

# Catalytic properties of several palladium complexes covalently anchored onto silica for the aerobic oxidation of alcohols

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A series of novel silica-supported palladium catalysts bearing N–N, N–S and N–O chelating ligands have been prepared and tested for the aerobic oxidation of alcohols to carbonyl compounds. The most active catalyst, **1**, was used for the oxidation of a series of primary and secondary alcohols to carbonyl compounds. The catalyst is highly selective and no over-oxidation products were detected. The catalyst **1** can also be used for the oxidation of primary benzyl alcohols to carbonyl compounds with comparable yields in the presence of atmospheric air.

## Introduction

In recent years, the search for environmentally benign chemical processes or methodologies has received much attention from chemists, because they are essential for the conservation of the global ecosystem.<sup>1</sup> The development of heterogeneous catalysts for fine chemical synthesis has become a major area of research, as the potential advantages of these materials (simplified recovery and reusability; the potential for incorporation in continuous reactors and microreactors) over homogeneous systems can lead to novel environmentally benign chemical procedures for academia and industry.<sup>2,3</sup>

The selective oxidation of alcohols to aldehydes and ketones is a highly desirable and much sought after transformation both in industrial chemistry as well as in organic synthesis, due to the wide-ranging utility of these products as important precursors and intermediates for many drugs, vitamins and fragrances.<sup>4,5</sup> In particular, the controlled oxidation of primary alcohols to aldehydes without forming over-oxidized products is a challenging task for chemists. Numerous methods are available for alcohol oxidation,<sup>6</sup> however, the development of newer methods and methodologies is currently gaining much attention due to the significance of this reaction. Traditional alcohol oxidations use toxic, corrosive and expensive oxidants such as DMSO-coupled reagents,<sup>7</sup> hypervalent iodines,<sup>8</sup> and chromium(VI) and manganese complexes, stringent conditions like high pressure or temperatures and the use of strong mineral acids.<sup>4,9</sup> Unfortunately, these oxidations result in large quantities of noxious wastes and call for the use of (at least) stoichiometric quantities of moisture-sensitive, unrecoverable and expensive reagents. Due to increasing environmental concerns, oxidations using environmentally friendly oxidants such as molecular oxygen and hydrogen peroxide are more desirable these days. Hydrogen peroxide oxidation, however, is relatively less economical due to its cost

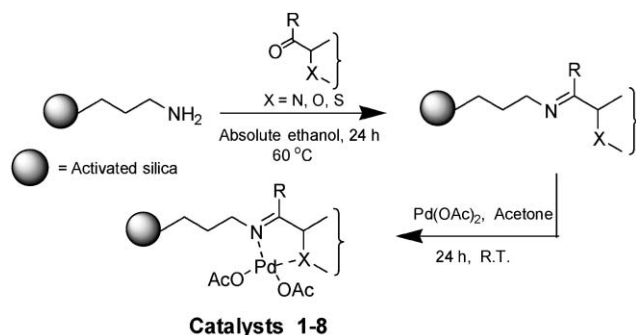
and comparatively poor efficiency and presents safety problems in transportation and storage.<sup>10</sup> Oxidations using molecular oxygen are highly attractive alternatives,<sup>6,11</sup> since they are atom efficient and produce water as the only by-product.<sup>12</sup> Recently, I<sub>2</sub>–KI–K<sub>2</sub>CO<sub>3</sub>–H<sub>2</sub>O<sup>13</sup> has been reported as a green reagent system for the selective oxidation of alcohols to carbonyl compounds.

Palladium is known to be an active catalyst for oxidations,<sup>14,15</sup> and some supported palladium catalysts have been shown to be stable in organic reaction systems. However, there are few examples of oxidations using supported palladium catalysts. Recently, it has been reported that a Pd(II) complex physisorbed onto hydrotalcite effects the aerobic oxidation of alcohols to the corresponding carbonyl compounds in the presence of pyridine as the exogenous base.<sup>16</sup> While this method is the first example of a Pd(II)-supported catalyst for application in the aerobic oxidation of alcohols, the catalyst suffers from the drawback of reduction of its activity caused by the leaching of the reactive centre (poor anchoring). Moreover, owing to the presence of a soluble ligand (pyridine) and the physisorbed nature of the Pd(II), it seems that oxidation with leached homogeneous palladium species, whereby the Pd(II) species is redeposited back on the heterogeneous surface at the end of the reaction, could be responsible.<sup>17</sup> Sahle-Demessie *et al.*<sup>18</sup> have also reported Pd/MgO as a quite efficient heterogeneous catalyst for the selective oxidation of alcohols to carbonyl compounds using molecular oxygen. However, long reaction times, low conversion and thus low turn-over frequencies (TOF) for the catalyst, make this catalytic system less practical. Palladium supported on alumina by an adsorption method has also been reported as an efficient and recyclable heterogeneous catalyst for the oxidation of alcohols using molecular oxygen.<sup>19</sup>

