STUDIES ON ALKANE OXIDATION USING TRANSITION METAL COMPLEXES

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BY
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UNDER THE GUIDANCE OF
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Certificate

This is to certify that, the work incorporated in the thesis entitled **“Studies on Alkane Oxidation using Transition Metal Complexes”** submitted by Mr. Makarand Madhukar Diwakar, for the degree of Doctor of Philosophy, was carried out by the candidate under my supervision, in the Chemical Engineering and Process Development Division, National Chemical Laboratory, Pune-411008, India. Such material as has been obtained from other sources has been duly acknowledged in the thesis.

Dr. R. M. Deshpande
(Research Guide)

April 2011
Pune

Declaration by the candidate

I hereby declare that the thesis entitled **“Studies on Alkane Oxidation using Transition Metal Complexes”** submitted by me for the degree of Doctor of Philosophy, to the University of Pune, is the record of work carried out by me under the guidance of Dr. R. M. Deshpande and has not formed the basis for the award of any degree, diploma, associateship, fellowship, titles in this or any other University or other institution of higher learning.

I further declare that the material obtained from other sources has been duly acknowledged in this thesis.

Makarand Madhukar Diwakar
(Candidate)

April 2011
Pune

Dedicated to

My Beloved Father

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Abstract of the Thesis

Title: "Studies on alkane oxidation using transition metal complexes".

The growth of the chemical industry is influenced by several factors like availability of feedstock, development of new competitive technologies and environmental acceptance, besides economics. Catalysis has played a vital role in developing new technologies as well as in providing solutions for environmental problems.

Catalysis is generally classified into two types depending on the nature of the catalyst employed viz, (a) Heterogeneous, in which the catalyst is immiscible with the reaction medium or present as a separate phase and (b) Homogeneous, in which the catalyst is soluble in the reaction medium. Catalytic reactions, using transition metals, both in the homogeneous and heterogeneous form have found diverse applications in chemical industries. Successful commercialization of many catalytic reactions such as hydroformylation, carbonylation, oxidation, hydrogenation etc. has proved the importance of catalysis, and will continue to gain more importance from environmental point of view. The motivation for further research in the field of catalysis is via the development of new selective, efficient and environmentally acceptable catalysts for industrial processes.

Oxidation is a core technology for converting petroleum-based materials to useful chemicals. Transition metal catalyzed oxidation of olefins, alcohols and alkanes is a convenient route for the synthesis of epoxides, diols, aldehydes, alcohols, and ketones and has great industrial potential for bulk chemicals as well as fine and pharmaceutical products.[1] However, oxidation is among the most complex processes. The major issues in oxidation reactions have been poor reaction rates and selectivity. Many textbook oxidation methods are unacceptable for practical synthesis, as the heavy metal oxidants form toxic wastes, while the known organic stoichiometric oxidants are usually very expensive.[2] Nitric acid, the most conventional industrial oxidant, is cheap but invariably forms various nitrogen oxides. Molecular oxygen, hydrogen peroxide or alkyl hydrogen peroxides can be the ideal choices for environmentally benign synthetic technologies with high atom economy for oxidation reactions.

The alkane oxidation reaction is an important route for the conversion of saturated hydrocarbons to corresponding secondary alcohols and ketones. These oxygen-functionalized alkanes find applications in various fields such as plasticizers, solvents, and as intermediates for biodegradable alcohol based detergents. The detergent range alcohols can be obtained via oxidation of C_{12}-C_{16} alkanes. Other routes to synthesize detergent grade alcohols are i) hydrogenolysis of fatty acid esters, ii) hydroformylation of olefins and iii) from petrochemicals by Ziegler alcohol process based on ethylene and aluminium alkyl catalyst. The alkane oxidation route if feasible, is more attractive as it employs an easily obtainable alkane feed stock and cheaply available oxidants, like air or oxygen.

A general view that can be drawn on the basis of the published results is that, alkali, alkaline and rare earth metals are mainly used for the selective oxidation of alkanes, but these metals need high reaction temperatures, i.e. above 400^0C and are ideal systems for obtaining acids. Transition metals, because of their high activity are used for the total combustion of alkane, particularly in emission control.[3] They are also used for the partial oxidation of cyclo alkanes under mild conditions.[4] However, no reports are available on the application of transition metal catalysts for partial oxidation of linear higher alkanes ($>C_{10}$). The development of metal complex catalysts operating under mild conditions for the oxidation of higher alkanes using molecular oxygen will be extremely attractive from industrial point of view.

From the available literature the following issues in the oxidation of alkanes stand out.

i) Use of stoichiometric oxidants needs to be avoided, as this is a major cost center. Use of stoichiometric oxidants other than hydroperoxides produce a number of byproducts in large quantities.

ii) Partial oxidation to alcohols/ ketones poses difficulties due to the tendency for over oxidation and difficult control over the reaction.

iii) Lack of detailed mechanistic studies on oxidation of alkanes, particularly with molecular oxygen.

iv) Scanty literature on oxidation of higher alkane, which is of industrial importance.

Considering the above facts, the present study was focused on the oxidation of alkanes using transition metal complexes. The main objective of this work was to develop a highly active and selective catalytic system for the oxidation of linear alkanes. Further to this, the development of immobilized catalyst systems for the oxidation of higher linear alkanes to achieve high activity, selectivity, and stability was also investigated. The mechanistic study of these reactions was also carried out for a deeper understanding of reaction system. For this study the following problems were chosen for the present work.

- Oxidation of alkanes using palladium metal complex catalysts. Synthesis and characterization of palladium complex catalysts, screening of catalysts to achieve high activity, selectivity for the oxidation of higher alkanes, followed by optimization of reaction conditions.
- Mechanistic study of the activation of alkanes with palladium catalysts and molecular oxygen as oxidant.
- Synthesis and characterization of novel heterogenized catalysts for the oxidation of alkanes. Screening of catalysts to achieve high activity, selectivity followed by the optimization of reaction conditions.

The thesis will be presented in four chapters, a brief summary of which is given below.

Chapter 1: Introduction and Literature Survey

Chapter 1 presents a detailed survey of the literature on the oxidation reaction. From the literature it is realized that, majority of the literature available on the use of molecular oxygen as oxidant is either on the oxidation of lower alkanes, mainly pertaining to the treatment of exhaust gases, which contain the alkanes in low concentrations, or oxidation of linear alkanes upto C_8, cycloalkanes and aromatic compounds. Most of these studies are invariably on the conversion and selectivity issues because over oxidation is common and the oxygenated products are more reactive than the substrate.

Use of transition metals as well as non transition metals as catalysts in the oxidation of alkanes along with various oxidants is reviewed in this chapter. Literature on use of metal oxides, rare earth oxides, heteropoly compounds and heterogeneous catalysts in oxidation of alkanes is also covered in this chapter. The techniques of heterogenization of homogeneous complex catalysts and its use in alkane oxidation are also reviewed in this chapter. A detailed survey on mechanism of alkane oxidation is also presented.

Chapter 2: Oxidation of alkanes using palladium metal complexes:

Chapter 2 presents the experimental results on the oxidation of alkanes using palladium complex catalysts. Various complexes of palladium were synthesized, characterized and screened for alkane oxidation using molecular oxygen. For this purpose, decane was chosen as a model substrate.

The Comparison of best-selected ligands from each screened ligand group is given in the Figure 1

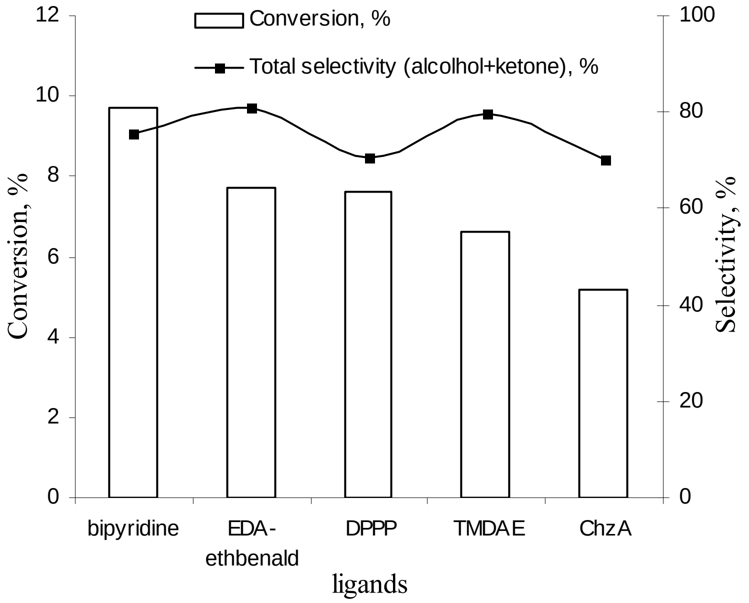

Figure 1: Comparison of best-selected ligands from each screened ligand group

The $PdCl_2Bipy$ was found to be the best catalyst for oxidation of alkane out of the various palladium complex catalysts screened.

The influence of the reaction parameters such as reaction temperature, reaction time, catalyst concentration, concentration of molecular oxygen, mode of molecular oxygen introduction has been studied. With the variation in reaction parameters the change in the rate of reaction was observed, however, no major influence was observed on distribution of alcohol and ketone in the product. The recycle study of the catalyst showed no change in the activity and selectivity of the catalyst.

Chapter 3: Studies on the mechanism of alkane oxidation using palladium metal complexes:

Chapter 3 presents the mechanistic study of activation of alkane based on the in situ FTIR studies using DRIFT.

The interaction of alkane with the palladium catalyst ($PdCl_2Bipy$, $PdBr_2Bipy$) was studied at 150ºC both, in the absence as well as presence of oxygen the chemisorption of alkane on catalyst surface in presence of oxygen stream was observed, which confirms the activation of oxygen as an initial step prior to activation of alkane.

The catalytically active and stable species 'C' was isolated from the reaction mixture and recycled. The structure of the initial complex and catalytically active species 'C' was determined using infrared spectroscopy in far and mid IR region. The disappearance of Pd-Cl bond and formation of Pd-O bond in the active catalyst was confirmed in far IR region.

The mid IR of the isolated species C showed a peak for OH group, for C-O, alkane The retention of oxidation state of Pd(II) was confirmed by ESCA. The XPS study of the used catalyst confirmed the oxidation state of Pd to be +2.

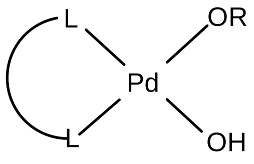

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Figure 2: The probable structure of the species 'C'

Based on this study it was proposed that the catalyst precursor A reacts with molecular oxygen replacing the halide ligands and forms species B. Species B reacts with alkane to form the catalytically active species C wherein the oxygen of the alkoxy group (OR) is bound to an internal carbon in the alkane. The position of the oxygen will thus dictate the location of the hydroxyl or ketonic function giving rise to the isomeric secondary alcohols and ketones.

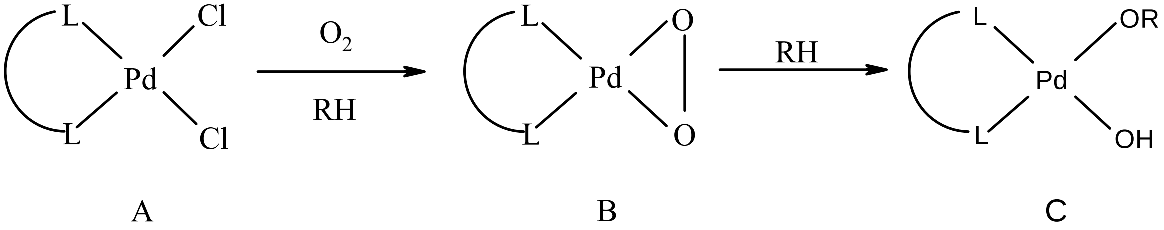

Figure 3: Proposed mechanism for the activation of the alkane

Based on the product profile a mechanism is proposed for the oxidation of alkane to the corresponding products

Chapter 4: Oxidation of alkanes using heterogenized catalysts:

Chapter 4 presents the synthesis, characterization and catalytic activity of novel hetrogenised catalyst for the oxidation of alkanes. The concept involves the precipitation of the water soluble palladium catalysts as it is insoluble Gr.2 metal (Ca, Sr or Ba) salt. This new concept of heterogenization is termed as ‘ossification’. The precipitation of the complex is also possible on porous supports and such catalysts are termed as ‘supported ossified catalyst’. This technique yields a highly dispersed catalyst with a much larger surface area. The supported ossified catalysts were characterized by powder XRD, SEM, TEM, EDX and XPS. The BET surface area, pore size and pore volume were also determined. The catalysts were tested for the oxidation of alkanes. The important feature of this catalyst was the improvement in the activity and selectivity for the oxidation of alkanes compared to the non-supported catalysts reported in chapter 2.

The catalyst was found to be stable and the activity and selectivity of the catalyst was maintained during several recycles. The ICP analysis shows negligible leaching to the organic phase even after five reuses. The ossified catalysts supported on SiO_2, Al_2O_3, ZrO_2, TiO_2, La_2O_3 and MgO also show good oxidation activity.

Typical results of decane oxidation reactions using ossified catalysts are given in Table 1.

Table 1: Results of screening of catalysts for decane oxidation reaction

Sr. No.	Catalyst concentration, mole	Conversion, %	Selectivity, %				TOF, h^{-1}
			Alcohols	Ketones	Lower alkanes	●Other products	
1	SOC-PdBD	8.54	40.98	45.44	7.97	5.09	305
2	Pd-TPP	5.71	42.43	41.55	10.34	4.95	386
3	SOC-PdSSA	4.55	39.39	38.55	12.37	8.63	179

Reaction conditions: decane- 25mmole, cat: (ossified 1% Pd)-0.100g, temperature - 150 ^{0}C, time- 5 hr, oxidant- O_2 in bladder ● other products- Esters of alcohols, lower acids, diketones, dialkyl ethers

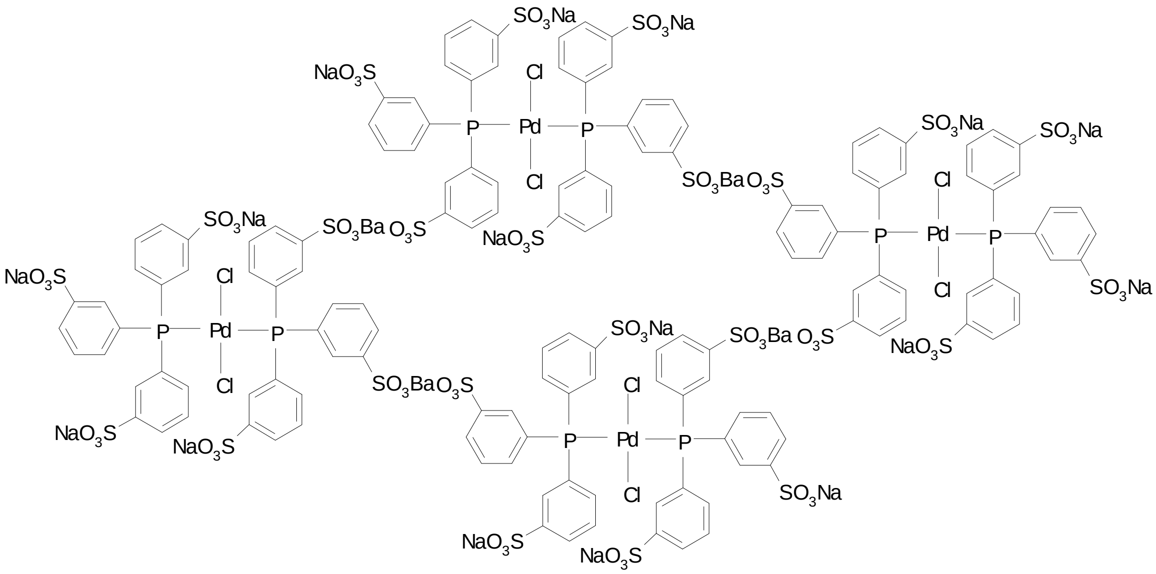

Figure 1: Ossified $PdCl_2$-TPPTS-Ba

The ossified Pd-TPPTS catalyst was recycled for five times with no loss in activity or selectivity.

Reference:

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Chapter 1

Introduction and Literature Survey

1.1 Introduction:

The growth of chemical industry is influenced by several factors like availability and type of feedstock, development of new competitive technologies and environmental acceptance, besides economics. Catalysis has played a vital role in developing new sustainable technologies as well as in providing solutions for environmental problems. In spite of the enormous development in catalytic chemistry, there is still a need of newer environmentally friendly processes, catalytic technologies for the efficient conversion of available feedstock to chemicals, and in the removal of pollutants and waste minimization, even today.

Catalysis is generally classified into two types depending on the nature of the catalyst employed viz, (a) Heterogeneous, in which the catalyst is immiscible with the reaction medium or present as a separate phase and (b) Homogeneous, in which the catalyst is soluble in the reaction medium.

1.1.1 Heterogeneous catalysts:

Heterogeneous catalysis has been the basis of a majority of the chemical processes so far, e.g. synthesis of ammonia, Ziegler- Natta polymerization, mineral oil processing etc.[1] Some of the general features of heterogeneous catalysts are, long catalyst life, easy catalyst-product separation and solid catalysts which facilitate a continuous mode of operation. However, compared to the homogeneous catalysts there are a few drawbacks in heterogeneous catalysts which are their poor selectivity, generally severe temperature and pressure conditions employed for the reaction and metal leaching, etc., which restrict the applications of heterogeneous catalysts in fine, pharmaceutical and specialty chemicals manufacture.

1.1.2 Homogeneous catalysts:

Homogeneous catalysis by soluble metal complexes has been practiced in industry for several years for a number of processes involving carbonylation, hydroformylation, hydrogenation, oligomerization, isomerization, polymerization and oxidation.[2] The unique features of these catalysts are high activity and selectivity under mild operating conditions, ability to activate substrates such as CO, hydrogen, olefins, alkanes, alcohols and plausible characterization at a molecular level. While the industrial potential of homogeneous catalysis was realized several decades ago with the development of catalytic processes like hydroformylation (oxo process), Wacker process, carbonylation of methanol to acetic acid (Monsanto process), and *p*-xylene oxidation to terephthalic acid, it is only in recent years that the true potential of homogeneous catalysts has become evident with widely expanding applications in the synthesis of fine chemicals, pharmaceuticals and specialty chemicals.

The main drawback of homogeneous catalysis is the separation of the catalyst and products, which is often a tedious task involving precipitation of the catalyst by adding nonpolar solvents, high vacuum distillation or extraction of products into a second phase. Consequently, only 20% of the industrial catalytic reactions involve homogenous catalysis, while 80% employ the classical heterogeneous catalysis involving supported metal catalysts

The motivation for further research in the field of catalysis is the development of new selective, efficient and environmentally acceptable industrial processes. Recent developments on new metal complexes, ligands, bimetallic systems, solid supports etc, indicate a strong potential of catalysis for new synthetic routes and economical processes for a wide variety of fine, specialty and pharmaceutical products.

Transition metal catalyzed oxidation of olefins, alcohols and alkanes is a convenient and environmentally benign route for the synthesis of epoxides, diols, aldehydes, alcohols, and ketones and has great industrial potential for bulk chemicals as well as fine and pharmaceutical products. The alkane oxidation reaction is an important route for the conversion of saturated hydrocarbons to corresponding secondary alcohols and ketones. These oxygen-functionalized alkanes find applications in various fields such as plasticizers, solvents, and as intermediates for biodegradable alcohol based detergents. The detergent range alcohols can be obtained via oxidation of C_{12}-C_{16} alkanes. Other routes to synthesize detergent grade alcohols are i) hydrogenolysis of fatty acid esters, ii) hydroformylation of olefins and iii) from petrochemicals by Ziegler alcohol process based on ethylene and aluminium alkyl catalyst. The alkane oxidation route if feasible, is more attractive as it employs an easily obtainable alkane feed stock and cheaply available oxidants, like air or oxygen. Several researchers have worked in this field on the development of catalysts, alternative routes, and reaction mechanism. The major issues in most cases were lower reaction rates, and poor selectivity.

Considering the issues mentioned above in the catalytic oxidation of alkanes the main objective of this thesis was to investigate the catalytic aspects of partial oxidation of alkanes to alcohols and ketones. Oxidation of linear alkanes, cyclic alkanes and alkyl aromatic compounds were chosen as reaction systems with the goal of understanding the performance of various catalytic systems followed by its mechanistic study and further heterogenization of the catalyst on solid inorganic supports.

This chapter presents a brief literature survey on oxidation of alkanes with respect to catalysis and reaction mechanism.

1.2 Oxidation reactions and processes based on oxidation reaction:

The functionalization of naturally occurring petroleum components via a reaction with air i.e. oxidation reactions, was naturally seen as the simplest way to derive useful chemicals. Therefore, the processes, which convert petroleum feedstocks such as alkanes, olefins, and aromatics into industrially important chemicals, are of great importance. Some notable examples of such processes are the oxidation of *p*-xylene to terephthalic acid and dimethyl terephthalate, oxidation of cyclohexane to cyclohexyl hydroperoxide, cyclohexanol and cyclohexanone, oxidation of cumene to cumene hydroperoxide, oxidation of *iso*-butane to *tert*-butyl hydroperoxide and *tert*-butyl alcohol, and oxidation of butane to acetic acid. Some of the commercialized processes based on oxidation reaction[3] are listed in Table 1.1

Table-1.1: Industrial oxidation processes

Product	**Primary raw material**	**Volume ($\times 10^6$ ton)**	**Oxidant / Reaction phases**
Ethylene oxide	Ethylene	2.9	O_2 / G
Propylene oxide	Propylene	1.4	ROOH / L
Acetone	Propylene	1.2	O_2 / L
Vinyl acetate	Ethylene	1.3	O_2 / L; G
Acrylonitrile	Propylene	1.4	O_2 / G
Methyl ethyl ketone	1-Butene	0.3	O_2 / L
Methyl methacrylate	Isobutene	0.5	O_2 / G
Acrylic acid	Propylene	0.5	O_2 / G
Terephthalic acid	*p*-Xylene	3.9	O_2 / L
Phthalic anhydride	*o*-Xylene	0.7	O_2 / G
Benzoic acid	Toluene	1.0	O_2 / L
Formaldehyde	Methanol	3.8	O_2 / G
Acetic acid	n-Butane/ Ethylene	1.8	O_2 / L
Maleic anhydride	n-Butane	0.3	O_2 / G
Adipic acid	Benzene	0.7	O_2 / L
Acetaldehyde	Ethylene	-	O_2 / L

The major developments in hydrocarbon oxidations have most often been motivated by the availability of feedstock and catalysis has played a major role in the development of such oxidation processes.

The synthesis of carbonyl compounds by direct oxidation of olefins is one of the most important and widely used processes in chemical industries. Use of homogeneous as well as heterogeneous catalysts in oxidation of olefins to aldehydes and ketones is very well-known. Oxidation of ethylene to acetaldehyde using aqueous solution of palladium and cupric chloride in presence of oxygen is known as Wacker reaction. The same system can also be applied to other olefins such as propene butene, styrene, cyclohexene, etc.

Oxiranes, particularly ethylene and propene oxides, are key raw materials for a variety of chemicals and polymers. The simplest oxirane, ethylene oxide is manufactured by vapor phase oxidation of ethylene with air or oxygen over a supported silver catalyst.[4] However for the production of propene oxide, molybdenum catalyst in presence of alkyl hydroperoxide is used.[5] Shell uses silica supported Ti catalyst for the production of the same.[6] The oxirane process, for the oxidation of propylene to propylene-oxide developed by Atlantic Richfield (ARCO), in the late 1960s, uses a co-oxidation principle. Oxygen is incorporated into the propylene molecule by reaction with a hydroperoxide, which is produced by a liquid-phase air oxidation of isobutane or ethylbenzene.[7] The utility of oxirane synthesis was further extended by a development of the titanium tartarate catalyst for the asymmetric epoxidation of allylic alcohols with tert butyl hydroperoxide (TBHP).[8]

Quinones and in particular, naphthoquinone derivatives are industrially valuable products, prepared by oxidation of corresponding arenes. In general, quinones are still prepared by using stoichiometric oxidants such as CrO_3/H_2SO_4, ceric ammonium nitrate or sulfate, manganese dioxide, etc. Attempts have been made to achieve these reactions catalytically, by using supported palladium and peroxyacetic acid,[9] or hydrogen peroxide (H_2O_2) in presence of transition metal catalysts.[10] However selective oxidation of arenes is still a challenge for catalysis research.

Catalytic oxidation of the aldehydes is an efficient and well-known route for the production of C_3-C_{10} carboxylic acids. The most effective catalysts for the liquid phase oxidation of aldehydes in presence of air, are the salts of Co, Cu and Mn.[11] The production of unsaturated acids such acrylic or methacrylic acid is done by vapor phase oxidation of the corresponding aldehydes utilizing heterogeneous catalyst systems such as Mo-V- Al-Cu oxides.[12]

Similar to the olefin oxidation, the selective oxidation of alcohols to the corresponding carbonyl compounds plays an important role in organic synthesis. New catalytic systems based on clean oxidants and effective catalysts, which are active over a broad range of alcohols, are reported for alcohol oxidation reactions. Aerobic oxidation of alcohols using a $RuCl_2(PPh_3)_3$ and 2,2',6,6'-tetramethylpiperidine-*N*-oxyl (TEMPO) is an effective catalyst for the conversion of a broad range of primary, secondary, and allylic alcohols to the corresponding aldehydes or ketones.[13] The titanium (IV)-silicalite (TS-1) catalyst developed by Enichem[14] also is a versatile catalyst for the alcohol oxidations with 30% aqueous hydrogen peroxide.

The discovery of the "Mid-Century" catalysts and the subsequent development of the Mid-Century (MC) process for the oxidation of *p*-xylene to terephthalic acid were in the period of 1950.[15] In terms of tonnage, the conversion of *p*-xylene to terephthalic acid (PTA) and dimethyl terephthalate (DMT) ranks as the largest among the oxidation processes. The oxidation of *p*-xylene using a catalyst system containing cobalt, manganese, and bromide (for example, cobalt acetate, manganese acetate, and hydrogen bromide) in acetic acid solvent, (composition around 10% water and 90% acetic acid) gives 90% yield of the final product. This combination offers a high activity and high selectivity over a wide temperature range.[3]

The liquid-phase oxidation of cumene is a unique example of "uncatalyzed" reaction that is being commercially practiced.[3] Typically, oxidation is carried out at around 135°C and a pressure of the order of 3-4 atmospheres at the top of the reactor. An optimized overall level of conversion is about 30%; above this level, the yield decreases because of side reactions associated with decomposition of the hydroperoxide to the carbinol, cleavage to acetophenone and methanol, etc.

The processes for the oxidation of cyclohexane are important for the manufacture of adipic acid, an intermediate for Nylon-6 and Nylon- 66. Today, practically the entire world output of adipic acid is via the liquid-phase oxidation (LPO) of cyclohexane by air, followed by the further oxidation of the products using nitric acid.[16]

Liquid phase oxidation of linear alkanes (C_{12-16}) is emerging as an important route for the manufacture of fatty alcohols. These alcohols have a lot of demand because of their use in the production of biodegradable detergents. The oxidation process contributes to a very small extent in the overall manufacture of detergent grade alcohols. Nippon Shokubai Ltd. in Japan uses the boric acid modified oxidation technology for the direct oxidation of alkanes.[17] The Bashkirov principle of using boric acid to produce alcohol esters of boric acid, and thereby gain alcohol selectivity, was first developed for the oxidation of *n*-paraffins as one of the routes to linear secondary alcohols in the C_{10}-C_{20} range. Atmospheric operation at 140-190°C, in the presence of about 0.1%

potassium permanganate and 4-5% metaboric acid, to conversion levels of 15-25% is used. The borate esters are later hydrolyzed with sodium hydroxide. The oxidation yields *sec*-alcohols almost exclusively, with a statistical distribution of OH groups, on the carbon chain.

1.3 Oxidation of alkanes:

The chemical industries use hydrocarbons as primary building blocks to produce chemical intermediates and polymers. Significant advances in the chemistry of the hydrocarbons have been made since the 1970s, which are particularly relevant to the development of low temperature, selective catalysts for functionalization of hydrocarbon.[18] Still there has been and continues to be intense interest in incorporating the C-H activation reaction into catalytic cycles to convert hydrocarbons to more useful functionalized products. However, to date, relatively few catalyst systems have been developed that allow the functionalization of C-H bonds in hydrocarbons and there are still lacunae in our fundamental knowledge on designing such catalysts.[19]

1.3.1 Alkane oxidation using homogeneous catalysts:

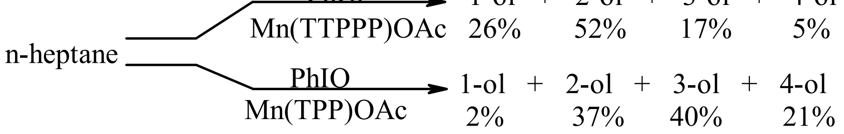
The development of coordination chemistry and catalysis has lead to increased success in the activation of various molecules, such as molecular hydrogen, olefins, aromatics, carbon monoxide, molecular nitrogen, etc. by metal complexes. For some time saturated hydrocarbons remained outside the purview of these processes because of the absence of double or triple bonds, lone pairs, and also due to the strength of covalent C-H and C-C σ-bonds in the alkanes. In spite of these difficulties, various catalytic systems were developed for the oxidation of alkanes using homogeneous catalysis.[20]

1.3.1.1 Oxidation of alkanes using chemical models of biological enzymes:

The construction of chemical models of biological enzyme for alkane oxidation is an established approach in the search for new ways for activation of alkanes and their functionalization.

The hydroxylation of C-H bonds of alkanes in almost all living organisms such as mammals, microorganisms, or plants is catalyzed by cytochrome P-450 dependent monooxygenases.[21] They are β-type cytochromes containing iron porphyrin complex in the active enzyme center. The cytochrome P-450 is able to catalyze the insertion of an oxygen atom into C-H bonds, double or triple bonds, aromatic rings, and heteroatoms of various substrates.[22] Similar to cytochrome *P*-450, ω-hydroxylases catalyzes hydroxylation of alkane, while the methane monooxygenases hydroxylate methane and its analogues. The most useful information derived from attempts to mimic enzymatic systems is that high oxidation state iron intermediates are the active sites for alkane oxidation.[23]

Iron porphyrins with single oxygen atom transfer reagents such as iodosylbenzene or organic peroxides, was one of the approach to develop the biomimitic catalytic system.[24] Groves et al.[25] first demonstrated that iron-meso-tetraarylporphyrins are able to catalyze the transfer of the oxygen atom of iodosobenzene into many substrates in a manner very similar to cytochrome *P*-450. For eg. alkane hydroxylation occurs with high isotopic effects,[26] retention of configuration of the C-H bond of cis-decalin,[27] and a preferential reaction on the tertiary C-H bonds. However, these porphyrins are not stable and get oxidatively destroyed during alkane hydroxylation. Major improvements in stability of these model systems were obtained by using tetraarylporphyrins containing halogen substituted aryl groups such as the pentafluorophenyl[28] and 2,6-dichlorophenyl[29] groups. More recently the even more robust Fe[tetrakis(2,6-dichlorophenyl)octabromoporphyrin]Cl complex was found able to hydroxylate norbornane with a 75% yield based on iodosobenzene and without loss of catalyst.[30] With the very hindered Mn(TTPPP)OAc, (acetate[tetrakis(2,4,6triphenyl)phenylporphyrin] Mn(III)) catalysts, the hydroxylation of linear alkanes occurs mainly in ω-1 position but also to a great extent in the ω-position.[31] The hydroxylation of the n-heptane catalyzed by the non hindered catalyst Mn(TPP)OAc, (acetate[triphenylporphyrin]Mn(III)) occurs mainly in the ω-2 and ω-1 positions but rarely in ω-position.



Eq. - 1

Other oxidants containing a single oxygen atom such as hypochlorite, $KHSO_5$, tertiary amine-oxides associated with Mn or Fe-porphyrin catalysts have led to results similar to those obtained with iodosobenzene.[32]

The most difficult substrate for the demonstration of regioselectivity by any catalyst are the n-alkanes, which lack any functionality or polarity with which the catalyst may differentiate one site from another. Only relatively modest, anisotropic differences in the shape of n-alkanes may allow for the distinction of one methylene from another, or, even more challenging, for the selection of terminal groups. In all cases involving modestly hindered metalloporphyrins (TTMPP) only very modest shape selectivity has been possible, and no significant production of primary alcohols was seen.[32]

Other biomimetic work concerned with the enzyme cytochrome P-450 has used molecular oxygen as the oxidant with sacrificial reductant to deliver the electrons normally supplied in the enzyme by NADH. Biomimetic alkane oxidation using iron porphyrins with dioxygen has been practically ignored and has been unsuccessful even with the use of expensive co-reductants mainly because the stoichiometric addition of electrons and protons to an operating catalytic alkane oxidation is not economically viable for the production of fuel additives or commodity chemicals. Even the use of the least expensive source of two electrons and two protons, i.e. molecular hydrogen, is economically unacceptable.[33]

$$RH + O_2 \xrightarrow[M^{n+}]{2H^+,\ 2e^-} ROH + H_2O \qquad \text{Eq.-2}$$

Another serious problem with biomimetic oxidation systems is their susceptibility to oxidative and thermal destruction. Although nature has the ability to replace and regenerate dysfunctioning proteins, no such mechanism is available in a commercial process based on an abiotic synthetic catalyst.

Activation and functionalization of alkanes to some extent using biomimetic organometallic complexes has been successfully achieved in the past few years. The developments in this field have demonstrated possibilities for new selective reactions that produce an interesting chemistry of alkanes. In spite of the ease of oxidation, biomimetic organometallic complexes have above mentioned drawbacks, which restricts their application.

1.3.1.2 Oxidation of alkanes by the Gif and Gif-Orsay systems:

The selective functionalization of saturated hydrocarbons under mild conditions became a stimulating research area in organic chemistry since the discovery of monooxygenases.[34] The existence of an enzymatic system in nature that could catalyze the monooxygenation of nonactivated carbon-hydrogen bonds has promoted the consideration that their organic counterparts could be developed. An ideal system for the oxidation of alkanes would be capable of regio and chemoselective oxidation under mild conditions. Thus the oxidation of the carbon-hydrogen bond calls for the presence of a reducing agent, protons, a catalytically active metal ion, oxygen, and a solvent.

Preliminary experiments with pyridine in the presence of iron powder, oxygen, and a carboxylic acid (acetic acid, tartaric acid, citric acid, etc.) possessed an unusual oxidizing power and attacked selectively secondary, not tertiary positions.[35] The optimum reaction temperature was 30^0C. Above 80^0C there is no oxidation reaction and below -20^0C, the reaction is very slow. A series of experiments were done to develop this system and the most developed one was called Gif III system. The oxidation of spherically symmetrical hydrocarbon adamantane showed a nonradical mechanism.[36] A series of oxidation reactions of adamantane in pyridine-acetic acid, using zinc as a reducing agent gave an efficient catalytic system (Gif IV) giving turnover numbers of over 2000.[37] These catalytic systems when tested for regio and chemoselective oxidation of trans-1,4-dimethylcyclohexane (a symmetrical hydrocarbon having primary, secondary and tertiary positions) gave mainly ketone, along with small quantity of aldehyde.[38]

Oxidation of cyclohexane and cyclohexene under Gif system showed little difference in the reactivity. Furthermore, cyclohexene was oxidized in the allylic position and no epoxidation was seen. When oxidation of cyclohexanol was attempted under similar reaction conditions, only 14% of ketone was observed, which indicated the pathway for ketone formation is not via alcohol formation. An important thing about the Gif system was the dependence of the selectivity ratio (C-2 / C-3), on the partial pressure of oxygen, where, C-2 is the total of the oxidation product formed at secondary carbon atom, and C-3 is the total of the oxidation product formed at tertiary carbon atom.[39] Using air instead of pure oxygen resulted in a higher C-2/C-3 for the oxidation of adamantane. The selectivity of the Gif system (secondary>> tertiary ~ primary) can be explained by a combination of C-H bond strengths (primary > secondary > tertiary) and steric resistance to insertion (tertiary > secondary > primary). The balance normally favors the secondary positions. Insertion into the tertiary position is seen only when the C-H bond is specially exposed.[38]

The most valuable members of this Gif family of catalytic oxidation systems are Gif ^{IV} [Fe(II) catalyst, dioxygen, Zn powder, in pyridine acetic acid], GoAgg ^{II} [Fe(III) catalyst, hydrogen peroxide in pyridine-acetic acid], and GoAgg ^{III} (GoAgg ^{II} + picolinic acid). Although less important, the Gif ^{III} system involves Fe powder and dioxygen, in pyridine-acetic acid. These iron-based models are able to activate saturated hydrocarbons in quantitative yields at l0-25% conversions. Ketones are the major product of the reaction. Ketone to alcohol ratios ranges between 15:l (for Gif ^{IV} reactions) to 4:1 (for GoAgg ^{II} reactions).[40]

The main features of all Gif systems are: i) the oxidation of secondary C-H bonds occurs mainly to ketones, alcohols are not reaction intermediates; ii) the excess of alcohols or other easily oxidizable compounds does not suppress significantly the oxidation of alkane iii) cyclic olefins are not epoxidized, but yield conjugated ketones iv) the selectivity order for C-H bonds is secondary > tertiary > primary v) secondary alkyl radicals are not intermediates in the activation process; the reaction proceeds smoothly, even in the presence of different radical trapping reagents (which do not interfere with the activation process but yield functionalized hydrocarbons).[41]

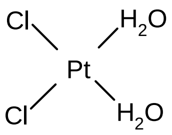
The GoChAgg system, employing a Cu(II) catalyst, $Cu(Cl_4)_2.6H_2O$, catalyzes ketonisation of saturated hydrocarbons in pyridine by hydrogen peroxide. GoChAgg system was then modified by substituting $Cu(Cl_4)_2.6H_2O$ with $Cu(OAc)_2.H_2O$ and by adding acetic acid.[41] By analogy with the Gif^{III} system [Fe^0, dioxygen, pyridine-acetic acid solution] the activation of saturated hydrocarbons coupled to the oxidation of copper powder by dioxygen (1 atm) in pyridine-acetic acid. It was observed that cyclohexane is efficiently oxidized to cyclohexanone and cyclohexanol.

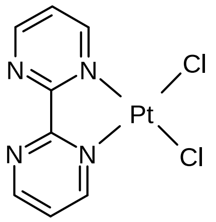
1.3.1.3 Oxidation of saturated hydrocarbons using organometallic complexes:

In last few decades, new methods of alkane functionalization with the participation of various transition metal complexes have been discovered and developed.[41] In 1970s Goldshleger[42], showed that platinum (VI) complexes catalyze the oxidation of alkanes. These are the first examples of alkane functionalization catalyzed by homogeneous complexes. Further investigations on alkane oxidation in the presence of platinum complexes were conducted in several research groups (Garnett et. al.[43], Webster et. al.[44], Rudakov et. al.[45], Shilov et. al.[46]). Following these reactions a number of new reactions of alkanes have been discovered in solutions of organometallic complexes of metals. Some of them are hydromethylation of carbon monoxide to acetaldehyde and to ethyl methyl ketone in presence of ethylene. [47]

$$\begin{aligned} CH_4 + CO &\longrightarrow CH_3COH \\ CH_4 + CO + C_2H_4 &\longrightarrow CH_3COC_2H_5 \end{aligned} \qquad \text{Eq. - 3}$$

The stability of the metal complex in highly acidic, oxidizing and high temperature conditions is the main problem in alkane oxidation reaction, which was well addressed by tailoring of ligands. The Shilov system,[48] which is catalytically unstable due to irreversible decomposition of Pt complex to Pt metal, or due to insoluble, polymeric Pt salts such as $(PtCl_2)_n$, becomes a stable one when used with bipyrimidine (bpym) ligand, $Pt(bpym)Cl_2/H_2SO_4$ system is stable and active for the conversion of methane to methanol in concentrated sulfuric acid and gave yield of over 70% methanol (based on methane) with selectivity of >90% and turnovers of >300.





Many researchers then suggested the catalytic systems to overcome the degradation or decomposition of the catalysts. Fish et al.,[49] used 2,2'-dipyridyl (dipy), a relatively oxidation resistant ligand and prepared dipyridyl-substituted manganese cluster complexes for oxidation of CH_4, C_2H_5, and C_6H_{12} using t-BuOOH as an oxidant. Crabtree et al.,[119] also developed a $[Mn_3O_4(dipy)_4(OH_2)_2](ClO_4)_4$ cluster for the oxidation of alkanes, alkenes, and alkylated arenes with alkyl hydroperoxides in CH_3CN, which gives up to 700 turnovers/h at 0^oC.

Komiya et al.,[50] examined highly stable metal phthalocyanine (Pc) complexes for the aerobic oxidation of cyclohexane, hexane, indane in the presence of acetaldehyde, at room temperature. They found that the catalytic activity of Pc complexes is strongly dependent upon both central metal and ligand. In general, the Fe, Co, Mn, and Ni complexes with substituted Pc ligands show better catalytic activity. The corresponding Mg(II), Zn(II), Sn(II), and Al(III) complexes show no catalytic activity. Haloganated Pc ligands favored the reaction due to enhancement of robustness of the ligands during reaction. Conversion of 20% with almost 50% selectivity to alcohol and ketone respectively was achieved for cyclohexane and around 6% conversion with 16% and 33% yield of alcohols and ketones was obtained for hexane oxidation. The maximum TON obtained was up to 11000. The oxidation of alkanes with $KHSO_5$ was also reported in the presence of water-soluble metal phthalocyanines.[51]

Rh and Ru complex catalyzed oxidation of saturated hydrocarbons to alcohols, ketones, and acids is well reported in the literature.[52] Brian et al., have reported the rhodium phosphino complex catalysts for the aerobic and anaerobic oxidation of hydrocarbons.[120] Sen et al., showed that $RhCl_3$, in the presence of several equivalents of Cl^- and I^- ions, catalyzes low temperature ($<100^0C$), hydroxylations and hydroxycarbonylations of C-H and C-C bonds in lower alkanes with dioxygen as the oxidant. $RhCl_3$ at $80\text{-}85^0C$ in a 6:1 mixture of perfluorobutyric acid and water catalyzes direct formation of methanol and acetic acid from methane, carbon monoxide, and dioxygen, (approximate turnover rate: 2.9/h based on Rh). They also showed that it is possible to selectively form either methanol or acetic acid by a simple change in the solvent system. It was found that ethane is more reactive than methane, and under similar reaction conditions formed methanol, ethanol, and acetic acid (approximate turnover rate: 7.5/h based on Rh),[53] when propane was used as the substrate, a mixture of *n*- and isopropyl esters and acetone were formed, in addition, significant quantities of acetic acid, ethanol, and methanol derivatives were formed through C-C cleavage. With n-butane as a substrate, C-C cleavage was predominantly observed, giving following products, $C_3F_7CO_2CH_2CH_3$, CH_3CH_2OH, CH_3CO_2H, CH_3CHO, $C_3F_7CO_2CH_3$, CH_3OH, and HCO_2H. The overall yield was 85.0% based on carbon content of *n*-butane.

Kuwabaraa et al., [54] examined the catalytic activity of various metal complexes for the oxidation of n-decane with TBHP. They found that $RuCl_2(PPh_3)_3$ and $RuH_2(PPh_3)_4$ are good catalysts for the formation of decanones and decanols. $RuCl_2(PPh_3)_3$ gives around 28% conversion of decane with around 40% combined selectivity of corresponding alcohols and ketones. The use of other catalysts such as $RuCl_3.nH_2O$, $RuCl_2(bpy)_2$, $Ru_3(CO)_{12}$, and $RhCl(PPh_3)_3$ gave unsatisfactory results. The effect of oxidants when examined for the oxidation of n-decane in the presence of $RuCl_2(PPh_3)_3$ catalyst, alkyl hydroperoxides such as TBHP and cumyl hydroperoxide gave good results. Other oxidants such as hydrogen peroxide, m-chloroperbenzoic acid, sodium hypochlorite, iodosyl benzene, and N-methylmorpholine N-oxide are ineffective for the decane oxidation reaction.

Co, Mn, and Br and salt of Ru(III), Rh(III), Ir(III), Pd(II), Pt(II), as a cocatalyst are well reported for the oxidation of alkyl aromatics to corresponding carboxylic acids.[55] Use of Pd, Rh, or Pt for the selective oxidation of methane to methanol or formaldehyde at elevated pressures is also well documented.[56]

Meyer[57] Takeuchi,[58] and Che[59] studied ruthenium metal complexes with polypyridyl ligands for the catalytic oxidation of organic compounds with dioxygen and showed that these complexes form stable ruthenium oxo species, $(Ru(O))^{2+}$ and $(Ru(O)_2)^{2+}$, which are good metal oxygen atom-transfer reagents for numerous substrates.[60] These highly oxidized species catalyze hydroxylation of alkanes under O_2 atmosphere. Mechanistic studies, performed showed that a high-valent ruthenium oxo species rather than a peroxo species as the probable oxidant; radical trapping experiments with benzoquinone inhibited the reaction, indicating a radical mechanism.[61]

Hirobe et al.,[62] showed that in the presence of small amounts of HCl or HBr, the catalytic property of the ruthenium porphyrins for the oxidation of alkanes or alkyl alcohols with pyridine N-oxides, enhances drastically. With 2,6-dichloropyridine N-oxide as the oxidant and $RuTMP(O)_2$, TMP-(tetramesitylporphyrinato) as the catalyst, (room temperature, under argon atmosphere, 24 h), almost 100% conversion of adamantane took place with the formation of adamantan- 1-ol, adamantane-l,3-diol, and adamantan-2-one in yields of 68%, 25%, and 1% based on adamantane, respectively. In contrast, without the addition of these acids, only a 4% yield of oxidation products was obtained and most of the adamantane remained intact after the reaction for 24 h. With this system oxidation of ethylbenzene gave almost 88% acetophenone, while 1-methylcyclohexanol was selectively obtained in the oxidation of methylcyclohexane with 94% yield. RuTMP$(CO)_2$ is more effective catalyst, compare to the RuTMP$(O)_2$, as it catalyzes adamantane oxidation more faster, completed it in 6 h compare to the 24 hr for RuTMP$(O)_2$**.** According to the authors HCl or HBr plays two roles in this system. The first is to convert the dioxo or CO complexes of ruthenium porphyrins into the appropriate catalytic complexes, and the second is to accelerate the deoxygenation of N-oxide by ruthenium porphyrins or to enhance the reactivity of generated active intermediates.

The Catalyst methyltrioxorhenium (MTO),[63] efficiently oxidizes alkanes in the presence of pyrazin-2-carboxylic acid. Metal-catalyzed alkane oxidations in solutions give directly valuable products such as alkyl hydroperoxides, alcohols, ketones, and carboxylic acids under mild conditions.[64]

Although iron plays an extremely important role in oxidations occurring in living cells and methanemonooxygenase (MMO), iron complexes and especially simple salts of this metal do not usually exhibit high activity in oxidations. Iron complexes (especially polynuclear derivatives) containing N-ligands are more powerful catalysts. The H_2O_2–$FeCl_3$–bipyridine system in acetonitrile efficiently oxidizes alkanes predominantly to alkyl hydroperoxides. (Turnover numbers attain 400 after 1 h at 60^0C).[65] Martell et al.,[66] developed, iron(II) complexes of macrocyclic ligands. (L24), 24 membered macrocycle containing phenol, pyridine and amino donor groups, and (L30), a 30-membered macrocycle containing phenol, bipyridine, and amino donor groups, for the effective oxidation of cyclohexane and adamantane, with H_2S as a two-electron reductant. The oxidation of cyclohexane gave cyclohexanol and cyclohexanone. The turnovers were 24.4 after 6 h for the L24 complex and 21.4 after 6 h for L30 complex.

Mayer and co-workers[67] described stoichiometric and catalytic oxidations of alkanes with OsO_4. This osmium derivative has been used as a catalyst in oxidation of isobutane with $NaIO_4$ in aqueous solution (pH ~ 4.3; 168 h at 85^0C), with the TON being only 4. A carbonyl osmium(0) complex with π-coordinated olefin, (2,3-g-1,4-diphenylbut-2-en-1,4-dione), efficiently catalyzes oxygenation of alkanes (cyclohexane, cyclooctane, n-heptane, isooctane, etc.) with hydrogen peroxide, as well as with tert-butyl hydroperoxide and *m*-chloroperoxybenzoic acid in acetonitrile solution. Alkanes are oxidized to corresponding alcohols, ketones (aldehydes) and alkyl hydroperoxides. Thus, heating cyclooctane with the above catalyst–H_2O_2 combination at 70^0C gave products with turnover number as high as 2400 after 6 h. The maximum obtained yield of all products was equal to 20% based on cyclohexane and 30% based on H_2O_2.[68]

Shulpin et al.,[69] studied n-heptane oxidation using *n*-Bu_4NVO_3 with aqueous 30% as well as anhydrous hydrogen peroxide in acetonitrile at room temperature. In aqueous hydrogen peroxide the internal peroxides obtained after 24 h have 86% selectivity and did not decompose under reaction conditions. The internal alcohols and carbonyls formed had 4% and 10% selectivity, respectively. The total turnover number was 282 with 6% n-heptane conversion. Using anhydrous hydrogen peroxide, conversion of n-heptane increased to 13.5% and the selectivity for the hydroperoxides was reduced to 71%. The turnover number was 623.

Sulman,[70] has cited the effect of ultrasound on the liquid-phase oxidation of *n*-tetradecane at 115^0C in the presence of 0.3% cobalt stearate as a catalyst. Ultrasound appears to increase the production of oxygenated compounds by 15-30%. The maximum acceleration of the oxidation is reached at a frequency of 300KHz. The oxidation rate under these conditions does not vary with time, whereas it shows a maximum in the absence of ultrasound (silent reaction).

1.3.2 Alkane oxidation using heterogeneous catalysts:

Selective oxidation reactions catalyzed by heterogeneous catalysts are of great industrial significance, especially for the production of bulk organic chemicals. Heterogeneous catalysts used for oxidations are often based on active species (notably transition metals, metal ions or metal complexes) adsorbed on supports (such as carbon, aluminas, silicas, zeolites, clays and ion exchange resins).[71] Chemically modified support materials offer great scope for the development of new catalysts.[72]

Oxidation of ethane to acetic acid using titania-supported vanadium phosphorus oxide (VPO) catalysts,[73] propane to acrylic acid using mixed-metal oxides such as MoVNbTe[74] and MoVNbSb,[75] the conversion of *n*-butane to maleic anhydride over (VPO) catalysts are some examples of well-established commercial processes.[76]

1.3.2.1 Alkane oxidation using solid supported metal catalysts:

Use of mixed metal oxides for the selective oxidation of alkanes is well studied area in catalysis. Use of heteropolyacids and their polyoxometalate derivatives have been extensively studied for many different catalytic applications. Polyoxometalates and phosphomolybdates, in particular, have been extensively investigated for the selective oxidation of light alkanes.[77] Most of these studies have focused on the effect of different exchange cations or the incorporation of different amounts of vanadium in the polyoxometalate structure. Ueda and Suzuki,[78] demonstrated that a molybdovanadophosphoric acid (denoted as $PMo_{11}V$) treated with pyridine resulted in an active and selective catalyst for the conversion of propane to acrylic acid. Subsequently, Li and Ueda[79] found that treating molybdophosphoric acid (denoted as PMo_{12}) with pyridine and then activating in nitrogen at 420^0C improved activity for the selective oxidation of propane to acrylic acid. Holles et al.,[80] showed that niobium and pyridine-exchanged salts of molybdophosphoric acid and molybdovanadophosphoric acid ($NbPMo_{12}pyr$ and NbPMo11Vpyr) are active and selective catalysts for the selective oxidation of propane to acrylic acid and *n*-butane to maleic acid.

The oxidation of *n*-hexane in presence of molecular oxygen has been carried out in the temperature range of 150–200^{0}C by Thomas et al.,[81] using cobalt and manganese deposited on aluminophosphate zeolite (Co-$AlPO_4$). No isomerization or cracking of alkanes were observed, and the oxidation products were mainly alcohols, acids, aldehydes and ketones of *n*-hexane. The main disadvantage of this catalyst is the extremely low conversion of n-hexane. Similar results were obtained for oxidation of *n*-pentane and *n*-octane with this catalyst. In the temperature range of 200–350^{0}C, the $LaMO_3$ (M: Mn, Fe, Co) perovskite catalyst[82] and Pt, Ni/Al_2O_3 in the temperature range of 350–500^{0}C have been used for total combustion of *n*-hexane.[83] Molecular Sieves (SAPO-5, SAPO-11, BEA and MCM-41) have been used for partial oxidation of n-heptane in the temperature range of 300–400^0C and the products formed are 2,3- and 4-heptanones and hetrocyclic compounds (cyclohexanol, benzyl alcohols, furans and pyrans).[84]

Stoylkova et al. studied the activity of SAPO-5, SAPO-11, BEA and MCM-41 for the partial oxidation of *n*-heptane by air at 250^0C and 300^0C.[85] The main products of *n*-heptane partial oxidation in the presence of air were 2-, 3- and 4-heptanones, 2-methyl-5-ethyl-furan, 2,6-dimethyl-pyran, 1-hepten- 4-ol and branched dienes. The authors found that SAPO molecular sieves are more active than BEA and MCM-41 when compared the conversions of *n*-heptane. SAPO gave 49.3% conversion of n-heptane with around 4.5% of heptanone, 32.5% of heterocycles, 12.3% of dienes, and 3.03% of coke, no formation of heptanols was observed.

Among the catalytic oxidation systems for the deep oxidation of alkanes to carbon monoxide, carbon dioxide, and water in aqueous medium using dioxygen as the oxidant that have been studied most extensively are the TiO_2-catalyzed photooxidations[86] and the "Fenton" systems involving H_2O_2 and a soluble transition metal catalyst.

1.3.2.2 Alkane oxidation using heterogenized catalysts:

Immobilization of transition metal catalysts on solid supports facilitates easy handling and recovery and could result in improved activities and selectivities through support effects.[87] Metal complexes of porphyrins, salens, phthalocyanines, etc. have been heterogenized using various supports like clays, [200] microporous silica,[88] mesoporous zeolites[89] and polymers. [90]

Assis et al.,[91] have reported the heterogenization of $Fe(PCl_8)Cl$, on aminopropylated silica and oxidation of cyclohexane and adamantane by iodosylbenzene and hydrogen peroxide. The supported poly-halogenated iron porphyrin was less efficient as a catalyst than the homogeneous analogue. This is probably due to the increase in steric hindrance of the catalytic site on the support that restricts the access of the oxidant and substrate to the iron center. [149]

A Schiff base [1,2-bis(salicylidine amino)-phenylene] cobalt complex catalyst bonded to carbamate modified silica gel, oxidizes alkanes using molecular oxygen at moderate reaction conditions and gives an entirely different product distribution.[92] The oxidation of *n*-hexane gives isomerization and dehydrocyclization along with low oxygenated products. As opposite to this, the *n*-heptane oxidation gives, only oxygenated products without any cracking or isomerization. The oxygenated products for this case were found to be 4-heptanone, 2-heptanone, 2-heptanol and 1-heptanoic acid with selectivity of 8.4, 33.6, 16.3 and 6.3%.

Use of heterogeneous catalysis for shape selective oxidation is an approach with much promise. There are two classes of catalysts in this area. First, the microheterogeneous systems that utilizes micelles or lipid bilayers to achieve a steric isolation of the catalytic center, and second, microporous solids with interior catalytic sites.

A number of researchers have incorporated porphyrins into micellar or bilayer structures to induce shape selective oxidation. Shilov and co-workers used long-tailed iron porphyrin complex tetrakis(4-hexadecyloxphenyl)porhyrin, (T(4-HDP)P), incorporated into Triton X-100 micelles or phospholipid vesicles to hydroxylate hexane. The preference for hydroxylation to give 2-hexanol in both the cases was good but terminal hydroxylation occurs only to a limited extent. Several other groups have also incorporated metalloporphyrins into lipid bilayer vesicles for both O_2 binding, oxidations, and for epoxidation.[93] In most of the systems selectivities are not very high and removal of product from the active site is also difficult, which limits the catalytic utility of such systems.

Oxidation of olefins, alkanes and alkyl benzenes in the cages of zeolites NaY, CaY, BaY, KL and BaL by oxygen at room temperature is well documented.[94] Auto-oxidation of cyclohexane to hydroperoxide and its decomposition to cyclohexanol and cyclohexanone with Y zeolites at relatively low temperature (150^0C) and under pressure (1.0MPa) gave around 3.5% conversion of cyclohexane.[95] Cyclohexane was dehydrogenated to cyclohexene and then oxygenated to cyclohexanone and cyclohexene-2-one by air in the presence of mesoporous MCM-41molecular sieves.

Various workers have recently begun an exploration of the use of modified zeolites as shape-selective heterogeneous catalysts for hydrocarbon oxidation.[96] In one study, an iron phthalocyanine was synthesized in situ within a large pore zeolites and examined as an alkane hydroxylation system.[97] No terminal hydroxylation was observed, but due to the incorporation into the zeolite, the stability of the complex improved, compared to iron phthalocyanine.

Fe(II)/Pd(II) exchanged zeolite 5A catalysed hydroxylation of alkanes in the presence of H_2/O_2 mixture.[98] Good shape selectivity was observed for the product formed within the zeolite. The primary selectivity index for terminal hydroxylation of octane was extremely high [0.54 to 0.67 vs 0.53 for MnTTPPP(OAc)]. If larger pore zeolite is used (such as ZSM-5), the products can be removed without zeolite dissolution, but the selectivities are reduced. However this approach has a tremendous potential for future industrial application.

