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ORIGINAL PAPER

Sonochemical fabrication of Pd/TiO_2-nanotubes/Ti plate as a green catalyst for oxidation of alkylarenes and benzyl alcohols

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Abstract

A facile and fast strategy has been employed to fabricate Pd nanoparticles supported on TiO_2 nanotubes/Ti plate via sonochemical deposition. Microstructure studies showed the homogeneous deposition of Pd nanoparticles on the walls of TiO_2 nanotubes/Ti plate. The synthesized plate was applied as a novel catalyst for the oxidation of benzyl alcohol and ethylbenzene derivatives. The results of catalytic experiments demonstrated that the modified plate was an efficient green catalyst for the oxidation of benzyl alcohols to benzoic acid derivatives in H_2O. The oxidation of alkylarenes was carried out in EtOH:H_2O (1:1) ended up with the formation of the corresponding ketone as the sole product. High yields and excellent selectivities were obtained for the oxidation reactions in green solvents using green oxidant. Superior catalytic activity, easy catalyst recovery, and reusability of the catalyst are some advantages of the modified PdNPs/TiO_2 nanotubes/Ti plate, indicating a potential application of the catalyst in the industrial oxidation reactions.

Keywords Titania · Nanotubes · Catalyst · Oxidation · Heterogeneous catalyst

Introduction

The oxidation of organic substrates into a valuable organic products is one of the most important reactions in the organic synthesis both for laboratory and industry proposes [1, 2]. Hundreds of different catalysts and reagents have been introduced for the oxidation of organic chemicals [3]. Many industrial oxidation reactions were reported with stoichiometric amounts of reagents that gave a big amount of hazardous chemical wastes [4–6]. In recent years, transition metal catalysts have attracted a great deal of attention for the oxidation of various saturated and unsaturated organic chemicals in the presence of cheap and green oxidant such as O_2 or H_2O_2 [7, 8]. The oxidation of alkylarenes and alcohols to the corresponding carbonyl compounds have been carried out with catalytic amounts of Pd using O_2 or H_2O_2 as the oxidant [9]. These reactions are performable with homogeneous and heterogeneous Pd species such as Pd(0), Pd(II), and Pd(IV) [10]. It has been known that homogeneous Pd catalysts due to the existence of catalyst in the same phase with starting material can give high yields [11–13]. Today, heterogeneous catalytic systems have been widely employed for the various catalytic transformations due to significant advantages of heterogeneous catalysts compared to the homogeneous systems [14, 15]. Powdery catalysts containing Pd nanoparticles (PdNPs) have been found to be effective catalysts for the oxidation reactions, but the oxidation reactions with these catalysts have some drawbacks such as stirring during the reaction, separation of the catalyst from the reaction solvent after each run, and the particle aggregation. It seems the immobilizing Pd nanoparticles on a suitable plate as a support can be considered as an excellent strategy for inhibiting from some extra processes for recovery of the catalyst like sedimentation, centrifugation and filtration. Moreover, the mesoporous properties of the support can significantly affect microstructures of palladium, leading to the low size and, therefore, high active catalyst which can improve the performance of the catalyst. Among various types of plates, TiO_2 nanotubes/Ti fabricated by anodizing of titanium plate can be considered as a suitable substrate because of its high

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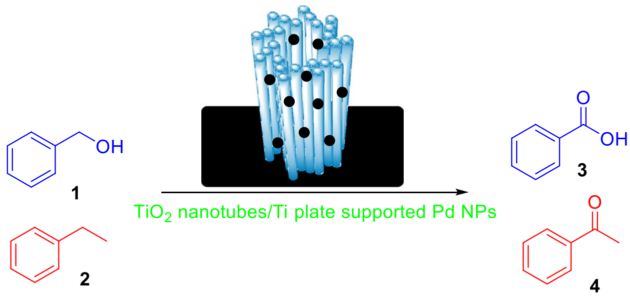
specific surface area, inexpensiveness, good mechanical and chemical stability, controlled pore structure and non-toxicity [16].

