Chapter 3

Aerobic Oxidation of Benzyl Alcohols

$R_1 = H, 4-\text{NO}_2, 3-\text{OMe}, 4-\text{Br, 4-Cl, 2-Br, 4-Me, 2,4-OMe, 2,5-OMe, 4-OMe}$

$R_2 = H \& \text{Me}$
3.1 Introduction:
Oxidation of organic compounds is important and widely used reaction in organic chemistry [Tsuji (2000)]. Among various oxidation reactions, oxidation of alcohols (Figure 1) is a fundamental organic transformation in synthetic organic chemistry [Hudlicky (1990); Larock (1999); Smith and March (2001)] since carbonyls have huge industrial applications as solvents, perfumes, intermediates in the manufacture of dyes and in pharmaceuticals [Pillai and Sahle-Demessie (2003)].

![Figure 1. General Scheme for the oxidation of alcohols](image)

Traditionally, stoichiometric oxidants having transition metals notably chromium based reagents (such as PCC, PDC etc.) [Lee and Spitzer (1970), Cainelli and Cardillo (1984); Muzart (1992)], permanganates [Regen and Koteel (1977); Menger and Lel (1981)], ruthenium (VIII) oxide [Berkowitz and Rylander (1958); Griffith (1992)], DMSO-coupled reagents [Mancuso and Swern (1981)], Dess-Martin periodinane [Dess and Martin (1983)], tert-butylhydroperoxide [Krohn et al.(1996)] and TPAP/NMO system [Ley et al. (1994)] are used to affect the oxidation of alcohols which are often toxic and demonstrate poor atom efficiency and their use causes significant environmental issues which render them impractical. For this reason, there has been a strong move toward the development of catalytic reactions using benign oxidizing reagents.

3.2 Different metal catalyzed protocols using green oxidants:
From economical and environmental viewpoint, there is a definite need for catalytic oxidation reactions that use dioxygen ($O_2$) or hydrogen peroxide as oxidants. The use of oxygen has great benefits from both economic and green chemistry viewpoints in oxidation reactions because oxygen is relatively cheap and produce water as the only by product. In this context, significant progress has been made in the field of transition metal catalyzed oxidations [Chen et al. (2010); Ji et al. (2007); Li et al. (2007); Kockritz et al. (2006)]
particularly utilizing molecular oxygen as green oxidant. The catalysts including heterogenized complexes, mixed oxides and nanoparticles, containing transition metals such as vanadium [Jiang and Ragauskas (2007)], cobalt [Sharma et al. (2003)], copper [Marko et al. (1996)], ruthenium [Yamaguchi and Mizuno (2002)], palladium [Jensen et al. (2003)], platinum [Wang et al. (2007)], iron [Martin and Suarez (2002)] etc. have been screened for oxidation reactions. Among them, palladium based catalysts have very interesting and promising catalytic activity and different types of palladium based homogeneous and heterogeneous catalysts in the form of metal complexes or nanoparticles have been developed for oxidation reactions which are discussed in details as below:

3.2.1 Homogeneous palladium-catalyzed aerobic oxidation of alcohols:

Oxidation of primary and secondary allylic and benzylic alcohol to aldehyde and ketone has been achieved [Peterson and Larock (1998)] using catalytic Pd(OAc)$_2$ in dimethyl sulfoxide (DMSO) with oxygen gas as the sole oxidant. Nishimura et al. have described an improved system of simple combination of commercially available reagents, Pd(OAc)$_2$/pyridine/MS3A$^\circ$ for aerobic oxidation of benzylic and aliphatic alcohols using O$_2$ [Nishimura et al. (1999)]. This approach could also be employed using catalytic amount of a novel perfluoroalkylated-pyridine as a ligand in a fluorous biphasic system (FBS) composed of toluene and perfluorodecalin [Nishimura et al. (2000)]. The fluorous phase containing the active palladium species reused several times without significant loss of catalytic activity. Further Schultz et al. have developed a convenient aerobic alcohol oxidation using Pd(OAc)$_2$/TEA system at room temperature and found that triethylamine (TEA) is best additive or base for oxidation than pyridine. The initial mechanistic studies provided evidence that the active catalyst may be a palladium complex of TEA (Scheme 1) [Schultz et al. (2002)].

![Scheme 1. Palladium-catalyzed aerobic oxidation of alcohols](image)

Brink et al. have demonstrated that water-soluble complexes of palladium (II) with phenanthroline derivatives are stable and recyclable catalysts for the selective aerobic
Application of solid supported

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oxidation of a wide range of alcohols in a biphasic liquid-liquid system and the active
catalyst found to be a dihydroxy-bridged palladium dimer (Scheme 2) [Brink et al. (2002)].

\[
\begin{align*}
R_1 OH &\xrightarrow{\text{PhenS*Pd(OAc)}_2\text{, air, NaOAc, H}_2\text{O}} R_1 \text{O} \\
R_1 &= \text{alkyl, aryl} \\
R_2 &= H, \text{CH}_3
\end{align*}
\]

**Scheme 2. PhenS*Pd(OAc)_2-catalyzed aerobic oxidation of alcohols**

Buffin et al. have described the application of an aqueous palladium catalyst that is
stabilized by a water-soluble biquinoline-based ligand for the aerobic oxidation of primary
and secondary alcohols in water and air as oxidant. The catalyst system was recycled
(Scheme 3) [Buffin et al. (2005)].

