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Selective Oxidation of Benzyl Alcohol Over Hydroxyapatite – Supported Au-Pd Nanoparticles

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ABSTRACT

The selective oxidation of alcohols to the carbonyl compounds is of great importance as aldehydes and ketones are valuable intermediates for the production of fine chemicals. Au and Pd are highly active for the oxidation of primary alcohols. However, traditional oxidants are often toxic and release a considerable amount of by-products. Here we report the synthesis of bimetallic Au-Pd nanoparticles supported on hydroxyapatite (HAP) as a heterogeneous catalyst for the selective oxidation of benzyl alcohols to benzaldehydes under air atmosphere without using any oxidant. Under optimal conditions, bimetallic Au-Pd/HAP catalyst showed remarkably enhanced catalytic activity and selectivity as compared with their monometallic counterparts. The catalyst was found to be highly stable, passes hot filtration test successfully and could be recycled several times without significant loss of activity. The catalyst was characterized by TGA, FTIR, AAS, XRD, SEM and TEM.

Keywords: Oxidation of benzyl alcohols, Au-Pd/HAP, Heterogeneous catalysis, Recyclability, Benzaldehydes.

INTRODUCTION

Tremendous efforts have been devoted in the recent years for developing heterogeneous noble metal catalysts from the viewpoints of atomic efficiency and environmentally benign processes [i(a-f)]. In recent time, nanoparticles has emerged as excellent sustainable alternatives to conventional solid supports [ii], since they increase the exposed surface area of the active component of the catalyst, thus enhancing the contact between the reagents and the catalytic center [iii], as it happens in homogeneous catalysis. However, if nanoparticles are immobilized on a solid, insoluble support, they can be easily separated from the reaction mixture [iv], which is the main advantage of heterogeneous catalysis over homogeneous systems which lead to novel environmentally benign chemical procedures for academia and industry. The selective oxidation of organic compounds, such as alcohols or hydrocarbons, to carbony compounds is a primary and essential transformation in organic synthesis [v] and industrial chemistry due to the wide ranging utility of these products as important precursors and intermediates for many drugs, vitamins and fragrances. Traditionally, benzyl alcohol oxidations are achieved by utilizing stoichiometric oxygen donors, such as toxic metal oxides [vi] like chromium trioxide [vii], ammonium permanganate [viii], tert-butyl hydroperoxide [ix], halides [x] or ozone [xi], etc. However, these stoichiometric oxygen donors are expensive, toxic, corrosive, and produce waste. Recently, the use of oxidants, such as aqueous H_2O_2 and molecular O_2, has attracted considerable attention because of economic and environmental concerns [xii]. Molecular oxygen is the most desirable oxidant [xiii] because it is cheap, safe, readily available, and above all, produces water as the sole byproduct. Compared with those oxidants, undoubtedly, air is the most ubiquitous, atom economical and environmentally benign oxidant. Nowadays, catalytic oxidations with ambient air as the ultimate oxidant represent one of the most critical technologies in chemical industry. However, due to the triplet ground state structure of oxygen, air is unreactive and difficult to activate, especially towards the strong C-H bond of hydrocarbons. Recently, breakthrough in Au and Pd catalysis provided new opportunities for aerobic oxidation chemistry [xiv]. Bimetallic nanoparticles are of greater interest than monometallic ones for improving the catalytic properties due to synergetic effects between two elements [xv]. Recently, several research groups have examined supported Au–Pd bimetallic catalysts, which have remarkably enhanced catalytic activity and product selectivity in various alcohol oxidation reactions [xvi]. Enache et al. reported an extraordinarily high TOF (269,000 h^{-1}) of Au–Pd/TiO_2 in 1-phenylethanol selective oxidation, showing that the combination of gold and palladium in an alloyed nanoparticle configuration led to a 25-fold improvement in catalytic activity [xvii]. The advantage of bimetallic catalysts is attributed not only to electronic interaction between the two metals but also to the complex structure of bimetallic nanoparticles [xviii]. Several studies tested different bimetallic nanoparticle structures, such as core–shell structure [xix], cluster-in-cluster structure [xx], and single-alloy structure [xxi]. However, these catalysts are generally prepared by multistep procedures and further require high temperatures and strong reductants during their preparation.

