



Photocatalytic Oxidation of Alcohols Using Bimetallic Ag-Pd/TiO₂ Catalyst in Presence of Visible Light Irradiation

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Bimetallic Ag-Pd nanoparticles supported on TiO₂ have been prepared using *Ocimum tenuiflorum* leaf extract and characterized by UV-visible, SEM, SEM-EDS, TEM, SAED pattern and XPS analysis. This heterogeneous catalyst is efficient for oxidation reactions of alcohol and can be reused upto 5th cycles. Use of low cost and non-toxic TiO₂ as support is an additional advantage to this catalyst.

Keywords: Silver, Palladium, Bimetallic nanoparticles, TiO₂, Heterogeneous, Alcohol oxidation.

INTRODUCTION

Noble metal nanoparticles have found extensive use in several technological applications [1,2]. There is a great interest in synthesizing metal and semiconductor nanoparticles due to their remarkable properties which differ from when they are in bulk. In recent years, growing attention has been paid to bimetallic catalysts, composed of two metal elements in either alloy or intermetallic form, with catalytic properties different from mono-metallic nanoparticles catalysts. In comparison to mono-metallic nanoparticles, bimetallic systems frequently shows significantly improved catalytic activity for several chemical reactions, even at low temperatures [3]. The increased catalytic activity of hybrid nanoparticles could be directly attributable to electronic coupling between two different metals together with geometric effects caused by the different lattice constants [4]. On the other hand, inexpensive, chemically stable and non-toxic TiO₂ powders have been used as white pigment from ancient times. TiO₂ has no absorption in visible range and active only under UV light irradiation because of its wide band gap [5]. Since UV light accounts only a small fraction of (14 %) of sun's energy compared to visible light [6], so shift in optical response of TiO₂ from UV range to visible range increases its practical use. It is needed to develop a TiO₂ photocatalyst activated by visible light sensitive nanoparticles, which results in growth of photogenerated electrons in the conduction band of TiO₂ [7]. Recently, photocatalytic activity of TiO₂ modified with

bimetallic nanoparticles including Pt-Au [8], Pt-Pd [9], Pd-Au [10], Pt-Cu [11] and Cu-Ag [12] has been studied by different researchers. Depending on the processing parameters, miscibility and reduction kinetics of metal ions a bimetallic particle can be synthesized as an alloy or intermetallic structure, heterostructure, core-shell or multi-shell structure. The structure of bimetallic nanoparticles deposited on TiO₂ largely depends on the amount of metal loaded and preparation procedure [13].

Moreover, oxidation reactions are among the most important and widely used reactions in industrial processes [14]. Particularly, the oxidation of primary and secondary alcohols to the corresponding carbonyl compounds is of significant importance in organic synthesis, since it is at the core of numerous synthetic methods [15]. The products obtained in alcohol oxidation reactions have wide utility as important precursors and intermediates for many drugs, vitamins and fragrances [16]. Many reagents and catalysts exist for this transformation reaction, but some methods still have significant scale-up issues. Due to this reason, in spite of being a fundamentally important reaction, the oxidation of an alcohol to a carbonyl compound is generally avoided by the pharmaceutical industry and so looking for new, facile, economical and mild procedures which avoid the use of large excess of toxic and expensive stoichiometric metal oxidants has attracted extensive attention.

Herein, we report oxidation of alcohols to aldehydes and ketones using TiO₂ (anatase) supported bimetallic Ag-Pd nanoparticles as catalyst, *t*-BuOOH (*tert*-butyl hydroperoxide)

as oxidizing agent under visible light and using H₂O as solvent system.

EXPERIMENTAL

All the chemicals used in this study such as Ag(NO₃), Pd(NO₃), titanium isopropoxide, ethyl acetate, methanol, toluene, *t*-butyl hydroperoxide (TBHP), Na₂CO₃, ethanol, NaOH and various substrates used in this study were purchased from Merck, Rankem, Sigma Aldrich, *etc.* and used without additional purifications.