The problem of leaching of metals, such as palladium species, into the solution can be avoided by covalently anchoring the palladium species onto the surface of a suitable support. More recently, a palladium catalyst covalently anchored onto the surface of silica gel was reported for the selective oxidation of alcohols to carbonyl compounds.<sup>20</sup> This is a quite efficient and reusable supported palladium catalyst for the selective oxidation of alcohols to carbonyl compounds

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Scheme 1

using molecular oxygen. This catalyst can be used for the oxidation of primary benzylic alcohols using atmospheric air but is less effective for aliphatic and secondary alcohols. However, with this catalyst, longer reaction times (4–14 h) are required.

In our earlier communication, we have reported<sup>21</sup> the preparation and structure–activity relationship of a series of novel, covalently anchored, silica-supported palladium catalysts bearing N–N, N–S and N–O chelating ligands for the Suzuki reaction. Keeping in view the importance of the selective oxidation of alcohols to carbonyl compounds in academia and industry, and that of heterogeneous catalysis, we report our results on the use of eight palladium catalysts covalently anchored onto the surface of silica gel (with N–N, N–S and N–O chelating ligands), for the selective oxidation of alcohols to carbonyl compounds with molecular oxygen, with a view to developing completely heterogeneous, reusable and more effective catalysts and also to further reducing the reaction time and increasing the TON. More importantly, there is interest in the development of a catalyst which could be used for the oxidation of alcohols in the presence of atmospheric air instead of molecular oxygen, which in turn could further reduce the cost and hazards of the oxidation process.

## Results and discussion

The general procedure for the synthesis of catalysts **1–8** is indicated in Scheme 1. It involves the preparation of 3-aminopropylsilica from activated silica and (3-aminopropyl)trimethoxysilane followed by the preparation of Schiff bases from 3-aminopropylsilica and *n*-butyl 2-pyridyl ketone,

**Table 1** Oxidation of benzyl alcohol to benzaldehyde using molecular O<sub>2</sub> and K<sub>2</sub>CO<sub>3</sub> in the presence of catalysts **1–8** (3 mol% of Pd) at 90 °C.<sup>a</sup>

Catalyst	Time/h	Yield <sup>b</sup> (%)
1	2.5	95
2	6	80
3	15	55
4	4.5	91
5	3.5	89
6	3.25	88
7	10	90
8	15	93

<sup>a</sup> The molar ratio of benzyl alcohol : K<sub>2</sub>CO<sub>3</sub> : catalyst is 1 : 1 : 0.03.

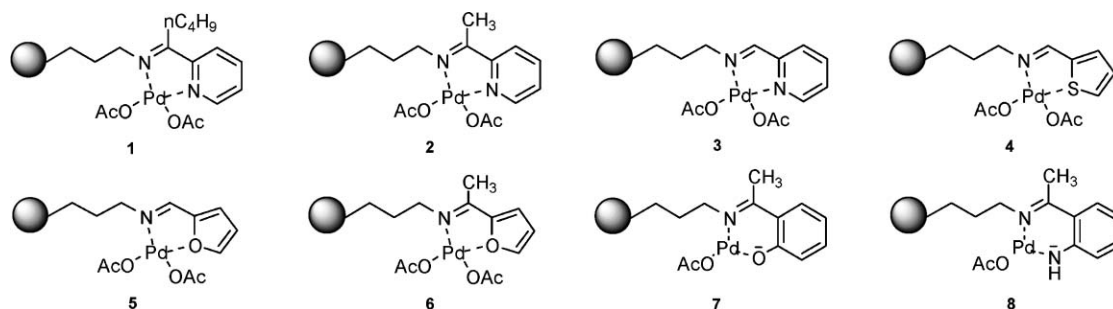
<sup>b</sup> Yield of isolated products.

