Journal of Catalysis 382 (2020) 305–319

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Design and synthesis of a versatile cooperative catalytic aerobic oxidation system with co-immobilization of palladium nanoparticles and laccase into the cavities of MCF

Sirvan Moradi, Zahra Shokri, Nadya Ghorashi, Aso Navaee, Amin Rostami *

Department of Chemistry, Faculty of Science, University of Kurdistan, Zip Code 66177-15175, Sanandaj, Iran

ARTICLE INFO

Article history:
Received 1 October 2019
Revised 13 December 2019
Accepted 16 December 2019

Keywords:
Reusable cooperative catalytic system
Palladium
Laccase
Hydroquinone
Aerobic oxidative dehydrogenation

ABSTRACT

We have designed a versatile reusable cooperative catalyst oxidation system, consisting of palladium nanoparticles and laccase with unprecedented reactivity. This biohybrid catalyst was synthesized by the stepwise immobilization of laccase as an enzyme and Pd as a nanometallic component into the same cavity of siliceous mesocellular foams (MCF). MCF and nanobiohybrid catalyst were characterized by BET, SAXS, SEM, EDX elemental mapping, ICP-OES, TEM, TGA, FT-IR, and XPS techniques and the stepwise immobilization of laccase enzyme and Pd onto MCF was evaluated through several compelling electrochemical studies. The present catalytic system exhibits high activity toward (i) aerobic oxidation of alcohols to the corresponding carbonyl compounds, (ii) aerobic oxidation of cyclohexanol and cyclohexanone to phenol and (iii) aerobic dehydrogenation of important *N*-heteocyclic compounds (tetrahydro quinazolines, quinazolonones, pyrazolines and 1,4-diydropyridines) in the presence of catalytic amount of hydroquinone (HQ) as mediator in phosphate buffer (0.1 M, pH 4.5, 4 mL)/THF (4%, 1 mL) as solvent under mild conditions. The immobilization of both oxygen-activating catalyst (laccase) and oxidizing catalyst (Pd) onto the same support makes the present catalyst system superior to other currently available heterogeneous palladium based catalytic aerobic oxidation systems.

1. Introduction

The selective oxidation of organic compounds is an easy way to transform simple precursors into valuable products. Among the various reactions of organic chemistry, oxidation reactions have always been a challenge and have been discussed. Since most of these reactions have low selectivity and by-products are seen when oxidizing stoichiometric values are used. In this regard, the development of aerobic oxidation in a liquid phase with high chemoselectivity, regioselectivity and stereoselectivity can have a great impact on the synthesis of drugs, agrochemicals, and fine chemicals [1]. Also, the industry's need for environmentally friendly processes has increased demand for eco-friendly oxidants today, with H_2O_2 and O_2 meeting this need [2]. Aerobic oxidation in the presence of palladium dates back to the late 1950s when Wacker process was discovered. In the decades following the discovery of the Wacker process, these reactions have been considered and developed often in the direction of oxidative alkene functionalization, but over the past two decades, the oxidation reactions in the presence of homogeneous palladium catalysts have led to many other reactions, including oxidation of alcohols, dehydrogenation of C-C bonds and oxidative C-H functionalization's [1]. Although these reactions proceed in good to high yields, in most of aerobic oxidation reactions catalyzed by palladium, organic solvents, high pressure and/or temperature [3], expensive ligands [1] and strongly basic pH are required. As well, because of the unfavorable electron transfer between Pd^0 and O_2, palladium-catalyzed oxidation reactions with direct reoxidation of Pd^0 by molecular oxygen sometimes fail. Thus, the use of Electron Transfers Mediators (ETMs) for many Pd-catalyzed aerobic oxidation reactions are required to obtain high selectivity and high efficiency [2,4].

Recently, cooperative catalyst systems have been developed as highly promising sustainable alternatives to traditional catalysts. In these catalysts, two or more catalytic centers cooperate to reduce the energy of chemical transformations. In nature, such systems are abundantly seen in metalloenzymes that use a metal and an organic cofactor [5]. Several research groups designed bioinspired oxidation cooperative catalytic systems to carry out reac-

* Corresponding author.
E-mail address: a.rostami@uok.ac.ir (A. Rostami).

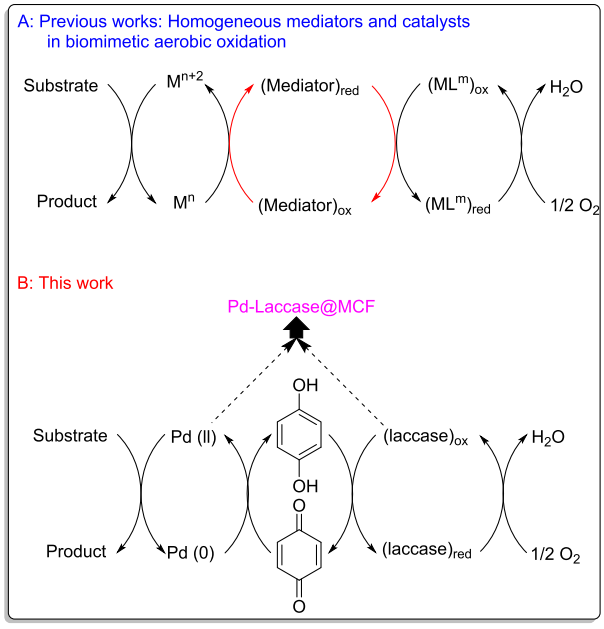
https://doi.org/10.1016/j.jcat.2019.12.023
0021-9517/

tions under mild conditions [4,6]. Although these protocols represent considerable advances, there are still other drawbacks, such as homogeneity of the catalyst systems, and the use of transition metal complexes and expensive ligands (Scheme 1A). Therefore, the development of intramolecular heterogeneous cooperative catalytic systems with simple separation and recycling in the ligand-free and benzoquinone-free aerobic oxidation of organic compounds under mild conditions is highly desirable.

Recently, several one-pot tandem catalytic systems have been developed, which combine the reactivity of transition metal catalysis and the selectivity of enzymatic catalysis [7]. Despite these developments, there has been no report on the design of heterogeneous cooperative catalyst systems that make use of both biocatalysis and transition metals being employed in the oxidation of organic compounds.

Laccases, multi-copper-containing oxidoreductase enzymes, are highly attractive biocatalysts in modern organic synthesis. They catalyze the oxidation of various compounds such as benzenediols, aminophenols, polyphenols, polyamines, and lignin-related molecules using oxygen as an electron acceptor and producing water as by-product. The most efficient strategy to extend the range of laccase substrates is the simultaneous use of the enzyme and redox mediators [8].

Recently, Bäckvall and co-workers reported Pd@MCF as an efficient nanocatalyst for aerobic oxidation of alcohols [9] and bifunctional biomimetic catalyst in which Pd nanoparticles and lipase are co-immobilized on MCF for dynamic kinetic resolution of an amine [10]. These works and our previously published results on the application of laccase and laccase-mediated catalytic system in organic reactions [11] prompted us to design a heterogenous cooperative catalyst system, consisting of palladium nanoparticles and laccase enzyme for biomimetic oxidation of organic compounds (Scheme 1B). In this work, we used mesocellular foams (MCF) as a support because of features such as simple preparation, large channel size, high surface areas, and the presence of a large number of silanol groups that contribute to high catalyst loading. Also, it is important to keep in mind that we use catalytic amount of hydroquinone [12] instead of stoichiometric amount of benzoquinone, a toxic mediator (Scheme 1B).



Scheme 1. Cooperative catalytic aerobic oxidation systems.

2. Experimental

2.1. Material and instrumentation

All substances, reagents and solvents except *N*-heterocyclic compounds were bought from the Merck and Aldrich Chemical Companies and used without further purification. The *N*-heterocyclic compounds were synthesized using previous methods in our research lab [13]. FT-IR and ^{1}H, ^{13}CNMR spectra were recorded on Thermo Nicolet Nexus 670 and BrukerAvance spectrometers (300 MHz). The physical properties of mesoporous materials were determined from N2 adsorption/desorption isotherms using an ASAP 2010 instrument. The particle size was determined by SEM using FESEM-TESCAN. The chemical composition of the prepared nanocatalyst was measured by EDX (Energy Dispersive X-ray Spectroscopy) performed in SEM. The loading and size of the Pd nanoparticles on the support was determined by inductively coupled plasma-optical emission spectrometry (ICP-OES, Optima 7300D) and Transmission Electron Microscopy (Microscope an acceleration voltage of 80 kV), respectively. X-ray photoelectron spectroscopy (XPS) was used to determine the oxidation states of the Pd nanoparticles and the elements types on Pd-Laccase@MCF.

The electrochemical tests were performed by a Zahner electrochemical workstation equipped with a conventional three electrode system. A glassy carbon electrode (GCE) with diameter of 2 mm was used as a support electrode. The desired materials were well dispersed in ethanol with concentration dispersion of 1 mg mL^{-1}. For each experiment, 3 μL of dispersed suspension were cast on the electrode surface and dried at room temperature. The voltammetry and electrochemical impedance spectroscopy (EIS) were carried out in the 0.1 M KCl solution containing 1 mM $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ as redox probe. EIS was taken in the frequency range of 1 Hz to 100 kHz using a modulation voltage of 5 mV with applying the ΔE of redox peaks as constant voltage. The Zview modeling program (version 3.5f) was used to fit the faradaic impedance spectra. All electrochemical measurements were performed at room temperature.

2.2. Synthesis of siliceous mesocellular foams (MCF)

MCF particles were prepared according to a previously reported method [14] with slight modifications. P123 (2.0 g, 0.4 mmol) was dissolved in an acidic HCl solution (1.6 M, 75 mL) at room temperature. Then, NH_4F (23 mg, 0.6 mmol) and 1,3,5-trimethylbenzene (2.0 g, 17 mmol) were added. After stirring for 45 min at 35–40 °C, tetraethoxysilane (4.4 g, 21 mmol) was added and stirring continued for 20 h. Subsequently, the mixture was placed at 100 °C for 24 h. The resulting product was filtered, washed and dried. Finally, the obtained sample was calcined at 550 °C in air for 6 h to give the MCFs. The synthesized MCFs exhibited the following characterstics: window size = 7 nm, Cell size = 24 nm, specific pore volume = 1.1 cm^3 g^{-1} and BET surface area = 503 m^2 g^{-1} (Fig. S1 in the Supplementry information). The characterstics of the synthesized MCFs in this work are in agreement with those previously reported in the literatures (Table S1, p. S4). Furthermore, the prepared MCFs also have been analyzed using small-angle X-ray scattering (SAXS). Based on this technique, the cell size was obtained about 26 nm, which is in good agreement with the value obtained from nitrogen sorption.

2.3. Synthesis of aminopropyl-functionalized MCF (AmP-MCF)

The synthesized MCFs (1 g) was dispersed in 20 mL dry toluene, then a solution of 3-aminopropyltrimetoxysilane (2.7 mL) in

toluene (10 mL) was added to the reaction mixture. The mixture was stirred under argon (10 min) and then refluxed for 24 h. The resulting solid was filtered and washed several times with toluene, ethanol, and dichloromethane and dried [9].

