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PAPER

Palladium containing periodic mesoporous organosilica with imidazolium framework (Pd@PMO-IL): an efficient and recyclable catalyst for the aerobic oxidation of alcohols†

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The application of a novel palladium containing ionic liquid based periodic mesoporous organosilica (Pd@PMO-IL) catalyst in the aerobic oxidation of primary and secondary alcohols under molecular oxygen and air atmospheres is investigated. It was found that the catalyst is quite effective for the selective oxidation of several activated and non-activated alcoholic substrates. The catalyst system could be successfully recovered and reused several times without any significant decrease in activity and selectivity. Moreover, the hot filtration test, atomic absorption spectroscopy (AA) and kinetic study with and without selective catalyst poisons showed that the catalyst works in a heterogeneous pathway without any palladium leaching in reaction solution. Furthermore, nitrogen-sorption experiment and transmission electron microscopy (TEM) image proved the superior stability of high-ordered PMO-IL mesostructure during reaction process. TEM image also confirmed the presence of well-distributed Pd-nanoparticles in the uniform mesochannels of the material. These observations can be attributed to the ionic liquid nature of PMO-IL mesostructure which facilitates the reaction through production, chemical immobilization and stabilization of active palladium nanoparticles, as well as preventing Pd-agglomeration during overall process.

Introduction

The selective oxidation of alcohols into their corresponding carbonyl compounds is one of the most significant and fundamental transformations from both synthetic and industrial points of view, because the corresponding carbonyl compounds are versatile intermediates of valuable compounds such as pharmaceuticals, agricultural chemicals and fine chemicals.[1,2] Traditionally, the oxidation of alcohols has been achieved with stoichiometric inorganic oxidants, notably Cr^{VI}- and Mn^{VII}- based reagents.[2,3] However, these reagents are not only very expensive but there are serious toxicity problems associated with them.[1,4] As a consequence, due to increasingly stringent environmental standards and economical pressures, much attention has recently been directed toward the use of transition-metal catalysts in the oxidation of alcohols with molecular oxygen as the sacrificial oxidant.[5,6] However, most of the earlier examples which have been investigated for aerobic oxidation of alcohols were homogeneous, and catalyst separation, high catalyst loading, catalyst recycling, and product contamination with traces of heavy metals are often problematic in these systems. In comparison with the homogeneous catalysts, heterogeneous catalysts possess the advantages of easier product isolation and catalyst recycling, and have received much attention for the oxidation of alcohols using molecular oxygen in recent years.[7] Solid catalysts based on precious metals such as Pd,[8] Au,[9] Ru,[10] and Pt[11] are particularly promising for the liquid phase aerobic oxidation of alcohols. Various solids such as organic polymers, silica, carbons, metal oxides, and inorganic mixed oxides have been employed as supports. to address the recyclabilities of the transition-metal-based catalyst whilst keeping their performances. Although, noticeable improvements in terms of selectivity and performance have been achieved, there is still a major challenge to develop new recoverable catalyst systems and especially for the aerobic oxidation of less reactive aliphatic alcohols under mild conditions.

Ionic liquids (ILs) are considered to be environmentally acceptable solvents for organic reactions, because they have a very low vapor pressure and can be used to replace volatile organic solvents.[12] Imidazolium-based ionic liquids have been extensively utilized as reaction media for a number of palladium-catalyzed reactions that in fact act as *in situ* *N*-heterocyclic carbene ligands with transition metals[13] and could also effectively stabilize certain transition-metal nanoclusters.[12,14] However, despite promising

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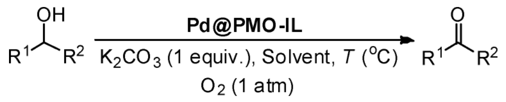
† Electronic supplementary information (ESI) available: Details of experimetal procedure, N_2 adsorption-desorption isotherm for **1**, **2**, and the recovered **2**, BJH diagrams, and TEM image of the recovered **2**. See DOI: 10.1039/c1ob05752a

