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1. Introduction

Within a survey among various porous materials, silicates could play particular roles in fine chemical industries.¹⁻³ For the running of miniaturized-scale syntheses, namely through pores as nanoreactors,4-7 these pioneering catalysts have found a highlighted place across the chemistry world. Despite their excellent aptitude to facilitate different reactions inside pores, for instance, condensation types,⁸⁻¹⁰ there is still a lack of enough versatility. Hence, as a helpful tool to provoke chemists' minds, their structural modifications have always been embedded in their outlines. Requirements for the use of a green reductant-oxidant¹¹⁻¹⁶ for redox processes, based on green chemistry protocols, have led researchers to have a replacement of the catalytic methods with traditional ones.17-20 One group of significant products via the partial oxidation of the carbon-hydrogen (C-H) bond, specifically aldehydes, is of considerable importance as precursors.²¹ Air, because of the accessibility, economic viability, more effortless exploitation than other reagents, and the low number of

Efficient strategy for interchangeable roles in a green and sustainable redox catalytic system: IL/Pd^{II}-decorated SBA-15 as a mesoporous nanocatalyst

Time and again, SBA-15-based composites as mesoporous materials and the incorporation of transition metals in them have been attracting dramatic attention in the field of catalysis due to their remarkable features. In this paper, the activity of SBA-15 supported ionic liquid–Pd(II) has been investigated in the catalytic transfer hydrogenation of nitroarenes with formic acid as a hydrogen donor at room temperature in water medium, and the oxidation of benzyl alcohols to benzaldehyde derivatives under atmospheric oxygen at high temperature. This novel nanocatalyst was characterized by FT-IR, SA-XRD, BET, BJH, TGA, FE-SEM, TEM, and ICP as the most commonplace techniques for analyzing its characteristics to be revealed as truth. Furthermore, the EDX analysis illustrates the grafting of the ionic liquid–Pd(II) into SBA-15. The catalyst showed high stability under reaction conditions, and can be recovered and reused for at least 15 and 6 reaction runs in oxidation and reduction reactions, respectively.

undesirable side reactions, is more noteworthy than other green oxidants. These attributes encourage researchers to develop desirable and, of course, robust catalytic systems for aerobic oxidation.²² However, due to several challenges, industrial oxidation processes have extended far less than the reduction processes.²³

Concerning reduction reactions, molecular hydrogen is the most appropriate reducing agent. However, endangering its application, storing problems, and restrictions on the use of gaseous processes can be addressed as a unique source for its merits and demerits. Therefore, the investigation of catalytic systems based on alternative green hydrogen donors is one of the researchers' vital interests in this field.¹¹ In the middle of a vast number of options, formic acid with its intriguing properties, such as ease of transportation and use, availability, lack of hazardous wastes, economic efficiency, and high atom-economy, is one of the most critical compounds used as a reducing agent.²⁴ Accordingly, various approaches and methods for developing suitable catalysts in reduction processes using this reductant have been studied.¹¹

Since most homogeneous catalysts have not been reusable in chemical processes, extensive endeavours have been allocated to studying different immobilization methods.^{25–27} Catalysts, including one or more grafted or inserted transition metals, especially precious metals, such as palladium, are tremendously regarded because of their ability to perform both oxidation and

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reduction.11,28,29 Fundamental studies on the employment of palladium as a catalyst on oxidation-reduction reactions by the aid of green oxidants-reductants, such as molecular oxygenhydrogen (O_2/H_2) , indicate its extraordinary catalytic potential. However, the formation of palladium(0) and the debilitation of the catalytic centres bring about the retardation of reaction kinetics, which has been observed over time. Therefore, its immobilization has two purposes: (i) heterogeneity to accelerate separation, (ii) prevention of the formation of Pd (0) and deactivating catalytic centres has been the basis of research. As mentioned, ordered mesoporous silicates, especially functionalized ones, have an outstanding potential due to their high surface area with the hydroxyl groups to be used as much more efficient catalysts.^{30,31} In the present study, due to the advantages of ordered mesoporous silica, SBA-15 was functionalized through a solvent-free green pathway using the tetrachloropalladate anion, [PdCl₄]²⁻, based on ionic liquid. Various characterization techniques, such as FT-IR, SA-XRD, BET, BJH, TGA, SEM-EDX, TEM, and ICP, have been carried out to assess the achievement of imposed corrections. As no solvent is used in this process, further steps, such as extraction to remove waste liquid is eliminated. The functionalized ordered mesoporus silica was then used as a catalyst in the aerobic oxidation reaction of the C-H bonds of benzylic, aliphatic, and allylic alcohols. The highly desirable efficiency of the catalyst in the aerobic oxidation process led us to investigate its ability in the green transfer hydrogenation (TH) of nitroarenes. This reduction process was investigated in an aqueous medium using formic acid as a green hydrogen-donor. The results showed the high efficiency of the catalyst for this process in green conditions, and at ambient temperature. Besides, the reusability of the catalyst was estimated to be 15 and 6 times for the oxidation and reduction processes, respectively, which confirms its high stability under both associated conditions.

