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# A Bipyridyl Palladium Complex Covalently Anchored onto Silica as an Effective and Recoverable Interphase Catalyst for the Aerobic Oxidation of Alcohols[⊥]

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*Summary: A new silica-based Pd(II) interphase catalyst 2 efficiently catalyzes the aerobic oxidation of various types of structurally diverse alcohols to the corresponding carbonyl compounds. The catalyst is also quite effective for the oxidation of primary benzylic alcohols under atmospheric pressure of air. The catalyst shows high thermal stability (up to 200 °C) and is also stable under the oxidation reaction conditions. To our knowledge this work is the first example of the application of a palladium complex covalently anchored to silica for the aerobic oxidation of alcohols.*

## Introduction

The selective oxidation of alcohols to the corresponding carbonyl compounds is a prominent and frequently used transformation in laboratory and industrial synthetic chemistry, and hence a plethora of procedures have been developed for this transformation.[1] However, until recently this transformation is normally achieved using stoichiometric reagents such as chromium salts,[1a,2] DMSO-coupled reagents,[3] or hypervalent iodines.[4] Unfortunately, these oxidations bring about large quantities of noxious wastes and call for at least the stoichiometric use of moisture-sensitive and unrecoverable expensive reagents. Thus, from the standpoint of environmental and economic concerns, a better approach is to construct cleaner and cheaper oxidation systems. *Dioxygen-coupled* strategies are attractive alternative means of attaining this goal,[5] since they are atom efficient and produce water as the only byproduct.[6] The use of palladium catalysts for the oxidation of alcohols to aldehydes and ketones in the presence of various types of reoxidants is well known.[7] Recently, the advantages of using molecular oxygen as the oxidant in the Pd-catalyzed oxidation of alcohols has been explored.[8,9] However, the reports on this particular subject are still scarce, and the vast majority of them still use homogeneous palladium catalysts.[8] 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 exogenous base.[10a,b] While this method is

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[⊥] Dedicated to Professor Mohammad Yalpani on the occasion of his 66th birthday.

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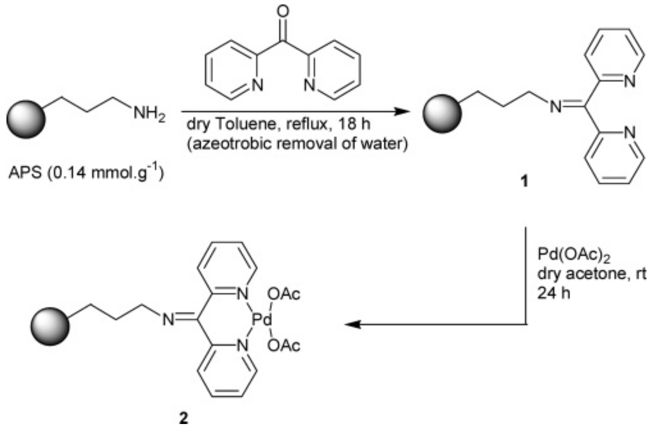
the first example of Pd(II)-supported catalyst for application in the aerobic oxidation of alcohols, the catalyst suffers from the drawback of reduction of its activity caused by the leaching of the reactive center (poor anchoring). Moreover, owing to the presence of a soluble ligand (pyridine) and the physisorbed nature of the Pd(II), it seems that oxidation with leached homogeneous palladium species could be responsible whereby the Pd(II) species is redeposited back on the heterogeneous surface at the end of the reaction.[11] An important strategy to transform a homogeneous process into a heterogeneous one is to covalently incorporate the active site onto a large surface area solid through an organic entity (flexible spacer) to create organic−inorganic hybrid (interphase) catalysts.[12] An interphase is defined as a *region* within a material in which a stationary (organic−inorganic hybrid catalyst) and mobile component (solvent and reactants) penetrate each other on a molecular level. According to the definition, an interphase catalyst is composed of three parts: an inert matrix (support), a flexible organic spacer, and an active center.[12b] In contrast to traditional physisorbed heterogeneous catalysts, in the interphase counterparts, the organic spacer provides sufficient mobility of the reactive center and diminishes any desired steric effect of the matrix over the accessibility of the reactive center. Therefore, these systems are able to simulate homogeneous reaction conditions, and at the same time they have the advantage of easy separation and recovery of the heterogeneous catalysts. Although there are a small number of examples of palladium complexes covalently anchored to silica for application in C−C bond forming reactions,[12,13] to our knowledge examples do not exist of the application of palladium-based interphase catalysts for the aerobic oxidation of alcohols. In the present work, we wish to report the results obtained with a new bipyridyl palladium complex covalently anchored onto a silica surface as a heterogeneous and recoverable interphase catalyst for the oxidation of various types of alcohols using molecular oxygen.

