Syntheses of Monometallic and Bimetallic PD(II) Catalysts Supported on Polymer Surface and Their Applications in Organic Syntheses

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SYNTHESES OF MONOMETALLIC AND BIMETALLIC PD(II) CATALYSTS
SUPPORTED ON POLYMER SURFACE
AND THEIR APPLICATIONS IN ORGANIC SYNTHESES

A THESIS SUBMITTED TO
THE FACULTY OF THE GRADUATE SCHOOL
IN CANDIDACY FOR THE DEGREE OF
MASTER OF SCIENCE
DEPARTMENT OF CHEMISTRY

BY
QIN JIAN YU

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TO MY PARENTS AND WIFE
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ABSTRACT

The first part of this project involves the synthesis and elucidation of heterogeneous mono- and bi-metallic Pd(II) catalysts on an aromatic polymer film coated on Celite. In the polyphenylene polymers used in the present studies, FT-IR and IR studies confirmed that the potential modification site, a methyl ester group was not reacted during polymerization and curing process. After chemical modification, a new set of infrared peaks characteristic of $\beta$-diketone ($d$, 1697.5 cm$^{-1}$) and $\beta$-triketone ($t$, 1699.4 cm$^{-1}$) replaced the absorption of the methyl ester group (1720 cm$^{-1}$). Due to coordination with Pd(II) ions, the $\beta$-diketone and $\beta$-triketone absorptions shifted down about 44.4 to 46.3 cm$^{-1}$ as compared to their original wavenumbers before Pd(II) uptake. As evidenced by the palladium precipitate, the heterogeneous bi-Pd(II) catalyst was more stable than the mono-Pd(II) catalyst because of the cooperative action between two Pd(II)'s in the bi-metallic species.

The second part of this project involved catalytic organic syntheses by mono- and bi-metallic Pd(II) catalysts. The results obtained from the mono- and bi-Pd(II) catalysts were compared to see if the bi-metallic catalyst could catalyze reactions that the mono-metallic partner cannot. Thus useful novel organic syntheses would be developed. Olefin oxidation by mono- and bi-Pd(II) catalysts was studied in several solvents. In the low
dielectric constant acetic acid solvent, the mechanism of the mono-Pd(II) catalysis was the usual Wacker-type oxidation. Only unsaturated products, such as vinyl, isopropenyl, allyl, and cyclohexenyl acetate, were produced. For the bi-Pd(II) catalysis in acetic acid, new products were formed because of the cooperative action between two palladiums. Since Pd(I)-Pd(I) dimers were good leaving groups, this route gave saturated products, such as ethylene glycol diacetate, ethylene glycol monoacetate, cis-1,2-cyclohexyl diacetate and trans-1,2-cyclohexyl diacetate. This mechanism competes with the β-elimination of the oxypalladation adduct to give the unsaturated esters. The final ratio of the saturated esters to unsaturated esters from olefin oxidation is determined by the competition of those two reaction pathways.

In high dielectric constant solvents, such as methanol and water, the bimetallic catalyst does not give 1,2 disubstituted products. The same product, acetaldehyde dimethyl acetal, was formed for both mono- and bi-metallic Pd(II) oxidations of ethene. In water, mono-Pd(II) is readily decomposed so it only gave 4-pentene-1-ol product while bi-Pd(II) produced both ketones and aldehydes.

In the presence of cupric chloride, the mechanism most consistent with Pd(II) chemistry is oxypalladation followed by the reaction of the oxypalladation adduct with cupric chloride to produce saturated esters. Thus the bimetallic catalyst gives the same results as the monometallic catalyst. In water solution, using cupric chloride as re-oxidant, 2-chloro-1-propanol, 1-chloro-2-propanol and acetol were obtained from propylene
oxidation catalyzed by both mono- and bi-metallic-Pd(II) catalysts. In the presence of lithium chloride, vinyl acetate, 2-chloro-ethyl acetate and ethylene glycol diacetate were formed from the ethylene oxidation catalyzed by the mono-Pd(II) catalyst.

The stereochemistry of bi-Pd(II) species was also investigated using the cyclohexene oxidation reaction. The ratio of cis-1,2-cyclohexan-diacetate to trans-1,2-cyclohexan-diacetate was 14 to 1.

The overall rate constants of the ethylene and propylene oxidation catalyzed by the polymer supported mono-Pd(II) catalyst were 0.0194 M$^{-1}$s$^{-1}$ and 0.0094 M$^{-1}$s$^{-1}$ at 25°C, respectively. The rate constant of the ethylene oxidation catalyzed by the supported mono-Pd(II) catalyst in acetic acid was about 10 times faster than that of the homogeneous Pd(II) catalyzed one in the similar reaction according to literature data. While the overall rate constants of the ethylene and propylene oxidation catalyzed by the polymer supported bi-Pd(II) catalyst were 0.0297 M$^{-1}$s$^{-1}$ and 0.0137 M$^{-1}$s$^{-1}$ at 25°C, respectively.

The initial rate of ethylene oxidation by 0.0535 g (0.0503 mmole) of the mono-Pd(II) catalyst in acetic acid with 1.0 M CuCl$_2$ and 2.0 M LiCl was 85.7 uMh$^{-1}$. The rate constants of the ethylene oxidation by the supported mono- and bi-Pd(II) catalysts in methanol were 0.00206 and 0.00391 M$^{-1}$s$^{-1}$ at 25°C, respectively. The values of reaction rate constants for the propylene oxidation by the supported mono- and bi-Pd(II) catalysts in water and THF mixture solvents were 0.0673 and 0.074 M$^{-1}$s$^{-1}$. 

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CHAPTER I
INTRODUCTION

I.1. Catalysis-General

I.1.1. The Importance of Catalysis

A catalyst is a substance that can selectively accelerate the reaction rate without itself being consumed during the process. Since the discovery of the first large-scale catalytic technology, the synthesis of ammonia in Germany in 1913,\textsuperscript{1,2} catalysis has made great studies.\textsuperscript{3} Presently, catalysis plays a vital role, not only in modern chemical industry, but also in energy production,\textsuperscript{4-8} environmental protection\textsuperscript{9,10} and pharmaceuticals.\textsuperscript{11-13}

Largely because of the commercial importance of catalysis, the field has received considerable attention. However, until three decades ago, most catalysts were developed by empiricism. Because of innovations in instrumentation and technology,\textsuperscript{14} including high resolution NMR, FT-IR, SEM, and \textit{in situ} characterization techniques of reaction intermediates, catalytic mechanisms are now much better understood. It has been possible to understand catalyst composition, structure, and performance on the molecular level.\textsuperscript{15,16} All these techniques are moving catalyst synthesis into the age of molecular design.\textsuperscript{17-20}
I.1.2. *Two Basic Kinds of Catalysts*

There are two basic modes of catalysts, homogeneous and heterogeneous. Homogeneous catalysts exist in the same phase as reactants and products while heterogeneous ones do not. There are several examples of homogeneous catalytic processes in industry. These include Wacker-type reactions, asymmetric hydrogenations, enantioselective reactions, and new polymerization processes. However, use of homogeneous catalysis is limited in industry because the reaction equipment is complicated and catalyst recovery is often difficult. However these homogeneous reactions are more easily studied than heterogeneous ones. Therefore, one of the most important contributions of homogeneous catalysis is to elucidate the elementary steps in catalytic processes on the molecular level. With a knowledge of catalytic mechanisms, catalysts can be specifically designed for industrial catalytic processes and laboratory organic syntheses.

In heterogeneous catalysis, the catalytic active site is located at a phase boundary and interfacial phenomena now becomes important. The fact that a two-phase system is involved complicates the reaction mechanism, but commercial heterogeneous catalysts are conveniently prepared, transported, and packed in reactors. A principal advantage is the easy of recovery of the catalyst. For these reasons, the majority of industrial catalytic processes are heterogeneous.
I.1.3. **Organometallic Complexes**

Transition metal organometallic complexes, are the actual catalysts in many catalytic reactions. Notable advancements in the knowledge of catalytic mechanisms by organometallics have made in the last three decades.\(^{34,35}\) For example, elementary steps such as oxidation-addition or its reverse, insertion reaction or its reverse, have been defined as important steps; also a more complete definition of coordination structures between central metal and its organic ligands has been achieved. Most catalyzed processes consist of one or a series of these elementary steps which can often be studied in isolation in organometallic chemistry. In addition to the theoretical importance, organometallic complexes themselves are often used as practical catalysts, especially in asymmetric organic synthesis.\(^{24,36-38}\) These examples demonstrate the power of organometallics in both catalytic system design and practical applications.

I.2. **Catalysis by Palladium Complexes**

The sub-field of palladium(II) catalysis has received much more attention than most other metal-catalyzed reactions because of the commercial success of the Wacker process for directly converting ethylene to acetaldehyde in the early 1960's. Consequently, our knowledge of the palladium(II) catalytic reactions has grown more rapidly than that of other homogenous catalysis. Palladium catalysis has served as a model to define the features of contemporary metal-complex catalytic processes. Thus it is necessary to review palladium chemistry before we discuss Pd(II) catalysis.
I.2.1 **Properties of Palladium**

Palladium chemistry has been discussed by Hartley and Henry. Palladium is one of the Group VIII elements which have a $5d^{10}$ electron structure. Its oxidation states are Pd(0), Pd(I), Pd(II), and Pd(IV). The Pd(IV) oxidation state is not related to this project. The following discussion will concentrate on the remaining oxidation states of palladium.

The properties of atomic Pd(0) in complexes are quite different from those of the bulk metal. The first Pd(0) complexes with phosphines and arsines were found by Malatesta and Angoletta in 1957. Presently Pd(0) complexes can be prepared by several procedures. Transition metal catalysis usually involves cycling of the metal catalyst between two oxidation states. Since Pd(II) is the most common oxidation state of palladium and since palladium in catalysis tends to react in two-electron steps, the zero oxidation state is very important in catalytic chemistry. Certain reactions would not proceed unless the Pd(0) state could be stabilized and prevented from forming bulk metal. Complexing Pd(0) can be looked upon as a means of keeping the Pd(0) in a monomeric atomic reactive form.

The zero oxidation state occurs only when stabilized by certain types of ligands called $\pi$-acid ligands. These ligands will donate a pair of electrons to the transition metals, to form regular $\sigma$-bonds. For zero valent metals this would result in a considerable electron density on the metal which usually lead to instability. The $\pi$-acid ligands can also
accept electron density from the metal, which is called \( \pi \)-back bonding, to give stable zero valent compounds.

**Scheme I-1**

\[
\begin{array}{c}
\text{M} \\
\Rightarrow \\
\text{L}
\end{array}
\]

Carbon monoxide and unsaturated hydrocarbons are common \( \pi \)-acid ligands since they have empty \( \pi^* \) orbitals to form \( \pi \)-back bonds with the zero valent transition metal as demonstrated by the following orbital diagrams (\( X = O, C \)) in Scheme I-2.

**Scheme I-2**

Another important series of \( \pi \)-acid ligands in catalytic chemistry of the transition metals is the trivalent compounds of P, As and Sb. These compounds have empty \( d \)-orbitals of proper symmetry and energy to overlap with the filled metal \( d \)-orbitals.

Pd(0) is implicated in a number of palladium-catalyzed reactions. The states of Pd(PPh\(_3\))\(_4\) in solution were investigated by Tolman,\(^{47}\) and those of Pd(PMePh\(_2\))\(_4\), Pd(PEt\(_3\))\(_4\), Pd(PBu\(_3\))\(_4\) and Pd(PhCH\(_2\))\(_3\))\(_4\) by Musco.\(^{48}\)

Pd(I) is the least common oxidation state for palladium. Pd(I) is chemically labile since it has an unpaired electron in its \( 5d \) orbital. The Pd(I) oxidation state was first found by Gel'man and Meilakhin in 1942, as the carbonyl anion, [PdCl\(_2\)CO].\(^{49}\) Next the
binuclear complexes, $[\text{PdAl}_2\text{Cl}_7(\text{C}_6\text{H}_5)_2]_2$, $[\text{PdAlCl}_4(\text{C}_6\text{H}_5)_2]_2$, were synthesized and characterized.\textsuperscript{50,51} They all contain Pd(I)-Pd(I) bonds and no bridging ligands.\textsuperscript{52,53} Recent studies have indicated that both Pd(I)-Pd(I) bond and the bridging P atom exist in some stable palladium(I) dimers, such as $[\text{Pd}_2(\mu-\text{PBu}^1_2)(\text{PPh}_3)_2(\mu,\pi^2:\pi^2-\text{CS}_2)]X$ (X=BF$_4$ or CF$_3$SO$_3$) and $[\text{Pd}_2(m-\text{PBu}^1_2)(\text{PPh}_3)_3]X$.\textsuperscript{54} Goggin and coworkers have found the carbonyl-bridged structures in $[\text{Pd}_2\text{X}_4(\text{CO})_2]^2-$ and CO and X bridges alternately between a palladium(I) atoms in polymeric complex $[\text{Pd(I)X(CO)}]_n$ (X = Cl or Br).\textsuperscript{55,56} Pd(I) may be important in palladium catalysis since there is some evidence that the organopalladium intermediate may well initially decompose to give unstable univalent palladium species,\textsuperscript{57} especially when the Pd(I) intermediate can form binuclear species.

