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Selective Catalytic Oxidation in the Liquid Phase by Gold-Palladium Catalysts

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Summary

The selective oxidations of cinnamyl alcohol, *trans*-stilbene and 3-pyridinemethanol were investigated using Au-Pd catalysts. These reactions were carried out under industrially relevant conditions. The tested monometallic and bimetallic heterogenous Au-Pd catalysts were prepared by sol-immobilisation (SIm) and impregnation (Imp) methods.

Oxidation of cinnamyl alcohol performed at elevated temperatures leads to autoxidation hence its role has been examined in the catalytic process using supported AuPd nanoparticles. 0.50 %(wt)Au 0.50 %(wt)Pd/ TiO_2 (SIm) catalyst was shown to prevent the autoxidation process while promoting the selective catalytic pathway. 0.50 %(wt)Au 0.50 %(wt)Pd/ TiO_2 (Imp) catalyst appeared to only limit autoxidation enabling co-existence of these two processes. Further optimisation of metal ratio revealed that the most active catalyst is 0.75 wt.% Au- 0.25 wt.% Pd/ TiO_2 (SIm). Furthermore, this metal ratio was found to be stable under the reactions conditions with only minor change observed over multiple uses, highlighting the synergistic effect.

The effectiveness of the Au-Pd system for cinnamyl alcohol oxidation has been contrasted with that of *trans*-stilbene and 3-pyridinemethanol oxidation due to the different chemical nature of these substrates. 0.50% Au 0.50% Pd/TiO_2 (SIm) catalyst demonstrated similar behaviour in the oxidations of cinnamyl alcohol and *trans*-stilbene regarding excluding undesired non-selective reactions under optimised conditions, despite the difference in the mechanisms of these two processes. This is suggested to be due to the effectiveness of smaller nanoparticles in limiting uncontrolled oxidation pathways.

3-Pyridinemethanol oxidation using Au-Pd supported nanoparticles is extremely difficult due to the chemical stability of this substrate. The presence of N- heteroatom in the structure presumably leads to the catalyst poisoning due to interaction between N and Pd. Despite this, the Au-Pd catalysts were found to be more active than monometallic ones which indicates synergistic effect. Furthermore, optimisation of reactions conditions enabled total selectivity to the desired aldehyde product.

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Chapter 1

1. Introduction

1.1. Catalysis

While the phenomenon of catalysis was always present in nature, it was first observed by Swedish chemist J.J. Berzelius. This eminent chemist suggested based on his scientific work the existence of a force, which he called the “catalytic force” and he called “catalysis” the process caused by this force. He wrote in his paper published in 1836[1]:

“It is, then, proved that several simple or compound bodies, soluble and insoluble, have the property of exercising on other bodies an action very different from chemical affinity. By means of this action they produce, in these bodies, decompositions of their elements and different recombination of these same elements to which they remain indifferent.”

The earliest recorded example of catalytic activity is associated with decomposition of ammonia into nitrogen and hydrogen when passed over red-hot metals. It was first observed by Louis Jacques Thenard in 1813 and then ten years later Pierre Dulong determined metal activity for the process to be in the order Fe>Cu>Ag>Au>Pt. L.J. Thenard was working also on the decomposition of hydrogen peroxide and as an effect of his work he announced in 1818 the existence of a chemical substance that speeds up a chemical reaction without being changed.[1]

Fermentation and enzymes in human body are the examples of homogeneous biocatalysis. In general, pioneers in the rationalisation of the theory of homogeneous catalysis were Charles Bernard Desormes and Nicolas Clement.[1] The researchers studied the homogeneous catalytic effect of nitrogen oxides in the lead chamber process to produce sulphuric acid in large amounts and were the authors of the intermediate compound theory. The process of sulphuric acid synthesis by this method was discussed later in detail by Humphry Davy who is also known as the inventor of the Davy lamp (miner’s safety lamp for use in flammable atmospheres). During the research work on safety lamp, Davy made phenomenal observations of heterogeneous catalytic oxidation. In the safety lamp, the platinum wire was attached over the flame. Davy observed that after the introduction of coal gas into the lamp the flames went out, while the platinum wire remained hot for a long time. In addition, the hot wire introduced into the mixture of coal gas and oxygen became incandescent. Davy drew the conclusion that oxygen and coal gas combined in the presence of a platinum wire and the heat generated by the reaction kept the wire hot. The description of this phenomenon, namely the chemical reaction between two gaseous reactants on the surface of the metal without its chemical change, was published by the Royal Society in 1817. Thus, Davy started the foundations of heterogeneous catalysis.[1]

The brief historical outline described above provides information only on the first mention of catalysis. Since then, a huge amount of scientific information has been accumulated. Despite numerous theoretical discussions, the catalytic process is still a mystery. Many factors influence every catalytic process in a different way, which points to the need for a separate and systematic investigation of each process. Catalysis still remains a challenge to the chemist since Davy's discovery in 1817. Nevertheless, the huge progress made in this area has led to the situation where catalytic processes have found a comprehensive application in today's global industry to produce materials (e.g. plastics), pharmaceuticals, fine chemicals, fuels and to remove pollutants from car engines. According to the American Chemical Society, 60 % of global chemical production takes place as a result of catalytic processes, accounting for 90 % of all chemical processes. The current definition of a catalysis and a catalyst presented by American Chemistry Society[2] is:

"Catalysis has been defined as the process by which chemical reaction rates are altered by the addition of a substance (the catalyst) that is not itself changed during the chemical reaction".

A catalyst can change the kinetic pathway of the reaction by lowering activation energy of the reaction and creating other intermediates/transition complexes in relation to the reaction carried out in a non-catalytic manner (figure 1-1). Then, the catalyst regenerates to its original form completing a catalytic cycle. Catalysts enable a different reaction pathway (shown in red) with a lower activation energy, however, does not change the overall thermodynamics (the equilibrium constant).[3]

A homogeneous catalyst is one that is in the same phase as the reagents (dissolved in solution), while the heterogeneous catalyst forms a separate phase (e.g., V_2O_5 catalyst in the oxidation of SO_2 to SO_3; solid Fe catalyst in the Haber process).

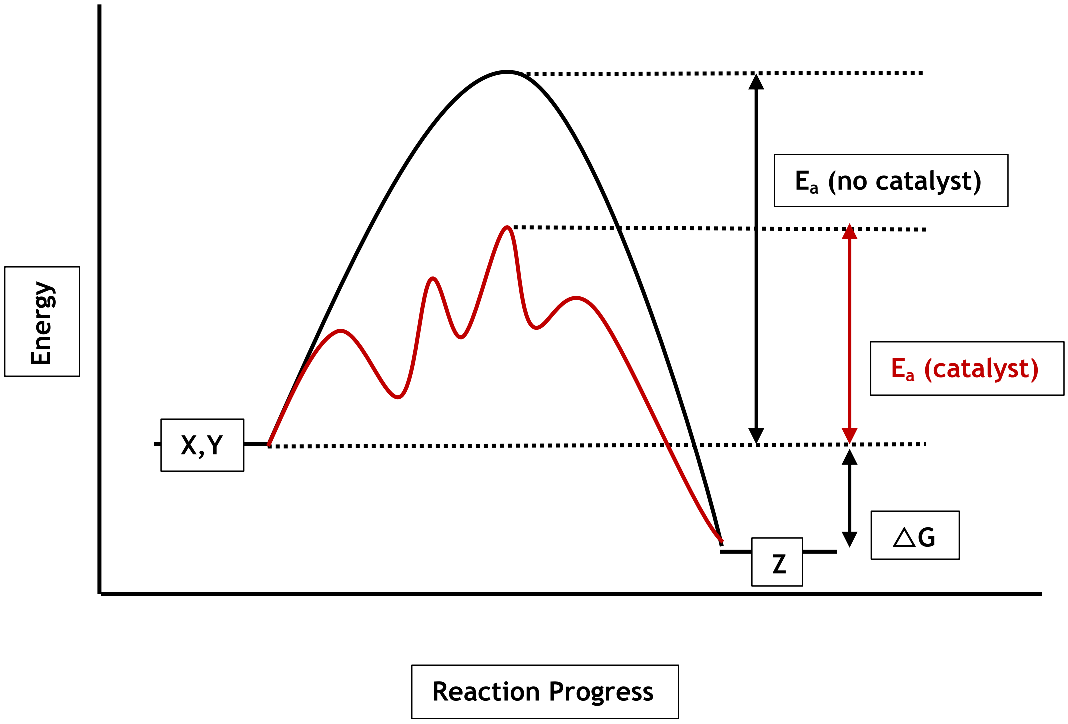

Figure 1-1 *General diagram presenting the basis of catalysis. Catalyst lowers activation energy (shown in red) by different reaction pathway leading to the same Z-products.*

From a kinetic point of view, catalytic reactions are chemical reactions therefore the reaction rate depends on the rate-determining step. Usually, the catalyst is involved in the slowest step and rates are limited by its activity. However, in heterogeneous catalysis also the diffusion of reagents to/ from the surface can be rate determining. Figure 1-2 shows the catalytic cycle at the molecular level for CO oxidation on a metal surface. This reaction is extremely important as it takes place in automobile exhaust catalysts. The first step is diffusion of the molecules (CO and O_2) to the metal surface (figure 1-2: 1) where the adsorption process takes place (figure 1-2: 2). In the case of O_2, dissociative adsorption (figure 1-2: 3) enables surface diffusion of oxygen molecules (figure 1-2: 4). CO is fairly stable compared to O_2, which dissociates easily; the reason of different behaviour of these two molecules is the different internal bond strength: 1076 kJ and 500 kJ, respectively. The surface reaction step (figure 1-2: 5) is very often the rate determining step in heterogeneous catalysis; in the described example oxygen atoms combine with CO to form the adsorbed product CO_2 (figure 1-2: 6). In the last step, CO_2 undergoes desorption from the catalyst surface (figure 1-2: 7).[4]

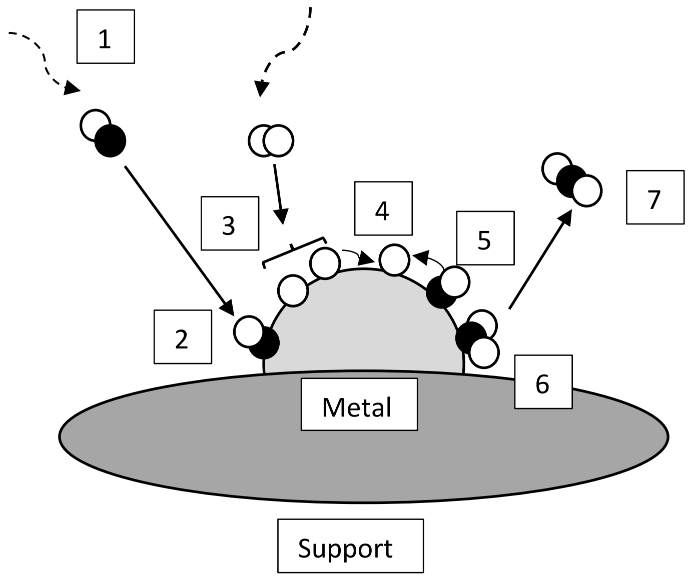

Figure 1-2 *Molecular and atomic steps during catalytic oxidation of CO to CO_2 with molecular oxygen.* [4] *1: gas phase diffusion; 2: molecular adsorption; 3: dissociative adsorption; 4: surface diffusion; 5: surface reaction; 6: adsorbed product; 7: product desorption*

Another example of a catalytic process is alcohol oxidation in liquid phase utilizing a heterogeneous catalyst. The mechanism is widely accepted in academic circles and is the so-called "classical" dehydrogenation mechanism consisting of two steps (figure 1-3).[5] In the first step, the O-H bond of alcohol breaks upon adsorption on the catalyst surface resulting in an adsorbed alkoxide and hydrogen. In the second step, which is considered to be rate-determining, the ß-C-H bond in the adsorbed alkoxide breaks (as this bond is weaker than other C-H bonds due to the electron withdrawing effect of oxygen) yielding the corresponding aldehyde. Co-product hydrogen is oxidised by adsorbed oxygen shifting the equilibrium toward the carbonyl compound and liberating active sites on the catalyst surface.

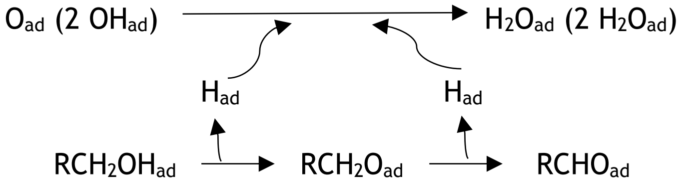

Figure 1-3 *Classical dehydrogenation mechanism of alcohol oxidation over Pt-group metal catalysts.*[5]

1.2. Phenomenon of gold as a catalyst

Gold nanoparticles have been produced by mankind for over 2000 years. In Indian ayurvedic medicine, a powdered substance called Swarna bhasma contains gold nanoparticles (around 56 nm) and was used to treat a lot of diseases e.g. asthma and arthritis. Romans applied nanoparticles to colour glass (4th century glass beaker, the Lycurgus cup, can be seen in the British Museum in London). Similar techniques were often used to colour church windows. Interestingly, Michael Faraday reported in 19th century that a rosy glow could observed by aqueous solutions of gold particles and he also mentioned their dimensions.[6], [7]

Nevertheless, the catalytic value of gold was overlooked for years in modern chemistry laboratories. Indeed, bulk gold is catalytically inactive, however nanoparticles of gold have been found to be extremely active for many reactions, especially oxidations. The high electrode potential of gold (E=+1.69 V) is the reason of its high stability and selectivity as a catalyst compared even to traditional precious metal catalysts such as platinum (E=1.20V) and palladium (E=0.99 V).[8]

The first work where gold was successfully employed as a catalyst was reported by Bond *et al.* and was related to the hydration of olefins.[9] Nevertheless, this publication did not receive much interest at the time. A real gold rush began 10 years later after discoveries made by Haruta and Hutchings. Haruta *et al.* proved high catalytic activity of gold supported on iron oxide for CO oxidation. Their detailed study revealed the importance of preparation method, depending on which it was possible to obtain different sizes of nanoparticles, hence different catalytic activity.[10] In the same year, 1985, Hutchings reported the best catalyst available for the hydrochlorination of acetylene to vinyl chloride, which turned out to be supported gold catalyst.[11] Other important applications of gold catalysts were found in following processes: oxidation of propene to propylene oxide (by Haruta *et al.*)[12], selective oxidations of diols (by Prati and Rossi)[13] and direct synthesis of hydrogen peroxide under non explosive conditions (by Hutchings and Kiely)[14].

Many valuable scientific papers have been published since these breakthrough studies. All these works stress the importance of many factors necessary for the synthesis of highly active and selective gold catalyst such as preparation method, particle size, support, alloying of gold to another metal and employed conditions. The following literature review presents the latest reports on the use of precious metals as catalysts in liquid phase oxidation reactions.

1.3. Selected preparation methods of heterogeneous catalysts.

There are many methods for synthesizing heterogeneous catalysts. The design of a heterogeneous catalyst containing precious metals is demanding for several reasons. Alloying Au with Pd enables to obtain more active catalysts, however preparation method is the key as it enables tailoring of the necessary features of nanoparticles. The biggest challenges in catalyst synthesis are the following: control of the particle morphology, control of the particle size distribution and control of the nanoparticle composition.[15]

In general, the most common methods applied in synthesis of heterogeneous Au-Pd bimetallic catalysts are: impregnation, modified impregnation, sol-immobilisation and deposition-precipitation. Modifications, variations and optimizations of these methods are common.[16]–[22]

The impregnation method seems to be relatively straightforward. Suitable aqueous salts ($HAuCl_4$ and $PdCl_2$) are simply impregnated on the support by stirring at elevated temperature forming a smooth paste. The paste undergoes further heat treatment stages (drying and calcination), which control the final morphology. Obtained nanoparticles have a broad range of sizes from 5 to 25 nm and even larger clusters are observed. In general, the nanoparticles exist as alloys, however the small nanoparticles contain mainly Pd and the large mainly Au. Moreover, in this method the support plays an important role. It has been shown that random Au-Pd nanoalloys are formed on carbon while following the same procedure core-shell structures are formed on oxides (Au-rich core, Pd-rich shell). Nanostructures are formed during calcination step. The temperature of calcination should be optimised as too high will decrease the catalyst activity due to sintering. In case of Au-Pd/ TiO_2, 400 °C allows full formation of core-shell structures without significant loss of activity. Moreover, during calcination the oxidation of Pd surface takes place, which influences the active sites. Even though the metals are not very well dispersed, it is still possible to synthesise active catalysts for many reactions utilizing this method. Au-Pd/TiO_2 prepared by impregnation has been found to be active for the oxidation of alcohols under solvent-less mild conditions and also for the direct synthesis of hydrogen peroxide.[15], [23], [24]

The sol-immobilisation method allows to obtain a very narrow particle size distribution, usually 4-6 nm. The nanoparticles are synthesized by a reduction of a metal precursor with a reducing agent (*e.g.*, BH_4^-) in the presence of a protective agent to prevent aggregation (*e.g.*, PVA or PVP). The nanoparticles can be easily supported and dried without significant change in the mean particle size. As in the case of impregnation method the nature of support influences the behaviour of nanoparticles. Nanoparticles do not appear to wet carbon, which means that sintering takes place easily above 200 °C. Contrary to carbon, TiO_2 interacts with the nanoparticles which makes them resistant to sintering. Generally, sol-immobilisation method allows to obtain homogeneous Au-Pd nanoalloys, however, small nanoparticles contain mainly Au and large nanoparticles mainly Pd (opposite trend to impregnation method). Core-shell structures might be obtained simply by forming either Au or Pd nanoparticles first and then using these as templates for the deposition of another metal. An important observation is that the composition of the nanoparticle is often related to the nanoparticle size.

A drawback for sol-immobilisation method is presence of stabilizing/ coating agent. A possible way of removing PVA/PVP is heat treatment in air, however this would result in the loss of the small nanoparticles through sintering. The other solution might be removing of water-soluble polymer by treatment with water at elevated temperature. The presence of coating agent should not be a massive issue for the reactions performed in the liquid phase, however problem escalates in case of gaseous reactants e.g. oxidation of CO.[15], [16], [25], [26]

In the modified impregnation method, an excess of anion is being used by addition of aqueous HCl to the metal precursor solutions, $PdCl_2$ and $HAuCl_4$. It has been proposed by Sankar *et al.*[18] that the presence of Cl^- ions facilitates the formation of $AuCl_4^-$ and $PdCl_4^{2-}$ species whose coexistence in the aqueous medium enables a homogeneous mixture of metal ions, hence better dispersion of the metals onto the support. In the case of standard impregnation method, in the absence of excess Cl^-a $[Au(OH)_x(Cl)_{4-x}]^-$ species is formed and $PdCl_2$ which is only partially soluble in water, therefore the observed dispersion in the catalysts is rather poor and the formation of large nanoparticles is very common. Presence of the halide during synthesis increases the dispersion of Au as the occurrence of large clusters is significantly limited (the mean value of Au-Pd nanoparticles is around 2.9 nm). Modified impregnation method allows to obtain AuPd nanoparticles with the character of random alloy and particle sizes ranging from 2 to 6 nm. Nevertheless, halide needs to be removed from the material by a reduction treatment in order to obtain the most active catalysts.

In general, two steps in the synthesis of catalysts by modified impregnation method are crucial and influence massively the formation of nanoparticles: heat treatment and the concentration of the HCl.

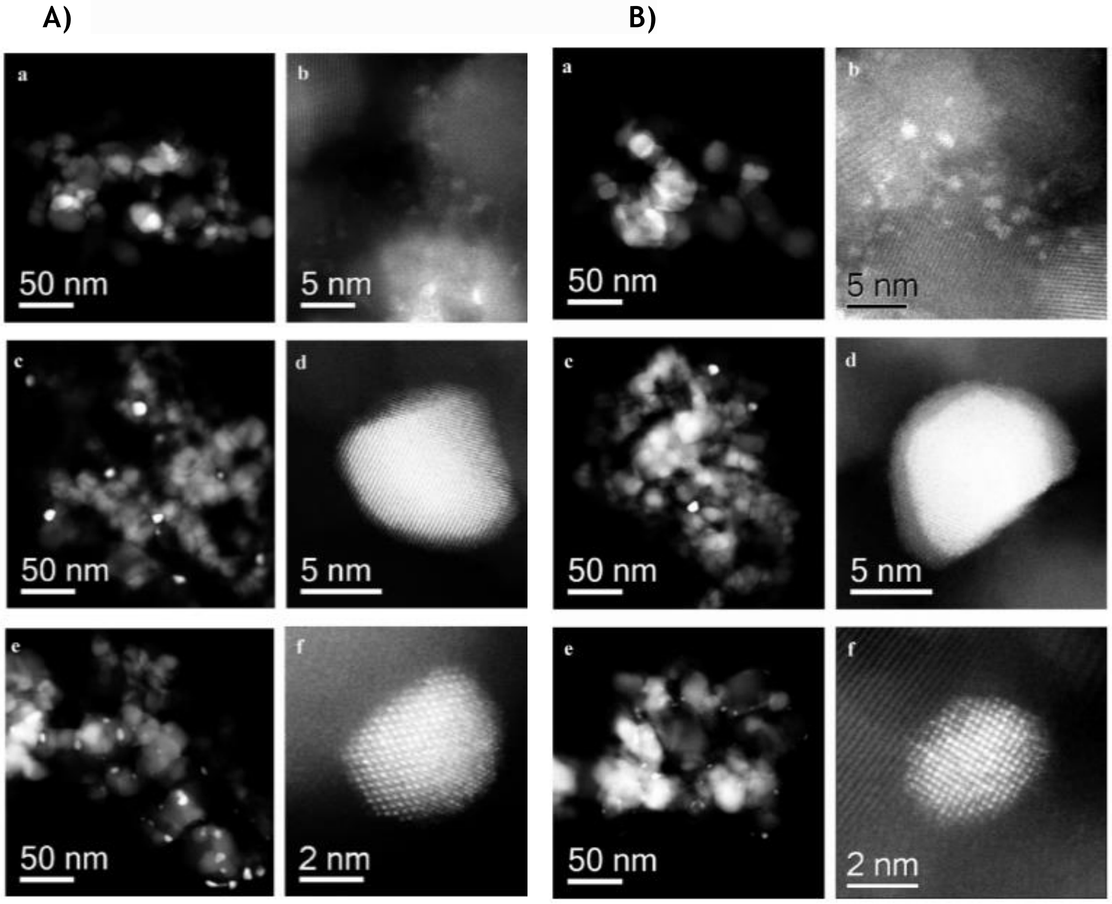

Figure 1-4 *HAADF-STEM images of 0.50 %Au 0.50 %Pd/ TiO_2 catalysts:* ***A*** *– catalyst prepared by standard impregnation method* ***B****- catalyst prepared by modified impregnation method with 0.58 M HCl.* ***a,b****- dried only at 120 °C;* ***c,d****- calcined in air at 400 °C;* ***e,f****- reduced in 5 % H_2/Ar at 400 °C. Experiment carried out by Sankar at al.*[18]

It has been presented by Sankar *et al.* [18] that dried only 0.50 wt % Au 0.50 wt% Pd/TiO_2 catalysts prepared by impregnation and modified impregnation showed rather similar morphologies with vast majority of Pd-rich nanoparticles being 1-2 nm and some large Au-rich particles being in micrometre range (figure 1-4, A-a,b and B-a,b). After calcination at 400 °C in air, also similar morphologies (Au-core, Pd-shell) have been observed with larger particles being in the range of 5-10 nm (figure 1-4, A-c,d and B-c,d). Applying reduction in 5 % H_2/Ar instead of calcination in air allows for enhanced dispersion in case of modified impregnation method and also impacts the morphology as observed structures are rather random alloys. Also, particle size distribution varies with the mean value for the reduced catalyst prepared by standard impregnation method being 4.7 nm and 2.9 nm for the reduced catalysts prepared by modified impregnation method (figure 1-4, A-e,f and B-e,f).

Second factor, Cl^- concentration, influences the composition of nanoparticles. It has been observed that after reduction varying Cl^- concentration results in systematic change in Au-Pd ratio (the higher Cl^- concentration, the higher Au content within Au-

Pd nanoalloy). However, the amount of Cl^- used influences the activity and reusability of catalysts prepared by modified impregnation method. An optimal concentration of HCl used in the preparation of AuPd catalysts tested in the oxidation of benzyl alcohol and also in the direct synthesis of hydrogen peroxide has been established to be 0.58 M. In summary, the composition and particle size can be tuned by the excess of chloride anion. The researchers tested different palladium precursors and the excess of anion methodology seems to be beneficial only if chloride ions are applied.[15], [18]

In the deposition- precipitation method, the support is suspended in a solution containing metal salts. The nanoparticles are precipitated onto the support after the addition of base to the solution. The particle size distribution is narrower than in previous method, usually 1-10 nm. Here, the synthesis is more detailed as there are more steps and different factors such as temperature and pH that should be controlled throughout the whole process. In this thesis the catalysts have been prepared using methodologies described earlier hence the reader should refer to the literature if interested in deposition- precipitation method. [27]–[31]

1.4. Literature review

It is extremely difficult to compare and contrast the literature reports due to the variety of catalytic systems, catalysts synthesis and applied conditions. Neverthless the key scientific knowledge has been presented as the basis to the experimental work on Au-Pd supported nanoparticles in the oxidation reactions discussed in this thesis.

1.4.1. Alcohol oxidation: Cinnamyl alcohol

The desired product of cinnamyl alcohol oxidation, cinnamaldehyde, is an insecticide and common additive in food and perfume industry. Moreover, the reaction network is interesting hence this reaction is a model reaction from an academic viewpoint. In general, aldehydes are extremely important compounds due to their applications, however existing methods of carbonyl compound synthesis utilise toxic and stoichiometric oxidants such as chromate and permanganate. Precious metals have been found to be active in oxidation of alcohols thus being an alternative, greener route for these reactions.

Baiker *et al.*[32] published in 1994 their work on the oxidation of cinnamyl alcohol to cinnamaldehyde with air using Bi-Pt/Alumina catalysts. The bimetallic Bi-Pt system has been found to be more active than the counterpart monometallic Pt system.

The researchers reported that the presence of Bi limited but did not stop the formation and irreversible adsorption of by-products. It was also mentioned that the partial coverage of active sites with oxygen enabled oxidative removal impurities from the surface. The scientists suggested that Bi acted as a geometric (blocking) element which decreased the size of Pt clusters. Adsorption of cinnamyl alcohol on the noble metal was pointed as a possible reason of the catalyst deactivation. Also, chemisorption of by-products limited the number of available free Pt^0 active sites.

A few years later, Baiker and co-workers[33] investigated the positive effect of Bi as a promoter in the oxidation and dehydrogenation of alcohols over Pt-group metal catalysts. The promoter itself was inactive. The researchers tested Pd/Al_2O_3 and Bi-Pd/Al_2O_3 in the oxidation of phenylethanol and cinnamyl alcohol. It was found that higher conversion was obtained for phenylethanol than for cinnamyl alcohol in the same conditions. The researchers suggested that it might be due to side reactions in case of cinnamyl alcohol, mostly decarbonylation of cinnamaldehyde which was intensified at higher temperature. The conversion of cinnamyl alcohol using Pd/Al_2O_3 was close to 100 % after an hour, however Bi-Pd/Al_2O_3 catalyst showed much lower conversion at the same time (below 30 %). It was suggested that coverage of the Pd surface by Bi decreased the availability of active sites for hydrogen adsorption and hence alcohol dehydrogenation in the Bi-promoted catalyst.

Bi has also been investigated by Prati and co-workers[34] in the oxidation of glycerol and by Besson and co-workers[35] in the oxidation of 3-pyridinemethanol as a promoter improving overall activity of noble metals catalysts. In both cases, Bi was deposited on preformed precious metal nanoparticles and did not interfere with the size of the nanoparticles or interfere with the formation of homogeneous metallic phases. Also, in both cases Bi enhanced processes by interaction with active sites leading to switching off undesired side reactions and processes.

Baiker[36] and co-workers carried out studies on the oxidation of cinnamyl alcohol using different catalysts, including 5 %wt Pd/Al_2O_3. Generally, the reported mechanism of the reaction was in line with the principles of classical dehydrogenation mechanism. The reaction scheme has been shown in figure 1-5.

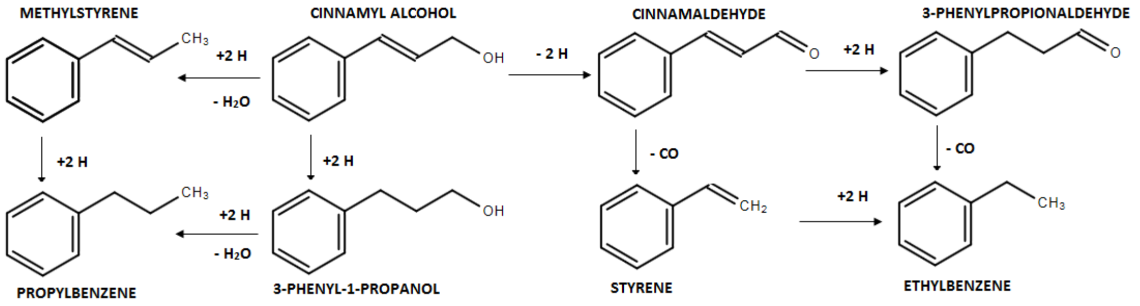

***Figure 1-5** Reaction network in the oxidation of* trans-*cinnamyl alcohol over alumina-supported Pd proposed by Baiker and co-workers.*[36]

The researchers stated that cinnamaldehyde was formed as the effect of dehydrogenation; 3-phenyl-1-propanol and dihydrocinnamaldehyde were formed as the effect of hydrogenation of the substrate and major product (cinnamaldehyde) respectively; methylstyrene was formed as the effect of hydrogenolysis of C-O bond; styrene and ethylbenzene were formed in the process of decarbonylation. Based on the presented reaction network, the researchers stretched that Pd is particularly active for two processes in the case of allylic alcohols: hydrogen transfer and an aldehyde decarbonylation. The presence of an allylic bond in aromatic allylic alcohols results in them behaving like hydrogen donors and acceptors on the surface of Pt group metals, including Pd.

Baiker and Mallat[37] studied also the epoxidation of various allylic alcohols, including cinnamyl alcohol using titania-silica aerogel. It was reported, that cinnamyl alcohol was oxidised mostly to cinnamaldehyde, regardless of the conditions applied.

The researchers concluded based on their wide studies on the cinnamyl alcohol oxidation that many factors influence the course of the reaction: catalyst composition, reaction atmosphere, solvent, and the reaction temperature.[36] Baiker's further work focused mainly on studying these factors, determining the role of oxygen and the origin of the catalyst deactivation. The change of the reaction conditions led to different selectivities, nevertheless the general reaction network remained valid for all cases[36]. Interestingly, further oxidation of cinnamaldehyde to cinnamic acid has not been observed in toluene, which was explained by the differences in the reactivity of the carbonyl group. In general, the direct oxidation of the carbonyl group is slow, and dehydrogenation through hydration of the carbonyl group (the predominant mechanism in the aqueous environment) is faster. Thus, the hydration of the carbonyl group in toluene is hindered not only because of the availability of water, but also by the stability of the aldehyde and the inert apolar organic medium. The scientists focused on determining the role of oxygen in the oxidation of cinnamyl alcohol, as it is generally accepted that oxygen may be directly involved in hydrogen abstraction from the adsorbed alcohol. In a specially designed experiment, cinnamyl alcohol was oxidised in an atmosphere of argon for 90 minutes and then in air. The reaction temperature remained the same, 65°C and the amount of substrate was 1 g in 30 ml toluene. It can be seen from figure 1-6 that the reaction profile in argon was rather steady within 90 min with conversion around 15 % and selectivity around 60 %. When the atmosphere was switched to air the selectivity to cinnamaldehyde slightly increased, however the conversion increased significantly up to 100 % in a short period of time (around 100 minutes). The results of Baiker's work have shown that the reaction takes place under inert gas hence oxidation of the co-product hydrogen by oxygen is not necessary. Further investigation using *in situ* Attenuated Total Reflectance- Infrared Spectroscopy (ATR-IR) spectroscopic analysis of adsorbed species on Pd/Al_2O_3 under reaction conditions revealed that oxygen is necessary to oxidise and remove strongly adsorbed CO (formed as by-products during decarbonylation) from the catalyst surface. Furthermore, the researchers proposed that the active sites in this process are Pd^0.

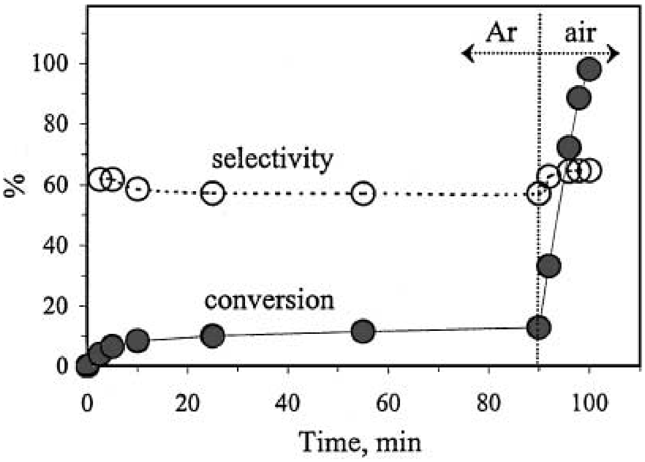

Figure 1-6 *Oxidation of cinnamyl alcohol carried out in argon and then in air. Conditions: 5 wt% Pd/Al_2O_3;1.0 g cinnamyl alcohol; 30 ml toluene; reaction temperature, 65 °C; mixing frequency, 1250 min−1; air flow rate, 60 ml min−1.*[36]

Baiker *et al.*[36] suggested two possible reasons for catalyst deactivation. The first would be CO poisoning, which can be easily reversed by air (leading to higher reaction rates anyway). However, the researchers suggested that the catalyst may undergo so called overoxidation leading to decreased yield of the process. The second suggested reason of catalyst deactivation is also poisoning by short-chain hydrocarbons (degradation products formed during the decarbonylation processes), impossible to remove by oxygen under reaction conditions.

Baiker and co-workers[38] carried on their works on the oxidation of alcohols using heterogeneous Pd supported catalyst. Based on their observations they stated that aldehydes decarbonylate on Pd surface to form CO and hydrocarbon fragments which adsorb strongly causing catalyst deactivation. To remove hydrocarbon residue, one needs to apply reducing conditions while to remove CO adsorbed oxygen is needed. The authors pointed an amazing feature of the aerobic oxidation of alcohols on Pt-group metals, that under specific conditions these two processes may run parallel leading to a high yield of the reaction. This work has shown that complete removal of degradation products is not necessary to obtain good reaction rates. ATR-IR spectroscopic analysis revealed the presence of carboxylate species, even at low alcohol conversion. Carboxylic acid adsorbed strongly on the catalyst surface, mainly on the support, and was not found in the liquid phase by GC analysis.

The researchers also discussed the importance of water in the alcohol oxidations. Water is formed from the oxidation of hydrogen in equimolar amounts to formation of the aldehyde. Water may also be formed as the effect of hydrogenolysis of the C-O bond. Their ATR-IR study confirmed presence of water on the catalyst surface even if the reaction has been carried out in a non-aqueous media. In that case water removal from the catalyst is extremely important. In case of aqueous reaction solutions, water speeds up further oxidation of aldehyde to carboxylic acid through hydration of the carbonyl group followed by dehydrogenation of the geminal diol as this is a faster route than direct oxidation.

In his later paper, Baiker[39] investigated structural changes of a Pd/Al_2O_3 catalyst during oxidative dehydrogenation of cinnamyl alcohol using *in situ* Extended X-ray Absorption Fine Structure (EXAFS) and quick EXAFS (QEXAFS) techniques. Additionally, the reactions carried out in batch and in flow fixed-bed cell of EXAFS reactor have been contrasted (the results were fairly comparable). High selectivity to the major product has been obtained (around 58-63 %) and also a large amount of 1-phenyl-3-propanol has been detected (20-35 %) which indicated that the substrate played the role of hydrogen acceptor. This hypothesis has been confirmed further by EXAFS analysis. Interestingly, the QEXAFS study revealed that the 5 %wt Pd/Al_2O_3 catalyst has been reduced within 1 hour during exposure to cinnamyl alcohol in toluene under an argon atmosphere. When the atmosphere was switched to oxygen, a similar product distribution was still observed. Moreover, hydrogenation and hydrogenolysis processes took place even though there was oxygen available in the feed. It is quite intriguing as according to the classical dehydrogenation mechanism, hydrogen abstraction is catalysed from the adsorbed reactant and then hydrogen is oxidised by adsorbed oxygen.

In his next publication, Baiker and co-workers[40] oxidised cinnamyl alcohol to cinnamaldehyde in a continuous fixed-bed reactor with molecular oxygen using 0.5

%Pd/Al_2O_3 catalyst in supercritical carbon dioxide with toluene as a co-solvent. This method has been found to be especially effective for solid alcohols. A slightly different reaction network was observed compared to that reported previously, mostly due to benzaldehyde presence (figure 1-7). *In situ* X-ray Absorption Near Edge Structure (XANES) and EXAFS revealed that alcohol dehydrogenation was the first reaction taking place in the process after which hydrogenated by-products were formed as the effect of internal hydrogen transfer reactions. During the same analysis, the researchers also observed that Pd was mainly in a reduced state and it was possible to oxidise its surface only in the complete absence of cinnamyl alcohol in the feed. Detailed study of the catalyst surface and bulk phase of the reaction mixture revealed the presence of cinnamaldehyde and carbon dioxide inside the porous catalyst, but no toluene and cinnamyl alcohol; these last two compounds were present only in the reaction mixture.

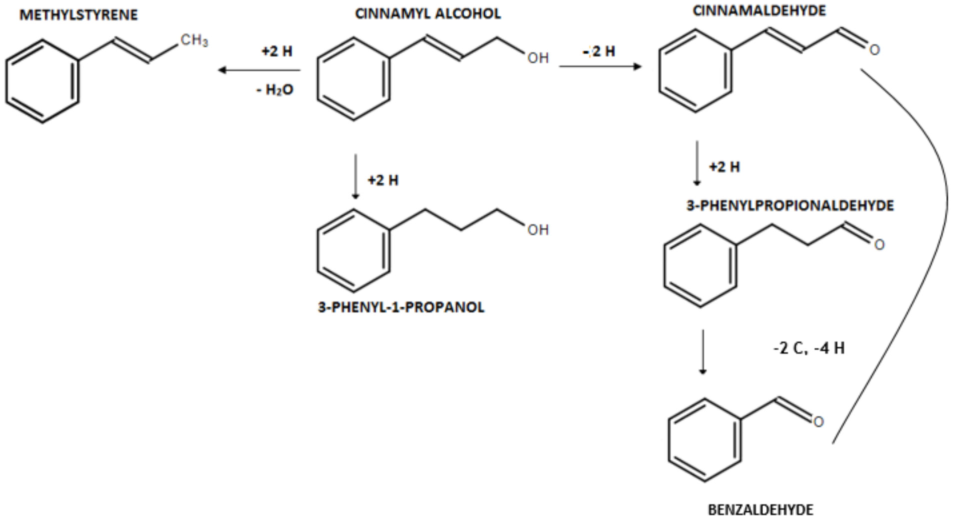

Figure 1-7 *Reaction network in the oxidation of cinnamyl alcohol in supercritical CO_2 over supported Pd catalyst proposed by Baiker et al.*[40]

The scientists observed a strong dependence of reaction rate on pressure and oxygen concentration (table 1-1).

Table 1-1 *Influence of oxygen on the oxidation of cinnamyl alcohol at 80 °C (0.15 mol% alcohol, 1.9 mol% toluene in CO_2 (0.233 mol/min), 2.5 g of 0.5 wt% Pd/Al_2O_3.*[40]

Gas pressure and oxygen content	**Conversion (%)**	**Selectivity (%)**			
		Cinnamaldehyde	**3-Phenyl-1-propanol**	**Methylstyrene**	**Benzaldehyde**
120 bar absence O_2	12.4	57.6	11.2	30.9	-

120 bar 0.15%mol O_2	58.7	79	19	traces	-
120 bar 10 mol% O_2	51.4	82.2	3.6	traces	11.7
150 bar 10%mol O_2	53	72.9	5.2	traces	20

Conditions: temperature, 80°C; 0.15 mol% alcohol; 1.9 mol% toluene in CO_2 (0.233 mol/min); 2.5 g of 0.5 wt% Pd/Al_2O_3

Generally, with increasing oxygen partial pressure, the amounts of MS and PP decreased, and the amount of benzaldehyde increased. The researchers linked this fact with the greater availability of surface oxygen on the palladium active sites. It was mentioned that benzaldehyde might be formed from toluene and from cinnamic acid (by oxidative cleavage of the C=C double bond), however it was excluded as these both reactions take place in extremely harsh conditions.

The nature of active sites is not clear in the oxidation of cinnamyl alcohol. Baiker determined throughout his research that Pd^0 is the active species in the process. However, a different suggestion was made by Lee *et al.*[41] pointing to PdO as an active site in the oxidation of cinnamyl alcohol. During this study, Pd was deposited onto alumina grafted SBA-15 support which showed the high dispersion and surface oxidation typical for alumina as well as the high surface area of SBA-15. The obtained activity data have been shown in table 1-2.

***Table 1-2** Cinnamyl alcohol oxidation using supported Pd catalysts.*[41]

Catalyst	Conversion	Cinnamaldehyde [%]	TOF (h^{-1})
Pd/Al-SBA-15	95	64	13600
Pd/meso-Al_2O_3	56	39	13391
Pd/SBA-15	21	16	6108

Conditions: temperature, 90 °C; time, 30 minutes; oxygen, 1bar; catalyst mass, 0,05g; 8.4 mmol cinnamyl alcohol; toluene, 10 ml.

The researchers performed operando liquid-phase XAS measurements based on which the strong correlation between dissolved oxygen and the oxidation state of Pd has been noted. It was observed that flowing oxygen under ambient pressure hindered the reduction of PdO to Pd^0, while under static oxygen rapid PdO reduction was taking place. High catalytic activity was observed under flowing oxygen for the first 30 minutes whereas the catalyst deactivation occurred instantly under static oxygen. The catalyst tested under flowing air deactivated after 30 minutes leading to the same results as the catalyst tested under static air. The scientists suggested that the reason of deactivation might be a formation of decarbonylation products (CO and hydrocarbons) that adsorb strongly on the catalyst surface, which is in line with Baiker's observations. High yield to cinnamaldehyde was linked to the presence of PdO, however full suppression of the catalyst reduction with flowing oxygen was unsuccessful. The group carried on research on the oxidation of allylic alcohol using Pd nanoparticles supported over various supports (C, Al_2O_3, KIT-6, SBA-16, SBA-15) and they noted similar observations regarding active sites being PdO.[42]-[48] It was stated mostly based on the analysis of the reaction rate, product distribution and catalyst characterization techniques (XPS and EXAFS).

Prati and co-workers[49] tested monometallic and bimetallic Pt, Pd and Au systems supported over carbon in the oxidation of alcohols. The only observed products were cinnamaldehyde and 3-phenyl-1-propanol. The reactions were carried out at 60 °C, under 1.5 atm O_2 in both toluene and water. The researchers tested monometallic Au, Pt, Pd catalysts and bimetallic Au-Pt, Au-Pd catalysts. The results presented in table 1-3 revealed that the most suitable solvent in the oxidation of cinnamyl alcohol in mild conditions is water, however the activity in toluene is considerable. Moreover, bimetallic Au-Pd system have been found to be more active than their monometallic counterparts (table 1-3). Interestingly, although Au-Pd demonstrated a positive/synergistic effect, Au-Pt showed a negative effect, as the conversions in case of Au-Pt were even lower than for their monometallic counterparts (table 1-3). It was also noted that a decreased selectivity to cinnamaldehyde when using Pt as opposed to Pd indicates the ability of the latter metal to promote hydrogen transfer.

Table 1-3 *Oxidation of cinnamyl alcohol.*[49]

Catalyst	**Solvent**	**Conversion (%)**	**Sel. Cinnamaldehyde (%)**	**Sel. 3-phenyl-1-propanol (%)**	**TOF (h^{-1})**
0.73 %Au-0.27 %Pd	Toluene	72	85	13	180
0.6 %Au-0.4 %Pt		5	100	0	12
1 %Au		0	0	0	0
1 %Pd		24	86	14	61
1 %Pt		15	100	0	38
0.73 %Au-0.27 %Pd	Water	95	83	17	237
0.6 %Au-0.4 %Pt		18	100	0	45
1 %Au		0	0	0	0
1 %Pd		36	86	14	90
1 %Pt		27	100	0	67

Conditions: cinnamyl alcohol, 0.3M; cinnamyl alcohol/metal, 1/500 (mol/mol); temperature, 60°C; oxygen, 1.5 atm; time, 2 hours.

In their other work, the group under the leadership of Prati[50] studied the effect of the base in the oxidation of alcohols, including cinnamyl alcohol using various ratios of Au-Pd nanoalloys supported on carbon. The results (table 1-4) revealed that bimetallic catalysts are more active than their monometallic counterparts, especially for 9:1, 8:2, 6:4 Au-Pd ratios. TEM analysis demonstrated uniform alloyed phases in these catalysts opposed to 2 Au: 8 Pd where inhomogeneity in the structure was noticed. Generally, the addition of base improved the activity of all tested catalysts, however the increase observed was especially significant for Au-rich catalysts. The addition of base also changed the product distribution as the formation of ester has been observed. The different behaviour of Au-rich and Pd-rich catalysts in the presence of base indicated possibly two different mechanisms. The authors noted that in case of Pd, transfer of H atom to the β-carbon of the adsorbed alkoxide leading to the aldehyde and a Pd-hydride is the rate determining step. In case of Au, the rate determining step is the H-abstraction by a superoxo-like oxygen species adsorbed on Au. Other research groups have reported similar observations and hypotheses supporting Prati's work.[51]-[53] In summary, base seems to be involved in the hydride abstraction and also in the hydration of the aldehyde intermediate which leads to the formation of the corresponding carboxylate.

Table 1-4 *Oxidation of cinnamyl alcohol as reported by Prati and co-workers.*[50]

		Selectivity at 90 % conversion			
Catalyst	**Base**	**TOF (h^{-1})**	**CinnALD**	**3-phenyl-1-propanol**	**Ester+ acid**
1% Au/AC	-	25	80	18	-
1% $Pd_{10}@Au_{90}$/AC		520	77	22	-
1% $Pd_{20}@Au_{80}$/AC		630	75	24	-
1% $Pd_{40}@Au_{60}$/AC		539	75	24	-
1% $Pd_{80}@Au_{20}$/AC		394	74	25	-
1% Pd/AC		120	70	28	-
1% Au/AC	1 equiv. NaOH	470	27	10	63
1% $Pd_{10}@Au_{90}$/AC		858	28	16	56
1% $Pd_{20}@Au_{80}$/AC		861	32	21	47

1% $Pd_{40}@Au_{60}$/AC	669	50	24	26
1% $Pd_{80}@Au_{20}$/AC	480	58	23	19
1% Pd/AC	143	62	25	13

Conditions: cinnamyl alcohol, 0.3M; cinnamyl alcohol/metal, 1/500 mol/mol; temperature, 60°C; oxygen, 1.5 atm.

Rossi and Costa[54] investigated the solventless oxidation of cinnamyl alcohol using Au-Ag nanotubes. The reactions have been carried out at 100 °C under different oxygen pressures. The only observed products were cinnamaldehyde and benzaldehyde with negligible traces of unidentified substances. The researchers noticed the dependence of oxygen pressure and selectivity: the higher oxygen pressure, the higher benzaldehyde formation (figure 1-8).

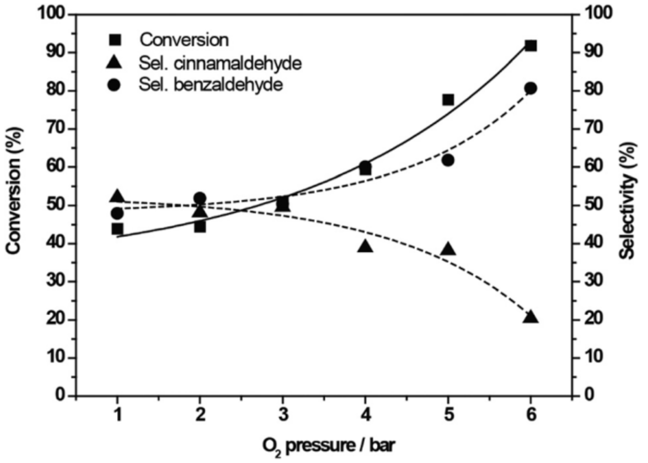

Figure 1-8 *The influence of oxygen pressure on the oxidation of cinnamyl alcohol using Au-Ag supported catalyst.*[54]

It was suggested that benzaldehyde might be formed through oxidative cleavage of the C=C double bond in two possible ways: an epoxidation involving a cis-diol intermediate or *via* a radical mechanism. The scientists carried out a set of experiments to investigate this, the results of which have been presented in table 1-5.

Table 1-5 *Oxidation of cinnamyl alcohol.*[54]

Entry	Catalyst	BHT	Conv. (%)	CinnALD (%)	BenzALD (%)	Other (%)
1	Au-Ag NT	-	99.1	21.1	73	5.9
2		-	28	53	44	3
3		present	69.2	96.7	0.9	2.4
4		-	2.6	63.8	36.2	0
8		-	28	44.5	53	2.5

9	No catalyst	present	10.4	94.7	3.9	1.4

Conditions: temperature, 100 °C; oxygen, 6 bar; time, 2.5 hours; cinnamyl alcohol, 10 mmol; catalyst/alcohol, 1/2000.

The standard reaction carried out at 100 °C under 6 bar O_2 achieved 99.1 % conversion after 2.5 hours, only 21.1. % selectivity to cinnamaldehyde and 73.0 % selectivity to benzaldehyde (entry 1, table 1-5). The same reaction stopped earlier (after 1 hour) showed only 28 % conversion, however higher selectivity to cinnamaldehyde (53 %) and lower selectivity to benzaldehyde 44.0 % was observed (entry 2, table 1-5). The addition of a radical trap (BHT = Butylated hydroxytoluene; 2,6-di-tert-butyl-4-methylphenol) to the standard reaction massively influenced the reaction product distribution; the conversion (69.2 %) was lower compared with the standard reaction, however the selectivity to cinnamaldehyde was 96.7 % and selectivity to benzaldehyde was below 1 % (entry 3, table 1-5). The reaction carried out under an inert atmosphere had only 2.6 % conversion, and still large amounts of benzaldehyde had been identified (entry 4, table 1-5). Based on these experiments, the researchers linked the formation of benzaldehyde with a radical-chain oxidation pathway. The researchers carried out the autoxidation of cinnamyl alcohol (blank reaction) under the given conditions and they reported 28 % conversion with 44.5 % selectivity to cinnamaldehyde and 53 % selectivity to benzaldehyde (entry 8, table 1-5). The blank reaction carried out under the same conditions but with the addition of the radical scavenger showed lower conversion, 10.4 %, however mostly cinnamaldehyde was formed (94.7 %) and only minor amounts of benzaldehyde (below 4 %) (entry 9, table 1-5). The researchers suggested that the trace amounts of hydroperoxides (from the substrate or by the activation of oxygen over Au surface) played the role of the chain initiator. The absence of epoxides pointed to polyperoxides which can decompose *via* cleavage of the O-O bond (and an adjacent C-C bond) yielding the products of oxidative cleavage. The group focused also on identification of other small molecules by-products. For this purpose, the reactor gas phase was transferred to a gas cell and analysed by FT-IR. The researchers identified CO_2 and formaldehyde. In the next step, the gas phase was frozen and reacted with 2,4-dinitrophenylhydrazine (DNPH) which reacts with aldehydes yielding hydrazones. Hydrazones were then dissolved with an organic solvent and analysed by High Performance Liquid Chromatography (HPLC). This experiment confirmed the presence of formaldehyde. The reaction scheme presents the obtained product distribution (figure 1-9).

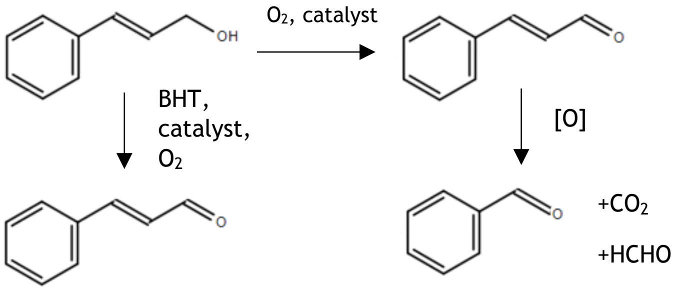

Figure 1-9 *Reaction network for the oxidation of cinnamyl alcohol using Au-Ag NT proposed by Rossi and Costa.*[54]

Moreover, the researchers investigated the dynamic of product formation using Surface-enhanced Raman spectroscopy (SERS). The results of their studies have shown that cinnamaldehyde was formed on the catalyst surface as a product of metal catalysed oxidation. However, benzaldehyde was not observed on the catalyst surface, hence it was suggested that its formation takes place in the bulk solution *via* a radical chain pathway. These observations are in line with the activity data.

Rossi and Costa drew attention to a very important aspect in organic chemistry and also in catalysis, i.e. autoxidation. Although in different context, Niklasson *et al.*[55] studied stability of cinnamyl alcohol in detail. The researchers designed a set of experiments, where the samples of cinnamyl alcohol were exposed to air under different conditions. The conclusion drawn from these experiments was that cinnamyl alcohol undergoes autoxidation no matter what conditions are applied. The topic of autoxidation will be discussed in more detail later in this chapter.

1.4.2. Alcohol oxidation: 3-pyridinemethanol oxidation

Heterocyclic carbonyl derivatives are used in the pharmaceutical industry as precursors of important drugs e.g. antiviral and antitumor. In general, the aerobic oxidation of pyridine-derived alcohols is challenging due to the presence of heteroatom in the structure which stabilizes the molecule making it more difficult to oxidise. Therefore, many different approaches have been applied.

Rostami *et al.*[56] prepared VO(ephedrine)$_2$ supported over magnetic nanoparticles which allows for easy separation of the catalyst by a magnet. The researchers pointed to the fact that alcohols containing a heterocyclic atom in the structure very often interact with transition metals which leads to the deactivation of the catalyst. VO(ephedrine)$_2$@MNPs was found to be very active for the oxidation of 3-pyridinemethanol with the use of TBHP as oxidant. The isolated yield of 3-pyridinecarboxyaldehyde after 15 hours was 92 %. The reaction was carried out at 80

°C in PEG as solvent. The catalyst showed only mild deactivation after 6 reuses for benzyl alcohol oxidation.

Karimi and Esfahani[57] demonstrated an unusual approach in performing the catalytic oxidation of alcohols at room temperature. Here, rather than immobilising gold nanoparticles onto a support prior to reaction, the researchers simply added $NaAuCl_4$ and Cs_2CO_3 to the reaction mixture of a substrate in toluene. It was observed that under reaction conditions, nanoclusters of gold were formed, followed by their immobilisation on Cs_2CO_3 (3 equiv.) which acted as a solid support. Oxidation of 3-pyridinemethanol did not take place under air (1 atm), however under the oxygen the isolated yield after 16 hours was 87 %, with 100 % selectivity to the aldehyde. This *in-situ* formed $Au–Cs_2CO_3$ catalyst was recovered by simple filtration and reused without any further treatment. The catalyst remained active for 3 runs, after which its activity significantly decreased as a result of agglomeration. The choice of the type of base was crucial, as in the presence of K_2CO_3 agglomeration of gold nanoparticles occurred instantly resulting in no conversion and in the presence of Cs_2CO_3 the reactions took place. Optimisation of the reaction time and ratio of alcohol to $NaAuCl_4$ enhanced the catalytic process.

Zhou *et al*. oxidised a range of alcohols in the presence of isobutyraldehyde with the use of metalloporphyrin-intercalated hydrotalcites CoTSPP-Zn_2Al-LDH, originated from metalloporphyrins (MTSPP; M = Co, Fe, and Mn). The reactions were carried out in acetonitrile at 60°C with the addition of 3 mmol isobutyraldehyde per 1 mmol of substrate. Oxygen was bubbled through the reaction mixture (10 ml/min). The conversion of 3-pyridinemethanol to its aldehyde after 40 min was 44 % with a selectivity of 89 %.[58] The basic properties of hydrotalcite can be simply altered by substituting cations and anions. The same group studied the influence of basicity on the oxidation of various alcohols by replacing Ni^{2+} by Mg^{2+} in a series of hydrotalcites: CO_3^{2-}-Ni_2Mg_xAl-LDHs, x = 0, 0.5, 1.0, 1.5, and 2.0. The researchers proved that the type of basic site affects the catalytic performance with only Bronsted OH basic sites being able to accelerate the reaction.[59] Zhou *et al*. continued works on Co-containing hydrotalcites for oxidation of alcohols by changing the Co/Fe ratio. Exchanging Al with Fe improved the catalytic performance of CO_3^{2-}–Co_xFe–LDHs hydrotalcites. The increase in activity was found to be caused by a synergistic effect between Co and Fe and also between their cations. Oxidation of 3-pyridinemethanol performed in acetonitrile at 60 °C with TBHP as an oxidant gave almost 100 % conversion to 3-pyridinecarboxyaldehyde within 12 hours.[60]

Chen and co-workers synthesised and tested Cu(II)-based metal-organic frameworks (MOFs)for the oxidation of alcohols to aldehydes in the presence of TEMPO. Oxidation of 1 mmol of 3-pyridinemethanol was carried out for 16 hours at 75 °C in acetonitrile (5ml) with the addition of TEMPO (0.5 equiv.) and Na_2CO_3 (1 equiv.). This resulted in an isolated yield of 83 % to 3-pyridinecarboxyaldehyde. The MOFs were easily recovered from the liquid phase and reused.[61]

Besson *et al.*[35], [62]–[64] tested 1.95 wt% Pt/C for the oxidation of pyridine-derivative alcohols. The catalyst showed different activity towards various substituted alcohols. The choice of solvent influenced massively the overall catalyst performance in terms of activity and product distribution. The problem of Pt- group metals being poisoned by N-containing compounds has been highlighted. Findings reported by Besson are described in detail in Chapter 5, where they were then contrasted to the experimental results obtained in the oxidation of 3-pyridinemethanol using Au-Pd supported nanoparticles.

1.4.3. Alkene epoxidation: *trans*-stilbene

Supported nanoparticles of precious metals have been shown to be efficient not only in the selective oxidation of alcohols but also in the oxidation of alkenes. Epoxides are important intermediates used in various syntheses on the industrial scale. One model reaction is the oxidation of *trans*-stilbene.

Lignier *et al.*[65] tested heterogeneous Au/TiO_2, Au/Fe_2O_3 and Au/C catalysts in the process of *trans*-stilbene epoxidation under atmospheric pressure of air at 80 °C. Pt/ C was found to be inactive under these conditions and Au/TiO_2 showed the highest activity among tested catalysts. The authors investigated the effect of the solvent and they reported its significant influence on the course of the reaction. Au/TiO_2 tested in toluene and acetonitrile yielded less than 5 % epoxide while in methylcyclohexane the yield to epoxide was 53 %. The researchers proved a free-radical mechanism of the studied reaction by carrying out a set of experiments. In the first experiment, the oxidation of *trans*-stilbene was performed in the absence of TBHP which resulted in no conversion (less than 1 % epoxide). In the next experiment, 5 mol% TBHP was used instead of 400 mol% which resulted in significantly decreased conversion. In the last experiment, the reaction has been carried out with the addition of radical scavenger, which led to less than 5 % trans-stilbene oxide in 24 h. The researchers proved that the molecular oxygen from the air is necessary as less than 5 % *trans*-stilbene oxide has been obtained in the reaction carried out under argon (in standard conditions). Moreover, it was noted that oxygen activation is related to the nature of the solvent as the epoxidation of *trans*-stilbene involves a co-oxidation of the solvent (methylcyclohexane).

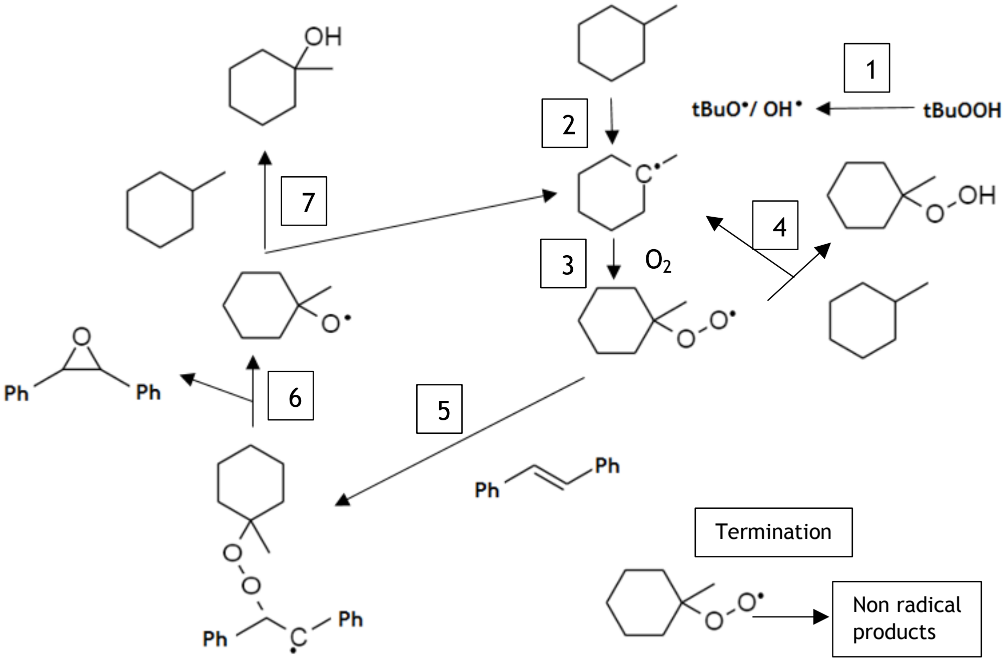

Figure 1-10 *Mechanism for the oxidation of trans-stilbene in methylcyclohexane proposed by Lignier et al.*[65]

The scientists proposed the following mechanism that has also been shown in figure 1-10: Initiation- thermolysis of TBHP (1) → Formation of the methylcyclohexyl radical (2) → Propagation- formation of the methylcyclohexyl peroxy radical (3) → Reaction with *trans*-stilbene (5) → Regeneration of the methylcyclohexyl radical and then methylcyclohexyl hydroperoxide (4) → Decomposition: formation of the epoxide and a methylcyclohexoxy radical (6) → Abstraction of the tertiary hydrogen from methylcyclohexane to produce methylcyclohexan-1-ol and regeneration of the methylcyclohexyl radical → Termination: *via* recombination of the peroxo radicals.

Direct addition of hydroxyl radicals to *trans*-stilbene is also possible in excess of TBHP. The researchers performed another experiment where instead of TBHP, H_2O_2 has been used obtaining 30 % conversion however no epoxide was detected. This indicated that the excess of hydroxy radicals (also in case of TBHP) led to an unselective degradation process in which products of a total oxidation such as CO_2 have been detected. Therefore, the selective epoxidation reaction was induced by the *tert*-butoxy radical.

The same group tested Au/TiO_2 in the oxidation of both forms, *trans*-stilbene and *cis*-stilbene.[66] Interestingly, the produced epoxide was formed always in *trans* form. This was explained by adsorption effects to a solid surface where steric hindrance forces the formation of specific products by decreasing symmetry and accessibility of the molecule. The group carried out the reaction using 50 ppm of free gold and they reported its inactivity towards epoxide formation which indicated that the reaction was heterogeneous. Moreover, it was suggested that both gold and titania take part in the mechanism, by trapping the unselective hydroxyl radicals, catalysis of radical formation and stabilisation the intermediate (adduct of the methylcyclohexyl peroxy radical to the *trans*-stilbene).

Lignier *et al.*[67] extended their research on *trans*-stilbene epoxidation using 1.5 %Au/TiO_2 with systematic studies of solvents and radical initiators. The applied conditions remained the same: 80 °C, 24 h, and atmospheric air pressure. Three radical initiators were tested: tert-Butylhydroperoxide (70 % TBHP in H_2O), di-tertbutylperoxide (98 % DTBP) and hydrogen peroxide (29-32 % H_2O_2 in H_2O). It can be seen from table 1-6 that di-tertbutylperoxide and hydrogen peroxide degraded about 20 % of *trans*-stilbene. TBHP has been found to be an effective radical initiator for the oxidation of *trans*-stilbene.

Table 1-6 *Influence of radical initiators on the oxidation of trans-stilbene in methylcyclohexane.*[67]

Entry	Peroxide	Catalytic properties		
		Conv. (%)	Yield (%)	Sel. (%)
1	TBHP	42	27	64
2	DTBP	20	0.5	3
3	H_2O_2	24	0.5	2

Conditions: trans-stilbene, 1 mmol; solvent, 20 ml; Au/TiO_2, 27+/- 2 mg/ 2.1+/- 0.2 µmol Au; TBHP, 0.05 mmol; air, atmospheric pressure; temperature, 80 °C; time, 24 hours.

The researchers drew interesting conclusions based on the solvent studies presented in table 1-7.

Table 1-7 *Influence of solvent on the oxidation of trans-stilbene.*[67]

Entry	Solvents	Catalytic properties (%)		
		Conversion	Yield	Selectivity
1	n-Heptane	13	2.4	19
2	Cyclohexane	1.6	1	61
3	Methylcyclohexane	42	27	64
4	1,3-Dimethylocyclohexane	67	43	63
5	1,4-Dimethylocyclohexane	63	41	65
6	Toluene	3.2	2	61
7	1-Methylpiperidine	0.2	<0.1	-
8	Piperidine	3.1	<0.1	-
9	Benzyl alcohol	2.1	0.2	9.5
10	Acetophenone	5.6	1.7	31

11	Propionitrile	9.4	4.7	50
12	Dimethylformamide	3.7	0.4	10
13	Acetonitrile	3.8	2.5	67
14	Dimethylsulfoxide	6.7	<0.1	-

Conditions: trans-stilbene, 1 mmol; solvent, 20 ml; Au/TiO2, 27+/- 2 mg/ 2.1+/- 0.2 μmol Au; TBHP, 0.05 mmol; air, atmospheric pressure; temperature, 80 °C; time, 24 hours.

It can be noted, that only mono- and di-substituted cyclohexanes are efficient as solvents to achieve high yields of epoxide. Polarity does not seem to play a significant role. The researchers suggested that the molecular structure of the solvent, especially the presence of tertiary alkyl groups enables to obtain higher epoxide yields. Keeping in mind that epoxide formation was associated with partial oxidation of the solvent molecule (tertiary C-H bonds: 1-Methylcyclohexanol, 1,3-dimethylcyclohexanol and 1,4-methylcyclohexanol) it was stated that the epoxidation process and the oxidation of the solvent are interconnected.

The group decided to investigate the anatase titania morphology in gold catalysts on the epoxidation of *trans*-stilbene.[68] Three kinds of TiO_2 with similar surface areas have been tested: AK350 (less hydroxylated), UV100 and PC500. All tested catalysts showed similar selectivity, however with a different overall yield of the epoxidation of stilbene. Au catalysts supported over PC500 and UV 100 have been found to be more active than when supported over AK500 due to the presence of titanol groups. Moreover, the researchers linked the higher activity of Au/ UV100 to the presence of boron and its possible role as a promoter. It has been shown that UV100 is more suitable support in the oxidation of stilbene by gold than TiO_2-P25.

Fkiri *et al.*[69] tested unsupported monodisperse gold octahedra in polyol (PVP K30 as a stabilizing agent) using an excess of TBHP as oxidant in the selective oxidation of *trans*-stilbene. 1,3-propanediol served as both solvent and reducing agent. The addition of a small amount of surfactant played a significant role in this process. It was reported that the carbon balance was only 5 % for the uncatalyzed reaction which means that 95 % of the substrate has been changed into total oxidation products. The other reported product was benzaldehyde (around 3 % yield), no epoxide was observed. The researchers stated that their method of gold nanoparticles synthesis utilizing PVP coupled with 1,3-propanediol allows to control the shape and monodispersity. A low PVP/Au molar ratio R=0.03 has been suggested to be optimal for the oxidation of *trans*-stilbene (table 1-8).

Table 1-8 *Influence of a stabilizing agent on the oxidation of trans-stilbene.*[69]

R(PVP/Au)	Induction period [min]	Conversion (%)	Benzaldehyde yield (%)	Epoxide yield (%)
0.025	400-500	66	7	Below 1
0.035		62	7	
0.02		50	7	
0.045		50	7	
0.015	no	82	15	40
0.03	no	66	15	40

Conditions: trans-stilbene, 1mmol; Au colloidal solution in ethanol, 2 ml/2 µmol Au; methylcyclohexane, 18 ml; TBHP, 909 µl of the 5-6 M decane solution/ 5 mmol; air, atmospheric pressure; temperature, 80 °C; time, maximum 97 hours.