TiO₂ supported Ag-Pd bimetallic nanoparticles: Aqueous leaf extract of *Ocimum tenuiflorum* plant, collected from the garden of the Department of Chemistry, Dibrugarh University was used to synthesize Ag-Pd bimetallic nanoparticles. To prepare the plant extract, first 10 g of collected leaves were washed and finely crushed using a mortar. Then 50 mL distilled water was added and heated at 40 °C for 2 h. To synthesize Ag-Pd nanoparticles, 15 mL of an aqueous mixture of AgNO₃ and Pd(NO₃)₂ (0.5 mM AgNO₃ and 0.5 mM Pd(NO₃)₂) was heated at 80 °C with stirring rate of 700 rpm. Then 10 mL of plant extract was added dropwise to this precursor solution and vigorously stirred for 2 h and end products were obtained.

To synthesize TiO₂ supported Ag-Pd bimetallic nanoparticles, 15 mL acetic acid (glacial) was taken in a beaker. Then 9.3 mL of titanium isopropoxide was hydrolyzed using acetic acid solution at room temperature. After that 200 mL water was added to it under vigorous stirring for 1 h, (after adding 100 mL water, 5 mL of Ag-Pd bimetallic nanoparticles were added dropwise). It was stirred for 30 min followed by ultrasonication for 15 min. The stirring was continued for further 1 h. The prepared solution was then kept in dark for 24 h to allow the nucleation process. After this period, the solution was placed in an oven at 100 °C for gelation and aging process and afterward crushed into fine powder to get the required catalyst [6].

General method for oxidation of alcohols: The oxidation (photocatalytic oxidation) of alcohol was carried out under visible light in a round bottomed flask surrounded by circulating water jacket using 100 W LED light (400-700 nm) as light source equivalent to 0.16 sun (distance of light source from the reaction flask is 28 cm) at room temperature. 1 mmol of alcohol was taken in a 50 mL round bottom flask. To it, 3 mL of H₂O as solvent, 20 mg catalyst (Ag-Pd/TiO₂) and 0.2 mL oxidant (*t*-butyl hydroperoxide) were added. Then the mixture was stirred using magnetic stirrer under visible light irradiation. The progress of the reactions were monitored by thin layer chromatography using alumina coated TLC plates under visible light. After completion of the reaction, the catalyst was separated by filtration and the residual solid was washed several times with the solvent H₂O used in the reaction. The filtrate was diluted with water and extracted with ethyl acetate. The extract was then dried over anhydrous Na₂SO₄. The solvent was then evaporated and using column chromatography purified products were obtained.

RESULTS AND DISCUSSION

Characterization of Ag-Pd/TiO₂

UV-visible spectroscopy analysis: Primarily, formation of nanoparticle is characterized by UV-visible spectroscopy

and this technique has been widely used in synthesis of nanoparticles with surface plasmon resonance (SPR) bands. The UV-visible absorbance behavior of bare TiO₂ and TiO₂ supported Ag-Pd bimetallic nanoparticles are shown in Fig. 1. Generally, AgNPs exhibits characteristic SPR band centered at 426 nm and PdNPs does not show any absorption peak in the range 300 to 800 nm. Occurrence of a broad absorption peak around 440 nm is indicative of the formation of bimetallic nanoparticles [17].