Pd(II) is the most common and stable oxidation state for palladium and also the most important in Pd catalytic chemistry. It is a soft metal in the Pearson soft acid and base theory.\textsuperscript{58} Thus Pd(II) will complex more strongly with polarizable soft ligands such as, phosphines, carbon monoxide, olefins, and acetylene. Much of the catalytic chemistry of Pd(II) is related to its ability to coordinate unsaturated organic molecules. Palladium(II) is a $d^8$ ion and prefers to form four-coordinate square planar complexes. As would be predicted from crystal field splitting diagrams,\textsuperscript{59} these complexes are diamagnetic. There are numerous methods regarding the preparation and characterization of Pd(II) complexes.\textsuperscript{60-71}
1.2.2. **Palladium Catalysis**\(^{34}\)

In analogy to other transition metals, Pd(II) catalysis involve one or both of the basic reactions of catalysis: (A) oxidation-addition or its reverse, reduction-elimination; (B) the insertion reaction or its reverse. The main features of those elementary steps have been used to explain the mechanism of various reactions catalyzed with palladium and other metals.\(^{72}\)

**Oxidative-Addition**

The main feature of oxidation-addition is oxidation of the metal at the same time as the coordination number is increased. Generally both of the oxidation and coordination numbers are increased by two, as shown by the Equation I-1:

\[
\text{LnM}^n + \text{XY} \rightarrow \text{LnM}^{n+2}(\text{X})(\text{Y}) \quad (\text{I - 1})
\]

Thus, at the same time as the oxidation number is increased, new bonds are formed to X and Y. The addendum, XY, can be either a symmetrical or an unsymmetrical molecule. Examples are H\(_2\), O\(_2\), SO\(_2\), C\(_2\)H\(_4\), CH\(_3\)I, Cl\(_2\). These reaction occurs mainly with \(d^8\) and \(d^{10}\) metal systems. Examples of \(d^8\) systems are Rh(I), and Ir(I), Pd(II) and Pt(II), while \(d^{10}\) systems include Ni(0), Pd(0) and Pt(0). This kind of the oxidation addition reaction gives stable adducts.\(^{73-75}\) The numerous cases of oxidation addition and its reverse reaction catalyzed by the palladium complexes have been discussed by Henry.\(^{34}\)
**Insertion Reaction**

The second basic process in catalysis is the insertion reaction. The reaction can be defined as the insertion of an unsaturated molecule between two bonded atoms of another molecule. Pd(II) catalysis includes 1,2-insertion of carbon-carbon multiple bonds of olefins and acetylene and 1,1-insertion of carbon monoxide. The well-studied insertion reactions involve oxymercuration, M-OH, and additions of M-H and M-C.

\[
\begin{align*}
LnM^nA + XY &\rightarrow LnM^nXY-A & LnM^nA + XY &\rightarrow LnM^nX_A \\
1,2\text{-Insertion} & & 1,1\text{-Insertion}
\end{align*}
\]

Organic oxidation is a fundamental process in both organometallic chemistry and industry. Much of palladium catalytic chemistry is based on the fact that Pd(II) is a good oxidant and the ease of the palladium(II) $\leftrightarrow$ palladium(0) redox interconversion makes the reactions catalytic. The following sections will focus on the palladium-catalyzed olefin oxidations related to this thesis.

**1.2.3 Olefin Oxidation - Wacker Process**

The Wacker process for the oxidation of ethylene to acetaldehyde was discovered by Smidt and coworkers in the late fifties. Actually it is a combination of a series of known reactions.
Scheme I-3

\[
PdCl_4^{-2} + C_2H_4 + H_2O \rightarrow Pd^0 + CH_3CHO + HCl + Cl^-
\]

\[
Pd^0 + 2CuCl_2 + 2Cl^- \rightarrow 2CuCl + PdCl_4^{-2}
\]

\[
2CuCl + \frac{1}{2}O_2 + 2HCl \rightarrow 2CuCl_2 + H_2O
\]

\[
C_2H_4 + \frac{1}{2}O_2 \rightarrow CH_3CHO
\]

The in situ reoxidation of Pd(0) to Pd(II) by the Cu(II), which is rapidly regenerated by O₂, completes a catalytic cycle. Equation I-3 gives the rate expression for the Wacker process.  

\[
\frac{-d[C_2H_4]}{dt} = \frac{k [PdCl_4^{-2}][C_2H_4]}{[H^+][Cl^-]^2} \quad (I - 3)
\]

The mechanism of the Wacker process is complicated and considerable effort has been spent by many groups. There is no doubt the chloride squared inhibition results from the following two rapid equilibria where the value of $K_1$ has been measured by fast reaction techniques.

\[
PdCl_4^{-2} + C_2H_4 \overset{K_1}{\rightleftharpoons} PdCl_3(C_2H_4)^{-1} + Cl^{-1} \quad \frac{1}{[Cl^-]} \text{ term} \quad (I - 4a)
\]

\[
PdCl_3(C_2H_4)^{-1} + H_2O \overset{K_2}{\rightleftharpoons} PdCl_2(C_2H_4)(H_2O) + Cl^{-1} \quad \frac{1}{[Cl^-]} \text{ term} \quad (I - 4b)
\]

The proton inhibition is the term which causes controversy. Two reasonable possibilities are trans attack of water in an equilibrium step or an acid - base equilibrium
followed by cis attack of coordinated hydroxide in the rate determining step as shown in Scheme I-4 on the next page.

The original proposal of a cis mechanism is based on kinetic isotope effects. The value of $k_H/k_D$ is equal to 1.07. This result indicates hydroxpalladation is rate determining so equilibrium hydropalladation is unlikely. This would leave the cis hydroxide insertion from the coordination sphere of Pd(II) as the most likely mechanism.

However, very convincing stereochemical studies indicated that the Wacker process addition was actually trans. One example is the work of Bäckvare, Åkermark and coworkers. They ran the Wacker-type reaction with specifically deuterium labeled ethylene and determined that the stereochemistry of 2-chloroethanol at high chloride concentrations (>3 M) is only consistent with trans addition (Scheme I-5). Assuming that the intermediate leading acetaldehyde is the same one intercepted by CuCl$_2$ they suggested trans hydroxypalladation under Wacker reaction conditions.

The Cu(II) pathway can be explained by the concept of the metal species as a "leaving group". Certain metal ions interact with olefins in hydroxylic solvents to give oxymetallation adducts (equation I-5: $R = OH, OR', O_2CR'$) as shown below.

\[
M^{+n} + \text{C} = \text{C} + \text{HOR} \rightarrow \text{RO} - \text{C} - \text{C} - M^{+(n-1)} + \text{H}^+ \quad (I-5)
\]

The stability of the intermediate depends on the oxidizing power of the metal ion as well as its ability to leave with its electrons. In well-known case of Tl(III), the intermediates are very unstable because Tl(III) is vigorous oxidizing agent and Tl(I),
Scheme I-4

\[
\begin{align*}
\text{Cl} & \quad \text{Pd} \\
\text{Cl} & \quad \text{OH}_2 \\
+ & \quad \text{H}_2\text{O} \\
\text{K} & \quad \rightleftharpoons
\end{align*}
\]

\[
\begin{align*}
\text{Cl} & \quad \text{Pd} \\
\text{Cl} & \quad \text{OH}_2 \\
\text{Cl} & \quad \text{OH} \\
+ & \quad \text{H}_2\text{O} \\
\text{H}^+ & \quad \text{Slow}
\end{align*}
\]

Products
Scheme I-5

\[
\begin{align*}
\text{Scheme I-5} & \\
\text{[Diagram]} & \\
\end{align*}
\]
which is a stable species in aqueous solution, is a "good" leaving groups as shown in Equation I-6.

\[
\text{I-6} \quad (\text{CH}_3\text{CO}_2)_2\text{Tl} - \text{O}_2\text{CCH}_3 \quad \text{CH}_3\text{CO}_2 \quad \text{I-6} \quad (\text{CH}_2\text{O}_2\text{CCH}_3)_2 + \text{TlO}_2\text{CCH}_3
\]

On the other hand when the metal ion is Hg(II), the leaving group will be Hg(0) which would be a "poor" leaving group since monatomic zero valent metal species are unstable in hydroxylic solvents. Thus the Hg(II) oxymercurials are stable compounds even though Hg(II) is a fairly strong oxidizing agent. Their stability can be decreased by adding excess Hg(II) because the mercury can now leave as Hg(I)-Hg(I) dimers which are stable species.

In oxidations by Pd(II), decomposition of the oxypalladation adduct by a carbonium ion mechanism would give Pd(0) which is also an unstable species like Hg(0) and a "poor leaving group". Thus oxypalladation adducts would not decompose by carbonium ion mechanisms the way oxythallation adducts do. However, there is another type of oxidative decomposition available to the Pd(II) species which is not available to Hg(II). This decomposition is $\beta$-hydride elimination which will give the unsaturated
products. An example of ethylene oxidation by Pd(II) in aqueous solution is described in Equation I-7.\textsuperscript{92}

\[
\begin{align*}
\text{CH}_2\text{C}O_2\text{CCH}_3 & \quad \xrightarrow{\text{Pd}^{+2} \rightarrow \text{H}} \quad \text{CH}_2\text{CHO}_2\text{CCH}_3 + \text{HPd}^+ \quad \rightarrow \quad \text{H}^+ + \text{Pd}^0 \\
\end{align*}
\]

(Equation I-7)

Apparently the restriction on Pd(0) as leaving group can be removed by adding other redox species which can withdraw two electrons from the palladium in the transition state for decomposition so Pd(II) rather than Pd(0) is the leaving group. Thus in high concentrations of aqueous CuCl\textsubscript{2} solution, the CuCl\textsubscript{2} can interact with Pd(II) in the transition state removing two electrons from the Pd(II) and give the main 2-chloroethanol product from carbonium ion type decomposition. The decomposition of the oxypalladation adduct by a carbonium ion mechanism would gives saturated products. The scheme is shown in Equation I-8.

\[
\begin{align*}
\text{CuCl}_2 + \text{Cl}_3\text{PdCH}_2\text{CH}_2\text{OH}^- & \quad \rightarrow \quad \text{ClCu}-\text{Cl} \quad \text{Cl} \quad \text{Pd-CH}_2\text{CH}_2\text{OH} \\
\end{align*}
\]

(Equation I-8)

Now the assumption must be made that the same intermediate that decomposes to acetaldehyde is the one intercepted by CuCl\textsubscript{2}. This certainly seems like a reasonable
assumption since 2-chloroethanol is only formed at high concentrations of chloride (>3 M) and cupric chloride. The detailed stereochemical mechanism of Wacker-type reaction has been studied by Henry, using a series of olefins as probes. The hydroxypalladation under the Wacker conditions is apparently a \textit{cis} process at low [Cl\textsuperscript{-}] while it will be \textit{trans} at high [Cl\textsuperscript{-}].\textsuperscript{93} Thus the stereochemistry of hydroxypalladation at high and low [Cl\textsuperscript{-}] are different.

In the bimetallic Pd(II) catalyst system there is an opportunity for a similar electron transfer in the transition state for decomposition to give a Pd(I) dimer which is a stable species and thus a "good leaving group". More details will be discussed in I-3.

\textit{Effects of Substrate in Wacker-Type Oxidation}

The Wacker-type chemistry is not limited to ethylene. Many olefins are either oxidized to various products or else react to give other products in non-oxidative reactions.\textsuperscript{94, 95} Unsubstituted \(\alpha\)-olefins can form ketones resulting from Markovnikov hydroxypalladion followed by decomposition. The reaction conditions will also affect the rate and product distribution.

\textit{Effects of Various Reoxidants in Wacker-Type Oxidation}

In the catalytic cycle, rapid Pd(0) reoxidation occurs only in the \textit{in situ} system. The reason that Pd(0) is reoxidized rapidly to Pd(II) in the \textit{in situ} system is, of course, the fact that atomic Pd(0) is being reoxidized before it has a chance to polymerize into solid palladium metal which is much less reactive. If the Pd(0) is allowed to precipitate and the reoxidant then added, the regeneration of Pd(II) is very slow. A number of oxidants,
including K$_2$Cr$_2$O$_7$, NaNO$_2$, CuBr$_2$, Pb(OAC)$_4$, benzoquinone, Fe(III) salts, and O$_2$, were found to be effective re-oxidants in catalytic olefin oxidation.$^{96}$

Benzoquinone is worthy of special mention because it does not change either the rate or product distribution of the olefin oxidation.$^{96}$ For these reasons quinone has been used as an oxidant in kinetic studies. The fact that benzoquinone does not change the rate of oxidation indicates that the rate of reoxidation of Pd(0) to Pd(II) is faster than the rate of oxidation. Another advantage of quinones in mechanistic studies in that the hydrogen ion concentration also does not change during the course of a kinetic run. Thus the H$^+$ formed in the oxidation of ethylene by Pd$^{2+}$ is used up in the regeneration step.

\[
Pd^0 + HCl + Cl^- + O=\rightarrow PdCl_4^{2-} + HO\rightarrow OH (1-9)
\]

Assuming the same mechanism as the Wacker reaction, the reaction rate expression is simplified from Equation 1-3 to Equation 1-10 in chlorine-free and constant [H$^+$] system.

\[
-\frac{d[C_2H_4]}{dt} = \frac{k[Pd^{2+}][C_2H_4]}{[H^+]} = k_{obs}[Pd^{2+}][C_2H_4] (1-10)
\]

where $k_{obs} = k / [ H^+ ]$

CuCl$_2$ is another common reoxidant. However, copper salts affect the free chloride concentration in an uncertain fashion by forming Cu(I) and Cu(II) chloride species such as CuCl$_n^{(n-1)-}$ and CuCl$_n^{(n-2)-}$. Since, as shown in equation 1-3, the rate of ethylene oxidation by PdCl$_4^{2-}$ depends on both free chloride and free proton, the rates in the presence and
absence of copper salts are very difficult to compare quantitatively. Moreover, CuCl₂, as described above, can act as cocatalyst with Pd(II) and changes the courses of the oxidation reactions.