Caps and co-workers[70] designed and developed a reference catalyst that is suitable to be used in apolar media. $Au(PPh_3)Cl$ was employed as a gold precursor in three different protocols of catalyst synthesis. Commercially available silica functionalized with dimethylsiloxane, Aerosil R972 was successfully used as a hydrophobic support. Enhanced wettability of the catalyst in the organic solvent leading to minimal diffusion limitations allowed to obtained high yield in *trans*-stilbene epoxidation as opposed to the gold nanoparticles supported over TiO_2 (table 1-9, Protocol no 2 has been shown). Moreover, the catalyst can be easily scaled-up to 5 g and more.

Table 1-9 *Influence of support on the oxidation of trans-stilbene using Au nanoparticles (catalysts prepared by Protocol 2).*[70]

Support	24 h		72 h	
	Conver. (%)	Sel. (%)	Conver. (%)	Sel. (%)
Aerosil R812	25	60	>60	>60
Aerosil R972	53	74	97	73
TiO_2 (P25)	36	56	50	82

Conditions: trans-stilbene, 1 mmol; Au catalyst, 1 µmol; methylcyclohexane, 20 ml; tert-butyl hydroperoxide, 0.05 mmol/7 µl of a 70 % TBHP in water; temperature, 80 °C; air, atmospheric pressure.

In their next work, the group focused on determining a key reaction intermediate in aerobic epoxidation of *trans*-stilbene in methylcyclohexane using optimised Au/SiO_2-R972 catalyst.[71] The researchers monitored the concentration of 1-methylcyclohexyl hydroperoxide (GC–MS in SIM (selective ion monitoring) mode by triphenylphosphine titration followed by ^{31}P NMR) and found that the autoxidation and epoxidation pathways co-exist in the process. Moreover, it was noted that 1-methylcyclohexyl hydroperoxide accumulates during the reaction. It was suggested that the Au catalysed decomposition of hydroperoxide might be the limiting step in the oxidation of *trans*-stilbene in methylcyclohexane.

Crites *et al.*[72] carried out epoxidation of *cis*-stilbene in cumene using Au/TiO_2. The reactions were performed at 80 °C, for 24 hours, using TBHP as a radical initatior. Interestingly, the formation of two forms of oxides, *cis*- and *trans*-stilbene oxide, have been reported (table 1-10).

Table 1-10 *Oxidation of cis-stilbene in cumene.*[72]

Catalyst	**Conversion (%)**	**Yield *trans*-stilbene oxide (%)**	**Yield *cis*-stilbene oxide (%)**
Au/ TiO_2	18.7	16.3	2.6
TiO_2	48	0	0
No catalyst	0	0	0

Conditions: temperature, 80°C; time, 24 h; 0.5 mmol cis-stilbene; cumene, 10 ml; AuNO@TiO_2.

Electron Paramagnetic Resonance (EPR) spin trap technique was employed to identify the radical species. It can be seen from table 1-10 that oxides were obtained only when the catalyst was used. Previous work[73] of this group provided the proof that peroxyl radicals can be decomposed on the surface of gold nanoparticles leading to the formation of surface-oxygen species. Based on that and on the activity data, the researchers put forward the hypothesis that a cumyl peroxyl radical can decompose on the Au nanoparticles surface followed by an electron transfer from *cis*-stilbene to the oxygen bound Au nanoparticle adduct (figure 1-11). The reported epoxide stereochemistry would be a result of the suggested mechanism.

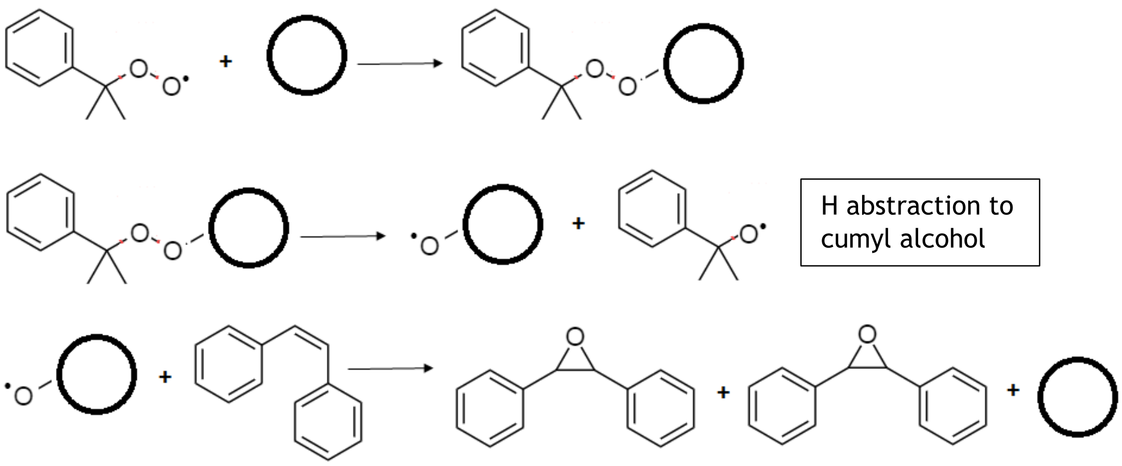

Figure 1-11 Mechanism for the epoxidation of cis-stilbene using Au nanoparticles proposed by Crites et al.[72]

The proposed pathway is in contradiction with previous literature reports regarding the direct involvement of a free peroxyl radical in the attack and epoxidation of stilbene.

1.5. Synergy between Au and Pd

It has been shown above that bimetallic Au-Pd supported catalysts have been found to be superior to their monometallic counterparts in the oxidation of cinnamyl alcohol. However, this synergistic effect between Au and Pd has been observed for several other reactions which have been briefly described below.

The desired product in the oxidation of benzyl alcohol is benzaldehyde, a common food and perfume additive (almond flavour and aroma), and also a precursor to the wide range of chemicals.[74] Hutchings and co-workers carried out thorough research on the oxidation of benzyl alcohol using Au, Pd and Au-Pd heterogeneous catalysts prepared by different methods, immobilized on different supports, applying various conditions.[17], [18], [82], [83], [20], [75]–[81] In general, the most active catalysts for the oxidation of benzyl alcohol were prepared by sol-immobilisation method (1 % Au-Pd/TiO_2 showed 70 % conversion and 80 % selectivity after 3 hours under 1 bar O_2 at 120 C)[78]. As an example of enhanced yield to benzaldehyde using bimetallic Au-Pd system, the work of Enache *et al.*[84] has been presented in the table 1-11 below.

Table 1-11 *Oxidation of benzyl alcohol and direct synthesis of hydrogen peroxide using bimetallic Au-Pd supported catalysts.*[84]

Catalyst	**Benzyl alcohol oxidation**					**H_2O_2 synthesis**
	Conversion (%)		**Selectivity (%)**		**Productivity [mol/(hour/kg$_{cat}$)]**	**Productivity [mol/(hours/kg$_{cat}$)]**
	0.5 hour	**8 hours**	**0.5 hour**	**8 hours**		
2.5%Au-2.5%Pd/Al_2O_3	2.6	83.3	90.5	86.6	174	23
2.5%Au-2.5%Pd/TiO_2	3.7	74.5	95.2	91.6	165	64
2.5%Au-2.5%Pd/SiO_2	3.6	35.7	97.3	88	76	80

2.5%Au-2.5%Pd/Fe_2O_3	3.6	63.4	74.9	66.4	102	16
2.5%Au-2.5%Pd/C	2.9	69.2	53.9	46.4	78	30
2.5%Au/TiO_2	0.6	15.3	96.7	63.9	24	<2
2.5%Pd/TiO_2	13.4	60.1	51.3	54.4	79	24

Conditions: temperature, 100 °C; oxygen, 0.2 MPa; catalyst

The catalysts have been prepared by impregnation method, followed by calcination process during which the segregation of the metals occurred leading to a Pd-rich shell and Au-rich core. The researchers suggested that some Au atoms were still present at the surface based on the activity data indicating that Au is more than just a Pd promoter and the enhancement is related to bifunctional active sites. Moreover, it can be seen from table 1-11 that the support plays a significant role and its optimization can improve the overall yield of the catalytic process. In this case, the most efficient support has been found to be TiO_2 compared to the Al_2O_3 and Fe_2O_3 supports. The researchers linked the inferior behaviour of the latter oxides with their acidic character leading to enhanced by-product formation. The group proved in their other publications[85]-[87] that simply by changing support from TiO_2 to MgO or ZnO, it is possible to switch off the formation of toluene as a side reaction in the oxidation of benzyl alcohol. Moreover, as they showed later, the addition of Pt to the supported AuPd nanoparticles switches off the formation of toluene immediately.[88] The researchers hypothesised that the reason for that lies in the relative stability of Pt hydride compared to Pd hydride. The characterisation of this trimetallic catalyst revealed the presence of a homogeneous nanoalloy.

Another process where bimetallic Au-Pd system has been employed is glycerol oxidation.[89], [90] Glycerol is a by-product of biodesel production, one of the major alternatives to petroleum fuels. Glycerol is a highly functionalized molecule that can be used as a platform chemical for the synthesis of fine chemicals and pharmaceuticals.[26], [91]-[94] However, the current supply of glycerol greatly outstrips demand and therefore its transformation into other useful compounds is of great academic interest. Prati and co-workers[89] designed and synthesised 1% Pd@Au/C catalyst with homogeneous alloy by two step synthesis: preformed metallic sol of Au was immobilised on carbon followed by deposition of Pd. EDX and HRTEM techniques confirmed no phase segregation, random character of Au-Pd alloy, and metal ratio Au-Pd being 6: 4. The catalyst has been tested in the oxidation of glycerol and it was reported that TOFs measurements showed a six fold increase from about 1000 h^{-1} for monometallic to 6400 h^{-1} for bimetallic. The researchers linked enhanced activity with homogeneous alloyed phased. Moreover, it was highlighted that the increase in selectivity of the bimetallic system was significant with respect to monometallic Au and close to the selectivity of monometallic Pd. In terms of conversion, the worst performance was demonstrated by monometallic Pd, whereas bimetallic and Au were more active. It was suggested that deactivation of Pd was caused by poisoning. It was also suggested that Au-Pd bifunctional sites were responsible for the enhancement in catalytic activity as the number of Pd and Au monomers decreased. The researchers linked their results with the report about active sites for CO adsorption[95] determined at the edge of Au islands on Pd(111) surface. Therefore, the overall improved activity should be considered a result of two effects: electronic and geometric. A year later, the group published their further findings.[90] A series of catalysts with various Au-Pd metal ratio (9.5:0.5, 9:1, 8:2, 6:4, and 2:8) were prepared in the same way as described above. The characteristic studies have been correlated with the oxidation of glycerol to glyceric acid. The synergistic effect has been observed based on the activity data (figure 1-12). The most active catalyst was the 9: 1 ratio of Au-Pd.

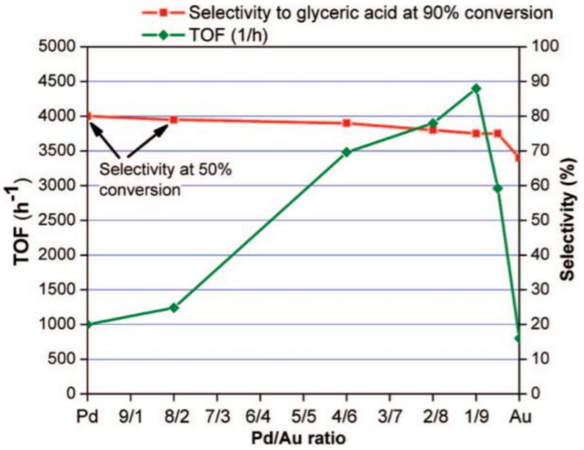

Figure 1-12 *Influence of Au-Pd metal ration on the oxidation of glycerol.*[90]

In general, all tested catalysts had similar particles sizes. Pure Au and Au-rich catalysts showed multiply twinned structure with mainly (111) surfaces and occasionally (100); good Pd dispersion was observed. However, in the monometallic Pd catalyst, Pd-rich 2Au: 8Pd and 9.5Au:0.5 Pd, the researchers noticed irregularities in shape. They pointed to the fact that the surface Au-Pd ratio can be different from the nominal calculated value simply due to an insufficient number of atoms, for example 2 Au: 8Pd, hence Pd segregation is expected. The scientists linked high catalytic activity with uniformed alloyed bimetallic particles observed in Au-Pd 9:1, 8:2, and 6:4 ratios. The inhomogeneity of Pd in other studied ratios was indicated as a reason of inferior activity due to depletion of isolated Pd monomer sites. Many other scientific reports confirmed the validity of the hypothesis about greatly enhanced catalytic activity of the highly dispersed Pd sites diluted with Au.[96]–[98]

Hydrogen peroxide has been known for years as a domestic chemical used mostly as a bleach and disinfectant. For chemists, hydrogen peroxide is an excellent oxidant, considered as green oxidant, hence widely used in the production of fine chemicals. The major problem of the currently used anthraquinone process used for production of hydrogen peroxide is the generation of harmful wastes: oxanthrones and anthrones, and also the requirement for this process to be conducted on large scales.[99] The direct synthesis of hydrogen peroxide from O_2 and H_2 is therefore of great academic and industrial importance. Active catalysts used for the direct synthesis of H_2O_2 are effective hydrogenation catalysts (hydrogenation of oxygen). This fact implies the consequences of further hydrogenation of hydrogen peroxide to water.[100] Initially, the direct synthesis of hydrogen peroxide from H_2 and O_2 has been investigated with the use of catalysts containing mostly Pd. Growing interest in the catalysis of gold has led to breakthrough discoveries for the discussed process. It was reported that only a small amount of added Pd is enough to significantly increase the activity of Au catalysts (table 1-11).[84], [90]

The great advantage of bimetallic Au-Pd catalysts over monometallic Pd catalyst is the fact that no promoters (e.g. halide, acid) are needed to obtain high rates and high concentrations of hydrogen peroxide formed. Extensive research is being undertaken by many groups to improve the direct synthesis of hydrogen peroxide by Au-Pd nanoparticles.[24], [101]–[106]

Carter *et al.*[107] contrasted reactions for which addition of Au to Pd leads to a synergistic effect (such as mentioned earlier) with the reactions that Au-Pd shows anti-synergy such as CO oxidation. The case of CO oxidation using bimetallic Au-Pd system is confusing because there are a lot of theoretical reports[108], [109] that predict high activity of the system, however experimental reports[110], [111] seem to be in contradiction with theoretical works. The authors noticed that electronic effect is presumably responsible for the synergistic effect for alcohol oxidations and hydrogen peroxide synthesis which does not play a role in the oxidation of CO. CO Diffuse Reflectance Infrared Fourier Transform Spectroscopy (CO-DRIFTS) and X-ray Photoelectron Spectroscopy (XPS) techniques were used to determine the active sites which were called rather *active centres* due to their structure: metal atoms placed at the periphery of the nanoparticles placed closely to adsorption sites on the support material. Therefore, enhancing this interface by optimisation of support and maximizing by using nanoparticles is a way to design highly active catalysts. In view of these observations, the addition of Pd to Au system in the oxidation of CO is not beneficial due to the formation of less active Pd sites at the metal-support interface.[107]

Based on the presented processes, the synergy of the Au-Pd nanoparticles is clearly visible. Metal ratio, coordination and electronic configuration plays an enormous role in nanoparticles catalytic activity. Understanding of the synergistic effect at atomic level would enable conscious and targeted optimization/tuning of catalysts. However, the origin of this phenomenon is still not clear and is under debate.[21], [84], [112] The literature reports suggest that the synergy of Au and Pd is caused by two effects: ensemble and ligand effects. The ensemble effect is simply related to the dilution of one metal by another, e.g. more active Pd diluted by less active Au. Therefore, isolated Pd can form active sites on increased surface. Moreover, side reactions are limited due to absence of Pd ensembles which improves selectivity. The ligand effect is related to the electronic interaction between Au and Pd (by charge transfer or by changing in bond lengths).[21]

Petkov *et al.*[113] studied Au-Pd nanoparticles supported on carbon for CO oxidation in the context of the synergy between Au and Pd (using resonant High-Energy X-ray Diffraction (HEXRD). The researchers supported their experimental work also with theoretical DFT calculations based on a refined version of d-band centre theory. They reported that the activity enhancement is due to formation a specific "skin" on top of the nanoalloys involving atomic pairs. Their research confirmed previous reports about electronic effect of Au and Pd in the outer layer: Au atoms shrink and acquire a partial positive charge of 5d-character whereas Pd atoms expand and become 4d-electron deficient. The reactivity of Au increases whereas Pd atoms become less reactive, hence some reactions are intensified and some reactions are limited (side reactions caused by Pd).

Detailed investigation of d- band centre theory allows for deeper understanding the phenomenon of metals catalytic activity. The mechanism of reactions utilizing metals as catalysts is described in the literature as breaking bonds between valence electrons at the Fermi level of surface metal atoms and frontier orbitals of reactants. Therefore, the catalytic properties of metals and their alloys depend on the number and character of valence electrons at the Fermi level. It is possible to calculate the valence electrons available for bonding for Au and Pd knowing their number of the respective row in the periodic table (m) and applying to the formula: md, (m+1)s and (m+1)p. Thus, the electron configuration for Au is 5d10s1(11 valence electrons altogether) and for Pd is 4d10s0 (10 valence electrons). It was noted that at the bulk scale sp-d hybridization occurs which pushes into higher-energy s and p states a small number of the valence d electrons of Pd and Au. As a result, bulk Pd has actual valence electron structure: $4d^{9.4}5(sp)^{0.6}$ and the actual valence structure for Au is: $5d^{9.6}6(sp)^{1.4}$ Valence electrons of s- and p-character and their interactions with the adsorbate orbitals are fairly similar for all transition metals with regard to bonding. Valence electrons of d-character in metals show differences in binding. Moreover, it has been shown that the catalytic activity and selectivity of transition metals, including Au, Pd and their alloys, are influenced by sp-d hybridization, width and position of d-electron bands with respect to the Fermi energy. From this point of view, the low reactivity of Au can be explained by the fact that its 5d band is fully occupied and positioned below the Fermi energy, hence the valence electrons of 5 d- character responsible for chemisorption are inaccessible. Following this path, the 4d band of Pd extends through the Fermi level hence strong chemisorption bonds can be easily formed, which explains high reactivity of Pd. [21], [113], [114]

Gao and Goodman[21] explained catalytic activity of Au-Pd system by combined ensemble and ligand effects: Au gains 6(sp) electrons and loses 5d electrons, whereas Pd loses 5(sp) electrons and gains 4d electrons. Chemisorption and catalytic properties of transition metals (including Pd and Au) are determined rather by the d-character than s,p-character, hence in case of Pd gaining d electrons shifts the d band centre away from the Fermi level. The authors linked this fact to enhanced activity as “self-poisoning” is eliminated by weaker binding of reactants and products to Pd. Interestingly, catalytic activity of diluted Pd with Au is close to the catalytic activity of pure Pd.[21] The observations and activity data based on model reactions have been supported by theoretical calculations.[112], [115], [116]

In summary, it has been shown that the size of nanoparticles, their shape, interaction with the support and oxidation state determine the catalytic performance. Morphology of nanoparticles seems to be crucial element to understand, as it massively influences the activity and selectivity nanometals by affecting the availability of active sites, binding strength of reactants, metal-support interaction, and both electronic and geometric effects. Another issue would be determination of nanoparticles interaction under realistic reaction conditions. There is a possibility that morphology may change during a reaction due to high temperature or interactions with the reactants in an unexpected and unpredictable way which means that the state of the catalyst during a reaction is different than that determined by characteristic techniques before and after a reaction. Development of operando and in-situ techniques coupled with experimental chemistry seems to be necessary to fully understand the dynamic nature of supported heterogeneous nanoparticles.[117]–[120]

1.6. Autoxidation

Oxidation reactions are used to produce all kinds of chemicals, from fine chemicals, through additives to food, to pharmaceuticals. Oxidations performed with the use of supported nanoparticles of noble metals are characterized by two features: conversion and selectivity. Currently, research is focused on achieving the highest possible conversion and selectivity, which is very often linked to the catalyst design, such as particle size, nanoalloy formation and metal-support interaction. The lack of selectivity in catalytic process is a complex issue. One of the reasons of low selectivity (apart of the catalyst itself and active sites issue) in oxidation reactions is related to the presence of oxygen and presence of radical species very often leading to the side-reactions or autoxidation processes.[121]

Autoxidation is not always an undesirable process. Partial oxidation of hydrocarbons, autoxidations, mediated by free radical intermediates are challenging reactions in an industry. Examples of this type of processes used deliberately in bulk scale are: the oxidation of *p*-xylene to terephthalic acid (44×10^6 tons per year), the oxidation of cyclohexane to cyclohexanol and cyclohexanone (6×10^6 tons per year), and the synthesis of ethylbenzene hydroperoxide (6×10^6 tons per year).[122]

Oxidation of cyclohexane is especially interesting as the products, cyclohexanol and cyclohexanone (figure 1-13), are precursors of nylon-6,6 and nylon-6 respectively. The reaction is performed industrially at elevated temperature (140 °C) using Co(II)-naphthenate, Co(II)-$(acac)_2$ or Fe(III)-$(acac)_3$ and the conversion is deliberately maintained at around 4-5 %. The reason for that is to maintain selectivity to alcohol and ketone above 85 % and to limit the formation of by-products. The catalyst Co(II)-naphthenate acts rather as a promoter of a free radical autoxidation pathway (in a Haber-Weiss cycle), hence selectivity is almost impossible to control at higher conversion. [121], [123], [124]

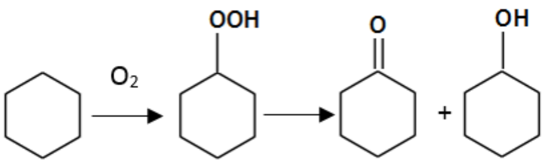

Figure 1-13-*Scheme for the autoxidation of cyclohexane using air and metal salts proposed by Hermans et al.*[105]

Another benchmark reaction is oxidation of the renewable olefin α-pinene, the products of which (figure 1-14) have found applications in the fragrance and flavour industry. For example, the epoxide is the starting material for the synthesis of sandalore (Givaudan) and polysantol (Firmenich)- sandalwood-like aroma.[122], [125]

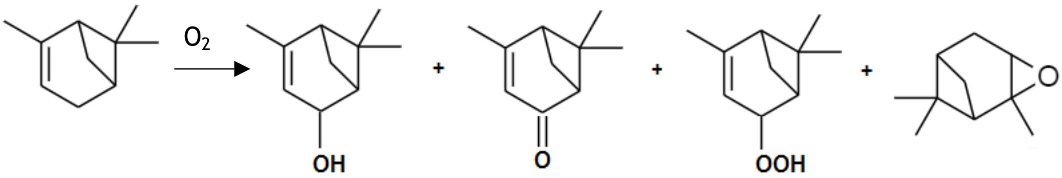

Figure 1-14 *Scheme of the thermal a-pinene oxidation proposed by Hermans.* [103]

Also oxygenated compounds such as aldehydes can be subjected to autoxidation. The aerobic oxidation of valeric aldehyde (*n*-pentanal) leads to the formation of valeric acid (*n*-pentanoic acid) applied in the production of lubricants, PVC stabilizers and fragrances (scheme 1-15). The scale of this process is about 2×10^4 t/a worldwide.[126]

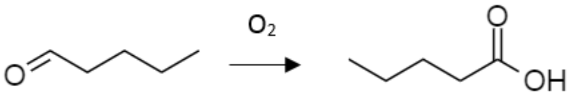

Figure 1-15 *Thermal autoxidation of valeric aldehyde.*[126]

The autoxidation pathways are possible thanks to the *diradical* nature of molecular oxygen. O-O bond is relatively weak (about 40 kcal $mol^{-1)}$ and can be thermally activated at elevated temperatures. Therefore, several activated oxygen species can be present over heterogeneous oxides supported catalysts, such as O_2 (adsorbed or peroxide group), O^{2-}(oxide anion), O_2^{2-} (peroxide anion), and O_2^- (superoxide).[121], [126]

A general oxidation mechanism *via* radical chain[126] has been shown in figure 1-16, which can be summarized in a few steps: 1a,b) Initiation of a dialkylperoxide (ROOR) or a hydroperoxide (ROOH) with a substrate molecule (RX) → 2) formation of alkoxyl (RO•) and alkyl (R•) radicals → 3,4) abstraction of hydrogen from the substrate and generation an alkyl radical → 5) termination[126]

1a) $ROOR \rightarrow 2\ RO\bullet$ 1b) $ROOH + RH \rightarrow RO\bullet + H_2O + R\bullet$
2) $R\bullet + O_2 \rightarrow ROO\bullet$
3) $ROO\bullet + RH \rightarrow ROOH + R\bullet$
4) $RO\bullet + RH \rightarrow ROH + R\bullet$
5) $ROO\bullet \rightarrow ROH + Q{=}O + O_2$

Figure 1-16 *General mechanism of autoxidation proposed by Neuenschwander and Hermans.*[126]

It has been shown in this brief review that autoxidation is a valued process in industry. However, its presence is very often negligible or overlooked during catalytic studies. Conte *et al.*[127] investigated the mechanism of benzyl alcohol oxidation by unsupported and supported Au nanoparticles. The researchers employed Electron Paramagnetic Resonance (EPR) spectroscopy and spin trapping to confirm the formation of Au-H intermediates formed as the effect of C-H cleavage in the alcohol molecule. C-H bond cleavage has been pointed as a rate determining step occurring *via* transfer of either a hydrogen atom or hydride. The role of oxygen was identified as a catalyst activity regenerator (removing H from the catalyst surface) rather than direct oxidant. Also, the support was found to play a role as an oxygen activator, which facilitates faster restoration of the supported catalysts as opposed to unsupported Au. Nevertheless, the most interesting finding proved the existence of autoxidation products during the catalytic oxidation of benzyl alcohol by Au. Despite the minor character of the observed process and very little amount of formed by-products, reported peroxyl radicals were in line with a free radical autoxidation mechanism. This work confirmed the co-existence of two mechanisms: catalytic and radical (figure 1-17). The mechanism of alcohol formation is in line with the classical dehydrogenation mechanism and formation of free peroxyl radicals is much slower than hydride transfer, hence the catalytic reaction is dominant.[127]

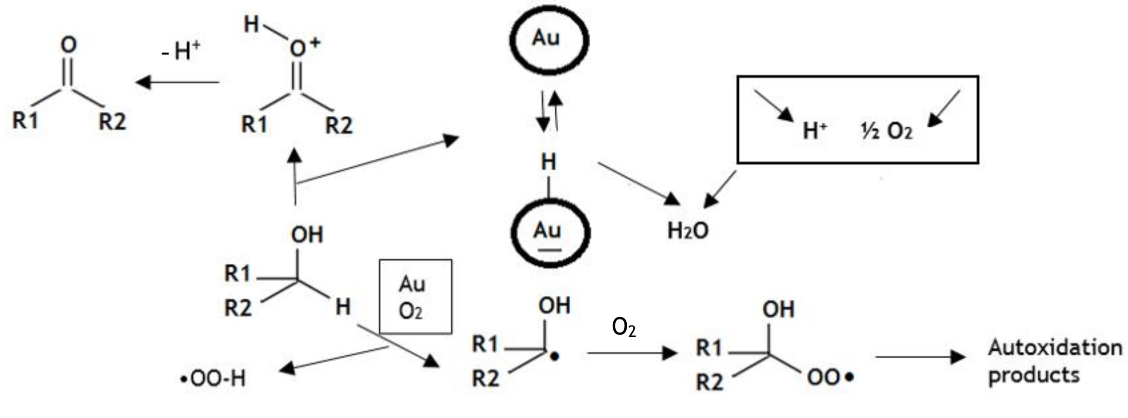

Figure 1-17 *Mechanism for the oxidation of alcohols catalysed by Au proposed by Conte et al.*[127]

In summary, transition metals have been found to be extremely active catalysts in oxidation reactions especially coupled with molecular oxygen as an oxidant. However, activated oxygen at elevated temperature and in the presence of metals can produce trace amounts of peroxides. This fact can cause further consequences in regard to the selectivity and mechanism of the process. Oxidation reactions are complex, and every factor should be taken into consideration during catalytic studies, even autoxidation pathways, to gain unadulterated insight into the process.

The above oxidation reactions are currently performed industrially using stoichiometric toxic oxidants such as permanganates and chromates. Bimetallic Au-Pd catalysts have been found to be extremely active for the oxidation reactions carried out in line with green chemistry rules. The reactions described in the literature are usually performed at low temperatures for long times which is undesirable from an industrial point of managing energy. Supported precious metal catalysts will be employed under elevated, industrially relevant temperatures with the aim of high activity and selectivity over shorter reaction times. The catalysts will be tested for a range of substrates with regards to their chemical reactivity and stability.

1.7. Aims of the study

The aim of this project is to utilize bimetallic Au-Pd supported nanoparticles inspired from recent advances in field of heterogeneous catalysis for the production of value-added chemicals in industrially relevant conditions, in a green and sustainable manner.

The first reaction to be investigated is the oxidation of cinnamyl alcohol to yield cinnamaldehyde carried out in toluene in the absence of any additives under autoxidation conditions. The third chapter contains a detailed study of both catalytic and radical pathways.

The fourth chapter examines the effect of Au-Pd ratio on cinnamaldehyde yield.

In the fifth chapter, the oxidations of trans-stilbene and 3-pyridinemethanol will be carried out to investigate the effect of the chemical nature of the substrate on the catalytic activity of Au-Pd supported nanoparticles. Trans-stilbene is an example of alkenes and the desired product is trans-stilbene oxide. The Au-Pd system is also studied in the oxidation of N- containing and chemically stable 3-pyridinemethanol to yield 3-pyridinecarboxyaldehyde. The reaction has been described in the literature as challenging due to rapid deactivation of Pd catalysts, hence alloying Au with Pd is investigated.

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Chapter 2

2. Experimental

2.1. Chemicals

Listed below chemicals were used as received:

- Cinnamyl Alcohol (98 %, Sigma Aldrich)
- Cinnamaldehyde (Sigma Aldrich)
- 3-Phenyl-1-propanol (Sigma Aldrich)
- Methylstyrene (Sigma Aldrich)
- Styrene (Sigma Aldrich)
- 3-Phenyl-1-propanol (Sigma Aldrich)
- Benzaldehyde (Sigma Aldrich)
- Benzoic Acid (Sigma Aldrich)
- Toluene (HPLC grade, Fisher Scientific)
- Water (HPLC grade, Fisher Scientific)
- Titania (Degussa P25)
- Sodium Borohydride (98 %, Sigma Aldrich)
- Palladium Chloride (Johnson Matthey)
- Hydrogen tetrachloroaurate (III) hydrate (49% Au assay, Strem)
- Activated Carbon
- Mesoporous silica (Sigma Aldrich)
- Mesoporous alumina (Sigma Aldrich)
- Xylene (HPLC, Fisher Scientific)
- Mesitylene (HPLC, Fisher Scientific)
- 3-Pyridinemethanol (HPLC, Sigma Aldrich)
- 3-Pyridinecarboxyaldehyde (HPLC, Sigma Aldrich)
- Niacin (99 % Sigma Aldrich)
- Trans-Stilbene (99% Sigma Aldrich)
- Trans-Stilbene oxide (99% Sigma Aldrich)
- Benzil (99% Sigma Aldrich)
- Water (HPLC, Fisher Scientific)

2.2. Definitions

Conversion of tested substrates was calculated with the use of following equation (C subA, C subB- represent the substrate concentrations [mol/dm^3] at the beginning of the reaction and at the end of the reaction, respectively):

$$Conversion = \frac{C\ subA - C\ subB}{C\ subA} \text{ x } 100\ \%$$

Selectivity to each compound has been calculated according to the following equation:

$$Selectivity = \frac{C\ compound}{\sum C\ observed\ products} \text{ x } 100\ \%$$

S:m ratio has been evaluated using following formula:

$$s{:}m = \frac{number\ of\ moles\ of\ substrates}{number\ of\ moles\ of\ metal\ on\ catalyst\ used}$$

Turnover frequency (TOF) has been calculated using following formula:

$$TOF = \frac{{}^{moles\ of\ reactant}\!/_{moles\ of\ metal\ in\ catalyst}}{time\ (h)}$$

2.3. Acronyms

Listed below acronyms have been used throughout this thesis:

TOF	Turnover Frequency
PVA	Polyvinyl Alcohol
NMR	Nuclear Magnetic Resonance
SEM	Scanning Electron Microscope
XPS	X-ray Photoelectron Spectroscopy
MP-AES	Microwave Plasma – Atomic Emission Spectroscopy
ICP-OES	Inductively Coupled Plasma – Optical Emission Spectroscopy
GC	Gas Chromatograph/Chromatography
HPLC	High Performance Liquid Chromatography
GC/MS	Gas Chromatography/Mass Spectrometry
FID	Flame Ionisation Detector
MS	Methylstyrene
PP	3-Phenyl-1-propanol
CinnALD	Cinnamaladehyde

BenzACID	Benzoic acid
BenzALD	Benzaldehyde

2.4. Catalyst preparation

Catalysts have been prepared according to the procedures described in papers where oxidation of benzyl alcohol has been studied.[1], [2]

2.4.1. Sol-immobilisation method

The catalysts have been synthesised according to the protocol described by Prati and co-workers.[2]–[5]

For preparation of a 0.50 %Au 0.50 %Pd/TiO_2 catalyst, aqueous solutions of $PdCl_2$ (1.1494 ml, concentration: 4.35 mg/ml) (Alfa Aesar) and $HAuCl_4 \cdot H_2O$ (0.4082 ml, concentration: 12.25 mg/ml) (Strem) were added to deionized water under vigorous stirring, followed by PVA (1wt% aqueous solution, Aldrich, MW= 10,000) (PVA/(Au + Pd) (wt/wt) = 1) and a freshly prepared solution of $NaBH_4$ (0.1 M, $NaBH_4$/(Au + Pd) (mol/mol) = 5). After an hour, the formed nanoparticles were immobilised onto a TiO_2 support by addition of TiO_2 and acidification of the solution to pH=1 with sulphuric acid. The solid was filtered and washed with 800 ml distilled water followed by drying overnight at 110 °C in an oven. The obtained solid was then ground in pestle and mortar. These values were changed accordingly to prepare catalysts with various metal ratios.

2.4.2. Impregnation method

The catalysts have been prepared according to the protocol described by Hutchings and co-workers.[6]–[8]

For preparation of a 0.50 %Au 0.50 %Pd/TiO_2 catalyst, $PdCl_2$ (0.0083 g) (Alfa Aesar) was dissolved in an aqueous solution of $HAuCl_4 \cdot H_2O$ (0.4082 ml, concentration: 12.25 mg/ml) (Strem). TiO_2 (0.99 g) (Evonik, P25) was added to the solution with the addition of small amount of water. The slurry was heated at 90 °C until the consistency of toothpaste was obtained. The paste was dried overnight at 110 °C in an oven after which the solid was ground in a pestle and mortar and calcined in static air at 400 °C for 3 h. These values were changed accordingly to prepare catalyst with various metal ratios.

2.4.3. Modified Impregnation method

The catalysts have been synthesised according to the protocol described by Sankar *et al.*[8]

For preparation of a 0.50 %Au 0.50 %Pd/TiO_2 catalyst, first stock solutions have been prepared. $PdCl_2$ (Alfa Aesar) was dissolved in an aqueous solution of 0.58 M HCl resulting in a Pd concentration of 9 mg/ml. As a precursor of Au, $HAuCl_4 \cdot H_2O$ in water (concentration: 12.25 mg/ml) (Strem) has been used. The requisite amounts of Pd and Au solution were charged into the round bottom flask with the addition of water (to a total volume of 16 ml) and heated in oil bath up to 60 °C under stirring. In the next step, TiO_2 (0.99 g) (Evonik, P25) was slowly added to the solution and heated at 60 °C for another 30 minutes. After that time, the temperature was raised to 90 °C and the slurry was further heated under stirring for 16 hours. Obtained solid powder was ground in a pestle and mortar and calcined at 400 °C in 5 %H_2 in Ar for 4 hours at a heating rate of 10 °C/min.

2.4.4. Alumina grafted SBA-15 support preparation

Alumina grafted SBA-15 support has been prepared according to the protocol described by Landau and Wilson.[9], [10] Aluminium-tri-sec butoxide (14.5 g) was dissolved in anhydrous toluene (100 ml) at 85 °C under stirring. In the next step triethylamine (2.1 ml) and SBA-15 (1 g) have been added to the solution. After 6 hours of stirring the slurry was filtered and dried. Obtained solid was washed with toluene (35 ml) 3 times in total. Subsequently, the solid has been placed in ethanol (318 ml) mixed with small amount of water (1.6 ml) and hydrolysed for 24 hours at room temperature. The slurry was filtered, washed with ethanol (300 ml) and dried under vacuum (0.25 bar) at 50°C on a rotary evaporator. The powder was dried at 110 °C followed by a 3-step calcination sequence with ramp rate 1 °C min^{-1}: 1 hour at 250°C, then 1h at 400°C and finally 4 hours at 500°C. Three grafting cycles have been performed.

2.5. Catalyst Evaluation

2.5.1. Cinnamyl alcohol oxidation

The oxidation of cinnamyl alcohol was carried out in Radleys starfish reactor at 120 °C under an oxygen pressure of 3 bar. Cinnamyl alcohol (0.5 M in toluene, 5 ml) was charged into the reactor, followed by addition of the catalyst (0.01 g). The glass reactor flasks were purged with oxygen 3 times before caps were sealed and placed on the hot plate. The stirring rate was set to 1000 rpm. Following the reaction, a sample of product mixture was centrifuged to separate the catalyst. Samples were diluted with mesitylene as internal standard and analysed by gas chromatography (Agilent Technologies 7820 A) fitted with a CPwax 52 CB capillary column and a flame ionization detector. Conversion and selectivity values are reported within ± 3 % error (calculated as a standard deviation).

2.5.2. 3-Pyridinemethanol oxidation

The oxidation of 3-pyridinemethanol was carried out in Radley reactor at various temperatures under an oxygen pressure of 3 bar. 3-pyridinemethanol (0.5 M in toluene, 5 ml) was charged into the reactor, followed by addition of the catalyst (0.06 g). The glass reactor flasks were purged with oxygen 3 times before caps were sealed and placed on the hot plate. The stirring rate was set to 1000 rpm. The collected mixture of products was centrifuged to separate the catalyst. Samples were diluted with mesitylene as internal standard and analysed by gas chromatography (Agilent Technologies 7820 A) fitted with a CPwax 52 CB capillary column and a flame ionization detector. Conversion and selectivity values are reported within ± 5 % error (calculated as a standard deviation).

2.5.3. Trans-Stilbene oxidation

The oxidation of trans-stilbene was carried out in Radley reactor at various temperatures under an oxygen pressure of 3 bar. Trans-stilbene (0.05 M in methylcyclohexane or cyclohexane, 5 ml) was charged into the reactor, followed by addition of the catalyst (0.06 g). The glass reactor flasks were purged with oxygen 3 times before caps were sealed and placed on the hot plate. The stirring rate was set to 1000 rpm. The collected mixture of products was centrifuged to separate the catalyst. Samples were diluted with mesitylene as internal standard and analysed by gas chromatography (Agilent Technologies 7820 A) fitted with a CPwax 52 CB capillary column and a flame ionization detector. Conversion and selectivity values are reported within ± 5 % error (calculated as a standard deviation).

2.6. Catalyst Characterisation

2.6.1. Scanning Electron Microscopy (SEM)[11]

In the characterization of heterogeneous catalysts, various microscopic methods are used, such as Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM) and Scanning Transmission Electron Microscopy (STEM).

Scanning electron microscopy is a very useful technique for imaging surface microstructures. A simplified diagram of a SEM system is shown in figure 2-1. The idea of this technique is to scan the surface of the sample with an electron beam formed by the electron-optical microscope system. This beam is focused by a system of condenser lenses to be deflected over a rectangular area of the sample surface using scanning coils. The signal from the surface of the sample, usually in the form of secondary or backscattered electrons, reaches the detector consisting of, most importantly, a scintillator and a photomultiplier. The scintillator converts the energy of secondary electrons into light pulses, which are then amplified by a photomultiplier. The signal coming from the detector controls the brightness of the image generated on the monitor.

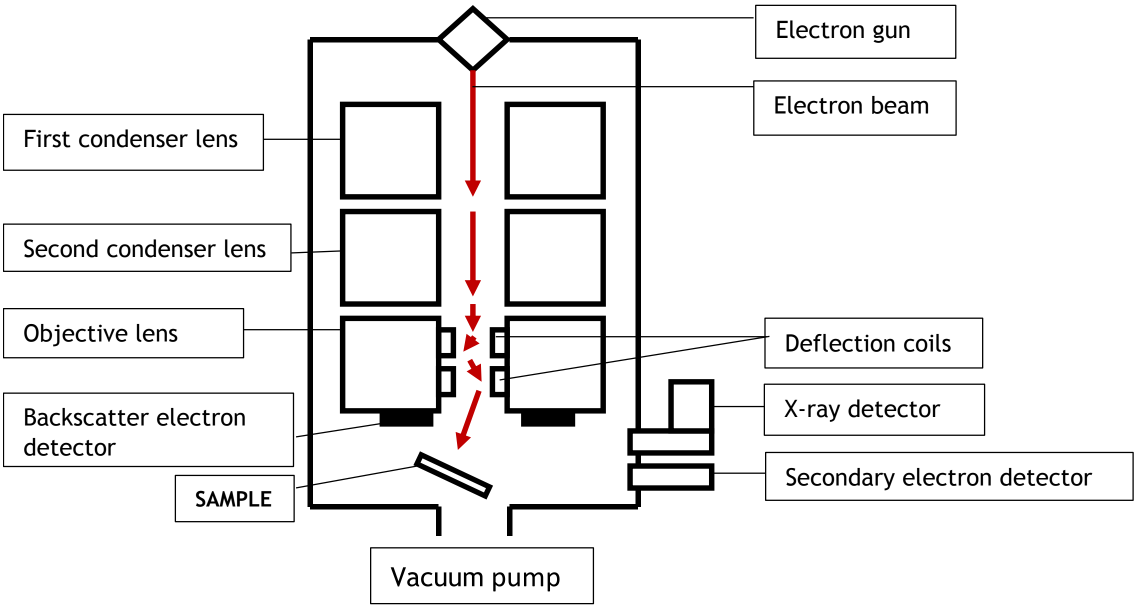

Figure 2-1 *Simplified diagram of an SEM system.*

There are three main types of electron sources used in the electron microscope: tungsten, lanthanum hexagon (LaB_6) and Field Emission Gun (FEG). Usually, an electron beam is emitted from an electron gun fitted with a tungsten filament cathode, heated in a vacuum of 10^{-4} Pa to a temperature of 2800 K, in order to provide electrons with more energy than the work function. When creating the primary electron beam, in addition to the electron source, an electron accelerating field is also needed. The electrons produced by the cathode (source) are accelerated by being attracted by the anode and passing through the hole in it. The typical anode potential for SEM is usually 1-20 kV, and for TEM 100-200 kV (and sometimes even more). The generated electron beam has a wave-particle duality nature.

The interaction between electrons and the sample has the shape of a pear (figure 2-2) and is understood as the interaction volume in which 95 % of the primary electrons have been scattered. A sample made of material with a high atomic number will show a smaller depth of electron penetration compared to a sample made of material with a lower atomic number. Electrons falling on a sample collide with its atoms, resulting in:

- loss of kinetic energy;
- being completely absorbed;
- deflection from the sample;
- emission of radiation;
- penetration through the sample.

Thus, several signals can be obtained from the effect of the primary beam on the sample (figure 2-2): secondary electrons, backscattered electrons, Auger electrons and X-rays.

Secondary electrons (SE) have low energy (conventionally kinetic energy is less than 50 eV), most often knocked out of the atoms closest to the surface of the material in a phenomenon called secondary emission. The number of SE electrons is very large in relation to the number of backscattered electrons. The efficiency of the SE emission strongly depends on the magnitude of the accelerating voltage. There are two subtypes of secondary electrons: SE I - emitted as a result of the interaction of the primary beam with the electrons of the sample; SE II - emitted from electrons of the sample with backscattered electrons.

Backscattered electrons (BSE) are high-energy electrons that have been resiliently reflected and at the same time left the surface of the material with virtually no loss of kinetic energy. The number of BSE electrons is very small in relation to the number of secondary electrons. The efficiency of BSE emission strongly depends on the atomic number. With the increase of the atomic number, the number of emitted backscattered electrons increases. It is possible to estimate the hemispherical region from which backscattered electrons are emitted.

Auger electrons are low energy electrons (100-1000 eV conventionally) emitted as a result of a nonradiometric jump of another electron to a lower electron shell. The excited atom emits excess energy, which can cause the emission of the Auger electron or X-rays. For this reason, the emission of the Auger electron is competitive to the emission of characteristic X-rays and more often occurs in light materials. Auger electrons are not collected in the standard equipment of a scanning electron microscope. The Auger spectrometer can be a separate device or act as an additional module in SEM.

X-rays - an excited atom gives off excess energy by emitting X-rays with a given energy. The energy of radiation results from the difference in energy between the energy levels of electrons.

The specific feature of SEM images, especially in the contrast of secondary electrons, is their "three-dimensional" character. The reason for this phenomenon is the significant depth of sharpness of scanning images, often compared to images seen with the human eye.

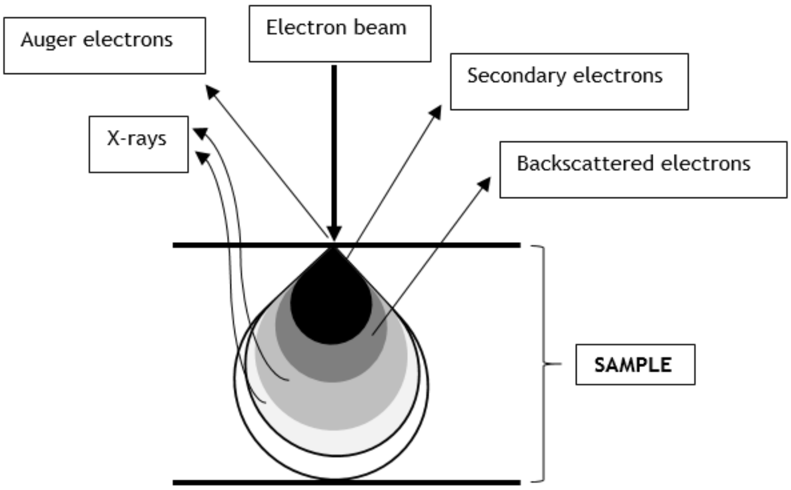

Figure 2-2 *Interactions between electrons and the sample in SEM technique.*

Experimental

Microscopy was performed by a technician on a Tescan Maia3 field emission gun scanning electron microscope (FEG-SEM) operating at 15KV. Images were obtained using the backscattered electron detector. Samples were dispersed as a powder onto 300 mesh copper grids coated with holey carbon film.

2.6.2. X-ray photoelectron spectroscopy (XPS)[12], [13]

X-ray photoelectron spectroscopy (XPS) is a surface characterization technique that can analyse a sample to a depth of 2 to 5 nanometres (nm). In XPS, a focused X-ray beam bombarding the sample causes the emission of electron from the inner shell of the atom (figure 2-3).

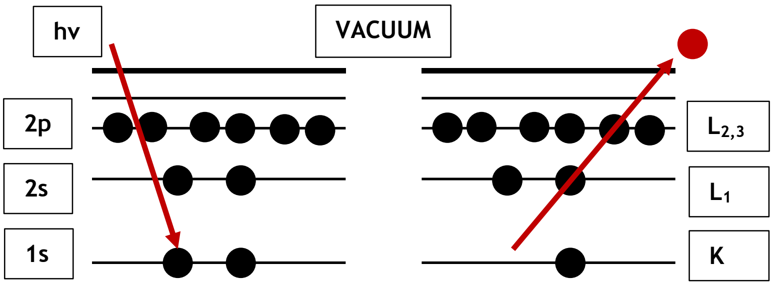

Figure 2-3 *Basic principle of XPS.*

The photo-ejected electrons become excited enough to escape the atom with a certain energy $E_{kinetic}$. The basic equation that describes the photoelectric effect on which photolelectron spectroscopy is based is the Einstein equation:

$$E_{photon}=E_{kinetic}+E_{binding}$$

where $E_{binding}$ is the binding energy of the electron measured against the level of vacuum, E_{photon} is the energy of the X-ray photons being used, $E_{kinetic}$ is the kinetic energy of the electron measured by the instrument.

As a result of electrical contact, the Fermi levels of the sample and the spectrometer equalize. The kinetic energy of the emitted photoelectron depends on its binding energy on the corresponding electron shell of the atom and is described by the dependence:

$$E_{kinetic} = E_{photon} - E_{binding} - \Phi$$

where Φ is the work function dependent on both the spectrometer and the material. It is an adjustable instrumental correction factor. In electron spectrometers, electron binding energy in a solid sample is measured relatively to the Fermi level of the analyser material. The above equation shows that if the kinetic energy Ek of photoelectrons is measured, it becomes possible to determine the binding energy of electrons on individual shells. The energy of an X-ray with particular wavelength is known (for Al K_α X-rays, E_{photon} = 1486.7 eV), hence:

$$E_{binding}= E_{photon} - E_{kinetic} - \Phi$$

The XPS idea seems quite simple. However, the technical conditions that the apparatus must meet are quite restrictive (high vacuum, $P \sim 10^{-8}$ millibar), therefore unique apparatus is necessary to carry out the XPS measurement. A simplified diagram of the XPS test instrument is given in the figure below (figure 2-4). The basic components of the apparatus are: a vacuum system, an X-ray source, an electron energy analyser and a detector.

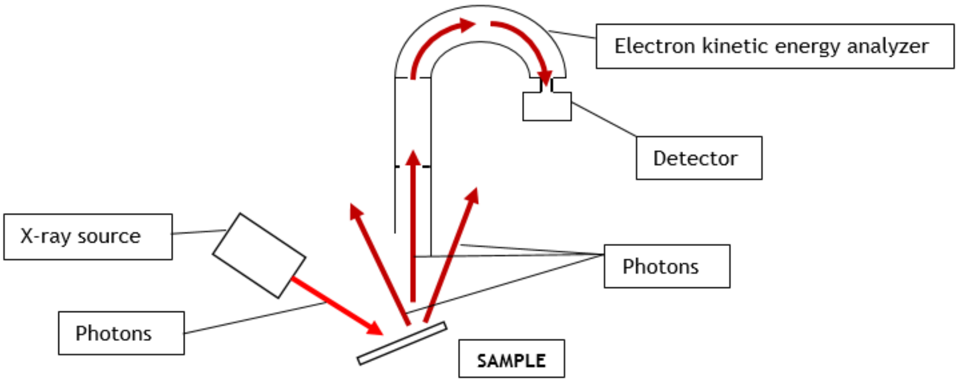

Figure 2-4 *Simplified diagram of XPS apparatus.*

The radiation beam is directed to the sample which results in the emission of electrons (photoelectrons) from atoms located on the surface of the tested material. Once these photo-ejected electrons are in the vacuum, they are collected by an electron analyzer and then the detector measures their kinetic energy. An electron energy analyzer generates an energy spectrum of intensity (number of photo-ejected electrons versus time) versus binding energy. The binding energy of the characteristic photoelectron peaks (1s, 2s, 2p) are standardized and therefore XPS allows for an easy qualitative analysis of the chemical composition of the surface layer. Quantitative analysis is also possible by measuring peak intensities.

The advantages of this method are measurement capabilities. XPS enables detection and quantitative analysis of all elements with a good sensitivity (except hydrogen); allows to identify chemical and electronic states of elements; enables determination of the type of chemical bonds of elements in the surface. The main disadvantage of this XPS is occurrence of thermal effects (surfaces with poor thermal conductivity), e.g. local surface level, thermal desorption, layer decomposition, segregation. It should be kept in mind that the surface being analysed is large due to the difficulty of focusing the X-ray beam (in fact we get an average result from a large area). As mentioned earlier, XPS can only probe to approximately 3-5 nm and therefore can only be considered as a surface sensitive technique.

Experimental

X-ray photoelectron spectroscopy (XPS) data was collected on a Thermo-Fisher Scientific K-Alpha+ X-ray photoelectron spectrometer using a monochromatic Al Kα X-ray source operating at 72 W. Survey scans and high-resolution scans were obtained at a pass energy of 150 eV and 40 eV respectively. Charge neutralization was achieved using a combination of low energy electrons and argon ions, resulting in a C(1s) binding energy of 284.8 eV; experimental binding energies are quoted ±0.2 eV

2.6.3. Gas Chromatography[14], [15]

Gas chromatography is a relatively "young" method, as the first works appeared in 1952. Gas chromatography is a fast and effective method of separating mixtures of volatile compounds. It has found wide application in the identification and quantification of complex mixtures, control of technological processes, determination of some physicochemical constants and reaction kinetics studies.

Gas chromatography, as any chromatographic method, is based on the occurrence of intermolecular interactions between the chemical compounds being components of the analysed mixture and that which fills the column. In the case of gas chromatography, the mixture to be analysed is first converted into a vapor phase in a vaporizer, which is a key element of the injection system (if the analysed sample is a gas it can be fed to the column without the vaporizer). Then, the sample is swept by a carrier gas (usually helium or nitrogen) and passes through a long column where the mixture is separated into individual chemical compounds. At the output there is a detector by means of which the concentration of subsequent components of the mixture in the carrier gas is detected and measured. The rate at which a given chemical compound progresses throughout the column is called retention time and depends on the strength of adsorption. Conditions of the analysis have a very strong influence on the retention time, such as the temperature and velocity of the carrier gas, forced by the pressure applied to the top of the column. The retention time under given conditions is a specific value for each component of the analysed mixture. This allows a very approximate identification of the component, by comparison with a known, pure substance. The sample components analysed by gas chromatography must be volatile and stable at the analysis temperature.

The basic elements of gas chromatography are: injector, column, detector (figure 2-5).

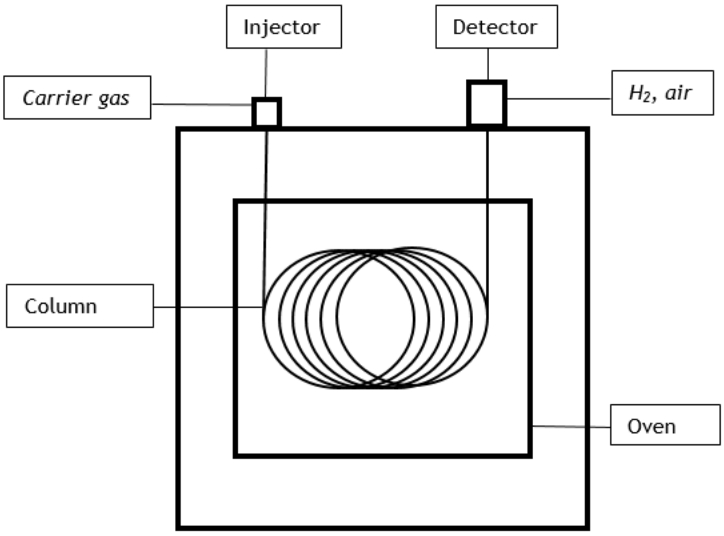

Figure 2-5 *Simplified scheme of gas chromatography apparatus.*

Injector (figure 2-6). The traditional injection system usually consists of a membrane, which is punctured with a needle of a special chromatographic syringe and a vaporizer, in which all components of the analysed sample evaporate. The steam separator is a short (5-10 cm) metal or glass tube surrounded by a heating coil that allows the tube to be heated to over 200 °C. In some devices the vaporizer works constantly at the same temperature, while in others it is possible to regulate its temperature in a wide range. Injections are done manually or automatically. The following injection systems are distinguished: split dispenser and on-column dispenser. In the case of split dispenser the injected sample goes to a special distributor, in which only a strictly determined part of the injection is directed to the vaporizer, while the rest goes to the so-called dead loop; this system guarantees that the column always gets a repeatable amount of the sample. On-column dispenser means that the whole sample goes straight to the column. The split dispenser allows to reduce the load by setting large division ratios (e.g., 50: 1, 100: 1 or 500: 1, i.e. it is discarded 50, 100 or 500, respectively, and one part of the sample goes to the column). The on-column dispenser is usually used when the sample being tested is thermally unstable so that it could decompose at the temperature of the split dispenser.

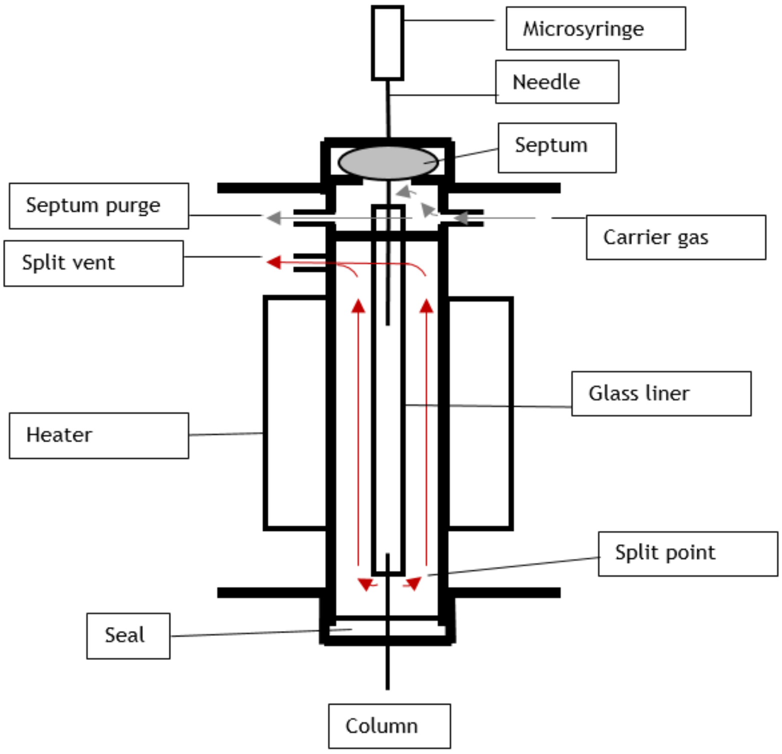

Figure 2-6 *Scheme of injection system in GC apparatus.*

Column. Capillary columns for GC are most often made of molten quartz or silicon dioxide. Molten quartz is easy to mold, flexible and much stronger than other glasses, which means that an inner diameter of capillaries can be 0.1 to 1 mm with a length of 10 to 30 m. The capillary columns are stored in a roll in protective holders to prevent damage. Adsorbents used in gas chromatography are carbon adsorbents, gels, siliceous, molecular sieves, porous polymers. Stationary phases in capillary columns can be both adsorbents and liquids and can be deposited on the capillary walls in a variety of ways.

Detector (figure 2-7). The flame ionisation detector (FID) is a universal detector and reacts with a signal for the presence of organic compounds. It uses a change in the electrical conductivity of the flame atmosphere (hydrogen - air) when the organic compound formed in the combustion process appears in the flame. The resulting ionization current is amplified and registered by the computer. The signal from this detector is proportional to the number of carbon atoms not related to oxygen, and hence to the mass of the substance. It also depends on the nature of the compounds, generally is a very sensitive detector and allows detection in a low range (10^{-12} g) of the test substance. Unfortunately, it is not sensitive to inorganic compounds as well as to such carbon compounds as: CO, CO_2, CS_2, HCOOH and $COCl_2$. In the case of FID, the most suitable carrier gas is nitrogen and helium.

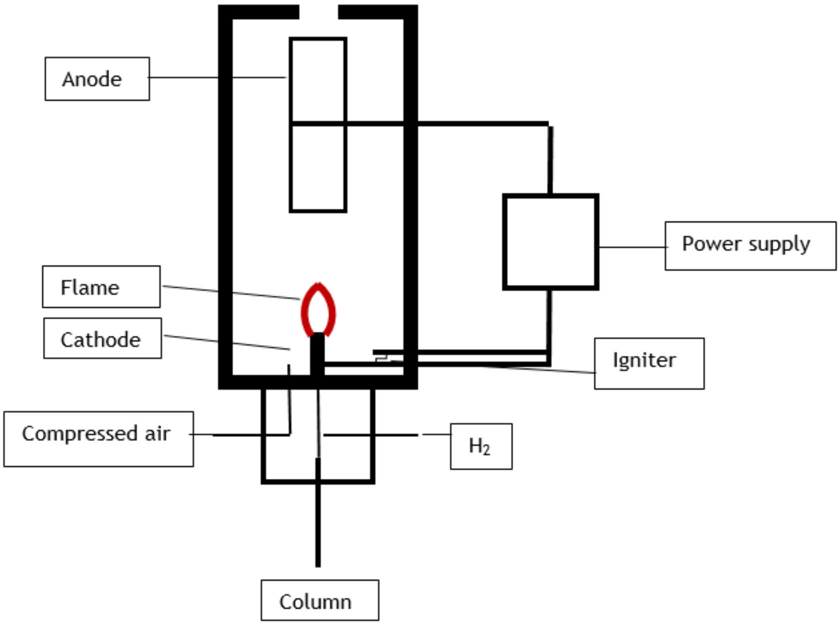

Figure 2-7 *Scheme of FID detector in GC apparatus.*

Previously, analog recorders were used as recorders, sometimes provided with an integrator, which simply "drew" changes in the electrical voltage generated by the detector. These charts are traditionally called chromatograms. Chromatograms usually take the shape of a series of sharp peaks whose height corresponds to the instant concentration of a chemical coming out of the column, and the area under the peak can be converted into the total concentration of a given chemical in the whole sample analysed. Nowadays, PCs are used as recorders with software enabling both the control of the work parameters of the whole apparatus and the automatic collection and analysis of chromatograms. The software using numerical methods determines the maximum peak (retention time) and the beginning and end of the peak, then by integration in the beginning and end of the peak, calculates the area of the field.

Experimental

GC analysis was carried out using an Agilent 7280A chromatograph equipped with an autosampler and a CP-wax 52 column. Products were identified by comparison with authentic samples. For the quantification of the amounts of reactants consumed and products generated, an external calibration method was used.

2.6.4. High Performance Liquid Chromatography[16]

High performance liquid chromatography (HPLC) is, as in the name, a type of liquid column chromatography. This means that the analysed sample is dissolved in a suitably chosen solvent, which is dependent on the properties of the substance and the system used, and is in the form of a solution of known concentration and volume is directed to a column that is filled with a special adsorbent material. The carrier liquid (mobile phase) is a properly selected mixture (the so-called eluent). As a result of varying extents of intermolecular interactions between analytes and the column filling, the analytes can be separated. Depending on the system used, several retention mechanisms can be distinguished, e.g. analytes that interact more strongly with the adsorbent (they have so-called higher affinity to the adsorbent) and less with the mobile phase: flow slower through the column; analytes that have less impact on the filling of the column and more strongly with the mobile phase: flow faster. However, in some specific HPLC systems retention mechanisms are more complex.

HPLC differs from the usual liquid chromatography by the pressure at which the eluent is applied to the columns. These are quite significant pressures, exceeding 100 atm. The high pressure in the HPLC system results from the construction of HPLC pumps (narrow capillary sections), column filling grains (several micrometres) and the mobile phase flow used in the application (from fractions ml / min to even tens mL / min in the case of preparative chromatography). Small particle size distribution of the stationary phase results in more favourable parameters of efficiency and separation of the HPLC system. As a result, it is possible to separate the analysed mixtures into individual chemical compounds in a much shorter time, with less consumption of the eluent and smaller amount of the analysed sample than in classical column chromatography.

In HPLC, phase polarity is of great importance for the separation. Initially, a normal phase system (NP) was used, in which the stationary phase is much more polar than the mobile phase (eg, the system: silica gel - hexane). Currently, the reversed phase system (RP) is most often used, in which the stationary phase is less polar than the mobile phase, e.g. the system: silica gel with chemically modified surface (octadecylsilane groups, octylosilane, diols, modified substituents and others, more complex) - a mixture of methanol, acetonitrile, water, specially selected buffers, etc. The separation depends on the binding of hydrophobic molecules dissolved in the mobile phase to immobilized, hydrophobic ligands bound to the stationary phase. The strength and nature of interaction between sample molecules and the stationary phase depends both on hydrophobic interactions and polar interactions. The dissolved substances are eluted in the order of increasing molecular hydrophobicity. RP systems have more durable fillings, are characterized by a lower cost of the mobile phase and, above all, are characterized by different selectivity than NP systems, which are used in the analysis of samples with a large polar range of components.

A basic flowchart showing the principle of HPLC operation is shown in figure 2-8. The pump draws the mobile phase from the tank (or tanks) and pushes it into the chromatographic column. The column is sometimes placed in the thermostat. The analyzed sample is injected at the top of the chromatographic column, and then the mixture of components is separated in the column and at the exit from it the components are detected by the detector. Column flow and pressure are carefully controlled factors and are extremely important during the method optimisation process.

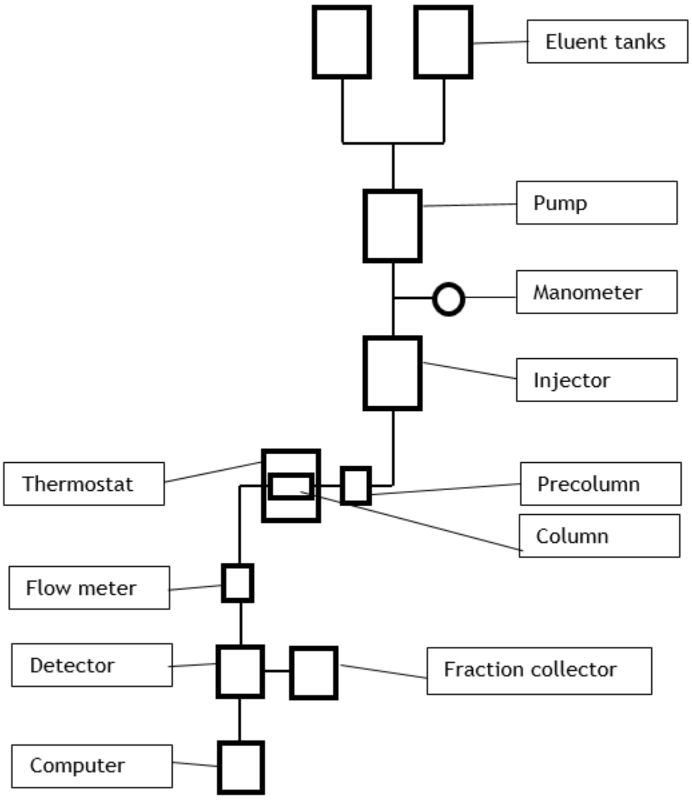

Figure 2-8 *Simplified flowchart of HPLC system.*

Ultraviolet (UV) or ultraviolet and visible (UV-VIS) light detectors are the best and most common detectors used in HPLC. They are used to detect compounds containing unsaturated bonds and chromophore groups, olefins, aromatic compounds and dyes in the molecule. The UV-VIS radiation absorption is related to transitions of valence electrons and electrons of free electron pairs from a lower energy orbital to a higher energy orbital.

The simplest monochrome UV detectors enable the detection of chromatographed substances at one wavelength - 254 nm. It is the wavelength of light absorbed by most organic substances (about 65 %). Currently, spectrophotometric detectors are widely used, in which it is possible to smoothly adjust the wavelength (e.g. Diode Array

Detector- DAD). Such a detector, after stopping the mobile phase flow, makes it possible to register the absorption spectrum of the substance and to determine the wavelength at which the absorption maximum occurs therefore the substance can be detected with maximum sensitivity.

The light from a deuterium lamp is focused by the optical system in a flow cell in which part of the light is absorbed by the substances contained in the sample. Then a beam of light split on a diffraction grating falls on the diode array. The diodes of this matrix can record the intensity of light in the range of 190-600 nm in 10 ms. The sensor has, for example, 211 photodiodes, each of which is designed to measure a narrow spectrum of light. Simultaneous recording of currents from individual photodiodes enables the recording of the entire absorption spectrum of the analyzed chemical. This spectrum can be represented in a three-dimensional system - retention time, wavelength and absorbance. It is also possible to record a normal chromatogram with the maximum absorbance for each component of the sample recorded in the chromatogram as a peak. The UV spectrophotometric detector is insensitive to changes in the mobile phase flow and temperature changes. Detection of the analysed substance at a well-chosen ultraviolet wavelength is on average 1 ng in the sample.

Another widely used detector is RID- Refractive Index Detector, which is based on the deflection principle of refractometry and measures the change in refractive index of the effluent passing through the flow-cell.

Experimental

HPLC analysis was carried out using an Agilent 1260 Infinity instrument equipped with an autosampler and a C18 column with a mobile phase being a mixture of acetonitrile and water. Products were identified by comparison with authentic samples. For the quantification of the amounts of reactants consumed and products generated, an external calibration method was used.

2.6.5. Inductively Coupled Plasma- Mass Spectrometry (ICP-MS)[17]

Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) is a technique of mass spectrometry for the detection of elements (mainly of metals and a few non-metals) in very small concentrations (one part in 10^{15}, part per quadrillion, ppq). This is achieved by complete vaporisation, atomisation and ionization of the sample in an inductively coupled plasma, after which the the mass spectrometer determines the amounts of ions (figure 2-9).