2.4. Synthesis of Pd nanoparticles onto AmP-MCFs (Pd(0)-AmP-MCF)

The aminopropyl-functionalized MCF (500 mg) was dispersed in pH-adjusted deionized water solution by adding 15 mL LiOH (0.1 N, pH 8). Then, the mixture was stirred at room temperature for 5 min. On the other hand, Li_2PdCl_4 was prepared by mixing $PdCl_2$ (145.41 mg, 0.82 mmol) and LiCl (69.52 mg, 1.64 mmol) in 10 mL distilled water, the suspension was stirred at 80 °C until a homogeneous solution was achieved. The resulting solution was filtered, pH-adjusted (pH 8), and then added to the mixture of AmP-MCFs in water. The reaction mixture was stirred for 24 h. Then, the suspension was centrifuged, and the resulting solid (the Pd(II)-precatalyst) was washed with distilled water. The Pd (II)-precatalyst was then re-dispersed in water (15 mL), and a solution of $NaBH_4$ (310.2 mg, 8.2 mmol) in distilled water (5 mL) was added slowly to reduce Pd(II) to Pd(0). After the completion of the reduction, the Pd(0)-AmP-MCFs was isolated by centrifugation and washed with water, acetone, and dried overnight [9].

2.5. Synthesis of glutaraldehyde-functionalized Pd(0)-AmP-MCF

Pd(0)-AmP-MCF (0.5 g) was dispersed in 30 mL of sodium phosphate buffer (100 mM, pH 8.0), and allowed to stir with glutaraldehyde solution (50% in H_2O, 0.23 g, 0.99 mmol) at r.t. for 24 h. The reaction mixture was then centrifuged and the resulting solid was washed with phosphate buffer (3 × 45 mL, 100 mM, pH 8.0) and acetone (3 × 45 mL), and finally dried under reduced pressure [8].

2.6. Immobilization of laccase enzyme on glutaraldehyde-functionalized Pd(0)-AmP-MCF (Pd-Laccase@MCF)

Glutaraldehyde-functionalized Pd(0)-AmP-MCF (0.5 g) was dispersed in sodium phosphate buffer (1 mL/100 mg support, 100 mM, pH 7.2), followed by a solution of laccase enzyme (30 U) in distilled water (3 mL). The reaction mixture was stirred at room temperature for 12 h. The final product was then separated by centrifugation, washed with phosphate buffer (2 × 5 mL, 100 mM, pH 7.2) and dried under reduced pressure.

2.7. Activity assays of immobilized laccase in Pd-Laccase@MCF

The activity of laccase in Pd-Laccase@MCF was assayed spectrophotometrically with 2,2-azino-bis-3-ethylbenzothiazoline-6-sulfonic acid (ABTS) as substrate (5 mM) in 100 mM Na-acetate buffer (pH 5) by measuring absorbance increase at 420 nm at a temperature of 25 °C. Suitable amount of Pd-Laccase@MCF in Na-acetate buffer (100 mL) was added to the mixture and the initial rate was immediately measured as increase in optical density at 420 nm [15]. The molar extinction coefficient for the oxidation of ABTS at 420 nm is $3.6 \times 10^4\ M^{-1}\ cm^{-1}$. One unit of activity is defined as the amount of enzyme required to oxidize 1 mmol of ABTS per minute. Based on this procedure, the amount of immobilized Laccase onto support was obtained 24 U per 0.5 g of solid support.

2.8. General procedure for the aerobic oxidation of alcohols

A 25 mL round-bottomed flask equipped with a magnetic stirrer was charged with alcohol (1 mmol), Pd-Laccase@MCF (0.2 g, 0.27 mmol Pd), hydroquinone (HQ, 0.27 mmol) and NaPBS/THF (5 mL, 4/1 v/v). The reaction mixture was stirred under the O_2 (balloon) or in an open-air round-bottom flask at room temperature for the time specified (Scheme 2). After completion of the reaction (monitored by TLC), the catalyst was separated using filtration and washed with CH_2Cl_2 and the product was extracted with CH_2Cl_2 (2 × 5 mL). The organic phase was dried over anhydrous $MgSO_4$. After evaporation of the solvent under reduced pressure, the crude product was purified by recrystallization from ethanol or chromatography on silica gel (*n*-hexane-EtOAc = 3:1).

2.9. General procedure for the aerobic oxidation of cyclohexanol and cyclohexanone

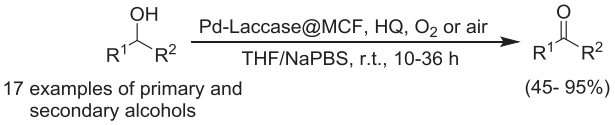
A 25 mL round-bottomed flask equipped with a magnetic stirrer was charged with substrate (1 mmol), Pd-Laccase@MCF (0.25 g, 0.34 mmol Pd), HQ (0.34 mmol) and NaPBS/THF (5 mL, 4/1 v/v). The reaction mixture was stirred under the O_2 (balloon) at room temperature for the time specified (Scheme 3). After completion of the reaction (monitored by TLC), the catalyst was separated using filtration and washed with CH_2Cl_2 and the product was extracted with CH_2Cl_2 (2 × 5 mL). The organic phase was dried over anhydrous Na_2SO_4. After evaporation of the solvent under reduced pressure, the crude product was purified by chromatography on silica gel (*n*-hexane-EtOAc = 5:1).

2.10. General procedure for the aerobic dehydrogenation of N-heterocycle compounds (2-substute-1,2,3,4-tetrahydroquinazolines, 1,4 dihydropyridines and pyrazolines)

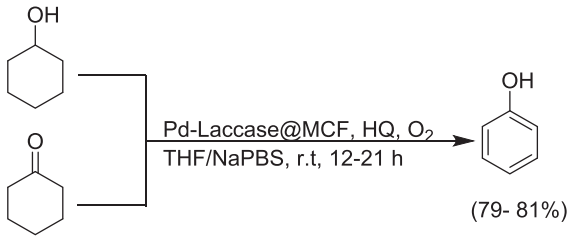
To a mixture of substrate (1 mmol), catalyst (0.2 g, 0.27 mmol Pd), and HQ (0.27 mmol), NaPBS/THF (4/1 mL) were added. The reaction mixture was stirred under O_2 (balloon) at room ambient for an appropriate time (Scheme 4). After being finished (monitored by TLC), the catalyst was separated using filtration and washed with CH_2Cl_2 and the product was extracted with CH_2Cl_2 (2 × 5 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure. The crude product was purified by chromatography on silica gel using *n*-hexane/ethyl acetate (3:1).

2.11. General procedure for aerobic dehydrogenation of 2-substute-2,3-dihydroquinazolin-4(1H)-ones

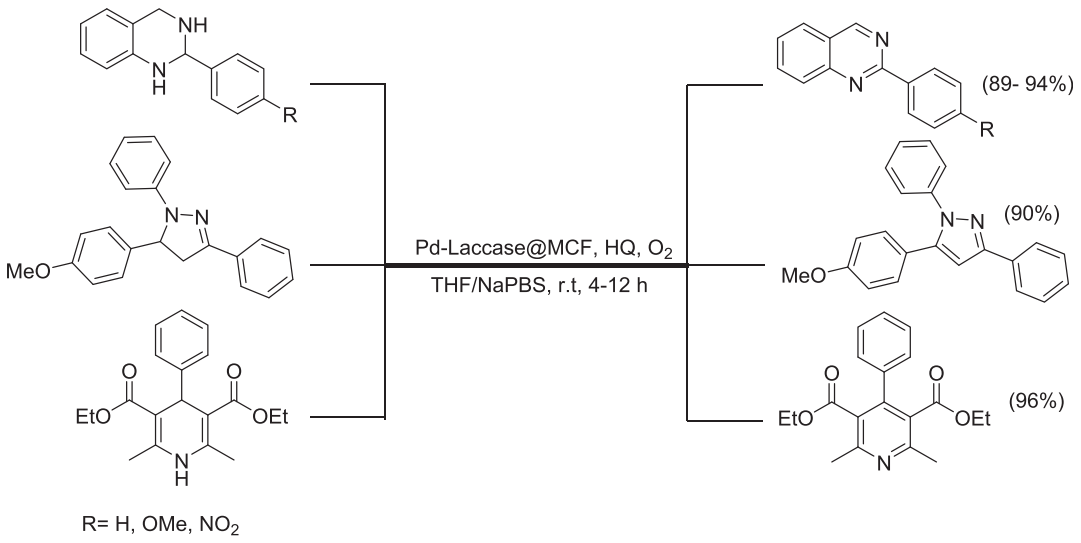
To a mixture of substrate (1 mmol), catalyst (0.25 g, 0.34 mmol Pd), and HQ (0.34 mmol), NaPBS/THF (4/1 mL) were added. The



Scheme 2. Pd-Laccase@MCF catalyzed the aerobic oxidation of alcohols to the corresponding carbonyl compounds.



Scheme 3. Pd-Laccase@MCF catalyzed the aerobic oxidation of cyclohexanol or cyclohexanone to phenol.



Scheme 4. Pd-Laccase@MCF catalyzed the dehydrogenation of *N*-heterocycle compounds.

reaction mixture was stirred under O_2 (balloon) at 45 °C for an appropriate time (Scheme 5). After being finished (monitored by TLC), the catalyst was separated using filtration and washed with CH_2Cl_2 and the product was extracted with CH_2Cl_2 (2 × 5 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure. The crude product was purified by recrystallization from ethanol or chromatography on silica gel using *n*-hexane/ethyl acetate (3:1).

3. Results and discussion

3.1. Catalyst preparation

In order to prepare the Pd-Laccase@MCF, firstly palladium nanoparticles were immobilized in aminopropyl-functionalized MCF. Then, further functionalization of the aminopropyl groups that are uncoordinated to Pd was carried out with glutaraldehyde. Finally, laccase was covalently linked to the support by the bond formation between the remaining —CHO group of glutaraldehyde and —NH_2 group situated on the enzyme surface. The synthetic route was depicted in Scheme 6. The Pd-Laccase@MCF was characterized using FESEM, TEM, EDS, ICP-OES, FT-IR, TGA, EIS and XPS.

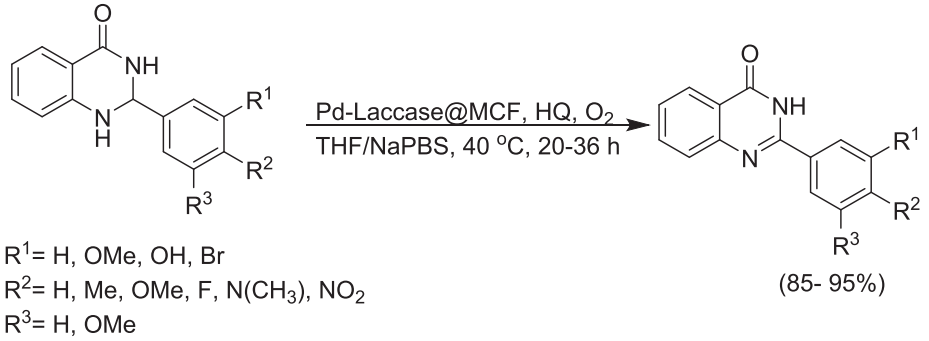
3.2. Catalyst characterization

The SEM characterization images of MCF and Pd-Laccase@MCF are shown in Fig. 1. According to the SEM images, the bare MCF particles had discrete spherical morphology in the size range of 8–96 nm. Also, based on this technique the particle size of the Pd-Laccase@MCF has determined to be 44–83 nm.

