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# Nanocrystalline Magnesium Oxide Stabilized Palladium(0): An Efficient Reusable Catalyst for Room Temperature Selective Aerobic Oxidation of Alcohols

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**Abstract:** 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 green oxidant at room temperature. Various alcohols could be transformed into their corresponding aldehydes or ketones in good to excellent yields using a set of optimal conditions. NanoActive™ Magnesium Oxide Plus, [NAP-MgO] with its three-dimensional

structure and well-defined shape acts as an excellent support for well dispersed palladium(0) nanoparticles. This catalyst can be recovered and reused for several cycles without any significant loss of catalytic activity.

**Keywords:** aerobic oxidation; alcohols; aldehydes; catalyst recycling; heterogeneous catalysis

## Introduction

The selective oxidation of alcohols to aldehydes and ketones is a very important organic transformation both in industrial chemistry and in organic synthesis due to the utility of these products as important precursors and intermediates for many drugs, fine chemicals, vitamins and fragrances.<sup>[1]</sup> Numerous methods are available for the selective oxidation of alcohols<sup>[2]</sup> but the development of mild reaction conditions with a greener approach from the environmental point of view has been an ever challenging task for chemists. Traditional oxidation methods use toxic, corrosive and expensive oxidants such as DMSO-coupled reagents, hypervalent iodine, Cr(VI), and manganese complexes leading to environmentally hazardous wastes.<sup>[3]</sup>

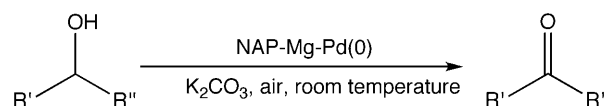
From the green chemistry viewpoint, there remains an urgent need to develop a catalytic system using molecular oxygen or air as the oxidant, because these oxidants are atom efficient and produce water as the only by-product.<sup>[4]</sup> Palladium is a well known catalyst for oxidation, and in view of this, a number of both heterogeneous and homogeneous catalysts including

Pd(II) salts or complexes have been investigated for the selective aerobic oxidation of alcohols.<sup>[5]</sup> The first palladium-catalyzed aerobic oxidation of alcohols at room temperature was reported by Sigman et al. using a homogeneous catalytic system containing palladium acetate with triethylamine as an organic additive.<sup>[6]</sup> Heterogeneous catalysts are more industrially important than homogeneous catalysts because of their easy separation and reusability. The use of the heterogeneous palladium catalysts for the selective oxidation of alcohols using oxygen or air as oxidant is known but most of the reported catalyst systems work at high temperatures.<sup>[7]</sup> Recently, Rhee et al. reported the Pd/C-catalyzed selective oxidation of alcohols using molecular oxygen at room temperature which required an NaBH<sub>4</sub> additive to regenerate the catalytic surface, which inevitably generates borates as by-product.<sup>[8]</sup> The heterogeneous palladium-catalyzed oxidation of alcohols using air or oxygen at ambient room temperature conditions without any additives and ligands is more environmentally friendly, but to the best of our knowledge, there has been no such report at ambient temperature with air as green oxidant.

Most of the recent studies have shown that supported palladium nanoparticles are excellent catalysts for selective aerobic oxidation of alcohols by oxygen or air.<sup>[9]</sup> For example, Zhang et al. have reported the aerobic oxidation of various alcohols catalyzed by SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-supported palladium nanoparticles with a mean size of 3.6 nm. Demessie et al. reported MgO support with a BET surface area of 39 m<sup>2</sup>g<sup>-1</sup> containing 1% palladium nanoparticles of mean size 6.9 nm to be an active heterogeneous catalyst for the oxidation of various alcohols. Wang et al. reported the aerobic oxidation of alcohols catalyzed by zeolite-supported palladium nanoparticles. He also showed that palladium nanoparticles with a mean size of 5 nm dispersed on alumina were catalytically active for the solvent-free aerobic oxidation of a variety of alcohols. Uozumi et al. reported the catalytic oxidation of allylic and benzylic alcohols in aqueous medium using polystyrene-PEG-supported palladium nanoparticles with a mean diameter of 9 nm for the selective oxidation of various alcohols. Palladium nanoparticles entrapped in aluminium hydroxide with sizes between 2–3 nm have also been shown to be effective for aerobic alcohol oxidation reactions. It is to be noted that the major drawback of these nano-Pd(0) dispersed heterogeneous catalysts is that they require high temperatures (65–150 °C) for the selective oxidation of alcohols to corresponding aldehydes and ketones.

Our previous works have shown that nanocrystalline magnesium oxide (NAP-MgO)-supported palladium nanoparticles, [NAP-Mg-Pd(0)], is a very active heterogeneous catalyst for a plethora of organic reactions, such as Suzuki and Stille cross-coupling of aryl halides,<sup>[10a]</sup> Heck and Sonogashira coupling of aryl halides,<sup>[10b]</sup> selective reduction of nitro compounds,<sup>[10c]</sup> and one-pot synthesis of dibenzyl and alkyl phenyl esters.<sup>[10d]</sup> Studies with NAP-MgO have revealed that there are several characteristics<sup>[11]</sup> that make NAP-MgO a superior support for applications in heterogeneous catalysis. Firstly, the very small particle size of the palladium nanoparticles which are well dispersed on NAP-MgO is responsible for the excellent catalytic activity for many reactions reported by our group.<sup>[12]</sup> Another reason is that the high surface area [590 m<sup>2</sup>g<sup>-1</sup>] and high basicity of NAP-MgO further enhances the catalytic performance in these heterogeneous reactions. These advantages are further complemented by the presence of edge-corner and other defect sites which allow the NAP-MgO to possess a high concentration of reactive surface ions.