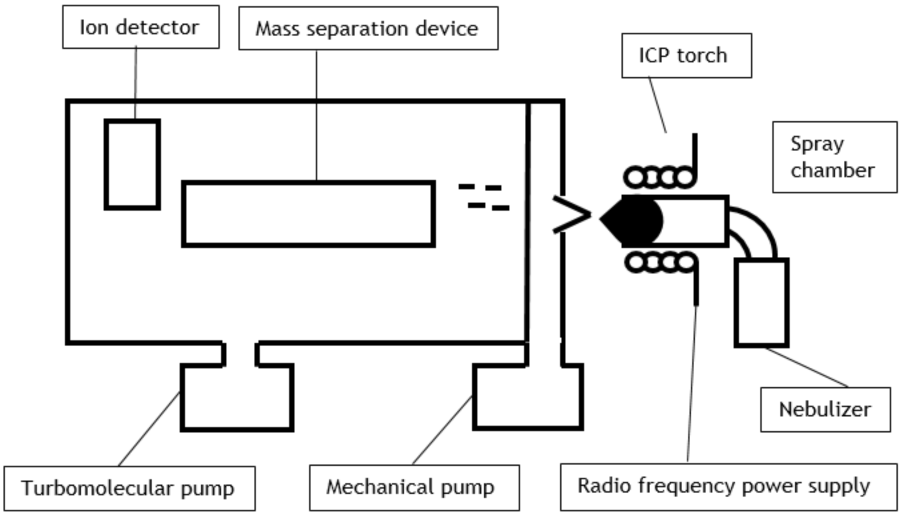

Figure 2-9 *Scheme of ICP-MS apparatus.*

A liquid sample must be sprayed by a nebuliser prior to ionisation in the plasma. The basic task of the nebuliser (igure 2-10) is to convert the analysed solution into an aerosol form, i.e. a suspension of fine droplets (with diameter in the range of 5-10 micrometres). The most common method of aerosol generation is to pass a gas (argon) through a perpendicular liquid stream (figure 2-10).

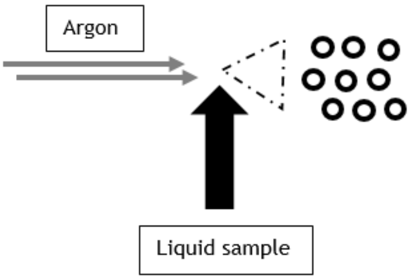

Figure 2-10 *Nebulized sample*

Plasma is generated in a specially designed plasma torch (figure 2-11). Argon (usually 13-18 liters per minute) flows tangentially within the torch tube (figure 2-11A). The generation of an electromagnetic field occurs as a result of a high-frequency current passing through the generator's coil which is placed at the end of the torch (figure 2-11B). As a result, electric discharge is initiated in the area of the alternating electromagnetic field which results in the formation of free electrons figure(2-11C). Free electrons are accelerated in the electromagnetic field (Lorentz force), collide with the atoms of argon and cause its ionization (figure 2-11D). At the plasma torch output a plasma is formed in which the sample is introduced through the sample injector (figure 2-11E). The temperature of the plasma is very high (10 000 K) and also ultraviolet light is produced so for safety reasons it should not be viewed directly.

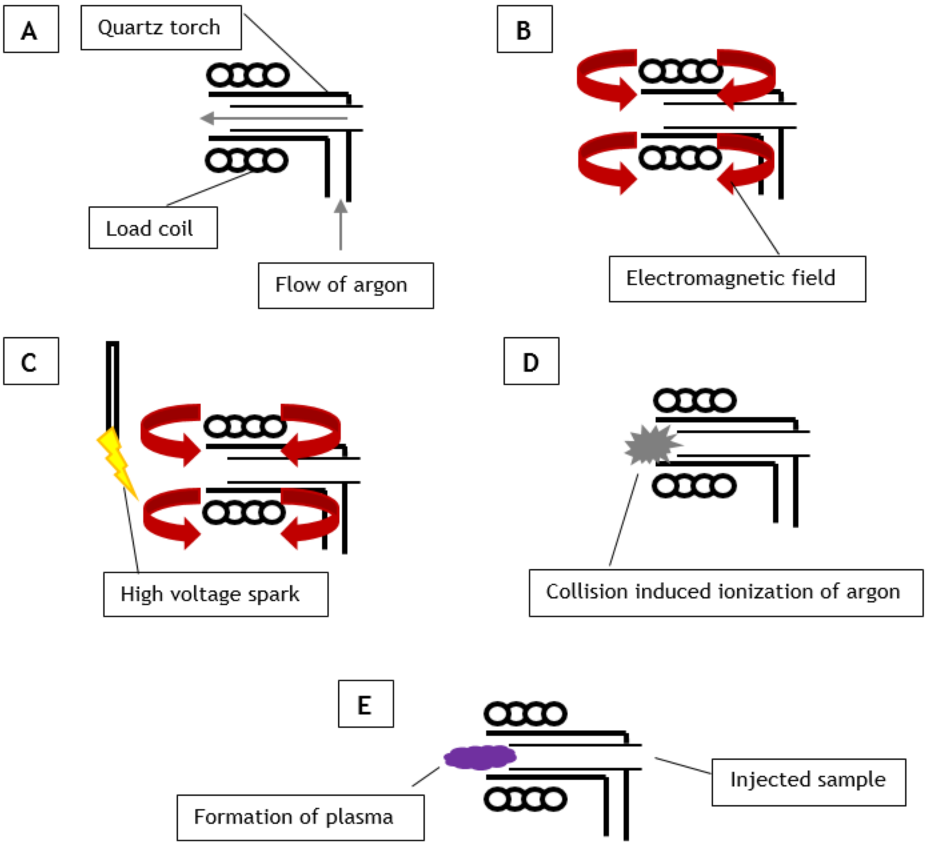

Figure 2-11 *Simplified process of plasma generation.*

Positive ions generation (from sample injector to mass spectrometer) takes places in four steps:

1) evaporation of water (desolvation)
2) evaporation of a solid sample (vaporization)
3) dissociation into atoms (atomization)
4) ionization

Analytical problems in ICP-MS measurements are related mostly with spectral interferences, matrix effect and charge-related effects. A solution to the problem of spectral interference is the collision/reaction chamber which is placed in front of the quadrupole analyser. The collision/reaction cell eliminates some of the interfering ions by ion-neutral reactions with gases such as ammonia, methane, oxygen or hydrogen:

$$Ar^{+} + NH_3 \rightarrow NH_3^{+} + Ar$$

$$Ca^{+} + NH_3 \rightarrow \text{no reaction}$$

The ions from the plasma are extracted into a mass spectrometer, usually a quadrupole where the ions are separated on the basis of their mass-to-charge ratio and a detector receives an ion signal proportional to the concentration. The concentration of a sample can be determined by calibration with standard (reference) material.

Experimental

The analyses were carried out by a technician using Agilent 7900 ICP-MS with I-AS autosampler. Five point calibration using Certified Reference material from Perkin Elmer (1000/100/10/1/blank ug/l) and Internal Standard also certified from Agilent. All calibrants were matrix mapped with samples.

2.6.6. Microwave Plasma - Atomic Emission Spectroscopy (MP-AES)[18]

MP-AES is an elemental analysis technique used for simultaneous multi-analyte determination of major and minor elements. MP-AES measurement protocol is rather straight forward (figure 2-12). The injected sample is nebulized prior to further interaction with the plasma. A nitrogen plasma is formed within a quartz torch and heated to around 5000 K using microwave and magnetic excitation techniques. After atomisation, electrons are promoted to the excited state in the plasma. After relaxation of the electrons, emitted photons of defined energies and wavelengths which are characteristic for each element are separated into a spectrum and the intensity of each emission line measured at the detector. The main advantage of this method is a high sensitivity and low interference for each element as each wavelength can be analysed individually and sequentially using a monochromator detector. It is also possible to use multiple emission wavelengths for each element which is useful in case of analysed solutions containing more than one element to avoid interferences and hence mistakes in analysis. Most commonly determined elements can be analysed within a range of low part per million (ppm) to weight percent. The main limitation of this method is the necessity of analysed samples being in liquid form e.g. soluble or digestible catalysts. In comparison, inductively coupled plasma optical emission spectrometers can analyse solid samples *via* a laser ablation system.

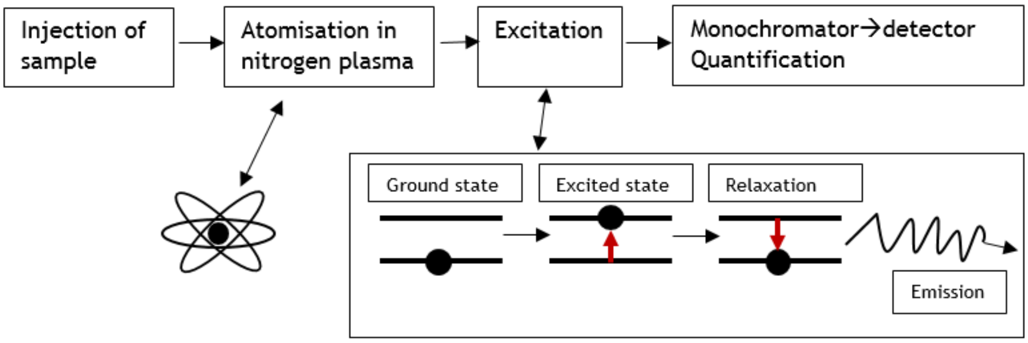

Figure 2-12 *Basic principles of MP-AES.*

Experimental

MP-AES technique has been used to evaluate leaching of Au and Pd in heterogeneous catalysts during oxidations of alcohols in water. Post reaction mixtures were diluted using deionised water (to the desired order of magnitude metals contained) and filtered using PTFE syringe filters (0.45 µm). Samples were then analysed using an Agilent MP-AES 4100 and tested for Au and Pd using multiple wavelength calibrations for each element.

2.6.7. Nuclear Magnetic Resonance (NMR)[19], [20]

Nuclear Magnetic Resonance is a spectroscopic technique of observing local magnetic fields around atomic nuclei. The sample is placed in a strong magnetic field and nuclei are perturbed by a weak oscillating magnetic field. The intramolecular magnetic field around the atom in the molecule changes the resonance frequency, thus giving information about the details of the electronic structure of the molecule and its individual functional groups. Because fields are unique and highly characteristic of individual compounds, NMR spectroscopy is a precise method for identifying organic compounds. Moreover, NMR provides detailed information on the structure and chemical environment of molecules. The most common types of NMR are proton and carbon-13 NMR spectroscopy.

In the case of a substance consisting of only one type of atoms - *e.g.* hydrogen gas, the spectrum of electromagnetic radiation usually consists of one sharp line, because all nuclei are equal and are in the same magnetic field. In the case of a substance consisting of more complex molecules, *e.g.* ethanol, different hydrogen atoms will emit electromagnetic radiation at a slightly different frequency. This is due to the screen effect of the electrons around these nuclei. The electrons are also in constant motion and also have an electric charge, which is why their motion generates a magnetic field with a different polarity than the external magnetic field generated by the NMR apparatus. As a result, the nuclei of atoms are actually in a slightly different field than that generated by the NMR apparatus: the field being the resultant field of the apparatus and the field generated by electrons. This resultant field is different for each of the nuclei of the atoms forming the given molecule, because around each of them is a different set of electrons, resulting from the system of chemical bonds. Therefore, the same type of nuclei (*e.g.* hydrogen), but placed elsewhere in the molecule, generates electromagnetic radiation at a slightly different frequency and the result is a set of sharp signals in the spectrum, the number of which corresponds to the number of chemically different atoms in a given molecule. The position of the signal in the NMR spectrum is determined by the so-called chemical shift. Chemical shifts in NMR are expressed in ppm. The ranges of chemical shifts corresponding to absorption by nuclei in the environment of specific chemical groups are tabulated. Comparison of recorded chemical shifts with table values enables identification of the chemical structure of the tested compound.

Experimental

^{1}H NMR spectra were obtained using a Bruker Avance 400 MHz DPX spectrometer, equipped with Silicon Graphics workstation running X win 1.3. All chemical shifts for ^{1}H NMR were recorded in deuterated chloroform (*d*-$CDCl_3$).

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Chapter 3

3. Cinnamyl alcohol oxidation: an investigation of the autoxidation and catalytic pathways with the use of bimetallic Au-Pd supported nanoparticles.[1]

3.1. Introduction

Alcohol oxidation is an important reaction both in academia and in industry. A considerable number of experiments have been performed with the use of bimetallic catalysts consisting of gold and palladium, which were found to be highly active for oxidation reactions with molecular oxygen.[2] The application of Au-Pd catalysts in the process of oxidation is an excellent alternative to existing methods of carbonyl compound synthesis which utilise toxic and stoichiometric oxidants such as chromate and permanganate. The oxidation of cinnamyl alcohol has attracted much attention as a model reaction. Cinnamyl alcohol is an example of an allylic alcohol and represents one of the main components of plant biomass derivatives. The transformation of alcohols to carbonyl products is meaningful for industrial applications. Cinnamaldehyde, the desired product of cinnamyl alcohol oxidation, is an insecticide and common food/perfume additive. The reaction network is also interesting from an academic viewpoint, due to the formation of different by-products and the substrate being prone to the process of autoxidation.

Autoxidation is very common and advantageous in the chemistry of hydrocarbons, such cyclohexane[3], [4], p-xylene[5], α-pinene[6], [7] and cumene[8] as it enables the formation of oxygenated derivatives. A lot of effort has been made to understand the mechanism of autoxidation.[9]-[11] However, despite these extensive investigations, there is still a lot of uncertainty surrounding this process as it strongly depends on the conditions and character of the substrate which makes it hard to predict and design.

3.2. Reaction network

It is known from the literature that the reaction network for cinnamyl alcohol oxidation is extremely interesting due to its complexity. Depending on the catalyst used and /or the applied conditions, the product distribution varies considerably. Corma and co-workers achieved an excellent yield to cinnamaldehyde (99 %) by using an Au/nCeO$_2$ catalyst[12]. Prati and co-workers obtained a high conversion of cinnamyl alcohol over AuPd/TiO$_2$ to cinnamaldehyde and 3-phenyl-1-propanol at only 60 °C under oxygen[13]. Baiker and co-workers oxidised cinnamyl alcohol with the use of Pd/Al$_2$O$_3$ at 65 °C in air and detected the presence of numerous products: methylstyrene, 3-phenyl-1-propanol, propylbenzene, ethylbenzene, 3-phenylpropionaldehyde[14] (Figure 3-1). Also benzaldehyde was observed as a by-product in several investigations[15]–[17]. Most of the studies on oxidation of cinnamyl alcohol have been conducted at a temperature not exceeding 90 °C. From an environmental point of view, researchers are stressing the need to develop chemical processes taking place under mild conditions. However, from an industrial point of view, running a process at a temperature higher than the room temperature, but lower than the boiling point of water is considered as a waste of energy, and thus money. Usually, the chemical plant is designed so that it is possible to collect heat (energy) and further transfer it where needed. Assuming that the chemical process is conducted at 60 °C, this means that energy must be delivered to the system, but it is too low to be recovered. To ensure the industrial relevance, the studies presented in this thesis have been performed at elevated temperature (120 °C).

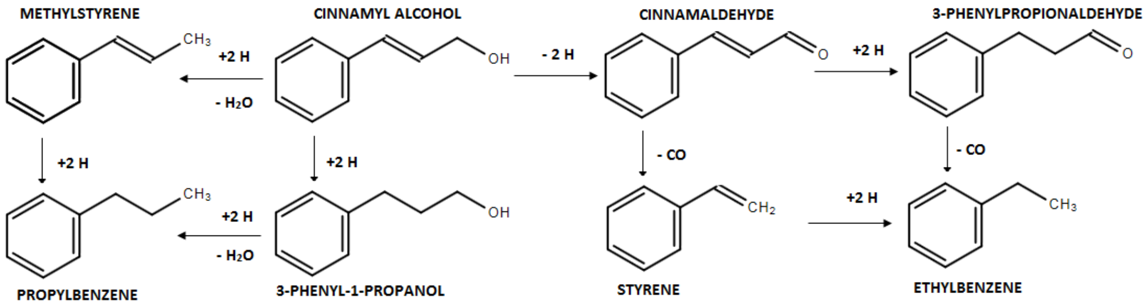

Figure 3-1 *Reaction network presented by Baiker et al.*[14]

Due to the remarkable variety of possible products, it was important to establish the reaction network and product distributions for the experiments conducted during my studies. The oxidation of cinnamyl alcohol was carried out at 120°C in a Radley reactor under oxygen pressure of 3 bar. Reactions were performed in the absence and presence of the 0.50 %wt Au 0.50 %wt Pd/ TiO$_2$ catalysts prepared with two different methods: impregnation (Imp) and sol- immobilisation (SIm).

In general, the reaction network observed was similar with that in the literature although not identical (Figure 3-2). The following products have been detected: cinnamaldehyde (**CinnALD**), benzaldehyde (**benzALD**), 3-phenyl-1-propanol (**PP**), methylstyrene (**MS**), styrene, benzoic acid (**BenzACID**), CO, CO$_2$ and unidentified organic substances were observed in traced amounts hence neglected (usually less than 5 %). Other compounds reported in the literature such as propylbenzene, ethylbenzene, and 3-phenylpropionaldehyde have not been observed. Moreover, oxidation process was taking place in the absence of a catalyst (due to elevated temperature) which has been taken into consideration and carefully studied.

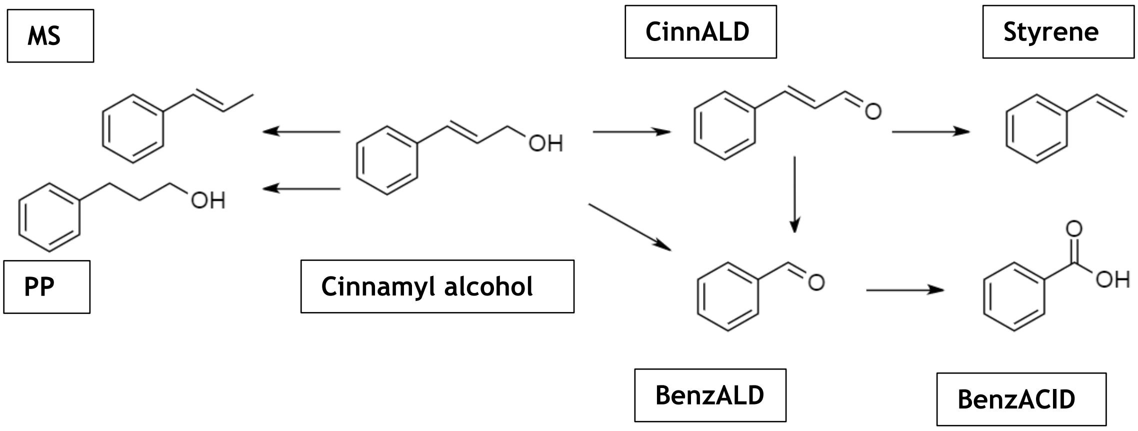

Figure 3-2 *Products obtained during current investigation.*

3.3. Results and discussion

3.3.1. Reaction network and product distributions in the presence and absence of a catalyst

Unless otherwise stated, the reactions have been performed according to the procedure described in chapter 2.

Figure 3-3 plots the conversion and selectivity as a function of time-online for the blank reaction of cinnamyl alcohol oxidation. Interestingly, the reaction carried out in the absence of any catalyst showed significant conversion and high selectivity to 3 major products: cinnamaldehyde, benzaldehyde and benzoic acid. As can be seen, the conversion after 4 hours was exceptionally high at 60 %. Selectivity to cinnamaldehyde was at 30 %, benzaldehyde reached 60 %, benzoic acid was 10 % and PP was below 1 %. The obtained values were high enough to be taken into consideration and therefore this phenomenon was further investigated as part of this work. Figure 3-4 displays the results for the reaction carried out with the use of catalyst prepared by impregnation method (0.50 %Au 0.50 %Pd/TiO_2 (Imp).

After careful analysis of Figures 3-3 and 3-4, it is clear that the reaction with the use of the 0.50 %Au 0.50 %Pd/TiO_2 (Imp) catalyst had a lower conversion than the blank reaction, which is most notable during the first two hours. The difference in conversion diminished after 4 hours of reaction (blank: 57 %, catalysed: 48 %). Importantly however, a higher selectivity to cinnamaldehyde (60 %) is observed in favour of the catalysed reaction. Furthermore, the formation of benzoic acid decreased and selectivity to benzaldehyde was lower (30%). The selectivity to products, which indicate hydrogen transfer processes (methylstyrene and 3-phenyl-1-propanol), was below 5%.

As detailed in Figure 3-5 the reaction carried out with the use of the catalyst made by sol-immobilisation method (0.50 %Au 0.50 %Pd/TiO_2 (SIm) had a high conversion (85 %) and high selectivity to cinnamaldehyde (80 %). No benzoic acid was detected and the amount of benzaldehyde was low (around 3 %) compared to the reactions described previously. The amount of PP formed as the effect of hydrogenation was slightly higher (10 %), and the selectivity to MS through hydrogenolysis was relatively low (3 %).

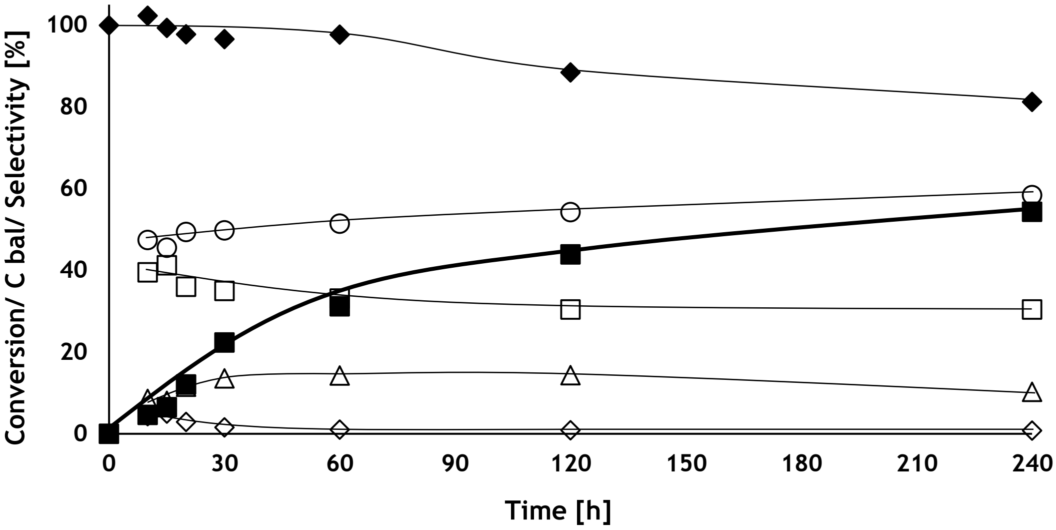

Figure 3-3** Time online profile for the autoxidation of cinnamyl alcohol. Reaction conditions: oxygen pressure: 3 bar; temperature, 120 °C; 0.5 M cinnamyl alcohol in toluene.* ***Conversion (■); Carbon balance (◆); CinnALD (□); BenzALD (○); PP (◇); BenzACID (△)

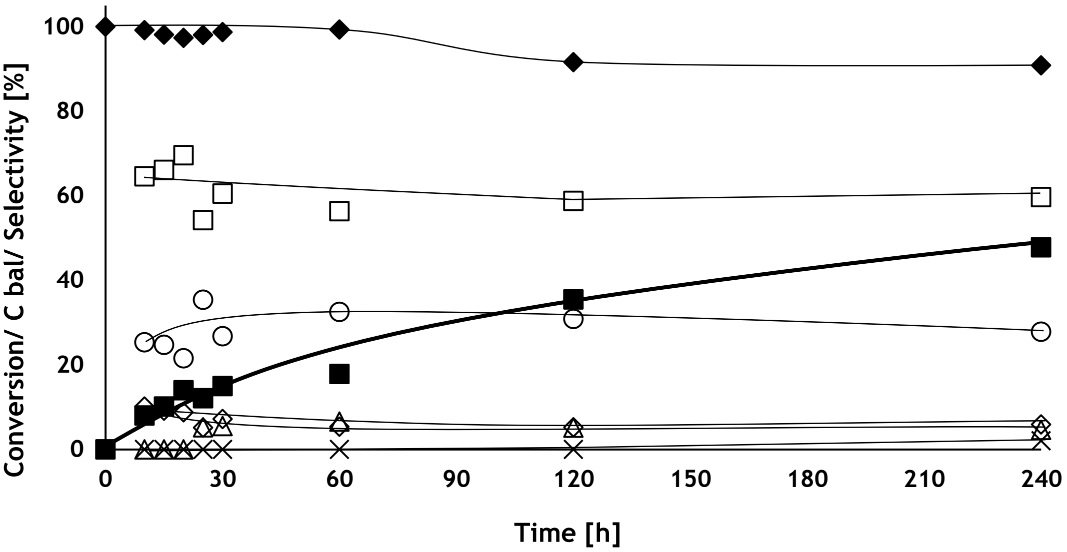

Figure 3-4 *Time on-line profile for the catalytic oxidation of cinnamyl alcohol using 0.50 %Au 0.50 %Pd/TiO$_2$ (Imp). Reaction conditions: catalyst, 10 mg; oxygen pressure, 3 bar; temperature, 120 °C; 0.5 M cinnamyl alcohol in toluene.* ***Conversion (■); Carbon balance (◆); CinnALD (□); BenzALD (O); PP (◇); BenzACID (△); MS (×)***

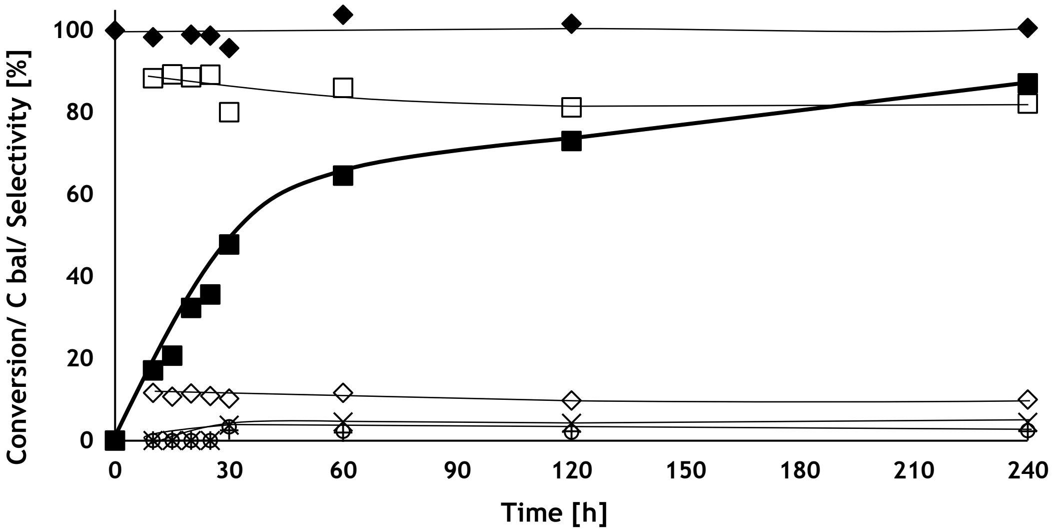

Figure 3-5 *Time on-line profile for the catalytic oxidation of cinnamyl alcohol using 0.50 %Au 0.50 %Pd/TiO$_2$ (SIm). Reaction conditions: catalyst, 10 mg; oxygen pressure, 3 bar; temperature, 120 °C; 0.5 M cinnamyl alcohol in toluene.* ***Conversion (■); Carbon balance (◆); CinnALD (□); BenzALD (O); PP (◇); MS (×); Styrene (I)***

These time on-line studies revealed that the selectivity to major products achieved after 30 minutes was stable for the continuation of the reaction. The bare support, namely TiO$_2$, did not play the role in the oxidation of cinnamyl alcohol as the results were the same (within ± 3 % experimental error) as the results of the reaction carried out in the absence of the catalyst (see Figure 3-3 and Figure 3-6).

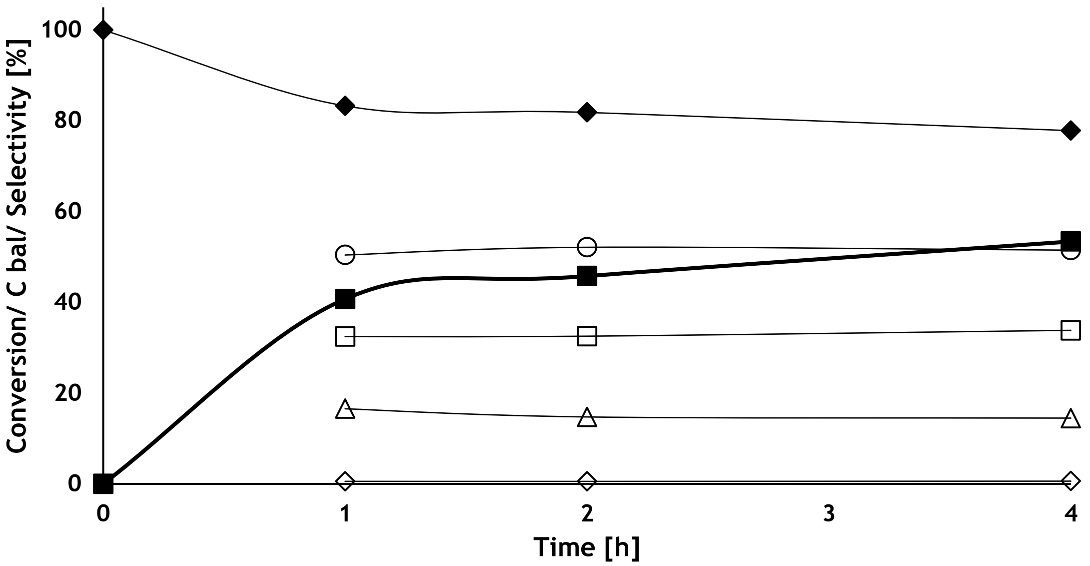

Figure 3-6 *Time on-line profile for the oxidation of cinnamyl alcohol using TiO_2. Reaction conditions: TiO_2, 10 mg; oxygen pressure, 3 bar; temperature, 120 °C; 0.5 M cinnamyl alcohol in toluene.* ***Conversion (■); Carbon balance (◆); Cinnamaldehyde (□); Benzaldehyde (○); 3-Phenyl-1-propanol (◇); Benzoic acid (△)***

3.3.2. Purity of the substrate

The high conversion of cinnamyl alcohol in the absence of the catalyst led to the presumption that the substrate could be contaminated. To exclude this possibility, cinnamyl alcohol was first purified by crystallization in pentane[18], and then used in reaction. Figure 3-7 compares the conversion of cinnamyl alcohol when using the as received and purified substrate.

Considering, that the experimental error is ± 3 %, the purification process did not improve the results of the experiment. In addition, measurements of NMR of cinnamyl alcohol were done before and after purification. Based on the spectra (Figure 3-8a and 3-8b), it can be stated, that cinnamyl alcohol as received is free of impurities and can be used without prior treatment.

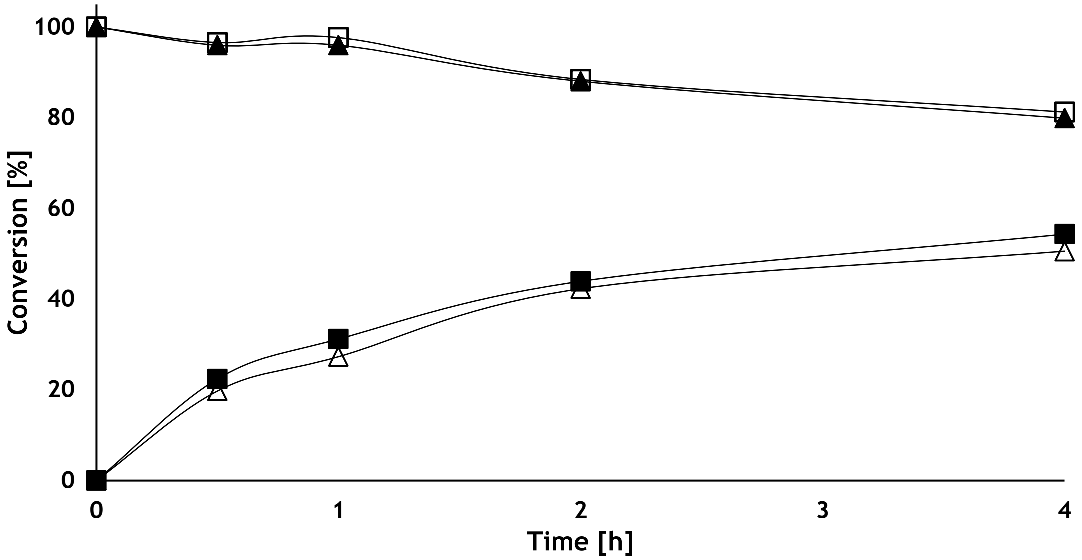

Figure 3-7 *Time on-line for the oxidation of cinnamyl alcohol (as received and purified) carried out in the absence of a catalyst. Reaction conditions: oxygen pressure, 3 bar; temperature, 120 °C; 0.5 M cinnamyl alcohol in toluene.* ***Conversion-substrate as received (■); Carbon balance- substrate as received (□); Conversion- purified substrate (△); Carbon balance- purified substrate (▲)***

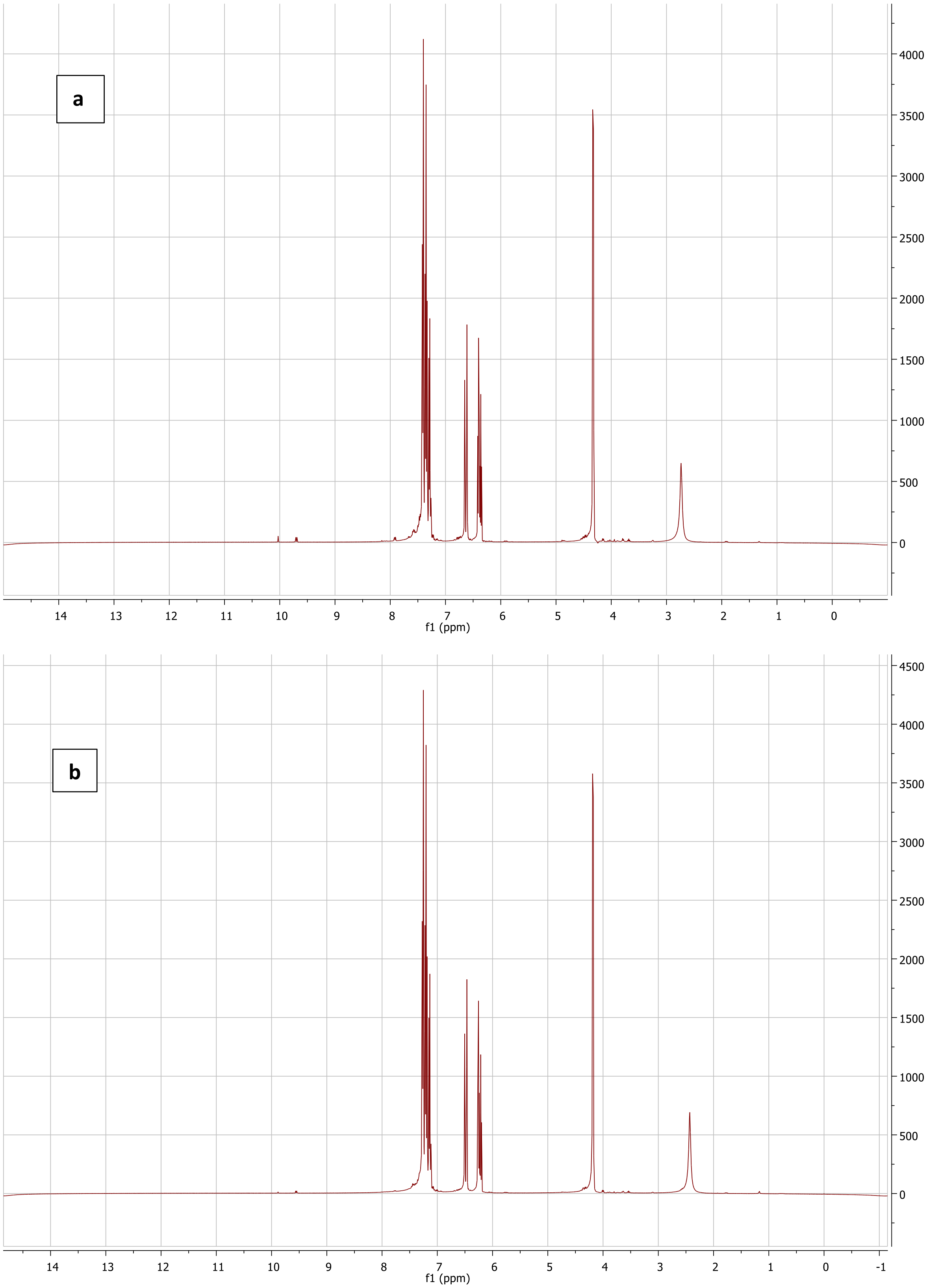

Figure 3-8 *NMR spectra of cinnamyl alcohol* ***(a)*** *before and* ***(b)*** *after purification.*

3.3.3. Catalyst characterisation

3.3.3.1. SEM

Following the confirmation of a significant blank reaction, an in-depth study of the catalysts was conducted to investigate the discrepancies observed between preparation methods and their influence on this reaction. The detailed analysis of catalysts at the molecular level has been carried out using the SEM technique. The SEM images obtained for the catalysts prepared with the same ratio of Au-Pd but by two different preparation methods are presented in figure 3-9, showing significant differences in the particles size. Figure 3-9A shows an image of the 0.50 %Au 0.50 %Pd/TiO_2 (Imp) from which one can immediately see an extremely large ~100 nm metal particles. Strangely, no smaller metal particles were detected which might suggest that there are either no smaller nanoparticles or they are sufficiently small that they are below the detection limit of the SEM. Another explanation refers to the morphology of AuPd nanoparticles, obtained by impregnation method, comprising mostly of a Pd-rich core and an Au-rich shell. The poor detection of Au suggests the presence of core-shell structures as Au would be 'coated' by Pd. The impregnation method has been widely used for catalyst synthesis and generally gives a broad particle size distribution with large particles but also small particles < 20 nm.[19] In the studied case of the impregnation catalyst, a particle size distribution was impossible to be determined due to the size of the metal clusters. In contrast to the impregnation method, the nanoparticles synthesised by sol-immobilisation method were very well dispersed and easily detectable (figure 3-9B). As expected, the nanoparticles were all smaller than 10 nm, with the majority being 2-4 nm. This is in good agreement with previous reports.[20]

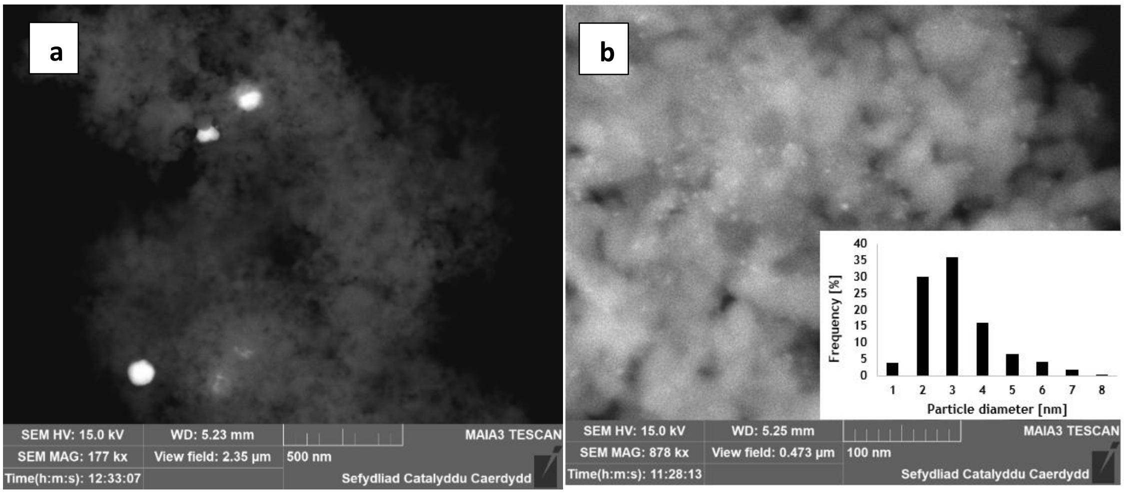

Figure 3-9 a) *BSD-SEM image of the 0.50 %Au 0.50 %Pd/TiO_2 (Imp) catalyst;* ***b)*** *BSD-SEM image and associate particle size distribution of the 0.50 %Au 0.50 %Pd/TiO_2 (SIm) catalyst.*

3.3.3.2. XPS

The conclusions drawn from the SEM imaging were confirmed by XPS analysis. Figure 3-10 shows the Au(4f) and Pd(3d)/Au(4d) core-level spectra for both catalysts. In the case of 0.50 %Au 0.50 %Pd/TiO_2 (Imp) catalyst, the Au(4f) signal is weak, which can be explained by the fact that the nanoparticles are large and poorly dispersed. Gold is found in its metallic state and the Pd is mostly present as Pd(II), which based on the Pd(3d5/2) binding energy of 336.2 eV, is assign as PdO. However, the presence of Pd-Cl bonds is possible as Cl is found at a binding energy of *ca.* 198 eV, consistent with metal chlorides.[21]

In contrast to the Imp catalyst, the SIm catalyst shows an intense Au and Pd signal, corresponding to the smaller particle size and improved dispersion correlating with results obtained from SEM. The predominant binding energies of Au(4f7/2) at 82.9 eV and Pd (3d5/2) at 334.3 eV are consistent with their metallic states.[21] Trace amounts of Pd(II) were found at 335.8 eV.

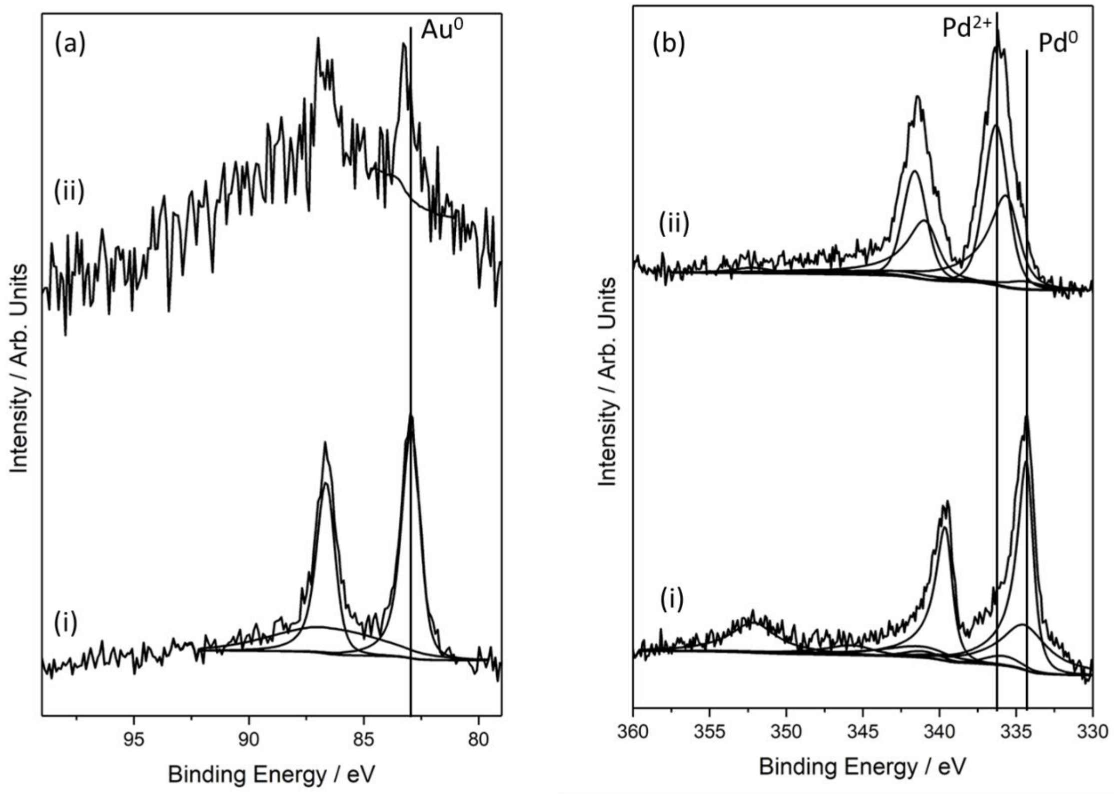

Figure 3-10 *XPS* ***(a)*** *Au(4f) and* ***(b)*** *Pd(3d)/Au(4d) core-level spectra for (i) 0.50 %Au 0.50 %Pd/*TiO_2 *(SIm) and (ii) 0.50 %Au 0.50 %Pd/*TiO_2 *(Imp) catalysts.*

3.3.4. Support comparison study

Several supports with different surface areas, pore volume and pH have been tested using Au-Pd system deposited by sol-immobilisation method for the oxidation of cinnamyl alcohol. The reactions were carried out under standard conditions for 4 hours. Au-Pd nanoparticles supported over TiO_2 (P25, Evonik) showed high activity in the preliminary test, nevertheless the other supports have been tested towards optimisation of the process and understanding of the role of support.

The most common material used as a catalyst support is carbon due to its stability in both acidic and basic media, high corrosion resistance, surface properties and high surface area. Vulcan XC-72R (Cabot) has been chosen as a representative of carbon materials. It consists of an aggregation of spherical particles within the size range of 30 to 60 nm. It has a large surface area (S_{BET}) of 238 m^2/g and a total pore volume of 0.38 cm^3/g.[22] It can be seen from figure 3-11 that 0.50 %Au 0.50 %Pd/ C catalyst showed higher conversion (94 %) than its counterpart supported over TiO_2 (87 %), however lower selectivity to cinnamaldehyde was observed. Furthermore, the carbon balance was significantly lower for the carbon supported catalyst, and the fact that the formation of any other compounds has not been observed suggests possibility that combustion processes are taking place. The other possibility is that the reactants are adsorbed onto carbon as it is known that aromatic compounds can absorb strongly onto high surface area carbon supports.[23]

Other tested supports were chosen inspired by work related to oxidations using mesoporous silicas and aluminas as catalysts supports carried out under leadership of Lee. Mesostructured aluminas exhibit the high dispersion and surface oxidation whereas high surface area and thermal stability is typical for mesoporous silicas. Lee and co-workers[24] were the first to report the use of alumina- grafted SBA-15 as a catalyst support for oxidation reactions. The researchers tested Pd nanoparticles deposited by incipient wetness impregnation and observed an enhanced catalytic performance when Pd was supported over alumina-grafted SBA-15 than either pure alumina (mesoporous) or SBA-15 (table 1). This was ascribed to higher nanoparticle dispersions and surface PdO concentrations on the modified support. This was said to be crucial as the researchers suggest that PdO species are an active site for the oxidation of cinnamyl alcohol.

***Table 1** Catalysts comparison.*[24] [25] [26]

Catalyst	Conversion [%]	Selectivity to cinnamaldehyde [%]
Pd/Al-SBA15	95	64
Pd/m-Al_2O_3	56	39
Pd/SBA15	21	16

Conditions: Radley reactor; catalyst mass, 50 mg; substrate, 8.4 mmol in 10 cm^3 toluene; temperature, 90 °C; oxygen pressure, 1bar; time, 0.5 h.

Catalysts with 1 % total metal loading (1:1 by weight) of Au-Pd have been prepared by sol-immobilisation method using purchased mesoporous aluminium oxide and SBA-15 (Sigma Aldrich). Alumina grafted SBA-15 was prepared from purchased powders according to the procedure described in the literature[24] and shortly presented in the experimental 2.4.3. section in chapter 2. The results have been presented in figure 3-11. Au-Pd/ m-Al_2O_3 demonstrated a relatively low conversion (64 % after 4 hours) and acceptable carbon balance (92 %), while Au-Pd/ SBA-15 led to a higher conversion (99 % after 4 hours), however carbon balance was relatively low (86 %). One on the reasons of lower carbon balance might be adsorption of the reactants or products on the catalyst surface (due to high surface area). Baiker and co-workers proved that very small amounts of carboxylic acids are able to be adsorbed on the catalyst, especially on the support and their presence is not detectable on GC.[27] Au-Pd nanoparticles supported over m-Al_2O_3/SBA-15 demonstrated 75 % conversion thus the resultant value between those two pure powders. Surprisingly, the selectivity to cinnamaldehyde was higher than for both pure supports and carbon balance was closed. The results differ from the results reported in the literature because the conversion for m-Al_2O_3/ SBA-15 is not the highest, however by showing higher selectivity to cinnamaldehyde the overall catalytic performance has been enhanced compared to the pure powders.

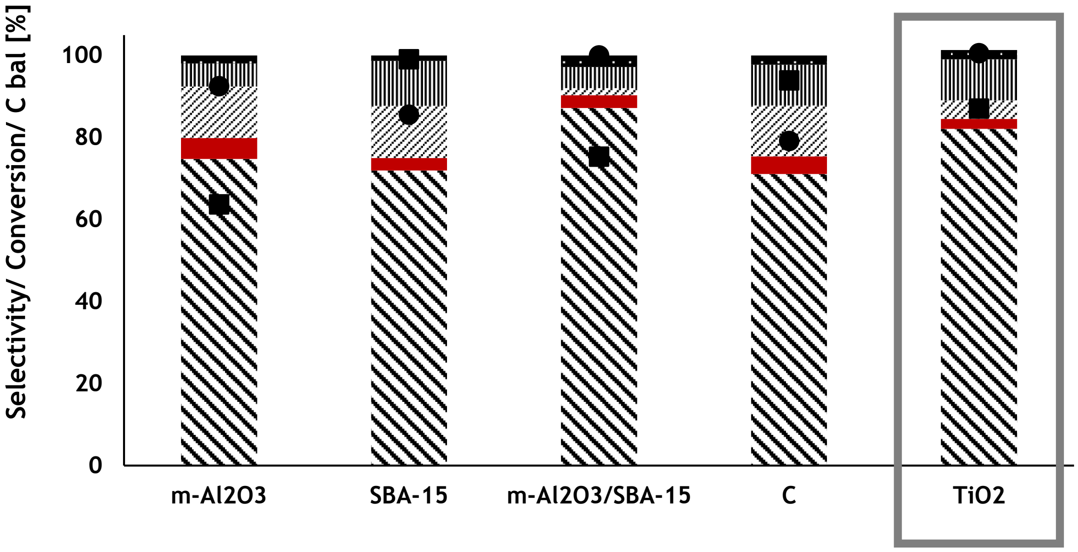

Figure 3-11 Catalysts screening for the oxidation of cinnamyl alcohol. Reaction conditions: catalyst*s prepared by sol-immobilisation method*, 10 mg; oxygen pressure, 3 bar; temperature, 120 °C; 0.5 M cinnamyl alcohol in toluene; time, 4 hours. **Conversion (■) ; Carbon balance (●); Cinnamaldehyde (▧); Benzaldehyde (▬); Styrene (▬); 3-Phenyl-1-propanol (▨); Methylstyrene (▥)**

The influence of bare m-Al_2O_3/SBA-15 support was tested on the oxidation of cinnamyl alcohol (figure 3-12) and has been contrasted with the blank reaction. The support leads to a lower conversion during the first 2 hours, however after 4 hours the conversion is the same as for the blank reaction. The selectivity is also comparable to the blank reaction (figure 3-13). Taking into consideration that TiO_2 does not influence the blank reaction, different behaviour of m-Al_2O_3/SBA-15 implies different radical scavenging properties. The reason might be related to the adsorption effect as the surface area of TiO_2 (35-65 m^2/g) is lower than the surface area of m-Al_2O_3/SBA-15 (224 m^2/g). Radical species are more likely to be quenched due to its collision with the support surface what would explain why the autoxidation is limited during the first 2 hours.

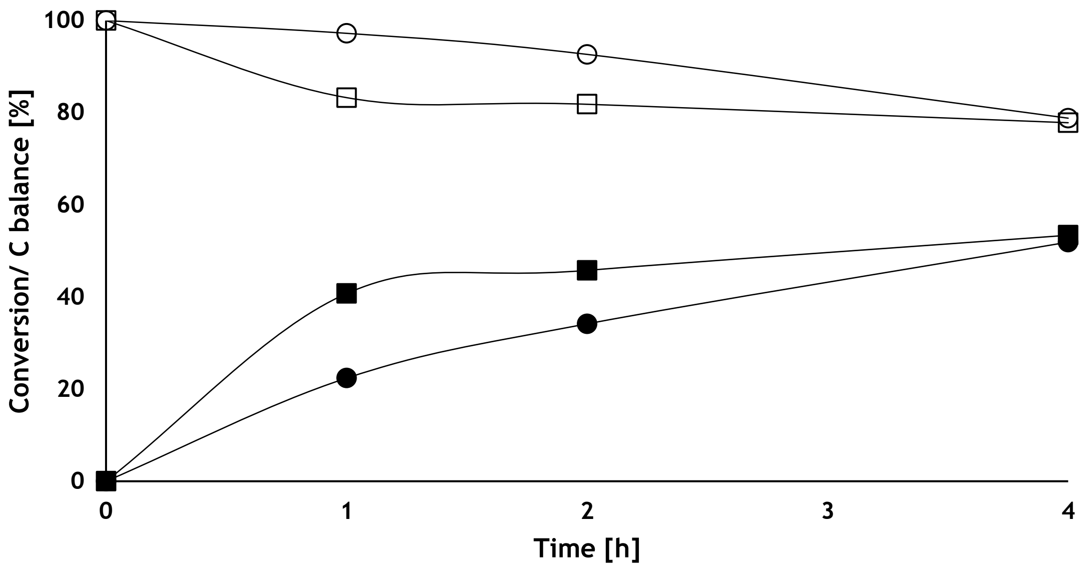

***Figure 3-12** Effect of (m-Al_2O_3/SBA-15) on the conversion in the process of cinnamyl alcohol oxidation. Reaction conditions: support, 10 mg; oxygen pressure, 3 bar; temperature, 120 °C; 0.5 M cinnamyl alcohol in toluene.* **Full figures- conversion: blank reaction (■); reaction carried out using bare *m-Al_2O_3/SBA-15 support* (●). Empty figures- carbon balance: blank reaction (☐); reaction carried out using bare *m-Al_2O_3/SBA-15 support* (○)**

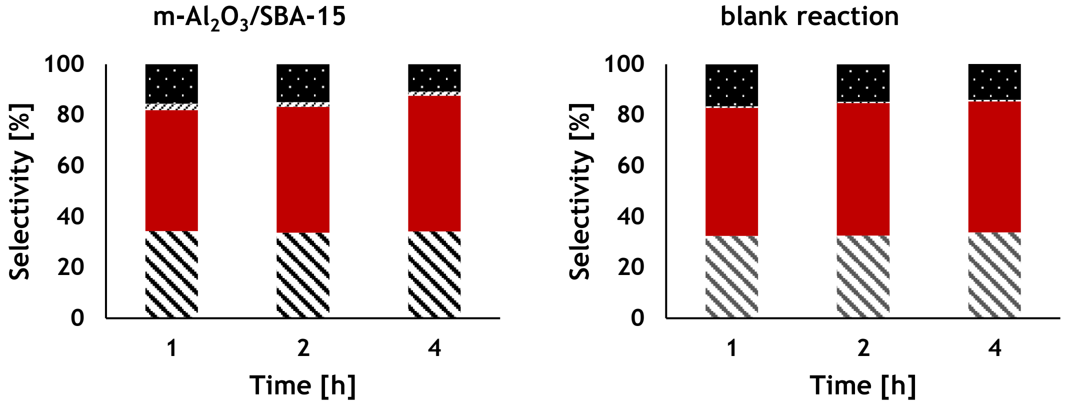

Figure 3-13** Effect of (m-Al_2O_3/SBA-15) on the selectivity in the process of cinnamyl alcohol oxidation. Reaction conditions: support, 10 mg; oxygen pressure, 3 bar; temperature, 120 °C; 0.5 M cinnamyl alcohol in toluene. **Cinnamaldehyde (▧); Benzaldehyde (🟥); Benzoic acid (■); 3-Phenyl-1-propanol (▨)

To decide which support is more beneficial for the studied process, more detailed experiments have been carried out. Figures 3-14 and 3-15 present time online studies using Au-Pd nanoparticles supported over m-Al_2O_3/SBA-15 and TiO_2 by sol-immobilisation method. It can be seen that the 0.50 %Au 0.50 %Pd/ TiO_2 (SIm) has higher conversion than 0.50 %Au 0.50 %Pd/(m-Al_2O_3/SBA-15) (SIm). The latter displays higher selectivity towards cinnamaldehyde, however the difference is not significant enough to compensate lower conversion.

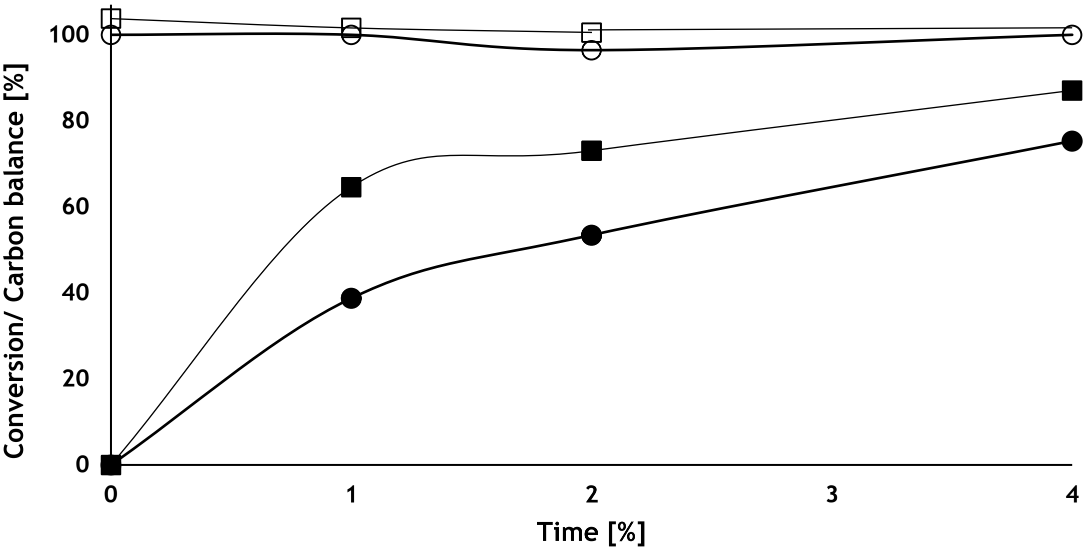

Figure 3-14 *Time on line profile for the oxidation of cinnamyl alcohol using catalysts prepared by sol-immobilisation method. Reaction conditions:* catalyst, *10 mg; oxygen pressure, 3 bar; temperature, 120 °C; 0.5 M cinnamyl alcohol in toluene*. **Full figures-conversion: *0.50 %Au 0.50 %Pd/(m-Al_2O_3/SBA-15) (●); 0.50 %Au 0.50 %Pd/TiO_2 (■).*** **Empty figures- carbon balance: *0.50 %Au 0.50 %Pd/(m-Al_2O_3/SBA-15) (○) ; 0.50 %Au 0.50 %Pd/ TiO_2 (□).***

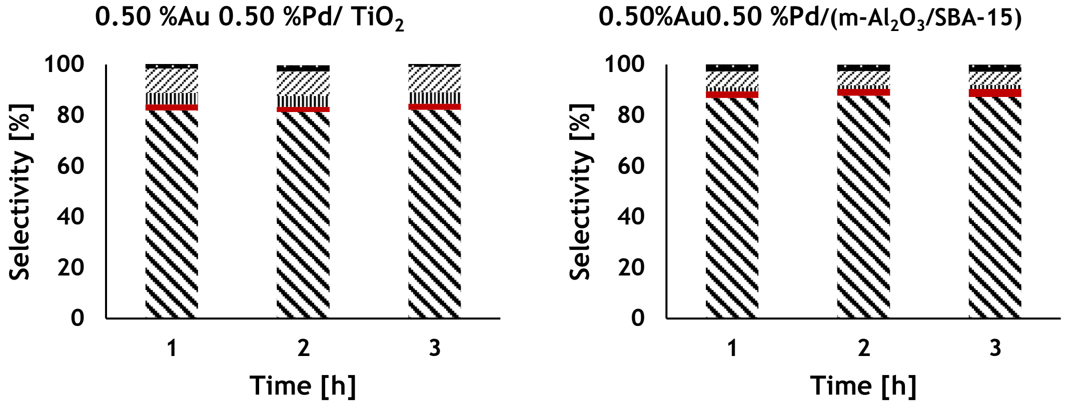

Figure 3-15 Effect *of catalysts prepared by sol-immobilisation method on the selectivity in the process of cinnamyl alcohol oxidation. Reaction conditions:* catalyst, *10 mg; oxygen pressure, 3 bar; temperature, 120 °C; 0.5 M cinnamyl alcohol in toluene*. ***Cinnamaldehyde (▧); Benzaldehyde (▬); Styrene (■); 3-Phenyl-1-propanol (▨); Methylstyrene (▥)***

The activity of the catalysts prepared by impregnation method have been found to be at a comparable level with only minor differences during the first two hours; the activity lined up in fourth hours of the experiment (figure 3-16). Interestingly, Au-Pd nanoparticles deposited by impregnation method over m-Al_2O_3/ SBA-15 showed higher selectivity than supported over pure m-Al_2O_3 and SBA-15 (figure 3-17).

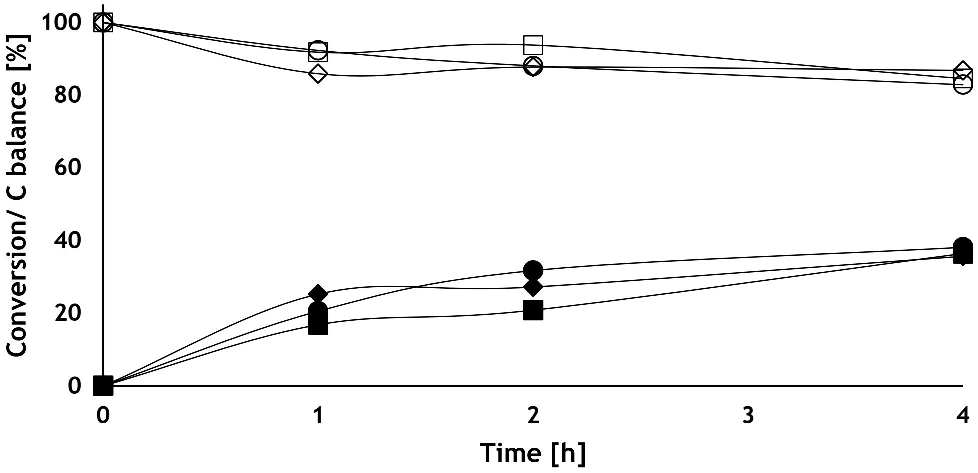

Figure 1-16** Time on line profile for the oxidation of cinnamyl alcohol using catalysts prepared by impregnation method. Reaction conditions: catalyst, 10 mg; oxygen pressure, 3 bar; temperature, 120 °C; 0.5 M cinnamyl alcohol in toluene.* ***Full figures-conversion: 0.50 %Au 0.50 %Pd/ m-Al_2O_3 (■); 0.50 %Au 0.50 %Pd/ SBA-15 (◆); 0.5 %Au 0.5 %Pd/(m-Al_2O_3/SBA-15) (●). Empty figures- carbon balance: 0.50 %Au 0.50 %Pd/ m-Al_2O_3 (□); 0.50 %Au 0.50 %Pd/ SBA-15 (◇); 0.50 %Au 0.50 %Pd/(m-Al_2O_3/SBA-15) (○)

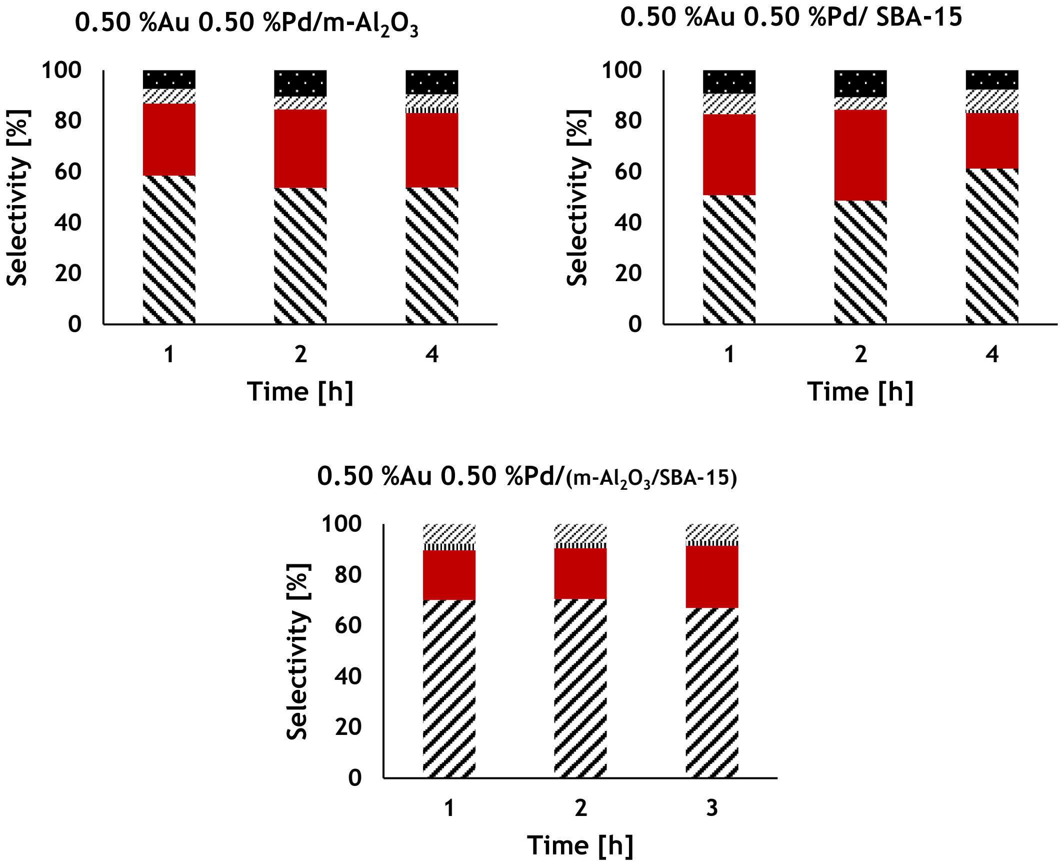

***Figure 3-17** Effect of catalysts prepared by impregnation method on the selectivity in the process of cinnamyl alcohol oxidation. Reaction conditions: catalyst, 10 mg; oxygen pressure,*

3 bar; temperature, 120 °C; 0.5 M cinnamyl alcohol in toluene. ***Cinnamaldehyde (▧); Benzaldehyde (🟥); Benzoic acid (■); 3-Phenyl-1-propanol (▨); Methylstyrene (▥)***

Summarizing the considerations on the selection of the best support, TiO_2 is definitely more beneficial than carbon, m-Al_2O_3, SBA-15 or m-Al_2O_3/ SBA-15. Therefore, other experiments have been carried out using Au-Pd nanoparticles supported over TiO_2.