results, their widespread application in practical and process chemistry is still hampered because many of them are very expensive.[15] Since ionic liquids are very expensive, and because of the high viscosity of ionic liquids in many liquid–liquid biphasic reactions, only a small fraction of the ILs ("the diffusion layer") participates in the process, it is desirable to keep the amount of used to a minimum; here immobilization on solid supports is an interesting option.[16] Although, the use of supported ionic liquid phase (SILP) concept significantly reduces the amount of IL in a typical process, low loading and to some extent non-uniform distribution of immobilized ionic liquids on solid surfaces are fairly commonplace. Very recently, we have addressed these problems by synthesis of a novel periodic mesoporous organosilica with alkyl imidazolium ionic liquid framework (PMO-IL).[17] We have demonstrated that the PMO-IL could be effectively used for the immobilization and stabilization of palladium nanoparticles (Pd@PMO-IL) suitable for the Suzuki cross coupling of arylhalides with arylboronic acids in water as green solvent.[17] In this study, we also found that although PMO-IL nanostructure acts as a source for the soluble Pd-species, it can simultaneously operate as a *nano-scaffold* to re-capture the Pd-nanoparticles into the mesochannels, thus preventing undesired agglomeration of Pd nanoparticles. In another investigation, we explored the first use of a **S**elf-**A**ssembled organic-inorganic hybrid silica with **I**onic **L**iquid **P**hase (SAILP) as a novel support for chiral $Yb(OTf)_3$-pybox catalyst system in which the catalyst remains active, and highly selective, over extended periods, in the catalytic enantioselective Strecker reactions of imines with trimethylsilyl cyanide (TMSCN) to afford the corresponding chiral α-aminonitriles.[18] It is interesting to note that this heterogeneous catalyst system consistently showed higher enantioselectivities and chemical yields in comparison with our previously reported homogeneous $Yb(OTf)_3$–pybox under the same reaction condition (–40 to –60 °C).[19] In continuation of our studies in this field, we wish to disclose that our new multifunctional Pd@PMO-IL material is a highly efficient catalyst for the selective oxidation of a wide variety of alcohols, including not only benzylic and allylic, but also alicyclic and aliphatic alcohols in the presence of molecular oxygen/or air as the oxidant (Scheme 1).



Scheme 1 Aerobic oxidation of alcohols in the presence of Pd@PMO-IL catalyst.

Results and discussion

The Pd@PMO-IL nanocatalyst was prepared by hydrolysis and co-condensation of 1,3-bis(3-trimethoxysilylpropyl)imidazolium chloride[20] and tetramethoxysilane in the presence of Pluronic P123 as template under acidic condition followed by immobilization of Pd precursor according to our previous reported procedure.[17] The nitrogen adsorption-desorption isotherm and PXRD analysis of the Pd@PMO-IL catalyst clearly revealed successful incorporation of the palladium species inside the nanopores of the PMO-IL material (ESI,† Figs. 2*S*,3*S*). The nitrogen sorption analysis showed a type IV isotherm with a relatively sharp H1 hysteresis loop which is characteristic of highly ordered mesoporous materials with 2-dimensional hexagonal pore structure. The appreciable decreases in BET surface areas, mesoporous volume and BJH pore diameter of the materials from 671 $m^2 g^{-1}$, 1.21 $cm^3 g^{-1}$, and 7.0 nm for the parent PMO-IL to 458 $m^2 g^{-1}$, 0.88 $cm^3 g^{-1}$ and 5.3 nm for Pd@PMO-IL, respectively, indicate that the cavities of PMO-IL are partly occupied by highly dispersed Pd species (ESI,† Table 1*S*). The powder X-ray diffraction (PXRD) pattern of the Pd@PMO-IL material illustrated a single high intensity peak at $2\theta \approx 1.1–1.3$ which matches with the materials having long range periodicity. This single peak is indexed as the d_{100} reflection and usually observed for hexagonally ordered mesoporous materials. After loading of Pd, a partial loss of intensity in diffraction peak of Pd@PMO-IL is observed as compared with those of parent PMO-IL (ESI,† Fig. 3*S*). This data is in good agreement with the nitrogen-sorption experiments and confirms the successful incorporation.