As a continuation of our work in this direction, herein we report highly basic NAP-MgO containing palladium nanoparticles [NAP-Mg-Pd(0)] as an efficient ligand-free heterogeneous catalytic system for the selective oxidation of both primary and secondary alcohols using air as oxidant at room temperature (see Scheme 1).



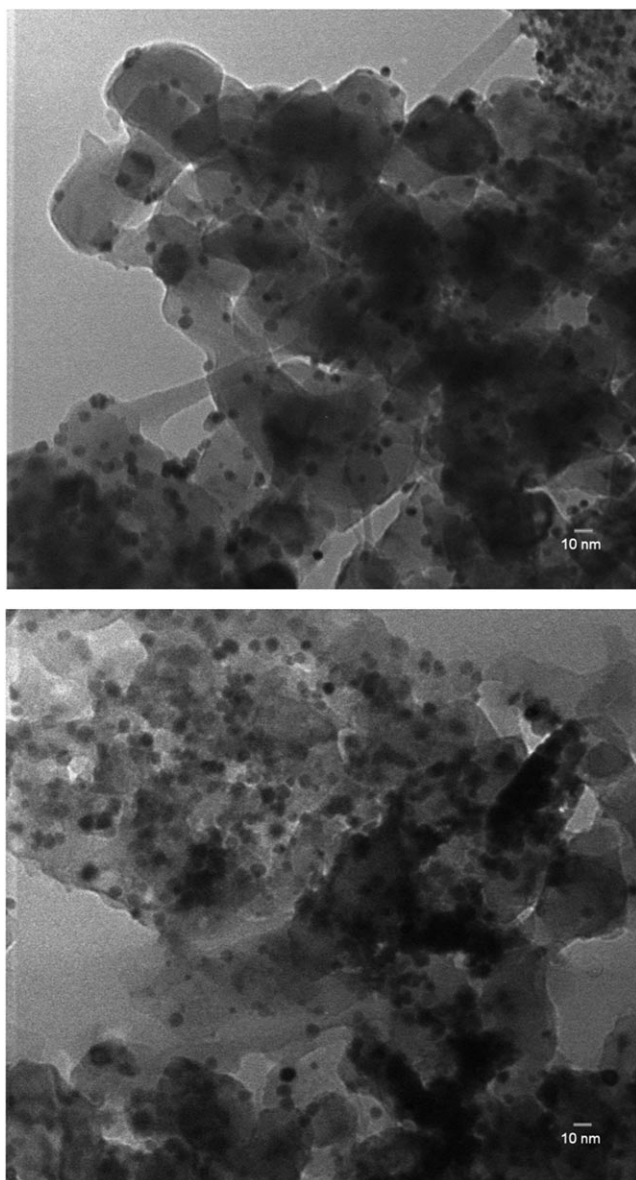
**Scheme 1.** Oxidation of primary and secondary alcohols in the presence of air as oxidant.

## Results and Discussion

### Characterization of NAP-Mg-Pd(0)

NAP-MgO [commercial name: NanoActive™ Magnesium Oxide Plus, specific surface area (BET)  $\geq$  590 m<sup>2</sup>g<sup>-1</sup>] was purchased from NanoScaleMaterials, Inc. (Manhattan, USA). The NAP-Mg-Pd(0) was synthesized by following a modified procedure reported earlier by our group.<sup>[13]</sup> The average size of palladium nanoparticle reported earlier was 40 nm.<sup>[13]</sup> Since on decreasing the particle size, the number of reactive palladium species on the support increases, and hence the available surface area of the reactive site increases, the reaction proceeds at a faster rate. Our studies have shown that the oxidation of benzyl alcohol to benzaldehyde with the 40 nm size palladium nanoparticles on NAP-MgO took 20 h for 99% conversion, whereas using NAP-Mg-Pd(0) with 5–7 nm size palladium nanoparticles the same could be accomplished in 7 h under the same reaction conditions. In this particular work, we have succeeded in decreasing the particle size of the palladium nanoparticles that are dispersed on NAP-MgO from the previously reported size of 40 nm<sup>[13]</sup> by stirring the reaction contents at 3–5 °C using sodium borohydride as the reducing agent. Although the role of sodium borohydride in decreasing the particle size is not specifically known, lower temperatures are well-known to play a significant role in controlling the particle size. This is because upon decreasing the temperature, the mean particle size of Pd(0) decreases due to the increase in nucleation rate.<sup>[14]</sup> These studies reveal that the particle size of Pd(0) dispersed on NAP-MgO decreased drastically from the previously observed size of 40 nm<sup>[13]</sup> to about 5–7 nm as deduced from detailed transmission electron micrograph (TEM) studies [see Figure 1 for TEM images of both freshly prepared NAP-Mg-Pd(0) and spent catalyst]. The synthesized catalyst was well characterized by XRD, FTIR, SEM-EDX, TEM and XPS. (see Supporting Information).