We herein report a recyclable Au-Pd nanoparticles supported on hydroxyapatite (HAP) solid support prepared from readily available reagent, like $HAuCl_4$ and $Pd(OAc)_2$ at room temperature and without the use of strong reducing agents.

MATERIALS AND METHODS

$HAuCl_4$, $Pd(OAc)_2$, K_2CO_3 and all benzyl alcohols were purchased from Merck (Germany) and Aldrich Chemical Company. All melting points were determined on a Perfit melting point apparatus and are uncorrected. ^1H NMR spectra were recorded on a Brucker DPX-200 NMR spectrometer (200 MHz) in $CDCl_3$ using tetramethylsilane as an internal standard and IR spectra were recorded on Perkin-Elmer FTIR spectrophotometer using KBr discs. Mass spectral data was recorded on Bruker Esquire 3000 (ESI). Thermal analysis was carried out on Linseis Thermal Analyser with heating rate of 10 °C/min. SEM was recorded using Jeol make T-300 Scanning Electron Microscope and Transmission Electron Micrographs (TEM) in a H7500 Hitachi. The amount of Au and Pd was determined on GBC Avanta-M Atomic Absorption Spectrometer manufactured by GBC Scientific agencies.

Preparation of Au-Pd supported hydroxyapatite: Bimetallic Au-Pd/HAP catalyst was prepared via sol-immobilization (SI) and adsorption–reduction (AR) methods. A well mixed aqueous solution of $HAuCl_4$ (0.5 mM) (25 mL) and acetone solution of $Pd(OAc)_2$ (0.5 mM) (25 mL) were mixed and stirred at room temperature for 24 h. Freshly prepared solution of sodium borohydride ($NaBH_4$) (1.6 mM) was added dropwise to the resulting solution under vigorous stirring at room temperature, where spontaneous reduction resulted in the formation of bimetallic Au-Pd bimetallic sols. After 1 h of complete sol generation, an amount of hydroxyapatite HAP (2 g) solid support was added under vigorous stirring for 6 h. Thereafter the suspension was filtered, washed thoroughly with deionized water and dried subsequently in vaccum oven at 50 ^{0}C for 6 h.

An amount of HAP (2 g) support was initially immersed in a 50 mL well-mixed aqueous solution of $HAuCl_4$ (0.5 mM) and acetone solution of $Pd(OAc)_2$ (0.5 mM) at room temperature and stirred for 24 h for the AR method. Afterwards, a freshly prepared solution of sodium borohydride (1.6 mM) was added dropwise during stirring. The suspension was stirred vigorously for another 1 h and finally filtrated; the solids were then post-treated as in the SI method.