Table 1 The effect of solvent, reaction temperature and Pd-loading in the aerobic oxidation of 1-phenylethanol using Pd@PMO-IL catalyst[a]

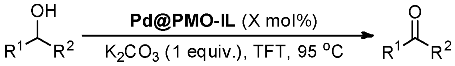
Solvent	*T*/°C	Pd (mol%)	Time (h)	Yield (%)[b]
H_2O	80	1	12	—
H_2O	95	1	12	14
Toluene	80	1	12	12
Toluene	95	1	12	68
TFT	80	1	12	66
TFT	95	1	1:40	>99
TFT	95	0.75	2:20	>99
TFT	95	0.5	2:50	>99
TFT	**95**	**0.25**	**3:00**	**>99**
TFT	95	0.1	12	52

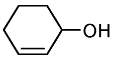
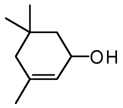
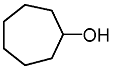
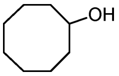
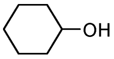
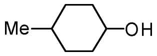
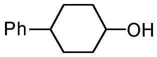
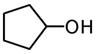
[a] Reaction conditions: 1-phenylethanol (1 mmol), K_2CO_3 (1 mmol), solvent (2.5 mL). [b] GC yields.

The application of the Pd@PMO-IL nanocatalyst was of Pd-species into mesoporous channel then investigated in the aerobic oxidation of alcohols under oxygen and air atmospheres. Initially, the aerobic oxidation of 1-phenylethanol was used as a model reaction in the presence of Pd@PMO-IL as the catalyst (Table 1). This study demonstrated that the reaction was significantly affected by catalyst loading, reaction temperature, and type of solvent used in the reaction. After several screening experiments with different combination of solvents, catalyst loading, and temperature, the best conditions were found to be 1-phenylethanol (1 mmol), Pd@PMO-IL (0.25 mole% of Pd), K_2CO_3 (1 mmol), O_2 (1 atm) in α,α,α-trifluorotoluene (TFT, 2.5 mL) at 95 °C during 3.5 h.[21]

Using the optimized reaction conditions, the activity of Pd@PMO-IL catalyst was further confirmed in the aerobic oxidation of a variety of different primary and secondary alcohols under normal pressure of oxygen and air atmospheres (Table 2). This study showed that benzyl alcohol was selectively oxidized to benzaldehyde in quantitative yields in the presence of 0.25 mol% of catalyst without the formation of any over oxidation products (Table 2, entry 1). Moreover, both electron rich (Table 2, entries 2–4) and electron deficient (Table 2, entries 5–7) derivatives of benzyl alcohol also demonstrated excellent reactivity and afforded the corresponding aldehydes in excellent yields under the same reaction conditions. It is noteworthy that, benzyl alcohol derivatives bearing sterically demanding substituents such as

Table 2 Aerobic oxidation of alcohols using Pd@PMO-IL catalyst in TFT in the presence of molecular oxygen and air[a]

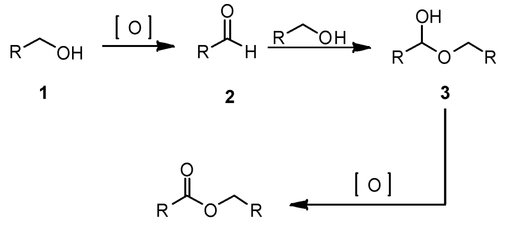


			Pd@PMO-IL (mol%)		Time (h)		Yield (%)[b]	
Entry	R^1	R^2	O_2	Air	O_2	Air	O_2	Air
1	C_6H_5	H	0.25	0.35	3	8	>99	>99
2	4-MeO-C_6H_4	H	0.25	0.35	3	7	>99	>99
3	4-Me-C_6H_4	H	0.25	0.35	3	8	>99	>99
4	2-Me-C_6H_4	H	0.35	—	6	—	92	—
5	4-NO_2-C_6H_4	H	0.35	—	7	—	94	—
6	4-Cl-C_6H_4	H	0.35	0.6	5	12	>99	95
7	2-Cl-C_6H_4	H	0.5	—	5	—	90	—
8	2-Furyl	H	0.5	0.75	5	7.5	94	93
9	4-MeS-C_6H_4	H	0.5	—	11	—	65	—
10	3-Pyridyl	H	0.5	—	8	—	85	—
11	C_6H_5	Me	0.25	0.35	3.5	7.5	>99	>99
12	C_6H_5	Et	0.25	0.35	4	9	>99	>99
13	C_6H_5	C_6H_5	0.4	0.7	7	16	97	93
14	4-Cl-C_6H_4	C_6H_5	0.4	—	9	—	95	—
15	C_6H_5	$CO\ C_6H_5$	0.5	0.7	9	19	93	87
16	$C_6H_5CH{=}CH$	H	0.5	—	6	—	88	—
17	$C_6H_5CH{=}CH$	Me	0.5	0.7	6	12	93	85
18		0.5	0.7	4.5	8	92	90	
19		0.5	—	6	—	90	—	
20	n-C_5H_{11}	$CH_2{=}CH$	0.5	—	5	—	90	—
21	n-C_6H_{13}	Me	0.5	0.75	10	14	93	80
22		0.5	0.75	7	12	97	85	
23		0.5	—	8	—	96	—	
24		0.5	—	5	—	95	—	
25		0.5	0.75	5.5	14	93	86	
26		0.5	—	5.5	—	94	—	
27		0.5	0.75	5	10	95	87	
28	n-C_7H_{15}	H	1	—	12	—	84[c]	—
29	$C_6H_5(CH_2)_3$	H	1	—	12	—	>99[c]	—
30	$C_6H_5(CH_2)_2$	H	1	—	12	—	94[c]	—