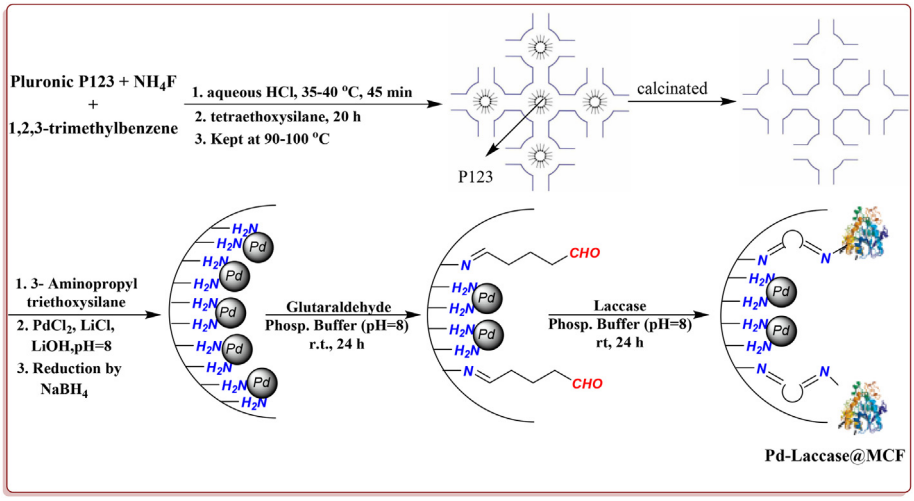
The morphology and distribution of Pd nanoparticles onto the surface of the catalyst was surveyed by TEM analysis. As indicated in Fig. 2, the Pd-Laccase@MCF catalyst contained many small well-dispersed spheres with a particle size range of 2–3 nm due to the presence of Pd nanoparticles.

In order to determine the elemental composition of the Pd-Laccase@MCF nanocomposite, EDX technique was applied. The EDX spectrum confirmed the presence of Pd, C, N, O, Si and Cu elements in the synthesized nanocomposite (Fig. 3). The presence of Cu atom in this analysis verified the successful immobilization of laccase. Further, the presence of Pd, C, N, O, Si and Cu elements was approved using the elemental mapping images (Fig. 4). Also, the inductively coupled plasma-optical emission spectrometry (ICP-OES) analysis was used to determine the Pd and Cu contents of the synthesized nanocomposite. This analysis indicated that the weight percentage of Pd and Cu was 14.5 and 0.035%, respectively.

Fig. 5 displays FT-IR spectra of MCF, aminopropyl-functionalized MCF (AmP-MCF), glutaraldehyde-functionalized Pd (0)-AmP-MCF (GA-Pd-AmP-MCF) and Pd-Laccase@MCF. As can be seen, MCF exhibit two intense bonds at 3465 and 1132 cm^{-1} correspond to the O-H stretching vibrations from silanol and stretching vibration Si-O-Si respectively. Also, the bonds at 1654 and 821 cm^{-1} probably attributed to adsorbed water molecules and Si-O bending vibrations respectively [16].



Scheme 5. Pd-Laccase@MCF catalyzed the dehydrogenation of 2-substute-2,3-dihydroquinazolin-4(1*H*)-ones.



Scheme 6. Synthetic diagram of the Pd-Laccase@MCF nanocatalyst.

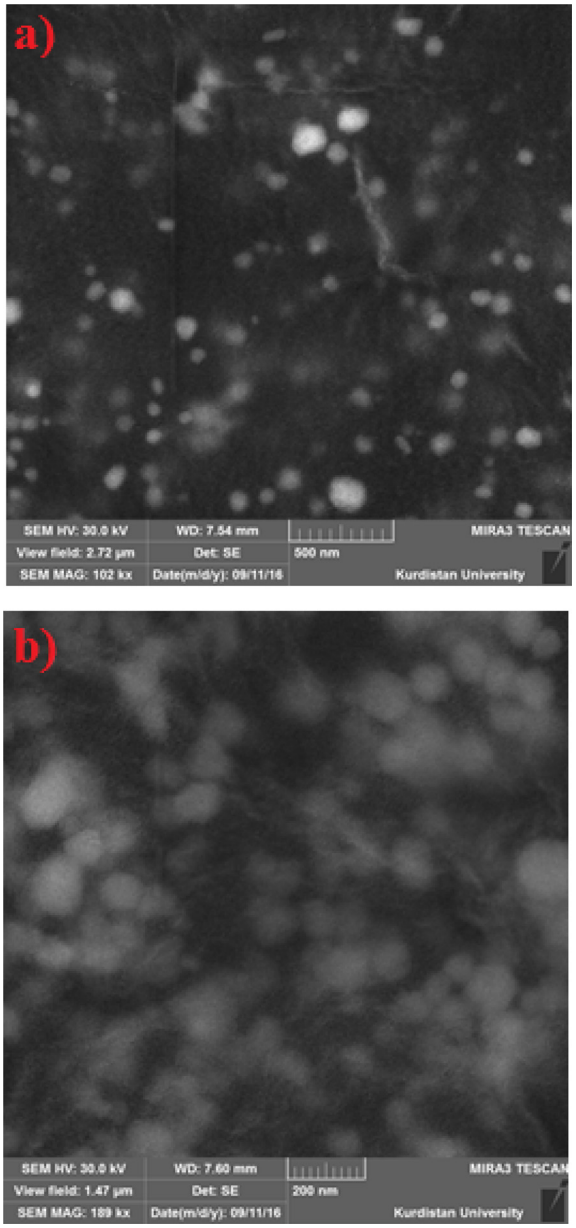


Fig. 1. SEM images of (a) MCF and (b) Pd-Laccase@MCF.

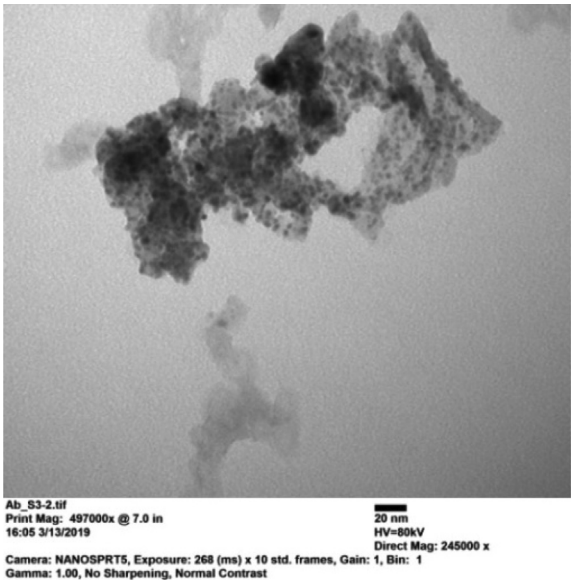


Fig. 2. TEM image of Pd-Laccase@MCF.

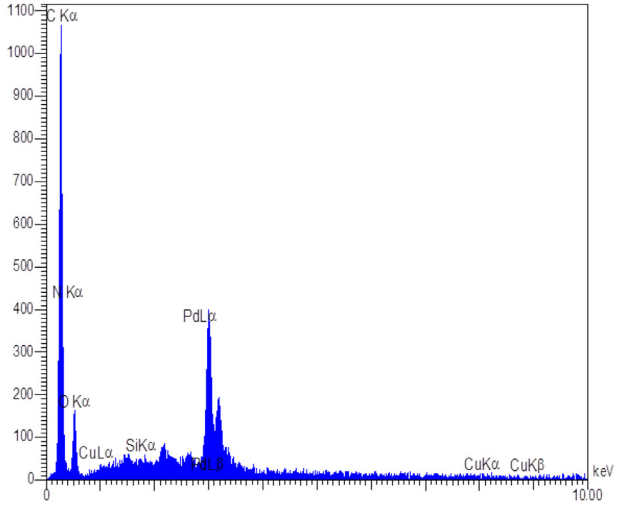


Fig. 3. EDX spectrum of Pd-Laccase@MCF.

In FT-IR spectrum of AmP-MCF, all the peaks of MCFs can be seen. Also, the presence of anchored aminopropyl groups was confirmed by the appearance of several peaks at 2960 cm^{-1}, 2881 cm^{-1} and 1484 cm^{-1} attributed to $-CH_2$ groups of the aminopropyl chain [9].

In FT-IR spectrum of GA-Pd-AmP-MCF, the Schiff-base forming reaction between free $—NH_2$ group of Pd-AmP-MCF and –CHO group of glutaraldehyde was confirmed by the C═N stretching vibration that appeared at 1658 cm^{-1} [17].

Based on the above observations, we think that FT-IR is a useful technique for characterizing MCF, Amp-MCF, GA-Pd-AmP-MCF, but in the case of FT-IR spectrum of Pd-Laccase@MCF (Fig. 5d), no indicative peaks for laccase were observed and this spectrum was quite similar to the FT-IR spectrum of GA-Pd-AmP-MCF spectrum.

The TGA curves for MCF and different synthesis steps of Pd-Laccase@MCF (AmP-MCF, Pd-AmP-MCF, GA-Pd-AmP-MCF and Pd-Laccase@MCF) are shown in Fig. 6. In the all samples, the weight loss below 200 °C is owing to the removal of the surface hydroxyl groups or physically adsorbed water, and the other weight loss appeared between 200 and 800 °C corresponds to the decomposition of the organic functional groups, palladium nanoparticles and laccase grafted on MCF nanoparticles.