In continue of the our research group efforts to introduce new efficient heterogeneous catalytic systems for the oxidation reactions [17–20], herein, we investigated the catalytic applications of TiO_2 nanotubes/Ti plate modified with Pd NPs as a new heterogeneous catalyst in the oxidation of organic substrates. The catalyst was prepared via a simple surface sonochemical modification of TiO_2 nanotubes/Ti plate with Pd NPs. To the best of our knowledge, this work is the first report about use of sonochemically modified TiO_2 nanotubes/Ti plate with Pd NPs as a catalyst for the oxidation of benzyl alcohols and alkylarenes (Scheme 1).



Scheme 1 Oxidation of benzyl alcohol and ethylbenzene in the presence of the catalyst

Experimental

Catalyst preparation

Highly oriented TiO_2 nanotubes/Ti plates were obtained via electrochemical anodizing of Ti metal plates with a geometric area of 3 cm^2 using a DC power source in a two-electrode electrochemical cell. Briefly, prior to each anodizing, Ti plates were polished with emery papers, cleaned in deionized water in an ultrasonic bath, and subsequently were dried in air at room temperature. Electrochemical anodizing of the cleaned plates was conducted at 20 V for 2 h in an electrolyte containing of glycerol/water (75:25, vol%) + 0.5 wt% NH_4F at room temperature using a conventional two-electrode configuration with platinum foil with a geometric area of 9 cm^2 as a counter electrode. The distance between the electrodes was maintained at 2 cm. After the anodizing process, the anodized plates were rinsed by deionized water, dried in the air at room temperature, and finally were annealed at 450 °C for 2 h to crystallize the anodized plates from an amorphous phase to anatase phase. The loading of PdNPs on the TiO_2 nanotubes plate was carried out by electroless-plating under sonication condition for 30 s in a bath containing 4.5×10^{-4} M of $PdCl_2$ at pH 1 s (pH value was adjusted with HCl). It has been believed that the reduction of metal ions can be carried out by sonolysis of water to primary reducing radicals, i.e., H atoms [21, 22]. The major outcomes for nanomaterial synthesis via sonochemical procedure are high catalytic performance due to an increase in specific surface area and narrow size distribution [23, 24]. Sonochemical deposition is a more effective route towards the synthesis of PdNPS with much smaller size, homogeneously Pd dispersion, and higher surface area than those prepared by traditional methods [25, 26].

Characterization and electrochemical studies

The surface morphology of the plate was characterized with a scanning electron microscope (Philips, Model XL30). In addition, elemental mappings were detected by an energy dispersive X-ray spectrometer (EDS) attached to the SEM. Electrochemical impedance spectroscopy (EIS) measurements were carried by Autolab PGSTAT302N potentiostat.

Typical procedure for the oxidation of benzyl alcohol

Benzyl alcohol (0.10 g, 1.00 mmol) was added to a round-bottomed flask containing of H_2O (5 mL) and PdNPs/TiO_2 nanotubes/Ti plate. The mixture was heated to 90 °C, and H_2O_2 (3 mmol) was added dropwise to the reaction vessel during 0.5 h. After 24 h, the plate was removed, the solvent was evaporated under vacuum, and the product was analyzed by GC. The conversions were calculated in the presence of internal standard using integrals of the GC analyses.

Typical procedure for the oxidation of ethylbenzene

Ethylbenzene (0.10 g, 1.00 mmol) was added to a round-bottomed flask containing of H_2O:EtOH (1:1) (5 mL), PdNPs/TiO_2 nanotubes/Ti plate, and KOH (0.03 g, 0.5 mmol). The mixture was heated to 90 °C, and H_2O_2 (3 mmol) was added dropwise to the reaction vessel during 0.5 h. After 24 h, the plate was removed, the solvent was evaporated under vacuum, and the product was analyzed by GC. The convesions were calculated in the presence of internal standard using integrals of the GC analyses.

