

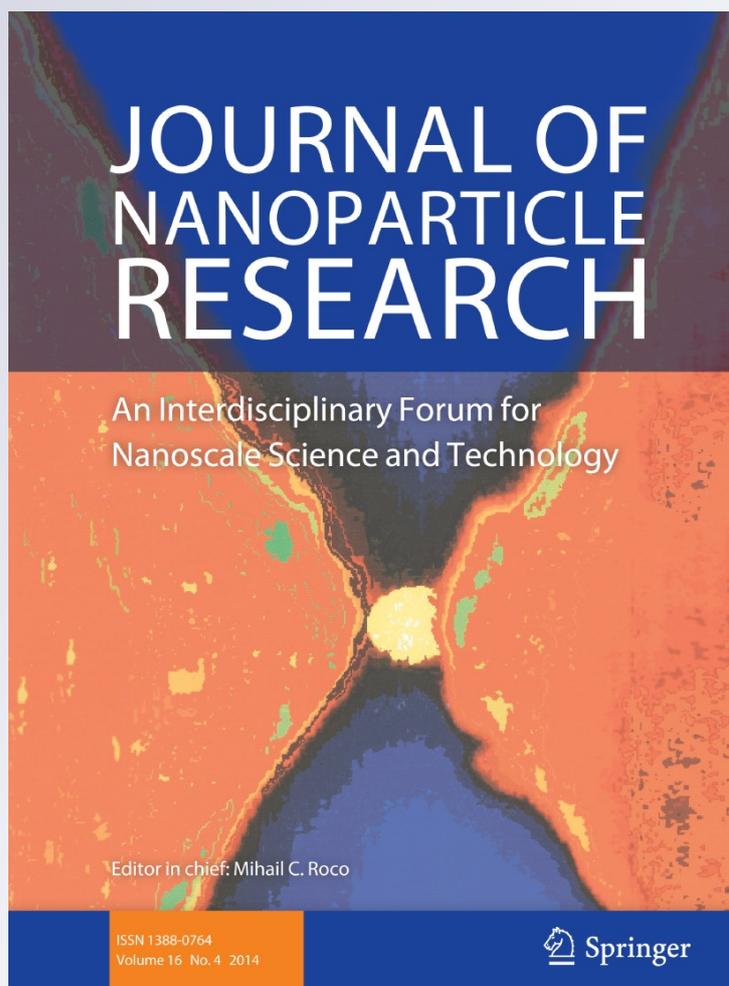
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Palladium nanoparticles in ionic liquids: reusable catalysts for aerobic oxidation of alcohols

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Abstract The search for more efficient catalytic systems that might combine the advantages of both homogenous (catalyst modulation) and heterogenous catalysis (catalyst recycling) is still the challenge of modern chemistry. With the advent of nanochemistry, it has been possible to prepare soluble analogues of heterogenous catalysts. These nanoparticles are generally stabilized against aggregation into larger less active particles by electrostatic or steric protection. In the present case, we demonstrate the use of room temperature ionic liquids (ILs) as effective agents of dispersion of palladium nanoparticles (prepared from palladium chloride with 5 ± 0.5 nm size distribution) that are recyclable catalysts for aerobic oxidation of alcohols under mild conditions. The particles suspended in ILs show no metal agglomeration or loss of catalytic activity even on prolonged use. An attempt has been made to elucidate the reaction mechanism of

aerobic alcohol oxidation using a soluble palladium catalyst.

Keywords Palladium · Nanoparticles · Oxidation · Agglomeration · Ionic liquid · Nanostructured catalysts

Introduction

The field of nanocatalysts has become active with numerous books and articles published since 1990s (Hadjipanayis and Siegel 1994; Collier et al. 1999; Liz-Marzan and Kamat 2003; Narayan and El-Sayed 2003; Yang et al. 2006). Metal particles with nano sizes have been intensely investigated as they have application in various fields like optics, electronics, magnetic devices, photocatalysts, adsorbents, sensors, etc. The small size of these particles makes them attractive in catalysis due to their large surface to volume ratio. Palladium nanoparticles stabilized with tetraalkyl ammonium salts (Reetz et al. 1996), polyvinyl pyrrolidone (Li et al. 2000), dendrimers (Li and El-Sayed 2001), chitosan (Adlin et al. 2004), cyclodextrin (Strimbu et al. 2003), kaolinite (Papp and Dekany 2001) and montmorillonite clay materials (Patel et al. 2008) have been reported in literatures.