First, to identify the best heterogeneously supported Pd(0) for selective oxidation of alcohols at room temperature, a diverse range of supported heterogeneous palladium catalysts were prepared using reported procedures<sup>[15]</sup> and then screened using benzyl alcohol as the model substrate with air as oxidant at ambient temperature. The results from this screening study are summarized in Table 1. For these reactions, benzyl



**Figure 1.** Transmission electron micrograph of (top) fresh [NAP-Mg-Pd(0)] and (bottom) used [NAP-Mg-Pd(0)] (after third cycle). Pd nanoparticles are clearly seen as small black spots deposited onto NAP-MgO support.

alcohol was used neat under solvent free conditions. Various bases and solvents were also screened using 4-nitrobenzyl alcohol as the model substrate and the best result was obtained using toluene as the solvent and potassium carbonate as the base (see Supporting Information). As can be seen from Table 1, yields as high as 99% for benzaldehyde and a turnover number (TON) of 73.17 were obtained using [NAP-Mg-Pd(0)] as the catalyst (Table 1, entry 1) at room temperature under our set of experimental conditions. Pd-HAP and Pd-FAP have almost similar palladium contents (0.022 and 0.024 mmol g<sup>-1</sup>, respectively) but Pd-FAP

gives slightly higher TON and yield than Pd-FAP because of its higher BET surface area (Table 1, entries 2 and 3). It is also very interesting to note that Pd-Mg-LaO although it has a very low BET surface area of 40.3 m<sup>2</sup> g<sup>-1</sup>, gives a 60% yield of benzaldehyde because of its very high palladium content of 0.748 mmol g<sup>-1</sup> (Table 1, entry 5). No products were formed when the reaction was carried out with simple NAP-MgO and in the absence of NAP-Mg-Pd(0). Eventually the catalytic system consisting of NAP-Mg-Pd(0) as catalyst, K<sub>2</sub>CO<sub>3</sub> as base and toluene as solvent (for solid alcohols only) was chosen for the oxidation of various alcohols.

To better understand the scope of the reaction, various primary alcohols were then subjected to the above optimized reaction conditions. The results are shown in Table 2. For convenience, primary alcohols in the liquid state (Table 2, entries 1, 7, 10, 11 and 12) were used as neat liquids under solvent-free conditions as described earlier for benzyl alcohol. For alcohols in the solid state (Table 2, entries 2, 3, 4, 5, 6, 8 and 9), reactions were conducted using toluene as solvent. To test the electronic influence of substituents on the phenyl ring of benzylic alcohols, both electron-withdrawing and electron-donating groups at various aromatic positions were tested (Table 2, entries 2–9). Among the various substituted benzylic alcohols that were screened for the study, *ortho*-substituted benzylic alcohols afforded comparatively lower yields (70–77%) of the corresponding oxidized products with longer reaction times (Table 2, entries 3, 5 and 7: 12–18 h) when compared to substrates that have substituents at the *para* substitution (Table 2, entries 2, 4 and 9: 10–12 h). It is likely that this observation may be due to the steric hindrance of *ortho*-substituted groups at the OH centre of the benzylic group. In particular, when the OH group is directly attached to the phenyl ring of benzyl alcohol, we observed selective oxidation of the benzyl OH group (Table 2, entries 6, 7 and 9). Overall, the presence of electron-donating or electron-withdrawing groups on the phenyl ring of benzylic alcohols does not seem to show much of an appreciable effect on the yield of oxidation products. For example, 4-nitrobenzyl alcohol with an electron-withdrawing nitro group at the *para* position gave 80% of the oxidized product, and 4-hydroxybenzyl alcohol with an electron-donating hydroxy group at the *para* position gave 81% of the oxidized product. For primary aliphatic alcohols decent yields (68–72%) were obtained, but required longer reaction times (20–22 h). In particular, octanol gave 68% of the oxidized product in 20 h; both nonanol and dodecanol gave 73% and 72% of the oxidized aldehyde products, respectively, in 22 h (Table 2, entries 10–12). These results show that nanocrystalline NAP-Mg-Pd(0) catalyst exhibits especially high catalytic activity and selectivity for both benzylic and aliphatic alco-

**Table 1.** Screening of supported palladium catalysts for the aerobic oxidation of benzyl alcohol at room temperature.<sup>[a]</sup>

Entry	Catalyst	BET surface area of the support [m <sup>2</sup> g <sup>-1</sup> ]	Palladium content [mmol g <sup>-1</sup> ]	Conversion <sup>[b]</sup> [%]	Yield <sup>[c]</sup> [%]	Selectivity [%]	TON <sup>[d]</sup>	TOF <sup>[e]</sup> [hour <sup>-1</sup> ]
1	NAP-Mg-Pd(0)	590	0.048	100	99	>99	73.17	10.45
2	PdHAP	271	0.022	41	37	99	65.46	9.35
3	PdFAP	379	0.024	50	45	92	68.65	9.80
4	Pd-C	485	0.100	82	78	98	28.7	4.10
5	Pd-Mg-LaO	40.3	0.748	65	60	95	2.94	0.42

<sup>[a]</sup> *Reaction conditions:* Benzyl alcohol (1 mmol) in neat form, catalyst (30 mg), K<sub>2</sub>CO<sub>3</sub> (1.2 mmol), stirred under air at room temperature for 7 h. Pd-C was procured commercially and was used as received. Pd-HAP, Pd-FAP, and Pd-Mg-LaO were prepared using literature procedures.<sup>[15]</sup>

<sup>[b]</sup> Analyzed by GC.