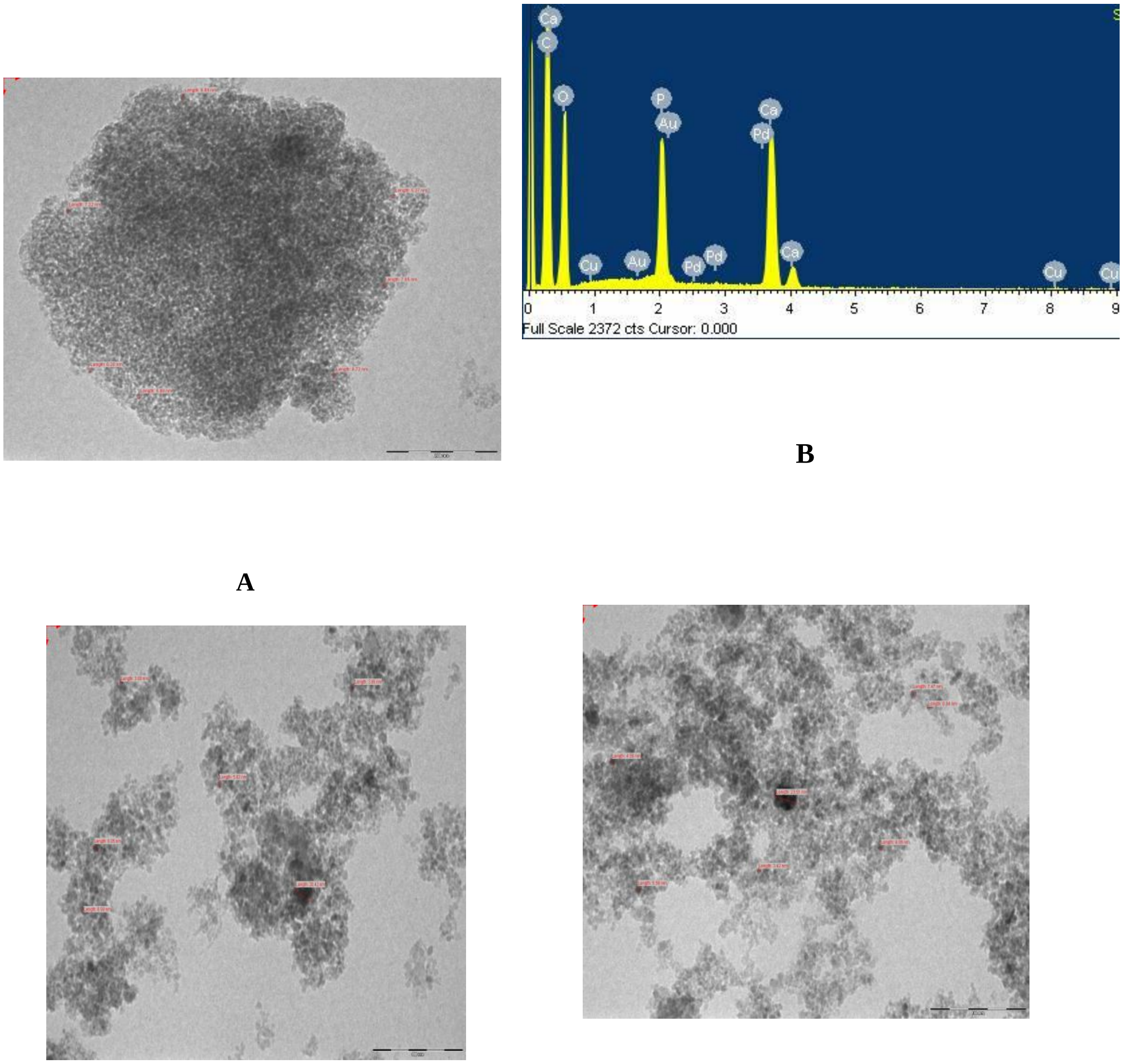
Several bimetallic catalysts with different Au/Pd molar ratios were prepared by varying the concentrations of $HAuCl_4$ and $Pd(OAc)_2$, and labeled by the Au/Pd molar ratio. For instance Au(1)Pd(1)/HAP/SI corresponds to the HAP supported catalyst prepared by sol-immobilization method with an Au/Pd molar ratio of 1:1. The amount of support material for all prepared catalysts was calculated to maintain the final metal load of 2.5 wt%. The catalytic activities of these two types of catalysts were studied on the oxidation of benzyl alcohols. The most active catalyst (Au-Pd/HAP)/SI was employed to study the scope of the substrates.

General procedure for the selective oxidation of benzyl alcohols to benzaldehydes: To a mixture of benzyl alcohol (1 mmol), Au-Pd/HAP (0.2 g, 2.5 mol% Au and Pd), K_2CO_3 (0.208 g, 1.5 mmol) in a round bottom flask (25 mL), toluene (5 mL) was added and the reaction mixture was stirred at 100 ^oC. On completion (monitored by TLC), the reaction mixture was cooled to room temperature and filtered. The residue was washed with hot ethyl acetate (3×10 mL) followed by distilled water (200 mL). The organic layer was washed with water and dried over anhydrous Na_2SO_4. Finally, the product was obtained after removal of the organic solvent on a rotavapor at 60 °C followed by passing through column of silica gel and elution with ethylacetate : pet ether. The structures of the products were confirmed by spectral data and comparison with authentic samples obtained commercially or prepared according to the literature methods.

RESULTS AND DISCUSSION

Characterization of Au-Pd/HAP: The characterization of Au-Pd/HAP was done on the basis of simultaneous thermal analysis (TGA), Fourier transform infrared spectroscopy (FTIR), atomic absorption spectroscopy (AAS), X-ray Diffractometry (XRD), Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM).