The oxidations with phthalocyanine catalysts are limited to the reactions with peroxides in the presence of heterogeneous, immobilized metal phthalocyanine catalysts. T*ert*-butylhydroperoxide and iodosylbenzene have been used for the oxidation of alkanes in the presence of zeolite-encapsulated metal phthalocyanines,[99] iron complex embedded in a polymer membrane,[100] MCM-41 supported metalphthalocyanines,[101] and activated carbon black supported metalphthalocyanines.[102]

Cationic metalloporphyrins (MePs) have been studied as catalysts for the oxidation of a wide range of substrates.[103] However, their use in homogeneous systems is restricted as they are prone to oxidative self-destruction. One way to obtain efficient, selective and easy-to-recover cationic MePs for oxidation of organic substrate is the combination of electron withdrawing substituents in the porphyrin ring with catalyst immobilization on inorganic matrices.[104] A new approach consisting of MeP encapsulation in a size- and shape-selective mineral matrix framework such as zeolites, using the ship-in-a-bottle approach has been demonstrated.[105] Nakamura et al., [106] were the first to describe how iron III and manganese III 5,10,15,20-tetramethylporphyrin complexes could be synthesised within the cages of NaY zeolite and the catalytic activity of these materials in the oxidation of saturated hydrocarbons with hydrogen peroxide. More recently, the synthesis of a faujasite-Y confined MeP, and its catalytic activity in the oxidation of cyclohexene has been reported.

Heterogeneous catalysts, normally employed at elevated temperatures, are able to affect the oxidation of alkanes with air or oxygen but promote deeper oxidation to products such as carboxylic acids, anhydrides, CO_2, water etc.[107]

A literature survey on use of metal complex and oxidant in alkane oxidation is given in the Table 1.2

Table1.2: Metal complex / oxidant used in alkane oxidation

Sr. No.	Substrate	Oxidant	Catalyst system	Product	Ref.
1	Saturated paraffin oil	Air, O_2	Non catalytic and in presence of salts of Cu, Fe, Ni, Zn, Pt, Pb, NiO, CuO	CO, CO_2, peroxides, ketones, acids, (no alcohol)	108
2	Paraffin	Dry air	Non catalytic 140-160^{0}C	Alcohol, acid, ketone, peroxides	109
3	Decane,	O_2, air,	Non catalytic, 150^{0}C	Alcohol, ketone	110
4	C_{17}-C_{28} n-alkane	Air	0.07-0.1 wt.% KX-MX_4 (X = 1/2O_2, OH, fatty acid residue; M = Ti, Zr, Hf) at 115-22° C	23.9-38.7% fatty acids	111
5	C_{12-35} alkanes	Air	a) $KMnO_4$, b) NH_4VO_3, Cu, 70 wt.% HNO_3, at 80-85°C	a) 42 mol% conversion, 39 mol% selectivity to monocarboxylic acids, b) 75 mol % selectivity to monocarboxylic acids	112
6	C_{10}-C_{14} n-alkanes	O_2	Co naphthenate, at 140°C	Monocarboxylic acids	113

Sr. No.	Substrate	Oxidant	Catalyst system	Product	Ref.
7	C_{12-14}, n-alkanes	Gaseous mixture. of NH_3 0.01, O_2 3.5, and N_2 96.5 vol. %	HBO_2 2.5g, and Ti (>325 mesh) 2.5 g 170°C	82.5% selectivity for the alcohols and 16.4% conversion	114
8	Hydrocarbons	Air	0.075-0.12% Co and/or Mn C_6-C_{12} α-hydroxycarboxylate and 0.04-0.06% Na and/or K α-hydroxycarboxylate, At 120-140°C	Fatty acids	115
9	Linear alkanes	Air in presence of 4 volume % O_3	Mixed K and Mn salts of C_{5-9} monocarboxylic acids and a mixed K-Mn^{3+} acetylacetonate	Carboxylic acids	116
10	C_4-C_{10} n-alkanes	O_2	H_3PO_4, V_2O_5, MoO_3, $CuCl_2.2H_2O$, NiO, $CoCl_2.6H_2O$, CrO_3, $BaCl_2.2H_2O$, CeO_2, Nd_2O_3, Y_2O_3, and Sm_2O_3. at 395°C	Corresponding anhydrides butane- maleic anhydride	117
11	C_{10}-C_{40}	O_2-contg. Gas	Cr, Mn, and an alkali metal in the form of oxides and salts at 100-160°C	Aliphatic acids	118

Sr. No.	Substrate	Oxidant	Catalyst system	Product	Ref.
12	C_{11-23} n-alkanes	Air	Cr-naphthenate, K- naphthenate	Corresponding carboxylic acids	119
13	Ethane	O_2, HCl	$AgMn_2O_4$ at 350°C	Acetaldehyde and acetic acid 2.7 mol % conversion, 42% selectivity to acetaldehyde and 15% acetic acid	120
14	Cyclohexane,	O_2	Mn(TPP)(Cl) ascorbate as a reducing agent	Alcohol, aldehyde,	121
15	Hexane Cyclohexane Benzyl alcohol	Air	Mn(TPP)(Cl) (TPP = tetraphenylporphyrin dianion) phase-transfer agent-[Me(CH2)7]3N+Me Cl- ascorbate as a reducing agent	1-hexene gave 30% 1,2-epoxyhexane, cyclohexane gave 40% cyclohexanol and 30.0% cyclohexanone, and $PhCH_2OH$ gave 87.00% PhCHO	122
16	Adamantane, EB, methyl cyclohexane	2,6 dichloropyridine N-oxide	$RuTMP(O)_2$ TMP: tetramesitylporphyrinato	Corresponding alcohols and ketones, HCl or HBr is used as an additive	123

Sr. No.	Substrate	Oxidant	Catalyst system	Product	Ref.
17	ethane, cyclohexane	Air	CrO+	Alcohols, less than 40%, olefins	124
18	Hexane, cyclohexane, Toluene,Ethyl benzene	Air, O_2	$FeCl_3$, Under UV-Visible light	Ketone, alcohol	125
19	cyclohexane, hexane, ethylbenzene, toluene, styrene	O_2, air	$CuCl_2$	Corresponding alcohols and carbonyl compounds	126
20	Cyclic, alkyl substituted, olefins	TBHP	Cluster $[Mn_3O_4(dipy)_4(OH_2)_2](C1O_4)_4$	Corresponding alcohols and ketones	127
21	cyclohexane, hexane, toluene ethylbenzene,	Air	anhydrous $CuCl_2$, photochemical oxidation	Alcohol, ketone	128
22	Alkane, olefin	O_2	$RuCl_2(H_2O)^{4+}$	Alcohols, ketones	129

Sr. No.	Substrate	Oxidant	Catalyst system	Product	Ref.
23	Alkanes	Molecular oxygen, aldehyde	Iron powder	Corresponding alcohols and ketones, Acetic acid used in catalytic amount in dichloromethane at RT	130
24	cyclohexane, pentane,hexane, heptane, 3-methylhexane	Air	$FeCl_3$, in alcohol as solvent	Alcohols, ketones	131
25	Linear, cyclic, aryl alkyl alkanes	TBHP	$RuCl_2PPh_3)_3$	Corresponding alcohols and ketones, maximum 28% conversion for decane with around 40% yield	132
26	Adamantane, ethylbenzene, and cyclohexane	O_2	PW_9-Fe_2Ni heteropolyanion	Alcohols and ketones	133
27	n-pentane, n-hexane	O_2	VO^{2+} Schiff's base modified silica	Alcohols, and acids with	134

Sr. No.	Substrate	Oxidant	Catalyst system	Product	Ref.
28	Linear, cyclic, alkyl aromatic	30% solution of peracetic acid in ethyl acetate	Ru on charcoal	Main oxidation product ketone with alcohol in minor amount, at RT in ethyl acetate solvent, oxidizes all alkanes	135
29	cyclohexane	TBHP	μ-oxo dinuclear Fe or Mn complexes	Cyclohexanol and cyclohexanone with almost 1:1 ratio	136
30	Methane, ethane	O_2	Cs–M/SiO2 catalysts (M = Fe, V, Bi).	Formaldehyde, Acetaldehyde, acroline around 60% selectivity at 4-5 % conversion	137
31	Cyclohexane	TBHP, peracetic acid, air	$CuCl_2$/ crown ether, $CuCl_2$ /crown ether/alkaline metal salt	Ketone, alcohol	138
32	Cyclohexane	O_2/ aldehyde	nanostructured iron and cobalt oxides and iron oxide supported on titania	ketone	139
33	Cyclohexane, decane	TBHP, O_2/aldehyde	Cu/Co-perchlorophthalocyanine immobilized MCM-41	Around 12-15% conversion with selectivity to ketone	140

Sr. No.	Substrate	Oxidant	Catalyst system	Product	Ref.
34	Lower alkanes	O_2	Niobium and pyridine-exchanged molybdophosphoric acid (NbPMo12pyr) and molybdovanadophosphoric acid (NbPMo11Vpyr)	Corresponding acids	141
35	Adamentane, n-pentane,	iodosylbenzene and hydrogen peroxide	Fe(PCl$_8$)Cl,	Selectivity to oxidation of alkane	142
36	Linear alkanes, C_{8-25}	Alkyl hydroperoxide	Supported iron catalyst	60-90% selectivity to alcohols and ketones	143
37	Cyclohexane	O_2	Co-salen encapsulated in NaY	Cyclohexane conversion 24% with selectivity to Adipic acid,	144
38	Paraffins	H_2O_2, TBHP	vanadosilicate molecular sieves	Chemoselective oxidation of terminal CH bond	145
39	Ethyl benzene	TBHP	Co- MCM41	Selectivity to acetophenone,	146

1.3.3 Oxidation of alkanes using soluble organometallic complexes and heterogeneous form of palladium:

Palladium in the form of $PdSO_4.2H_2O$ in 20% oleum is reported by Griffin et al.,[147] for the oxidation of methane to $MeOSO_3H$. Use of palladium in a bimetallic system along with copper chloride, in a solvent mixture of trifluoroacetic acid and water is reported by Sen et al., [148] for the oxidation of methane, ethane, and butane to corresponding acids and alcohols in presence of dioxygen and carbon monoxide. Here CO is used as a sacrificial reductant, to enhance the rate of reaction.

Palladium along with copper chloride catalyzes the oxidation of methane, ethane, and butane to corresponding acids and alcohols in presence of dioxygen and carbon monoxide.[149] The oxidation of alkyl aromatics to corresponding carboxylic acids is selectively catalyzed by Co, Mn, and Br and salt of Ru(III), Rh(III), Ir(III), Pd(II), and Pt(II), as a cocatalyst.[150] Pd, Rh, or Pt selectively catalyzes oxidation of methane to methanol or formaldehyde at elevated pressures.[151]

The literature on the use of Palladium metals in the form of heterogeneous catalyst on various supports, with or without various co-metals and promoters is well documented. Supported palladium metal catalysts like Pd on Al_2O_3,[152] Pd foil,[153] Pd on titania[154] catalyze alkane oxidation to acids with 5-10% conversion. Oxidation of pentane, octane, and decane to corresponding acids has been reported using palladium with Fe in zeolite.[155] Rh and Pd metal coated monoliths are also used for the partial oxidation of alkanes to syngas in the presence of air or O_2 at atmospheric pressure and at 25°C.[156]

Oxidation of methane to formic acid and ethane to acetic acid and formic acid in presence of molecular oxygen has been reported using metallic Pd in aqueous media at 70^0-110^0C.[157] It has also used in the form of an alkyl orthosilicates stabilized palladium on Al_2O_3 support for methane oxidation to syngas.[158] Palladium in the form of Pd/γ-alumina and Pd foil have been reported for oxidation of methane to formic acid.[159] Pd/Al_2O_3 catalyst has used for the oxidation of propane.[160] Palladium loaded titania as catalyst is used for oxidation of linear paraffin (n-hexane).[161] A palladium with Fe in zeolite is used as a catalyst for the oxidation of pentane, octane, and decane to corresponding alcohol, ketone.[162] Rh and Pd metal coated monoliths are used for the oxidation of alkanes to syngas in the presence of air or O_2 at atmospheric pressure and at 25°C.[163] Similar to Palladium, Rhodium is also used in heterogeneous form for oxidation reaction.

A general view that can be drawn on the basis of the published results is that, alkali, alkaline and rare earth metals are mainly used for the selective oxidation of alkanes, but these metals need high reaction temperature i.e. above 400^0C and are ideal systems for obtaining acids. Transition metals, because of their high activity are used for total combustion of alkane, particularly in emission control. In few reports they are also used for the partial oxidation of cyclo alkanes under mild conditions. However, no reports are available on the application of transition metal catalysts to partial oxidation of linear higher alkanes ($>C_{10}$).

A literature survey on use of palladium in alkane oxidation is given in the Table 1.3

Table 1.3: Palladium in the oxidation of alkanes

Sr. No.	Substrate	Oxidant	Catalyst system	Product	Ref.
1	Methane, ethane	Air	Pd/TiO_2	Mechanism of the oxidation of alkane on palladium surface is proposed	164
2	Exhaust gases	Air	Palladium containing metal oxides	Treatment of exhaust gases	165
3	Cyclohexane	O_2/H_2	$FeCl_2$ or $FeCl_3$ with Pd/ Al_2O_3	Ketone, alcohol,	166
4	Lower alkenes	Air	Pd foil	Kinetic study of complete oxidation of alkanes	167
5	Methane, lower alkane	O_2 and CO	$CuCl_2$ and metallic palladium	Methanol, acetic acid	168

Sr. No.	Substrate	Oxidant	Catalyst system	Product	Ref.
6	Mixture of gases	Air	Pt-, Pd-, Rh-, Sn-, and Ag-metal, and mixtures, supported on high surface area acid-zeolites.	For oxidation of volatile organic compounds	169
7	Flue gas	Air	Fluidized palladium catalyst	For the destruction of BTEX and poly aromatic hydrocarbons and capturing particles	170
8	Mixture of alkanes	Air	mixed Cu-Zn oxide and noble metals, namely Pt, Pd and Ru,	Waste water treatment	171
9	Mixture of alkanes	H_2O_2, TBHP, m-chloroperbenzoic acid	tetrakis(methyldiphenylphosphine) palladium	Mechanism of oxidation is proposed	172
10	Linear alkane, cycloalkanes	O_2/H_2	Pd(II) with heteropoly tungstate,	Mechanism of interaction of oxygen with metal and alkanes	173

1.4 Oxidants used in oxidation of alkanes:

A large number of oxidants, which can function as oxygen donors, DO, have been extensively investigated in context of catalytic oxidation processes. The primary characteristics that define the attractiveness of an oxidant are the percentage active oxygen (the higher the better) and the selectivity associated with its use, in addition to the practical issues of cost and effect on the environment. Some of the major oxidants, particularly those with oxygen atom donor capabilities, along with salient features and liabilities are summarized in Table1.4

In oxidation reactions, the oxidants such as $KMnO_4$, Ag_2O and CrO_3 have been reported. These form inorganic wastes and hence there is a current interest in environmentally benign oxidants. The need to develop alternative environmentally friendly catalytic oxidations derives not only from the nature and potential toxicity of the metal present in the stoichiometric oxidant, but also from the general principle of green chemistry, which occurs to reduce the amount of byproducts formed in any overall synthetic route.

In catalytic oxidations, the oxidants generally used are molecular oxygen, hydrogen peroxide, alkyl hydroperoxide, persulfate, percarbonate, perborate, hypochlorite, etc. The brief discussion on these oxidants is given in next section.

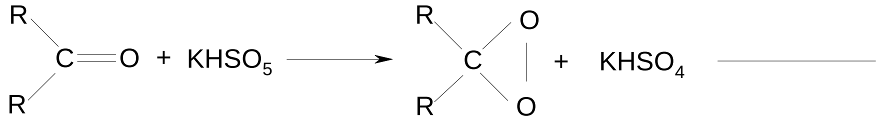
Hydrogen peroxide, H_2O_2, is a very attractive oxidant for liquid phase reactions.[174] H_2O_2 is an adduct of H_2 and O_2 which is also viewed as adduct of an O atom and H_2O molecule. It can oxidize organic compounds with an atom efficiency of 47% and with the generation of water as the only theoretical co product. It is relatively cheap and about 2.4 million metric tones are produced for use, mainly as bleach.[189] The generation of hydrogen peroxide has been achieved directly from gaseous hydrogen and oxygen under the atmospheric conditions in water solvent, the in-situ generation of hydrogen peroxide was also reported using bifunctionalized supramolecularly assembled zeolite catalyst.

Reagents such as alkyl hydroperoxides are more convenient for lab scale oxidations and have a fairly good selectivity towards oxidation. Nowadays these oxidants are reported to catalyze oxidations at low temperatures, which also helps to avoid the unwanted decomposition of these reagents.

Alkyl hydroperoxides are not only used as oxidizing agents but also used as important precursors for the synthesis of important chemicals. For instance, the ethylbenzene hydroperoxide (EBHP) obtained by aerobic oxidation of ethylbenzene (EB) is used as an active oxygen carrier in the epoxidation of propylene, known as propylene oxide/styrene co-production (PO/SM) process. Similarly in the cumene–phenol process (Hock process), cumene hydroperoxide is used worldwide to produce phenol.[175]

Similar to hydrogen peroxide, another extensively employed oxidant is iodosylbenzene, PhIO.[176] PhIO has proved itself as a valuable reagent for formation of oxometalloporphyrins and thus as an oxygen source in catalytic oxygenations of organic substrates. The PhIO is a polymeric solid with I-O-I bonds and is sparingly soluble in most organic solvents. In methanol it forms $PhI(OMe)_2$, which is readily hydrolyzed to PhIO. Groves, et. al.,[177] found that in CH_2C1_2, Fe(TPP)Cl catalyzes alkane hydroxylation by PhIO. The radical character of the process was suggested by the 12:1 ratio for tertiary: secondary products in adamantine oxidation. Chang's initial report concerned hydroxylation of the alkyl chain of a "strapped" iron porphyrin with PhIO.[178] Hill showed that Mn(TPP)X (X = C1, Br, I, N_3) gave similar chemistry with cyclohexane and PhIO.[179]

Dioxiranes are three-membered ring strained peroxides used as O-transfer reagents. The reaction of simple ketones with potassium caroate ($KHSO_5$) = K^+ $^-OSO_3OH$, p*K*a 9.2) at a pH close to neutrality (7.5 - 8.0) generates dioxiranes.[180]



Eq. - 4

The dioxirane generated in solution can be attacked further by caroate ion yielding sulfate ion and molecular oxygen. However, it can also be attacked by a variety of electron-rich substrates, yielding oxidation products. In both reactions, the parent ketone is regenerated, so it returns to the catalytic cycle.[181] A variety of applications, including enantioselective oxidations using suitable chiral ketones,[182] have utilized dioxiranes generated in situ. Dioxiranes thus generated from several D-fructose-derived carbonyls, as well as from C_2 symmetric ketones by the chiral binaphthalene scaffold, have been shown to yield often-remarkable enantioselectivity in the asymmetric epoxidation of prochiral alkenes.[183]

A number of oxohalogen species known as perhalates function as oxygen donors.[184] The oxidizing power of perhalates decreases in the order BrO_4^- (1.85 V) > H_5IO_6 (1.60 V) > ClO_4^- (1.20 V).[185] Of the various oxyhalides, chlorate and hypochlorite are the most frequently used. Periodic acid is a more reactive oxidant because of greater oxygen lability. The catalytic oxidation of olefins via oxomanganese species employs ClO^- as the oxygen source.[186]

Molecular oxygen is an ideal oxidant, considering the cost, cleanliness and availability. However, aerobic oxidation is often difficult to control and sometimes results in combustion and therefore the reaction is performed with a low conversion to avoid over oxidation. Furthermore, although both oxygen atoms in O_2 may be utilized for oxidation (100% atom efficiency),[187] only one oxygen atom has been used in most of the reactions (50% atom efficiency),[188] and hence oxidation often requires presence of reducing agents to capture the extra oxygen atom.[189] In some cases, the initial oxidation products such as (hydro)peroxides are reduced to obtain the desired products.

Molecular oxygen does indeed have considerable oxidation potential, but at room temperature it does not react with most organic compounds owing to high activation barriers. At higher temperatures, oxygen, which exists as diradical in the ground state, takes part preferably in nonselective radical reactions, like for example, the auto-oxidation of hydrocarbons. To achieve selective oxidations with oxygen, transition-metal complexes have been developed as catalysts.

Besides oxygen, amongst the various possible oxygen atom donors susceptible to transfer their oxygen atom to hydrocarbons, H_2O_2, is particularly interesting since it is a readily available and cheap oxidant and since it gives only water as a secondary product.

Table 1.4 - Oxygen donors generally used in oxidation reactions

Oxygen donors	% Active oxygen	Byproduct	Comments
O_2	100	None	A commercially successful nonradical chain system does not exist
H_2O_2	47	H_2O	Attractive environmentally. Fairly attractive, minimally used, and inexpensive oxidant. Usually kinetically unreactive. May become more expensive soon
O_3	33.3	O_2	Potentially environmentally attractive, Short lived and hard to store, corrosive.
ClO_2	23.9	ClO^-, Cl^-	Inorganic salt by-products,
ClO^-	21.6	Cl^-	Toxic and carcinogenic chlorinated by-products.
$(CH)_3CO_2$	21.6	$(CH)_3CO$	Highly reactive with metal
t-BuOOH (TBHP)	17.8	t-BuOH	Still commercially important
N- methylmorpholine N-oxide ($C_5H_{11}NO_2$)	13.7	$C_5H_{11}NO$	Expensive, but the oxidant of choice
ClO_3^-	13.1	ClO_2^-, Cl^-	Inorganic salt and chlorinated organic by-products.
HSO_5^-	10.5	HSO_4^-	Undesirable inorganic salt product

Oxygen donors	% Active oxygen	Byproduct	Comments
$ClC_6H_4CO_3H$ (MCPBA)	10.2	$ClC_6H_4CO_2H$	Fairly expensive
$NCC_6H_4N(CH_3)_2O$	9.9	$NCC_6H_4N(CH_3)_2$	Fairly selective in metal catalyzed oxidations; expensive
IO_4^-	1.5	IO_3^-	Undesirable inorganic salt product.
C_6H_5IO (PhIO)	1.3	C_6H_5I	Often quite selective in metal catalyzed oxidations. Prohibitively expensive.

1.5 Mechanistic studies

The role of transition metal complexes in the activation of oxygen is complicated because of many different reaction pathways that are available. Widely differing conditions are required to oxidize selectively different substrates to desired products, often with no marked patterns in the role the metal plays.[190] Detailed mechanisms generally are not known. In those cases where kinetic studies have been carried out, complicated reaction mechanisms are often needed to account for the reactivity.

In the following section the different fundamental pathways whereby transition metal complexes can catalyze the selective oxidation of organic substrates are grouped into classes. In general the role of the transition metal complex is discussed without concern for the detailed reaction mechanisms of the particular substrates.

1.5.1 Oxidation of alkanes catalyzed by metals using O_2 as oxidant

Based on the role of the metal in oxidations using O_2, the mechanisms are divided into five classes

Class I: metal-bound O_2

Following are the few examples in which substrates are oxidized using metal bound oxygen: substituted phenols are converted to quinones as well as diphenoquinone,[191] substituted indoles are converted to ketoamides,[192] flavanols are oxidized readily to CO and ring-opened products,[193] while lignosulfonate and isoeugenol are converted to vanillin.[194]

The analysis of the metal bound oxygen showed that coordination of oxygen to metal enhances both the nucleophilicity and radical reactivity of oxygen. The established reaction paths for this class involve hydrogen atom abstraction to initiate the reaction as shown in the equation 5.

$$\text{S-H} + \text{LMO}_2 \longrightarrow \text{S}^{\bullet} + \text{LMO}_2\text{H} \longrightarrow \text{LM} + \text{HO}_2 \qquad \text{Eq.-5}$$

Where in L is ligand, S-H is hydrogen-containing substrate and MO_2 is oxygen bound metal. After hydrogen atom abstraction by the metal bound O_2, LMO_2H

dissociates to HO_2, regenerating the catalyst. HO_2 disproportionates rapidly into O_2 and H_2O_2. Reaction of the radical in equation (5) with LMO_2 (or, in some cases, O_2) then occurs. The former is shown in the equation (6)

$$S^{\bullet} + LMO_2 \longrightarrow LMO_2S \qquad \text{Eq. - 6}$$

The LMO_2S then further under go reaction to give the oxidation product and regenerated catalyst.[195] Thus in this class the metal complex coordinates with O_2, enhancing its basicity and radical reactivity. Further the substrate reacts with the coordinated O_2 molecule for oxidation.

Class II: metal oxo via dioxygen

Class II systems involve formation of a high-valent metal oxo species by reaction of a metal complex with O_2. Both oxygen atoms of O_2 are used productively to oxidize the substrate. The catalysts that productively use both oxygen atoms of O_2 to oxidize the substrate are referred as dioxygenates**.** The metal oxo complex undergoes oxygen atom transfer or other type of reactions in the oxidation of organic substrates, regenerating the lower oxidation state of the metal. Formal oxidation state cycles of the metal from two to four, three to five and four to six are commonly involved.

The formation of high-valent metal oxo species from O_2 can proceed via several paths. A peroxo dinuclear complex formed by two spin pairing interactions of O_2 with two metal complexes decomposes to form the metal oxo as shown by the equation 7

$$M^{II}L + O_2 \longrightarrow LM^{III} - O_2 \longrightarrow LM^{III}\text{-O-O-}M^{III}L \longrightarrow LM^{IV}O \qquad \text{Eq. - 7}$$

Complexes with III and IV oxidation states do not form stable O_2 adducts. These complexes are converted by oxygen to V and VI oxo complexes, respectively, by reactions other than eqn. (7). Possibilities include unstable O_2 intermediates or reactions of ion paired O^- and O^{2-} species generated by metal to O_2 electron transfer. Another possibility involves oxidation of the metal by electron transfer, converting coordinated water to metal hydroxo and metal oxo systems.

$$M(H_2O)^{n+} \longrightarrow M(OH)^{(n+1)+} + H^+$$

Eq. - 8

$$M(OH)^{(n+1)+} \longrightarrow MO^{(n+2)+} + H^+$$

Several different reactions of high-valent metal oxo compounds with organic substrates can occur. Specific examples of reactions utilizing O_2 that fall into Class II are relatively few. Groves et al. [196] report a ruthenium(II) porphyrin complex that reacts with O_2 to form the Ru(IV)O and trans-Ru(Vl)$(O)_2$ complex. This system is a catalyst for the selective aerobic oxidation of norbornene to epoxide. Ellis and Lyons[197] have reported that Mn(TPP)N, where TPP is meso-tetraphenylporphyrinate, and the pentafluoro analogue, Mn(TFPP)N_3 catalyze the reaction of O_2 with isobutane to produce isobutanol with dioxygenate results.

Class III: metal oxo via peroxides

For reactions in this class, either kinetic or thermodynamic factors prevent O_2 from converting the low oxidation state complex $M^{(n)}$ to the high oxidation state $M^{(n+2)}$. However, the oxidation does occur with the stronger oxidants like hydrogen peroxide or alkyl hydroperoxides. Thus, if a sacrificial reducing agent is available to convert oxygen to hydrogen peroxide or an alkyl hydroperoxide (often, but not necessarily, metal-complex catalyzed), the high oxidation state metal oxo species can form and undergo the oxidation reactions with organic substrates. With two oxidizing equivalents of the O_2 molecule reacting with the sacrificial reducing agent to form the peroxide, only one of the oxygen atoms (two oxidation equivalents) of O_2 is available for productive substrate oxidation. These reactions take advantage of the stronger oxidizing ability of H_2O_2 than O_2, to oxidize lower-valent metal complexes to metal oxo species.

Metals that have stable oxidation states that differ by one (Mn^{2+}, Fe^{3+}, Cu^{2+}) are very effective catalysts for the decomposition of hydrogen peroxide. The metal functions as both an oxidizing and reducing agent in the catalyzed decomposition mechanism

$$H_2O_2 + 2M(III) \longrightarrow 2M(II) + O_2 + 2H^+$$

Eq-9

$$2H^+ + H_2O_2 + 2M(II) \longrightarrow 2M(III) + 2H_2O$$

When H_2O_2 is decomposed by metals in the presence of organic substrates, some of the hydroxyl radicals react with the substrate. This reaction, called Fenton chemistry, [198] belongs to Class IV. More effective utilization of H_2O_2 occurs if H_2O_2 can be used efficiently to form high-valent metal oxo species instead of the oxidized metal being reduced by H_2O_2 in the second step of the decomposition cycle (Equation 9).

Class IV: metal peroxo systems

This class of reaction differs from Class III because metal peroxo complexes are involved as reactive intermediates instead of high-valent metal oxo complexes. Hydroperoxo (MOOH) and alkyl peroxo (MOOR) complexes of the early transition metals are well characterized. [199] The reactions to form alkyl hydroperoxides are catalyzed by metal complexes through radical chain mechanisms, which belong to Class IV.

The alkyl hydroperoxide, metal alkylhydroperoxo complex or the metal peroxo complex can undergo three main types of reaction that constitute a further subdivision of this class of reaction. These are:

(1) Metal-catalyzed peroxide decomposition (Haber-Weiss or Fenton chemistry)
(2) Nucleophilic attack on peroxo or alkylperoxo complexes
(3) Other reactions of metal peroxo intermediates

Class V: metal-centered oxidizing agents

A very important reaction in this category involves the Wacker process for oxidizing ethylene to acetaldehyde.[200] The reaction is assigned to Class V because the metal is doing the oxidation and the oxygen functions to regenerate the initial high oxidation state of the metal. Nucleophiles other than H_2O or OH^- can attack the coordinated alkene, making this a diverse reaction type. In palladium catalyzed oxidation of Methane with H_2O_2 in trifluoroacetic acid, an electrophilic attack on the C-H bond by Pd(II) take place forming $CF_3CO_2CH_3$. Here the role of H_2O_2 is to regenerate Pd(II), putting this reaction into the Class V category.[201] Another reaction that would be placed in this category involves the catalytic, selective oxidation of alcohols to aldehydes by O_2 using $Ru_3O(CH_3CH_2CO_2)_6(H_2O)_3^+$ as a catalyst.[202]

1.5.2 Oxidation of alkanes catalyzed by metal using peroxides as oxidizing agent

Peroxide based oxidation reactions proceed through free radicals. In traditional radical chain oxidation of alkanes (RH), dioxygen causes an initiation and propagation of chains:

$$\text{a)}\quad RH + O_2 \longrightarrow \quad + HO_2^{\cdot}$$

$$\text{b)}\quad R^{\bullet} + O_2 \longrightarrow RO_2^{\bullet} \qquad \text{Eq. - 10}$$

$$\text{c)}\quad RO_2^{\bullet} + RH \longrightarrow RO_2H + R^{\bullet}$$

Transition metal compounds (M) can participate in the chain initiation and branching via 1e$^-$ stages, e.g.,

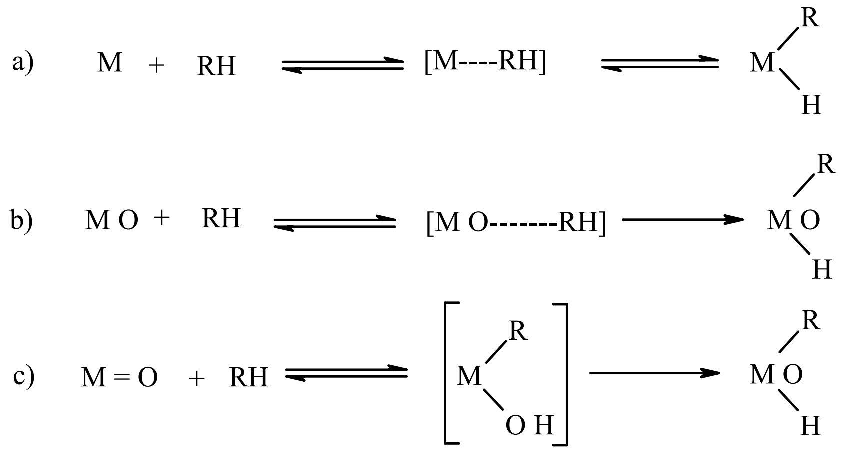
$$\text{a)}\quad RO_2H + M^{n} \longrightarrow M^{n+1} + RO^{-} + {}^{\bullet}OH$$

$$\text{Eq. - 11}$$

$$\text{b)}\quad RH + 2e^{-} + 2H^{+} + O_2 \longrightarrow ROH + H_2O$$

The whole process is usually nonselective, since radicals, particularly such active ones as $^{\bullet}$OH, do not discriminate different C-H bonds; for less active radicals, the secondary (2°) and tertiary (3°) C-H bonds are more reactive than the primary (1°) one; i.e., bond selectivity is $1° < 2° < 3°$

Another mechanism of alkane oxidation with transition metal compounds involves direct interaction of an alkane with a metal core in a 2e$^-$ process (Equation 12)



Eq. -12

The example of such a mechanism was the reaction of Pt(II) complexes with alkanes via oxidative addition

The factors, which distinguish free radical mechanisms from non-free radical mechanisms, are product selectivity, regioselectivity, retention of configuration, kinetic isotope effects and structure reactivity correlations. In addition, radical chain initiators and inhibitors as well as radical traps can be employed.

The free-radical chain theory of autoxidation in hydrocarbon oxidation in the liquid phase is mediated by free-radical intermediates.[203] According to this theory, the radical mechanism is based on the three elementary processes of initiation, propagation, and termination.

Initiation:

The reaction may be initiated either by the hydrocarbon itself or by the decomposition of an initiator such as peroxide

a) $RH + O_2 \longrightarrow R\cdot + HO_2\cdot$

Eq. -13

b) $2RH + O_2 \longrightarrow 2R\cdot + H_2O_2$

When no initiator is used, either or both the reactions Eq.-13 a) and Eq. –13 b) may be important. For example, reaction a) has been shown to be prominent in cyclohexane, cumene, and *o*-xylene, oxidation and reaction b) in the case of tetralin oxidation. These reactions are endothermic and quite slow. Therefore, induction periods are often observed in oxidations without added initiators.

Propagation:

The following two reactions represent the general chain-propagation mechanism:

c) $R^{\bullet} + O_2 \longrightarrow RO_2^{\bullet}$

Eq. -14

d) $RO_2^{\bullet} + RH \longrightarrow ROOH + R^{\bullet}$

Reaction Eq. –14 c) is usually much faster than reaction Eq. –14 d), so that the R* radicals are effectively scavenged, and the overall reaction shows a zero-order behavior in oxygen. The rate of reaction c) depends on the nature of the hydrocarbon as well as on the nature of the radical. The peroxy radicals are relatively stable, and abstract preferentially only the most weakly bound hydrogen atom. Thus, the ease of hydroperoxide formation decreases in the order: tertiary C > secondary C > primary C.[204b] Thus, for example, in the oxidation of cumene, attack always occurs on the tertiary C in the isopropyl group, with negligible attack on the ring or the methyl carbons.

On the other hand, the reactivity of the alkylperoxy radical strongly depends on its structure, being influenced by steric as well as polar effects. In general increasing the electron-withdrawing capacity of the R-substituent increases the reactivity of the alkylperoxy radical. For example, acyl peroxy radicals are much more reactive than alkylperoxy radicals. Thus, autoxidation rates and selectivity depend not only on the nature of the hydrocarbon itself, but also on the structure of the peroxy radical derived from it.

Termination

Given the relative abundance of the peroxy type of free radicals under normal circumstances, the dominant mode of termination would be by ("Russell mechanism") reactions of the type[192]

$$RO_2^{\bullet} + RO_2^{\bullet} \longrightarrow RO_4R + O_2 + \text{non radical product} \qquad \text{Eq. -15}$$

It is possible that mutual termination between different types of radicals becomes important under conditions of extremely low oxygen partial pressures, when types of radicals other than peroxy radicals can also accumulate in solution. The tetroxide that forms in the reaction shown above undergoes decomposition in a manner that depends on its structure. Thus, the tetroxides derived from secondary and primary alkylperoxy radicals decompose by disproportionation to the corresponding alcohol and carbonyl compound. However, when chains are long, most of the observed concentrations of alcohols and ketones in the reaction mixture derive from the decomposition of the hydroperoxide. The termination mechanisms associated with *t*-alkylperoxy radicals lead to dialkyl peroxides.[204]

The mechanism of ruthenium complex, $RuC1_2(PPh_3)_3$, catalyzed oxidation of alkanes using TBHP as oxidant is proposed based on the cytochrome P-450 type mechanism.[205]

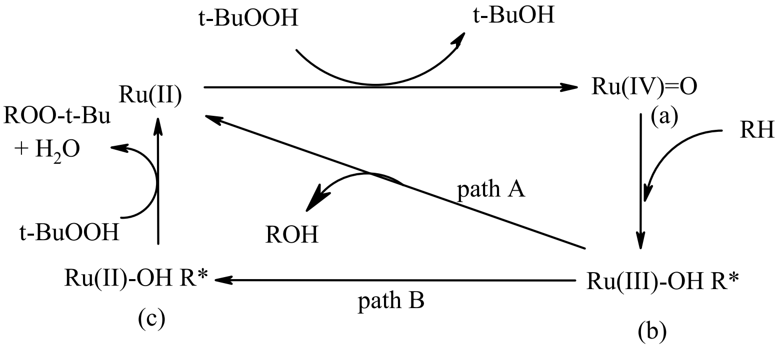


Figure 1.1: Proposed mechanism for $RuCl_2(PPh_3)_3$ and TBHP catalyzed oxidation of alkane

The $RuC1_2(PPh_3)_3$ reacts with TBHP to give oxoruthenium(IV) species (See Figure l.1, (a)),[206] which abstracts hydrogen atom from an alkane to give radical pair (b). Transfer of hydroxy ligand of caged alkyl radical (path A) would afford an alcohol and Ru(II) species to complete the catalytic cycle. Secondary alcohols can be converted into ketones under the same conditions. (Cyclooctanol was oxidized to give cyclooctanone (78%) under the same reaction conditions. t-butyl-dioxycyclohexane prepared independently could not be converted into cyclohexanone under the same reaction conditions, indicating that the possibility of ketone formation via cleavage of t-butyldioxyalkanes is ruled out in the present reaction.) When a radical formed is stable, electron transfer oxidation of the caged alkyl radical (b) would give cation (c) (path B), which undergoes electrophilic reaction with TBHP and Ru(II) species will formed again to continue the catalytic cycle.

1.5.3 Reaction mechanism with palladium catalysts:

Various palladium species mediate the aerobic oxidation of organic substrates. Some of the more important examples are the conversion of alkenes to aldehydes or ketones (Wacker process), the oxidation of alcohols to carbonyl compounds, the hydroxylation and further oxidation of primary C–H bonds, and the deep oxidation of toxic organics. In alkene and alcohol oxidations, the oxidant responsible for substrate oxidation is the palladium(II) ion which is then reduced to a palladium(0) species. The latter is subsequently reoxidized to palladium(II) by dioxygen. Copper compounds have sometimes been employed to aid this reoxidation step.[207] The two-electron oxidation of palladium(0) to palladium(II) by dioxygen simultaneously generates a second, potentially powerful, oxidant: free peroxide (O_2^{2-} or H_2O_2) as shown in Figure 1.2.

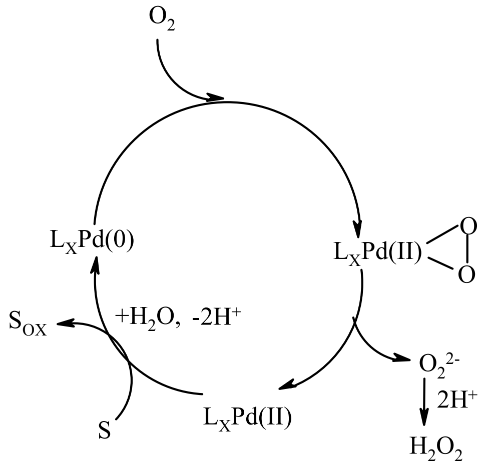
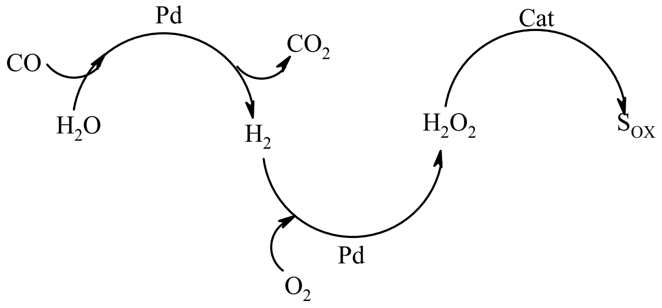


Figure 1.2: Proposed mechanism for the Pd(II) catalyzed aerobic oxidation

Both metallic palladium, as well as discrete palladium compounds, catalyze the oxidation of alkenes and alcohols as per the mechanism given above, however a coreductant is required for the hydroxylation of strong primary and aromatic C–H bonds. The aerobic oxidation of palladium(0) to palladium(II) also produces hydrogen peroxide and does not need a coreductant, however, the continued catalytic generation of hydrogen peroxide requires the rereduction of palladium(II) to palladium(0). In case of oxidation of alkenes and alcohols, it is achieved by the oxidation of these substrates to carbonyl compounds. In these cases, no sacrificial coreductant is necessary and the hydrogen peroxide appears to play no significant part in the oxidation of these substrates. On the other hand, palladium(II) does not readily oxidize primary or aromatic C–H bonds thereby preventing its reduction by them. Thus, a sacrificial coreductant is required to reduce palladium(II).[208] Carbon monoxide and dihydrogen fulfill this role, being oxidized to carbon dioxide and water, respectively as shown in Figure 1.3



(S = substrate, S_{OX} = oxidized substrate, cat = Pd or second catalyst)

Figure 1.3: Proposed mechanism for the reduction of Pd(II) species

The hydrogen peroxide generated in these cases is subsequently used to effect the oxidation of the alkane and arene either by palladium(II) or by a second catalyst.

Similarly a catalytic system consisting of metallic palladium, dioxygen and carbon monoxide in aqueous medium catalyses direct, low temperature, oxidation of lower alkanes at 70-100°C. Carboxylic acids are the initial products, and the ultimate oxidation products are carbon monoxide and carbon dioxide. Mechanistic studies reported indicate that the overall transformation encompasses three catalytic steps in tandem. The first is the water-gas shift reaction involving the oxidation of carbon monoxide to carbon dioxide with the simultaneous formation of dihydrogen. The second catalytic step involves the combination of dihydrogen with dioxygen to yield hydrogen peroxide (or its equivalent, M-OOH). The third step in the oxidation process involves the metal catalyzed oxidation of the substrate by the hydrogen peroxide. It is possible to replace carbon monoxide and dioxygen by hydrogen peroxide; however, unless the latter is added slowly the amount of substrate oxidized relative to the hydrogen peroxide consumed is low due to the catalytic decomposition of hydrogen peroxide occurring in parallel with the oxidation. It is this latter undesirable reaction that made the combination of carbon monoxide and dioxygen more effective than hydrogen peroxide. The requirement of a coreductant (carbon monoxide) makes the overall reaction formally analogous to the monooxygenases in which only one of the two oxygen atoms in the dioxygen molecule is used for substrate oxidation.

Heterogeneous oxidation reactions are complex multistep reactions. For example the selective transformation of n-butane to maleic anhydride is a 14-electron oxidation with abstraction of 8 hydrogen atoms and insertion of 3 oxygen atoms, however the transformation apparently occurs in one step without the appearance of detectable intermediates in the gas phase.[209] Literature data indicate that the dynamics of surface reactions of adsorbed species play a central role in determining selectivity during heterogeneous alkane oxidation. An optimized vanadyl pyrophosphate catalyst is an example of a catalyst, which has a property of activation of paraffinic C-H bond, and of controlled oxidation to give selective oxidation of n-butane to maleic anhydride, and oxidation of n-pentane to phthalic anhydride, and maleic anhydride.[210]

1.6 Scope and objective:

Metal complex catalyzed oxidation of alkanes, olefins, alcohols and aldehydes is a convenient and environmentally benign route for the synthesis of variety of chemicals and their derivatives and is of great industrial potential for bulk chemicals as well as fine and pharmaceutical products. Extensive work has been carried out by several research groups in this field with respect to catalysts development from activity and selectivity point of view. The major issues in most cases were lower reaction rates, turnovers and selectivity. Consequently, the objective of this thesis is to investigate palladium / complex metal catalyzed oxidation of linear alkanes to corresponding alcohols and ketones with the goal of developing improved catalyst systems with high activity and selectivity and to explore the use of heterogeneous catalysis.

With these objectives, the following specific problems were chosen for the present work

1. Synthesis and characterization of the palladium metal complexes containing nitrogen, phosphorous, ligands and their application as catalysts for alkane oxidation reaction
2. Investigation of the mechanistic study of palladium catalyst catalyzed oxidation of alkane

3. Synthesis and characterization of the heterogenized dispersed palladium metal complex catalysts and study of effect of dispersion of metal complex on rate of reaction

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Chapter 2

Oxidation of Alkanes
Using
Palladium Metal Complexes

2.1 Introduction:

The oxidation of alkanes is an important route to obtain oxygen-functionalized products. However, the radical mechanism and uncontrollable over-oxidation results in poor selectivity to the desired products particularly at higher conversions. This problem is more pronounced for oxidation of higher linear alkanes where scission of the carbon chain gives a wide variety of unwanted oxygenated products. In living organisms, selective oxidations are achieved under mild conditions by enzymes such as methane monooxygenases,[1] cytochrome P-450[2] and flavoenzymes.[3] In cytochrome P-450 system, activation of molecular oxygen takes place, followed by its transfer to the substrate. Simulation of the function of cytochrome P-450 with transition metal catalysts such as ruthenium, iron, copper, etc has resulted in the discovery of biomimetic reactions for alkane oxidation using peroxides and molecular oxygen or aldehyde as oxidants. In spite of the ease of oxidation and selectivity, biomimetic organometallic complexes have inherent drawbacks, which restrict their application.

Thus metal complexes have been used in a variety of different ways to activate dioxygen to form a metallooxidant to oxidize hydrocarbons.[4] However, despite numerous examples of hydrocarbon oxidation catalysis by metal-oxo species, only a limited number have been found or proposed to catalyze the oxidation of hydrocarbons solely with dioxygen.[5] The goal of this chapter, therefore, has been to select and evaluate metal complexes with the primary requirement of dioxygen activation and oxidation catalysis.

The detailed literature search on alkane oxidation is presented in chapter 1. It was found that majority of studies have centered on activation of oxygen and oxidation of adamantane, cyclohexane, aryl alkanes and lower alkanes (methane, ethane, butane, iso-butane). Oxidation of higher linear alkanes using hydroperoxides is also well reported (section 1.3.1.4) however, transition metal complexes catalyzed oxidation of alkanes using molecular oxygen, as oxidant has not been investigated in detail. Besides, there are also practically no reports on palladium catalyzed oxidation of higher linear alkanes.

In this work, we have developed an efficient catalyst for the selective partial oxidation of higher linear alkanes. This is a first report on use of palladium complex catalyst for the oxidation of alkanes using molecular oxygen as oxidant and without any co-reductant and solvent. The effect of different process parameters on the activity and selectivity of the $PdCl_2Bipy$ catalyst in the oxidation of alkanes was studied. The effect of ligands, oxygen concentration, reaction temperature, and reaction time on alkane conversion and ketone, alcohol selectivity has been studied.

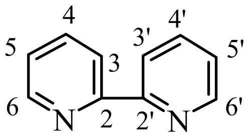
2.2 Materials:

Palladium chloride ($PdCl_2$) and palladium acetate ($Pd(OAc)_2$) were obtained from Hindustan Platinum and used as received. N-hexane, n-decane, n-dodecane, n-tetradecane, n-hexadecane, ethylbenzene, propylbenzene, cyclohexane, 5,6-dimethyl-1,10-Phenanthroline, 4,7-diphenyl-1,10-Phenanthroline, N,N,N',N'-tetramethylethylenediamine, triphenylamine, N,N'-dibenzylethylenediamine, 1,2-dianilinoethane, 1,2-diphenylphosphinoethane, 1,3-diphenylphosphinopropane, diphenyl-2-pyridylphosphine, dibenzylamine, tribenzylamine, 4-ethyl benzaldehyde were procured from Sigma-Aldrich USA and used without further purification. Pyridine, bipyridine, 1, 10-phenanthroline, 2,6-lutidine, ethylenediamine, 1,3-diaminopropane, cyclohexylamine, aniline, triphenylphosphine, benzaldehyde, were purchased from Loba Chemie India and used without further purification. The solvents ethanol, methanol, tetrahydrofuran obtained from Merck, India were freshly distilled prior to use. Oxygen, air and nitrogen gas supplied by Indian Oxygen, Mumbai were used directly from the cylinders. The mixtures of oxygen in nitrogen (60% and 5%) were prepared by mixing the gases in a reservoir vessel.

2.2.1 Synthesis of Palladium metal complexes:

2.2.1.1 Synthesis of $PdCl_2$Bipyridine ($PdCl_2$Bipy) complex:

Synthesis procedure:



The $PdCl_2Bipy$ complex was prepared by using following procedure. In a 50 ml round bottom flask containing 10 ml methanol, 0.266g (1.33mmol) $PdCl_2$ was added followed by 0.234g (1.33mmol) 2,2'-bipyridine. The mixture was stirred at room temperature for 15 hr. The precipitated orange yellow colored $PdCl_2Bipy$ complex was filtered and washed with methanol and then dried under vacuum. Practical yield of the complex was 0.440g (88%)

Characterization:

Microanalysis:

The elemental analysis of $PdCl_2Bipy$

Found: C=36.19%; H=2.38%; N= 8.32%, Cl=22.43%

Theoretical: C=36.01%; H=2.42%; N=8.40%, Cl=22.36%

IR analysis:

The IR spectra of 2,2'-bipyridine and $PdCl_2Bipy$ complex are shown in Figure 2.1 and Figure 2.2 respectively (See Annexure I)

In the complex, the coordination of 2, 2'-bipyridine ligand was confirmed by the characteristic absorption peak between 1579 to 1415 cm^{-1} for bipyridyl ring, with a blue shift ranging between 1601 to 1448 cm^{-1}. The IR spectra of the complex also showed the shift in vibration peak at 757cm^{-1} to 761cm^{-1} and Pd–N stretching vibrations in the range of 540 to 580 cm^{-1}.[6]

Far IR spectrum for $PdCl_2Bipy$ complex was also recorded which showed strong peaks at 479.9, 445.7, 412.7, and 359.3 cm^{-1}, which are typical for Pd–N stretching vibrations. The Pd-Cl stretching vibration occurs at 340 and 347 cm^{-1}

Proton NMR analysis:

^1H NMR spectra of 2,2'-bipyridine and $PdCl_2Bipy$ complex are shown in the Figure 2.3 and Figure 2.4 respectively. (See Annexure I)

Proton NMR data for the ligand - 2,2'-bipyridine and the $PdCl_2Bipy$ complex are presented in Table 2.1

Table 2.1: Proton NMR data of the bipyridine ligand and $PdCl_2Bipy$ complex

Atom	Ligand (2,2'-bipyridine) δ ppm	Catalyst [$PdCl_2Bipy$ complex] δ ppm	Shift δ ppm
$H_{5,5'}$	7.35 ppm, 2 H, doublet of triplet, (J=1.8,3.6,1.8,3.6,1.8Hz)	7.70ppm, 2 H, doublet of triplet, (J=1.3,5.9,1.3,5.9,1.3Hz)	0.35
$H_{4,4'}$	7.84 ppm, 2 H, doublet of triplet, (J=1.8,5.9,1.8,5.9,1.8Hz)	8.25 ppm, 2 H, doublet of triplet, (J=1.3,6.4,1.3,6.4,1.3Hz)	0.41
$H_{3,3'}$	8.29 ppm, 2 H, d, (J=7.7Hz)	8.48 ppm, 2 H, d, (J=7.7Hz)	0.19
$H_{6,6'}$	8.59 ppm, 2 H, d, (J=3.6Hz)	9.02 ppm, 2 H, d, (J=5.9Hz)	0.43

The aromatic protons corresponding to pyridyl rings for the compounds were found between δ = 7 to 9 ppm. From the Table 2.1 it can be seen that there is substantial chemical shift observed when the ligand gets coordinated with Pd metal. The shift is more towards the downfield region to that of the ligand. The chemical shift values of proton NMR of ligand were also compared with the reported values, and were found to be similar. (Reported values of chemical shift for ligand are-7.3ppm, 7.8ppm, 8.4ppm, and 8.6ppm for $H_{5,5'}$, $H_{4,4'}$, $H_{3,3'}$, $H_{6,6'}$ respectively). The multiplicity of the protons remains the same after complexation, whereas the shift in coupling constant (J value) is observed.

Carbon NMR analysis:

^{13}C NMR spectra of 2,2'-bipyridine and $PdCl_2Bipy$ complex are shown in the Figure 2.5 and Figure 2.6 respectively. (See Annexure I)

In the ^{13}C NMR of the $PdCl_2Bipy$ complex, the shift observed is more towards the downfield region to that of the free ligand - 2,2'-bipyridine in the range of 0.4 to 4.0 ppm. A plausible assignment of each aromatic carbon is shown in Table 2.2

A shift in the signal position with respect to the free ligand occurs because of the coordination to the metal via two pyridyl nitrogens in the complex.

Table 2.2: Carbon NMR data of $PdCl_2$Bipyridine complex

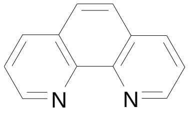
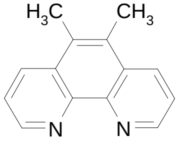
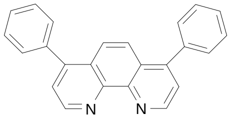
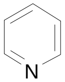
Atom	Ligand (2,2'-bipyridine) δ ppm	Catalyst ($PdCl_2$Bipyridine complex) δ ppm	Shift δ ppm
$C_{2,2'}$	155.40	156.61	1.21
$C_{6,6'}$	149.46	149.88	0.42
$C_{4,4'}$	137.48	141.42	3.94
$C_{3,3'}$	124.37	127.50	3.13
$C_{5,5'}$	120.60	124.08	3.48

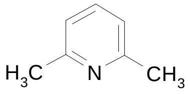
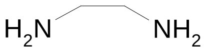
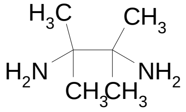
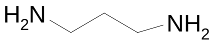
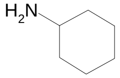
2.2.1.2 General procedure for the synthesis of the complex $PdCl_2L_2$:

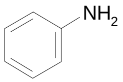
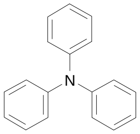
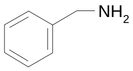
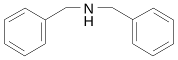
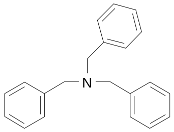
In a 50 ml round bottom flask 0.266g (1.33mmol) $PdCl_2$ was added followed by 10 ml methanol and an appropriate quantity of the ligand, i.e. 2.66mmol in case of a monodentate ligand and 1.33mmol in case of a bidentate ligand. The mixture was stirred at room temperature for 15 hr. The precipitated $PdCl_2L_2$complex was filtered and washed with methanol and then dried under vacuum.

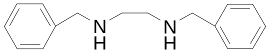
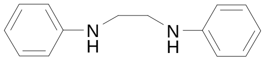
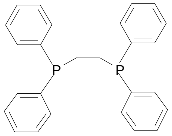
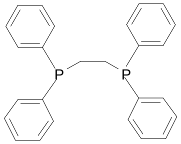
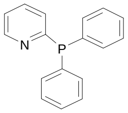
The Table 2.3 illustrates the elemental analysis of the respective complexes and the relevant absorption frequencies in IR spectra (see Annexure I for IR spectra), which indicate coordination of the ligand with palladium centre.