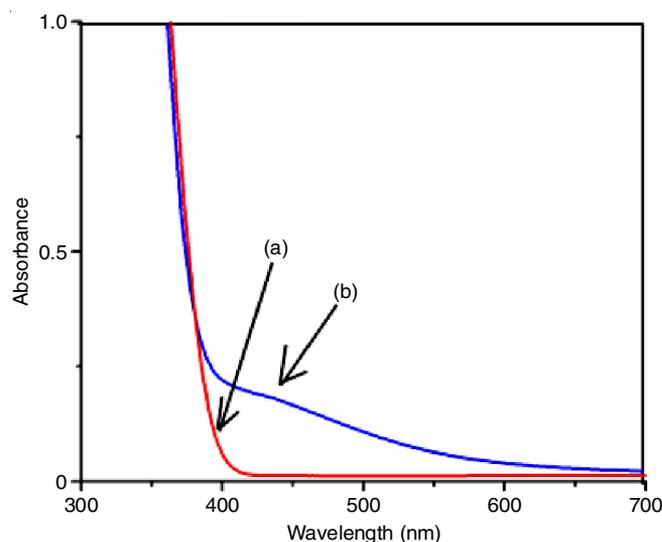


Fig. 1. UV-visible absorption spectra of (a) TiO₂ and (b) Ag-Pd/TiO₂

XRD pattern analysis: Crystalline nature of Ag-Pd/TiO₂ and TiO₂ were studied by XRD analysis. Powder X-ray diffraction (XRD) pattern of Ag-Pd/TiO₂ and TiO₂ are shown in Fig. 2(a) and (b), respectively. In this XRD patterns, similar Bragg's reflection values were observed for both TiO₂ and Ag-Pd/TiO₂ due to low loading of metal nanoparticles in TiO₂. The presence of strong diffraction peaks in the XRD patterns at 2θ values of 25°, 38.1°, 47.8°, 54.1°, 62.7°, 69.1° and 74.9° corresponding to the crystal plane (101), (004), (200), (211), (204), (220) and (215), respectively indicates that TiO₂ is in anatase phase. Since metal loading is less than 0.5 mol %, so XRD pattern of pure TiO₂ nanoparticles and bimetallic Ag-Pd nanoparticles incorporated TiO₂ catalyst look almost similar (JCPDS card No.21-1272) [18,19].

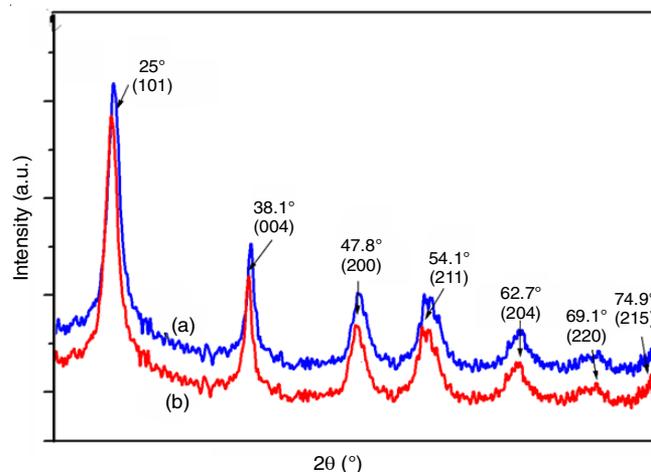


Fig. 2. XRD pattern of (a) TiO₂ and (b) Ag-Pd/TiO₂

SEM-EDS analysis: SEM image in Fig. 3(a) shows clear image of morphology of prepared Ag-Pd/TiO₂. This catalyst was further investigated by energy dispersive X-ray spectroscopy analysis. In EDS spectrum, characteristic peaks confirm the presence of metals Ag and Pd along with Ti and O (Fig. 3b).

ICP-AES analysis: From ICP-AES analysis the loading of palladium and silver is found to be 0.004 mol % and 0.0048 mol % in 20 mg of solid Ag-Pd/TiO₂ catalyst.

TEM analysis: In Fig. 4, TEM images of Ag-Pd/TiO₂ are shown. The TEM images indicate the morphology and size of