Electrochemical Impedance Spectroscopy (EIS) can be used as a powerful technique to reveal the proficiency of biomolecules immobilization on the solid surfaces [18]. The EIS analysis clearly demonstrated the existence and the effects of each material on the electrode resistance. Hence, different steps of biocatalyst preparation process were evaluated by recording the Nyquist plots of EIS. As schematically shown in Fig. 7A, the resulted material in each step of catalyst synthesis was assembled on an electrode and examined in presence of a redox probe. Fig. 7B shows the impedance Nyquist plots of GCE before (a) and after assembling with AmP-MCF (b), Pd-Amp-MCF (c), GA-Pd-AmP-MCF (d) and Pd-Laccase@MCF (e) in 0.1 M KCl electrolyte and presence of 1 mM $Fe(CN)_6^{4-/3-}$. The corresponding cyclic voltammograms are also given in Fig. 7C, in which for each of modified electrode a pair redox peak is seen. However, through increasing the surface resistance, the anodic and cathodic peaks are shifted to the higher overpotentials. The resulted Nyquist plots were fitted with a Randles

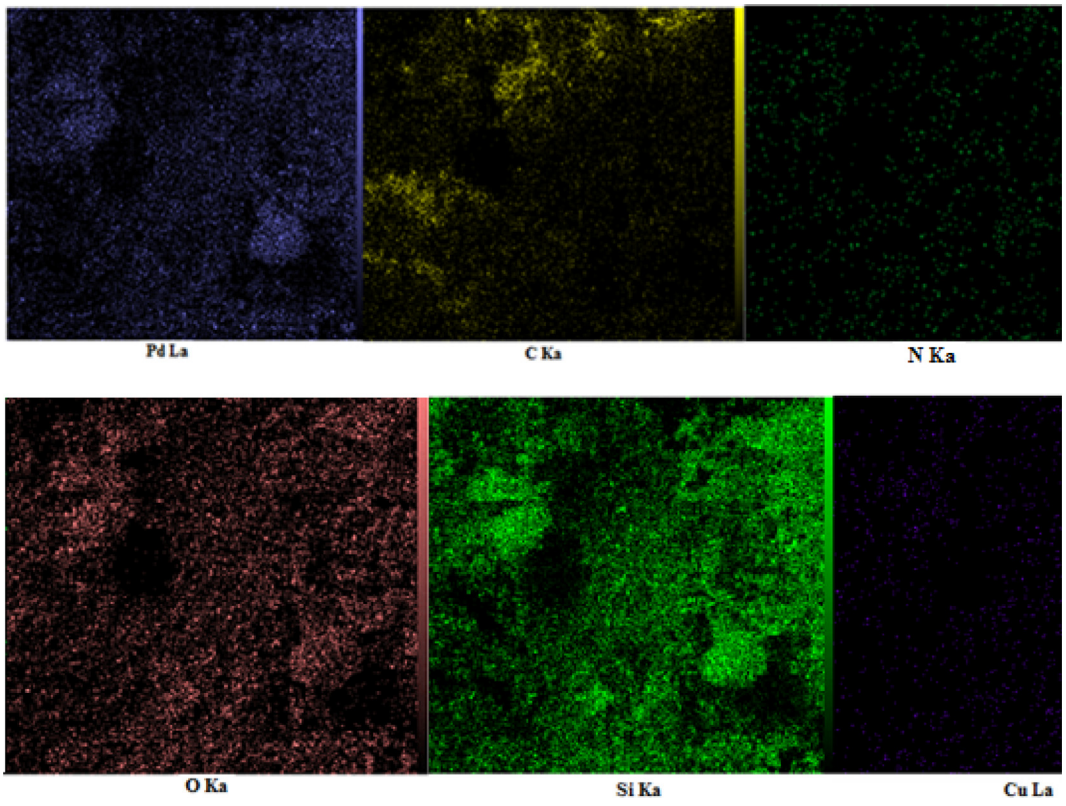


Fig. 4. Elemental mapping of the Pd-Laccase@MCF.

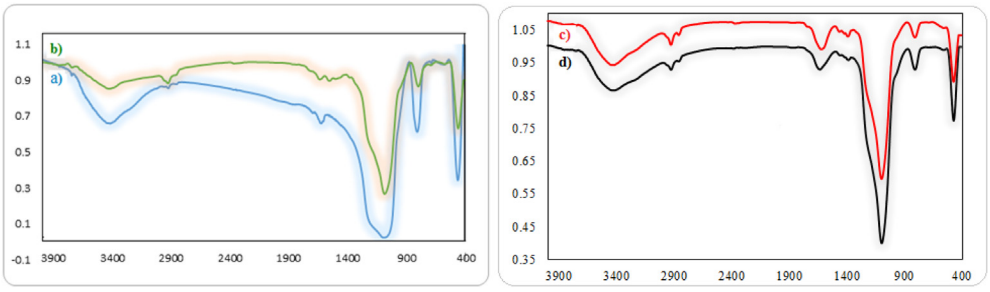


Fig. 5. FT-IR spectra of (a) MCF, (b) AmP-MCF, (c) GA-Pd-AmP-MCF, (d) Pd-Laccase@MCF.

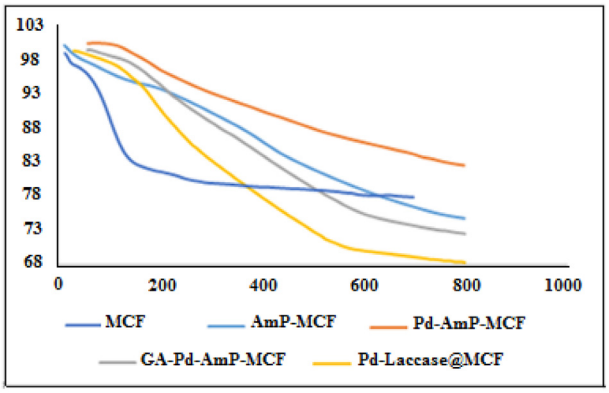


Fig. 6. TGA curves of different synthesis steps of Pd-Laccase@MCF.

equivalent circuit model, as shown in the inset of Fig. 7B to obtain the fitting parameters. The resulted equivalent circuit is involved four elements; solution resistance (R_s), charge transfer resistance (R_{ct}), Warburg element (W_o, related to the diffusion resistance of double layer at electrolyte/electrode interface) and constant phase element (CPE) related to the double layer capacitance. Among them, R_{ct} is a key parameter in EIS since it directly related to the hindrance of species against the electron transfer from probe Fe $(CN)_6^{4-/3-}$ to the electrode surface. R_{ct} can be visually estimated from the semicircle of Nyquist plot. As illustrated, the GCE displays a Nyquist plot with R_{ct} of 1.0 KΩ, where after assembling the amino-propyl-functionalized-MCF (AmP-MCF) on the surface of GCE, R_{ct} is increased to 6.2 KΩ. The assembling the Pd-Amp-MCF on the surface of GCE, R_{ct} is twice increased to 19.2 KΩ, indicating the increase of electron transferee resistance at the electrode surface. Interestingly, after incubation of electrode surface with Glutaraldehyde-functionalized Pd-AmP-MCF (GA-Pd-AmP-MCF), R_{ct} value is decreased from 19.2 KΩ (in Pd-Amp-MCF) to 10 KΩ, which it may be explained as follows: GA linkers can diffuse between Pd nanoparticles to interact with amino moieties around of MCF and consequently, lead to the distributed arrangement of Pd nanoparticles on the MCF core. The well-arrangement of Pd nanoparticles leads to decrease in electron transfer resistance at electrode surface. Finally, a significant increase in R_{ct} is seen through incubation of GCE with Pd-Laccase@MCF, where R_{ct} reaches to 27.7 KΩ, indicating the hindrance of electron transfer kinetics because of presence a nonconductive species such as Laccase (see Fig. 7A). These variations in R_{ct} (in EIS) and over-potential (in voltammetric peaks) noticeably clarify the immobilization of laccase enzyme on glutaraldehyde-functionalized Pd-AmP-MCF.

The XPS technique is demonstrated to be extremely useful not only to ascertain the elemental composition of the Pd-

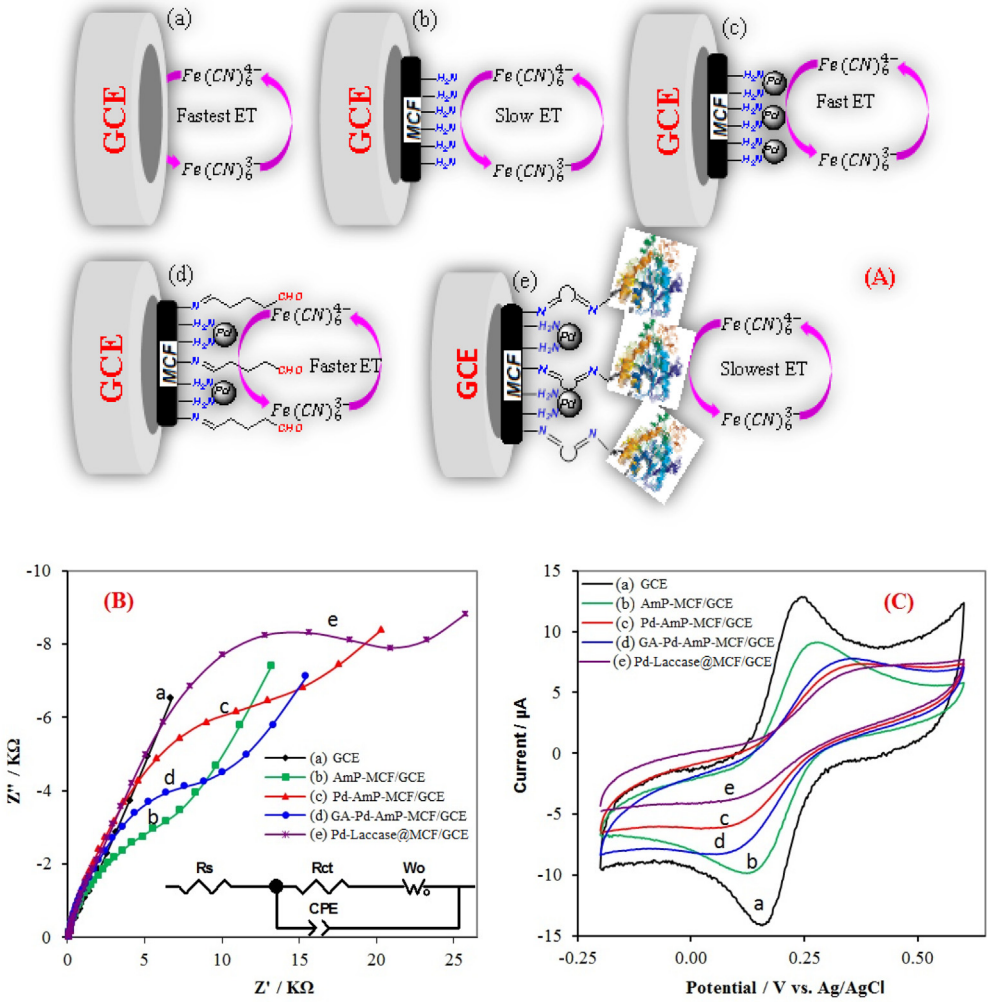


Fig. 7. (A) Schematic of electrochemical tests and electron transfer (ET) of $Fe(CN)_6^{4-/3-}$ at GCE; (B) Electrochemical impedance spectra of bare GCE before (a); and after assembling of AmP-MCF (b); Pd-Amp-MCF (c); GA-Pd-AmP-MCF (d); Pd-Laccase@MCF (e) on it; C) Cyclic voltammograms with scan rate 0.1 V s^{-1} corresponding to the EIS studies which presented in A.

Laccase@MCF, but also to determine the oxidation state of the Pd. The XPS of the reduced Pd nanocatalyst (Pd^0- Laccase@MCF) is given in Fig. 8. In Fig. 8a, silicon, carbon, oxygen, nitrogen, and palladium peaks are clearly detected in elemental survey scan. As shown in Fig. 8b, the surface of the nano-Pd particles have both Pd(0) and Pd(II) atoms.

Two strong peaks at 335 and 340 eV, are due to the Pd(0) absorptions and two peaks at 343 and 338 eV, which are consistent with Pd(II) [9]. As it was indicated, the major part of the Pd(II) has been reduced to Pd(0).