Although a large number of investigations deal with palladium containing systems as catalysts for hydrogenation reactions (Mastalir et al. 2000; Le-Bras et al. 2004; Mukherjee 2008; Lee et al. 2011),

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comparatively fewer articles deal with oxidation of alcohols involving metal nanoparticles (Kaneda et al. 2004; Stahl 2004; Corma et al. 2006; Garcia et al. 2008; Sheldon et al. 2010; Feng et al. 2010). In most instances, this transformation is performed with stoichiometric and toxic inorganic oxidizing agents (i.e. KMnO_4 , Cr(VI) compounds, HNO_3 , etc.) and in organic solvents which are volatile, toxic and flammable. Moreover, purification of the reaction products is often demanding and laborious. Due to the industrial importance of this process and the ever-growing environmental concerns, the development of effective, greener catalytic systems is an important challenge. Over the last several years, the ambient temperature ionic liquids (ILs), especially those based on 1-alkyl-3-methylimidazolium cations, have emerged as promising alternative green solvents for the chemical synthesis because of their solvating ability, negligible vapour pressure, easy recyclability and reusability (Welton 1999; Wasserscheid and Keim 2000; Sheldon 2001; Dyuba and Bartsch 2001, 2003; Pernak et al. 2004). With the increasing environmental consciousness many transition metals including palladium have been used as catalysts for alcohol oxidation with ILs as green solvents (Ganchequi et al. 2002, 2004; Muzart 2006; Han et al. 2009). Recently, several new ILs have been synthesized by changing the anions or properties of the cations for the investigation of the oxidation of alcohols, such as heteropoly acid-type ILs (Chhikara et al. 2005), aryliodinediacetate-type ILs (Qian et al. 2005) and hexaalkylguanidinium-type ILs (Xie et al. 2004). In those cases, ILs have been used not only as solvents but also as catalysts. Although the yield and conversion of alcohols reported in most cases are quite excellent (>90 %), none of them made an attempt to establish the mechanistic pathway involving the metal nanoclusters. Also in most reported literatures nitrogen-based additives like triethylamine, pyridine, triethylenediamine (Sigman et al. 2001, 2002) to enhance the yield of products, or sodium hypochlorite, sodium perchlorate, aqueous hydrogen peroxide as source of oxygen (Han et al. 2009) were employed. Our present study includes preparation and characterization of $[\text{PdCl}_2(\text{PhNH}_2)_2]$ and palladium nanoparticles which were separately used as catalysts for oxidation of alcohols using O_2 as source of oxidant at room temperature. An attempt has been made to elucidate

the reaction mechanism using the soluble variety $[\text{PdCl}_2(\text{PhNH}_2)_2]$ (*trans*-dichloro dianiline palladium(II)). Use of $[\text{BMIM}]\text{BF}_4$ as dispersion medium to stabilize and recycle the palladium nanoparticles has also been discussed.

Experimental

Catalyst preparation and characterization

The soluble catalyst *trans*- $\text{Pd}(\text{C}_6\text{H}_5\text{NH}_2)_2\text{Cl}_2$ was prepared from PdCl_2 by the method described earlier (Mukherjee 2003). Aniline (1.5 g, 16.2 mmol) was added to a hydrochloric acid solution (100 ml) of palladium(II) chloride (1.0 g). Solution was warmed gently for 30 min and the yellow crystals of the desired compound separated out on cooling (0–5 °C). This was recrystallized from acetone. Anal. found: C, 40.4 %; H, 3.8 %; N, 2.5 %, Pd, 29.06 %, FTIR (CsBr , cm^{-1}) 450 (vPdN), 350 (vPdCl).

Palladium nanoparticles were prepared from palladium(II) chloride using tetraalkyl ammonium salts following the literature methods (Reetz and Maase 1999; LeBras et al. 2004). Elemental analysis (average of two concordant determinations) of the palladium-based nanoparticles indicate that the salt tetra-*n*-butyl ammonium bromide is only present in the protecting layer of these particles. This is further supported by ^1H NMR, ^{13}C NMR and FTIR studies which are in fact identical to the spectra of $\text{Bu}_4\text{N}^+\text{Br}^-$. Anal. (particles prepared from PdCl_2) found: C, 53.88 %; H, 10.78 %; N, 3.86 %; Pd, 6.76 %; Br, 22.28 %. ^1H NMR (CDCl_3 , TMS); 1.1 (3H,t), 1.4–1.5 (2H,m), 1.6–1.7 (2H,m), 3.4 (2H,br); ^{13}C NMR (CDCl_3 -TMS); 15.1, 22.8, 26.3, 61.1; FTIR (CDCl_3 dispersion, cm^{-1}); 925, 1384, 1468, 1488, 2875, 2962. The weight percentage of palladium was determined by inductively coupled plasma (ICP) in a optima 3200 RL multicanal Perkin Elmer machine at standard conditions. Weight percentage of palladium for particles prepared from PdCl_2 was determined and found to be 6.76 %. Strong evidence of the existence of nanoparticles in the studied samples comes from transmission electron microscopy (TEM) conducted on the colloidal particles suspended in acetonitrile. The soluble palladium aniline complex and the palladium nanoparticles derived from PdCl_2 are abbreviated as Pd_s and Pd_n throughout the text.