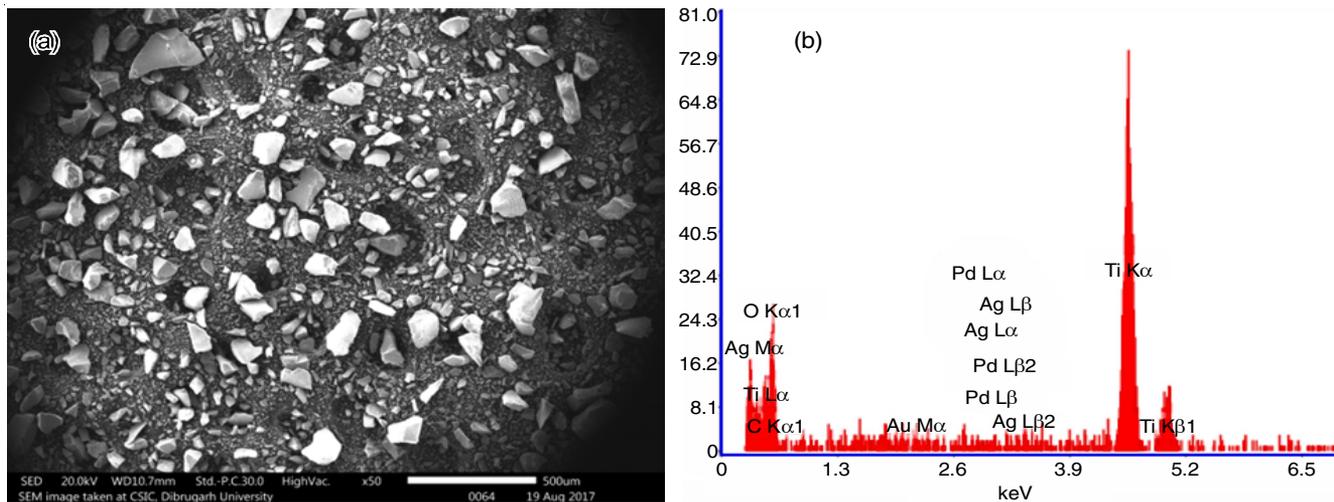


Fig. 3. (a) SEM image and (b) EDS spectrum of Ag-Pd/TiO₂

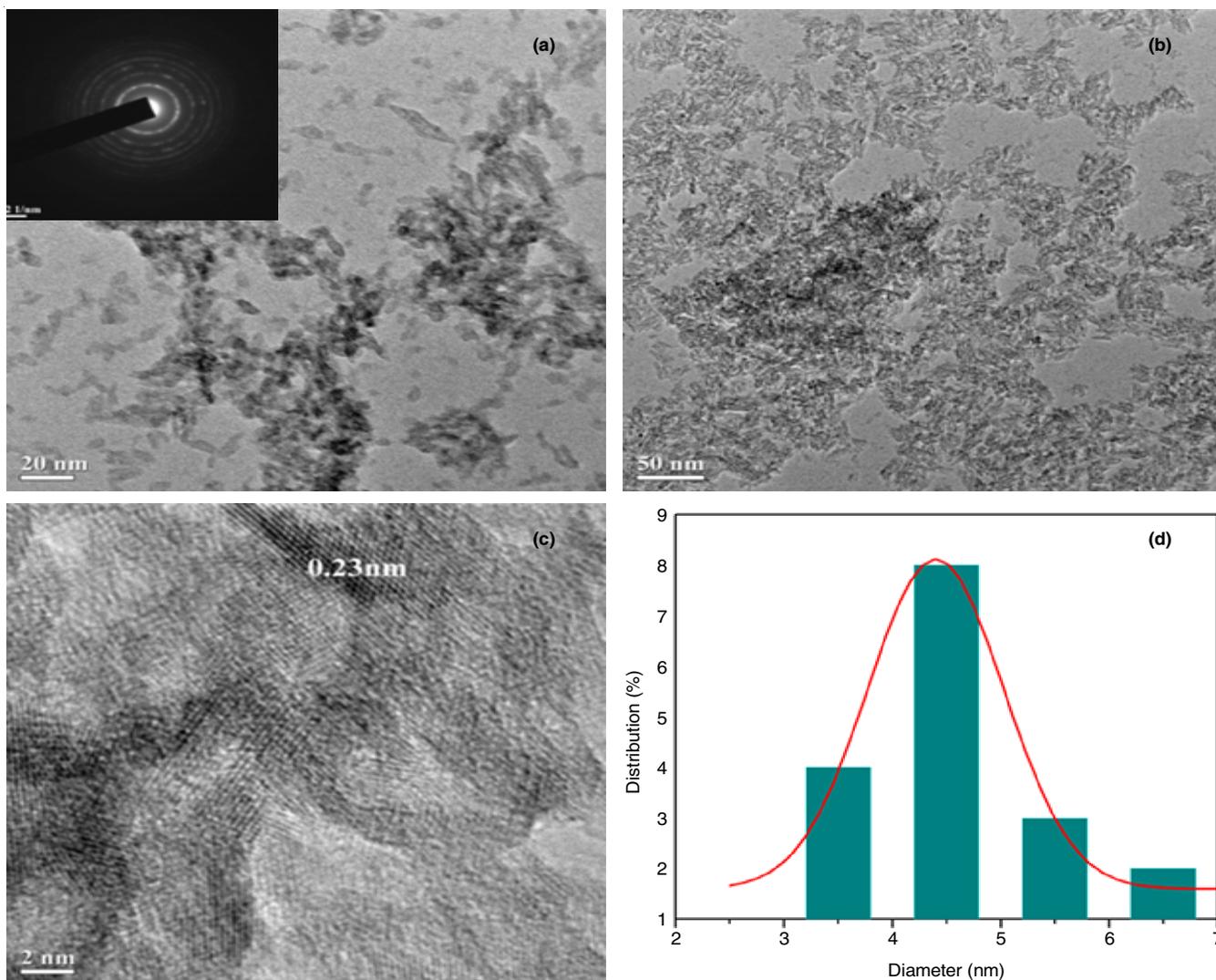


Fig. 4. TEM image of Ag-Pd/TiO₂ (a), (b), (c) at different resolutions and (d) particle size distribution histogram

Ag-Pd/TiO₂ nanoparticles. In Fig. 4a(inset), clearly visible lattice fringes indicate the high crystallinity of the nanostructure. The width of lattice fringes of 0.230 nm in HRTEM images of Ag-Pd/TiO₂ is close to (111) lattice spacing of fcc Pd (about 0.224 nm) and Ag (about 0.235 nm). It could be indicative of alloy structure of prepared alloy Ag-Pd bimetallic nanoparticles supported on TiO₂ [20].

X-ray photoelectron spectroscopy: XPS is a highly surface sensitive technique and was performed to study the elemental composition of the surface [21]. In Fig. 5, XPS photoelectron spectrum of Ag-Pd/TiO₂ is shown. Palladium 3d_{5/2} peak at 335.3 eV and 3d_{3/2} peak at 340.11 eV are attributed to metallic palladium. The peaks at 368.21 and 374.18 eV can be ascribed

to 3d_{5/2} and 3d_{3/2} of silver, respectively. Thus, these XPS spectra prove the presence of metallic palladium and silver in the catalyst [22].

Catalytic activity: Using 1-phenylethanol as model substrate, we optimized the reaction variables such as solvent, amount of catalyst and with different oxidants in presence of visible light. The results of optimization process are summarized in Table-1. First we performed the reaction in aerobic condition in water using 20 mg of catalyst. Under this condition, the product isolated is 32% (Table-1, entry 1). However, the yield of product increased as we used H₂O₂ and TBHP as oxidant (Table-1, entries 4-9). We also found that in absence of oxidant reaction didn't take place (Table-1, entry 11). During optimi-

