and the $^{\bullet}OOH$ radicals can abstract $H^{\bullet}$ from toluene forming hydrogen peroxide with the resulting toluene derived alkyl radical reacting with surface $^{\bullet}OH$ to form benzyl alcohol. (iii) Formation of O_2^- surface species *via* $HOO^{\bullet}$ deprotonation ($HOO \rightarrow H^+ + O_2^-$),[19] adsorption of toluene on the metal or metal/support interface and activation *via* O_2^- surface radicals (or other surface ROS) for transformation of toluene to oxygenated species. In these pathways the surface $^{\bullet}OH$ radicals can easily be produced by the decomposition of hydrogen peroxide on the metal surface and $tBu^{\bullet}$ radicals can react with $^{\bullet}OH$ radical and form *tert*-butanol. (iv) Finally, the possibility cannot be excluded that $tBuO^{\bullet}$ and $^{\bullet}OH$ radicals are also formed *via* homolytic thermal decomposition of TBHP in the absence of catalyst. Nevertheless, the consideration will be taken that these species play a minor role in the activation process of toluene since a very low conversion TBHP was observed in the blank reaction (i.e. in the absence of catalyst).

The next step after the formation of alcohol is described in (Scheme 4.2). This reaction is a dehydrogenation with the metal, which is acting as an H acceptor.[20] The corresponding alcohol can coordinate on the metal sites forming M-alcoholate species. The metal alcoholate species will transform to the corresponding carbonyl compound resulting in the formation of M-hydride spesies. In this reaction, water acts as a weak base (nucleophile). Finally, the M-hydride species will be oxidised in the presence of adsorbed oxygen to obtain the initial metal sites.

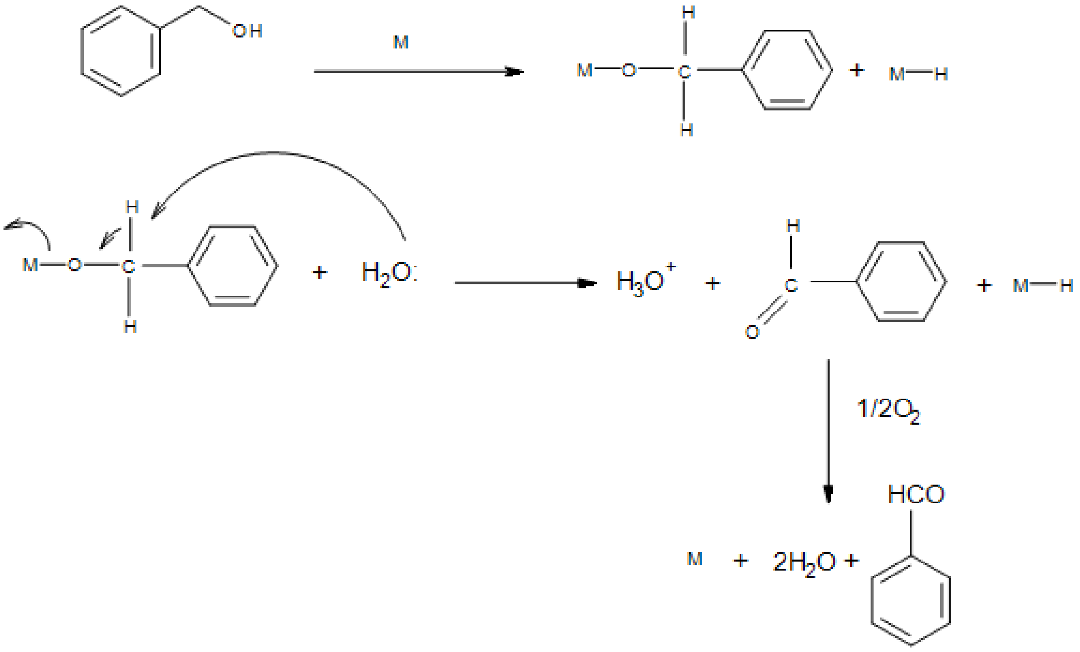
Other reaction pathway was the oxidation of benzyl alcohol leads in the first instance to the formation of benzaldehdye. Further oxidation of this molecule leads to the production of benzoic acid, as shown in scheme 4.3. However, other side reactions are also possible. One pathway is reaction between generated aldehyde and water, which is catalysed by the acid-basic sites present on the catalyst (scheme 4.3). This generates an enol (aldehyde hydrate) and subsequently oxidized to the corresponding benzoic acid.

The formation of carboxylic groups can be the result of the following parameters as it is shown in Scheme 4.4: (i) due to the presence of water, interaction between the solvent and the carbonyl group to form the germinal glycol which is more reactive than the aldehyde under oxidation conditions, [21] (ii) $tBuO^\bullet$ surface radical will abstract $H^\bullet$ from the carbonyl group to form surface $RC^\bullet O$ species and the subsequent oxidation with surface $^\bullet OH$ radical will form RCOOH. (iii) $^\bullet OOH$ will abstract $H^\bullet$ from the carbonyl group and will form H_2O_2 and $RC^\bullet O$ followed by H_2O_2 decomposition on the metal surface to produce $^\bullet OH$ radicals which combine with the $RC^\bullet O$ to yield RCOOH. (iv) The oxidation of carbonyl group with adsorbed oxygen and the subsequent formation of the carboxylic group and further desorption could be also possible.

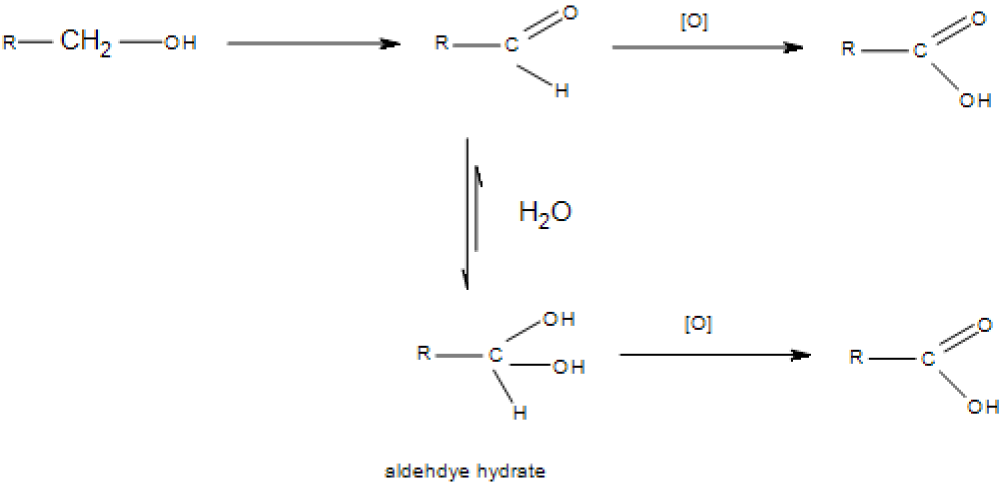


(iii) $RCH_3 + O_{2\,ad}^{-} \longrightarrow RCHO + H_2O$

Scheme 4.1. Possible reaction pathways for the activation of toluene in the presence of TBHP



Scheme 4.2**:** Possible reaction pathways for the oxidation of alcohol



Scheme 4.3**:** Possible other reaction pathways for the oxidation of alcohol via acid formation.

$$\text{(i)}\quad RCHO_{ad} + H_2O \rightleftharpoons RCH(OH)_{2,ad}$$

$$RCH(OH)_2ad \rightleftharpoons RCOOH_{ad} + 2H_{ad}$$

$$\text{(ii)}\quad RCHO_{ad} + tBuO^{\circ}{}_{ad} \longrightarrow RC^{\circ}O_{ad} + tBuOH$$

$$RC^{\circ}O_{ad} + {}^{\circ}OH_{ad} \longrightarrow RCOOH$$

$$\text{(iii)}\quad RCHO_{ad} + {}^{\circ}OOH_{ad} \rightleftharpoons RC^{\circ}O_{ad} + H_2O_2$$

$$H_2O_2 \longrightarrow 2\ {}^{\circ}OH_{ad}$$

$$\text{(iv)}\quad RCHO_{ad} + O_{ad} \rightleftharpoons RCOOH_{ad}$$

$$RCOOH_{ad} + OH^{-}{}_{ad} \rightleftharpoons RCOO^{-} + H_2O$$

Scheme 4.4: Possible reaction pathways for the oxidation of the carbonyl group in the presence of TBHP

4.4.4. Identification of radical species present in the catalytic system using Electron Paramagnetic Resonance (EPR)

EPR radical trapping techniques have been used to identify the radical species available in the reaction solution. In this experiment 5,5-dimethyl-pyrroline N-oxide (DMPO) was used as a radical trap and it was added to the reaction filtrate after collecting the liquid solution from the toluene reaction. The reaction was carried out in the presence of 1%wt(Au-Pd)/TiO_{2SI} catalyst prepared by sol-immobilisation method. The experiment was performed for 4 hours before adding DMPO.

Therefore, to investigate the nature of the aforementioned surface based ROS, CW-EPR spectra were recorded for the 1%wt (Au-Pd)/TiO_{2SI} sample in the presence and absence of TBHP. The solid state EPR spectra of the dried samples are shown in figure 4.10, after the appropriate treatment. The background EPR spectrum of the untreated sample (figure 4.10a) contains signals arising from bulk Ti^{3+} centres ($g_{\perp} = 1.978$, $g_{\parallel} \approx 1.962$)[21] and Pd^{+} ions ($g_1 \approx 2.80$, $g_2 = 2.13$, $g_3 = 2.080$).[23] Owing to the broad profile of the axially symmetric Ti^{3+} signal, it is not possible to assign these centres specifically to the anatase or rutile component of the P25 (TiO_2); nevertheless formation of Ti^{3+} centres in P25 by gentle annealing is not uncommon.[24] The Pd^{+} signal suggests small amounts of Pd-oxide or isolated Pd centres exist on the catalyst. Following treatment with TBHP, the EPR spectrum changes markedly (Figure 4.10b); the majority of the Pd^{+} signal disappears, the bulk Ti^{3+} remains visible and a new signal assigned to the superoxide radicals (O_2^{-}) is observed; the measured g values of $g_1 = 2.003$, $g_2 = 2.004$ and $g_3 = 2.024$ and line width are consistent with a non-vacancy $Ti^{4+}...O_2^{-}$ coordinated site for a ‘side-on’ ionically bonded conformation.[25] This species is considered to be derived directly (from TBHP decomposition) or indirectly (by reduced Ti^{3+} centres reacting with molecular oxygen) from TBHP, as it is not present when THBP is absent; *e.g.* direct exposure of the Au-Pd/TiO_2 catalyst to oxygen does not generate this signal in the absence of TBHP. There was no evidence of a hydroperoxy ($HO_2^{\bullet}$) species or other oxygen centered radical (peroxy) which have been previously identified on P25.[26]

When the sample was subsequently treated with TBHP/toluene (figure 4.10c), the superoxide signal disappeared completely and a new inhomogeneously broadened symmetric signal with $g = 2.004$ was formed. Coupled with the relatively large linewidth, one may conclude that the radical responsible for this signal is surface based. Surface O_2^- radicals can oxidise various organic substrates over TiO_2 (P25), although oxidation by other surface ROS such as acryl or organo-peroxyl radicals is more facile.[27] Whilst the former ionic species (O_2^-) are stable on TiO_2, the latter species are more difficult to detect directly on the oxide support,[27] let alone on a metal particle where spin polarization would considerably broaden any signal, hence they may be formed but are not observed in the current experiments. Nevertheless these EPR results at least demonstrate the role of surface O_2^- radicals in the oxidation of toluene. This is clearly evidenced by the fact that when it recovered and dried the catalysts after TBHP addition (figure 4.10b) the O_2^- signal remained. After subsequent toluene addition, the O_2^- signal disappeared, thus proving the reaction of toluene with this surface bound radical species. However, the possible role of other unobserved surface ROS cannot be precluded.