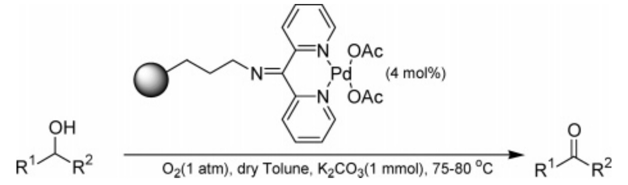
## Results and Discussion

The preparation procedure to obtain catalyst **2** is indicated in Scheme 1. Catalyst **2** was characterized by atomic absorption spectroscopy (AA), thermo-gravimetric analysis (TGA), and DRIFT-IR spectroscopy.[14] From the TGA analysis of **1**, it is calculated that the loading of the bipyridyl ligand bound to the silica surface was 0.13 mmol·g$^{-1}$. TGA analysis of anchored palladium **2** shows a first weight loss due to the desorption of water below 100 °C. This is followed by a second weight loss centered at 325 °C, corresponding to the loss of the surface-bound bipyridyl ligand. The loading of palladium itself was determined using AA and shows a loading at 0.12 ± 0.01 mmol·g$^{-1}$. This indicates that more than 90% of the surface-bound ligands were complexed with palladium.

**Scheme 1**



**Scheme 2**



To test the activity of **2** as a heterogeneous catalyst, we selected the oxidation of alcohols using molecular oxygen (Scheme 2). Thus, benzyl alcohol was oxidized in the presence of **2** (0.33 g, 4 mol %) and $K_2CO_3$ (1 equiv) in toluene (5 mL) at 75−80 °C for 8 h. After filtration of the mixture, the catalyst was rinsed twice with a small volume of $CH_2Cl_2$ and reused. Evaporation of the solvent from the filtrate furnished benzaldehyde in 85% isolated yield (Table 1, entry 1), the purity of which was analyzed by GC to be more than 99%. It is worth mentioning that the oxidation of benzyl alcohol in the presence of lower amounts of $K_2CO_3$ led to less satisfactory yields of the products accompanied by the rapid formation of palladium black (Table 1, entries 2, 3). As summarized in Table 1, catalyst **2** also efficiently catalyzes the aerobic oxidation of a wide variety of alcohols.

The catalyst exhibits especially high catalytic activity for both benzylic and aliphatic alcohols, giving the corresponding carbonyl compounds in good to excellent yields. Under similar reaction conditions, even sterically encumbered alcohols furnished the corresponding carbonyl compounds in good to excellent yields (Table 1, entries 12, 17). The double bond in allylic alcohols apparently coordinates strongly to palladium, as would be expected, and this slows the reaction with concomitant formation of palladium black. While the addition of more $K_2CO_3$ further increases the reaction rate, the formation of palladium black could not be prevented. When using a heterogeneous catalyst, there are important issues to be resolved. The first is the possibility that some active metal leaches from the solid to the solution and that this leached Pd is responsible for all

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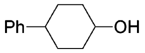
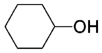
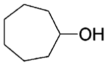
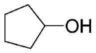
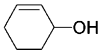
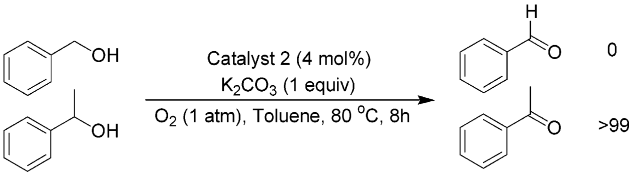
**Table 1. Oxidation of Alcohols to Carbonyl Compounds Using Molecular Oxygen in the Presence of a Bipyridyl Palladium Complex Covalently Anchored onto Silica 2**