Results and discussion

Structural and morphological characteristics

The SEM images in Fig. 1 show significant differences in the morphologies of the fabricated plates. The SEM images in Fig. 1a show an array of highly ordered TiO_2 nanotubes formed after anodic oxidation and calcination at 450 °C,

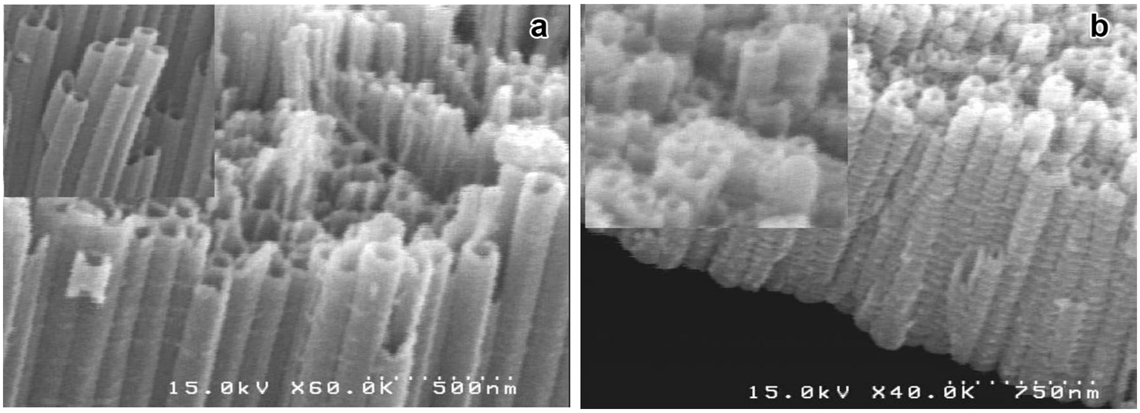


Fig. 1 SEM images of bare TiO_2 nanotubes/Ti plate (**a**), PdNPs/TiO_2 nanotubes/Ti plate (**b**)

where the nanotubes are 140–210 nm and 20–30 nm in the diameter and wall thickness, respectively. Figure 1b shows SEM micrograph of the PdNPs-loaded TiO_2 nanotubes, where NPs of Pd grown on the walls of TiO_2 nanotubes and especially on the top section are observed. The wall thickness of the Pd/TiO_2 nanotubes' plate is 30–40 nm. To probe the chemical composition, the plate material was further characterized by EDX-MAP analysis. Figure 2 shows the EDX spectrum of the PdNPs-TiO_2 nanotubes/Ti plate that confirms the presence of palladium on TiO_2 nanotubes/Ti. In addition, Pd is uniformly distributed on the TiO_2 nanotubes/Ti plate, suggesting that the current synthesis strategy is effective to modify the surface of TiO_2 nanotubes/Ti plate.

The EIS measurements were carried out in aqueous solution containing 10 mM $K_3[Fe(CN)_6]$:$K_4[Fe(CN)_6]$ (1:1) and 0.1 M KCl plates at open-circuit potential (OCP) in the frequency range of 100 kHz–10 mHz to evaluate the charge transfer characteristics of the prepared plates. As can be seen from Fig. 3, the Nyquist plots consist of a depressed semicircle, corresponding the charge-transfer resistance (R_{ct}) in the interface of the plates with electrolyte [27]. The PdNPs/TiO_2 nanotubes/Ti plate possesses lower R_{ct} than TiO_2 nanotubes/Ti plate, indicating the highly network structure formed by PdNPs.

Catalytic activity

The catalytic activity of PdNPs/TiO_2 nanotubes/Ti plate was evaluated in the oxidation reaction of benzyl alcohol. Therefore, the oxidation of benzyl alcohol (**1**) with H_2O_2 was investigated for the optimization of the reaction conditions in the presence of synthesized PdNPs/TiO_2 nanotubes/Ti plate. It was found that H_2O as the solvent and three equivalents of H_2O_2 as the oxidant at 90 °C is the best reaction conditions for the oxidation of benzyl alcohol (Table 1). Oxidation of benzyl alcohol (1 mmol) proceeded to give benzoic acid (**2**) as the sole product with > 99 conversion in 24 h without any byproduct such as benzaldehyde. The oxidation reaction of benzyl alcohol needs Pd and gave lower yields in the absence of Pd (Table 1, entry 5). The reaction needs 3 mmol H_2O_2 for obtaining high yields, and the yields decreased in low amounts of H_2O_2 (Table 1, entries 3 and 4). The reaction temperature is an important factor for the reaction and the yield was decreased in low temperatures especially at room temperature (Table 1, entries 5 and 6). After screening a variety of solvents, H_2O was determined to be the best solvent (Table 1, entries 7–12). The reaction in H_2O, CH_3CN, and CH_2Cl_2 gave benzoic acid selectively. Low yields of the benzoic acid were obtained in solvent free conditions, *o*-xylene, MeOH, and EtOH, also benzaldehyde produced as the by-product. The reaction was examined for excess of benzyl alcohol for obtaining the quantitative conversion ability of the plate which 12 mmol of benzoic acid was produced during 24 h. Excellent selectivity of the reaction in green solvent, high yield, easy work up, green oxidant, and stirring-free oxidation conditions are important features for this approach.