The data that have been observed for the reaction of toluene and TBHP can therefore be rationalised on the basis of free radical chemistry, although many of the radicals concerned should be regarded as surface bound ROS. It is possible that a number of potential pathways exist for the formation of the primary product, *i.e.* benzyl alcohol involving free radical formation and termination. However, based on the data generated, the consideration has been taken that these products arise from interactions of surface-bound ROS that behave chemically like radicals. Therefore it is clear from our results that for $AuPd/TiO_2$ the bi-functional role of Au/Pd sites and Ti^{4+} centres on the surface of titania facilitates the activation of toluene and affects the product distribution.

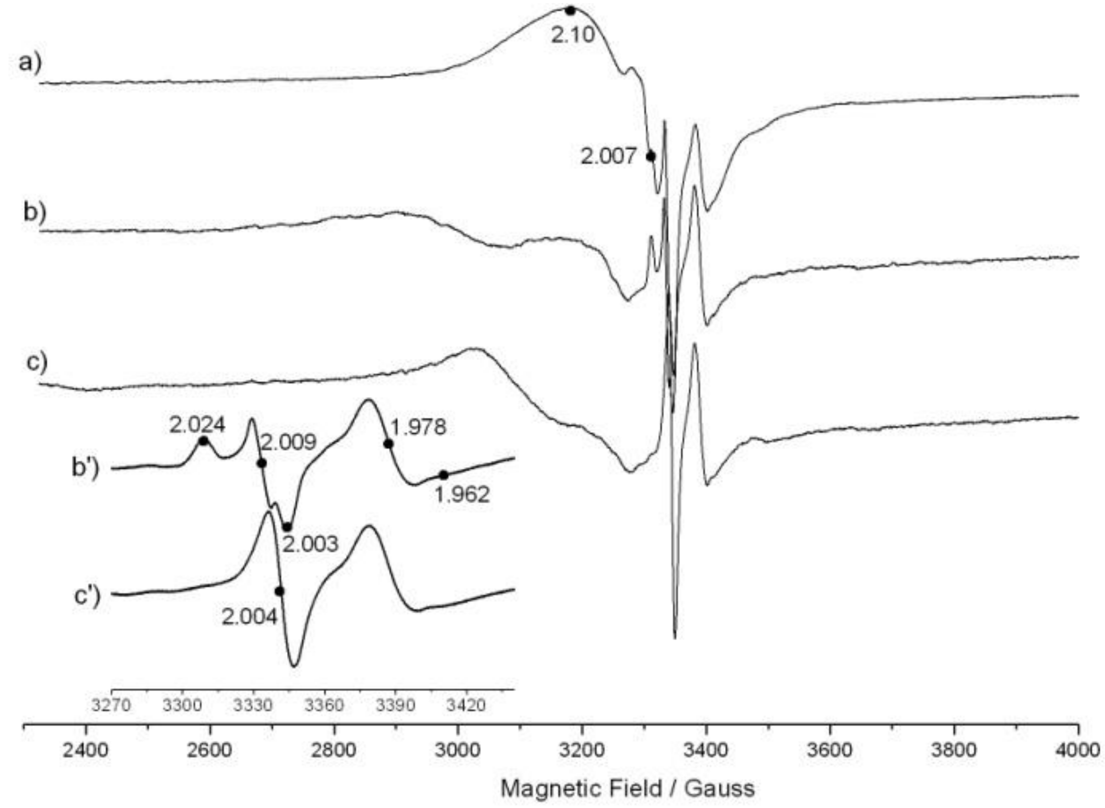


Figure 4.10: X-band CW-EPR spectra (140K) of a) Au-Pd/TiO_2, b) Au-Pd/TiO_2 after treatment with TBHP, and c) Au-Pd/TiO_2 after treatment with TBHP + toluene. The expanded views of the centre field regions of b) and c) are shown in the inset (labelled b' and c').

4.5 Conclusions

In this chapter, toluene has been examined by oxidation reactions with the addition of TBHP using supported Au-Pd nanoparticles catalysts. The obtained experimental and catalytic data are well correlated with catalyst structure as well as the reaction parameters. Initial studies showed that TBHP is successfully as oxidant to toluene oxidation at mild reaction conditions. Furthermore, the reaction was set up at 80 °C of temperature due to the good conversion was observed rather than using at higher temperature (~90 °C). Further, it was proved by experimental that air could give effect for the reaction activity. The synergistic effect also contributes to the increase in the activity when bimetallic Au-Pd was used to perform the reaction. By increasing the reaction time from 4 to 48 hours, an increase in toluene conversion is observed; nevertheless a drop in the selectivity of benzyl alcohol and benzaldehdye due to consecutive reaction to form benzoic acid.

Au-Pd/TiO_2 synthesized via impregnation and sol-immobilisation technique was also found to be stable when reused. Variation of the support also was studied and it showed that carbon as a support gives more conversion for both preparation techniques.

Decomposition of TBHP was studied with the series of the experiments performed. The oxidation of toluene and TBHP without using catalyst gives minimal conversion of the reactant as compared to full catalytic system. When adding the catalyst, it was showed that catalyst had major influence on both the conversion of toluene and selectivity profile of the products. Further studies identified the importance of reactive oxygen species (ROS) and radical generated or bound to the metal surface.

Furthermore, plausible reaction mechanism pathways were proposed to clarify the role of TBHP towards the toluene oxidation. These pathways included the formation of radical species such as *tert*-butyl peroxy (*t*-BuOO$^\bullet$) and *tert*-butyloxy (*t*-BuO$^\bullet$) directly derived from surface metal mediation with the metal sites forming M-alcoholate species and formation of carboxylic group as well.

For further conformation of the radical species in toluene oxidation, an EPR technique was employed and the results showed that superoxide species (O_2^-) was detected when the reaction of TBHP and catalyst was performed. After subsequent toluene addition, the O_2^- species' signal disappears, indicating the role of these surface species in the oxidation of toluene. Unfortunately, no surface bound hydroperoxy ($HO_2^{\bullet}$) species or other oxygen centre radical (peroxy) has been detected through that process. This does not preclude the role of solution based hydroperoxy of peroxy racidals in the oxidation mechanism. Further work using radical inhibitors/scavengers such as sodium sulphite, $NaSO_3$, butylated hydroxytoluene (BHT), and N-*tert*-butyl-α-phenylnitrone (PBN) may be useful in investigating the solution species.

At present, it has not been able to delineate fully the contributions to the overall oxidation reactions by the surface bond radicals, but the mere observation of this new pathway will aid and inform future catalyst design and reaction mechanism study.

4.6 References

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CHAPTER 5

Oxidation of other aromatic organic compounds using Au-Pd catalysts

5.1 Introduction

In this chapter other type of aromatic hydrocarbons, such as substituted benzenes, possessing electron-donating and electron-withdrawing groups, were studied using Au-Pd supported TiO_2 catalyst using impregnation and sol-immobilisation methods. These studies were preformed to investigate the wider applicability of the Au-Pd catalysts for selective oxidation of other aromatic molecules as well as toluene oxidation. In keeping with previous work all reactions in this chapter were performed using TBHP as an oxidant with same conditions of temperature and amount of catalyst as used previously.

5.2 Effect of an electron donating group- reactions with 2, 3, 4 – methoxytoluene

It is well known that substituting toluene with electron donating groups should result in higher activity as compared to toluene for reactions in which the transition state is more easily accessed when electron density at the reactive carbon is high. This argument is based on the substituent effects on toluene aromatic ring affecting the strength of C-H bond dissociation energies of system. In the benzylic system, bond dissociation energies of the methyl C-H bond is dependent on two effects; ground state effect and radical effect. [1] The former is a polar effect whereas the latter is based on a spin delocalization effect. Since the methyl group of toluene is a weak donor; electron donating substituents at the *ortho, meta* and *para- positions* causes destabilization of ground state but stabilizes the benzyl radical formed during the oxidation reaction thereby reducing the effective benzylic C-H bond dissociation energies. Hence, the presence of methoxy (OCH_3) substituents, a strong electron-donating group, at carbon *ortho, meta* and *para* in toluene aromatic ring will reduce the C-H bond dissociation energies of system. This facilitates the activation of C-H bond and therefore it is easier to activate 2,3,4-methoxy toluene compared to toluene.

It can be seen in Table 5.1 that the conversion of 4-methoxytoluene was higher compared with 3 and 2-methoxytoluene when using the impregnation catalyst in 4 hours reaction. The main product formed was *n*-methoxybenzaldehyde for each catalyst. This trend was completely different when sol-immobilisation catalyst was using in the reaction. Comparison of catalytic activity for the methoxytoluenes shows the following order of activity: 4-methoxytoluene>3-methoxytoluene>2-methoxytoluene. The main product detected was *n*-methoxy benzoic acid due the over-oxidation process. It clearly shows that small nano particles from sol-immobilisation catalyst affect the product distribution greatly. This effect was already explained in detail in chapter 3 and 4, respectively. From this data set the effect position of the methoxy substituent is not clear as the order of catalytic activity differs between the two catalysts. This may be due to the difference in the morphology of the catalysts prepared with the sol-immobilisation method.

Table 5.1: Liquid phase oxidation of methoxytoluenes and TBHP as an oxidant at 80 °C for 5 wt % Au-Pd/TiO_{2Iw} prepared by impregnation method and sol immobilization methods.[a]

Substrate	Conv. [%]	Selectivity [%]			TOF $[h^{-1}]$[h]
		n-Methoxy benzyl alcohol	*n*-Methoxy benzaldehyde	*n*-Methoxy benzoic acid	
4-methoxytoluene[b]	6.2	38.9	60.5	0.6	83.8[d]
3-methoxytoluene[b]	2.9	28.9	68.0	3.1	21.6[d]
2-methoxytoluene[b]	2.8	36.8	58.0	5.2	2.2[e]
4-methoxytoluene[c]	6.7	36.0	39.8	24.2	254.0[f]
3-methoxytoluene[c]	4.5	19.3	40.3	40.4	112.5[f]
2-methoxytoluene[c]	7.3	20.1	35.1	44.8	136.9[g]

[a] Reaction conditions: Substrate = 10 ml, Substrate/TBHP molar ratio = 1:1, T = 80 ºC, Catalyst = 0.2g, Reaction time = 4 h, [b] I: Impregnation method, [c] SI: Sol-immobilization method, [d] Substrate/metal molar ratio = 1096, [e] Substrate/metal molar ratio = 1114, [f] Substrate/metal molar ratio = 5479, [g] Substrate/metal molar ratio = 5570, [h] TOF (h^{-1}) at 0.5 hours. TOF numbers were calculated on the basis of total loading of metals.