Table 2.3: The details of the ligand used and characterization of the palladium metal complexes

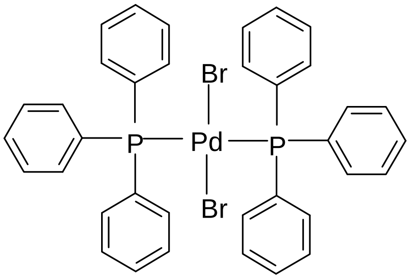
Sr. No	Ligand, L	Elemental analyses, %		Absorption region in IR spectrum, cm^{-1}	Practical yield of the complex, %
		Calculated	Found		
1	 1,10-Phenanthroline (phen)	C-40.31 H-2.26 N-7.84	C- 40.39 H-2.31 N-7.72	1600 to 1400 cm^{-1} 900 to 700 cm^{-1} (Figure 2.7, Annexure I)	90
2	 5,6-dimethyl-1,10-Phenanthroline (m-phen)	C-43.61 H-3.14 N-7.27	C-43.70 H-3.21 N-7.35	1600 to 1400 cm^{-1} 900 to 700 cm^{-1} (Figure 2.8, Annexure I)	53
3	 4,7-diphenyl-1,10-Phenanthroline (p-phen)	C-56.55 H-3.16 N-5.50	C-56.64 H-3.24 N-5.41	1600 to 1400 cm^{-1} 900 to 700 cm^{-1} (Figure 2.9, Annexure I)	50
4	 pyridine (Py)	C-35.80 H-3.00 N-8.35	C-35.91 H-3.03 N-8.29	1600 to 1400 cm^{-1} 900 to 700 cm^{-1} (Figure 2.10, Annexure I)	86

Sr. No	Ligand, L	Elemental analyses, %		Absorption region in IR spectrum, cm^{-1}	Practical yield of the complex, %
		Calculated	Found		
5	 2,6-lutidine (Lut)	C-42.94 H-4.73 N-7.59	C-43.01 H-4.86 N-7.65	1600 to 1400 cm^{-1} 900 to 700 cm^{-1} 2900 to 3070 cm^{-1} (Figure 2.11, Annexure I)	87
6	 ethylenediamine (EDA)	C-10.12 H-3.40 N-11.80	C-10.08 H-3.45 N-11.92	2800 to 3100 cm^{-1} 1132 cm^{-1} (Figure 2.12, Annexure I)	80
7	 N,N,N’,N’-tetramethylethylenediamine (TMEDA)	C-24.55 H-5.50 N-9.54	C-24.49 H-5.61 N-9.60	2800 to 3100 cm^{-1} 1125 cm^{-1} (Figure 2.13, Annexure I)	80
8	 1, 3-diaminopropane (DAP)	C-14.33 H-4.01 N-11.14	C-14.37 H-4.13 N-11.21	2800 to 3100 cm^{-1} 1031 cm^{-1} (Figure 2.14, Annexure I)	79
9	 Cyclohexylamine (ChA)	C-38.37 H-6.98 N-7.46	C-38.42 H-7.01 N-7.53	2800 to 3100 cm^{-1} 1146 cm^{-1} (Figure 2.15, Annexure I)	80

Sr. No	Ligand, L	Elemental analyses, %		Absorption region in IR spectrum, cm^{-1}	Practical yield of the complex, %
		Calculated	Found		
10	 aniline (An)	C-39.64 H-3.88 N-7.71	C-39.71 H-3.93 N-7.69	1600 to 1400 cm^{-1} 900 to 700 cm^{-1} (Figure 2.16, Annexure I)	80
11	 triphenylamine (TPA)	C-64.73 H-4.53 N-4.19	C-64.82 H-4.61 N-4.26	1600 to 1400 cm^{-1} 900 to 700 cm^{-1} (Figure 2.17, Annexure I)	70
12	 benzylamine (BzA)	C-46.01 H-4.82 N-6.71	C-46.12 H-4.90 N-6.66	1600 to 1400 cm^{-1} 900 to 700 cm^{-1} (Figure 2.18, Annexure I)	70
13	 dibenzylamine (DbzA)	C-58.81 H-5.29 N-4.90	C-58.95 H-5.36 N-5.01	1600 to 1400 cm^{-1} 900 to 700 cm^{-1} (Figure 2.19, Annexure I)	75
14	 tribenzylamine (TbzA)	C- 67.07 H- 5.63 N- 3.73	C- 67.13 H- 5.71 N- 3.80	1600 to 1400 cm^{-1} 900 to 700 cm^{-1} (Figure 2.20, Annexure I)	70

Sr. No	Ligand, L	Elemental analyses, %		Absorption region in IR spectrum, cm^{-1}	Practical yield of the complex, %
		Calculated	Found		
15	 N,N’-dibenzylethylenediamine (DBzEDA)	C-46.01 H-4.83 N-6.71	C-46.14 H-4.91 N-6.68	1600 to 1400 cm^{-1} 900 to 700 cm^{-1} (Figure 2.21, Annexure I)	75
16	 1,2-dianilinoethane (DAnE)	C-43.16 H-4.14 N-7.19	C-43.21 H-4.09 N-7.21	1600 to 1400 cm^{-1} 900 to 700 cm^{-1} (Figure 2.22, Annexure I)	92
17	 1,2-diphenylphosphinoethane (DPPP)	C-54.24 H-4.20 Cl-12.32	C-54.19 H-4.25 Cl-12.26	1600 to 1400 cm^{-1} 900 to 700 cm^{-1} (Figure 2.23, Annexure I)	76
18	 1,3-diphenylphosphinopropane (DPPE)	C-54.99 H-4.44 Cl-12.02	C-55.09 H-4.51 Cl-12.23	1600 to 1400 cm^{-1} 900 to 700 cm^{-1} (Figure 2.24, Annexure I)	76
19	 diphenyl-2-pyridylphosphine (DPhPyP)	C- 46.34 H- 3.20 N- 3.18	C- 46.41 H- 3.26 N- 3.30	1600 to 1400 cm^{-1} 900 to 700 cm^{-1} (Figure 2.25, Annexure I)	80

2.2.1.3 Synthesis of $PdBr_2(PPh_3)_2$ complex:



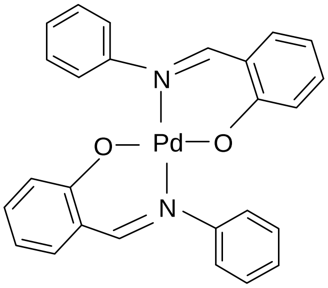
0.583 g (2.6mmol) $Pd(OAc)_2$ was dissolved in 5ml ethanol under constant stirring and heating. To it 0.28ml, 48% HBr solution (3.2mmol) was added slowly under constant stirring. After complete addition of HBr, the solution turned dark red. This mixture was then dried under vacuum. To it then 5 ml ethanol was added and then it was added to 5ml ethanol containing 1.37 g (5.2mmol), triphenylphosphine. This mixture was then stirred for 3 hr at 60^0C, and then for 10 hr at room temperature. Precipitated yellow coloured $PdBr_2(PPh_3)_2$ was filtered and washed with ethanol and dried under vacuum. Practical yield of the complex was found to be 1.16g (45%)

The elemental analysis of $PdBr_2(PPh_3)_2$
Found: C= 54.74%; H= 3.90%;
Calculated: C= 54.68%; H=3.82%

The coordination of the ligand triphenylphosphine with palladium was confirmed by the absorption in the region 1600 to 1400 cm^{-1} for the aromatic group and absorption in the region 900 to 700 cm^{-1}, (See Annexure I, Figure 2.26).

2.2.1.4 Preparation of Pd(salicylideneaniline)$_2$ complex (Pd-SaAn):

The Schiff's base containing metal complex was synthesized in two steps. First Schiff's base was synthesized and in second step using this base and metal precursor, metal complex was synthesized

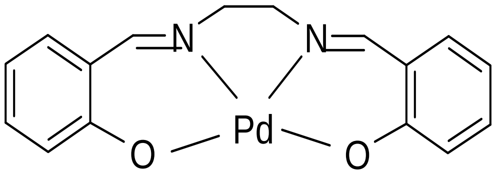


For the synthesis of Pd-SaAn, to a solution of 0.187g (2.0mmol) aniline in 5ml methanol, 0.24g (2.0mmol) salicylaldehyde was added drop wise under stirring. On addition of salicylaldehyde the initial colorless solution turned reddish yellow. The mixture was then stirred at RT for 12 hr. To this mixture then 0.177g (1.0mmol) $PdCl_2$ was added in equal lots under stirring. The mixture was then stirred at RT for a further 12 hr. The precipitated metal complex was then filtered and washed with 5 ml cold methanol and then dried under vacuum. Practical yield of the complex was 0.30g (60%)

The elemental analysis of Pd-SaAn:
Found: C= 62.51%; H= 4.11%; N= 5.70%,
Calculated: C= 62.60%; H=4.04%; N=5.62%

The coordination of the ligand salicylideneaniline (SaAn) with palladium was confirmed by the absorption in the region 1600 to 1400 cm^{-1} for the aromatic group and absorption in the region 900 to 700 cm^{-1} (See Annexure I, Figure 2.28)

2.2.1.5 Preparation of Pd(bissalicylideneethylenediamine) complex (Pd-bSaEDA):

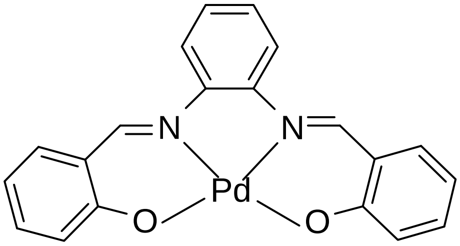


The Pd-bSaEDA was synthesized by a similar procedure used for the synthesis of Pd-SaAn. The charge taken for the metal complex preparation was 0.080g (1.3mmol) ethylenediamine, 0.327g (2.6mmol) salicylaldehyde, 0.326g (1.3mmol) $PdCl_2$, and 5 ml methanol. Practical yield of the complex was 0.350g (70%).

The elemental analysis of Pd-bSaEDA:
Found: C= 51.49%; H= 3.81%; N= 7.48%
Calculated: C= 51.56%; H=3.79%; N=7.52%

The coordination of the ligand bissalicylideneethylenediamine (bSaEDA) with palladium was confirmed by the absorption in the region 1600 to 1400 cm^{-1} for the aromatic group and absorption in the region 900 to 700 cm^{-}, (See Annexure I, Figure 2.29)

2.2.1.6 Preparation of Pd(bissalicylidenephenyldiamine) complex (Pd-bSaPhDA):

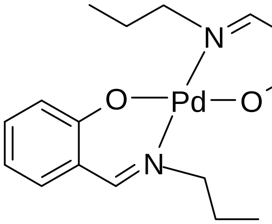


The Pd-bSaPhDA complex was synthesized using procedure used for the synthesis of Pd-SaAn. The charge taken for the metal complex preparation was 0.080g (1.3mmol) o-phenylenediamine, 0.327g (2.6mmol) salicylaldehyde, 0.326g (1.3mmol) $PdCl_2$, and 5 ml methanol. Practical yield of the complex was 0.350g (70%).

The elemental analysis of Pd-bSaPhDA
Found: C= 57.20%; H= 3.40%; N= 6.69%,
Calculated: C= 57.09%; H=3.35%; N=6.66%

The coordination of the ligand bissalicylidenephenyldiamine (bSaPhDA) with palladium was confirmed by the absorption in the region 1600 to 1400 cm^{-1} for the aromatic group and absorption in the region 900 to 700 cm^{-1}, (See Annexure I, Figure 2.30)

2.2.1.7 Preparation of Pd(salicylidenepropylamine)$_2$ complex (Pd-SaPA):

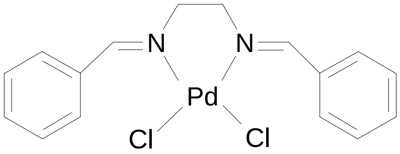


The Pd(salicylidenepropylamine)$_2$ complex was synthesized using procedure used for the synthesis of Pd-SaAn. The charge taken for the metal complex preparation was 0.137g (2.3mmol) n-propylamine, 0.283g (2.3mmol) salicylaldehyde, 0.205g (1.15mmol) $PdCl_2$, and 5 ml methanol. Practical yield of the complex was 0.330g (66%).

The elemental analysis of Pd-SaPA
Found: C= 55.83%; H= 5.70%; N= 6.44%,
Calculated: C= 55.76%; H=5.61%; N=6.50%

The coordination of the ligand salicylidenepropylamine (SaPA) with palladium was confirmed by the absorption in the region 1600 to 1400 cm^{-1} for the aromatic group and absorption in the region 900 to 700 cm^{-1}, (See Annexure I, Figure 2.31)

2.2.1.8 Preparation of Pd(bisbenzyylideneethylenediamine) complex (Pd-bBeEDA):

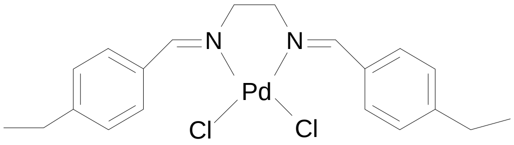


The Pd-bBeEDA complex was synthesized using procedure used for the synthesis of Pd-SaAn. The charge taken for the metal complex preparation was 0.073g (1.2mmol) ethylenediamine, 0.258g (2.4mmol) benzaldehyde, 0.214g (1.2mmol) $PdCl_2$, and 5 ml methanol. Practical yield of the complex was 0.30g (60%).

The elemental analysis of Pd-bBeEDA
Found: C= 46.46%; H= 3.90%; N= 6.77%,
Calculated: C= 46.53%; H=3.81%; N=6.86%

The coordination of the ligand bisbenzylideneethylenediamine (bBeEDA) with palladium was confirmed by the absorption in the region 1600 to 1400 cm^{-1} for the aromatic group and absorption in the region 900 to 700 cm^{-1}, (See Annexure I, Figure 2.32)

2.2.1.9 Preparation of Pd(bis(4-ethyl benzyylidene)ethylenediamine) complex (Pd-4EBeEDA):



The Pd-4EBeEDA complex was synthesized using procedure used for the synthesis of Pd-SaAn. The charge taken for the metal complex preparation was 0.063g (1.06mmol) ethylenediamine, 0.286g (2.12mmol) 4-ethyl benzaldehyde, 0.188g (1.06mmol) $PdCl_2$, and 5 ml methanol. Practical yield of the complex was 0.290g (58%).

The elemental analysis of Pd-4EBeEDA
Found: C= 51.26%; H= 5.19%; N= 6.03%,
Calculated: C= 51.14%; H=5.15%; N=5.96%

The coordination of the ligand bis(4-ethyl benzylidine)ethylenediamine (4EBeEDA) with palladium was confirmed by the absorption in the region 1600 to 1400 cm^{-1} for the aromatic group and absorption in the region 900 to 700 cm^{-1}, (See Annexure I, Figure 2.33)

2.3 Experimental procedure and setup for alkane oxidation reactions:

2.3.1 Experimental procedure:

In a typical reaction procedure the reaction vessel was charged with alkane and preformed catalyst. The reaction mixture was flushed with oxidant, and was then stirred at reaction temperature for particular reaction time. At the end of the reaction the reaction mixture was cooled to room temperature and diluted with THF to get 5%

reaction mixture in THF. This THF solution (diluted reaction mixture) was then analyzed on GLC.

2.3.2 General procedure for alkane oxidation at atmospheric pressure:

The oxidation reactions under atmospheric pressure of oxidant were carried out in a 50 ml round bottom flask equipped with a reflux condenser and an arrangement to fix a balloon to maintain a static oxidant (pure oxygen, air or mixture of N_2 and O_2). The reaction mixture was heated to the desired temperature in an oil bath connected to the PID controller and was stirred using a magnetic stirrer.

2.3.3 General procedure for alkane oxidation under continuous feeding of gaseous oxidant:

The oxidation reactions with continuous feeding of oxidant were carried out in a glass reactor of 20 ml capacity equipped with thermowell, a gas sparger and a reflux condenser. The reactor was heated in an oil bath controlled by the PID controller and reaction mixture was stirred using a magnetic stirrer. The oxidant (pure oxygen, air or mixture of N_2 and O_2) was bubbled through the reaction mixture at a constant flow controlled by differential flow controller.

2.3.4 General procedure for alkane oxidation reactions in an autoclave under pressure:

Pressure reactions were carried out in an autoclave (Parr) of 50 ml capacity, equipped with stirrer, thermowell, pressure gauge, and automatic temperature controller. The substrate and the catalyst were charged into the reactor. The reactor was closed and flushed with nitrogen. The reaction was heated to desired temperature under slow stirring and then the oxidant (air or 5% O_2 in N_2) was fed into the reactor up to desired pressure through a reservoir. The reaction was initiated by increasing the stirrer speed to fixed value (600 rpm). Reaction was carried out for a fixed reaction time. Then the reactor was cooled to room temperature. The gas was vented and again the fresh oxidant was charged into the reactor and reaction was continued for a fixed period. This was done a number of times.

2.4 Analytical methods:

Elemental analysis of the complexes was carried out on a CHNS-O EA1108, elemental analyzer of Carlo Erba Instruments, Italy.

IR spectra were obtained using a Perkin Elmer Spectrum-2000 in transmission mode using KBr pellets.

NMR spectra were obtained on a Bruker AC-200 or MSL-300 spectrometer at room temperature. FT-IR spectra were recorded on a Bio-Rad Spectrophotometer 175C. The reaction products were identified using GCMS, Agilent GC 6890N with 5973 mass selective detector instrument

The quantitative analysis of the reactant and oxidation products was carried out by an external standard method using a gas chromatographic technique. For this purpose, HP 6890 gas chromatograph controlled by the HP Chemstation software and equipped with an auto sampler unit, fitted with FFAP capillary column (30M × 320μm × 0.25 μm film thickness with a stationary phase of fatty acids) and FID detector was used. Authentic standards were prepared in the range of concentrations studied, and a calibration-table was constructed for the quantification. The standard GC conditions for the analysis of products of different reactions are given in Table 2.4.

Table 2.4: Conditions for GC analysis

Injector (split) Temperature	250ºC		
Flame ionization detector Temp	250ºC		
Inlet flow–total (He)	20.2 ml/min		
Split ratio for Injector	50:1		
Column Temperature	Rate (ºC /min)	T (ºC)	Hold time (min)
	-	100	20
	40	190	5
Column Pressure	Rate (psi/min)	Pressure (Psi)	Hold time (min)
	-	5	25

A typical GC chart of decane oxidation (See Annexure II, Fig. 2.34) shows the reactant and products under the analysis condition given in Table 2.4.

Complete mass balance of the liquid phase components (substrate and products) was thus obtained from the quantitative GC analysis. The percent conversion, selectivity, turnover number (TON) and frequency (TOF h^{-1}) were calculated using the formulae (Equations 2.1-2.4) given below. The percent conversion was calculated based on the liquid substrate charged.

$$\text{Conversion, \%} = \left(\frac{\text{Initial concentration of substrate - Final concentration of substrate}}{\text{Initial concentration of substrate}}\right) \text{X } 100 \qquad \text{Eq. -2.1}$$

$$\text{Selectivity, \%} = \left(\frac{\text{Number of moles of product formed}}{\text{Number of moles of substrate converted}}\right) \text{X } 100 \qquad \text{Eq. -2.2}$$

$$\text{TON} = \left(\frac{\text{Number of moles of product formed}}{\text{Number of moles of catalyst}}\right) \qquad \text{Eq. -2.3}$$

$$\text{TOF, } h^{-1} = \left(\frac{\text{Number of moles of product formed}}{\text{Number of moles of catalyst X time in hour}}\right) \qquad \text{Eq. - 2.4}$$

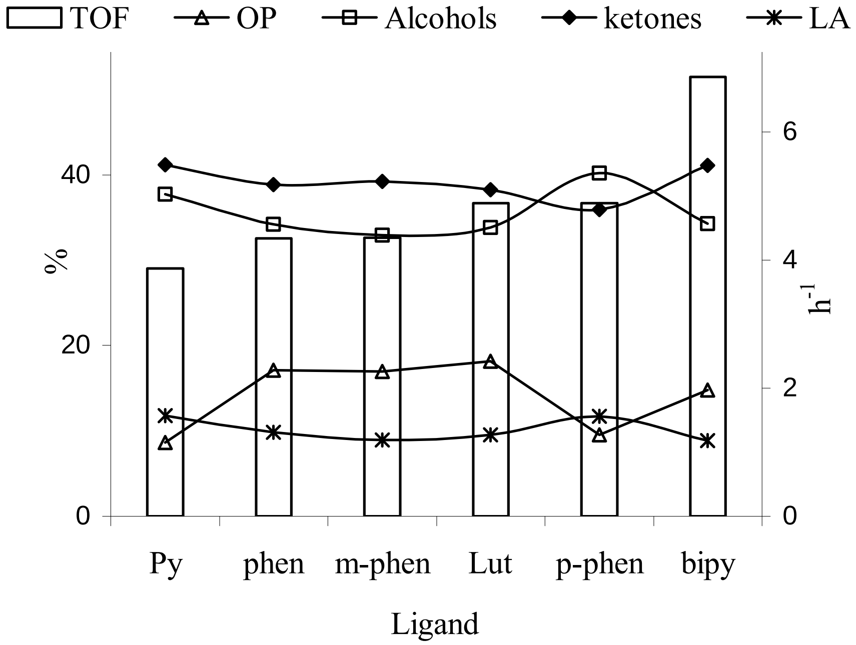
2.5 Results and discussion:

The type and nature of ligand can have a dramatic influence on the activity and selectivity of catalytic reaction.[7] Therefore ligand screening was carried out to find out effect of ligands on alkane oxidation reaction. All ligand screening was done with decane as the model substrate, under atmospheric reaction conditions. The optimization of reaction conditions was also done with decane, however a few reactions involving parameters like temperature effect, high pressure reactions etc. were carried out with hexadecane as its boiling point is high which has an important factor to consider while carrying out high temperature reactions.

2.5.1 Decane oxidation using palladium metal complexes of aromatic nitrogen containing ligands

The results of screening of palladium complexes of aromatic nitrogen containing ligands in decane oxidation are given in Figure 2.35

Figure 2.35: Results of decane oxidation using Palladium metal complexes of nitrogen containing aromatic ligands



Reaction conditions: decane- 25mmol, cat- 0.08mmol, temperature - 150^{0}C, time- 5 hr, oxidant- O_2 in bladder, ∗ OP means other products, like ethers, diketones, esters, carboxylic acids and LA means lower alkanes formed by the scission of substrate alkane.

The results of ligand screening show, lutidine is a better ligand compared to pyridine ligand. This is might be due to the +I effect of methyl group attached in lutidine at 2 and 6 positions, which, increases the electron density on metal compared to pyridine. The graph showed that the decane conversion is more with bipyridine ligand compared to pyridine ligand. This increase in decane conversion might be because, bipyridine is a bidentate ligand which forms a chelate with the central metal atom thus giving more stability and a fixed cis geometry to the metal complex. This fixed geometry might be favoring the activation of O_2 thereby increasing the rate of reaction, compared to the metal complex with monodentate pyridine ligand. The graph for phenanthroline and substituted phenanthroline ligands show that the decane conversion with these ligands is low compared to the bipyridine ligand. This could be attributed to the structural arrangement of metal complexes. With bipyridine ligand the metal is forming a chelate, which is comparatively more flexible because of possible rotation between two pyridine rings connected by a sigma bond, thereby allowing metal to get oriented in the space during reaction suitably to enhance the reaction. However, with phenanthroline type of ligands such movement to adjust the orientation in space during reaction is not possible due to the fixed planar structure of the ligands resulting in lower reaction rates compared to bipyridine ligand.

Thus the ligand screening study showed that the alkane conversion increases with increased electron density on central metal through electron-donating substituents on the ligand. However, no considerable change in the alcohol and ketone selectivity was observed.

It was observed that among the nitrogen containing aromatic ligands screened for the oxidation of decane, the best TOF was obtained with 2,2-bipyridine (TOF is $6.86h^{-1}$).

2.5.2 Decane oxidation using Palladium metal complexes of aliphatic nitrogen containing ligands

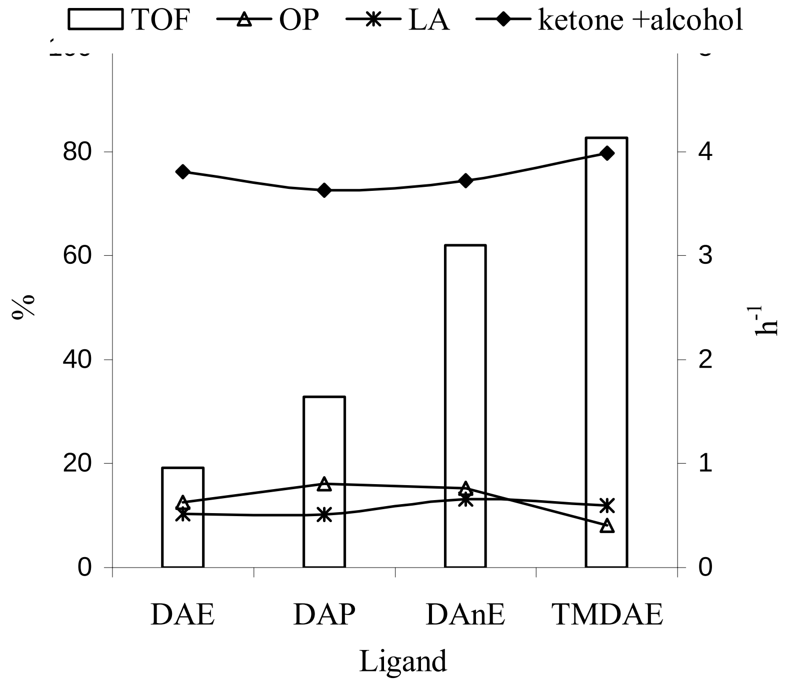
The results of screening of palladium complexes of nitrogen containing aliphatic ligands in decane oxidation reaction are given in Figure 2. 36

The screening of aliphatic ligands for decane oxidation reaction also showed that enhanced electron density on central metal atom increases the rate of decane oxidation. The results for 1,2-diaminoethane and tetramethyl-1,2-diaminoethane showed four-fold increase in decane conversion with tetrametyl-1,2-diaminoethane. Because of +I effect of four methyl groups in tetrametyl-1,2-diaminoethane the decane conversion with this ligand is greater than the conversion with 1,2-diaminoethane. The graph for 1,2-diaminoethane and 1,3-diaminopropane showed better conversion with 1,3-diaminopropane. The reason for better conversion with 1,3-diaminopropane, other than presence of extra alkyl group (+I effect) in the ligand, might be the effect of numbers of atoms forming the chelate.

With 1,3-diaminopropane, palladium forms a six-membered ring, while with 1,2-diaminoethane it forms a five-membered ring which has high energy associated with it.

This explains the better conversion with 1,3-diaminopropane as ligand. The enhanced rate of reaction on use of DAnE compared to DAE can be attributed to the enhanced electron density on the coordinated palladium due to the presence of aromatic rings in case of DAnE.

Figure 2.36: Results of decane oxidation using Palladium metal complexes of nitrogen containing aliphatic ligands



Reaction conditions: decane- 25mmol, cat- 0.08mmol, temperature - 150^0C, time- 5 hr, oxidant- O_2 in bladder

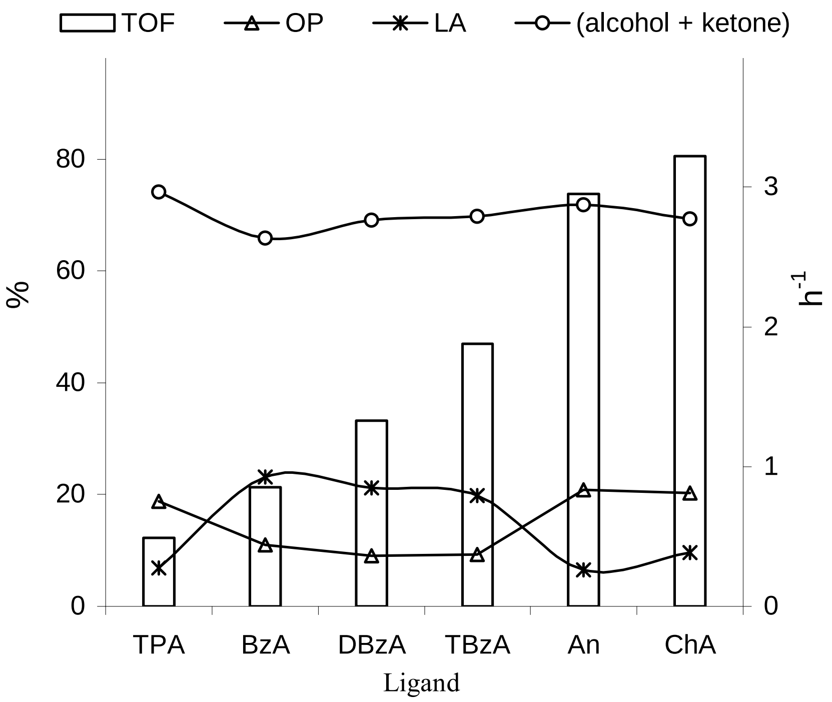
Thus in the screening of nitrogen containing aliphatic ligands for the oxidation of decane, maximum TOF was obtained with tetramethyl-1,2-diaminoethane ligand.

However, this TOF is considerably lower than the TOF obtained with bipyridine ligand (TOF is 4.13 h^{-1}, with alcohol + ketone selectivity 79.67%).

2.5.3 Effect of steric strain around coordinating nitrogen atom on decane oxidation reaction

To understand the effect of the substituent groups present on the ligand on the activity and selectivity in decane oxidation, a study was carried out with ligands where the number of rings around nitrogen atom was varied. The results of the study are given in Figure 2.37

Figure 2.37: Results of effect of steric strain around coordinating nitrogen atom on decane oxidation reaction



Reaction conditions: decane- 25mmol, cat- 0.08mmol, temperature - 150 ^{0}C, time- 5 hr, oxidant- O_2 in bladder

The effect of steric strain was carefully studied with two different categories of ligands, one in which benzyl substitution was increased (benzyl amine, dibenzyl amine and tribenzyl amine), and the other in which number of phenyl rings were increased (aniline and triphenyl amine) In the Figure 2.37, the trends obtained are very distinct. The steric strain at nitrogen atom has an inverse relationship with the rate of reaction. The TOF increases in the order benzyl amine > dibenzyl amine > tribenzyl amine. A similar result is observed for aryl group substitution, i.e. TOF with ligand phenylamine > triphenyl amine. It is also notable that the TOF value obtained for tribenzyl amine is more than that obtained for triphenyl amine, which is expected since the steric strain is more in case of triphenyl amine.

The effect of replacement of the aromatic ring by an aliphatic ring with the same numbers of carbon atom was also checked. A better conversion was observed for cyclohexyl amine in comparison to aniline due to the +I effect of an aliphatic ring on coordinating atom, which increases the electron density on central metal atom giving rise to better decane conversion.

Thus in the study of effect of steric strain on oxidation of decane, maximum TOF was obtained with cyclohexyl amine ligand. However, this TOF is way below to the TOF obtained with bipyridine ligand (TOF is $3.22h^{-1}$ with alcohol + ketone selectivity 70.18%).

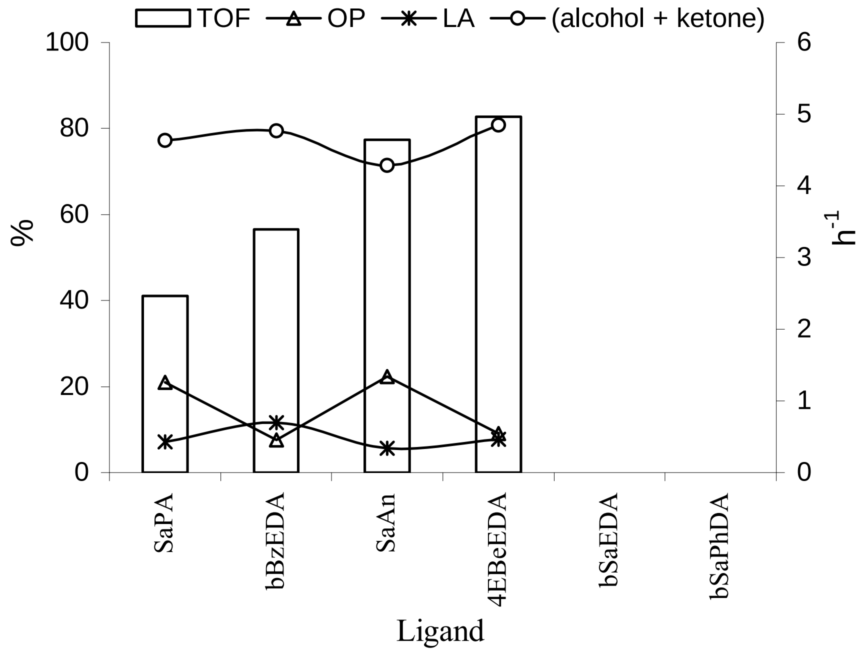
2.5.4 Decane oxidation using Palladium metal complexes of Schiff's base ligands

The effect of Schiff's base ligands, which will serve both as an electron donating ligand and as chelating ligand on decane oxidation, was carried out.

The previously done ligand screening study showed us that if we increase the electron density on central metal atom the decane conversion increases. Therefore, Schiff's base ligands were chosen for the study, which are multidentate ligands and have O^- as one of the coordinating atom. These ligands form a stable complex with metal and also increase the electron density on the metal atom and hence were expected to be suitable ligands for the study. The results obtained are illustrated in the Figure 2.38.

In the screening of Schiff's base ligands no decane oxidation was observed with bSaEDA and bSaPhDA. However moderate decane oxidation was observed with SaAn and SaPA ligands. With bSaEDA and bSaPhDA the metal forms rigid planer structure, which may not allow the oxidation to takes place, whereas with SaAn and SaPA the metal has freedom to adjust itself in such a way that the reaction will facilitate.

Figure 2.38: Results of screening of Palladium complexes of Schiff's base ligands in decane oxidation reaction



Reaction conditions: decane- 25mmol, cat- 0.08mmol, temperature - 150^0C, time- 5 hr, oxidant- O_2 in bladder

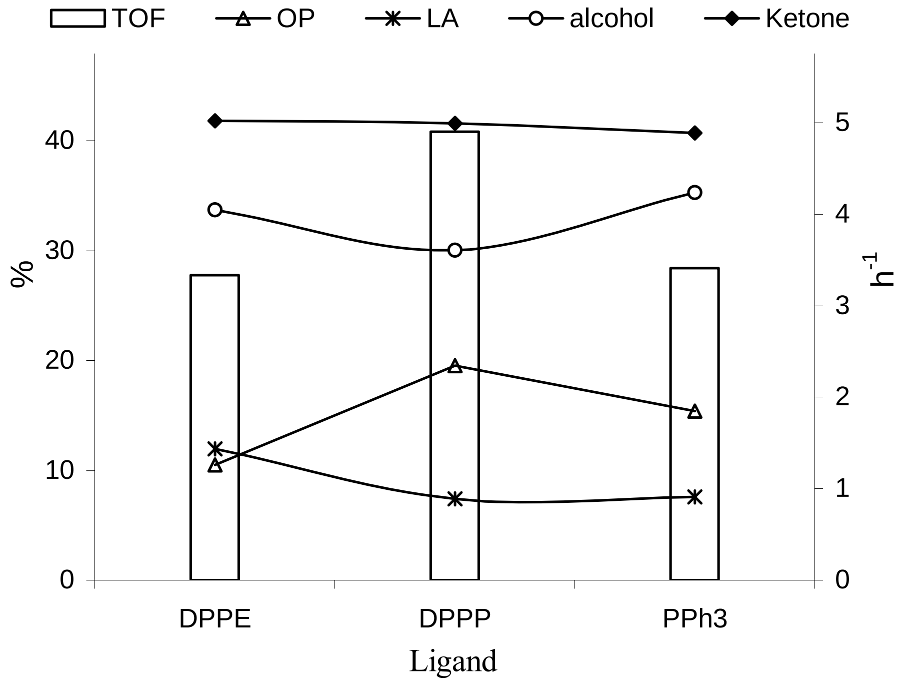
The ligand 4EBeEDA showed the +I effect of electron donating group on the coordinated ligand on decane oxidation. A better TOF was obtained with 4EBeEDA ligand compared to bBeEDA ligand.

Thus in the screening of imine ligands for the oxidation of decane, a maximum TOF was obtained with bis(4-ethyl benzylidene)ethylenediamine) [4EBeEDA] ligand. However, this TOF is less than the TOF obtained with bipyridine ligand (TOF is 4.96 h^{-1} with alcohol+ ketone selectivity 80.75%).

2.5.5 Decane oxidation using Palladium metal complexes of phosphorous based ligands

Phosphorous-based ligands are well known for their coordinating ability and for offering stability to the metal complex. Therefore phosphorous-based ligands were also screened for decane oxidation reaction. The results of the screening of Palladium metal complexes of phosphorous ligands are shown in Figure 2.39.

Figure 2.39: Results of screening of Palladium complexes of phosphorous-based ligands in decane oxidation reaction



Reaction conditions: decane- 25mmol, cat- 0.08mmol, temperature - 150^{0}C, time- 5 hr, oxidant- O_2 in bladder

In the screening of phosphorous based ligands, the effect of size of chelate on decane oxidation was observed. A better TOF was observed with DPPP ligand compared to DPPE ligand, this is attributed to the less energy associated with six membered ring of DPPP ligand compared to the five membered ring with DPPE ligand. This leads to the difference in reactivities of these ligands. With the monodentate ligand PPh_3 a moderate decane conversion was observed.

In the study of screening of phosphorous-based ligands for the oxidation of decane, maximum TOF was obtained with DPPP ligand (TOF is 4.9h-1 with alcohol + ketone selectivity 71.67%). However, this conversion is less than the conversion obtained with bipyridine ligand.

2.5.6 Comparison of best ligands obtained from the ligand screening study

The graph of comparison of best ligands selected from each screened groups is given in the Figure 2.40

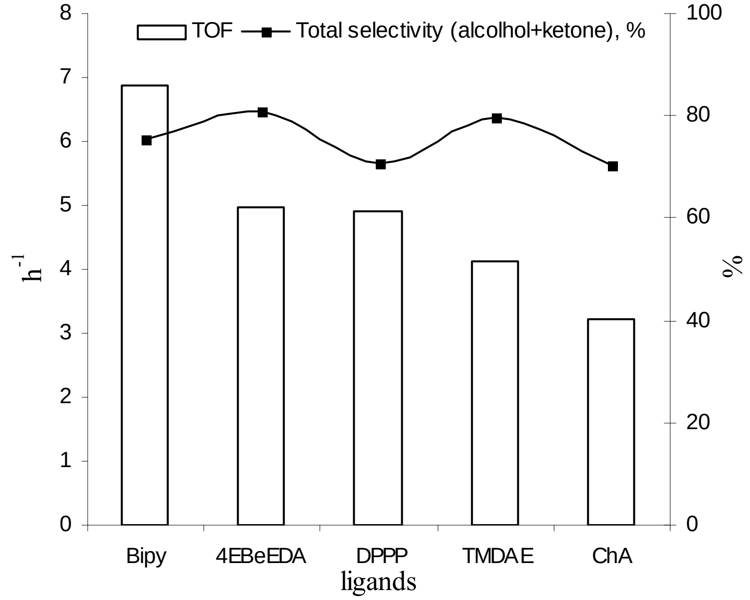


Figure 2.40: Comparison of best-selected ligands from each screened ligand group

Thus in the ligand screening study, nitrogen and phosphorous-based monodentate as well as bidentate ligands were screened. During this study it was observed that if we increase the electron density on the central metal atom by attaching electron-donating groups to the coordinating ligands, the conversion of decane oxidation increases and if we decrease the electron density on the metal by using electron-withdrawing groups on the ligand the decane conversion decreases. Similarly the effect of the structure of the complex on the reaction was also observed. The metal complexes with lower energy, due to structural arrangement or due to chelate formation are more reactive towards decane oxidation reaction. The metal complexes having less crowding around central metal atom are more active for decane oxidation compared to that having more crowding around metal. Within all the screened ligands the highest conversion and selectivity was obtained with bipyridine ligand i.e. with $PdCl_2Bipy$ complex. Therefore further optimization of reaction conditions and other screening studies were carried out with $PdCl_2Bipy$ complex.

2.5.7 Effect of catalyst concentration on decane oxidation reaction

In the study of optimization of reaction conditions, first the optimization of concentration of the catalyst in the reaction was carried out. The results of the catalyst concentration optimization study are given in Table 2.5

Table 2.5: Effect of catalyst concentration on decane oxidation reaction

Sr. No.	Catalyst concentration, mmol	Conversion, %	Selectivity, %				TOF, h^{-1}
			Alcohols	Ketones	Lower alkanes	●Other products	
1	0.04	6.05	36.65	39.66	9.52	13.80	7.82
2	0.08	9.73	34.27	41.11	8.84	14.77	6.86
3	0.16	11.35	33.51	42.36	7.68	14.52	3.62
4	Blank	0.74	23.17	35.26	17.39	21.23	-

Reaction conditions: decane- 25mmol, catalyst: $PdCl_2Bipy$, temperature - 150^0C, time- 5 hr, oxidant- O_2 in bladder ● other products- Esters of alcohols, lower acids, diketones, dialkyl ethers

The optimization of catalyst concentration was carried out in the range of 0.04 to 0.16mmol of catalyst. The results showed that the decane conversion increases with increase in catalyst concentration. However the increase in the decane conversion is not directly proportional to catalyst concentration. This is likely to be due to the poor solubility of the catalyst in neat alkane resulting in its poor dispersion in the reaction mixture. Hence the reaction is taking place only at the surface of the catalyst and not in the bulk of the catalyst.

No major variation in the alcohol and ketone selectivity was observed due to variation in catalyst concentration.

A blank reaction gave 0.73 % decane conversion with (alcohol + ketone) selectivity 58.43%

To be able to monitor a change in the conversion of decane and change in selectivity during other optimization study, the catalyst concentration was fixed to 0.08mmol.

2.5.8 Effect of reaction temperature on hexadecane oxidation reaction

The effect of reaction temperature was carried out with hexadecane as substrate. This is done from safety aspects. If the boiling point of reactant is close to the reaction temperature; the vapor composition is likely to be in the explosion range. The boiling point of decane is 174.1^0C, whereas that of hexadecane is 287^0C. Therefore these reactions were conducted using hexadecane.

The effect of reaction temperature on hexadecane oxidation reaction is given in Table 2.6

It was observed that, this reaction has a temperature threshold of 140^0C, below which reaction does not take place. It was also observed that with increase in reaction temperature the hexadecane conversion increases. The total selectivity to alcohol and ketone also decreases from 80% to 72 % for increase in temperature from 140^0C to 170^0C.

Table 2.6: Effect of reaction temperature on hexadecane oxidation reaction

Sr. No.	Reaction temperature, ^0C	Conversion, %	Selectivity, %				TOF, h^{-1}
			Alcohols	Ketones	Lower alkanes	Other products	
1	120	0	0	0	0	0	0
2	130	0	0	0	0	0	0
3	140	9.48	37.14	43.17	3.27	16.02	6.00
4	150	11.66	40.31	37.57	4.07	16.27	7.29
5	170	14.48	44.07	33.34	4.22	16.91	9.04

Reaction conditions: alkane: hexadecane- 25mmol, catalyst: $PdCl_2Bipy$ – 0.08mmol, time- 5 hr, oxidant- O_2 in bladder

Based on the results of this study, 150^0C reaction temperature was fixed as the optimized reaction temperature. 140^0C is the minimum temperature below which the reaction does not take place.

2.5.9 Effect of oxygen concentration on decane oxidation reaction

The oxygen concentration effect was carried out in the range of 100% oxygen to 5% oxygen in N_2. The mixtures of O_2 in N_2 were prepared separately in the gas reservoir and were analyzed on GC. The results of the variation in oxygen concentration on activity and selectivity of the $PdCl_2Bipy$ catalyst are given in Table 2.7

The results of decane oxidation with variation in oxygen concentration showed that as the concentration of O_2 in the reaction system increases the rate of reaction increases. This is expected because, as the concentration of O_2 in the atmosphere increases the concentration of O_2 in the reaction mixture will increase and more oxygen will be available for the catalyst to carry out oxidation reaction.

Table 2.7: Effect of oxygen concentration on decane oxidation reaction

Sr. No.	Oxidant	Conversion, %	Selectivity, %				TOF, h^{-1}
			Alcohols	Ketones	Lower alkanes	Other products	
1	100% O_2	9.73	34.27	41.11	8.84	14.77	6.86
2	60% O_2 in N_2	6.40	36.23	37.60	12.91	12.20	3.98
3	20% O_2 in N_2	2.43	41.15	37.23	12.81	7.04	1.53
4	*5% O_2 in N_2	2.07	24.82	29.32	18.78	25.85	0.45

Reaction conditions: alkane: decane-25mmol, cat: $PdCl_2$Bipy- 0.08mmol, temp- 150^0C, time- 5 hr, oxidant in bladder, * reaction time is 15 hr

Hence, with increase in O_2 concentration the decane conversion will increase. It was also observed that as the oxygen concentration in the reaction system decreases the percentage of alcohol in the product increases. For 100% O_2 the alcohol selectivity was 34% and at 20% O_2 it was 41%. The decane oxidation reaction under 5% O_2 in N_2 was carried out for longer time to achieve measurable alkane conversion. However, oxidation of the products is more predominant compared to alkane oxidation. Hence, lower selectivity towards oxidation product was observed under these conditions.

The oxidant concentration was fixed to 100% O_2, for all further reactions to ensure reproducible results.

2.5.10 Effect of reaction time on hexadecane oxidation

In alkane oxidation reactions it is well known that if alkane oxidation reactions are carried out for longer reaction time to achieve high alkane conversions, selectivity of the product decreases. This is because the products are more reactive than the alkanes and hence oxidation of product takes place instead of substrate. So to optimize reaction time, reactions were carried out for longer reaction time. Results of these reactions are given in Table 2.8

Table 2.8: Effect of reaction time on hexadecane oxidation reaction

Sr. No.	Reaction time	Conversion, %	Selectivity, %				TOF, h^{-1}
			Alcohols	Ketones	Lower alkanes	Other products	
1	5	11.66	40.31	37.57	4.07	16.27	7.29
2	16	18.38	36.58	39.74	9.41	12.59	3.80
3	48	24.04	35.30	36.09	10.03	18.04	1.61
4	96	35.96	33.42	35.61	11.18	18.51	1.17

Reaction conditions: alkane: hexadecane-25mmol, catalyst: $PdCl_2$Bipy- 0.08mmol, temp- 150^0C, oxidant: O_2 in bladder

The results in the Table 2.8 showed that with increase in reaction time the hexadecane conversion increases, however no much variation in the product profile was observed. After 5 hrs reaction the hexadecane conversion was 11.66% with alcohols and ketones combined selectivity to 70%, and after 96 hr reaction time the conversion was 35.96% with alcohols and ketones combined selectivity of 67%. So 24% increase in hexadecane conversion resulted in only 3% decrease in the selectivity.

If we look at the TOF values in Table 2.8 then we will find that the rate of oxidation has slowed down over the reaction period. The TOF value is 7.29 in the initial 5 hr period then it gradually decrease to the value 1.17 at 96 hr. That means, over the period the rate of reaction has slowed down. This may be due to catalyst deactivation. To find out the extent of catalyst deactivation the catalyst recycle study was carried out.

2.5.11 Catalyst recycle study:

The alkane oxidation reactions are carried out in neat alkane, without use of any solvent. Most of the organometallic complexes including the organometallic complexes of palladium are insoluble in alkanes. In this case also the catalyst is heterogeneous catalyst, and simple filtration is sufficient to separate the catalyst from the reaction mixture. Therefore during the catalyst recycle study, after the virgin run, the catalyst was filtered from the reaction mixture and washed with acetone followed by hexane and dried under vacuum at RT. This catalyst was then charged into fresh hexadecane and the reaction was carried out using previously mentioned procedure.

The $PdCl_2Bipy$ catalyst used for hexadecane oxidation reaction was recycled for five times using this procedure. The results of the catalyst recycle study are given in Figure 2.41

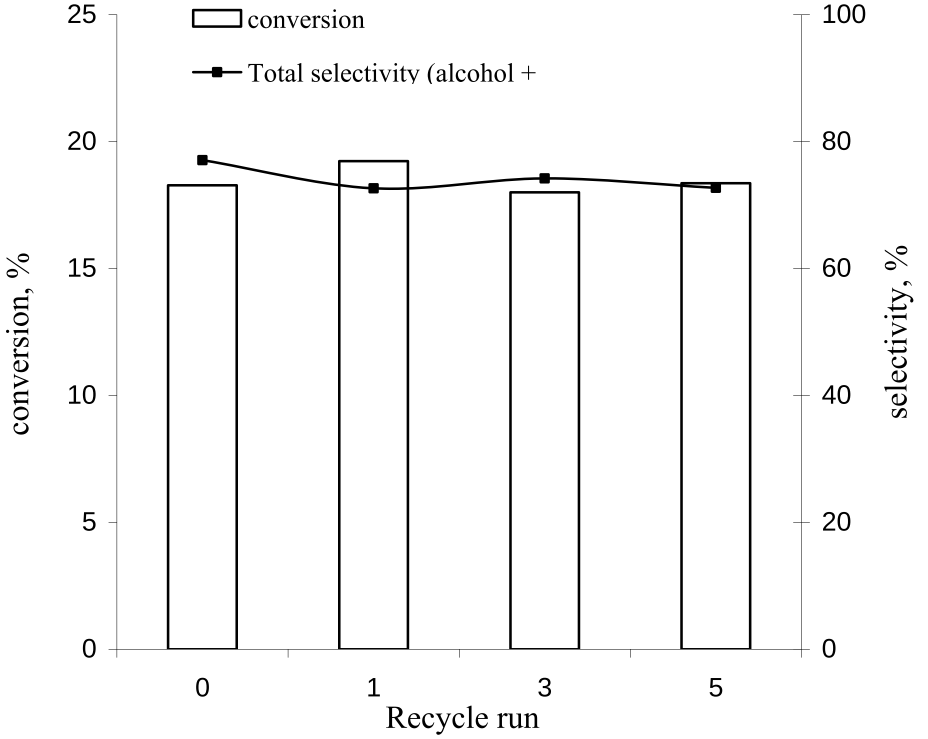


Figure 2.41: Catalyst recycle study

Reaction conditions: alkane: hexadecane-25mmol, catalyst: $PdCl_2$Bipyridine-0.08mmol, temp- 150^0C, oxidant: O_2 in bladder, time: 16 hr

The results of the catalyst recycle study showed that the catalyst is active even after five recycles. No much variation in the activity and selectivity of the catalyst was observed.

The leaching of catalyst was also checked by ICP of the reaction mixture (filtered solution). The ICP analysis of the reaction mixture separated from the catalyst of the virgin run and 1st recycle study showed negligible presence of palladium in the reaction mixture (<1ppm).

The catalyst recycle study showed that the catalyst is not deactivated during reaction. This suggest that in the course of reaction the catalyst surface is getting temporarily covered by the adsorption of reaction mixture components, which get removed on washing with hexane and acetone. To confirm this possibility, the catalyst after virgin run was separated from the reaction mass and used as such without washing for another reaction with fresh hexadecane charge. The results of this study are given in Table 2.9

Table 2.9: Hexadecane oxidation using used catalyst without catalyst washings

Sr. No.	Reaction particulars	Conversion, %	Selectivity, %				TOF, h^{-1}
			Alcohols	Ketones	Lower alkanes	Other products	
1	Virgin run	18.21	37.31	40.29	8.55	12.66	3.67
2	1st recycle	16.85	37.53	40.15	9.45	12.48	3.49

Reaction conditions: alkane: hexadecane-25mmol, catalyst: $PdCl_2$Bipyridine-0.08mmol, temp- 150^0C, oxidant: O_2 in bladder, time: 16 hr

The results of the run 2 in Table 2.9 showed that even the unwashed catalyst has the same activity as that of fresh catalyst. This also showed that the adsorption on the catalyst surface is temporary as the catalyst surface get washed even in hexadecane under stirring.

To understand whether the products that are forming during reaction are poisoning the catalyst surface and to identify this, few reactions were carried out in which the products like ketone, alcohol, and water were added separately in the fresh hexadecane charge before beginning of the reaction and then the reactions were carried out using normal procedure. The results of these reactions are given in Table 2.10.

Table 2.10: Effect of products on conversions of hexadecane oxidation reaction

Sr. No.	Additional component	Conversion, %	Selectivity, %				TOF, h^{-1}
			Alcohols	ketones	lower alkanes	Other Products	
1	Normal reaction	18.38	35.58	38.84	9.41	11.59	3.80
2	2-undecanol	18.46	32.95	37.04	9.88	10.56	3.81
3	Water	16.33	34.46	42.25	9.05	12.74	3.39
4	2-decanone	18.22	33.56	37.23	9.10	11.43	3.77

Reaction conditions: alkane: Hexadecane – 25mmol, catalyst: $PdCl_2Bipy$- 0.08mmol, 2-undecanol - 1.8mmol, water – 1.8mmol, 2-decanone – 1.8mmol, temperature - 150^0C, time- 16 hr, oxidant- O_2 in bladder,

The results of these reactions did not show major influence of these components on the conversion and selectivity of the reaction, which suggests that these particular classes of products are not poisoning the catalyst. It is likely that the other products, which are forming at very low concentrations in the course of reaction, may poison the catalyst. The other products that were observed in the reaction medium were diketones, carboxylic acids, and ether. Out of these components the chances of ether poisoning the catalysts are rare and the fact that washing the catalyst with hexane, regenerates the catalyst showed that the poisonous material temporarily binding the catalyst. Hence the probability of diketones poisoning the catalyst is more compare to carboxylic acids.

2.5.12 Effect of mode of introduction of oxidant on activity and selectivity of catalyst

To find out effect of mode of introduction of oxidant on hexadecane oxidation few reactions were carried out under purging of oxidant. The results of the study are given in Table 2.11

Table 2.11: Oxidation of hexadecane under the purging of oxidant

Sr. No.	Oxidant	Conversion, %	Selectivity, %				TOF, h^{-1}
			Alcohols	Ketones	Lower alkanes	Other products	
1#	100% O_2	11.66	35.71	39.67	6.07	15.27	7.29
2*	100% O_2	12.35	34.59	39.54	5.50	16.66	8.03
3#	20% O_2 in N_2	2.43	40.15	37.23	12.81	6.04	1.53
4*	20% O_2 in N_2	5.91	39.65	36.99	9.90	8.34	3.78

Reaction conditions: alkane: hexadecane-25mmol, catalyst: $PdCl_2Bipy$- 0.08mmol, temperature- 150^0C, oxidant purging rate- 5-10 ml / min, time: 5 hr, # reactions under atmospheric pressure of oxidant, *reactions under purging of oxidant

Entries 2 and 4 in Table 2.11 showed that in both these reactions the hexadecane conversion has increased compared to the reactions carried out under static oxidant atmosphere. This is expected because in purging mode the concentration of oxygen in solution will always remain more than that of static mode, resulting in more alkane conversion. However in both these cases the total selectivity of alcohols and ketones has remained almost constant.

Based on the results of the reaction conditions optimization study the optimized reaction conditions for the alkane oxidation reactions are given in the Table 2.12

Table 2.12: Optimized reaction conditions for alkane oxidation reaction

Sr. No.	Reaction parameter	Optimized value
1	Catalyst concentration	0.08 mol
2	Temperature	150^0C
3	Oxidant	O_2
4	Time	5.0 hr

2.5.13. Screening of alkanes

PdCl$_2$Bipy catalyst was tested for the oxidation of other alkanes under the optimized reaction conditions. The products of these all reactions were identified by GCMS.

2.5.13.1 Screening of linear alkanes

With PdCl$_2$Bipy catalyst the oxidation of n-hexane to n-hexadecane was carried out. The results of the reaction are given in the Table 2.13

Table 2.13: Screening of linear alkanes using PdCl$_2$Bipy catalyst

Sr. No.	Substrate	Conversion, %	Selectivity, %				TOF, h^{-1}
			Alcohols	Ketones	Lower alkanes	Other products	
1	n-hexane*	3.57	37.05	35.38	-	15.87	61.00
2	n-decane	9.73	34.27	41.11	8.84	14.77	6.86
3	n-dodecane	10.26	35.97	37.62	7.68	17.06	6.56
4	n-tetradecane	11.17	34.01	39.06	8.16	15.69	7.13
5	n-hexadecane	11.66	35.71	39.67	6.07	15.27	7.29

Reaction conditions: alkane- 25mmole, catalyst: PdCl$_2$Bipy- 0.08mmol, temperature - 150^{0}C, time- 5 hr, oxidant- O$_2$ in bladder, * reaction carried out in autoclave under 200 psi pressure of air for 1hr

The substrate screening showed that as the number of carbon atoms in the alkane chain increases, the rate of reaction increases. At the same time no much effect of alkane chain length was observed on the selectivity of alcohols and ketones. The combined selectivity of alcohols and ketones remains almost constant for all substrates. (Total selectivity, alcohol + ketone is in the range of 70 – 75%). [As a representative example for the oxidation of linear alkanes, the oxidation of hexane along with observed products is shown in scheme 2.1, Annexure III.]

2.5.13.2 screening of aryl alkanes and cyclic alkanes

The PdCl2Bipy catalyst was also tested for aryl alkanes and cyclic alkanes. The results of the screening of alkanes are given in Table 2.14

Table 2.14: Screening of aryl alkanes and cyclic alkanes using $PdCl_2$Bipy catalyst

Sr. No	Substrate	Conversion, %	Selectivity, %				TOF, h^{-1}
			Alcohols	Ketones	Lower alkanes	Other products	
1	ethylbenzene	22.28	22.52	69.75	-	1.26	4.44
2	propylbenzene	23.75	9.14	70.38	-	16.63	4.73
3	cyclohexane*	4.34	33.44	47.63	-	11.35	83.61

Reaction conditions: alkane- 25mmole, catalyst: $PdCl_2$Bipy- 0.08mmol, temperature - 150^0C, time- 16 hr, oxidant- O_2 in bladder, * reaction carried out in autoclave under 200 psi pressure of air for 1hr

The alkane screening study showed that in addition to the oxidation of linear alkanes the catalyst was also found to be active for the oxidation of cycloalkanes and aryl alkanes**.** [The reaction and products for oxidation of ethyl benzene, propyl benzene and cyclohexane are shown in scheme 2.2-2.3, Annexure III]

2.6 Conclusions:

The oxidation of alkanes was performed using palladium metal complexes. The oxidation products of alkanes were identified by GC-MS. Various organic ligands were screened for oxidation of decane. It was observed that as we increase the electron density on central metal atom the activity of catalyst towards alkane oxidation increases. The $PdCl_2$Bipyridine catalytic system was found to give the highest activity (TOF = 6.86 h^{-1}) and combined selectivity of (~75 %) to alcohol and ketone for oxidation of decane. The palladium catalysts is insoluble in reaction medium therefore its recycle study also tested. The catalyst showed no loss in activity and selectivity in five recycles. The role of temperature, reaction time, oxygen concentration on the activity and selectivity of oxidation of decane has been investigated. The $PdCl_2$Bpyridine catalyst system is also an efficient catalyst for oxidation of aryl alkanes, cyclic alkanes in addition to linear alkanes.

References:

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Chapter 3

Studies on the Mechanism of Alkane Oxidation Using Palladium Metal Complexes

3.1 Introduction:

The role of transition metal complexes in the activation of oxygen and alkanes is very complex. Many different reaction pathways have been proposed to explain the widely differing process conditions required to oxidize different substrates selectively to the desired products using metal complexes.[1]

The detailed literature related to the mechanism proposed in the oxidation of alkanes is covered earlier (Chapter 1, section 1.5).