<sup>[c]</sup> Isolated yields.

<sup>[d]</sup> TON = turnover number (mole product per mole catalyst)

<sup>[e]</sup> TOF = turnover frequency (mole product per mole catalyst per hour)

hols, giving the corresponding aldehydes in good to excellent yields.

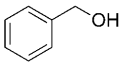
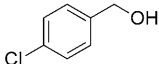
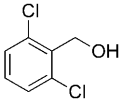
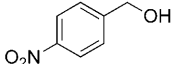
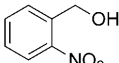
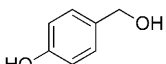
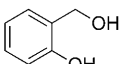
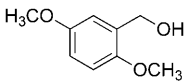
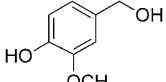
After thoroughly studying the aerobic oxidation of primary alcohols to their corresponding aldehydes, we tested the catalytic activity of the NAP-Mg-Pd(0) system for the selective oxidation of secondary, allylic and *N*-heterocyclic alcohols (Table 3, entries 1–17). As was the case with reactions of primary alcohols studied in Table 2, the reactions of liquid state alcohols were conducted under solvent-free neat conditions (Table 3, entries 1, 2, 4–10, 12, and 14–16) and the reactions of those of solid state alcohols (Table 3, entries 3, 11, 13 and 17) were conducted using toluene as solvent. Among the secondary alcohols tested, the less reactive substrates such as alicyclic alcohols were oxidized to the corresponding ketones with good to excellent yields (Table 3, entries 1–6). For example cyclohexanol, which is known to be a less reactive substrate, smoothly undergoes oxidation at room temperature and gave cyclohexanone in 85% yield in 18 h (Table 3, entry 1). We have also studied the oxidation reaction of substituted cyclohexanols using NAP-Mg-Pd(0) catalyst. As can be seen, cyclohexanols with functional groups such as methyl or phenyl at the 2 or 4 positions showed higher reactivity than the unsubstituted cyclohexanol (Table 3, entry 1 vs. entries 2–4). For example, 4 phenylcyclohexanol gave 92% yield of the oxidized product in 12 h under our experimental conditions (Table 3, entry 3). Quite notably, in these reactions no aldol products were formed. Interestingly, when cyclopentanol was employed as a substrate, only a moderate yield of 65% was obtained for cyclopentanone. However, when the reaction of cyclopentanol was performed at an elevated temperature of 100 °C an excellent yield was obtained for cyclopentanone (Table 3, entry 6). The oxidation of 1-phenylethanol to acetophenone using our catalytic system proceeded smoothly in the presence of air affording 88% yield of the product. It is significant to note that the presence of CO<sub>2</sub> in air did not poison our catalyst

system (Table 3, entry 7). The presence of either electron-withdrawing or electron-donating groups at the *para*-position of the phenyl ring of 1-phenylethanol affects the course of the reaction. For example, electron-donating groups such as methyl and methoxy groups at the *para* position gave excellent yields of the oxidized product, 92% and 89%, respectively in 10 h, whereas the presence of an electron-withdrawing nitro group at the *para* position gave 81% of 4-nitroacetophenone in 18 h. (Table 3, entries 8–10). As can be seen from Table 3, bulky *sec*-alcohol substrates such as benzhydrol also undergo oxidation to benzophenone quantitatively in 10 h under our experimental conditions (Table 3, entry 11). Other *sec*-alcohols such as *trans*-cinnamyl alcohol and other allylic alcohols also gave decent yields of the products without affecting the double bond (Table 3, entries 12–14).

To further explore the catalytic activity of our system we have checked the oxidation of methyl-2-hydroxyphenylmethyl acrylate. We were pleased to see that our catalytic system selectively oxidized the OH group to provide methyl 2-benzoylacrylate. Quite notably, only a moderate yield of 65% of the product (methyl 2-benzoylacrylate) was obtained even after 28 h, but interestingly, as for the cyclopentanol substrate described earlier, at 100 °C, an 80% yield was obtained for methyl 2-benzoylacrylate in 12 h (Table 3, entry 15). Similarly, *N*-heterocyclic alcohols like pyridine-3-ylmethanol and 1-(pyridin-3-yl)ethanol were oxidized to the corresponding aldehyde and ketone but needed longer reaction times (40–44 h) when compared to other secondary alcohols. Very notably, the yield of pyridine-3-carbaldehyde and 1-pyridin-3-yl-ethanone was further increased when the reaction was performed at 100 °C (Table 3, entries 16 and 17).