The catalyst application was extended to the oxidation of various benzyl alcohols, including 4-nitrobenzyl alcohol, 2-chlorobenzyl alcohol, and 4-methylbenzyl alcohol (Table 2). High conversions were obtained for the oxidation of benzyl alcohols derivatives.

The catalytic activity of PdNPs/TiO_2 nanotubes/Ti plate was evaluated also in the oxidation reaction of ethylbenzene. The reaction conditions were optimized for the oxidation of ethylbenzene (**3**) with KOH as a base and H_2O_2 as an oxidant in the presence of PdNPs/TiO_2 nanotubes/Ti plate. It was found that H_2O:EtOH (1:1) as the solvent, 3 equivalents of H_2O_2 as the oxidant, and 0.5 mmol KOH as the base at 90 °C is the best reaction conditions for the oxidation of ethylbenzene (Table 3). Oxidation of ethylbenzene (1 mmol) proceeded to give acetophenone (**2**) as the sole product with > 99 conversion in 24 h without any byproduct. The oxidation reaction of ethylbenzene needs Pd and did not proceed

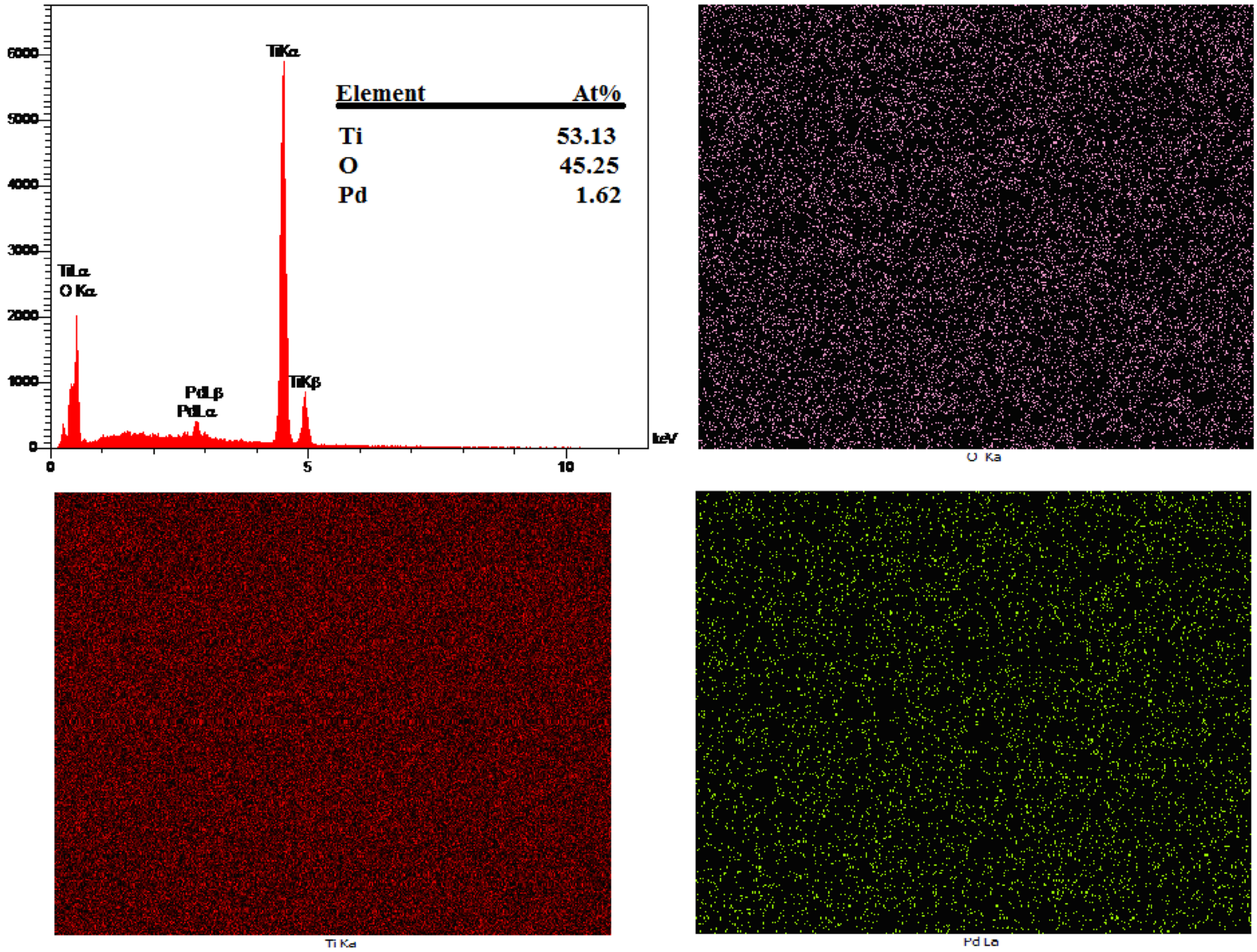


Fig. 2 EDX spectra obtained of PdNPs/TiO_2 nanotubes/Ti plate as well as EDX mapping

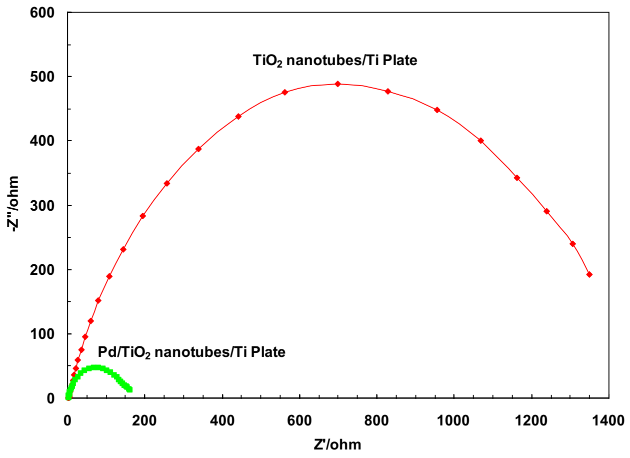


Fig. 3 Impedance Nyquist plots for the PdNPs/TiO_2 nanotubes/Ti plate and TiO_2 nanotubes/Ti plate