2. Experimental section

2.1. Chemical, instrumentation and analysis

All starting materials and correlated apparatuses were purchased from credible commercial suppliers, and used without further purification or manipulating in their proceeding styles, respectively. The catalyst was characterized using spectroscopic and different affordable analytical techniques, including FT-IR, X-ray diffraction (XRD), inductively coupled plasma (ICP), Brunauer-Emmett-Teller (BET), Barrett-Joyner-Halenda (BJH), thermal gravimetric analysis (TGA), and scanning electron microscopy joined with energy-dispersive X-ray analysis (SEM-EDX). The FT-IR spectra reached an acquisition step of the basic spectra over the region 400-4000 cm⁻¹ with NICOLET IR100 FT-IR. Here, spectroscopic-grade KBr was harnessed. The powder X-ray diffraction spectrum was marked at room temperature by a Philips X'pert 1710 diffractometer using Cu-K α (α = 1.54056 Å) *via* charted Bragg–Brentano geometry $(\theta - 2\theta)$. The ICP analysis was performed using a VISTA-PRO, CCD simultaneous ICP system. The running of the thermal destruction was analysed

and sketched on a plot through a gradual heating rate of 20 $^{\circ}$ C min⁻¹ over a temperature range of 25–1000 $^{\circ}$ C under a stream of purified N₂. The SEM images were observed using Philips XL 30 and S-4160 instruments with gold-aided coating, which was laid out on nanoparticles within the EDX test. The primary results for the reaction progress were surveyed by gas chromatography (GC) (Yonglin 6100; BP-5; 30 m × 0.25 mm × 0.25 µm) with toluene as a general solvent for injection, and nitrogen as an inert carrier gas. All yields referred to isolated and purified products. ¹H-NMR and ¹³C-NMR spectra were recorded on a Bruker Avance (DRX 400 MHz) in pure deuterated CDCl₃ solvent with a commercially introduced internal standard, namely tetramethylsilane (TMS).

2.2. Synthesis of SBA-15

Exploiting a general procedure out of the literature, the support SBA-15 prepared using Pluronic P-123 as a template was casted by a diluting and initiating agent, TEOS (tetra ethyl oxy silane), for polymerization across such framework as a silica source, which was fulfilled in an acidic medium.32 In a typical procedure, 4 g of the Pluronic P-123 surfactant was dissolved in 20 g of water, followed by adding 80 g of 2 M HCl. To the above solution, 8 g of TEOS was added gently, and stirring was continued for the next 24 h at 40 °C. The gel mixture was then transferred to a polypropylene bottle, and hydrothermally treated at 100 °C for 48 h. The solid residue was passed through a paper and then a ceramic sieve, washed with water, and finally dried at 60 °C for 8 h. The volatile template was removed by calcination at 550 $^\circ C$ (heating rate = $2 \degree C \min^{-1}$) for 6 h in the presence of air as an in situ decomposer. The obtained porous material is denoted as SBA-15 nanoparticles.

2.3. Synthesis of 3-methyl-1-(3-(trimethoxysilyl)propyl)-1*H*-imidazol-3-ium

In a typical procedure for the preparation of the interior decoration of the catalyst, trichloropropyltrimethoxysilane (20 mmol) and *N*-methyl imidazole (20 mmol) were mixed together and poured into a round-bottom-flask, as a container. The mixture was stirred for 24 h at 100 °C under reflux and neutral gas atmosphere. The obtained yellow viscous liquid was dried at 80 °C and under vacuum for 24 h (Scheme 1A).

2.4. Synthesis of (3-methyl-1-(3-(trimethoxysilyl)propyl)-1*H*-imidazol-3-ium)2 monopalladium(II) tetrachloride

To the prepared ionic liquid (2 mmol), $PdCl_2$ (0.17 g, 1 mmol) was added. A 6 h swirling was carried out at 100 °C under reflux and argon atmosphere until a transparent brown liquid appeared. The obtained brown viscous liquid was dried at 80 °C under vacuum for 24 h (Scheme 1B).

2.5. Synthesis of Pd-sites linked onto SBA-15 (SBA-15-IL/Pd)

To the prepared Pd^{II} -containing ionic liquid (20 mmol), SBA-15 (0.25 g) was added and agitated overnight at 100 °C under reflux and argon atmosphere. The obtained brownish precipitate was centrifuged and washed three times with ethanol. Finally, all remaining solvents and rinsed solutions



were wiped out at 80 $^{\circ}$ C under vacuum condition for 24 h (Scheme 1C).

2.6. General imposed approach for the aerobic oxidation of alcohols using SBA-15-IL/Pd

Benzyl alcohol (1 mmol) was added gradually to a mixture of the catalyst, SBA-15-IL/Pd, (40 mg, 3 mol% of Pd), and NaOH (1 mmol) in water (2 mL). The reaction mixture was whirled for six hours at 80 °C inside of a condensed-air chamber, and thinlayered chromatography (TLC) was used to check the finalized reaction. After the perfecting of the reaction, the catalyst was separated from the reaction mixture by centrifugation. As a work-up step, it was washed four times with ethanol. The final mixture was added to a new flask and diluted with ethyl acetate, and the organic phase containing the product was decanted. Finally, the organic layer was isolated by the aid of column chromatography on a silica gel. All refined compounds were checked out using the melting point test, FT-IR, ¹H-NMR, and ¹³C-NMR. The spectral data of the known compounds were compared with the reported patterns and a number of previous reports.