Transmission electron microscopy studies: TEM observations were performed to examine the mean particle size and size distribution of bimetallic (Au–Pd/HAP) catalysts. The images are shown in fig.1. The bimetallic Au–Pd nanoparticles (10.3 ± 2.2 nm) for the catalyst prepared by the SI method were much smaller than both Au (20.42 ± 3.85 nm) and Pd (23.51 ± 3.42 nm) monometallic nanoparticles, suggesting the chemical combination of Au and Pd to form the bimetallic nanoparticles rather than physical combination. The particle sizes of the Au catalysts and bimetallic catalysts decreased slightly with the AR method. This feature is attributed probably to the different pathways of loading the metal precursors on the support where the size of the bimetallic nanoparticles with the AR method can be restricted to the pore size of the support. No metal particle for the Pd/HAP/AR catalyst was large enough to be detected by TEM. however, the corresponding EDX analysis revealed the presence of Pd, indicating a highly dispersed Pd phase on the support. TEM images (Figure 1) showed the uniform distribution of gold and palladium onto surface of hydroxyapatite.



B

A

C

D

Figure 1. TEM images of bimetallic Au-Pd/HAP catalyst with corresponding nanoparticles size distributions. Insets: (a) Au-Pd/HAP/SI (b) EDX spectra of the catalysts with the Cu and Ca signal because of the copper grid holder and support HAP. (c) Au/HAP/SI, (d) Pd/HAP/SI

Thermogravimetric analysis: Thermal analysis curve for the Au-Pd/HAP showed initial weight loss up to 100 ^{o}C which may be due to the loss of residual water trapped onto the surface of HAP. Further, a negligible weight loss (0.29%) was observed up to 395 ^{o}C. Thus, catalyst is stable up to 395 ^{o}C and hence, it is safe to carry out the reaction up to 100 ^{o}C.

Fourier Transform Infra-Red Spectroscopic studies : In FTIR spectra, strong absorption peaks at 473, 569, 602, 3572 cm^{-1} and weak intensity peaks at 1412 and 2924 cm^{-1} were observed. Further, wide absorption bands also appear at 1047 and 3421 cm^{-1} (Figure 2). All these peaks are characteristic of HAP (hydroxyapatite) indicating that during the formation of Au-Pd/HAP, structure of hydroxyapatite remained intact.

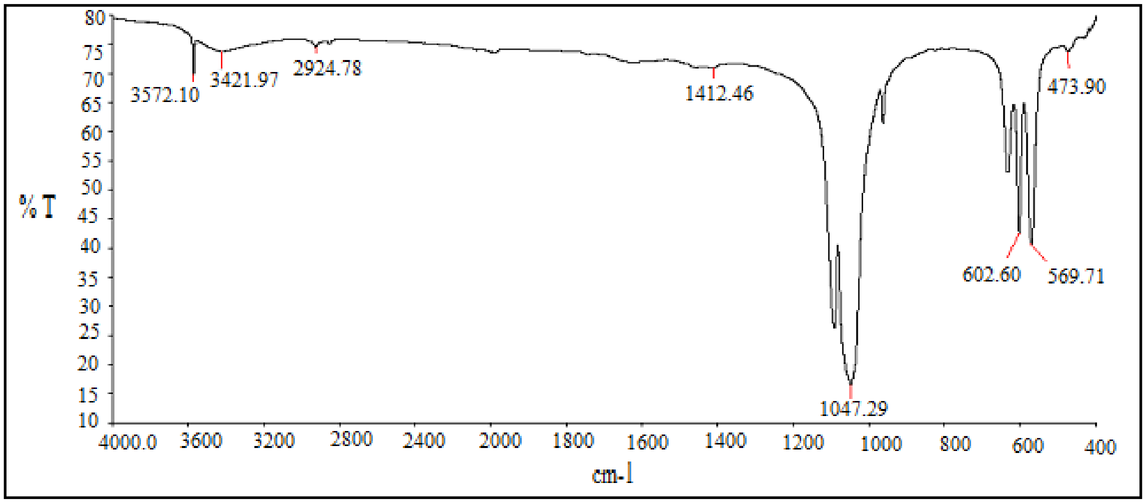


Figure 2. FTIR spectra of Au-Pd/HAP.