The cooperation of two metallic species introduces a new dimension to catalysis by transitional metal complexes. Thus bi- or polymetallic complexes might cause some organic transformations that monometallic species do not. Recently a number of studies involved in bi- and polymetallic complexes.¹⁰⁷-¹⁰⁵

**Effects of Solvents on Olefin Oxidation**

The catalytic olefin oxidation by Pd(II) complexes can be carried out in several solvents such as methanol and acetic acid. As expected, the nature of the products depends on the reaction medium. In the presence of quinone as re-oxidant, the catalytic oxidation of ethylene in methanol at 25 °C by palladium(II) chloride plus LiCl was found to yield mainly CH₃CH(OCH₃)₂ (dimethylacetal).¹⁰⁶ The reaction in acetic acid produces vinyl acetate.

The states of palladium(II) complexes will change with the dielectric constant of the medium. These various species may have different reactivities. With the lower dielectric constant acetic acid solvent (6.15 at 25 °C)¹⁰⁷, palladium(II) exists as a polymeric species.¹⁰⁸ Equilibrium studies indicate that palladium(II) chloride in acetic acid exists as chloride-bridged binuclear complexes.¹⁰⁹,¹¹⁰ Palladium(II) acetate in acetic acid in the absence of acetate ion exists as the trimeric species [Pd₃(OAc)₆]. This unreactive trimer will first be converted to a more reactive dimer [Pd₂(OAc)₄], and then to a monomeric
species $[\text{Pd(OAc)}_4]^{2-}$, by successive increases in sodium acetate concentration.$^{111,112}$ Water has a dielectric constant of 78.36 and there is no evidence for a dimeric species. Above a chloride concentration of 0.1 M, the Pd(II) exists almost entirely as $\text{PdCl}_4^{2-}$ in water.$^{113,114}$ Methanol has a dielectric constant of 32.63, between that of water and acetic acid. $[\text{PdCl}_4]^{2-}$ was found to obey the following equilibrium in methanol.$^{106}$

$$\text{PdCl}_4^{2-} + \text{CH}_3\text{OH} \rightleftharpoons K_H \text{PdCl}_2(\text{CH}_3\text{OH})^- + \text{Cl}^- \quad (\text{I-11})$$

At 25 °C, the equilibrium constant $K_H$ has a value of $1\times10^{-2}$ L mol$^{-1}$ at $[\text{Cl}^-] = 0.002$ M.

**Stereochemistry in Olefin Oxidation**

As mentioned earlier, there has been considerable interest in the stereochemistry of catalytic olefin oxidation by metal complexes since it is closely tied to the mechanism.$^{115-125}$ The configuration of the products depends on the stereochemistry of the nucleophile attack. *Syn*-attack occurs on same side as the metal. *Anti*-attack occurs on the side remote from the metal or from the solvent.

The catalytic oxidation of cyclohexene was investigated by Henry.$^{126,127}$ Cyclohexene was chosen as a mechanism probe for this study for several reasons. The complication of Pd(II)-catalyzed olefin isomerization is avoided. The stereochemistry of products can be determined directly by NMR, since vicinal coupling constants can be used to determine *cis* or *trans* configurations in substituted cyclohexanes.$^{128}$ In general *cis* protons in rapidly interconversion mixtures of conformers give vicinal coupling constants in the 3.5-4.0 Hz range. *Trans* coupling constants are much large, usually at least 6.5-7.0
Hz. The stereochemical results are easier to interpret in terms of mechanism because there cannot be free rotation around the carbon-carbon bonds in any reaction intermediates.

The oxidation of cyclohexene by a mixture of Pd(II) and Cu(II) in acetic acid gives both saturated disubstituted cyclohaxane acetate and unsaturated 2-cyclohexene-1-ol acetate and 3-cyclohexene-1-ol acetate. The last two are the only products in the absence of Cu(II). The saturated esters were either chloroacetates or diacetates. The diacetates were all of cis stereochemistry. The 1,3 and 1,4 chloroacetates were exclusively trans while the 1,2 chloro acetates were an approximately equal molar mixture of cis and trans isomers. Oxidation of cyclohexene-3,3,6,6-d₄ gave 3-cyclohexen-1-ol acetate and trans-1,3 and -1,4 chloro acetates which retained all four deuteriums. The distribution of deuterium in these products was stereospecific. A reaction scheme was proposed which involves trans acetoxy-palladation followed by stepwise movement of Pd(II) around the ring by cis palladium(II) hydride eliminations and re-additions. The decomposition of the Pd(II) adduct occurs by reaction with Cu(II). This decomposition is believed to involve transfer of electrons from the Pd(II)-carbon bond in the adduct directly to Cu(II) as shown in Equation I-8.

1.2.4 Oxidation of Alcohols

Alcohols are oxidized by palladium(II) complexes to give carbonyl compounds. In the 1960s, Harrod and Chalk found acetaldehyde as a by-product from the oxidation of the palladium(II)-catalyzed ethylene reaction in ethanol solvent. Lloyd reported primary and secondary alcohols were readily oxidized in good yield. This reaction has precedent
in alcohol oxidation catalyzed by other transition metal complexes. Among the primary alcohols the only relatively stable species was methanol which gave methyl formate as the oxidation product. Lloyd suggested a ligand dehydrogenation involving the alcoholic hydrogen and the α-hydrogen.

\[
Pd^{+2} + RCH_2OH \rightleftharpoons R\overset{\cdot}{C}O \text{Pd}^{+2} + H^+ \rightarrow HPd^+ + R\overset{\cdot}{C}O \quad (1-12)
\]

1.3. Polymer supported Pd(II) catalysis

Although most commercial catalysts are heterogeneous, the determination of their mode of operation is much more difficult than that of homogeneous catalysts. Thus it would be instructive to attach active homogeneous catalytic species to solid supports.

Catalytic active sites on supports may not only simply duplicate the activities of their homogeneous counterparts but also have their own novel reactivities. Many metallic heterogeneous catalysts on supports appear to have crystallites which are very small, containing only a few metal atoms. These atoms can interact cooperatively to readily carry out reactions which cannot be achieved by homogeneous, mononuclear catalysts. Examples on platinum surfaces include the oxidation of methanol,\textsuperscript{131} the four electron reduction of dioxygen at fuel cell electrodes,\textsuperscript{132} and the isomerization of alkanes.\textsuperscript{133} These catalysts may have a further advantage. As they are surface species, they would have bare coordination sites and thus be more reactive than completely coordinated soluble catalysts.
Two categories of supports can be used as catalytic carriers. One is an inorganic support, such as inorganic oxides or salts. The other is organic polymers. Inorganic supports have high surface area for coating catalysts and good mechanical and thermal stabilities. However, the internal pore distribution in inorganic carriers is not easily controlled, which may affect the internal selectivity and diffusion of substrates. Moreover, the supports are sometimes themselves active catalysts. In contrary, the organic supports often are thermally and mechanically unstable. On the other hand, organic polymers are chemical inert and themselves are not catalysts. The organic supports can also be functionalized to give ligands which can coordinate with metal species. Considerable efforts have been made in preparing polymer supported catalysts in the last twenty years. Examples include catalysts for asymmetric hydroformulation, ruthenium catalyzed oxidation of organics, and Fischer-Tropsch methanol homologation. Most of these used only monomeric metallic species and none involved the type of surface ligand discussed in this thesis.

Recently, Henry's group coated thermally stable chemically modified organic polymers on inorganic supports. These heterogeneous polymeric surfaces are the subject of this thesis.

1.3.1. **Catalyst System**

One ligand which strongly binds a large variety of metal species is the β-diketone group. A closely related binucleating ligand is the β-triketone group which is capable of holding two metal species in a known geometry. Preliminary studies have shown this
binuclear complex is suitable for joint catalysis in several reactions. The strategy for attaching diketone and triketone groups to a surface involves the preparation of polyphenylene polymers by the aromatization polymerization shown in Equation I-13. These copolymers can be prepared by known methods and are very thermally stable.\textsuperscript{152,153}

\[ \begin{align*}
&\begin{align*}
&\text{O} \\
&\text{CCH}_3 \\
&\text{O}
\end{align*} \\
&\begin{align*}
&\text{X} \\
&\text{H} \text{ or } \text{CO}_2\text{CH}_3
\end{align*}
\end{align*} + \begin{align*}
&\begin{align*}
&\text{O} \\
&\text{CCH}_3 \\
&\text{O}
\end{align*} \\
&\begin{align*}
&\text{H} \text{ or } \text{CO}_2\text{CH}_3
\end{align*}
\xrightarrow{HCl\text{(gas)}}
\begin{align*}
&\begin{align*}
&\text{O} \\
&\text{CCH}_3 \\
&\text{O}
\end{align*} \\
&\begin{align*}
&\text{X} \\
&\text{H} \text{ or } \text{CO}_2\text{CH}_3
\end{align*}
\end{align*}
\text{ (I-13) }
\]

meta or para

X = H or CO\textsubscript{2}CH\textsubscript{3}

Originally the \( \beta \)-di- and tri-ketone surface ligands were introduced by modification of the acetyl end groups but a newer, more effective means has been developed for placing these groups on the polymer surface using the methyl benzoate groups, which do not take part in the polymerization and thus will not be consumed during the course of the polymerization. These ester functional groups react with base plus ketone or \( \beta \)-diketone to give diketone (B) and triketone (C) surface ligands. These surface ligands can complex with metal ions to give monometallic (D) and bimetallic (E) surface complexes as shown in Scheme I-6 on the next page. These mono- or bi-metallic complex structures have considerable analogy with homogeneous systems.\textsuperscript{138,139}
Scheme I-6

Polymer $\text{CO}_2\text{CH}_3$ Base

A

O

CH$_2$CCH$_3$

$\text{CO}_2\text{CH}_3$

Base

$\text{CH}_2\text{CCH}_3$

$\text{CH}_2\text{CH}_3$

B

$\text{M}^{+\left(n+1\right)}$

$-\text{H}^+$

$\text{D}$

$\text{M}^+$

$-\text{H}^+$

$2\text{M}^{+\left(n+1\right)}$

$2\text{H}^+$

C

$\text{E}$
These can be selectively modified with two types of ligand groups. Studies on low molecular weight model systems, which space does not permit describing in detail, indicate that the ester groups are not destroyed in the original polymerization and that surface chemical modification has occurred quantitatively. In addition to these studies, there is the chemical evidence of catalytic activity, discussed in the next section, to demonstrate that these surfaces are catalytically active and that the activity depends on the identity of the surface ligand.

1.3.2 **Modes of Polymetallic Catalysis**

An appealing design for a catalytic site is a polymetallic environment which can allow enhanced rate effects. It is the goal of this research to improve the catalytic capability of the chosen metal ions by designing a complex setting which allows for cooperative interaction between metal species. There are a number of possible mechanisms for this cooperation but in this section only those of direct importance to this project will be considered.

**Absorption of Substrate**

One such mechanism involves absorption of the substrate by one metal center, bringing the second metal close to the reactive site on the organic. A normal example is the alcohol oxidation by the bi-metallic species. The reaction would most likely involve adherence to one metal and hydride extraction by another metal so that the hydride abstraction and $\beta$-hydride elimination should occur more readily. This occurs because the
carbon $\beta$-hydrogen bond will be polarized resulting in a partial negative charge on the hydrogen as shown in Equation I-14.

\[
Pd" \longrightarrow Pd" + RCH_2OH \rightarrow Pd" \longrightarrow Pd" + RCHO + H^+ \]

Absorption would be especially important for those organic substances which have more than one functional group and is capable of bonding to the metal species. Examples would be glycols, allylic alcohols and catechol.

**Cooperative Electron Transfer**

A second possible mechanism is cooperative electron transfer. This mechanism is especially important since it converts two one-electron metal oxidants into a two electron oxidants. Organic oxidations which occur readily usually involve two electron transfer. Cooperative electron transfer can convert one electron oxidants such as Fe$^{+3}$ and Cu$^{+2}$ into two electron catalytic species.