Oxidation in an organic solvent

A mixture of the substrate (2.0 mmol), palladium nanoparticles (15 mg) or $[\text{PdCl}_2(\text{PhNH}_2)_2]$ (0.05 mmol) in tetrahydrofuran (THF) or dichloromethane (CH_2Cl_2) (2 ml) was stirred in a 50 ml round bottomed flask under oxygen atmosphere (gas bag) at room temperature for the stipulated time. Petroleum ether was added and after filtration the products were purified by column chromatography (silica; petroleum ether–AcOEt 95:5) and then analyzed in each case by ^1H NMR (250 MHz, CDCl_3) and gas chromatographic studies (Yonglin YL6500). The intermediate samples were withdrawn from the reaction mixture at an interval of 15 min and analyzed immediately by GC equipped with a carbowax capillary column and flame ionization detector. Temperature programming was done in the range 80–140 °C at the rate of 5 °C/min.

Oxidation in $[\text{bmim}]\text{CH}_3\text{COO}^-$ (1-butyl-3-methyl imidazolium acetate)

A similar procedure as described above was used but with $[\text{bmim}]\text{OAc}$ (2 ml) as the solvent. At the end of the reaction (usually 2 h), the mixture was extracted with dry diethyl ether (3×10 ml). The organic phase was concentrated and purified as described above. The IL was dried on a rotary evaporator, then used for recycling experiments or stored in the refrigerator. $[\text{bmim}]\text{BF}_4$ (*1-butyl-3-methyl imidazolium tetrafluoroborate*) was also used as solvent for oxidation reaction under similar conditions. The ILs were prepared and purified as per literature methods (Grätzel et al. 1996) and their ^1H NMR spectra have been provided as Electronic Supplementary Information.

TEM analysis of a recovered sample

The quantity of IL in the sample was so large that observation of the palladium nanoparticles was obscured. Separation of the IL from the nanoparticles was therefore necessary and was performed as follows: the sample after reaction was suspended in acetone and sonicated for 5 min, then centrifuged and the supernatant phase was removed; this procedure was repeated 3–4 times until the acetone was colourless. The resulting black solid was suspended in acetonitrile and sonicated for 3 min. A drop of the

suspension was placed on the specially produced structureless carbon support film and dried in air.

Results and discussion

The use of palladium catalysts for the oxidation of alcohols to aldehydes and ketones is well documented. The use of molecular oxygen as oxidant in Pd-catalyzed oxidation reaction of alcohols has also been reported. The use of molecular oxygen as oxidant is ideal because it is readily available, soluble in common organic solvents and even in the ILs and generates environmentally benign by-products. However, Pd-catalyzed aerobic oxidations are often limited by the use of high temperatures (60–80 °C), pressures (30–50 bar) and high catalyst loadings (Sheldon et al. 2006; Sigman et al. 2001). The development of more active palladium catalysts is therefore desirable for improving the utility of these oxidations. Palladium nanoparticles prepared from PdCl_2 and tributylamine in molten tetrabutylammonium bromide have been found to be effective oxidation catalysts at room temperature.

The initial investigation was carried out using benzyl alcohol as the substrate to optimize the reaction conditions and the results are summarized in Table 1. Both the soluble variety $\text{PdCl}_2(\text{PhNH}_2)_2$ and the nanoparticles suspended in organic solvents were found to be effective in oxidation of benzyl alcohol to benzaldehyde within 30 min of reaction. The only difference with the soluble variety is that a minimum O_2 pressure (20 bar, stainless steel autoclave fitted with pressure adaptor) is necessary to initiate the oxidation reaction while the nanoparticles yield products at oxygen balloon pressure (1 bar). No additives were required in either case to initiate the reaction and the oxidation occurs smoothly under room temperature to the aldehyde stage only. No overoxidized products were noticed even after 4 h of catalytic reaction. Both THF and CH_2Cl_2 were found to be equally efficient as solvents while use of pyridine, DMSO and water as solvents or solvent combination was found to inhibit oxidation of benzyl alcohol. Although Stahl and coworkers (Stahl et al. 2002) conducted catalytic studies on the Pd/DMSO and Pd/pyridine systems and found that both pyridine and DMSO had a positive effect on the reoxidation of palladium(0), we noticed complete deactivation of the