To be sure of the product assignments the filtered reaction solution was analyzed using GC-MS to confirm the product distributions (Figure 5.1). It clearly shows that formation of the n-methoxybenzyl alcohol and n-methoxybenzaldehyde with higher retention time in the GC-MS trace. A small peak was observed which is identified as an aromatic ester. Unfortunately, this peak is not clearly observed in the normal GC data. The reason is maybe the possibility of the sensitivity of GC-MS equipment to detect the other products is much higher than the GC used in the analysis. The details of the time of the products also have been given in Table 5.2. These data are based on the reaction of 4-methoxytoluene using impregnation catalyst and notably a peak for *n*-methoxybenzoic acid was not detected due the small conversion as shown clearly in Table 5.1.

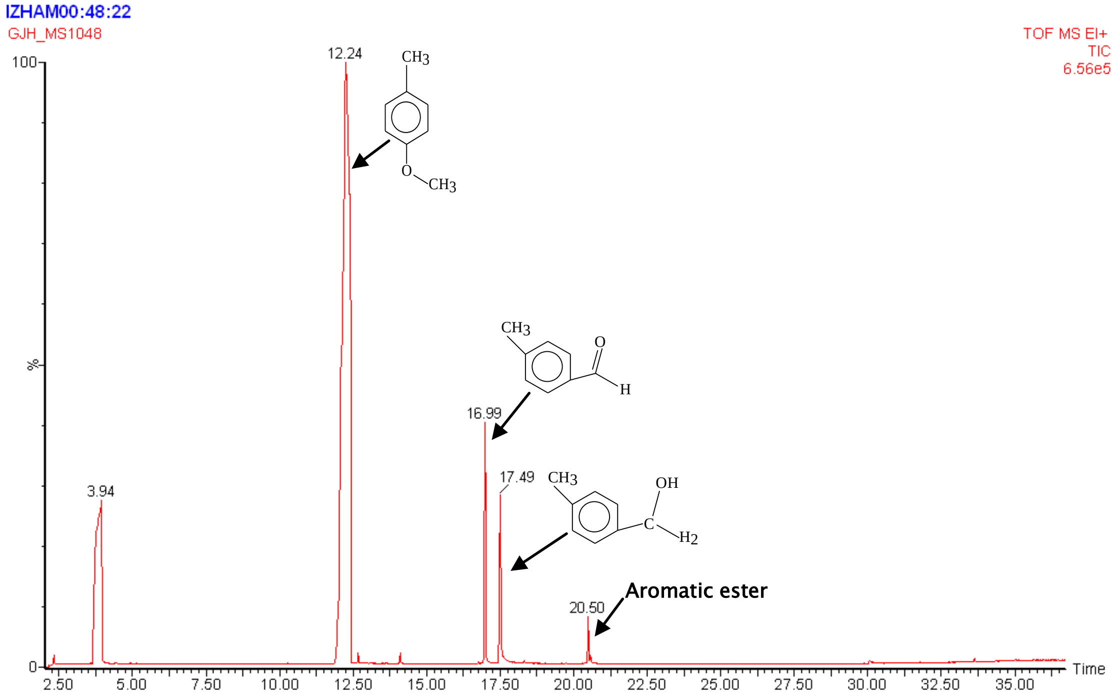


Figure 5.1: GC-MS graph for 4-methoxytoluene reaction using TBHP as oxidant

Table 5.2: GC-MS data for 4-methoxytoluene and product distributions

Name of product	Time
4-methoxytoluene	12.24
4-methoxybenzaldehyde	16.99
2-methoxybenzyl alcohol	17.49
Aromatic ester	20.50

5.3 Effect of electron withdrawing substituents- reactions with 2,3,4 –nitrotoluene

It was noted that the nitro group is a very strong deactivating substituent because of the combined electronegativities of the nitrogen and oxygen atoms, it is a powerful electron-withdrawing group[2]. It is possible that NO_2 group will give lower conversion result compared to the methoxy group (as a electron donating group). In Table 5.3, the conversion is similar for a particular substituent position when using the two catalysts. Interestingly only the 4-nitro group resulted in a lack of benzoic acid products. Based on TOF, the activity of both catalysts is higher for the meta substituent (4-nitrotoluene), 14.3 and 134.5 h^{-1}. In general the TOF is higher with the methoxy substituent (Table 5.3 versus Table 5.1) which is in line with the hypothesis that a strong electron withdrawing group will lower the oxidation rate.

Table 5.3: Liquid phase oxidation of nitrotoluene and TBHP as an oxidant at 80 °C for 5 wt % Au-Pd/TiO_{2Iw} prepared by impregnation method and sol immobilization methods.[a]

Substrate	Conv. [%]	Selectivity [%] *n*-Nitro benzyl alcohol	 *n*-Nitro benzaldehyde	 *n*-Nitro benzoic acid	TOF [h^{-1}][j]
4-nitrotoluene[b]	2.3	20.6	79.4	0	14.3[d]
3-nitrotoluene[b]	2.8	12.1	41.7	46.2	14.2[e]
2-nitrotoluene[b]	1.0	28.2	40.0	31.8	5.8[f]
4-nitrotoluene[c]	2.9	18.7	81.3	0	134.5[g]
3-nitrotoluene[c]	1.7	22.0	57.0	21.0	61.6[h]
2-nitrotoluene[c]	1.7	25.8	56.9	17.3	72.9[i]

[a] Reaction conditions: Substrate = 10 ml, Substrate/TBHP molar ratio = 1:1, T = 80 ºC, Catalyst = 0.2g, Reaction time = 4 h, [b] I: Impregnation method, [c] SI: Sol-immobilization method, [d] Substrate/metal molar ratio = 1402, [e] Substrate/metal molar ratio = 1163, [f] Substrate/metal molar ratio = 1172, [g] Substrate/metal molar ratio = 7013, [h] Substrate/metal molar ratio= 5818, [i] Substrate/metal molar ratio= 5818, [j] TOF (h^{-1}) at 0.5 hours. TOF numbers were calculated on the basis of total loading of metals.

The products that have been produced are *n*-nitrobenzyl alcohol, *n*-nitrobenzaldehdye and *n*-nitrobenzoic acid (see Table 5.3) as confirmed by GC-MS analysis of the reaction solution (Figure 5.2 and the products distribution in Table 5.4).

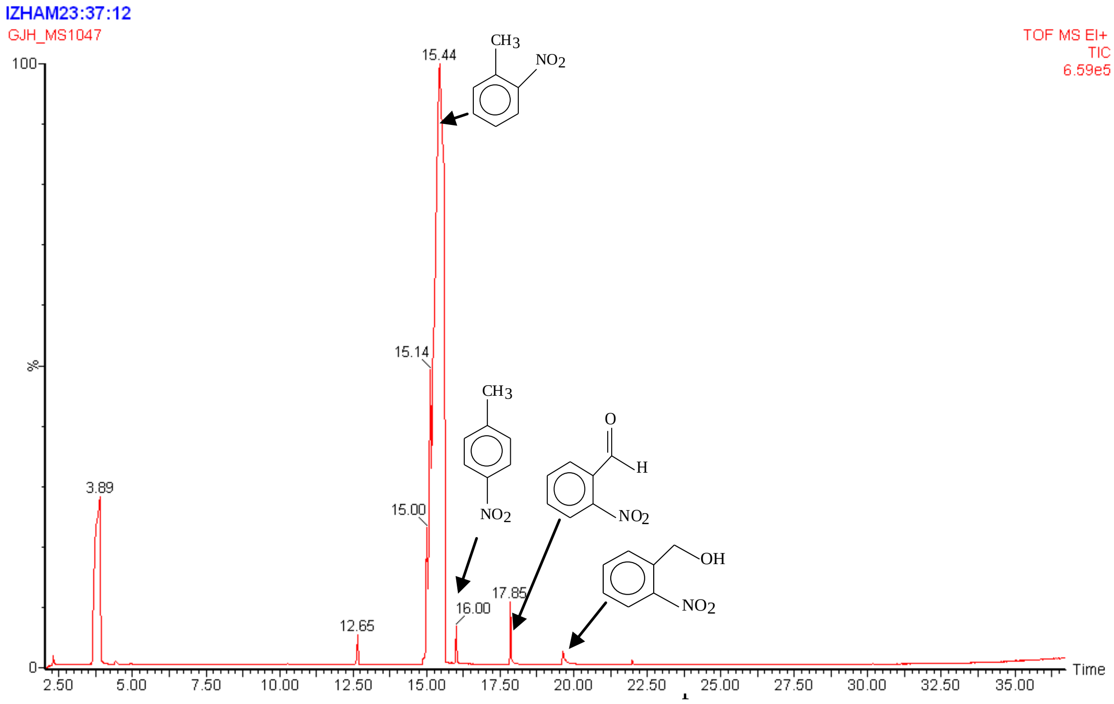


Figure 5.2: GC-MS graph for 2-nitrotoluene reaction using TBHP as oxidant

Table 5.4: GCMS data for 2-nitrotoluene and product distributions

Name of product	Time
2-nitrotoluene	15.44
4-nitrotoluene	16.00
2-nitrobenzaldehyde	17.85
2-nitrobenzyl alcohol	21.00

5.4 Ethyl benzene

Another aromatic substrate which is interesting to study is ethyl benzene due to the probability of oxidation at two C's of the ethyl group. Two catalysts, bimetallic Au-Pd/ TiO_2 prepared by different methodologies, were studied in this reaction with the data given in Table 5.5. Based on table 5.5, the sol-immoblisation catalyst gives higher conversion (11.5%) if compared than impregnation catalyst (9.3%). Specifically sol-immoobilisation technique has been employed to obtain Au/Pd metal nanoparticles with smaller and narrower particle size distribution (3-5 nm, median at 3.8 nm)[3] compared to the bimodal distribution of particle size with small size distribution (2-10 nm) and minority (ca. 8%) of larger particles (35-80 nm) using the impregnation technique and calcined in static air. [4-6]. It is again hypothesized that the smaller size and shape of the former results in higher activity. The major product was acetophenone formed by conversion of 1-phenyl ethanol. No 2-phenyl ethanol and phenylacetic acid was detected in any of these reactions. This is due to the greater stability of benzylic radical or faster oxidation of ethyl benzene to the benzylic radical as compared ot the primary carbon based radical (Scheme 5.1). It is beneficial that acetophenone was formed in appreciable yield since this molecule is very useful as a precursor in resin, pharmaceuticals and fragrances. Figure 5.3 and table 5.6 clearly shows the correct assignments of the products have been made according to GC-MS analysis of the reaction products and authentic commercial standards. Furthermore, a products such as benzoin and 1-phenyl ether ester also was appeared in that chromatograph due to sensitivity of the equipment. This data also was matched with run the standard each of the products and reactant (see Figure 5.4 and Table 5.7).

Table 5.5. Liquid phase oxidation of ethyl benzene and TBHP as an oxidant at 80 °C for bimetallic supported catalysts prepared by impregnation and sol immobilisation[a].