The success of the above results with NAP-Mg-Pd(0) encouraged us to investigate their catalytic activity for the chemoselective oxidation of various alcohols under competitive conditions. When an equi-

**Table 2.** Aerobic oxidation of primary alcohols using NAP-Mg-Pd(0).<sup>[a]</sup>

Entry	Alcohol	Time [h]	Conversion <sup>[b]</sup> [%]	Yield <sup>[c]</sup> [%]	Selectivity [%]	TON <sup>[d]</sup>	TOF <sup>[e]</sup> [hour <sup>-1</sup> ]
1		7	100 100 <sup>[f]</sup> 88 <sup>[g]</sup>	99 99 <sup>[h]</sup> 86 <sup>[i]</sup>	> 99	73.17 73.17 <sup>[j]</sup> 64.39 <sup>[k]</sup>	10.45 10.45 <sup>[l]</sup> 9.19 <sup>[m]</sup>
2 <sup>[n]</sup>		12	89	85	99	65.12	5.42
3 <sup>[n]</sup>		12	80	77	98	57.94	4.82
4 <sup>[n]</sup>		10	83	80	> 98	60.24	6.02
5 <sup>[n]</sup>		14	73	70	98	52.87	3.77
6 <sup>[n]</sup>		12	84	81	99	61.46	5.12
7		18	77	75	99	56.34	3.13
8 <sup>[n]</sup>		12	98	94	> 99	71.99	5.99
9 <sup>[n]</sup>		10	99	96	> 99	73.02	7.30
10	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub> CH <sub>2</sub> OH	20	73	68	> 95	51.36	2.56
11	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> CH <sub>2</sub> OH	22	77	73	> 97	55.35	2.51
12	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>10</sub> CH <sub>2</sub> OH	22	76	72	96	53.95	2.45

<sup>[a]</sup> Reaction conditions: alcohol (1 mmol), NAP-Mg-Pd(0) (30 mg), K<sub>2</sub>CO<sub>3</sub> (1.2 mmol) stirred under air at room temperature for the appropriate time

<sup>[b]</sup> Analyzed by GC.

<sup>[c]</sup> Isolated yields.

<sup>[d]</sup> TON = turnover number (mole product per mole catalyst).

<sup>[e]</sup> TOF = turnover frequency (mole product per mole catalyst per hour).

<sup>[f]</sup> Conversion after fourth cycle.

<sup>[g]</sup> Conversion after fifth cycle.

<sup>[h]</sup> Isolated yield after fourth cycle.

<sup>[i]</sup> Isolated yield after fifth cycle.

<sup>[j]</sup> TON after fourth cycle.

<sup>[k]</sup> TON after fifth cycle.

<sup>[l]</sup> TOF after fourth cycle.

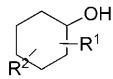


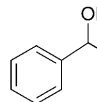
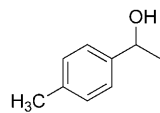
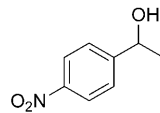
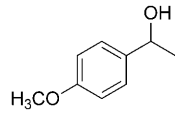
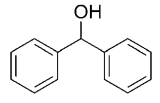
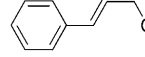
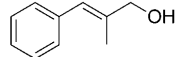
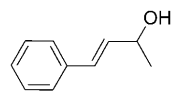
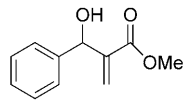
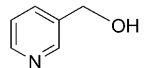
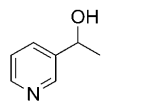
<sup>[m]</sup> TOF after fifth cycle.

<sup>[n]</sup> 3 mL of toluene were used as a solvent.

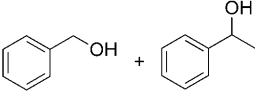
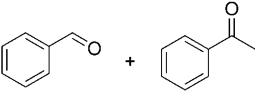
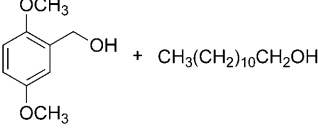
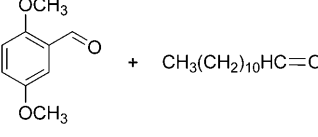
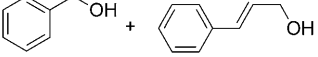
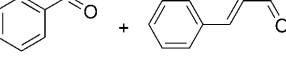
molar mixture of benzyl alcohol and 1-phenylethanol was used for the oxidation, benzyl alcohol was almost completely oxidized to the corresponding aldehyde in 99% yield, with only 15% of 1-phenylethanol undergoing oxidation to acetophenone (Table 4, entry 1). Similarly, when an equimolar mixture of 2,5-dimethoxybenzyl alcohol and dodecanol was subjected to oxidation, 2,5-dimethoxybenzyl alcohol was selective-

ly oxidized to the corresponding aldehyde in 16 h (Table 4, entry 2). When an equimolar ratio of benzyl alcohol and 3-phenylprop-2-en-1-ol was taken as substrate, benzyl alcohol was selectively oxidized to benzaldehyde in 99% yield (Table 4, entry 3). From these results, it can be clearly stated that primary benzyl alcohols are more reactive than secondary benzyl alcohols, aliphatic alcohols and allylic alcohols.