3.3.5. Catalyst mass studies

The investigation of the effect of substrate to metal ratio has been carried out using 0.50 %Au 0.50 %Pd/TiO_2 (SIm) catalyst. As is presented in figures 3-18 and 3-19, the conversion increases with decreasing s:m (an equivalent to the increase in the amount of catalyst) which is in line with other catalytic reactions.[28], [29]

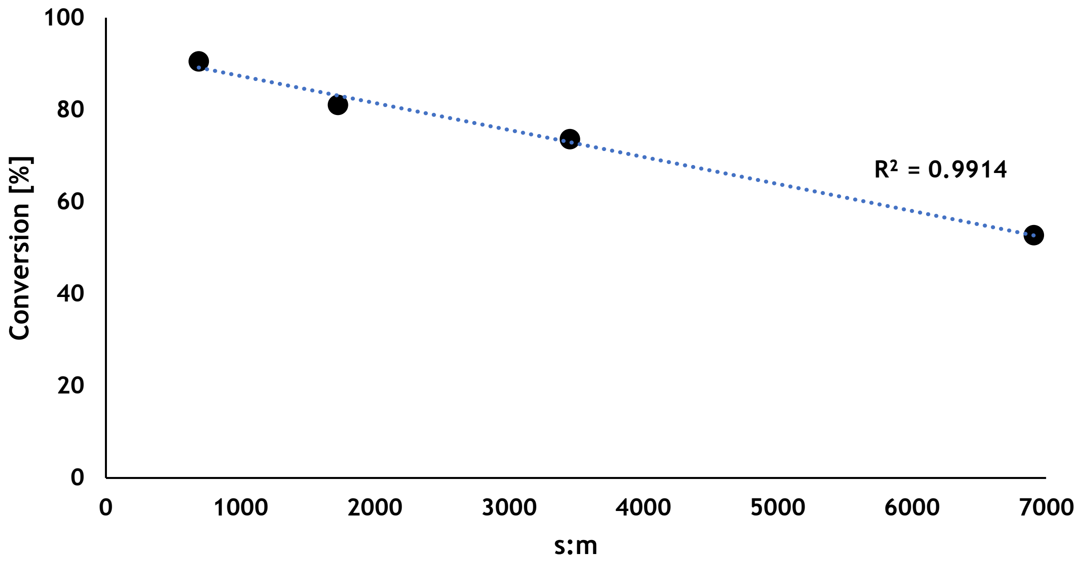

Figure 3-18 *The effect of substrate metal ratio on the conversion of cinnamyl alcohol. Reaction conditions: 0.50 %Au 0.50 %Pd/TiO_2 (SIm) catalyst; oxygen pressure, 3 bar; temperature, 120 °C; 0.5 M cinnamyl alcohol in toluene; reaction time, 2h.*

The mass transfer limitation means that the catalyst in a given process is not being effectively used. To assess whether the process of cinnamyl alcohol oxidation is mass transfer limited, the test reactions have been carried out (figure 3-19). It can be seen, that the conversion is not proportional to the catalyst mass when extremely low amount of the catalyst has been applied (below 10 mg). The conversion of cinnamyl alcohol increased proportionally to the increasing mass of the catalyst when 10 mg to 50 mg has been used. The presented research aims to underpin the work towards developing of greener alcohols oxidations methods hence low metal loading and low catalyst usage are the key points. When 50 mg of the catalyst has been tested, the carbon balance was relatively low (91 %). The difference in conversion between 10 and 20 mg of the catalyst was only 6 % (carbon balance was closed) hence it was reasonable to do further work using 10 mg which is efficient, transfer limited free and is beneficial from an environmental point of view.

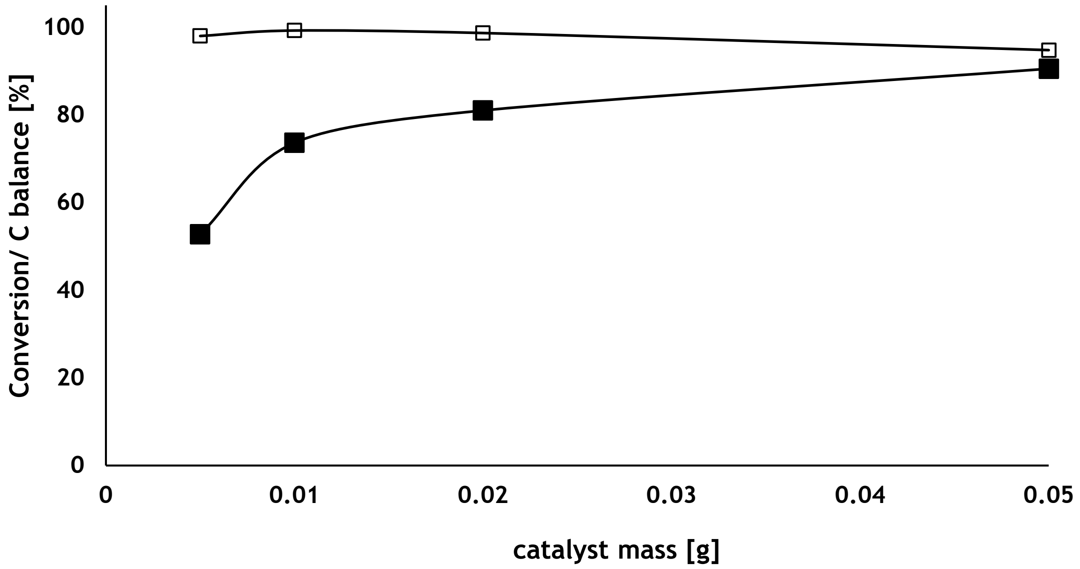

Figure 3-19 *The effect of catalyst mass on the oxidation of cinnamyl alcohol. Reaction conditions: 0.50 %Au 0.50 %Pd/TiO$_2$ (SIm) catalyst; oxygen pressure, 3 bar; temperature, 120 °C; 0.5 M cinnamyl alcohol in toluene; reaction time, 2h.* ***Conversion (■); Carbon balance (□)***

As can be seen in figure 3-20, the catalyst mass of the catalyst does not affect massively the selectivity.

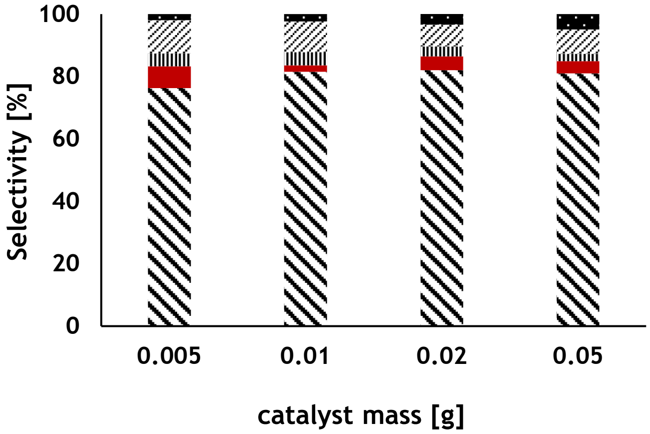

Figure 3-20 *The effect of catalyst mass on the selectivity in the oxidation of cinnamyl alcohol. Reaction conditions: 0.50 %Au 0.50 %Pd/TiO$_2$ (SIm), 10 mg; oxygen pressure, 3 bar; temperature, 120 °C; 0.5 M cinnamyl alcohol in toluene; reaction time, 2h.* ***Cinnamaldehyde (▧); Benzaldehyde (🟥); Styrene (■); 3-Phenyl-1-propanol (▨); Methylstyrene (▥)***

3.3.6. Effect of scavengers

Niklasson *et al.* proved that cinnamyl alcohol undergoes autoxidation under various conditions.[30] In addition it was pointed out that the process of autoxidation starts easily and has a high rate of reaction once started.[30] Costa *et al.* also reported the phenomenon of autoxidation of cinnamyl alcohol in their work on the catalytic oxidation of alcohols by Au-Ag nanotubes. Furthermore, researchers obtained large amounts of benzaldehyde which was suggested to be formed from cinnamaldehyde *via* a radical pathway in the liquid phase, not on the catalyst surface.[17] The reaction was carried out at elevated temperature (100 °C) and under a relatively moderate oxygen pressure (6 bar). The reaction performed in the absence of a catalyst demonstrated 28 % conversion after 2.5 h with a selectivity profile of 44.5 % to cinnamaldehyde and 53 % to benzaldehyde. The reaction catalysed by Au-Ag NT showed 99.1 % conversion with slightly different selectivity profile of 21.1 % cinnamaldehyde and 73 % benzaldehyde. The researchers hypothesised two possible reasons for the activation of a radical pathway: the presence of hydroperoxides originating from the substrate or due to the activation of molecular oxygen by Au.

In my opinion, the formation of benzaldehyde was not clear enough and this phenomenon required further investigation. To confirm the radical mechanism, the oxidation of cinnamyl alcohol was performed with the addition of radical scavengers in the absence of a catalyst. Two types of scavengers were tested: hydroquinone as a scavenger for oxygen centred radicals[31] and diphenylamine as a scavenger for carbon centred radicals[32]. As evidenced in Figure 3-21, scavengers significantly decreased the conversion of cinnamyl alcohol, indicating the radical character of the reaction which is in good agreement with the literature. Moreover, reaction in the absence of a catalyst did not take place in the atmosphere of inert gas hence we can be sure that autoxidation was taking place due to the presence of oxygen.

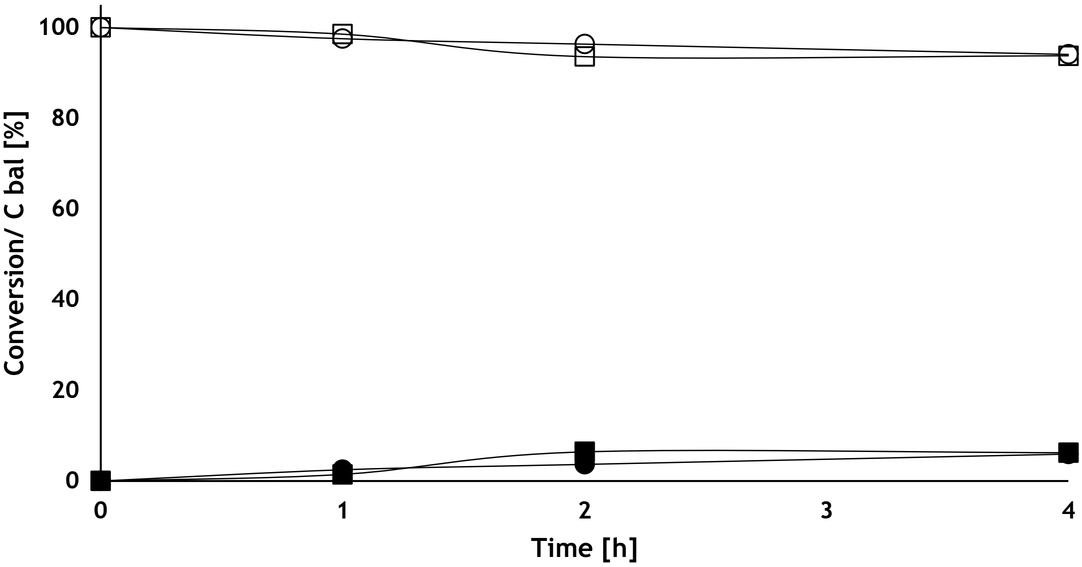

Figure 3-21 *Reaction carried out in the absence of a catalyst with the addition of scavengers. Conditions: oxygen pressure, 3 bar; temperature, 120 °C; 0.5 M cinnamyl alcohol in toluene; scavengers: hydroquinone/ diphenylamine, 2 mg.* ***Full figures- conversion; empty figures- carbon balance: reaction with diphenylamine (●), reaction with hydroquinone (■)***

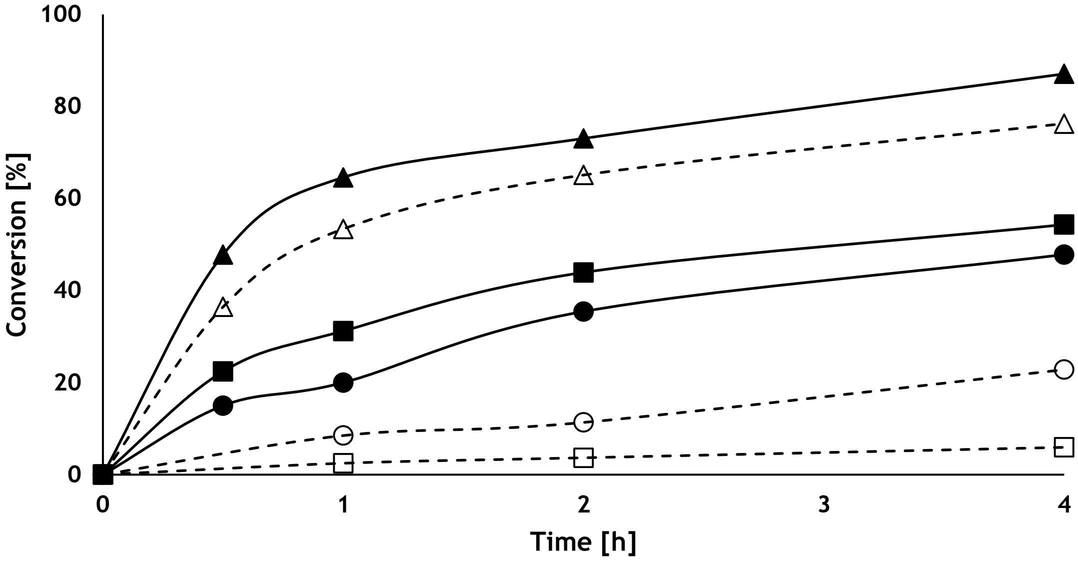

Figure 3-22 *Time on-line for the oxidation of cinnamyl alcohol with the addition of scavenger (hydroquinone). Reaction conditions: catalyst, 10 mg; oxygen pressure, 3 bar; temperature, 120 °C; 0.5 M cinnamyl alcohol in toluene; scavengers: hydroquinone/ diphenylamine, 2 mg.* ***Blank (■)****; 0.50 %Au 0.50%Pd/TiO$_2$ (SIm)* ***(▲)****; 0.50 %Au 0.50 %Pd/TiO$_2$ (Imp)* ***(●)****;* ***blank + scavenger (□)****; 0.50 %Au 0.50%Pd/TiO$_2$ (Imp) +* ***scavenger (○)****; 0.50 %Au 0.50 %Pd/TiO$_2$ (SIm) +* ***scavenger (△)***

The presence of scavengers only slightly decreased the conversion for the reaction utilising the 0.50 %Au 0.50 %Pd/TiO$_2$ (SIm) (figure 3-22) whereas the drop for blank and for the 0.50 %Au 0.50%Pd/TiO$_2$ (Imp) catalyst was dramatic.

Figures 3-23 and 3-25 summarise selectivity to products for the catalysed reactions carried out with the addition of scavengers. It can be seen from Figure 3-23, that both scavengers completely inhibit the formation of benzaldehyde in case of the reaction with the 0.50 %Au 0.50 %Pd/TiO_2 (SIm) catalyst.

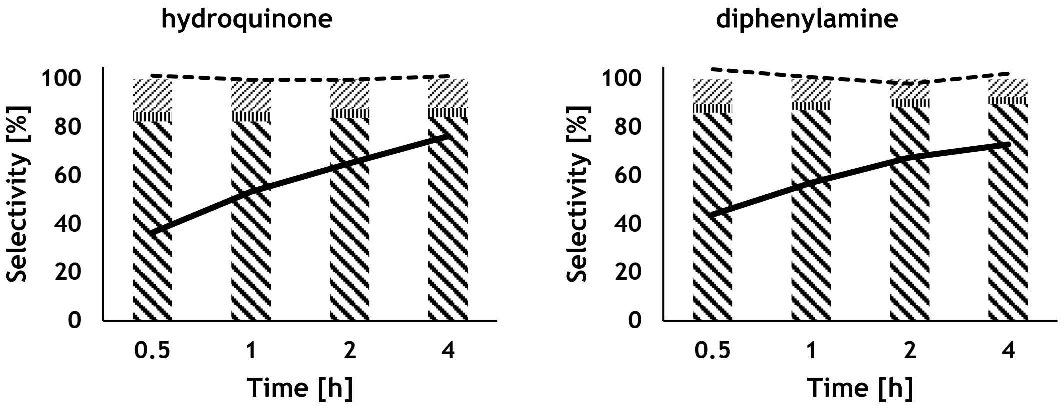

Figure 3-23 Time on-line for the *oxidation of cinnamyl alcohol using of 0.50 %Au 0.50 %Pd/ TiO_2 (SIm) catalyst. Reaction conditions: catalyst; 10 mg; oxygen pressure, 3 bar; temperature, 120 °C; 0.5 M cinnamyl alcohol in toluene; scavenger, 2mg.* ***Conversion (——); Carbon balance (-----); Cinnamaldehyde (▧); 3-Phenyl-1-propanol (▨); Methylstyrene (|||||||)***

Addition of scavengers to the reaction carried out with the use of the 0.50 %Au 0.50%Pd/TiO_2 (Imp) catalyst provided interesting results (Figure 3-24). In addition to lowering conversion, the scavengers significantly reduced formation of benzaldehyde, simultaneously increasing selectivity to cinnamaldehyde (80 %). It seems reasonable to suggest that the scavengers limit the autoxidation of cinnamyl alcohol and therefore leads to a low selectivity to benzaldehyde and low conversion (20 % after 4 hours). It supports the hypothesis that benzaldehyde might be formed in more than one way, not only from cinnamaldehyde but also from cinnamyl alcohol. If benzaldehyde was created only from cinnamaldehyde, addition of scavengers would differently affect the profile of benzaldehyde and cinnamaldehyde. There is a possibility that benzaldehyde plays a promoting role on the oxidation of cinnamyl alcohol.[33] To test this hypothesis, the catalysed and uncatalysed oxidations of the substrate with the addition of benzaldehyde were performed. The results revealed that the presence of additional benzaldehyde had no influence on the oxidation of cinnamyl alcohol. The experiment was carried out twice using two types of benzaldehyde: standard benzaldehyde and F-benzaldehyde which showed no difference compared to the standard compound.

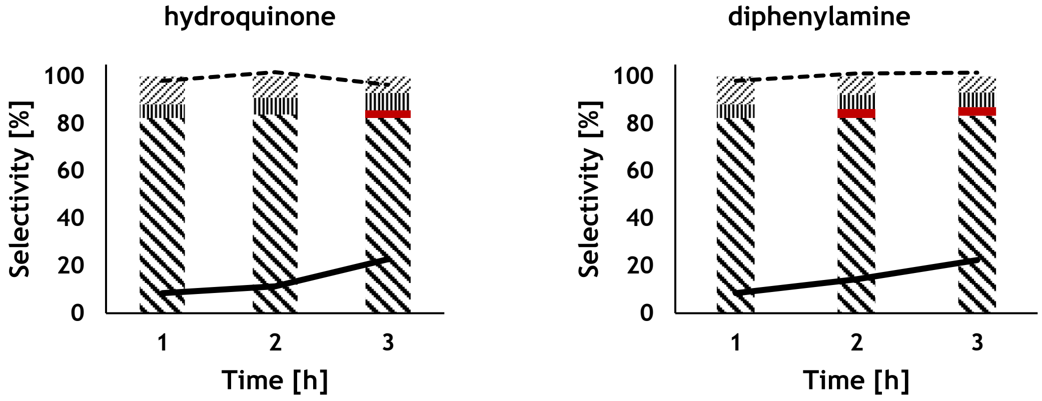

Figure 3-24 *Oxidation of cinnamyl alcohol using of 0.50 %Au 0.50 %Pd/ TiO_2 (Imp) catalyst. Reaction conditions: catalyst; 10 mg; oxygen pressure, 3 bar; temperature, 120 °C; 0.5 M cinnamyl alcohol in toluene; scavenger, 2mg.* ***Conversion (—); Carbon balance (- - - -); Cinnamaldehyde (▧); Benzaldehyde (🟥); Benzoic acid (■); 3-Phenyl-1-propanol (▨); Methylstyrene (|||)***

It is known from literature that metal ions (e.g. $Co^{2+}/Co^{3+}/ Mn^{2+}/Mn^{3+}$, Fe^{2+}/Fe^{3+}, Cu^{+}/Cu^{2+}) are able to split the hydroperoxides which prevents the processes of autoxidation.[34] It seems that the studied Au-Pd system has similar properties which depend on the size of metal nanoparticles. Based on the gathered knowledge, the formation of benzaldehyde has been considered as a proof of autoxidation taking place in the selective oxidation of cinnamyl alcohol.

3.3.7. Atmosphere of inert gas

There is a big gap in understanding the role of oxygen in the oxidation of cinnamyl alcohol. Several groups of researchers have different views and put different hypothesis in relation to this issue. Baiker and co-workers oxidised cinnamyl alcohol with the use of Pd/Al_2O_3 catalyst.[35] Their detailed studies delivered very important findings. One of many significant observations was confirmation of the dehydrogenation mechanism for this reaction. Moreover, the researchers proved that the process is independent of the presence of oxygen in the system. Increased selectivity to the products being formed under anaerobic conditions due to the effect of hydrogen transfer, namely 3-phenyl-1-propanl and methylstyrene, showed that cinnamyl alcohol acts as a hydrogen acceptor.[12], [35] It was concluded that the oxygen takes part in the process as a "cleaner" for catalyst surface from e.g. excess of hydrogen.[34] Another group under the leadership of Lee suggested that PdO is the active centre hence oxygen plays a direct and important role in the catalytic process to constantly regenerate the active sites.[26]

To examine the influence of oxygen under the currently studied conditions, reactions of cinnamyl alcohol oxidations were carried out under nitrogen and under oxygen. The studies on the aerobic oxidation have been shown in the later part of this work. Anaerobic conditions have been discussed in this section.

As stated before autoxidation did not take place under nitrogen (anaerobic) conditions. The results for the catalysed reactions carried out under either oxygen or nitrogen (4 hours) have been contrasted in table 2. Time online studies were also conducted for the same reactions to get a better insight into the process (Figure 3-25 and 3-26). Analysing those two figures one can see the same trend as for the reactions carried out under standard conditions and that the selectivity to each product is fairly steady over time.

The 0.50 %Au 0.50 %Pd/TiO$_2$ (Imp) catalyst (table 2, figure 3-25) was less active under nitrogen than under oxygen. Interestingly, the formation of benzaldehyde was stopped and the selectivity to cinnamaldehyde remained the same. Higher selectivities to 3-phenyl-1-propanol and methylstyrene indicate that the processes of hydrogenation and hydrogenolysis were more prevalent under nitrogen than under oxygen. This result is in excellent agreement with Baiker's work.[14], [35] It can be seen from table 2, that there was only a minimal difference in conversion for the reactions with 0.50 %Au 0.50 %Pd/TiO$_2$ (SIm) catalyst carried out under nitrogen and oxygen whereas the difference in selectivity was significant, especially towards formation of methylstyrene (see table 2 and Figure 3-26). The results of experiments carried out under inert gas are in line with mentioned above literature.[14], [35] It seems very likely that hydrogen is abstracted on the catalyst surface, followed by another molecule of the substrate acting as a hydrogen acceptor. Overall, the studied process is in good agreement with the mechanism of oxidative dehydrogenation/ dehydrogenation described in the literature.[35]

Table 2 *Effect of oxygen and nitrogen on catalysed and uncatalysed reaction of cinnamyl alcohol oxidation under standard conditions after 4 h.*

Reaction	Conversion [%]	C bal [%]	Selectivity [%]					
			CinnALD	BenzALD	PP	MS	BenzACID	Styrene
Blank- O$_2$	54	81	31	58	1	-	10	-
Blank-N$_2$	-	-	-	-	-	-	-	-
Imp-O$_2$	48	91	60	28	6	2	5	-

Imp-N_2	19	103	56	-	27	18	-	-
SIm-O_2	87	100	82	2	10	5	-	2
SIm-N_2	86	100	58	-	13	30	-	-

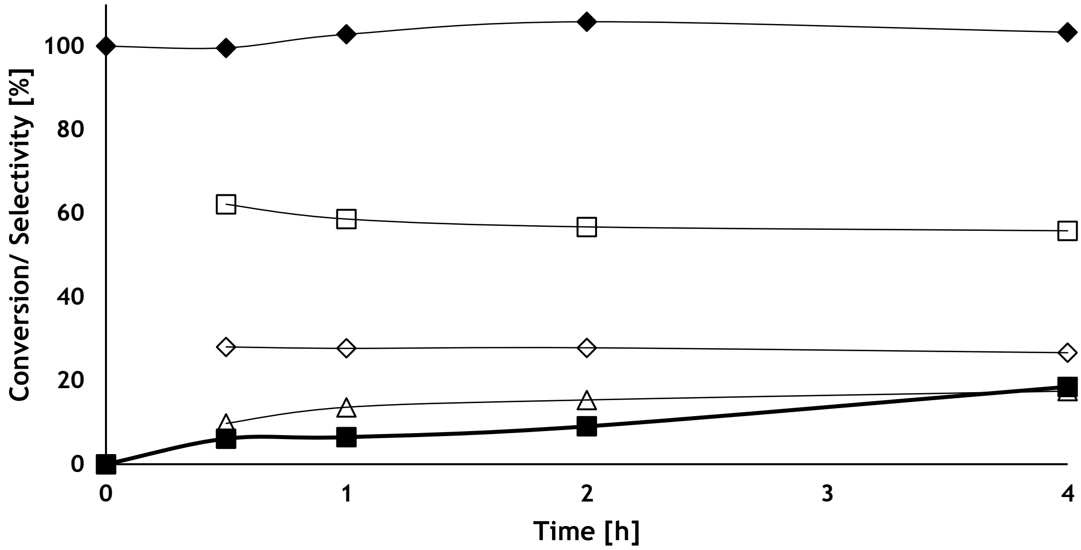

Figure 3-25 *Time on-line for the oxidation of cinnamyl alcohol using 0.50 %Au 0.50 %Pd/TiO_2 (Imp). Conditions: catalyst, 10 mg; nitrogen pressure, 3 bar; temperature, 120 °C; 0.5 M cinnamyl alcohol in toluene.* ***Conversion (■); Carbon balance (◆); Cinnamaldehyde (□); 3-Phenyl-1-propanol (◇) ; Methylstyrene (△).***

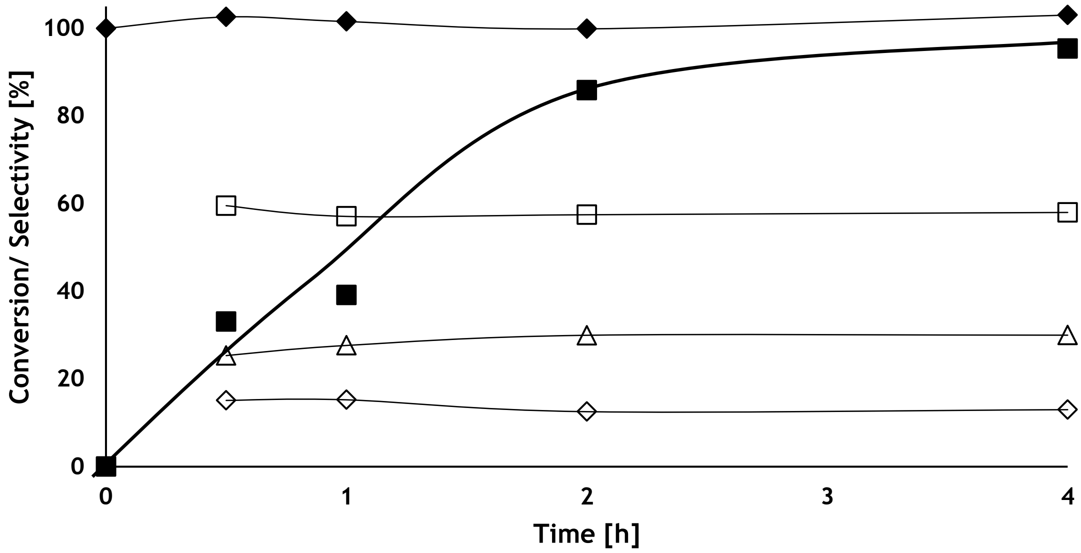

Figure 3-26 *Time on-line for the oxidation of cinnamyl alcohol using 0.50 %Au 0.50 %Pd/TiO_2 (SIm). Conditions: catalyst,* 10 mg; nitrogen pressure, 3 bar; temperature, 120 °C; 0.5 *M* cinnamyl alcohol in toluene. **Conversion (■); Carbon balance (◆); Cinnamaldehyde (□); 3-Phenyl-1-propanol (◇); Methylstyrene (△).**

3.3.8. Effect of oxygen and oxygen pressure

Following the significant differences observed between nitrogen and oxygen, further studies were conducted to investigate the role of the latter. Figure 3-27 illustrates the influence of oxygen pressure on the conversion for the reaction carried out in the absence and presence of the 0.50 %Au 0.50 %Pd/TiO_2 (Imp) catalyst. It can be seen that on increasing pressure, a higher conversion is achieved. This is particularly notable in the case of catalysed reaction (Imp).

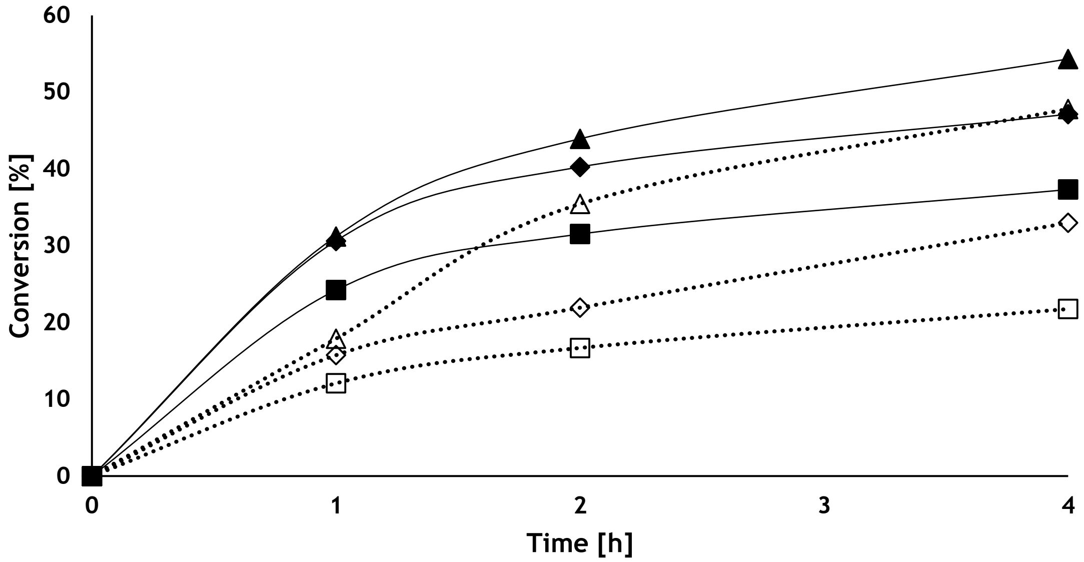

Figure 3-27 *Time on-line for the oxidation of cinnamyl alcohol under different oxygen pressure carried out in the presence and absence of the 0.50 %Au 0.50 %Pd/TiO_2 (Imp) catalyst. Reaction conditions: catalyst, 10 mg; oxygen pressure, 1-3 bar; temperature, 120 °C; 0.5 M cinnamyl alcohol in toluene.* ***Full figures- reactions carried out in the absence of a catalyst: 1 bar (■); 2 bar (◆), 3 bar (▲); empty figure- reactions carried out in the presence of a catalyst: 1 bar (□); 2 bar (◇); 3 bar (△)***

Figures 3-28 and 3-29 demonstrate the selectivities to major products as a function of oxygen pressure. The results for the catalysed (Imp) and uncatalysed reactions have been combined in order to emphasize the partly similarity in the mechanisms for both. In the case of the blank reaction, the mechanism is purely radical and increased pressure only slightly influenced the product distribution. The relation of selectivities to pressure is plotted in figure 3-29 from which it is clear that selectivity to benzaldehyde increased with increasing pressure at the expense of cinnamaldehyde. Pressure massively influenced the reaction carried out with the use of catalyst prepared by impregnation method. The selectivity to cinnamaldehyde under 1 bar oxygen pressure was high (around 70 %). The increase in pressure to 2 bar resulted in decreased selectivity to cinnamaldehyde (around 60 %) and increased selectivity to benzaldehyde (15 % under 1 bar and 25 % under 2 bar). A further increase in pressure to 3 bar led to significant decrease in selectivity to cinnamaldehyde (ca. 30 %) and an even higher selectivity to benzaldehyde (ca. 50 %). Interestingly, there is no benzoic acid at low pressure (1 bar) and quite large amounts have been formed at higher pressures (ca. 10 % under 2 bar and 15 % under 3 bar).

In general, the increase in pressure resulted in increased selectivity to benzaldehyde at the expense of cinnamaldehyde which is consistent with the findings reported by Costa and co-workers[17]. The conversion under 3 bar is significantly higher than at lower pressures and selectivity to benzaldehyde is especially high. These experiments imply that benzaldehyde might be formed from cinnamaldehyde at lower pressures and additionally from cinnamyl alcohol at higher pressure.

The product distribution for catalysed reactions is different from blank reaction in the range of lower pressure: 1 bar and 2 bar. However, under the pressure of 3 bar the product distributions are almost identical for both reactions. Moreover, the low conversion for the 0.50 %Au 0.50 %Pd/TiO_2 (Imp) catalyst under 1 and 2 bar increased dramatically under 3 bar. The described dependencies indicate that catalyst plays a role of a radical scavenger under low pressure. Presumably, the increase in pressure to 3 bar ensured high availability of oxygen which coupled with high temperature enabled quicker formation of active oxygen species. As a result, the radical pathway has dominated the catalytic performance and autoxidation of cinnamyl alcohol took place. This is indicated by higher conversion and larger amount of formed benzaldehyde.

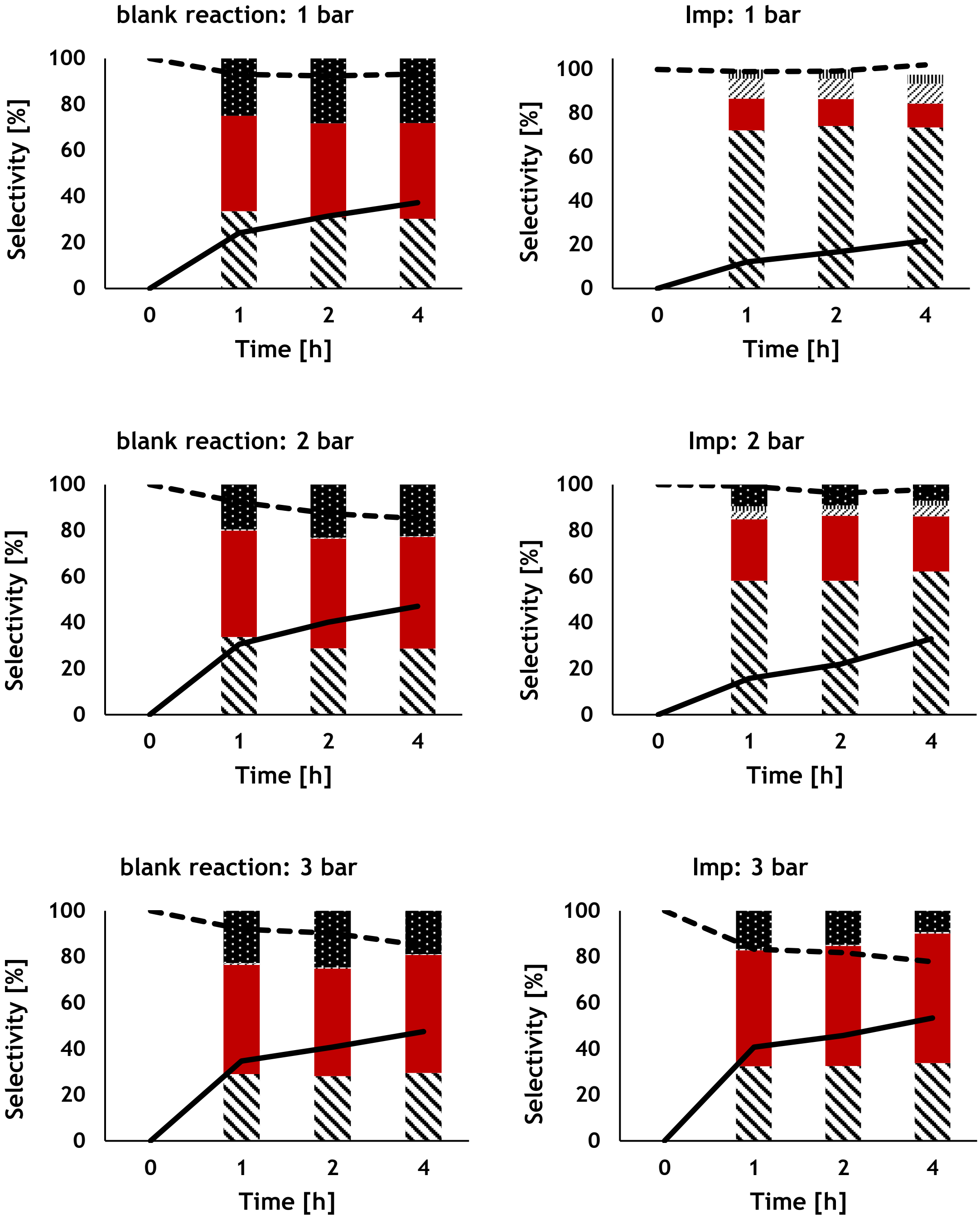

Figure 3-28 *The effect of pressure on the oxidation of cinnamyl alcohol; time on-line. Reaction conditions: oxygen pressure,1, 2 and 3 bar; temperature, 120 °C; 0.5 M cinnamyl alcohol in toluene; 0.50 %Au 0.50 %Pd/TiO*$_2$ *(Imp), 10 mg.* ***Conversion (—); Carbon balance (-----); Cinnamaldehyde (▧); Benzaldehyde (🟥); Benzoic acid (■); 3-Phenyl-1-propanol (▨); Methylstyrene (▥)***

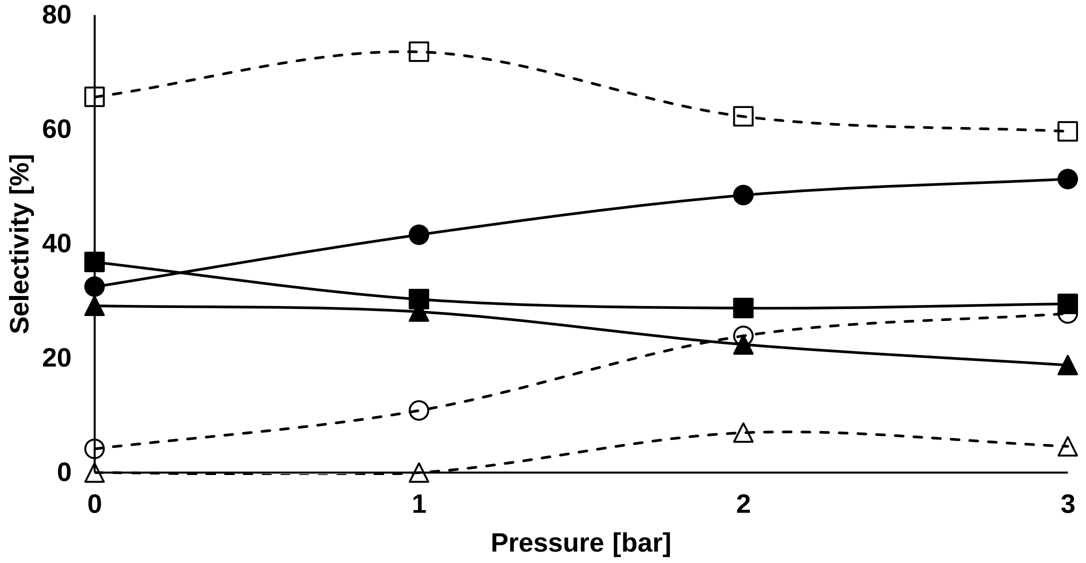

Figure 3-29 *Oxidation of cinnamyl alcohol under different oxygen pressure carried out in the presence and absence of the catalyst. Selectivity to cinnamaldehyde and benzaldehyde as a function of oxygen pressure. Reaction conditions: 0.50 %Au 0.50 %Pd/TiO*$_2$ *(Imp), 10 mg; oxygen pressure, 1-3 bar; temperature, 120 °C; 0.5 M cinnamyl alcohol in toluene.* ***Full figures- reactions carried out in the absence of the catalyst: CinnALD (■); BenzALD (●); BenzACID (▲); empty figure- reactions carried out in the presence of the catalyst: CinnALD (□), BenzALD (○); BenzACID (△)***

The pressure to a lesser extent determined the process of cinnamyl alcohol oxidation performed using 0.50 %Au 0.50 %Pd/TiO$_2$ (SIm) catalyst. Figure 3-30 shows the conversions of cinnamyl alcohol at 120 °C and under two pressures: 1 and 2 bar. Taking into account the experimental error of 3%, the difference is minimal. Despite the negligible difference in conversion, the analysis of selectivity showed subtle but interesting differences (figure 3-31). Whereas benzaldehyde is formed from the very beginning during a reaction carried out at 3 bar, at lower pressure (1 bar), benzaldehyde is formed only in the second hour of the experiment. In addition, a slightly increased selectivity towards MS and PP can be observed under reduced pressure. Although the pressure effect in the case of 0.50% Au 0.50% Pd / TiO$_2$ (SIm) catalyst is relatively low, it can be seen that the influence of oxygen is not without significance on the course of the reaction. The slightly increased amount of hydrogen transfer compounds suggests that more hydrogen is present at the surface of the catalyst at a pressure of 1 bar, and thus cinnamyl alcohol behaves like a hydrogen acceptor. There are two views in the literature about the role of oxygen in the oxidation of alcohols: oxygen is directly involved in the oxidation of alcohols, and oxygen purifies the surface of the catalyst from excess of hydrogen. More thought about the role of oxygen is presented in Chapter 4 of this thesis.

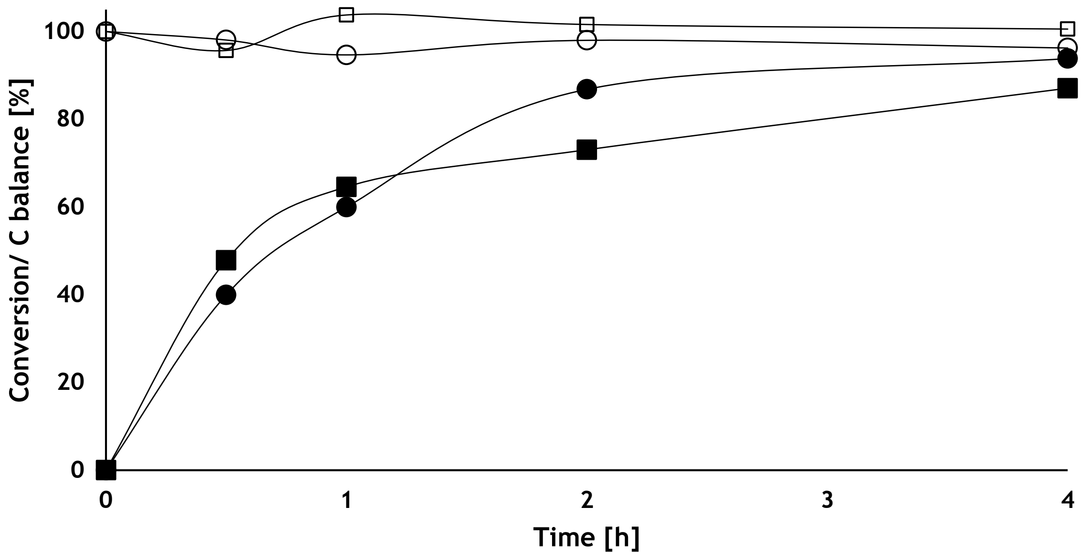

***Figure 3-30** Time on-line for the oxidation of cinnamyl alcohol using 0.50 %Au 0.50 %Pd/TiO$_2$ (SIm) under different oxygen pressure. Reaction conditions: catalyst, 10 mg; oxygen pressure, 1 and 3 bar; temperature, 120 °C; 0.5 M cinnamyl alcohol in toluene.* **Full figures- conversion: 3 bar (■); 1 bar (●); Empty figures- carbon balance: 3 bar (☐); 1 bar (○)**

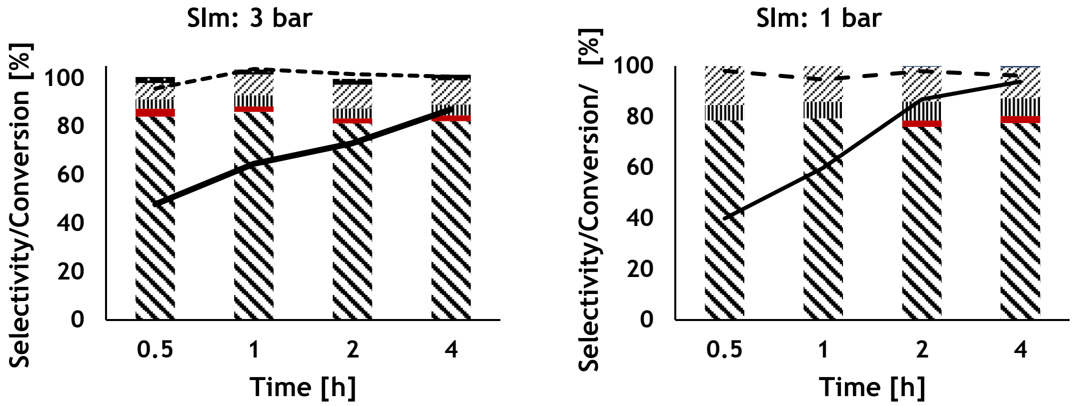

Figure 3-31** The effect of pressure on the oxidation of cinnamyl alcohol; time on-line. Reaction conditions: oxygen pressure,1 and 3 bar; temperature, 120 °C; 0.5 M cinnamyl alcohol in toluene; 0.50 %Au 0.50 %Pd/TiO$_2$ (SIm), 10 mg. **Conversion (—); Carbon balance (- - - -); Cinnamaldehyde (▨); Benzaldehyde (▬); Benzoic acid (▬); 3-Phenyl-1-propanol (▨); Methylstyrene (▥)

3.3.9. Effect of temperature

Considering the acquired knowledge from the literature and from the current work, the questions arose as to what conditions should be applied to avoid autoxidation, whether the autoxidation should be avoided and how important is the process in terms of catalysis. To elucidate these points, a number of detailed experiments were designed. Initially, a series of one-hour reactions were conducted at different temperatures under an oxygen pressure of one bar to check the influence of temperature on the process of autoxidation. The lower pressure was applied to minimise the effect of oxygen radicals. The results revealed that the autoxidation process took place between 60 and 70 °C, and above (Table 3) and that the temperature has a large influence on the product distribution. The only products detected at 80 °C and below were cinnamaldehyde and 3-phenyl-1-propanol. Benzaldehyde and benzoic acid appeared at 90 °C and above.

Table 3 *The presence of autoxidation of cinnamyl alcohol at low temperatures and low oxygen pressure (1 bar), in the short term (1h). The conversion and selectivity are reported within ± 3 % error.*

Temperature [°C]	Conversion [%]	C bal [%]	Selectivity [%]			
			CinnALD	BenzALD	PP	BenzACID
60	-	-	-	-	-	-
70	7	95	80	-	20	-
80	10	99	80	-	20	-
90	8	99	46	46	8	-
100	9	101	39	47	4	10
120	31	98	33	51	1	14

The autoxidation increases with temperature even under low oxygen pressure. Also, it is clear that autoxidation is very hard to be avoided as it takes place at low temperatures.

Figure 3-32 presents the process of autoxidation time on-line at different temperatures. Generally speaking, the higher the temperature, the higher the conversion caused by the autoxidation process. As expected, the conversion increases with time.

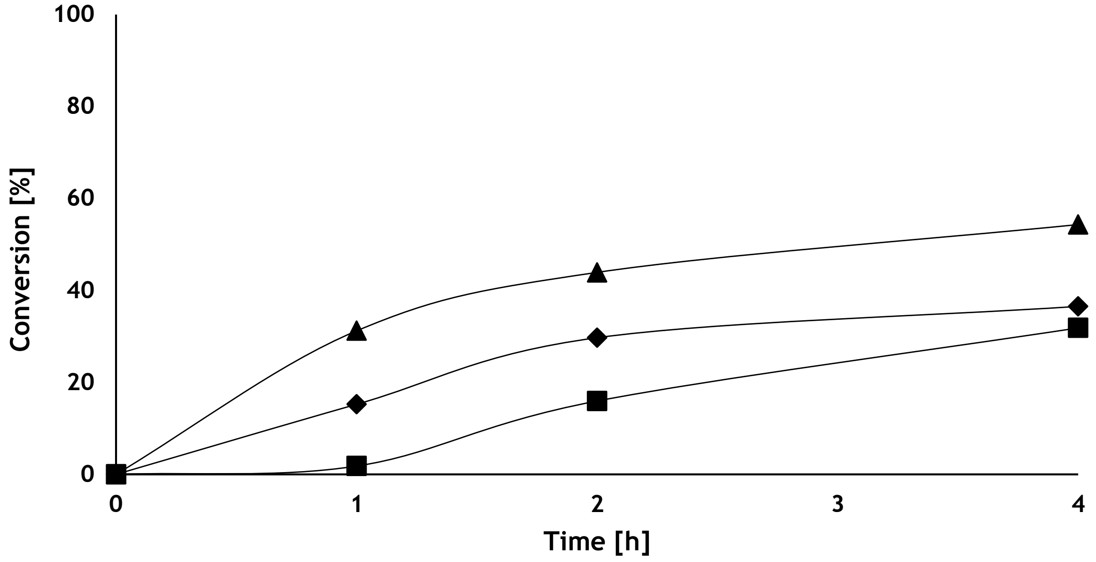

Figure 3-32 *The influence of the temperature on the oxidation of cinnamyl alcohol carried out in the absence of a catalyst. Reaction conditions: oxygen pressure, 3 bar; 0.5 M cinnamyl alcohol in toluene.* ***Temperature: 80 °C (■); Temperature: 100 °C (◆); Temperature: 120 °C (▲)***

It can be seen from figure 3-33 that the temperature influences the reaction carried out with the use of the catalyst prepared by impregnation method. The presence of the catalyst limited the autoxidation significantly at 80 °C and 100 °C as the conversion did not exceed 20 % after 4 hours. This trend can be compared with the results of experiments carried out for the blank reaction presented in figure 3-32 from which it can be seen that the conversion was lower than 40 % after 4 hours. Increasing the temperature to 120 °C resulted in an increase in conversion of catalysed reaction to ca 50 % thereby achieving the value similar to the blank reaction at that temperature. It has been suggested before that the Au-Pd nanoparticles acts as a scavenger, which would explain the behaviour of the catalyst in this case. The number of radicals formed at lower temperatures was lower compared with elevated temperatures, therefore the catalyst was able to efficiently decompose these to prevent autoxidation.

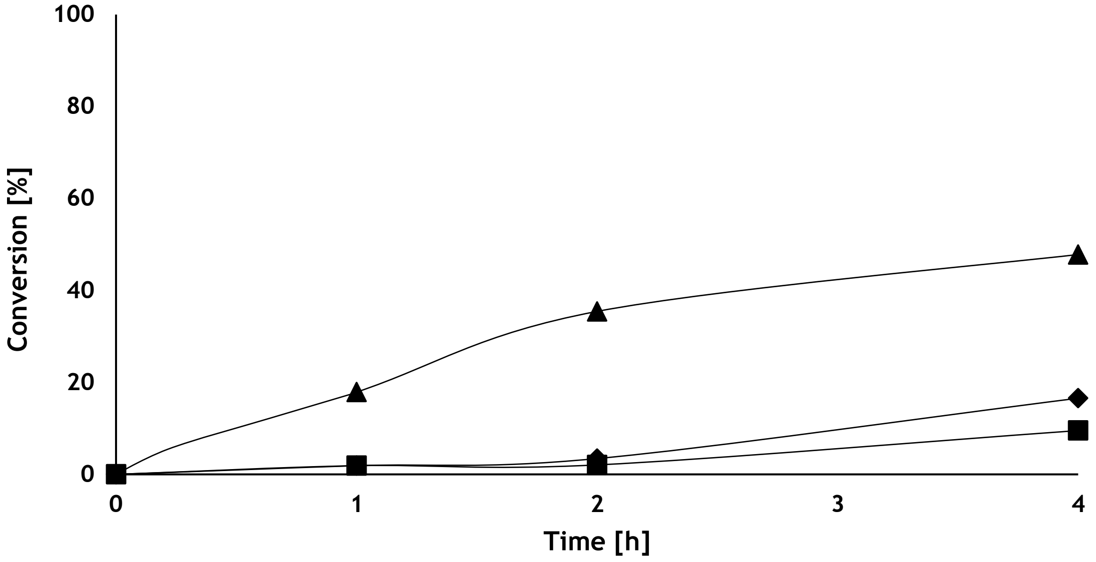

Figure 3-33** The influence of the temperature on the oxidation of cinnamyl alcohol using 0.50 %Au 0.50 %Pd/TiO$_2$ (Imp). Reaction conditions: catalyst, 10 mg; oxygen pressure, 3 bar; 0.5 M cinnamyl alcohol in toluene. **Temperature: 80 °C (■); Temperature: 100 °C (◆); Temperature: 120 °C (▲)

Figure 3-34 plots the conversion against the temperature for the reactions carried out in the absence and presence of the 0.50 %Au 0.50 %Pd/TiO$_2$ (Imp) catalyst. It can be clearly seen that there is a similar pattern of dependence for the catalysed (Imp) and blank reactions. Conversion increases with temperature in both reactions. As mentioned earlier the increase at 120 °C is particularly noticeable, possibly due to the formation of radicals overwhelming the effect of the catalyst.

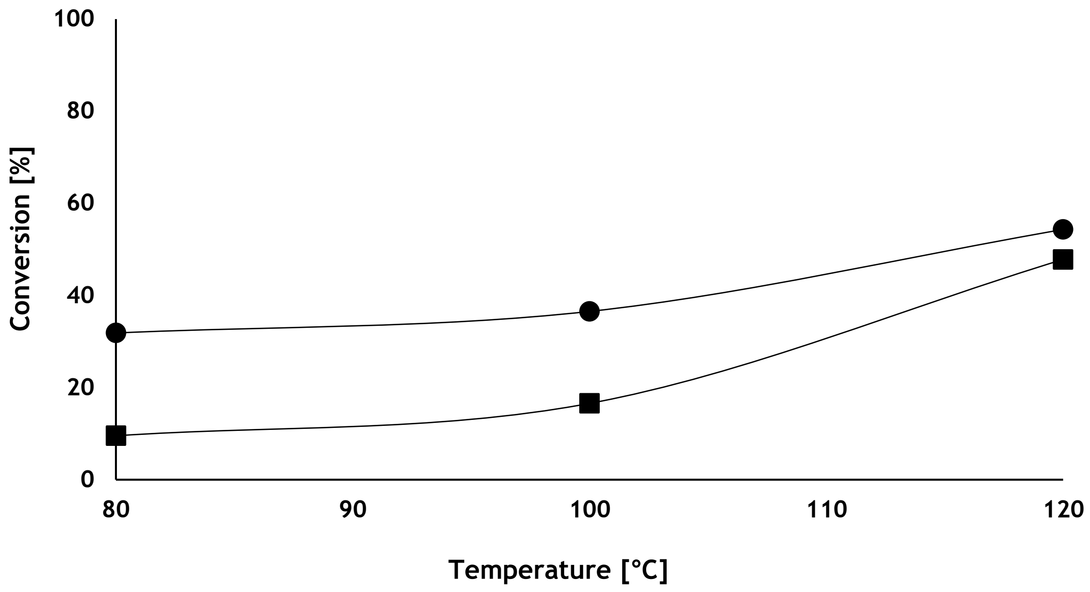

Figure 3-34 *Dependence of activity on the temperature for the process of cinnamyl alcohol oxidation performed in the absence and presence of the 0.50 %Au 0.50 %Pd/ TiO_2 (Imp) catalyst. Reaction conditions: catalyst, 10 mg; oxygen pressure, 3 bar; 0.5 M cinnamyl alcohol in toluene; time, 4h.* ***Blank reactions (●); reactions carried out in the presence of 0.50 %Au 0.50 %Pd/ TiO_2 (Imp) catalyst (■)***

Analysis and comparison of the product distribution for each reaction is presented in Figure 3-35. Generally, the product distribution for the reactions carried out in the absence of a catalyst was fairly steady over time: the selectivity profile was around 45 % benzaldehyde, 30-35 % cinnamaldehyde and around 10-15 % benzoic acid.

As expected, the selectivity to the desired product for the catalysed reactions decreased with increasing temperature (around: 80 % at 80 °C, 70 % at 100 °C and 60 % at 120 °C) which is related to the intensification of the autoxidation reaction and hence non-selective oxidation to benzaldehyde. Also, the formation of benzoic acid and 3-phenyl-1-propanol took place at elevated temperatures (above 80 °C). A lower carbon balance was observed for the blank reaction, which is caused by decarbonylation of the substrate in the radical pathway.[27], [35] Improvement of carbon balance could be noticed for catalysed reaction.

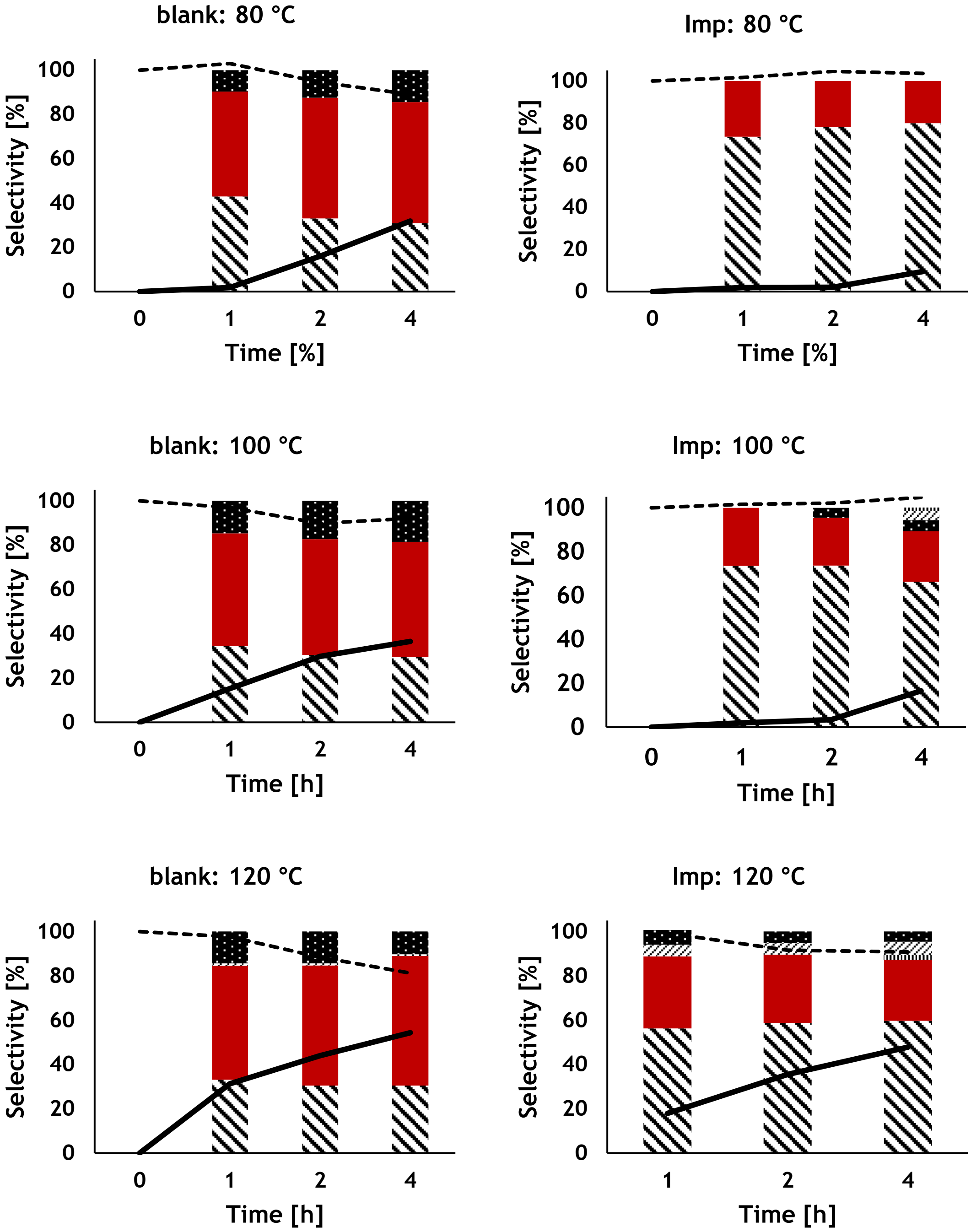

Figure 3-35 *The influence of the temperature on the selectivity in the process of of cinnamyl alcohol oxidation conducted in the absence and presence of the 0.50 %Au 0.50 %Pd/TiO*$_2$ *(Imp) catalyst. Reaction conditions: catalyst, 10 mg; oxygen pressure, 3 bar; 0.5 M cinnamyl alcohol in toluene.* ***Conversion (——); Carbon balance (-----); Cinnamaldehyde (▧); Benzaldehyde (🟥); Benzoic acid (■); 3-Phenyl-1-propanol (▨); Methylstyrene (||||||||||)***

Similarly, the temperature influenced the activity of the 0.50 %Au 0.50 %Pd/TiO$_2$ (SIm) catalyst considerably. The conversion has been compared over various temperatures in figure 3-36. The catalyst was the most active at 120 °C. The reactions carried out under the same oxygen pressure (3 bar) but at lower temperatures (100 °C) gave significantly lower conversions.

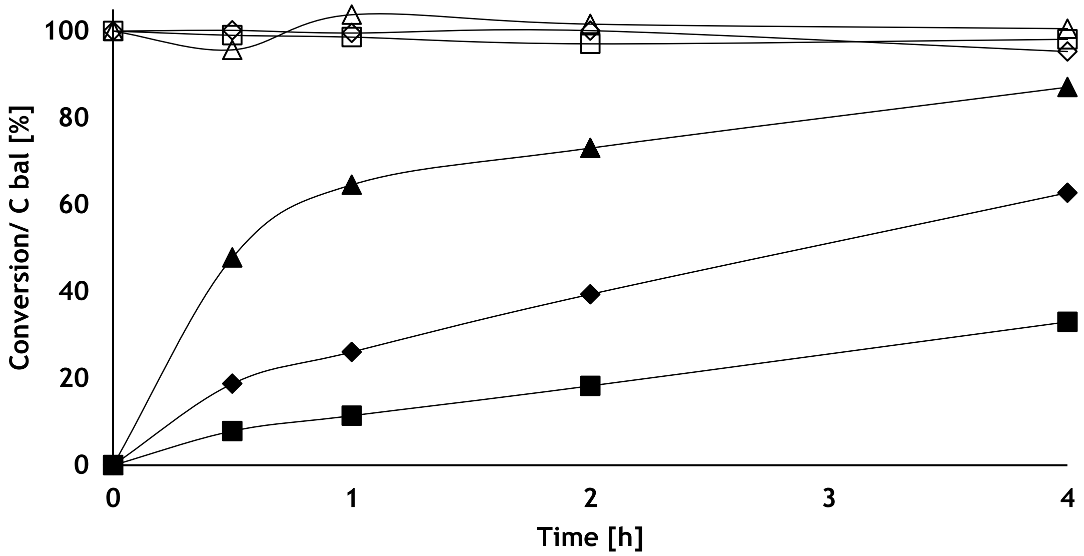

Figure 3-36 *The influence of the temperature on the oxidation of cinnamyl alcohol using 0.50 %Au 0.50 %Pd/TiO_2 (SIm). Reaction conditions: oxygen pressure, 3 bar; 0.5 M cinnamyl alcohol in toluene. Full figures- conversion:* ***Full figures- temperature: 80 °C (■); 100 °C (◆); 120 °C (▲); Empty figures- carbon balance: 80 °C (□); 100 °C (◇); 120 °C (△)***

Interestingly, the only products formed at 100 °C and below are cinnamaldehyde, and a side product of hydrogenation: 3-phenyl-1-propanol (figure 3-37). The increase in the temperature to 120 °C led to the formation of small amounts of benzaldehyde and styrene at the expense of cinnamaldehyde. Nevertheless, the improvement in the activity of the catalyst is high enough to warrant a small decrease in the selectivity to cinnamaldehyde. The presence of benzaldehyde is puzzling as it might be formed as a result of two different pathways: transformation of cinnamaldehyde or in the radical pathway as result of autoxidation of cinnamyl alcohol. The formation of benzaldehyde has been discussed in detail in the next section.

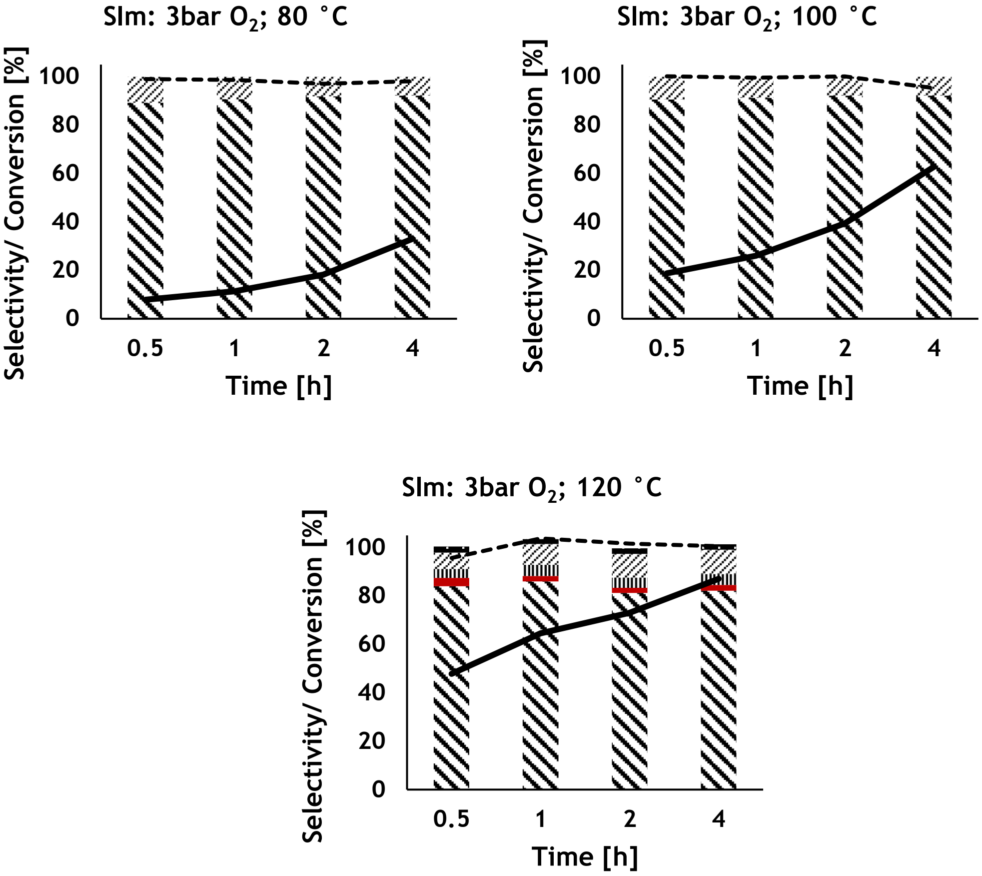

Figure 3-37 The influence of the temperature on the selectivity in the process of cinnamyl alcohol oxidation conducted in the presence of the 0.50 %Au 0.50 %Pd/TiO_2 (Slm) catalyst. Reaction conditions: catalyst, 10 mg; oxygen pressure, 3 bar; 0.5 M cinnamyl alcohol in toluene. ***Conversion** (—); **Carbon balance** (-----); **Cinnamaldehyde** (▧); **Benzaldehyde** (🟥); **Benzoic acid** (■); **3-Phenyl-1-propanol** (▨); **Methylstyrene** (▥)*

3.3.10. Cinnamaldehyde oxidation

Few studies have reported that benzaldehyde might be formed from cinnamaldehyde and it has been proved that benzaldehyde is formed in the bulk phase of the reaction mixture, not on the catalyst.[14], [15], [17] The time online data for the reactions carried out in the presence and absence of a catalyst presented at the beginning of this chapter (Figure 3-3 and 3-4) suggest that all the products have been obtained simultaneously, which is especially confusing for the formation of benzaldehyde. As this is not a trivial issue, an attempt was made to elucidate the possible routes of benzaldehyde formation. As a starting point, the oxidation of cinnamaldehyde was carried out under standard conditions in the absence of a catalyst (figure 3-38). The results revealed that cinnamaldehyde was transformed into benzaldehyde. The analysis of molar concentrations of both compounds suggests that cinnamaldehyde is converted directly to benzaldehyde. Subsequently, benzaldehyde is further oxidised to benzoic acid. Side reactions were also present, however the contribution towards selectivity is minor, as carbon balance after 4 hours was 90 % (not shown in figure).