Catalyst	Reaction Time/h	Conv. (%)	Selectivity (%)				TOF (h^{-1})[d]
			1-phenyl ethanol	2-phenyl ethanol	Aceto-phenone	Ph-acetic acid	
2.5%Au2.5%Pd/TiO_{2I}	0.5	2.4	50.6	0.0	49.4	0.0	53.3[b]
	1	2.7	47.8	0.0	52.2	0.0	30.4[b]
	2	5.9	45.4	0.0	54.6	0.0	33.2[b]
	4	9.3	40.5	0.0	59.5	0.0	26.2[b]
0.5%Au0.5%Pd/TiO_{2SI} (1:1 wt ratio)	0.5	2.7	41.6	0.0	58.4	0.0	303.7[c]
	1	4.3	40.5	0.0	59.5	0.0	240.6[c]
	2	7.1	38.7	0.0	61.3	0.0	198.9[c]
	4	11.5	34.3	0.0	65.7	0.0	162.3[c]

[a] Reaction conditions: ethylbenzene = 81.6mmol, catalyst = 0.2g, ratio ethyl benzene(mol): TBHP(mol) = 1:1, T = 80 ºC, Reaction time = 4 hours, I: Impregnation method, , SI: Sol-immobilisation method, [b] Substrate/metal = 1127, [c] Substrate/metal = 5638, [d] TOF (h^{-1}) at 4 hours. TOF numbers were calculated on the basis of total loading of metals

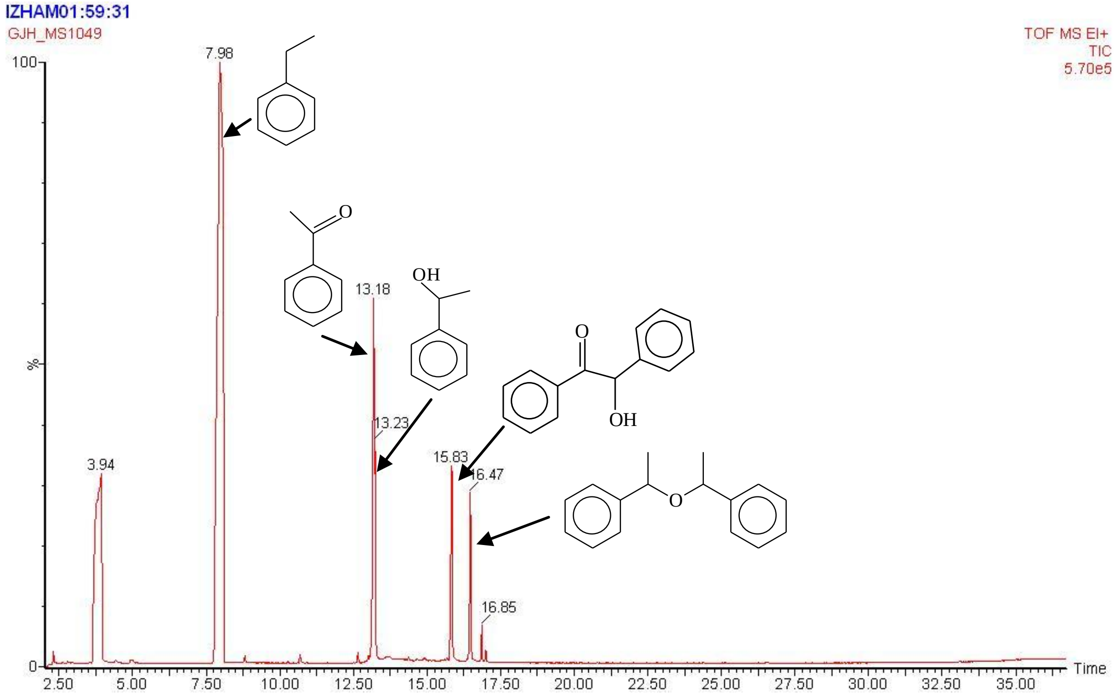


Figure 5.3: GCMS graph for ethyl benzene reaction using TBHP as oxidant

Table 5.6: GCMS data for ethyl benzene and product distributions

Name of product	Time
ethylbenzene	7.98
acetophenone	13.18
1-phenylethanol	13.23
benzoin	15.83
1-phenyl ethyl ester	16.47

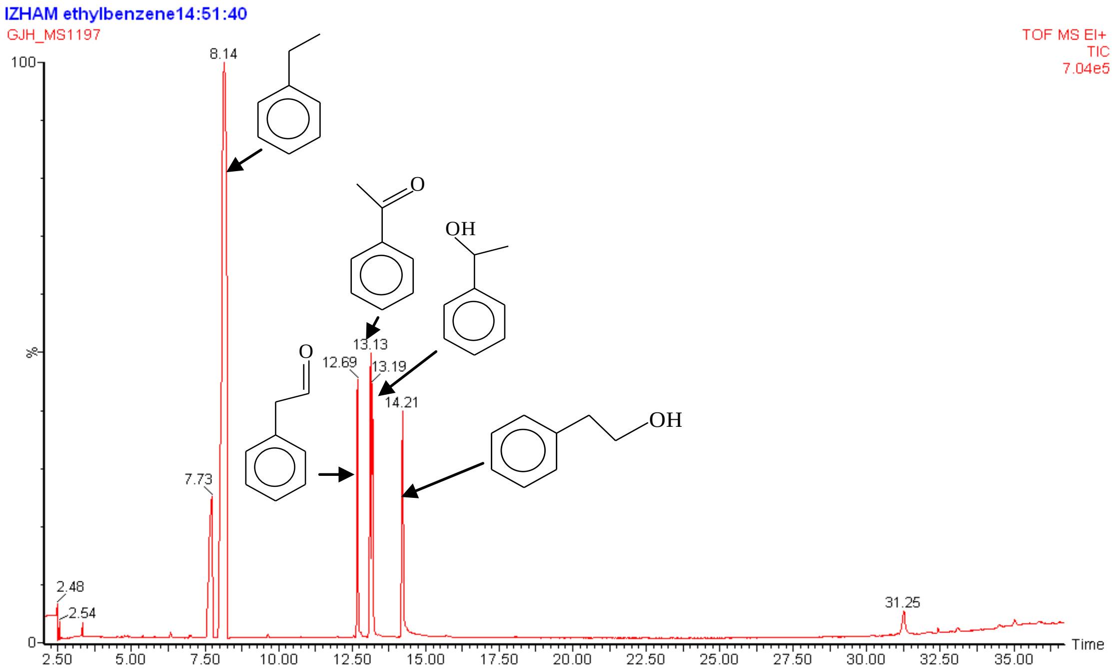
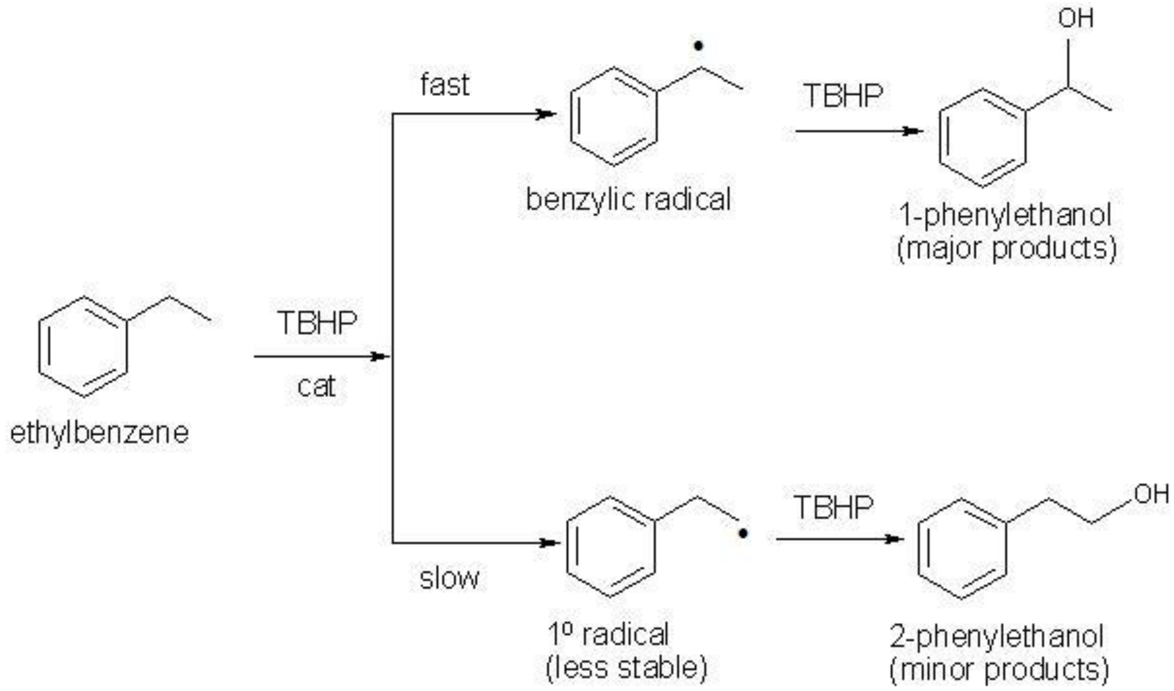


Figure 5.4: GCMS graph for ethyl benzene standard

Table 5.7: GCMS data for ethyl benzene and product distributions standard

Name of product	Time
ethylbenzene	8.14
phenylacetaldehyde	12.69
acetophenone	13.13
1-phenylethanol	13.19
2-phenylethanol	14.21



Scheme 5.1: Plausible mechanism for ethylbenzene reaction using TBHP as an oxidant.[2]

5.4.1 Oxidation of n--phenyl ethanol

To probe the hypothesis that the acetophenone was formed simply by consecutive oxidation of 1-phenylethanol, the oxidation of the latter was performed. This study on the oxidation of 1-phenylethanol showed 100 % conversion of acetophenone (Table 5.8). As a comparison, 2-phenyl ethanol was also studied and as expected the formation of phenyl-acetaldehyde was clearly discovered (Table 5.9).

Table 5.8. Liquid phase oxidation of 1-phenyl ethanol and TBHP as an oxidant at 80 °C for bimetallic supported catalysts prepared by impregnation and sol immobilisation[a]. Reaction performed for 4 hours

Catalyst	Reaction Time/h	Conv. (%)	Selectivity (%)				TOF (h^{-1})[d]
			Ethyl benzene	2-phenyl ethanol	acetophenone	Ph-acetic acid	
2.5%Au2.5%Pd/ TiO$_{2I}$	1	6.6	0	0.0	100	0.0	75.8[b]
	2	9.1	0	0.0	100	0.0	51.9[b]
	4	12.7	0	0.0	100	0.0	36.2[b]
0.5%Au0.5%Pd/ TiO$_{2SI}$ (1:1 wt ratio)	1	2.8	0	0.0	100	0.0	162.0[c]
	2	5.0	0	0.0	100	0.0	142.5[c]
	4	10.9	0	0.0	100	0.0	155.6[c]

[a]Reaction conditions: 1-phenylethanol = 41.4mmol, catalyst = 0.1g, ratio 1-pheth(mol): TBHP(mol) = 1:1, T = 80 ºC, I: Impregnation method, , SI: Sol-immobilisation method, [b]Substrate/metal = 1144, [c]Substrate/metal = 5721, [d]TOF (h^{-1}) at 4 hours. TOF numbers were calculated on the basis of total loading of metals

Table 5.9. Liquid phase oxidation of 2-phenyl ethanol and TBHP as an oxidant at 80 °C for bimetallic supported catalysts prepared by impregnation and sol immobilisation[a]. Reaction performed for 4 hours

Catalyst	Reaction Time/h	Conv. (%)	Selectivity (%)				TOF (h^{-1})[d]
			Ethyl benzene	1-phenyl ethanol	Ph-acetaldehyde	Ph-acetic acid	
2.5%Au2.5%Pd/ TiO$_{2I}$	1	3.7	0	0.0	87.7	12.3	42.3[b]
	2	4.1	0	0.0	86.6	13.4	23.5[b]
	4	5.6	0	0.0	85.8	14.2	16.2[b]
0.5%Au0.5%Pd/ TiO$_{2SI}$ (1:1 wt ratio)	1	2.7	0	0.0	84.9	15.1	157.6[c]
	2	3.6	0	0.0	85.7	14.3	105.6[c]
	4	4.7	0	0.0	86.2	13.8	68.0[c]

[a]Reaction conditions: 2-phenylethanol = 41.9mmol, catalyst = 0.1g, ratio 2-pheth(mol): TBHP(mol) = 1:1, T = 80 ºC, I: Impregnation method, , SI: Sol-immobilisation method, [b]Substrate/metal = 1158, [c]Substrate/metal = 5790, [d]TOF (h^{-1}) at 4 hours. TOF numbers were calculated on the basis of total loading of metals.