X-ray diffraction studies : The XRD (Figure 3) showed reflection patterns corresponding to 2θ = 38.3°, 44.6° which were attributed to Au and 2θ =33.8° which corresponds to Pd. The diffraction peaks of the bimetallic catalyst at 38.6◦ located between Au(1 1 1) and Pd(1 1 1) is assigned to the Au–Pd stable alloy phase.

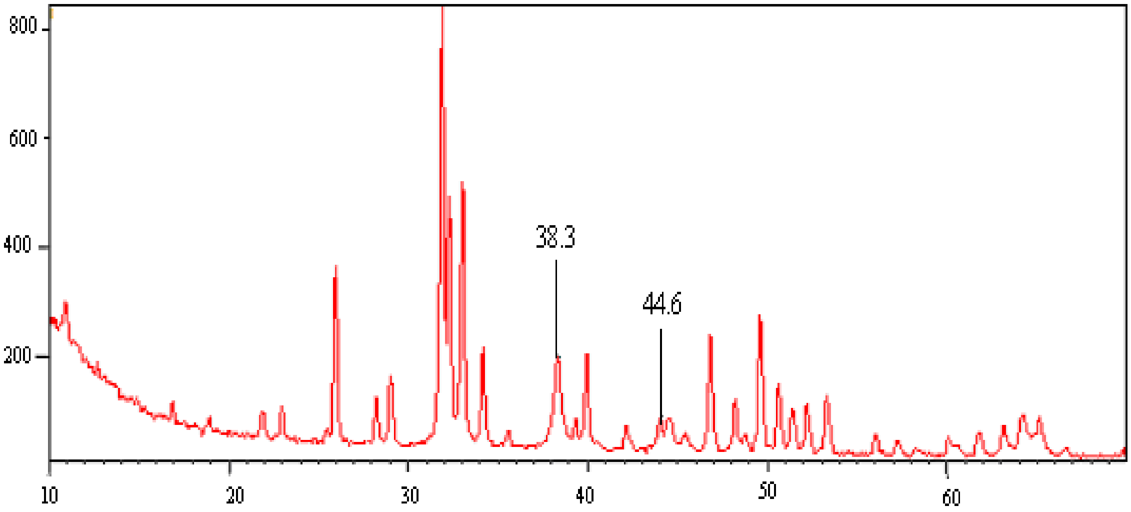


Figure 3. XRD spectra of Au-Pd/HAP.

Atomic Absorption Spectroscopy: The amount of gold and palladium loaded onto the surface of hydroxyapatite was determined by AAS analysis. The catalyst was stirred in dil. HNO_3 and then subjected to AAS analysis. It was found that Au-Pd/HAP contained 0.02461 g of Au and Pd per gram of the catalyst.

Scanning Electron Microscope studies : The physical form of the catalyst was characterized by using Scanning Electron Microscope. SEM image of Au-Pd/HAP shown in (Figure 4) indicates that it is a homogeneous powder.

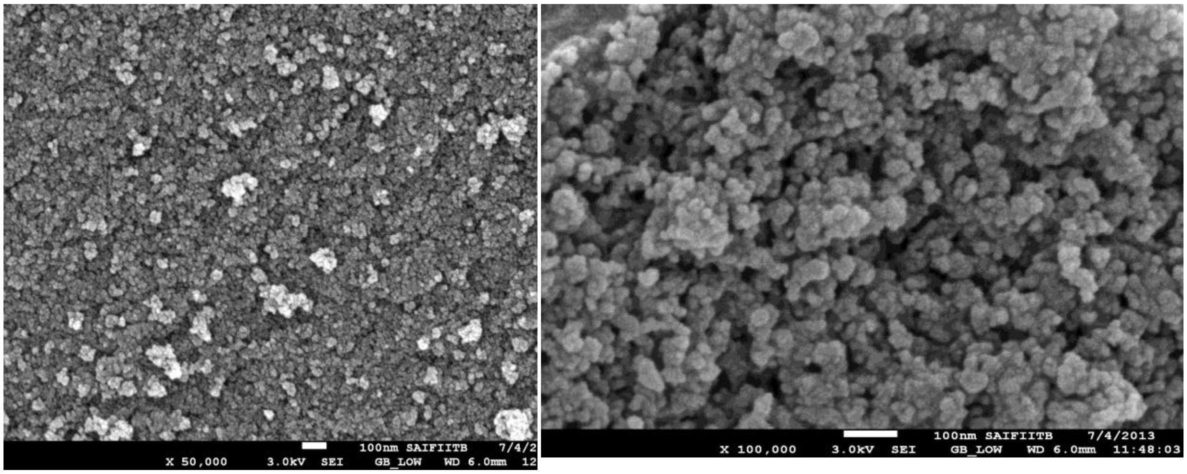


Figure 4. SEM images of Au-Pd/HAP/SI.