Table 1 Optimization of the reaction condition for oxidizing benzyl alcohol to benzaldehyde

Entry	Solvent	Catalyst	Additives ^a	Conv %/ yield % ^b	TOF (h ⁻¹)
1	THF	Pd _s	–	Recovery	–
2	CH ₂ Cl ₂	Pd _s	–	Recovery	–
3	CH ₂ Cl ₂	Pd _s	CH ₃ COONa	Recovery	–
4	CH ₂ Cl ₂	Pd _s ^c	–	85/77	1,360
5	CH ₂ Cl ₂	Pd _s ^d	–	84/79	1,360
6	CH ₂ Cl ₂	Pd _s ^c	Et ₃ N	80/78	1,280
7	THF	Pd _n	–	98/94	1,600
8	CH ₂ Cl ₂	Pd _n	–	97/92	1,550
9	CH ₂ Cl ₂	Pd _n	Et ₃ N	89/85	1,424
10	CH ₂ Cl ₂	Pd _n ^c	–	92/88	1,470
11	CH ₂ Cl ₂	–	–	Recovery	–
12	H ₂ O	Pd _n	–	Recovery	–
13	DMSO/ H ₂ O (1:1)	Pd _n	–	10/8	160
14	CH ₂ Cl ₂	PdCl ₂	–	Recovery	–

2 mmol benzyl alcohol, 2 ml solvent, room temperature, O₂ balloon pressure, run for 30 min

^a Additives, 1 mmol was used

^b Gas chromatographic analysis after isolation by flash chromatography

^c O₂ (20 bar pressure) in stainless steel reactor

^d O₂ (40 bar pressure)

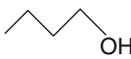
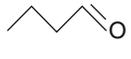
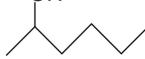
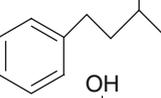
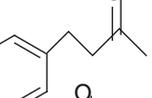
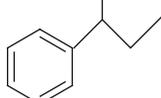
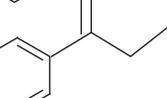
catalysts using these solvents. PdCl₂ or Pd(OAc)₂ as such are not viable catalysts for oxidation reaction under the existing conditions as no conversion was noticed even after 6 h and almost 90 % substrate recovery was observed using GC (Table 1).

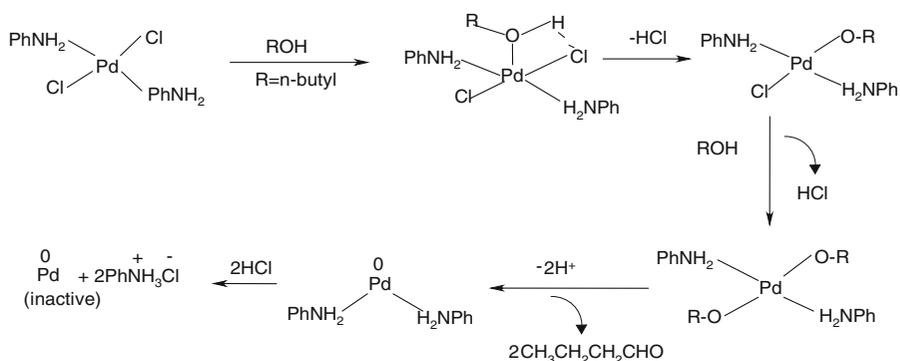
Having optimized the reaction condition, the oxidation of other alcohols using Pd_n as catalyst under oxygen balloon pressure at RT was then examined. All the primary aromatic alcohols investigated gave excellent yields ranging from 88 to 94 % (Table 2) and the products could be substantially purified by flash chromatography as indicated by ¹H NMR and GC analysis. The oxidation of both secondary aliphatic alcohols and aromatic alcohols were low and incomplete even after 4 h of catalytic run. The catalytic activities in terms of turn over frequencies (mole product/mole palladium catalyst, h⁻¹) indicate that though the

two variety of catalysts show nearly quantitative transformation of the substrate benzyl alcohol into benzaldehyde, palladium nanoparticles were superior to [Pd(PhNH₂)₂Cl₂] as far as oxidation of various alcohols is concerned under mild conditions. It is evident that as the chain length increases (run no 3–6) % conversion as well as TOF decreases. It is presumed that this decrease in activity is due to the presence of butyl ligands on the surface of the palladium nanoparticles. Since the alkyl groups create a hydrophobic layer around these particles, the polar hydroxyl group remains in the hydrophilic solvent media while the hydrophobic tail of the substrates extends through the hydrophobic area and reaches the surface of the nano catalyst. As the chain length increases, the –OH group moves away from the metal centre and the rate of oxidation reduces to a considerable extent. Increasing the concentration of the catalyst has, however, no effect on the rate of oxidation of aliphatic or aromatic alcohols. Bonding of the polar hydroxyl group in a polar solvent like water may also be a reason why water does not favour oxidation reactions under similar conditions.