3.3. Investigation of the catalytic activity of the Pd-Laccase@MCF nanoparticles

The catalytic activity of Pd-Laccase@MCF was investigated in the most important oxidation reactions such as aerobic oxidation of alcohols, the production of phenol from cyclohexanone and cyclohexane and aerobic oxidative dehydrogenation of *N*-heterocycle compounds.

3.4. The aerobic oxidation of alcohols to the corresponding carbonyl compounds

The selective oxidation of alcohols to the corresponding carbonyl compounds is one of the most fundamental reactions in the synthetic organic chemistry [19]. However, many oxidizing reagents have been traditionally employed to accomplish this transformation, their use is associated with serious drawbacks, such as use of toxic and/or hazardous reagents, and generation of large amount of waste. To overcome these drawbacks, catalytic protocols employing O_2 or H_2O_2 as the terminal oxidant have been developed [20]. Recently, heterogeneous Pd catalysts have attracted more attention for the aerobic oxidation of alcohols [9,21]. Although these procedures have been successfully applied

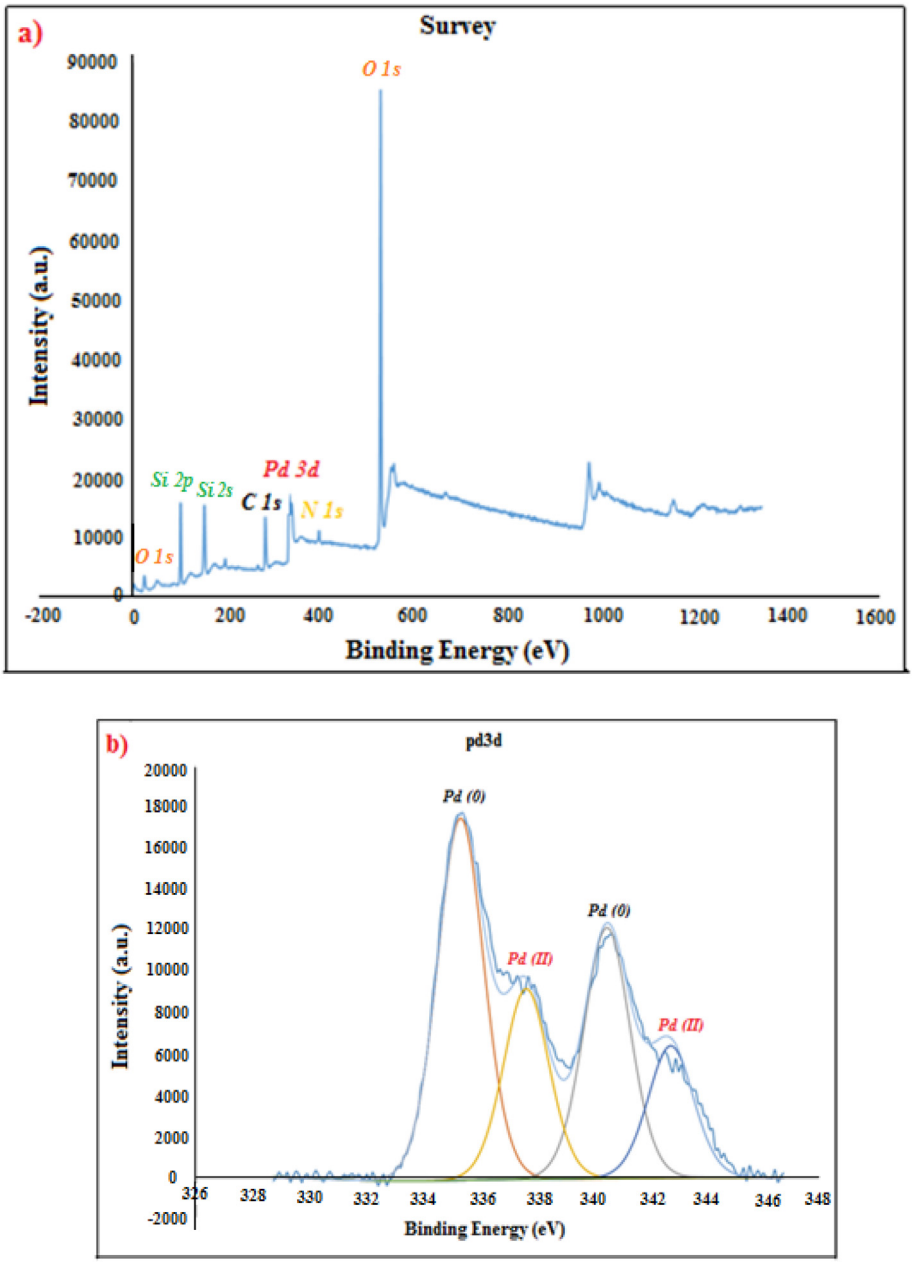


Fig. 8. Survey XPS spectrum of Pd^0-Laccase@MCF (a) Pd3d (b) Orbitals.

in the field of aerobic oxidation of alcohols, the use of catalysis that allows processes to occur under mild reaction conditions is intensely encouraged. Therefore, in the present study, we report for the first time the aerobic oxidation of various alcohols in the presence of Pd-Laccase@MCF under mild conditions.

To optimize the reaction conditions, the catalytic activity of Pd-Laccase@MCF was first surveyed for the oxidation of 1-phenyl ethanol using molecular oxygen as a terminal oxidant. When the reaction was performed in the presence of Pd-Laccase@MCF (0.2 g) in phosphate buffer (0.1 M, pH 4.5, 4 mL)/THF (4%, 1 mL) at room temperature, the corresponding product was isolated in 45% (Table 1, entry 1). In order to increase the yield of product, the aerobic oxidation of 1-phenyl ethanol was investigated in the presence of different mediators including hydroquinone (HQ), 3,5-di-tert-butylcatechol (DTBC) and *p*-benzoquinone (BQ). It was found that the yield of the oxidation of 1-phenyl ethanol could be improved to 99% in the presence of all of them (Table 1, entries 2–4). Although the reaction time in the presence of DTBC and BQ were shorter, HQ was applied as an electron transfer mediator for the subsequent experiments because of its low cost and toxicity and easily handled. These results indicated that both the heterogeneous Pd-Laccase@MCF catalyst and HQ are essential to complete the aerobic oxidation of 1-phenyl ethanol under mild conditions. Also, a number of solvents were tested for this reaction (Table1, entries 2 and 5–7). Both mixtures of THF/NaPBS and CH_3CN/NaPBS led to high yields of the product, but THF/NaPBS was selected as the reaction medium due to less toxicity. Afterward, the effect of the amount of the Pd-Laccase@MCF and mediator was studied upon the reaction. When the amount of catalyst or HQ was reduced, the GC yield dropped (Table 1, entries 8–10).

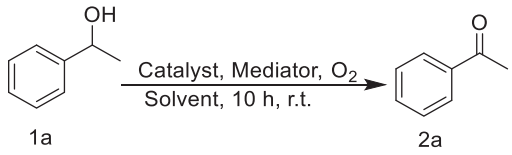
Further experiments devoted to the influence of the temperature (Table 1, entries 11–15) revealed that when the reaction temperature was increased to 40 and 60 °C, the reaction time was decreased to 9 and 6 h, respectively (Table 1, entries 11 and 12). A further increase of the temperature to 80 °C leads to a decrease in the yield of the product, which could be attributed to the enzyme deactivation in high temperatures (Table 1, entry 13). The oxidation of 1-phenyl ethanol at 60 °C tolerates the reduction of the amount of catalyst and mediator without any loss of yield (Table 1, entry 15). This result shows that turnover number (TON) could be increased by raising temperature to 60 °C.

However, we have found that in terms of time and product yield, the best result was obtained for aerobic oxidation of 1-phenyl ethanol using MCF@Pd-Lacasse (0.2 g), HQ (0.27 mmol) in phosphate buffer (0.1 M, pH 4.5, 4 mL)/THF (4%, 1 mL) under O_2 at room temperature (Table 1, entry 2).

Additional control studies were also performed to demonstrate palladium nanoparticles and laccase immobilized into the cavities of MCF (heterogeneous catalyst) and HQ obtain a stepwise electron transfer from substrate to molecular oxygen and act cooperatively to facilitate the aerobic oxidation under mild conditions. We examined the aerobic oxidation of 1-phenyl ethanol with HQ in the absence of Pd-Laccase@MCF and found that the desired product was not formed (Table 2, entry 1). With argon instead of air only 10% of the desired product was obtained (Table 2, entry 2). These results clearly demonstrate that this transformation requires the triple action of Pd-Laccase@MCF, HQ and air. We also examined other catalysts such as bare MCF, Pd@MCF, and Laccase@MCF in the aerobic oxidation of 1-phenyl ethanol (Table 2, entries 3–7) under same reaction conditions. As expected, MCF failed to catalyze the desired oxidative reaction (Table 2, entry 3). It is worth mentioning that similar results were obtained using Pd@MCF as a catalyst in the presence or absence of HQ as a mediator (Table 2, entries 4–5). Using Laccase@MCF as catalyst led to 10% conversion into the desired product (Table 2, entry 6). Increasing the temperature to 60 °C in the presence of Laccase@MCF increased the yield only to 20% (Table 2, entry 7).

With the optimal reaction conditions in hand, we then investigated the scope of this aerobic oxidation protocol for structurally diverse alcohols (Table 3). As shown in Table 3, various types of primary benzylic alcohols were selectively oxidized to the corresponding benzaldehyde derivatives without any over-oxidation to corresponding carboxylic acids (Table 3, entries 1–5). The present catalyst system showed a higher reactivity for primary benzylic alcohols with electron-donating (Table 3, entry 2) than for the electron-withdrawing ones (Table 3, entries 3–5). Also, the present catalyst system was applicable for the aerobic oxidation of substituted secondary benzylic alcohols, to afford the respective

Table 1
Optimization of reaction conditions for aerobic oxidation of 1-phenylethanol. [3a,b]



Entry	Catalyst (g)	Solvent	Mediator (mmol)	Temperature (°C)	Time (h)	GC Yield (%)
1	Pd-Laccase@MCF (0.2)	THF/NaPBS	–	r.t.	10	45
2[a]	Pd-Laccase@MCF (0.2)	THF/NaPBS	HQ (0.27)	r.t.	10	99
3	Pd-Laccase@MCF (0.2)	THF/NaPBS	DTBC (0.27)	r.t.	8	99
4	Pd-Laccase@MCF (0.2)	THF/NaPBS	BQ (0.27)	r.t.	9	99
5	Pd-Laccase@MCF (0.2)	CH_3CN/NaPBS	HQ (0.27)	r.t.	10	98
6	Pd-Laccase@MCF (0.2)	THF	HQ (0.27)	r.t.	10	87
7	Pd-Laccase@MCF (0.2)	CH_3CN	HQ (0.27)	r.t.	10	68
8	Pd-Laccase@MCF (0.2)	THF/NaPBS	HQ (0.15)	r.t.	10	87
9	Pd-Laccase@MCF (0.1)	THF/NaPBS	HQ (0.27)	r.t.	10	81
10	Pd-Laccase@MCF (0.15)	THF/NaPBS	HQ (0.27)	r.t.	10	90
11	Pd-Laccase@MCF (0.2)	THF/NaPBS	HQ (0.27)	40	9	99
12	Pd-Laccase@MCF (0.2)	THF/NaPBS	HQ (0.27)	60	6	99
13	Pd-Laccase@MCF (0.2)	THF/NaPBS	HQ (0.27)	80	10	38
14	Pd-Laccase@MCF (0.08)	THF/NaPBS	HQ (0.108)	40	10	73
15	Pd-Laccase@MCF (0.08)	THF/NaPBS	HQ (0.108)	60	10	99

[a] Reaction conditions unless stated otherwise: 1-phenylethanol (1 mmol), phosphate buffer (0.1 M, pH 4.5, 4 mL)/THF (4%, 1 mL), O_2 (balloon), r.t.