The studies on the oxidation of alkanes using $PdCl_2Bipy$ complex using molecular oxygen (Chapter-2) shows the formation of alcohol, ketone and other products like ether, ester, lower alkanes and water. As also seen in the Table 2.8 we can see that the formation of the alcohols and ketones is linearly increasing with reaction time. The ratio of alcohol: ketone is also invariant throughout the course of the reaction. In conventional oxidation reactions particularly for the reactions involving peroxo radicals one finds that the product profile changes during reaction. The first product being more reactive undergoes reaction in preference to the alkane. This results in the variation in the selectivity with conversion.

In order to understand the mechanism of the $PdCl_2Bipy$ catalyzed alkane oxidation, a number of reactions were carried out, reaction intermediates isolated and characterized.

In this chapter a mechanism is proposed for the palladium catalyzed aerobic oxidation of alkanes. An active palladium species was isolated from the reaction mixture and characterized by IR and XPS analysis. Based on the IR, in-situ IR studies and XPS analysis of the catalyst, a probable mechanism is proposed for activation of alkane. The observations and results obtained in the previous chapter were also used to deduce and propose the mechanism that may be operative for this reaction.

3.2 Materials:

Palladium chloride ($PdCl_2$) and palladium acetate ($Pd(OAc)_2$) were obtained from Hindustan Platinum and used as received. Triphenyl phoshine, 2,2'-bipyridine, n-decane were purchased from Aldrich. Pet ether, acetone, were purchased from Loba chemicals and used as received.

3.2.1 Synthesis of Palladium metal complexes:

3.2.1.1 Synthesis of $PdCl_2$Bipy:

The $PdCl_2$Bipy complex was prepared by using following procedure. In a 50 ml round bottom flask containing 10 ml methanol, 0.266g (1.33mmol) $PdCl_2$ was added followed by 0.234g (1.33mmol) 2,2'-bipyridine. The mixture was stirred at room temperature for 15 hr. The precipitated orange yellow colored $PdCl_2$Bipy complex was filtered and washed with methanol and then dried under vacuum. Practical yield of the complex was 0.440g (88%)

The complex was characterized and the details are given in Chapter II, section 2.2.1.1

3.2.1.2 Synthesis of $PdBr_2(PPh_3)_2$:

0.583 g (2.6mmol) $Pd(OAc)_2$ was dissolved in 5ml ethanol under constant stirring and heating. To it (3.2mmol) 0.28ml, 48% HBr solution was added slowly under constant stirring. After complete addition of HBr, the solution turned dark red. This mixture was then dried under vacuum. To this 5 ml ethanol was added. Further this solution was added to 5ml ethanol containing 1.37 g (5.2mmol), triphenylphosphine. This mixture was then stirred for 3 hr at 60^0C, and then for 10 hr at room temperature. The precipitated yellow colored $PdBr_2(PPh_3)_2$ was filtered and washed with ethanol and dried under vacuum. Practical yield of the complex was 1.16g (45%)

The complex was characterized and the details are given in Chapter II, section 2.2.1.3

3.2.2 Analytical methods:

IR spectra were obtained using a Perkin Elmer Spectrum-2000 spectro photometer in transmission mode using KBr pellets. FT-IR spectra were recorded on a Bio-Rad Spectrophotometer 175C. The alkane adsorption study on the catalyst surface was done on IR instrument Shimatzu-8300, with DRIFT accessory.

The reaction products were identified using Agilent GC 6890N with 5973 mass selective detector (GCMS).

The quantitative analysis of the reactant and oxidation products was carried out by an external standard method using a gas chromatographic technique. For this purpose, HP 6890 gas chromatograph controlled by the HP Chemstation software and equipped with an auto sampler unit, fitted with FFAP capillary column (30M × 320μm × 0.25 μm film thickness with a stationary phase of fatty acids) and FID detector was used.

3.3 Results and discussion:

In Chapter 2, a detailed study on use of organometallic complexes of palladium in oxidation of alkanes was carried out. It was observed that the palladium complexes, in presence of molecular oxygen selectively catalyze the oxidation of alkanes to corresponding alcohols and ketones. Out of the palladium complexes screened in Chapter 2 a maximum decane conversion obtained was with $PdCl_2$Bipy complex (9.73% conversion and total selectivity to alcohol and ketone is 75.38%). In addition to the desired products (alcohol and ketone), the other products formed are lower alkanes, alcohol and ketone derivatives of lower alkanes, diketones and carboxylic acids. The product contribution from the lower alkanes inclusive of the corresponding oxygenates was ≤15% of the alkane converted. Besides the alcohol and ketone, ethers (≤4%) diketones, acids (≤2%) and esters (≤6%) were also detected along with the by-product water (The GC-MS of the reaction mass is given in Annexure-IV). The carbon dioxide formation was found to be negligible, as confirmed by gas analysis of the reaction on GC.

The $PdCl_2$Bipy catalyst was found to catalyze the oxidation reaction in neat alkane in presence of molecular oxygen, without the use of any co-reductant or co-catalyst. It was therefore decided to investigate the reaction mechanism.

The $PdCl_2$Bipy complex is insoluble in alkane (generally most of the metal complexes are insoluble or sparingly soluble in neat alkane) and it could be conveniently separated by filtration. The robustness of the catalyst was checked through a recycle study. For recycle study the catalyst was separated after oxidation reaction by filtration of the reaction mass and washed several times with hexane followed by acetone. This washed catalyst was then dried under vacuum for 5 hrs at room temperature and then used for the recycle study. This catalyst could be successfully recycled for five times with no considerable loss in activity and selectivity (Chapter 2, section 2.5.11). This observation suggests that the filtered catalyst is one of the active catalytic species, involved in the reaction. Therefore, this active species was analyzed to elucidate the structure.

The IR spectrum of the isolated active species was recorded and compared with the IR spectrum of the unused $PdCl_2Bipy$ catalyst. The IR spectra are shown in Figure 3.1 and 3.2.

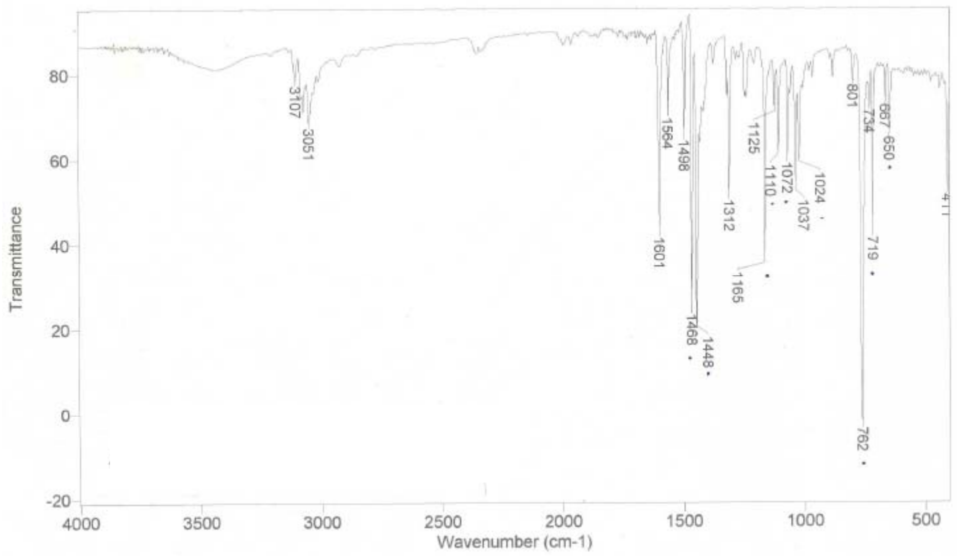


Figure 3.1: IR spectra of the unused $PdCl_2Bipy$ catalyst

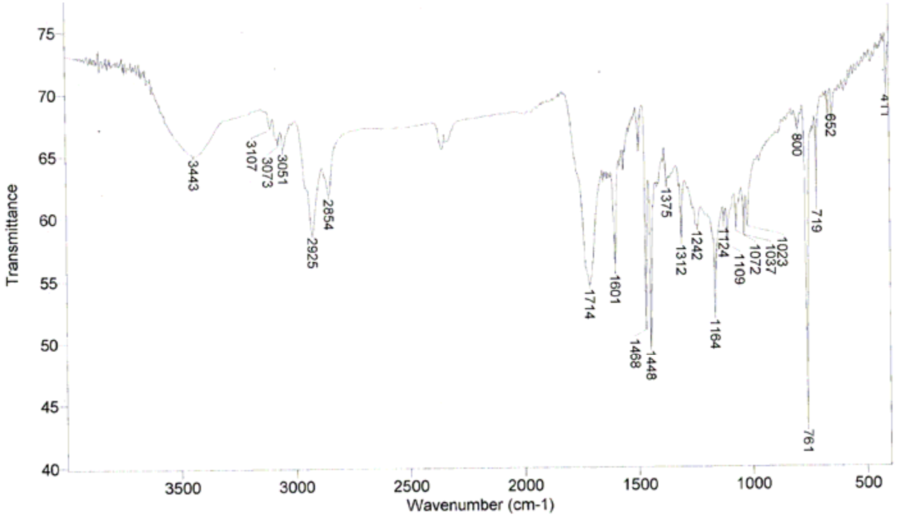


Figure 3.2: IR spectra of the isolated active species (i.e $PdCl_2Bipy$ catalyst after reaction)

In comparison to the IR spectrum of the unused $PdCl_2$Bipy catalyst new peaks are observed in the IR spectrum of the $PdCl_2$Bipy catalyst after reaction. The new peaks observed are at $1714cm^{-1}$, at $3443cm^{-1}$, and in the region $2854cm^{-1}$ to $2956cm^{-1}$. The peak at $1714cm^{-1}$ showed the presence of C-O functionality in the complex, the peaks at 2854, 2924 and $2956cm^{-1}$ showed the presence of the alkyl group and the peak at $3443cm^{-1}$ indicated presence of OH group. Thus the isolated catalytic species has an alkane moiety, C-O moiety and an OH group attached to it.

The ESCA analysis of the isolated catalyst was carried out to find out the oxidation state of the palladium. The results of the ESCA analysis are shown in Figure 3.3a and Figure 3.3b

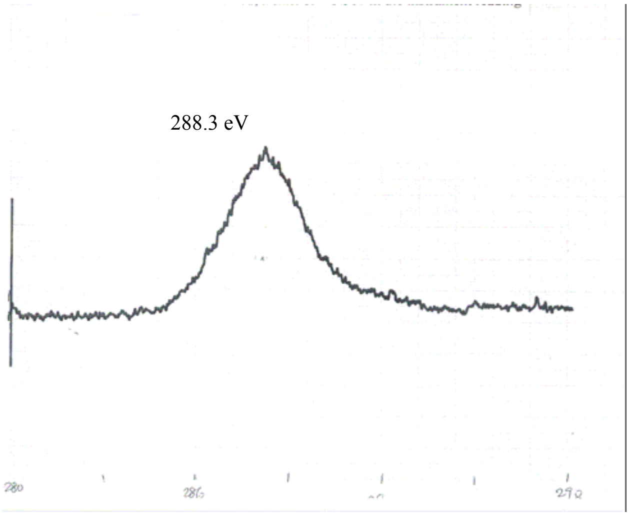


Figure 3.3: a) ESCA of the carbon

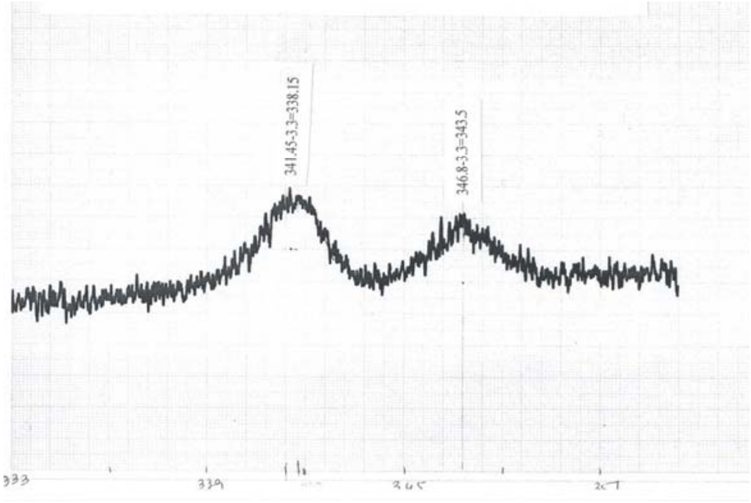


Figure 3.3: b) ESCA of the $PdCl_2$Bipy catalyst after reaction

Table 3.1: XPS analysis of $PdCl_2Bipy$ catalyst after reaction

Values (eV)	C	Pd	
	1s	$3d_{5/2}$	$3d_{3/2}$
Observed	288.3	341.4	346.8
Corrected*	285	338.1	343.5
Literature	285	336.4	341.7

*All the values were corrected to $C_{(1s)}$ with binding energy of 285eV using adventitious carbon.

The XPS of the used catalyst showed energy of Pd 3d π/2 to be 338.15ev and energy of Pd 5d π/2 to be 343.5ev, which are comparable with the reported binding energy values of 336.4eV for the Pd(II) (3d5/2) and 341.7eV for the Pd(II) (3d3/2).[2] This showed that in the isolated catalytic species the oxidation state of the palladium is +2.

The elemental analysis of the $PdCl_2$bipy before reaction and that of the catalyst isolated after reaction were carried out to check the presence of chloride ion. The results of the halide content analysis are as given below

1. Theoretical % Cl^- in $PdCl_2$bipy before reaction = 21.32 %
2. Experimental % Cl^- in $PdCl_2$bipy before reaction = 21.54%
3. Experimental % Cl^- in isolated catalyst after reaction = 1.12 %

The results show the removal of both the chloride ions from the $PdCl_2$Bipy catalyst during reaction. The small chloride content in the catalysts may be attributed to some unconverted catalyst. This is likely to occur as the catalyst is heterogeneous in nature and hence some catalyst may not take part in the reaction.

To find out the interaction of alkane with the catalyst during reaction, an in-situ DRIFT IR study of the catalyst under alkane oxidation reaction conditions was carried out. In this study, first the catalyst was heated to 150^0C under a flow of nitrogen gas. Then decane was allowed to pass over the catalyst along with the nitrogen stream, and the far IR of the catalyst was recorded at regular time intervals under constant temperature (150^0C) and nitrogen flow. The far IR showed that the alkane does not get chemisorbed on the catalyst surface in presence of nitrogen gas, indicating no activation of alkane. However, when the same study was carried out in presence of oxygen instead of nitrogen, chemisorption of alkane was observed on the catalyst surface indicating the activation of alkane. This study thus showed that as a first step initial activation of oxygen is taking place on the catalyst surface followed by the activation of alkane giving rise to a catalytically active species.

Thus the above study showed that, during reaction the catalyst first activates the oxygen, following which the alkane is activated. The elemental analysis showed the removal of Cl^- ions during reaction, which suggest that during the activation of oxygen on catalyst surface, the Cl^- ions from $PdCl_2Bipy$ get detached by the oxygen molecule to form Pd-O bond. To confirm this hypothesis the far IR study of the catalyst before reaction and that of the catalyst isolated after reaction were carried out. The results of the far IR study are shown in the Figure 3.5 and Figure 3.6 respectively for the virgin complex and isolated complex. For comparison the far IR of the $Pd(OAc)_2$ and that of the $PdCl_2$ were also recorded. The Pd-O frequency is observed at 390 and 403cm^{-1} and the Pd-Cl frequency is observed at 364cm^{-1}. (Figure 3.4).

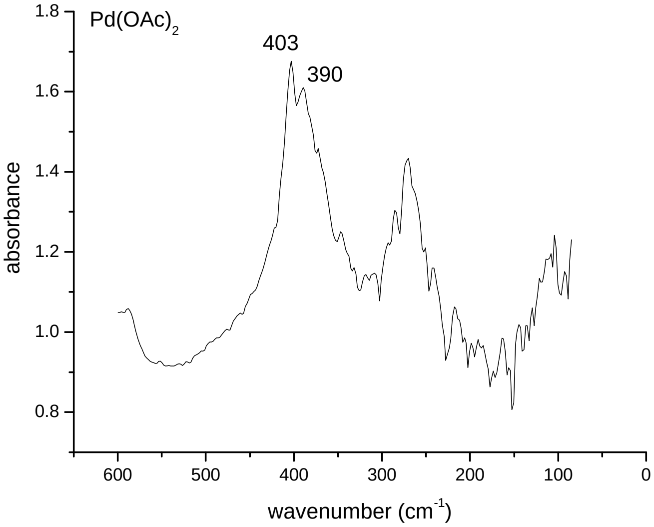


Figure 3.4: Far IR spectrum of Pd $(OAc)_2$ complex

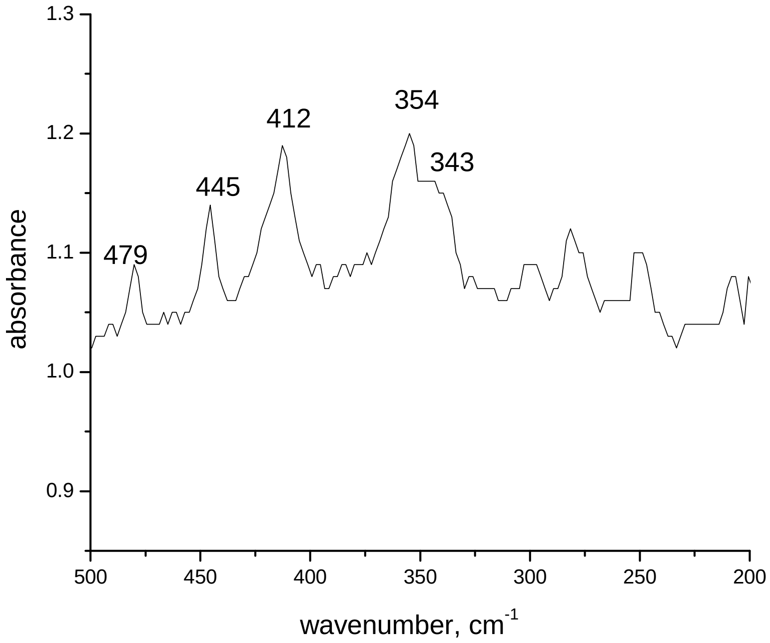


Figure 3.5 Far IR spectrum of the virgin PdCl$_2$Bipy complex

In the far IR spectrum of the virgin PdCl$_2$Bipy complex, peaks are observed at 343, 354, 412, and 445cm^{-1}. These peaks are for the Pd-Cl and Pd-N bond vibrations.[3]

Similarly the far IR spectrum of the catalyst isolated after reaction showed peaks at 279.62, 346.64, 358.71, 412.73, 445.30 and 479.2cm^{-1}.

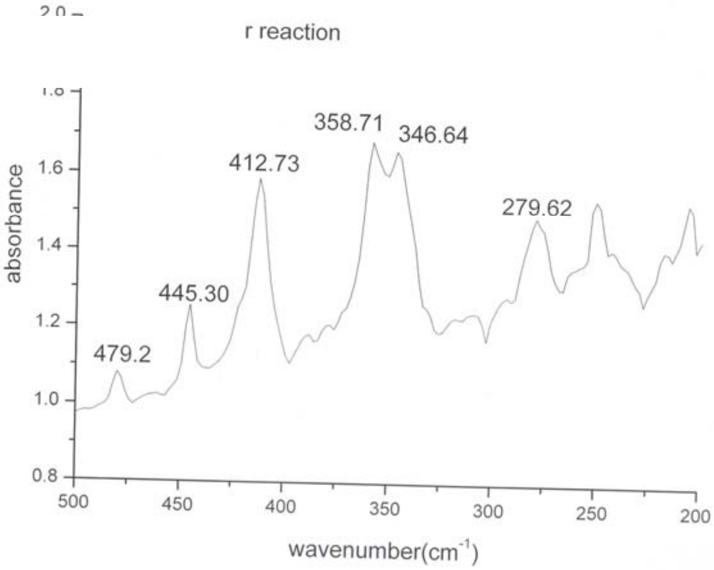


Figure 3.6: Far IR spectrum of PdCl$_2$Bipy catalyst after reaction

In the far IR study of $PdCl_2Bipy$ catalyst the Pd-N bond frequency and Pd-Cl frequency are found to interfere with Pd-O absorption frequencies, thus not allowing the monitoring of the disappearance of the Pd-Cl bond and formation of Pd-O bond.

To solve this problem, instead of using $PdCl_2Bipy$ catalyst the same study was carried out with $PdBr_2(PPh_3)_2$ catalyst. This catalyst was also found to be active for the oxidation of alkane (Table 2.8) and the mechanism derived could be extrapolated to that for $PdCl_2Bipy$. The far IR spectra of $PdBr_2(PPh_3)_2$ catalyst before reaction and after reaction are given in Figure 3.7 and 3.8 respectively.

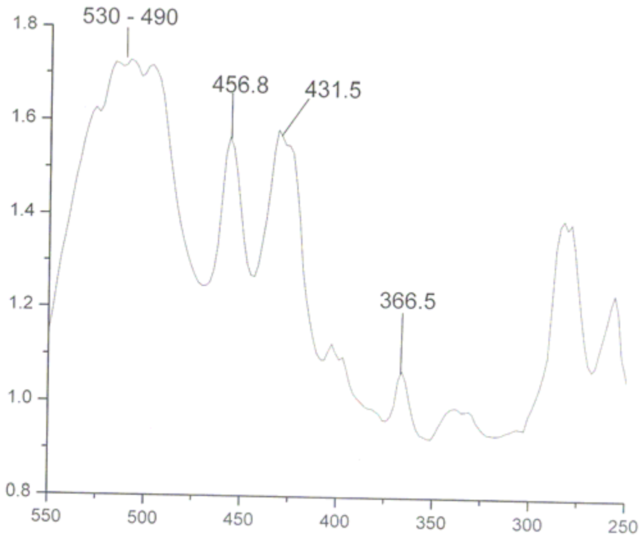


Figure 3.7: Far IR spectrum of $PdBr_2(PPh_3)_2$ catalyst before reaction

In the far IR spectrum of the virgin $PdBr_2(PPh_3)_2$ catalyst peaks are observed at 431.5, 456.8 cm^{-1} and a broad multiplet in the range 490-530 cm^{-1} for $Pd\text{-}PPh_3$[4] and a peak at 366.5 cm^{-1} for Pd-Br (confirmed from IR of the $PdBr_2$).

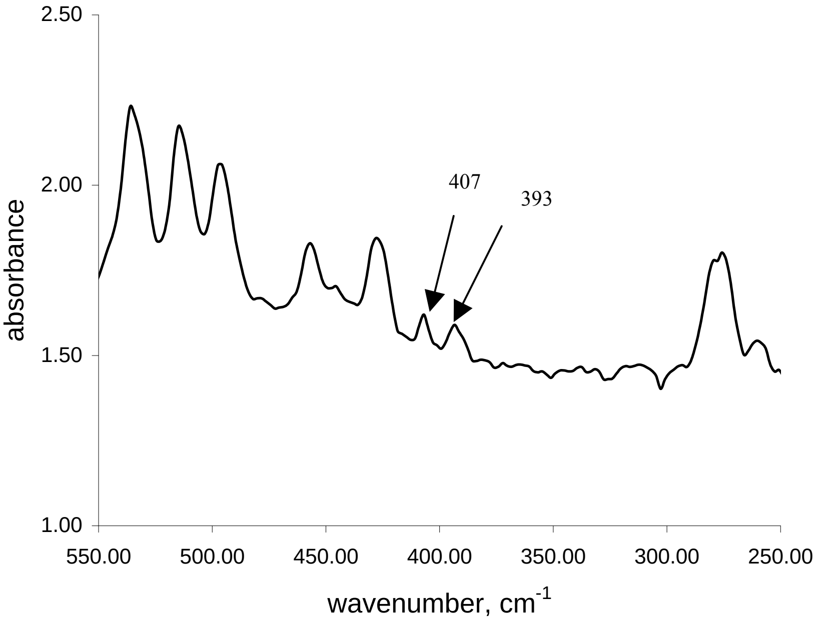


Figure 3.8: Far IR spectrum of $PdBr_2(PPh_3)_2$ catalyst after reaction

In the far IR spectrum of the isolated complex (from $PdBr_2(PPh_3)_2$) , the Pd-PPh_3 peaks are observed at 427.6, 456.9 cm^{-1} and the multiplet well resolved into three peaks at 496.5, 514.4 and 535.5 cm^{-1}. However, the peak at 366.3 cm^{-1} for Pd-Br is absent indicating removal of halides and instead peaks at 407.3 and 393.2 cm^{-1} are observed which are assigned to Pd-O stretching frequencies (by comparison with $Pd(OAc)_2$).

Thus all the above study indicates the structure of the catalytically active species (assigned as species ‘C1’) isolated from the reaction crude to be of the type given in the Figure 3.9. In case of the $PdCl_2Bipy$ complex the species is more likely to be similar to ‘C’ (Figure 3.9).

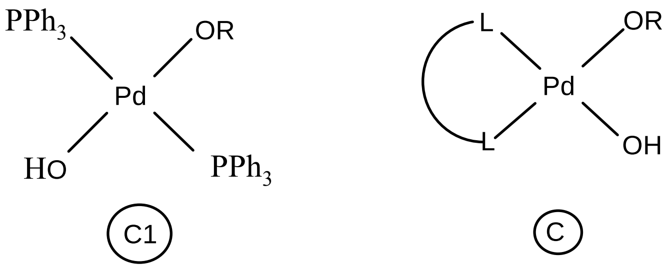
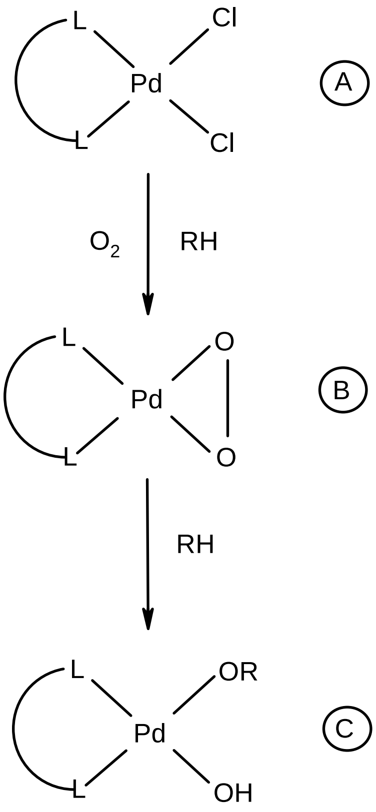


Figure 3.9: Probable structure of the catalytically active species ‘C1’ and ‘C’

Where, L represents the chelating ligand (bipy) and 'OR' represents the alkyl chain attached to the metal atom via oxygen molecule attached to any of the carbon atom from the alkyl chain. The formation of the 'OR' at the terminal carbon is likely to be rare, considering the electronic and thermodynamic stability of the species 'C'.

Based on the experimental results and spectroscopic characterizations, the mechanism for the palladium-catalyzed activation of alkane was proposed which starts with the activation of the oxygen followed by the activation of alkane. The probable mechanism is given in Scheme 1.



Scheme 3.1: Proposed mechanism for activation of alkane on palladium metal complex

In this proposed mechanism the catalyst precursor 'A' reacts with the molecular oxygen in presence of alkane replacing the halide ligands and forms species 'B'.[5] Species B being reactive, immediately reacts with alkane to form the catalytically active species 'C', wherein the oxygen of the alkoxy group (OR) is primarily bound to an internal carbon in the alkane. The position of the oxygen thus decides the location of the hydroxyl or ketonic function-giving rise to the isomeric secondary alcohols and ketones. Species ‘C’ is stable and active as it can be isolated and recycled easily.

In presence of oxygen and alkane the species ‘C’ further gives the products –viz- alcohols, ketones, ethers, diketones, esters and acids. The reaction data showed that the percentage formation of alcohols and ketones during reaction is independent of each other. Which implies different reaction pathways are followed for the generation of these products. The further reaction thus proceeds through the interaction of species ‘C’ with the alkane and oxygen. This can be shown schematically as given in Figure 3.10.

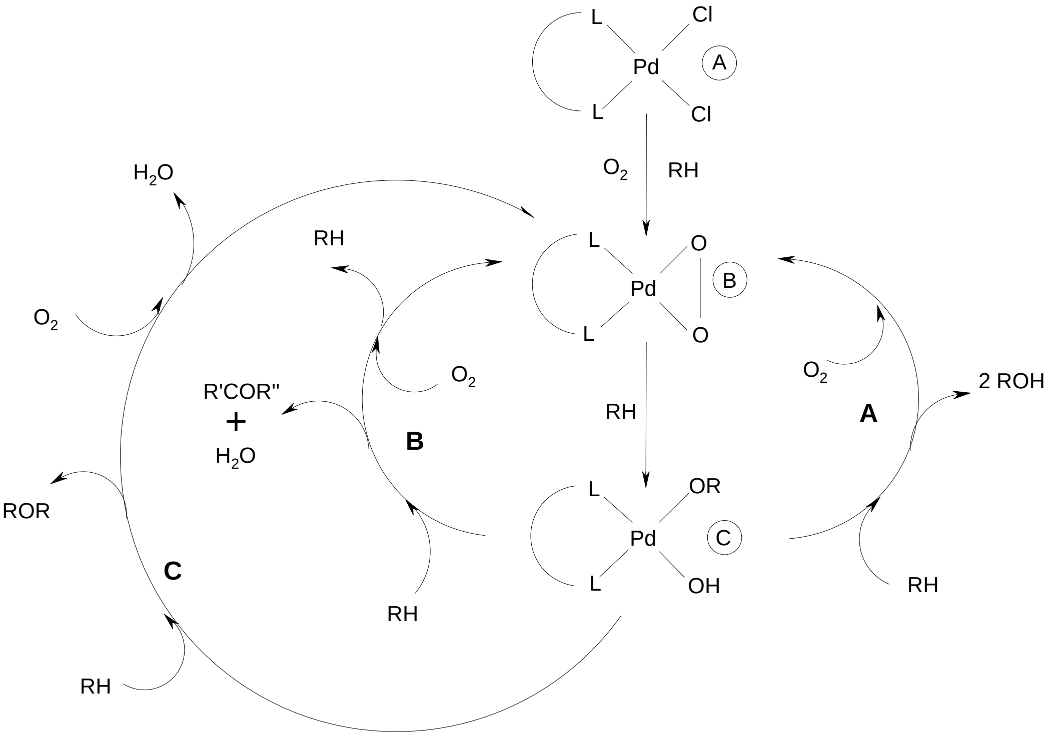


Figure 3.10: The probable mechanism for the generation of products from the species ‘C’

Path A: If the species ‘C’ follows the path ‘A’, then on interaction with RH it generates 2 moles of alcohols. Further on interaction with oxygen will generate the species ‘B’, and the catalytic cycle will continue.

The intermediate species after the elimination of the two alcohols will be highly coordinatively unsaturated and reacts with oxygen to generate species ‘B’. This is more likely to be a concerted mechanism wherein a single alcohol is liberated. The second alcohol is liberated along with formation of species ‘B’ by interaction with oxygen.

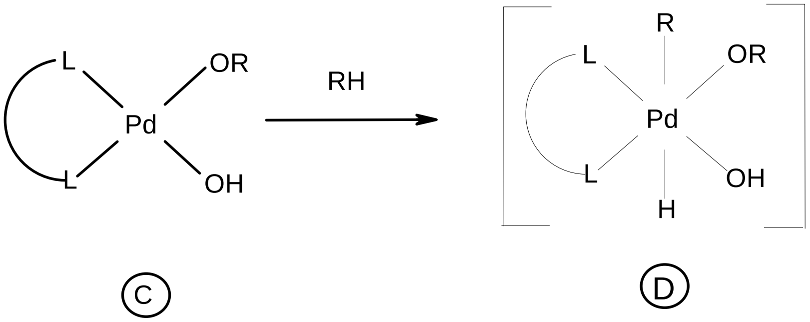
Path B: If species ‘C’ follows the path ‘B’ then it will give rise to ketone and water on interaction with RH and further on interact with oxygen to form the species ‘B’ by liberating an alkane (RH)

Path C: If the species ‘C’ follows the path ‘C’ then on interaction with RH it will generate the ether. Further interaction with oxygen will liberate water molecule to form the species B and thus the catalytic cycle will continue.

This proposed mechanism thus explains the invariance in the product profile with conversion and also explains the formation of ether.

In all the possible routes for the formation of the different major products –viz- alcohols, ketones, ether, water the initiation is similar, till the formation of the complex ‘C’. Further to this formation all the pathways envisage an interaction with alkane (RH), following which either alcohol, ketone, ether or water get liberated. Thus it is seems likely that all these pathways proceed through a common intermediate.

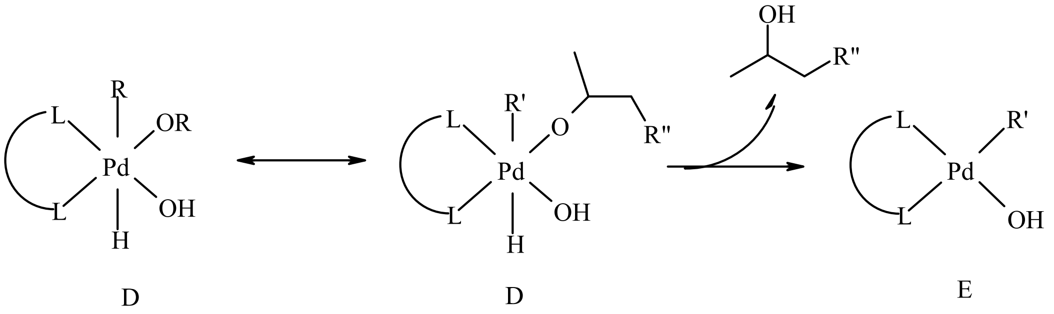
The interaction of species ‘C’ with alkane can form a six coordinated Pd (IV) transient species ‘D’ (Scheme 3.2) that can liberate any two coordinated moieties to form alcohols, ketones, water or ethers.



Scheme 3.2: The probable path away and the structure of the transient species ‘D’

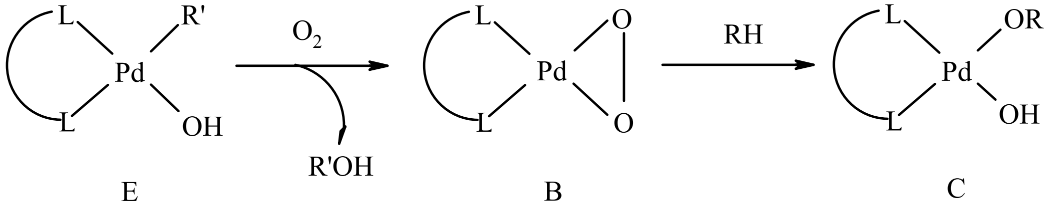
Based on the products formed during reaction, the probable routes for the generation of these products from species 'D' are discussed below in detail.

1. Generation of alcohol from the species 'D':



Scheme 3.3: Probable mechanism for the generation of alcohols

In the transient intermediate species 'D' the elimination of alkoxy group (OR") and the hydride will generate alcohol and the species 'E'. In the alkoxy group, since oxygen atom is generally attached to the internal carbon it will generate secondary alcohol. For a less probable case if the oxygen is attached to a terminal carbon atom it will generate primary alcohol. Primary alcohols being more reactive further get converted to the corresponding acids and further on, may also react with primary or secondary alcohol to form corresponding esters. All these products are observed in the analysis of the reaction mass and have been characterized by GC mass (see Annexure III). The species 'E' on interaction with oxygen will liberate one more alcohol to form species 'B', which can form species 'C' on reaction with alkane (RH) and regenerate the catalyst (Scheme 3.4).

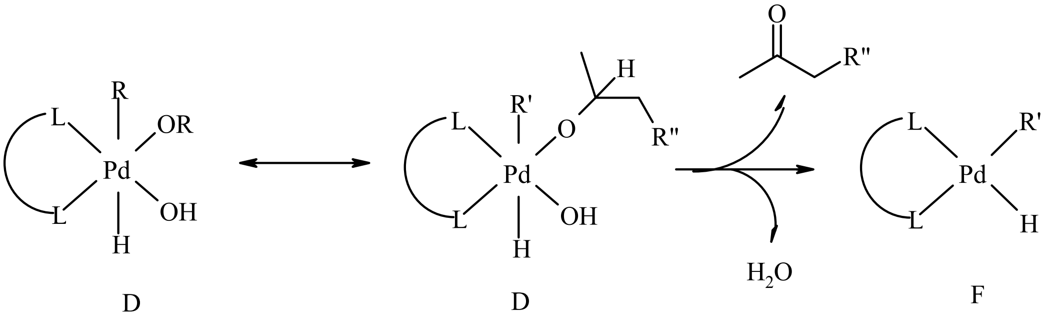


Scheme 3.4: Probable mechanism for the regeneration of species 'C' from species 'E'

Since the probability of forming terminal alkoxy species is low, the formation of the terminal alcohol is very low, as are the products derived from the terminal alcohol i.e. acid/ester

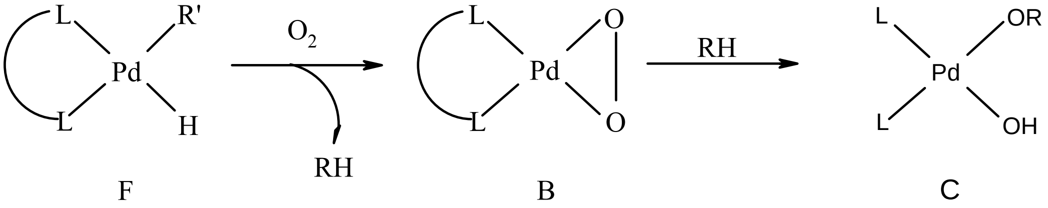
2. Generation of ketone from the species 'D':

For ketone formation, simultaneous elimination of alkoxy along with OH has to occur to form ketone and water.



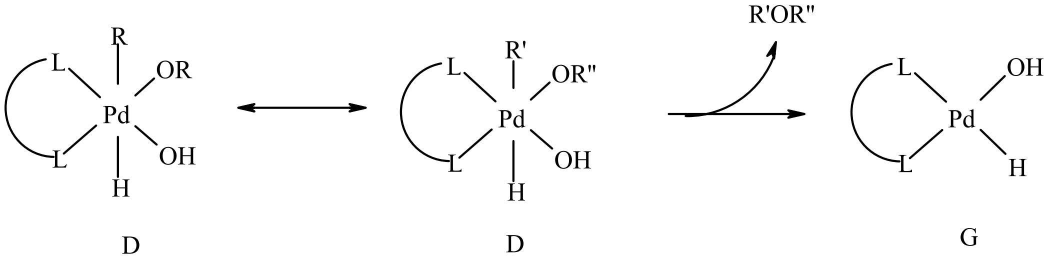
Scheme 3.5: Probable mechanism for the generation of ketones

The resulting species 'F' will in presence of oxygen liberate an alkane and form the species 'C' thus continuing the catalytic cycle (Scheme 3.6).



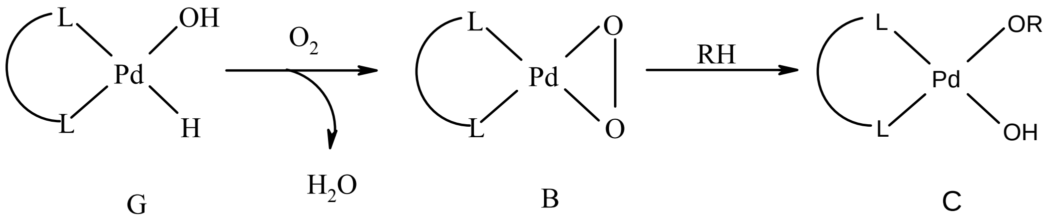
Scheme 3.6: Probable mechanism for the regeneration of species 'C' from species 'F'

3. Generation of ether from the species ‘D’:



Scheme 3.7: Probable mechanism for the generation of ethers

The ether can form from species ‘D’, by elimination of an alkoxy and alkyl group from complex ‘D’. After formation of the ether molecule, the species formed ‘G’ in presence of oxygen will convert to the species ‘B’.



Scheme 3.8: Probable mechanism for the regeneration of species ‘C’ from species ‘G’

As mentioned in the main catalytic cycle, species ‘B’ form the active complex ‘C’ via addition of alkane (RH) (Scheme 3.8).

Due to the chelating nature of Bipy, all the groups attached to the palladium are cis to each other, facilitating their elimination hence, during reaction the ketone and alcohol formation is expected to be much easier than the formation of ether. The results of the reaction also showed the same trend. The percentage formation of alcohol and ketone is ~35 – 40 % each and that of ether is < 4%.

The alcohol and ketone are the major products. It is likely that the alkyl and the alkoxy groups being bulky would prefer trans position. As a result elimination of alcohol

(OR, H/ R, OH) or ketone (OR/ OH), would be favored since they are cis to each other. The elimination of OR and R to generate ether would require a high-energy situation. As a result the formation of ether is very low.

Reactions were carried out with neat alcohol/ ketone/ ether to see whether these products could convert to further oxidized products. It was observed that they could not react further. These results suggest that the alcohol/ ketone/ ether and other products are formed independent of each other, via interaction of alkanes and oxygen with the Pd complex.

Solmonov, et. al.[6] have reported the presence of Pd(IV) species in the reaction of methane with dihalobis(phosphine)palladium(II) complexes. Authors have studied the electrophilic replacement of H, oxidative halogenation of methane, and oxidative addition of methane CH bonds to the palladium atom using the GAMESS program (non-empirical MO method). The geometry and relative stability of six diastereomeric reaction products, hydridomethyl Pd(IV) complexes $CH_3Pd(H)X_2(PPh_3)_2$, were calculated. The energy of oxidative addition of secondary and primary CH bonds of propane to $PdCl_2(PPh_3)_2$ was also calculated. The oxidative addition is a concerted process with a late transition state. The results of the calculations are in qualitative agreement with experimental data.

Crabtree et. al.[7] have proposed the mechanism involving the Pd(IV) species in the $Pd(OAc)_2$ catalyzed acetoxylation of arenes using PhI(OAc) as oxidant at 100^0C for 21hr reaction period (See Figure 3.11).

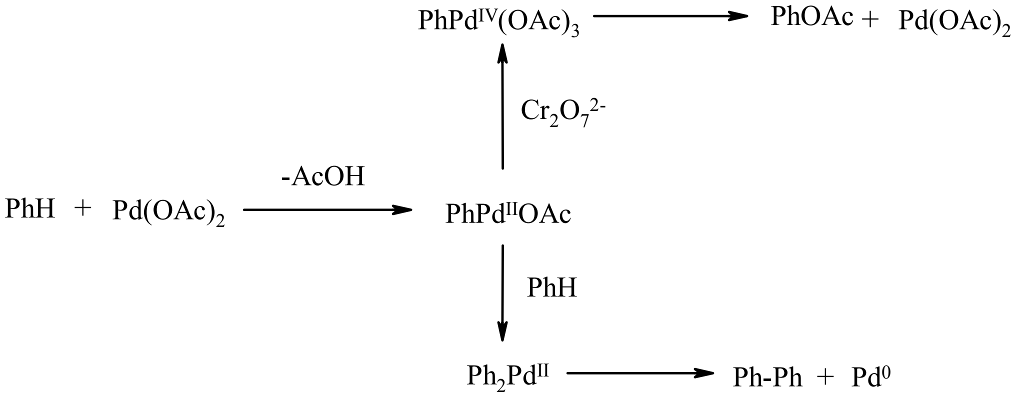


Figure 3.11: Reaction mechanism proposed for the acetoxylation of benzene using dichromate as oxidant

Sanford et. al[8] have also reported the formation of Pd(IV) species during Pd(II) catalyzed oxidative functionalization of sp^2 and sp^3 C-H bonds using PhI(OAc) as oxidant at 100^0C (See Figure 3.12).

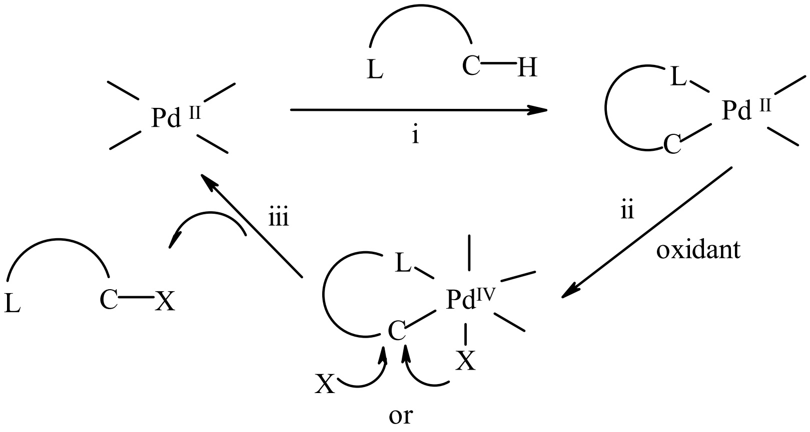


Figure 3.12: A proposed mechanism in chelate directed C-H activation of the substrate.

Stahl, et. al.,[9] have reported the probable presence of Pd (IV) species in the Pd(II)/ pyridine catalyzed aerobic oxidation of alkane, however the energies calculated for the Pd(IV) states were high in comparison to the experimental reaction pathway and hence, the probability of involvement of these species in the reaction would be less.

Six coordinated species of palladium would be very high energetically and hence their formation is expected to be difficult. The palladium catalyzed alkane oxidation reaction is found to have a temperature threshold of 140^0C (See Chapter 2, Table 2.10). This means that unless the necessary energy is provided the reaction cannot take place. This could also suggest that the intermediate species would require high temperature to form.

The feasibility of formation of species 'D' was analyzed by DFT study. In DFT study using Turbomole 6, the energies related to the probable molecules were calculated. The method used was b-p (Burke Perdew functional), using basis set TZVP. The study showed that the formation of such molecules is energetically possible.

The electronic energy values of the substrate and the palladium species ‘C’ and species ‘D’ obtained from the DFT study are given in the Table 3.2

Table 3.2: Electronic energy values obtained from DFT study

Sr. No.	Molecule	Energy, hartree
1	Decane	-394.46
2	Species ‘C’	-1168.59
3	Species ‘D’	-1563.06

The probable structure of the species ‘C’ for the reaction with decane given by the DFT study is shown in the Figure 3.13

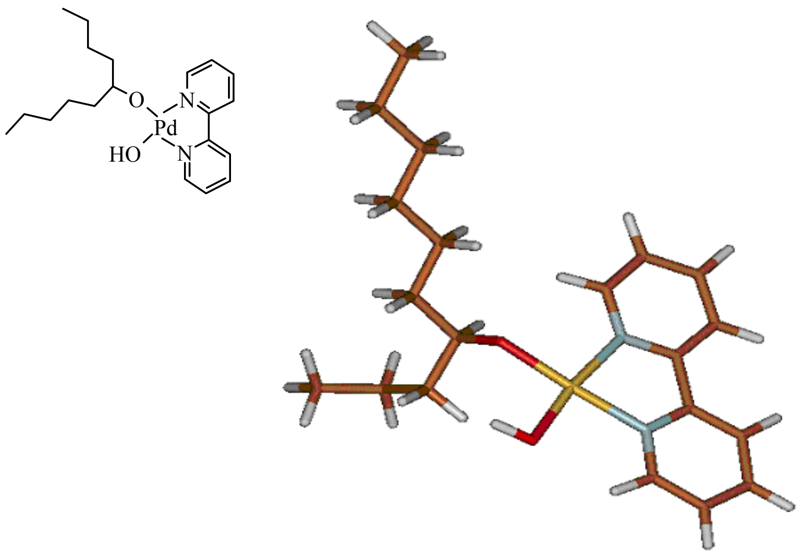


Figure 3.13: The probable structure of the species 'C'

The probable structure of the species ‘D’ given by the DFT study is shown in the Figure3.14

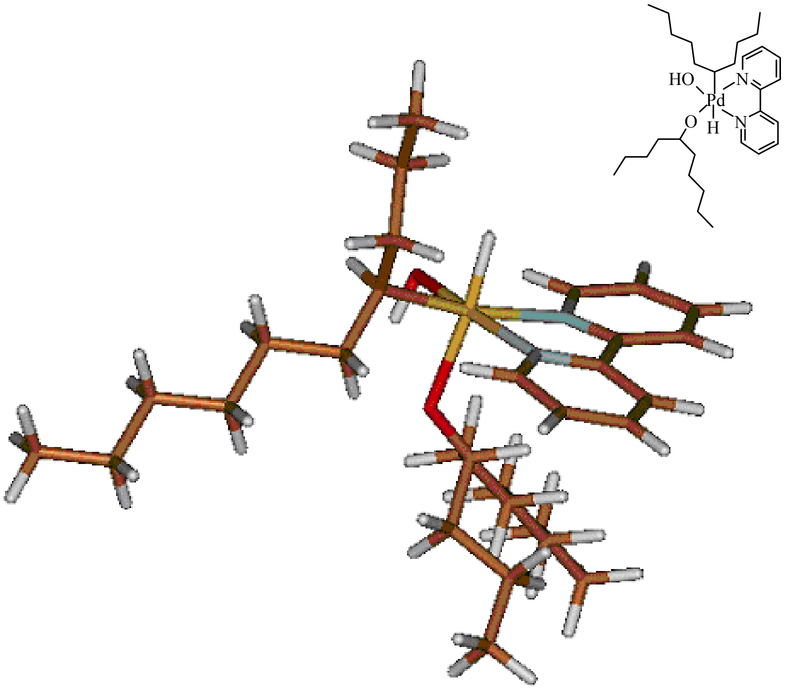


Figure 3.14: The probable structure of the species 'D'

The DFT study showed that the energy difference between the species ‘C’ and species ‘D’ is 47.4Kcal/mol (The energy difference was calculated as [energy of the decane + energy of the species ‘C’] - energy of the species ‘D’), which means the activation energy of the reaction has to be equal to or more than this value for any reaction to take place. The activation energy was calculated for the $PdCl_2$Bipy catalyzed oxidation of alkane using a neat catalyst complex (See Table 2.6). The activation energy was found to be 1.06 Kcal/mol. Such low value for the activation energy is obtained since the reaction is mass transfer controlled and also not representative, as all the catalyst is not employed in the reaction.

The activation energy was calculated for the supported palladium complex catalyzed alkane oxidation reaction (See Table 4.9). This was used, as the catalyst is highly dispersed and would provide better temperature dependence (The activation energy was 26.47 Kcal/mol).

Although the calculated activation energy is far improved compare to the earlier value, this data may not be representing true kinetics. Although the metal complex is highly dispersed (as reflected in the TOF's) the reactions are in neat alkane, which can lead to apparent kinetics and not true kinetic dependence. To obtain true kinetics dependence and calculate the activation energy with the predicted values, it would be essential to study the reaction in gas phase.

Based on the earlier discussed probable formation of a common intermediate, the proposed mechanism incorporating this species is shown in Figure 3.15.

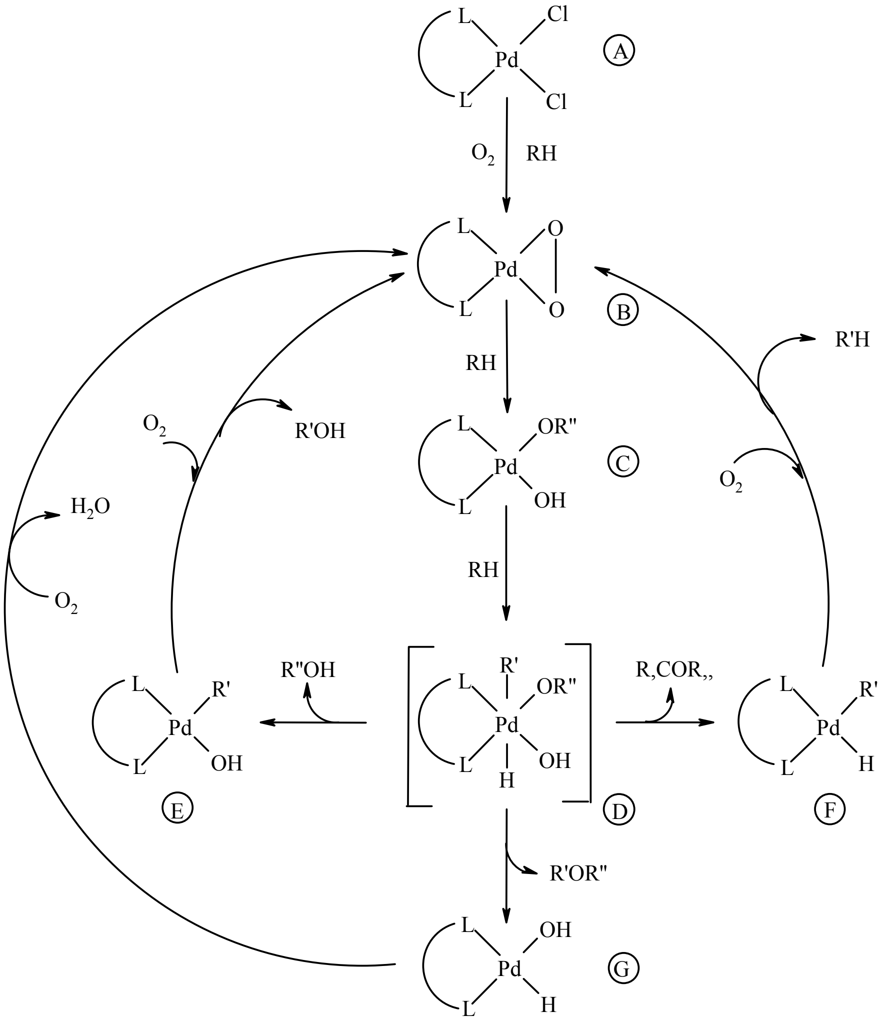


Figure 3.15: Proposed reaction mechanism for the $PdCl_2$Bipy catalyzed alkane oxidation

This mechanism thus explains the formation of alcohols and ketones as well as the ethers, and the invariance of the selectivity with conversion of alkane.

3.4 Conclusion:

A probable mechanism is proposed for the $PdCl_2$Bipy catalyzed alkane oxidation. An active metal species was isolated from the reaction nurture and characterized using various techniques. Based on the spectroscopic analysis and ESCA study a mechanism is proposed for the palladium-catalyzed activation of alkane. During oxidation of alkane, first the activation of oxygen takes place followed by the alkane. Based on the product profile and DFT study the probable reaction mechanism is also proposed. An octahedral Pd (IV) species is proposed from which, the generation of alcohols, ketones and of ethers is shown. This particular mechanism explains the invariance in the profile of alcohol and ketone with alkane conversion and also explains the formation of ether.

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Chapter 4

Synthesis, Characterization and Catalytic Activity of Heterogenized Catalysts for Oxidation of Alkanes

4.1 Introduction:

Homogenous catalytic systems have immense advantages in processes like high activity and selectivity, milder reaction conditions and better understanding of the process at molecular level. Despite these advantages their industrial application is limited by the difficulties in recovery and reusability of the catalyst.[1] Heterogenization of the tailor-made catalytic complexes offers great potential in this regard, and has been attracting considerable attention.[2] Some of the most prominent modes of heterogenization of transition metal complexes include anchoring organometallic complex on solid support[3] and biphasic reaction systems.[4] A more detailed account of the literature survey on heterogenization of metal complexes, their characterization and application for chemical reactions is presented in Chapter 1 in the section 1.3.2.

It was observed in the earlier chapter 2, that $PdCl_2Bipy$ complex can catalyze the oxidation of alkanes to alcohol and ketone. Since this complex works as a heterogeneous catalyst, only the surface of the catalyst is active for the reaction. Since the bulk of the catalyst is unavailable to the reactant, reactivity is low (maximum TOF obtained is 6.86 h^{-1})

In this chapter, the organometallic complexes of palladium were heterogenized using three different heterogenization techniques.

1) Exchange of the metal complex $PdCl_2(TPPTS)_2$ in the hydrotalcite by ion exchange
2) Tethering of $PdBr_2(PPh_3)_2$ on silica
3) Supported ossified catalyst

4.1.1 Metal complex exchanged Layered Double Hydroxides (LDH) as catalyst:

Layered double hydroxides (LDH) or more conveniently called as hydrotalcite (HT) like anionic clays have recently gained interest as catalysts, catalyst supports, ion-exchangers and composite materials in catalysis.[5] This material belong to the class of anionic, basic clays having the general formula,

$[M^{(II)}_{(1-x)}\ M^{(III)}_x\ (OH)_2]^{x+}\ [(A^{n-})_{x/n}\ yH_2O]^{x-}$ where x = 0.1-0.33, $M^{(II)}$ = Mg, Cu, Ni, Co, and Mn, $M^{(III)}$ = Al, Fe, Cr, and Ga and A^{n-} is an interlayer anion such as CO_3^{2-}, NO_3^- and SO_4^{2-}. Their calcination at 450^0C gives rise to the decomposition of the layer structure and formation of basic mixed oxides having high surface area. These ‘spinel type’ oxides have shown promise as catalysts.[6] The characteristic double-layered structure can be associated with different cations and offers a pronounced versatility with regard to the elemental composition. Transition metals, that are expected to act as active sites of catalysts can also be introduced in the brucite layer.[7] Hydrotalcites containing metals like Ni, Cu, Co, Pd etc., have already been reported in the literature.[8] Hydrotalcites with zirconium incorporated into the layers have been used for the selective oxidation of phenol to catechol with H_2O_2.[9] Kaneda et. al.[10] reported the use of Ru-Co-Al- CO_3 HT for the oxidation of alcohols. Choudhary and co-workers[11] have found out that Ni-Al hydrotalcite is active in the oxidation of alcohols using molecular oxygen. Choudhary et. al.[12] investigated the application HTs for asymmetric C-C bond-forming reactions. Narayanan et. al.[13] have studied the hydrogenation of phenol to cyclohexanone over Pd(II) containing Mg-Al hydrotalcites. Very recently, a single-pot biomimic synthesis of chiral diols mediated by a newly developed trifunctional solid catalyst consisting of active palladium, tungsten, and osmium species embedded in a single layered double-hydroxide matrix has been achieved by Choudary et. al.[14] Another important development in LDH catalysis is the nano-palladium immobilized layered double hydroxide (LDH-$Pd^{(0)}$) catalyzed Heck olefination, Suzuki coupling and Sonogashira reactions of chloroarenes .[15] Narayan et.al. have reported the effect of calcination temperature on dispersion of palladium on LDH and also have studied its effect on hydrogenation of phenol.[16] Choudary et al. have developed a $PdCl_2(TPPTS)_2$ immobilized LDH by ion exchanged method and have used it for Heck arylation of olefins.[17] Unlike other supported Pd catalysts, hydrotalcites incorporated with palladium in their structure could be good catalysts for alkane oxidation.