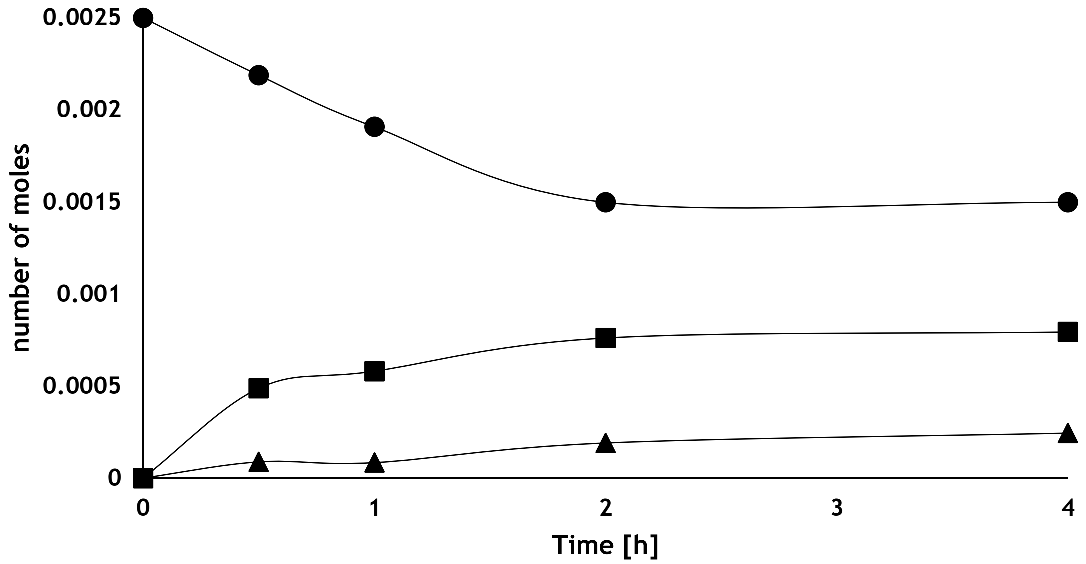

Figure 3-38*: The molar concentration of cinnamaldehyde and benzaldehyde during the oxidation of cinnamaldehyde carried out in the absence of a catalyst as a function of reaction time. Reaction conditions: oxygen pressure, 3 bar; temperature, 120 °C; 0.5 M cinnamaldehyde in toluene.* ***Cinnamaldehyde, (●); Benzaldehyde (■); Benzoic acid (▲)***

Following these results, a set of experiments were performed to evaluate the influence of the studied catalysts on the oxidation of cinnamaldehyde (figure 3-39a). Surprisingly, the amount of benzaldehyde formed was nearly the same for the blank reaction and for the catalysed reactions. In the case of 0.50 %Au 0.50 %Pd/TiO_2 (SIm) catalyst, the amount of consumed cinnamaldehyde was smaller which is related to reduced side reactions. From the comparison of the number of moles of benzaldehyde formed during cinnamyl alcohol oxidation in figure 3-39b one can see that the 0.50 %Au 0.50 %Pd/TiO_2 (SIm) catalyst enabled the highest conversion of alcohol and in the same time, only small amount of benzaldehyde has been formed. The blank reaction and 0.50 %Au 0.50 %Pd/TiO_2 (Imp) catalyst gave very similar results, which supports the hypothesis that the mechanisms taking part in those two reactions are similar.

It is clear, that the oxidation of cinnamyl alcohol and cinnamaldehyde are different. The reason why the 0.50 %Au 0.50 %Pd/TiO_2 (SIm) catalyst is so highly selective to cinnamaldehyde during cinnamyl alcohol oxidation is presumably the ability of radical quenching coupled with a competitive adsorption effect. The presented studies might indirectly imply that benzaldehyde is formed not only from cinnamaldehyde but also from cinnamyl alcohol.

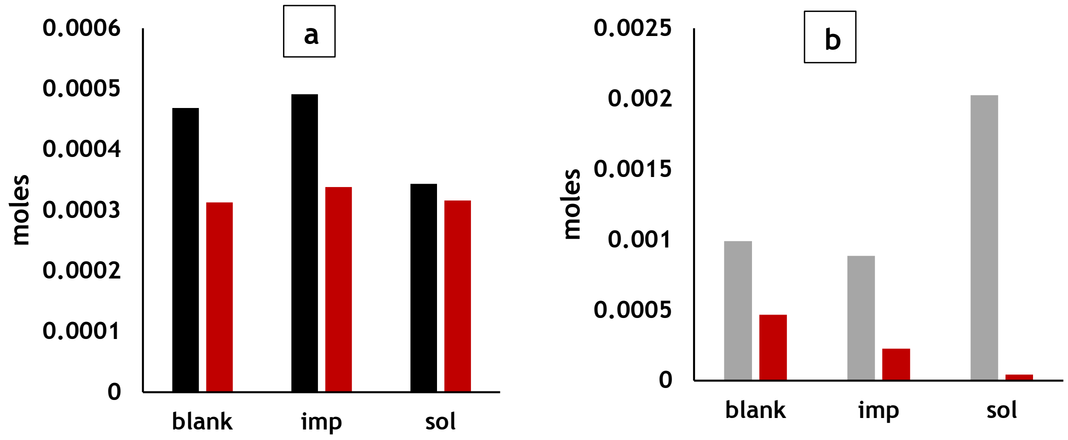

Figure 3-39 Oxidation of cinnamaldehyde **(a)** carried out in the presence and absence of a catalyst as a function of reaction time contrasted with the reaction of cinnamyl alcohol oxidation **(b)**. Reaction conditions: 0.50 %Au 0.50 %Pd/ TiO_2 (SIm) or (Imp), 10 mg; oxygen pressure, 3 bar; temperature, 120 °C; 0.5 M cinnamaldehyde or cinnamyl alcohol in toluene. **Cinnamaldehyde consumed (■); Benzaldehyde (■ *)* ; Cinnamyl alcohol consumed (■ *)***

The presented experimental data is in line with the general knowledge gathered in Ullmann's Encyclopedia of Industrial Chemistry regarding oxidation.[34] All organic structures (paints, polymers and various chemicals) have one feature in common: aging. From a chemical point of view, the aging is natural as all organic matter strive to achieve a stable state and only CO_2 is stable.[34] Although, this fact is the reason of autoxidation, the actual mechanism is unknown or at least not clear. Clearly, the process depends on the conditions and on the character of the substrate. Cinnamyl alcohol represents an allylic alcohol, which means that contains chemically active allylic group in its structure. The reason of this activity is the difference in strength between normal sp^3 C-H bonds and allylic C-H bonds, which are roughly 15 % weaker.[36] In theory, direct reaction of oxygen with hydrocarbon is spin-forbidden[37], however there is a possible way of breaking allylic C-H bonds by oxygen. It was mentioned before that the conditions play a very important role as in the presence of oxygen and at elevated temperatures, radicals (peroxides, hydroperoxides) are formed quickly and easily.[34], [37] The radical pathway does not require activation energy hence the reaction of hydrocarbons with oxygen is possible.[34]

The oxidation of cinnamyl alcohol has been performed in this work at elevated temperature above the boiling point of water. Taking into consideration the chemical constitution of the substrate containing weaker allylic C-H bonds, the heat is most likely the initiation factor for autoxidation.[34] Radicals are easily attached to the double bond what is the cause of its cleavage.[34] Experimental data presented in this section coupled with the literature supports the hypothesis that benzaldehyde is formed from cinnamyl alcohol in the radical pathway as a result of autoxidation.

3.3.11. Effect of water

It has previously been demonstrated that in the oxidation of alcohols by permanganate, the presence of moisture is beneficial and enables higher yields of the desired product.[38] Kozhevnikov and Stuchinskaya managed to enhance the activity of Pd-M oxide catalysts in the oxidation of alcohols by addition of water.[39] Studies by Mullins and co-workers showed examples of various reactions where the enhancement effect of water is explained by the presence of oxygen adatoms and hydroxyl species on gold surfaces.[40] Hermans and Neuenschwander extensively studied autoxidation of hydrocarbons where water was formed as a by-product. The researchers reported that water is an effective shield between radicals and might be hydrogen-bonded to the alkoxyl radical.[11] By following this route, water can prevent recombination of radicals and the interaction of a radical with a substrate or other compounds in the system. Qiu and co-workers demonstrated the promotion effect of water on the oxidation reaction of alcohols over Au/TiO_2, including cinnamyl alcohol, although base was also required here. It was suggested that water facilitates the adsorption of oxygen on TiO_2 which leads to the formation of active oxygen species. Activated oxygen can further react with the alcohol and as the effect, hydrogen abstraction takes place more easily.[41] Prati and co-workers used water instead of toluene in the oxidation of cinnamyl alcohol and obtained higher yields to cinnamaldehyde. The researchers suggested that the water might behave as a weak base, which supports dehydrogenation.[13]

In this work, the influence of water was examined by adding a small amount (2 ml) to the standard reaction mixture. The results are summarised in Table 4 from which it can be seen that the conversion of the blank reaction decreased significantly after addition of water. Keeping in mind that blank reaction has a purely radical character, the understanding of the role of water given by Hermans and Neuenschwander seems to be reasonable. Water may possibly be able to quench and deactivate radicals to some extent, decreasing conversion from 54 to 17% after 4 hours. This is supported by an increased selectivity to cinnamaldehyde and also by the formation of benzoic acid which was completely stopped. Time on-line data for the reactions carried out with 0.50 %Au 0.50 %Pd/TiO_2 (Imp) catalyst is shown in figures 3-40 and 3-41. The addition of water resulted in only slightly different conversion, although the selectivity to cinnamaldehyde increased significantly. Moreover, the formation of benzoic acid has been stopped. The result of this experiment suggests that the water deactivated radicals, which enabled activation of a catalytic mechanism that led to a relatively high selectivity towards cinnamaldehyde.

Oxidation of cinnamyl alcohol performed with 0.50 %Au 0.50 %Pd/TiO_2 (SIm) catalyst takes place on the catalytic route. Figure 3-40 shows that water significantly enhanced the activity of 0.50 %Au 0.50 %Pd/TiO_2 (SIm) catalyst. The comparison of two reactions with 0.50 %Au 0.50 %Pd/TiO_2 (SIm) catalyst shown in figure 3-42 suggests that the addition of water caused moderately decrease in selectivity to cinnamaldehyde in favour of 3-phenyl-1-propanol. This appears to be in accordance with the results reported by Prati that water acts as a weak base facilitating the abstraction of hydrogen, which is further transferred to another molecule of the substrate causing further hydrogenation and higher selectivity to by-products, as 3-phenyl-1-propanol. Small amounts of benzaldehyde have been presumably formed from cinnamaldehyde as radical pathway is switched off.

In conclusion, the results of experiments with the addition of water and the behaviour of the reactions support the hypothesis that the autoxidation is a radical process which does not occur when the sol catalyst is employed.

Table 4 *Effect of the small addition of water (2 ml) on catalysed and uncatalyzed reaction of cinnamyl alcohol oxidation under standard conditions after 4 h.*

Reaction	Conversion [%]	C bal [%]	Selectivity [%]					
			CinnALD	BenzALD	PP	MS	BenzACID	Styrene
Blank	54	81	31	59	1	-	10	-
Blank+water	17	95	41	54	5	-	-	-
Imp	47	91	60	28	6	2	5	-
Imp+water	36	100	87	10	3	-	-	-
SIm	87	100	82	2	10	5	-	2
SIm+water	100	100	72	7	19	2	-	-

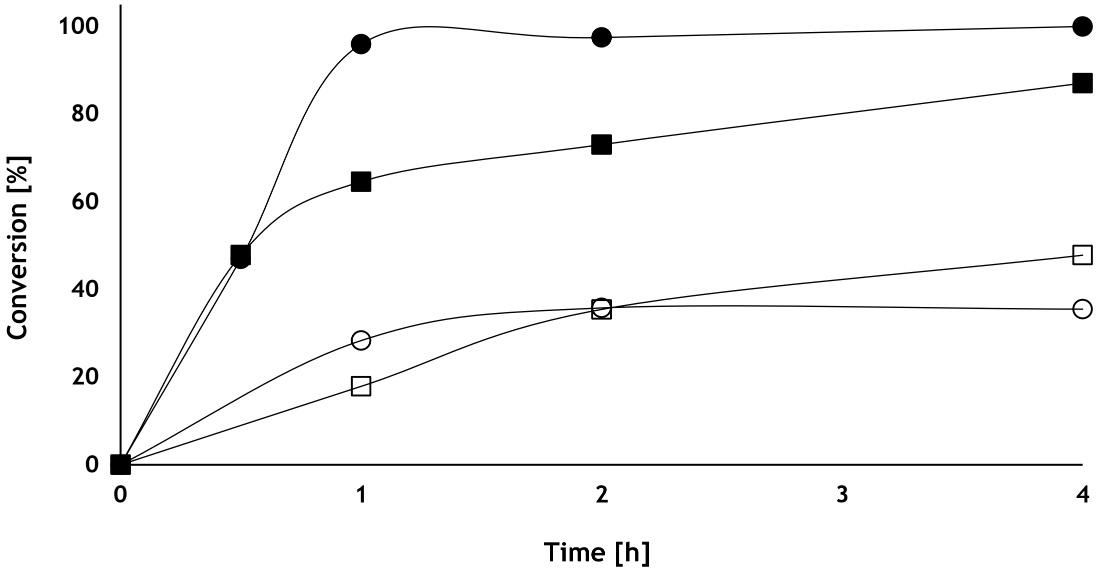

Figure 3-40** The influence of water on the catalysed (SIm and Imp) oxidation of cinnamyl alcohol as a function of reaction time. Reaction conditions: oxygen pressure, 3 bar; temperature, 120 °C; 0.5 M cinnamyl alcohol in toluene; water, 2 ml; catalyst, 10 mg.* ***Full marker: reactions carried out using 0.50 %Au 0.50 %Pd/TiO$_2$ (SIm): catalysed reaction (■), catalysed reaction with the addition of 2 ml water(●). Empty markers: reactions carried out using 0.50 %Au 0.50 %Pd/TiO$_2$ (Imp): catalysed reaction (□), catalysed reaction with the addition of 2 ml water (○).

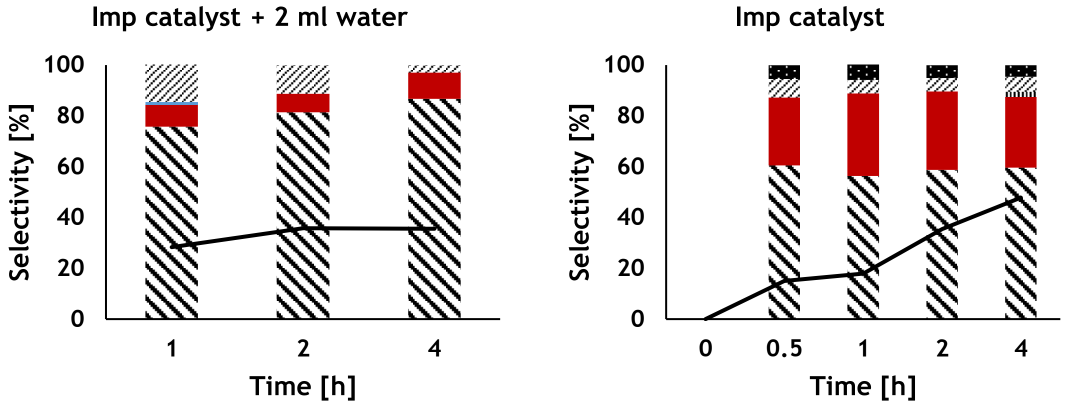

Figure 3-41** The influence of water on the selectivity in catalysed oxidation of cinnamyl alcohol using 0.50 %Au 0.50 %Pd/TiO$_2$ (Imp). Reaction conditions: oxygen pressure, 3 bar; temperature, 120 °C; 0.5 M cinnamyl alcohol in toluene; water, 2 ml; catalyst, 10 mg.* ***Conversion (▬); Cinnamaldehyde (▧); Benzaldehyde (🟥); Benzoic acid (■); 3-Phenyl-1-propanol (▨); Methylstyrene (▥)

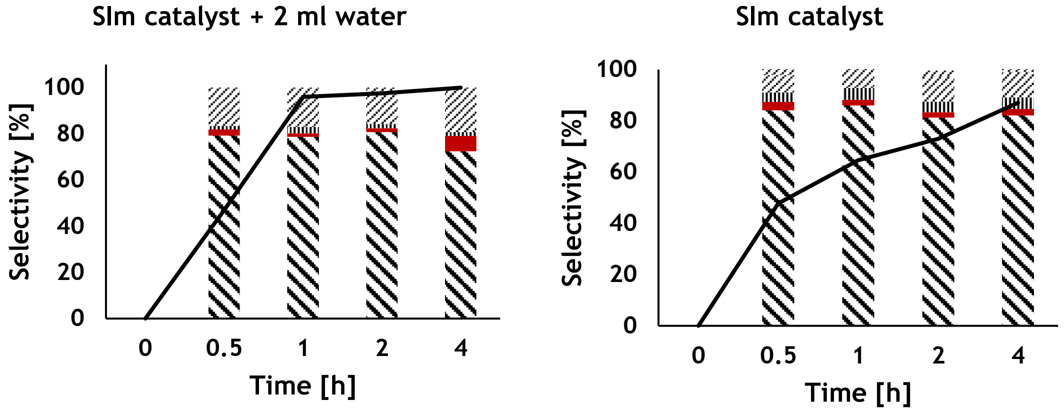

Figure 3-42 *The influence of water on the selectivity in catalysed oxidation of cinnamyl alcohol using 0.50 %Au 0.50 %Pd/TiO$_2$ (SIm). Reaction conditions: oxygen pressure, 3 bar; temperature, 120 °C; 0.5 M cinnamyl alcohol in toluene; water, 2 ml; catalyst, 10 mg.* ***Conversion (—); Cinnamaldehyde (▧); Benzaldehyde (🟥); 3-Phenyl-1-propanol (▨); Methylstyrene (▥)***

Another point worth considering is solubility of oxygen in different media. In general, the solubility of oxygen is higher in organic solvents than in water. An attempt has been made to calculate the amount of oxygen that could be dissolved in the experimental system, nevertheless this theoretical consideration has not been evaluated experimentally. The amount of dissolved oxygen in 2 ml of water was calculated based on the following equation (taking into account the pressure and temperature) developed by Tromans[42]:

$$C\ aq = P\ oxygen\ \frac{0.046T^2 + 203.357T ln\left(\frac{T}{298}\right) - (299.378 + 0.092T)(T - 298) - 20.591 * 10^3}{(8.3144)T}$$

The amount of dissolve oxygen in toluene has been calculated based on the method developed by Liang[43]:

$$X_{O_2} = \frac{\boldsymbol{n}\ oxygen\ in\ toluene}{(\boldsymbol{n}\ toluene) + (\boldsymbol{n}\ oxygen\ in\ toluene)}$$

*X=mole fraction of oxygen: a) temperature, 10.71 °C; O$_2$ pressure, 1 bar: X$_{O2}$: 0.000922; b) temperature, 120 °C; O$_2$ pressure, 3 bar: X$_{O2}$: 0.00359

Calculated values have been compared in the table 5.

***Table 5** Theoretical amounts of dissolved oxygen in 2 ml of water and in 5 ml of toluene in different conditions.*

Medium	**Amount of dissolved oxygen [g]**	
	25 °C; 1 bar O_2	**120 °C; 3 bar O_2**
Water: 2 ml	4.60E-05	8.78E-05
Toluene: 5 ml	0.001388	0.005419

It can be seen, that the possible amount of dissolved oxygen in water is very small and increases around twice as much in its order of magnitude under reaction conditions. The solubility of oxygen is significantly higher in toluene and increases almost five times under elevated reaction conditions. Hypothetically, adding water may reduce the solubility or available amount of oxygen in the reaction mixture. Lower oxygen availability hinders its activation, hence the formation of radicals.

3.3.12. Kinetics

Reaction rates of a process can be determined by observing the changes in the concentrations of reactants over a specific time. In order to establish the order of the reaction of cinnamyl alcohol oxidation, the consumption of the substrate with time has been calculated based on the experimental data.

The rate constants have been determined using the following expressions:

0 order: $k_0 = \frac{C0-C}{t}$

1st order: $k_1 = \frac{1}{t} \ln \frac{C0}{C}$

2nd order: $k_2 = \frac{1}{t} \left(\frac{1}{C} - \frac{1}{C0}\right)$

3rd order: $k_3 = \frac{1}{2t} \left(\frac{1}{C^2} - \frac{1}{C0^2}\right)$

The results for these calculations have been shown in table 6 below:

Table 6 *Kinetic data for cinnamyl alcohol oxidation at 120 °C.*

Time [min]	0	5	10	15	20	25	30	Standard deviation
Concentration [mol/l]	0.5	0.46	0.41	0.4	0.34	0.32	0.29	
zero order	0	**0.007213**	**0.00856**	**0.00691**	**0.00808**	**0.00712**	**0.0071**	**0.000724**
first order	0	0.014973	0.018785	0.015487	0.019517	0.017613	0.018507	**0.001854**
second order	0	0.031095	0.041331	0.034867	0.047748	0.044257	0.049486	**0.007248**
third order	0	0.07259	0.097442	0.075	0.116263	0.115313	0.13151	**0.023932**

The calculated values are based on the experimental data hence remain affected by error to some extent. In theory, the identical values should be obtained for the actual order of the reaction. It can be seen from the table 6 that the closest values for each time are presented for zero order.

Another way to confirm the order of the reaction is to plot the change in concentration of the substrate vs time and a straight line should be obtained. Figure 3-43 confirms that the oxidation of cinnamyl alcohol using 0.50 %Au 0.50 %Pd/TiO$_2$ (SIm) catalyst is the zero order reaction as the R^2=0.99.

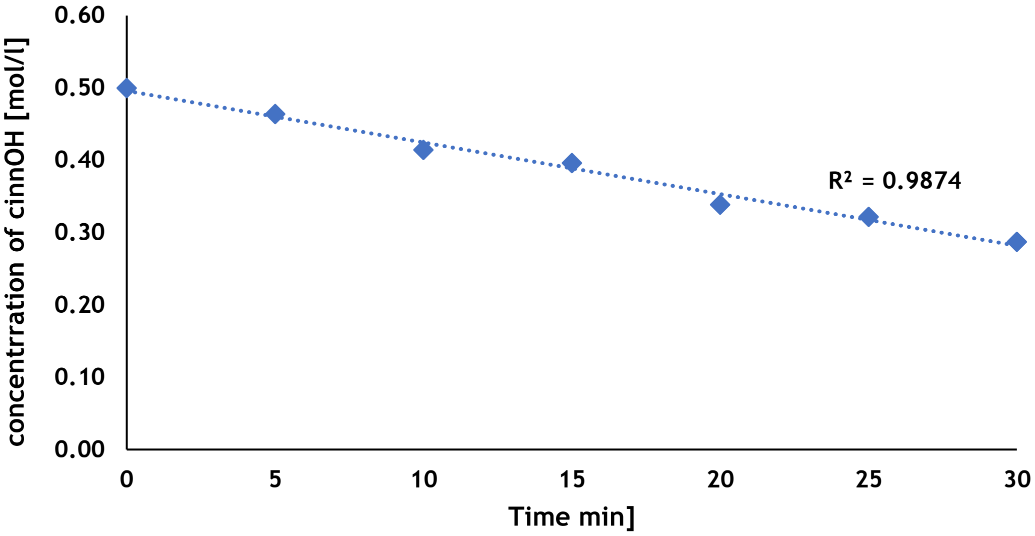

Figure 3-43 *Reaction order determination for the reaction of cinnamyl alcohol oxidation using 0.50 %Au 0.50 %Pd/TiO$_2$ (SIm).*

The activation energy can be calculated using Arrhenius Equation:

$k=Ae^{-Ea/RT}$

The rate constants for the reactions carried out at different temperatures have been calculated based on the data presented in previous section (figure 25 and 26).

Taking the natural log of both sides of Arrhenius Equation gives the following:

$$\ln k = \ln A - \frac{Ea}{RT}$$

Plotting ln k vs 1/T gave a straight line (R^2=0.97) with a slope of -Ea/R and y-intercept of ln A (figure 3-44). As the gradient of the line tgα was equal to -Ea/R, the activation energy was calculated giving a value of 58 kJ.

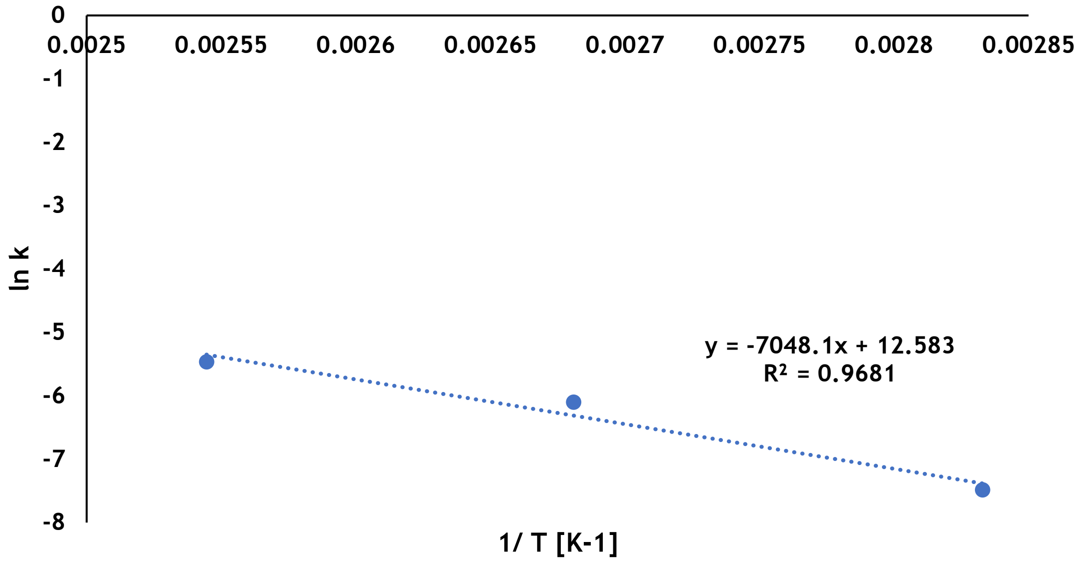

Figure 3-44 *Activation energy determination. Arrhenius plot.*

The activation energy can also be calculated given two known temperatures and a rate constant at each temperature:

$$\ln k_1 = \ln A - \frac{Ea}{RT1} \quad \text{and} \quad \ln k_2 = \ln A - \frac{Ea}{RT2}$$

Ln k_2 has been subtracted from ln k_1: $\ln k_2 - \ln k_1 = \left(-\frac{Ea}{RT1} + \ln A\right) - \left(-\frac{Ea}{RT2} + \ln A\right)$

After rearrangement: $\ln\left(\frac{k1}{k2}\right) = \left(\frac{1}{T2} - \frac{1}{T1}\right)\frac{Ea}{R}$

The activation energy directly calculated taking into account the lowest tested temperature (80 °C) and the highest tested temperature (120 °C) gave the same value of 58 kJ. The reaction of cinnamyl alcohol oxidation carried out in the absence of a catalyst and the reaction carried out using Au-Pd catalyst prepared by impregnation method have not been analysed as their character is radical and partly radical, respectively. An Arrhenius plot of a radical reaction has no slope and is independent of temperature. The reaction rate does not depend on the concentration of the reagents but possibly on the surface area of the catalyst, metal ratio, metal loading, and catalyst mass.

3.4. Conclusions

The approach used in this study aimed to examine the autoxidation phenomenon and its influence on the catalytic oxidation of cinnamyl alcohol. Although the oxidation of cinnamyl alcohol has been widely studied in the literature, usually mild conditions were applied. From an industrial viewpoint, it is economically more efficient to perform oxidation processes at elevated temperature for the purpose of heat recapture. However, these conditions very often lead to the autoxidation of the substrate. Autoxidation in terms of catalysis is reluctantly discussed in academia, however it is extremely important issue in the industry.

The conversion of cinnamyl alcohol carried out at 120 °C under molecular oxygen was relatively high, however non-selective to the desired product, cinnamaldehyde. Instead, a large amount of benzaldehyde was formed, hence close attention has been paid to the mechanism of its formation. Au-Pd supported nanoparticles have been tested to limit the autoxidation and enhance the selectivity to cinnamaldehyde. Catalysts have been prepared by two different methods (sol-immobilisation and impregnation) to obtained nanoclusters in various sizes.

The oxidation of cinnamyl alcohol occurred *via* two mechanistic pathways as indicated by the product distributions and dependence on the method of catalyst preparation. The nature of blank reaction has been proven to be purely radical. The size of Au-Pd nanoparticles appeared to have a strong influence on the reaction mechanism. Small particles (3-5 nm confirmed by SEM and XPS) obtained by sol-immobilisation method were suggested to be able to split peroxides/hydroperoxides caused by the autoxidation process thus enabled high selectivity to cinnamaldehyde. Autoxidation seemed to be switched off and high conversion could be achieved. Larger particles (100 nm confirmed by SEM and XPS) achieved *via* impregnation method were less active in the oxidation of cinnamyl alcohol and the product distribution suggested that autoxidation and catalytic mechanisms were taking place simultaneously. Conversion was lower than for the blank reaction, however higher selectivity to cinnamaldehyde has been obtained. There was still large amount of benzaldehyde, a by-product which serves as proof of autoxidation, which means that larger particles were able only to limit autoxidation and not stop entirely.

Large amounts of benzaldehyde have been obtained at elevated temperatures and at higher pressures in the case of blank and catalysed reactions using 0.50 %Au

0.50%Pd/ TiO_2 (Imp). Larger clusters prepared by impregnation method were able to limit the autoxidation at milder conditions, however their catalytic activity was significantly lower at 120 °C and 3 bar. 0.50 %Au 0.50%Pd/ TiO_2 (SIm) catalyst have been found to be extremely active and selective, the product distribution remained fairly steady in different conditions, however the temperature significantly influenced the conversion.

Small addition of water improved the overall yield of the process in case of blank reaction and catalysed reaction using 0.50 %Au 0.50%Pd/ TiO_2 (Imp) confirming radical/ partly radical nature respectively. The same addition of water to the reaction using 0.50 %Au 0.50%Pd/ TiO_2 (SIm) improved significantly conversion without major differences in selectivity.

The presented findings are proof that the autoxidation is an important issue that should be taken into consideration while establishing the mechanism of a catalytic process under industrially relevant conditions. Moreover, the selectivity and overall yield of the process can be finely tuned by proper design of a heterogeneous catalyst. Therefore, the further optimisation of this catalytic system is described in the following chapter 4.

3.5. References

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Chapter 4

4. Cinnamyl alcohol oxidation using supported bimetallic Au-Pd nanoparticles under autoxidation conditions continued: an optimization of metal ratio and investigation of deactivation behaviour.

4.1. Introduction

In the previous chapter the phenomenon of autoxidation of cinnamyl alcohol in terms of catalysis has been studied. The effect of reaction conditions and the impact of Au-Pd catalysts obtained by two different methods on the reaction have been investigated.[1] Bimetallic Au-Pd nanoalloys supported over titania were found to be superior to monometallic supported nanoparticles. The size of nanoparticles appeared to influence the reaction and resulted in large differences in selectivities between the two sets of catalysts. The sol immobilisation catalyst was found to be extremely selective to the desired product, cinnamaldehyde. It is known that these two preparation methods vary not only in the size of the nanoparticles obtained, but also in the morphology and composition, which subsequently effects activity and selectivity. Furthermore, the chosen bimetallic ratio has been found to heavily influence catalyst performance in a number of reactions. This chapter considers the aforementioned variables in an attempt to optimise the present catalytic system.

There are numerous studies, which have investigated the effect of bimetallic ratio on both activity and selectivity for a number of reactions. The study of benzyl alcohol oxidation has demonstrated a large synergistic effect between Au and Pd with the optimum ratio being 50:50 (wt:wt).[2] Similar results have been obtained in the synthesis of hydrogen peroxide.[3] Carter *et al.* contrasted reactions for which addition of Au to Pd leads to a synergistic or anti-synergistic effect.[4] Synergy between Au and Pd was observed for e.g. selective oxidation of benzyl alcohol, which is explained by the electronic interaction around active sites. So called anti-synergy was suggested to be a result of different active centres/ sites for specific reactions.

Prati and co-workers have carried out fascinating studies on the glycerol oxidation reaction using gold and palladium nanoparticles supported over carbon. A detailed review of their studies is included in Chapter 1, section 1.4. It has been confirmed that also in this case bimetallic catalysts were more active than their monometallic counterparts.[5] The authors ascribed the higher activity to the Au-Pd bifunctional sites and in general to a combination of electronic and geometric effects.

It was observed that the separated Pd phases forming inhomogeneity in certain metal ratios might be the cause of inferior catalytic performance for the oxidation of glycerol, as the synergistic effect between Au and Pd is weakened. The researchers demonstrated that optimization of the metal ratio is extremely important in order to obtain the best possible results.[6]

Prati and co-workers studied oxidation of cinnamyl alcohol at 60 °C under oxygen. Here, the researchers tested monometallic and bimetallic Au- Pd and Au-Pt systems supported over TiO_2 by the sol-immobilisation method, with products of cinnamaldehyde and 3-phenyl-1-propanol. The conversion and selectivity varied for mono- and bimetallic catalysts. The Au-Pd system was more active than Au-Pt for the oxidation of cinnamyl alcohol both in water and in toluene. 0.73 wt% Au-0.27 wt% Pd catalyst was found to be superior to its monometallic counterparts (conversion was 72 % after 2 h, selectivity to cinnamaldehyde was 85 % and selectivity to 3-phenyl-1-propanol was 13 %).[7]

In their other work, Prati and co-workers extended their studies by examining the influence of previously tested Au-Pd metal ratios on the oxidation of benzyl alcohol, cinnamyl alcohol, 2-octen-1-ol and 1-octanol. The reactions were performed in water at 60 °C under 1.5 atm of oxygen pressure. These conditions were relatively mild, therefore no autoxidation was observed. The only products detected during cinnamyl alcohol oxidation under these conditions were cinnamaldehyde and 3-phenyl-1-propanol. The optimum ratio for synergy was for 80 Au: 20 Pd (mol:mol) in case of benzyl and cinnamyl alcohols, whereas the most effective metal ratio for aliphatic alcohols was found to be 60 Au: 40 Pd (mol:mol).[8]

It is clear from the literature reports that the activity of catalysts can be tuned by optimisation of Au-Pd metal ratio under relatively mild conditions. The data presented in this chapter address whether a similar optimisation is possible under harsher, autoxidation conditions.

4.2. Results and discussion

4.2.1. Metal ratio studies

The influence of metal ratio in bimetallic catalysts prepared by wet impregnation (Imp) and sol immobilisation (SIm) has been tested for the oxidation of cinnamyl alcohol under autoxidation conditions. The following metal ratios of TiO_2 supported Au-Pd nanoparticles have been studied: 1 %Au/ TiO_2; 0.95 %Au 0.05 %Pd/ TiO_2; 0.75 %Au 0.25 %Pd/ TiO_2; 0.50 %Au 0.50 %Pd/ TiO_2; 0.25 %Au 0.75 %Pd/ TiO_2; 1

%Pd/ TiO_2. In the case of the impregnation catalysts the amount of converted alcohol is the resultant of the autoxidation and catalytic processes taking place simultaneously. It has been demonstrated in Chapter 3 that the formation of benzaldehyde might be an indicator that autoxidation is present. Therefore, the investigation of the influence of Au-Pd metal ratio on the reaction should be focused on the selectivity profile.

4.2.1.1. Impregnation method

Figure 4-1 presents the results of the catalytic oxidation of cinnamyl alcohol with the use of a number of catalysts prepared by impregnation method. The reference point is the blank reaction (marked as a blue line on the graph) from which the catalysed reactions have been contrasted.

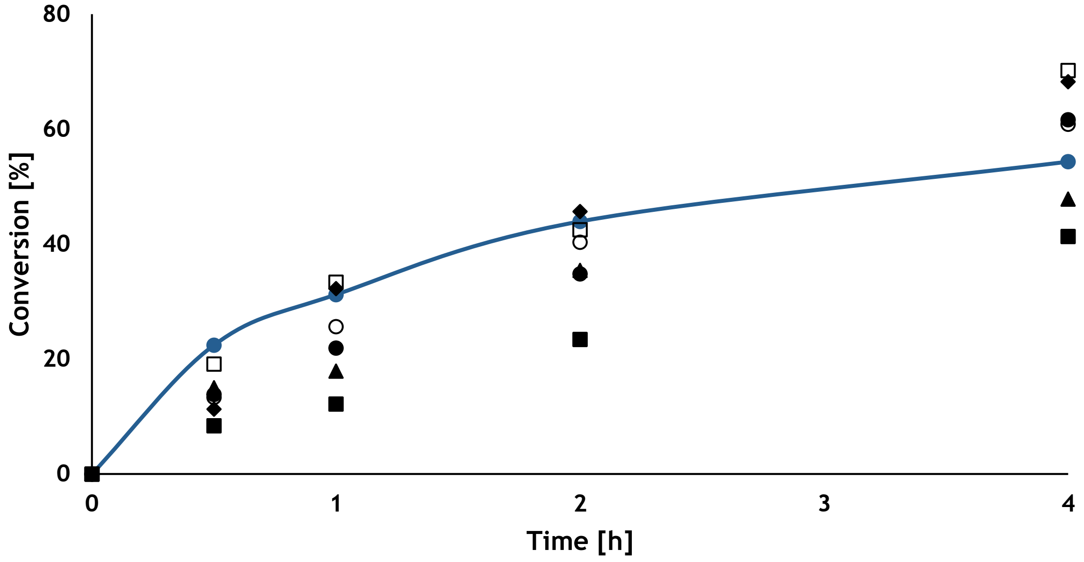

Figure 4-1 *Time on-line for the oxidation of cinnamyl alcohol using the range of catalysts prepared by impregnation method. Reaction conditions: catalyst, 10 mg; oxygen pressure, 3 bar; temperature, 120 °C; 0.5 M cinnamyl alcohol in toluene.* ***Blank reaction (blue line); 1 %Au/ TiO_2(■); 0.95 %Au 0.05 %Pd/ TiO_2 (○); 0.75 %Au 0.25 %Pd/ TiO_2 (●); 0.50 %Au 0.50 %Pd/ TiO_2 (▲); 0.25 %Au 0.75 %Pd/ TiO_2 (□); 1 %Pd/ TiO_2 (◆).***

It can be seen, that all tested impregnation catalysts limited conversion in the first hour of the experiment when compared to the blank reaction. The analysis of the results in the following hours of the experiment showed that Pd- rich catalysts are most active. Conversion of Pd-rich catalysts (1 %Pd/ TiO_2 (Imp), 0.25 %Au 0.75 %Pd/ TiO_2 (Imp)) is comparable to the blank reaction during the second and the third hours of the experiment, however the selectivity profile differs significantly (figure 4-2). The selectivity to benzaldehyde for the blank reaction is around 57 % after 4 hours and selectivity to cinnamaldehyde is below 40 % (Chapter 3).

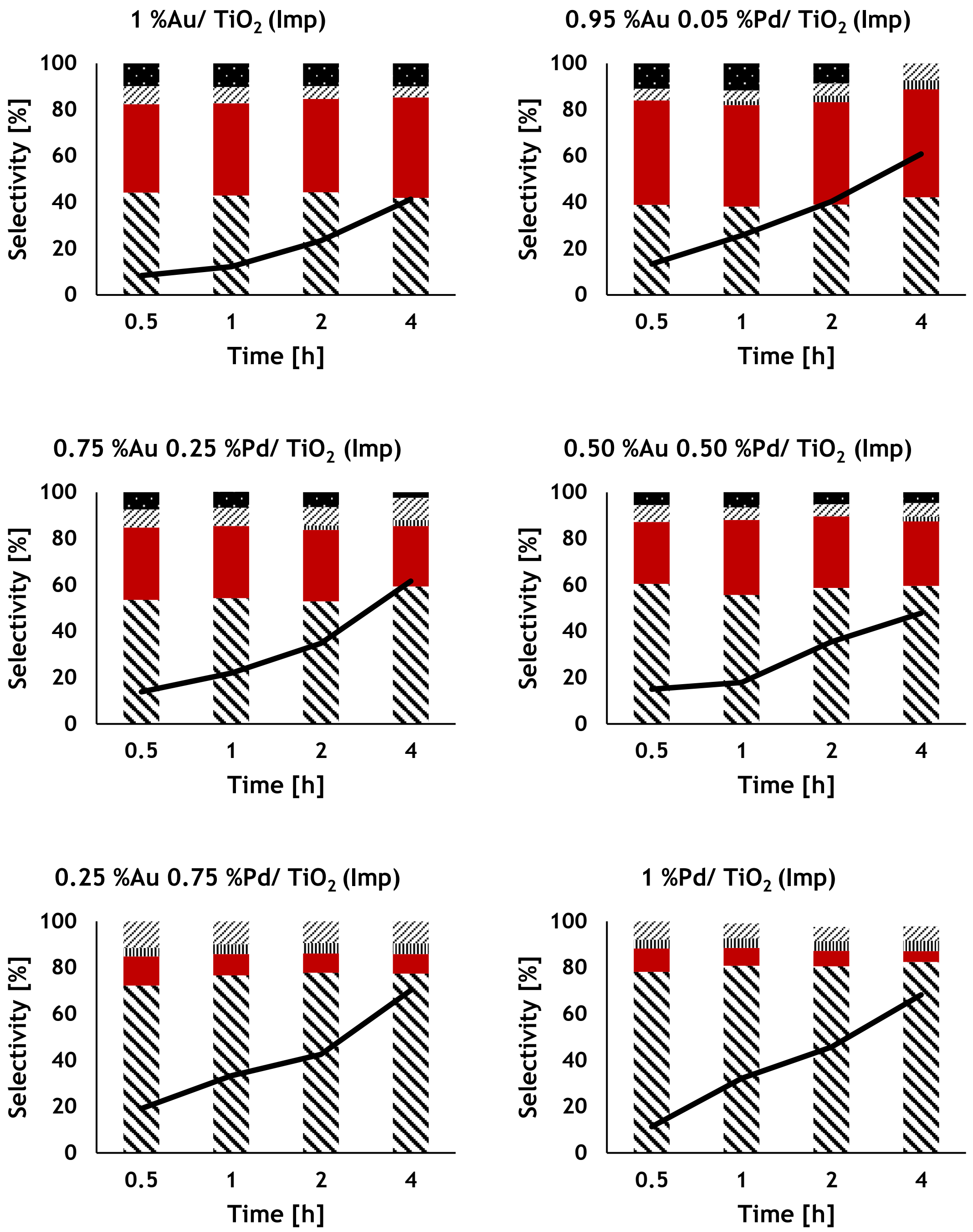

Figure 4-2 *Time on-line profile for the oxidation of cinnamyl alcohol using the range of catalysts prepared by impregnation method. Reaction conditions: catalyst, 10 mg; oxygen pressure, 3 bar; temperature, 120 °C; 0.5 M cinnamyl alcohol in toluene.* ***Conversion (——); Cinnamaldehyde (▧); Benzaldehyde (🟥); Benzoic acid (■); 3-Phenyl-1-propanol (▨); Methylstyrene (|||||||)***

Pd-rich (Imp) catalysts limited formation of benzaldehyde to around 10 %, which suggests that the catalytic mechanism is dominant over autoxidation. As a result, the selectivity to cinnamaldehyde is high (around 75-80 %). Moreover, Pd-rich (Imp) catalysts not only significantly reduced formation of benzaldehyde but also completely stopped formation of benzoic acid. The advantage of the catalytic process over autoxidation is manifested in carbon balance which is almost closed for the Pd-rich (Imp) catalysts (figure 4-3).

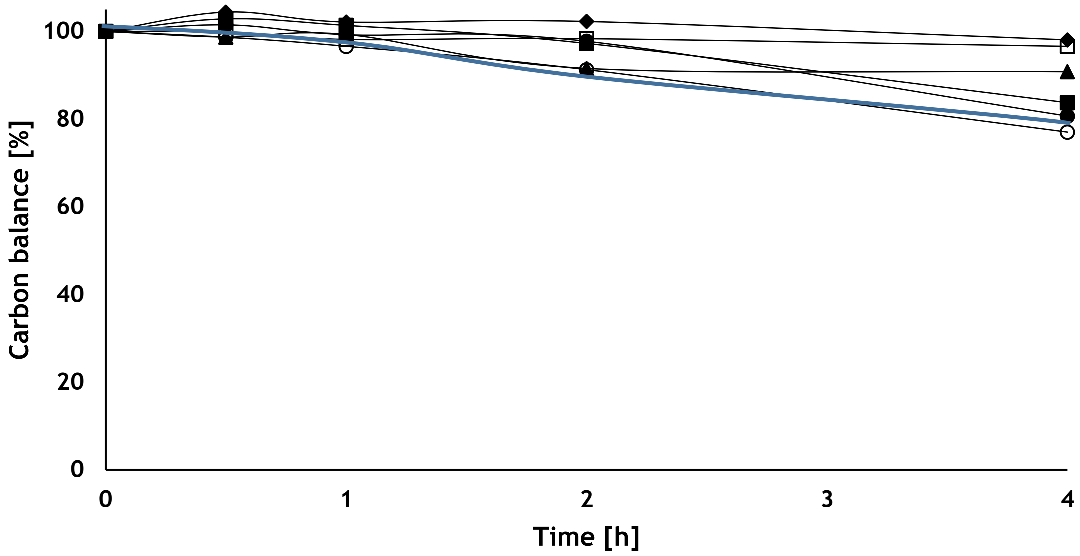

Figure 4-3** Carbon balance for the oxidation of cinnamyl alcohol using the range of catalysts prepared by impregnation method. Reaction conditions: catalyst, 10 mg; oxygen pressure, 3 bar; temperature, 120 °C; 0.5 M cinnamyl alcohol in toluene.* ***Blank reaction (blue line) ; 1 %Au/ TiO_2(■); 0.95 %Au 0.05 %Pd/ TiO_2 (○); 0.75 %Au 0.25 %Pd/ TiO_2 (●); 0.50 %Au 0.50 %Pd/ TiO_2 (▲); 0.25 %Au 0.75 %Pd/ TiO_2 (□); 1 %Pd/ TiO_2 (◆).

1 %Au/TiO_2 imp catalysts limited the conversion in comparison with the blank reaction (figure 4-1), however the large amount of benzaldehyde (figure 4-2) suggests that autoxidation was still taking place. Presumably, the catalyst acted as a scavenger to some extent but was not active enough to perform catalytic dehydrogenation towards cinnamaldehyde. This has been explained in Chapter 3 with reference to the larger size of gold nanoparticles and their poor dispersion in the absence of palladium, which is typical for the impregnation method.

The activity of 0.95 %Au 0.05 %Pd/ TiO_2 (Imp) is interesting and is an ideal example of the phenomenon studied in the literature on the dispersion properties of palladium against gold. Miedziak *et al.*[9], [10] proved that even a small addition of palladium improves significantly dispersion of gold and therefore activity of the catalyst. From figure 4-1 it is clear, that an extremely small amount of Pd changed the activity of pure Au catalyst in such a way that selectivity (figure 4-2) remained the same but conversion increased (by 20 % after 4 hours). This is not a particularly great achievement with respect of enhancement of overall yield of the studied process, however it implies that even a minimal change of Au-Pd metal ratio can possibly change the properties of bimetallic nanoalloys. This observation is in line with the previously cited literature in that the combination of alloying Au with Pd and better dispersion leads to an enhanced catalytic activity of nanoclusters.

Increasing the percentage of palladium to 25 %, and then up to 50 %, resulted in the limiting of autoxidation, evidenced by the product distribution, as the selectivity to cinnamaldehyde was higher in each case (figures 4-1 and 4-2). This indicates a relatively strong synergistic effect and implies that every metal ratio varies in terms of electronic properties. From figure 4-2 it can be seen, that Au-rich (Imp) catalysts are not active enough to prevent autoxidation and C=C cleavage hence the carbon balance is lower than in the case of Pd-rich (more active) catalysts. Even though 0.75 %Au 0.25 %Pd/ TiO_2 (Imp) and 0.50 %Au 0.50 %Pd/ TiO_2 (Imp) catalysts have been found to be more suitable for the oxidation of cinnamyl alcohol than 1 %Au/ TiO_2 (Imp) and 0.95 %Au 0.05 %Pd/ TiO_2 (Imp) catalysts, large amounts of benzaldehyde were still formed, which suggests that the impregnation catalysts are not ideal to effectively suppress the autoxidation.

Figure 4-4 plots catalytic activity and yield of cinnamaldehyde produced in relation to weight percentage of gold. It can be seen, that the conversion trend is reflected in the yield to cinnamaldehyde trend. Pd-rich catalysts are the most effective towards formation of cinnamaldehyde; initial activity of 0.25 %Au 0.75 %Pd/TiO_2 (Imp) (after 0.5 h) is especially noteworthy. Surprisingly, 0.50 %Au 0.50 %Pd/TiO_2 (Imp) catalyst demonstrated a lower activity compared to other metal ratios, which is particularly noticeable after longer reaction times (4h). In conclusion, the change in metal ratio leads to significant differences in the activity of impregnation catalysts as well as in the product distribution. A point worthy of further emphasis is that it is possible to increase the selectivity of even poor activity catalysts by optimising the metal ratios.

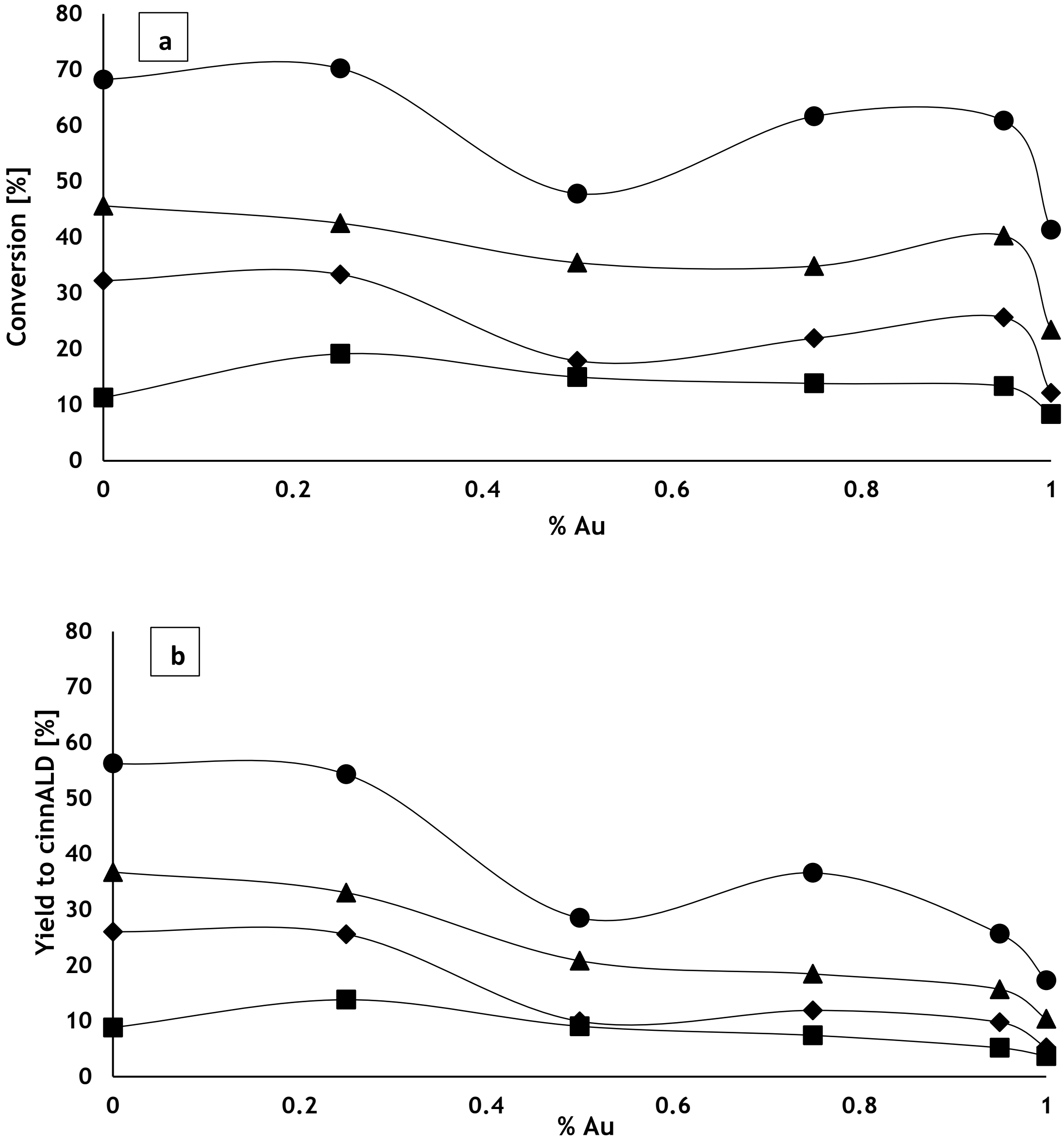

Figure 4-4 *Influence of Au-Pd metal ratio on the oxidation of cinnamyl alcohol: a) conversion vs gold percentage b) yield to cinnamaldehyde vs gold percentage. Reaction conditions: catalysts made by impregnation method, 10 mg; oxygen pressure, 3 bar; temperature, 120 °C; 0.5 M cinnamyl alcohol in toluene.* ***0.5 hour (■); 1 hour (◆); 2 hours (▲); 4 hours (●).***

4.2.1.2. Sol-immobilisation method

In Chapter 3 it has been shown that the 0.50 %Au 0.50 %Pd/TiO_2 (SIm) catalyst was extremely active for the studied reaction. Moreover, the catalyst was highly selective resulting in only a small amount of undesired benzaldehyde, which is formed in large amounts as a by-product of non-selective oxidation.

Extended research on various Au-Pd metal ratio supported over titania by sol-immobilisation showed that this method allows the formation of extremely active catalysts for the oxidation of cinnamyl alcohol. Analysing the data presented in figure

4-5 it can be seen that monometallic 1 % Au/ TiO_2 (SIm) has low activity in comparison to the other tested catalysts. As in the case of the (Imp) catalyst, the small addition of Pd sufficiently improved the activity of pure Au catalyst.

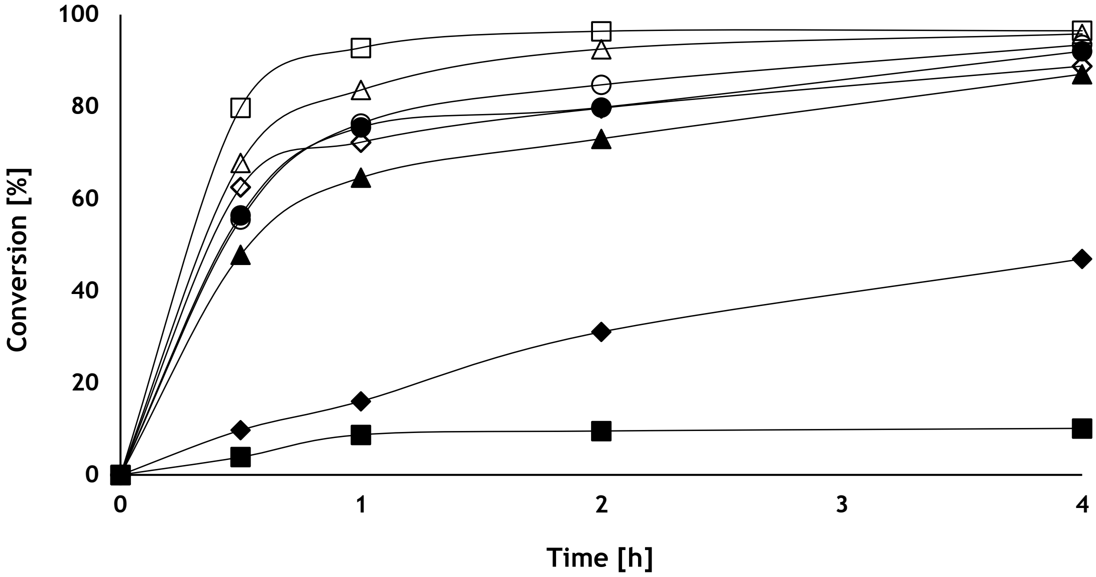

Figure 4-5 *Time on-line for the oxidation of cinnamyl alcohol using the range of catalysts prepared by sol-immobilisation method. Reaction conditions: catalyst, 10 mg; oxygen pressure, 3 bar; temperature, 120 °C; 0.5 M cinnamyl alcohol in toluene.* ***1 %Au/ TiO_2(■); 0.95 %Au 0.05 %Pd/ TiO_2 (◆); 0.75 %Au 0.25 %Pd/ TiO_2 (□); 0.50 %Au 0.50 %Pd/ TiO_2 (▲); 0.25 %Au 0.75 %Pd/ TiO_2 (●); 1 %Pd/ TiO_2 (◇); 0.60 %Au 0.40 %Pd/ TiO_2 (○); 0.85 %Au 0.15 %Pd/ TiO_2 (△).***

The effect of Pd addition is also noticeable in product distribution (figure 4-6). 0.95 % Au 0.05 %Pd/ TiO_2 (Imp) significantly decreased formation of benzaldehyde (around 7 %) in comparison to the 1 % Au/ TiO_2 (SIm) (around 35 %).

Further analysis of the data presented in figures 4-5 and 4-6 shows that the highest conversion (nearly 96 % after 4 hours) and selectivity to cinnamaldehyde (80 %) was achieved using the 0.75 %Au 0.25 %Pd/ TiO_2 (SIm) catalyst. This finding is in good agrement with Prati's work reporting 0.73 wt% Au-0.27 wt% Pd/C catalyst made by sol-immobilisation which was more active than monometallic catalysts.[7]

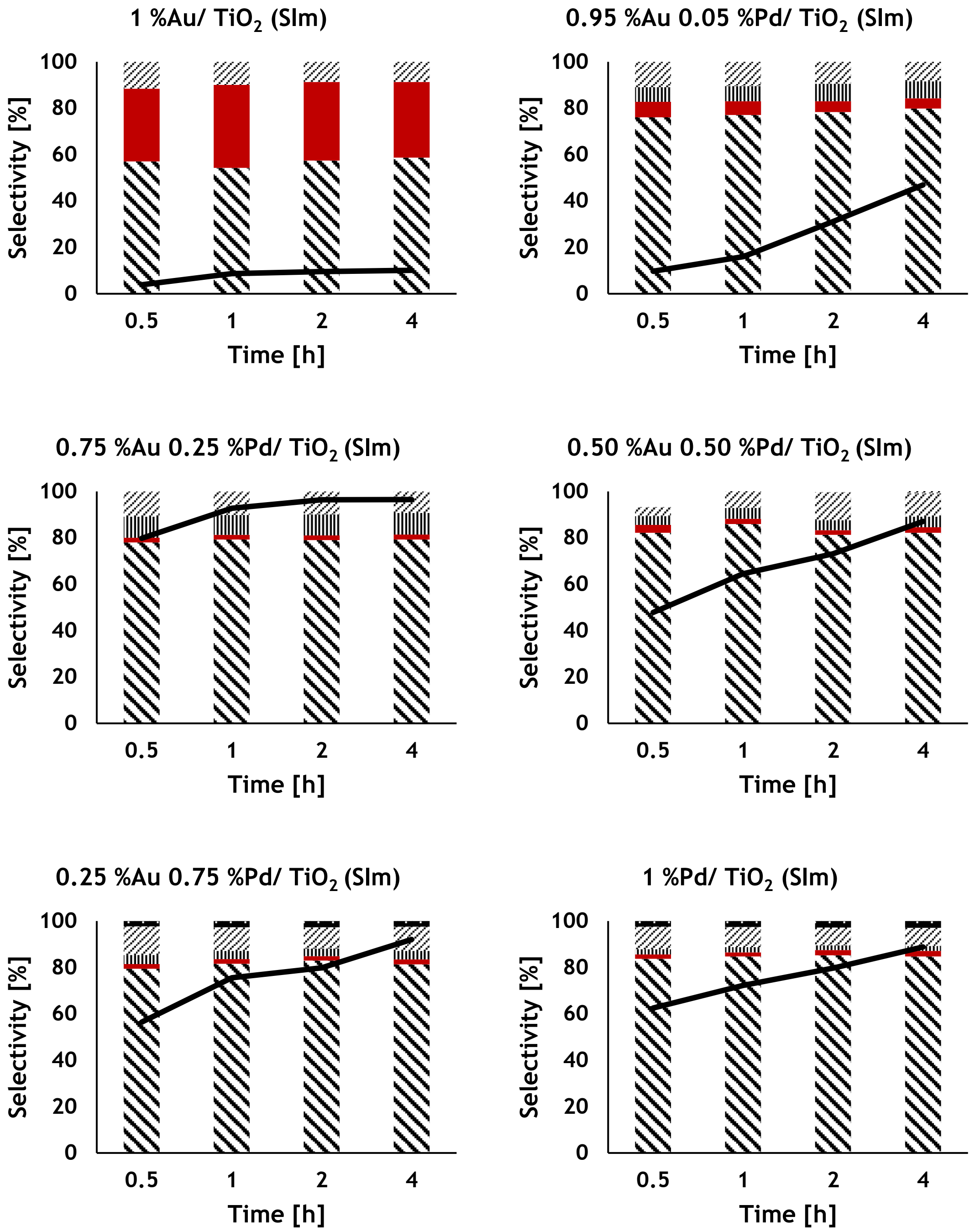

Figure 4-6 *Time on-line profile for the oxidation of cinnamyl alcohol using the range of catalysts prepared by sol-immobilisation method. Reaction conditions: catalyst, 10 mg; oxygen pressure, 3 bar; temperature, 120 °C; 0.5 M cinnamyl alcohol in toluene.* ***Conversion (▬); Cinnamaldehyde (▧); Benzaldehyde (▬); 3-Phenyl-1-propanol (▨); Methylstyrene (|||); Styrene (■)***

To be sure that exactly this composition (75Au:25Pd) is optimal to obtain the best possible results, an additional two catalysts have been prepared: 0.60 %Au 0.40 %Pd/ TiO_2 (SIm) and 0.85 %Au 0.15 %Pd/ TiO_2 (SIm). The data presented in figure 4-7 revealed that the tested catalysts are active but still not as active as 0.75 %Au 0.25 %Pd/ TiO_2 (SIm).

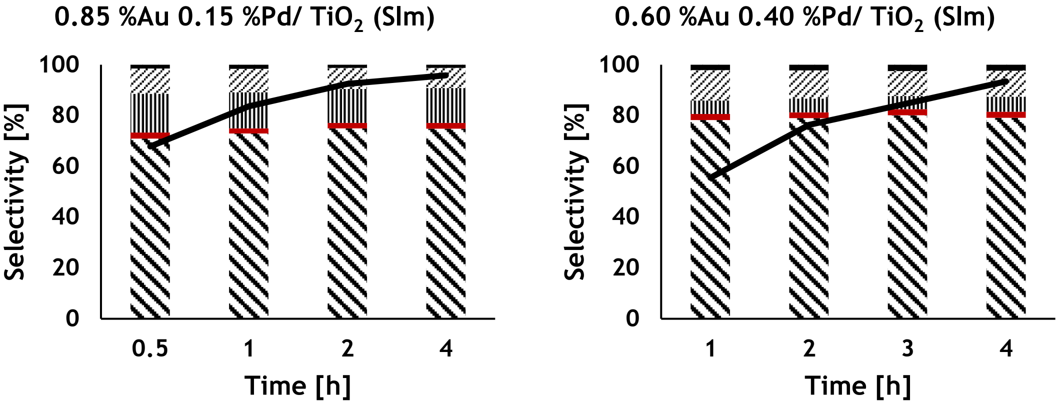

Figure 4-7** Time on-line profile for the oxidation of cinnamyl alcohol using the catalysts prepared by sol-immobilisation method. Reaction conditions: catalyst, 10 mg; oxygen pressure, 3 bar; temperature, 120 °C; 0.5 M cinnamyl alcohol in toluene. **Conversion (—); Cinnamaldehyde (▧); Benzaldehyde (▬); 3-Phenyl-1-propanol (▨); Methylstyrene (▥); Styrene (■)

Interestingly, the correlation in metal ratio and activity again dipped at 50Au:50Pd as with the impregnation catalysts. The data suggests a strong synergistic effect between Au-Pd leading to an excellent catalytic performance towards obtaining cinnamaldehyde from cinnamyl alcohol. The product distribution (figure 4-6) and closed carbon balance (figure 4-8) strongly indicate that the dominating process is catalytic dehydrogenation over autoxidation which is presumably switched off.

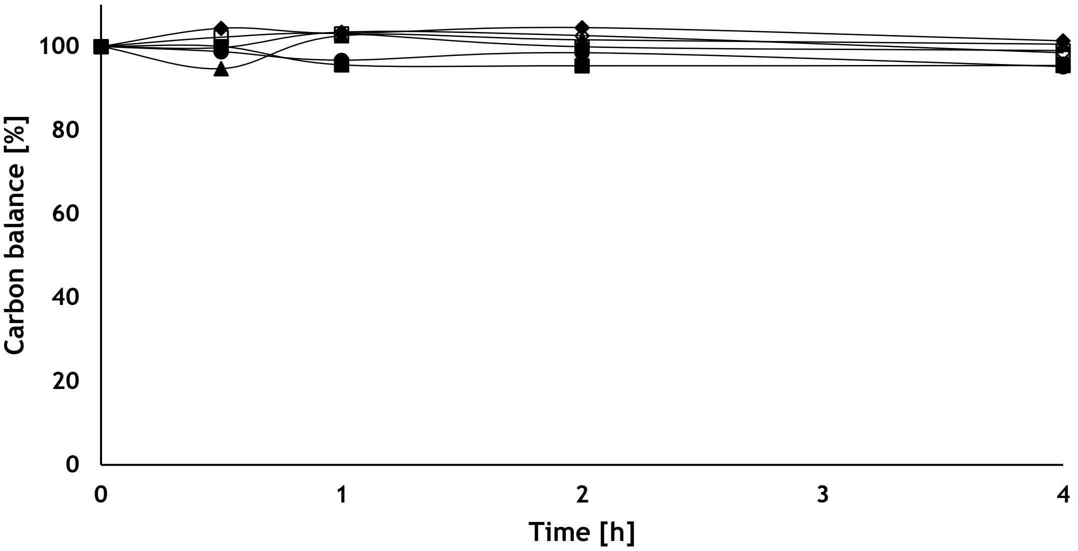

Figure 4-8** Carbon balance for the oxidation of cinnamyl alcohol using the range of catalysts prepared by sol-immobilisation method. Reaction conditions: catalyst, 10 mg; oxygen pressure, 3 bar; temperature, 120 °C; 0.5 M cinnamyl alcohol in toluene. **1 %Au/ TiO$_2$ (■); 0.95 %Au 0.05 %Pd/ TiO$_2$ (◆); 0.75 %Au 0.25 %Pd/ TiO$_2$ (□); 0.50 %Au 0.50 %Pd/ TiO$_2$ (▲); 0.25 %Au 0.75 %Pd/ TiO$_2$ (●); 1 %Pd/ TiO$_2$ (◇); 0.60 %Au 0.40 %Pd/ TiO$_2$ (○)

Figure 4-9 plots catalytic activity and yield of cinnamaldehyde produced in relation to weight percentage of gold.