\[
\begin{align*}
R_1 OH &\xrightarrow{\text{Pd(II) biquinoline catalyst, O}_2, \text{NaOAc, H}_2\text{O}} R_1 \text{O} \\
R_1 &= \text{alkyl, aryl} \\
R_2 &= H, \text{CH}_3
\end{align*}
\]

**Scheme 3. Palladium(II)biquinoline catalyzed aerobic oxidation of alcohols**

Steinhoff et al. have studied the effect of molecular sieves on the Pd(OAc)_2/pyridine and
Pd(OAc)_2/DMSO catalytic systems for aerobic oxidation of alcohols. It has been found
that molecular sieves enhance the rate of the Pd(OAc)_2/pyridine-catalyzed oxidation due to
ability of molecular sieves to serve as a bronsted base, but no rate enhancement was
observed for the Pd(OAc)_2/DMSO catalyzed reaction [Steinhoff et al. (2006)]. It has been
observed that both catalytic systems exhibit improved catalytic stability in the presence
of molecular sieves. The performances of palladium complexes with phenanthroline ligands
have been studied for alcohol oxidation in water as well as in water/polar co-solvent
mixtures [Arends et al. (2006)]. The Pd(OAc)_2-neocuproine catalyst has been found
efficient in water or polar co-solvents for oxidation of alcohols and tolerates a wide variety
of functional groups in the alcohol (Scheme 4).

\[
\begin{align*}
R_1 OH &\xrightarrow{\text{Pd (II) neocuproine, air}} R_1 \text{CO} \\
R_1 &= \text{aryl, alkyl} \\
R_2 &= \text{alkyl, aryl} \\
\text{DMSO/ H}_2\text{O} &\quad 80 ^\circ \text{C}
\end{align*}
\]

**Scheme 4. Palladium-neocuproine catalyzed aerobic oxidation of alcohols**
Zhou et al. have investigated the use of palladium-diamine catalyst in the aerobic oxidation of alcohols (Scheme 5). The electronic properties, rigidity and steric hindrance of ligands have remarkable influence upon the catalytic activity of the palladium complexes [Zhou et al. (2008)]. It has been found that the catalyst showed high efficiency for the oxidation of benzylic alcohols than secondary aliphatic and cyclic alcohols.

\[
\begin{align*}
\text{Pd (OAc)}_2 / \text{diamine, O}_2 & \quad \text{R}_1 = \text{aryl, alkyl} \\
\text{K}_2\text{CO}_3, \text{DMA} & \quad \text{R}_2 = \text{alkyl, aryl} \\
100 \, ^\circ \text{C}
\end{align*}
\]

**Scheme 5. Palladium-diamine catalyzed aerobic oxidation of alcohols**

Water-soluble palladium nanoparticles stabilized by the functionalized-poly(ethylene glycol) [Feng et al. (2010)] as a protective ligand has been demonstrated for aerobic oxidation of alcohols (Scheme 6). UV/Vis and XPS study proved the electronic interactions between the bidentate nitrogen ligand and palladium atoms. It has been found that both the size and surface properties of palladium nanoparticles are important in affecting catalytic performance and the catalyst can be recycled at least four times without any loss of catalytic activity.

\[
\begin{align*}
\text{R}_1 \text{OH} & \quad \text{Pd nanoparticles} \\
\text{O}_2, \text{K}_2\text{CO}_3, 80 \, ^\circ \text{C} & \quad \text{R}_2 = \text{H, CH}_3 \\
\end{align*}
\]

**Scheme 6. Aerobic oxidation of alcohols using water soluble palladium nanoparticles**

Palladium pincer complexes have been used as catalysts for aerobic oxidation of secondary benzyl alcohols in PEG-400 and showed good catalytic activity (Scheme 7) [Urgoitia et al. (2011)].

\[
\begin{align*}
\text{R}_1 \text{OH} & \quad \text{Pd pincer complex, O}_2 \\
\text{NaOAc,PEG-400} & \quad \text{R}_2 = \text{alkyl, aryl} \\
120 \, ^\circ \text{C}
\end{align*}
\]

**Scheme 7. Oxidation of secondary benzyl alcohols using palladium pincer complex**

Although homogeneous catalyst (typically a soluble metal complex) acquire the advantage of having all catalytic sites accessible to all reagents. However, their use in industrial
applications is limited by the difficulties encountered in catalyst separation from the final products. To overcome the separation problems encountered in homogeneous catalysis, efforts have been made to develop heterogeneous catalysts which can be easily separated from the reaction mixture and reused several times.