4.1.2 Tethering of metal complex on silica:

Tethering means chemical anchoring of the complex to the support surface via suitable modifications is another technique extensively used to heterogenize the homogeneous catalysts on inorganic supports. In this method the metal complex is anchored to the support material such as SiO_2 through a ligand. The surface of silica materials can be functionalized with various organic moieties, by reaction of the silanol groups on the silica surface with chloro- and alkoxysilanes.[18] Many different silanes with a large variety of organic moieties are commercially available for that purpose. An organic group, which is often used for functionalization, is 3-aminopropyltrimethoxysilane.[19] Use of tethered catalyst in catalysis is well reported in the literature. Clark et. al. [20] have used tethered cobalt complex for oxidation of alky aromatics. Singh et. al.[21] have used the Mn and Co salen tethered on solid support for the oxidation of olefins. Brunel et. al. [22] have tethered modified salen to polymeric supports/SiO_2. Similarly tethered palladium metal complexes are also expected to work in the oxidation of alkanes.

4.1.3 Supported ossified catalysts:

A novel approach has been demonstrated by Hu et. al.[23] for the development of heterogenized hydrogenation catalyst. Here, the simplistic approach of precipitating the homogeneous catalyst as its insoluble salt has been applied. The precipitation of ruthenium and rhodium complexes of phosphonated BINAPs as the zirconate species has resulted in providing a heterogenized catalyst for chiral hydrogenation of aromatic ketones and β-keto esters. This catalyst is very stable and recyclable.

The technique of ossification of catalysts involves heterogenization of homogeneous water soluble metal complex catalysts by its precipitation as sulphites of group II elements such as Ca, Sr or Ba. The resulting heterogenized catalyst is not only insoluble in water but also in a majority of organic solvents.[24] In a typical case, the catalyst is formed by interaction of barium nitrate with an aqueous solution of $PdCl_2(TPPTS)_2$ to form a precipitated Ba^{+2} salt of $PdCl_2(TPPTS)_2$. It is also possible to obtain such catalyst on solid supports termed as ‘supported ossified catalyst’.[25] This catalyst is formed by interaction of $Ba(NO_3)_2$ impregnated support with an aqueous solution of $PdCl_2(TPPTS)_2$, to form a precipitated Ba^{+2} salt of $PdCl_2(TPPTS)_2$ and free TPPTS-$Ba_{3/2}$ where Ba^{+2} is adsorbed on the support surface by physical adsorption. This method of immobilization is generic in nature and can be applied to a variety of catalysts supports, and catalytic reactions. Moreover, precipitation onto a support using a pre-adsorbed Ba^{+2} species provides a highly dispersed, active and stable form of catalyst with a much larger surface area. This technique of heterogenization of the homogeneous complex catalysts is expected to give enhanced activity in alkane oxidation.

The prime objective for investigation of these techniques was to explore the effect of dispersion of organometallic complex on solid surface and the effect of support on activity of the catalyst. The ability of the heterogenized homogeneous complexes to retain the activity and selectivity for the oxidation of alkanes was also explored.

A detailed investigation on this heterogenized palladium complex catalyst for oxidation of various classes of alkanes (in particular higher linear alkanes) has been presented in this chapter to demonstrate the activity, selectivity and stability of these catalysts. Characterization of the catalysts has also been discussed in the chapter.

4.2 Experimental:

4.2.1 Materials:

Palladium chloride ($PdCl_2$), obtained from Arora-Matthey was used as received. n-hexane, n-decane, n-dodecane, n-tetradecane, n-hexadecane, cyclohexane, ethylbenzene, propylbenzene (> 99% pure), ZrO_2 and La_2O_3 were obtained from Sigma-Aldrich, USA. $Mg(NO_3)_2.6H_2O$, $Al(NO_3)_26H_2O$, $Ba(NO_3)_2$, NaOH, Na_2CO_3, $Ca(NO_3)_2$, $Sr(NO_3)_2$, PPh_3, SiO_2, TiO_2, Al_2O_3 and MgO were procured from Loba Chemie, India. The solvents, acetone, dichloromethane, etc. were freshly distilled, dried and degassed prior to use. Oleum of 65% (w/w of SO_3 in H_2SO_4) strength was prepared by dissolving the SO_3 gas (produced from the reaction of H_2SO_4 with P_2O_5) in concentrated H_2SO_4 in required proportion. Distilled degassed water was used in all operations. Oxygen, air and nitrogen gas supplied by Indian Oxygen, Mumbai, India (> 99.8% pure, Matheson Gas, USA) were used directly from the cylinders. The oxidant mixtures (O_2+N_2) in (60:40, 20:80) ratio were prepared by mixing O_2 and N_2 in a reservoir vessel.

4.2.2 Synthesis of silica anchored $PdBr_2(PPh_3)_2$ using tethering procedure:

The synthesis of silica anchored $PdBr_2(PPh_3)_2$ was done in three steps.

1. Synthesis of $PdBr_2(PPh_3)_2$ complex
2. Synthesis of 10% APTS functionalized silica
3. Synthesis of 1% $PdBr_2(PPh_3)_2$ anchored silica

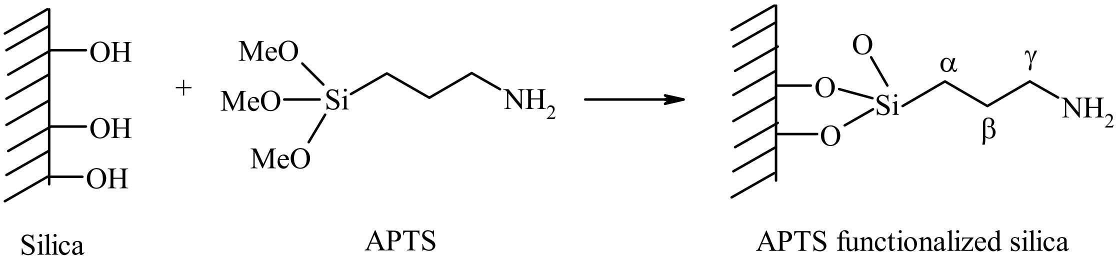
4.2.2.1 Synthesis of $PdBr_2(PPh_3)_2$ complex

0.583 g (2.6mmol) $Pd(OAc)_2$ was dissolved in 5ml ethanol under constant stirring and heating. To it 0.28ml, 48% HBr solution (3.2mmol) was added slowly under constant stirring. After complete addition of HBr, the solution turned dark red. This mixture was then dried under vacuum. To it then 5 ml ethanol was added and then it was added to 5ml ethanol containing 1.37 g (5.2mmol), triphenylphosphine. This mixture was then stirred for 3 hr at 60^0C, and then for 10 hr at room temperature. Precipitated yellow coloured $PdBr_2(PPh_3)_2$ was filtered and washed with ethanol and dried under vacuum. Practical yield of the complex was found to be 1.16g (45%)

The complex was characterized and the details are given in Chapter II, section 2.2.1.3

4.2.2.2 Synthesis of 10% APTS-functionalized silica (Si-APTS)

Reaction scheme:



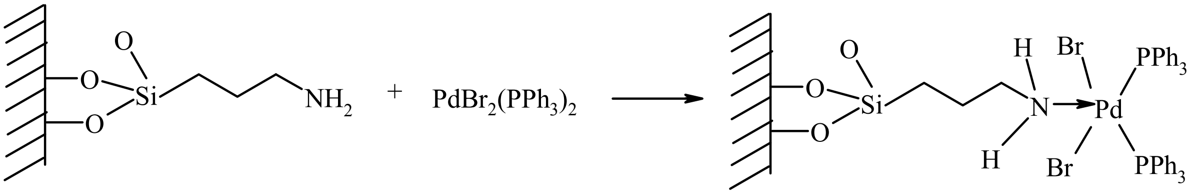
Scheme 4.1: Synthesis of 10% APTS functionalized silica

The APTS functionalized silica was prepared by the procedure reported by Mukhopadhyay et. al.[26]

1.0 g of silica was suspended in 15 ml of dry dichloromethane and to this 0.1g (5.73 mmol) 3-aminopropyltrimethoxysilane (APTS) was added dropwise under stirring. The mixture was stirred for further 24 hr at 40^0C. Then the contents were filtered and washed with dichloromethane repeatedly and dried under vacuum for 5 hr at room temperature.

4.2.2.3 Synthesis of 1% $PdBr_2(PPh_3)_2$ anchored silica

Reaction scheme:



APTS functionalized silica Pd catalyst SA-Pd

Scheme 4.2: Synthesis of 1% $PdBr_2(PPh_3)_2$ anchored silica

1.0 g of 10% APTS-functionalized silica was added to a $PdBr_2(PPh_3)_2$ solution in methanol (0.1g (0.095mmol) in 20 ml of methanol) and stirred for 16 hr at room temperature. The light yellow solid was then filtered under vacuum and washed several times with methanol, soxhlet-extracted thrice with methanol to remove any Pd-complex adhered to the support, then dried under vacuum for 5hr at room temperature.

The catalyst thus prepared (labeled as **SA-Pd**), was used as such for alkane oxidation reaction.

4.2.2.4 Characterization:

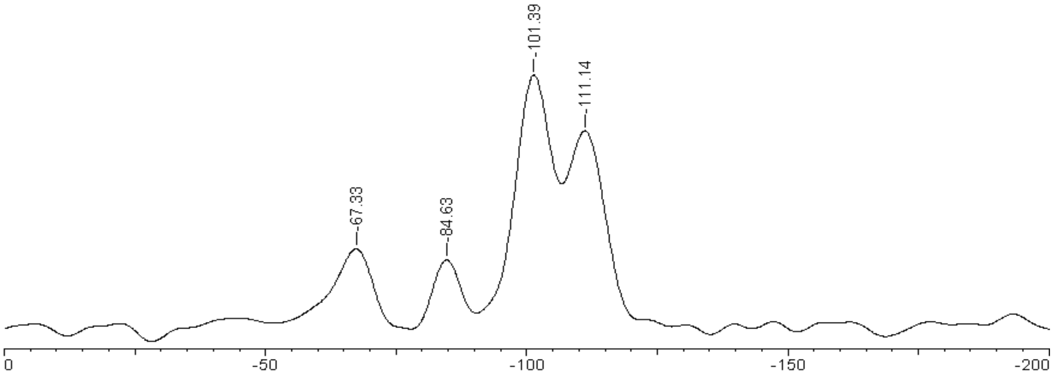
The APTS functionalized silica and the SA-Pd thus prepared were characterized using ^{13}C and ^{29}Si CP/MAS NMR, X-ray Photoelectron Spectroscopy (XPS) measurements and ICP analysis.

A. CP/MAS NMR analysis:

^{29}Si MAS NMR of Si-APTS:

The ^{29}Si MAS NMR of Si-APTS is shown in the Figure 4.1

The prominent signals at -111.14 ppm, -101.39 ppm, -84.63 ppm can be assigned as the Q_4 [$Si(OSi)_4$] and Q_3 [$Si(OSi)_3OH$] sites of fumed silica. The spectrum of fumed silica has already been reported in the literature and is known to have peaks at -109, -100, and -91 ppm corresponding to the Q_4, Q_3, and Q_2 [$Si\text{-}(OSi)_2(OH)_2$] sites.[27] The Q_4 structural units represent interconnected SiO_4 tetrahedrons, while the Q_3 and Q_2 structural units represent the silanol groups associated with the silica surface.



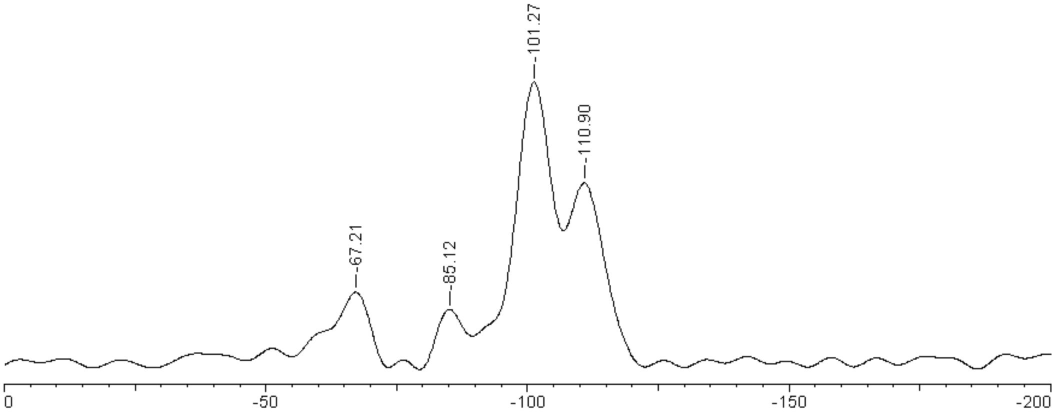
ppm

Figure 4.1: ^{29}Si MAS NMR of Si-APTS

The intensity of the Q_2 site at -84.63 ppm is much less in the functionalized silica because most of the silanol groups associated with Q_2 sites of the fumed silica were reacted with 3-aminopropyltrimethoxysilane. The peak at δ= -67.33 ppm indicates the formation of Si-O-Si linkage of the 3-aminopropyltrimethoxysilane group on the surface of silicon atoms of fumed silica through three siloxane bonds.[28] This shows that APTS molecule is covalently bonded to the silica surface via Si-O-Si linkage.

^{29}Si MAS NMR of Si-APTS-Pd:

The ^{29}Si MAS NMR of Si-APTS-Pd is shown in the Figure 4.2

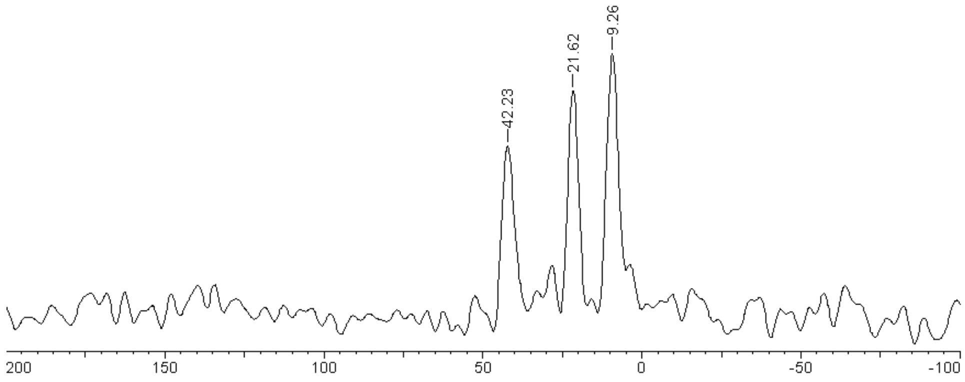


ppm

Figure 4.2: ^{29}Si MAS NMR of Si-APTS-Pd

Since the amino molecules are expected to coordinate with the palladium atoms in the complex, we do not expect any change in the Si spectra of Si-APTS-Pd from the Si-APTS, which is observed in Figure 4.2

^{13}C CP MAS NMR of Si-APTS:

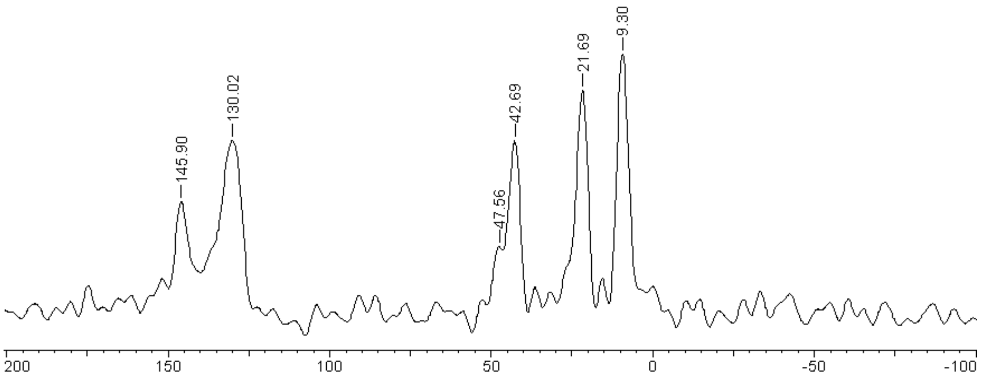


ppm

Figure 4.3: ^{13}C CP MAS NMR of Si-APTS

In the ^{13}C CP/MAS NMR of Si-APTS the signals at 9.26 ppm, 21.62 ppm and 42.23 ppm correspond to the α carbon, β carbon and γ carbon respectively (the numbering of carbon is given in the Scheme 4.1. This shows the presence of APTS molecule on the silica surface.

^{13}C CP MAS NMR of Si-APTS-Pd:



ppm

Figure 4.4: ^{13}C CP MAS NMR of Si-APTS-Pd

In the ^{13}C CP MAS NMR of Si-APTS-Pd the signals for α carbon, β carbon and γ carbon are observed at 9.30 ppm, 21.69 ppm and 42.69 ppm respectively. The tethering of palladium to the silica support via NH_2 group in the APTS will cause a shift in the γ carbon signal. A shoulder at 47.56 ppm shows the coordination of palladium by the NH_2 group in the APTS. As the percentage of palladium coordinated APTS is around 1% on silica, the signal for γ carbon in non- coordinated APTS is more predominant than the signal for γ carbon in metal coordinated APTS. The broad signals at 130.02 ppm and 145.90 ppm correspond to the phenyl ring present in the palladium metal complex $PdBr_2(PPh_3)_2$. This shows the coordination of palladium complex to the APTS molecule present on the silica surface.

B. XPS analysis of Si-APTS-Pd:

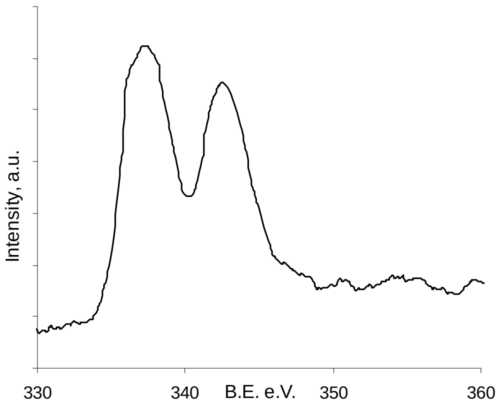


Figure 4.5: X-ray photoelectron spectrum of Si-APTS-Pd

X-ray photoelectron spectrum of Si-APTS-Pd is as shown in Fig. 4.6. The binding energies for palladium observed are 337.6eV and 342.8eV. The reported values for the 3d levels of Pd(II) are 336.4eV (3d5/2) and 341.7eV (3d3/2),[29] which are comparable with the observed binding energy values. This showed that all the palladium is present as Pd(II).

C. ICP analysis:

The ICP study of the Si-APTS-Pd catalyst shows that the Pd content in the catalyst is 0.73%.

Thus the CP/MAS NMR, XPS and ICP study showed that the $PdBr_2(PPh_3)_2$ complex is tethered to the silica surface via APTS molecule.

4.2.3 Synthesis of $PdCl_2(TPPTS)_2$ exchanged hydrotalcite:

The synthesis of $PdCl_2(TPPTS)_2$ exchanged hydrotalcite was done in four steps.

1. Synthesis of Mg-Al hydrotalcite (MA-LDH)
2. Synthesis of triphenylphenyl phosphine trisulfonate sodium salt (TPPTS)
3. Synthesis of $PdCl_2(TPPTS)_2$ complex
4. Synthesis of $PdCl_2(TPPTS)_2$ exchanged LDH

4.2.3.1 Synthesis of Mg-Al hydrotalcite (MA-LDH):

MA-LDH was synthesized according to the procedure reported by Choudary et. al. with minor modifications.[30] In a 250ml round bottom flask, a solution of 15g (0.0596mol) of $Mg(NO_3)2.6H_2O$ and 8.77g (0.0234mol) of $Al(NO_3)_2.6H_2O$ was prepared in 60ml distilled water (solution A). In another 500ml round bottom flask a solution of 7.56g (0.189mol) NaOH and 5.84g (0.055 mol) of Na_2CO_3 was prepared in 250ml distilled water (solution B). The solution A was then slowly added to the solution B under constant vigorous stirring. The addition was done over the period of 3hr. The contents were then heated at 65^0C for 6hr. The precipitate formed was filtered and washed with hot distilled water until the pH of the filtrate was neutral. The precipitate was then dried in the oven at 80^0C for 15hr. The activation of hydrotalcite was carried out at 450^0C under a flow of air for 8hr. The calcination temperature was attained at a heating rate of 10^0C per minute. The calcined hydrotalcite was then cooled under the flow of dry nitrogen and then rehydrated at room temperature under the flow of nitrogen gas saturated with water vapor. The flow of wet nitrogen was maintained for 12hr.

4.2.3.1.1 Characterization:

The MA-LDH was analyzed using XRD, TG and DT analysis

A. XRD of MA-LDH:

The powder X-ray diffraction patterns of hydrotalcite samples were recorded on RIGAKU MINI FLEX instrument from $2\theta = 5^0$ to 80^0. The XRD of the MA-LDH is given in the Figure 4.9

B. TGA and DTA:

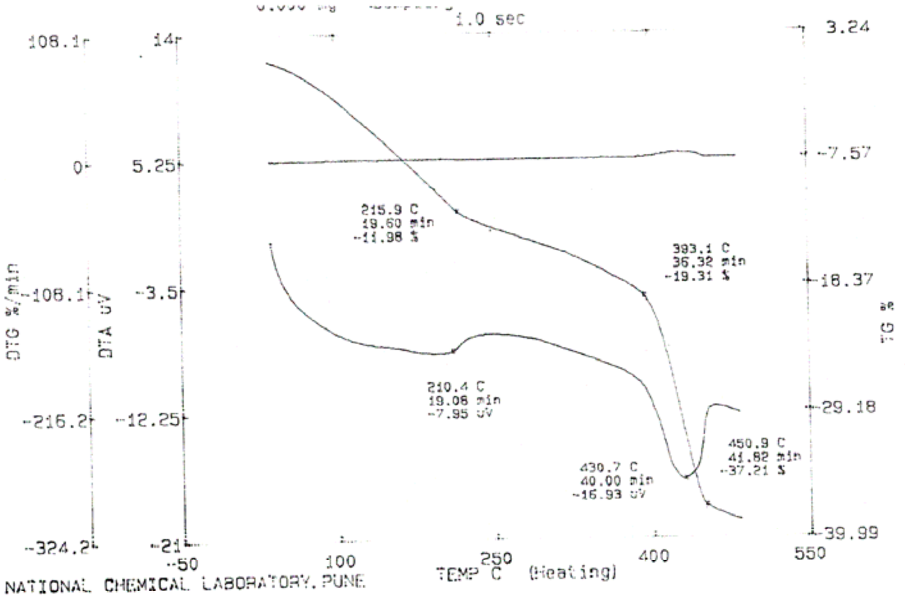


Figure 4.6: TG/DT analysis of MA-LDH

TG analysis:

The TGA data of the MA-LDH (Fig 4.6) showed two stages of weight loss, which is a characteristic property of LDH like material.[31] The first weight loss is observed between 82 to 220^{0}C due to the loss of interlayer water molecules. The second weight loss between 230 to 440^{0}C is due to the loss of condensed water molecule and carbon dioxide.

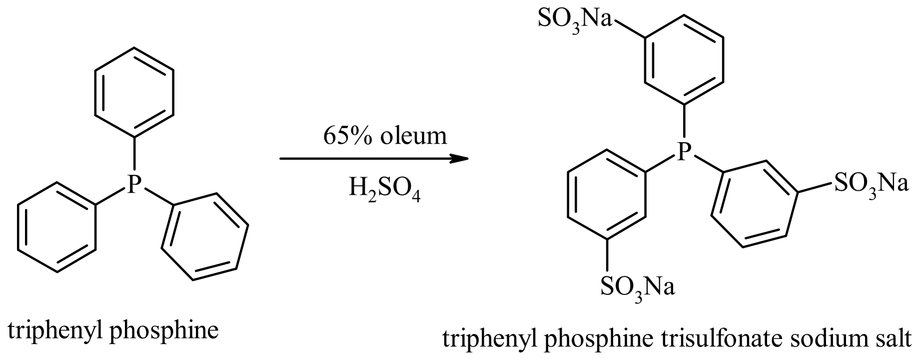
DT analysis:

In the DT analysis data of the MA-LDH (Figure 4.6), the observed broad endothermic peak related to the dehydration of MA-LDH between 82 to 220^{0}C and second endothermic peak corresponds to the weight loss due to condensed water molecules and carbon dioxide form the carbonate anion present in the brucite layer, matches well with the reported values.[32]

4.2.3.2 Synthesis of TPPTS:

For synthesis of triphenyl phosphine trisulfonate (TPPTS), a double-jacketed 1 L glass reactor equipped with a high-speed half-moon stirrer was used. This reactor was designed so that operation under argon atmosphere was possible. The temperature was controlled by circulation of water using a cryostat. A similar reactor of larger volume was used for neutralization of the crude reaction mixture. The procedure used was similar to that reported in the literature.[33]

Reaction scheme:



Scheme 4.3: Synthesis of TPPTS

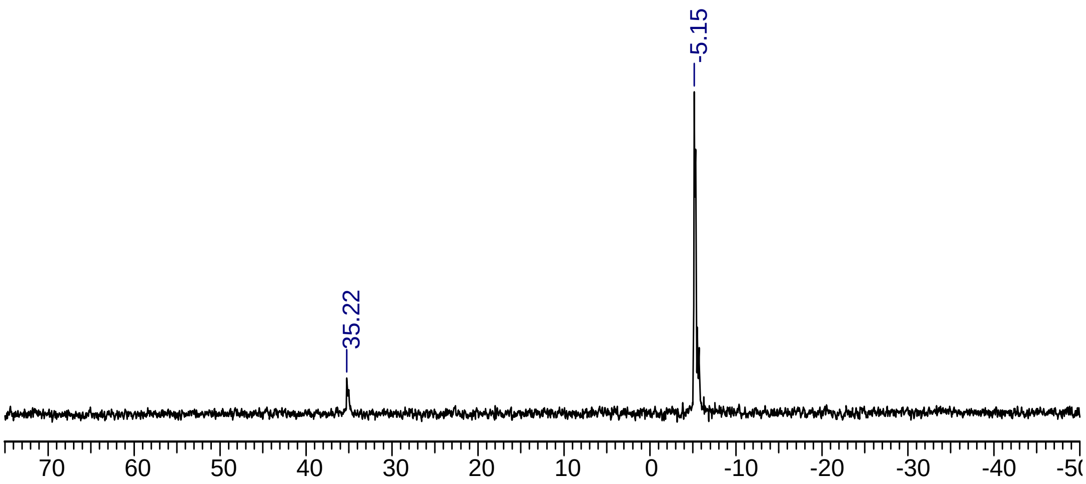
Procedure for the synthesis of TPPTS:

200g of 98% pure sulfuric acid was introduced into the sulfonation reactor. The acid was cooled under constant stirring to 12-15ºC by means of a cryostat. 50g of triphenyl phosphine (TPP) (190.75 mmol) was introduced slowly at 15ºC over a period of 30-45 min. This gave a homogeneous yellow coloured solution of TPP in sulfuric acid. 280g (141.48ml, d=1.98 at 35ºC) of 65% oleum (SO_3 content: 2.275 mol) was transferred into the addition funnel from the oleum receiver. This oleum was then introduced in the sulfonation reactor containing TPP solution in sulfuric acid, over a period of 40-45 minutes maintaining a maximum temperature of 15ºC with rapid stirring. The temperature of the reaction mixture was then raised to 22ºC and was maintained for 76 hr using a cryostat. This step of keeping the reaction mixture at 22ºC is critical for optimum yield of TPPTS. Thereafter, the temperature of the reactor was lowered to ~ 10ºC and 50g of distilled water was introduced while maintaining the temperature at 10ºC. This addition is necessary to quench the excess SO_3 present after the sulfonation reaction is complete. The addition of water is highly exothermic, and hence temperature was maintained at <10ºC while adding water. This gave a solution of sulfonated triphenyl phosphine in sulphuric acid. This reaction mixture was further diluted to approximately 800 ml under cooling (10ºC). This diluted solution was then transferred into a 3 lit neutralization reactor under argon atmosphere. The solution was neutralized using 50% (w/w) degassed sodium hydroxide solution maintaining 10ºC temperature. The reaction mixture obtained was in a slurry form. The neutralized mixture was then filtered and the filtrate was evaporated under reduced pressure at 50-60ºC till the volume reduced to about 250 ml from the initial two liters. 1.5 liters of methanol was added to the above solution and the mixture was refluxed under argon atmosphere for 2 hr. TPPTS dissolved in methanol completely. The methanol was filtered hot, with the solid residue comprising only sodium sulphate. The filtrate was evaporated under reduced pressure. The solid TPPTS obtained was recrystallized from ethanol, weighed and stored under argon atmosphere. The yield was found to be 80-85%.

4.2.3.2.1 Characterization:

A. ^{31}P NMR analysis:

^{31}P NMR analysis (Figure 4.7) shows singlet at δ= -5.15 (TPPTS) and δ= 35.22 (OTPPTS) which is consistent with that reported in the literature, showing approximately 95% TPPTS and 5% OTPPTS formation. No further purification of TPPTS was undertaken for use as a ligand for the preparation of water-soluble catalyst precursors.



ppm

Figure 4.7: ^{31}P NMR spectrum of TPPTS

4.2.3.3 Synthesis of $PdCl_2(TPPTS)_2$ complex

Structure:

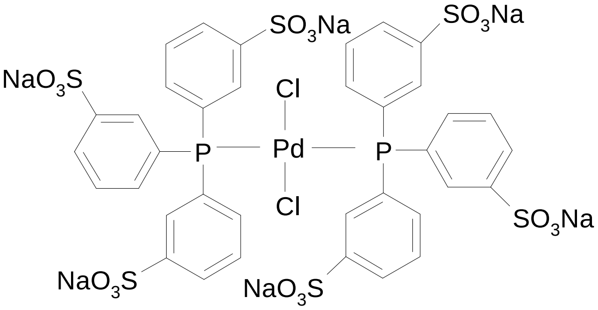


Figure 4. 8: Structure of $PdCl_2(TPPTS)_2$

Procedure:

0.1g $PdCl_2$ and 2ml of 2M HCl were added into the 50ml round bottom flask and the mixture was stirred for 50^0C until $PdCl_2$ dissolved completely. The flask was cooled to room temperature and flushed with argon. 0.8g TPPTS was added into the flask under stirring. The colour of the solution changed from dark red to bright yellow immediately. After 10 min of stirring, 15ml absolute ethanol was added and stirred for another 30min. The light yellow precipitate formed was filtered under vacuum, washed with warm ethanol thrice and dried under vacuum.

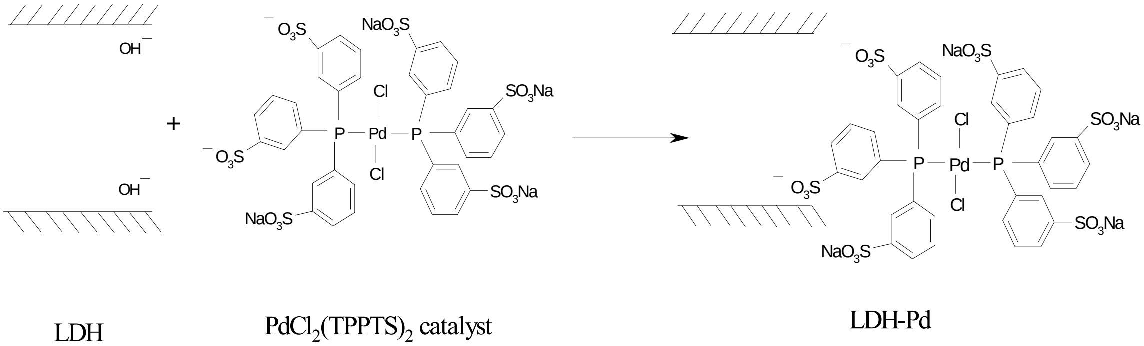
Yield of the complex was 73% based on the quantity of $PdCl_2$ charged

The elemental analysis of $PdCl_2(TPPTS)_2$

Found: C=36.19%; H=2.38%; N= 8.32%, Cl=22.43%

Calculated: C=36.01%; H=2.42%; N=8.40%, Cl=22.36%

4.2.3.4 Synthesis of $PdCl_2(TPPTS)_2$ exchanged LDH (LDH-PdTPP):



Scheme 4.4: Synthesis of LDH-PdTPP

Slurry of 1.0g LDH was prepared in 50ml distilled-deionised water and then a bed of LDH was prepared in a narrow diameter column. The packed LDH was then washed with 50ml distilled-deionised water. A solution of 2.84g (5.0mmol) of $PdCl_2(TPPTS)_2$ in 10 ml of distilled-deionised water was then passed through the LDH bed. The basic pH (pH=9-10) of the elute confirmed the exchange of OH^- with the $PdCl_2(TPPTS)_2$ complex. The LDH bed was then washed with distilled water till the pH of elute was neutral followed by acetone. The LDH-PdTTP thus synthesized was dried under vacuum at room temperature for 5 hr and used as such for alkane oxidation reaction.

4.2.3.4.1 Characterization:

A. XRD analysis:

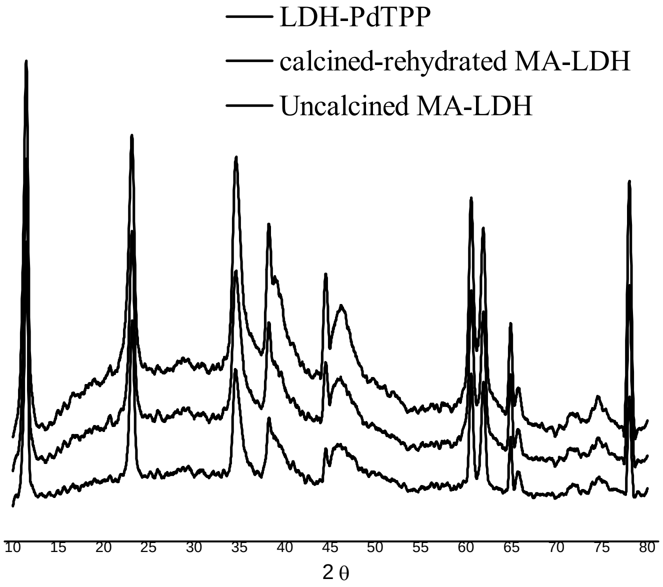


Figure 4. 9: Powder XRD pattern of the M A-LDH and MA-LDH-Pd

The X-ray powder diffraction patterns of the MA-LDH and MA-LDH-Pd (Fig 4.9) hardly differ in the range 2θ = 0-80^0. The observed d_{003} basal spacing of the support that appeared at 7.8A remained unchanged after the anion exchange, which indicates that $PdCl_2(TPPTS)_2$ is mainly located on the edge of LDH.[8]

B.XPS analysis:

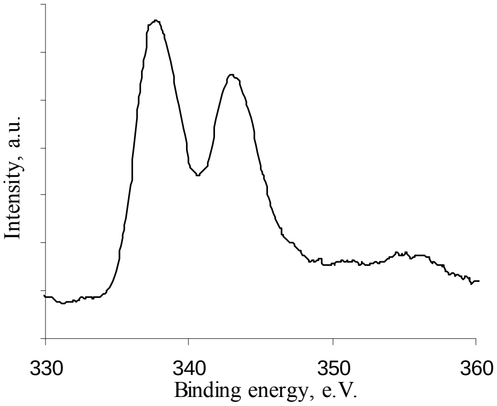


Figure 4.10: X-ray photoelectron spectroscopy (XPS) analysis of MA-LDH-Pd

X-ray photoelectron spectrum of MA-LDH-Pd catalyst is as shown in Figure 4.10. The binding energies for palladium observed are 338eV and 343.3eV. The reported values for the 3d levels of Pd(II) are 336.4eV (3d5/2) and 341.7eV (3d3/2), which are comparable with the observed binding energy values and chlorine binding energy (197.8eV) reveals that it is in metal chloride form.

4.2.4 Synthesis of supported ossified catalysts:

Three different supported ossified catalysts were synthesized

1. Silica supported ossified $[PdCl_2(TPPTS)_2]_2$-Ba catalyst
2. Silica supported ossified $[PdCl_2(bathophends)]_2$-3Ba catalyst
3. Silica supported ossified $[Pd(sulfosalicylidineaniline)_2]_2$-3Ba catalyst

4.2.4.1 Preparation of supported ossified $[PdCl_2(TPPTS)_2]_2$-Ba catalyst:

The supported ossified $[PdCl_2(TPPTS)_2]_2$-Ba catalyst was prepared in the following steps

1. Preparation of 20% $Ba(NO_3)_2$ loaded silica
2. Preparation of TPPTS
3. Preparation of $PdCl_2(TPPTS)_2$ complex
4. Preparation of supported ossified $[PdCl_2(TPPTS)_2]_2$-Ba catalyst

Structure:

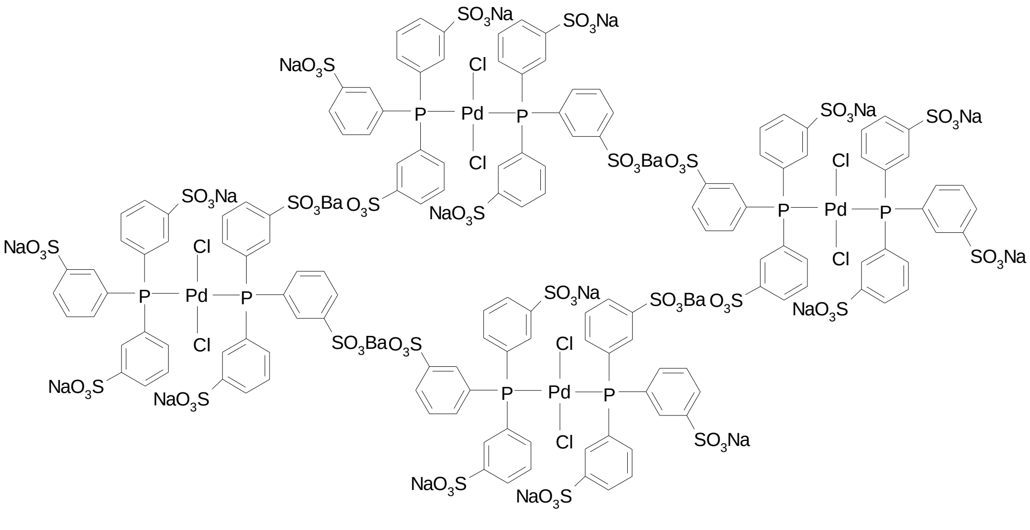


Figure 4.11: Supported ossified $[PdCl_2(TPPTS)_2]_2$-Ba catalyst

4.2.4.1.1 Preparation of 20% $Ba(NO_3)_2$ loaded silica

In a 50 ml round bottom flask containing 10ml distilled water, 0.4 g (1.5 mmol) $Ba(NO_3)_2$ was dissolved. To this solution then 2.0g silica was added under constant stirring. The mixture was stirred for 5 minutes and then water was evaporated under vacuum to get 20% $Ba(NO_3)_2$ loaded silica.

Practical yield of the 20% $Ba(NO_3)_2$ loaded silica was 2.4 g

4.2.4.1.2 Preparation of TPPTS

The detailed procedure of TPPTS synthesis is given in section 4.2.3.2

4.2.4.1.3 Preparation of $PdCl_2(TPPTS)_2$ catalyst:

The detailed procedure for the synthesis of $PdCl_2(TPPTS)_2$ is given in section 4.2.3.3

4.2.4.1.4 Preparation of supported ossified $[PdCl_2(TPPTS)_2]_2$-Ba

In a 50 ml round bottom flask containing 10 ml distilled water and 0.020 g $PdCl_2(TPPTS)_2$ and 100mg TPPTS, 2.00g 20% $Ba(NO_3)_2$ loaded silica was added. The mixture was stirred for 24hr and then filtered under vacuum over the Buckner funnel. The filtered solid was washed with distilled water and then with acetone followed by ether. The solid was dried under vacuum.

Practical yield of the silica supported ossified $[PdCl_2(TPPTS)_2]_2$-Ba was 2.0 g.

The catalysts thus prepared (labeled as **SOC-PdTPP**), were used as such for alkane oxidation reaction.

4.2.4.1.5 Characterization:

A. ^{31}P solid state NMR:

In literature, the supported catalysts have been characterized by a variety of methods, but multinuclear solid state NMR has turned out to be a particularly useful method. In order to understand the interactions of the different components of the heterogeneous catalyst system, (metal complex to support) and seek conclusive evidence of the heterogeneous nature of complexes, ^{31}P solid state NMR of the catalyst was recorded.

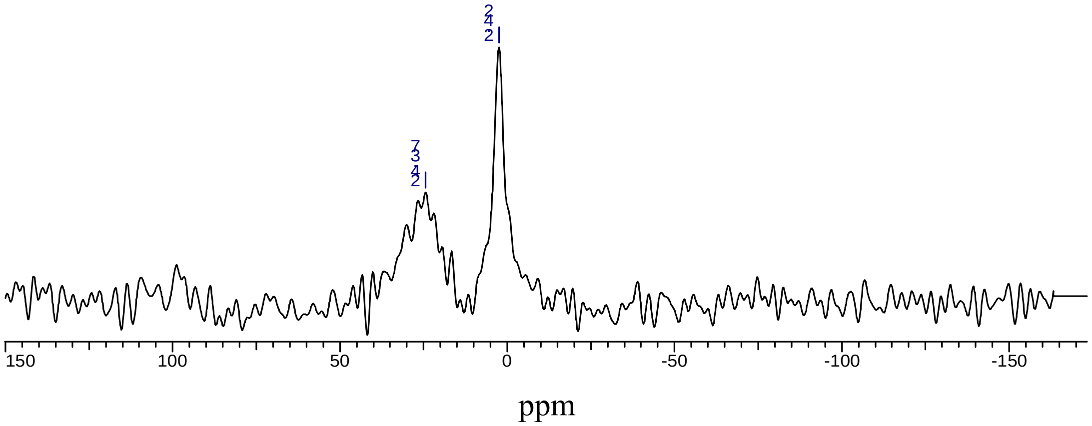


Figure 4.12: Solid state ^{31}P NMR spectrum of SOC-PdTPP catalyst

The ^{31}P solid state NMR (Figure 4.12) of the silica supported ossified catalyst shows a signal at 2.42 δ and a multiplet at 24.37 δ. The signal at 2.42 δ is due to the free TPPTS-$Ba_{3/2}$ as an excess of TPPTS is used in the preparation of the supported complex and the multiplet at 24.37 δ may arise from the mixing of the signals from the coordinated phosphine and phosphine oxide.

To confirm the chemical shifts in the supported ossified catalyst the supported ossifiedTPPTS-$Ba_{3/2}$ (SOC-TPP) was synthesized separately and its ^{31}P solid state NMR was recorded.

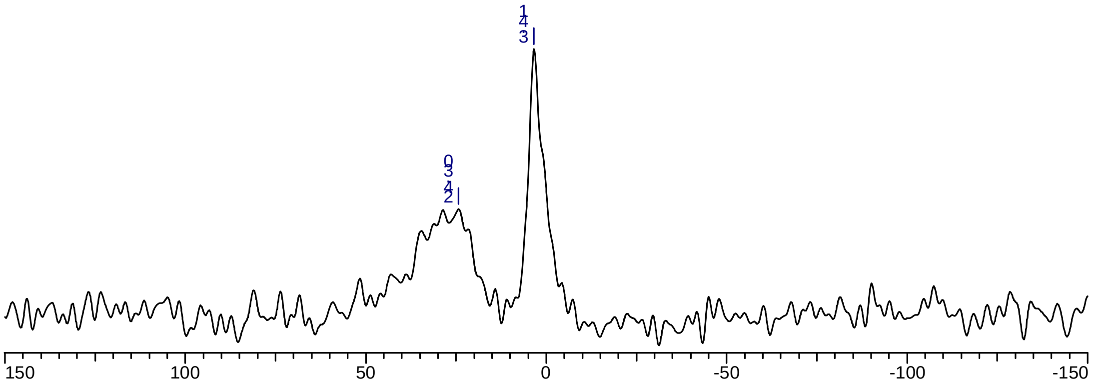
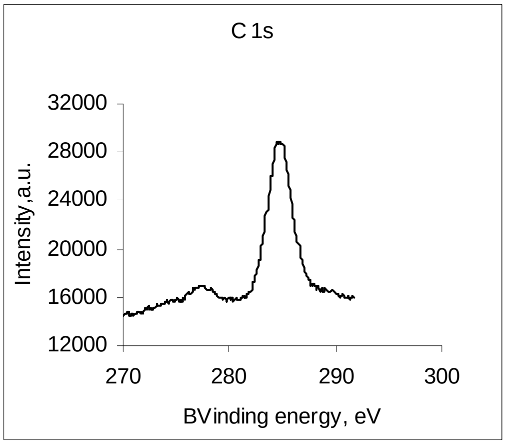


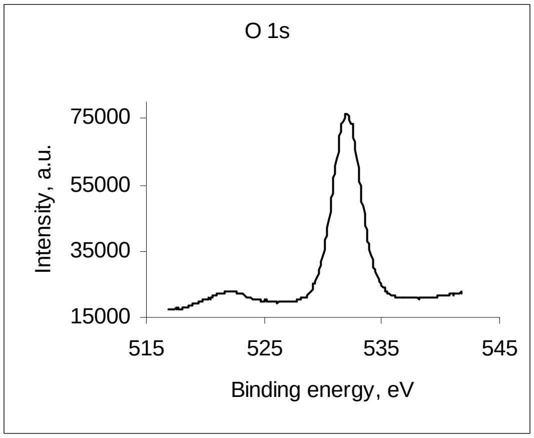
Figure 4.13: Solid state ^{31}P NMR spectrum of SOC-TPP

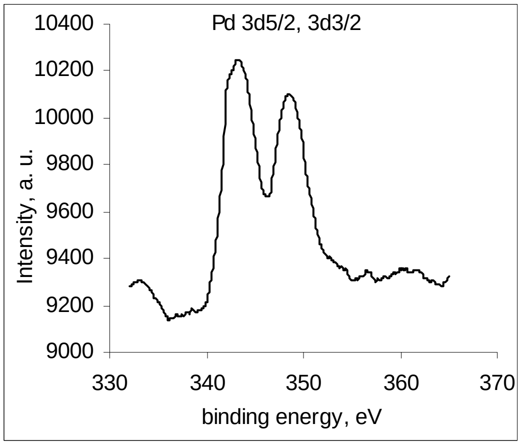
The solid state ^{31}P NMR of TPPTS-Ba$_{3/2}$ (Figure 4.13) shows a singlet at 3.41 δ due to the free phosphine i.e P^{III} (deshielded compared to TPPTSNa (-5.15 δ (s)) and a singlet at 24.30 δ due to the OTPPTSBa$_{3/2}$ i.e P^{V} (deshielded compared to the OTPPTSNa 35.22 δ (s)).

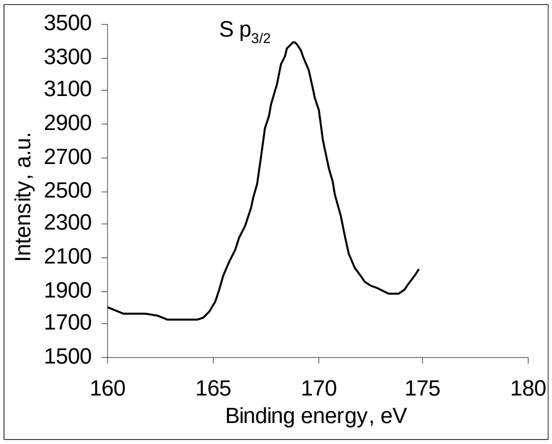
B. X-ray photoelectron spectroscopy (XPS) analysis

Surface analysis by XPS spectra was carried out in terms of the binding energy values of various elements present (palladium, phosphorus, carbon, oxygen and barium) in the catalyst, and the supports after the necessary C$_{(1s)}$ correction (Figure 4.14). These were in compliance with the literature values (Table 4.1).









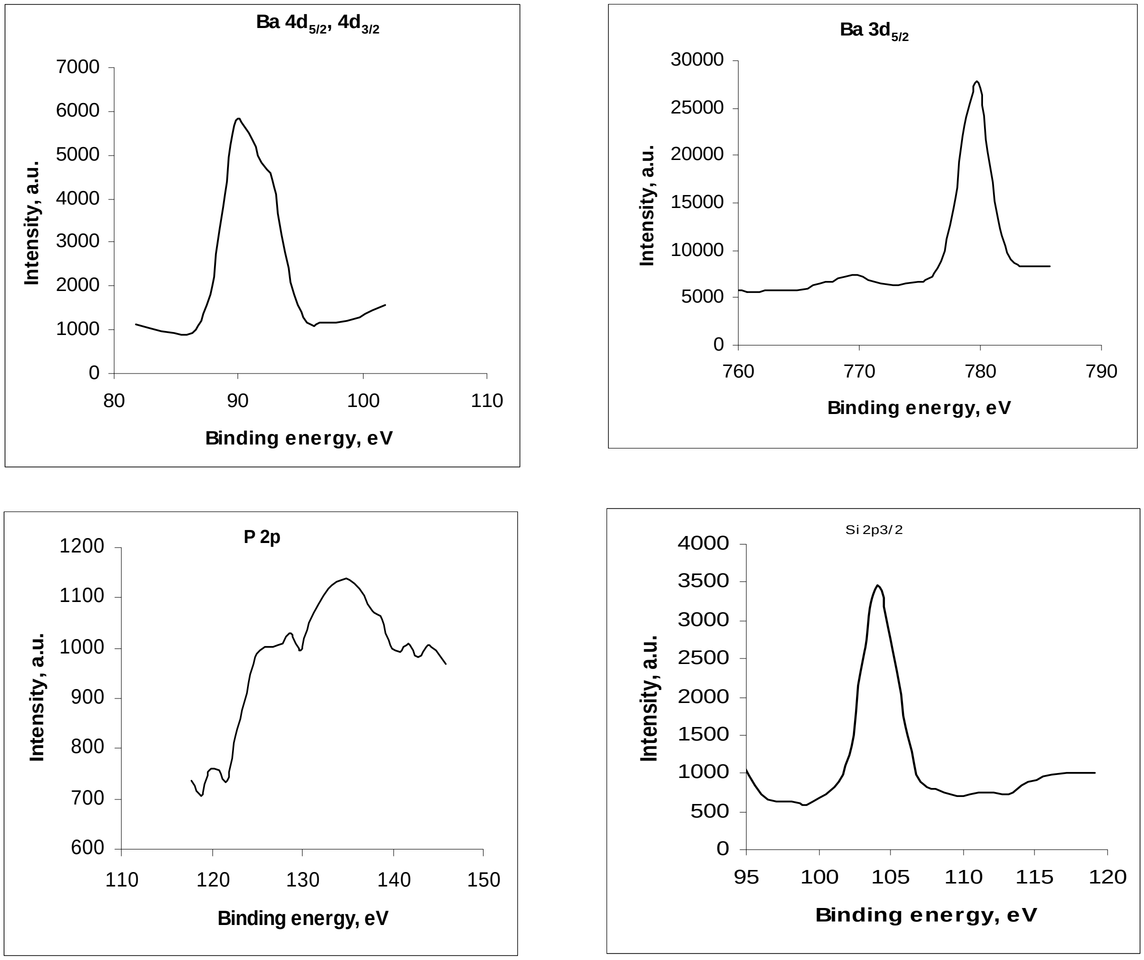


Figure 4.14: Representative X-ray photoelectron spectra (XPS) of catalyst SOC-PdTPP

Table 4.1: XPS analysis of SOC-PdTPP Catalyst

Values	C	Ba			P	S	Si	O	Pd	
(eV)	1s	$3d_{5/2}$	$4d_{3/2}$	$4d_{5/2}$	2p	$2p_{3/2}$	$2p_{3/2}$	1s	$3d_{5/2}$	$3d_{3/2}$
Observed	291.9	787	99	97.0	135.9	176	110	540	345.4	350.3
Corrected*	285	780.1	92.1	90.1	129.0	169.1	103.1	533.1	338.1	343.4
Literature	285	780.6	92.8	90.5	131.2	168.3	102.5	531	336.4	341.7

*All the values were corrected to $C_{(1s)}$ with binding energy of 285 eV using adventitious carbon.

C. SEM:

Topography and morphology of the catalyst samples were investigated using scanning electron microscopy (SEM). Topography gives the surface features of an object, its texture and morphology gives the shape, size and arrangement of the particles making up the object that are lying on the surface of the sample or have been exposed by grinding or chemical etching. The micrograph of the supported ossified catalyst is shown in Figure 4.15. The micrograph of supported ossified catalyst shows that the catalyst particles are unevenly distributed on the support. The SEM image of the catalyst shows catalyst particle as a white spots on the support.

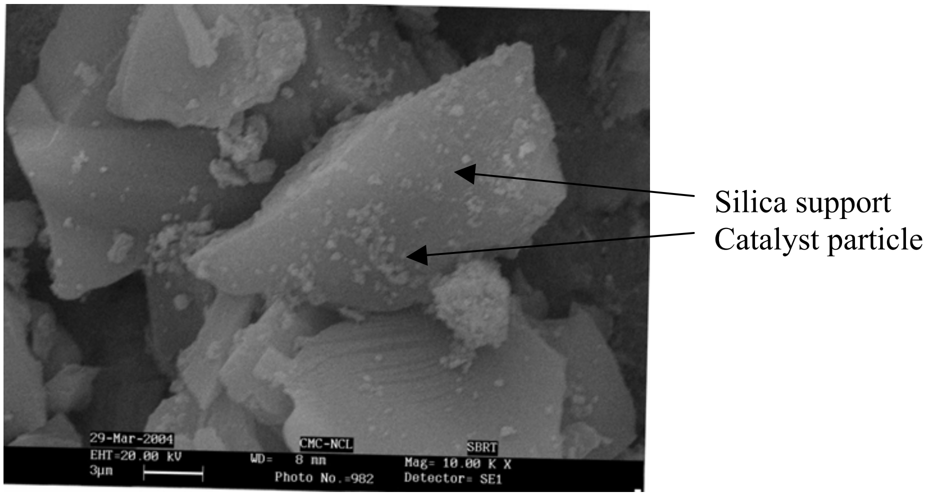


Figure 4.15: SEM image of silica supported ossified catalyst

The data interpretation using the above instrumental techniques reveals the physical interaction between precipitated complex and the support. The catalyst is also in a true heterogenized form, unevenly distributed onto the support.

4.2.4.2 Preparation of supported ossified [$PdCl_2$Bathophends]$_2$-Ba catalyst

The supported ossified ($PdCl_2$Bathophends)$_2$-Ba catalyst was prepared in three steps

1. Preparation of 20% $Ba(NO_3)_2$ loaded silica
2. Preparation of supported ossified (Bathophends)$_2$-Ba
3. Preparation of supported ossified [$PdCl_2$Bathophends]$_2$-Ba

Structure:

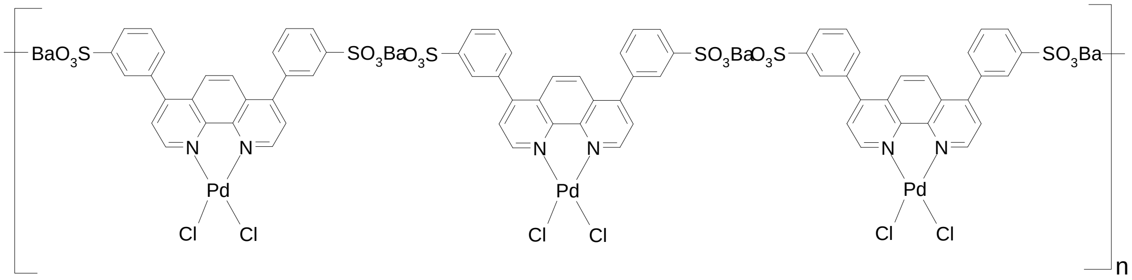


Figure 4.16: supported ossified ($PdCl_2$bathophends$)_2$-Ba catalyst

4.2.4.2.1 Preparation of 20% $Ba(NO_3)_2$ loaded silica

The procedure for the preparation of 20% $Ba(NO_3)_2$ loaded silica is mentioned in the section 4.2.4.1.1

4.2.4.2.2 Preparation of supported ossified (Bathophends$)_2$-Ba

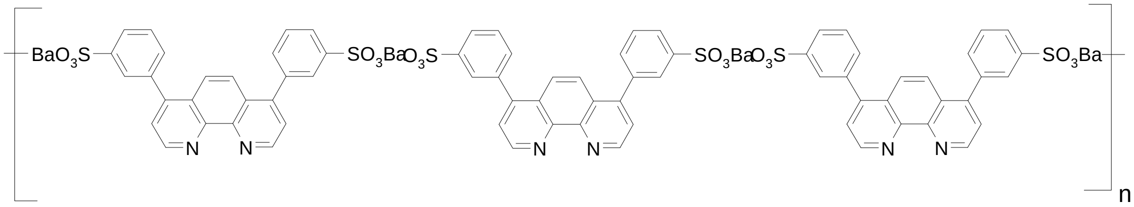


Figure 4.17: Supported ossified (bathophends$)_2$-Ba ligand

Procedure:

In a 50 ml round bottom flask containing 10ml distilled water, 0.050g (75 mmol) bathophends was dissolved. To this solution then 2.0 g 20% $Ba(NO_3)_2$ loaded silica was added under constant stirring. The mixture was stirred for 24hr and then filtered under vacuum through a Buckner funnel. The filtered solid was washed with distilled water and then with acetone followed by ether. The solid was dried under vacuum for 5 hr.