Catalyst testing for the selective oxidation of benzyl alcohols to aldehydes : The reaction conditions for catalytic oxidation of benzyl alcohols to corresponding aldehydes were optimized by selecting 4-chlorobenzyl alcohol as the test substrate and Au-Pd/HAP/SI as the heterogeneous catalyst. Addition of base was found to be necessary for the efficient and selective conversion. Due to its inexpensiveness and mild nature, K_2CO_3 was selected as the base. Further, initially air was used as a source of molecular O_2 and to make the process green and economic. A further improvement in the efficiency of aerobic oxidation was achieved by using the molecular oxygen in place of atmospheric oxygen. For the optimization of the solvent, the reaction was carried out in polar and non-polar solvents (Table 1). Among toluene, acetonitrile and water, best results in term of yield, reaction times and selectivity were observed in toluene. Whereas in more polar solvents like acetonitrile and water, only 20% and 15% yields of the corresponding aldehyde was obtained respectively, and this loss of activity may be a result of the leaching of gold or palladium in polar solvents. Thus, toluene was selected as the solvent for the oxidation of benzyl alcohols. Further, the reaction was carried out at different temperatures, 25, 50, 80, 100 and 110^{o}C and found that 100 °C was the optimum reaction temperature in terms of activity and selectivity. The reaction was found to be sluggish at low temperatures and at high temperature the selectivity was reduced. The reaction with the test substrate was also carried out using different molar ratios of the catalyst (Table **1**) and found that 2.5 mol% of Au and Pd in Au-Pd/HAP was efficient to carry out the reaction with good selectivity.

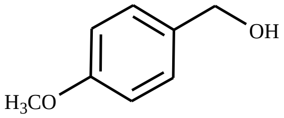
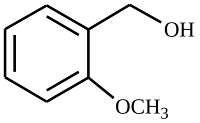
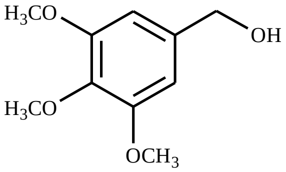
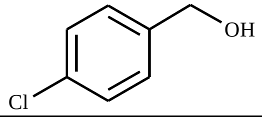
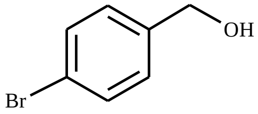
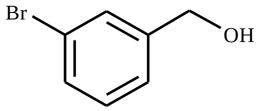
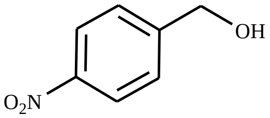
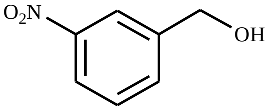
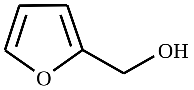
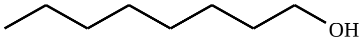
Table 1. Effect of solvents and catalyst loading in the oxidation of 4-chlorobenzyl alcohol to aldehyde$^{\mathbf{a}}$

Effect of solvent			**Effect of catalyst loading**		
Entry	Solvent	Yield (%)^b	Entry	Catalyst (mol% Au and Pd)	Yield (%)^b
1	Acetonitrile	20	1	1	65
2	Water	15	2	1.5	70
3	**Toluene**	**95**	3	2	85
			4	**2.5**	**95**
			5	3	95

$^{\mathbf{a}}$Reaction conditions: 4-chlorobenzyl alcohol (0.1869 g, 1 mmol), Au-Pd/HAP (0.2 g, 2.5 mol%), K_2CO_3 (1.5 mmol), toluene (5 mL), 100 ^{o}C as the reaction temperature. The reaction was carried out under air atmosphere for 5 h.
$^{\mathbf{b}}$Yield refer to column chromatography yield.