3.2.2 Heterogeneous palladium-catalyzed aerobic oxidation of alcohols:
Kakiuchi et al. have described the aerobic oxidation of primary and secondary alcohols into the corresponding aldehydes and ketones with atmospheric pressure of air under mild conditions in toluene using a heterogeneous Pd(II)-hydrotalcite catalyst (Scheme 8) [Kakiuchi et al. (2001)].

\[
\begin{align*}
&\text{R}_1 \text{OH} \quad \text{Pd(II)hydrotalcite, O}_2 \\
&\text{Pyridine/ Toluene} \\
&\text{R}_1 = \text{aryl, alkyl} \\
&\text{R}_2 = \text{H, alkyl, aryl}
\end{align*}
\]

Scheme 8. Aerobic oxidation of alcohols using palladium hydrotalcite catalyst

Mori et al. have described the formation of palladium hydroxyapatite (PdHAP-0) as a heterogeneous catalyst by grafting of monomeric PdCl\(_2\) species on the surface of stoichiometric hydroxyapatite and its application in aerobic alcohol oxidation (Scheme 9) [Mori et al. (2004)].

\[
\begin{align*}
&\text{R}_1 \text{OH} \\
&\text{PdHAP-0, O}_2 \\
&TFT, 90^\circ \text{C} \\
&\text{R}_1 = \text{aryl, alkyl} \\
&\text{R}_2 = \text{H, alkyl, aryl}
\end{align*}
\]

Scheme 9. Aerobic oxidation of alcohols using palladium hydroxyapatite catalyst

Kwon et al. have prepared a recyclable aluminium hydroxide-supported palladium catalyst by a one-pot synthesis through nanoparticle generation and gelation which have catalytic activity for aerobic alcohol oxidation (Scheme 10) [Kwon et al. (2005)]. A silica-based Pd(II) interphase catalyst having high thermal stability has also been applied for the oxidation of alcohols [Karimi et al. (2005)].

\[
\begin{align*}
&\text{R}_1 \text{OH} \\
&\text{Pd catalyst, O}_2 \\
&Toluene or TFT \\
&80-100 \degree \text{C} \\
&\text{R}_1 = \text{alkyl, aryl} \\
&\text{R}_2 = \text{H, CH}_3, \text{alkyl, aryl}
\end{align*}
\]

Scheme 10. Oxidation of alcohols using supported palladium catalyst with O\(_2\)
Alumina supported palladium (Pd/Al₂O₃) catalyst has been prepared by the adsorption method [Wu et al. (2005)] which results in mononuclear or oligonuclear palladium species stabilized on Al₂O₃ surface after calcination and found to be efficient in the solvent-free selective oxidation of alcohols (Scheme 11). The catalyst was recycled and palladium species transformed to small Pd nanoparticles during the course of oxidation.

Scheme 11. Aerobic oxidation of alcohols using Pd/Al₂O₃

The biphasic aerobic oxidation of alcohols by using palladium nanoparticles in a poly(ethylene glycol) (PEG) matrix as the catalyst and supercritical carbon dioxide (scCO₂) as the substrate and product phase has been established (Scheme 12) [Hou et al. (2005)]. It was observed that the PEG matrix effectively stabilizes and immobilizes the active particles, whereas the solubility and mass-transfer properties of scCO₂ allow continuous processing at mild conditions.

Scheme 12. Aerobic oxidation using PEG stabilized palladium nanoparticles

An efficient and recoverable palladium-based catalyst for the aerobic oxidation of alcohols has been developed [Karimi et al. (2006)]. It has been demonstrated that the combination of an organic ligand and ordered mesoporous channels resulted in an interesting synergistic effect that led to enhanced activity, the prevention of the agglomeration of the Pd nanoparticles and the generation of a durable catalyst. Choudhary et al. have prepared a series of silica-supported palladium catalysts bearing N-N, N-S and N-O chelating ligands for the aerobic oxidation of alcohols [Choudhary et al. (2006)] and found that N-N ligands were highly selective for oxidation without forming over-oxidation products (Scheme 13).

Scheme 13. Aerobic oxidation of alcohols using palladium catalyst
An amphiphilic polystyrene-poly(ethylene glycol) (PS-PEG) resin-dispersion of palladium nanoparticles [Uozumi and Nakao (2003); Uozumi et al. (2007)] has been prepared by Uozumi et al. and the catalytic oxidation of alcohols has been achieved in water under atmospheric pressure of molecular oxygen (Scheme 14). The catalyst was recycled up to four runs and catalyst leaching into the aqueous phase under the reaction conditions was not observed.

\[
\begin{align*}
&\text{Scheme 14. Aerobic oxidation of alcohols using ARP-Pd} \\
&\text{Chen et al. have prepared SiO}_2\text{-Al}_2\text{O}_3\text{-supported Pd nanoparticles by adsorption of PdCl}_4^{2-}
\end{align*}
\]

ions onto the support followed by calcination and reduction with either hexanol or H\textsubscript{2}. The supported Pd nanoparticles catalyzed the aerobic oxidation of benzyl alcohols under solvent free conditions [Chen et al. (2008)]. The Pd/SiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3} catalyst with appropriate Si/Al ratios showed significantly higher benzyl alcohol conversions than both the Pd/SiO\textsubscript{2} and the Pd/Al\textsubscript{2}O\textsubscript{3}. Hara et al. have synthesized a NiZn-Pd nanocomposite catalyst containing highly stable divalent Pd species by simple intercalation of the anionic Pd(II) hydroxyl complex. The intercalated anionic palladium hydroxide complex rigidly fixed by the strong electrostatic interactions between the NiZn host and anionic Pd(II) species could act as an efficient heterogeneous catalyst for the oxidation of alcohols under an air atmosphere (Scheme 15) [Hara et al. (2009)].

\[
\begin{align*}
&\text{Scheme 15. Pd/SiO}_2\text{-Al}_2\text{O}_3\text{ or Pd/ NiZn catalyzed aerobic oxidation of alcohols} \\
Pd/\text{NiZn, air} &\text{ or } \text{Pd/SiO}_2\text{-Al}_2\text{O}_3, \text{O}_2 \\
&\text{Pd/ NiZn, air} \\
&TFT
\end{align*}
\]