Practical yield of the silica supported ossified (Bathophends$)_2$-Ba was 2.0g

4.2.4.2.3 Preparation of supported ossified [PdCl$_2$Bathophends]$_3$-4Ba

Procedure:

In a 50 ml round bottom flask containing 10 ml distilled water and 0.020 g PdCl$_2$, 2.00g (Bathophends)$_2$-Ba loaded silica was added. The mixture was stirred for 24hr at room temperature and then filtered under vacuum over the Buckner funnel. The filtered solid was washed with distilled water and then with acetone followed by ether. The solid was dried under vacuum.

Practical yield of the silica supported ossified [PdCl$_2$Bathophends]-Ba was 2.0 g.

The catalysts thus prepared (labeled as **SOC-PdBD**), were used as such for alkane oxidation reaction.

4.2.4.3 Preparation of silica supported ossified [Pd(Sulfosalicylideneaniline)$_2$]$_2$-Ba catalyst:

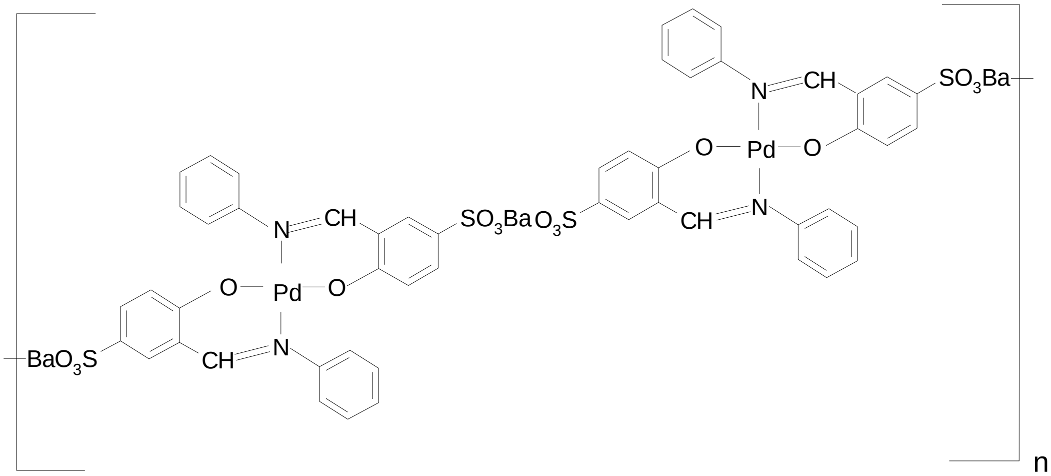


Figure 4.18: Ossified [Pd(sulfosalicylideneaniline)$_2$]$_2$-Ba

The silica supported ossified [Pd(Sulfosalicylideneaniline)$_2$]$_2$-Ba catalyst was prepared in three steps

1. Preparation of 20% Ba(NO$_3$)$_2$ loaded silica
2. Preparation of Pd(Na-sulfosalicylideneaniline)$_2$ complex
3. Preparation of silica supported ossified [Pd(sulfosalicylideneaniline)$_2$]$_2$-3Ba

4.2.4.3.1 Preparation of 20% $Ba(NO_3)_2$ loaded silica:

The procedure for the preparation of 20% $Ba(NO_3)_2$ is mentioned in the section 4.2.4.1.1

4.2.4.3.2 Preparation of Pd(Na-sulfosalicylideneaniline)$_2$ complex:

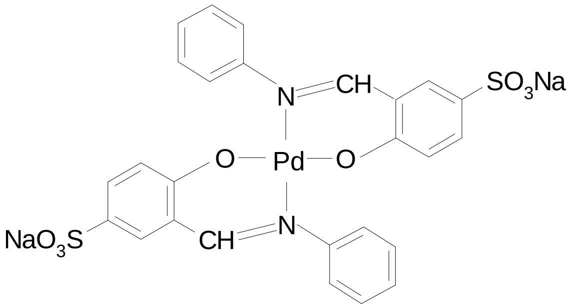


Figure 4.19: Pd(sulfosalicylideneaniline) complex

The preparation of Pd(Na-sulfosalicylideneaniline)$_2$ complex was done in three steps.

1. Preparation of 5-sulfosalicylaldehyde
2. Preparation of Schiff's base sulfosalicylideneaniline
3. Preparation of Pd(Na-sulfosalicylideneaniline)$_2$ complex

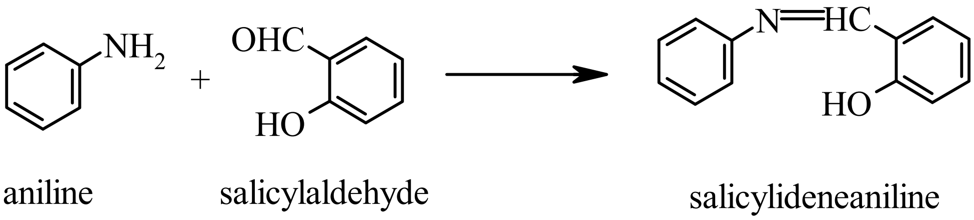
4.2.4.3.1.1 Preparation of 5-sulfosalicylaldehyde:

Preparation of 5-sulfosalicylaldehyde was done in three steps.

1. Preparation of Schiff's base of aniline and salicylaldehyde i.e. salicylideneaniline
2. Sulfonation of the salicylideneaniline using conc. sulfuric acid
3. Hydrolysis of sulfosalicylideneaniline and precipitation of sulfosalicylaldehyde as its sodium salt

4.2.4.3.1.1.1 Preparation of Schiff's base salicylideneaniline

Reaction:



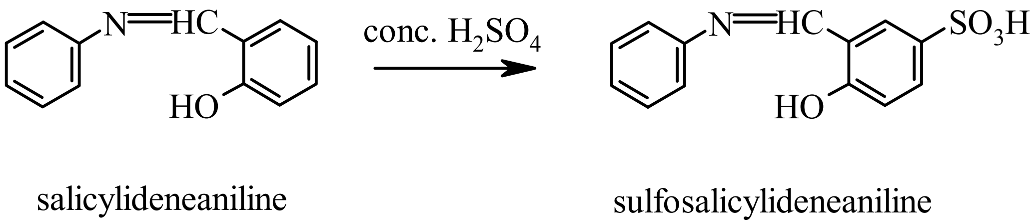
Scheme 4.5: Preparation of Schiff's base salicylideneaniline

Procedure:

In a 100 ml round bottom flask containing 12.5 ml (0.12 mol) of salicylaldehyde in 50 ml benzene, 10.9 ml (0.12mol) aniline was added drop wise. The solution was refluxed overnight and H_2O was removed as a benzene-water azeotrope with the use of dean stark apparatus. The volume of water collected was 2.10 ml, which was as per the reaction stoichiometry. The benzene was then evaporated to get orange oil, which solidified on cooling to a yellow solid. The solid was then recrystallized from methanol to get 17.3g salicylideneaniline. (73% yield)

4.2.4.3.1.1.2 Sulfonation of salicylideneaniline:

Reaction:



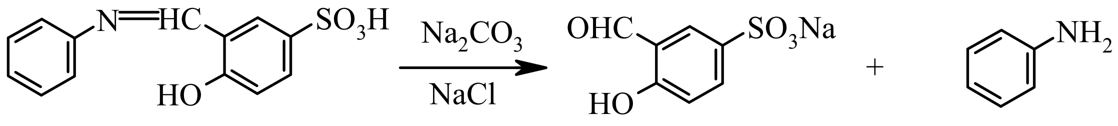
Scheme 4.6: Preparation of sulfosalicylideneaniline

Procedure:

17.3 g (0.0875mol) of salicylideneaniline was first heated to 64^0C in the water bath to get oily mass. To this yellow liquid, then 24.4 ml of 96% H_2SO_4 was added drop wise and heated on a steam bath for two hours. 50 ml H_2O was added drop wise to this solution with continued heating. The solution was cooled slowly and was allowed to stand for a period of 48 hr. A yellow colored precipitate was then filtered and washed with saturated sodium carbonate solution and then with water. The yellow solid was recrystallized from water and dried in vacuum at 78^0C. The practical yield was 11.9g (69%).

4.2.4.3.1.1.3 Hydrolysis of sulfosalicylideneaniline and precipitation of sulfosalicylaldehyde as its sodium salt

Reaction:



sulfosalicylideneaniline sulfosalicylaldehyde aniline

Scheme 4.7: Preparation of sulfosalicylaldehyde

Procedure:

8.5g (0.0305mol) sulfosalicylideneaniline was mixed with 200 ml water and 5g Na_2CO_3 was added to it. This solution was then heated for 1.5 hr and the aniline was removed by steam distillation. The volume of the solution was made strongly acidic with conc. HCl. This acidic solution was then concentrated on rotavapour to its half volume. To this solution NaCl was added to precipitate sulfosalicylaldehyde as its sodium salt. The precipitate was then redissolved in methanol and the solution was filtered to remove excess NaCl. The filtrate was then concentrated to obtain sulfosalicylaldehyde. The second crop of crystals was obtained by reducing the volume of filtrate. Recrystallization from hot H_2O yielded a flocculant precipitate, which was dried under vacuum at 130^0C. The practical yield was 5.1g (71%)

4.2.4.3.1.1.3.1 Characterization:

The characterization of the sulfosalicylaldehyde was done by its C-NMR and IR analysis

A. C-NMR analysis:

The C-NMR of the sodium sulfosalicylaldehyde (Figure 4.20) shows signal at 209.88ppm corresponding to aldehyde carbon and another signal at 174.84ppm for the carbon carrying the hydroxyl group that matches with the literature values.[34]

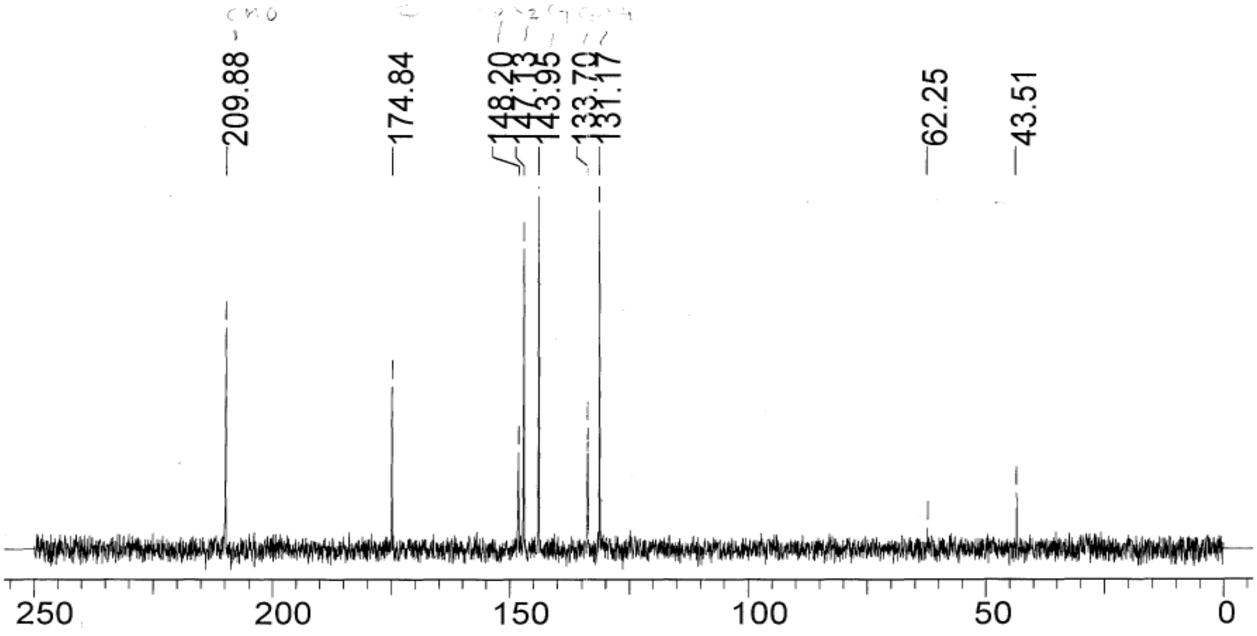


Figure 4.20: C-NMR of sodium salt of sulfosalicylaldehyde

B. IR analysis:

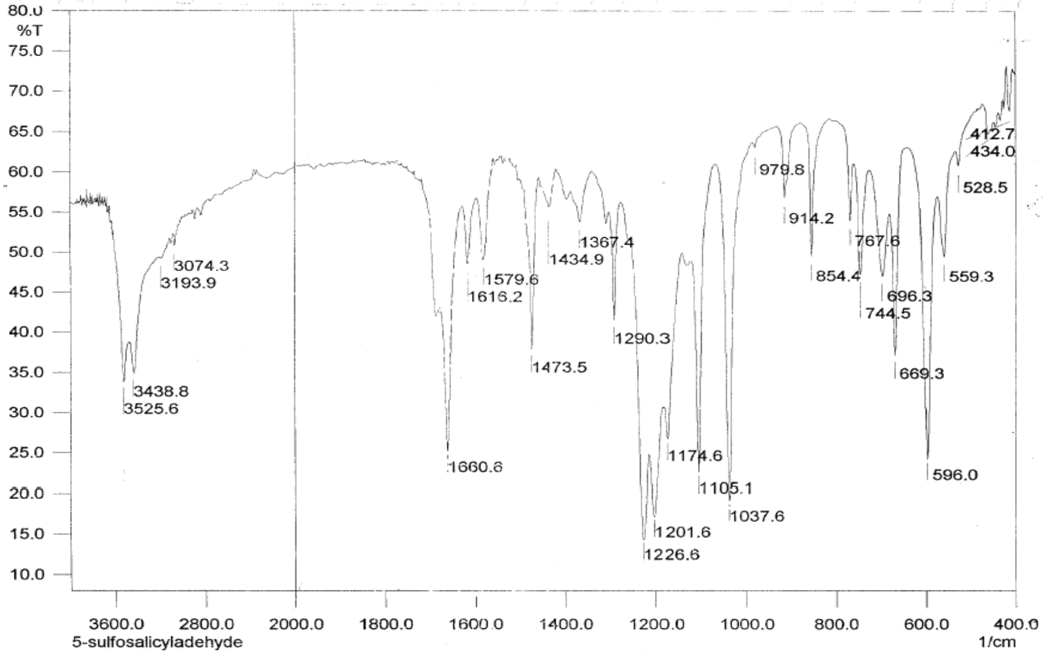
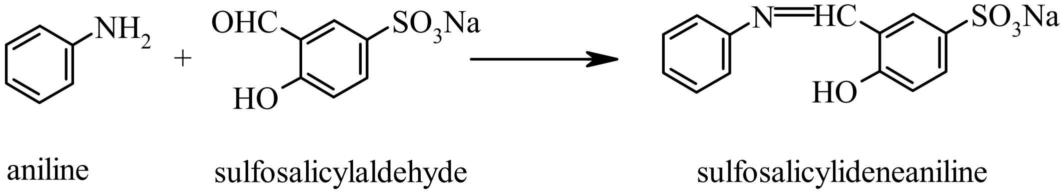


Figure 4.21: FTIR spectrum of the sodium salt of sulfosalicylaldehyde

In the IR spectrum of the sulfosalicylaldehyde, (Figure 4.21) a peak at 1037.6cm^{-1} which confirmed the presence of SO_3^- in the molecule. Other characteristic absorption peaks are ν_{OH} = 3525.6cm^{-1}, $\nu_{C=O}$ = 1660.6cm^{-1}, $\nu_{C=C}$ = 1616.2 cm^{-1}, $\nu_{S\text{-}O}$ = 1037.6 cm^{-1}

4.2.4.3.2.2 Synthesis of Schiff's base sulfosalicylideneaniline using sulfosalicylaldehyde and aniline:

Reaction:



Scheme 4.8: Preparation of sulfosalicylidineaniline

Procedure:

1.0047 g (4.47 mmol) sodium salt of 5-sulfosalicylaldehyde was added to 10 ml methanol. To this solution then 0.65 ml (4.48 mmol) aniline was added dropwise. The mixture was stirred for 4hr at room temperature. The yellow coloured sulfosalicylideneaniline was filtered and washed with methanol and then dried under vacuum. Yield of the ligand was 0.687g (68%)

4.2.4.3.2.2.1 Characterization:

A. IR analysis:

The IR spectrum of the sulfosalicylideneaniline, (Figure 4.22) shows a peak at 1029.9cm^{-1} confirmed the presence of SO_3^- in the molecule. Other characteristic absorption peaks are $\nu_{C=C}$ = 1608.5cm^{-1}, $\nu_{C=N}$ = 1660.6cm^{-1}

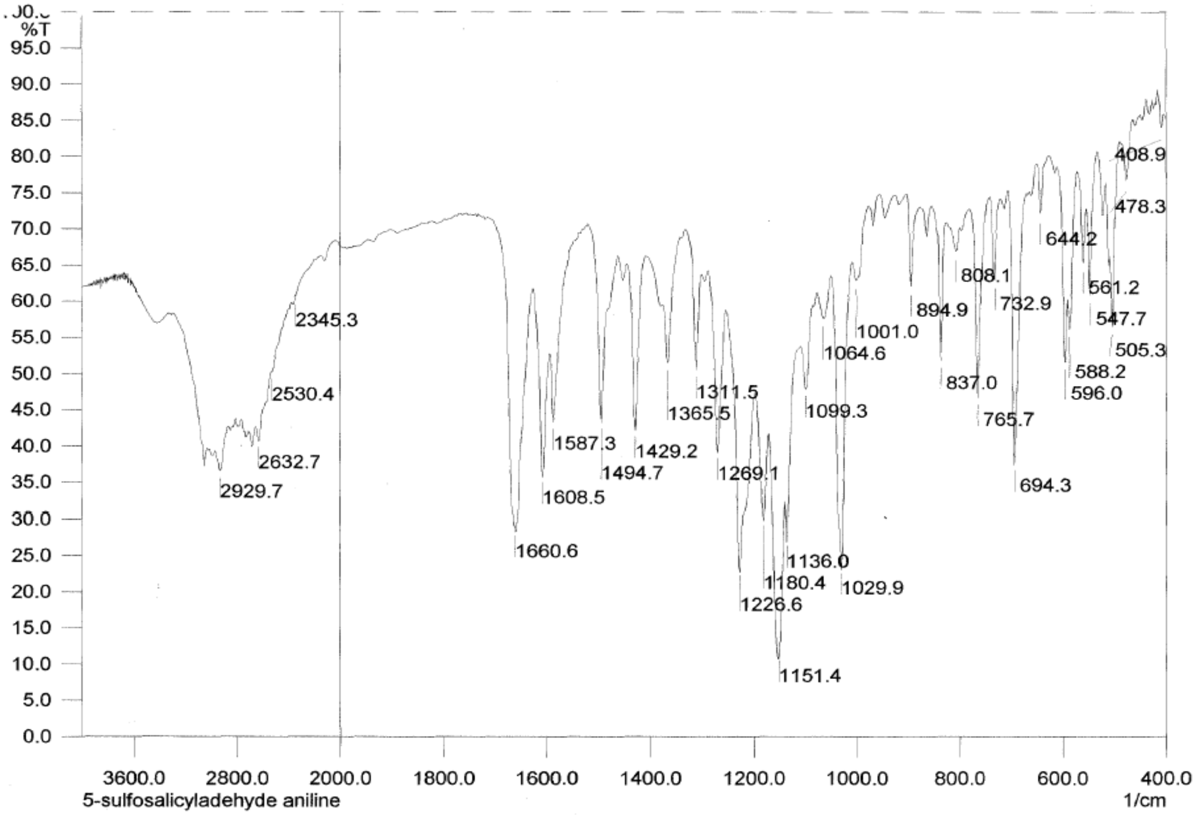
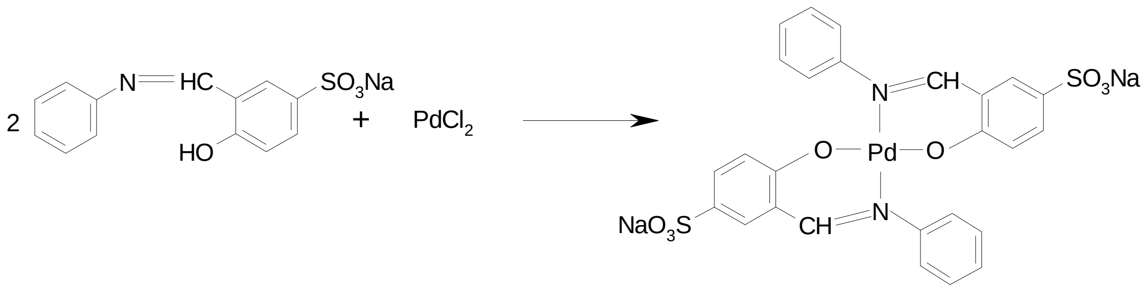


Figure 4.22: FTIR spectrum of sulfosalicylideneaniline

4.2.4.3.2.3 Preparation of Pd(Na-sulfosalicylideneaniline)$_2$ complex

Reaction:



Scheme 4.9: Preparation of Pd(sulfosalicylideneaniline)$_2$

Procedure:

In a 50ml round bottom flask containing 10ml methanol, 0.059g (0.334mol) sulfosalicylideneaniline was added and stirred for 5 min. To this mixture 0.020 g (0.668mol) $PdCl_2$ was added and the reaction mixture was stirred for 4 hr at room temperature. The precipitated metal complex was filtered under vacuum and washed with methanol and dried under vacuum for 5 hr.

Practical yield of the complex was found to be 80 %

4.2.4.3.2.3.1 Characterization:

A. IR spectrum:

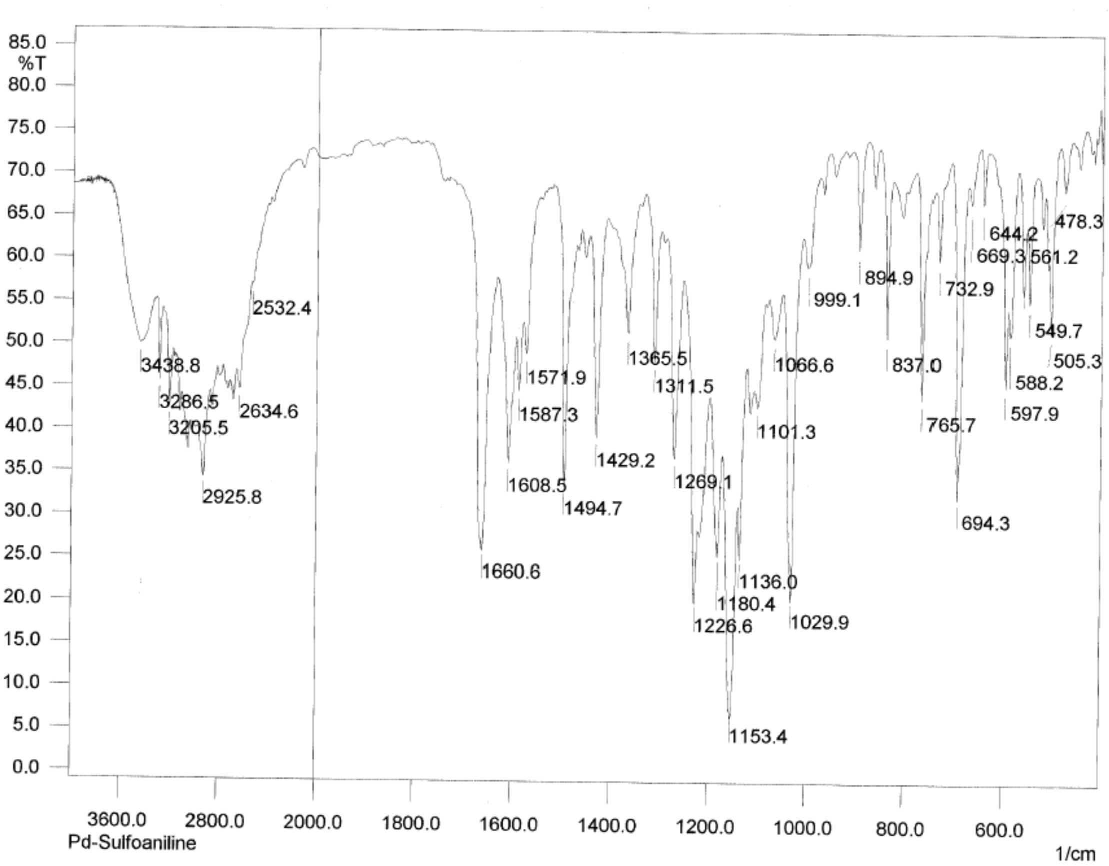


Figure 4.23: FTIR spectrum of Pd(sulfosalicylideneaniline)$_2$

In the IR spectrum of the Pd(sulfosalicylideneaniline)$_2$, characteristic absorption peaks observed are $\nu_{C=N}$ = 1608.5cm^{-1}, $\nu_{C=C}$ = 1608.5 cm^{-1}, $\nu_{S\text{-}O}$ = 1029.9 cm^{-1}, $\nu_{C\text{-}N}$ = 1153.4 cm^{-1}

4.2.4.3.3 Preparation of supported ossified [Pd(sulfosalicylideneaniline)$_2$]$_2$-Ba

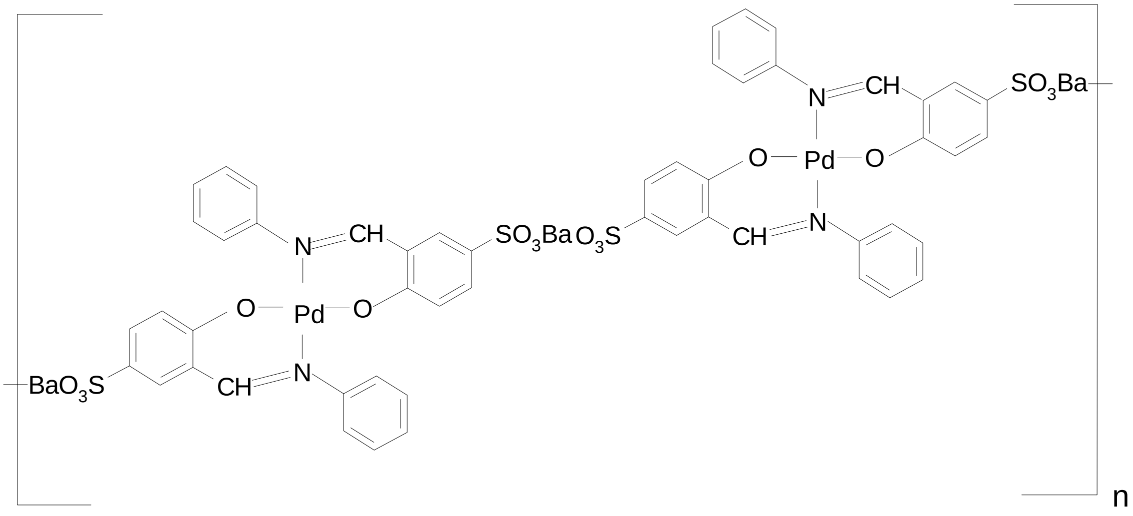


Figure 4.24: Ossified [Pd(sulfosalicylideneaniline)$_2$]$_2$-3Ba

In a 50 ml round bottom flask containing 10 ml degassed water 0.020g (0.28mmol) Pd(Sulfosalicylideneaniline)$_2$ was added. To this solution 2.00g 20% Ba(NO$_3$)$_2$ loaded silica was added and the mixture was stirred for 24h. The solid was filtered under vacuum over the Buckner funnel. The filtered solid was then washed with water followed by acetone and ether. The solid was then dried under vacuum for 5 hr.

The catalyst thus prepared thus was named as (**SOC-PdSSA**) and used for alkane oxidation reaction without any further treatment.

4.2.5 Experimental set up and procedure:

The experimental setup and procedure for performing oxidation reactions was the same as described in Chapter-2, section 2.3

4.2.6 Analytical methods:

FT-IR of the catalysts was recorded on a Bio-Rad Spectrophotometer 175C. Liquid ^{31}P NMR spectra were obtained on a Bruker AC-200 or MSL-300 spectrometer in D$_2$O at room temperature. ^{31}P solid state NMR (CP-MAS) spectra of all the heterogeneous materials were obtained on a UXNMR, Bruker Analytische

Messtechnik GmbH FT-NMR spectrometer at 5 or 8 kHz. The chemical shifts were referred to H_3PO_4 at 0 ppm and the spectra were collected with a flip angle of 45° and 6000 real data points. X-ray photoelectron spectroscopy (XPS) measurements were recorded using a VG Microtech ESCA 3000 instrument at 10^{-10} torr Pressure, a pass energy of 50 eV, and using unmonochromatized Mg-K_α (photon energy –1253.6 eV) as the radiation. Powder X-ray diffraction (XRD) spectra were obtained at room temperature on a Rigaku D MAX III VC diffractometer using Ni-filtered Cu-K_α radiation, $\lambda = 1.5404$ Å, where 2θ ranges were from 2° to 80° at a scan rate of 8°/min. Elemental analysis of the complexes was carried out on a CHNS-O EA1108, elemental analyzer of Carlo Erba Instruments, Italy. Inductively coupled plasma with atomic emission spectra (ICP-AES) analysis (Perkin-Elmer 1200 instrument) or GFAAS analysis (GBC Avanta Sigma Instruments Australia, with photo multiplier tube (PMT) as detector) was performed for quantifying palladium leaching. The quantitative analysis of reactants and products was carried out by a gas chromatographic method on a FFAP (free fatty acids as a stationary phase) capillary column. For this purpose, HP 6890 gas chromatograph was used. The standard GC conditions for the analysis of reactant and oxidation products of different alkanes are as described in Chapter 2, section 2.4. All the alkane oxidation products were identified by GC-MS (Agilent GC 6890N with 5973 mass selective detector instrument).

4.3 Results and discussion:

The objective of this work was to synthesize heterogenized catalysts by immobilization of the homogeneous complex catalyst, their characterization using various spectroscopic techniques and evaluation of their performance for the oxidation of alkanes. Here, we have synthesized the heterogenized catalysts using three different techniques viz.

1. Tethering on silica
2. Immobilization in LDH using ion exchange method
3. Ossification technique

4.3.1 Oxidation of alkanes using heterogenised catalysts:

4.3.1.1 LDH supported catalyst (LDH-PdTPP):

To check the feasibility of oxidation of alkanes using LDH supported catalyst, oxidation of decane was carried out at 150^0C under air with MA-LDH and LDH-PdTPP catalyst. The results of the reaction are given in the Table 4.2.

Table 4.2: Decane oxidation using LDH and LDH-PdTPP

Sr. No.	Catalyst	Oxidant	Conversion, %	Selectivity, %			
				Alcohols	Ketones	Lower alkanes	Other products
1	MA-LDH	air	0.69	21.61	13.79	8.02	3.66
2	LDH-PdTPP	air	1.04	35.24	39.55	14.35	6.54
3	LDH-PdTPP	oxygen	1.25	29.59	30.21	23.43	8.32
4*	LDH-PdTPP	oxygen	1.39	33.21	31.68	27.21	8.17
5#	LDH-PdTPP	oxygen	1.63	25.87	32.92	33.42	10.25

Reaction conditions: decane- 25mmol, cat- 100mg, temperature - 150^0C, time- 5 hr, * reaction at 160^0C, # reaction time 10 hr.

Both the catalysts show very little activity for alkane oxidation reaction. Not much difference in the decane conversion was observed when molecular oxygen was used instead of air and also with 160^0C reaction temperature. Extending the reaction time to 10hr instead of 5hr also did not improve the alkane conversion.

The probable reason for inactivity of the catalyst towards alkane oxidation might be because of the difference in polarity of the substrate and catalyst surface. The alkanes are nonpolar molecules and the catalyst surface is polar compared to the alkane. As the oxidation reactions are carried out in neat alkane this difference in polarity plays a major role. The difference in polarity probably does not allow the substrate to come in contact with the catalyst hence restrict the activity of the catalyst.

4.3.1.2 Tethered catalyst (SA-Pd)

To check the feasibility of tethered catalyst for oxidation of alkanes, the oxidation of decane was carried out at 150^0C under air using tethered $PdBr_2(PPh_3)_2$ catalyst (SA-Pd) (see Table 4.3 for the results).

When SA-Pd catalyst was tested for decane oxidation using oxygen, surprisingly no alkane conversion was observed. No alkane oxidation was also observed when plain silica was used for decane oxidation reaction under same reaction condition.

Table 4.3: Decane oxidation using SA-Pd catalyst

Sr. No.	Catalyst	Oxidant	Conversion, %	Selectivity, %			
				Alcohols	Ketones	Lower alkanes	Other products
1	Plain silica	oxygen	nil	-	-	-	-
2	SA-Pd	oxygen	nil	-	-	-	-

Reaction conditions: decane- 25mmol, cat- 100mg, temperature - 150^0C, time- 5 hr, oxidant- oxygen

For this catalyst also the probable reason for inactivity towards alkane oxidation might be because of the polar surface of the catalyst. The silica surface is polar in nature, which is not allowing the substrate to react with the catalyst, and hence no oxidation reaction was observed.

Therefore to have the active heterogeneous catalyst for alkane oxidation reaction the catalyst surface has to be relatively nonpolar in nature or has to be masked with nonpolar compound. The supported ossified catalyst would have all these requirements and would be worth attempting. In supported ossified catalyst the surface of the catalyst is covered with the organic ligand and the metal is coordinated to this surface bound ligands. This results in a relatively nonpolar catalyst where we can expect the reaction.

4.3.1.3 Supported ossified catalysts:

The supported ossified catalysts were tested for decane oxidation at 150^{0}C under oxygen atmosphere (see Table 4.4 for the results).

Table 4.4: Screening of supported ossified catalysts for decane oxidation reaction

Sr. No.	Supported ossified catalyst	Conversion, %	Selectivity, %				TOF, h^{-1}
			Alcohols	Ketones	Lower alkanes	•Other products	
1	SOC-PdBD	8.54	40.98	45.44	7.97	5.09	305
2	SOC-PdTPP	5.71	42.43	41.55	10.34	4.95	386
3	SOC-PdSSA	4.55	39.39	38.55	12.37	8.63	179

Reaction conditions: decane- 25mmole, cat: (ossified 1% Pd)-0.100g, temperature - 150^{0}C, time- 5 hr, oxidant- O_2 in bladder ● other products- Esters of alcohols, lower acids, diketones, dialkyl ethers

The results in Table 4.4 showed that all the three supported ossified catalysts are active (TOF 179 to 386 h^{-1}) for oxidation of decane with a good combined selectivity (>79 to 86 %) of alcohols and ketones.

The synthesized supported ossified catalysts showed that it is active and also selective for decane oxidation reaction. In order to check the stability of the catalyst in decane oxidation reaction, a catalyst recycle study was carried out. Out of the three tested catalysts SOC-PdTPP catalyst was used for this study as it gave better TOF compared to the other two catalysts as seen in Table 4.4.

For the recycle study, the supported catalyst was filtered after oxidation reaction through buckner funnel over filter paper, washed with n-hexane and then with acetone and dried under vacuum for 10 mins. The washed catalyst was then again charged into the fresh decane and the oxidation reaction was carried out as per the previously mentioned procedure. The results of the catalyst recycle study are given in Table 4.5

Table 4.5: Results of the recycle study of the ossified catalyst for decane oxidation reaction

Sr. No.	Recycle numbers	Conversion, %	Selectivity, %			
			Alcohols	Ketones	Lower alkanes	Other products
1	Virgin run	5.71	42.43	41.55	10.34	4.95
2	1	5.37	40.47	43.52	9.97	5.12
3	3	5.43	39.81	42.91	10.52	4.56
4	5	5.52	40.45	43.64	9.38	5.54

Reaction conditions: decane- 25mmole, cat: 1% SOC-PdTPP-0.100g, temperature - 150^0C, time- 5 hr, oxidant- O_2 in bladder

The results of the catalyst recycle study showed that the catalyst is stable on recycle and the activity and selectivity of the catalyst was maintained during several recycles. The ICP analysis shows negligible leaching to the organic phase, at the end of fifth recycle. The palladium content of reaction crude was <0.1 ppm, which shows almost nil leaching of palladium.

4.3.2 Comparison of the performance of the supported ossified catalysts

A comparison of the performance of the supported ossified catalysts with the conventional non supported metal complexes under identical reaction conditions showed a drastic increase in the activity of the catalyst. The three supported ossified catalysts were tested against $PdCl_2(TPPTS)_2$, $PdCl_2$Bathophends and $PdCl_2$(sulfosalicylideneaniline)$_2$. The results of the activity comparison study are shown in Table 4.6 and in the Figure 4.25.

From the Table 4.6 it is clear that the activity of the supported ossified catalyst is higher than that of non supported metal complex catalyst by 30 to 80 times!

Table 4.6: Results of the comparison of activity of supported ossified catalysts with non-supported metal complexes.

Sr. No.	Catalyst concentration, mole	Conversion, %	Selectivity, %				TOF, h^{-1}
			Alcohols	Ketones	Lower alkanes	•Other products	
1	SOC-PdTPP	5.71	42.43	41.55	10.34	4.95	386
2	$PdCl_2(TPPTS)_2$	7.51	33.14	41.99	8.05	9.51	4.71
3	SOC-PdBD	8.54	40.98	45.44	7.97	5.09	305
4	$PdCl_2$Bathophends	6.54	37.70	43.51	6.11	8.71	4.08
5	SOC-PdSSA	4.55	39.39	38.55	12.37	8.63	179
6	$PdCl_2$ (sulfosalicylideneaniline)$_2$	6.23	40.39	39.68	9.52	8.08	5.44

Reaction conditions: decane- 25mmole, cat: (ossified 1% Pd)-0.100g, non supported metal complex – 0.08mmol, temperature - 150^0C, time- 5 hr, oxidant- O_2 in bladder ● other products- Esters of alcohols, lower acids, diketones, dialkyl ethers

The probable reason for the drastic increase in the activity of the supported catalyst is that the non-supported organometallic complexes used for alkane oxidation are insoluble in alkane and formed lumps in the neat alkane during oxidation reaction. Therefore the catalyst molecules that are on the surface of the lumps are the ones only available for reaction, giving rise to low reaction rates. In the supported ossified catalyst on contrary the catalyst molecules are highly dispersed with relatively high surface area, which provides easy accessibility of the catalyst. The reaction can take place to a large extent due to the large number of sites available.

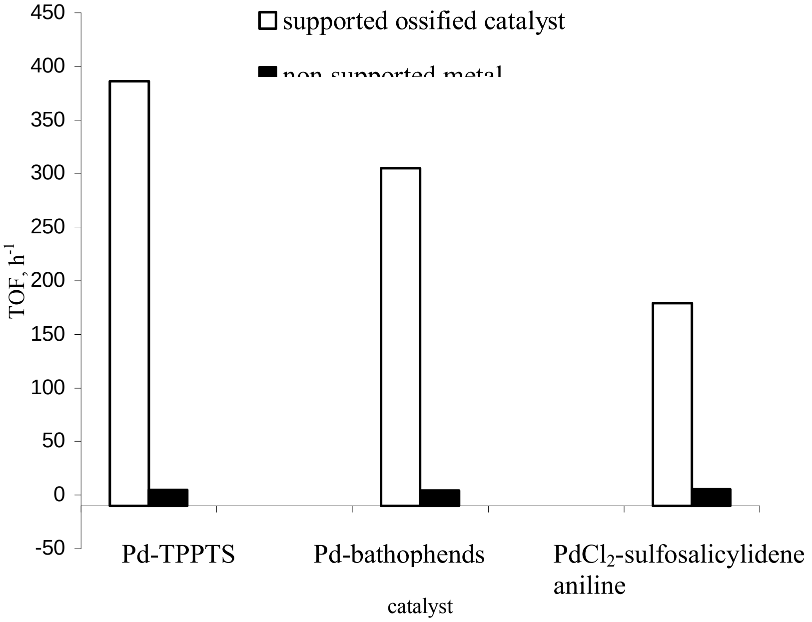


Figure 4.25: comparison of activity of supported ossified catalysts with non supported metal complexes

4.3.3 Role of Support

In heterogeneous catalytic systems, the support is known to play a major role in dictating the activity and selectivity of the catalyst. As in the ossified catalyst the water soluble organometallic complex is precipitated on surface of the support it is of interest to observe the role of supports on the activity and selectivity of the catalyst for oxidation reaction. In this context barium salt of $PdCl_2(TPPTS)_2$ supported on various inorganic supports like SiO_2, TiO_2, Al_2O_3, ZrO_2, La_2O_3 and MgO was prepared and their activity was assessed for the oxidation of n-decane.

The supported ossified catalysts prepared on different supports were tested for the oxidation of n-decane and the results are presented in Table 4.7. All the catalysts showed good oxidation activity.

Table 4.7: Results of support screening in oxidation of n-decane

Sr. No.	Support	Conversion, %	Selectivity (%)				TOF h^{-1}
			Alcohol	Ketone	Lower alkanes	Other products	
1	SiO_2	5.71	42.43	41.55	10.34	4.95	386
2	Al_2O_3	5.59	41.69	42.24	9.69	5.33	378
3	ZrO_2	5.34	42.58	42.65	10.35	4.18	363
4	TiO_2	3.46	40.12	40.28	11.23	7.01	234
5	La_2O_3	4.97	41.54	39.21	9.77	6.59	336
6	MgO	4.23	39.01	40.38	10.98	7.58	285

Reaction conditions: decane- 25mmole, catalyst: 0.10g, temperature - 150^0C, time- 5 hr, oxidant- O_2 in bladder

SiO_2, Al_2O_3, La_2O_3, ZrO_2, supported catalysts show relatively higher activity than TiO_2 and MgO supported catalysts. Comparatively high leaching (~0.5 ppm) of the palladium metal to the organic phase was observed in case of the catalyst supported on MgO and TiO_2. No much variation was observed in alcohol and ketone selectivities in all the catalyst screened. The catalyst supported on silica is sufficiently active and stable and shows negligible leaching.

The above results showed that the supported ossified catalysts are active for the oxidation of alkanes and are stable and can be reused. Therefore further detailed studies in alkane oxidation using silica supported ossified catalyst were carried out. For detailed study decane was used as a model substrate.

4.3.4 Effect of the variation in palladium concentration in supported ossified catalyst for n-decane oxidation

The effect of change in palladium concentration in silica supported ossified catalyst on n-decane oxidation was checked in the range of 1%w/w to 3%w/w of palladium. The results of the palladium content on decane oxidation reaction are given in Table 4.8

Table 4.8: Effect of change in palladium content in silica supported ossified catalyst on decane oxidation reaction

Sr. No.	Pd content, % w/w	Conversion, %	Selectivity, %				TOF, h^{-1}
			Alcohols	Ketones	Lower alkanes	●Other products	
1	1	5.71	42.43	41.55	10.34	4.95	386
2	2	12.03	41.01	41.14	11.25	5.41	813
3	3	18.67	40.87	41.05	10.85	6.91	1270

Reaction conditions: decane- 25mmole, catalyst: silica supported SOC-PdTPP, temperature - 150^0C, time- 5 hr, oxidant- O_2 in bladder ● other products- Esters of alcohols, lower acids, diketones, dialkyl ethers

The study of effect of palladium content in supported ossified catalyst on decane oxidation reaction showed that the decane conversion increases with increase in catalyst concentration. The increase in the decane conversion with the increase in the palladium content is linear. No much variation in the in the selectivity of alcohol and ketone was observed.

4.3.5 Study of effect of reaction temperature on activity of silica supported ossified catalyst on hexadecane oxidation reaction

The reaction temperature effect was carried out with hexadecane as substrate. The results of effect of reaction temperature on hexadecane oxidation are given in Table 4.9.

It was observed that, this catalyst also has a temperature threshold of 140^0C, below which reaction does not take place. It was also observed that with increase in reaction temperature the hexadecane conversion increases. This increase in conversion is almost double for 10^0C rise in temperature. The total selectivity to alcohol and ketone does not vary much for increase in temperature from 140^0C to 160^0C.

Table 4.9: Effect of reaction temperature on activity of silica supported ossified catalyst on n-hexadecane oxidation reaction

Sr. No.	Reaction temperature, ^0C	Conversion, %	Selectivity, %				TOF, h^{-1}
			Alcohols	Ketones	Lower alkanes	Other products	
1	120	nil	0	0	0	0	0
2	130	nil	0	0	0	0	0
3	140	5.98	42.86	42.68	9.82	8.19	404
4	150	12.17	43.08	43.15	15.61	8.28	823
5	160	24.76	41.67	41.96	17.23	8.69	1673

Reaction conditions: alkane: hexadecane- 25mmole, catalyst: 1% silica supported SOC-PdTPP – 100mg, temperature - 150^{0}C, time- 5 hr, oxidant- O_2 in bladder

4.3.6 Effect of change in oxygen concentration on activity of silica supported ossified catalyst for decane oxidation reaction

The oxygen concentration effect was carried out in the range of 100% oxygen to 5% oxygen in N_2. The mixtures of O_2 in N_2 were prepared separately in the gas reservoir and were analyzed on GC. The results of the study of change in oxygen concentration variation on activity of SOC-PdTPP are given in Table 4.10

The results of oxygen concentration variation showed that as the concentration of O_2 in the reaction system increases the rate of reaction increases. This is obvious because, as the concentration of O_2 in the atmosphere will increase the concentration of O_2 in the reaction mixture will increase. Hence, with increase in O_2 concentration the decane conversion will increase. No much variation in the percentage of alcohol and ketone was observed with change in oxygen concentration.

Table 4.10: Effect of change in oxygen concentration on activity of silica supported ossified catalyst on n-decane oxidation reaction

Sr. No.	Oxidant	Conversion, %	Selectivity, %				TOF, h^{-1}
			Alcohols	Ketones	Lower alkanes	Other products	
1	100% O_2	5.71	42.43	41.55	10.34	4.95	386
2	60% O_2 in N_2	3.41	42.69	42.37	14.51	7.35	231
3	20% O_2 in N_2	1.11	43.15	41.96	14.18	7.68	74

Reaction conditions: alkane: decane-25mmol, cat: silica supported SOC-PdTPP- 1%, temp- 150^0C, time- 5 hr, oxidant in bladder

4.3.7 Screening of alkanes

The SOC-PdTPP catalyst was also tested for the oxidation of linear alkanes, cyclic alkanes and aryl substituted alkanes. The results of alkane screening are discussed below in detail.

4.3.7.1 Screening of linear alkanes

With 1% SOC-PdTPP catalyst the oxidation of alkane ranging from n-hexane to n-hexadecane was carried out. The results of the reaction are given in the Table 4.11

The substrate screening showed that as the number of carbon atoms in the alkane chain increases the rate of reaction increases. At the same time no much effect of alkane chain length was observed on the selectivity of alcohols and ketones. The combined selectivity of alcohols and ketones remains almost constant for all substrates.

Table 4.11: Screening of linear alkanes using SOC-PdTPP catalyst

No	Substrate	Conversion, %	Selectivity, %				TOF, h^{-1}
			Alcohols	Ketones	Lower alkanes	Other products	
1	n-decane	5.71	42.43	41.55	10.34	4.95	386
2	n-dodecane	7.64	42.26	42.79	14.33	8.97	514
3	n-tetradecane	9.81	42.67	42.93	16.05	8.20	664
4	n-hexadecane	12.17	43.08	43.15	15.61	8.28	823

Reaction conditions: alkane- 25mmole, catalyst: silica supported SOC-PdTPP-1%, temperature - 150^0C, time- 5 hr, oxidant- O_2 in bladder,

4.3.7.2 Screening of aryl alkanes and cyclic alkanes

The 1% SOC-PdTPP catalyst was also tested for aryl alkanes and cyclic alkanes. The results of the screening of alkanes are given in Table 4.12

Table 4.12: Screening of aryl alkanes and cycloalkanes using SOC-PdTPP catalyst

No	Substrate	Conversion, %	Selectivity, %				TOF, h^{-1}
			Alcohols	Ketones	Lower alkanes	Other products	
1	ethylbenzene	19.87	28.31	63.45	-	1.26	1291
2	propylbenzene	21.33	19.74	67.38	-	11.43	1386
3	cyclohexane*	5.63	37.49	43.49	-	13.35	364

Reaction conditions: alkane- 25mmole, catalyst: silica supported SOC-PdTPP-1%, temperature - 150^0C, time- 16 hr, oxidant- O_2 in bladder, * reaction carried out in autoclave under 200 psi pressure of air for 1hr

In addition to the oxidation of linear alkanes the catalyst was found to be also active for the oxidation of cycloalkanes and aryl alkanes**.**

4. 4 Conclusions:

A methodology for immobilization of palladium complex catalysts which gives finely dispersed heterogeneous catalysts has been applied for oxidation of alkanes. The method (ossification) involves conversion of a water-soluble Pd complex catalyst (containing sulfonate groups) to its heterogeneous form as a barium salt on solid support. The catalysts were characterized by the various techniques such as FTIR, solid state ^{31}P NMR, TEM, and XPS. The detailed characterization shows the catalyst is truly a heterogenized form of his homogeneous analogous $PdCl_2(TPPTS)_2$.

The supported ossified catalyst was tested for oxidation of various classes of alkanes and showed significant improvement of catalytic activity as compared to their conventional homogeneous analogues. The effects of nature and type of support and reaction parameters were also investigated. The supported ossified catalyst is stable and can be recycled without any loss in activity. The silica supported ossified catalyst was found to have a higher activity and the stability compared to the other heterogenised palladium catalysts synthesized using other heterogenization technique.