[a] Conditions: Alcohol (1 mmol), Pd@PMO-IL (0.25–1 mol%), K_2CO_3 (1 mmol), α,α,α-trifluorotoluene (TFT, 2.5 mL), at 95 °C. [b] GC yields using internal standard (biphenyl) method. [c] The yields of the corresponding esters.

2-methyl- and 2-chloro- groups also gave the corresponding aldehydes in high yields (Table 2, entries 4, 7). Although, several types of heterogeneous palladium catalysts have been recently reported for the aerobic oxidation of alcohols under oxygen atmosphere, to date only a few of them have been shown to be suitable for the oxidation of alcohols bearing heteroatoms. Gratifyingly, we found that heteroaromatic alcohols such as furfuryl alcohol (Table 2, entry 8) and pyridine-3-yl-methanol (Table 2, entry 10) as well as 4-(methylthio)phenyl methanol (Table 2, entry 9) were efficiently converted to their corresponding aldehydes.

As expected, secondary alcohols were more difficult to oxidize. Secondary benzylic alcohols such as 1-phenylpropanol also furnished excellent yields of corresponding ketones under optimized reaction conditions, though it was necessary to increase the reaction time and the loading of Pd@PMO-IL to 0.5 mol% to ensure complete conversion (Table 2, entries 11–15). In particular, hindered substituted benzhydrols (Table 2, entries 13, 14) and benzoin (Table 2, entry 15) were cleanly oxidized within 7–9 h, giving the corresponding carbonyl products in high yields and selectivities. In the case of benzoin, no C–C bond cleavage was observed under the reaction conditions. It is also noteworthy that, the present catalyst system showed also high activity in the oxidation of primary and secondary allylic alcohols to the respective α,β-unsaturated carbonyl products in excellent yields and selectivities, while $C{=}C$ survived intact without an intramolecular hydrogen transfer (Table 2, entries 16–20). This observation confirms the impressive efficiency of Pd@PMO-IL catalyst in the selective aerobic oxidation of sensitive substrates. Furthermore, this catalyst system also showed outstanding activity for the selective aerobic oxidation of different kinds of highly challenging aliphatic alcohols to afford the corresponding carbonyl products in good yields (Table 2, entries 21–30). Although several heterogeneous catalytic systems have been recently reported for such reactions,[8–11] the yields and selectivities are not always satisfactory. Secondary linear and cyclic aliphatic alcohols were smoothly converted into the corresponding ketones in excellent yields in the presence of 0.5 mol% of Pd@PMO-IL (Table 2, entries 21–27). More importantly, primary aliphatic alcohols were successfully oxidized to their corresponding esters in excellent yields under the applied reaction conditions (Table 2, entries 28–30).[8g] In this case, it seems plausible that after the initial oxidation of primary aliphatic alcohol **1** to give aldehydes **2**, a rapid reaction with unreacted starting alcohol then ensues, leading to the corresponding hemiacetal **3**, which further oxidizes to produce the respected ester **4** (Scheme 2).



Scheme 2 Possible pathway for the formation of esters through the aerobic oxidation of primary aliphatic alcohols using Pd@PMO-IL catalyst.