Palladium catalysts supported on TUD-1 mesoporous molecular sieves functionalized with various organosilanes (APS, ATMS, HMDS and MPTMS) have been prepared using a post-synthesis grafting method combined with a metal adsorption-reduction procedure. The catalytic activity has been explored in the solvent-free selective oxidation of benzyl alcohol using molecular oxygen (Scheme 16). Among all the catalysts, 1Pd/1.2APS-TUD
1Pd/1.2APS-TUD catalyzed aerobic oxidation of benzyl alcohols

Palladium-charcoal (Pd/C) has been used as a heterogeneous catalyst along with NaBH$_4$ in aqueous ethanol or methanol and either K$_2$CO$_3$ or KOH as base at room temperature under molecular oxygen or air for oxidation of alcohols (Scheme 17). The catalyst was recycled upto ten times without the loss of activity [An et al. (2010)].

Pd/C catalyzed aerobic oxidation of alcohols

Karimi et al. have demonstrated the efficiency of ionic liquid based PMO material in the production and stabilization of active palladium species for aerobic oxidation of alcohols (Scheme 18). The catalyst was easily recovered and reused even after ten runs [Karimi et al. (2011)]. The hot filtration test, atomic spectroscopy and the results of the effect of poisons have confirmed that the Pd@PMO-IL catalyst operated through a heterogeneous pathway.

Pd@PMO-IL catalyzed aerobic oxidation of alcohols

Nanocrystalline magnesium oxide-stabilized palladium(0) [NAP-Mg-Pd(0)] as an efficient catalytic system has been employed for the selective oxidation of alcohols using atmospheric oxygen as a oxidant at room temperature (Scheme 19). This catalyst was recovered and reused for several cycles without any significant loss of catalytic activity [Layek et al. (2011)].
Scheme 19. NAP-Mg-Pd(0) catalyzed aerobic oxidation of alcohols

The supported palladium catalyst based on ligand functionalized amorphous and ordered mesoporous silica (SBA-15) has been prepared and applied for the oxidation of alcohols [Karimi et al. (2009)]. Recently Zang et al. have prepared mesoporous SBA-15 supported catalyst PdLn@SBA-15 via click route in which the click-triazole acted as a stable linker and good chelator [Zang et al. (2012)]. The obtained solid catalyst demonstrated a promising catalytic activity for the aerobic oxidation of benzyl alcohols (Scheme 20). The catalyst was recovered by simple filtration and reused up to seven cycles with a consistent catalytic activity.

Scheme 20. Aerobic oxidation of benzylic alcohols using PdLn@SBA-15

In view of the above literature precedents, it would be apparent that a majority of the prevalent oxidation approaches employ additives and basic conditions. Although there have been noteworthy efforts to devise more benign oxidation conditions with various improvements, but these have also been found to be constrained by the use of complicated ligands which are not commercially available or require multiple steps for their synthesis. On the other hand, various metal free approaches mainly employ oxidants such as TEMPO or hypervalent iodine based reagents. But the utility of TEMPO mediated system is limited due to its expensiveness and lengthy work up procedures [Jiang and Ragauskas (2005); Mannam et al. (2007); He et al. (2009)]. In this context, it would be highly desirable to develop a mild methodology for oxidation of benzyl alcohols using green oxidants.

Hence, we have investigated the scope of our previously synthesized heterogeneous SS-Pd(0) catalyst in the oxidation of benzyl alcohols to the corresponding aldehydes and ketones using molecular oxygen as the oxidant. Moreover, the catalyst system was recycled up to five runs without significant loss of activity.
3.3 Results and discussion:
Initially concentration based studies of solid supported palladium catalyst were performed to optimize the concentration of palladium required to give best performance of the catalyst for aerobic oxidation of benzyl alcohols. In this regard, solid supported palladium catalysts (SS-Pd) were prepared following our previously described procedure with different concentrations of Pd(OAc)$_2$ on solid surface (5 mg/g and 10 mg/g) and analyzed by scanning electron micrographs (SEM) (Figure 2 and 3). With the change of concentration, no significant particle size changes were observed but 10 mg Pd(OAc)$_2$ on 1 g solid surface gave the best result with good recyclability. Through these studies, we realized that 10 mg/g concentration of catalyst occupied sufficient space of the solid surface which showed highest interaction with the substrate required for heterogeneous catalyst to give high performance of the catalyst. With decrease of concentration (5mg/g) huge space of the solid surface remained unoccupied by the catalyst and decrease the optimal interaction with substrate, thereby, decreasing the rate of reaction.

Figure 2. (a) SS-Pd (10 mg Pd(OAc)$_2$/g solid surface) (b) SEM of SS-Pd (10 mg Pd(OAc)$_2$/g solid surface)

Figure 3. (a) SS-Pd (5 mg Pd(OAc)$_2$/g solid surface) (b) SEM of SS-Pd (5 mg Pd(OAc)$_2$/g solid surface)
The solid surface of the catalyst (SS-Pd) behaves as an interface where liquid and gaseous molecules such as alcohols and oxygen interacted with each other to produce corresponding carbonyls (Figure 4).