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Annexure I

IR spectrum of the palladium metal complexes:

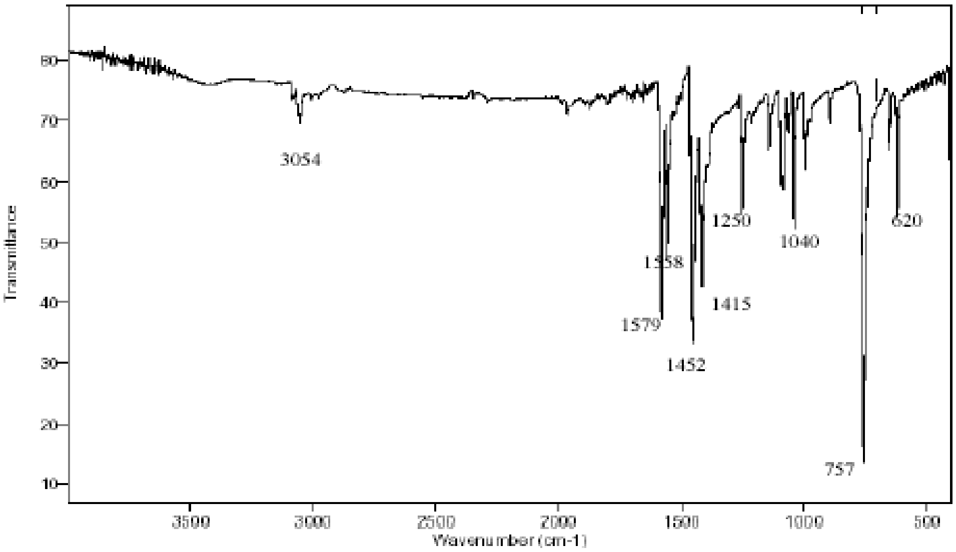


Figure 2.1: IR spectrum of 2, 2’-bipyridine, ligand

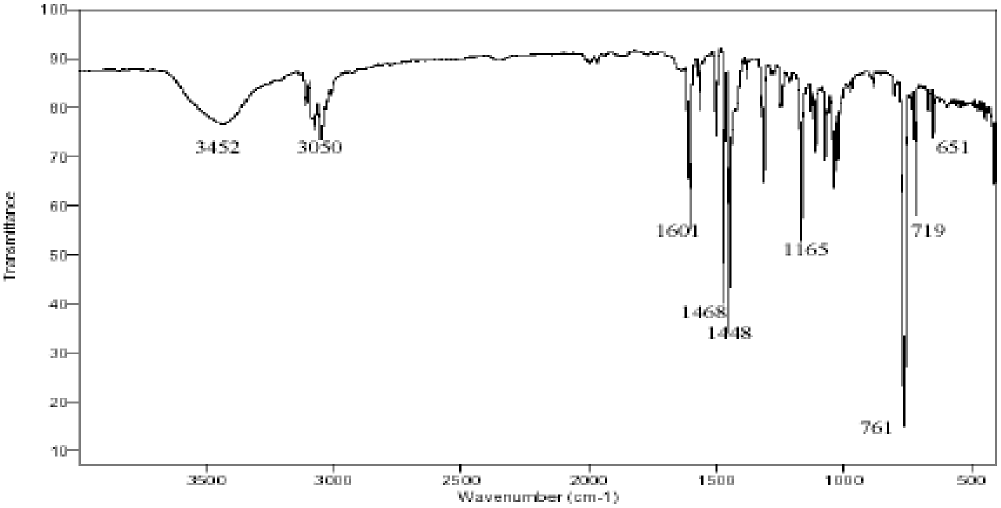


Figure 2.2: IR spectrum of $PdCl_2$Bipy complex

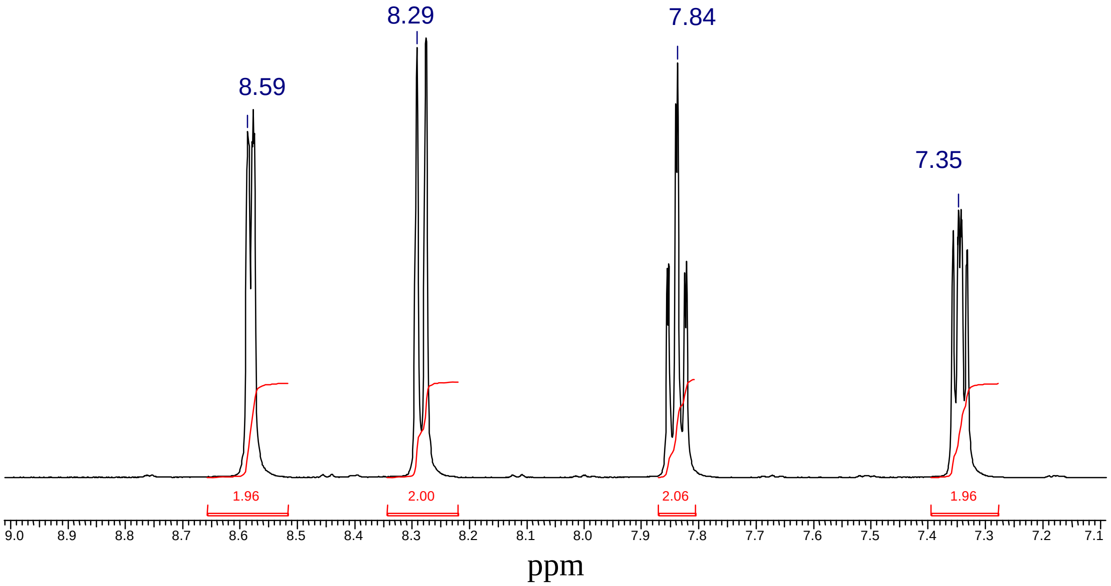


Figure 2.3: Proton NMR spectrum of 2,2’-bipyridine ligand

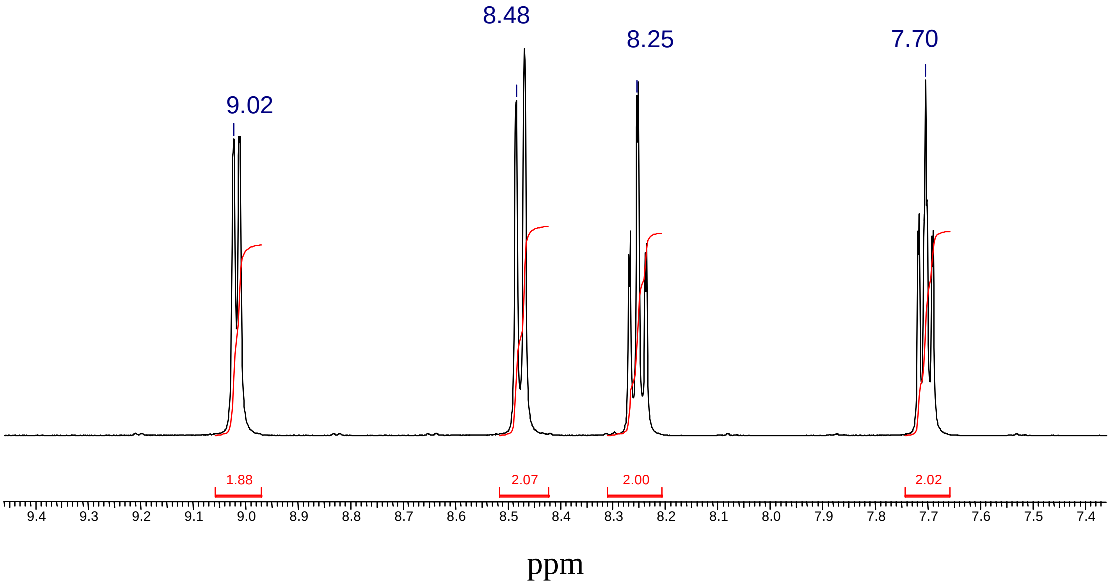


Figure 2.4: Proton NMR spectrum of PdCl2Bipy complex

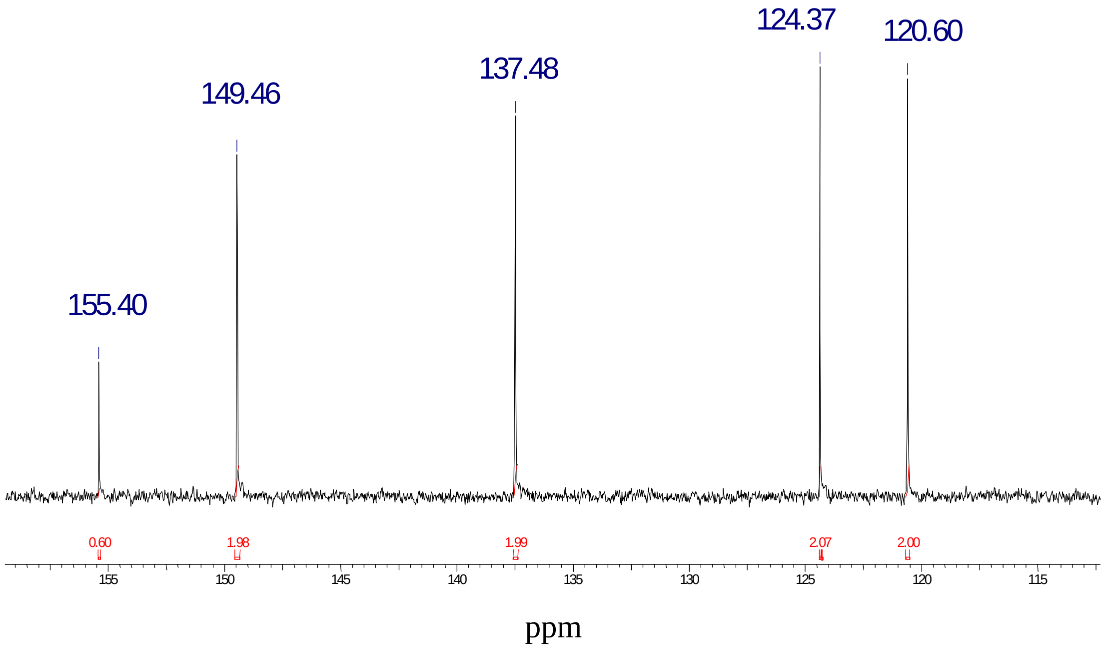


Figure 2.5: Carbon NMR spectrum of 2,2’-bipyridine ligand

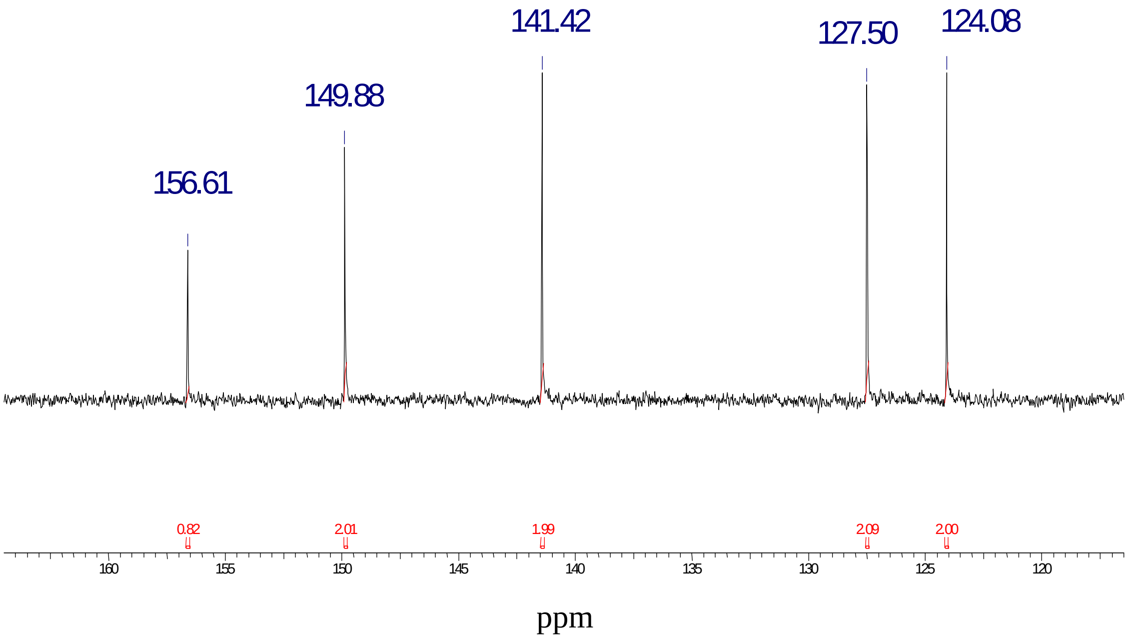


Figure 2.6: Carbon NMR spectrum of $PdCl_2$Bipyridine complex

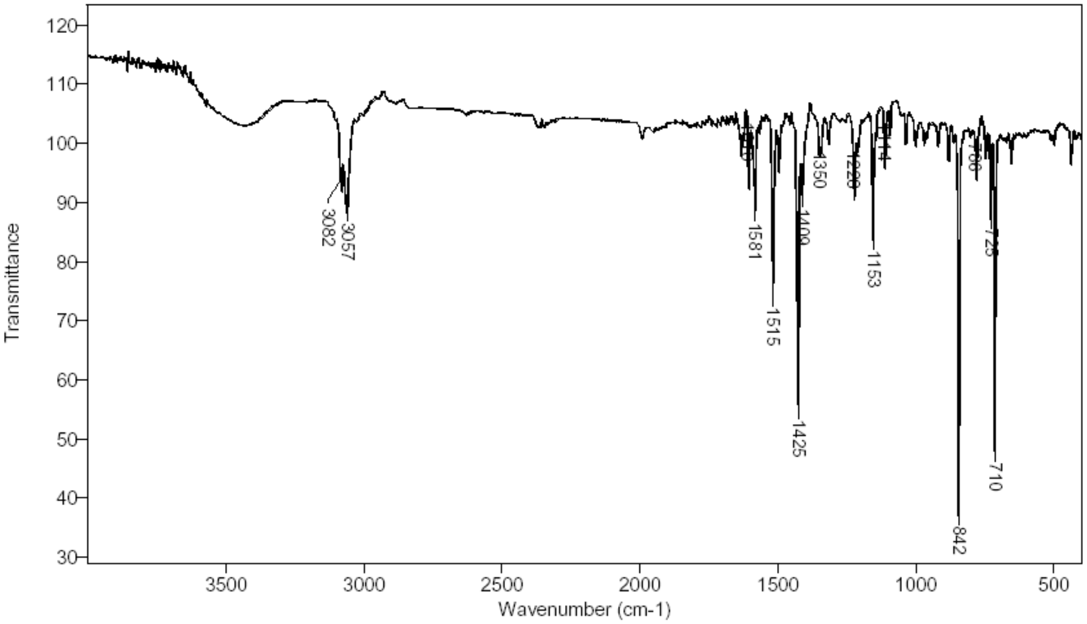


Figure 2.7: FTIR spectrum of $PdCl_2$Phenanthroline

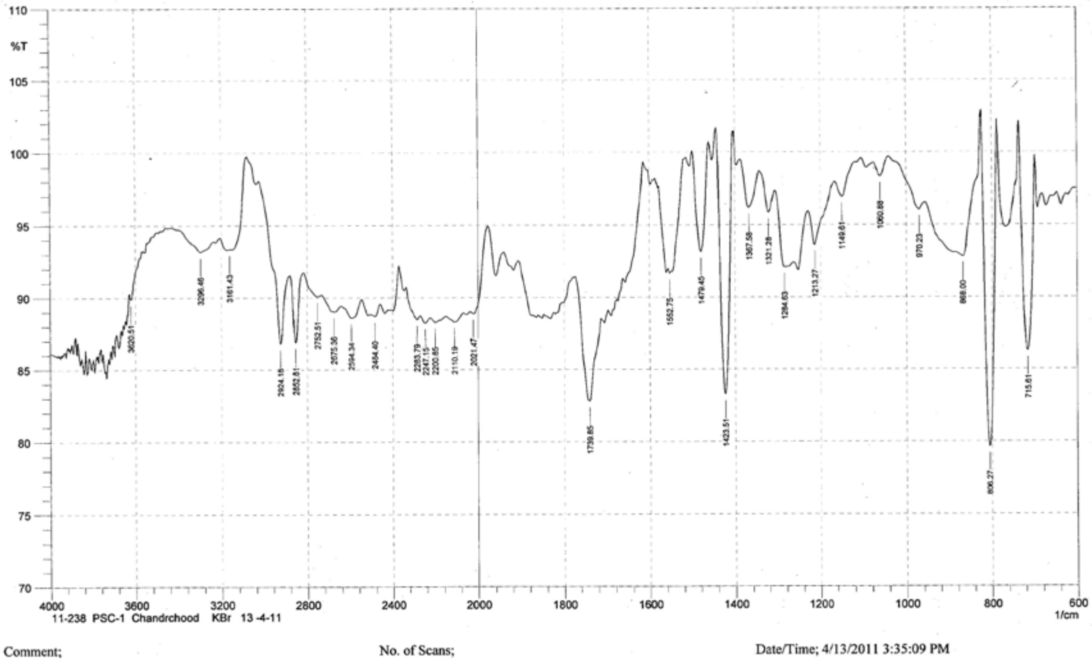


Figure 2.8: FTIR spectrum of $PdCl_2$(5,6-dimethyl-1,10-Phenanthroline)

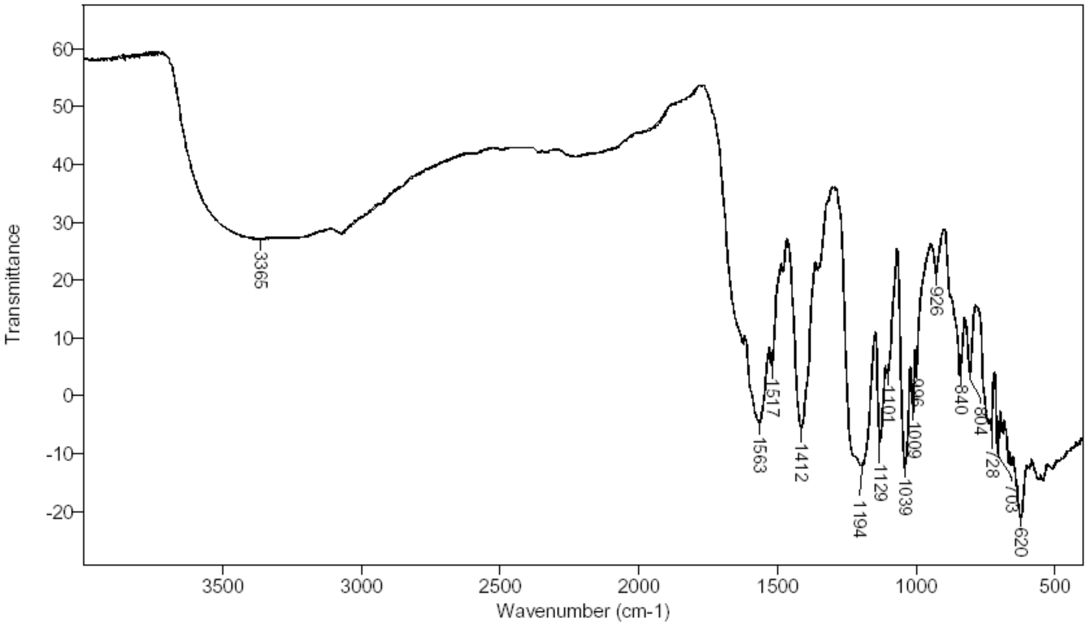


Figure 2.9: FTIR spectrum of $PdCl_2$(4,7-diphenyl-1,10-Phenanthroline)

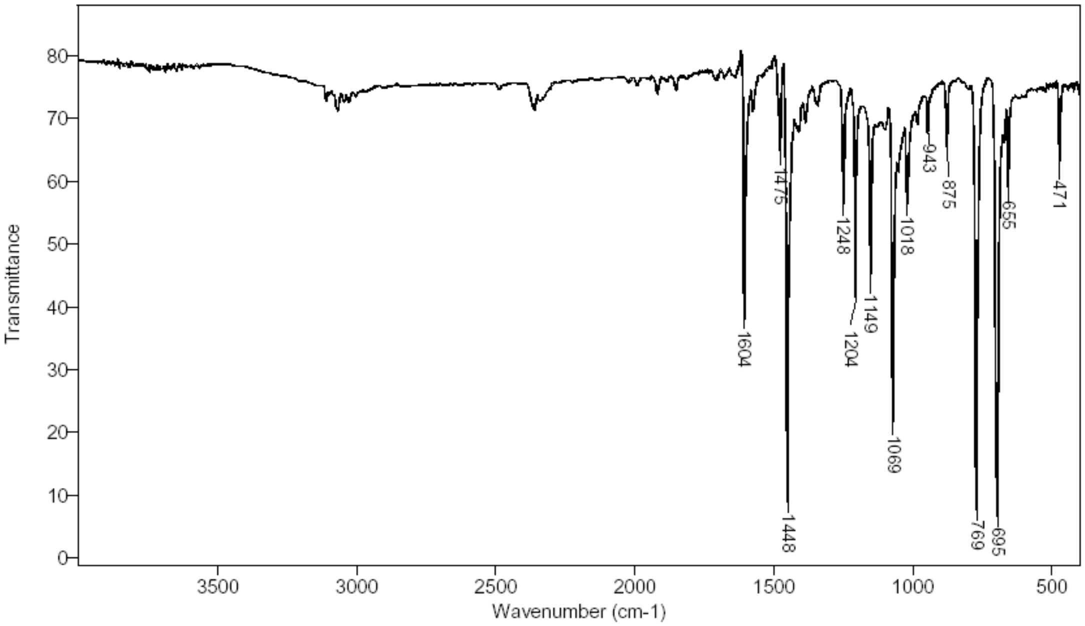


Figure 2.10: FTIR spectrum of $PdCl_2(pyridine)_2$

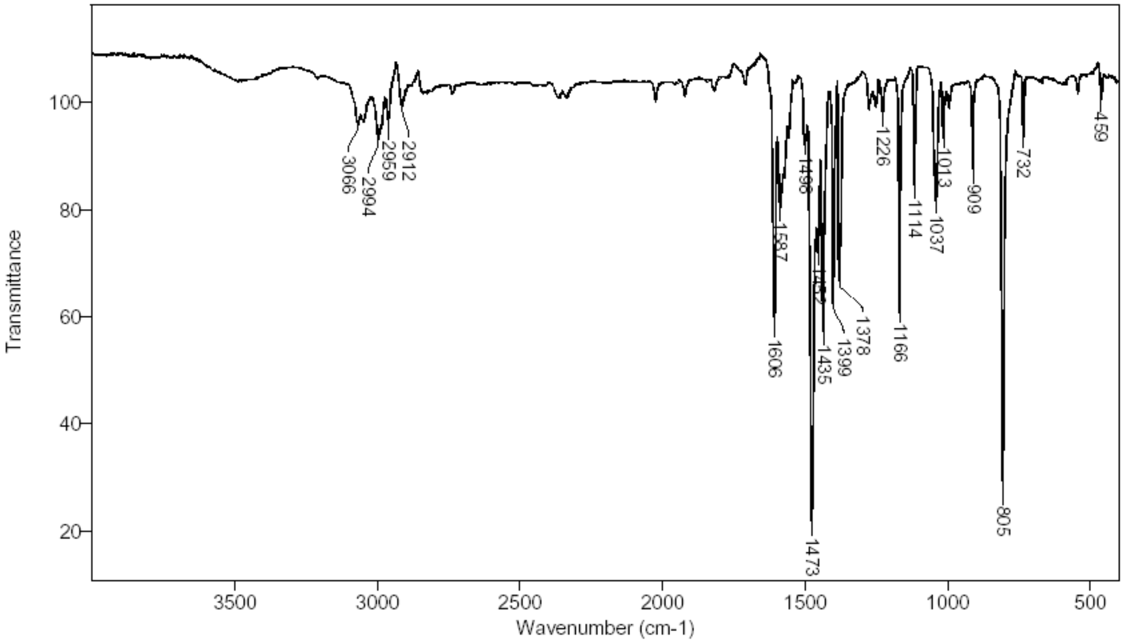


Figure 2.11: FTIR spectrum of $PdCl_2(2,6\text{-lutidine})_2$

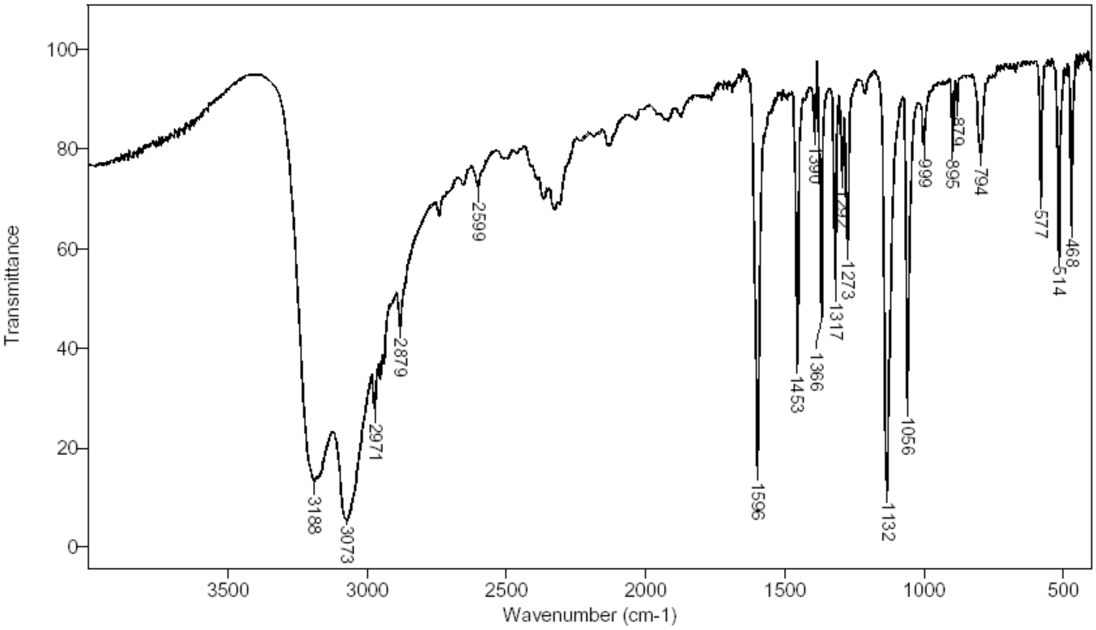


Figure 2.12: FTIR spectrum of $PdCl_2$ethylenediamine

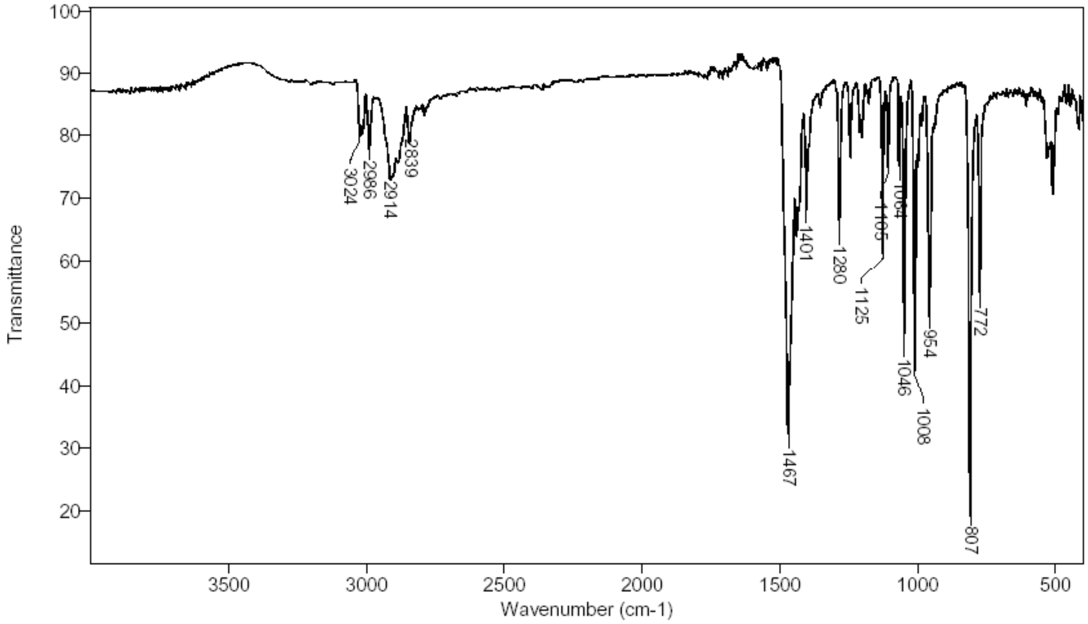


Figure 2.13: FTIR spectrum of $PdCl_2$(N,N,N’,N’-tetramethylethylenediamine)

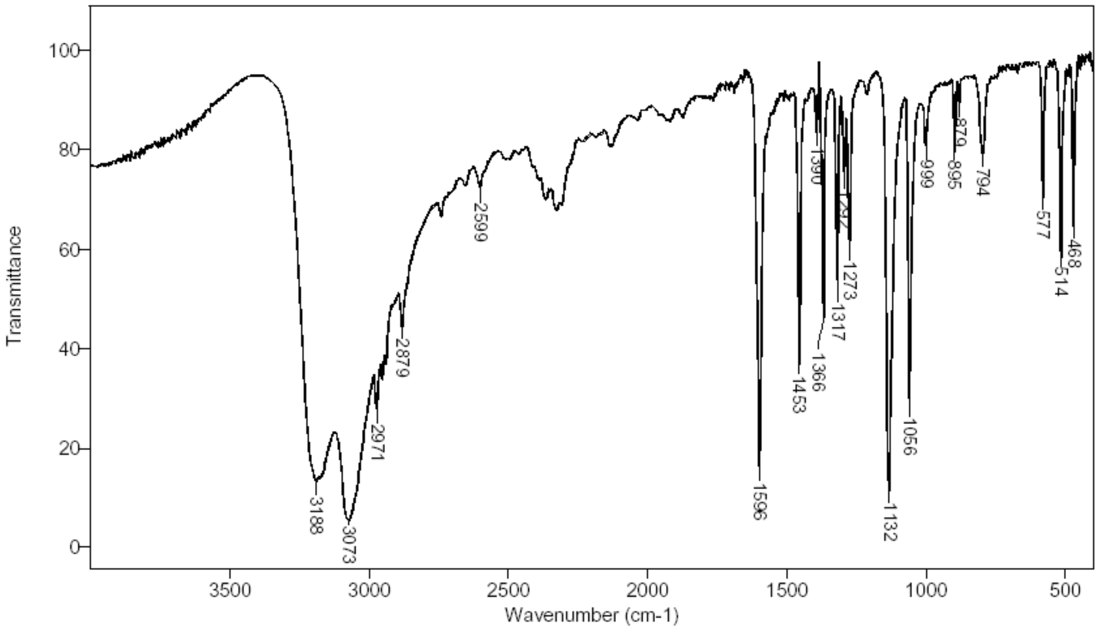


Figure 2.14: FTIR spectrum of $PdCl_2$(1,3-diaminopropane)

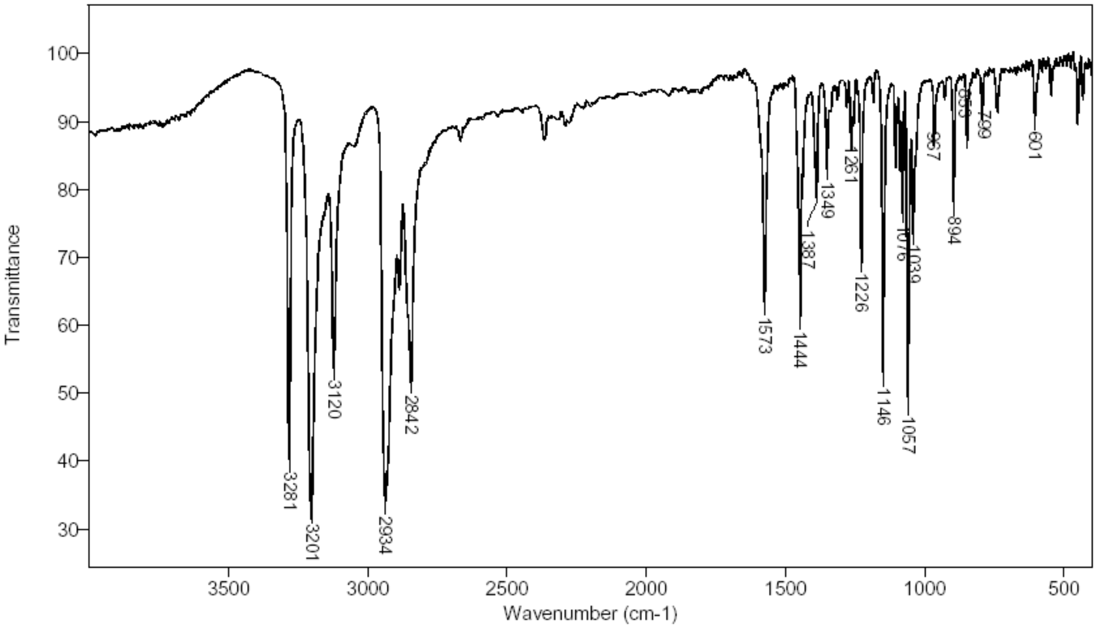


Figure 2.15: FTIR spectrum of $PdCl_2(cyclohexylamine)_2$

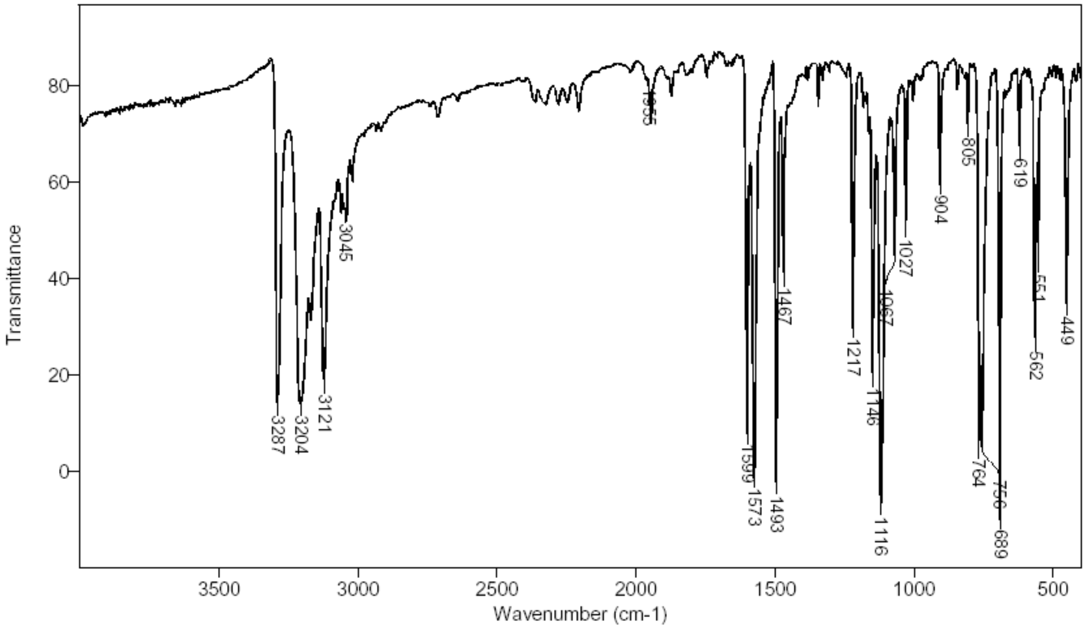


Figure 2.16: FTIR spectrum of $PdCl_2(aniline)_2$

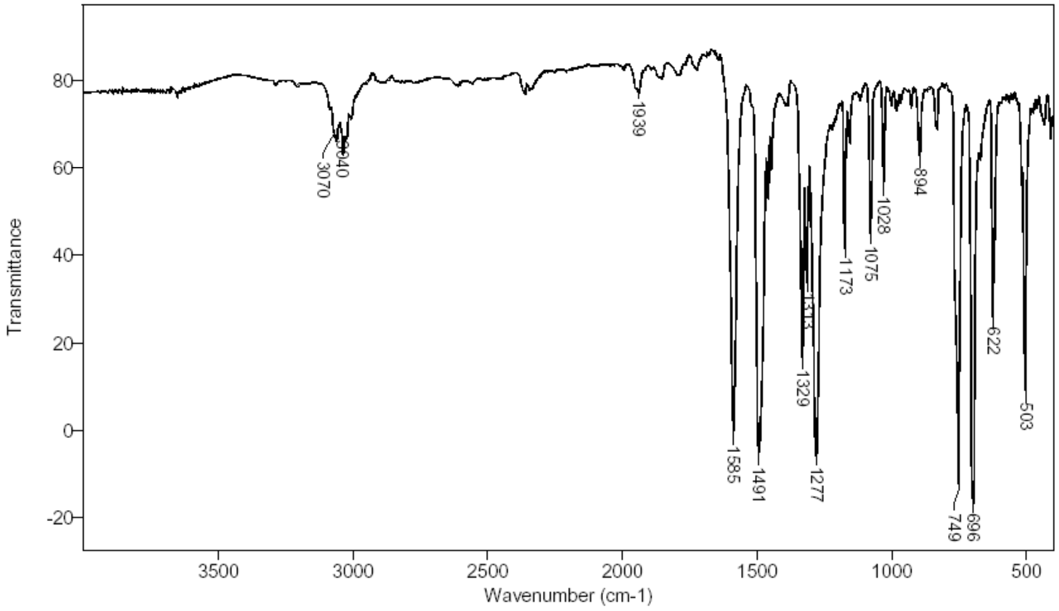


Figure 2.17: FTIR spectrum of $PdCl_2$(triphenylamine)$_2$

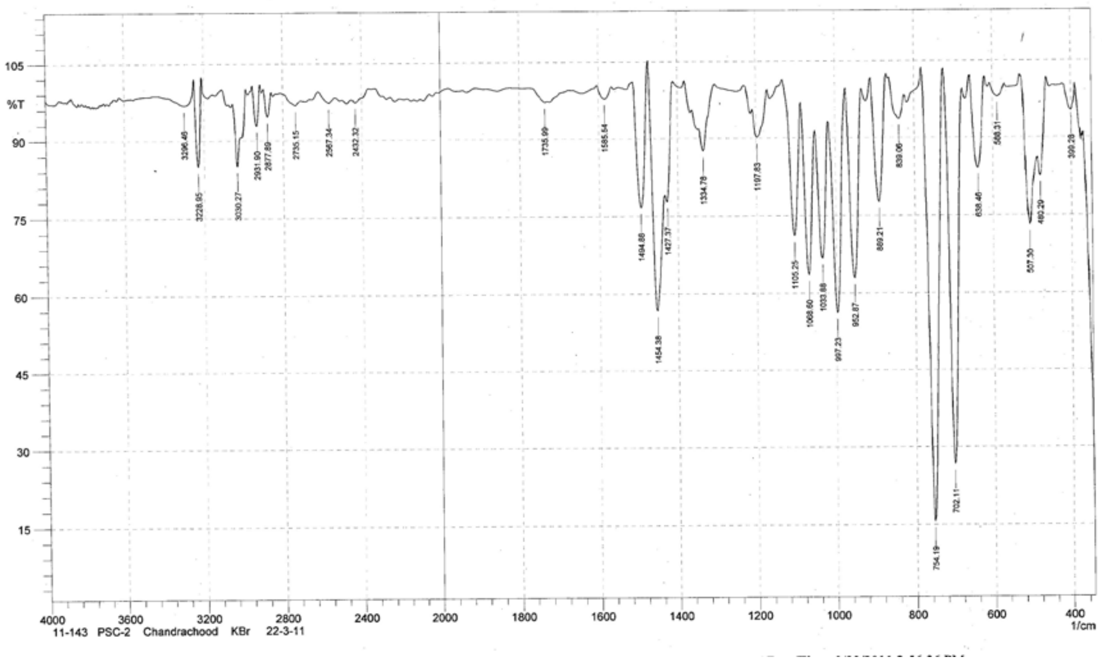


Figure 2.18: FTIR spectrum of $PdCl_2$(benzylamine)$_2$

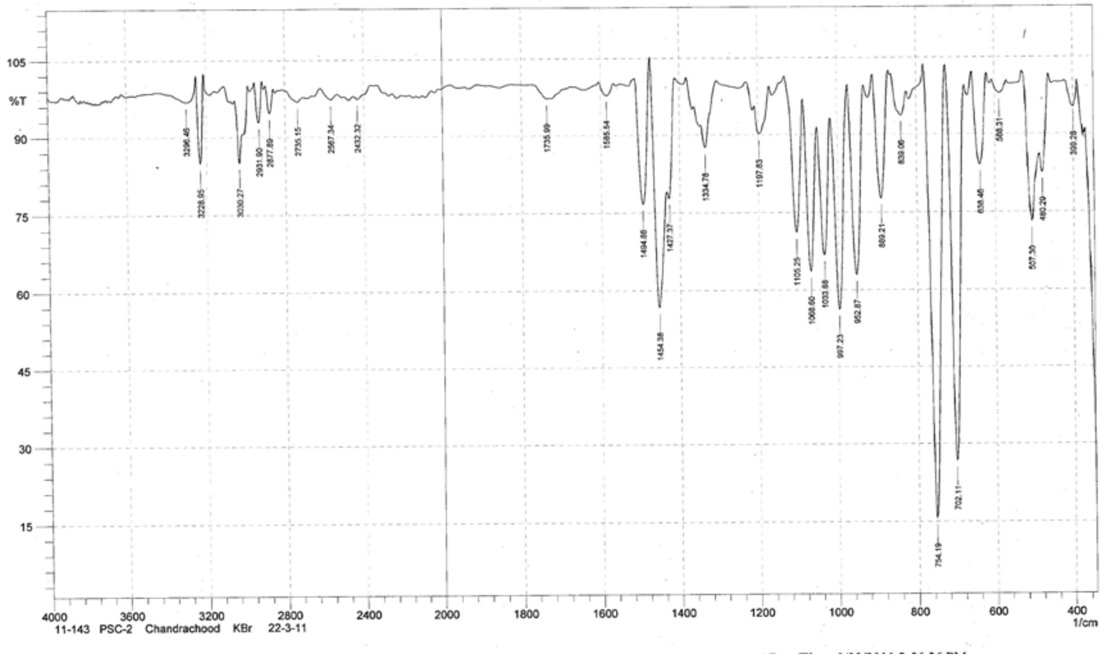


Figure 2.19: FTIR spectrum of $PdCl_2$(dibenzylamine)$_2$

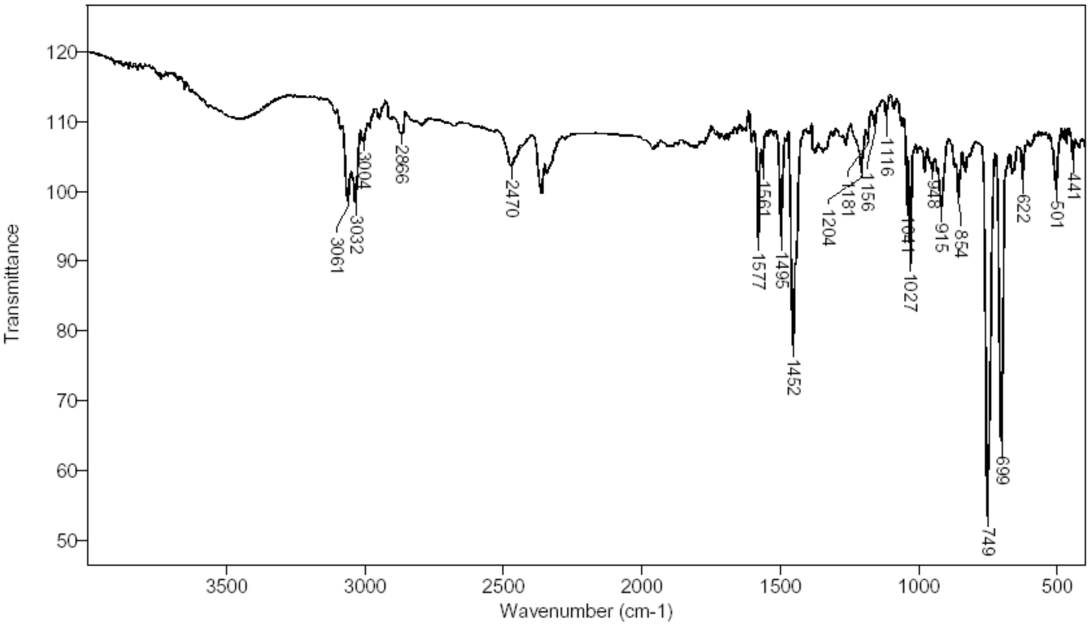


Figure 2.20: FTIR spectrum of $PdCl_2$(tribenzylamine)$_2$

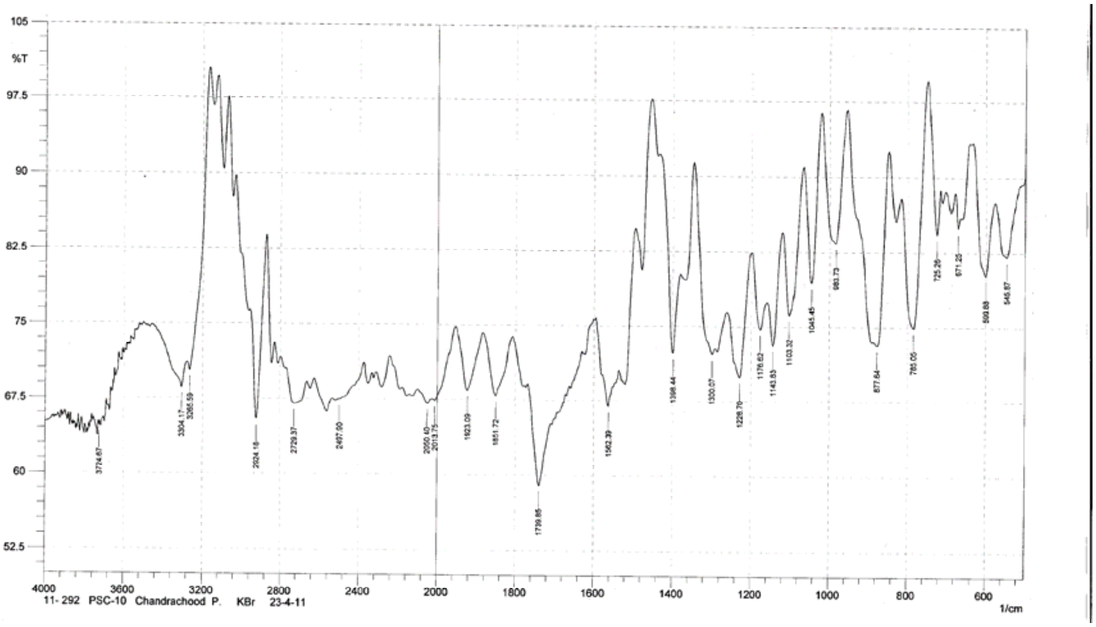


Figure 2.21: FTIR spectrum of $PdCl_2$(N,N’-dibenzylethylenediamine)

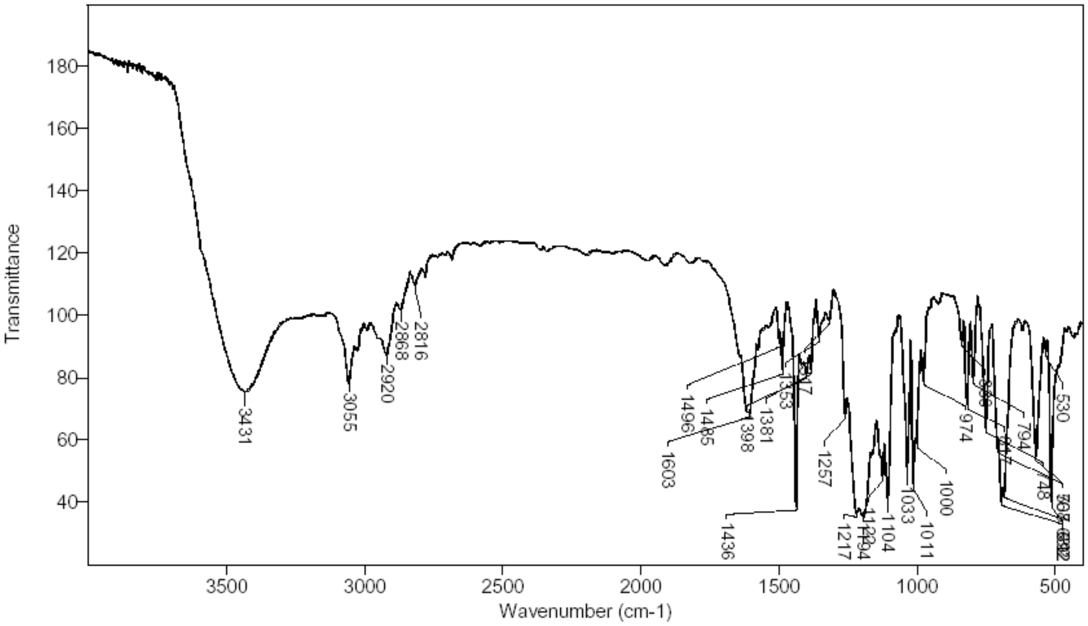


Figure 2.22: FTIR spectrum of $PdCl_2$(1,2-dianilinoethane)

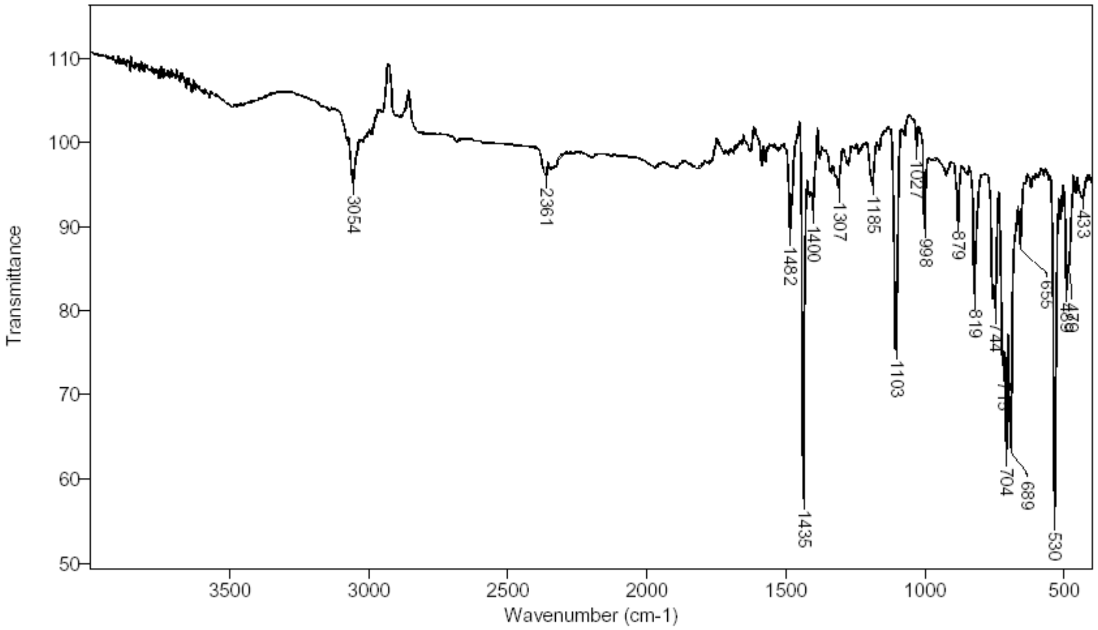


Figure 2.23: FTIR spectrum of $PdCl_2$(1,2-diphenylphosphinoethane)

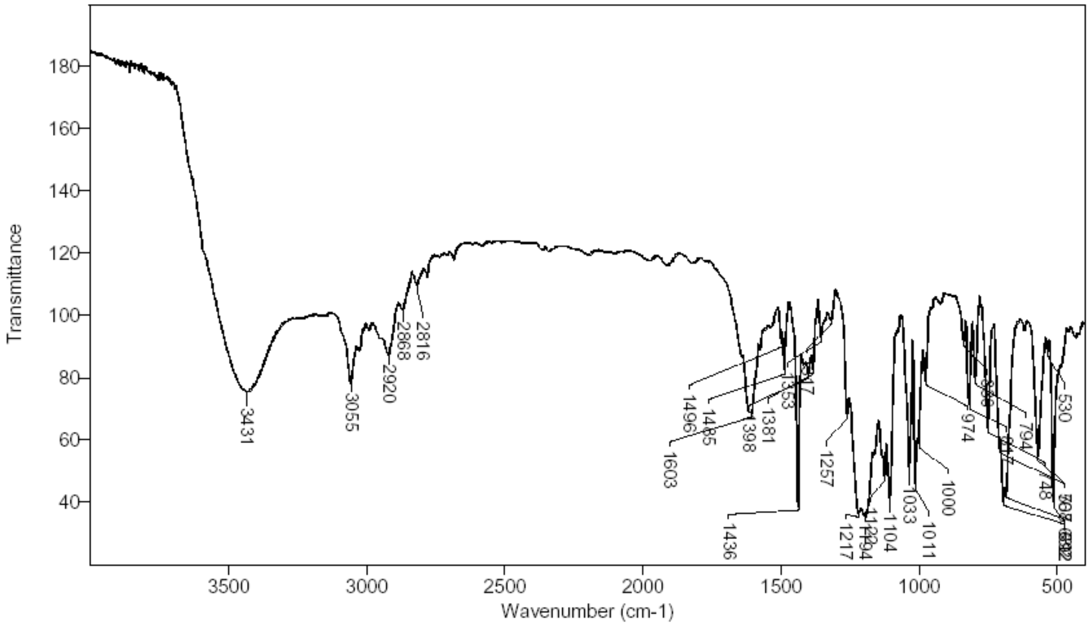


Figure 2.24: FTIR spectrum of $PdCl_2$(1,3-diphenylphosphinopropane)

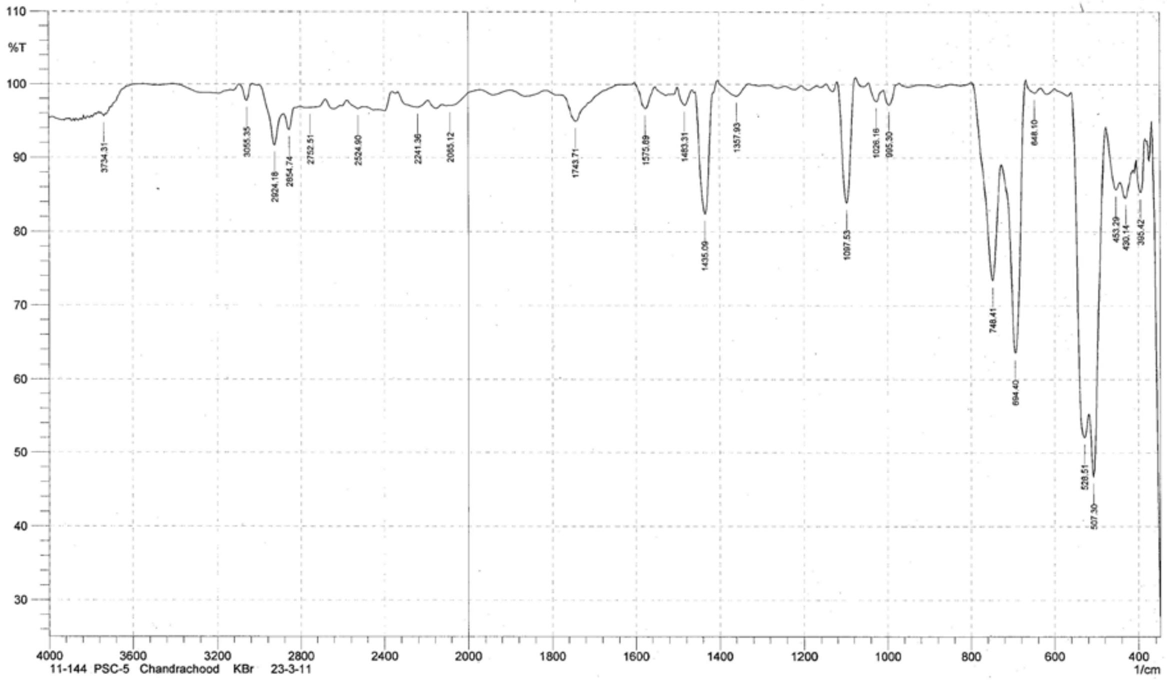


Figure 2.25: FTIR spectrum of $PdCl_2$(diphenyl-2-pyridylphosphine)

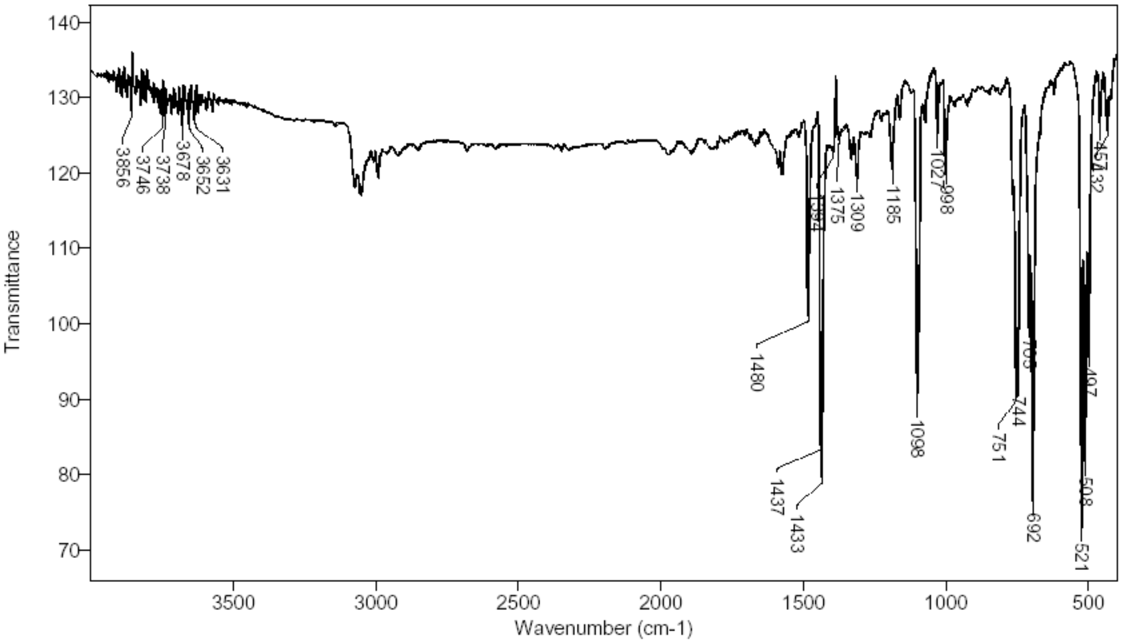


Figure 2.26: FTIR spectrum of $PdBr_2(PPh_3)_2$

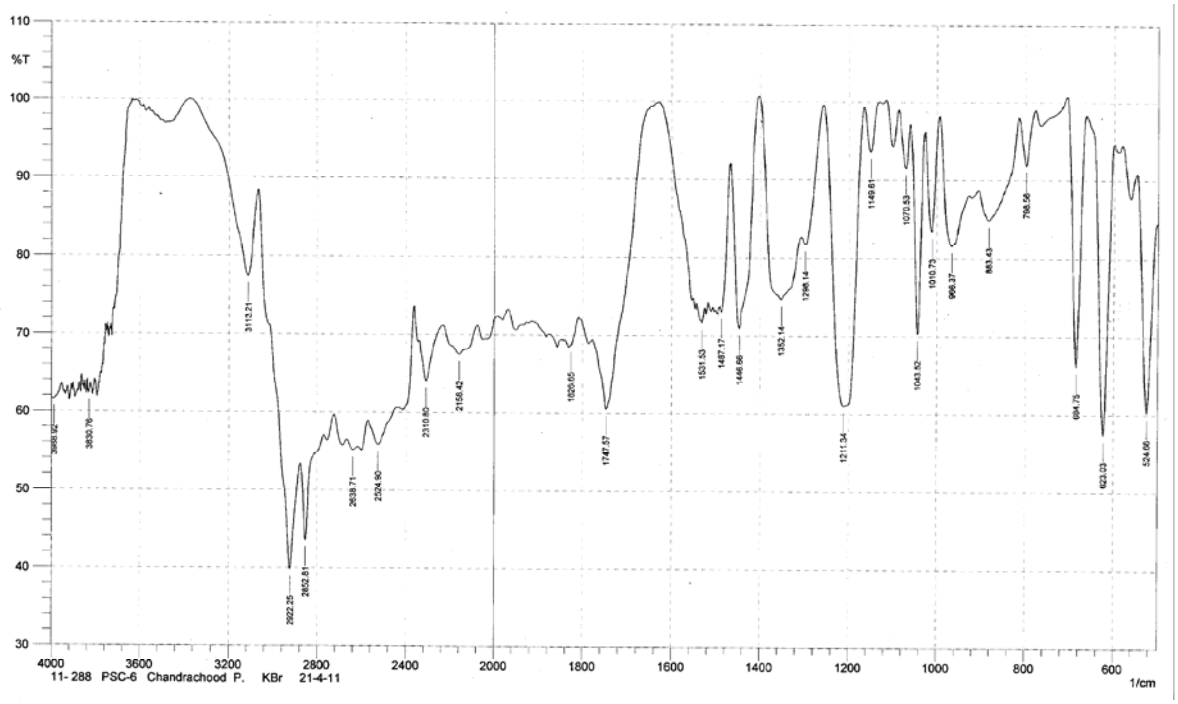


Figure 2.27: FTIR spectrum of $PdCl_2(TPPTS)_2$

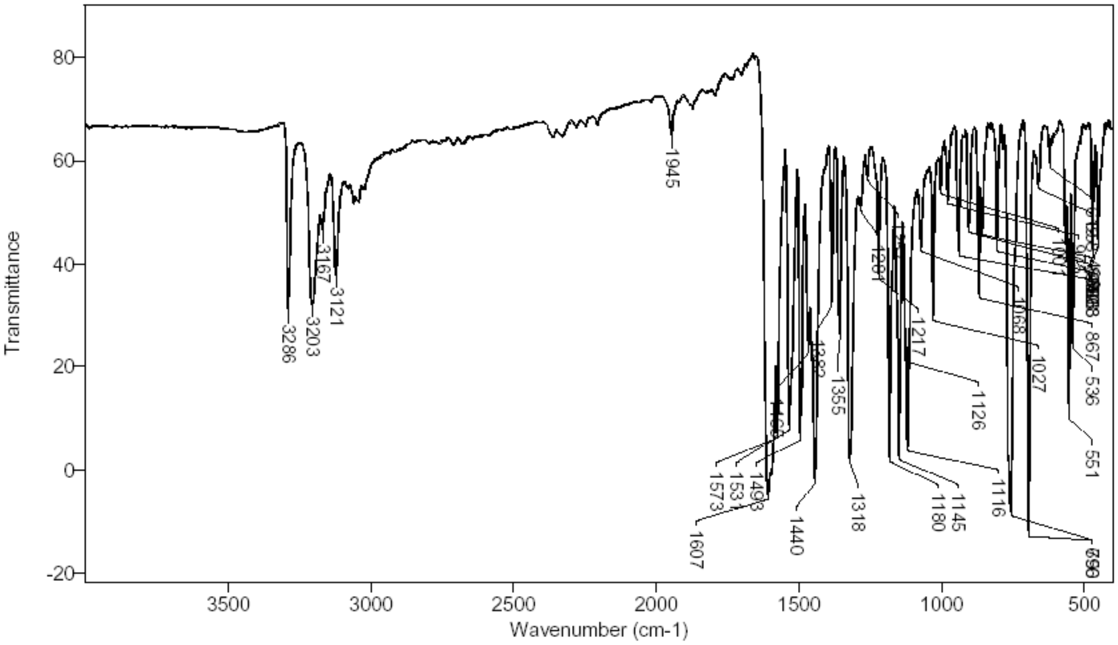


Figure 2.28: FTIR spectrum of $Pd(Salicylidineaniline)_2$

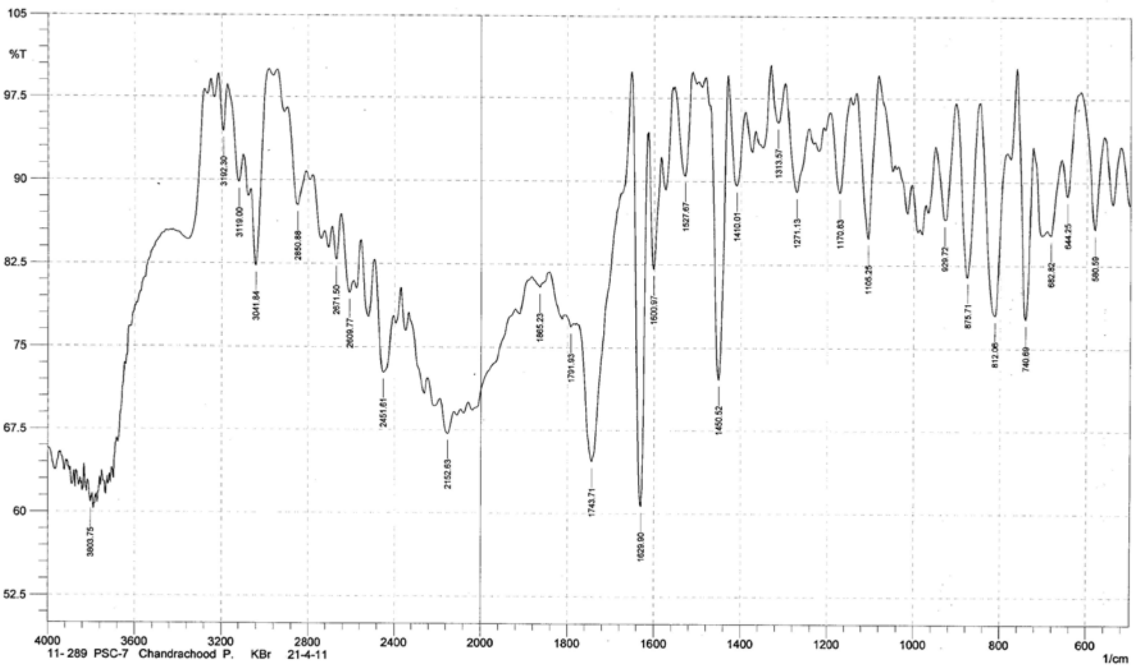


Figure 2.29: FTIR spectrum of Pd(bissalicylidineethylenediamine)$_2$

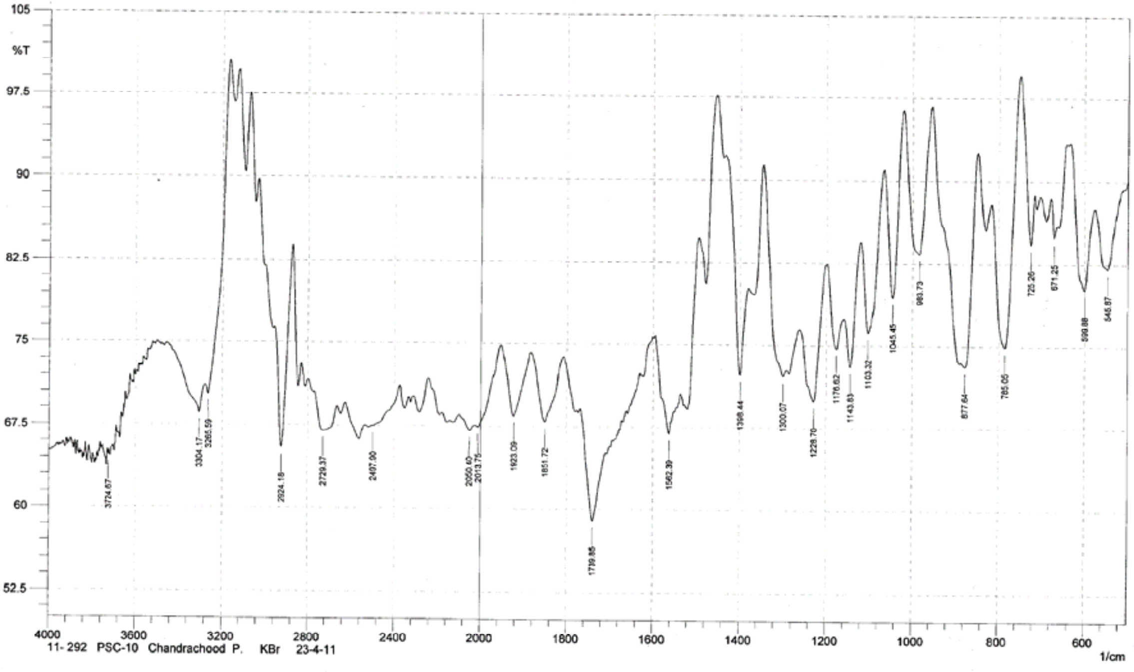


Figure 2.30: FTIR spectrum of Pd(bissalicylidinephenyldiamine)