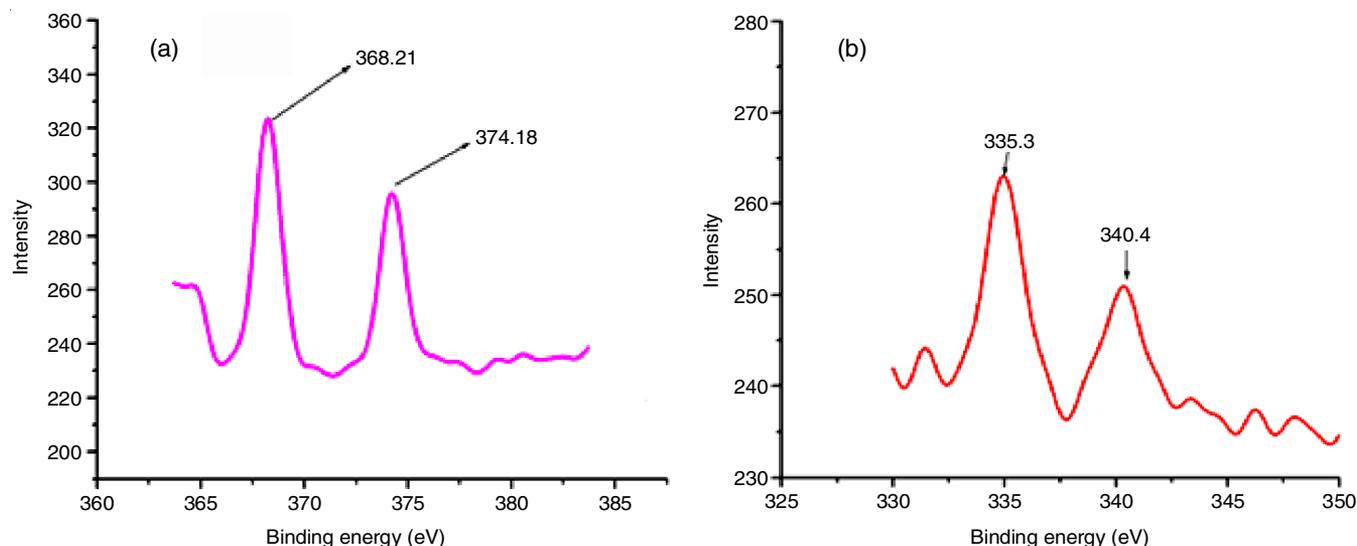
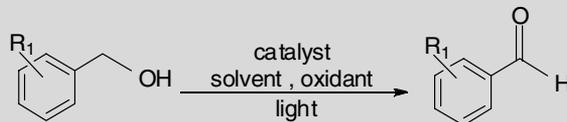


Fig. 5. X-ray photoelectron spectrum of (a) Ag, (b) Pd

TABLE-1
OPTIMIZATION OF THE REACTION CONDITIONS



Entry	Solvent	Oxidant	Catalyst (mg)	Time (h)	Isolated yield ^a (%)
1	H ₂ O	Air	Ag-Pd/TiO ₂	8	32
2	CH ₃ CN	Air	Ag-Pd/TiO ₂	8	29
3	MeOH	Air	Ag-Pd/TiO ₂	8	26
4	H ₂ O	H ₂ O ₂ (0.2 mL)	Ag-Pd/TiO ₂	9	90
5	CH ₃ CN	H ₂ O ₂ (0.2 mL)	Ag-Pd/TiO ₂	7	79
6	MeOH	H ₂ O ₂ (0.2 mL)	Ag-Pd/TiO ₂	8	75
7	H ₂ O	TBHP (0.2 mL)	Ag-Pd/TiO ₂	5	95
8	CH ₃ CN	TBHP (0.2 mL)	Ag-Pd/TiO ₂	6	82
9	MeOH	TBHP (0.2 mL)	Ag-Pd/TiO ₂	7	80
10	–	TBHP (0.2 mL)	Ag-Pd/TiO ₂	9	Trace
11	H ₂ O	–	Ag-Pd/TiO ₂	9	–
12	H ₂ O	TBHP (0.2 mL)	TiO ₂	8	23
13	H ₂ O	TBHP (0.2 mL)	–	6	15
14	H ₂ O	TBHP (0.2 mL)	Ag-Pd/TiO ₂ ^b	7	46
15	H ₂ O	TBHP (0.2 mL)	Ag-Pd/TiO ₂ ^c	7	69
16	H ₂ O	TBHP ^d	Ag-Pd/TiO ₂	8	95
17	H ₂ O	TBHP ^e	Ag-Pd/TiO ₂	6	75
18	H ₂ O	TBHP (0.2 mL)	Ag-Pd/TiO ₂	9	27 ^f
19	H ₂ O	TBHP (0.2 mL)	TiO ₂	7	27 ^g