![Figure 4](image)

**Figure 4.** Performance of reaction on solid surface of catalyst which act as interface

Using the standard SS-Pd catalyst (10 mg/g), further optimization studies were performed for oxidation of 2-ethoxybenzyl alcohol $\text{1a}$ as the model substrate (Table 1). The progress of reaction was monitored by TLC and GC-MS analysis. From standard SS-Pd catalyst (10 mg/g), different loadings of SS-Pd containing 1-6 mol% palladium with respect to substrate were investigated for the aerobic oxidation of 2-ethoxybenzyl alcohol. Highest turnover number (TON, 2266) and turnover frequencies (TOF, 453 h$^{-1}$) were calculated when SS-Pd (3 mol % Pd) was used for the oxidation reaction of $\text{1a}$ (Table 1, entry 2). However, only 68% yield of $\text{2a}$ was observed by GC-MS analysis. SS-Pd with 5 mol% Pd in toluene afforded 80% yield of $\text{2a}$ and TON/TOF was calculated as 1600/320 h$^{-1}$ (Table 1, entry 3). No further improvement of yield was observed by enhancing the catalyst loading up to 6 mol% Pd (Table 1, entry 4). Different solvents were investigated to see their effect on the product yield. Dioxane and THF were not found to be good solvents under the reaction condition. Moderate yield of product was obtained in benzene and acetonitrile. Among different solvents, toluene gave the best result under standard reaction condition. Comparative studies of different catalytic systems were also performed. The reaction with Pd/C and $\text{Pd}_2\text{C}_6\text{H}_{10}\text{Cl}_2$ gave poor yield of product while moderate yields
were obtained in presence of Pd$_2$(dba)$_3$ and Pd[P(C$_6$H$_5$)$_3$]$_4$. Pd(OAc)$_2$ was also found to be good but the best result was obtained using SS-Pd under the standard reaction condition. Hence SS-Pd (5 mol% Pd) in the presence of toluene was found to be optimum under the reaction conditions.

Table 1. Effect of catalysts and solvents for the oxidation of 2-ethoxybenzylalcohol

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst (mol % Pd)</th>
<th>Solvent</th>
<th>Yield (%)$^a$</th>
<th>TON</th>
<th>TOF h$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SS-Pd (1)</td>
<td>Toluene</td>
<td>11</td>
<td>1100</td>
<td>220</td>
</tr>
<tr>
<td>2</td>
<td>SS-Pd (3)</td>
<td>Toluene</td>
<td>68</td>
<td>2266</td>
<td>453</td>
</tr>
<tr>
<td></td>
<td>i. Toluene</td>
<td></td>
<td>80</td>
<td>1600</td>
<td>320</td>
</tr>
<tr>
<td></td>
<td>ii. THF</td>
<td></td>
<td>9</td>
<td>180</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>iii. Dioxane</td>
<td></td>
<td>3</td>
<td>60</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>iv. C$_6$H$_5$CN</td>
<td></td>
<td>23</td>
<td>460</td>
<td>92</td>
</tr>
<tr>
<td>3</td>
<td>SS-Pd (5)</td>
<td>Toluene</td>
<td>55</td>
<td>1100</td>
<td>220</td>
</tr>
<tr>
<td>4</td>
<td>SS-Pd (6)</td>
<td>Toluene</td>
<td>80</td>
<td>1333</td>
<td>267</td>
</tr>
<tr>
<td>5</td>
<td>Pd(OAc)$_2$ (5)</td>
<td>Toluene</td>
<td>69</td>
<td>1380</td>
<td>276</td>
</tr>
<tr>
<td>6</td>
<td>Pd/C (5)</td>
<td>Toluene</td>
<td>2</td>
<td>40</td>
<td>8</td>
</tr>
<tr>
<td>7</td>
<td>Pd$_2$C$<em>6$H$</em>{10}$Cl$_2$ (10)</td>
<td>Toluene</td>
<td>1</td>
<td>20</td>
<td>4</td>
</tr>
<tr>
<td>8</td>
<td>Pd$_2$(dba)$_3$ (10)</td>
<td>Toluene</td>
<td>20</td>
<td>400</td>
<td>80</td>
</tr>
<tr>
<td>9</td>
<td>Pd[P(C$_6$H$_5$)$_3$]$_4$ (5)</td>
<td>Toluene</td>
<td>39</td>
<td>780</td>
<td>156</td>
</tr>
</tbody>
</table>

$^a$Determined by means of GC, based on the 2-ethoxy benzyl alcohol  
TON = % conversion x mmole of substrate / mmole of catalyst, TOF = TON / time

Further investigations were performed to enhance the scope of oxidation reactions in different substituted primary and secondary benzyl alcohols (Table 2).
Table 2. Oxidation of primary and secondary benzyl alcohols to aldehydes and ketones