| Entry | $R^1$ | $R^2$ | Time (h) | Yield[a, b, c] (%) |
|---|---|---|---|---|
| 1 | Ph ($1^{st}$) | H | 8 | 100 (85) |
| 2 | Ph | H | 15 | 23[d] |
| 3 | Ph | H | 15 | 78[e] |
| 4 | Ph ($2^{nd}$) | H | 8 | 100 |
| 5 | Ph ($3^{rd}$) | H | 8 | >98 |
| 6 | Ph ($4^{rd}$) | H | 18 | 75 |
| 7 | Ph | H | - | 41[f] |
| 8 | 4-(Me)$C_6H_4$ | H | 5 | 100 (92) |
| 9 | 2-(Me)$C_6H_4$ | H | 8 | 100 (96) |
| 10 | 4-(MeO)$C_6H_4$ | H | 4 | 100 (92) |
| 11 | 4-(Cl)$C_6H_4$ | H | 5 | 100 (98) |
| 12 | 2,6-$(Cl)_2C_6H_3$ | H | 10 | 100 |
| 13 | PhCH=CH- | H | 18 | 33 |
| 14 | Ph | Me | 12 | 100 |
| 15 | Ph | Et | 12 | 100 |
| 16 | PhCO | Ph | 12 | 100 (97) |
| 17 | Ph | Ph | 12 | 79 |
| 18 | $PhCH_2$ | H | 10 | >95 (85) |
| 19 | $CH_3(CH_2)_5$ | H | 10 | >95 (78) |
| 20 | $CH_3(CH_2)_4$ | Me | 10 | 100 (95) |
| 21 |  | - | 12 | 80 |
| 22 |  | - | 12 | 100 (85) |
| 23 |  | - | 12 | 89 |
| 24 |  | - | 8 | 100 |
| 25 |  | - | 14 | 47 |

[a] GC yield unless otherwise stated. [b] Yields in parentheses refer to isolated pure products. [c] The molar ratios of substrate:$K_2CO_3$:**2** are 1:1:0.04 unless otherwise stated. [d] The reaction was carried out in the absence of $K_2CO_3$. [e] The reaction was carried out in the presence of 0.5 equiv of $K_2CO_3$. [f] The reaction was carried out in the presence of solid **2** for 2 h, and at that point the catalyst was filtered off and further stirring was done in the absence of catalyst for 8 h.

**Scheme 3**



or part of the reaction. To rule out the contribution of homogeneous catalysis, the reaction of benzyl alcohol was conducted in the presence of catalyst **2** for 2 h until a conversion of 41%. Then the solid was hot-filtered off and welded to another reaction vessel containing $K_2CO_3$ in toluene at 80 °C. The catalyst-free solution was then allowed to continue to react, but no further reaction took place even after 10 h (Table 1, entry 7). This result indicates that any Pd species that leached into the reaction mixture is not an active homogeneous catalyst and that the observed catalysis is truly heterogeneous in nature. Moreover, no palladium species was detected using atomic absorption spectroscopy of the reaction mixture. The second important point concerning heterogeneous catalysis is the deactivation and reusability of the catalyst. Our preliminary examination shows that catalyst **2** is reusable. When the oxidation of benzyl alcohol was repeated three times with the same sample of catalyst, benzaldehyde was produced at the same rate as that of the first run. However, in the fourth run, the formation of benzaldehyde is slightly reduced (Table 1, entries 1−4). This may be due to either the deactivation of active centers resulting from complexation with both starting materials and products or microscopic changes in the structure of the catalyst.

Secondary alcohols often oxidize faster than primary alcohols owing to the increased electron density on the former. However, as can be seen from the data in Table 1, using the present protocol, primary alcohols (mainly benzylic) react faster than secondary alcohols in *separate experiments*. This may be due to an increase in steric hindrance on the secondary alcohols. This observation encouraged us to investigate the possible chemoselective oxidation of primary alcohols in the presence of secondary alcohols. However, as shown in Scheme 3, when a 1:1 mixture of benzyl alcohol and 1-phenyl ethanol was allowed to react with molecular oxygen, in the presence of catalyst **2** (4 mol %) and $K_2CO_3$ (1 equiv) after 8 h, GC and NMR analysis of the reaction mixture showed it to consist of a 1:1 mixture of benzyl alcohol and acetophenone. This type of chemoselectiviy is in sharp contrast to the observation of Sheldon et al. using a water-soluble bathophenanthroline disulfonate Pd complex.[8j] While we do not exactly understand the reaction mechanism, there is at least one plausible explanation, which is in accordance with experimental evidence. When 1-phenylethanol was allowed to oxidize under $O_2$ atmosphere in the presence of benzaldehyde (1 equiv) instead of benzyl alcohol, after 5 h, 35% benzyl alcohol was detected by GC analysis of the reaction mixture. The formation of benzyl alcohol may be attributed to the oxidation of 1-phenylethanol by benzaldehyde through a *transfer-hydrogenation* process. This means that in a competition experiment, although the benzyl alcohol reacts faster to produce benzaldehyde, the benzaldehyde in turn assists the oxidation of 1-phenylethanol to the more thermodynamically stable acetophenone through a transfer-hydrogenation pathway. On the other hand, the formation of benzyl alcohol may also support the presence of a *reversible β-hydride elimination* in the reaction pathway.[15] However, further studies are currently underway in our group to clarify this issue.