2.7. General procedure for the transfer hydrogenation of nitroarenes to corresponding amines using SBA-15-IL/Pd

As a reverse role of the catalyst in promoting the oxidation reaction, in a typical transfer hedrogenation (TH) reaction, nitrobenzene (0.5 mmol) and formic acid (1 mmol) were combined together by making an aqueous solution (2 ml) in a glass vial. Then, using 20 mg of the added catalyst, the mixture was stirred at room temperature in contact with air for 3 h. Thin-layered chromatography (TLC) and GC were performed to ensure reaction completion. By the end of the completion of the reduction, the catalyst was separated by centrifugation, and the product underwent an eluting procedure by applying an aqueous–organic extraction stage (H₂O–ethylacetate). In the organic phase, the aniline product was separated and identified after the separation of the ethyl acetate solvent using a rotary evaporator and passing through the silica gel column. The identification of all compounds was rendered using the melting point (m.p.; for solid products), FT-IR, ¹H-NMR, and ¹³C-NMR. The spectral data of the known amines were checked with their authentic references.

3. Results and discussions

3.1. Validation of the synthesized SBA-15-IL/Pd

For the assessment of the precision of our first theoretical modification and synchronizing with former reports, a wide range of analyses were applied. For studying the prepared SBA-15-IL/Pd by different fundamental instrumental techniques, such as SA-XRD, FT-IR, BET, TGA/DTA, SEM, EDX, TEM, and ICP-AES, the quality and quantity information of the composite structure were measured.

3.1.1. FT-IR (Fourier-transform infrared) spectroscopy. The non-decorated SBA-15 includes a peak related to the Si-O bond in its infrared spectrum similar to that of silica. The (3-methyl-1-(3-(trimethoxysilyl)propyl)-1H-imidazol-3-ium)₂ monopalladium(II) tetrachloride has functional groups, such as aliphatic C-H, aromatic C-H, aliphatic C-C, aromatic C-C, aromatic C=C, aromatic C=N, aliphatic C-N, and aromatic C-N. The mentioned functional groups are quite apparent in FT-IR spectroscopy, and they are expected to remain unchanged after functionalizing SBA-15 (in fact, modifying the internal cavity surfaces). The FT-IR spectra of SBA-15 before (SBA-15) and after functionalization (SBA-15-Pd) were compared point-by-point, and as a result, the formation of the desired structure was verified (Fig. 1a). The FT-IR spectra of SBA-15 (black curve), IL-Pd (blue curve), and SBA-15-IL-Pd (red curve) have been illustrated in Fig. 1a. The peak at 1091 cm^{-1} is related to the stretching vibration of the Si-O bond and is apparent in all IR graphs for compounds that contained a silicate basis. This peak is present in all three IR diagrams, indicating the integrity and stability of the SBA-15 structure. The broad peak observed at the 3300-3600 cm⁻¹ region is ascribed to the O-H stretching vibration in Si-OH and water molecules absorbed on the



Fig. 1 (a) FT-IR spectra, (b) SA-PXRD and PXRD. (c) Nitrogen adsorptiondesorption isotherms, and (d) TGA pattern of SBA-15 and functionalized SBA-15.

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nanoparticles in the preparation process. In the FT-IR spectrum of treated SBA-15 (after complete preparation), there is no peak in the range of 2900–3000 cm^{-1} , which confirms the absence of the surfactant Pluronic P123 used in its preparation process, or its complete removal from the structure during the separation and calcination process. After the functionalization of SBA-15 using the (3-methyl-1-(3-(trimethoxysilyl)propyl)-1H-imidazol-3ium)₂ monopalladium(II) tetrachloride, the discriminating peaks of this ligand or ionic liquid were appeared in the infrared spectrum of the noted catalyst. In particular, the IR absorption peaks at 1500-1700 cm⁻¹ and 1300-1500 cm⁻¹ ranges could be allocated to the $\nu_{asym}(C=C)$ and $\nu_{sym}(C=C)$ stretching modes of the imidazole aromatic ring of 3-methyl-1-(3-(trimethoxysilyl)propyl)-1H-imidazol-3-ium, in similar sequence. The observation of a peak around 1593 cm^{-1} could be eloquently assigned to the stretching vibration along the C=N bond presented in the imidazole, which after IL formation, is shifted to 1627 cm^{-1} . Such a phenomenon can conclude that the IL formation has occurred. The presence of a peak in the 2250-2400 cm⁻¹ region could also be another evidence of the conjugated C=N functional group being shifted to higher frequencies because of the IL formation. Moreover, the vibrational frequency found at 3130 cm⁻¹ is related to the aromatic C-H group (imidazole). The bands at 2977, 2923, and 2877 cm⁻¹ belong to the aliphatic (propyl chain) C-H bonds in the FT-IR spectrum.