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Time (h)</th>
<th>Product</th>
<th>Yield (%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>TON / TOF&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1a</td>
<td>5</td>
<td>2a</td>
<td>78</td>
<td>1560/312</td>
</tr>
<tr>
<td>2</td>
<td>1b</td>
<td>5</td>
<td>2b</td>
<td>96</td>
<td>1963/393</td>
</tr>
<tr>
<td>3</td>
<td>1c</td>
<td>3</td>
<td>2c</td>
<td>70</td>
<td>1400/467</td>
</tr>
<tr>
<td>4</td>
<td>1d</td>
<td>3</td>
<td>2d</td>
<td>90</td>
<td>1800/600</td>
</tr>
<tr>
<td>5</td>
<td>1e</td>
<td>3</td>
<td>2e</td>
<td>80</td>
<td>1600/533</td>
</tr>
<tr>
<td>6</td>
<td>1f</td>
<td>3</td>
<td>2f</td>
<td>83</td>
<td>1660/553</td>
</tr>
<tr>
<td>7</td>
<td>1g</td>
<td>3</td>
<td>2g</td>
<td>85</td>
<td>1700/567</td>
</tr>
<tr>
<td>8</td>
<td>1h</td>
<td>5</td>
<td>2h</td>
<td>90</td>
<td>1800/360</td>
</tr>
<tr>
<td>9</td>
<td>1i</td>
<td>5</td>
<td>2i</td>
<td>93</td>
<td>1860/372</td>
</tr>
<tr>
<td>10</td>
<td>1j</td>
<td>5</td>
<td>2j</td>
<td>90</td>
<td>1800/360</td>
</tr>
<tr>
<td>11</td>
<td>1k</td>
<td>5</td>
<td>2k</td>
<td>90</td>
<td>1800/360</td>
</tr>
<tr>
<td>12</td>
<td>1l</td>
<td>5</td>
<td>2l</td>
<td>74</td>
<td>1480/296</td>
</tr>
<tr>
<td>13</td>
<td>1m</td>
<td>5</td>
<td>2m</td>
<td>90</td>
<td>1800/360</td>
</tr>
</tbody>
</table>

<sup>a</sup>Isolated Yield
Both the primary and secondary benzyl alcohols on oxidation gave satisfactory to good yields of the corresponding aldehydes and ketones. Secondary benzyl alcohol was also found to be reactive toward oxidation under the same reaction condition and the product \( \text{2b} \) was obtained in excellent yield (Table 2, entry 2). Primary benzyl alcohols with electron donating and withdrawing groups afforded products \( \text{2c and 2d} \) in good yields (Table 2, entries 3 and 4). Primary benzyl alcohols bearing halogen groups were also successfully oxidized to benzaldehydes \( \text{2e-g} \) with satisfactory yields (Table 2, entries 5-7). Secondary benzyl alcohols with electron donating groups afforded products \( \text{2h-k} \) in good yields (Table 2, entries 8-11) and halogen substituted secondary benzyl alcohols also gave products \( \text{2l and 2m} \) in satisfactory yields (Table 2, entries 12 and 13).

Evaluation of recyclability was done on the same test substrate \( \text{1a} \). After completion of reaction, the product was extracted with ethyl acetate and the recovered catalyst was washed with acetone, dried and used for further reactions. The catalytic activity of SS-Pd remained almost the same up to five runs as indicated by the yields of the corresponding aldehyde \( \text{2a} \). Gradual decrease in yield was encountered after six to seven runs of SS-Pd catalyst. As shown in Table 3, on recycling, from the first to the seventh run the TONs drop from 1600 to 1000 and total turnover number over the seven cycles was 10400.

**Table 3. Recyclability experiments of \( \text{2a} \) using SS-Pd**

<table>
<thead>
<tr>
<th>Run</th>
<th>1(^{st})</th>
<th>2(^{nd})</th>
<th>3(^{rd})</th>
<th>4(^{th})</th>
<th>5(^{th})</th>
<th>6(^{th})</th>
<th>7(^{th})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield (%)(^\text{a})</td>
<td>80</td>
<td>80</td>
<td>79</td>
<td>79</td>
<td>78</td>
<td>74(^\text{b})</td>
<td>50(^\text{b})</td>
</tr>
<tr>
<td>TON</td>
<td>1600</td>
<td>1600</td>
<td>1580</td>
<td>1580</td>
<td>1560</td>
<td>1480</td>
<td>1000</td>
</tr>
<tr>
<td>TTON over seven cycles</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10400</td>
</tr>
</tbody>
</table>

\(^{a}\) Determined by means of GC  
\(^{b}\) Isolated Yield  
TTON = total turnover number; procedure followed as described for \( \text{2a} \)

### 3.4 Conclusion:

Aerobic oxidation of benzyl alcohols using SS-Pd has been developed. Different primary and secondary benzyl alcohols afforded corresponding products in good yields. Due to the stability of SS-Pd catalyst in moisture and air, it is very easy to handle under reaction conditions. This methodology will find interest in both academic as well as industry due to
Application of solid supported----------

its atom-economy and cost-effective process by using heterogeneous nano and microparticles as a ligand free catalyst.

3.5 Experimental section:
3.5.1 General procedure:
Reagents of high quality were purchased from Sigma Aldrich. Silica gel (60-120 mesh size) for column chromatography was procured from SD Fine-Chem. Ltd. Commercial reagents and solvents were of analytical grade and were purified by standard procedures prior to use. Thin layer chromatography was performed using precoated silica gel plates 60 F254 (Merck) in UV light detector. 1H and 13C NMR spectra were recorded using a Bruker Avance 300 spectrometer operating at 300 MHz (1H) and 75 MHz (13C). Spectra were recorded at 25 °C in CDCl3 [residual CHCl3 (δH 7.26 ppm) or CDCl3 (δC 77.00 ppm) as international standard] with TMS as internal standard. Chemical shifts were recorded in δ (ppm) relative to the TMS and CDCl3 signal, coupling constants (J) are given in Hz and multiplicities of signals are reported as follows: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad singlet.