This mechanism of cooperative two electron transfers will be particularly effective when the transfer can occur via the coordination of two functional groups on the same
molecule to each of the two metal centers. Preliminary studies have shown that such cooperative electron transfer actually occurs. A special example is the oxidation of catechol which can be oxidized by both mono- and bi-metallic species to give o-quinone. However only the bimetallic catalyst can give the second two electron transfer to give ring cleavage shown in Scheme I-7.

Scheme I-7

One question is whether the bimetallic catalyst can give cooperative electron transfer with monofunctional molecules. This might be another type of cooperative electron transfer that could occur to give completely different types of products. Compared with the Pd(II) - Cu(II) system, one reasonable assumption is that bi-Pd(II) species has an opportunity for a similar electron transfer in the transition state for decomposition giving a Pd(I) dimer which is a stable species and thus a "good leaving group". Thus, as in the case when CuCl₂ present in a hydroxyl solvent, the bi-Pd(II) species should give saturated
products resulting from carbonium ion decomposition mechanisms as shown in Scheme I-8 on page 28.

1.4. **Scope of This Work**

1.4.1. *The Development of Novel Pd(II) Catalysts on Polymer Film*

This project is to develop novel heterogeneous mono- or bi-Pd(II) catalysts supported by polymers for organic synthesis. The strategy involves the absorption of Pd(II) species on the \( \beta \)-diketone and \( \beta \)-triketone surface ligands on the polymeric supports as discussed earlier. The polymer supported catalysts have been prepared many times in our laboratory. In this project, we will test the reactivity of heterogeneous Pd(II) catalysts.

In addition, in the new systems we would also like to elucidate the structure of the mono-metallic and bi-metallic polymer supported Pd(II) catalysts. The prepolymer can be analyzed by NMR and IR spectroscopy. Since the high molecular weight aromatic polymer cannot be dissolved in any solvent, the polymers and their Pd(II) complexes will be largely characterized by infrared spectra and FT-IR techniques.\(^{154}\)

1.4.2 **Catalytic Olefin Oxidation By Heterogeneous Mono- and Bi-Pd(II) Species**

The mechanism of catalytic oxidation of certain olefins by mono- and bi-metallic catalysts will be studied by reaction kinetics and distribution of products. The results obtained for the mono- and bi-Pd(II) catalysts will be compared to see if the bi-metallic species can catalyze reactions which the mono-metallic species cannot. Stereochemistry of the products from the two types of catalysts will also be investigated.
Scheme I-8

OAc\(^{-}\) + Pd\(^{II}\)→CH\(_2\) + OAc\(^{-}\) → Pd\(^{I}\)→Pd\(^{I}\) + AcO\(-\)-CH\(_2\)-CH\(_2\)-OAc
II.1. Description of Instruments

NMR Studies

The NMR spectra were recorded on a Varian VXR-300 NMR spectrometer. The instrument was equipped with a 5 mm multinuclear probe. A standard single pulse sequence was employed to obtain the NMR spectra of all the samples. All chemical shifts for the $^1$H and $^{13}$C spectra were measured at ambient temperature and referenced to TMS or solvents.

FT-IR Studies

The FT-IR spectra were recorded using an ATI Mattson Genesis FTIR™ Instrument or an IBM FT-IR Model #98 spectrometer (University of Illinois at Chicago). The resolution of the FT-IR instruments was set at 4 cm$^{-1}$. IR spectra of liquid samples were taken in NaCl cells while IR spectra of solid samples were taken on KBr plates.

Gas-Liquid Chromatography

The reaction products were identified by GLC. The GLC spectra were measured by a GOW-MAC Series 350 Gas Chromatograph instrument equipped with a 20-inch
80/100 Chrom. WHP column and a thermal conductivity detector or GOW-MAC Series 580 Gas Chromatograph instrument equipped with a 10 inch 80/100 C20 M column and a hydrogen flame detector. The products were separated and collected by the GOW-MAC Series 350 GC instrument.

**GC-MS Studies**

GC-MS spectra were recorded using the Hewlett Packard 5890 Series II Plus GC instrument equipped with 5972 Series Mass Selective Detector and HP5 column.

**TLC Method**

Thin liquid chromatography was analyzed by Aldrich silica gel 60 F 254 aluminum TLC plates.

**Kinetic Studies**

Oxidation and kinetic studies were carried out in gas burets and a creased flask agitated by means of magnetic stirring bars. A schematic apparatus is shown in Figure II-1 on page 30. The creased flask was intended to increase stirring efficiency. The reaction temperature was maintained at 25 ± 0.2 °C in a water bath using a Messgeräte-Werk Lauda model B-1 thermostat. All reactions were run in the presence of re-oxidant (quinone, cupric chloride, or oxygen) and at a constant pressure of 1 atm by adjusting the Hg reservoir in Figure A-1.

The rates of oxidation of gaseous olefins were followed by olefin uptake measured by the gas buret. Since none of the reactant concentrations changed during the
Figure 1  Schema of Creased Flask Reactions
course of a run, the kinetics was pseudo zero order. Thus, the olefin uptake was linear with time until all the re-oxidant had been reduced or heterogeneous catalysts had been decomposed. From the rate of linear uptake, the rate constant can readily be calculated from the known concentrations of reactants. The solubilities of olefins were measured by gas uptake of solutions of the same composition as the reactions mixtures but from which the palladium catalysts were omitted. The reported data are mean values of at least two runs.

II.2. Materials

II.2.1 Chemicals

Palladium sponge (99.9%), triethylorthoformate (98%), 1,4-diacytbenzenene (98%), 1,4-acetyl benzoic acid (99%), p-toluene sulfonic acid monohydrate (99%), 3,3-dimethyl-2-butanone (pinacolone) (98%), 2,4-pentanediene (99%), 4-penten-1-ol, ethylene (99.5+%), propylene (99%), ethyl ether (anhydrous), petroleum ether, methylene chloride ethanol (absolute 200 proof), methanol, hexane, benzene, tetrahydrofuran, acetonitrile, 2,4-dinitrophenyl hydrazine, nitrosyl tetrafluoroborate acetic acid, acetic anhydride, hydrochloric acid, sulfuric acid, gaseous hydrogen chloride (99%), calcium hydride, sodium hydride (dispersion in mineral oil, 60%), magnesium sulfate (anhydrous), sodium hydrate, sodium carbonate, sodium bicarbonate, sodium sulfate, sodium chloride, lithium acetate, Celite (high-purity analytical grade), and silica gel (70-230 mesh, 60 Å) were purchased from Aldrich Chemical Company. Argon, helium, and oxygen were obtained from Airco.
Acetonitrile, tetrahydrofuran and benzene were dried over calcium hydride. 1,4-Diacetylbenezene was recrystallized from n-hexane and dried under vacuum. All other chemicals were of reagent grade and were used as received unless specified otherwise in the text.

II.2.2. Reagent

The 2,4-DNP solution was prepared by dissolving 3.0 g of the reagent in 15 ml of concentrated H₂SO₄ at room temperature. This solution was carefully added to 80 ml of water, stirred for 10 minutes and filtered.

II.3. Syntheses of Mono- and Bi-Pd(II) Catalysts on the Surface of the Polymer

Supported on Celite

1,4-Acetyl benzoic acid and 1,4-diacetylbenezene were selected as monomers. Since the high molecular weight polymer can not be dissolved in any solvent, the lower molecular weight pre-polymer was synthesized first and coated on the surface of celite. After curing to form a high molecular weight cross-linked structure on the celite; the polymer was modified to introduce β-diketone and β-triketone ligands on the polymer coated celite. The last step was treatment with [Pd(CH₃CN)₄]²⁺ species to give the surface catalytic species.

II.3.1 Preparation of Monomers

Synthesis of 4-Acetyl Methylbenzoate

Gaseous hydrogen chloride (HCl) was bubbled through 210 ml of methanol for 30 min. A 5.5278 g of 4-acetyl benzoic acid was added to the methanol in a 500 ml three
necked round bottom flask. The 4-acetyl benzoic acid dissolved immediately to give a yellow solution. It was refluxed for 3.5 hours and then cooled to room temperature. The solution was diluted with 150 ml of CH₂Cl₂ and 170 ml of brine. The layers were separated. The aqueous layer re-extracted with 3x25 ml of CH₂Cl₂, and all the organic layers were combined. The organic layer was washed with 3 x 150 ml of saturated NaHCO₃ until blue litmus paper showed no change and then washed with 2 x 125 ml of brine. The organic layer was dried with anhydrous MgSO₄ overnight. After filtering off the drying agent the solvent was removed with a vacuum pump. The best yield of the crude product was 81.4 %. The crude product was purified using a 100 g silica column and CH₂Cl₂ as the only eluant. A 4.67 g sample of the purified product was obtained (yield: 95.7 %). The pure product was analyzed by 300 MHz NMR and infrared.

II.3.2. Polymerization of 4-Acetyl Methylbenzoate and 1,4-Diacetylbenzene

Prepolymer Preparation

A 1.00 g (6.17x10⁻³ mole) sample of 1,4-diacetylbenzene and a 1.01 g (5.68x10⁻³ mole) sample of 4-acetylbenzoate were dissolved completely in 50 ml of dry benzene. Then a 5.34 g (3.602 x 10⁻² moles) sample of the triethyl orthoformate (TEOF) was added. The molar ratio of 4-acetyl benzoic methylbenzoate to 1,4-diacetylbenzene was 0.928 and that of the TEOF to all the acetyl groups present was 2. The HCl gas was bubbled slowly through the solution at room temperature for 20-45 minutes. The color of solution changed from yellow, to red, then to dark red. At regular intervals 0.5 ml portions of the reaction solution were transferred into 5 ml of ethanol. Initially, there is no precipitate, then light
yellow precipitate formed, and finally a brown yellow precipitate appeared. At this time, the reaction was stopped, before the gel point of the polymerization.

The solution was poured into 400 ml of absolute ethanol to precipitate the prepolymer. The yellow precipitate was filtered and washed quickly with ethanol, saturated sodium carbonate solution, water and finally with copious amounts of ethanol until the wash contained no yellow color, indicating there was no monomer and low molecular weight product in the prepolymer. The solid was dried first in a stream of argon and then on a vacuum pump. After drying, it was partially dissolved in benzene and stirred in a mixed solvent containing benzene and methylene chloride for 12 hours. The undissolved fraction was removed by filtration. This prepolymer was only partially dissolved in benzene but completely dissolved in chloroform. The melting point of the prepolymer was 205 to 230 °C. The prepolymer was further analyzed by NMR and IR.

**High Molecular Polymer Polymerization**

In the same method as described as above, a 1.50 g (9.25x10^{-3} mole) sample of 1,4-diacylbenzene and a 1.46 g (8.22x10^{-3} mole) sample of 4-acetyl methylbenzoate were polymerized at room temperature in 40 ml of dry benzene until the light brown high molecular weight polymer precipitated. The molar ratio of 4-acetyl methylbenzoate to 1,4-diacylbenzene was 0.889. After the precipitate was washed with water, saturated sodium carbonate solution and ethanol, it was dried in a vacuum oven at 80 °C.
This precipitate cannot be melted and is insoluble in any solvent. It was analyzed by FT-IR using a KBr dish (1 % concentration). The yield is not affected by the molar ratio of TEOF to acetyl group. However, the reaction rate increased as the ratio increased.

II.3.3. Coating of the Prepolymer onto Celite

First, the prepolymer was coated onto a 1 g sample of celite. A 0.050 g sample of prepolymer was dissolved in the 95 ml of a mixed solvent containing methylene chloride and benzene (1:1.8). It was stirred at room temperature and 5-10 ml portions of the prepolymer solution was added to the 1 g sample of celite every four to eight hours until the color of the supernatant did not change. The amount of coated prepolymer was calculated to be 0.023 g of prepolymer per gram of celite. In the same way, the prepolymer was coated onto 40.0 gram of celite. The supernatant was removed and the polymer coated celite was dried in a rotary evaporator and then in a vacuum oven overnight.

II.3.4. Curing of the Prepolymer on the Supported Materials

The polymer coated celite was sprayed with 5.0 g of p-toluene sulfonic acid in 100 ml of ethanol and cured in a vacuum oven at 138-140 °C for 24 hours. After curing, the melting point of polymer is over 400 °C. In the same fashion, the polymer film was coated on NaCl plates and cured. After curing, the celite and NaCl plates were washed with copious quantities of absolute ethanol.
II.3.5. *Chemical Modification to Place $\beta$-Diketone and $\beta$-Triketone Ligands on the Polymer Surface*

The $\beta$-diketone and $\beta$-triketone groups have been modified in homogeneous systems.\textsuperscript{157-159} The prepolymer and polymer were modified by several procedures to determinate the best heterogeneous modification conditions. Then the polymer films on NaCl plates and celite were modified under this best modification conditions.