5.5 *p*-tertbutyltoluene

p-tertbutytoluene was also studied using the two Au-Pd/TiO_2 catalysts with TBHP as an oxidant. In keeping with the trend for all molecules previously discussed the sol-immoblisation AuPd/TiO_2 catalyst gave higher conversion (9.23%) after 4 hours compared to impregnation method (6.09%). In a similar way to ethylbenzene, toluene and *n*-methoxytoluene the acid product, *p*-tertbutyl benzoic acid, was the major product for sol-immobilisation catalyst whereas and *p*-tertbutylbenzaldehyde for impregnation catalyst (Table 5.10). This trend has been explained before as being facilitated by the smaller particle size and different morphology of the nanoparticles in the former catalyst.

Additionally, these results are an improvement on the data of Wangyi Li *et al*.[7]In that case the reaction was performed using Co/MCM-41 as a catalyst, hydrogen peroxide as an oxidant and use of various solvent at 90 ºC for 4 hours. From their data, 2-3 % conversion of *p*-tertbutyltoluene was observed with 4 to 44 % selectivity to *p*-tertbutylbenzaldehdye with acetonitrile, dichloromethane, methanol, ethanol as a solvent. Although conversion of 15% has been reported with high selectivity to *p*-tertbutylbenzaldehdye (82%), the use of acetic acid solvent make this process undesirable due to the high corrosion of the facilities.[7] It is generally a benefit if a solvent-less system can be used for organic oxidation reactions. It was noted that p-tertbutylbenzaldehyde is an important intermediate in production of Lilestral (BBA) or Lilial (Givaudan, Kingston, UK) which is an important fragrance compound used in large quantities in soap and cosmetic perfumes.[8] Hence the ability to produce this molecule selectively in short reaction time at moderate temperature without the use of a solvent system is a clear advantage of using the Au-Pd/TiO_2 as a heterogeneous catalytic system. Further work on optimization of this system should be undertaken to increase the yield of the desired product.

Table 5.10. Liquid phase oxidation of *p*-tertbutyltoluene with TBHP as an oxidant at 80 °C using bimetallic supported catalysts prepared by sol-immobilisation and impregnation[a].

Catalyst	Reaction Time/h	Conv. (%)	Selectivity (%) *p*-tertbutyl benzyl alcohol	*p*-tertbutyl benzaldehdye	*p*-tertbutyl benzoic acid	Benzyl benzoate	unknown	TOF (h^{-1})[d]
0.5%Au0.5%Pd/TiO_{2SI} (1:1 wt ratio)	0.5	2.74	31.3	62.2	6.1	0.5	0.0	219.54[b]
	1	4.11	28.5	52.0	19.1	0.4	0.0	164.4[b]
	2	5.96	24.2	45.3	29.3	0.3	1.0	119.14[b]
	4	9.23	17.4	34.7	46.8	0.1	1.0	92.29[b]
2.5%Au2.5%Pd/TiO_{2I}	0.5	1.39	31.6	68.4	0.0	0.0	0.0	22.18[c]
	1	2.06	31.4	68.6	0.0	0.0	0.0	16.50[c]
	2.5	4.01	30.9	64.7	4.2	0.3	0.0	12.85[c]
	4	6.09	30.2	52.9	16.5	0.4	0.0	12.18[c]

[a]Reaction conditions: *p*-tertbutyltoluene = 57.9mmol, catalyst = 0.2g, ratio p-tbtol(mol): TBHP(mol) = 1:1, T = 80 ºC, Reaction time = 4 hours, SI: Sol-immobilisation method, I: Impregnation, [b]Substrate/metal = 4001, [c]Substrate/metal = 800, [d]TOF (h^{-1}) at 4 hours. TOF numbers were calculated on the basis of total loading of metals

5.6 Dibenzyl ether

From the discussion in chapter 4, it was explained that it is difficult to form benzyl benzoate from the toluene oxidation using TBHP as an oxidant at mild conditions. However it was discovered by Lokesh Kesavan *et al.*.[9] that more than 90% conversion of benzyl benzoate could be achieved using bimetallic AuPd/C catalyst prepared by sol-immoblisation. This toluene oxidation reaction was performed at much higher temperature (160 ºC) using , 10 bar O_2 for 7 hours and higher amount of catalyst.[9] In Table 5.11, it shows that the benzyl benzoate can be produced from dibenzylether in moderate conversion and above 40% selectivity using Au-Pd/catalyst after 4 hours of reaction. By comparison to previous work it can be assumed that if the reaction was prolonged it may be possible to obtain very high conversion (>90%) with benzyl benzoate as a major product.

Table 5.11. Liquid phase oxidation of dibenzylether and TBHP as an oxidant for bimetallic supported catalysts prepared by impregnation and sol-immobilisation[a].

Catalyst	Reaction Time/h	Conv. (%)	Selectivity (%)				TOF (h^{-1})[d]
			Benzyl alcohol	Benzaldehyde	Benzoic acid	Benzyl Benzoate	
2.5%Au2.5%Pd/TiO_{2I}	0.5	4.90	19.9	41.8	0.0	38.3	71.2[b]
	1	6.10	19.7	39.1	0.0	41.2	44.50[b]
	2	10.10	20.1	39.2	0.0	40.6	36.70[b]
	4	16.60	19.8	37.1	0.0	43.1	30.2[b]
0.5%Au0.5%Pd/TiO_{2SI} (1:1 wt ratio)	0.5	11.00	15.8	36.4	0.0	47.7	71.2[c]
	1	11.90	16.6	35.9	0.0	47.6	44.50[c]
	2	17.60	17.6	35.9	0.0	46.4	37.80[c]
	4	28.80	18.7	37.2	0.0	44.1	29.70[c]

[a]Reaction conditions: dibenzylether= 52.6mmol, ratio substrate(mol): TBHP(mol) = 1:1, catalyst = 0.2g, T = 80 ºC, Reaction time = 4 hours, I: Impregnation method, SI: Sol-immobilisation method, [b]Substrate/metal = 727, [c]Substrate/metal = 3634, [d]TOF (h^{-1}) at 4 hours. TOF numbers were calculated on the basis of total loading of metals.

5.7 Benzyl alcohol reaction

Oxidation of benzyl alcohol to benzaldehdye is an industrially important reaction as it provides chlorine-free benzaldehyde required in perfumery and pharmaceutical industries. Catalytic vapor phase oxidation of benzyl alcohol has been widely investigated. [10-14] However since the carbon loss in the vapor phase benzyl alcohol oxidation is very appreciable due to the formation of carbon oxides, it is preferable to produce benzaldehyde more selectively by catalytic liquid phase oxidation of benzyl alcohol. A few studies have been reported for the liquid phase oxidation benzyl alcohol to benzaldehyde over supported Pd[15-16], heteropolyacid[17] and Ni-Al-hydrotalcite[18] catalysts, using molecular oxygen or aqueous H_2O_2 as the oxidant, in the present of solvent. It is environmentally beneficial to perform the benzyl oxidation in the absence of any solvent.

One of the most significant advances in the field of alcohol oxidation using Au catalyst has been the observation of Corma and coworkers [19-20] showing that an Au/CeO_2 catalyst is active for the selective oxidation of alcohol to aldehyde and ketones and the oxidation of aldehyde to acids. In these studies the catalyst is active at relatively mild conditions, without the addition of a solvent, using O_2 as oxidant without the requirement for the addition of NaOH to achieve high activity. The results were shown to be comparable to, or higher than, the highest activities that had been previously observed with supported Pd catalyst.[4] The Au-Pd/TiO_2 catalyst were very active for benzyl alcohol reaction, and the selectivity to benzaldehyde was >96%, with the only by-product being benzyl benzoate. This reaction was performed at 100 ºC with O_2 as oxidant in the absence of solvent.[4] Recently, the sol-immobilisation version of this catalyst has been of interest due to the formation of smaller nanoparticles Au-Pd which achieves higher conversion.[21-24]

The use of TBHP as oxidant for oxidation of benzyl alcohol was mostly studied by Choudhary *et al.* [25-28]. In earlier studies, they focused using MnO_4^{-1} exchanged Mg-Al-hydrotalcites [29] and transition metals containing different layered double hydroxides (LDH) and/or mixed metal oxides [27] as a catalyst. After the discovery of supported nanosized gold as a highly active low-temperature (< 273 K) CO oxidation catalyst, greater attention has been given to exploring various organic reactions using gold catalyst.[30] Recently, Choudhary and co-workers reported the use of different monometallic nanogold catalysts using a variety of supports (TiO_2, MnO_2, Fe_2O_3, CoOx, NiO, CuO, ZnO, ZrO_2, La_2O_3, Sm_2O_3, Eu_2O_3, and Yb_2O_3). [25] The Au/TiO_2 and Au/ZrO_2 were discovered as promising catalysts that showed high activity and selectivity in the oxidation of benzyl alcohol to benzaldehyde.

In this study, the blank reaction in the absence of catalyst was performed primarily in order to verify the contribution from homogeneous reactions which possibly occurred when using TBHP as oxidant at elevated temperature. The experiment was conducted in an air atmosphere conditions using round bottom flasks, and the blank reaction gave 3.1% conversion after 4 hours of reaction. The consecutive reaction involved in the catalytic process is as follows:[27]

$C_6H_5CH_2OH + (CH_3)_3COOH \rightarrow C_6H_5CHO + (CH_3)_3C\text{-}OH + H_2O$ (Equation 1)

$C_6H_5CHO + (CH_3)_3COOH \rightarrow C_6H_5COOH + (CH_3)_3C\text{-}OH$ (Equation 2)

$C_6H_5COOH + C_6H_5CH_2OH \rightarrow C_6H_5COOCH_2C_6H_5 + H_2O$ (Equation 3)

Since, benzaldehdye is an intermediate product in the oxidation process, its selectivity is decreased with increasing the reaction time depending upon the reaction temperature. At lower temperature, the benzaldehyde selectivity is higher.