3.5.2 Procedure of aerobic oxidation:

1-Phenyl ethanone (2b): A mixture of 1-phenyl ethanol 1b (100 mg, 0.818 mmol), SS-Pd (918 mg, 0.04 mmol Pd) and 3 ml of toluene was purged with molecular oxygen and stirred at 110 °C for 5h. The progress of reaction was monitored by TLC. After completion of reaction, the reaction was cooled, diluted with ethyl acetate and filtered through cotton bed. The combined organic layer was evaporated under reduced pressure and crude residue was purified by silica gel (mesh 60-120) column chromatography (hexane:EtOAc :: 95:5) afforded 1-Phenyl ethanone 2b as colourless liquid (94 mg, 96%); 1H NMR (300 MHz, CDCl3-d1) δ 2.59 (s, 3H), 7.44-7.55 (m, 3H), 7.93-7.96 (m, 2H); 13C NMR (75 MHz, CDCl3-d1) δ 26.49, 128.22 (2C), 129.48 (2C), 133.01, 137.06, 198.07.

2-Ethoxy benzaldehyde (2a): Prepared as described for 2b; starting from 2-ethoxybenzyl alcohol 1a (100 mg, 0.66 mmol) gave, after purification with silica gel column chromatography (hexane:EtOAc :: 95:5) 2a as colourless liquid (81 mg, 78%); 1H NMR (300 MHz, CDCl3-d1) δ 1.27-1.35 (m, 3H), 4.10-4.21 (m, 2H), 6.97-7.05 (m, 2H),
7.52-7.57 (m, 1H), 7.85 (d, J = 7.6 Hz, 1H), 10.53 (s, 1H); \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}-d\textsubscript{1}) δ 35.02, 64.92, 113.16, 116.67, 121.28, 125.66, 129.06, 136.64, 190.77.

\textbf{4-Nitro benzaldehyde (2c):} Prepared as described for 2b; starting from 4-nitrobenzyl alcohol 1c (100 mg, 0.66 mmol) gave, after purification with silica gel column chromatography (hexane:EtOAc :: 97:3) 2c as a brown solid (70 mg, 70%), mp 106-107 °C; \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}-d\textsubscript{1}) δ 8.09 (brs, 2H), 8.41 (brs, 2H), 10.17 (s, 1H); \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}-d\textsubscript{1}) δ 124.29 (2C), 130.71 (2C), 140.04, 151.12, 190.23.

\textbf{3-Methoxy benzaldehyde (2d):} Prepared as described for 2b; starting from 3-methoxy benzylalcohol 1d (100 mg, 0.72 mmol) gave, after purification with silica gel column chromatography (hexane:EtOAc :: 95:5) 2d as colourless liquid (89 mg, 90%); \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}-d\textsubscript{1}) δ 3.90 (s, 3H), 7.20-7.21 (m, 1H), 7.42-7.49 (m, 3H), 10.01 (s, 1H); \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}-d\textsubscript{1}) δ 55.48, 112.02, 121.55, 123.57, 130.03, 137.81, 160.16, 192.13.

\textbf{4-Bromo benzaldehyde (2e):} Prepared as described for 2b; starting from 4-bromobenzyl alcohol 1e (100 mg, 0.54 mmol) gave, after purification with silica gel column chromatography (hexane:EtOAc :: 96:4) 2e as white solid (80 mg, 80%), mp 56-57 °C; \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}-d\textsubscript{1}) δ 7.61-7.71 (m, 2H), 7.75-7.78 (m, 2H), 9.99 (s, 1H); \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}-d\textsubscript{1}) δ 129.77, 130.95 (2C), 132.43 (2C), 135.06, 191.04.

\textbf{4-Chloro benzaldehyde (2f):} Prepared as described for 2b; starting from 4-chlorobenzyl alcohol 1f (100 mg, 0.70 mmol) gave, after purification with silica gel column chromatography (hexane:EtOAc :: 96:4) 2f as white solid (82 mg, 83%), mp 46-47 °C; \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}-d\textsubscript{1}) δ 7.43-7.46 (m, 2H), 7.45-7.77 (m, 2H), 9.91 (s, 1H); \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}-d\textsubscript{1}) δ 129.45 (2C), 130.89 (2C), 134.71, 140.96, 190.84.

\textbf{2-Bromo benzaldehyde (2g):} Prepared as described for 2b; starting from 2-bromobenzyl alcohol 1g (100 mg, 0.54 mmol) gave, after purification with silica gel column chromatography (hexane:EtOAc :: 95:5) 2g as colourless liquid (85 mg, 85%); \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}-d\textsubscript{1}) δ 7.40-7.45 (m, 2H), 7.60-7.63 (m, 1H), 7.86-7.89 (m, 1H),
10.31 (s, 1H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)-d\(_1\)) δ 126.88, 127.73, 129.68, 132.82, 133.37, 135.12, 191.48.