3.1.2. SA-PXRD (small-angle powder X-ray diffraction). Pattern Fig. 1b indicates the SA-PXRD patterns of SBA-15 before and after modification by this palladium-activated linker. The SA-PXRD pattern of the bar SBA-15 shows three distinguishing Bragg peaks below 2.5, indicating its well-ordered mesostructure that expanded toward twodimensional layers. Three strong peaks at $2\theta = 0.986$, 1.630, and 1.859 with d-spacings of 89.47, 54.15, and 47.49 Å, respectively, were assigned to reflections of the 100, 110, and 200 associated with the hexagonal structure. In other words, the 100 and 110 peaks are related to the long silica sequence (the length of the honeycomb hexagons), and the 200 peak was assigned to the crystal plates associated with the hexagonal widths (the width of the honeycomb hexagons). After functionalization, the correlation between the reduction of the peak intensity and the overall decrease in the electron density contrast confirmed the Pd-IL's placement on the silica wall.³³⁻³⁵ It also shows a prominent effect by loading the ligand and the metal. The diffraction peak (100) width and intensity have become broader and weaker, respectively, and the change to 2θ values related to the SA-PXRD pattern of pure SBA-15. The blockage of a part of the open anchor catalyst pores decreased the long-range order of SBA-15.

3.1.3. Nitrogen adsorption-desorption test. Nitrogen adsorption-desorption, namely BET (Brunauer-Emmett-Teller), measurements were carried out for SBA-15 (black curve) and SBA-15-IL-Pd (red curve) to evaluate their casted properties. The isotherms and pore size distributions are given and depicted in Fig. 1c. All of the materials exhibited type IV isotherms, and H1 hysteresis loops were detected as a characteristic of mesoporous

solids that revealed the identity of the SBA-15 structures. A sharp capillary condensation step confirmed by a narrow pore size distribution in the mesoporous range appeared at $P/P_0 = 0.5-0.8$ as the fractional pressure, and proved the presence of a regular mesopore in the network of the catalyst (Fig. 1c).³⁶ The results obtained for the analysis of the textural characteristics (BET surface area, average pore size, and pore volume) of the samples are summarized in Table 1. As shown in Table 1, the specific surface area and the pore volume of bar SBA-15 decreased after the functionalization, proving the immobilization of (3-methyl-1-(3-(trimethoxysilyl)propyl)-1*H*-imidazol-3-ium)₂-monopalladium(π) tetra chloride inside of the SBA-15 pores.

3.1.4. TG/DTA (thermo-gravimetric degradation via differential thermal) analysis. The thermal stability of functionalized SBA-15 with (3-methyl-1-(3-(trimethoxysilyl)propyl)-1Himidazol-3-ium)₂ monopalladium(II) tetrachloride was evaluated by TG/DTA analysis at the temperature range of 25 °C to 800 °C (Fig. 1d). Moreover, the ratio of organic matter to mineral content in the catalyst was calculated by this technique. According to the diagram, the first step, including the slight weight loss (6 w%) below 200 °C, can be considered to correspond to the loss of water and organic groups absorbed physically. The second step, which indicates 24% weight loss at the range of 200-400 °C, is most likely due to the decomposition of organic molecules (imidazolium ionic liquids) grafted to the SBA-15 surface. In the third step, there is a 20% weight loss at the range of 400–800 $^\circ C$ because of organic residue contents. Through the TGA analysis, the organic motif, particularly the 3-methyl-1-propyl-1H-imidazol-3ium chloride content of the functionalized SBA-15 nanoparticle was evaluated to be 200 mg g^{-1} . The amount of 200 mg per 1000 mg equals 1.25 mmol of 3-methyl-1-propyl-1H-imidazol-3ium chloride and 0.75 mmol Pd(0) per 1000 mg of modified catalyst.

3.1.5. SEM (scanning electron microscopy). We investigated the morphology, size, and texture of SBA-15 (Fig. 2a), and functionalized SBA-15 (Fig. 2b) by SEM (Fig. 2). These images demonstrate that the bare SBA-15 has a worm-like morphology and a striated appearance, indicating the presence of surfaces caused by surfactants during structure synthesis. The SEM analysis indicated that the synthetic SBA-15-IL-Pd had a unified surface of worm-shaped nanoparticles. These micrographs confirmed the formation of the free form and functionalized SBA-15 arranged in a style of curved worm.

3.1.6. Energy-dispersive X-ray spectroscopy (EDX). An EDX spectrum can prove the presence of stabilized $Pd(\pi)$ ions and other expected elements inside the functionalized SBA-15 pores. It gives the atomic percent of elements that are present

Table 1 Textural properties of SBA-15 and SBA-15-IL/Pd samples					
Name of sample	BET surface area $(m^2 g^{-1})$	Langmuir specific surface area $(m^2 g^{-1})$	Pore volume $(cm^3 g^{-1})$	Pore size (Å)	
SBA-15 SBA-15-IL/Pd	736.85 318.47	3994.5489 1291.07	1.27 0.241	69.39 21.71	



Fig. 2 SEM images of (a) SBA-15, (b) SBA-15-IL/Pd. (c) Weight percent of various elements on the surface of SBA-15-IL–Pd from EDX analysis. (d) EDX studied area. TEM illustration of (e) SBA-15SBA-15 and (f) SBA-15-IL/Pd.

on the surface of the catalyst. As shown in Fig. 2c, the EDX analysis approved the successful synthesis of SBA-15-IL–Pd with 0.16% palladium. The distribution of other elements was also obtained, including Cl, 0.57; Si, 2.45; N, 15.64; O, 23.02; C, 58.16%.