**Table 3.** Aerobic oxidation of secondary, allylic and N-heterocyclic alcohols using NAP-Mg-Pd(0).<sup>[a]</sup>

Entry	Alcohol	Time [h]	Conversion <sup>[b]</sup> [%]	Yield <sup>[c]</sup> [%]	Selectivity [%]	TON <sup>[d]</sup>	TOF <sup>[e]</sup> [hour <sup>-1</sup> ]
							
1	R <sup>1</sup> = H, R <sup>2</sup> = H	18	88	85	99	64.39	3.57
2	R <sup>1</sup> = H, R <sup>2</sup> = 4-CH <sub>3</sub>	12	94	91	99	68.78	5.73
3 <sup>[f]</sup>	R <sup>1</sup> = H, R <sup>2</sup> = 4-Ph	12	97	92	> 99	71.11	5.92
4	R <sup>1</sup> = 2-CH <sub>3</sub>	15	90	88	99	65.85	4.39
5		10	92	89	98	66.63	6.66
6		22 5 <sup>[g]</sup>	69, 96 <sup>[h]</sup>	65 92 <sup>[i]</sup>	97	49.46, 68.82 <sup>[j]</sup>	2.24, 13.76 <sup>[k]</sup>
7		12	91	88	> 99	66.78	5.56
8		10	94	92	99	68.78	6.87
9		18	85	81	99	62.19	3.45
10		10	92	89	> 99	67.72	6.72
11 <sup>[f]</sup>		10	100	99	> 99	73.31	7.33
12		14	93	89	98	67.36	4.81
13 <sup>[f]</sup>		14	93	91	99	68.04	5.23
14		26	92	88	97	65.95	2.53
15		28, 12 <sup>[g]</sup>	68 84 <sup>[h]</sup>	65 80 <sup>[i]</sup>	97	48.75 60.22 <sup>[j]</sup>	1.74 5.01 <sup>[k]</sup>
16		44 8 <sup>[g]</sup>	55 79 <sup>[h]</sup>	50 76 <sup>[i]</sup>	98	39.83 57.22 <sup>[j]</sup>	0.90 7.15 <sup>[k]</sup>
17 <sup>[f]</sup>		40 8 <sup>[g]</sup>	65 88 <sup>[h]</sup>	62 85 <sup>[i]</sup>	98	47.08 63.73 <sup>[j]</sup>	1.17 7.96 <sup>[k]</sup>

**Table 4.** Selective competitive oxidation of primary alcohols using NAP-Mg-Pd(0).<sup>[a]</sup>

Entry	Alcohol	Product	Time [h]	Yield <sup>[b]</sup> [%]
1			8	99 + 15
2			16	94 + no reaction
3			12	99 + 15

<sup>[a]</sup> Reaction conditions: alcohols (1 mmol), NAP-Mg-Pd(0) (30 mg), K<sub>2</sub>CO<sub>3</sub> (1.2 mmol) and 3 mL of toluene stirred under air at room temperature for the appropriate time.

<sup>[b]</sup> Isolated yields.

### Oxidation of Isopropyl Alcohol

Up to now we have explored the catalytic activity of our system using NAP-Mg-Pd(0) only to high boiling point alcohols. To further explore the efficiency of our catalytic system to comparatively low boiling point alcohols we chose isopropyl alcohol (boiling point: 82.5 °C) as the substrate for oxidation. When 3 mL of isopropyl alcohol were subjected to aerial oxidation at room temperature using NAP-Mg-Pd(0), we could not isolate any oxidized product. Apparently, the reason behind this was that during the course of the reaction isopropyl alcohol was getting oxidized to acetone and acetone having a low boiling point (56 °C) escaped from the reaction vessel. To further confirm our reasoning, we performed the same reaction in a sealed vessel using an oxygen balloon. After 14 h we withdrew a portion of the reaction mixture from the vessel and analyzed it by GC-MS. The molecular ion peak corresponding to  $m/z = 58$  confirmed the presence of acetone. The reaction was 100% selective with a 77.62% conversion of the substrate. The TON and TOF obtained for this reaction were 56.91 and 4.06 hour<sup>-1</sup>, respectively. (see Supporting Information).

### Reusability of the Catalyst

The spent catalyst was recovered from the reaction mixture by simple filtration after the completion of the reaction. Then the recovered catalyst was first washed with water and then with diethyl ether to remove any excess base and any organic material. It was then dried at room temperature and used as it is for reusability studies. It was observed that the NAP-Mg-Pd(0) catalyst showed consistent activity for four cycles (Table 2, entry 1). No quantifiable amount of leached Pd was detected in the filtrate as determined by atomic absorption spectrometry (AAS) studies of both fresh and spent catalyst. Furthermore, the TEM images of the used catalyst did not show any significant change in the shape and size of the support as well as the particle size of the active species, Pd(0). This suggests that the morphology of the catalyst remains the same even after multiple reaction cycles (Figure 1, top and bottom panels).

<sup>[a]</sup> Reaction conditions: alcohol (1 mmol), NAP-Mg-Pd(0) (30 mg), K<sub>2</sub>CO<sub>3</sub> (1.2 mmol) stirred under air at room temperature for the appropriate time.

<sup>[b]</sup> Analyzed by GC.

<sup>[c]</sup> Isolated yields.

<sup>[d]</sup> TON = turnover number (mole product per mole catalyst).

<sup>[e]</sup> TOF = turnover frequency (mole product per mole catalyst per hour).

<sup>[f]</sup> 3 mL of toluene were used as a solvent.