Given that the baseline reaction was established, the reaction was carried out with 1% (Au-Pd)/TiO_2 (1:1 wt ratio) using sol-immobilisation method and 5% (Au-Pd)/TiO_2 via an impregnation technique. Results showing the influence of reaction time on the conversion of benzyl alcohol and TBHP, and product selectivity in the oxidation over the catalyst which showed good performance are presented in Table 5.12. With increasing reaction time, the selectivity to benzaldehdye is decreased while the conversion of benzyl alcohol and selectivity of benzoic acid and benzyl benzoate are increased. As expected based on previous work the selectivity to benzoic acid was higher (17.8% versus 7.5%) via sol-immobilisation catalyst. Though the conversion is similar for both catalysts (32-33%) the turn over frequency (TOF) value for sol catalyst was much higher throughout the reaction (e.g. 1142 versus 168 h^{-1} after 0.5 hours of reaction). The selective formation of benzaldehyde over these Au-Pd catalysts may be due to the plausible mechanism as shown in Scheme 4.1 (see Chapter 4). The Au-Pd catalysts react with TBHP and invariably proceed by the initial formation of radical *tert*-butyl peroxy (*t*-BuOO$^{\bullet}$) and *tert*-butyloxy radicals (*t*-BuO$^{\bullet}$). Further, the *tert*-butyloxy radical reacts with benzyl alcohol to form benzyl radical. The benzyl radical combines with *tert*-butyl peroxy radical to yield benzaldehyde. Another general mechanism proposed by Choudhary *et al* propose that the benzyl alcohol oxidation over the catalyst seems to be initiated by the decomposition of TBHP, which leads to the formation of highly reactive atomic species, which are responsible for the oxidation of benzyl alcohol to benzaldehyde and benzoic acid.[25] These processes involve the following elementary reactions:

$(CH_3)_3COOH \rightarrow (CH_3)_3COH + O$ (Equation 5)

$C_6H_5CH_2OH + O \rightarrow C_6H_5CHO + H_20$ (Equation 6)

$C_6H_5CHO + O \rightarrow C_6H_5COOH$ (Equation 7)

Table 5.12. Liquid phase oxidation of benzyl alcohol and TBHP as an oxidant at 80 °C for bimetallic supported catalysts prepared by impregnation and sol-immobilization methods.[a]

Catalyst	Time [h]	Conversion [%]	Selectivity [%]			TOF [h^{-1}][d]
			Benzaldehyde	Benzoic acid	Benzyl benzoate	
TBHP/No catalyst	0.5	0.5	100.0	0.0	0.0	
	1	1.0	100.0	0.0	0.0	
	2	1.9	98.4	1.5	0.1	0.0
	4	3.1	96.2	3.2	0.6	0.0
1%Au-Pd/TiO_{2SIw}	0.5	8.6	99.2	0.4	0.4	1142.0[b]
	1	12.0	95.2	3.7	1.7	
	2	18.1	88.0	9.1	3.0	
	4	32.8	76.8	17.8	5.4	
5%Au-Pd/TiO_{2Iw}	0.5	6.3	98.6	1.0	0.3	167.94 [c]
	1	9.6	97.9	1.6	0.5	
	2	19.6	91.8	3.0	5.2	
	4	33.1	84.7	7.5	7.8	

[a] Reaction conditions: ratio benzyl alcohol(mol):TBHP(mol) = 1:1, catalyst = 0.2g, T = 80 ºC, I: Impregnation method, SI: Sol-immobilization method, Reaction time = 4 h, [b] Substrate/metal = 6675, [c] Substrate/metal = 1335, [d] TOF numbers were calculated on the basis of total loading of metals.

5.8 Benzaldehyde oxidation

Further experiments utilising benzaldehyde as a substrate with TBHP as an oxidant were performed. As discussed earlier, the role of TBHP is to form radical species which facilitate the consecutive formation of benzoic acid from benzaldehyde. A trace of benzyl alcohol was detected in the blank reaction without catalyst and the sol immobilisation catalyst was slightly lower than blank reaction. As expected, the major product was benzoic acid (almost 100%) and a small amount of benzyl benzoate observed due the lower temperature (80 ºC) at which the reaction was performed. It was indicated previously in literature that the higher temperature (120-160 ºC) of reaction is beneficial in obtaining high selectivity to benzyl benzoate.[9] Both catalysts studied showed similar conversion levels and product selectivities (Table 5.13).

Table 5.13. Liquid phase oxidation of benzaldehyde and TBHP as an oxidant at 80 °C for bimetallic supported catalysts prepared by sol-immobilisation and impregnation[a]. Reaction performed for 4 hours

Catalyst	Reaction Time/h	Conv. (%)	Selectivity (%)				
			toluene	Benzyl alcohol	Benzoic acid	Benzyl benzoate	TOF (h^{-1})[d]
TBHP/no catalyst	0.5	3.90	0	5.7	94.3	0.0	0
	1	6.10	0	3.1	96.9	0.0	0
	2	13.40	0	1.5	98.4	0.0	0
	4	22.30	0	0.9	99.0	0.0	0
0.5%Au0.5%Pd/TiO_{2SI} (1:1 wt ratio)	0.5	19.70	0	0.3	97.0	2.7	2674.4[b]
	1	30.10	0	0.3	99.0	0.7	2045.57[b]
	2	43.40	0	0.2	99.5	0.2	1475.88[b]
	4	59.80	0	0.0	100.0	0.0	1015.81[b]
2.5%Au2.5%Pd/TiO_{2I}	0.5	7.50	0	0.1	94.1	5.7	205.4[c]
	1	16.90	0	0.0	96.8	3.2	229.31[c]
	2.5	35.00	0	0.0	99.8	0.2	237.76[c]
	4	51.50	0	0.0	99.8	0.2	175.12[c]

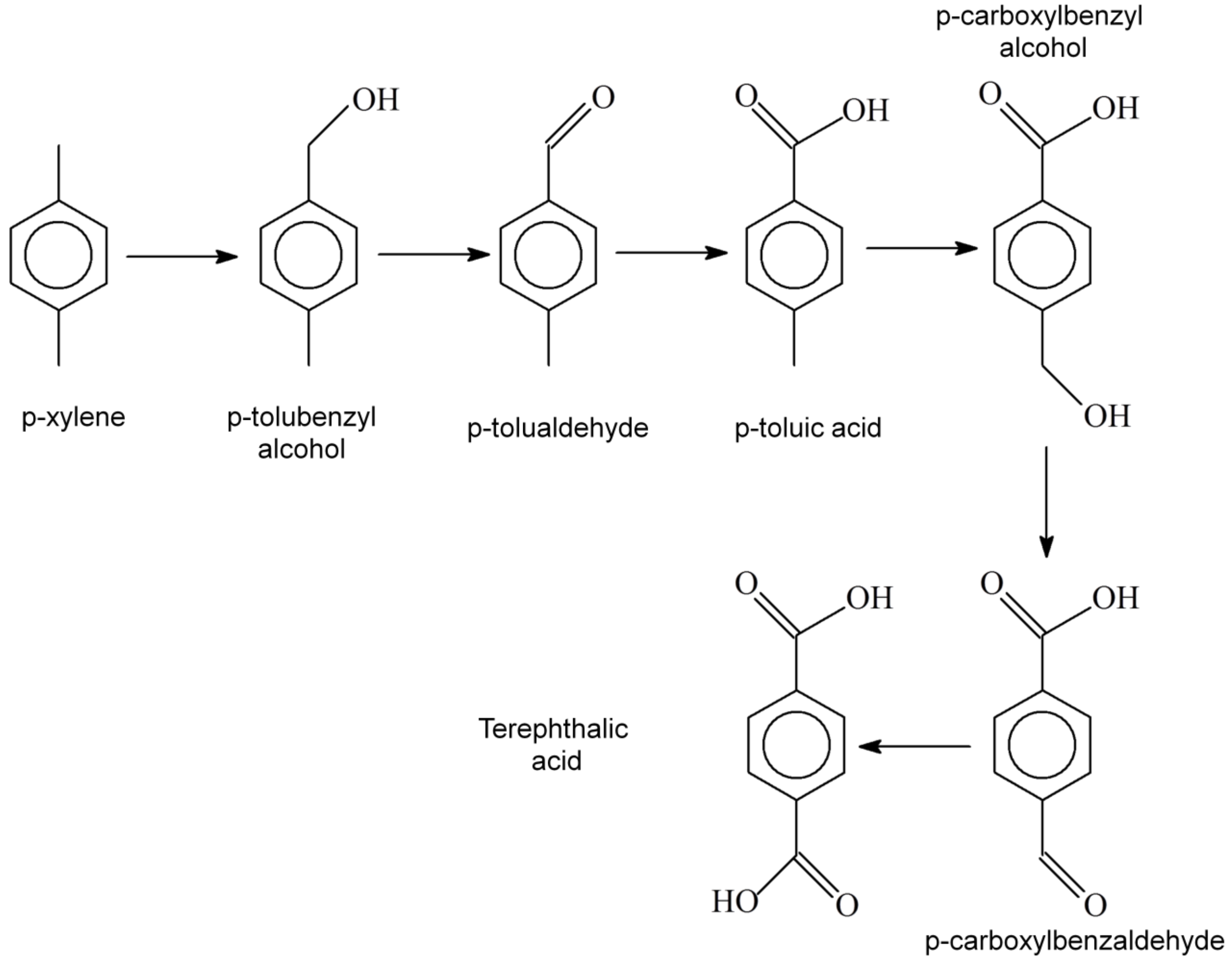
[a]Reaction conditions: benzaldehdye = 98.4mmol, catalyst = 0.2g, ratio benzaldehyde(mol): TBHP(mol) = 1:1, T = 80 ºC, SI: Sol-immobilisation method, I: Impregnation, [b]Substrate/metal = 6799, [c]Substrate/metal = 1360, [d]TOF (h^{-1}) at 4 hours. TOF numbers were calculated on the basis of total loading of metals.

5.9 Oxidation of *p*-xylene using THBP as an oxidant.

Terepthalic acid (TPA) is one of the most important chemicals industrially, with annual production capacity of more than 24 million tons in the year 2000[31]. TPA, the raw material polyester, is usually produced commercially by liquid phase oxidation of *p*-xylene with air, using catalyst combining cobalt, manganese and bromide ions in acetic acid at around 170-210 ºC. [32-33] Considering the huge production capacity of TPA, one realizes that even a small improvement of the process is very important in terms of economic productivity. The desirable improvements of TPA process include the following: [33]

i) Decrease of the destruction of raw materials and solvent
ii) Increase of the selectivity of reaction to eliminate the purification step and hydrogenation of the water solvent
iii) Replacement of the corrosive acetic acid and HBr with water and some non-corrosive free radical carriers, respectively.

A better understanding of the mechanism and effects of process parameters are essential to improve a process. However, there is limited expected further improvement of that process is because the TPA process has been optimized for the last several decades. [34] The interest in the synthesis of terepthalic acid in high temperature water (HTW) via the selective partial oxidation of *p*-xylene stemmed from a demonstration of this reaction [35]. The economic and environmental benefits that could result from replacing acetic acid, the medium used in commercial terepthalic acid manufacturing processes, with HTW provided additional motivation. An HTW- based process operating at 300 ºC with air separation prior to compression would likely be both economically competitive with and less energy and pollutant-intensive than the current technologies [36], if terepthalic acid can be produced in high yield at 300 ºC (or below).