Table 2
Control studies for aerobic oxidation of 1-phenylethanol.[a]

Entry	Catalyst (g)	Solvent	Mediator (mmol)	Temperature (°C)	Time (h)	GC Yield (%)
1	–	THF/NaPBS	HQ (0.27)	r.t.	10	–
2[b]	Pd-Laccase@MCF (0.2)	THF/NaPBS	HQ (0.27)	r.t.	10	10
3	MCF (0.2)	THF/NaPBS	HQ (0.27)	r.t.	10	–
4[c]	Pd@MCF (0.2)	THF/NaPBS	HQ (0.27)	r.t.	10	30
5[c]	Pd@MCF (0.2)	THF/NaPBS	–	r.t.	10	30
6[d]	Laccase@MCF (0.2)	THF/NaPBS	HQ (0.27)	r.t.	10	10
7[d]	Laccase@MCF (0.2)	THF/NaPBS	HQ (0.27)	60	10	20

[a] Reaction conditions unless stated otherwise: 1-phenylethanol (1 mmol), phosphate buffer (0.1 M, pH 4.5, 4 mL)/THF (4%, 1 mL), O_2 (balloon).
[b] Under an atmosphere of argon.
[c] The amount of Pd@MCF (0.2 g, 27 mol% Pd).
[d] The amount of Laccase@MCF (0.2 g, 40 U laccase).

Table 3
Aerobic oxidation of structurally diverse alcohols.[a]

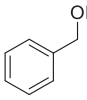
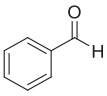
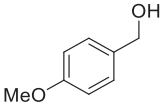
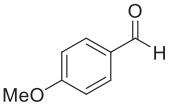
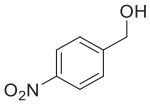
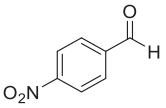
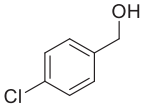
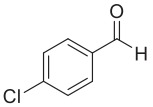
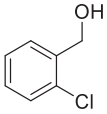
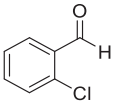
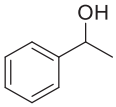
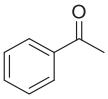
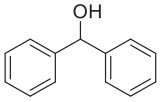
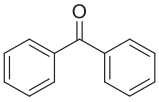
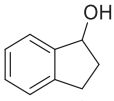
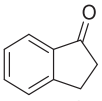
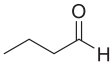
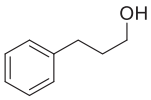
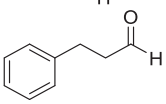
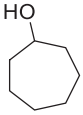
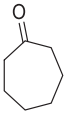
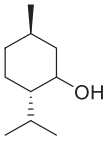
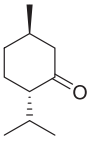
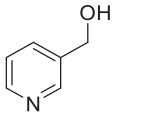
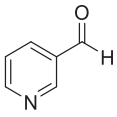
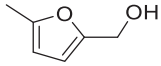
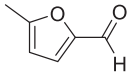
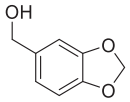
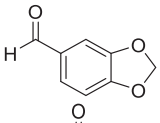
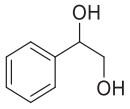
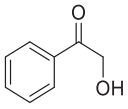
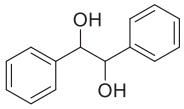
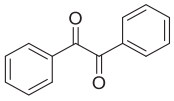
Entry	Substrate	Product	Time (h)	Isolated yield (air) (%)[b]
1			14	86 (78)
2			11	89 (80)
3			36	80 (69)
4			23	83 (75)
5			18	88 (81)
6			10	95 (89)
7			13	83 (77)
8			19	84 (71)
9			24	75 (61)
10			21	81 (63)
11			20	80 (70)
12			23	81 (73)

Table 3 (*continued*)

Entry	Substrate	Product	Time (h)	Isolated yield (air) (%)[b]
13			24	65 (50)
14			12	91 (87)
15			16	91 (80)
16			14	86 (75)
17			30	45 (–)

[a] General procedure: Substrate (1 mmol), Pd-Laccase@MCF (0.2 g), HQ (0.27 mmol), O_2 (balloon), phosphate buffer (0.1 M, pH 4.5, 4 mL)/THF (1 mL), r.t.
[b] Isolated yields in an open-air round-bottom flask are shown in parentheses.

ketones (Table 3, entries 6–8). Similarly, both primary and secondary aliphatic alcohols were selectivity oxidized to the respective carbonyl compounds in good to high yields (Table 3, entries 9–12). Remarkably, we found that our catalyst system is also highly effective for the oxidation of heterocyclic alcohols and gives the corresponding products in good to excellent yields with high selectivity (Table 3, entries 13–15). It is noteworthy that in the case of 1-phenylethane-1,2-diol containing secondary benzylic alcohol and primary aliphatic alcohol, a perfect selectivity was observed. The secondary benzylic alcohol group in this compound was selectively converted into ketone whereas the primary aliphatic alcohol remained untouched (Table 3, entry 16). We have found that the reactions in an open-air round-bottom flask give the desired products in medium to good yields in most cases (Table 3).

In order to gain further insight into the mechanism concerning if the reaction is catalyzed by homogenous or heterogeneous palladium, we have carried out heterogeneity tests including leaching test (hot filtration test) and three-phase test in the presence of the Pd-Laccase@MCF catalyst. Experimental details and results and discussion of these tests were provided in the Supplementary Information. As mentioned in the Supplementary Information (p. S5), the hot filtration and three phase tests confirmed that there was no significant leaching of Pd species during the reaction, which rules out that leached Pd species catalyze the reaction as a homogeneous catalyst [22]. Generally, immobilization of enzyme on support *via* covalent binding prevents enzyme leaching. However, to evaluate the possibility of the laccase leaching, the Pd-Laccase@MCF catalyst was shook with the phosphate buffer/THF for 2 h. The catalyst was separated by filtration and ABTS (500 μL of 1 mM) as substrate was added to detect laccase in the phosphate buffer/THF solution. UV–Vis analysis indicated that the absorbance at 420 nm was not increased [23]. This result shows that no leaching of laccase has taken place from the Pd-Laccase@MCF into the liquid phase.

For practical purposes, the recovery and reusability of the catalyst is highly desirable. Therefore, to evaluate the long-term stability and reusability of Pd-Laccase@MCF, we performed the aerobic oxidation on a 3 mmol scale of 1-phenyl ethanol to give acetophenone in the presence of Pd-Laccase@MCF as catalyst and HQ as mediator under both optimized conditions (Table 1, entry 2) and 60 °C (Table 1, entry 15). After completion of the reaction, the catalyst was centrifuged followed by washing and drying. The recycled catalyst exhibited consistent efficiency in 8 (corresponding to a total TON = 29) and 12 (corresponding to a total TON = 111) subsequent reaction runs without any significant change in activity under optimized conditions and 60 °C, respectively (Fig. 9).

3.5. The aerobic oxidation of cyclohexanol and cyclohexanone to phenol

Phenol, an important industrial chemical, is produced mainly using the three-step cumene process [24]. However, the development of a novel alternative approach for producing phenol is highly desirable. In this perspective, dehydrogenation of cyclohex-

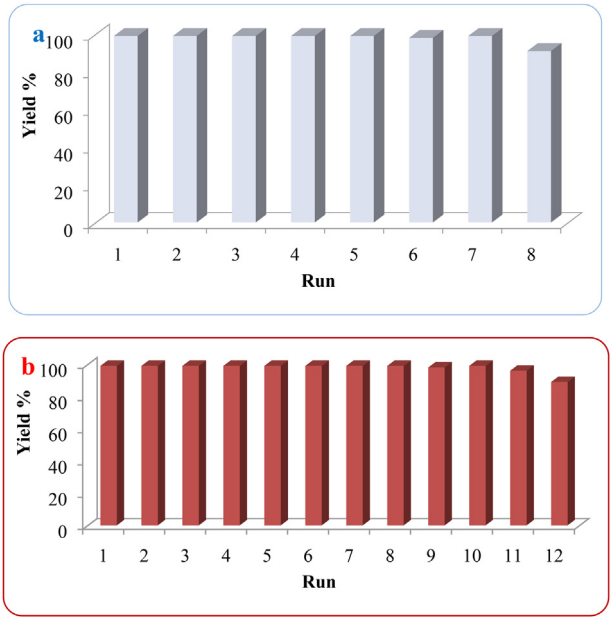
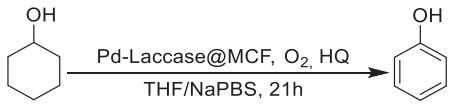


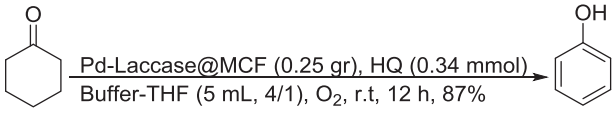
Fig. 9. Recycling runs for aerobic oxidation of 1-phenyl ethanol (3 mmol) using: (a) Pd-Laccase@MCF (0.6 g), HQ (0.81 mmol) in phosphate buffer (0.1 M, pH 4.5, 12 mL)/THF (4%, 3 mL) at room temperature (b) Pd-Laccase@MCF (0.24 g) and HQ (0.324 mmol) in phosphate buffer (0.1 M, pH 4.5, 12 mL)/THF (4%, 3 mL) at 60 °C.

Table 4
The effect of the amount of catalyst on the aerobic oxidation of cyclohexanol.[a]



Entry	Pd-Laccase@MCF (g)	Solvent	HQ(mmol)	GC Yield (%)
1	0.2	THF/NaPBS	0.27	65
2	0.25	THF/NaPBS	0.34	85
3	0.3	THF/NaPBS	0.41	87

[a] Reaction conditions: cyclohexanol (1 mmol), Pd-Laccase@MCF (0.25 g), HQ (0.34 mmol), O_2 (balloon), phosphate buffer (0.1 M, pH 4.5, 4 mL)/THF (4%, 1 mL), 21 h, r.t.



Scheme 7. Aerobic oxidative dehydrogenation of cyclohexanone.

anone and cyclohexanol has attracted considerable attention [25,26]. Regardless of notable progresses in the dehydrogenation of cyclohexanone and cyclohexanol to phenols, the development of reusable catalytic systems to accomplish this transformation with useful yields under mild conditions is of great importance. It should be mentioned that the oxidation of cyclohexanol under the optimized conditions for the oxidation of alcohols exclusively delivered phenol in 65% yield; no cyclohexanone formation was detected. This result promoted us to investigate the effect of the amount of catalyst on the reaction yield (Table 4). The best result was obtained in the presence of Pd-Laccase@MCF (0.25 g) and HQ (0.34 mmol) in phosphate buffer (0.1 M, pH 4.5, 4 mL)/THF (4%, 1 mL) at room temperature (Table 4, entry 2). Under the same reaction conditions, aerobic oxidative aromatization of cyclohexanone was also studied. It was observed that phenol was formed exclusively in 87% yield (Scheme 7).