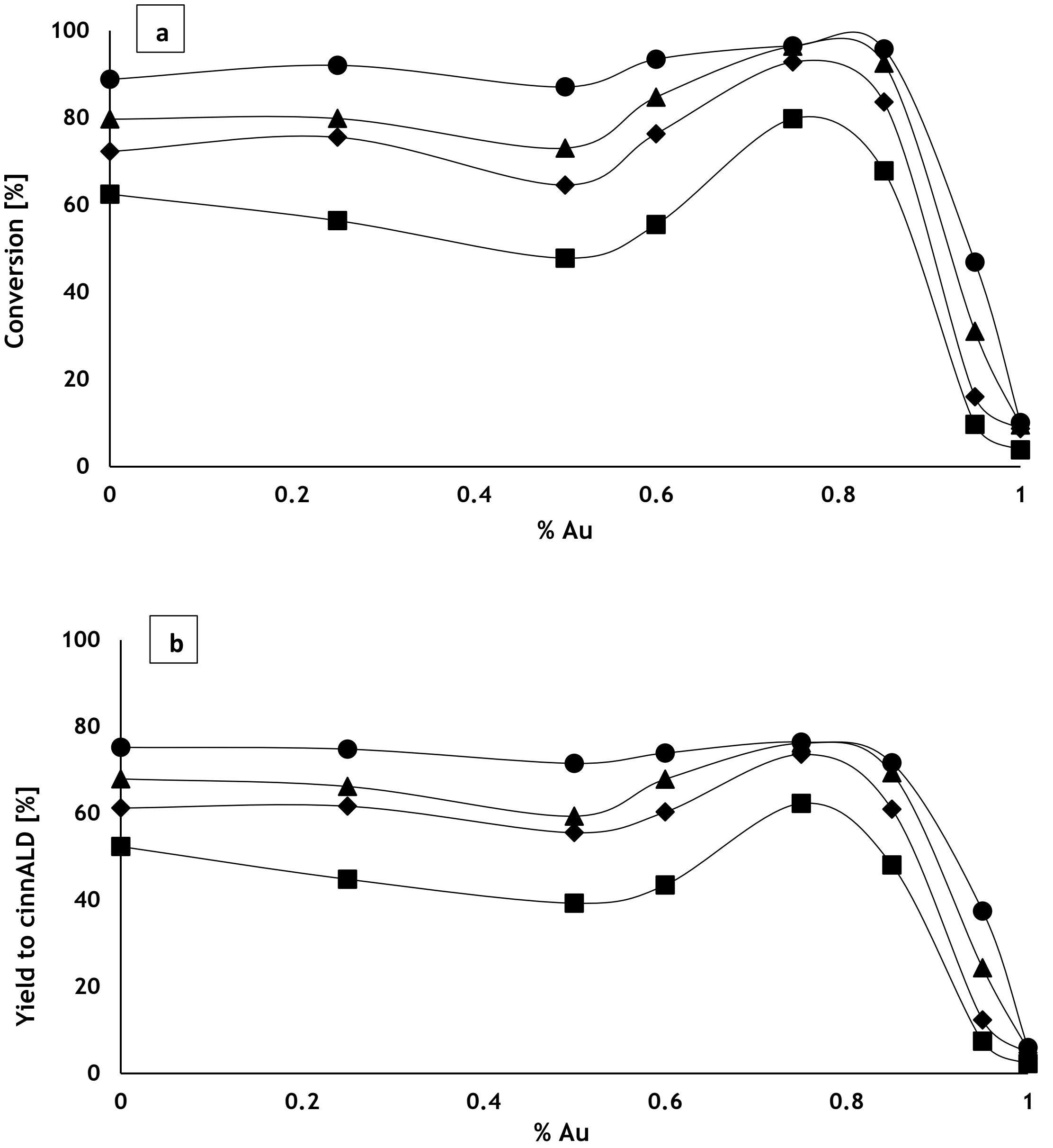

Figure 4-9 *Influence of Au-Pd metal ratio on the oxidation of cinnamyl alcohol:* ***a)*** *conversion vs gold percentage* ***b)*** *yield to cinnamaldehyde vs gold percentage. Reaction conditions: catalysts made by sol-immobilisation method, 10 mg; oxygen pressure, 3 bar; temperature, 120 °C; 0.5 M cinnamyl alcohol in toluene.* ***0.5 hour (■); 1 hour (◆); 2 hours (▲); 4 hours (●).***

It can be seen, that the conversion trend is reflected in the yield to cinnamaldehyde trend, similarly to the (Imp) catalysts. Whilst 0.75 %Au 0.25 %Pd/TiO_2 (SIm) showed the highest activity, 0.50 %Au 0.50 %Pd/TiO_2 (SIm) catalyst showed an unexpected drop in activity compared to other bimetallic catalysts. This observation is similar to the range of (Imp) catalysts. The presented results show that not only the size of nanoparticles is important but also their morphology and composition. However, after more careful consideration it should be stated that sizes of various alloys prepared by sol immobilisation method are similar but not identical, hence more detailed research should be performed to determine the effect of the size of the individual alloys on the oxidation of cinnamyl alcohol. It is not quite clear what causes different behaviour of bimetallic alloys with different metal ratio. In theory, a series of factors such as different extents of alloying, phase separation or presence of inhomogeneities might influence overall geometric and electronic effects. Prati and co-workers' work on glycerol and alcohols oxidations proved that inhomogeneities or segregation of Pd phase in bimetallic catalysts with certain metals ratios are the reason of weaker catalytic performance.[6], [8], [11], [12] These findings can be addressed to the presented research on the oxidation of cinnamyl alcohol under autoxidation conditions. Tested catalysts (both, SIm and Imp) with various metals ratios showed different catalytic activity, which may indicate different electronic properties caused by mutual interactions of different metals on each other. Prati reported the most suitable Au-Pd metal ratio being 80 Au: 20 Pd (by mol) supported over carbon for the oxidation of cinnamyl and benzyl alcohols under mild conditions. The results obtained during this investigation on the oxidation of cinnamyl alcohol under autoxidation conditions revealed that the most suitable metal ratio is 75 Au: 25 Pd by weight, which is 62 Au: 38 Pd by mol supported over titania. Prati has found very close metal ratio (60: 40 by mol) to be an ideal for the oxidation of aliphatic alcohols.[8] The difference regarding optimal metal ratio might be due to the fact, that harsher conditions have been applied in this study, which influences the behaviour of the catalysts. The additional reaction carried out using 85 Au: 15 Pd by weight, which is 75 Au: 25 Pd by mol again showed lower catalytic activity than 75 Au: 25 Pd by weight (62 Au: 38 Pd by mol). In addition to the reaction conditions, other differences in methodology could have an impact on the results. The catalysts in Prati's work have been prepared by a sequential deposition of Au and Pd while in this work, the precursors of metal have been reduced simultaneously. This should not be a major issue hence the group established that their alloys were homogeneous in certain ratios as described before. Moreover, in Prati's work the metal to substrate ratio was 500 while in this work s:m is 3455. Keeping in mind the differences in methodology and applied conditions it is expected to notice some differences in the results. However, by contrasting TOF's obtained during these two studies (table 4-1) it is possible to notice similar volcano trend throughout the whole range of Au-Pd catalysts.

Table 4-1 *Comparison of TOF for the range of Au-Pd catalysts prepared by sol-immobilisation method in the oxidation of cinnamyl alcohol.*

Source	Catalyst	TOF (h^{-1})
***This work**	1%Au/ TiO_2	248
	0.95 %Au 0.05 %Pd/ TiO_2	831
	0.85 %Au 0.15 %Pd (75 Au: 25 Pd by mol)/ TiO_2	3651
	0.75 %Au 0.25 %Pd (62 Au: 38 Pd by mol)/ TiO_2	4075
	0.50 %Au 0.50 %Pd/ TiO_2	2454
	0.25 %Au 0.75 %Pd/ TiO_2	2498
	1 % Pd/ TiO_2	2000
****Prati and co-workers[8]**	1% Au/AC	25
	1% $Pd_{10}@Au_{90}$/AC	520
	1% $Pd_{20}@Au_{80}$/AC	630
	1% $Pd_{40}@Au_{60}$/AC	539
	1% $Pd_{80}@Au_{20}$/AC	394
	1% Pd/AC	120

**Conditions: Reaction conditions: catalyst, 10 mg; oxygen pressure, 3 bar; temperature, 120 °C; 0.5 M cinnamyl alcohol in toluene. TOF calculated after 1 hour of reaction.*

***Conditions: cinnamyl alcohol 0.3 M, cinnamyl alcohol/metal 1/500 mol/mol,* T = *60 °C,* pO_2 *= 1.5 atm; stirring rate 1250 rpm. TOF calculated after 15 min of reaction.*

4.2.2. Reusability

Reusability is an essential property of any catalyst applied in the industry. Among various reasons of catalyst deactivation, the most common are metal leaching, surface changes and poisoning.[13] Reusability tests have been performed for the range of studied catalysts prepared by both methods, impregnation and sol-immobilisation (figures 4-10 and 4-11) for the oxidation of cinnamyl alcohol under autoxidation conditions. Elemental analysis (ICP-MS) of the post reaction mixtures (Imp and SIm catalysts) showed that leaching has been negligible (Au< 0.05 %; Pd~0.3 %).

Au-rich (Imp) catalysts (1 %Au/TiO_2 and 0.95 %Au 0.05 %Pd/ TiO_2) showed minimal loss of activity, however it should be emphasised that in case of impregnation method the autoxidation is dominant hence the catalytic performance is quite low for 0.95 %Au 0.05 %Pd/ TiO_2 (Imp) and negligible for 1 %Au/TiO_2 (Imp). A more pronounced loss of activity is noticeable for 0.75 %Au 0.25 %Pd/ TiO_2 (Imp) and 0.50 %Au 0.50 %Pd/ TiO_2 (Imp), however the selectivity seems to be maintained at similar level after every cycle. A significantly worse reusability is evident for Pd-rich (Imp) catalysts not only in regard of conversion but also selectivity. Larger amounts of benzaldehyde and benzoic acid have been formed after every use, which implies intensification of the autoxidation process due to weakening of catalytic performance.

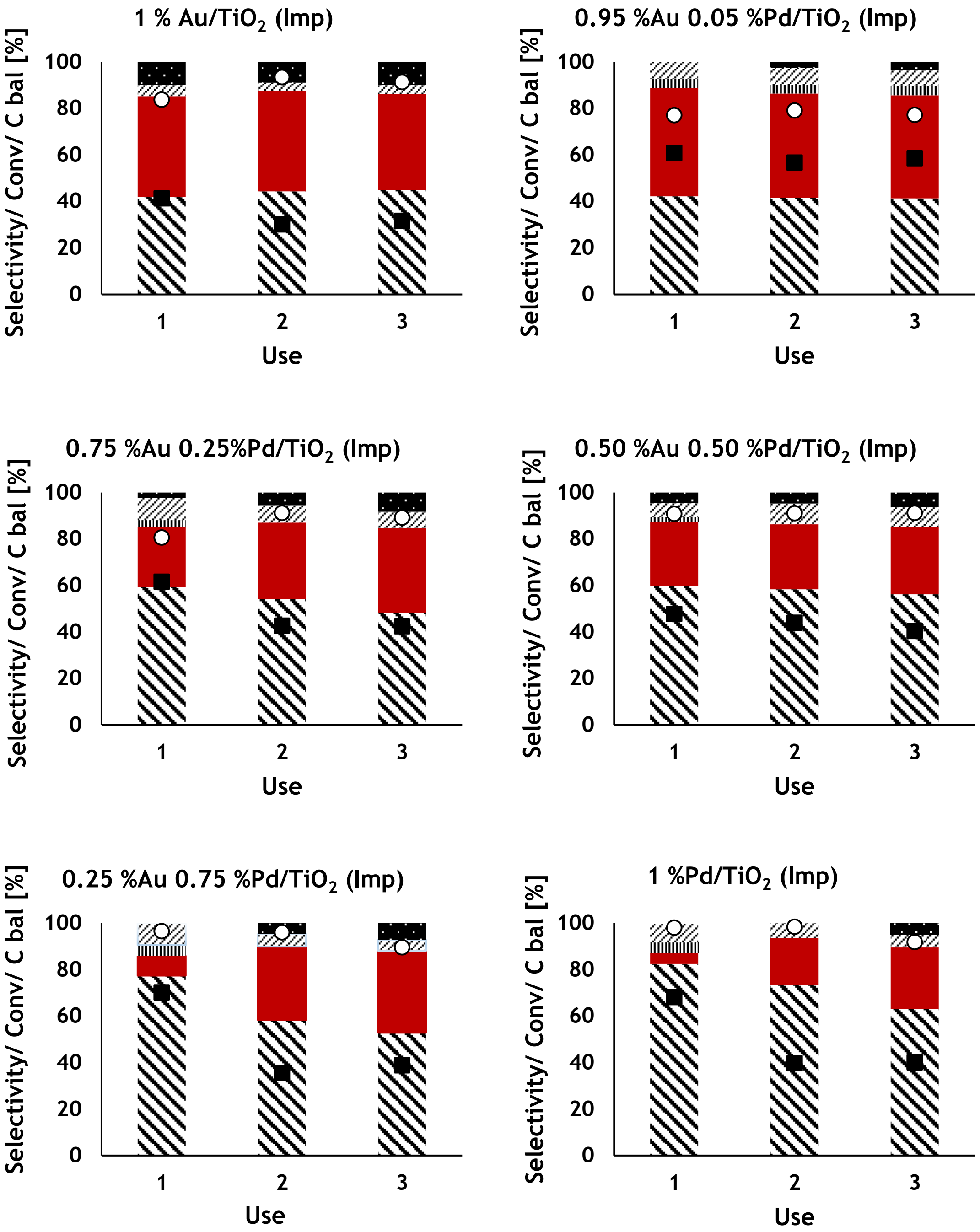

__Figure 4-10__ Reusability studies of the range of catalysts prepared by impregnation method. Reaction conditions: catalyst, 10 mg; oxygen pressure, 3 bar; temperature, 120 °C; 0.5 M cinnamyl alcohol in toluene; time, 4 hours. ***Conversion (■); Carbon balance (O); Cinnamaldehyde (▧); Benzaldehyde (🟥); Methylstyrene (▥); 3-Phenyl-1-propanol (▨); Benzoic acid (■)***

Reusability studies of (SIm) catalysts revealed gradual mild deactivation. Exceptionally low deactivation showed 0.75 %Au 0.25 %Pd/ TiO_2 (SIm): 94, 92 and 90 % after first, second and third use, respectively. This result can be understood as only slight deactivation or this catalyst is extremely stable within experimental error. To determine which hypothesis is true, the experiment would have to be repeated at low conversions (in this case at shorter time e.g. 15 or 30 minutes) to compare the initial rates. Nevertheless, as in the case of Au-rich (Imp) catalysts, Au-rich (SIm) catalysts have a low catalytic activity, hence autoxidation is dominant. It may seem that 1 %Au/TiO_2 (SIm) is more active with every use, however it is the opposite. The increased conversion is caused by autoxidation due to worse scavenging properties of the catalyst after every cycle, which is reflected in larger amount of formed benzaldehyde. Noticeably more benzaldehyde has been formed after every cycle using 0.95 %Au 0.05 %Pd/ TiO_2 (SIm), which also suggests that the autoxidation is taking place. In general, 0.50 %Au 0.50 %Pd/ TiO_2 (SIm) and Pd-rich (SIm) catalysts maintained high selectivity to cinnamaldehyde with every use, however conversion decreased. Especially high selectivity to cinnamaldehyde (97 %) has been obtained after third cycle using 1 %Pd/ TiO_2 (SIm). This reading appears to be incorrect due to analysis error, hence it should be repeated before drawing any conclusions.

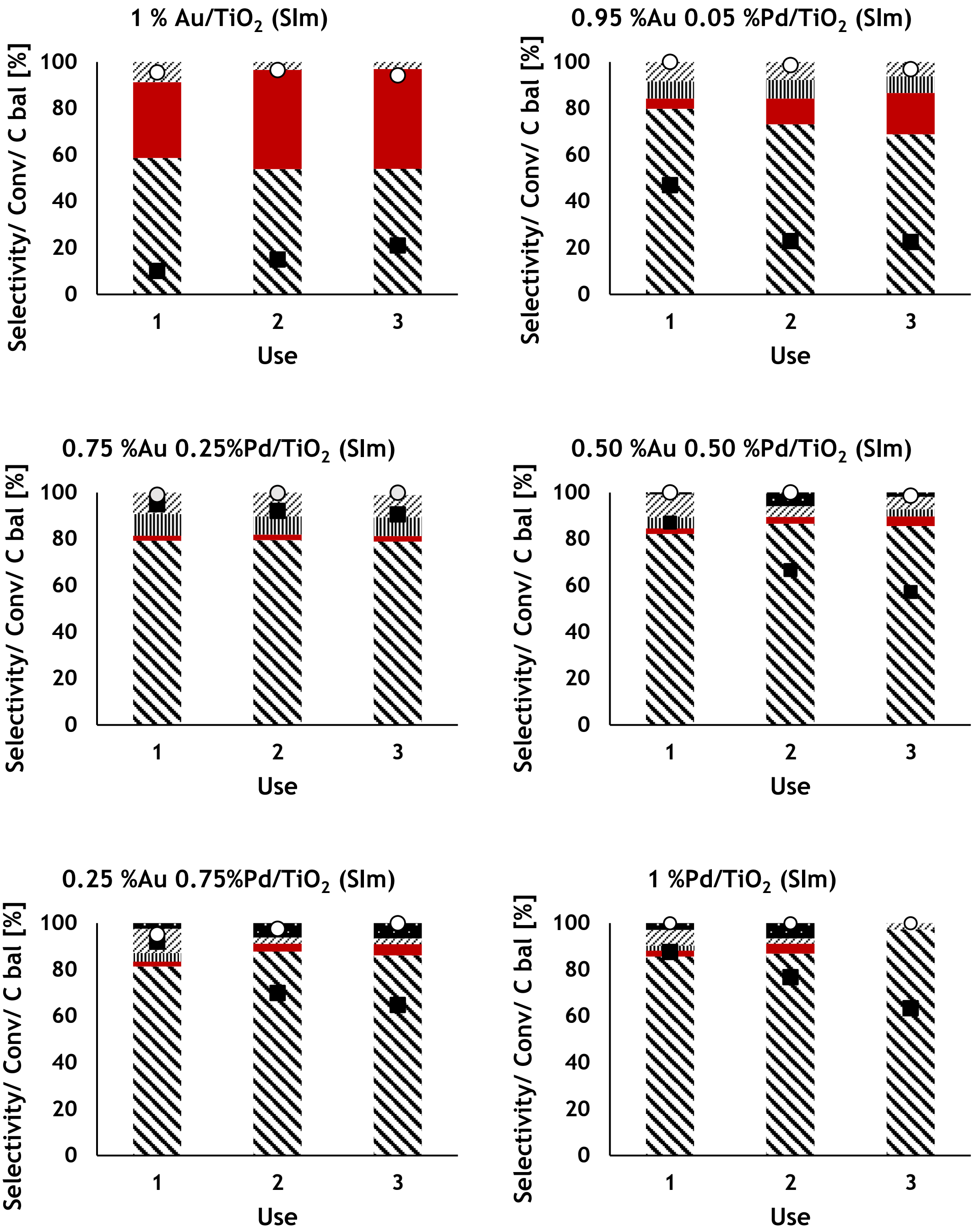

Figure 4-11 *Reusability studies of the range of catalysts prepared by sol-immobilisation method. Reaction conditions: catalyst, 10 mg; oxygen pressure, 3 bar; temperature, 120 °C; 0.5 M cinnamyl alcohol in toluene; time, 4 hours.* ***Conversion (■); Carbon balance (○); Cinnamaldehyde (▧); Benzaldehyde (▬); Methylstyrene (‖‖‖); 3-Phenyl-1-propanol (▨); Benzoic acid (▪▪▪)***

Poisoning is an especially common and difficult to manage reason of catalyst deactivation in the oxidation of allylic alcohols. Two research groups under the leaderships of Baiker and Wilson proved that CO formed during decarbonylation can adsorb on Pd, which diminishes overall yield of the catalytic process.[14]-[17] A small amount of CO is produced during the oxidation of cinnamyl alcohol, which can explain lower carbon balance in case of the range of (Imp) catalysts. Therefore, poisoning coupled with probable nanoparticle agglomeration might explain gradual loss of activity of the studied catalysts. To verify this hypothesis, detailed SEM and XPS analysis have been performed, which is presented in the next section.

4.2.3. Characteristics

4.2.3.1. SEM

It has been demonstrated in Chapter 3 that the size of Au-Pd nanoparticles obtained by impregnation and sol-immobilisation methods varies heavily as expected. In this chapter, SEM has been used to investigate the characteristics of the metal nanoparticles in used catalysts in 3 consecutive cycles. The analysis has been carried out on the example of following catalysts: 0.50 %Au 0.50 %Pd/ TiO_2 (Imp), 0.50 %Au 0.50 %Pd/ TiO_2 (SIm) and 0.75 %Au 0.25 %Pd/ TiO_2 (SIm). The catalysts prepared by impregnation method showed a similar deactivation pattern, hence 50:50 metal ratio has been chosen as an example. Deactivation of 0.75 %Au 0.25 %Pd/ TiO_2 (SIm) catalyst was unusally minor compared to the rest of the catalysts prepared by sol-immobilisation method, hence two catalysts have been chosen for the investigation.

From figure 4-12a it can be seen that the nanoparticles in 0.50 %Au 0.50 %Pd/ TiO_2 (Imp) are large (around 100 nm) with occasional occurences of smaller clusters (from 3 to 100 nm). Comparison of the size of nanoparticles on the fresh (4-12a) and used catalyst (4-12b) showed that there is no massive change noticed in the particle size. The poor gold dispersion has been confirmed by XPS results (section 4.2.3.2). Based on that and on the activity data it can be assumed that similar behaviour would show any other catalyst prepared by impregnation method.

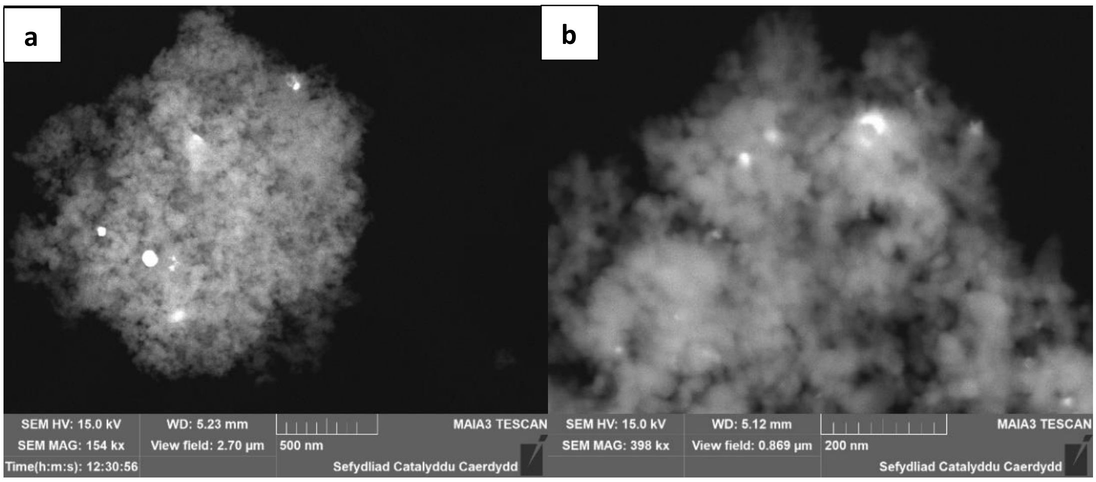

***Figure 4-12** BSD-SEM image of the 0.50 %Au 0.50 %Pd/ TiO_2 (Imp): a) fresh, b) spent*

In the case of the same catalyst but made by the sol-immobilisation method, the difference between the fresh and the catalyst used is significant. Figure 4-13 shows a comparison of catalyst after first use (4-13a) 0.50 %Au 0.50 %Pd/ TiO_2 (SIm), after second (4-13b) and third cycle (4-13c). Initially the nanoparticles were very small, in range 1-8 nm with an average of 2-3 nm. Slighlty larger clusters have been observed after second use, the size range has increased (3-13 nm) with the majority being 5-7 nm. After 3rd use a minimal particle growth has been obtained with more 7 and 8 nm clusters noticed.

From figure 4-14 it is clear that for 0.75 %Au 0.25 %Pd/ TiO_2 (SIm) the particle growth is neglible which can explain the extraordinary reusability of this catalyst. The nanoparticles were in range 1-8 nm after all 3 cycles, with an average of 2-3 nm after first and second use, and 4-5 nm after third use.

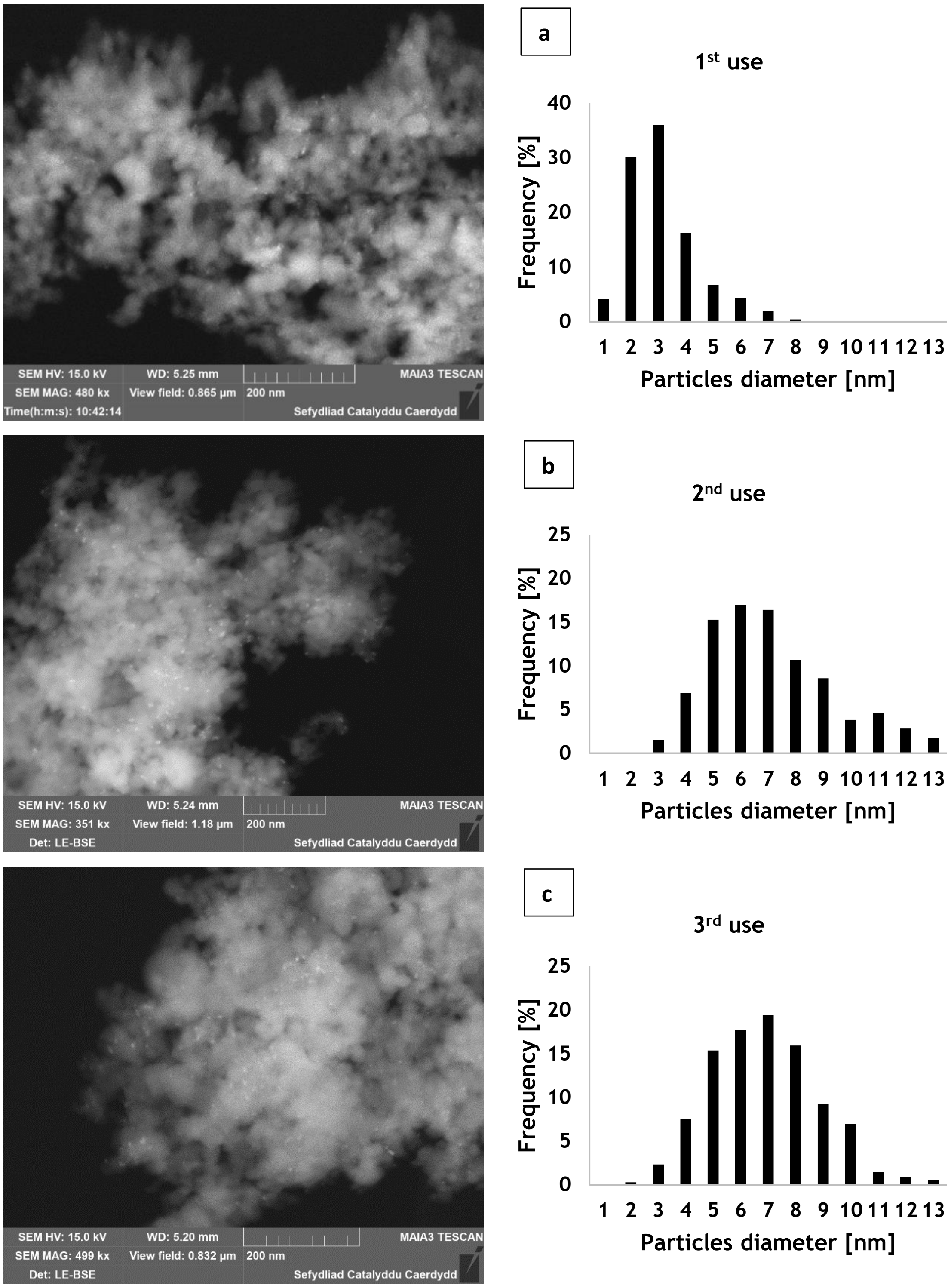

Figure 4-13 *BSD-SEM image of the 0.50 %Au 0.50 %Pd/ TiO_2 (SIm) and associated particle size distribution: a) fresh catalyst b) spent catalyst: 2nd use c) spent catalyst: 3rd use*

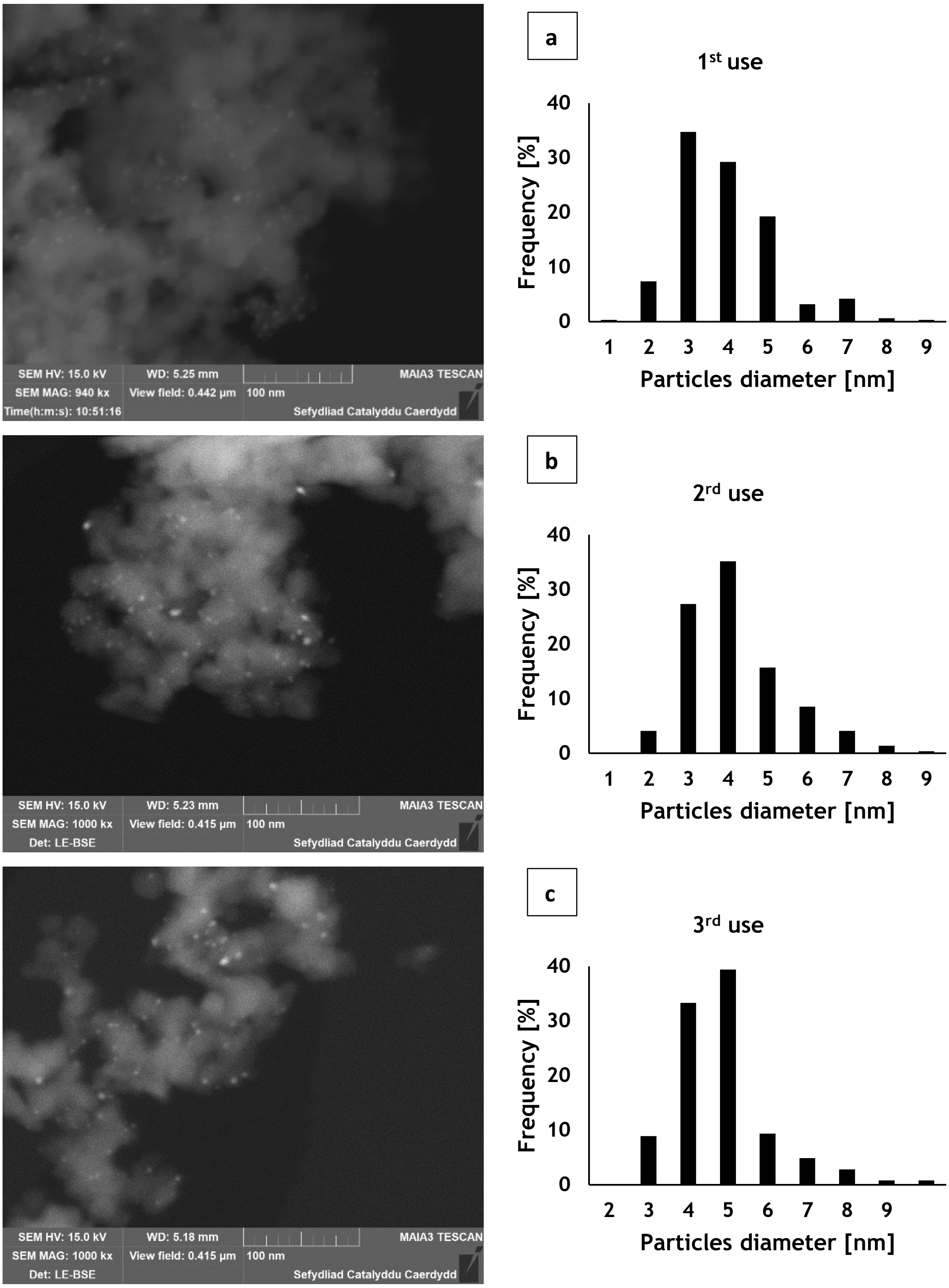

Figure 4-14 *BSD-SEM image of the 0.75 %Au 0.25 %Pd/ TiO_2 SIm and associated particle size distribution: a) fresh catalyst b) spent catalyst: 2nd use c) spent catalyst: 3rd use*

In conclusion, the agglomeration in case of 50Au:50Pd and minor particle growth in case of 75Au:25Pd can explain the deactivation of the range of 1 %AuPd/TiO_2 (SIm) catalysts with the exception of 75Au:25Pd ratio presenting outstanding stability and activity.

4.2.3.2. XPS

XPS analysis of catalysts prepared by the impregnation method revealed the existence of Pd (II) and Pd (0) species (with binding energies of 336.4 and 335.3 eV, respectively), which occur in approximately a 1:1 ratio (figure 4-15). Gold was found in its metallic form (binding energy of 83.2 eV). Moreover, the signal of Au (4f) for catalysts in the range of increasing gold content was very weak, which generally means poor dispersion of gold. Thus, the XPS analysis confirmed the results obtained from the SEM analysis that the nanoparticles are large and poorly dispersed.

In the case of the catalysts prepared by the sol-immobilisation method, the effect of gold dilution by palladium occurred, which was determined by lower Au coordination (lowering of the Au (4f) peak to a maximum of 0.4 eV). Furthermore, both Au (4f) and Pd (3d) peaks were observed for all bimetallic catalysts. The fact that Pd was detectable even in the case of low metal concentrations (e.g., 0.95% Au, 0.05% Pd / TiO_2 (SIm)) indicates excellent overall dispersion.

Pd (II) has not been detected in 0.75 %Au 0.25 %Pd/TiO_2 (SIm) catalyst, however the reason for this may be its low concentration. It can definitely be stated, that Pd (II) species are easily detectable in catalysts with a higher content of Pd, that is, above 0.25 %. The Pd (II) concentration is relatively low for 0.50 %Au 0.50 %Pd/TiO_2 (SIm), which may cause a relatively lower activity compared to other bimetallic catalysts (figure 4-16). The significance of PdO is discussed in more detail in the following section 4.2.4.

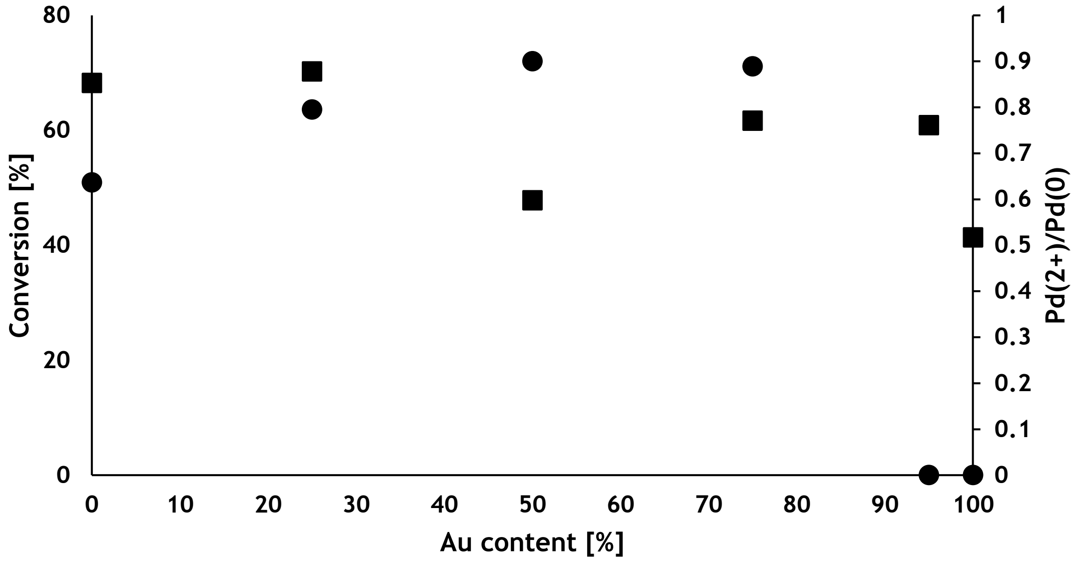

__Figure 4-15__ Presence of Pd (0) and Pd (2+) species in the range of catalysts prepared by impregnation method. ***Conversion after 4 hours (■); Pd (2+)/ Pd (0) ratio (●)***

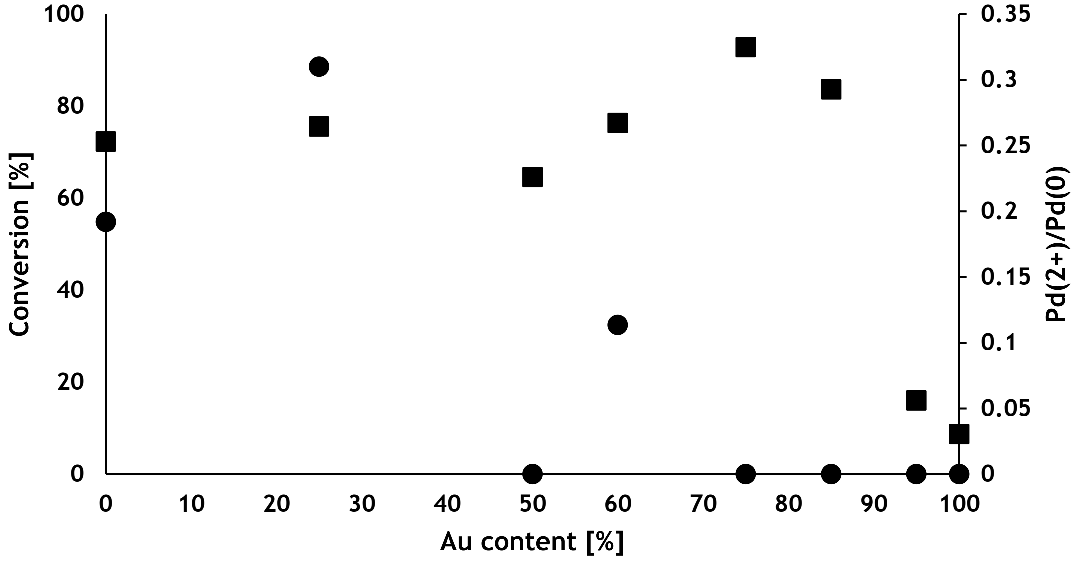

Figure 4-16 Presence of Pd (0) and Pd (2+) species in the range of catalysts prepared by sol-immobilisation method. **Conversion after 4 hours (■); Pd (2+)/ Pd (0) ratio (●)**

4.2.4. The importance of oxygen in the catalytic process

As already discussed in Chapter 3, the role of O_2 in the oxidation of cinnamyl alcohol (and other allylic alcohols) is contentious.[18], [19] Baiker *et al.* reported that dehydrogenation of cinnamyl alcohol over Pd/Al_2O_3 catalysts took place in the absence of oxygen in the system and increased selectivity to 3-phenyl-1-propanol and methylstyrene indicated that cinnamyl alcohol acted as a hydrogen acceptor. The researchers stated that oxygen might clean the catalyst surface and therefore takes a part in the process.[18] Lee *et al.* on the other hand suggested that PdO is the active centre and oxygen plays a direct, important role in the catalytic process.[19] In Chapter 3, the role of oxygen in cinnamyl alcohol oxidation has been investigated in terms of its influence on the products distribution. Little attention has been paid to the subtle matter of the influence of oxygen on the catalysts itself. It is extremely difficult to indicate active centres of the catalysts even with the participation of modern technologies. Lee and Wilson delivered valuable publications on the active site in Pd supported catalysts in the oxidation of various alcohols in mild conditions (air as an oxidant, low temperatures ~60 °C).[13], [20] The researchers investigated the structural changes in a Pd/C catalyst using *in situ* XAFS and XPS techniques. Their work confirmed Baiker's [21] report that cinnamyl alcohol rapidly reduces the surface palladium oxide. The most important observation concerned the correlation of catalytic activity with the oxidation state of Pd. A designed experiment with cycles of oxidation and catalyst reduction has shown that a palladium oxide surface layer was crucial for high catalytic performance.[20] In a later paper the scientists emphasize the importance of high Pd dispersion for enhanced catalytic activity.[13] Appreciable Pd dispersion was observed up to 1 wt% bulk loading; higher Pd content (up to 8.55 wt%) resulted in lower dispersion and occurrence of larger Pd particles. The phenomenon of dispersion was directly linked with the palladium oxide presence as the researchers noticed the relation between increasing TOF in cinnamyl alcohol oxidation with increasing surface layer of PdO (%).[13] Wilson *et al.* made efforts to improve Pd catalytic performance by changing support to mesoporous alumina and three-dimensional silicas (KIT-6, SBA-16). Indeed, these supports were found to be more suitable than SBA-15 or γ-Al_2O_3 which was explained by enhanced Pd nanoparticle stabilization hence a high concentration of palladium oxide has been maintained.[21] [22]

XPS analysis carried out during this study revealed the presence of PdO (section 4.2.3.2) however there is no actual trend in terms of the influence of PdO on the activity. The most active catalyst for the oxidation of cinnamyl alcohol under autoxidation conditions has been found to be 0.75 %Au 0.25 %Pd/TiO_2 (SIm) and no PdO has been detected on it. Anyway, small quantities may still be present, taking into consideration that XPS technique is not ideal for such subtle measurements. Moreover, XPS analysis should be carried out also after the reaction to verify the existence of PdO. Unfortunately, the role of oxygen is not fully understood. Nevertheless, some additional experiments have been carried out to verify whether the change of oxygen to air would benefit the overall yield of the studied reaction. Moreover, the catalyst has been tested in low temperature, where autoxidation did not take place.

From figure 4-17 it can be seen that, the use of oxygen allows to obtain higher reaction rate within the first 2 hours compared to the use of air. However, after this time the same results are possible to obtain using air as an oxidant. The reactions carried out at 60 °C gave considerably lower conversion than the reaction performed at standard temperature (120 °C) regardless of which oxidant has been used (molecular oxygen or air).

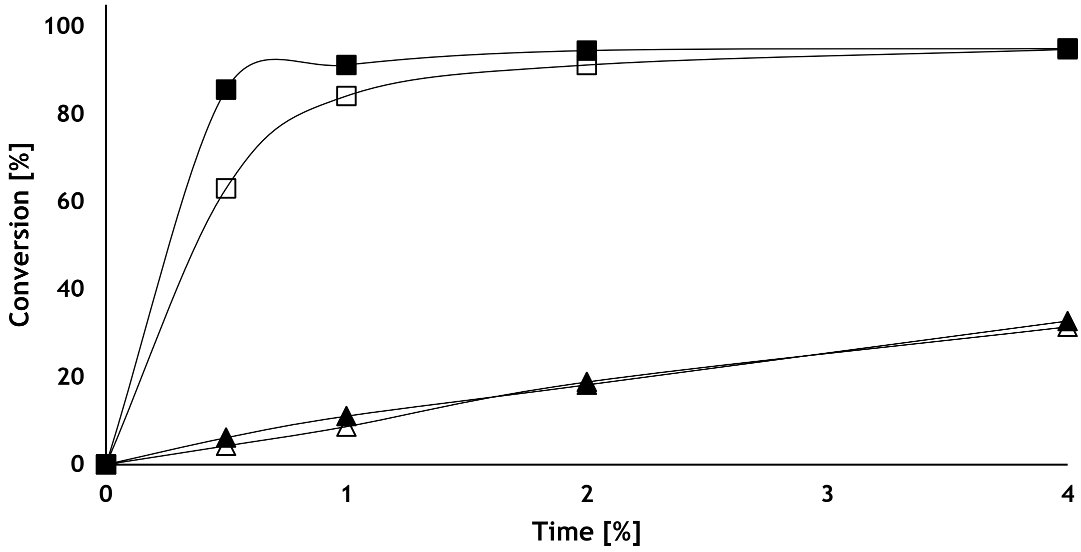

Figure 4-17 *Influence of different conditions on the oxidation of cinnamyl alcohol using 0.75 %Au 0.25 %Pd/ TiO_2 (SIm) catalyst. Reaction conditions: catalyst, 10 mg; oxygen pressure, 3 bar; temperature, 120 °C; 0.5 M cinnamyl alcohol in toluene.* ***Full markers- atmosphere of oxygen: 120 °C (■); 60 °C (▲). Empty markers- air: 120 °C, (□); 120 °C; 60 °C (△)***

Figure 4-18 presents selectivity profiles for the above discussed reactions. When oxygen has been replaced with air, benzaldehyde has not been immediately formed, however it is observed after 30 minutes of reaction. Interestingly, a higher selectivity to methylstyrene has been noticed at the expense of cinnamaldehyde. From this experiment it is clear, that oxygen is more suitable oxidant than air as it leads to lower formation of by-products from hydrogen transfer processes, which allows for higher selectivity to cinnamaldehyde.

The product distribution of the reaction carried out at 60 °C differed from the reaction carried out at 120 °C. The most noticeable difference is related to benzaldehyde. Benzaldehyde has been detected after 2 hours of the experiment under oxygen, while there was no benzaldehyde formed under air. Similar to the experiments performed at 120 °C, at 60 °C under oxygen the formation of methylstyrene was minimal and only appeared after 2 hours of the experiment, while under air the formation of methylstyrene was intensified. These observations support the hypothesis that oxygen may act not only as an oxidant but also as a cleaning agent, responsible for removing reactants of the catalyst surface. Smaller amounts of detected by-products generally mean better overall performance of the catalytic process hence the reaction has been carried out for longer to ensure higher conversion. Unfortunately, after 24 h the conversion did not exceed 32 %.

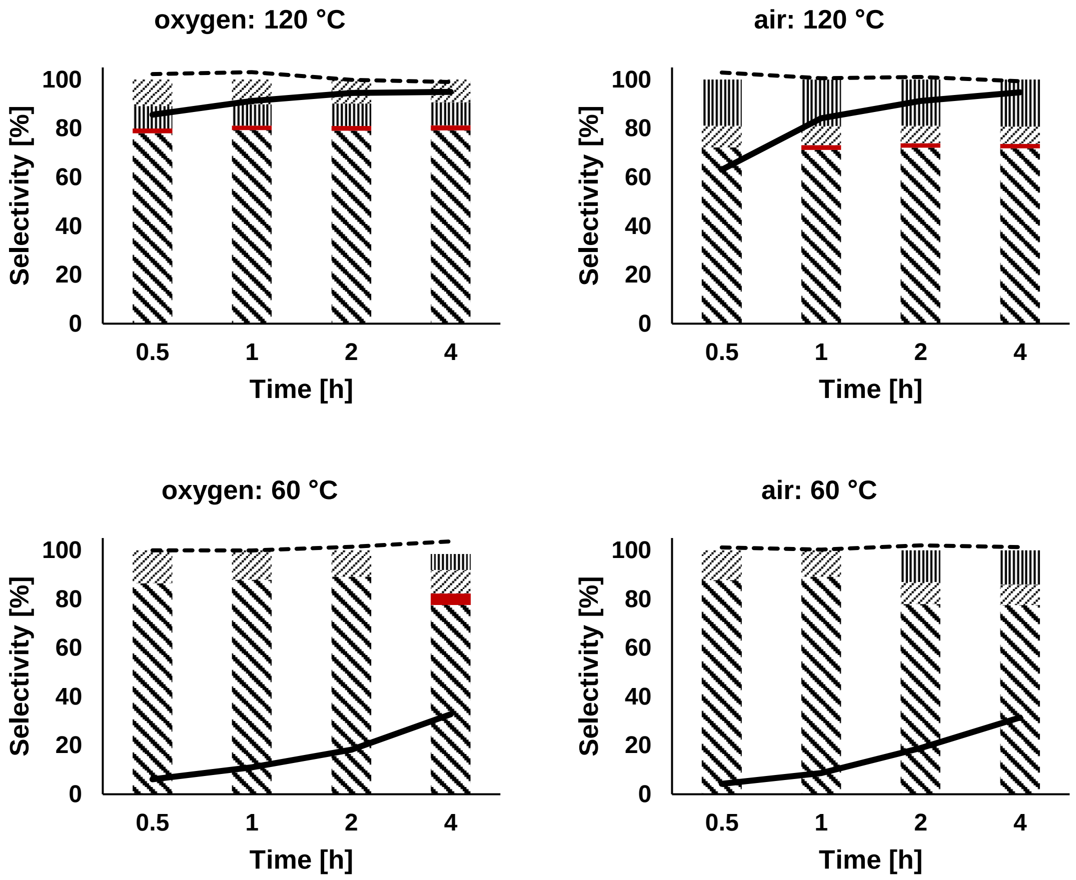

Figure 4-18** Influence of different conditions on the selectivity profile of the oxidation of cinnamyl alcohol using 0.75 %Au 0.25 %Pd/TiO_2 (SIm). Reaction conditions: catalyst, 10 mg; oxygen pressure, 3 bar; temperature, 120 °C; 0.5 M cinnamyl alcohol in toluene.* ***Conversion (—); Cinnamaldehyde (▧); Benzaldehyde (🟥); 3-Phenyl-1-propanol (▨); Methylstyrene (▥)

4.2.5. Studies of the most active catalysts prepared by sol-immobilisation and impregnation methods.

As already mentioned, the size of Au-Pd nanoparticles strongly influences their catalytic activity. However, as has been shown, variation in metal ratio also affects the course of the catalytic process, which implies different properties and possibly different morphologies of clusters with different metal content in the same size range. The most active (Imp) and (SIm) catalysts have been chosen and tested in detail to verify possible differences to the 50:50 (Imp) and (SIm) catalysts which have been analysed in Chapter 3. The main reason of these tests is relatively weaker activity of (SIm) and (Imp) catalysts with 50:50 metal ratio compared to the other bimetallic catalysts. An attempt has been made to investigate the behaviour of the most active catalysts and verify possible different trends in their performance.

4.2.5.1.Different Solvents

In this section, the most active catalysts 0.75 %Au 0.25 %Pd/ TiO_2 (SIm) and 0.25 % 0.75 %Pd/ TiO_2 (Imp) have been tested in two different solvents: xylene and water.

4.2.5.1.1. Xylene

It has been demonstrated in Chapter 3 that the increase in 0.50 %Au 0.50 %Pd/ TiO_2 (SIm) catalyst mass from 10 to 20 mg resulted in a minor increase in conversion (around 6 % after 4 hours) hence the lowest possible amount of catalyst showing satisfying results has been applied for further work. Also doubled mass (20 mg) has been tested in xylene. Three isomeric forms of xylene have been tested (*o*-, *m*- and *p*) showing the same results. Xylene (dimethylbenzene) has been chosen as an example of another organic solvent with variation in methyl groups in relation to toluene (methylbenzene).

The reaction carried out with the use of 10 mg 0.75 %Au 0.25 %Pd/TiO_2 (SIm) in toluene had 97 % conversion after 4 hours and selectivity profile to 80 % cinnamaldehyde, 3 % benzaldehyde, 10 % PP, and 7 % MS (figure 3-5). The change of solvent from toluene to xylene (figure 4-19) had a minimal influence on the process; the results after 0.5 and 4 hours are the same. A two-fold increase in catalyst mass resulted in increase of the conversion (from 75 % to 97 %) while maintaining the selectivity profile.

In the case of 0.25 %Au 0.75 %Pd/TiO_2 (Imp) catalyst, the conversion in toluene was 70 % after 4 hours with selectivity to cinnamaldehyde around 75 % and selectivity to benzaldehyde around 10 %. The selectivity to products, which indicate hydrogen transfer processes (methylstyrene and 3-phenyl-1-propanol), was below 5%. The course of the reaction in xylene (figure 4-20) is similar for the first 2 hours, however after 4th hour the conversion is lower (50 %). A two-fold increase in catalyst mass resulted in significant increase in conversion (93 % after 4 hours) while maintaining selectivity profile.

To conclude, the course of reaction has been found to be similar in tested organic solvents with a minimal advantage for toluene. Doubling the amount of catalyst led to minor improvement of the overall yield of the process in the case of (SIm) catalyst, however in the case of (Imp) catalyst the yield of the reaction increased significantly.

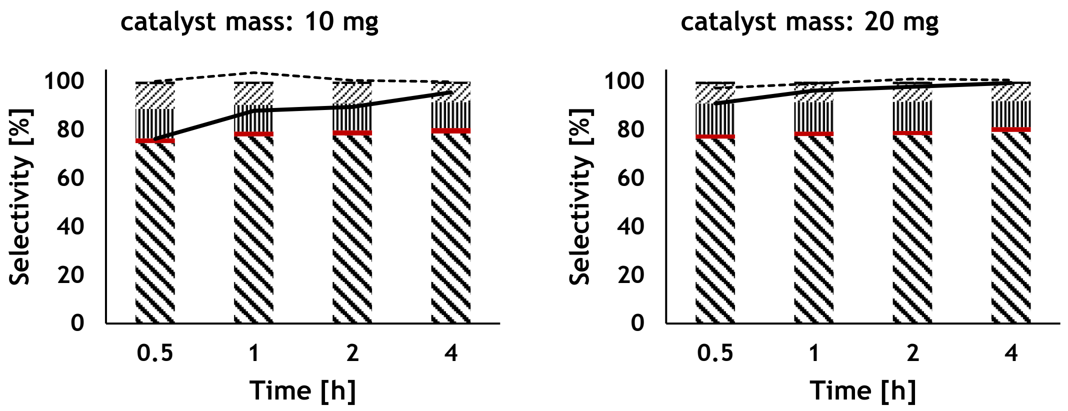

Figure 4-19 *Influence of the catalyst mass on the oxidation of cinnamyl alcohol using 0.75 %Au 0.25 %Pd/ TiO_2 (SIm). Reaction conditions: catalyst, 10 mg; oxygen pressure, 3 bar; temperature, 120 °C; 0.5 M cinnamyl alcohol in xylene.* ***Conversion (—); Cinnamaldehyde (▧); Benzaldehyde (🟥); 3-Phenyl-1-propanol (▨); Methylstyrene (▥); Styrene (■)***

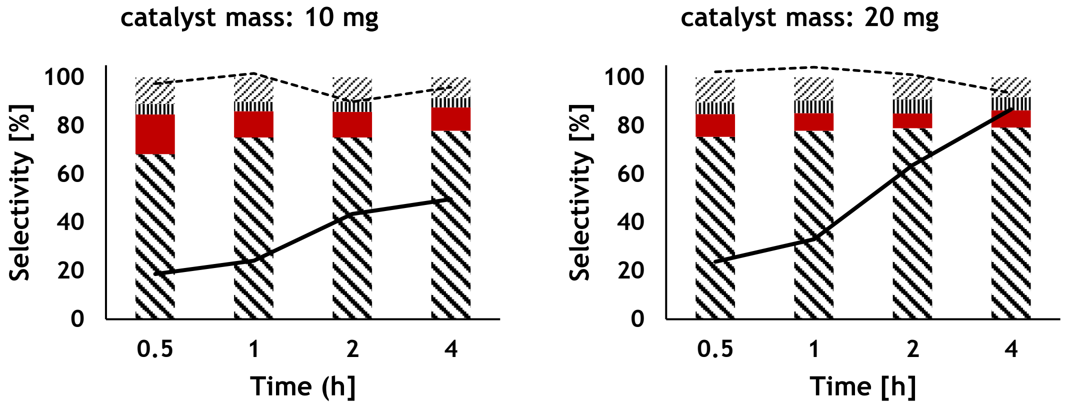

Figure 4-20 *Influence of the catalyst mass on the oxidation of cinnamyl alcohol using 0.25 %Au 0.75 %Pd/ TiO_2 (Imp). Reaction conditions: catalyst, 10 mg; oxygen pressure, 3 bar; temperature, 120 °C; 0.5 M cinnamyl alcohol in xylene.* ***Conversion (—); Cinnamaldehyde (▧); Benzaldehyde (🟥); 3-Phenyl-1-propanol (▨); Methylstyrene (▥); Styrene (■)***

4.2.5.1.2. Water

In addition to organic solvents, the reaction of cinnamyl alcohol oxidation has also been carried out in water using 0.75 %Au 0.25 %Pd/ TiO_2 (SIm). The compounds have been retrieved from aqueous phase by extraction with toluene. The table 4-2 contains obtained data compared with the reaction carried out in toluene under standard conditions.

***Table 4-2** Effect of water used as a solvent on the oxidation of cinnamyl alcohol.*

Experiment	Conversion [%]	C bal [%]	Selectivity [%]				
			CinnALD	BenzALD	PP	BenzACID	MS
Water as a solvent	99	47	50	28	12	10	-
Standard reaction	95	100	79	2	10	-	9

Reaction conditions: 0.75 %Au 0.25 %Pd/ TiO_2 (SIm) catalyst, 10 mg; oxygen pressure, 3 bar; temperature, 120 °C; 0.5 M cinnamyl alcohol in water or in toluene.

It can be seen, that the carbon balance of the extracted organic phase from water is rather low (47 %). One reason might be inefficient extraction process. The other reason might be large amount of cinnamic acid, the presence of which has been confirmed by GC-MS analysis, however cinnamic acid is undetectable during standard analysis on GC with CPwax column. Despite the fact, that the experiment with the use of water as a solvent is poor quality, it has not been repeated as these preliminary results were sufficient to evaluate the product distribution. The presence of benzaldehyde and benzoic acid in large amounts indicates that the process of autoxidation was taking place, which is not desirable. Moreover, cinnamic acid formation suggests that the mechanism of cinnamyl alcohol oxidation under autoxidation conditions in water is different to the mechanism in organics. It has been shown in Chapter 3 that a small addition of water to the organic reaction solution improved greatly the overall yield to cinnamaldehyde, presumably by quenching radical species. Interestingly, in this experiment using water as the only solvent not only did not improve the reaction but the opposite, large amounts of unwanted by-products have been detected.

Prati and co-workers tested various Au-Pd metal ratio on the oxidation of cinnamyl alcohol in water. The reactions have been performed at 60 °C under 1.5 atm of oxygen pressure. These conditions were relatively mild, there was no autoxidation observed and the only products detected were cinnamaldehyde and 3-phenyl-1-propanol. The researchers tested also the influence of base which led to the formation of acids and esters.[8] Earlier studies from the same group on the oxidation of cinnamyl alcohol using 0.73 %Au 0.27 %Pd/ C made by sol-immobilisation method showed that the catalyst is more active in water (95 % conversion) than in toluene (72 % conversion).[7] It is known, that the mechanism of oxidation in water and in toluene is different for Pt and Pd systems, which can be addressed to Au-Pd system accordingly. Better properties of water as a solvent have been explained by two possible reasons. First is mechanistically approach where water would react with aldehyde forming hydrate, which would react further with oxygen leading to carboxylic acid. This would explain why water applied as a solvent in the oxidation of cinnamyl alcohol under autoxidation conditions yielded large amounts of carboxylic acid. The other possible influence of water on the reaction is promoting reactivity by facilitating H abstraction from alcohol which is caused by the fact that water is a weak base.[7] This property of water might explain the higher activity of the Au-Pd supported catalyst in the oxidation of alcohols in mild conditions. In the presented research the small addition of water (2 ml) to the organic reaction solution led to significantly improved overall yield, which might be supported by this hypothesis.[7]

4.2.5.2. Inert gas

Another test that the most active catalysts have undergone is the oxidation of cinnamyl alcohol in an inert gas atmosphere. The same experiment has been performed for 0.50 %Au 0.50 %Pd/ TiO_2 (SIm) and (Imp) catalysts described in Chapter 3. In both cases significant differences have been noticed: the formation of benzaldehyde has been stopped and selectivity to the products being formed as the effect of hydrogen transfer (PP, MS) increased.[18], [23] The behaviour of the (Imp) catalyst differed from (SIm) catalyst in terms of conversion. The 0.50 %Au 0.50 %Pd/TiO_2 Imp catalyst (table 2, figure 3-25) was less active under nitrogen than under oxygen (19 and 48 %, respectively after 4 hours) whereas there was only a minimal difference in conversion (within an experimental error) for the reactions with the use of 0.50 %Au 0.50 %Pd/TiO_2 (SIm). Figure 4-21 shows the comparison of the most active (Imp) and (SIm) catalysts tested in oxygen and in nitrogen. It can be seen, that the trend for 0.25 %Au 0.75 %Pd/ TiO_2 (Imp) is similar to the studied earlier 50:50 (Imp), namely the conversion is lower under nitrogen than under oxygen with intensified role of cinnamyl alcohol as a hydrogen acceptor which is indicated by larger amounts of PP and MS (figure 4-22).[18], [24] The results for the 0.75 %Au 0.25 %Pd/TiO_2 (SIm) are somewhat more intriguing than would be expected given the previous 50:50 (SIm) tests. 0.75 %Au 0.25 %Pd/TiO_2 (SIm) tested under nitrogen demonstrated significantly lower conversion than under oxygen (figure 4-21). The selectivity profile is in line with expectations as large amounts of PP and MS have been detected (figure 4-23).

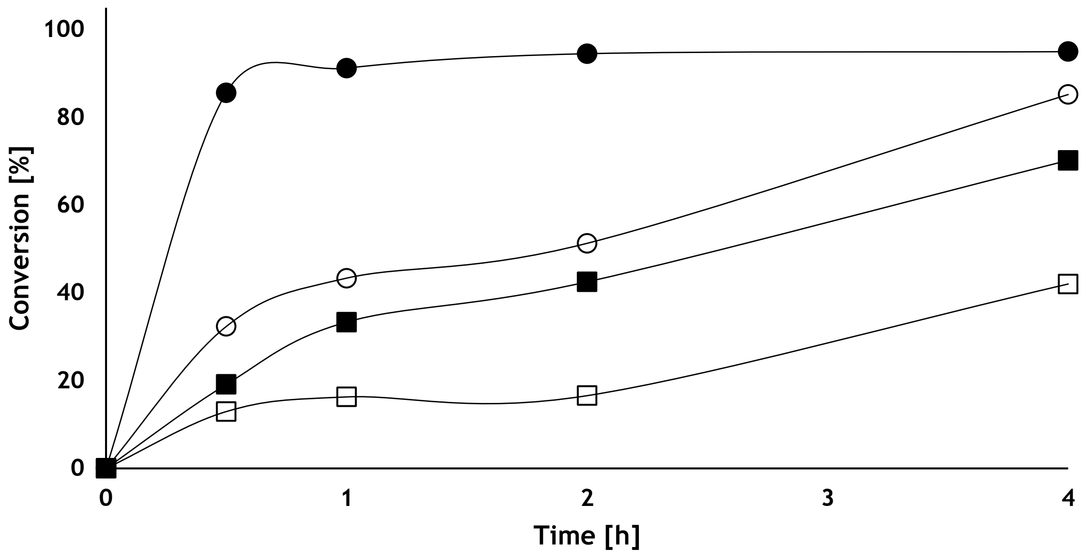

Figure 4-21 *Influence of inert gas on the conversion of cinnamyl alcohol using 0.75 %Au 0.25 %I TiO_2 SIm and 0.25 %Au 0.75 %I TiO_2 (Imp). Reaction conditions: catalyst, 10 mg; oxygen/ nitrogen pressure, 3 bar; temperature, 120 °C; 0.5 M cinnamyl alcohol in toluene.* ***Full markers- reactions carried in the atmosphere of oxygen: 0.25 %Au 0.75 %I TiO_2 (Imp) (■); 0.75 %Au 0.25 %I TiO_2 (SIm) (●). Empty markers- reactions carried out in the atmosphere of nitrogen: 0.25 %Au 0.75 %I TiO_2 (Imp) (□); 0.75 %Au 0.25 %I TiO_2 (SIm) (○)***

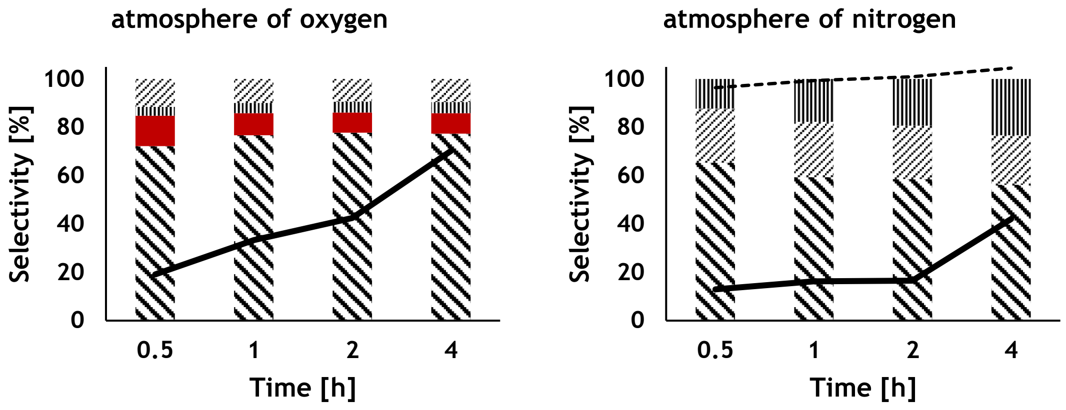

Figure 4-22 *Influence of inert gas on the selectivity profile in the oxidation of cinnamyl alcohol using 0.25 %Au 0.75 %Pd/ TiO_2 (Imp). Reaction conditions: catalyst, 10 mg; oxygen/nitrogen pressure, 3 bar; temperature, 120 °C; 0.5 M cinnamyl alcohol in toluene.* ***Conversion (—); Cinnamaldehyde (▧); Benzaldehyde (🟥); 3-Phenyl-1-propanol (▨); Methylstyrene (▥)***

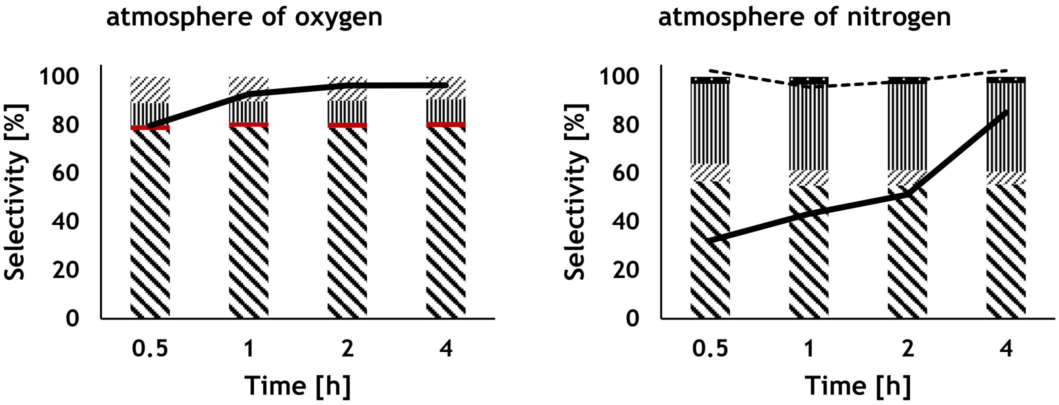

Figure 4-23 *Influence of inert gas on the selectivity profile in the oxidation of cinnamyl alcohol using 0.75 %Au 0.25 %Pd/ TiO_2 (SIm). Reaction conditions: catalyst, 10 mg; oxygen/nitrogen pressure, 3 bar; temperature, 120 °C; 0.5 M cinnamyl alcohol in toluene.* ***Conversion (▬); Cinnamaldehyde (▧); Benzaldehyde (▬); 3-Phenyl-1-propanol (▨); Methylstyrene (▥)***

These experiments confirmed what has been stated before that the process takes place according to the dehydrogenation mechanism.[18] However, the fact that 75: 25 (SIm) showed different trend to 50: 50 (SIm) in nitrogen leads to a discussion on the cause. There are two approaches to the role of oxygen in the literature; oxygen as a “cleaner” for catalyst surface from e.g. excess of hydrogen[18] and oxygen playing a direct and important role in the catalytic process to constantly regenerate the active sites.[19] Both hypotheses seem to be very likely and it is extremely difficult to verify the actual role of oxygen. In regard to the data presented, if the only role of oxygen was catalyst surface cleaning, the trend in activity for both, 50:50 and 75:25 (SIm) should be the same, that is minimal difference under oxygen and nitrogen. The fact that extremely active 75:25 (SIm) catalyst under oxygen has lost significantly its catalytic activity under nitrogen suggest that the oxygen plays direct role in the process. It also suggests that nanoclusters with various metal ratio interact differently with oxygen. Nevertheless, the presented results prove that the synergistic effect and hence the electronic effect between Au and Pd is an extremely important factor to consider in alcohols oxidations.

4.2.5.3. Influence of scavengers on the catalysed reaction

The radical mechanism of autoxidation in the non-selective oxidation of cinnamyl alcohol has been confirmed by the addition of radical scavengers to the system in the absence of a catalyst. Two types of scavengers were tested: hydroquinone as a scavenger for oxygen centred radicals[25] and diphenylamine as a scavenger for carbon centred radicals[26]. The presence of scavengers only slightly decreased the conversion for the reaction carried out with the use of 0.50 %Au 0.50 %Pd/TiO_2 (SIm) (figure 3-22) whereas the drop for blank and for the 0.50 %Au 0.50%Pd/TiO_2 (Imp) catalyst was dramatic. In the case of 0.75 %Au 0.25 %Pd/TiO_2 (SIm) catalyst, the addition of diphenylamine did not affect significantly the conversion, however hydroquinone caused decrease in conversion in a small but visible degree (figure 4-24). Similar to the previous experiments, scavengers limited formation of benzaldehyde. From figure 4-25 it can be seen that product distributions for the reactions carried out with both type of scavengers were almost identical. The exception is the 4 hour point in the experiment utilising diphenylamine, where small amount of benzaldehyde has been formed. It means that diphenylamine was able to quench radicals up to 2 hours after which its effectiveness decreased. The drop in conversion due to the addition of hydroquinone might be caused by a slower removal of hydrogen from the catalyst surface as a result of possible interaction of scavenger with oxygen.