Scheme 5.2: General reaction pathways for p-xylene oxidation.

In this study two catalysts made by different preparation techniques (impregnation and sol-immoblisation) were tested for the catalytic liquid phase oxidation of *p*-xylene. As usual, TBHP was used as an oxidant at mild conditions (80 ºC) under an air atmosphere conditions. Table 5.14 shows the conversion profile of the 1% (Au-Pd)/TiO_2 via sol-immoblisation methods gave 13.9% conversion higher compared to impregnation (7.3%). In term of selectivities, *p*-toluic acid as a major product using sol-immoblisation methods and impregnation catalyst shows higher formation of *p*-tolualdehyde. As the reaction proceeded, the selectivity to *p*-tolubenzyl alcohol decreased slowly, whereas the selectivity towards *p*-tolualdehdye and *p*-toluic acid increased progressively. Further, *p*-toluester also was detected as a small trace in this reaction. It observed that Au-Pd catalyst and TBHP successfully can give good conversion of *p*-xylene oxidation. However, the target was formation of the terepthalic acid as a product and it is apparently difficult to obtain this material at lower reaction temperature. As discussed earlier, though higher temperature condition was very favourable for TPA production it may be possibile to form TPA from p-toluic acid in a second step. In view of this, it was hypothesised that adding *p*-carboxylbenzaldehdye as a promoter and any solvent that can generate carboxyl group interactions to the reaction solution may improve TPA production. Further investigations are need to probe this hypothesis. In addition, *o*-xylene and *m*-xylene also was studied and it clearly shows that the similar pattern of conversion and product distribution was indicated (see Table 5.15 and 5.16).

Table 5.14. Liquid phase oxidation of *p*-xylene and TBHP as an oxidant at 80 °C for bimetallic supported catalysts prepared by impregnation and sol-immobilisition[a]. Reaction performed for 4 hours

Catalyst	Reaction Time/h	Conv. (%)	Selectivity (%)				
			p-tolualcohol	*p*-tolualdehdye	*p*-toluic acid	*p*-tolu-ester	TOF (h^{-1})[d]
Blank (without catalayst)	0.5	0.50	16.9	80.7	2.4	0.0	0
	1	0.70	15.6	79.3	5.1	0.0	0
	2	1.0	15.5	78.1	6.4	0.0	0
	4	1.4	14.8	77.5	7.7	0.0	0
2.5%Au2.5%Pd/TiO_{2I}	0.5	2.6	36.5	62.9	0.3	0.2	58.9[b]
	1	3.1	36.4	62.7	0.5	0.4	35.0[b]
	2	4.4	36.3	61.3	1.7	0.7	25[b]
	4	7.3	35.3	60.7	3.3	0.6	20.4[b]
0.5%Au0.5%Pd/TiO_{2SI} (1:1 wt ratio)	0.5	5.2	40.0	57.0	2.3	0.7	589.8[c]
	1	6.1	39.1	50.0	10.2	0.8	343.2[c]
	2.5	9.2	35.2	43.3	21.0	0.5	258.6[c]
	4	13.9	27.1	39.6	32.6	0.6	195.8[c]

[a]Reaction conditions: *p*-xylene = 81.6mmol, catalyst = 0.2g, ratio *p*-xylene(mol): TBHP(mol) = 1:1, T = 80 ºC, SI: Sol-immobilisation method, I: Impregnation, [b]Substrate/metal = 1127, [c]Substrate/metal = 5638, [d]TOF (h^{-1}) at 4 hours. TOF numbers were calculated on the basis of total loading of metals

Table 5.15. Liquid phase oxidation of *m*-xylene and TBHP as an oxidant at 80 °C for bimetallic supported catalysts prepared by impregnation and sol-immobilisition[a]. Reaction performed for 4 hours

Catalyst	Reaction Time/h	Conv. (%)	Selectivity (%)				
			m-tolualcohol	*m*-tolualdehdye	*m*-toluic acid	*m*-tolu-ester	TOF (h^{-1})[d]
Blank (without catalayst)	0.5	0.4	17.6	80.7	1.7	0.0	0
	1	0.5	17.4	80.2	2.4	0.0	0
	2	0.8	17.2	78.7	4.1	0.0	0
	4	1.0	16.9	78.0	5.1	0.0	0
2.5%Au2.5%Pd/TiO_{2I}	0.5	2.7	32.5	67.0	0.3	0.2	61.6[b]
	1	2.8	32.1	67.0	0.6	0.3	31.4[b]
	2	4.7	31.7	66.0	1.9	0.3	26.4[b]
	4	6.0	31.3	66.0	2.3	0.4	16.9[b]
0.5%Au0.5%Pd/TiO_{2SI} (1:1 wt ratio)	0.5	4.4	31.8	64.9	2.9	0.4	494.5[c]
	1	5.9	29.2	55.6	14.9	0.4	331.5[c]
	2	8.2	25.5	47.9	26.2	0.4	232.5[c]
	4	13.1	21.9	42.5	34.3	1.4	184.7[c]

[a]Reaction conditions: *m*-xylene = 81.8mmol, catalyst = 0.2g, ratio *m*-xylene(mol): TBHP(mol) = 1:1, T = 80 ºC, SI: Sol-immobilisation method, I: Impregnation, [b]Substrate/metal = 1130, [c]Substrate/metal = 5652, [d]TOF (h^{-1}) at 4 hours. TOF numbers were calculated on the basis of total loading of metals

Table 5.16. Liquid phase oxidation of *o*-xylene and TBHP as an oxidant at 80 °C for bimetallic supported catalysts prepared by impregnation and sol-immobilisition[a]. Reaction performed for 4 hours

Catalyst	Reaction Time/h	Conv. (%)	Selectivity (%)				
			o-tolualcohol	*o*-tolu aldehdye	*o*-toluic acid	*o*-tolu-ester	TOF (h^{-1})[d]
Blank (without catalayst)	0.5	0.7	16.5	81.5	2.0	0.0	0
	1	1.0	14.8	83.2	2.0	0.0	0
	2	1.3	14.7	83.2	2.1	0.0	0
	4	1.6	14.5	83.0	2.5	0.0	0
2.5%Au2.5%Pd/TiO_{2I}	0.5	3.2	37.3	62.3	0.4	0.0	72.8[b]
	1	3.3	37.1	62.2	0.6	0.0	38.2[b]
	2	6.7	36.1	62.1	1.8	0.0	38.5[b]
	4	10.6	35.4	56.8	7.7	0.1	30.4[b]
0.5%Au0.5%Pd/TiO_{2SI} (1:1 wt ratio)	0.5	6.0	42.9	54.0	3.1	0.0	689.7[c]
	1	8.7	40.7	50.2	9.1	0.0	496.3[c]
	2	12.1	38.5	43.3	18.2	0.0	346.0[c]
	4	19.0	31.1	41.6	27.3	0.0	271.9[c]

[a]Reaction conditions: *o*-xylene = 82.8mmol, catalyst = 0.2g, ratio *o*-xylene(mol): TBHP(mol) = 1:1, T = 80 ºC, SI: Sol-immobilisation method, I: Impregnation, [b]Substrate/metal = 1144, [c]Substrate/metal = 5721, [d]TOF (h^{-1}) at 4 hours. TOF numbers were calculated on the basis of total loading of metals

5.10 Conclusions

In this chapter, the selective oxidation of substituted toluenes and other aromatics using Au-Pd supported nanoparticles catalysts is briefly studied. The experimentals results are contrasted on the basis of catalyst preparation methods and TiO_2 as a support material. In general, supported Au-Pd nanoparticles are shown to be active for the oxidation of toluene derivates and aromatic organics under relatively mild solvent-free conditions with TBHP as an oxidant. Specifically, the reactions were carried out at lower temperature (80 ºC) without utilization of any initiator or co-catalysts.

Varying the catalyst preparation technique leads the significant differences in activity and product distribution. Depending on the nature of the metal and the reaction conditions, the distribution of the product could be tuned. Smaller particles size with narrow sized distribution and metallic oxidation state was observed to be responsible for high activity and formation of deeper oxidation products (without the production of carbon oxides). Therefore, AuPd supported catalyst synthesized via sol immoblisation method can generally be considered as more active compared to Au-Pd catalyst by the impregnation method.

TBHP as an oxidant may have an give important role to inhibit radical formation from available molecular oxygen in this study. It is suggested that the oxidation proceeds by the formation of oxidant based radicals such as radical *tert*-butyl peroxy (t-BuOO$^\bullet$) and *tert*-butyloxy radicals (t-BuO$^\bullet$). However, further investigations are need to explore this hypothesis in detail. Furthermore, contributions of O species from molecular oxygen as having an important role in the mechanism as discussed earlier in the chapter 4 cannot be disregarded.

Overall, the demonstration of the ability of Au-Pd supported nanoparticles in oxidizing a variety of aromatic compounds with TBHP is important to the wider applicability of this catalytic system. The wide applicability, mild environmentally benign conditions, high reaction rates, tunable selectivity and reusability of these catalysts suggests that industrial application of this catalytic system is possible.

5.11 References

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CHAPTER 6

Conclusions and Recommendations for Future Work

6.1. Conclusions

Activation of toluene and their catalytic oxidation into useful organic compounds is a major challenge for industry and academia. Due to the recent discoveries related to the ability of gold based nanoparticles to perform a variety of reactions, further work into the activation of toluene by gold and gold alloyed nanoparticles was the central topic of this study and has been addressed in this PhD thesis. The research intends to develop a catalytic system that can activate toluene under very mild conditions. In addition, environmentally benign catalysis has been also focused on these studies. An area of heterogeneous catalysis including catalyst characterisation, product analysis and validations, proposed reaction mechanisms and key reaction parameters for controlling selectivity and activity were briefly covered in this thesis.

It is clear from the work outlined in the preceeding chapters that the activation of toluene was successfully carried out using heterogeneous Au and Pd based catalyst. In **chapter 3**, the study was focused on the characterisation of the materials. The formation of presence Au-Pd alloy in catalyst was confirmed by XRD and XPS analysis, respectively. In term on the types of supported materials, nano ceria was discovered give higher value of support based on crystallite size compared to other tested support such as SiO_2, CeO_2, Al_2O_3 and activated carbon. Unfortunately, the activity from this support is not a best reaction toluene activity when compared with other different supports. Furthermore, carbon as a support looks more promising when adding Au with Pd as bimetallic catalyst. This was confirmed by the BET surface area where as the highest value of carbon via impregnation was 735.5 m^2/g and sol-immobilisation methods was 498.1 m^2/g. Based on conversion and activity of reaction, it has been investigated that carbon give highest value amongst others. Further, XPS data was confirmed formation of core shell structure by impregnation method and homogeneous random Au-Pd alloy via sol-immobilisation as a different technique.