The present catalyst system exhibits high catalytic activity even for the aerobic oxidation of alcohols under air rather than pure oxygen, affording the corresponding carbonyl products in high yields and with remarkable selectivities. As shown in Table 2, the reaction proceeded well with only slightly extended reaction times when using an atmospheric pressure of air. Several types of primary and secondary aromatic, heteroaromatic, allylic, and aliphatic alcohols were successfully oxidized to the corresponding carbonyl adducts in good to excellent yields and selectivities under the optimized reaction conditions (Table 2). Since the recycling and life time of the heterogeneous catalysts are significant issues for practical applications, the reusability of the Pd@PMO-IL catalyst was also studied with the aerobic oxidation of 1-phenylethanol as a model. Due to the unavoidable loss of solid catalyst during recovery and washing, the reaction scale was amplified 10 times to ensure enough catalyst was present to perform the consecutive recycling reactions. The catalyst was reused 9 times without showing significant loss of efficiency (Fig. 1). All recycling runs gave acetophenone in a purity greater than 99% by GC analysis. In order to show the impact of the mesoporous organosilica PMO-IL on the catalyst stability and recyclability, the same loading of Pd were immobilized on SBA-15[22] without any ionic liquid moiety through the same procedure to furnish Pd@SBA-15.[21]

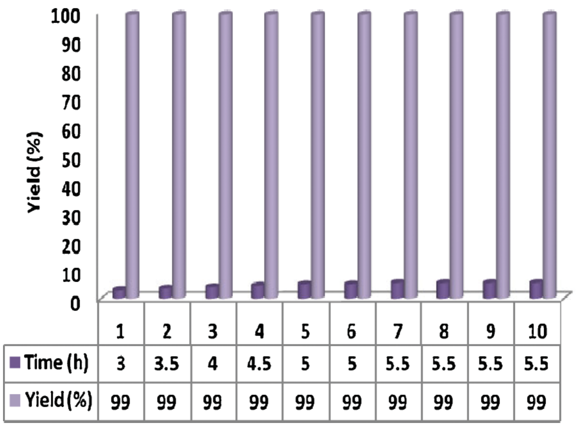


Fig. 1 The reusability of Pd@PMO-IL catalyst in the aerobic oxidation of 1-phenylethanol.

Comparative tests for the recyclability were then conducted using Pd@SBA-15 in the oxidation of 1-phenylethanol under the same condition as before. Within the same reaction time as Pd@PMO-IL, Pd@SBA-15 gave 99%, 45%, and 15% for the first, second and third reaction cycle, respectively. Obviously, the recyclability of Pd@PMO-IL was much better than that of Pd@SBA-15 and revealed that PMO-IL is an effective and powerful support for the immobilization and stabilization of palladium catalysts.

To determine the true nature of Pd species in our catalytic system, additionally a hot filtration test was also performed. To do this, the solid catalyst was filter out after the aerobic oxidation of 1-phenylethanol had run for 2 h (conversion 45%). The solid-free filtrate was then welded to another reaction vessel and continually stirred under standard reaction conditions (oxygen atmosphere, 95 °C, K_2CO_3). After 12 h, the analysis of the catalyst-free reaction showed that only 4% acetophenone was exceedingly obtained. This data was further confirmed by atomic adsorption analysis of the filtrate solution that showed any palladium content within the detection limit (less than 1 ppm). Based on these preliminary data, it is unlikely that the catalytic reaction was caused by leached Pd and Pd@PMO-IL operates in a heterogeneous pathway. However, it is very important to note that a negative result from the hot filtration test by considering the final yield alone can sometimes result in an erroneous conclusion and the absence of catalytic activity in the solid-free filtrate does not always imply no leaching of Pd species.[23–25] The reason for this uncertainty is that in many instances not only a leaching and re-deposition of a trace amount of active Pd species occur, but also the amount of leached palladium may be below the detection limit. Another powerful tool to assess the nature of the true active species is the study of reaction kinetics both in the presence and absence of catalyst poisons. Following to Jones findings,[23] very recently, we have demonstrated SBA-15-PrSH, and poly(4-vinylpyridine) (PVP) are efficient poisons for Pd-catalyzed Suzuki coupling reaction using Pd@PMO-IL.[17] Using this approach, we found that the addition of the above-mentioned poisons led to complete cessation of the catalytic activity of Pd@PMO-IL in the Suzuki coupling of 3-bromoacetophenone with phenylboronic acid in water at 60 °C. These results showed that for the Suzuki reaction, supported palladium catalyst Pd@PMO-IL serves as a reservoir for active Pd species which are dissolved from the solid catalyst under the described reaction condition. To assess whether our catalyst is working in a homogeneous or heterogeneous pathway in the course of the present aerobic oxidation of alcohols, the kinetic experiments were also conducted by using 4-chlorobenzylalcohol as a test model under our optimized reaction conditions in the presence of poisoning agents SBA-15-PrSH and PVP (Fig. 2). Notably, no significant suppression of catalysis by SBA-15-Pr-SH and PVP has been observed for catalyst. This study illustrated that for all control experiments, the reaction kinetic has the same pattern with an induction time of about 1.5 h, and after that the reactions are actually started to give 4-chlorobenzaldehyde in excellent yields (Fig. 2). The result suggests that the first 1.5 h after starting reaction, is a period for the generation of palladium nanoparticles which are actual active species in the catalytic process. This study also shows that the Pd@PMO-IL catalyst maintains its catalytic activity in the presence of excess amounts of poisons (poisons:Pd, 400 : 1) under vigorous stirring. The high activity of Pd@PMO-IL catalyst even in the presence of an excess of poisoning agents provides interesting evidence that active Pd-species are not leached during reaction process.