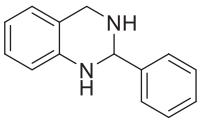
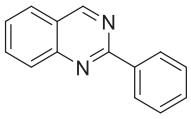
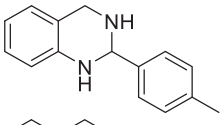
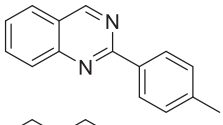
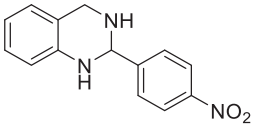
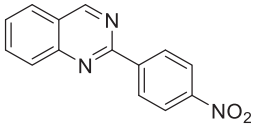
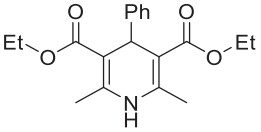
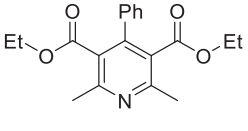
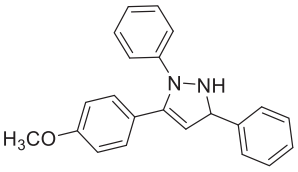
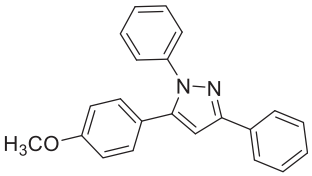
3.6. The aerobic oxidation of N-heterocycle compounds

N-Heterocycles are versatile intermediates in the preparation of pharmaceuticals, natural products, and synthetic materials. An effective procedure for synthesizing these compounds is the dehydrogenation of the corresponding saturated *N*-heterocycles [27]. Although many catalytic systems for dehydrogenation of *N*-heterocycles have been developed [28], it is highly desirable to investigate more convenient and environmentally friendly approaches. Therefore, we sought to accomplish this transformation with Pd-Laccase@MCF.

Under the optimized conditions for oxidation of alcohols, several *N*-heterocyclic compounds including 2-aryl-1,2,3,4-tetrahydro quinazoline, 1,4-dihydropyridine and pyrazoline were successfully dehydrogenated to the respective products with high yields. The results are summarized in Table 5.

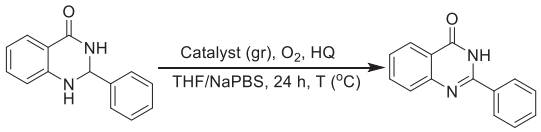
The catalytic activity of Pd-Laccase@MCF was also investigated for aerobic dehydrogenation of 2- substituted-2,3-dihydroquinazolin-4(1*H*)-ones. The oxidation of 2-phenyl-2,3-dihydroquinazolin-4(1*H*)-one was selected as a model reaction. Under optimized reaction conditions for oxidative dehydrogenation of other heterocyclic compounds (Table 5), the yield of the product was 65% (Table 6, entry 1). This result led us to optimize the reaction conditions required for this conversion. For this purpose, the effect of temperature on the reaction yield was studied, and it was found that raising the temperature to 40 °C increasing the yield of the product to 77% (Table 6, entry 2). Additional experiments dedicated to the influence of the amount of the catalyst and HQ obviously showed that the reaction was accomplished successfully in the presence

Table 5
Aerobic oxidative aromatization of *N*-hetrocyclic compounds in the presence of Pd-Laccase@MCF.[a]

Entry	Substrate	Product	Time (h)	Isolated yield (%)
1			10	94
2			8	91
3			12	89
4			4	96
5			6	90

[a] General procedure: substrate (1 mmol), Pd-Laccase@MCF (0.2 g), HQ (0.27 mmol), O_2 (balloon), phosphate buffer (0.1 M, pH 4.5, 4 mL)/THF (4%, 1 mL), r.t.

Table 6
Optimization of reaction conditions for oxidative dehydrogenation of 2-phenyl-2,3-dihydroquinazolin-4(1*H*)-one.[a]



Entry	Catalyst amount (g)	HQ (mmol)	Temperature (°C)	GC yield (%)[b]
1	Pd-Laccase@MCF (0.2)	0.27	25	65
2	Pd-Laccase@MCF (0.2)	0.27	40	77
3	Pd-Laccase@MCF (0.25)	0.34	40	98
4	Pd-Laccase@MCF (0.25)	0.34	50	98

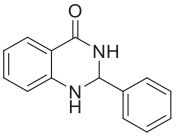
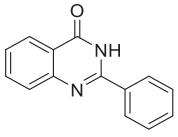
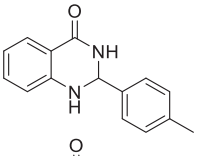
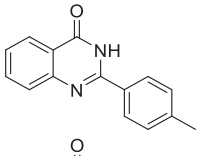
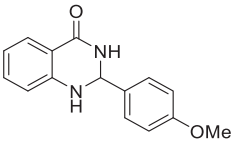
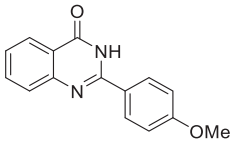
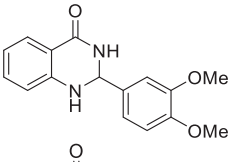
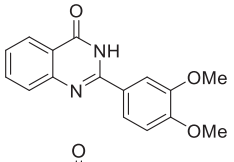
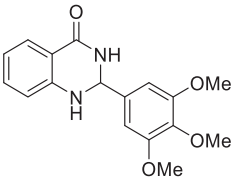
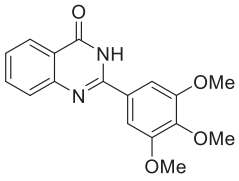
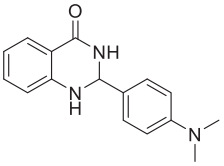
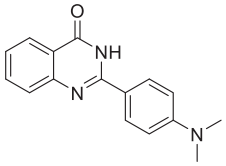
[a] Reaction conditions: Pd-Laccase@MCF (0.25 g), HQ (0.34 mmol), O_2 (balloon), phosphate buffer (0.1 M, pH 4.5, 4 mL)/THF (4%, 1 mL), 25 h.
[b] The conversion was determined by GC.

of Pd-Laccase@MCF (0.25 g), HQ (0.34 mmol) in phosphate buffer (0.1 M, pH 4.5, 4 mL)/ THF (4%, 1 mL) at 40 °C with 98% yield (Table 6, entry 3).

Under the optimized conditions (Table 6, entry 3), we studied dehydrogenation of various 2-substituted −2,3-dihydroquinazo lin-4(1*H*)-ones. The results are summarized in Table 7. It was observed that the presence of the electron-donating groups increased the reaction rate, regardless of their positions (Table 7, entries 2–7). Also, 2-substituted-2,3-dihydroquinazolin-4(1*H*)-one derivatives, carrying the electron-withdrawing groups gave the corresponding 2-substituted quinazolin-4(3*H*)-ones in excellent yields (Table 7, entries 8–10).

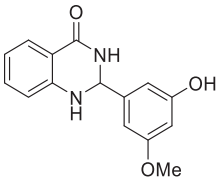
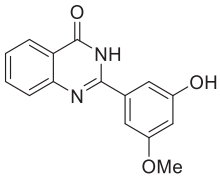
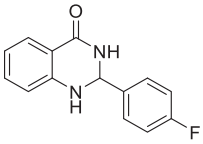
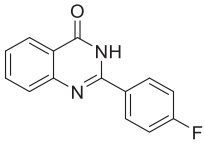
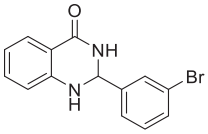
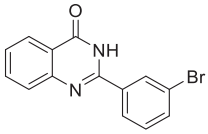
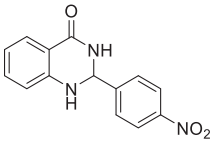
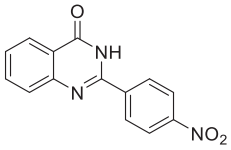
On the basis of previously reported mechanisms for the oxidation reactions in presence Pd@MCF/BQ system [22,9] and our reported mechanisms for the application of laccase in the aerobic oxidation of HQ in tandem reactions [11], it is proposed that Pd (II) atoms in the Pd-Laccase@MCF/HQ catalytic system are actual oxidizing agents. As shown in the XPS of Pd-Laccase@MCF, the

Table 7
Aerobic dehydrogenation of 2-substituted −2,3-dihydroquinazolin-4(1*H*)-ones.[a]

Entry	Substrate	Product	Time (h)	Isolated yield (%)
1			25	92
2			24	95
3			22	93
4			22	94
5			20	95
6			24	91

(*continued on next page*)

Table 7 (*continued*)

Entry	Substrate	Product	Time (h)	Isolated yield (%)
7			26	93
8			30	92
9			36	87
10			34	85

[a] Reaction conditions: substrate (1 mmol), Pd-Laccase@MCF (0.25 g), HQ (0.34 mmol), O_2 (balloon), phosphate buffer (0.1 M, pH 4.5, 4 mL)/THF (4%, 1 mL), in 40 °C.

nano-Pd particles continue both Pd(0) and Pd(II) atoms. Also, the active Pd (II) atoms required for the oxidation reaction are generated through adsorption of BQ to the palladium nanoparticles in Pd-Laccase@MCF [22]. The BQ is generated from aerobic oxidation of HQ in presence of laccase catalyst and laccase can be reoxidized by molecular oxygen, thus completing the catalytic cycle.

4. Conclusions

In conclusion, we have successfully synthesized a heterogeneous reusable artificial metalloenzyme by co-immobilization of palladium nanoparticles and laccase into the cavities of the mesocellular foams. This hybrid catalyst was applied in aerobic oxidative dehydrogenation of C—O, C—C and C—N bonds. The major advantages of these procedures are as follows: (1) this is the first report of Co-immobilization of laccase and palladium for use as a robust and highly efficient heterogeneous cooperative oxidative nanocatalyst system for aerobic oxidation of organic compounds, (2) this is the first time that a ligand-free and heterogeneous palladium- based catalytic system has been used for aerobic oxidative dehydrogenation of nitrogen heterocycles, (3) oxidation of important organic functional groups was performed using an ideal oxidant with good to high yields at ambient temperature and (4) the immobilization of the oxygen-activating catalyst (laccase) and oxidizing catalyst (Pd) onto MCF provide practical cooperative catalyst system that can be reused several times without a significant loss of activity (5) the methods conform to several of the guiding principles of green chemistry. The advantages of this novel cooperative catalyst system make it to accomplish other sustainable synthetic transformations. Further optimization and refinement of this catalyst is underway in our laboratory.

Declaration of Competing Interest

We declar that we have no competing interest.