in the absence of Pd plate (Table 3, entry 5). The reaction was performed with 3 mmol H_2O_2, and the yield decreased in low amounts of H_2O_2 (Table 3, entries 3 and 4). The reaction gave high yield at 90 °C and the yield was decreased in low temperatures, especially at room temperature (Table 3, entries 5 and 6). After screening a variety of solvents, EtOH and H_2O:EtOH (1:1) were recognized to be the best solvents which H_2O:EtOH (1:1) was selected due to more accordance with green chemistry principles (Table 3, entries 7–12). The reaction of excess ethylbenzene with the plate gave 9 mmol of acetophenone during 24 h. The reaction has advantages that observed in the oxidation of benzyl alcohol, including excellent selectivity, green solvent, high yield, easy work-up, green oxidant, and stirring free.

The catalyst application was extended to the oxidation of various alkylarenes (Table 4). High conversions were obtained for the oxidation of alkylarenes.

Potential Pd leaching into the reaction mixture was studied for oxidation of benzyl alcohol and ethylbenzene with

Table 1 Optimization of the reaction conditions for oxidation of benzyl alcohol

Entry	Solvent	Temp. (°C)	Conversion (%)	
			Benzaldehyde	Benzoic acid
1[a]	H_2O	90	0	19
2	H_2O	90	0	> 99
3[b]	H_2O	90	0	72
4[c]	H_2O	90	0	31
5	H_2O	80	0	95
6	H_2O	r.t.	0	39
7	–	90	22	31
8	*o*-Xylene	90	11	68
9	MeCN	90	0	> 99
10	MeOH	90	21	52
11	CH_2Cl_2	90	0	57
12	EtOH	90	5	74