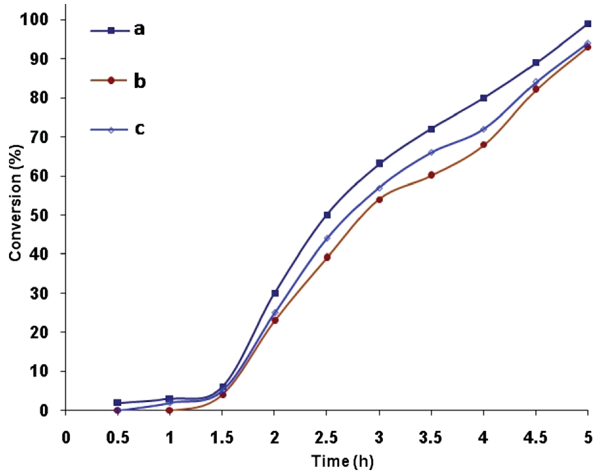


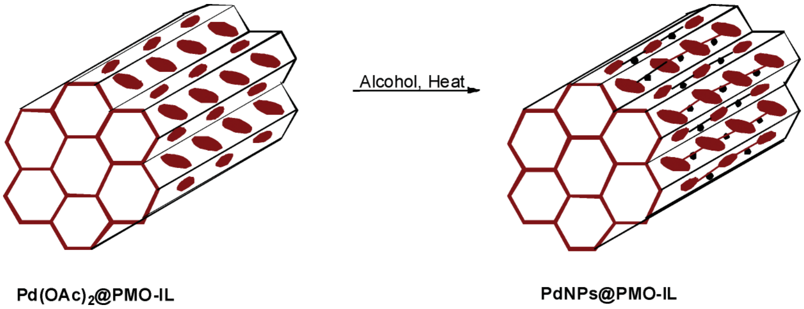
Fig. 2 Reaction progress as a function of time on the aerobic oxidation of 4-chlorobenzyl alcohol using **Pd@PMO-IL** catalyst in TFT: a) normal conditions; b) in the presence of 400 equivalents PVP; c) in the presence of 400 equivalents SBA-propyl-SH.

These results are in good agreement with those obtained from recovery and hot filtration experiments indicating that the main catalyst is probably immobilized palladium species operating in a truly heterogeneous pathway. In other words, these results confirm that PMO-IL is not a reservoir for the soluble palladium species in the described aerobic oxidation protocol but it is a powerful support for the generation and stabilization of active Pd-nanoparticles (PdNPs) which are chemically adsorbed into mesoporous channel walls (Scheme 3).[26]

In the next stage, N_2-sorption experiment and transmission electron microscopy (TEM) analysis of the recovered catalyst were investigated to further shed light to catalyst nature. Nitrogen adsorption-desorption isotherm of the recovered catalyst ROPd@PMO-IL revealed a type IV isotherm with a narrow hysteresis loop which shows high regularity of ROPd@PMO-IL remained during reaction process (ESI,† Fig. 5*S*).[21] Furthermore, the BET surface area and mesoporous volume for this sample were 303 $m^2\ g^{-1}$ and 0.58 $cm^3\ g^{-1}$, respectively, which are smaller than those for parent PMO-IL, and original Pd@PMO-IL materials (ESI,† Table 1*S*). Moreover, BJH calculations illustrated that the pore diameter of the recovered catalyst is reduced from 5.3 to 3.3 nm.[21] These results significantly confirm the generation of palladium species (nanoparticles) in the interior of the mesopores of PMO-IL. Transmission electron microscopy (TEM) image of recovered Pd@PMO-IL after the fifth reaction cycle proved that nanoarchitecture of the catalyst largely survived after reaction and recovery (Fig. 3).