*Modification of $\beta$-Diketone Ligand*

Under argon protection, 5.20 g of sodium hydride was refluxed in 180 ml of dry tetrahydrofuran (THF) for 45 minutes at 81°C. After cooling, 2.61 ml of 3,3-dimethyl-2-butanol was injected into the stirred gray sodium hydride slurry. The reaction solution was refluxed gently for 45 minutes at 80°C. At this point, a yellowish color indicated the formation of the anion. The reaction solution was then cooled to room temperature and a 2.00 g sample of polymer or prepolymer and 1.50 g of 18-crown-6 were added. The reaction mixture was refluxed for 18 hours at 81°C and then the deep brown solution was cooled to room temperature. Some of the solvent was removed under vacuum and the dull brown pasty residue was cooled to 0°C in ice-water bath. Then an 105 g ice-water mixture was added gradually to destroy the excess sodium hydride, and 10 ml of 1 N HCl and 15.4 ml of 6 N HCl were added to bring the pH of mixture below 7.00. The diketone product was filtered and washed with copious amount of water until the pH was equal to 7. Then the product was washed with ethanol and dried at 40°C in the vacuum oven to a constant weight. The product was a light orange brown color.
In the same fashion, the polymer films on the NaCl plates and celite were chemically modified with 3,3-dimethyl-2-butanone to form β-diketone ligands.

**Modification of β-Triketone Ligand**

Similarly, a 15.0 g sample of sodium hydride was refluxed in 185 ml of dry tetrahydrofuran (THF) for 2 hours at 80°C. After cooling, a 2.80 ml sample of 2,4-pentanedione was injected to this stirred gray sodium hydride slurry. The reaction solution was gently refluxed for 45 minutes at 80°C. At this point, the yellowish color indicated the formation of the anion. After cooling to room temperature, a 2.00 g sample of polymer or prepolymer and a 1.50 g sample of 18-crown-6 were added. The reaction mixture was refluxed for about 20 hours at 80°C and the deep brown solution was cooled to room temperature. Some of the solvent was removed and the brown pasty residue was cooled to 0°C in an ice-water bath. Then 106 g of ice-water mixture, 10 ml of 1 N HCl, and 61.5 ml of 6 N HCl were added. The triketone product was filtered and washed with copious amounts of water until the pH was equal to 7. Then the product was washed with ethanol and dried at 40°C in the vacuum oven to constant weight. The product was an orange brown solid.

In the same fashion, the polymer films on the NaCl plates and celite were chemically modified with 2,4-pentanedione to form β-triketone ligands. The KBr plates of the products (1 percent of sample) were made and characterized by FT-IR.
II.3.6. **Pd(II) Uptake by β-Diketone and β-Triketone on Supports**

**The Synthesis of Tetraacetonitrilepalladium(II) Tetrafluoroborate**

This compound was synthesized by a modification of Schramm and Wayland's method.\(^{160}\) To a degassed 250 ml two necked round bottom flask was charged 130 ml of redistilled acetonitrile and 0.66 g (6.2 mmoles) of palladium sponge. The system was then deoxygenated by vacuum de-gas and argon purge cycles three times. Under an argon atmosphere, a 1.80 g (15.4 mmoles) sample of nitrosyl tetrafluoroborate was added. The mixture was slowly bubbled with argon and stirred for about 48 hours until the palladium sponge was completely dissolved. The reaction mixture was a clear light yellow solution. The product was precipitated by addition of 250 ml of anhydrous ethyl ether and filtered. The solid was rinsed with 150 ml anhydrous ethyl ether and dried in vacuum oven at room temperature to constant weight. The whole process was carried out under argon.

The maximum yield of \([\text{Pd(II})(\text{CH}_3\text{CN})_4](\text{BF}_4)_2\) product was 93 %. The dry product was light yellow. It was characterized by \(^1\text{H NMR}\) in \(\text{CD}_3\text{NO}_2\) solvent and FT-IR with nujol.

**Pd(II) Uptake by High Molecular Weight Polymer**

The Pd(II) was coordinated with β-diketone and β-triketone sites on high molecular weight polymer by the modification of Sen's method.\(^{161}\) To a degassed 250 ml three necked round bottom flask was charged 115 ml of dry acetonitrile and 1.31 g β-diketone polymer. The system was then deoxygenated by vacuum de-gas and argon purge cycle three times. Then a 1.20 g (2.70 mmoles) sample of Pd(II) was added. The mixture
was slowly bubbled with argon and stirred for about 48 hours. The final product was filtered, washed with 39.5 ml dry acetonitrile, and dried in vacuum oven. The total 125.0 ml filtrate was saved for analysis to determine the amount of Pd(II) uptake.

In a manner similar to that described above, the Pd(II) ion uptake by the $\beta$-triketone was performed. The weights of triketone and $[\text{Pd(II)(CH}_3\text{CN)}_4](\text{BF}_4)_2$ were 1.30 g and 1.19 g, respectively.

**The Pd(II) Species Uptake by $\beta$-Diketone and $\beta$-Triketone Groups on Polymer Film Supported on NaCl Plates**

Prepolymer was prepared as described previously and coated on the NaCl plates. The plates were sprayed with 5 % of p-toluene sulfonic acid in 100 ml of ethanol and cured in a vacuum oven at 138-140°C for more than 24 hours. After curing, the polymer film was washed with absolute ethanol and dried in an oven. Those plates on which polymer film was deposited were immersed in a solution containing $\beta$-diketone and $\beta$-triketone anions to perform the modification. The excess basic reagent on the plates was rinsed with a 5 % solution of p-toluene sulfonic acid in 100 ml of absolute ethanol. After drying, the plates were modified with Pd(II) by the usual procedures. The surface structures of the plates were analyzed by FT-IR.
The Pd(II) Species Uptake by β-Diketone and β-Triketone Groups on Polymer Supported by Celite

Similarly, the prepolymer was coated and cured on celite. The β-diketone and β-triketone groups and Pd(II) species were attached as described above.

II.3.7. The Quantitative Analysis of Pd(II) Ion Uptake on Supports

The volume of the supernatant from the Pd(II) treatment was measured. Then, to a 50 ml or 25.0 ml aliquot was added 2.1 ml of 12 N HCl. The solution was diluted to 100 ml with distilled water. The mixture was titrated with 1 percent of dimethylglyoxime solution in 95 percent ethanol, until no more yellow crystalline precipitate formed. After standing overnight, the precipitate was washed with copious amounts of cold distilled water followed by hot water. It was dried in oven at 110°C to constant weight.

II.4. The Oxidation Reaction Catalyzed by Polymer Supported Mono- and Bi-Pd(II) Species

II.4.1. Propylene Oxidation by Mono- and Bi-Pd(II) Catalysts in De-ionized Water

A 250 ml two necked creased Erlenmeyer flask was charged with 0.05 to 0.17 g of mono- or bi-Pd(II) catalysts on bulk high molecular weight polymer or polymer coated celite. Benzoquinone was used as a re-oxidant. The reaction mixture was 50 ml of 0.2 M of benzoquinone in de-ionized water. The reaction flask was set in a thermostatted water bath at 25.0 ± 0.05°C for 30 min. Then, it was degassed by vacuum (22-inch-Hg vac.) and purged with propylene three times. The volume of propylene absorbed was read
periodically using a buret as shown in Figure II-1. All reactions were run under 1 atm of constant propylene pressure at 25°C.

**Identification of Products from Propylene Oxidation in De-ionized Water**

After enough product was collected, the 10 ml potions of reaction mixture were added to a 50 ml of 2,4-dinitrophenyl hydrazine (2,4-DNP) solution with stirring in ice-water bath. The 2,4-DNP derivative was identified by TLC and $^1$H NMR.

**II.4.2. 4-Penten-1-ol Oxidation by Mono- and Bi- Pd(II) Catalysts in De-ionized Water**

The catalyst was added to the reaction flask as described above (II.2.1). Oxygen was used as re-oxidant. The system was degassed by vacuum (22-inch-Hg vac.) and purged with oxygen three times. Then 0.13 ml or 0.21 ml of 4-penten-1-ol was injected. The volume of oxygen absorbed was recorded as described above. All reactions were run at 1 atm of constant oxygen pressure and 25.00 ± 0.05 °C.

**Identification of Products from 4-Penten-1-ol Oxidation in De-ionized Water**

The 2,4-DNP derivative of the products was identified by TLC. All products were analyzed by GC-MS spectrometer.

**II.4.3. Ethylene Oxidation by Mono- and Bi- Pd(II) Catalysts in Acetic Acid**

An argon-purged 250 ml two necked creased Erlenmeyer flask was charged with mono- Pd(II) catalyst (0.020 g, 0.031 g, and 0.100 g) or bi-Pd(II) catalyst (0.020, 0.030, 0.036 g with modified pure polymer; 0.061 g of the polymer coated celite) and 50 ml of 0.20 M recrystallized benzoquinone solution in acetic acid. The 0.20 M of benzoquinone solution was prepared by adding 0.3 ml of acetic anhydride to 1.08 g of the recrystallized
benzoquinone and diluting to 50 ml with acetic acid. The solution was transferred to the reaction flask which was immersed in a 25.0±0.05 °C thermostatically controlled water bath for 30 min. After the benzoquinone completely dissolved, the flask was degassed by vacuum (22-inch-Hg vac.) and purged with ethylene three times.

The reaction was run at a constant 1 atm ethylene pressure. A magnetic stirring bar was used for agitation. The ethylene uptake was measured by gas buret with readings taken periodically. The reaction mixture was transferred to a round bottom flask ten days later and allowed to react at room temperature until sufficient products for analysis were formed.

**Identification of the Products from Ethylene Oxidation in Acetic Acid**

After the reaction, the heterogeneous mono- or bi-Pd(II) catalyst was removed by filtration immediately. The reaction mixture was first diluted with 50 ml of distilled water then extracted with 50 ml of methylene chloride. The aqueous layer was re-extracted with three portions of 50 ml of methylene chloride and all organic layers were combined. The organic layer was washed with three 30 ml portions of saturated NaHCO₃ at which point pH paper showed the aqueous layer to be basic. Then the organic layer was washed with 20 ml of the saturated aqueous NaCl solution. The organic layer was dried over anhydrous Na₂SO₄ overnight and concentrated at 60°C to give 1 ml of product mixture at 60°C. Most of the benzoquinone was removed by adding petroleum ether.

The concentrated reaction mixture was analyzed by gas chromatography. The injector temperature was 99°C, the detector temperature was 99°C, and the column
temperature was 81 °C. The helium flow rate was 10 ml per minute. Vinyl acetate, which was identified by comparison with a standard sample, was the only product found. It was collected from GC at a column temperature of 50 °C and its identity was further confirmed by ¹H NMR.

For the analysis of the products from ethylene oxidation catalyzed by the bi-Pd(II) catalyst, a GOW-MAC 580 GC instrument with a 10-inch 80/100 Chrom GAW column was used. The injector temperature was 203 °C; the detector temperature was 213 °C; and the column temperature 186 °C. The helium flow rate was 25 ml/min. Three products were detected by GC. By comparison to standard samples, the major product was identified as ethylene glycol diacetate (tᵣ=3.75 min.). The other two products were ethylene glycol monoacetate (tᵣ=3.26 min.) and ethylidene diacetate (tᵣ=2.73 min.). The identity of the major product was confirmed by ¹H NMR.

II.4.4. Propylene Oxidation by Mono- and Bi-Pd(II) Catalysts in Acetic Acid Using Benzoquinone as Re-oxidant

A 250 ml two necked creased Erlenmeyer flask was charged with 0.040 g of mono-or bi-Pd(II) catalysts. The reaction solution was a 50 ml solution of 0.20 M recrystallized benzoquinone in acetic acid. Using the same procedure as described in II.2.3, the reaction flask was degassed by vacuum (22-inch-Hg vac.) and purged with propylene three times. The volume of propylene absorbed was read periodically from the buret. The reaction was run until sufficient products were accumulated for analysis.
Identification of the Products from Propylene Oxidation in Acetic Acid

The workup procedure was identical to that used for ethylene. Gas-liquid chromatography was used for product identification.

For the products from the mono-Pd(II) catalyst system, the GC injector temperature was 100 °C, the detector temperature was 100 °C, and the column temperature was 60 °C. The helium flow rate was 10 ml per minute. Isopropenyl acetate and allyl acetate ($t_R=9.70$ min.) were identified by comparison with standard samples. They were collected from GC at a column temperature of 60 °C and their identities were confirmed by $^1$H NMR.

For the products from bi-Pd(II) catalyst system, the injector temperature was 150 °C, the detector temperature was 150 °C, and the column temperature was 123 °C. Four peaks were found. The first peak ($t_R=3.73$ min) consisted of isopropyl acetate and allyl acetate. These products were collected by preparative GC and their identity was confirmed by $^1$H NMR. The other three products had retention times of 5.70, 7.82, and 9.80 minutes respectively, whose identity needs to be further confirmed.

II.4.5. Cyclohexene Oxidation by Mono- and Bi Pd(II) Catalysts in Acetic Acid

In the same fashion as described above, a reaction flask was charged with 0.050 g of mono-Pd(II) or 0.055 g of bi-Pd(II) catalyst and 50 ml of 0.2 M recrystallized benzoquinone-acetic acid solution. The flask was degassed by vacuum (22-inch-Hg vac.) and purged with oxygen three times. A 0.15 ml portion of the cyclohexene was injected
into the reaction mixture several times. All reactions were run at constant atmospheric oxygen pressure and at 25.0 °C.