^aisolated yield, ^b10 mg Ag-Pd/TiO₂, ^c15 mg Ag-Pd/TiO₂, ^d0.3 mL TBHP, ^e0.1 mL TBHP, ^fwithout visible light, ^gwith 20 mg commercially available TiO₂ (P25)

zation process when we increased the amount of TBHP to 0.3 mL, no significant increase of product yield was observed (Table-1, entry 16) however, on decreasing the amount of oxidant yield slightly decreased (Table-1, entry 17).

To study the role of solvent in our reaction, we carried out this reaction using different solvents such as water, acetonitrile and methanol. Among these three solvents, we found water is the most effective for this reaction. When we performed the reaction in water with TBHP and catalyst, amount of product isolated is 95 % (Table-1, entry 7). Moreover, in absence of solvent, trace amount of product is isolated (Table-1, entry 10). We have also studied the effect of amount of catalyst in this reaction and significant decrease in the product yield was seen on decreasing the amount of catalyst to 10 and 15 mg. (Table-1, entry 14, 15). Furthermore, when we performed the reaction using TiO₂ in place of Ag-Pd/TiO₂, yield is only 23 % (Table-1, entry 12). Similarly, in absence of any catalyst product obtained is negligible (Table-1, entry 13). In absence of visible light, decrease in product yield was observed (Table-1, entry 18). So, this study indicates the importance of Ag-Pd/TiO₂ as a good photo catalyst under visible light irradiation for alcohol oxidation reactions.

From the above observations, we optimized the reaction conditions for photocatalytic oxidation reaction of alcohols and to assess the scope of this protocol, we carried out the reaction

with different substrates including both primary and secondary alcohols and the results obtained are enlisted in Table-2.

From substrate study, we have seen that secondary alcohols gave (entry 1 and 9) higher yield than primary ones. Among the primary alcohols, 4-nitrobenzyl alcohol (Table-2, entry 4) gave lowest yield. Furthermore, when we used furfural alcohol (Table-2, entry 8) as substrate, product didn't form and in case of cinnamyl alcohol (Table-2, entry 6) trace amount of product was obtained.

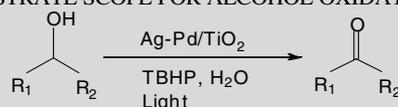
Conclusion

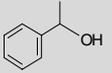
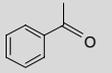
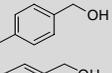
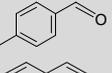
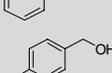
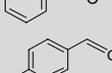
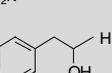
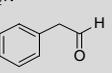
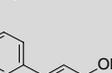
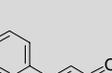
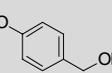
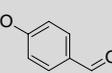
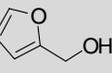
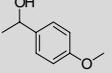
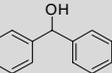
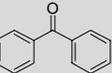
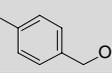
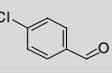
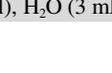
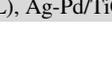
In this work, we presented a scheme for oxidation of both primary and secondary alcohol using TiO₂ supported Ag-Pd bimetallic nanoparticles as an effective heterogeneous photocatalyst and it showed good catalytic activity with a wide range of substrates in aqueous medium. The alcohol oxidation reactions were done under visible light irradiation at room temperature.

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TABLE-2
SUBSTRATE SCOPE FOR ALCOHOL OXIDATIONS^a



Entry	Substrate	Product	Time (h)	Yield ^b (%)
1			4.5	95
2			6	83
3			6	70
4			6	67
5			8	Trace amount
6			9	28
7			6.2	90
8		—	10	No reaction
9			5	89
10			5.5	86
11			6	71

^aReaction conditions: alcohol(1 mmol), H₂O (3 mL), TBHP (0.2 mL), Ag-Pd/TiO₂ (20 mg); ^bisolated yield

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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