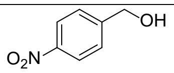
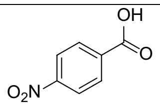
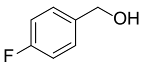
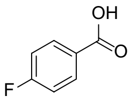
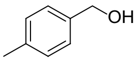
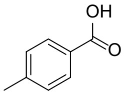
Reaction conditions: benzyl alcohol (1 mmol), catalyst, H_2O_2 (3 mmol), solvent (5 mL), 24 h

[a] Without catalyst

[b] H_2O_2 (2 mmol)

[c] Without H_2O_2

Table 2 Oxidation of various benzyl alcohol derivatives using PdNPs/TiO_2 nanotubes/Ti plate

Entry	Alcohol	Product	Conversion (%)
1			> 99
2			95
3			92

Reaction conditions: alcohol (1 mmol), catalyst, H_2O_2 (3 mmol), H_2O (5 mL), 24 h

FAAS analysis. For this purpose, after removing the plate, the solvents were evaporated, and the residues were dissolved in HNO_3. The analysis of these samples with FAAS showed that the Pd concentrations of the reaction solutions were less than the detection limit. These results indicate that virtually no Pd leach from the surface into the solutions.

Recyclability of the PdNPs/TiO_2 nanotubes/Ti plate was examined in the oxidation of benzyl alcohol. After carrying out the reaction, the catalyst was separated, washed with acetone (2 × 5 mL), and reused. Any decreases in the reaction yield were observed after six repetitive cycles for this reaction (Table 5).

Table 3 Optimization of the reaction conditions for oxidation of ethylbenzene

Entry	Solvent	Temp. °C	Conversion (%)
1[a]	EtOH:H_2O (1:1)	90	0
2	EtOH:H_2O (1:1)	90	> 99
3[b]	EtOH:H_2O (1:1)	90	86
4[c]	EtOH:H_2O (1:1)	90	39
5	EtOH:H_2O (1:1)	80	96
6	EtOH:H_2O (1:1)	r.t.	43
7	H_2O	90	46
8	*o*-xylene	90	64
9	MeCN	90	29
10	MeOH	90	83
11	CH_2Cl_2	90	61
12	EtOH	90	> 99

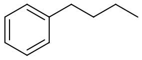
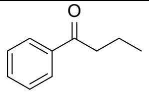
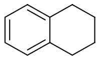
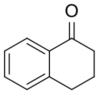
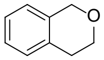
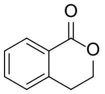
Reaction conditions: ethylbenzene (1 mmol), catalyst, H_2O_2 (3 mmol), KOH (0.5 mmol), solvent (5 mL), 24 h

[a] Without catalyst

[b] H_2O_2 (2 mmol)

[c] Without H_2O_2

Table 4 Oxidation of various alkylarenes using PdNPs/TiO_2 nanotubes/Ti plate

Entry	Alcohol	Product	Conversion (%)
1			> 99
2			94
3			91

Reaction conditions: alkylarene (1 mmol), catalyst, H_2O_2 (3 mmol), KOH (0.5 mmol), EtOH:H_2O (5 mL), 24 h

Table 5 Successive trials using recoverable PdNPs/TiO_2 nanotubes/Ti plate for oxidation of benzyl alcohol

Trial	Conversion (%)
1	> 99
2	> 99
3	> 99
4	> 99
5	> 99
6	> 99

Reaction conditions: benzyl alcohol (1 mmol), catalyst, H_2O_2 (3 mmol), 90 °C, 24 h