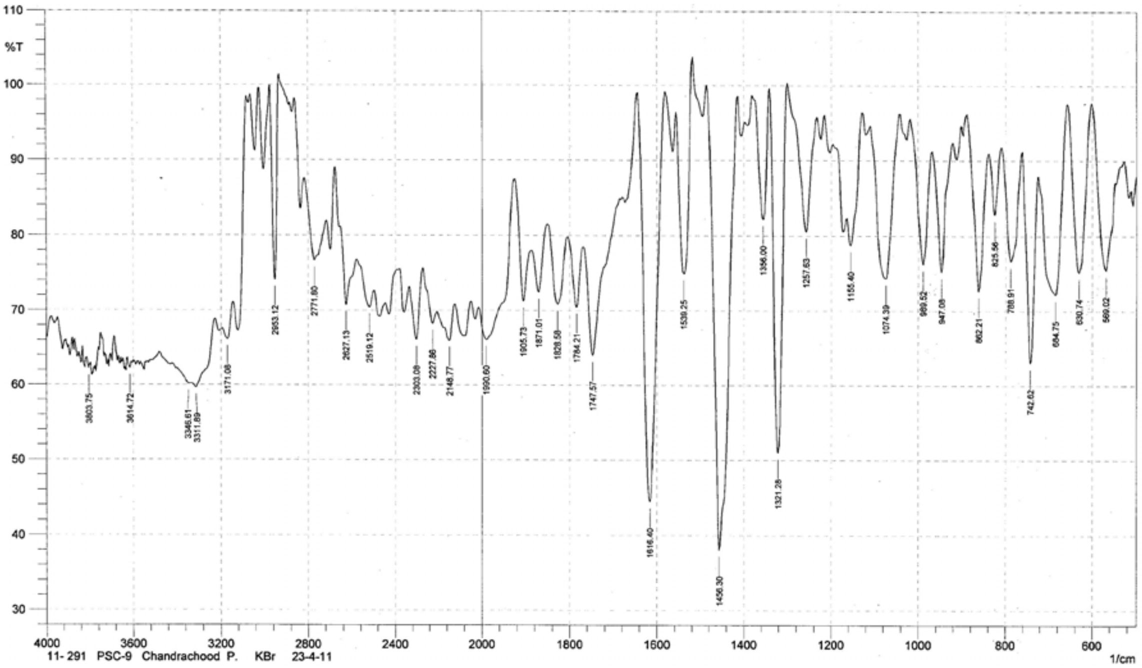


Figure 2.31: FTIR spectrum of Pd(salicylidinepropylamine)$_2$

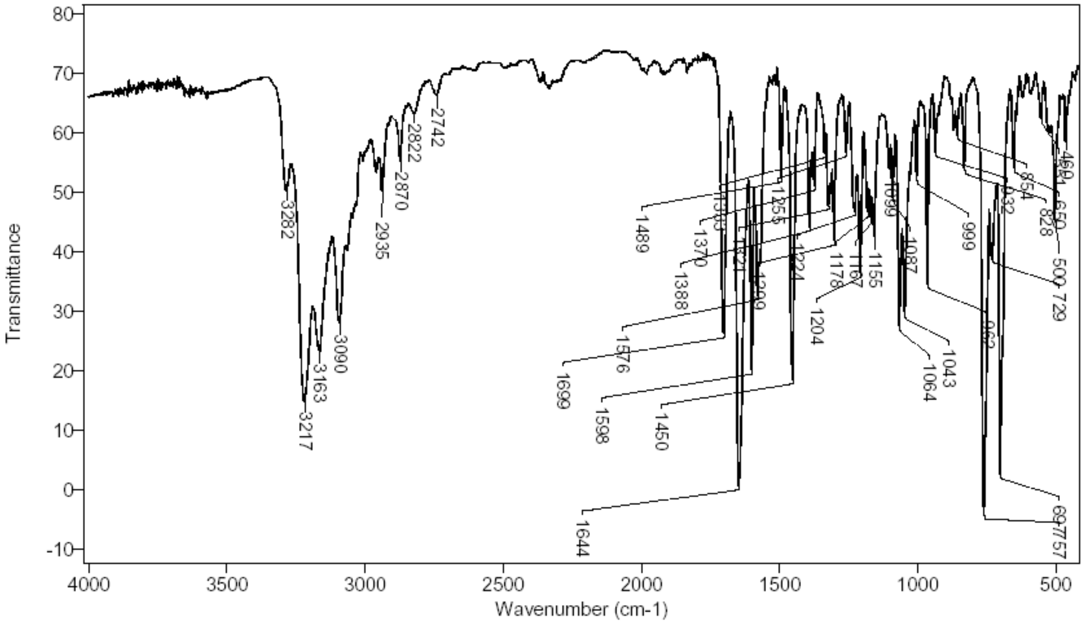


Figure 2.32: FTIR spectrum of Pd(bisbenzylidineethylenediamine)$_2$

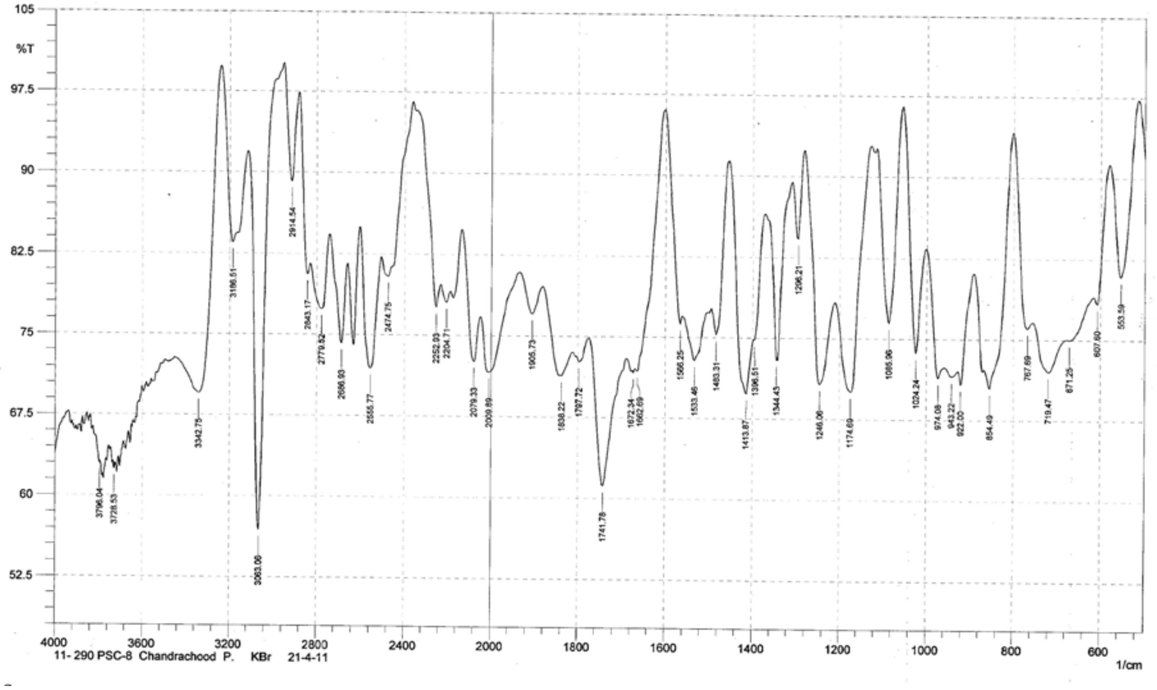


Figure 2.33: FTIR spectrum of Pd(bis(4-ethyl benzylidine)ethylenediamine))

Annexure II

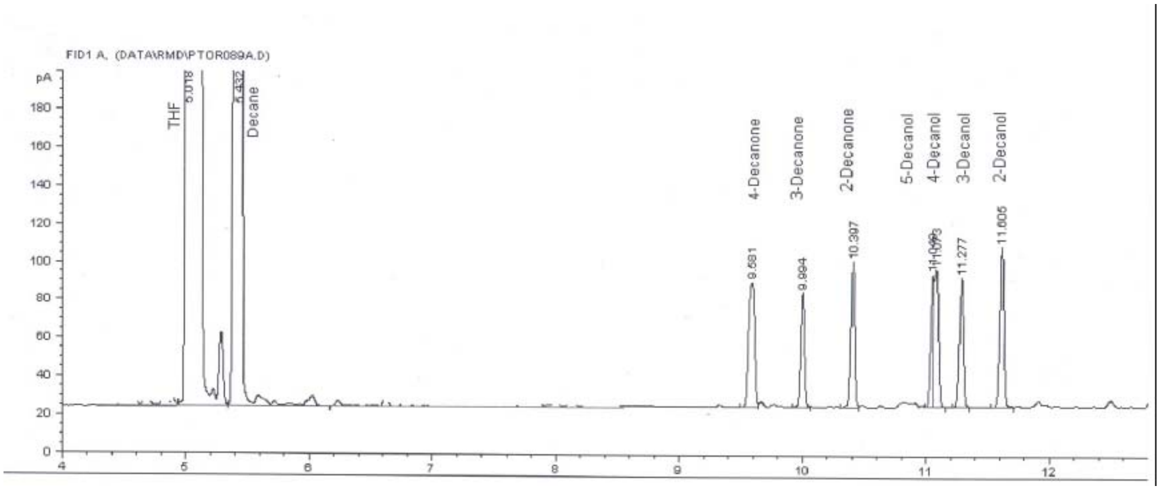
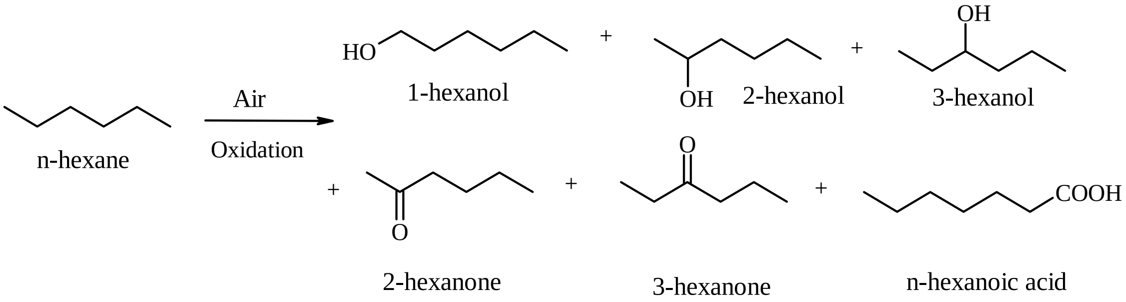


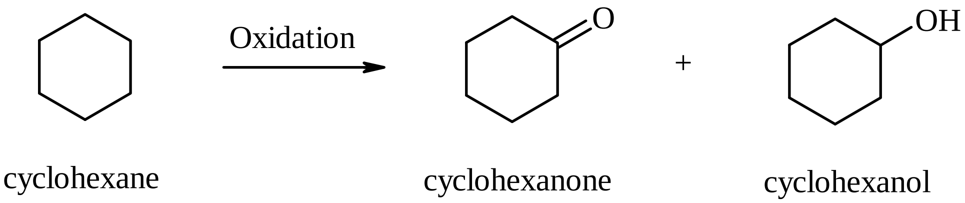
Figure 2.34: The GC chart of the decane oxidation

Annexure III

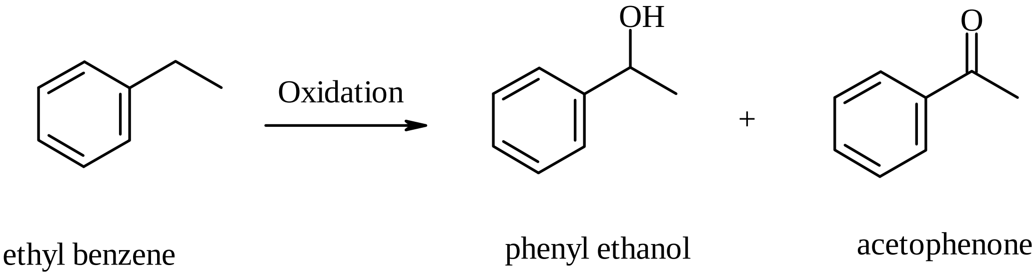
Possible products of n-hexane oxidation



Scheme 2.1: Possible oxidation products of n-hexane



Scheme 2.2: Possible oxidation products of cyclohexane



Scheme 2.3: Possible oxidation products of Ethyl benzene

Annexure-IV

GC mass spectra of the decane oxidation reaction

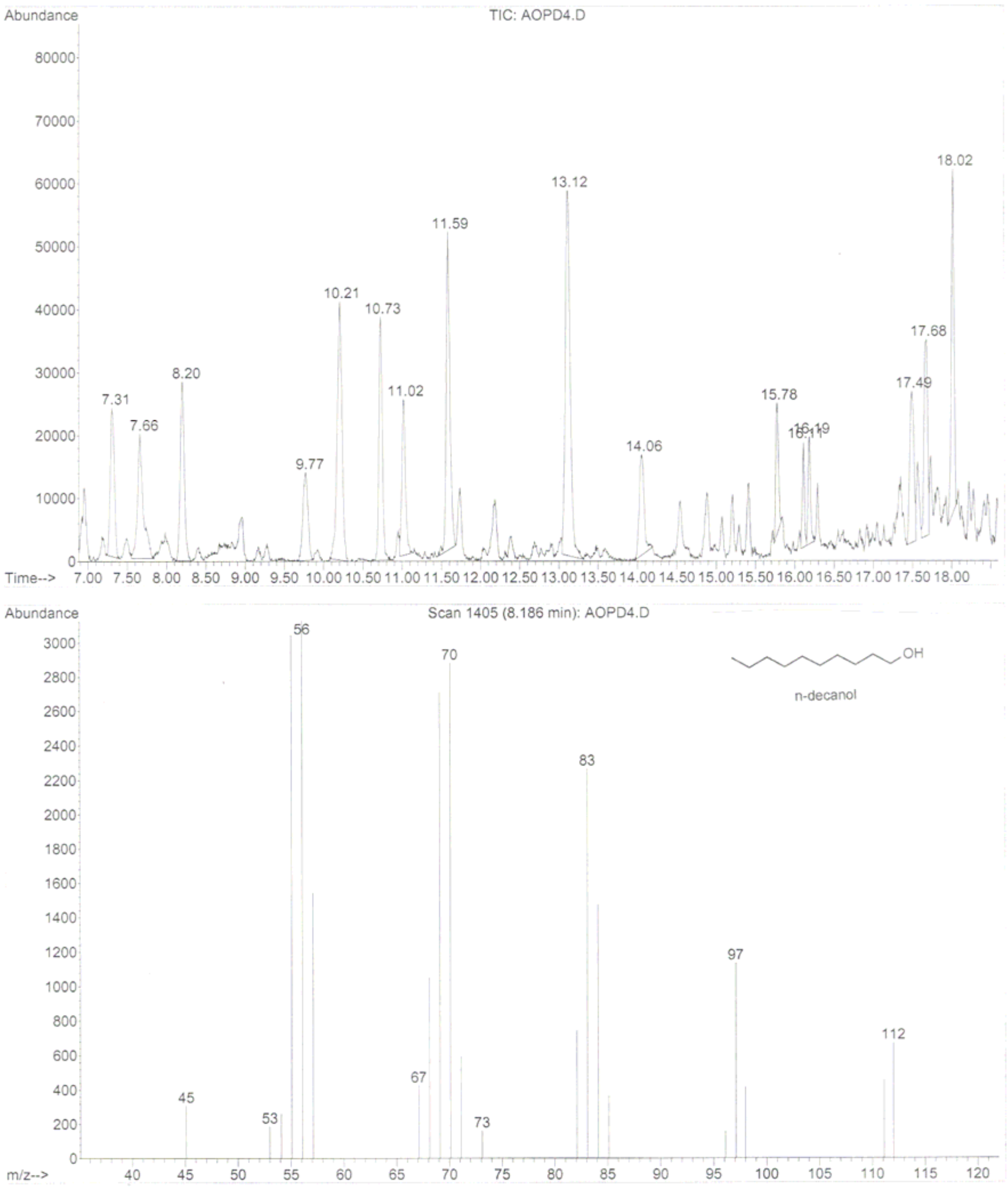


Figure 3.16: GC mass spectra of the n-decanol peak

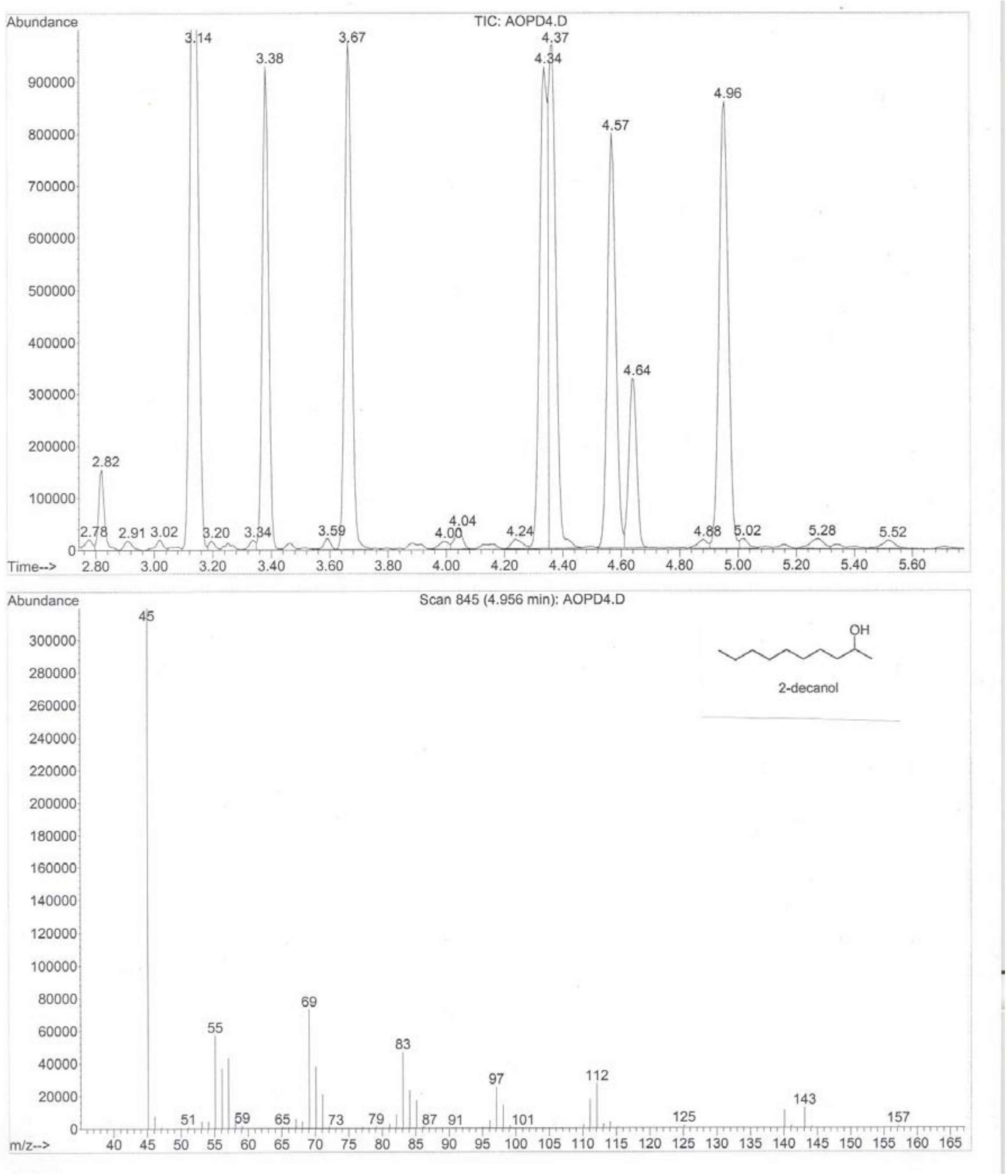


Figure 3.17: GC mass spectra of the 2-decanol peak

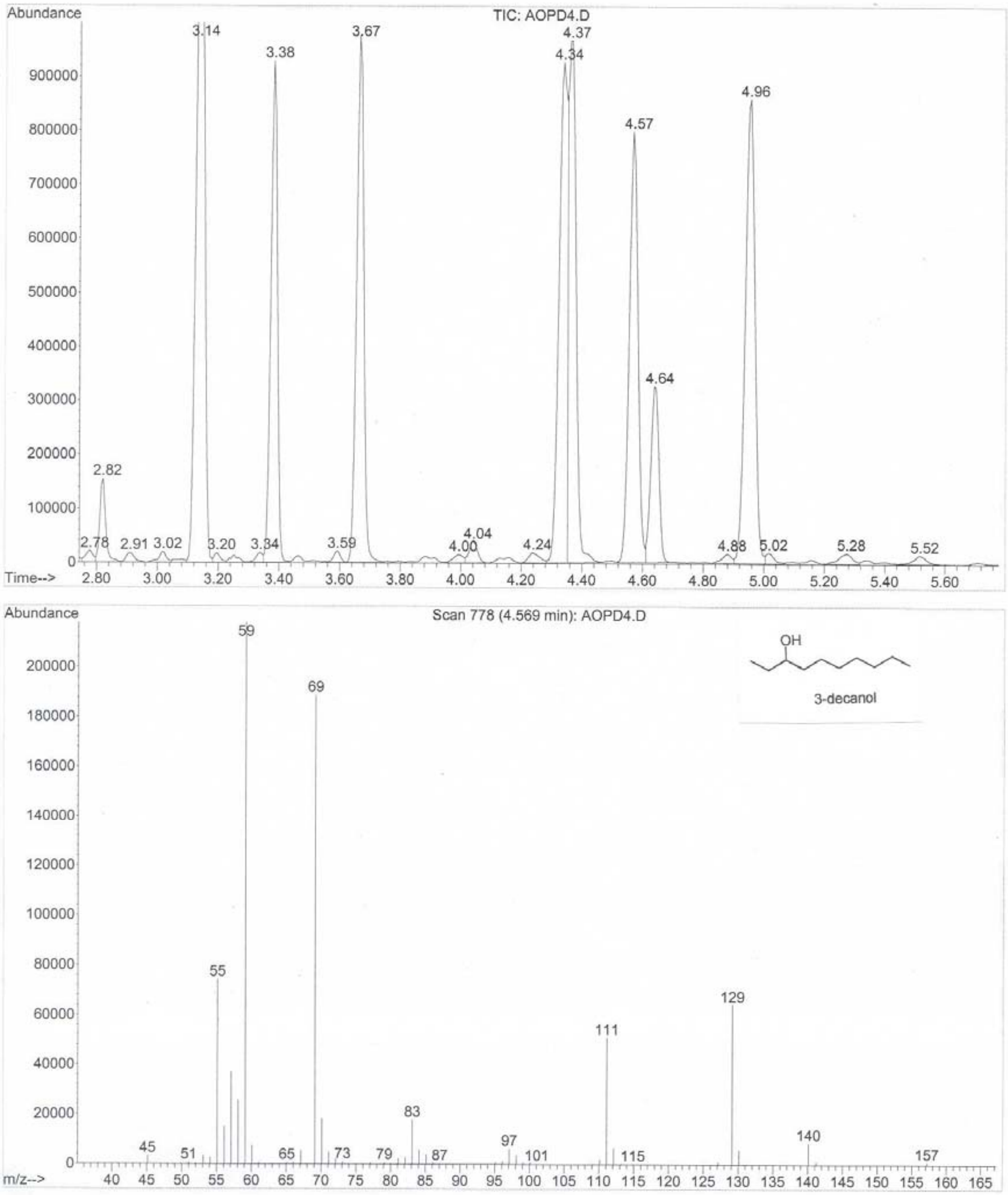


Figure 3.18: GC mass spectra of the 3-decanol peak

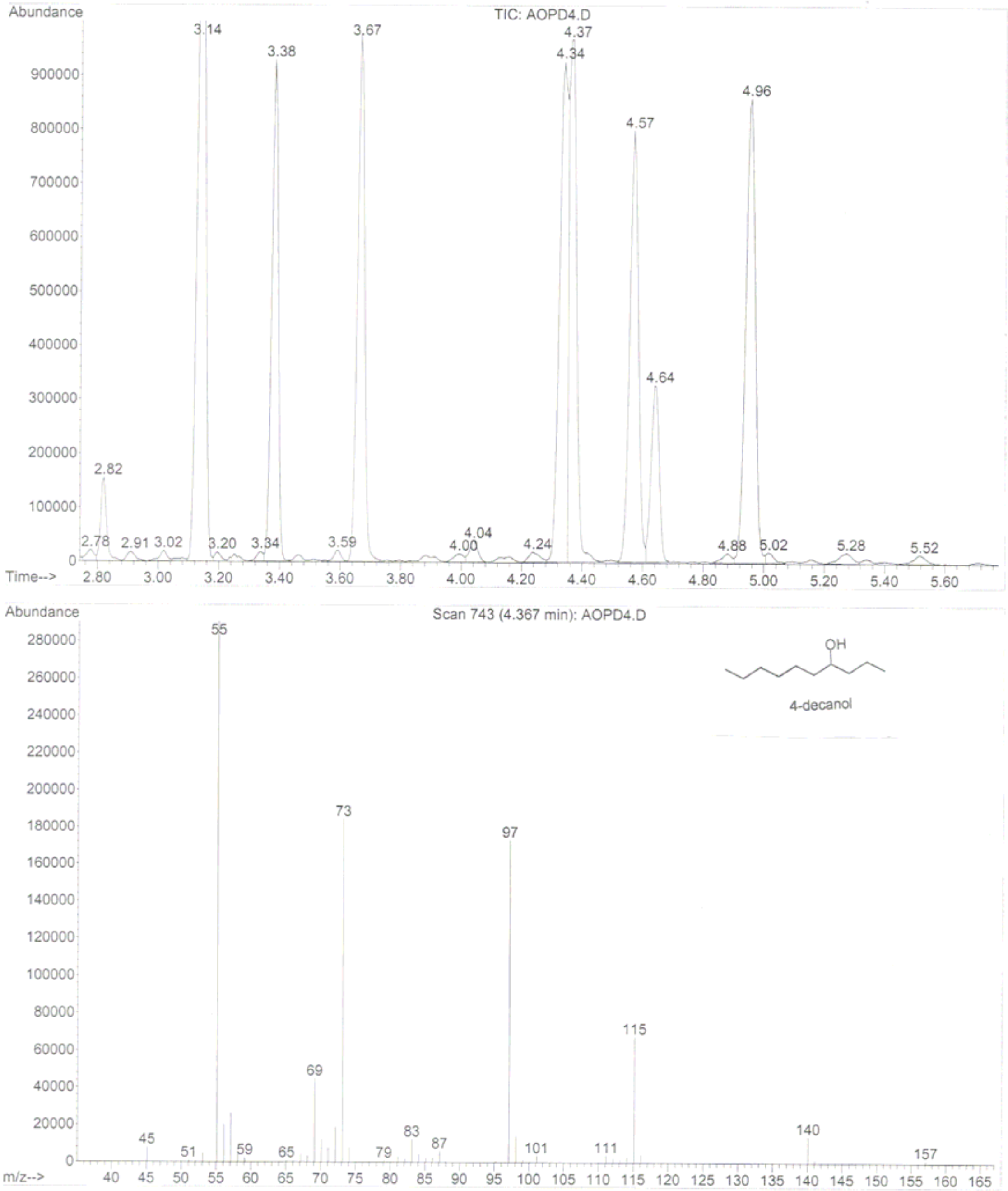


Figure 3.19: GC mass spectra of the 4-decanol peak

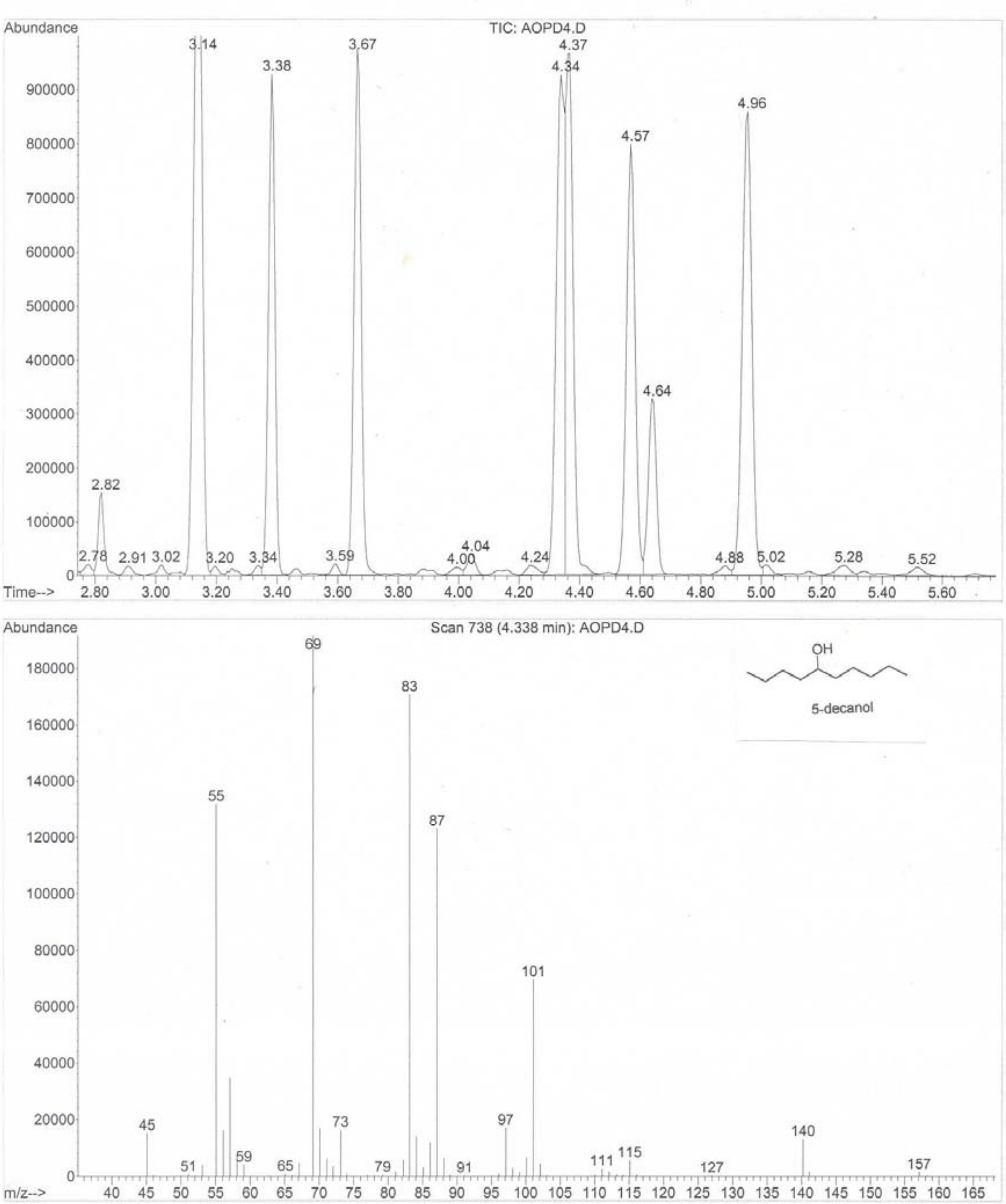


Figure 3.20: GC mass spectra of the 5-decanol peak

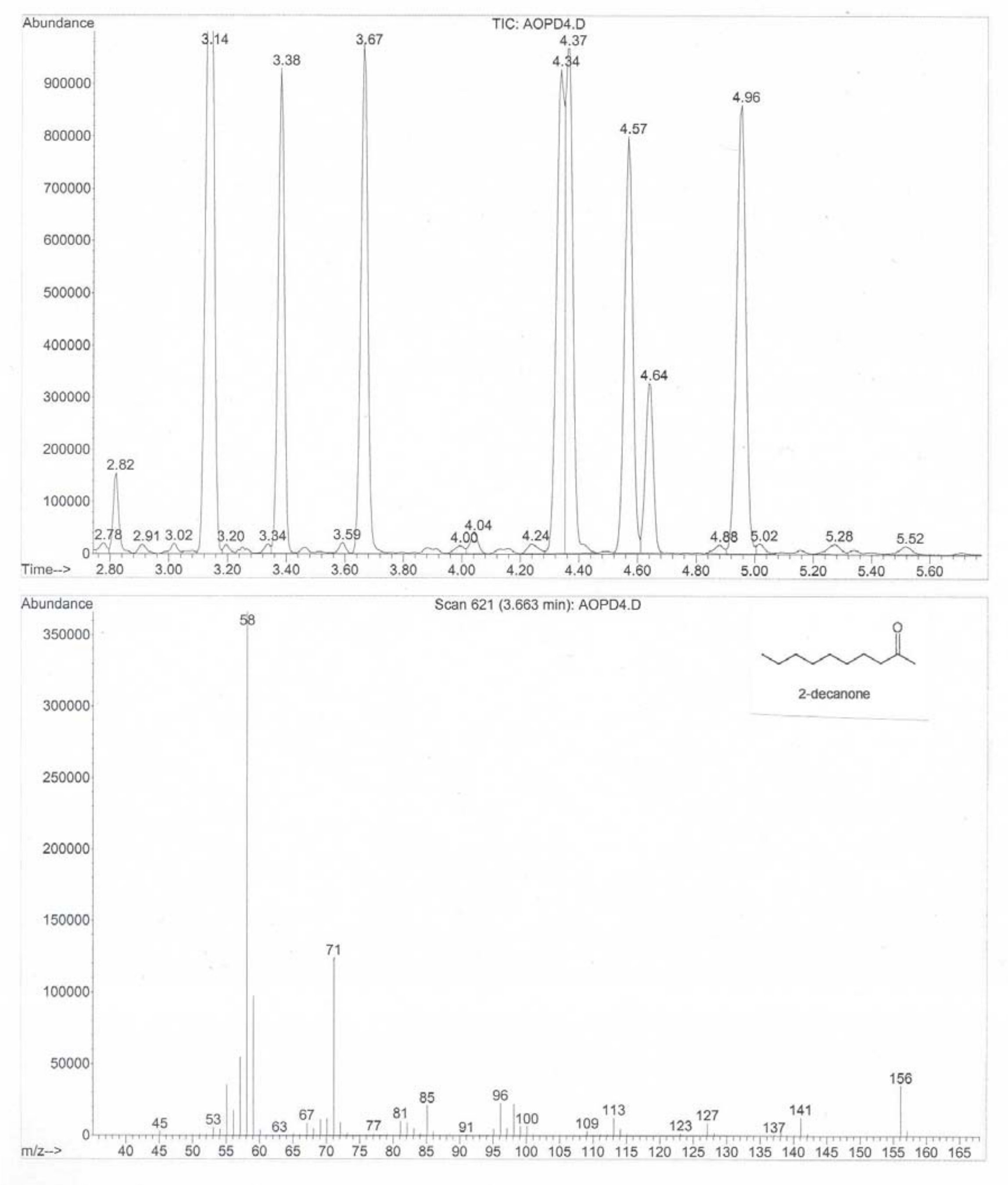


Figure 3.21: GC mass spectra of the 2-decanone peak

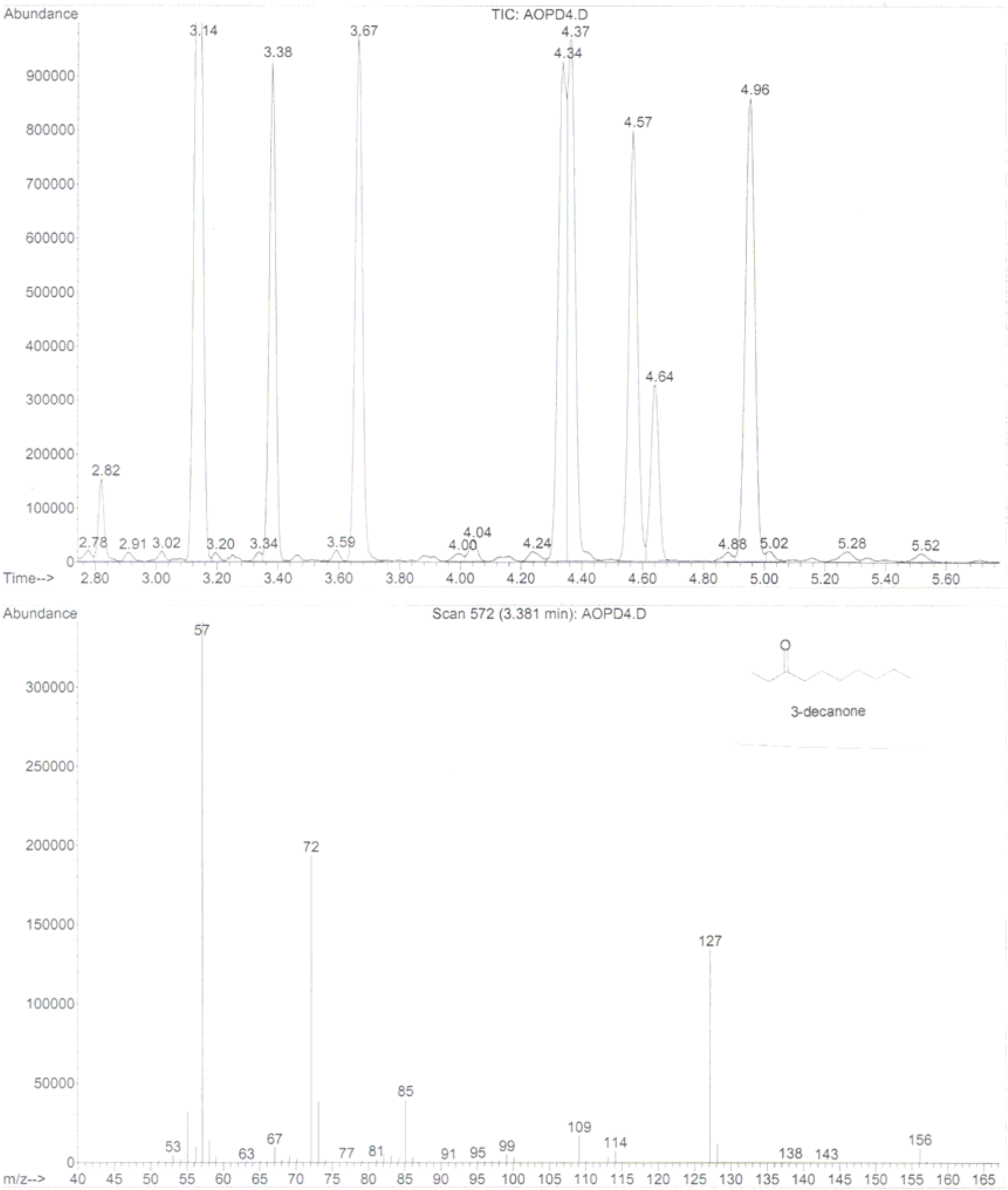


Figure 3.22: GC mass spectra of the 3-decanone peak

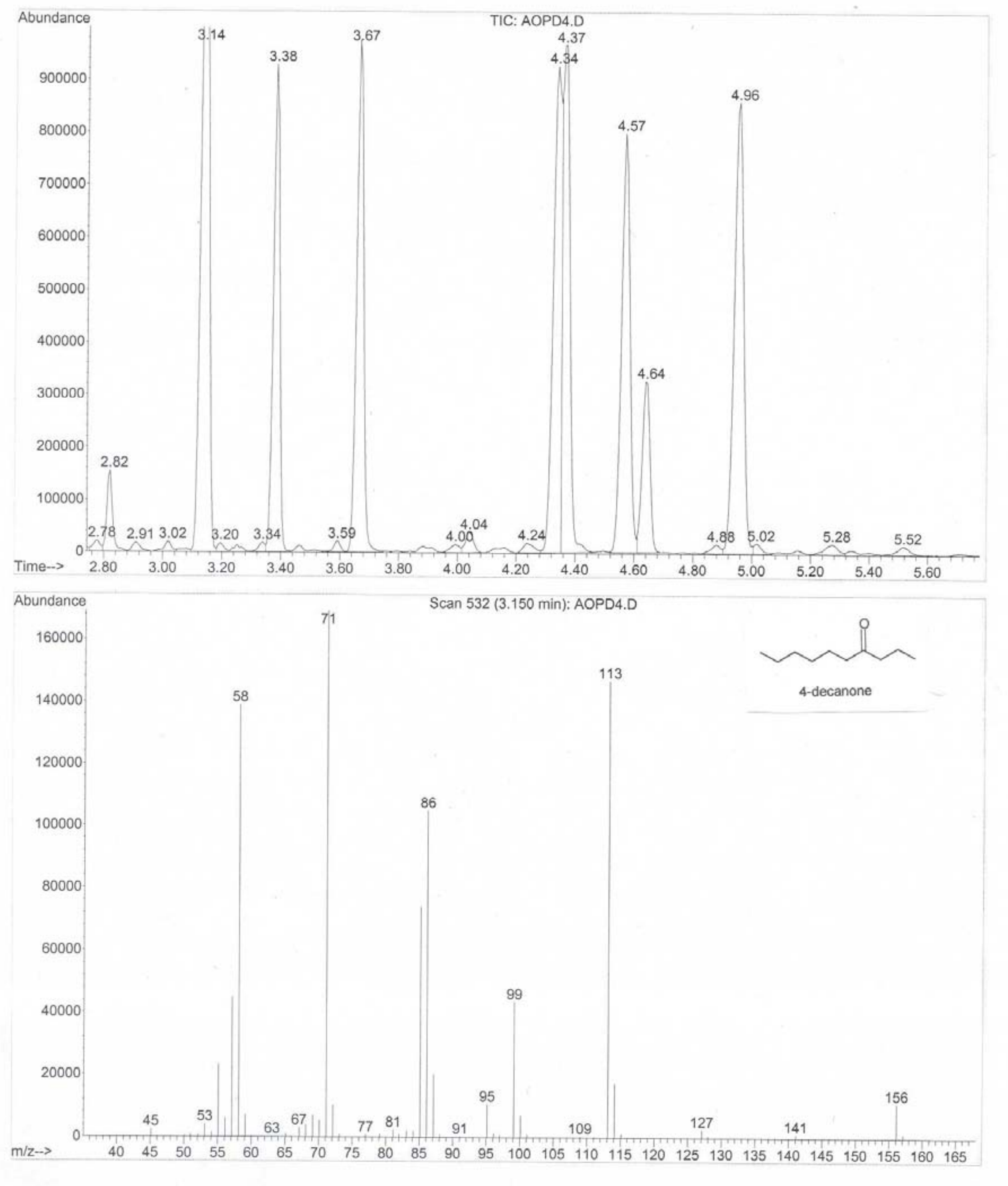


Figure 3.23: GC mass spectra of the 4-decanone peak

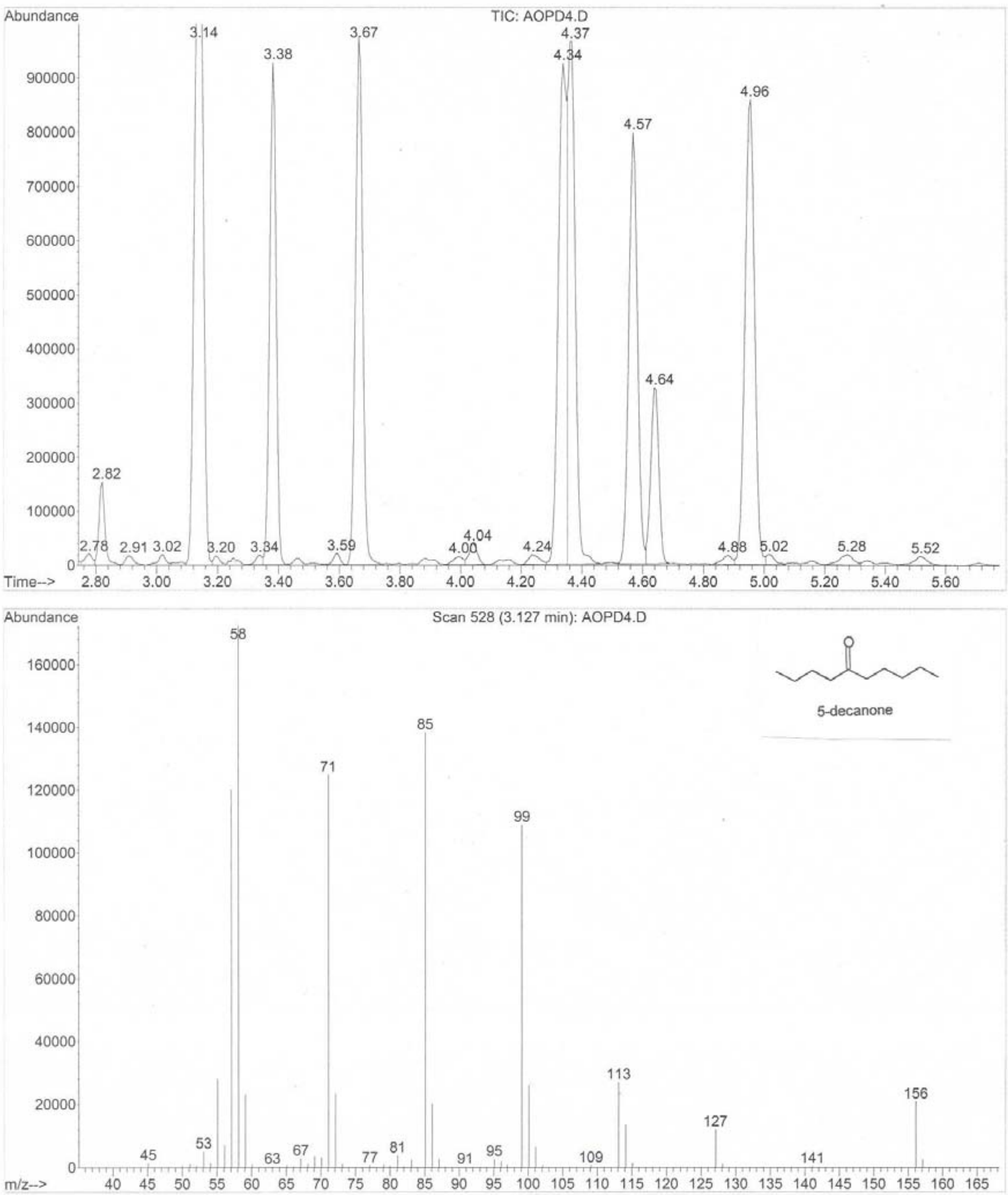


Figure 3.24: GC mass spectra of the 5-decanone peak

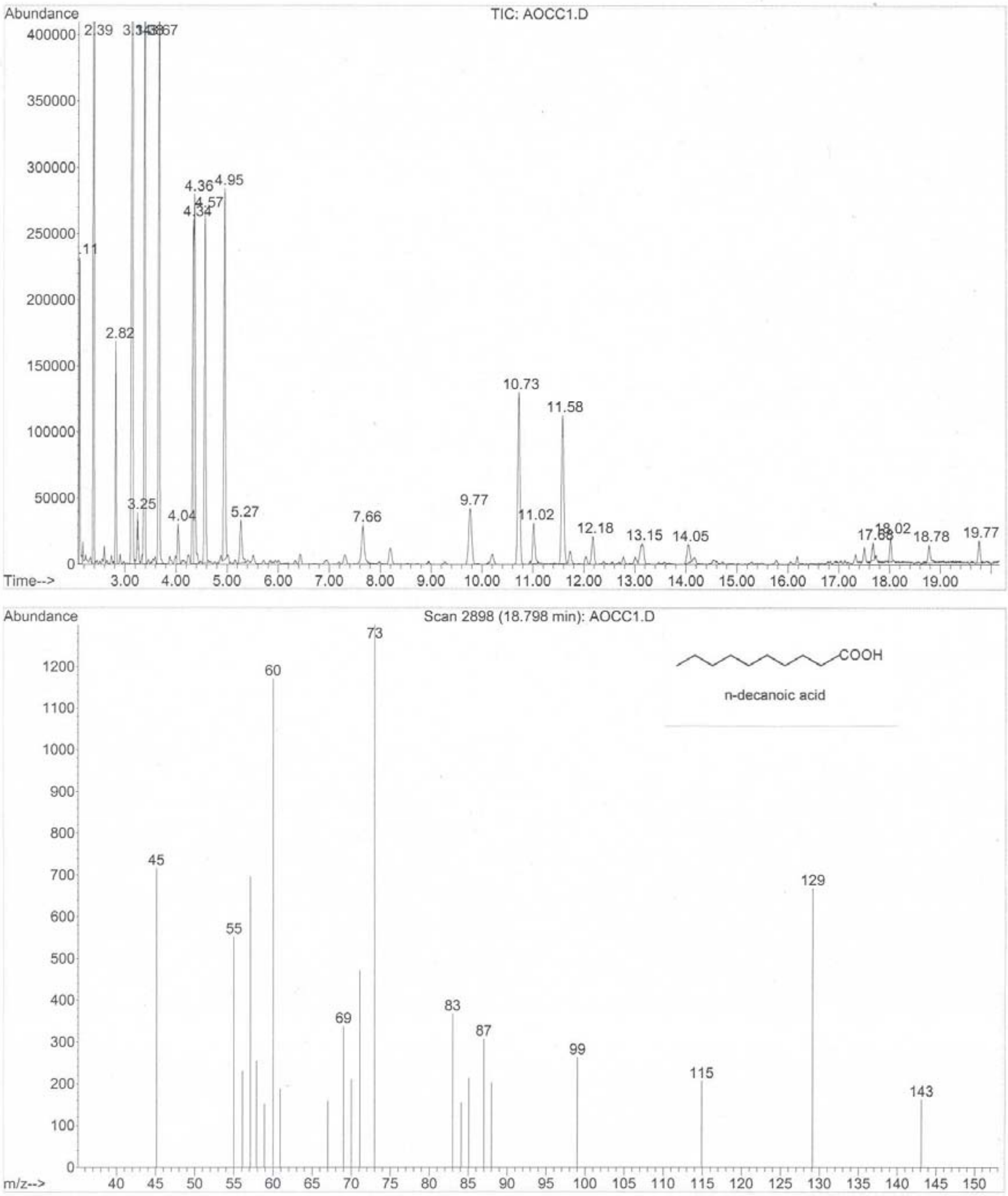


Figure 3.25: GC mass spectra of the n-decanoic acid peak

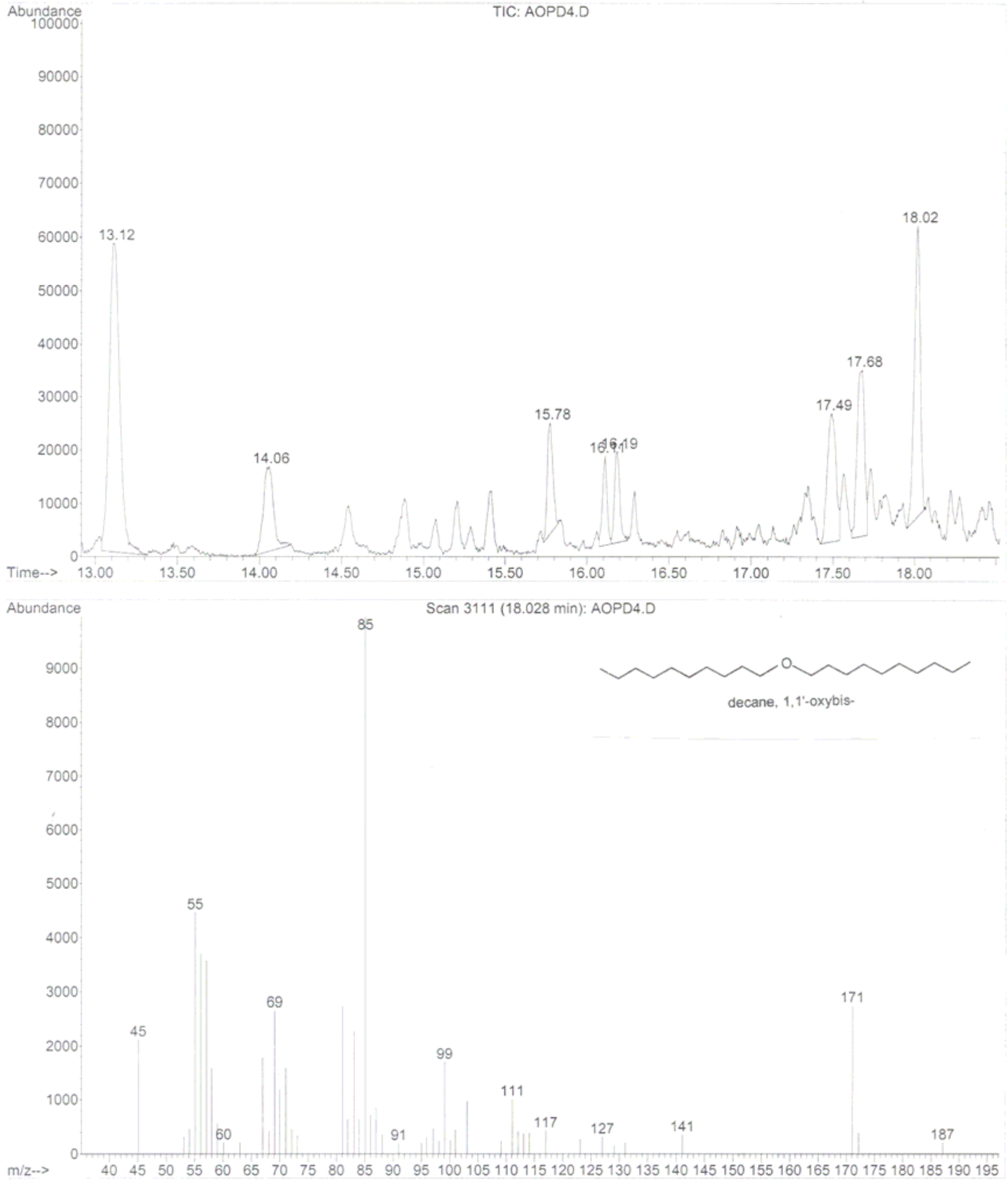


Figure 3.26: GC mass spectra of the decane, 1,1’-oxybis peak

List of Patent / Publication

Granted patent

1. A process for the oxidation of alkanes

   R.M.Deshpande, **M.M.Diwakar**, and R.V. Chaudhari

   US 7084307, 1 August 2006

Manuscript under preparation

1. Palladiun complex catalysts catalyzed aerobic oxidation of linear alkanes to secondary alcohols and ketones

   Makarand M. Diwakar, Raj M. Deshpande, Shubhangi B. Umbarkar and R. V. Chaudhari
2. Supported ossified Palladiun complex catalysts catalyzed aerobic oxidation of alkanes to secondary alcohols and ketones

   Makarand M. Diwakar, Raj M. Deshpande, and R. V. Chaudhari