For the reaction system catalyzed by the mono-Pd(II) species, no oxygen uptake was observed. Only a small amount of oxygen was absorbed by the bi-Pd(II) catalyst system.

Without benzoquinone, a similar reaction was run with oxygen as the only re-oxidant. No absorption of oxygen occurred for both mono- and bi-Pd(II) catalyst systems. As evidenced by the formation of a gray precipitate, the mono-Pd(II) catalyst had decomposed more quickly than the bi-Pd(II) catalyst.

**Identification of the Products from Cyclohexene Oxidation in Acetic Acid**

After the mono- or bi-Pd(II) catalyst was removed, the reaction mixture was diluted with 25 ml of water and 25 ml of saturated NaCl aqueous solution followed by extraction with five 40 ml portions of diethyl ether. The diethyl ether layers were neutralized, dried, and concentrated to give 1 ml of product solution.

The concentrated product mixture was analyzed by GLC. For the cyclohexene oxidation catalyzed by both mono-Pd(II) and bi-Pd(II) catalysts, the GLC injector temperature was 140 °C, the detector temperature was 132 °C, and the column temperature was 115 °C. The helium flow rate was 10 ml per minute. The product was collected and identified by \(^1\)H NMR.
11.4.6. *Ethylene Oxidation by Mono-Pd(II) Catalyst in Acetic Acid Using Cupric Chloride as Re-Oxidant*

To a 50 ml solution of 2.0 M lithium chloride in acetic acid in a 250 ml two-necked creased reaction flask, a 0.053 g sample of the mono-metallic Pd(II) and 6.72 g of cupric chloride were charged. The reaction flask was placed in 25.0 ± 0.05 °C water bath for 30 min. Then, it was degassed by vacuum (22-inch-Hg vac.) and purged with ethylene three times. The ethylene absorbed was read periodically from the buret. All reactions were run under the same reaction conditions as 11.2.3.

In the absence of lithium chloride, the mono-metallic or bi-metallic Pd(II) catalysts gave no gas uptake and no products were formed.

**Identification of Ethylene Oxidation Products Mono-Pd(II) Species**

After the heterogeneous mono-Pd(II) catalyst was removed, the reaction mixture was first diluted with 50 ml of water and 50 ml of saturated aqueous sodium chloride solution followed by extraction with diethyl ether for four days. The organic layer was washed with several portions of 20 ml saturated NaHCO₃ until litmus paper indicated the aqueous layer was basic. The organic layer was then washed with two 10 ml portions of the saturated NaCl solution. It was dried over anhydrous sodium sulfate overnight and concentrated at 60 °C to give 1 ml of product solution.

For the analysis of the products from ethylene oxidation catalyzed by mono-Pd(II) catalyst using CuCl₂ as re-oxidant, the GC injector temperature was 110 °C, the detector
temperature was 110 °C, and the column temperature 75 °C. The helium flow rate is 10 cm/s. The products were collected from GC and analyzed by \(^1\)H NMR.

**II.4.7. Ethylene Oxidation by Mono- and Bi-Pd(II) Catalysts in Methanol**

An argon purged 250 ml two necked creased flask was charged with the selected amount of mono-Pd(II) catalysts (0.061 g) or bi-Pd(II) catalysts (0.055 g) modified on pure polymer (0.02 g) or coated celite (0.61 g) and 50 ml of 0.20 M benzoquinone solution in methanol. The flask was immersed in a 25.00 \(\pm\) 0.05°C water bath for 30 min. It was then degassed by vacuum (22-inch-Hg vac.) and purged with ethylene (99 % Aldrich) three times.

All reactions were run at 1 atm ethylene pressure at 25 °C in the presence of 1,4-benzoquinone as the re-oxidant. A magnetic stirring bar was used for agitation. The gas uptake was measured by gas buret as described previously.

**Identification of Products from Ethylene Oxidation in Methanol**

After the reaction, the heterogeneous mono- or bi-Pd(II) catalyst was removed by filtration. A 10 ml portion of the reaction mixture was cooled to 5 °C in an ice-water bath and added to 50 ml of 2,4-DNP solution with stirring. The bright orange 2,4-DNP derivative was filtered and dried. The derivative was identified by TLC and purified by column chromatography. The column was packed with 10-20 g of silica gel (Aldrich, 70-230 mesh 60 A). About 0.1 g of the derivatives were dissolved in 10 ml of benzene and charged on the column. The first fraction eluted with benzene was the formaldehyde
derivative. The second fraction eluted with benzene-ethyl acetate (4:1 by volume) was benzoquinone.

The other portion of the original reaction solution was concentrated and most of the benzoquinone was removed by petroleum ether (Aldrich, 35-60 °C). A second product was separated and collected by GLC. The GLC temperatures of column, detector and injector were 65 °C, 100 °C and 100 °C respectively. The other conditions were the same as II.2.6.

II.4.8. Propylene Oxidation by Mono- or Bi-Pd(II) Catalysts in Water/THF Using Cupric Chloride as Re-Oxidant

To a reaction flask charged with 0.050 g of mono-Pd(II) or bi-Pd(II) catalyst, a 50 ml solution of 2.5 M of cupric chloride and 1.0 M of lithium chloride in water-tetrahydrofuran mixture (50 %) was added. The reaction flask was then purged with propylene three times and the reaction was run at 25.0 °C.

Identification of the Products from Propylene Oxidation

The heterogeneous mono- or bi-Pd(II) catalyst was removed by filtration. The reaction mixture was extracted with diethyl ether for five days. The ether layer was washed with distilled water, saturated NaHCO₃, and sodium chloride. It was dried over anhydrous sodium chloride and concentrated.

For gas chromatography analyses, the GC injector temperature was 120 °C; the detector temperature was 120 °C; and the column temperature 80 °C. The helium flow rate was 10 cm/s. The major products, 2-chloro-2-propanol, 1-chloro-2-propanol, and acetol,
were identified by comparison with standard samples. The products collected from GLC were further identified by $^1$H NMR. Both of the product mixtures from mono-Pd(II) and bi-Pd(II) had the same GC spectra and gave the same products.

II.5. **Control Experiments**

There were two kinds of control experiments. First, reactions were run under the same conditions as described above. The flask was charged with the same reaction mixture but without the mono- and bi-Pd(II) catalysts. No reactions were observed under the conditions of the control experiments. Second, the reaction mixtures were allowed to run after the heterogeneous mono- or bi-Pd(II) catalyst were removed. Also no reactions occurred.
CHAPTER III

RESULTS

III.1. **Structural Characterization of Polymer Supported Mono- and Bi-Pd(II) Catalysts**

**III.1.1. Characterization of Monomer-4-Acetyl Methylbenzoate**

This compound was characterized by standard $^1$H NMR spectroscopy in CDCl$_3$ and IR spectroscopy on NaCl plates.

$^1$H NMR: d 2.65 ppm (s, 3H; CH$_3$-CO-Ar); 3.97 ppm (s, 3H; CH$_3$-O-CO-Ar); 8.00, 8.03, 8.12, 8.15 ppm (s, 4H; -C$_6$H$_4$-).

IR: 3040-3043 cm$^{-1}$ (C-H stretch on aromatic ring); 2980-2940 cm$^{-1}$ (C-H stretch for CH$_3$ and CH$_2$); 1720.6 cm$^{-1}$ (C=O stretch for benzoate esters); 1684 cm$^{-1}$ (C=O stretch for the ketone group conjugating with the phenyl groups); 1273, 1217 cm$^{-1}$ (C-O asymmetric and symmetric coupled vibrations for C-CO-O groups conjugating with the phenyl groups).

**III.1.2. Characterization of Prepolymer**

The prepolymer was characterized by $^1$H NMR spectroscopy in CDCl$_3$ solution and IR and FT-IR spectroscopy both as a power and as a film on NaCl plates.
\(^1\)H NMR: d 1.21 ppm (t, 3H; -O-CH\(_2\)-CH\(_3\)); 1.6 ppm (s, 3H; CH\(_3\)-C-Ar); 2.66 ppm (s, 3H; CH\(_3\)-CO-Ar); 3.49 ppm (q, 2H; Ar-C-O-CH\(_2\)-CH\(_3\)); 3.96 ppm (s, 3H; CH\(_3\)-O-CO-Ar); 7.35 ppm region (s, H on the new 1,2,3-substituted benzene ring); 7.67 ppm region (s, H on the new 1,4-substituted benzene ring); 7.75 ppm - 8.13 ppm region (H; Ar-CO-O-CH\(_3\) and Ar-CO-CH\(_3\)).

IR: 3040-3043 cm\(^{-1}\) (C-H stretch on aromatic ring); 2980-2940 cm\(^{-1}\) (C-H stretch for CH\(_3\) and CH\(_2\)); 1720.6 cm\(^{-1}\) (C=O stretch for benzoate esters); 1682 cm\(^{-1}\) (C=O stretch for the ketone group conjugated with the phenyl groups); 1604.9 cm\(^{-1}\) (C = ring stretch); 1273, 1217 cm\(^{-1}\) (C-O asymmetric and symmetric coupled vibrations for C-CO-O groups conjugated with the phenyl groups). 880 cm\(^{-1}\) (w, Isolated H on 1,3,5-substituted benzene ring); 825.6 cm\(^{-1}\) (s, two adjacent H on 1,4-substituted benzene ring).

III.1.3. Characterization of High Molecular Weight Polymer

IR: 3031 cm\(^{-1}\) (C-H stretch on aromatic ring); 2948 cm\(^{-1}\) (C-H stretch for CH\(_3\) and CH\(_2\)); 1720 cm\(^{-1}\) (C=O stretch for benzoate esters); 1600 cm\(^{-1}\) (C = ring stretch); 1278, 1217 cm\(^{-1}\) (C-O asymmetric and symmetric coupled vibrations for C-CO-O groups conjugated with the phenyl groups). 880 cm\(^{-1}\) (w, isolated H on 1,3,5-substituted
benzene ring); 825 cm\(^{-1}\) (s, two adjacent H on 1,4-substituted benzene ring).

**III.1.4. Characterization of Prepolymers Before and After Curing**

After curing, the absorbance of the ketone groups (1684 cm\(^{-1}\), C=O stretch conjugated with the phenyl ring) disappeared from the prepolymer spectra. The other peaks remained the same as III.1.2.

**III.1.5. Characterization of Modified Polymer Film on NaCl Plates**

After chemical modification, a set of new IR bands were formed as following:

\[
\text{IR:} \quad 1697.5 \text{ cm}^{-1} (\beta\text{-diketone stretch, doublet}); 1699.4 \text{ cm}^{-1} (\beta\text{-triketone stretch, triplet}); 2925 \text{ cm}^{-1} (\text{CH}_2 \text{ stretch}).
\]

**III.1.6. Analysis of Mono- and Bi-Pd(II) Uptake on the Modified Polymer Supports**

\[
\text{IR:} \quad 1653.1 \text{ cm}^{-1} \ (\text{Pd(II)-} \beta\text{-diketone stretch, doublet}); 1699.4 \text{ cm}^{-1} \ (\text{Pd(II)-} \beta\text{-triketone stretch, triplet})
\]

**III.2. The Quantitative Analysis of Pd(II) Ion Uptake on Supports**

The method of quantitative analysis of Pd(II) ion in the residual solution was a standard gravimetric procedure using dimethylglyoxime. Since the amount of the initial Pd(0) used in the experiment was known precisely, the difference between this initial value and residual quantity in the solution gives the amount taken up by the polymer supports.
### III.3. Organic Syntheses by Supported Mono- and Bi-Pd(II) Catalysts

#### III.3.1. Propylene Oxidation by Mono- and Bi-Pd(II) Catalysts in De-ionized Water

According to TLC results, acetone is the only product of propylene oxidation catalyzed with bi-Pd(II) species on pure high polymer or on celite. The $R_f$ value of the 2,4-dinitrophenyl hydrazine derivative is 0.16 with methylene chloride as the eluting solvent. This derivative was further identified by proton NMR. Two single signals at $d$ 2.09 and 2.18 indicated the two isomers of the acetone 2,4-DNP derivative.

Acetone-2,4-DNP derivative: $2.09 \text{ ppm (s, 3h); } 2.18 \text{ ppm (s, 3H); } 7.95-7.99 \text{ ppm (d, 1H); } 8.28 \text{ ppm (d, 1H); } 9.15 \text{ ppm (d, 1H).}$

For propylene oxidation catalyzed by the mono-Pd(II) species on the pure high polymer or celite, no enough products could be accumulated before the mono-Pd(II) catalyst decomposed.

#### III.3.2. 4-Penten-1-ol Oxidation by Mono- and Bi-Pd(II) Catalysts in De-ionized Water

For the 4-penten-1-ol oxidation reaction catalyzed with bi-Pd(II), two products were found according to the TLC analysis. By comparison with standard GC-MS...
spectra, 4-pentenal and 5-hydroxyl-2-pentanone were identified as reaction products. The ratio of 4-pentenal and 5-hydroxyl-2-pentanone was 47 to 10. Therefore, the C=C double bond was oxidized by the bimetallic-Pd(II) catalyst to form ketones by the ordinary Wacker Process.