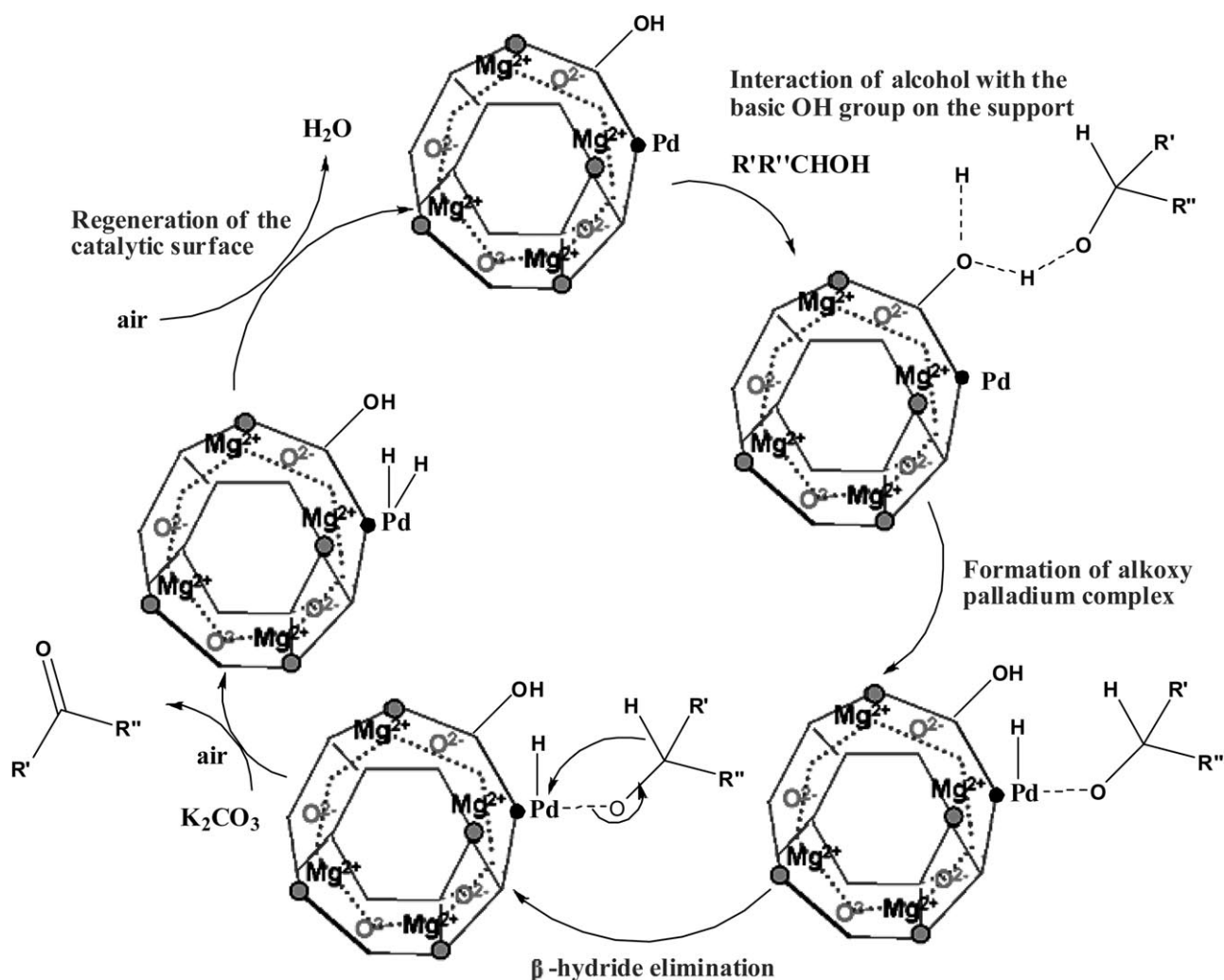
<sup>[g]</sup> Time required when reaction was carried out at 100 °C.

<sup>[h]</sup> Conversion at 100 °C.

<sup>[i]</sup> Isolated yield at 100 °C.

<sup>[j]</sup> TON at 100 °C.

<sup>[k]</sup> TOF at 100 °C.



**Figure 2.** Proposed mechanism for the oxidation of alcohols. (For the sake of convenience only one surface hydroxy group and only one palladium nanoparticle are shown on the support in the figure.)

### Proposed Catalytic Mechanism

The plausible mechanism of oxidation may be through the formation of an alkoxide by interaction of the alcohol with the isolated OH group (basic sites) of the NAP-MgO, followed by formation of an alkoxy palladium complex by the well dispersed palladium nanoparticles on the support. This complex then undergoes  $\beta$ -hydride elimination to give the carbonyl product in the presence of base and air. The palladium hydride intermediate thus formed then reacts with air to form water and regenerates the active catalytic surface.<sup>[16]</sup> This probable mechanistic pathway is shown in Figure 2.

### Role of Potassium Carbonate Base

Although the reaction proceeds even without the addition of base as the surface hydroxy groups on NAP-

MgO act as basic sites, still then, we observed that on adding potassium carbonate the reaction proceeded at a faster rate<sup>[8]</sup> and the reaction could be completed in lesser time than in the absence of base. This obviously implies that base plays a certain positive role in enhancing the reaction rate. Although the exact reason behind this is difficult to ascertain, we assumed that, since the palladium nanoparticles on NAP-MgO are surface bound and not pore bound, they may mask some of the surface basic sites, thereby, preventing the interaction of the surface OH groups with the substrate on NAP-MgO. In such a condition the addition of an external base definitely promotes the reaction.