Many alcohol oxidations are carried out in the presence of substantial amount of base because the reaction involves abstraction of a proton from an alcohol coordinated to the metal centre. In our experiments with added additives (Table 1), we found that addition of triethylamine, sodium acetate or potassium carbonate to the reaction medium does not improve the yield or the turn over frequencies. This led us to propose that coordinated hydroxide may abstract the proton from the alcohol resulting in the formation of palladium alkoxide species (Scheme 1). Preference of primary alcohol over secondary alcohol also hints at the presence of a metal-alkoxy species as an intermediate in the proposed catalytic cycle. This preference is due to the combined effects of decreased steric hindrance of the coordinated primary alkoxy group and higher acidity of the primary alcohol. The proposed mechanism in Scheme 1 would definitely have produced the aldehyde in absence of any oxygen in the system. However, this is not the case as a definite pressure of oxygen (20 bar) is required to initiate the oxidation reaction in the complex [PdCl₂(PhNH₂)₂]. Increasing the O₂ pressure to 40 bar, however, does

Table 2 Substrate scope in the Pd_n-catalyzed oxidation of alcohols in CH₂Cl₂ at RT

substrate	conv%	time(min)	products	TOF(h ⁻¹)
1) 	96	30		720
2) 	79	30		632
3) 	90	30		704
4) 	84	60		336
5) 	60	60		240
6) 	54	60		216
7) 	64	60		256
8) 	70	60		320

Scheme 1 Reaction of an alcohol with soluble Pd-catalyst in absence of O₂

not show any change in conversion or yield of products. Formation of palladium peroxo linkage of the type has therefore been proposed in the Scheme 2. Sheldon and coworkers (2006) have proposed formation of stable Pd (Fig. 1) species in their postulated mechanism for the Pd-phenanthroline catalyzed oxidation of alcohols. To substantiate that this type of peroxo-species can react with alcohols to form alkoxides, we kept barium peroxide and 1-butanol in a sealed glass vial for a few

minutes. Bubbles of hydrogen peroxide were observed and FTIR spectra of BaO₂ before and after the reaction with alcohol (1-butanol) show noticeable changes (Fig. 2). The O–O stretching mode present at 1066 cm⁻¹ for BaO₂ shift to a lower value addition of 1-butanol while the Ba–O stretching at 570 cm⁻¹ is present in both cases. The C–H stretching vibrations appear in the 2900 cm⁻¹ range in case of BaO₂ + 1-butanol (Abramowitz and Acquista 1971). All our attempts to isolate

Scheme 2 Reaction of alcohol with soluble Pd-catalyst in presence of O_2 .

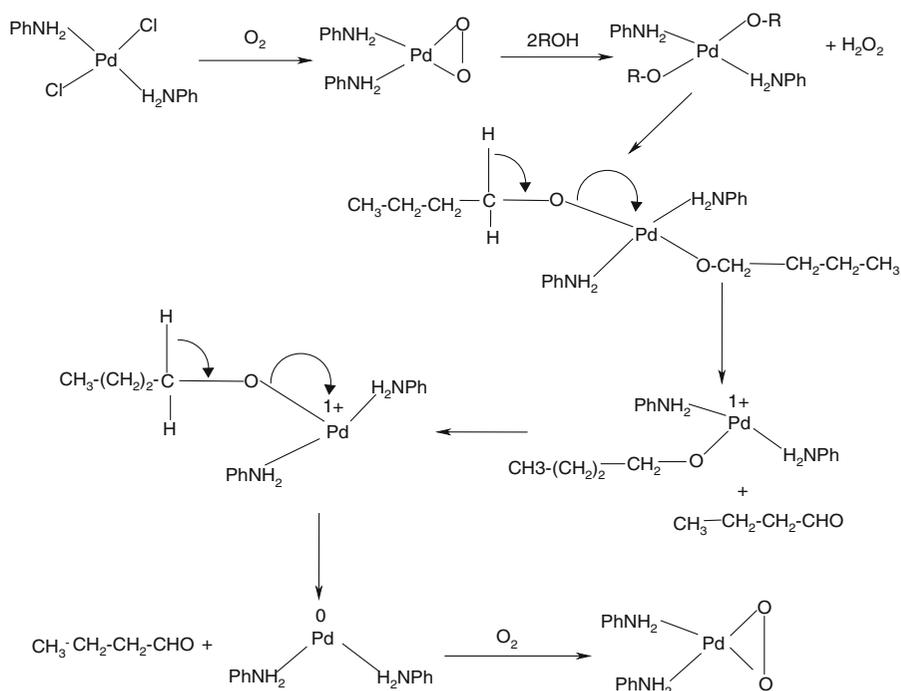
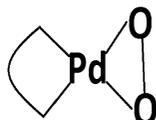


Fig. 1 Palladium-phenanthroline-peroxo intermediate



species of the type $[Pd(PhNH_2)_2(OR)_2]$, however, proved unsuccessful.