In **chapter 4**, liquid phase toluene oxidation was carried out using addition of TBHP as oxidant. It was clearly shows that the TBHP successfully as oxidant for toluene oxidation at mild conditions (80 °C). At the early stage, most of the experiments, Au-Pd supported TiO_2 via impregnation technique was use as a catalyst testing due the good activity that has been discovered from this catalyst.[1-3] It has been observed that air will give a small enhancement for toluene conversion when testing with and without He conditions. Synergistic effect of Au-Pd bimetallic catalyst has shown that where it is active and selective compared to monometallic catalyst counterpart. The selectivity to benzoic acid was discovered whereas the selectivity of benzyl alcohol and benzaldehyde was decreased when the time online of reaction was studied. It shows that there is a slight increase in activity when pre-treatment test of Au-Pd bimetallic catalyst was carried out in flowing H_2/Ar gas. The catalyst was tested and it shows a good data of reusability when it does not change significantly in conversion during 5 times of the reaction was performed for the same catalyst. From this data, it is believed that the use of this catalyst is very useful because it can be reused many times in reactor and it is a good opportunity in the petroleum industry. The nature of support is crucial in order to successfully utilised as bi-functional catalyst. The most active Au-Pd catalyst was prepared on activated carbon and the order of catalytic activity was the following: Carbon> ceria(nano) > SiO_2

> γ-Al_2O_3 > ZrO_2 > Graphite (Sigma Aldrich) > TiO_2 > CeO_2(Sigma Aldrich) >Graphite (JM).

The sol-immobilisation catalyst also was studied in this thesis due to that it is believe in the literature paper that it can be set to form small particles sizes and narrow particles size distribution and this observation was revealed that good in activity of oxidation reaction. [4-5]Two types of support (TiO_2 and carbon) was selected and studied in this technique and it was observed the good activities of catalysis performance especially carbon as a support. Hence, an impregnated Au-Pd supported catalyst with oxidised state of metal (*i.e.* PdO, Pd^{2+}) and bigger particle size was preferred than smaller and reduced state (Pd^0 and Au^0) of metal obtained in sol-immobilisation technique. The presence of metal in metallic state especially Pd was identified to accelerate the decomposition of TBHP subsequently increase the catalytic activity. Synergistic effect of Au and Pd was again proof the enhancement of activity was discovered comparing to mono catalysts. Further the oxidation of toluene with different Au/Pd metal ratio supported on carbon was also studied to see effect of different ratio of both metals loading. This was revealed that the addition of Pd to Au significantly enhance the catalytic performance, with the optimum Au-Pd composition being 1:1 by weight (0.5%wtAu-0.5%wt%Pd), where a compromise between catalytic activity and conversion toward benzoic acid has been achieved. Pd alone as the metal provides a low conversion and the resulting activity afterwards is reduced. The same trend was observed with the impregnation catalyst where benzoic acid is the major product followed by benzaldehyde, benzyl alcohol and trace of benzyl benzoate for the time online profile studies. At the same time, TBHP had 90% of conversion with carbon as a support compared to TiO_2 and without catalyst loading. This data suggested that role of TBHP could be important to form a radical and further interaction between toluene and catalyst to proceed the selectivity of the products distribution. Furthermore, decomposition of TBHP also was accelerated with the increase amount of the mass of catalyst and this subsequently affects the amount of oxidant available during the reaction and influence the rate of reaction too. The reused catalyst was studied and the results provide a similar pattern of conversion.

On the basis of the results obtained, mechanistic pathways have been proposed with 3 steps: a) formation of radical from TBHP, b) formation of alcohol in metal site catalyst and c) formation of carboxylic group from water, radical and O_2. A few experiments has been done to prove if the reactive oxygen species (ROS) was interact with surface on Au-Pd metal and TiO_2 as a support. EPR as a trapping radical technique has been used to prove this argument. The final finding was declared that for AuPd/TiO_2 the bi-functional role of Au/Pd sites and Ti^{4+} centres on the surface of titania facilitates the activation of toluene and it affects the product distribution. For the future, in-depth research will be carried out to focus more on ROS study in other variable technique discovery and hoping with the new findings, a strong statement that is more significant and relevant will be reported.

In view of the fact toluene has been successfully activated using TBHP as oxidant, in **chapter 5**, particular attention was made to generate the oxidation of other aromatic compounds was studied using Au-Pd/TiO_2 via impregnation and sol-immobilisation methods. As a result, the electron donating group such as methoxytoluene give a better result of conversion compared to the electron withdrawing groups, nitrotoluene. The other group such as ethyl benzene, *p-tert*butyltoluene, dibenzylether, benzyl alcohol, benzaldehyde was successfully discovered in this study. All this reaction was performed at mild condition reactions (80 °C). One interesting compound, *o, m, p*-xylene also was already studied and toluic acid as a major product was detected by using sol-immobilisation catalyst. Although, the target was formation of terephthalic acid as a product, it is apparently difficult to obtain this material at a lower reaction temperature.

6.2. Recommendations for future work

Further investigations are possible for all fields explored in this thesis. Brief recommendations are shown below:

1. It was demonstrated in this study that supported Au-Pd nanoparticles catalysts were successfully oxidised toluene using TBHP as oxidant. However, it is important in the future study to utilise other oxidant such as AIBN and it is possible to achieve by tuning the reaction conditions and morphology as well as characteristics of metal supported catalysts.
2. It has been proved in this study that Au-Pd supported catalysts are capable in oxidising other aromatics compounds using TBHP. Therefore another step could be taken to study deeper for Au-Pd system for other interest aromatics products.
3. The possible used of another characterisation technique such as STEM could further help in identifying the nature of developed catalyst especially on Au-Pd supported systems. Combination between STEM, XPS and XRD data might give a clear picture on any possible formation of alloy and also the average particle size of metal.
4. The possibility of carrying these oxidations in batch reactor system. Loading of TBHP need to be controlled for the explosion limit and run at mild conditions temperature.

5. In-depth research will be carried out to focus more on ROS study in other variable technique discovery.

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Publication for this study:

1. **Mohd Izham bin Saiman**, Gemma L.Brett, Ramachandra Tiruvalam, Michael M. Forde, Kate Sharples, Adam Thetford, Robert L. Jenskins, Nikaloas Dimitratos, Jose A. Lopez-Sanchez, Damien M. Murphy, Donald Bethell, David J. Willock, Stuart H. Taylor, David W.Knight, Christoper J. Kiely, and Graham J. Hutchings, *Angewandte Chemie International Edition*, 2012, **51**, 5981-5985.

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Appendixes

A.1 Preparation of standard for calibration of toluene oxidation and analysis using Gas chromatography.

i. Std 0.05
   - 0.05g Benzaldehyde + 0.05 g Benzyl alcohol + 0.0497 g benzoic acid + 0.05 g Benzyl benzoate + 1.8003 g Toluene

ii. Std 0.1
   - 0.1g Benzaldehyde + 0.1 g Benzyl alcohol + 0.1017 g benzoic acid + 0.1 g Benzyl benzoate + 1.5983 g Toluene

a) Mole, mole % and concentration have been calculated based on result from GC analysis. The concentrations of toluene were used in obtaining toluene calibration curve and the calibration factor calculated as follows;

$$\text{Calibration factor, CF} = \frac{mol\ (toluene)}{mol\ (2-propanol)} \times \frac{Area\ (2-propanol)}{Area\ (toluene)}$$

Mole of compound =

$$mol\ (2-propanol) \times calibration\ factor \times \frac{Area(toluene)}{Area\ (2-propanol)}$$

b) Based on the calculation, the graph was plotted:-

   i) Mole % Vs Area
   ii) Concentration Vs Area

c) Calibration Factor and R^2 data from the graph;

	CF / Mole %	R^2 / Mole %	CF / Concentration	R^2 / Concentration
Benzyl alcohol	22148.426	0.997	238168.174	0.998
Benzaldehyde	18038.930	0.998	193872.942	0.998
Benzoic acid	22068.701	0.998	237348.840	0.999
Benzyl benzoate	45175.702	0.999	485759.730	0.999
Toluene	19760.064	0.999	211880.547	1.000

d) Calibration factor, conversion (mol %), selectivity (%) and mass balance (%) based on internal standard.

Standard	0.05g				0.1g			
	Calibration factor	Selectivity (%)	Conversion (mol %)	Mass balance (%)	Calibration factor	Selectivity (%)	Conversion (mol %)	Mass balance (%)
Benzyl alcohol	0.381747558	30.92	8.92	100	0.368927145	29.63	17.14	99.99
Benzaldehyde	0.473043533	31.16			0.452452993	28.77		
Benzoic acid	0.386717247	23.37			0.368026858	25.19		
Benzyl benzoate	0.18866692	14.55			0.179719988	16.40		
Toluene	0.448038986	-			0.413127263	-		

Formula to calculate for conversion, selectivity and mass balance as shown as below:-

a) Conversion. mol % $= \frac{Total\ mole - mole\ (reac\tan t)}{Total\ mole} \times 100$

b) Selectivity, % $= \frac{mol(x)}{Totalmole - mole(reac\tan t)} \times 100$

c) Mass balance $= \frac{total\ mole\ (\exp eriment)}{total\ mole\ (theory)} \times 100$

B.1 Calculation of substrate/metal ratio

First, mol metal ratio (Au-Pd) was calculated as shown as below:

Assuming in

100g ⟶ 2.5g Au + 2.5g Pd

$$100\text{g} \longrightarrow \frac{2.5g}{196.97}\,\text{Au} + \frac{2.5g}{106.4}\,\text{Pd}$$

100g ⟶ 0.01269 mol Au + 0.023496 mol Pd = 0.036186 mol total

1g ⟶ 0.036186/100 = 3.6186×10^{-4} mol metal

For this reaction, amount of bimetallic catalyst was used (0.2g).

0.2g ⟶ 3.6186×10^{-4} x 0.2g = 7.2372×10^{-5} mol metal

Then, a substrate/metal ratio was calculated in following:

$$\frac{substrate}{metal\ ratio} = \frac{0.3764\ mol\ toluene}{7.2372\ x\ 10^{-5}\ \ mol\ metal\ (Au{-}Pd)} = 5200.9064$$

Based on same substrate/metal ratio was used for bimetallic Au-Pd, the amount of mono metallic Au or Pd catalyst was measured:

$\frac{substrate}{metal\ ratio}$ = 5200.9064, metal ratio = 7.2372×10^{-5} mol metal

100g ⟶ 2.5g Au or 2.5g Pd

$$100\text{g} \longrightarrow \frac{2.5g}{196.97}\,\text{Au} \quad \text{or} \quad \frac{2.5g}{106.4}\,\text{Pd}$$

100g ⟶ 0.01269 mol Au or 0.023496 mol Pd

1g ⟶ 1.269×10^{-4} mol Au or 2.3496×10^{-4} mol Pd

Amount of catalyst of mono Au catalyst = $\frac{7.2372\ x\ 10^{-5}}{1.269\ x\ 10^{-4}} = 0.570\text{g}$

Amount of catalyst of mono Pd catalyst = $\frac{7.2372\ x\ 10^{-5}}{2.3496\ x\ 10^{-4}} = 0.308\text{g}$

For the rest of the catalyst, this calculation was followed to get exactly amount of the catalyst used for each reaction was performed.

C. The Turn Over Frequency (TOF) and Turn Over Number (TON)

$$\text{TOF} = \frac{initial\ \ mol(reac\tan t)\ x\ conversion}{mole\ of\ \ metal} \Big/ time$$

$$\text{TON}= \frac{initial\ \ mol(reac\tan t)\ x\ conversion}{mole\ of\ \ metal}$$