In order to study the generality of the developed protocol, different benzyl alcohols with substituted electron-donating and electron-withdrawing substituents were chosen and good to excellent results were obtained. In case of 3,4,5-trimethoxybenzyl alcohol, 4-bromobenzyl alcohol, 4chlorobenzyl alcohol and 4-nitrobenzyl alcohol, the reaction was completely selective without over oxidation to acids (Table 2). However, in case of 4-methoxybenzyl alcohol and 2-methoxybenzyl alcohol very little amount of over oxidized product was formed. For 3-nitrobenzyl alcohol and furfuryl alcohol, the reaction was completely selective but didn't proceed to completion. To extend the application of the developed protocol for the oxidation of aliphatic alcohols, 1-octanol was selected as the test substrate. The reaction was found to be completely selective and no over oxidation was observed though reaction time was quite longer (Table 2, entry 10).

Table 2. Oxidation of benzyl alcohols to aldehydes in the presence of catalyst under air atmosphere[a]

Entry	Alcohol	Time (h)	Yield (%)[b]		m.p./lit. m.p. (°C)
			2	3	
1		5	85	10	liq./248 [34]
2		5	65	20	32-33/30-40[34]
3		4	92	0	72-73/72-74 [34]
4		5	95	0	45-46/47 [34]
5		8	92	0	55-56/55-58 [34]
6		12	65	0	22-23/20-22 [34]
7		6	95	0	liq./103 [34]
8		12	75[c]	0	55-56/55-58 [34]
9		18	55[c]	0	liq./162 [34]
10		20	85[c]	0	liq./171 [34]

[a]Reaction conditions: alcohol (1 mmol), Au(0)-Pd(0)/HAP (0.2 g, 2.5 mol%), K_2CO_3 (1.5 mmol), toluene (5 mL), 100 °C as the reaction temperature. Air was used as the source of O_2.

[b]Yield refer to column chromatography yield.

To determine the role of Au-Pd/HAP for oxidations, the test reaction was also carried out in the absence of the catalyst. The reaction didn't proceed in the absence of the catalyst, thus, indicating that Au-Pd/HAP is catalyzing the oxidation.

Heterogeneous catalysis and recyclability: To rule out the contribution of homogeneous catalysis, hot filtration test was carried out for these oxidation reactions. After 40% conversion of the test substrate (Table 2, entry 4), the reaction mixture was filtered and liquid phases were transferred to another flasks and allowed to react under the reaction conditions, but no further conversion was observed. The second point was the deactivation and recyclability of the catalyst, which becomes more important in case of oxidation reactions. To test this, series of five consecutive runs were carried out with the same test substrate for the oxidation of benzyl alcohol to benzaldehyde. It was found that for the oxidation to benzaldehyde, there occurred a very little drop in the activity of the catalyst which may be attributed to the microscopic changes on the structure of the catalyst.

APPLICATIONS

Benzaldehyde, a versatile intermediate, is one of the most valuable aromatic aldehydes in organic synthesis ranging from perfumery, pharmaceuticals, cosmetics, dyestuff, and agrochemical industries [xxii]. Currently, increasing environmental concerns necessitate the development of eco-friendly techniques for benzyl alcohol oxidation transformation [xxiii]. Accordingly, it is desirable to develop alternative processes and catalysts for the conversion of benzyl alcohol to benzaldehyde. The designs of alternative synthesis techniques that inject "greenness" into the three aspects of benzaldehyde production, specifically: (i) utilizing green oxidants, (ii) employing clean solvents, and (iii) designing environmentally benign catalysts with high activity and selectivity, is of supreme importance.

CONCLUSIONS

In conclusion, Au-Pd/HAP/SI as a heterogeneous catalyst for selective oxidation of alcohols to their respective aldehydes has been explored successfully using different oxidants like hydrogen peroxide, atmospheric oxygen and molecular oxygen. While gold alone is very effective catalyst for the selective oxidation of alcohols to an aldehydes, the alloying of gold with palladium leads to a more enhancement in activity with the simultaneous retention of selectivity over monometallic gold and palladium counterparts for the oxidation of benzyl alcohols to aldehydes in presence of molecular oxygen. The mild reaction conditions, high yield of products, ease of work-up, compatibility with various functional groups, and the ecologically clean selective procedure will make the present methodology a useful and important addition to the present methodologies for the oxidation of benzyl alcohols to aldehydes.

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