Catalyst recycling

The soluble palladium complex could not be recycled as it changes to the inactive form, presumably Pd^0 , by the reaction of liberated proton with the coordinated aniline to give $PhNH_3^+Cl^-$. Separation of palladium nanoparticles from the system to study their recyclability nature was tedious as they tend to stick to the stirring bar and to the sides of the reaction vessel. The turn over frequency calculated for the recycled colloidal nanoparticles with butan-2-ol (Table 3) show significant decrease under similar oxidation conditions. TEM of the nanoparticles collected after the first oxidation reaction show differences as far as average particle size distribution is concerned. Micrographs reveal considerable aggregation of the palladium particles on use and

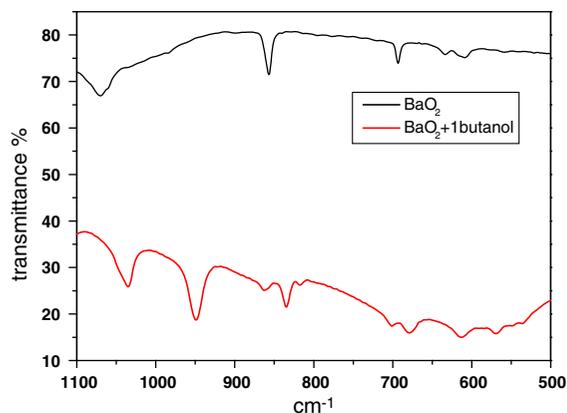
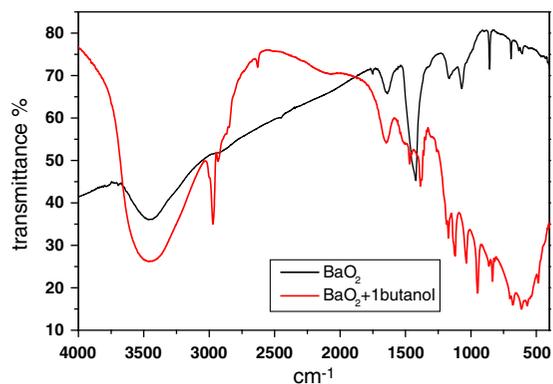


Fig. 2 FTIR spectra of product by reaction of BaO_2 and 1-butanol

Table 3 Recycling of the Pd-nano catalytic system for oxidation of butan-2-ol at RT

Entry	Solvent ^a	Conv %/ yield %	Remarks
Run 1	CH ₂ Cl ₂	90/87	Particles recovered for TEM analysis and recycling
Recycling of run 1	CH ₂ Cl ₂	30/24	–
Run 2	[bmim]OAc	82/79	–
Second cycle, run 2	–	80/77	–
Third cycle, run 2	–	80/74	Particles recovered for TEM analysis and recycling
Fourth cycle, run 2	–	78/74	–
Fifth cycle, run 2	–	77/70	–
Run 3	[bmim]BF ₄	70/66	–
Second cycle, run 3	–	67/64	–

All runs were conducted for 2 h under oxygen filled in gas bag

^a 2 ml solvent used for runs 1, 2 and 3

this is reflected in the increase in average size of recovered particles. Palladium particles freshly prepared from PdCl₂ had on an average a diameter of 5 ± 0.5 nm and this increased to around 8 ± 1 nm at the end of the first cycle (Figs. 3, 4). Lower catalytic activity observed with the reused particles in CH₂Cl₂ solution is due to a lower amount of small-sized nanoparticles present in active state in solution owing to aggregation into larger particles. Poisoning of the active sites of these nanoparticles by the product mixture could also be a reason of decreased catalytic activity. Oxidation of butan-2-ol with addition of 2-butanone (1 mol %) under similar conditions was next performed. As suggested by GC results, presence of 2-butanone do not inhibit the catalytic oxidation process and reduction of butan-2-ol was almost quantitative as noted before. Surface poisoning of palladium particles by the oxygenated products has therefore been ruled out. ¹H NMR spectra of the recovered nanoparticles still show the presence of tetra-*n*-butyl ammonium bromide in their protective layer. To prevent agglomeration of palladium particles during oxidation reactions, 2 ml of the IL [bmim]OAc was added to the system keeping all other parameters same. At the end of 2 h, the product mixture was extracted with diethylether and analyzed by GC (run 2, Table 3). Longer time period