\[
\begin{array}{c}
\text{4-Methyl acetophenone (2h): Prepared as described for 2b; starting from} \\
4\text{-methyl phenyl ethanol 1h (100 mg, 0.72 mmol) gave, after purification with silica gel} \\
column chromatography (hexane:EtOAc :: 95:5) 2h as colourless liquid (88 mg, 90%);} \\
^{1}\text{H NMR (300 MHz, CDCl}_{3}\text{-d}_{1}\text{)} \delta 2.43 (s, 3H), 2.60 (s, 3H), 7.27-7.29 (m, 2H), 7.87-7.89 (m,} \\
2\text{H);}^{13}\text{C NMR (75 MHz, CDCl}_{3}\text{-d}_{1}\text{)} \delta 21.61, 26.49, 128.44, 129.23, 134.78, 143.85, \\
197.81.
\end{array}
\]

\[
\begin{array}{c}
\text{2,4-Di-methoxy acetophenone (2i): Prepared as described for 2b; starting from} \\
(2,4-di-methoxy phenyl) ethanol 1i (100 mg, 0.54 mmol) gave, after purification with silica gel} \\
column chromatography (hexane:EtOAc :: 95:5) 2i as white solid (92 mg, 93%), mp 46-48 °C;} \\
^{1}\text{H NMR (300 MHz, CDCl}_{3}\text{-d}_{1}\text{)} \delta 2.53 (s, 3H), 3.80 (s, 3H), 3.84 (s, 3H), 6.34-6.48 (m, 2H), 7.73-7.79 (m,} \\
1\text{H);}^{13}\text{C NMR (75 MHz, CDCl}_{3}\text{-d}_{1}\text{)} \delta 31.57, 55.20, 55.25, 98.00, 104.95, 120.84, 132.74, 160.90, 164.36, 197.37.
\end{array}
\]

\[
\begin{array}{c}
\text{2,5 Di-methoxy acetophenone (2j): Prepared as described for 2b; starting} \\
from (2,5 di-methoxy phenyl) ethanol 1j (100 mg, 0.54 mmol) gave, after purification with} \\
silica gel column chromatography (hexane:EtOAc :: 95:5) 2j as colourless liquid (88 mg, 90%);} \\
^{1}\text{H NMR (300 MHz, CDCl}_{3}\text{-d}_{1}\text{)} \delta 2.64 (s, 3H), 3.80 (s, 3H), 3.90 (s, 3H), 6.90-7.06 \\
(m, 2H), 7.28-7.30 (m, 1H);}^{13}\text{C NMR (75 MHz, CDCl}_{3}\text{-d}_{1}\text{)} \delta 31.75, 55.79, 56.02, 113.20, \\
113.82, 120.31, 128.42, 153.41, 153.50, 199.34.
\end{array}
\]

\[
\begin{array}{c}
\text{4-Methoxy acetophenone (2k): Prepared as described for 2b; starting} \\
from (4-methoxy phenyl)ethanol 1k (100 mg, 0.64 mmol) gave, after purification with} \\
silica gel column chromatography (hexane:EtOAc :: 95:5) 2k as white solid (87 mg, 90%),} \\
mp 37-39 °C;}^{1}\text{H NMR (300 MHz, CDCl}_{3}\text{-d}_{1}\text{)} \delta 2.54 (s, 3H), 3.85 (s, 3H), 6.91 (d, J =} \\
8.72, 2H), 7.92 (d, J = 8.70 Hz, 2H);}^{13}\text{C NMR (75 MHz, CDCl}_{3}\text{-d}_{1}\text{)} \delta 26.65, 55.75, 113.96 \\
(2C), 130.57, 130.89 (2C), 163.77, 197.12.
\end{array}
\]
4-Chlorobenzophenone (2l): Prepared as described for 2b; starting from (4-chlorophenyl)-phenylethanol 11 (100 mg, 0.44 mmol) gave, after purification with silica gel column chromatography (hexane:EtOAc :: 95:5) 2l as white solid (73 mg, 74%), mp 76-78 °C; ¹H NMR (300 MHz, CDCl₃-d₁) δ 7.46-7.53 (m, 3H), 7.60-7.64 (m, 2H), 7.76-7.80 (m, 2H); ¹³C NMR (75 MHz, CDCl₃-d₁) δ 128.38 (2C), 129.61 (2C), 129.90 (2C), 131.44 (2C), 132.62, 135.86, 137.23, 138.87, 195.46.

4-Bromo acetophenone (2m): Prepared as described for 2b; starting from (4-bromophenyl) ethanol 1m (100 mg, 0.48 mmol) gave, after purification with silica gel column chromatography (hexane:EtOAc :: 95:5) 2m as white solid (87 mg, 90%), mp 47-49 °C; ¹H NMR (300 MHz, CDCl₃-d₁) δ 2.60 (s, 3H), 7.60-7.63 (m, 2H), 7.82-7.84 (m, 2H); ¹³C NMR (75 MHz, CDCl₃-d₁) δ 26.52, 128.28, 129.82 (2C), 131.87 (2C), 135.81, 197.00.

3.6 References:


NMR spectra of some compounds

$^1$H NMR (in CDCl$_3$) spectrum of 4-Bromo benzaldehyde

$^{13}$C NMR (in CDCl$_3$) spectrum of 4-Bromo benzaldehyde
$^1$H NMR (in CDCl$_3$) spectrum of 4-methoxy acetophenone

$^{13}$C NMR (in CDCl$_3$) spectrum of 4-methoxy acetophenone
$^1$H NMR (in CDCl$_3$) spectrum of 4-chlorobenzophenone

$^{13}$C NMR (in CDCl$_3$) spectrum of 4-chlorobenzophenone