A substantial practical improvement for aerobic oxidation is to replace pure $O_2$ with air since this reduces cost and is also safer. Interestingly, we found that with only slightly extended reaction times the oxidation of primary bezylic alcohols can be cleanly carried out under an atmospheric pressure of air instead of pure $O_2$ (Table 2). However, our preliminary examination showed that this method, in its present form, is not suitable for the efficient oxidation of nonbenzylic primary and secondary

**Table 2. Oxidation of Benzylic Alcohols to Carbonyl Compounds Using Atmospheric Air in the Presence of a Bipyridyl Palladium Complex Covalently Anchored onto Silica 2**

| entry | $R^1$ | $R^2$ | time (h) | yield[a,b] (%) |
|---|---|---|---|---|
| 1 | Ph | H | 12 | >99 |
| 2 | 4-(Me)$C_6H_4$ | H | 10 | >99 |
| 3 | 2-(Me)$C_6H_4$ | H | 12 | >99 |
| 4 | 4-(MeO)$C_6H_4$ | H | 7 | >99 |
| 5 | 4-(Cl)$C_6H_4$ | H | 12 | >99 |
| 6 | 2,6-$(Cl)_2C_6H_3$ | H | 14 | >99 |

[a] GC yield. [b] The molar ratios of substrate:$K_2CO_3$:**2** were 1:1:0.04.

alcohols in the presence of atmospheric air, and only low yields of the corresponding carbonyl compounds were produced. Further investigations to design and prepare new palladium-based interphase catalysts for application in aerobic oxidation of alcohols are currently ongoing in our laboratories.

## Conclusion

In conclusion, the novel silica-based Pd(II) interphase catalyst **2**, which can be prepared by a simple procedure, efficiently catalyzes the aerobic oxidation of various types of structurally diverse alcohols to the corresponding carbonyl compounds. The catalyst is also quite effective for the oxidation of primary benzylic alcohols under an atmospheric pressure of air. The catalyst shows high thermal stability (up to 200 °C) and is also stable under the oxidation reaction conditions. To our knowledge this work is the first example of the application of a palladium complex covalently anchored to silica for the aerobic oxidation of alcohols.

## Experimental Section

**General Remarks.** Chemicals were either prepared in our laboratories or purchased from Merck, Fluka, and Aldrich Chemical Companies. All yields refer to GC products unless otherwise stated. The products were characterized by comparison of their physical data with those of known samples or by their spectral data. $^1H$ NMR and $^{13}C$ NMR spectra were recorded on a 500 MHz spectrometer in $CDCl_3$ as the solvent and TMS as internal standard. Most of the products are known, and all of the isolated products gave satisfactory IR and NMR spectra.

**General Experimental Procedure.** A mixture of $K_2CO_3$ (1 mmol) and catalyst **2** (0.33 g, ~4 mol %) in toluene (5 mL) was prepared in a two-necked flask at 75−80 °C. The flask was then evacuated (water aspirator) and refilled with pure oxygen three times (balloon filled). To this solution the alcohol (1 mmol, in 1 mL toluene) was then injected, and the resulting mixture was stirred at 75−80 °C under an oxygen atmosphere for the indicated time in Table 1. After completion of the reaction, the reaction mixture was filtered off and the catalyst rinsed twice with $CH_2Cl_2$ (5 mL). The excess of solvent was removed under reduced pressure to give the corresponding carbonyl compounds (Table 1). In most cases, the purity of products was analyzed by GC to be more than 99% without any chromatographic purification.

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**Supporting Information Available:** This material is available free of charge via the Internet at http://pubs.acs.org.

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