Acknowledgements

We gratefully acknowledge financial support of this research by University of Kurdistan and the Iranian National Science Foundation (INSF, Grant Number: 96016233). We are also thankful to Prof. T. Hudlicky, Brock University, for editing the paper.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcat.2019.12.023.

References

[1] D. Wang, A.B. Weinstein, P.B. White, S.S. Stahl, Chem. Rev. 118 (2018) 2636–2679.
[2] J. Piera, J.E. Backvall, Angew. Chem. Int. Ed. 47 (2008) 3506–3523.
[3] a) M.S. Ahmed, D.S. Mannel, T.W. Root, S.S. Stahl, Org. Process Res. Dev. 21 (2017) 1388–1393;
b) M. Zhao, X.W. Zhang, C.D. Wu, ACS Catal. 7 (2017) 6573–6580.
[4] J.E. Backvall, R.B. Hopkins, H. Grennberg, M.M. Mader, A.K. Awasthi, J. Am. Chem. Soc. 112 (1990) 5160–5166.
[5] a) H. Yuan, W.J. Yoo, H. Miyamura, S. Kobayashi, J. Am. Chem. Soc. 134 (2012) 13970–13973;
b) H. Yuan, W.J. Yoo, H. Miyamura, S. Kobayashi, Adv. Synth. Catal. 354 (2012) 2899–2904.
[6] a) N. Gigant, J.E. Bäckvall, Org. Lett. 16 (2014) 4432–4435;
b) N. Gigant, J.E. Bäckvall, Chem. Eur. J. 20 (2014) 5890–5894;
c) C.M.R. Volla, J. Mazuela, J.E. Bäckvall, Chem. Eur. J. 20 (2014) 7608–7612;
d) M. Volla, J.E. Bäckvall, Angew. Chem. Int. Ed. 52 (2013) 14209–14213;
e) C. Zhu, B. Yang, T. Jiang, J.E. Bäckvall, Angew. Chem. Int. Ed. 54 (2015) 9066–9069;
f) Y. Mekmouche, L. Schneider, P.R. Pailley, B. Faure, A.J. Simaan, C. Bochot, M. Réglier, T. Tron, Chem. Sci. 6 (2015) 1247–1251;
g) B.M. Choudary, N.S. Chowdari, S. Madhi, M.L. Kantam, J. Org. Chem. 68 (2003) 1736–1746;
h) J.E. Bäckvall, A.K. Awasthi, Z.D. Renko, J. Am. Chem. Soc. 109 (1987) 4750–4752.
[7] Y. Wang, H. Zhao, Catalysts 6 (2016) 1–12.
[8] a) H.T. Abdel-Mohsen, J. Conrad, U. Beifuss, Green. Chem. 16 (2014) 90–95;
b) T. Kudanga, B. Nemadziva, M.L. Roes-Hill, Appl. Microbiol. Biotechnol. 101 (2017) 13–33;
c) J.R. Jeon, Y.S. Chang, Trends Biotechnol. 31 (2013) 335–341;

d) M.D. Cannatelli, A.J. Ragauskas, J. Mol. Catal. B: Enzym. 119 (2015) 85–89;
e) A.I. Cañas, S. Camarero, Biotechnol. Adv. 28 (2010) 694–705;
f) M. Mogharabi, M.A. Faramarzi, Adv. Synth. Catal. 356 (2014) 897–927;
g) S. Witayakran, A. Sudheendran, J. Ragauskas, Adv. Synth. Catal. 351 (2009) 1187–1209;
h) H.T. Abdel-Mohsen, K. Sudheendran, H.G. Imrich, J. Conrad, U. Beifuss, Green. Chem. 15 (2013) 1490–1495.
[9] E.V. Johnston, O. Verho, M.D. Kärkäs, M. Shakeri, C.W. Tai, P. Palmgren, K. Eriksson, S. Oscarsson, J.E. Bäckvall, Chem. Eur. J. 18 (2012) 12202–12206.
[10] K. Engström, E.V. Johnston, O. Verho, K.P.J. Gustafson, M. Shakeri, C.W. Tai, J.E. Bäckvall, Angew. Chem. Int. Ed. 52 (2013) 14006–14010.
[11] a) D. Habibi, A. Rahimi, A. Rostami, S. Moradi, Tetrahedron Lett. 58 (2017) 289–293;
b) S. Rouhani, A. Rostami, A. Salimi, O. Pourshiani, Biochem. Eng. J. 133 (2018) 1–11;
c) A. Rahimi, D. Habibi, A. Rostami, M.A. Zolfigol, S. Mallakpour, Tetrahedron Lett. 59 (2018) 383–387;
d) S. Saadati, N. Ghorashi, A. Rostami, F. Kobarfard, Eur. J. Org. Chem. (2018) 4050–4057;
e) A. Rostami, B. Mohammadi, Z. Shokri, S. Saadati, Catal. Commun. 111 (2018) 59–63;
f) D. Khaledian, A. Rostami, S.A. Zarei, Catal. Commun. 114 (2018) 75–78.
[12] B. Zheng, M.A. Schmidt, M.D. Eastgate, J. Org. Chem. 81 (2016) 3112–3118.
[13] a) A.E. Wendlandt, S.S. Stahl, J. Am. Chem. Soc. 136 (2014) 506–512;
b) M.A. Zolfigol, M. Safaiee, Synlett 5 (2004) 827–828;
c) D. Azarifar, M. Shaebanzadeh, Molecules 7 (2002) 885–895;
d) A. Rostami, A. Tavakoli, Chin. Chem. Lett. 22 (2011) 1317–1320.
[14] P.S. Winkel, W.W. Lukens, D. Zhao, P. Yang, B.F. Chmelka, G.D. Stucky, J. Am. Chem. Soc. 121 (1999) 254–255.
[15] a) M.M. Bradford, Anal. Biochem. 72 (1976) 248–254;
b) B.S. Wolfenden, R.L. Wilson, J. Chem. Soc., Perkin Trans. 2 (1982) 805–808.
[16] H. Iván Meléndez-Ortiz, N. Saucedo-Zuñiga, B. Puente-Urbina, G. Castruita-de León, J.A. Mercado-Silva, E. Saucedo-Salazar, Mater. Chem. Phys. 203 (2018), 333.
[17] S. Rouhani, A. Rostami, A. Salimi, RSC Adv. 6 (2016) 26709–26718.
[18] A. Navaee, A. Salimi, J. Mater. Chem. A 3 (2015) 7623–7630.
[19] C. Parmeggiani, C. Matassinia, F. Cardona, Green Chem. 19 (2017) 2030–2050.
[20] a) F.Z. Su, Y.M. Liu, L.C. Wang, Y. Cao, H.Y. He, K.N. Fan, Angew. Chem. Int. Ed. 47 (2008) 334–337;
b) Y. Sugano, Y. Shiraishi, D. Tsukamoto, I. Satoshi, S. Tanaka, T. Hirai, Angew. Chem. Int. Ed. 52 (2013) 5295–5299;
c) X. Yu, Y. Huo, J. Yang, S. Chang, Y. Ma, W. Huang, Appl. Surf. Sci. 280 (2013) 450–455;
d) Y. Li, Y. Gao, C. Yang, Chem. Comm. 51 (2015) 7721–7724;
e) K. Kędziora, A. Díaz-Rodríguez, I. Lavandera, V. Gotor-Fernández, V. Gotor, Green Chem. 16 (2014) 2448–2453;
f) I. Ibrahem, M.N. Iqbal, O. Verho, A. Eivazihollagh, P. Olsen, H. Edlund, C.W. Tai, M. Norgren, E.V. Johnston, Chem. Nano. Mat. 1 (2017) 1–6;
g) K. Rajabimoghadam, Y. Darwish, U. Bashir, D. Pitman, S. Eichelberger, M.A. Siegler, M. Swart, I. Garcia-Bosch, J. Am. Chem. Soc. 140 (2018) 16625–16634.
[21] a) K. Mori, T. Hara, T. Mizugaki, K. Ebitani, K. Kaneda, J. Am. Chem. Soc. 126 (2004) 10657–10666;
b) M.S. Kwon, N. Kim, C.M. Park, J.S. Lee, K.Y. Kang, J. Park, Org. Lett. 7 (2005) 1077–1079;
c) B. Karimi, S. Abedi, J.H. Clark, V. Budarin, Angew. Chem. Int. Ed. 45 (2006) 4776–4779;
d) F. Li, Q. Zhang, Y. Wang, Appl. Catal. A 334 (2008) 217–226;
e) B. Karimi, A. Zamani, S. Abedi, J.H. Clark, Green Chem. 11 (2009) 109–119;
f) T. Harada, S. Ikeda, F. Hashimoto, T. Sakata, K. Ikeue, T. Torimoto, M. Matsumura, Langmuir 26 (2010) 17720–17725;
g) C.M.A. Parlett, D.W. Bruce, N.S. Hondow, A.F. Lee, K. Wilson, ACS Catal. 1 (2011) 636–640;
h) B. Karimi, D. Elhamifar, J.H. Clark, A.J. Hunt, Org. Biomol. Chem. 9 (2011) 7420–7426;
i) M. Gholinejad, M. Afrasi, N. Nikfarjam, C. Nájerac, Appl. Catal. A Gen. 563 (2018) 185–195;
j) L. Chen, J. Yan, Z. Tong, S. Yu, J. Tang, B. Ou, L. Yue, L. Tian, Micropor. Mesopor. Mat. 266 (2018) 126–131.
[22] a) M.B. Li, D. Posevins, K.P.J. Gustafson, C.W. Tai, A. Shchukarev, Y. Qiu, J.E. Bäckvall, Chem. Eur. J. 25 (2019) 210–215;
b) M.B. Li, A.K. Inge, D. Posevins, K.P.J. Gustafson, Y. Qiu, J.E. Bäckvall, J. Am. Chem. Soc. 140 (2018) 14604–14608.
[23] V.V. Kumar, S. Sivanesan, H. Cabana, Sci. Total Environ. 487 (2014) 830–839.
[24] X. Jin, K. Taniguchi, K. Yamaguchi, N. Mizuno, Chem. Sci. 7 (2016) 5371–5383.
[25] T. Moriuchi, K. Kikushima, T. Kajikawa, T. Hirao, Tetrahedron Lett. 50 (2009) 7385–7387.
[26] (a) Y. Izawa, D. Pun, S. S. Stahl, Science 333 (2011) 209; (b) A.V. Iosub, S. S. Stahl, ACS Catal. 6 (2016) 8201–8213.
[27] E. Vitaku, D.T. Smith, J.T. Njardarson, J. Med. Chem. 57 (2014) 10257–10274.
[28] a) R. Yamaguchi, C. Ikeda, Y. Takahashi, K.I. Fujita, J. Am. Chem. Soc. 131 (2009) 8410–8412;
b) S. Muthaiah, S.H. Hong, Adv. Synth. Catal. 354 (2012) 3045–3053;
c) J. Wu, D. Talwar, S. Johnston, M. Yan, J. Xiao, Angew. Chem. Int. Ed. 52 (2013) 6983–6987;
d) D.V. Jawale, E. Gravel, N. Shah, V. Dauvois, H. Li, I.N.N. Namboothiri, E. Doris, Chem. Eur. J. 21 (2015) 7039–7042.