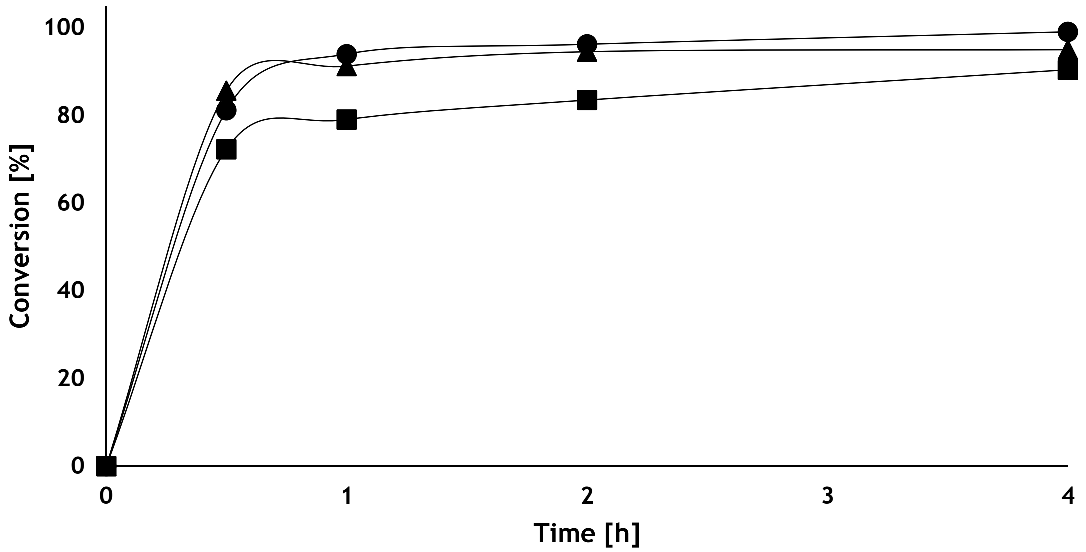

Figure 4-24 *Influence of the scavengers on the oxidation of cinnamyl alcohol using 0.75 wt%Au 0.25 wt%Pd/ TiO_2 (SIm). Reaction conditions: catalyst, 10 mg; oxygen pressure, 3 bar; temperature, 120 °C; 0.5 M cinnamyl alcohol in toluene; scavenger, 2 mg.* ***No scavengers addition (▲); diphenylamine (●); hydroquinone (■)***

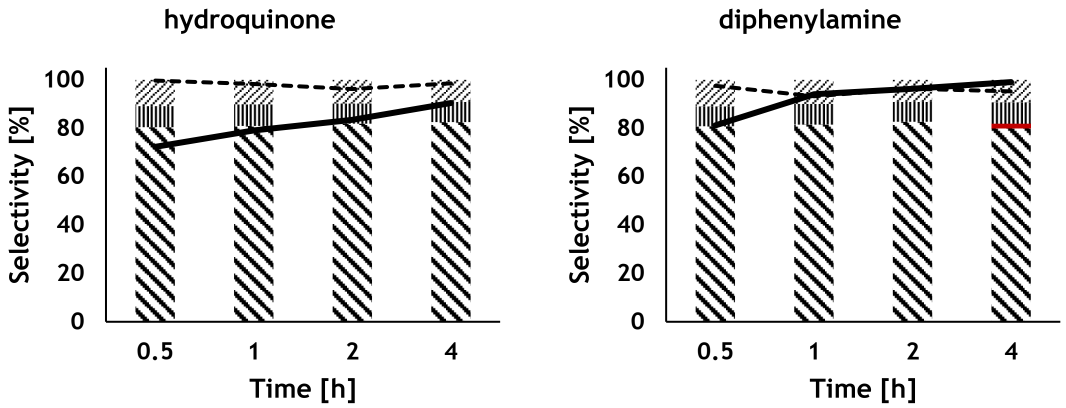

Figure 4-25** Influence of the scavengers on the selectivity profile in the oxidation of cinnamyl alcohol using 0.75 wt%Au 0.25 wt%Pd/ TiO_2 (SIm). Reaction conditions: catalyst, 10 mg; oxygen pressure, 3 bar; temperature, 120 °C; 0.5 M cinnamyl alcohol in toluene; scavenger, 2 mg.* ***Conversion (—); Cinnamaldehyde (▧); Benzaldehyde (▬); 3-Phenyl-1-propanol (▨); Methylstyrene (▥)

Addition of scavengers to the reaction carried out with the use of the 0.50 %Au 0.50%Pd/TiO_2 (Imp) catalyst (Figure 3-24) lowered conversion and significantly reduced formation of benzaldehyde, simultaneously increasing selectivity to cinnamaldehyde (80 %). Both scavengers, diphenylamine and hydroquinone gave reasonable similar results. In the case of 0.25 %Au 0.75 %Pd/TiO_2 (Imp) catalyst the trend is slightly different (figures 4-26 and 4-27). Scavengers completely stopped formation of benzaldehyde and selectivity to cinnamaldehyde was high (around 80 %). Diphenylamine did not affect massively the course of the reaction however hydroquinone has lowered greatly the conversion (figure 4-26), which presumably indicates stronger interaction of the latter scavenger with oxygen radicals.

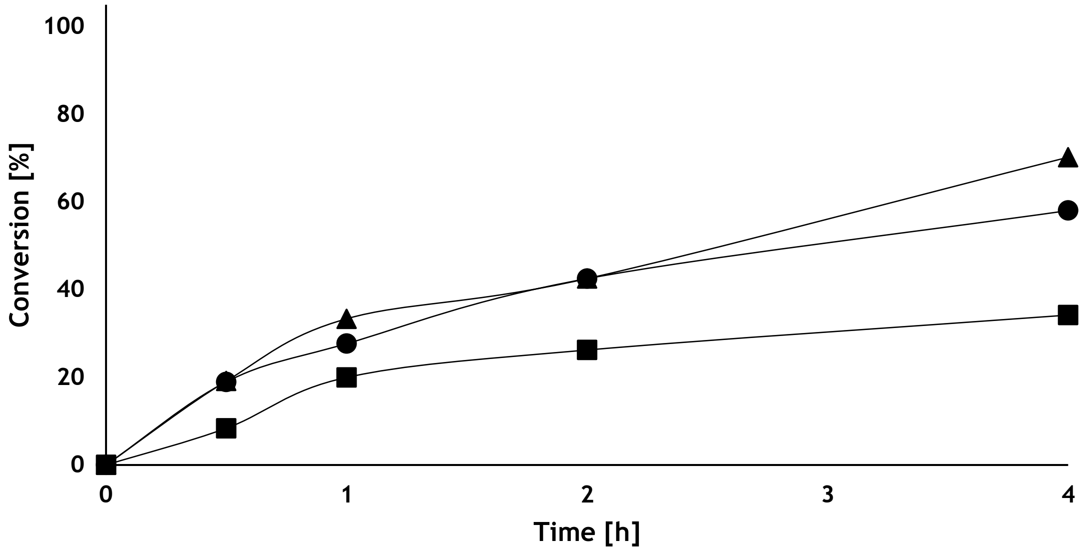

Figure 4-26 *Influence of the scavengers on the oxidation of cinnamyl alcohol using 0.25 %Au 0.75 %Pd/ TiO_2 (Imp). Reaction conditions: catalyst, 10 mg; oxygen pressure, 3 bar; temperature, 120 °C; 0.5 M cinnamyl alcohol in toluene; scavenger, 2 mg.* ***No scavengers addition (▲); diphenylamine (●); hydroquinone (■)***

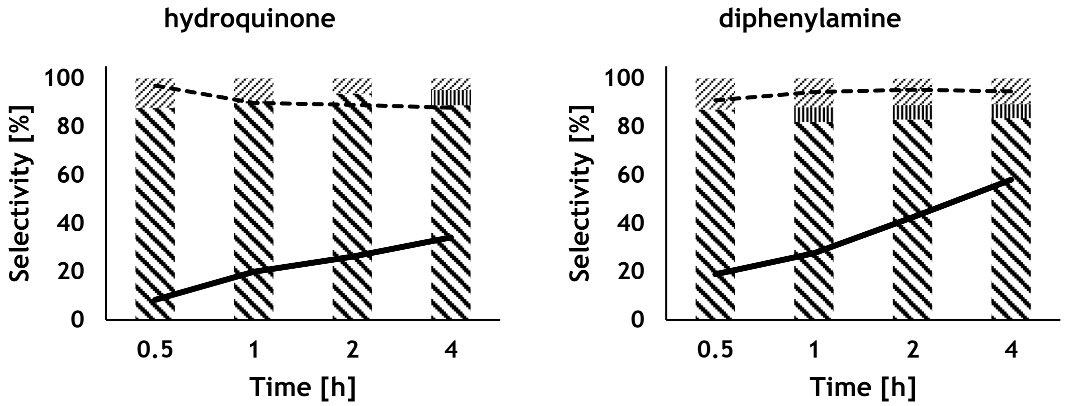

Figure 4-27 *Influence of the scavengers on the selectivity profile in the oxidation of cinnamyl alcohol using 0.25 wt%Au 0.75 wt%Pd/ TiO_2 (Imp). Reaction conditions: catalyst, 10 mg; oxygen pressure, 3 bar; temperature, 120 °C; 0.5 M cinnamyl alcohol in toluene; scavenger, 2 mg.* ***Conversion (——); Cinnamaldehyde (▧); 3-Phenyl-1-propanol (▨); Methylstyrene (▥)***

As in the case of 0.75 %Au 0.25 %Pd/TiO_2 (SIm) catalyst, the same questions arose about the role of oxygen. To be sure that the observed phenomenon concerns the oxygen-catalyst relationship only, the catalyst-scavenger possible interaction should be excluded. To investigate the influence of scavengers on the catalysts, the reactions have been carried out in the atmosphere of inert gas.

Figure 4-28 presents conversion of cinnamyl alcohol using 0.75 %Au 0.25 %Pd/TiO_2 (SIm) catalyst tested under nitrogen and contrasted with the same reactions carried out with the addition of scavengers. It can be seen, that scavengers decreased conversion of cinnamyl alcohol within first hour of the experiment after which the reactions proceeded in the same way as the control reaction (without scavengers). In terms of product distributions (figures 4-29 and 4-25), it is clear, that scavengers did not influence the selectivity profile in the atmosphere of nitrogen.

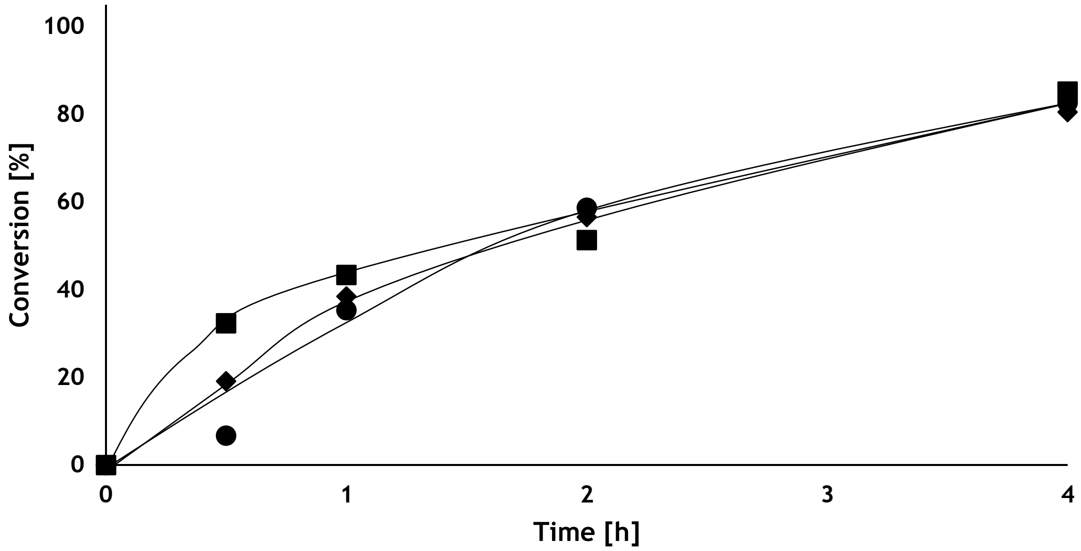

Figure 4-28 *Influence of the scavengers on the oxidation of cinnamyl alcohol using 0.75 %Au 0.25 %Pd/ TiO_2 (Slm). Reaction conditions: catalyst, 10 mg; nitrogen pressure, 3 bar; temperature, 120 °C; 0.5 M cinnamyl alcohol in toluene; scavenger, 2 mg.* ***No scavengers addition (■); diphenylamine (◆); hydroquinone (●)***

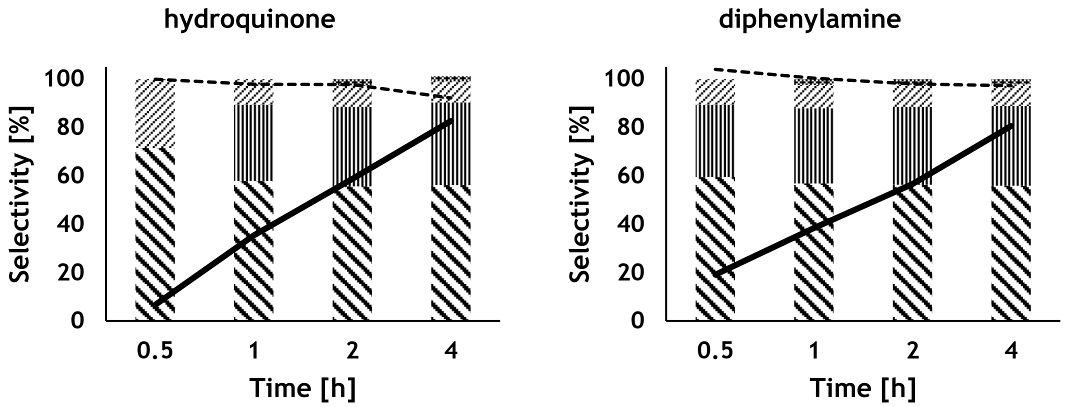

Figure 4-29 *Influence of the scavengers on the selectivity profile in the oxidation of cinnamyl alcohol using 0.75 wt%Au 0.25 wt%Pd/ TiO_2 (Slm). Reaction conditions: catalyst, 10 mg; nitrogen pressure, 3 bar; temperature, 120 °C; 0.5 M cinnamyl alcohol in toluene; scavenger, 2 mg.* ***Conversion (——); Cinnamaldehyde (▧); 3-Phenyl-1-propanol (▨); Methylstyrene (▥)***

Comparing the data shown in figure 4-30 where the 0.25 0.75%Au/TiO$_2$ (Imp) catalyst has been tested in the atmosphere of nitrogen and then the same reaction has been repeated with the addition of scavengers, one can see that there is no significant difference other than the experimental error (3 %) between sets of data. Also, selectivity profiles for the contrasted reactions are comparable within experimental error (figures 4-31 and 4-22).

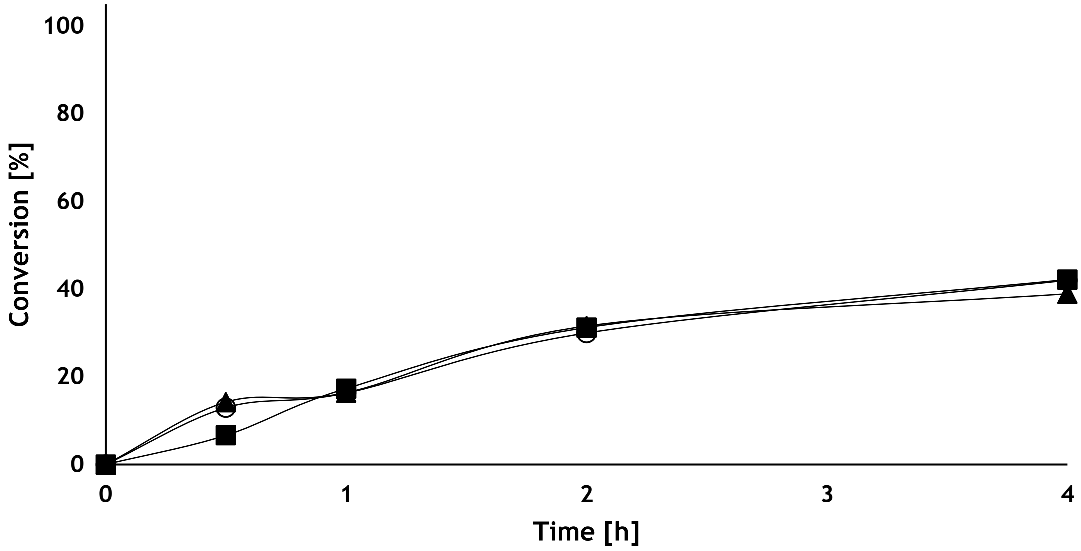

Figure 4-30** Influence of the scavengers on the oxidation of cinnamyl alcohol using 0.25 %Au 0.75 %Pd/ TiO$_2$ (Imp). Reaction conditions: catalyst, 10 mg; nitrogen pressure, 3 bar; temperature, 120 °C; 0.5 M cinnamyl alcohol in toluene; scavenger, 2 mg.* ***No scavengers addition (○); diphenylamine (▲); hydroquinone (■)

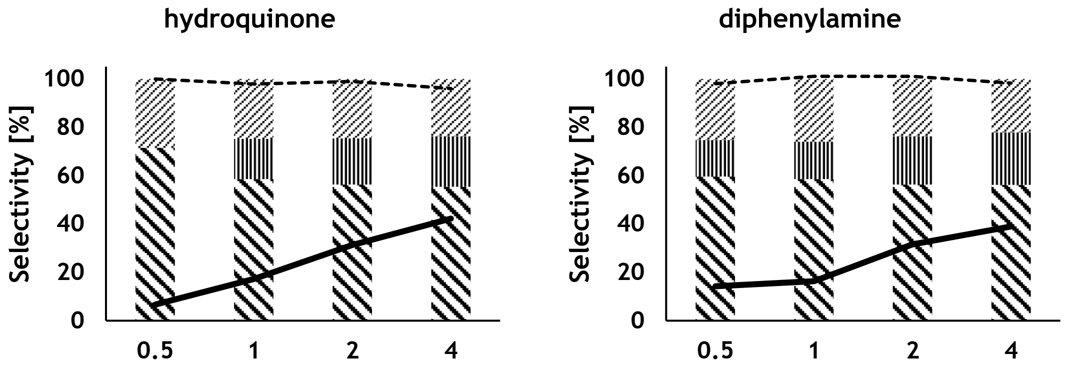

Figure 4-31** Influence of the scavengers on the selectivity profile in the oxidation of cinnamyl alcohol using 0.25 %Au 0.75 %Pd/ TiO$_2$ (Imp). Reaction conditions: catalyst, 10 mg; nitrogen pressure, 3 bar; temperature, 120 °C; 0.5 M cinnamyl alcohol in toluene; scavenger, 2 mg.* ***Conversion (▬); Cinnamaldehyde (▧); 3-Phenyl-1-propanol (▨); Methylstyrene (▥)

4.3. Conclusions

The catalyst synthesis method and metal ratio have an enormous impact on the size and morphology of nanoparticles, which in turn determines the catalyst's activity.

The sol-immobilisation method has been found to be more suitable to produce active and selective catalysts for the oxidation of cinnamyl alcohol than impregnation method under industrially relevant conditions. The highest conversion (nearly 96 % after 4 hours) and selectivity to cinnamaldehyde (80 %) was achieved using the 0.75 %Au 0.25 %Pd/ TiO_2 (SIm) catalyst. Generally SIm catalysts showed gradual mild deactivation within 3 cycles. Exceptionally low deactivation showed 0.75 %Au 0.25 %Pd/ TiO_2 (SIm): 94, 92 and 90 % after first, second and third use, respectively. SEM analysis revealed negligible particle growth within 3 cycles for this catalyst; the nanoparticles were in range 1-8 nm, with an average of 2-3 nm after first and second use, and 4-5 nm after third use. To highlight the extraordinary stability of 0.75 %Au 0.25 %Pd/ TiO_2 (SIm) catalyst, the SEM analysis has been shown and contrasted to re-used 0.50 %Au 0.50 %Pd/ TiO_2 (SIm), which revealed more prominent particle growth ranging from small particles 1-8 nm in fresh catalyst to slighlty larger clusters observed after second use (3-13 nm with the majority being 5-7 nm) and third use (mostly 7-8 nm clusters observed). The agglomeration observed for 50Au:50Pd metal ratio and minor particle growth in case of 75Au:25Pd can explain the deactivation of the range of 1 %AuPd/TiO_2 (SIm) catalysts with the exception of 75Au:25Pd ratio presenting outstanding stability and activity.

Study of various metal ratios in catalysts prepared by impregnation method proved that it is possible to increase the selectivity of even poor activity catalysts by simply optimising the metal ratio. Au-rich Imp catalysts showed low catalytic activity towards dehydrogenation to cinnamaldehyde and hence low selectivity due to co-existing autoxidation. Surprisingly, Pd-rich catalysts have been found to be much more selective towards formation of cinnamaldehyde and were able to significantly limit the autoxidation of the substrate. Unfortunately, one drawback of Pd-rich Imp catalysts is the relatively poor reusability with regards to both conversion and selectivity. Larger amounts of autoxidation products have been formed after every use, which implies intensification of the autoxidation process due to weakening of catalytic performance. Therefore, poisoning coupled with probable nanoparticle agglomeration might explain gradual loss of activity of the studied catalysts.

Experimental work presented in this thesis proved that optimisation of Au-Pd metal ratio is a crucial step towards improving the overall efficiency of oxidation in the liquid phase under autoxidation conditions. It is not quite clear what causes different behaviour of bimetallic alloys with different metal ratio. Significant difference in catalytic activity showed by tested catalysts (both, SIm and Imp) with various metal ratios may indicate the presence of geometric and electronic effects leading to different properties of each alloy. As suggested in the literature, a series of factors such as different extents of alloying, phase separation or presence of inhomogeneities might influence overall geometric and electronic effects.[6], [8], [11], [12] Observations of such small structures are very difficult and require specialized techniques and a lot of work and combined strengths from specialists in the field of chemistry, engineering, and physics. One of the most important challenges is the improvement of technologies to observe nanostructures without interfering. Recent achievements in the field of computational chemistry provide valuable guidance and information to come closer to achieving success in the design of excellent catalysts.

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Chapter 5

5. Evaluation of supported Au-Pd nanoparticles in the oxidation of different substrates: *trans*-stilbene and 3-pyridinemethanol.

5.1. Introduction

In the previous chapters, the oxidation of cinnamyl alcohol was studied under industrially relevant conditions where a high blank reaction is normally observed due to autoxidation. It was found that by using a bimetallic Au-Pd nanoalloys supported over titania, catalytic oxidation could dominate over the un-catalysed reaction. Furthermore, optimisation of the nanoparticle size and composition allowed higher activity and selectivity to the desired product, cinnamaldehyde, to be achieved. In this chapter the activity of a similar Au-Pd system has been tested in the oxidation of *trans*-stilbene and in the oxidation of 3-pyridinemethanol with molecular oxygen.

Catalytic oxidation is an extremely important process not only for the transformation of alcohols but also in many other processes such as the oxidation of alkenes.[1]–[3] Petroleum and biomass feedstocks can be converted into numerous types of chemicals and enriched with oxygen making them valuable intermediates and fine chemicals. Epoxides are especially useful intermediates on the industrial scale.[4]–[6] One model reaction used to study the epoxidation process is the oxidation of *trans*-stilbene. Various groups have studied the oxidation of *trans*-stilbene in many different ways.[7]–[10] The most common methods currently used in the industry are methods based on stoichiometric oxidants, analogous to the case of alcohol oxidation.[11] These methods are incredibly harmful for the environment, hence it is extremely important to develop green methods and to improve carbon efficiency.

3-Pyridinemethanol has been chosen as an example of an extremely stable molecule which does not easily undergo autoxidation. Moreover, the heterocyclic carbonyl derivatives are used in the pharmaceutical industry as precursors of important drugs e.g. antiviral and antitumor.[12] In general, the aerobic oxidation of pyridine-derivative alcohols using Pt-group metals is challenging which has been confirmed in this thesis.

5.2. Results and discussion

5.2.1. Epoxidation of *trans*-stilbene. Alcohol vs alkene.

The studies presented in Chapters 3 and 4 of this thesis concerned the oxidation of cinnamyl alcohol under autoxidation conditions. It has been shown that Au-Pd nanoparticles are able to significantly limit non-selective oxidation, thus directing selectivity to the desired product. As mentioned, cinnamyl alcohol is a representative of the allylic alcohol family, which means that the allylic C-H bonds are 15 % weaker in comparison to standard C-H bonds and thus reactions including dehydrogenation occur relatively easily. In this section, the oxidation of cinnamyl alcohol will be compared with the oxidation of an alkene with the example of *trans*-stilbene, which is more stable from a chemical point of view (figure 5-1).

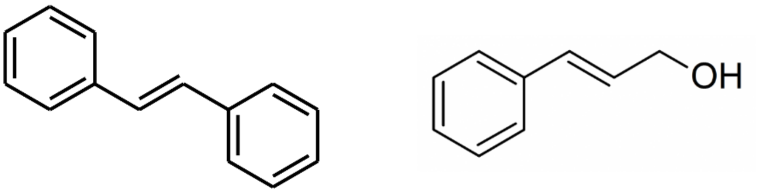

Figure 5-1 *Trans-stilbene and cinnamyl alcohol.*

The double bond C=C is surrounded on two sides by phenyl groups, which means that there are two possible isomeric forms, *cis*- and *trans*-, although the *cis*-form is sterically hindered and is possible to obtain from the *trans*- form photochemically. Nevertheless, the desired product of *trans*-stilbene oxidation, *trans*-stilbene oxide is obtained only in its *trans*- form, even if the substrate is *cis*-stilbene.[13], [14] *Cis*-stilbene oxide is definitely more difficult product to obtain, which is reflected in the relative price of each isomer: 1 g of *trans*- stilbene oxide costs less than £ 20 while 1 g of *cis*-stilbene oxide costs around £ 100.

Caps and co-workers carried out gold-catalysed aerobic oxidation of *trans*-stilbene in methylcyclohexane. The reaction has been performed under atmospheric pressure of air at 80 °C with the addition of a catalytic amount of TBHP and showed 65 % conversion after 24 hours with 45 % yield to *trans*-stilbene oxide.[15]

While testing the Au-Pd system for this reaction, my experimental work relied heavily on the work of this research group. A detailed literature review on this topic can be found in chapter 1 in section 1.4.3.

5.2.1.1. Influence of Au, Pd and Au-Pd supported nanoparticles on the oxidation of *trans*-stilbene

The main purpose of this short section on *trans*-stilbene epoxidation is to contrast the behaviour of Au-Pd catalysts with respect to the oxidation of cinnamyl alcohol. The most important point is the verification of the superiority of monometallic catalysts over bimetallic and the evaluation of selectivity. Therefore monometallic (1 %Au/TiO_2, 1 %Pd/TiO_2) and bimetallic (0.50 %Au 0.50 %Pd/TiO_2) catalysts prepared by impregnation and sol-immobilisation methods have been tested. Molecular oxygen has been used as a standard oxidant during my studies on the oxidation of cinnamyl alcohol hence further experiments have been carried out using oxygen instead of air. The most suitable solvents for the epoxidation of *trans*-stilbene have been determined in the literature cited before, hence only two solvents have been tested: cyclohexane and methylcyclohexane.[15] The reactions have been carried out at 80 °C under 3 bar oxygen pressure for 24 hours. The weight of the catalyst used was 50 mg, which is 5 times more than in the case of cinnamyl alcohol. The concentration of the reaction mixture was lower than for cinnamyl alcohol (0.5 mol/l) and was 0.05 mol/l 14 microliters of TBHP was added to every reactor loading for initiation of the reaction.

5.2.1.1a. Impregnation method

Monometallic and bimetallic Au-Pd nanoparticles supported over TiO_2 by impregnation method have been tested in cyclohexane and methylcyclohexane (figure 5-2). It can be seen, that the choice of solvent significantly influences the reaction profile. The reactions carried out in cyclohexane showed moderate conversions, however the carbon balance was closed. Large amounts of benzaldehyde (around 60 % selectivity) points to the conclusion that degradation (overoxidation of the substrate) is the dominant process. Selectivity to *trans*-stilbene oxide is relatively low (just below 20 %). Nevertheless, bimetallic 0.50 %Au 0.50 %Pd/TiO_2 (Imp) showed the highest conversion compared with its monometallic counterparts. The same reactions carried out in methylcyclohexane have a completely different course. Monometallic 1 %Au/TiO_2 (Imp) showed higher conversion in methylcyclohexane than in cyclohexane (40 % and 20 % respectively) and also selectivity was slightly higher in methylcyclohexane (around 25 %). Bimetallic 0.50 %Au 0.50 %Pd/TiO_2 (Imp) and monometallic 1 % Pd/TiO_2 (Imp) showed significantly higher conversion, however carbon balance has been found to be relatively low (70 % and 77 % respectively). Interestingly, in case of these two reactions, especially in case of the reaction utilising monometallic 1 %Pd/TiO_2 (Imp), formation of benzoic acid is significant. Clearly, bimetallic and monometallic Pd Imp catalysts are more active than monometallic Au imp catalyst which suggests that carbon might have been lost in favour of CO_2.

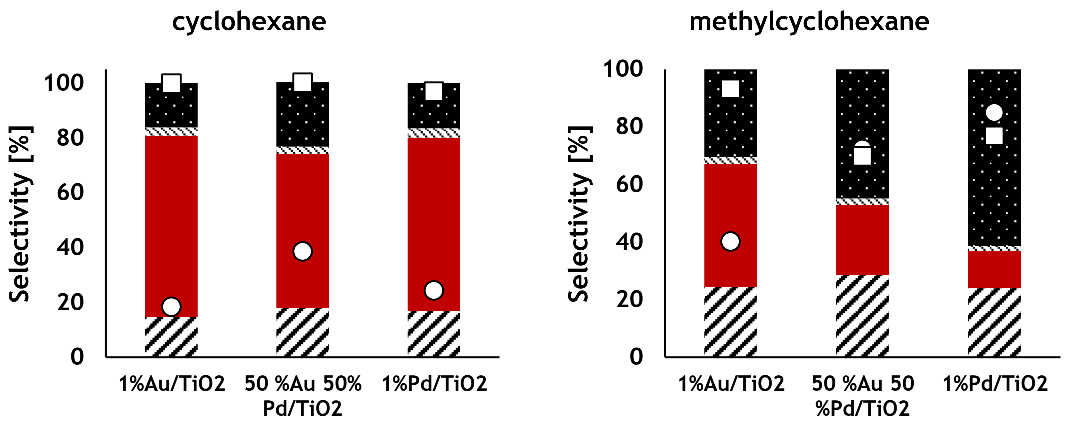

Figure 5-2 *Monometallic vs bimetallic imp catalysts in the oxidation of trans-stilbene in cyclohexane and methylcyclohexane. Reaction conditions: catalyst, 50 mg; oxygen pressure, 3 bar; temperature, 80 °C; 0.05 M trans-stilbene in methylcyclohexane or cyclohexane; time, 24 hours.* ***Conversion (○); Carbon balance (□); trans-Stilbene oxide (▨); Benzaldehyde (🟥); Benzoic acid (■); Benzil (▧)***

5.2.1.1b. Sol- immobilisation method

Analysing the data for cyclohexane shown in figure 5-2 and comparing them to the figure 5-3 it is clear, that the same catalysts prepared by sol-immobilisation method are more active. The highest conversion (60 %) and selectivity to *trans*-stilbene oxide (36 %) was obtained with the bimetallic 0.50 %Au 0.50 %Pd/ TiO_2 (SIm) catalyst. Based on the product distribution it might be reasonable to suppose that catalytic process and degradation processes take place simultaneously. The reactions carried out in methylcyclohexane using monometallic Au and Pd (SIm) catalysts showed similar conversion (just below 60 %), however Pd showed slightly higher selectivity to *trans*-stilbene oxide than Au (32 % and 26 %, respectively). Bimetallic 0.50 %Au 0.50 %Pd/TiO_2 (SIm) catalyst presented definitely the highest conversion (83 %), however carbon balance was incredibly low (65 %). Selectivity to *trans*-stilbene oxide was around 30 % and the amount of formed benzoic acid (55 % selectivity) at the expense of benzaldehyde (14 % selectivity) was large.

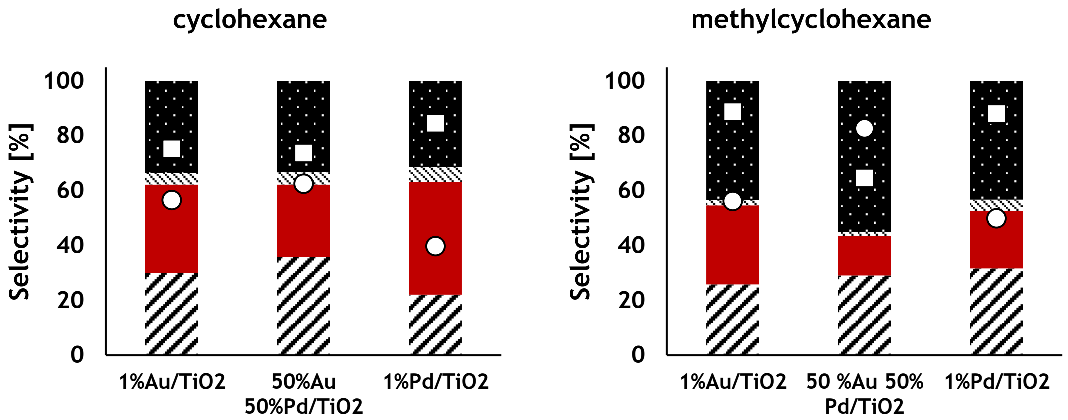

Figure 5-3 *Monometallic vs bimetallic (SIm) catalysts in the oxidation of trans-stilbene in cyclohexane and methylcyclohexane. Reaction conditions: catalyst, 50 mg; oxygen pressure, 3 bar; temperature, 80 °C; 0.05 M trans-stilbene in methylcyclohexane or cyclohexane; time, 24 hours.* ***Conversion (○); Carbon balance (□); trans-Stilbene oxide (▨); Benzaldehyde (🟥); Benzoic acid (■); Benzil (▨)***

One striking conclusion is that oxygen is not a suitable oxidant for the epoxidation of *trans*-stilbene due to excessive degradation of the substrate. The results presented in this section coupled with the literature findings make it clear that air is a better oxidant as it enables to achieve high selectivity to *trans*-stilbene oxide using Au-Pd supported nanoparticles.

Time on-line studies have been performed for *trans*-stilbene oxidation in cyclohexane using monometallic and bimetallic (SIm) catalysts (figure 5-4). In general, conversion increases with time for all tested catalysts. The reaction time found in the literature is even longer than 24 hours and can be up to 80 hours which suggests that prolonged reaction times leads to a correspondingly higher conversion.[15] The drop in carbon balance is observed mostly within the first 4 hours in all three experiments. Also, trends in selectivity profiles are similar. It can be noticed that selectivity to *trans*-stilbene oxide slightly increases with time. Selectivity to benzaldehyde decreased with time in favour of benzoic acid; benzaldehyde is transformed into benzoic acid. It is worth noting that benzaldehyde has been formed in large amounts within the first hours of the experiments, which is a similar trend to the oxidation of cinnamyl alcohol. Moreover, the size of Au-Pd nanoparticles influenced massively the process of cinnamyl alcohol oxidation. In the epoxidation of *trans*-stilbene under oxygen, the process of degradation is intense and the catalytic process does not take place selectively. External radical initiators coupled with pure oxygen as an oxidant are likely the reasons of dominant degradation/overoxidation over the catalytic process. Presumably, the reactions using the same catalysts carried out under low pressure of air would enable better catalytic performance which will be investigated in the next section.

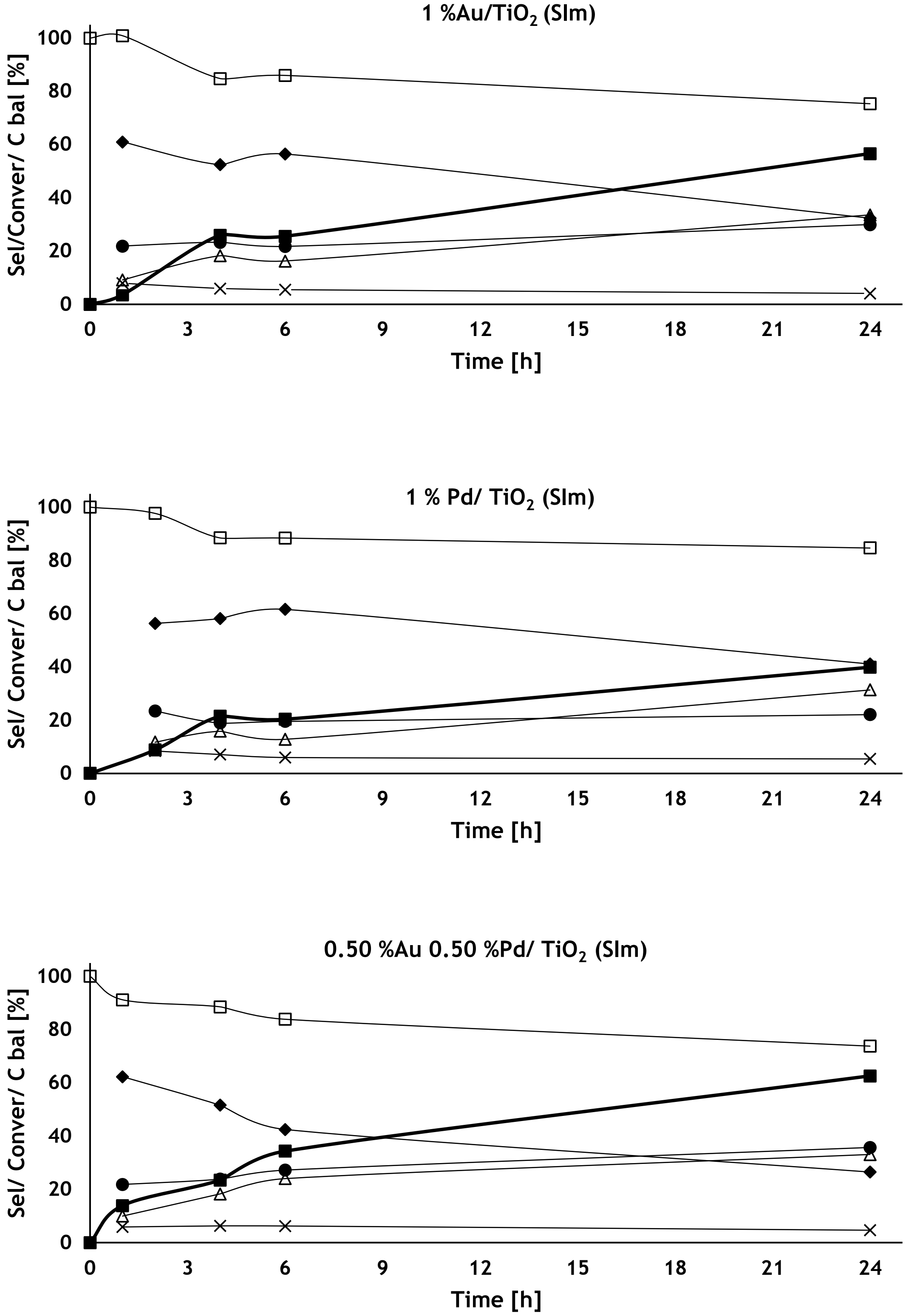

Figure 5-4 *Time on-line profile for the oxidation of trans-stilbene. Reaction conditions: catalyst, 50 mg; oxygen pressure, 3 bar; temperature, 80 °C; 0.05 M trans-stilbene in methylcyclohexane or cyclohexane.* ***Conversion (■); Carbon balance (□); trans-Stilbene oxide (●); Benzaldehyde (◆); Benzil (×); Benzoic acid (△)***

5.2.1.2. Optimisation of selected factors in the oxidation of *trans*-stilbene

The oxidation of *trans*-stilbene dissolved in methylcyclohexane carried out at 80 °C under 1 bar air in the absence of both catalyst and radical initiator showed no conversion. From the literature reports presented earlier, the addition of radical initiator is essential for the reaction to take place, which was reflected also in my experiment. It has been proved that the best possible radical initiator for the epoxidation of *trans*-stilbene is TBHP. Three different amounts of TBHP have been tested: 7, 14 and 100 microliters. The reactions have been performed in the absence (uncat) and in the presence of 0.50 %Au 0.50 Pd/ TiO_2 (SIm) catalyst. Keeping in mind that the oxidant pressure played an important role in the oxidation of cinnamyl alcohol, the same reactions of *trans*-stilbene epoxidation have been carried out also under higher air pressure (3 bar). These tests have surprisingly yielded much information (figure 5-5). In the presence of TBHP, the uncatalyzed reaction (uncat) demonstrated 20 % conversion under 1 bar air and around 40 % under 3 bar with around 35 % selectivity to *trans*-stilbene oxide in both cases. Similar to the reaction of cinnamyl alcohol oxidation, large amounts of benzaldehyde (43 % selectivity) and benzoic acid (20 % selectivity) have been found. To investigate the ongoing process, the reaction of *trans*-stilbene in methylcyclohexane has been carried out at 80 °C under 3 bar nitrogen. The conversion was lower than 1 % and only traces of *trans*-stilbene oxide have been detected, no presence of benzaldehyde or benzoic acid have been observed. These results suggest that in the epoxidation of *trans*-stilbene, even in the presence of radical initiator, oxygen is essential for the reaction to take place. The analysis of the selectivity profile for the catalysed reaction carried out under 1 bar air (figure 5-5) shows that the amount of added radical initiator is irrelevant as the results are roughly the same with the addition of 7, 14 or 100 microliters. The only difference that should be noticed is the lower carbon balance (80 %) for the reaction where excess of TBHP has been applied. It may be caused by total oxidation processes being intensified due to increased amount of radical initiator. The key observation is that the presence of the 0.50 %Au 0.50 %Pd/TiO_2 (SIm) catalyst significantly increased the conversion (60 %) and selectivity to the desired product (60 %) compared to the uncatalysed reaction, which is in excellent agreement with the results obtained in the oxidation of cinnamyl alcohol. Despite the differences in general mechanism of oxidation of *trans*-stilbene and cinnamyl alcohol, the way of catalyst behaviour showed the same pattern for these two processes. Moreover, the yield for the catalysed reaction carried out under 1 bar air is around 40 % which is in good agreement with the results obtained by Caps and co-workers (yield 45 %).[15]

Further analysis of the results obtained from the reactions performed under higher pressure of air (3 bar) revealed that even small increase in oxidant pressure massively influences the course of the process. It can be seen from figure 5-5 that increased pressure not only decreased selectivity to *trans*-stilbene oxide (around 40 %) but also significantly lowered carbon balance. As the conversion is significant (around 75 %), this indicates that the carbon has probably been lost due to the total combustion process which would be in line with the literature findings.[16]

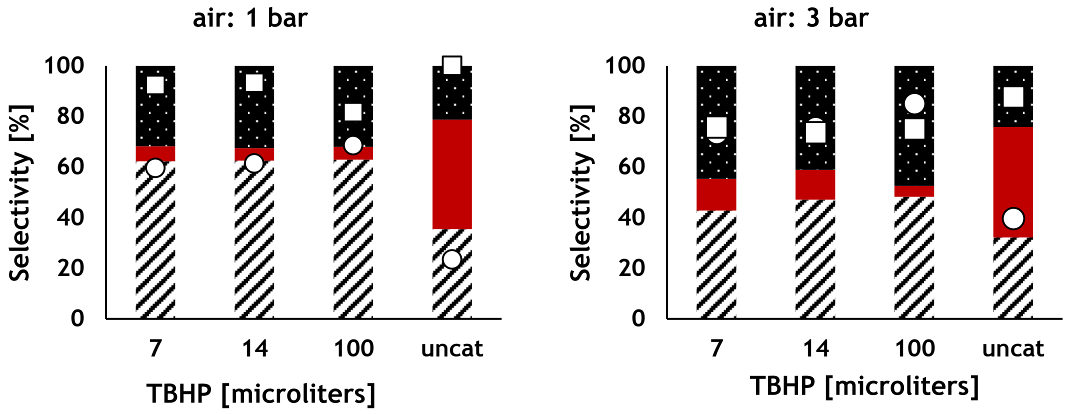

Figure 5-5 *The influence of the amount of radical initiator, 0.50 %Au 0.50 %Pd/ TiO_2 (SIm) catalyst and air pressure on the oxidation of trans-stilbene. Reaction conditions: catalyst, 50 mg; air pressure, 1 or 3 bar; temperature, 80 °C; 0.05 M trans-stilbene in methylcyclohexane; time, 24 hours.* ***Conversion (○); Carbon balance (□); trans-Stilbene oxide (▨); Benzaldehyde (🟥); Benzoic acid (■)***

Further optimisation of the reaction conditions and Au-Pd metal ratio could lead towards higher overall yield of the process.

5.2.2. Oxidation of 3-pyridinemethanol.

In this study, the product distribution for the oxidation of 3-pyridinemethanol was limited to aldehyde, 3-pyridinecarboxyaldehyde and the acid, niacin (figure 5-6). No other compounds have been observed during these experiments. The desired product in this process is the aldehyde, hence the optimisation has been conducted to achieve the maximum yield of 3-pyridinecarboxyaldehyde.

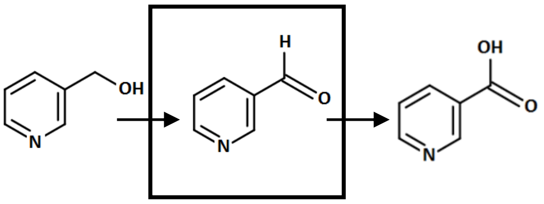

Figure 5-6 *Oxidation of 3-pyridine methanol to 3-pyridinecarboxyaldehyde and niacin.*

5.2.2.1. 3-Pyridinemethanol oxidation in water

5.2.2.1.1. Conditions establishing

The most desirable solvent in the design of the green chemical process is water. As both 3-pyridinemethanol and 3-pyridinecarboxyaldehde are soluble in water, this solvent was selected as first choice. Literature findings presented earlier suggested that the alkaline environment might be beneficial for the reaction therefore the effect of base and TBHP on the oxidation of 3-pyridinemethanol have been tested. From figure 5-7, it can be observed that the addition of TBHP does not play a role in the process. KOH slightly improved activity, however the aqueous alkaline environment promoted higher selectivity to niacin at the expense of 3-pyridinecarboxyaldehyde. Furthermore, the use of KOH with higher concentration (0.5 mol/l instead of 0.05 mol/l) during the reaction carried out in the absence of the catalyst (blank reaction) resulted in 63 % of conversion with selectivity profile of 5 % aldehyde and 95 % niacin (results not shown). The conclusion is that the reaction should be carried out in the absence both radical initiator and base as the aldehyde is the target molecule.

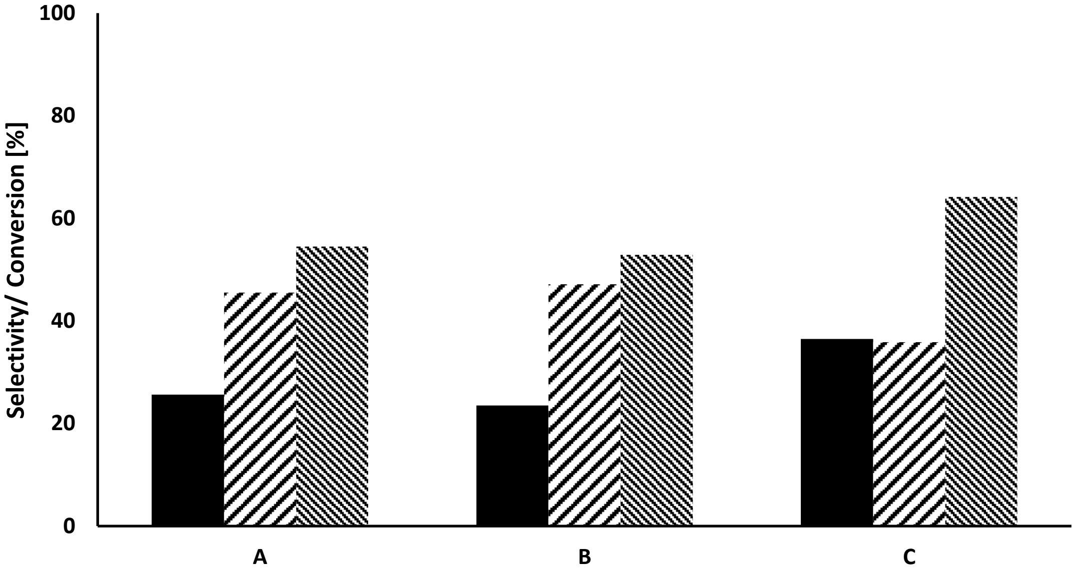

Figure 5-7 *Influence of KOH and TBHP on the oxidation of 3-pyridinemethanol using 0.5 %Au 0.5%Pd/ TiO_2 SIm: A) absence of TBHP and KOH B) presence of TBHP only C) presence of TBHP and 0.05 M KOH. Reaction conditions: 0.5%Au 0.5%Pd/TiO_2 (SIm), 60 mg; oxygen pressure, 3 bar; temperature, 120 °C; 0.5 M 3-pyridinemethanol in water; time, 24 h; TBHP, 14 µl.* ***Conversion, ■; 3-Pyrididnecarboxyaldehyde, ▨ ; Niacin, ▧***

The above data are in line with findings reported by Besson *et al.*[17] who tested 1.95 wt% Pt/C for the oxidation of benzyl alcohol, 2-pyridinemethanol and 4-pyridinemethanol under 10 bar of air at 100 °C. It was suggested that by tuning the solvent of the reaction, different product distributions can be obtained. The group synthetized aldehydes by applying dioxane and other organic solvents. Carboxylic acids have been formed in water or dioxane/water solvent mixtures with the addition of sodium hydroxide. The researchers observed relatively easy formation of corresponding acids in water, however, the catalytic activity towards formation of aldehydes in organic solvents was low (did not exceed 30 %). The proposed mechanism followed the rules of classical dehydrogenation mechanism where dehydrogenation of the adsorbed alcohol takes place on the catalyst surface followed by the reaction of formed metal hydride with the adsorbed oxygen. If water is present in the system, the aldehyde can easily form a hydrate which leads to the carboxylic acid. If there is a limited amount of water in the system, usually the aldehyde is yielded as the hydration and further dehydrogenation of an aromatic aldehyde is low due to conjugation of the carbonyl group. In general, organic solvents seem to prevent formation of the geminal diol and subsequent dehydrogenation to the acid. Also, high temperature might play a role in preferential formation of aldehyde in organics by the rapid removal of co-product water.

5.2.2.1.2. Base free, green reaction. Monometallic and bimetallic catalysts.

The exclusion of base and the lack of any additives such as radical initiators raised the possibility of developing a safer and greener process for the production of aldehydes. Moreover, the use of AuPd bimetallic catalysts could provide a highly efficient process. Although it is widely known that bimetallic Au-Pd catalysts are usually more active than their monometallic counterparts for oxidation reactions, mono- and bimetallic systems of Au, Pd and additionally Pt were tested to confirm this for the oxidation of 3-pyridinemethanol. It can be seen from table 5-1 that monometallic SIm catalysts are practically inactive for the studied reaction. Bimetallic Au-Pd and Au-Pt showed moderate conversion, 26 and 15 % respectively. The amounts of aldehyde and acid formed were roughly similar for both systems with selectivities of around 50 % to aldehyde and acid. The question arose whether acid is formed due to the catalytic pathway or rather as non-selective over oxidation of the aldehyde. To determine the mechanism, a blank reaction of 3-pyridinecarboxyaldehyde oxidation was performed under standard conditions. HPLC analysis showed only trace amounts of acid hence it is clear that the presence of the catalyst is necessary to further oxidise 3-pyridinecarboxyaldehyde to niacin.

***Table 5-1** Oxidation of 3-pyridinemethanol using monometallic and bimetallic catalysts.*

Catalyst [SIm]	Conversion [%]	C bal [%]	Selectivity [%]	
			Aldehyde	Acid
1 %Pt/TiO$_2$	1	102	*88**	*12**
1 %Au/TiO$_2$	4	100	*78**	*22**
1 %Pd/TiO$_2$	2	105	*68**	*32**
0.5 %Au 0.5 %Pt/TiO$_2$	15	101	49	51
0.5 %Au 0.5 %Pd/TiO$_2$	26	107	41	59

Reaction conditions: Sim catalysts, 60 mg; oxygen pressure, 3 bar; temperature, 120 °C; 0.5 M 3-pyridinemethanol in water; time, 24 h.

**The results are not fully reliable due to low conversion being within experimental error.*

The results discussed in the previous chapters on the oxidation of cinnamyl alcohol proved that optimisation of the catalyst metal ratio is one of the key factors towards achieving maximum yield of the desired product. Therefore, three batches of Sim prepared 1 wt% catalysts with the following Au:Pd metal ratios have been tested: 0.25:0.75 /TiO$_2$, 0.5:0.5/TiO$_2$, and 0.75:0.25/TiO$_2$ (figure 5-8). The results revealed significant fluctuations between 3 batches of the same catalyst in every case, especially with regard to selectivity. Therefore, all catalysts have been retested with the obtained results again varying significantly (figure 5-9).

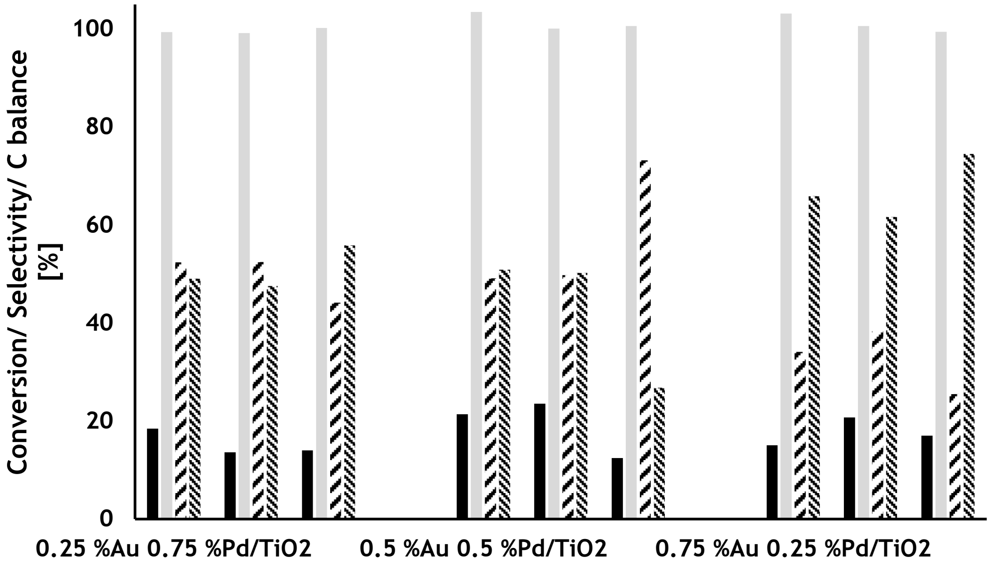

Figure 5-8 *Reproducibility of SIm catalysts. Reaction conditions: SIm catalysts, 60 mg; oxygen pressure, 3 bar; temperature, 120 °C; 0.5 M 3-pyridinemethanol in water; time, 24 h.* ***Conversion,■ ; Carbon balance, □; 3-Pyrididnecarboxyaldehyde, ▨ ; Niacin,▧***

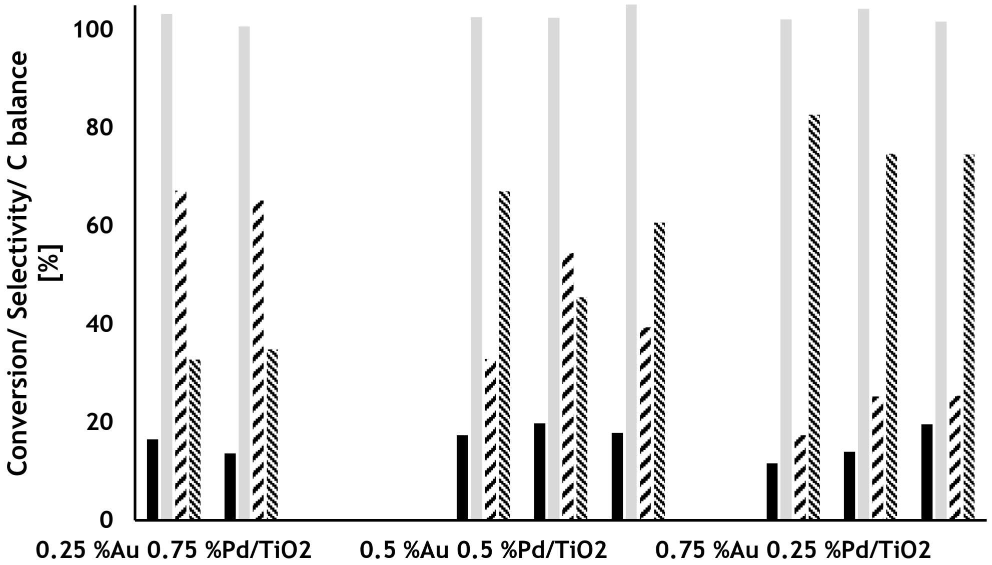

Figure 5-9 *Repeated reproducibility of SIm catalysts. Reaction conditions: SIm catalysts, 60 mg; oxygen pressure, 3 bar; temperature, 120 °C; 0.5 M 3-pyridinemethanol in water; time, 24 h.* ***Conversion,■ ; Carbon balance, □; 3-Pyrididnecarboxyaldehyde, ▨ ; Niacin,▧***

The above phenomenon was explored further by analysis of the post-reaction mixture for leaching using MP-AES (table 5-2). Surprisingly Au was found to be extremely stable, contrary to Pd which leached more than 80 %. A popular method to reduce leaching is thermal treatment of the catalyst.[18] Such attempts were made in this case with 0.5 %Au 0.5 %Pd/ TiO_2 SIm catalyst being calcined at 200 °C for 2 hours in static air. The leaching in this case was lowered by only 5 % under identical reaction conditions; calcination did not greatly influence the conversion which was 12 %. Due to the possibility that the temperature was too low, another catalyst 0.75 %Au 0.25%Pd/ TiO_2 SIm was calcined at 600 °C for 2 hours in static air. In this case leaching was lowered from 92 % to 61 %, however this is still unsatisfactory. The conversion was 13 % which is comparable with the results obtained for standard reactions. In the case of 1 %Pd/ TiO_2 Sim, the leaching observed was 100 %. Despite this, there was no conversion detected hence it is clear that there is no homogeneous catalysis contribution from Pd.

Table 5-2 *Determination of Pd leaching for SIm catalysts.*

Catalyst	Treatment	Leaching [%]
		Pd
0.25 %Au 0.75%Pd/ TiO_2	-	82
0.50 %Au 0.50%Pd/ TiO_2	-	90
	calcination: 200 °C	85
0.75 %Au 0.25%Pd/ TiO_2	-	92
0.75 %Au 0.25%Pd/ TiO_2	calcination: 600 °C	61
1 %Pd/ TiO_2	-	100

Further attempts at forming a stable catalyst were conducted by variation of the catalyst preparation methods described in experimental sections 2.4.2 and 2.4.3 in chapter 2. 0.5 %Au 0.5 %Pd/ TiO_2 catalysts were prepared by the standard impregnation (imp) and modified impregnation (mod imp) and were tested under standard conditions (table 5-3). The imp catalyst was found to be inactive and the mod imp catalyst gave 15 % conversion. In case of both catalysts, heavy Pd leaching of 67 % was observed; Au was stable. SEM analysis of the imp catalyst (figure 5-10 A) revealed presence of large nanoclusters (*ca.* 100 nm) which could explain its inactivity. Interestingly, nanoparticles obtained by modified impregnation method (figure 5-10 B) are quite well dispersed (1-6 nm) however showed lower activity (15 %) compared to the catalyst prepared by sol-immobilisation method (26 % average). If the leaching was minimal it would suggest that not only size but also morphology influences the catalyst activity, however it cannot be definitely stated, as the systems are not stable enough.

Table 5-3 *Au-Pd nanoparticles supported on TiO_2 using different methods.*

Method	Conversion [%]	C bal [%]	ALD [%]	Acid [%]	Pd leaching [%]
Standard impregnation		Inactive			67
Modified impregnation	15	107	27	73	67

Reaction conditions: 0.5 %Au 0.5 %Pd/ TiO_2 SIm, 60 mg; oxygen pressure, 3 bar; temperature, 120°C; 0.5 M 3-pyridinemethanol in water; time, 24 h.

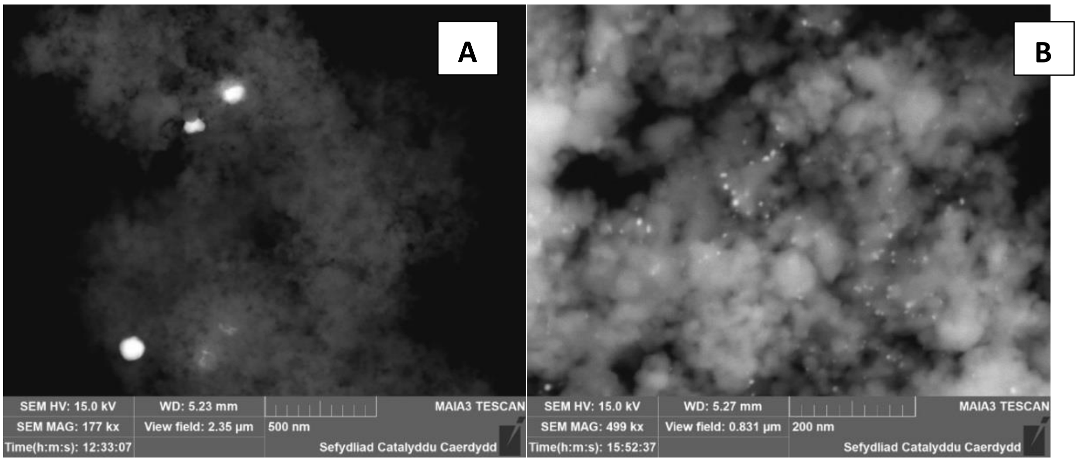

Figure 5-10 *BSD-SEM images:* ***A)*** *0.5 %Au 0.5 %Pd/ TiO_2 prepared by standard impregnation method;* ***B)*** *0.5 %Au 0.5 %Pd/ TiO_2 prepared by modified impregnation method*

5.2.2.2. 3-Pyridinemethanol oxidation in toluene.

5.2.2.2.1. Conditions establishing

In the previous section, the Au-Pd system was found to be unstable in water under the reaction conditions. Thermal treatment of the catalysts and variation of preparation method did not prevent heavy Pd leaching, with only slight improvements observed. Therefore, to optimise the effectiveness of Au-Pd supported nanoparticles in the oxidation of 3-pyridinemethanol and to minimise leaching, the solvent was switched from water to toluene. Toluene is generally regarded as one of the safer organic solvents (is still problematic due to its flammability but is not excessively hazardous)[19] and can be recovered after the reaction and reused. Therefore, it can be stated that the process remained relatively green even though the solvent was not water. Similar initial experiments were conducted in which, as in case of water as a solvent, the addition of base and/or TBHP was not beneficial to this process. The major advantage of performing the reaction in toluene is the ability to obtain 100 % selectivity to the desired product, 3-pyridinecarboxyaldehyde.

5.2.2.2.2. Support comparison study

Support studies for the oxidation of 3-pyridinemethanol were carried out in a similar way as that for the previously investigated oxidation of cinnamyl alcohol (chapter 3). Several supports with different surface areas have been tested using the Au-Pd system with 50:50 metal ratio deposited by the sol-immobilisation method. The supports studied were carbon (Vulcan XC-72R, Cabot), meso-alumina, meso-silica (SBA-

15), alumina grafted SBA-15 and titanium dioxide. The reactions were conducted at 140 °C for 24 hours under oxygen (3 bar).

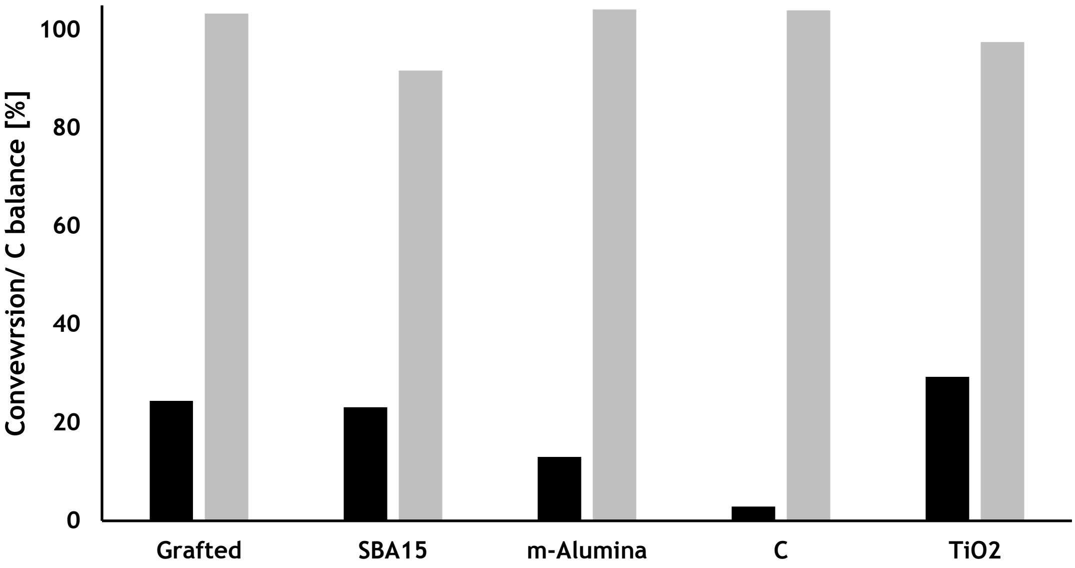

Figure 5-11 *Influence of support on the oxidation 3-pyridinemethanol using Au-Pd (50:50 wt.) system. Reaction conditions: 5 ml 0.5 M 3-pyridinemethanol in toluene; catalyst mass, 60 mg; oxygen pressure 3 bar; reaction time 24 h; temperature, 140 °C.* ***Conversion,*** ■ ; ***Carbon balance,*** ■

It can be seen from figure 5-11 that the lowest conversion was achieved when carbon was employed as a support. Other supports have allowed for reasonable catalytic activity. However, in case of SBA-15 the carbon balance was low (92 %) compared to the other systems tested (*ca.* 97-104 %). There are two possible explanations of this fact. The first one is an experimental error as the reactions have been carried out only twice and the presented result is an average for each reaction. The experimental error has been calculated for the oxidation of 3-pyridinemethanol in toluene as a standard deviation and was 5 %. The other reason might be related to the structure of SBA-15 and its high surface area (700 m^2/g compared to 238 m^2/g for carbon, 35-65 m^2/g for TiO_2 and 224 m^2/g for alumina grafted SBA-15) as the substrate might have interacted with the support and therefore be adsorbed.

A particularly noticeable difference in activity was observed between carbon and titania. The conversion for titania was the highest within the tested range of supports (29 %) while for carbon the activity is barely detectable (3 %). This particular type of carbon (Vulcan XC-72R) contains a mainly mesoporous structure but also contains around 30 % micropores. For this reason, it is not recommended for electrocatalysts due to sinking of nanoparticles into micropores which hinders accessibility of reactants.[20] Poor accessibility seemed not to be a case in the oxidation of cinnamyl alcohol therefore it should not be the case in the oxidation of 3-pyridinemethanol either as the sizes of these molecules are fairly comparable (Van der Waals radius of nitrogen is 155 pm and C-C bond in benzene ring are around 140 pm hence nitrogen should not be a steric hindrance).

The cause of the different behaviour of Au-Pd supported over titania and carbon might be a different metal-support interaction and morphology of the nanoparticle. It is well known that Au-Pd nanoparticles form ideal spheres on carbon while the same Au-Pd nanoparticles on titania form rather elongated shapes.[21] Detailed studies conducted by Xu *et al.*[22] confirmed that freshly prepared Au-Pd clusters were spherical, however immediately after immobilisation on TiO_2 their shape became elongated which indicates a strong metal-support interaction. This proves that the support plays an enormous role in nanoparticle behaviour during chemical processes. The resulting conclusion is that the support might influence the electronic properties of the Au-Pd clusters which points to the possibility of different active sites presence. The discussion about presumably different active site will be presented in further part of this chapter.

In conclusion, TiO_2 has been chosen as a suitable support for further studies as due to the fairly high conversion achieved. This allows reliable comparison of catalysts for the oxidation of 3-pyridinemethanol and furthermore allows for comparisons to be made to the use of this system with the previously studied cinnamyl alcohol oxidation.

5.2.2.2.3. Influence of temperature on the reaction

Temperature studies for 3-pyridinemethanol in toluene were performed using 0.50 %Au 0.50 %Pd/TiO_2 SIm catalyst in the standard set up. A Radleys starfish reactor was pressurised with oxygen (3 bar) and the reaction time was 24 h. For safety reasons associated with reactor design and operating with the use of organic solvent, the tested temperature range was limited to a maximum of 140 °C. The results have been presented in figure 5-12 from which it can be seen the general trend of increasing conversion with increasing temperature.

Taking into consideration safety reasons and the results of the temperature studies, it seems reasonable to be conducting a reaction at the level of 30 % conversion, i.e. at a temperature of 140 °C. The reaction carried out in the absence of a catalyst at 140 °C under oxygen (3 bar) gave no conversion; the substrate was stable for 24 hours.

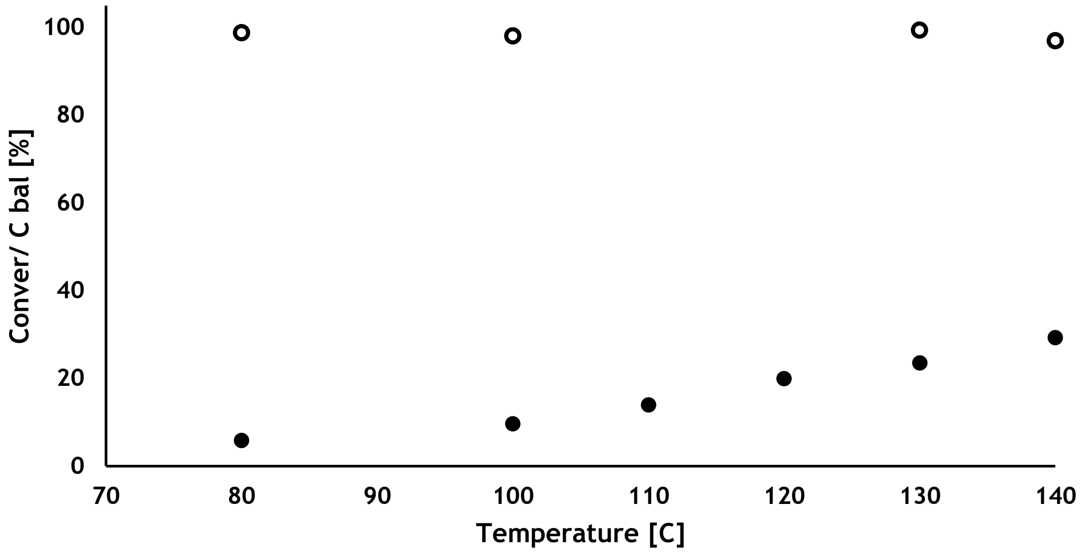

Figure 5-12 *Influence of temperature on the oxidation of 3-pyridinemethanol. Conditions: 5 ml 0.5 M 3-pyridinemethanol in toluene; 0.50 %Au 0.50 %Pd/TiO$_2$ SIm catalyst mass, 60 mg; oxygen pressure 3 bar; reaction time 24 h.* ***Conversion***, ● ; ***Carbon balance***, *O*

5.2.2.2.4. Catalyst mass studies

The results of the influence of the catalyst amount on the oxidation of 3-pyridinemethanol have been presented in figure 5-13. It is clear, that an increase in catalyst mass increases the overall conversion. In general, the trend line suggest linear increase. Discrepancies from linear trend appeared when 80 mg of catalyst was tested which was indicated by slightly lowered carbon balance (93 %). However, taking into consideration the experimental error being around 5 %, it can be assumed that only minor diffusion limitation occurred. The carbon balance for the tested catalyst in amount of 100 mg was significantly low (76 %). Here, the reaction has presumably become mass transport limited and therefore is not operating in the kinetic regime. To ensure a lack of mass transport limitations, relatively high conversion and high carbon balance, the amount of 60 mg of catalyst has been chosen for further studies.