### Conclusions

In conclusion, we have developed an efficient and reusable nano Pd(0) complex that is well dispersed and



stabilized on a nanocrystalline NAP-MgO catalyst system for the heterogeneous oxidation of various alcohols to the corresponding carbonyl products under oxidant and additive-free conditions at room temperature using air as an oxidant. This catalyst system shows excellent selectivity and yields towards the oxidation of both primary and secondary benzylic alcohols, primary aliphatic alcohols and heterocyclic alcohols. Using our catalytic system we also found that primary benzyl alcohols are more reactive than secondary benzyl alcohols, aliphatic alcohols and allylic alcohols. The NAP-Mg-Pd(0) catalyst is easy to handle, eco-friendly, shows consistent activity for multiple reaction cycles, and is cost effective for industrial use.

## Experimental Section

### General Remarks

NAP-MgO [commercial name: NanoActive™ Magnesium Oxide Plus, Specific surface area (BET)  $\geq 590 \text{ m}^2 \text{ g}^{-1}$ ] was purchased from NanoScaleMaterials, Inc. (Manhattan, USA). All chemicals were purchased commercially and were used as received. All solvents used for experiments were dried using standard procedures and distilled prior to use. The FT-IR spectra were recorded on a Perkin-Elmer spectrophotometer. XPS spectra were recorded on a Kratos AXIS 165 with a dual anode (Mg and Al) apparatus using the Mg K $\alpha$  anode. X-ray powder diffraction (XRD) data were collected on a Siemens/D-5000 diffractometer using Cu K $\alpha$  radiation. The particle size and external morphology of the samples were observed on a Philips TECNAI F12 FEI transmission electron microscope (TEM). SEM-EDX was performed on a Hitachi SEM S-520, EDX-Oxford Link ISIS-300 instrument to know the palladium content in the sample. BET surface areas were recorded on a Micromeritics ASAP 2020 Surface Area and Pore Analyzer instrument. Prior to surface area analysis all the samples were degassed at 100 °C. GC analysis was performed using Shimadzu GC-2010 and ZB-5 capillary column. GC-MS analysis was carried out in a Hewlett Packard 6890 series GC system using a HP-IMS column of 15 m  $\times$  0.25 mm  $\times$  0.25  $\mu\text{m}$ .  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on Bruker 200, Inova 500 and Avance 300 (300 MHz  $^1\text{H}$  and  $^{13}\text{C}$ ) spectrometers in  $\text{CDCl}_3$  using TMS as internal standard. ACME silica gel (100–200 mesh) was used for column chromatography purposes and thin layer chromatography was performed on Merck precoated silica gel 60-F254 plates. Other Pd(0)-containing heterogeneous catalysts, namely Pd-HAP, Pd FAP and Pd-Mg-LaO, were synthesized according to literature procedures.<sup>[14]</sup> Pd-C was purchased from commercial sources and has 10% Pd on carbon.

### Preparation of Nanocrystalline MgO stabilized Palladium Catalysts

**NAP-Mg-PdCl<sub>4</sub>:** NAP-MgO (BET  $590 \text{ m}^2 \text{ g}^{-1}$ , 1 g) was treated with  $\text{Na}_2\text{PdCl}_4$  (147 mg, 0.5 mmol) dissolved in 100 mL decarbonated water with vigorous stirring for 12 h at 5 °C under a nitrogen atmosphere to afford the brown colored

NAP-Mg-PdCl<sub>4</sub>. Then the catalyst was filtered and washed with deionized water and acetone and dried under vacuum.

**NAP-Mg-Pd(0):** NAP-Mg-PdCl<sub>4</sub> (1 g) was reduced with sodium borohydride (1.5 g, 39.6 mmol) in 20 mL dry ethanol for 3 h under a nitrogen atmosphere at 5 °C while vigorously stirring the reaction mixture. Then the reduced catalyst was filtered through a G-3 sintered glass funnel and washed with deionized water and acetone, and dried under vacuum to get the black-colored, air-stable NAP-Mg-Pd(0) (Pd  $0.048 \text{ mmol g}^{-1}$ ). The catalyst was well characterized by XRD, FTIR, SEM-EDX, TEM and XPS (see Supporting Information).

### General Procedure for the Oxidation Reaction

Alcohol (1.0 mmol), NAP-Mg-Pd(0) (30 mg, Pd  $0.048 \text{ mmol g}^{-1}$ ),  $\text{K}_2\text{CO}_3$  (166 mg, 1.2 mmol) were taken (for solid alcohols 3 mL of toluene were used as a solvent) in a 25-mL round-bottomed flask equipped with a teflon-coated magnetic stirring bead and stirred for an appropriate time under atmospheric air at room temperature. The progress of the reaction was monitored by TLC and on completion of the reaction; the reaction mixture was filtered to separate the catalyst. The solid residue was first washed with water and then with diethyl ether to remove any excess base and any organic material. It was then dried at room temperature and used as it is for further reactions. The reaction mixture was diluted with water (20 mL) and then extracted with EtOAc (3  $\times$  10 mL). The combined organic layers were washed with brine solution (10 mL) and then dried over anhydrous  $\text{Na}_2\text{SO}_4$ . Then, the solvent was evaporated under reduced pressure to yield the crude product, which was then purified by flash chromatography over silica gel (100–200 mesh) column using hexane/ethyl acetate as an eluent to afford the pure product. The products were characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and mass spectral analysis (see Supporting Information) and the data compared with those of authentic samples.

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