2-acetylpyridine, 2-pyridinecarboxaldehyde, 2-thiophene-carboxaldehyde, 2-furancarboxaldehyde, 2-acetylfuran, 2-hydroxyacetophenone and 2-aminoacetophenone. The silica-supported palladium catalysts **1–8** were then prepared by the complexation of the Schiff base with Pd(OAc)<sub>2</sub> in acetone. For detailed procedures, and characterizations of catalysts, see refs. 21 and 22.

The probable structures of the catalysts **1–8** are given in Scheme 2.

In our earlier report, we prepared eight catalysts and among those, the most active catalyst for the Suzuki reaction was found to be **2**, which contains –CH<sub>3</sub> groups at the carbon adjacent to the imino N, with the pyridyl N as the second co-ordinating ligand. If we compare the structures of catalysts **2** and **3**, the only difference is the presence of –CH<sub>3</sub> in **2**. But the interesting thing is that there is a tremendous difference in the activity of these two catalysts for the Suzuki reaction. So keeping in view this fact, we have prepared another catalyst **1**, which contains the –(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub> group in the place of –CH<sub>3</sub> in **2**, with a view to finding a more active catalyst.

To test the activity of these catalysts **1–8** as completely heterogeneous catalysts for the oxidation of alcohols, we selected benzyl alcohol as the test substrate. The oxidation of benzyl alcohol (1 mmol) was attempted in the presence of catalysts **1–8** (equivalent to 3 mol% of Pd) in toluene (5 mL) at 90 °C in the presence of K<sub>2</sub>CO<sub>3</sub> (1 mmol). The results are summarized in Table 1. From Table 1, it is clear that the most active catalyst is **1** (3 mol% of Pd), which oxidizes benzyl alcohol in the presence of molecular oxygen in 2.5 h at 90 °C with 100% conversion and 95% isolated yield of benzaldehyde. The high activity of catalyst **1**, compared to catalysts **2–8**, for the oxidation of alcohols to the corresponding carbonyl



Scheme 2

**Table 2** Oxidation of alcohols to the corresponding carbonyl compounds using molecular O<sub>2</sub> and K<sub>2</sub>CO<sub>3</sub> in the presence of catalyst **1** (3 mol% of Pd) at 90 °C.<sup>a</sup>

Entry	Alcohol	Time/h	Yield <sup>b</sup> (%)
1	Benzyl alcohol	2.5	95
2	4-(MeO)C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OH	2.5	96
3	4-(Me)C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OH	3.0	92
4	4-(Cl)C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OH	2.5	94
5	4-(F)C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OH	3.0	95
6	4-(NO <sub>2</sub> )C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OH	4.5	90
7	3-(NO <sub>2</sub> )C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OH	5	87
8	1-Pentanol	5.5	85
9	2-Butanol	5.0	82
10	Cyclohexanol	5.0	90
11	1-Phenyl ethanol	5.5	93
12	Cinnamyl alcohol	15	40

<sup>a</sup> The molar ratio of alcohol : K<sub>2</sub>CO<sub>3</sub> : **1** is 1 : 1 : 0.03. <sup>b</sup> Yield of isolated products.

compounds can be explained in a similar way to that reported in our earlier communication,<sup>21</sup> *i.e.* the presence of an alkyl group at the carbon adjacent to the imino N increases the stability of the catalyst by increasing the binding energy of Pd with the N atoms.

The oxidation of various substituted benzyl alcohols (containing both electron-withdrawing and electron-releasing groups) was attempted with catalyst **1** in toluene in the presence of K<sub>2</sub>CO<sub>3</sub> using molecular oxygen, and excellent results were found (Table 2, entries 1–7).

Once we were able to carry out the oxidation of benzyl alcohols efficiently, then attempts were made to perform the oxidation of other aliphatic alcohols. It was found that **1** is equally efficient for the oxidation of aliphatic primary and secondary alcohols as well. The results are given in Table 2 (entries 8–11). It is worth mentioning that oxidation of cinnamyl alcohol (entry 12) takes place very slowly with only 40% isolated yield of cinnamaldehyde in 15 h.