Furthermore, TEM image illustrates the presence of well distributed Pd-nanoparticles confined inside the mesoporous channels of PMO-IL.

The high efficiency of the PMO-IL nanostructure for powerful immobilization of recoverable Pd-catalyst significantly verifies the role of ionic liquid units inside mesochannel walls in the stabilization, size controlling, and activity tuning of Pd-nanoparticles. This conclusion is due to the fact that nonfunctionalized Pd@SBA-15 material, with the same loading of Pd-catalyst, loses its catalytic activity after the first reaction cycle. Based on these studies, a plausible schematic reaction pathway may be proposed for the aerobic oxidation of alcohols in the presence of Pd@PMO-IL nanocatalyst (Scheme 4).



Scheme 3 The proposed pathway for the generation and stabilization of Pd-nanoparticles inside PMO-IL matrix during reaction process.

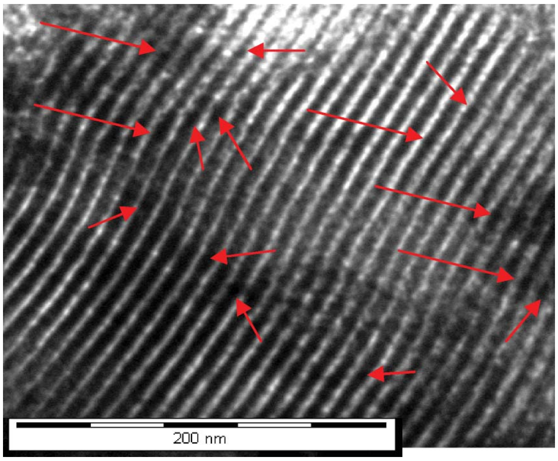
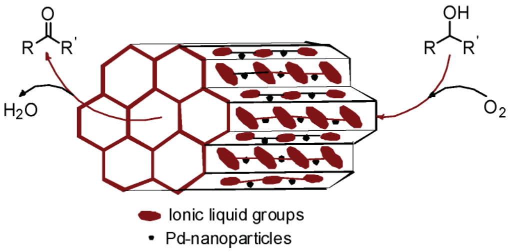


Fig. 3 TEM image of Pd@PMO-IL after five time uses, the arrows show a number of the Pd-nanoparticles in the mesochannels.



Scheme 4 A possible model for the aerobic oxidation of alcohols using Pd@PMO-IL.

Conclusions

In conclusion, we have demonstrated, for the first time, the significant efficiency of ionic liquid based PMO material in the production and stabilization of active palladium species in the aerobic oxidation of alcohols. The results showed that several types of primary and secondary aromatic, hetreoaromatic, allylic and aliphatic alcohols could be oxidized to their corresponding carbonyl compounds in the presence of a low loading of Pd@PMO-IL catalyst at short reaction times. Moreover, the catalyst could be easily recovered and reused to give quantitative yield of carbonyl adducts even after 10 recycling runs. The hot filtration test, atomic spectroscopy and the results of the effect of poisons were in good agreement with the recovery study and confirmed that the Pd@PMO-IL catalyst operated through a heterogeneous pathway. Furthermore, the nitrogen-sorption experiment and TEM analysis of the recovered catalyst also proved the high efficiency of the PMO-IL nanostructure in the successful immobilization of stable and well distributed active Pd-nanoparticles. This superior effectiveness of Pd@PMO-IL nanocatalyst may be attributed to isolated ionic liquid units incorporated in the mesochannels which could control the reaction mechanism through preventing the formation of agglomerated Pd-nanoparticles as well as stabilization of active catalytic palladium species (as shown by TEM image). It is also important to note that studies on some more practical applications of the Pd@PMO-IL catalyst in other organic transformations are currently underway in our laboratories.

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