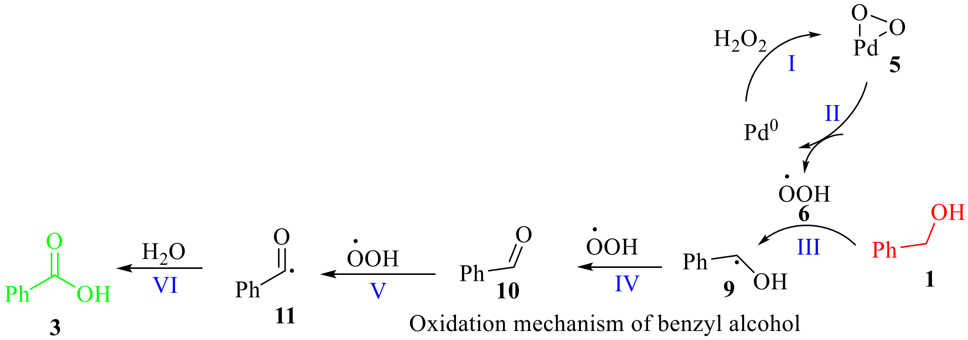
Although the mechanisms of these reactions have not been established experimentally, the formation of species **5** and **6** is conceivable in the oxidation reactions of benzyl alcohol and ethylbenzene in the presence of H_2O_2 and Pd (Scheme 2). These active spaces can perform the oxidation reactions as the procedure determined with Roman numbers.

The results for our catalyst are compared with some recent reports of Pd-catalysed oxidation of benzyl alcohol with respect to solvent, reaction duration, temperature, yield, and selectivity (Table 6). Performing the reaction in solvent-free conditions, and in short reaction times are the advantages for some of the previous reports. The oxidation reaction of benzyl alcohol with PdNPs/TiO_2 nanotubes/Ti plate has some advantages such as greener solvent compared to entry 1, and low reaction temperature compared to entries 2and 3. However, the method is a good oxidation reaction regarding high yield and excellent selectivity which are very important factors for oxidation reactions. The heterogeneity of the catalyst is also another advantage of this work which makes catalyst recovery easy. Regarding these results, we suggest that the introduced approach can be an interesting route for the production of benzoic acid from benzyl alcohol.

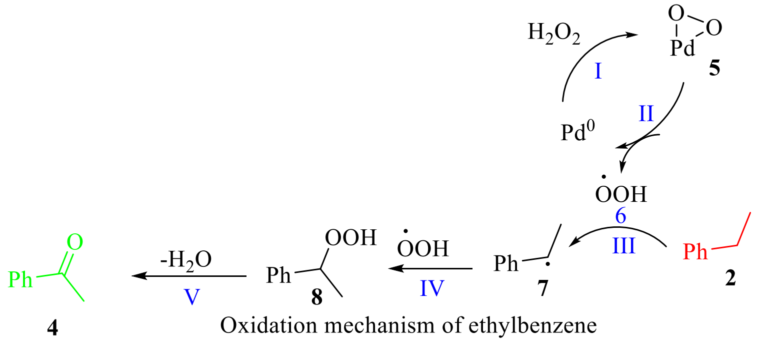
Conclusion

Synthesis and characterization of PdNPs/TiO_2 nanotubes/Ti plate were performed with a homogeneous distribution of Pd NPs on the TiO_2 nanotubes. Synthesis was conducted by sonochemical deposition of PdNPs onto TiO_2 nanotubes/Ti plate at room temperature. The plate showed good catalytic activity in the oxidation reactions of benzyl alcohol and ethylbenzene derivatives using H_2O_2 at 90 °C. The oxidation of benzyl alcohols in H_2O as a green solvent gave benzoic acid derivatives with high yield. The oxidation of alkylarenes in EtOH/H_2O led to the formation of corresponding ketones selectively in high yield. Use of a plate as a catalyst facilitated the oxidation reactions procedure with very easy separation of the catalyst from the reaction mixture and stirring-free conditions. The catalyst has a high stability and recyclable for several times.

Scheme 2 Proposed mechanism for the oxidation of ethylbenzene and benzyl alcohol



Oxidation mechanism of benzyl alcohol



Oxidation mechanism of ethylbenzene

Table 6 Comparison of the benzyl alcohol oxidation results with the previous report

Entry	Catalyst	Solvent	Time (h)	Temp. (°C)	Selectivity (%)	Yield (%)
1	Pd(II)-DPA@chitosan [28]	EtOH	24	80	100	96
2	Pd@CeO_2 [29]	–	1	160	88.9	20.8
3	Pd@NMC [30]	–	1	160	91.2	59.8
4	PdNPs/TiO_2 nanotubes/Ti plate	H_2O	24	90	100	> 99

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