For 4-penten-1-ol oxidation reaction catalyzed with mono-Pd(II), the GC-MS spectrum of 4-pentenal was found. The mono-Pd(II) catalyst was found to be readily decomposed in this reaction system.

**III.3.3. Ethylene Oxidation by Mono- or Bi-metallic Pd(II) Catalyst in Acetic Acid**

In the ethylene oxidation catalyzed by mono-Pd(II) catalyst in acetic acid, GLC indicated that the only product was vinyl acetate whose retention time was 5.95 minutes under the GC conditions. This result was confirmed by the $^1$H NMR spectrum:

Vinyl acetate: 2.10 ppm (s, 3H); 4.65 and 4.86 ppm (two d, 2H, vinylic);

7.28 ppm.(q, 1H).

In the reaction catalyzed by bi-metallic Pd(II) catalyst in acetic acid, three products were detected by GC. Their retention times were 3.80, 4.39, and 5.50 minutes under our GC conditions. Those products were identified as ethylidene diacetate, ethylene glycol diacetate, and ethylene glycol monoacetate by comparison with authentic samples. The ratios of the ethylidene diacetate to ethylene glycol diacetate to ethylene glycol monoacetate were 0.08 to 1 to 0.03. Therefore, the major product of the ethylene oxidation catalyzed in acetic acid was ethylene glycol diacetate. This identification was confirmed by the $^1$H NMR.
Ethylene glycol diacetate: 1.91 ppm (s, 6H); 4.12 ppm (s, 4H).

The kinetics of the ethylene oxidation was studied as described in II.1. In the present work, since none of the reactant concentrations changed during the course of a run, the reactions were pseudo zero order. Thus, the olefin uptake was linear with time until all the quinone had been reduced or the polymer supported Pd(II) catalysts had decomposed. From the rate of linear uptake the rate constant of Equation I-10 can readily be calculated from the known concentration of reactants. The data for olefin oxidation in acetic acid are summarized in Table 2.

**Table 2 Rate Constants for Olefin Oxidation in Acetic Acid**

<table>
<thead>
<tr>
<th>Catalyst Type</th>
<th>Substrate</th>
<th>$k_{obs}$ $^c$ (M$^{-1}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monometallic Pd(II)</td>
<td>Ethylene</td>
<td>0.0194</td>
</tr>
<tr>
<td>Bimetallic Pd(II)</td>
<td>Ethylene</td>
<td>0.0297</td>
</tr>
<tr>
<td>Monometallic Pd(II)</td>
<td>Propylene</td>
<td>0.0094</td>
</tr>
<tr>
<td>Bimetallic Pd(II)</td>
<td>Propylene</td>
<td>0.0137</td>
</tr>
</tbody>
</table>

$^a$ P-Quinone is used as re-oxidant. Concentration of this oxidant is 0.20 M.

$^b$ All runs at 25°C under 1 atm of olefin pressure.

$^c$ The $k_{obs}$ were calculated by pseudo first order reaction to the substrates and to the total [Pd(II)] in the mono- or bi-metallic catalyst.

III.3.4. *Propylene Oxidation by Mono- and Bi- Pd(II) Catalysts in Acetic Acid Using Benzoguinone as Re-oxidant*

In the propylene oxidation catalyzed by the mono-Pd(II) species in acetic acid, a large product peak ($t_R=9.70$ min.) was found in the GC trace. This peak contained two products which cannot be separated under the GC conditions. The peak was collected and
both products were identified by $^1$H NMR spectra. One product was isopropenyl acetate, the other product was allyl acetate. The ratio of those two products was 2.7.

Isopropenyl acetate: $1.94$ ppm (s, 3H), $2.15$ ppm (s, 3H), and $4.75$ ppm (d, 2H).

Allyl acetate: $2.10$ ppm (s, 3H), $4.58$ ppm (d, 2H), $5.30$ ppm (2 x d, 2H), $5.95$ (m, 1H).

For bi-metallic Pd(II) catalysis in the acetic acid, four product peaks were found by GC analysis. Their retention times were 3.73, 5.70, 7.82, and 9.80 minutes in the GC condition respectively. The first peak contained the same two products described above. The other products, which had high boiling points, will need to be further studied by $^1$H NMR. The kinetic data were shown in Table 2.

**III.3.5. Cyclohexene Oxidation by Mono- and Bi-Pd(II) Catalysts in Acetic Acid**

In the cyclohexene oxidation catalyzed by mono-Pd(II) catalyst in acetic acid, only one product peak was detected by GC. Its retention time was 22.9 minutes under the GC conditions. The $^1$H NMR signals confirmed that this product is 2-cyclohexene-1-yl acetate.

2-cyclohexene-1-yl acetate: $1.61$ ppm (m, 2H), $1.75$ ppm (m, 2H), $1.99$ ppm (m, 2H), $2.06$ ppm (s, 3H), $J_{1,2}=3.6$ Hz; $5.20$ ppm (m, 1H), $J_{2,3}=10.1$Hz), $5.70$ ppm (m, 1H); $5.90$ ppm (m, 1H),

In the cyclohexene oxidation catalyzed by the bi-Pd(II) catalyst, the main product was also 2-cyclohexen-1-yl acetate, which was collected by preparative GC and analyzed
by $^1$H NMR as described above. The higher boiling point products were also collected by preparative GC. By comparison with the standard samples and $^1$H NMR spectra, the main high boiling point product was cis-1,2-cyclohexyl-diacetate and a trace amount of product was trans-1,2-cyclohexyl-diacetate. The ratio of two products was 14 to 1.

- **Cis-1,2-cyclohexyl-diacetate:** 1.46 ppm (t, 2 x 4 H); 1.67 ppm (t, 2 x 2H); 2.08 ppm (s, 2 x 3 H); 5.03 ppm (d, 2 x 1 H).

- **Trans-1,2-cyclohexyl-diacetate:** 1.46 ppm (t, 2 x 4 H); 1.67 ppm (t, 2 x 2H); 2.08 ppm (s, 2 x 3 H); 4.81 ppm (two d, 2 x 1H).

### III.3.6. Ethylene Oxidation by Mono-and Bi-Pd(II) Catalysts in Acetic Acid Using Cupric Chloride as Re-Oxidant

Without lithium chloride, the heterogeneous mono- and bi-Pd(II) catalyst easily decomposed before enough amount of products was accumulated in the ethylene oxidation catalyzed by mono- or bi-Pd(II) catalyst in acetic acid.

With lithium chloride, three products were detected by GC. Their retention times were 7.40, 34.25, and 39.5 minutes. Those products were collected and identified by $^1$H NMR. The identification of NMR signals of the products is shown below:

- **Vinyl acetate:** 2.10 ppm (s, 3H); 4.65 and 4.86 ppm (two d, 2H, vinylic); 7.28 ppm (q, 1H).

- **2-chloroethyl acetate:** 2.16 ppm (s, 3H); 3.67 ppm (t, 2H); 4.30 ppm (t, 3H).

- **Ethylene glycol diacetate:** 2.03 ppm (s, 6H); 4.22 ppm (s, 4H).
The ratio of vinyl acetate to 2-chloro-ethyl diacetate to ethylene glycol diacetate was 0.044 to 0.3 to 1 according to the GC spectra.

Since the soluble \([\text{Cl}^+\)]\ in the reaction mixture was unknown, only the initial rate of the ethylene oxidation by the mono-Pd(II) catalyst are obtained in acetic acid with \(\text{CuCl}_2\) and \(\text{LiCl}\) according to the Equation I-3. The kinetic data are given in Table III.3.

**Table 3 Initial Rate of Ethylene Oxidation in Acetic Acid with \(\text{CuCl}_2\) and \(\text{LiCl}\)**

<table>
<thead>
<tr>
<th>Catalyst Type</th>
<th>Substrate</th>
<th>Initial Rate (Mh(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monometallic Pd(II)</td>
<td>Ethylene</td>
<td>0.00206</td>
</tr>
</tbody>
</table>

\(\text{a}\) Cupric chloride is used as re-oxidant. Concentration of this oxidant is 1.0 \(M\). Concentration of \(\text{LiCl}\) is 2.0 \(M\).

\(\text{b}\) All runs at 25\(^\circ\)C under 1 atm of olefin pressure.

\(\text{c}\) The \(k_{\text{obs}}\) were calculated by pseudo first order reaction to the substrates and to the total \([\text{Pd(II)}]\) in the mono- or bi-metallic catalyst.

**III.3.7. Ethylene Oxidation by Mono- and Bi-Pd(II) Catalyst in Methanol**

In the ethylene oxidation catalyzed by mono- or bi-Pd(II) species in methanol, the only product found was acetaldehyde dimethyl acetal by GC detection. The retention time was 3.70 minutes under the GC conditions used. This result was confirmed by the \(^1\text{H}\) NMR spectrum. In addition, formaldehyde was identified by its 2,4-DNP derivative.

Acetaldehyde dimethyl acetal: 3.31 ppm (s, 3H); 4.86 ppm (d,3H);

\[4.60 \text{ ppm (m,1H)}\]

Formaldehyde-2,4-DNP: 7.8 ppm (two s, 1H); 9.2 ppm (s, 1H).

As previously, the kinetic data for ethylene oxidation in methanol were given in Table 4.
Table 4 Rate Constants for Ethylene Oxidation in Methanol

<table>
<thead>
<tr>
<th>Catalyst Type</th>
<th>Substrate</th>
<th>(k_{obs}) (M(^{-1})s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monometallic Pd(II)</td>
<td>Ethylene</td>
<td>0.00206</td>
</tr>
<tr>
<td>Bimetallic Pd(II)</td>
<td>Ethylene</td>
<td>0.00391</td>
</tr>
</tbody>
</table>

\(\rho\)-Quinone is used as re-oxidant. Concentration of this oxidant is 0.20 M.

All runs at 25\(^\circ\)C under 1 atm of olefin pressure.

The \(k_{obs}\) were calculated by pseudo first order reaction to the substrates and to the total [Pd(II)] in the mono- or bi-metallic catalyst.

III.3.8. *Propylene Oxidation by Mono- or Bi-Pd(II) Catalysts in Water/THF Using Cupric Chloride as Re-Oxidant*

The same GC spectra were obtained from the propylene oxidation catalyzed with mono- or bi-Pd(II) catalyst. The first broad peak (\(t_R = 1.1\) min.) consisted of two isomers which could not be separated completely under the GC conditions used. They were identified as 2-chloro-1-propanol and 1-chloro-2-propanol. The ratio of 2-chloro-1-propanol to 1-chloro-2-propanol was 1 to 5.5. A second broad peak (\(t_R = 15.5\) min.) was identified as acetol.

\(^1\)H NMR:

1-chloro-2-propanol: 1.27 ppm and 1.30 ppm (d, 3H); 2.18 ppm (s, 1H); 3.45 to 3.63 ppm (m, 2H); 4.00 ppm (m, 1H).

2-chloro-1-propanol: 1.50 ppm and 1.52 ppm (d, 3H); 2.18 ppm (s, 1H); 3.64 ppm (m, 2H); 4.15 ppm (m, 1H).

Acetol: 2.33 ppm (s, 3H); 2.47 ppm (s, 1H); 4.09 ppm (s, 2H).

The relevant rate constants were presented in Table 5.
Table 5 Rate Constants for Propylene Oxidation in Solvent Mixture

<table>
<thead>
<tr>
<th>Catalyst Type</th>
<th>Substrate</th>
<th>$k_{obs}$ (M$^{-1}$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monometallic Pd(II)</td>
<td>Propylene</td>
<td>0.0673</td>
</tr>
<tr>
<td>Bimetallic Pd(II)</td>
<td>Propylene</td>
<td>0.0748</td>
</tr>
</tbody>
</table>

\[ \text{Cupric chloride is used as re-oxidant. Concentration of this oxidant is 2.5 M.} \]
\[ \text{Mixture solvent consists of THF and water at the volumetric ratio of 50 to 50.} \]
\[ \text{All runs at 25°C under 1 atm of olefin pressure.} \]
\[ \text{The } k_{obs} \text{ were calculated by pseudo first order reaction to the substrates and to the total [Pd(II)] in the mono- or bi-metallic catalyst.} \]

**IR, FT-IR and NMR spectra:** See Appendix.
CHAPTER IV
DISCUSSION

IV.1. Analyses of Polymer Supported Mono- and Bi-Pd(II) Catalysts

IV.1.1. Prepolymer

The mole ratio of 4-acetyl methylbenzoate and 1,4-diacetyl benzene in the copolymer was measured by $^1$H NMR integration. This ratio was determined not only by the mole ratio of the starting monomers, but also by the flow rate of the HCl gas, concentration of triethyl orthoformate and polymerization time. The prepolymers were mixed to give known compositions before coating the prepolymers on celite or NaCl plates. Since double bond groups exist in the prepolymer chain, the possible mechanism for the polymerization is shown in Scheme IV-1 (next page).