When using a supported metal catalyst, two important issues need to be addressed to qualify this as a purely heterogeneous catalyst. One is the possibility that some active metal migrates from the solid to the liquid phase, and that this leached palladium would become responsible for a significant part of the catalytic activity. To rule out the contribution of homogeneous catalysis in the results shown in Table 2, the oxidation of benzyl alcohol was carried out in the presence of **1** until the conversion was 35% and at that point, the solid was filtered off at the reaction temperature. The liquid was then transferred to another flask containing K<sub>2</sub>CO<sub>3</sub> and then again allowed to react, but no further significant conversion was observed. This indicates that no active species was present in the supernatant and that the observed catalysis is purely heterogeneous. The second important point concerning heterogeneous catalysis is the deactivation and reusability of the catalyst. To test this, a series of 7 consecutive runs of the oxidation of benzyl alcohol with catalyst **1** was carried out (1st use: 100% conversion after 2.5 h; 3rd use: 95% after 3.5 h; 5th use: 85% after 5 h; 7th use: 60% after 8 h). These results demonstrate that there is almost no change in the activity of **1** up to the 3rd use, a slight decrease in activity was observed up to the 5th use, but after the 5th use there is a tremendous

decrease in activity. This may be due to either the deactivation of active centres resulting from complexation with both starting materials and products, or microscopic changes in the structure of the catalyst.

A further improvement in the efficiency of the aerobic oxidation process can be achieved if molecular oxygen is replaced with atmospheric oxygen – then the process is more safe and economic. With catalyst **1**, we carried out the oxidation of benzyl alcohol in toluene using K<sub>2</sub>CO<sub>3</sub> (1 eq.) in the presence of atmospheric air. It was found that benzyl alcohol undergoes oxidation with 100% conversion in 7 h. However, lower yields were found in case of 1-pentanol and cyclohexanol. Thus, there is still a need to develop heterogeneous catalysts, which could be used for the oxidation of alcohols in the presence of atmospheric air. The development of new supported palladium catalysts is under active investigation in our laboratories.

## Experimental

### General

The chemicals used were either prepared in our laboratories or purchased from Aldrich Chemical Company. The products were characterized by comparison of their physical data with those of known samples or by their spectral data. The <sup>1</sup>H NMR data were recorded in CDCl<sub>3</sub> on a Bruker DPX 200 (200 MHz) spectrometer using TMS as an internal standard. The IR spectra were recorded on a Perkin–Elmer FTIR spectrophotometer using KBr windows.

**General procedure for the oxidation of alcohols to carbonyl compounds using catalyst **1**.** To a mixture of K<sub>2</sub>CO<sub>3</sub> (1 mmol) and catalyst **1** (0.260 g, 3 mol% Pd) in a three-necked round-bottomed flask, toluene (5 mL) was added. The flask was then evacuated with the help of a pump and twice refilled with oxygen (using oxygen-filled balloons). The reaction mixture was maintained at 90 °C, the alcohol (1 mmol) was injected into the flask using a syringe and the mixture was stirred under a pure oxygen atmosphere for an appropriate time (Table 2). On completion, the reaction mixture was filtered while hot and the residue was washed with hot toluene (5 mL). The product was obtained after removal of the solvent under reduced pressure. In most cases, the purity of the products was found to be greater than 98% (determined by <sup>1</sup>H NMR) without any chromatographic purification. The catalyst was recovered from the residue after washing with CH<sub>2</sub>Cl<sub>2</sub> (10 mL) followed by distilled water (200 mL) and then with CH<sub>2</sub>Cl<sub>2</sub> (15 mL). It was reused after drying at 100 °C for 5 h.

## Conclusions

In conclusion, we have reported the application of eight palladium/silica catalysts for the oxidation of benzyl alcohol using molecular oxygen and K<sub>2</sub>CO<sub>3</sub>. Out of these, the most active catalyst **1** was used for the oxidation of various types of structurally diverse alcohols to the corresponding carbonyl compounds. Catalyst **1** is completely heterogeneous, is more reusable and results in a faster reaction than the previously reported heterogeneous catalyst.<sup>20</sup> Further, it can be used for

the oxidation of primary benzylic alcohols under an air atmosphere, but is less efficient for the oxidation of other types of alcohols.

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