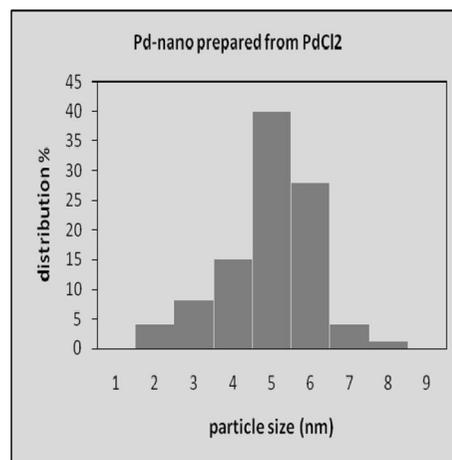
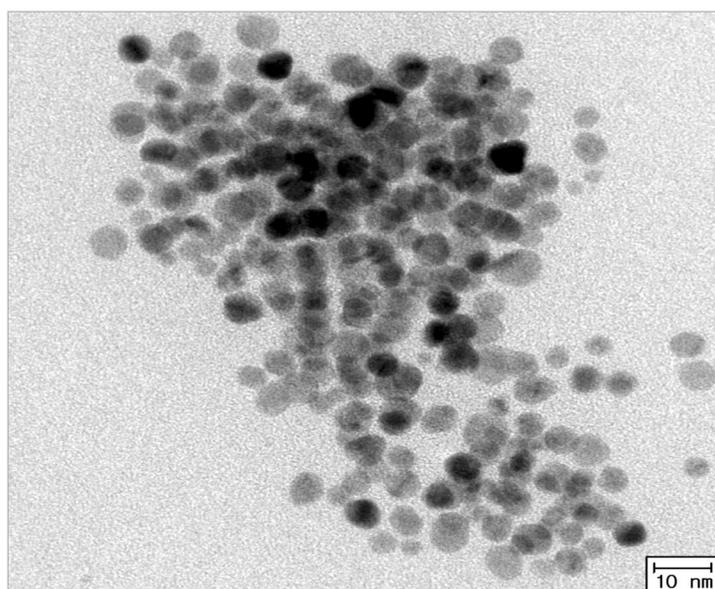
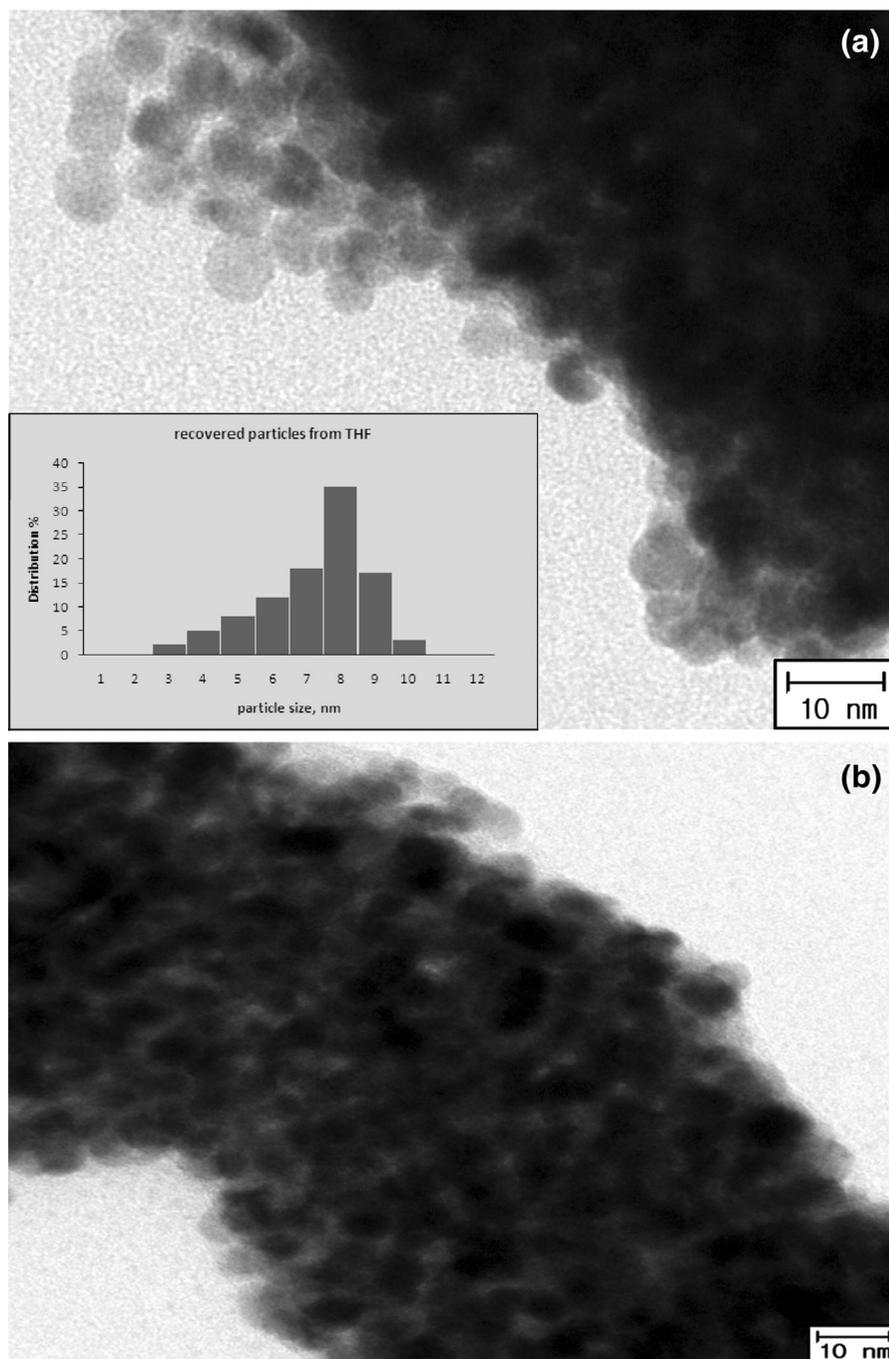
**Fig. 3** TEM picture of palladium particles obtained from PdCl₂