3.1.7. Transmission electron microscopy (TEM). TEM images of SBA-15 before and after binding of the silica-ended linker to the silicate surface were investigated to identify the size, morphology, and shape of the synthesized catalysts (Fig. 2e and f). Based on the investigated images, it can be seen that the dark halation inside the pores confirms the immobilization of (3-methyl-1-(3-(trimethoxysilyl)propyl)-1*H*-imidazol-3-ium)₂ monopalladium(II) tetrachloride in the pores. However, as observed in Fig. 2f, the assemblages of (3-methyl-1-(3-(trimethoxysilyl)propyl)-1*H*-imidazol-3-ium)₂ monopalladium(II) tetrachloride in the pores. However, are visible on the surface of SBA-15.^{32,37}

3.1.8. Inductively coupled plasma (ICP). The capacity of the catalyst about palladium in SBA-15-IL/Pd was measured by ICP-AES analysis. In a typical procedure, 1 g of the catalyst was dispersed in a mixture of hydrochloric acid and nitric acid (HCl/HNO₃, 3/1 v/v ratio), and then the remaining precipitate was separated by centrifugation. The remaining solution containing Pd²⁺ was analyzed by ICP. Eventually, the captivated palladium that is inserted inside of the catalyst was calculated to be equal to 0.73 mmol·g⁻¹, which is in good agreement with the results obtained from the TGA analysis.

3.2. Application of SBA-15-IL/Pd for the selective oxidative transformation of alcohols and nitroaromatic compound reduction

3.2.1. Optimization of the aerobic oxidation of alcohols. After the preparation and characterization of the catalyst, its ability was investigated in the aerobic oxidation of alcohols. Indeed, it is necessary to have a catalyst containing Pd(n) to run the reactions, and gain the best results. Recently, controlling the conversion of Pd(n) to Pd (0) has been a considerable challenge because this prevents the unique effect of a catalyst on the progression of the reaction. In several studies, the use of disparate ligands and co-catalysts has been considered.^{38–40} Moreover, many efforts have been assigned to investigate methods based on condition adjustment, not using auxiliary agents.^{41,42} According to the articles reported so far, many efforts have been made to find optimal oxidation conditions in an aqueous medium. Different parameters, such as the base, catalyst loadings, solvent, and temperature, have been considered for the optimization step (Scheme 2).

As a model reaction, we investigated the oxidation of benzyl alcohol to benzaldehyde in the company of SBA-15-L/Pd and air bubbling at room temperature. First, different solvents were examined to determine their effect on the yield of the model reaction. Water was selected as the best solvent for the aerobic oxidation reaction. Notably, toluene as a solvent had a similar effect, but due to the adherence to the requirements dictated by the green chemistry protocols, water was eventually used as the optimal solvent for the remaining processes. Interestingly, the catalyst had limited freedom to process in polar solvents, which could be repressed due to disturbance at the catalyst centers and catalyst poisoning (Fig. 3a). These studies also confirm that



Scheme 2 Model reaction for the aerobic oxidation of alcohols.



Fig. 3 Optimization of the base, catalyst loading, solvent temperature and catalyst heterogenity effect for the aerobic oxidation of alcohols (a–e respectively) and catalyst reusability (f).

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no aerobic oxidation product has been produced without a base, and NaOH could lead to the best results (Fig. 3b). Subsequently, the model reaction was investigated using different catalyst loadings. 40 mg of the catalyst led to the best results because we did not observe more significant progress by increasing the amount of catalyst. This slight increase is not a plausible justification for a 25% rise in the catalyst mass. Therefore, 40 mg was chosen as the optimal amount. It is probable that with increasing the mass, the catalyst starts to perform as an absorbent instead of a catalyst because of its porous structure (Fig. 3c). Further tests at higher temperatures indicated that increasing the temperature to 80 °C had a positive effect on the reaction process (Fig. 3d). Increasing the temperature can affect the reaction process in several ways. When the temperature climbs up, the solubility of the precursors in the aqueous medium increases.⁴³ In other words, the increased temperature leads to the diffusion of the species into the pores and more exposure to catalytic centres. In contrast, a further increase of the temperature reduces the solubility of oxygen in the reaction medium. As a result, a greater reaction progress was not observed. Eventually, the highest output in the field of product for the model reaction was gained using NaOH (1 equiv.) as a base, 0.04 g of catalyst (3 mol% of $Pd(\pi)$, and H_2O as solvent at 80 °C after 6 h (Scheme 2).

In another experiment, catalysts such as (1-butyl-3-methyl-1*H*imidazol-3-ium)₂ monopalladium(II) tetrachloride, Na₂PdCl₄ and PdCl₂ did not have a remarkable influence on model reaction efficiency. Indeed, using (1-butyl-3-methyl-1*H*-imidazol-3-ium)₂ monopalladium(II) tetrachloride, Na₂PdCl₄, and PdCl₂ as the catalyst yielded about 49, 31, and 21% of the desired products (Fig. 1e). The model reaction was surveyed *via* other comparable Pd-based catalysts. However, these catalysts were not as effective as SBA-15-IL/Pd.