IV.1.2. Curing Prepolymer

The prepolymer contains ester groups (1720.19 cm$^{-1}$, C=O stretch conjugated with the phenyl ring) and ketone groups (1684 cm$^{-1}$, C=O stretch conjugated with the phenyl ring). According to the FT-IR spectra, almost all of the ketone groups disappeared and the ester group still remained after curing. The ester group, a potential modification site, was not destroyed during the curing process.\textsuperscript{152,153,163}
IV.1.3. \textit{High Molecular Weight Polymer}

The FT-IR spectra of the high molecular weight polymer indicated that most of the C=O stretch (1684 cm\(^{-1}\)) in the ketone group conjugated with the phenyl ring disappeared and that of the ester group (1720.19 cm\(^{-1}\)) was not affected during polymerization.\textsuperscript{153, 154,}
IV.1.4. **Modification of Polymer and Polymer Film Cured on NaCl Plates**

After modification to give \( \beta \)-diketone and \( \beta \)-triketone groups on the prepolymer, polymer and cured polymer on NaCl plates, the IR and FT-IR spectra showed that the ester groups on the aromatic rings (1720.6 cm\(^{-1}\) C=O stretch for benzoate esters) decreased. They were replaced by a group of new bands at around 1697.5 cm\(^{-1}\) (doublet) attributed to the \( \beta \)-diketone and 1699.4 cm\(^{-1}\) (triplet) attributed to \( \beta \)-triketone. There was also a new \( \text{CH}_2 \) stretching band that appeared at 2925 cm\(^{-1}\). The peak intensities indicated that more diketone groups were placed on the polymer than triketone groups. IR results indicated that, under similar conditions, the modification procedure for introduction of \( \beta \)-diketone and \( \beta \)-triketone in solution can be used on solid surfaces. The \( \beta \)-diketone and \( \beta \)-triketone groups have been placed on the prepolymer, high polymer, and cured polymer film on NaCl plates using the chemical modification procedure.\(^{164}\)

IV.1.5. **Mono- and Bi-Pd(II) Uptake on the Modified Supports**

After Pd(II) ion uptake, a new triplet peak (around 1653.1) cm\(^{-1}\) attributed to the bimetallic Pd(II)-\( \beta \)-triketone complex and a doublet peak (around 1653.1) attributed to the monometallic Pd(II)-\( \beta \)-diketone complex appeared. The wavenumber shifted down 44.4 - 46.3 cm\(^{-1}\) from the uncomplexed triketone (1699.4 cm\(^{-1}\)) and diketone (1697.5 cm\(^{-1}\)).\(^{165}\) Thus Pd(II) have been successfully coordinated with \( \beta \)-diketone and \( \beta \)-triketone groups on the prepolymer, high molecular weight polymer and polymer film on celite or NaCl plates.
IV.2. **The Analysis of Pd(II) Uptake on Supports**

The quantities of Pd(II) uptake on the surface ligands were 0.94 for mono-Pd(II) on polymer, 1.56 mmole per gram for bi-Pd(II) on polymer; 0.064 mmole per gram for mono-Pd(II) on celite and 0.11 mmole per gram for bi-Pd(II) on celite. The theoretical ratio of bi-Pd(II) to mono-Pd(II) on the support is 2. The real ratios of bi-Pd(II) to mono-Pd(II) were 1.66 on the polymer and 1.71 on the celite. These results were reasonable because the FT-IR peak intensities indicated that more diketone groups were placed on the supports than triketone groups.

IV.3. **Organic Syntheses by Supported Mono- and Bi-Pd(II) Catalysts**

IV.3.1. *Propylene Oxidation in De-ionized Water*

Propylene oxidation by bi-Pd(II) species in water gave acetone. These results are expected in a Wacker-type oxidation. The possible mechanism is shown in Equation IV-1.

For propylene oxidation catalyzed by the mono-Pd(II) species on the pure high polymer or celite, the mono-Pd(II) catalyst was decomposed as evidenced by the bulk grey Pd(0) precipitate before enough products could be collected. Thus the mono-Pd(II) species are less stable than the bi-Pd(II) species.

IV.3.2. *4-Penten-1-ol Oxidation in De-ionized Water*

As discussed in IV-3.1, for the 4-pentene-1-ol oxidation, the double bond C=C was oxidized to form the ketone group C=O by the Wacker-type oxidation. The hydroxyl OH
group was oxidized to produce aldehyde groups by mono- and bi-Pd(II) catalysts as discussed in Introduction.

IV.3.3. Olefin Oxidation in Acetic Acid

In the olefin oxidation in acetic acid using benzoquinone as re-oxidant, the mechanism of the mono-Pd(II) catalysis was the expected Wacker type as discussed in the Introduction. Only unsaturated products, such as vinyl, isopropenyl, allyl and cyclohexenyl acetate, were produced.\textsuperscript{125, 126, 166}
With the bi-Pd(II) catalysis, saturated products, such as ethylene glycol diacetate, ethylene glycol monoacetate, cis-1,2-cyclohexyl diacetate and trans-1,2-cyclohexyl diacetate, were formed. These bi-Pd(II) catalysis results can be explained by the cooperative action between two Pd(II)s in the bi-Pd(II) species. The saturated products were formed because Pd(I) dimers are good leaving groups so this route is preferred over \(\beta\)-elimination. The detailed catalytic routes for ethylene oxidation are outlined in Scheme IV-2 on the next page. There is no such cooperative action in the mono-Pd(II) species. For that reason, the olefin substrates can only react through \(\beta\)-elimination by the mono-Pd(II) catalyst to give unsaturated products.

Since Pd(I)-Pd(I) dimers are good leaving groups the formation of saturated esters compete with the \(\beta\)-elimination pathway to give the unsaturated esters. The final ratio of saturated esters to unsaturated esters is determined by the competition of those two reaction mechanisms. Thus, in addition to the saturated products, isopropenyl acetate, allyl acetate and 2-cyclohexene-1-ol acetate were formed in propylene and cyclohexene oxidation by the bi-metallic Pd(II) catalyst in acetic acid using benzoquinone as re-oxidant.

**IV.3.4. Olefin Oxidation in Acetic Acid Using Cupric Chloride as Re-Oxidant**

The heterogeneous Pd(0) is not readily re-oxidized to Pd(II) in the solid phase reaction. Without lithium chloride, the concentration of soluble Cu(II) in the acetic acid is very low. Therefore, the heterogeneous mono- and bi-Pd(II) catalysts easily decomposed during the olefin oxidation if cupric chloride is used as the only re-oxidant.
Scheme IV-2

\[
\text{Pd}^{	ext{II}} \text{Pd}^{	ext{II}} + \text{OAc}^{-} \rightarrow \text{Pd}^{	ext{II}} \text{Pd}^{	ext{II}} + \text{AcOCH}_2\text{CH}_2\text{OAc}
\]
In this situation, no significant amount of products was detected in the ethylene oxidation catalyzed by mono- or bi-Pd(II) catalyst in acetic acid in the absence of LiCl.

With lithium chloride,\textsuperscript{167} the concentration of the soluble Cu(II) in acetic acid was increased. However, besides vinyl acetate, 2-chloroethyl acetate and ethylene glycol diacetate were formed in ethylene oxidation by mono-Pd(II). These results are expected for the normal Pd(II) chemistry involving oxypalladation adducts as intermediates. CuCl$_2$ can interact with the intermediates to remove two electrons from the Pd(II) and the adducts decompose by a carbonium ion pathway to give saturated products.\textsuperscript{168}

**IV.3.5. Propylene Oxidation in Water /THF Using Cupric Chloride as Re-Oxidant**

In the presence of cupric chloride, the mechanism most consistent with Pd(II) chemistry is oxypalladation, followed by reaction of the oxypalladation adduct with cupric chloride to produce the saturated esters. Therefore, with Cu(II) there is no advantage for the bi-Pd(II) species in olefin oxidation because saturated products are produced even with the monometallic catalyst. This mechanism would compete with decomposition by $\beta$-elimination to give unsaturated products. The concentration of soluble Cu(II) will mainly determine the reaction. In aqueous solution using cupric chloride as re-oxidant, 2-chloro-1-propanol, 1-chloro-2-propanol and acetol were obtained from propylene oxidation catalyzed by both mono- and bi-metallic-Pd(II) catalysts. The reaction pathway for the supported Pd(II) catalyst is the same as in the homogeneous system.\textsuperscript{169}
IV.3.6. **Ethylene Oxidation in Methanol**

In the ethylene oxidation catalyzed by mono- or bi-Pd(II) species in methanol, acetaldehyde dimethyl acetal is expected in a Wacker-process.\textsuperscript{106} Those results indicate that both mono- and bi-Pd(II) species have the same behavior in methanol since the dielectric constant of methanol is much higher than that of acetic acid. That is, the cooperation between two Pd(II)s in bi-Pd(II) species disappears in high dielectric constant media.

IV.3.7. **Stereochemistry of Bi-Pd(II) Catalysis**

In the cyclohexene oxidation by the bi-Pd(II) catalyst, the main saturated product was cis-1,2-cyclohexan-diacetate and a trace product was trans-1,2-cyclohexan-diacetate. The ratio of the two products was 14 to 1. The possible mechanism is shown in Scheme IV-3 on the next page.

IV.4. **Kinetic Studies**

The complete rate expression for the oxidation of olefins catalyzed by polymer supported mono- and bi-Pd(II) catalysts in chloride-free acetic acid using $p$-benzoquinone as reoxidant is described in equation I-10. The overall rate constant $k_{\text{obs}}$ of the ethylene oxidation catalyzed by the polymer supported mono-Pd(II) catalyst was 0.0194 M\textsuperscript{-1}s\textsuperscript{-1} at 25°C. The overall rate constant $k_{\text{obs}}$ of the propylene oxidation by the mono-Pd(II) catalyst was 0.0094 M\textsuperscript{-1}s\textsuperscript{-1}. In contrast, the overall rate constant $k_{\text{obs}}$ of the ethylene and propylene oxidation catalyzed by the polymer supported bi-Pd(II) catalyst were 0.0297 M\textsuperscript{-1}s\textsuperscript{-1} and 0.0137 M\textsuperscript{-1}s\textsuperscript{-1} at 25°C respectively. Ethylene is more reactive than propylene so that the
Scheme IV-3

\[
\text{\text{Pd}^{\text{II}}} \quad \text{\text{Pd}^{\text{II}}} + \text{\text{OAc}^-} \quad \text{\text{Pd}^{\text{II}}} \quad \text{\text{Pd}^{\text{II}}} \quad \text{\text{OAc}^-}
\]

\[
\text{\text{OAc}} \quad \text{\text{OAc}} \quad \text{\text{OAc}}
\]

\[
\text{\text{cAO} \quad \text{\text{OAc}}} \quad \text{\text{cAO} \quad \text{\text{OAc}}} \quad \text{\text{cAO} \quad \text{\text{OAc}}}
\]

\[
\text{\text{Pd}^{\text{II}}} \quad \text{\text{Pd}^{\text{II}}} \quad \text{\text{OAc}} \quad \text{\text{Pd}^{\text{II}}} \quad \text{\text{Pd}^{\text{II}}} \quad \text{\text{OAc}} \quad \text{\text{Pd}^{\text{II}}} \quad \text{\text{Pd}^{\text{II}}} \quad \text{\text{OAc}}
\]

\[
\text{\text{Pd}^{\text{II}}} \quad \text{\text{Pd}^{\text{II}}} \quad \text{\text{OAc}} \quad \text{\text{Pd}^{\text{II}}} \quad \text{\text{Pd}^{\text{II}}} \quad \text{\text{OAc}} \quad \text{\text{Pd}^{\text{II}}} \quad \text{\text{Pd}^{\text{II}}} \quad \text{\text{OAc}}
\]
former rate constant is larger than the latter in the same reaction conditions. It is difficult to compare the rate constants of the olefin oxidations between the polymer supported mono- and bi-Pd(II) catalysts because of different reaction mechanisms. However the rate constant of the ethylene oxidation catalyzed by the supported mono-Pd(II) catalyst in acetic acid is about 10 times faster than that of the homogeneous Pd(II) catalyzed one in the similar reaction, which was calculated to be 0.0019 M\(^{-1}\)s\(^{-1}\) from the literature data.\(^{96}\)

The initial rate of ethylene oxidation by the 0.0535 g (0.0503 mmole) of the mono-Pd(II) in acetic acid with 1.0M CuCl\(_2\) and 2.0 M LiCl was 0.0000857 Mh\(^{-1}\). The rate constant \(k_{\text{obs}}\) of the ethylene oxidation by the supported mono- and bi-Pd(II) catalysts in methanol were 0.00206 and 0.00391 M\(^{-1}\)s\(^{-1}\) at 25°C respectively. The values of \(k_{\text{obs}}\) for the propylene oxidation by the supported mono- and bi-Pd(II) catalysts in water and THF solvent mixture were 0.00206 and 0.00391 M\(^{-1}\)s\(^{-1}\). These kinetic data cannot be easily compared with those obtained from the literature of homogeneous reactions because of different rate expressions and different solvent systems.\(^{106, 108, 111, 112, 155, 168, 169, 170}\)
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