Fig. 4 a Palladium nanoparticles recovered from THF solution after catalytic oxidation.
b Palladium nanoparticles recovered from CH_2Cl_2 solution after catalytic oxidation



required when ILs were used as solvents is due to lower solubility of oxygen in these type of solvents at room temperature. The first four oxidation cycles carried out with palladium chloride-based nanoparticles dispersed in the IL medium [bmim]OAc show

that oxidation of butan-2-ol to ketone is to the extent of 80 % in all cases. TEM micrographs reveal the presence of palladium particles of average size distribution 5 nm after recovery from [bmim]OAc at the end of third cycle (Fig. 5).

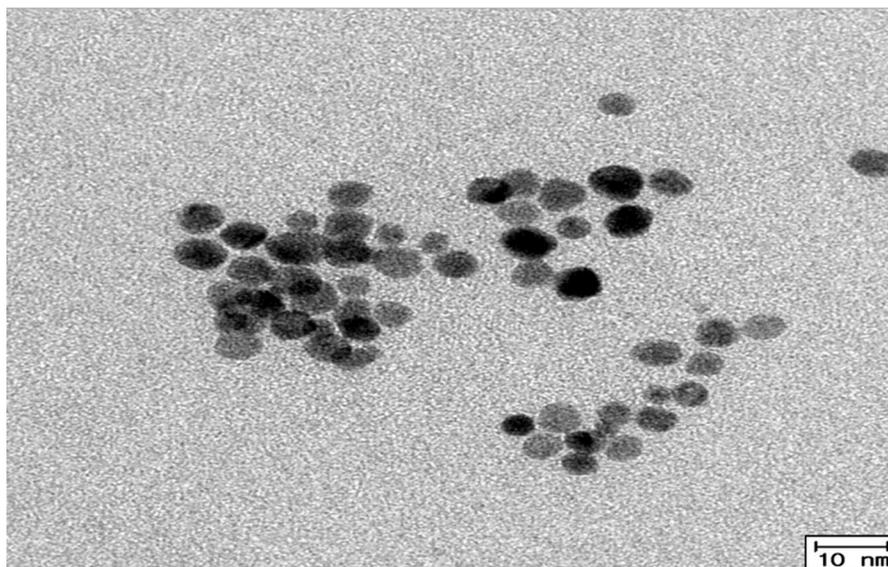


Fig. 5 Palladium particles recovered from [bmim]OAc after third cycle of oxidation

Conclusion

The findings demonstrate the higher catalytic activity of palladium nanoparticles compared to the soluble palladium complex. The result corresponded to the nano size and highly dispersed state of these particles. Though the rate of oxidation of various alcohols is much higher using the nano catalyst, it suffers from the serious drawback of aggregation and precipitation from the reaction system when common organic solvents are used. Recycling the nanoparticles becomes a tedious process then and shows reduced catalytic property. Dispersion of palladium nanoparticles in a room temperature IL prevent the phenomenon of agglomeration and retain their usual catalytic activity.

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