The performance and effectiveness of green SBA-15-IL/Pd were evaluated using various substrates with electron-donor and electron-withdrawer groups. The results of the efficiency and reaction time for the selective oxidation of alcohols to aldehydes are shown in Table 2. All of the substrates were successfully converted to the corresponding aldehydes at high conversion ratios (87–97%) without any byproducts, such as surplus oxidation products or aromatic acids, within a reaction time of 6 h.

Therefore, the most general, familiar, and eminently sensitive to the oxidation of alcohol derivatives were studied in the optimal redox conditions (Table 2). The accompanying of the electronwithdrawing groups (EWG) on the phenyl ring of the benzylic

Ar-NO-	нсоон	Ar NH	
AI-NO ₂	Solvent	AI-III2	
	base		
	r.t.		
	Cat. (mg)		

Scheme 3 Model reaction for the reduction of the nitroaromatic compounds.

alcohols led to the more favorable products (Table 2, entries 1e and 1f), and the electron-donating moieties had a slightly contrary impact (Table 2, entries 1b-1d). To investigate the steric effects on the performance of the secondary alcohols, 1-phenylethan-1-ol (reduced form of acetophenone) was selected as a sample substrate. It underwent the imposed oxidative condition successfully with high yield, containing a little steric hindrance (Table 2, entry 1n). Nevertheless, diphenylmethanol (reduced form of benzophenone), known as a bulky 2° alcohol, demonstrated a poor conversion into the product (Table 2, entry 10). The 1° and 2° aliphatic alcohols that are the problematic class of alcohol substrates in the usual aerobic oxidation reactions worked well in these optimal reaction conditions (Table 2, entries 1j-1m). However, the secondary aliphatic alcohols unveiled significantly low achievement because of the steric hindrance (Table 2, entry 1m). There should be an emphatic viewpoint that excellent chemoselectivity was observed regarding the primary alcohols, and just the aldehyde as a unique product was captured under these reaction conditions. After this time, the feasibility of the formation of acid or other corresponding byproducts was eliminated from the first estimations or predictions.

3.2.2. Aerobic oxidation mechanism study. According to the previous literature, the selective oxidation of alcohols to aldehydes relies on an essential medium, such as using NaOH to increase the oxidative activity of the catalysts, and can cause an enhancement around the selectivity towards BzH.44-46 From additional investigations, it was confirmed that the optimized basicity for the alteration of benzyl alcohol to benzyl aldehydes is ~9.2. Increasing it to a basic strength of ~9.5 can lead to the formation of benzoic acid.47 Therefore, the adjustment of the optimized basicity is remarkably essential to obtain the highest selectivity. Mori et al. reported that the reaction would occur if the hydroxyl (OH) group of benzyl alcohol was coordinated with the unsaturated Pd species. Subsequently, a Pd-alcoholate species, as a roughly stable complex, was formed. Then, during the hydride abstraction reaction, aldehydes and Pd-hydride (temporarily stable in contact with air molecules) were produced as products.48 The Pd-hydride species remains on its reaction pathway, and makes a Lewis acid-base coordination with O_{2} , thereby releasing the Pd species, and forming O_2 and H_2O . Additional investigations agreed on the same outcome. Prati et al. also suggested that surface oxygen can dissociate benzyl alcohol homolytically, and produce an alkoxy radical as the intermediate Ph-CH2-O• on the active site of noble metal surfaces. Then, H of Ph-CH2-O• was coordinated to vacant Pd sites to cause it to pass through oxidative carbonylation at the benzylic site. These sites are necessary for benzaldehyde embodying.^{49–52} In this study, the categorizations of the catalysts were settled in acid/base bi-functional heterogeneous division. Interaction between Pd²⁺ and the -OH of NaOH was considered as the Brønsted-Lowry base, while $-N^+=$ played a role as the Lewis acid site. The dominant mechanism is supposed to be an E1cB elimination process. In more detail, the single O-H bond of the alcohols was broken up by free coordinative Pd sites, and led to the conversion of benzyl alcohol to alkoxide, which is its conjugate base. Next, Pd would undergo a β-H elimination,

Table 2 Concocting of various carbonyl derivatives through SBA-15-IL/Pd catalyzed aerobic C-H oxidation^{ab}



^{*a*} Reaction conditions: alcohol (1 mmol), NaOH (1 equiv.), 0.04 g of catalyst (3 mol% of Pd(II)) and H₂O (2 ml) at 80 °C for 6 h under air bubbling condition. ^{*b*} The yields refer to the isolated pure products.

followed by a cleavage of the Pd-C-H bond from the alkoxide. After these two steps, the -OH- of NaOH caught the protons (H) from Pd-hydride and formed H₂O. Finally, the iminium site $(-N^{+})$ reacted with molecular oxygen to regain its Pd–O form. Eventually, the coordinative Pd sites were free from any ligand, completing the catalysis circle. An overall proposed mechanism is depicted in Fig. 5a. Inhibitors, such as thiophenol, quinoline, benzoic acid, HCl, cyclohexanone, and 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) with different concentrations, have been used to further investigate the mechanism of the aerobic oxidation reaction of benzyl alcohol, and performed using the prepared catalyst under optimized conditions. As can be seen from the results of the reaction under optimal conditions and in the presence of inhibitor agents, in the presence of thiophenol as a sulfur agent with a high affinity for the active catalytic centers of Pd, the catalyst is poisoned. With increasing amount of this inhibitor, the catalyst activity decreases significantly.