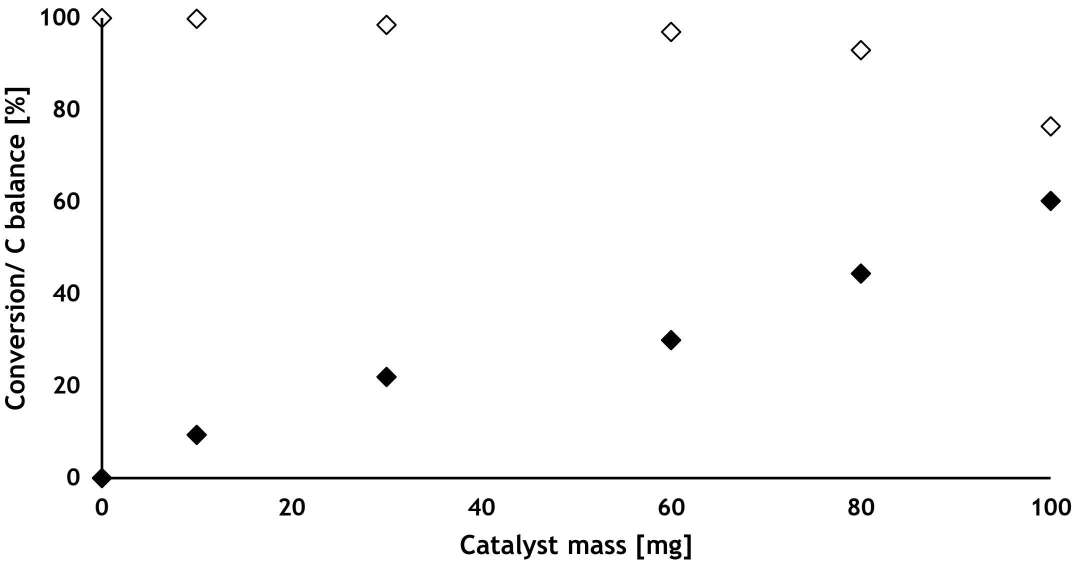

Figure 5-13 *Mass study using 0.50 %Au 0.50 %Pd/ TiO_2 SIm. Reaction conditions: oxygen pressure, 3 bar; temperature, 140°C; 0.5 M 3-pyridinemethanol in toluene; time, 24 h.* ***Conversion, ◆; Carbon balance ◇.***

The investigation of the effect of substrate to metal ratio has been carried out using 0.50 %Au 0.50 %Pd/TiO_2 (SIm) catalyst. As is presented in figures 5-13 and 5-14, the conversion increases with decreasing s:m (an equivalent to the increase in the amount of catalyst). The relationship is not a linear dependence that can be caused by not closed carbon balance due to diffusion limitations (presented in figure 5-13).

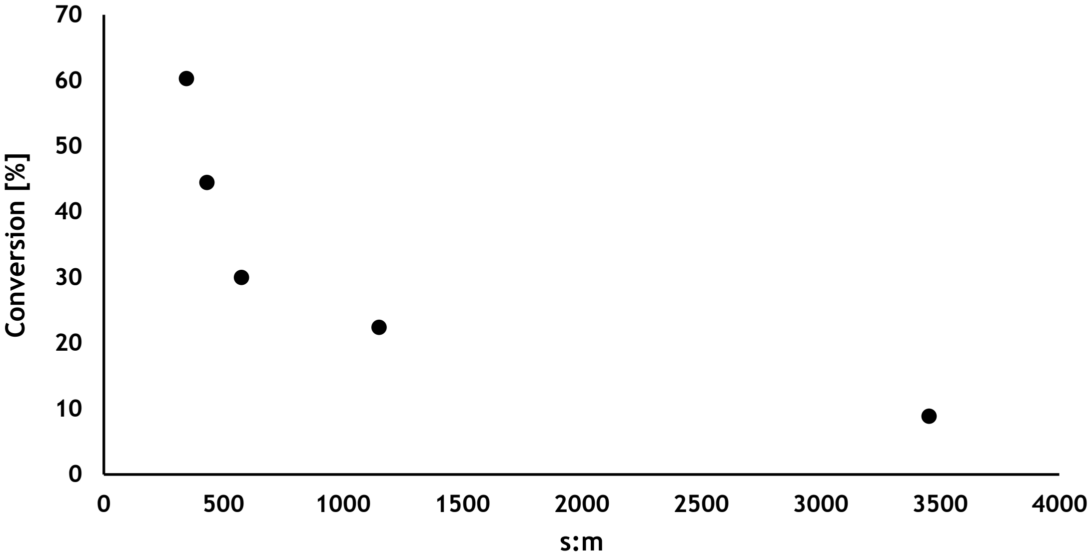

Figure 5-14 *The effect of substrate metal ratio on the conversion of 3-pyridinemethanol. Reaction conditions Reaction conditions: oxygen pressure, 3 bar; temperature, 140°C; 0.5 M 3-pyridinemethanol in toluene; time, 24 h.*

5.2.2.2.5. Time on-line

Using the optimised conditions, a time on-line study was conducted for the oxidation of 3-pyridinemethanol. The results are presented in figure 5-15 below:

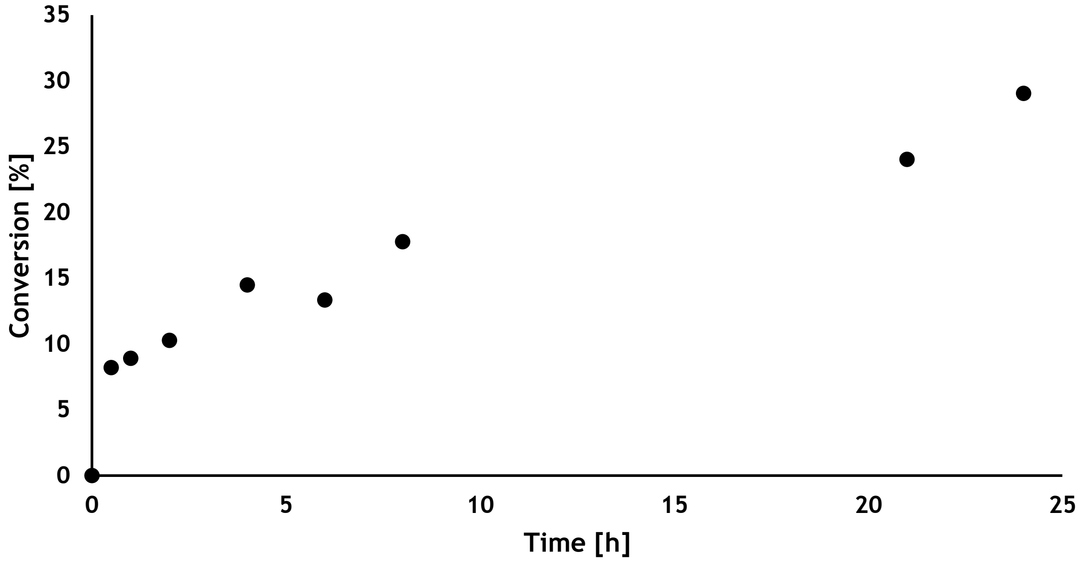

Figure 5-15 *Time-online in the oxidation of 3-pyridinemethanol. Reaction conditions: oxygen pressure, 3 bar; temperature, 140°C; 0.5 M 3-pyridinemethanol in toluene; time, 24 h; 60 mg catalyst 0.50 %Au 0.50 %Pd/*TiO_2 *SIm.*

Interestingly, one can observe relatively high conversion (8 %) within the first 30 minutes of the reaction. After this time the reaction progresses, however the increase in conversion is slow. To verify whether longer reaction time would allow for higher conversion, the process was conducted for 96 hours, and samples have been withdrawn every 24 hours. The results of further tests carried out over longer time periods revealed that no great increase in conversion occurred.

5.2.2.2.6. Influence of metal ratio on the oxidation of 3-pyridinemethanol.

According to the results obtained in earlier studies, the metal ratio comparison was performed (figure 5-16). It is clear from figure 5-16 that monometallic catalysts are active, however they are less active than the bimetallic analogues which indicates a synergistic effect. A physical mixture of monometallic catalysts (30 mg 1 %Au/TiO_2+ 30 mg 1 %Pd/TiO_2) showed 19 % conversion which is comparable with monometallic 1 %Pd/TiO_2 (16%) and 1 %Au/TiO_2 (13 %). The most active catalyst, 0.60 %Au 0.40 %Pd/ TiO_2 SIm resulted in 42 % conversion. The other tested bimetallic catalysts, 0.85 %Au 0.15 %Pd/ TiO_2, 0.75 %Au 0.25 %Pd/ TiO_2 and 0.50 %Au 0.50 %Pd/TiO_2 SIm showed similar conversions around 30 %. Pd-rich 0.25 %Au 0.75 %Pd/ TiO_2 SIm has been found less active than Au-rich bimetallic catalysts. Although differences in activity of bimetallic catalysts have occurred, they are not as significant as in the case of oxidation of cinnamyl alcohol. Also, a different metal ratio has been found to be optimal for the oxidation of 3-pyridinemethanol (60 Au:40 Pd) compared to the oxidation of cinnamyl alcohol (75 Au:25 Pd).

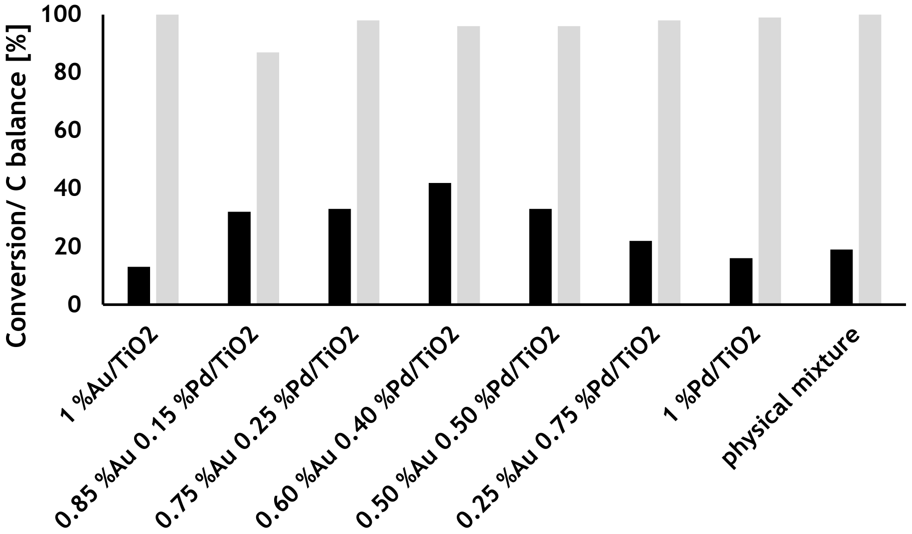

Figure 5-16 *Metal ratio study of SIm catalysts. Reaction conditions: SIm catalysts, 60 mg; oxygen pressure, 3 bar; temperature, 140 °C; 0.5 M 3-pyridinemethanol in toluene; time, 24 h. Conversion, ■; carbon balance, ▨.*

The possible reason of rather consistent conversion for all bimetallic catalysts might presumably be poisoning, which limits the catalytic activity of different alloys to a similar value. Nevertheless, bimetallic Au-Pd catalysts showed higher activity than their monometallic counterparts even in such a challenging process as oxidation of 3-pyridinemethanol.

The possibility of catalyst poisoning by the product, 3-pyridinecarboxyaldehyde, causing catalyst deactivation has been subjected for further investigation. To verify this hypothesis, 30 % (0.054 g/ 5ml) aldehyde has been added to the starting reaction solution and the reaction has been performed in standard conditions (oxygen pressure 3 bar; reaction time 24 h; temperature, 140 °C) using 60 mg 0.75 %Au 0.25 %Pd/TiO_2 SIm catalyst. The results of this experiment showed that the addition of the product had no influence on the reaction as the conversion was 29 % which is the same as for the standard reaction at 140 °C. Indeed, the poisonous effect of the product on the catalyst seemed to be excluded, however it cannot be completely ruled out. Hypothetically, small amounts of Pd present in the experimental set up could interact with small amount of product or even substrate (especially at 140 °C) which resulted in its poisoning hence further addition of larger amount of product would not make any difference.

The problem of Pt-group metals being poisoned by N-containing compounds is widely known, however the nature of the N- Pd interactions and the exact deactivation pathways in heterogeneous catalysts have not been clearly determined. Arrigo *et al.*[23] investigated the nature of the N-Pd interaction in nitrogen-doped carbon nanotube catalysts by a combined theoretical and experimental study. Their work was inspired by the fact that Pd has high affinity to form σ or π bonds with carbon and also with N-containing ligands enabling formation of organometallic complexes (with a variety of Pd(0) and Pd (II) species). In their carbon nanotubes, N species have been found in pyridine-like configuration with high thermal stability. The researchers used these N-doped carbon nanotubes as a support for Pd catalysts prepared by impregnation method. The result of their work stated that the interaction of pyridine N with Pd can be described as a covalent chemical bond with partial ionic character. Despite the fact that the quoted work was aimed at presenting the modification of carbon as an option for tuning selectivity by site-blocking strategies, it also shows the versatility and strength of the N-Pd interaction/ bond.

Prati and co-workers[24] investigated the role of N-heteroatom location in the activity of Pd-based catalysts for alcohol oxidation. The researchers reported that N groups in a solution or weakly bound to the support in the form of pyridine is detrimental to the catalytic activity and stability. However, simply by chemically/ covalently bonding of N moieties to the support structure (not to the Pd nanoparticles) improved catalytic performance by limiting the Pd leaching and coarsening of metal particles.

Besson in his extensive research on the oxidation of pyridine derivative alcohols using Bi-Pt system, also suggested complexation of N atoms with the catalyst as a major problem and challenge in this process.[12], [25]

In conclusion, the results of the presented work on the oxidation of 3-pyridinemethanol, in the context of several literature reports[12], [23], [25], lead to the hypothesis about the possibility of forming complex compounds between 3-pyridinemethanol/3-pyridinecarboxyaldehyde and Pd in the catalyst. Assuming, that there is some kind of interaction formed at elevated temperature between the pyridine N and Pd, it would explain the limitation of the conversion to 30 % in almost each performed experiment. Keeping in mind that water (even in small amounts) caused heavy Pd leaching it might suggest further hydration of complexes and hence deactivation of the catalyst. However, without further research, this is only a timid hypothesis that may be clarified further using diffuse-reflectance FTIR spectroscopy

(DRIFTS) with pyridine. This experiment would allow to determine whether specific active centres have been modified during the reaction.

5.2.2.2.7. Leaching

Keeping in mind that the studied reaction is extremely demanding due to possible interaction of pyridine N atoms with Pd in the catalyst, the metal leaching has been checked. The leaching of catalysts with different metal ratios has been evaluated using ICP MS technique and the results have been presented in table 5-4.

Table 5-4 *Leaching of SIm catalysts.*

Catalyst	Leaching [%]	
	Au	Pd
0.25 %Au 0.75%Pd/ TiO_2	0.1	1.9
0.50 %Au 0.50%Pd/ TiO_2	<0.1	2.1
0.75 %Au 0.25%Pd/ TiO_2	<0.1	2.4

Reaction conditions: SIm catalysts, 60 mg; oxygen pressure, 3 bar; temperature, 140 °C; 0.5 M 3-pyridinemethanol in toluene; time, 24 h.

The change of solvent from water to toluene significantly limited Pd leaching (from around 80 % to around 2 %), although this is still too high to meet industrial requirements. The loss of Au is again minimal (less than 0.1 %), hence it can be stated that Au leaching is negligible. The amount of leached Pd was only slightly influenced by the metal ratio of a catalyst (table 5-4).

The plateau in conversion occurred after 24 hours hence the samples have been analysed for metal leaching after 48 and 96 hours using 0.50 %Au 0.50 %Pd/TiO_2. The results revealed moderate Pd leaching after 48 hours (2.37 %) and quite heavy leaching after 96 hours (2.7-3.00 %); Au remained stable at all times. Unfortunately, progressing with time Pd leaching is a serious problem and might be a main reason of catalyst deactivation. Observed leaching can be a result of complexation or adsorption, however further studies are needed to fully determine the nature of these interactions.

Thermal treatments (calcination at 200, 400, and 600 °C under static air) were applied in an attempt to improve the stability of the 0.75 %Au 0.25 %Pd/TiO_2 SIm catalyst (table 5-5). Unfortunately, calcination at any of the tested temperatures did not stop Pd leaching. Moreover, the treated catalysts showed unusual results in terms of activity where the catalysts calcined at 200 and 400 °C have slightly higher conversion than the untreated catalyst and the catalyst calcined at 600 °C is essentially the same as the standard catalyst. It can be noticed that carbon balance varies and significantly influences the conversion and when the experimental error is taken into consideration (5 %), one can assume that the results for all compared catalysts are roughly similar. Another hypothesis is that the reaction depends on the size of nanoparticles, however to a small extent. SEM analysis confirmed the occurrence of particle growth (figure 5-17). It is clear from the graphs in figure 5-17 that as calcination temperature increases, larger clusters are obtained. Calcination at 200 °C did not greatly influence the size of nanoparticles compared to the uncalcined sample with the majority of particles being approximately 1.9-2.8 nm. Calcination at 400 °C clearly influenced the size of nanoparticles as the majority of clusters were approximately 2.8- 4.6 nm. As expected, calcination at 600 °C caused an even larger agglomeration as most particles were in the range of 5.2- 8.0 nm. Also, higher calcination temperatures caused larger range of size distribution than in catalyst calcined at lower temperature (200 °C).

Table 5-5 *Influence of calcination on Pd leaching for 0.75 %Au 0.25 %Pd/ TiO_2 SIm catalyst.*

Catalyst	Conversion [%]	C bal [%]	Pd leaching [%]
standard	30	97	2.4
200 °C	38	96	2.3
400 °C	35	97	2.3
600 °C	29	98	2.2

Reaction conditions: 0.75 %Au 0.25 %Pd/ TiO_2 SIm, 60 mg; oxygen pressure, 3 bar; temperature, 150°C; 0.5 M 3-pyridinemethanol in toluene; time, 24 h. Calcination: static air; time, 2 h.

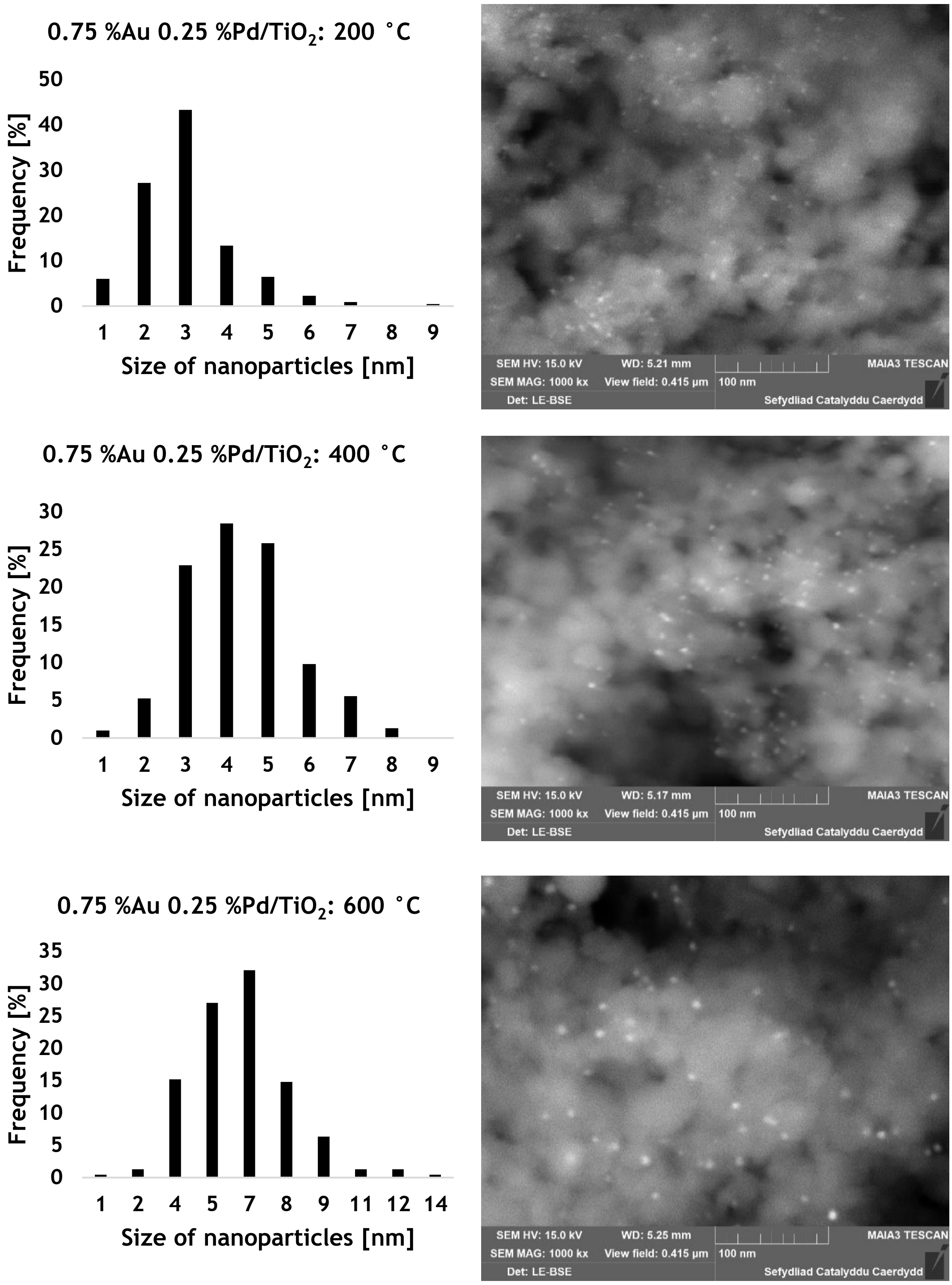

Figure 5-17 *SEM analysis of 0.75 %Au 0.25 %Pd/TiO$_2$ SIm after heat treatment. Conditions: temperature: 200, 400 and 600 °C; static air; time: 2h.*

The aim of this work was to evaluate and contrast the same Au-Pd system as a heterogeneous catalyst for various substrates with different chemical nature. Intrigued by the fact that calcination of catalysts did not influence conversions in the oxidation of 3-pyridinemethanol massively, the same catalysts were tested in the oxidation of cinnamyl alcohol. From figure 5-18 it is clear, that in the case of cinnamyl alcohol, calcination caused a significant drop in conversion. The catalyst calcined at 200 °C had similar activity to the standard fresh catalyst, however after calcination at 400 and 600 °C the activity and selectivity to the desired product decreased dramatically. This is particularly evident for 600 °C where the amount of benzaldehyde (product formed as a result of autoxidation) increased significantly.

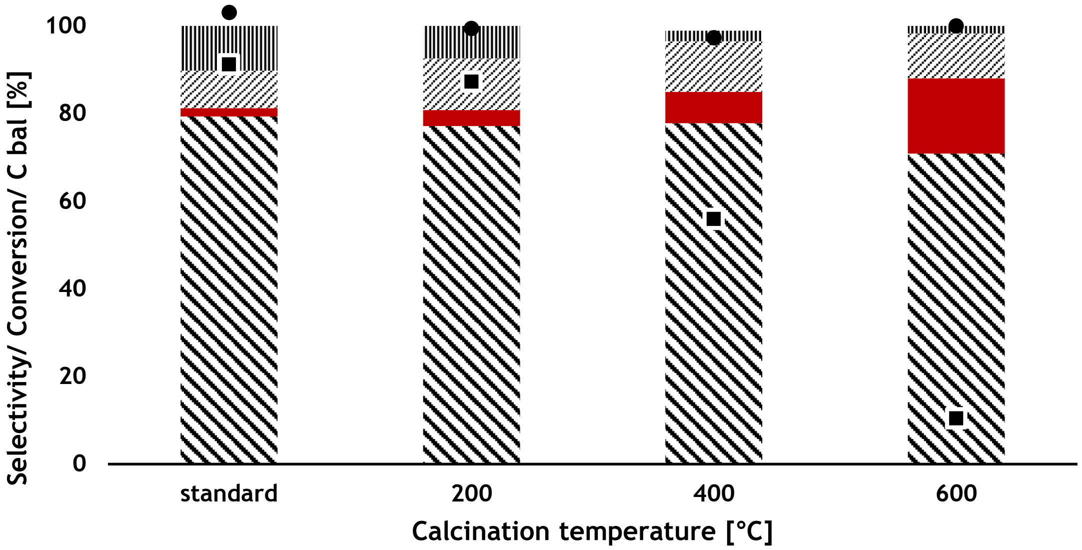

Figure 5-18** The influence of calcination on the activity of 0.75 %Au 0.25 %Pd/TiO$_2$ SIm in the oxidation of cinnamyl alcohol. Conditions: Radley reactor; temperature, 120 °C; O$_2$ pressure, 3 bar; catalyst mass, 10 mg; 5 ml 0.5 M cinnamyl alcohol in toluene; time, 1h.* ***Conversion (■); Carbon balance (●); Cinnamaldehyde (▧); Benzaldehyde (▬); 3-Phenyl-1-propanol (▨); Methylstyrene (‖‖‖)

Many of the literature reports mentioned and cited repeatedly in this thesis have proven the existence of a synergistic effect between Au and Pd. In addition to purely experimental work, many reports have been recently published based on computational chemistry and theoretical works supported by experiments with the use of modern techniques attempting to explain this challenging phenomenon.[26]–[29] It is tempting to put forward a hypothesis that the active sites in the oxidation of cinnamyl alcohol and 3-pyridinemethanol are different. In the case of cinnamyl alcohol oxidation it has been proven that the Au-Pd synergistic effect plays an enormous role in the process. This synergy is extremely sensitive to both metal ratio and preparation method. It has been also confirmed by the experiment with the calcined catalysts that agglomeration dramatically lowered catalytic activity for cinnamyl alcohol oxidation. In case of oxidation of 3-pyridinemethanol, calcination and hence changes in particles size and morphology influenced the catalytic activity only slightly. Based on these observations and contrasting the two different behaviours it may suggest that active sites for the oxidation of 3-pyridinemethanol are rather placed on the metal-support interface than on the Au-Pd alloy itself. It would also explain extremely low activity of Au-Pd system supported over carbon (section 5.2.2.2.2). Another explanation of the difference between these two studied processes might be that the oxidation of cinnamyl alcohol is more sensitive to the nanoparticles size and relies on a much smaller range than the oxidation of 3-pyridinemethanol.[30] To verify these hypotheses, further research would have to be done using advanced technology (e.g. operando spectroscopic techniques) and perhaps even to be supported by computational chemistry.[31]

5.2.2.2.8. Determination of pre-leaching

Following the literature reports regarding the interaction of N atom located in the alcohol with Pt group metal on the catalyst[12], it seems reasonable to suppose that this could be the reason of Pd leaching observed in this study. To verify how strong this interaction might be, the catalyst has been added to the stock solution of 3-pyridinemethanol in toluene and kept under stirring at room temperature for 2 hours. In the next step the catalyst was filtered off and the solution has been submitted for ICP. The results presented in table 5-6 revealed that Pd leaching occurred almost instantly, even at room temperature. In case of both tested catalysts, 0.50 %Au 0.50%Pd/ TiO_2 SIm and 0.75 %Au 0.25%Pd/ TiO_2 SIm, pre-leached Pd was approximately 0.12-0.22 % which shows that the substrate was able to strongly interact with metal, causing it to leach. The solvent has been excluded as a reason of leaching due to the fact, that no leaching has been observed in the oxidation of cinnamyl alcohol in toluene using the same catalyst.

Table 5-6 *Determining of pre-leaching in the oxidation of 3-pyridinemethanol.*

Catalyst	**Pd leaching [%]**	
	pre-leaching[a]	**standard reaction**[b]
0.50 %Au 0.50%Pd/ TiO_2	0.12	2.1
0.75 %Au 0.25%Pd/ TiO_2	0.22	2.4

[a] *Pre-leaching conditions: catalyst mass, 60 mg; room temperature; 0.5 M 3-pyridinemethanol in toluene; time, 2 h.*
[b] *Reaction conditions: catalyst mass, 60 mg; oxygen pressure, 3 bar; temperature, 140°C; 0.5 M 3-pyridinemethanol in toluene; time, 24 h.*

Interesting results were provided by an experiment carried out with a small addition of water. In the case of the oxidation of cinnamyl alcohol, the addition of 1 ml of water to 5 ml of the reaction mixture in toluene significantly improved the efficiency of the process. However, when 1 ml of water was added to the 3-pyridienemethanol mixture in toluene, the complete opposite effect occurred. First of all, there was a clear separation of the aqueous and organic phases, which was emphasized by the change in colour of the aqueous phase to yellow. Analysis by MP-AES of the yellow aqueous phase revealed the presence of Pd equivalent to 60 % of that in the catalyst used. Similar observations of yellow tinted mixture caused by leached Pt have been made by Besson and co-workers who studied the oxidation of 2-pyridienemethanol and 4-pyridinemethanol in various solvents[12], [17] Therefore it can be stated that even a small addition of water caused heavy Pd leaching which practically prevented the progress of the reaction. Comparison of this experiment for two different processes using the same Au-Pd catalyst suggests that 3-pyridinemethanol in the presence of water strongly interacts with Pd and, as a result, causes a particularly heavy leaching. The other reason might be higher temperature applied in the oxidation of 3-pyrididnemethanol (140 °C) than in the oxidation of cinnamyl alcohol which affected metal-support interaction and intensified Pd leaching.

In the earlier section (5.2.2.1), leached Pd was shown to be inactive when water was used as a solvent. To determine whether homogeneous catalysis took place in organic solvent, a hot filtration was carried out. The catalyst was filtered off after 2 hours of reaction and the solution was further oxidised for 22 h. The leaching was checked for the control reaction and for the supernatant (table 5-7). Taking into consideration 5 % experimental error, the conversion values for all reactions are in close proximity, hence it can be stated that leached Pd is inactive. No further reaction is observed after removal of the solid catalyst.

Table 5-7 *Investigation of homogeneous catalysis.*

	Conversion [%]	C bal [%]	Leaching [%]
Control reaction	11	103	2
After filtration (2h)	9	97	
After filtration (24)	13	98	3

Reaction conditions: 1 %Pd/ TiO_2 SIm, 60 mg; oxygen pressure, 3 bar; temperature, 140°C; 0.5 M 3-pyridinemethanol in water; time, 24 h.

5.2.2.2.9. Reusability studies in the oxidation of 3-pyridinemethanol

Reusability studies of the 0.50 %Au 0.50 %Pd/ TiO_2 SIm catalyst revealed gradual mild deactivation up to 5 reuses and massive drop after 6th use (table 5-8). Pd leaching has been monitored up to 6 cycles. ICP analysis revealed that Pd leaching remained at the same level after 3 reuses (around 2 %) and decreased after 5th (0.5%) and 6th cycle

(0.8 %). Gradual Pd leaching coupled with the observed particle growth (presented in figure 5-19) is presumably the reason of deactivation.

Table 5-8 *Reusability of 0.50 %Au 0.50 %Pd/ TiO_2 SIm catalyst.*

Run	**Conversion [%]**	**C bal [%]**	**Pd leaching [%]**
1	29	96	2.1
2	23	98	2.5
3	22	98	2.6
4	21	99	n/a
5	18	96	0.5
6	11	104	0.8

Reaction conditions: 0.50 %Au 0.50 %Pd/ TiO_2 SIm, 60 mg; oxygen pressure, 3 bar; temperature, 140°C; 0.5 M 3-pyridinemethanol in toluene; time, 24 h.

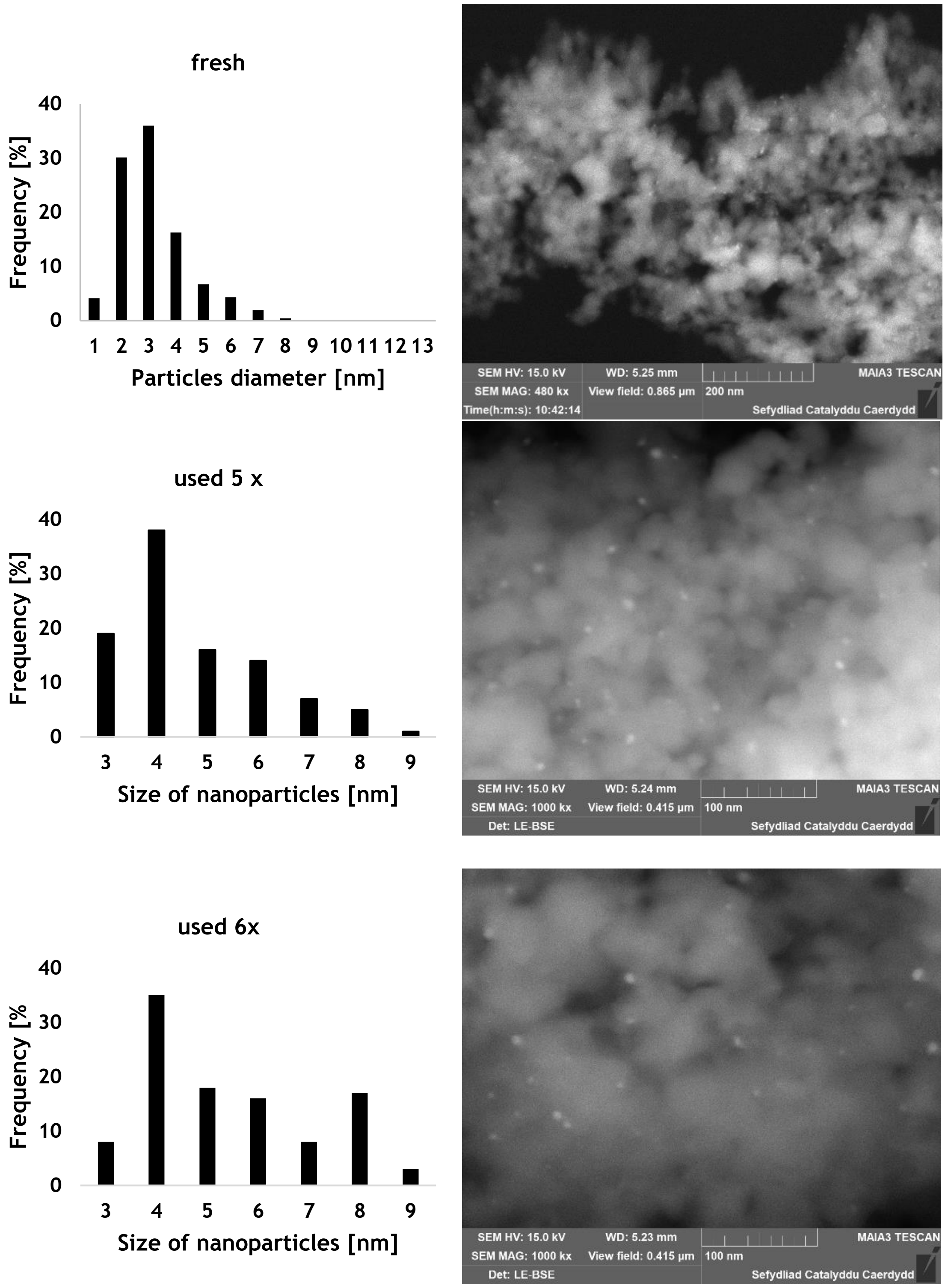

Figure 5-19 *SEM images of 0.50 %Au 0.50 %Pd/ TiO_2 SIm catalyst after 5th and 6th cycle.*

0.75 %Au 0.25 %Pd/ TiO_2 SIm has previously been found to be more stable than 0.5 %Au 0.5 %Pd/ TiO_2 SIm in case of cinnamyl alcohol oxidation. Therefore, reusability studies have been carried out for this catalyst in the oxidation of 3-pyridinemethanol (table 5-9). Interestingly, Pd leaching occurred only during the first cycle and decreased with every use. Therefore, the catalyst deactivation may be linked with Pd leaching. Similar to the oxidation of cinnamyl alcohol, 0.75 %Au 0.25 %Pd/TiO_2 is more stable than 0.50 %Au 0.50 %Pd/TiO_2. Once again, no leaching of Au was observed.

Table 5-9 *Reusability studies using 0.75 %Au 0.25 %Pd/ TiO_2 SIm*

Run	Conversion [%]	C bal [%]	Pd leaching [%]
1	30	97	2.5
2	30	100	0.9
3	33	101	0.0

*Au leaching: < 0.09 %

Reaction conditions: 0.75 %Au 0.25 %Pd/ TiO_2 SIm, 60 mg; oxygen pressure, 3 bar; temperature, 150°C; 0.5 M 3-pyridinemethanol in toluene; time, 24 h.

5.2.2.2.10. Different solvents

Besson and co-workers[12], [17] tested a 1.95 wt.% Pt/C catalyst in the oxidation of substituted aromatic alcohols with air under mild pressure (<20 bar) at 100 °C. The researchers focused their attention on the influence of solvents on the reaction. In case of benzyl alcohol and substituted benzyl alcohols (with electron donating and withdrawing groups), the reactions carried out in dioxane were highly selective, producing aldehydes only with almost total conversion (*ca.* 99 %). When dioxane was diluted with water (70/30 vol.% dioxane/water) and used as a solvent, the reaction rate increased significantly up to the total conversion of alcohol. The selectivity to benzaldehyde remained the same as for the pure dioxane. In a 50/50 vol.% mixture, benzoic acid was observed as the only product and addition of base caused even more rapid oxidation to benzaldehyde which was immediately oxidised further to benzoic acid. The same pattern was observed for other substituted benzyl alcohols with some minor differences for some compounds. The researchers tested in similar way the oxidation of 2-pyridinemethanol and 4-pyridinemethanol. The results revealed that conversions were lower compared to the oxidation of substituted benzyl alcohols. The reactions carried out in organic solvents such as dioxane, toluene, acetonitrile, THF, monoglyme and dichloromethane had low conversions, not exceeding 30 %. A slightly higher conversion, 46 %, was obtained in the oxidation of 4-pyridinemethanol carried out in THF. Addition of water to dioxane prevented the reaction to take place. Interestingly, the reactions performed in water only had high conversions (isolated yields about 80 %) to the corresponding acids which were the only products. The experiments carried out in water (section 5.2.2.1) yielded mostly niacin which is in line with reported observations by Besson. Substituted pyridinemethanol compounds (4-methoxy-3,5-dimethyl-2-pyridinemethanol and 3-hydroxy-6-methyl-2-

pyridinemethanol) showed behaviour similar to benzyl alcohols: relatively high conversions have been obtained in organic solvents; addition of water to dioxane increased the reaction rates; and corresponding acids have been obtained in pure water as the only products.[17]

The results presented in this thesis for the oxidation of 3-pyridinemethanol using Au-Pd/ TiO_2 catalysts are in line with Besson's work on the oxidation of pyridinemethanol derivatives using Pt-Bi system (table 5-10).[17] It has been shown that the solvent plays an important role in this process. Therefore, various solvents have been tested here in the oxidation of 3-pyridinemethanol. Besson *et al.*[17] reported dioxane as a suitable solvent for the oxidation of 4-pyridinemethanol (30 % conversion) and completely inefficient for the oxidation of 2-pyridinemethanol (no conversion) therefore it was implemented for the AuPt/TiO_2 system for the oxidation of 3-pyridinemethanol to evaluate its suitability. The results of the reaction carried out in dioxane have been contrasted to the standard reaction carried out in toluene in figure 5-20.

Table 5-10 *Effect of solvent on the oxidation of pyridinemethanol derivatives from Besson and co-workers.*[17]

	Conversion [%]			
Solvent	**2-pyridinemethanol**	**4-pyridinemethanol**	**4-methoxy-3,5-dimethyl-2-pyridinemethanol***	**3-hydroxy-6-methyl-2-pyridinemethanol***
Dioxane	0	30	40	100
Dioxane/water: 90/10 vol.%	-	-	70	100
Toluene	5	-	65	-
Acetonitrile	8	-	-	-
THF	20	46	50	-
Monoglyme	11	-	70	-
CH_2CL_2	18	-	27	-

Only aldehyde was detected. Conditions: substrate 50mmol/l, l g 1.95 wt.%Pt/C catalyst, 100 ml solvent, 100 °C, 20 bar, 15 h of reaction.
**Reaction conditions: the same as above but less catalyst: 0.15 g*

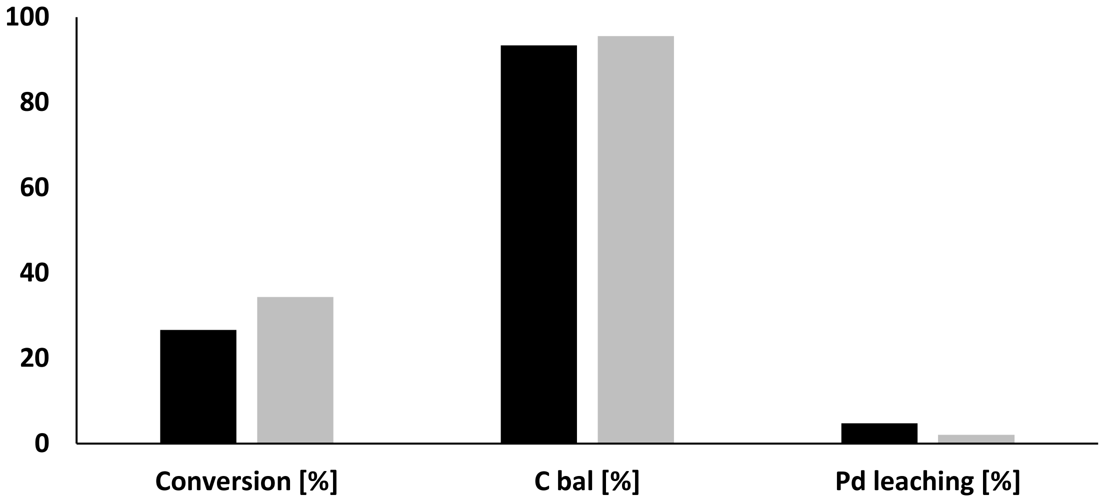

Figure 5-20 *Effect of dioxane used as a solvent on the oxidation of 3-pyridinemethanol. Reaction conditions: 0.50 %Au 0.50 %Pd/ TiO_2 SIm, 60 mg; oxygen pressure, 3 bar; temperature, 140°C; 0.5 M 3-pyridinemethanol in dioxane; time, 24 h.* ***Dioxane, ■; Toluene, ▨.***

Dioxane did not improve the efficiency of the catalytic performance using 0.5 %Au 0.5%Pd/ TiO_2 SIm and conversion was rather lower than in toluene. Furthermore, dioxane caused slightly higher Pd leaching than toluene. Taking into consideration that The United States Environmental Protection Agency classifies dioxane as a probable human carcinogen at high concentrations[32], [33], toluene is definitely a more suitable solvent. In addition to dioxane, other solvents have also been tested, table 5-10 shows the preliminary results.

Table 5-10 *Solvent testing for the oxidation of 3-pyridinemethanol.*

Solvent	Conversion [%]	C bal [%]
Toluene	29	96
o-Xylene	48	87
m-Xylene	43	165
Mesitylene	51	130
Acetonitrile*	<4	

**Solvent has partially evaporated (2 reactions have been carried out).*
Reaction conditions: 0.75 %Au 0.25 %Pd/ TiO_2 SIm, 60 mg; oxygen pressure, 3 bar; temperature, 140°C; 0.5 M 3-pyridinemethanol in toluene; time, 24 h.

3-Pyridinemethanol is miscible with toluene and acetonitrile and is not miscible with o-xylene, m-xylene, mesitylene. Miscibility problems affected the analysis and even addition of acetonitrile or acetone to make the reaction mixture homogeneous did not improve massively the accuracy of the results for some solvents. The addition of acetonitrile to xylene (reaction mixture: 70% vol toluene 30% vol acetonitrile) enabled to obtain reproducible results in two trials using various Au-Pd catalysts: 0.75 %Au 0.25

%Pd/ TiO_2 SIm, 0.50 %Au 0.25 %Pd/ TiO_2 SIm and 0.25 %Au 0.75 %Pd/ TiO_2 SIm (figure 5-21).

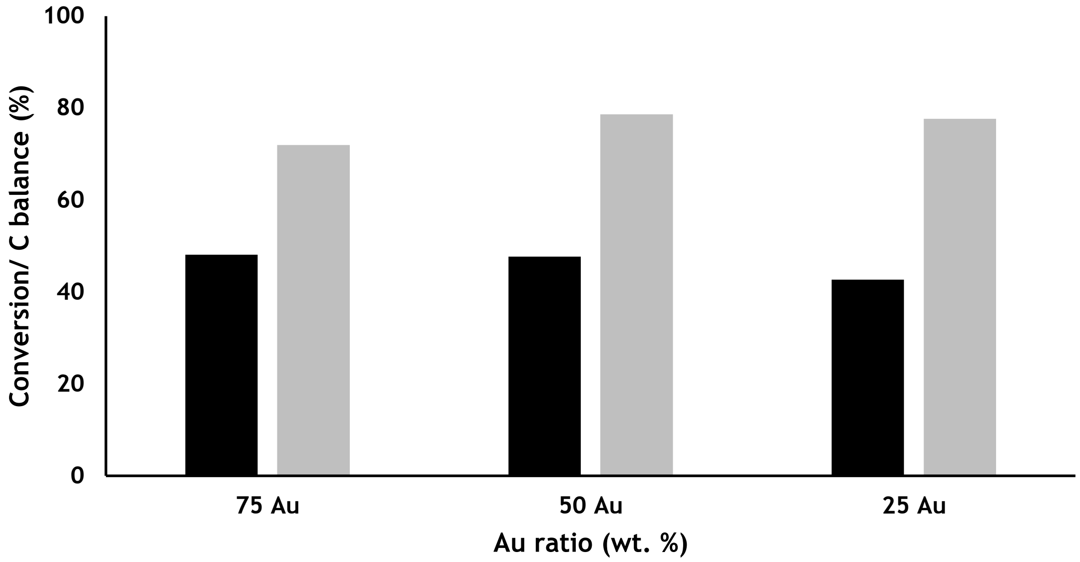

Figure 5-21 *Effect of xylene/acetonitrile used as a solvent in the oxidation of 3-pyridinemethanol. Reaction conditions: catalyst mass, 60 mg; oxygen pressure, 3 bar; temperature, 140°C; 0.5 M 3-pyridinemethanol in dioxane; time, 24 h.* ***Conversion,*** ■; ***Carbon balance,*** ▨

It can be seen from figure 5-21 that conversion in xylene/ acetonitrile is higher than in standard toluene for all tested catalysts (over 40 %), however carbon balance is low (around 70-80 %). Pd leaching has also been limited in xylene/acetonitrile to only 0.07 % while compared to 2 % in toluene. This observation highlighted further the tunability of these reaction systems by seemingly minor factors. Unfortunately, the discrepancies in carbon balance observed for this particular solvent mix ultimately limits its implementation. The cause for this is unknown however similar phenomena have been reported. Besson *et al.*[12] reported in his work lower carbon balance depending both on the substrate and product. It was hypothesised that insoluble by-products might be formed, or adsorption effect occurred on the catalyst surface. The oxidation of 1-phenylethanol has been contrasted to the oxidations of different alpha-substituted pyridinemethanol derivatives: alpha-methyl or phenyl pyridinemethanol. The oxidation reactions were performed using Pt/C and Pt-PBi/C catalysts under air (10 bar) at 373 K to the corresponding ketone. The catalytic activity in the oxidation of 1-phenylethanol increased by increasing the amount of water in the solvent with total conversion and selectivity to acetophenone. Addition Bi to Pt increased greatly the reaction rate. Moreover, no metal leaching has been detected. In general, N containing pyridinemethanol derivatives showed completely different behaviour to 1-phenylethanol. The solvent was selected depending on the solubility of the substrate:

either pure dioxane, water or mixture of both. Obviously, the presence of N dramatically changes the chemical nature of a compound in terms of its interaction with the Pt/ C catalyst. It is well known in the literature that N in N-containing compounds is able to adsorb on the metal surface and even coordinate strongly to the metal which is presumably the reason of catalyst deactivation.[25], it was more difficult to obtain high yields using a Pt/C catalyst. The other peculiarity presented in the discussed paper is the influence of the position of the substituent (*ortho*, *meta* or *para* position) in the substrate. The highest conversions have been obtained for ortho methyl- or phenyl-substituted pyridinemethanol (38 and 100 %, respectively). Bimetallic Pt-Bi/ C catalyst showed greater activity than monometallic Pt/C (enhancing conversions from 30 to 76 % in the case of the ortho methyl substituent). Conversions for the pyridinemethanol derivatives with the substituents in *meta* and *para* positions were significantly lower. The researchers suggested that the observed phenomenon can be related with different adsorption effects of the N and hydroxyl group in the compounds structure on the metal surface. The phenyl substituent in *ortho* position is a steric hindrance limiting the interaction of the pyridine N with the metal surface which makes the hydroxyl group more accessible thus dehydrogenation process is facilitated. The researchers hypothesised that also an internal hydrogen bond could be formed which would limit the N doublet to the metal. Substituents placed in the *meta* and *para* positions are more distant from N hence there is no steric hindrance and nitrogen doublet strongly interacts with metal surface which puts hydroxyl group away. In the oxidation of pyridinemethanol derivatives the researchers also noticed Pt leaching. The leaching was dependent on the nature of the substrate and also was correlated to the position of substituent. In case of the phenyl derivative, (which is a steric hindrance itself) leaching was negligible. In case of methyl substituent, the lowest leaching occurred when in the *ortho* position (5 %) which might be explained by lower accessibility of pyridine N to metal surface than in position *meta* (21 % leaching) and *para* (49 % leaching). The addition of Bi significantly reduced leaching for all *ortho, meta and para* substituents (from 5 to 1 %, from 21 to 8 % and from 49 to 18 %, respectively). The researchers explained the role of bismuth as a diluent for platinum, shielding Pt from interaction with pyridine N.

5.3. Conclusions

Au-Pd supported nanoparticles have been tested in the epoxidation of *trans*-stilbene and contrasted to the oxidation of cinnamyl alcohol. In this reaction, the choice of solvent plays an enormous role, hence the most suitable solvents reported in the literature have been chosen- cyclohexane and methylcyclohexane. As expected, catalyst preparation method influenced the course of the process. Similar to the oxidation of cinnamyl alcohol, the most active catalysts have been obtained by sol-immobilisation method. Large amounts of benzaldehyde obtained as a by-product suggested that degradation/ overoxidation of the substrate took place simultaneously next to the catalytic pathway.

The reactions carried out in cyclohexane using Au-Pd catalysts prepared by impregnation method showed that bimetallic 0.50 % 0.50 %Pd/TiO_2 (Imp) had the highest conversion compared to its monometallic counterparts. However, the change in solvent to methylcyclohexane resulted in higher conversion and selectivity of bimetallic 0.50 %Au 0.50 %Pd/TiO_2 (Imp) and monometallic 1 % Pd/TiO_2 (Imp). Analysis of the selectivity profile has shown increase in the formation of benzoic acid, which coupled with lower carbon balance (around 70-77 %) led to the conclusion that bimetallic and monometallic Pd Imp catalysts are more active than monometallic Au imp catalyst and combustion processes presumably took place.

The highest conversion and selectivity to *trans*-stilbene oxide was obtained with the bimetallic 0.50 %Au 0.50 %Pd/ TiO_2 (SIm) catalyst, however carbon balance was low (65 %), which indicated intense combustion processes. Replacement of an oxidant from oxygen to air enabled to maximise the formation of desired product, *trans*-stilbene oxide. The yield for the catalysed reaction carried out under 1 bar air was around 40 % which is in good agreement with the results obtained by Caps and co-workers (yield 45 %).[15] Moreover, increase in air pressure caused a significant drop in carbon balance, decrease in selectivity to *trans*-stilbene oxide and increase in conversion, which indicated intensified processes of total combustion. The key observation is that the presence of the 0.50 %Au 0.50 %Pd/TiO_2 (SIm) catalyst significantly increased the conversion and selectivity to the desired product compared to the uncatalysed reaction carried out under 1 bar air, which is in excellent agreement with the results obtained in the oxidation of cinnamyl alcohol. Despite the differences in general mechanism of *trans*-stilbene epoxidation and cinnamyl alcohol oxidation, the way of catalyst behaviour showed the same pattern for these two processes in terms of switching off undesired unselective reactions in optimised conditions.

3-pyridinemethanol oxidation using supported Au-Pd nanoparticles can be performed both in water and in organic solvents leading to the different product distributions. The reaction carried out in water yielded both aldehyde and carboxylic acid. The addition of base caused further oxidation of aldehyde to acid. Moreover, base caused the oxidation of 3-pyridinemethanol to acid even in the absence of a catalyst. Monometallic catalysts showed rather low activity in this case. Bimetallic Au-Pd catalysts showed synergistic effect and led to moderate conversion of 3-pyridinemethanol. Unfortunately, water caused heavy Pd leaching (more than 80 %) hence toluene had to be employed as an organic solvent to minimise this. Previous literature studies on Pt-Bi/C catalysts using toluene as a solvent resulted in little to no activity in pyridine methanol derived oxidations compared to other organic solvents such as dioxane. However, in this study activity was observed at temperatures as low as 80 °C, and by implementing raised reaction temperatures such as 140 °C, significant levels of oxidation can be achieved. Furthermore, 3-pyridinecarboxyaldehyde was obtained as the only product, with no acid formation detected. Bimetallic Au-Pd catalysts have been found to be more active than their monometallic counterparts indicating a synergistic effect. Pd leaching was found to be around 2 %, however the catalysts have been reusable up to 5 times with gradual loss of activity. Deactivation reason might be particle growth coupled with leaching. The efforts of catalysts stabilisation have been undertaken by calcination at different temperatures, however the outcome was rather poor. The most active and reusable tested catalyst for this reaction has been found to be 0.75 %Au 0.25 %Pd/ TiO_2 (SIm). The observed loss in activity within 3 cycles was extremely low. Nevertheless, the inhibition of the reaction took place as the reaction proceeded in case of all tested Au-Pd metal ratios catalysts. The reason of that is presumably catalyst poisoning due to strong interaction between Pt-group metal with N contained in pyridine structure of the reactants.

5.4. References

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Chapter 6

6. General Discussion, Conclusions and Future Work

6.1. Cinnamyl alcohol oxidation

6.1.1. General Discussion and Conclusions

Cinnamyl alcohol is an example of an allylic alcohol and represents one of the main components of plant biomass derivatives. The transformation of alcohols to carbonyl products is meaningful for industrial applications. The desired product of cinnamyl alcohol oxidation- cinnamaldehyde is an insecticide and common food/perfume additive. Also, the character of the substrate is very interesting as it is prone to the process of autoxidation.

Although the oxidation of cinnamyl alcohol has been widely studied in the literature, usually mild conditions are applied. From an industrial viewpoint, it is economically more efficient to perform oxidation processes at elevated temperature for the purpose of heat recapture.

Reactions have been performed with the use of bimetallic catalysts comprising of gold and palladium which were found to be very active for oxidation reactions with molecular oxygen. Platinum group metals have been studied for nearly 200 years due to several reasons such as their high catalytic activity under mild conditions, high selectivity towards a specific product, high stability under different reaction conditions and resistance to poisoning. Platinum has been utilised as a catalyst in many reactions, however palladium is another element gaining popularity as a catalyst as it is similar to platinum with regards to catalytic properties with the added economic benefit of being cheaper and more abundant. Since the discoveries made by Haruta[1] and Hutchings[2], it has been established that nanoparticles of gold alloyed with platinum group metals show unexpected, specific catalytic properties. It is widely accepted that electronic and geometric effects are responsible for the catalytic performance of Au-Pd bimetallic catalysts. Selectivity and resistance to deactivation are superior for bimetallic nanoparticles compared to monometallic Au catalysts.[3] Heterogeneous catalysts are more attractive from an industrial viewpoint than homogeneous catalysts mainly because they are easier to separate from the product mixture, possible to recycle hence cheaper and more sustainable. The research and development of heterogeneous catalysis provides promise for developing green, environment-friendly processes for producing commodity chemicals.

The presented process of cinnamyl alcohol oxidation using Au-Pd supported nanoparticles is potentially an excellent alternative to existing methods for the synthesis of carbonyl compounds based on procedures which use toxic and stoichiometric oxidants like chromate and permanganate.

The approach used in this study aimed to examine the autoxidation phenomenon and its influence on catalytic oxidation of cinnamyl alcohol. The conversion of cinnamyl alcohol in the blank reaction, carried out at 120 °C under molecular oxygen, was relatively high however non-selective to the desired product. Close attention has been paid to the mechanism of benzaldehyde formation, a by-product being proof of autoxidation process. The phenomenon of autoxidation in the blank reaction cannot be neglected and character of the substrate should be taken into consideration in this and every other process which is considered to be performed on the industrial scale. Oxidation of cinnamyl alcohol likely occurs *via* two mechanistic pathways as indicated by the product distribution. The size of Au-Pd nanoparticles has strong influence on the reaction mechanism. Small particles (3-5 nm) obtained by sol-immobilisation method are suggested to be able to split peroxides/hydroperoxides caused by autoxidation process thus enable high selectivity to cinnamaldehyde. Larger particles (around 20 nm) achieved *via* impregnation method are less active in the oxidation of cinnamyl alcohol and the product distribution suggests that autoxidation and catalytic mechanisms take place simultaneously.

Conditions also have strong impact on the reaction of cinnamyl alcohol oxidation. An important obstacle to overcome in order to apply Au catalysts on the industrial scale (especially for the oxidations) is the necessity of the presence of base, which is undesired.[4] In this reaction, the yield of the process was excellent in the absence of base. The activity of the catalysts depends on the preparation method and also on the metal ratio. The results revealed that catalysts made by sol-immobilisation method are more active for cinnamyl alcohol oxidation and more selective to cinnamaldehyde than catalysts made by impregnation method under industrially relevant conditions. The explanation is most likely related to the dramatically different particle sizes obtained during two preparation methods. The highest conversion (nearly 96 % after 4 hours) and selectivity to cinnamaldehyde (80 %) was achieved using the 0.75 %Au 0.25 %Pd/ TiO_2 (SIm) catalyst. Generally SIm catalysts showed gradual mild deactivation within 3 cycles. The 0.75 %Au 0.25 %Pd/ TiO_2 (SIm) catalyst demonstrated exceptionally low deactivation with 94, 92 and 90 % conversion after first, second and third use, respectively. SEM analysis revealed negligible particle growth within 3 cycles for this catalyst. The agglomeration observed for relatively unstable 50Au:50Pd metal ratio and lack of particle growth in case of the extremely stable 75Au:25Pd can help to explain the deactivation of the range of 1 %AuPd/TiO_2 (SIm) catalysts.

The experimental work presented in this thesis proved that optimisation of Au-Pd metal ratio and catalyst preparation method is essential towards improving the overall efficiency of oxidation in the liquid phase under autoxidation conditions.

Although the existence of a synergistic effect has been observed and reported based on experimental works, the nature of this phenomenon has not been entirely understood from a surface science viewpoint. The reason for this is the complexity of the processes and factors such as influence of the reactants, composition of the catalyst and experimental conditions.[5], [6]

Systematisation and rationalisation of the structure- activity relationship of bimetallic Au-Pd nanoparticles could provide guidelines for the development and fine-tuning of catalysts for crucial industrial reactions. This task is difficult and requires specialised techniques and a lot of work and combined strengths from specialists in the field of chemistry, engineering, and physics. Recent achievements in the field of computational chemistry coupled with experimental works would provide valuable guidance and information to come closer to achieving success in the design of excellent catalysts.

The presented findings are proof that there is plenty of room for greater improvement in understanding the mechanism of autoxidation and selective oxidation in general.

6.1.2. Future work

The most active and reusable catalyst for the oxidation of cinnamyl alcohol is 0.75 %Au 0.25% Pd/ TiO_2 prepared by sol-immobilisation method. Modifications to the synthesis of this catalyst should be investigated such as employment of other stabilising agents. An interesting idea would be to remove stabilising agent to achieve even higher yield. Calcinations of the catalysts led to a decrease in conversion, however it is possible to remove PVA by refluxing a catalyst prepared by sol-immobilisation in water.[7] This method prevents sintering of metal particles.

All tested catalysts had 1 % of total metal loading which was sufficient to achieve high yield in the oxidation of cinnamyl alcohol. Further tests could be performed by using Au-Pd catalysts with even lower metal loading. That would lower the cost of catalyst synthesis which is always desired in the industry.

It has been concluded that the reaction of cinnamyl alcohol oxidation is extremely particle size sensitive. Further research towards catalyst optimisation could be carried out by preparing a closer controlled nanoparticle size range using specific methods which would help to clarify the optimum particle size for activity and selectivity, as has been achieved in the analogous benzyl alcohol oxidation reaction.[8], [9]

Another step would be investigation of Au-Pd synergistic effect in detail by analysing various composition of metals on the molecular level. Here, in-depth characteristic investigation would be essential coupled with computational chemistry and experimental data.[10] Recent developments of microscopic techniques enable new insights into atomic-level catalytic mechanisms by employing enhanced detectors to capture structural and chemical changes in *operando* under synthesis and reaction conditions.[11]

It has been presented in section 4.2.2. of chapter 4 that monometallic 1 % Pd/ TiO_2 (SIm) showed high selectivity to cinnamaldehyde after being reused. This experiment should be repeated to exclude any possible reason such as analysis error. If the result would be positive, then it means that rearrangements of nanoparticles on the molecular level during reactions lead to optimal catalyst composition including size and oxidation state. This could direct future catalyst synthesis in order to achieve immediate high selectivity.

It has been demonstrated that catalysts can be applied under autoxidation conditions in order to increase selectivity to desired product in the oxidation of cinnamyl alcohol. Referring to this, Au-Pd supported nanoparticles could be used for other reactions where autoxidations take place or simply when harsh conditions can be applied. Keeping in mind that every process and every reaction is unique, optimisation of a catalyst and conditions should be carefully performed in every occasion.

6.2. Oxidation of *trans*-stilbene

6.2.1. General Discussion and Conclusions

In this part, the experimental conditions were based largely on the literature reports. The aim was to contrast the oxidation reactions of *trans*-stilbene with cinnamyl alcohol, due to the different chemical nature of these substrates, and study the effectiveness of the Au-Pd system. *Trans*-stilbene is an alkene and for the reaction to take place, the addition of a radical initiator is required. Also, choice of solvent is crucial, as it takes part in the reaction mechanism. The most suitable solvents for this process have been reported to be cyclohexane and methylcyclohexane.

As expected, the catalyst preparation method heavily influenced the reaction. Similar to the oxidation of cinnamyl alcohol, the most active catalysts were obtained by sol-immobilisation methods. Benzaldehyde has been also observed in this reaction as a by-product, formed as a result of degradation/overoxidation of the substrate. It is interesting that the catalytic reaction proceeded simultaneously with the degradation process. The highest conversion and selectivity to *trans*-stilbene oxide was obtained using 0.50% Au 0.50% Pd/TiO_2 bimetallic catalyst (SIm), however the carbon balance was low (65 %), which indicated intensive combustion processes. The change of one constituent in the system, namely replacement of oxygen with air, maximised the formation of the desired product, *trans*-stilbene oxide. The efficiency of the catalysed reaction carried out at 1 bar was approximately 40 %, which is consistent with the results obtained by Caps and co-workers (45 % yield).[12]

The key observation is that the presence of a 0.50% Au 0.50% Pd/TiO_2 catalyst (SIm) significantly increased the conversion and selectivity to the desired product compared to a non-catalysed reaction under air (1 bar), which is in perfect agreement with the results obtained in the oxidation of cinnamyl alcohol. Despite differences in the general mechanism of *trans*-stilbene epoxidation and cinnamyl alcohol oxidation, the catalyst behaviour showed the same pattern for these two processes in terms of excluding undesired non-selective reactions under optimized conditions.

6.2.2. Future work

It was found that milder conditions are more suitable for the oxidation of *trans*-stilbene. More work towards optimisation of this reaction could be carried out in terms of conditions and catalyst synthesis. Since solvent plays a direct role in the mechanism, various solvents or their mixtures could be tested. Low metal loading catalysts (below 1 %) could be prepared using various methods and compositions to investigate the influence of the nanoparticles size and morphology on the course of the reaction. Also, various supports could be tested as an important factor conditioning activity of embedded Au-Pd nanoparticles. Oxidation of *trans*-stilbene could be another case study where experimental work coupled with theoretical work would lead to deeper understanding of the nature of the Au-Pd synergistic effect.

6.3. Oxidation of 3-pyridinemethanol

6.3.1. General Discussion and Conclusions

3-Pyridinemethanol was selected due to the chemical stability of this substrate and the presence of N-heteroatom in its structure. Oxidation of 3-pyridinemethanol using Au-Pd nanoparticles is extremely difficult due to catalyst poisoning as the effect of the strong interaction between Pd and N- heteroatom present in pyridine-derivative reagents. This effect may also lead to Pd leaching, which is a huge obstacle in commercialisation of any catalyst.

The most active and reusable catalyst for this reaction was found to be 0.75% Au 0.25% Pd/TiO_2 (SIm). The observed loss of activity during 3 cycles was extremely low. Nevertheless, the inhibition of the reaction followed a similar trend to that of all tested Au-Pd supported catalysts.

The reaction conditions have a huge impact on the process. Literature reports on the oxidation of 3-pyridinemethanol using Pt-Bi/C catalysts in toluene indicated rather moderate catalytic activity. However, in this study the activity was observed at temperatures as low as 80 ° C, and by introducing elevated reaction temperatures, such as 140 °C, significant levels of conversion can be achieved. In addition, 3-pyridinecarboxaldehyde was obtained as the only product, without detection of acid formation. The acid, on the other hand, has been obtained in large quantities when water was used as a solvent.

Despite the fact, that the reaction is complicated, and difficulties are encountered mainly due to the possible poisoning of the catalyst, it can be concluded that the bimetallic catalysts are more active than monometallic ones. Once again, a synergistic effect has been observed.

6.3.2. Future work

An essential requirement for industrially employed catalysts is their stability and reusability. Pd leaching in the oxidation of 3-pyrididnemethanol was found to be around 2 %, however the catalysts have been reusable up to 5 times with gradual loss of activity. One possible cause for deactivation might be particle growth coupled with leaching. Calcination did not improve stabilisation of Pd. The fact that leaching has been limited in case of 0.75 % 0.25 %Pd/ TiO_2 (SIm) indicates that more work could be carried out to develop method of metals stabilisation. It has been suggested in the literature that sacrificially embedding Bi can shield Pd against leaching while maintaining access to the active sites.[13], [14] A similar procedure could be performed on the Au-Pd catalysts coupled with further optimisation of particles size and metal ratio. It was concluded that the reaction is less size sensitive, however if poisoning takes place then the effect of size is impossible to analyse. If there was possibility to introduce sacrificial protection without limiting the active sites, full catalyst optimisation would be possible.

Following that reasoning, a support study should be considered and performed in detail as perhaps they would enable designing more stable catalysts even at the expense of activity.

A Pyridine DRIFTS experiment could result in determination of active sites and would shed more light on the deactivation issues. Reacting pyridine with the catalyst would enable determination of whether N reacts with Pd leading to catalyst poisoning. XPS has been carried out on the fresh sample, however XPS of spent catalyst would enable detection of any carbon deposit leading to possible poisoning. This is important considering the incomplete carbon balance for these reactions. Moreover, this experiment would hopefully show any change in oxidation state of the metal leading to deactivation.

Finally, with comparison to Besson's work[13], 1 % Au-Pd/ TiO_2 catalysts could be tested for the other substituted pyridine- derivative alcohols to evaluate whether they are more active than the reference Pt-Bi/C catalysts.

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