This phenomenon indicates the importance of the presence of Pd catalytic centers in the reaction. Also, quinoline as a Lewis base, which can also act as a catalyst toxin, drastically reduces the catalytic activity. This indicates the importance of the coordination of the corresponding alcohol to the active catalytic centers of Pd for performing the reaction. In the presence of TEMPO, as a radical scavenger, the alkoxy radical is trapped and the reaction does not progress. The presence of benzoic acid in competition with alcohol did not significantly affect the oxidation reaction, indicating that this inhibitor does not interfere with the oxidation reaction. Since the oxidation reaction in the presence of this catalyst is associated with the release of HCl, it is predicted that the reaction progress will be slow in the acidic medium. The reaction dependency on the base also confirms this result. These results indicate the prominent role of palladium in catalyzing the oxidation reaction, and factors such as the coordination of alcohol to the active catalytic centers of

palladium and the need for the presence of a base in this reaction.

3.2.3. Optimization of the reduction of nitroaromatic compounds. Considering the desirable results and stability of Pd-IL-SBA-15 within the aerobic oxidation reaction of alcohols, we decided to investigate the performance of the catalyst for the transfer hydrogenation of nitroaromatic compounds in green orientation. Room temperature conditions and aqueous medium were chosen as a model reaction for the reduction of nitroarenes to evaluate the efficiency of SBA-15-IL/Pd as a catalyst in the presence of HCOOH as a hydrogen-donor. Initially, the reduction reaction was investigated in alphahydrogenated alcohols as a solvent. The first assumption was based on the role of the abovementioned alcohols as a solvent and reducing agent, simultaneously. However, this showed no desirable results (Fig. 4a). Then, other various solvents were investigated using formic acid as a green reducing agent. As shown in the optimization figure, the highest efficiency and catalytic performance were achieved in the aqueous medium (Fig. 4a). According to the results, the more reduction in solvents' polarity happens, the less efficiency will be obtained. This phenomenon can be due to the lower solubility of base used in these media reactions. Organic bases performed better than inorganic ones, and their efficiency was almost consistent with their strength. Among the organic bases, 1,8diazabicycloundec-7-ene (DBU) had the best performance. Interestingly, we also ran the model reaction in the absence of base, and aniline was successfully obtained with a comparable yield (Fig. 4b). Regarding the amount of catalyst, we investigated different masses and concluded that when 0.02 mg of catalyst was used in the model reaction, the highest yield was observed (Fig. 4c). According to the results, by the addition of 0.02 g of catalyst, the rate of the reaction and conversion values met a higher range for the desired products (Fig. 4c). Eventually, the highest product yield in the model reaction was obtained using 20 mg of the catalyst (1.5 mol% of $Pd(\pi)$ when the reaction components were immersed in H₂O as a solvent at room temperature after 3 h (Scheme 3).



Fig. 4 Optimization of the solvent, base and amount of catalyst for the reduction of nitroaromatic compounds (a-c) and catalyst reusability (d).

Since SBA-15-IL-Pd led to the high efficiency in the model reaction, we employed various nitroaromatic derivatives to be hydrogenated by this catalyst (Table 3). As shown in Table 3, halogens (such as chloro, bromo, and iodo) as substituents on the phenyl ring decreased the yield of the reaction, and prolonged the reaction time (Table 3, entry 2h, 2i, and 2m). In contrast, electron-donating (-OCH₃, -CH₂OH, -OH) substituents increased the yield of the reaction (Table 3, entries 2b, e, f, g, j, k, l, and 2n). We also compared the reduction of nitrobenzene in the presence of -OCH3 and -NH2 substituents in the meta and para positions using SBA-15-IL/Pd. Accordingly, the reduction of 3-methoxynitrobenzene produced 3-methoxyaniline after 5 h (Table 3, entry 2f), whereas the same substrate with a methoxy group on the para position gave 4-methoxyaniline after 2 hours (Table 3, entry 2g). The same trend was repeated for the -NH₂ group in the meta and para positions (Table 3, entries 2c-2e). The catalyst also quickly catalyzed the reduction of a bulky substrate, pyrene, with a good yield (Table 3, entry 20).

Table 3 List of various aniline derivatives that passed an attainment of the reduction of nitroaromatics in the presence of SBA-15-IL/Pd^{ab}



^{*a*} Reaction conditions: nitro compound (1 mmol), 20 mg of catalyst (1.5 mol% of Pd(π)), and H₂O as the solvent at the temperature of the peripheral conditions for 3 h. ^{*b*} The yields refer to the isolated pure products.

3.2.4. Mechanism study of the reduction of nitroaromatic compounds. Previous studies have assumed that, as the first step, the formate ion (HCOO⁻) is absorbed on the surface of the Pd-catalyst and forms Pd(HCOO⁻).^{53,54} Thoroughly, upon bubbling of the unbound CO₂ molecule and *in situ* formation of an activated metal hydride species (Pd-hydride; labeled as Pd(H⁻)ad), ammonium cations acting as Brønsted acid protonate these hydride species and create hydrogen and ammonium (amine) species. Alternatively, substrate molecules compete with RNH_3^+ ions for the $Pd(H^-)ad$ sites. Following the hydride transfer to the NO₂-group, the resulting intermediate captures the proton and RNH₃⁺ formed, which is associated with the release of the ammonium species (maybe in the form of ammonia gas). As a vital stage, these species, in the case of the isolated systems, re-enter the catalytic cycle. Eventually, the aniline product is excreted as an oily layer (Fig. 5b). Regarding the reduction reaction, the same inhibitors with different concentrations were used to determine its mechanism for nitrobenzene reduction and under optimized conditions. As shown in Fig. 5b, by using thiophenol as a sulfur-containing agent with a high affinity for the active catalytic centers of Pd, the catalyst is polluted. As the amount of this inhibitor increases, the catalytic activity of the catalyst decreases. This result confirms the great importance of the Pd catalytic centers as catalytic sites in the reaction. Similarly, the usage of quinoline as a Lewis base and inhibitor reduces the catalytic activity dramatically, indicating that the coordination of nitroarene to

the active catalytic center of Pd is a necessity for the reaction. Unlike the oxidation reaction, the presence of TEMPO has little effect on the reaction. In terms of benzoic acid, there is a competition between benzoic acid and formic acid, reducing the efficiency of the reduction reaction. Thus, the coordination of formic acid to palladium is quite essential to perform the reaction. Acidic media have little effect on the reaction. Also, this reaction does not rely on the presence of a base. Moreover, a significant decrease in the reaction efficiency in the presence of cyclohexanone as a hydride scavenger⁵⁵ was observed, indicating the primary role of hydride generation during the reaction mechanism. These results indicate the key role of Pd in catalyzing the reduction reaction, and factors such as the coordination of nitroarene and formic acid to the active catalytic centers of Pd, and the formation of hydrides in this reaction.

3.2.5. Catalyst reusability. Considering the importance of environmentally and eco-friendly catalytic systems, we concentrated on investigating the stability and reusability of the catalyst under the optimal reaction circumstances. The efficiency of the catalyst was surveyed in the model reaction. After completing the model reaction, in order to separate the heterogeneous catalyst, centrifugation was used, then washed with ethanol, and dried at 60 °C under vacuum suction. Finally, it was reused in the next run. As shown, after 15 (Fig. 3f) and 6 (Fig. 4d) cycles for the oxidation and reduction reactions, respectively, just a trivial dwindle in the catalytic activity was observed.



Fig. 5 Proposed mechanism for the aerobic oxidation (a) and reduction (b).



Fig. 6 FE–SEM and TEM images, and FT-IR, SA-PXRD and PXRD of SBA-15-IL/Pd after oxidation (a, c, e and f, respectively) and reduction (b, d, g and h, respectively) reactions.

The morphology and stability of the catalysts against the selfagglomeration were checked after the 15th and sixth runs (Fig. 6). As shown in Fig. 6a–h, the FE-SEM and TEM images and FT-IR, SA-PXRD and PXRD spectra of the recovered heterogeneous catalyst (after the 15th and sixth cycle) revealed that almost all SBA-15–L/Pd particles were uniquely wormlike in shape and stable in structure, as well as the intact catalyst. As a result, the accumulation of the particles was negligible.

Moreover, the applied catalyst was investigated by Inductively Coupled Plasma (ICP) analysis after the last run to determine the Pd leaching content. Accordingly, the amount of loaded Pd on the recovered catalyst was calculated at 0.72 mmol g^{-1} . Therefore, the ICP analysis after the 15th and sixth run showed less than 3% Pd leaching as a merit for such modified silicaaided framework. Furthermore, to determine the role of the Pd moiety for carrying out the model reaction, the hot filtration test (a common measurement for assessing the leakage of active sites into the mother solution of the reaction) was performed. Explicitly, when the reaction time reached the half time of the reaction quenching, the catalyst particles were separated from the mixture using centrifugation, and the residue solution was shaken under the reaction conditions. The monitoring of the reaction mixture by TLC witnessed no considerable progress. These results indicated that only a slight amount of Pd species might exist in the solution phase. Altogether, these data confirmed the high stability and capability of the catalyst under several tandem reaction conditions.

4. Conclusion

All in all, we have demonstrated a general, convenient, green, and highly efficient principle for the aerobic oxidation of alcohols and transfer hydrogenation of nitroaromatic compounds in the presence of SBA-15-IL/Pd as a robust and highly stable catalyst. There are numerous advantages of the green oxidants/ reductants, which are quite valuable because these compounds not only work as environmentally-benign alternatives to mineral oxidants, but can also be quickly produced and used. Other positive aspects of this catalytic system study include a significant improvement in the substrate and functional group sustainability and stability, highly preferable attack, environmental and economic efficiency, recovery, and reuse compared to former published methods. In spite of these unique properties, this catalytic methodology can have specific pharmaceutical applications, and lead to the synthesis of important biological compounds that bring safety, environmental, and financial benefits of paramount importance into the field of catalytic chemistry.

Conflicts of interest

There are no conflicts to declare.

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