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Alcohol Oxidation in Ionic Liquids Catalysed by Recyclable Platinum Nanoparticles: A Green Approach

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Abstract

The effect of particle size on the catalytic performance of materials in organic reactions is of scientific and industrial importance. In the present case we demonstrate the use of room temperature ionic liquids as effective agents of dispersion of platinum nanoparticles prepared from potassium tetrachloroplatinate. The platinum nanoparticles in the range 2.5±0.5 nm are recyclable catalysts for aerobic oxidation of alcohols under mild conditions. The particles suspended in ionic liquids show no metal agglomeration or loss of catalytic activity even on prolonged use. The protocol followed supports green chemistry as uses of hazardous, flammable organic chemicals have been limited.

Keywords: *Platinum, nanoparticles, oxidation, agglomeration, ionic liquid*

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INTRODUCTION

The preparation and use of particles of nanometer dimensions for catalytic applications has received intensive attention in recent decades [1, 2]. The nanoparticles not only demonstrate high surface to volume ratios but also different chemical and physical properties compared with the bulk. The metal nanoparticles prepared from noble metals (Au, Pt, Pd) or from base metal oxides like cobalt oxide [3], ferric oxide [4] have found applications in hydrogenation [5–7], oxidation [8], hydroformylation [9], Heck [10–12], Steam Methane Reforming reaction [13], Suzuki-Miyaura coupling reaction [10–12,14] and others, important in organic transformation reactions. These nano-sized particles are usually protected by surfactants like tetraalkyl ammonium salts [15], polyvinyl pyrrolidine [16], dendrimers [17], chitosan [18], cyclodextrin [19], Kaolinite [20] and montmorrilonite clay materials [21] or supported on common supports like activated carbon, alumina, polystyrene etc [22–24].TEM and SEM studies clearly depict that the particles of nano dimensions are well dispersed on the surface of the stabilizers and the kind of support can influence the electronic structure of the supported nanoparticles or interfere in the catalytic reactions.

The oxidation of alcohols is one of the important transformation reactions in organic synthesis because the corresponding carbonyl compounds are the versatile intermediates for the synthesis of fine chemicals [25, 26]. Since the pioneering study on the aerobic oxidation of alcohol in water using a palladium(II) bathophenanthroline complex by Sheldon and coworkers [27], numerous works using recyclable metal nanoparticles (Pd [28–31], Pt [32–35] and Au [36, 37]) have been reported in literatures. 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. Also in some reported literatures nitrogen-based additives like triethylamine, pyridine, triethylenediamine [38, 39] to enhance the yield of products, or sodium hypochlorite, sodium perchlorate, aqueous hydrogen peroxide as source of oxygen [40] were employed. Our present study is based on preparation and characterization of platinum nanoparticles from the commercially available K_2 [$PtCl_4$] which were used as catalysts for oxidation of alcohols using O_2 as source of oxidant at room temperature.

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 [41–44].With the increasing environmental consciousness many transition metals including palladium and platinum have been used as catalysts for alcohol oxidation with ionic liquids as green solvents [45–48]. Use of [BMIM]OAc (1-butyl-3-methyl-imidazolium acetate) as dispersion medium to stabilize and recycle the platinum nanoparticles has also been discussed in our present article.

EXPERIMENTAL

Platinum nanoparticles were prepared from Potassium tetrachloroplatinate using tetraalkyl ammonium salts following the literature methods [49, 50]. A mixture of K_2 [$PtCl_4$] (202 mg, 0.53 mmol) and *n*-Bu_4NBr (738mg, 2.29 mmol) was stirred under vacuum (0.1 mbar) at 120 ºC for 2 h. Then, the mixture was placed under nitrogen atmosphere and n-Bu_3N (318 mg, 1.72 mmol) was added with a syringe. After stirring at 120 ºC for an additional period of 3 h, the mixture was cooled to room temperature and then washed with diethyl ether (5 mL x 4). Drying the residue overnight under vacuum (0.1 mbar) gave Pt_n (742 mg, black powder). Elemental analysis (average of two concordant determinations) of the platinum 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 (Bruker 400 Spectrometer) and FTIR (Nicolet 800 Spectrometer) studies which are in fact identical to the spectra of $Bu_4N^+Br^-$. Anal (particles prepared from $K_2[PtCl_4]$): found C, 53.88%; H, 10.78%; N, 3.86%; Pt, 6.23%; 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); FTIR ($CDCl_3$ dispersion, cm^{-1}); 925, 1382, 1468, 1486, 2870, 2956. The weight percentage of platinum was determined by inductively coupled plasma (ICP) in a optima 3200 RL multicanal Perkin Elmer machine at standard conditions. Weight percentage of platinum for particles prepared from K_2 [$PtCl_4$] was determined and found to be 6.23%. Strong evidence of the existence of nanoparticles in the studied samples comes from High Resolution Transmission Electron Microscopy (HRTEM, CM30 microscope operating at 200 kV and expanded to 470 Pixels/cm) conducted on the colloidal particles suspended in acetonitrile. The soluble K_2 [$PtCl_4$] complex and the platinum nanoparticles prepared are abbreviated as Pt_s and Pt_n throughout the text.

Oxidation in an Organic Solvent

A mixture of the substrate (1.0 mmol), platinum nanoparticles (30 mg, 0.01mmol Pt content) or $K_2[PtCl_4]$(4 mg, 0.01 mmol Pt content) in THF or 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 (Younglin 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 ºC at the rate of 5 ºC /min.

Oxidation In [Bmim] CH_3COO^- (*1-butyl-3-methyl imidazolium acetate)*

A similar procedure as described above was used but with [bmim]OAc (2 mL) as the solvent. At the end of the reaction (usually 2 h), the mixture was extracted with dry diethyl ether (5x10 mL). The organic phase was concentrated and purified as described above. The ionic liquid was dried on a rotary evaporator, then used for recycling experiments or stored in the refrigerator. [bmim]PF_6 (*1-butyl-3-methylimidazolium hexafluorophosphate*) and [bmim] BF_4 (*1-butyl-3-methyl imidazolium tetrafluoroborate*) were also used as solvents for oxidation reaction under similar conditions. The ionic liquids were prepared and purified as per literature methods [51] and were dried under vacuum before reuse.

TEM Analysis of a Recovered Sample

The quantity of ionic liquid in the sample was so large that observation of the platinum nanoparticles was obscured. Separation of the ionic liquid 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 to 4 times until the acetone was colourless. The resulting black solid was suspended in acetonitrile and sonicated for 10 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 metal 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 ionic liquids and generates environmentally benign by-products. However metal catalyzed aerobic oxidations are often limited by the use of high temperatures (60–80 ºC), Pressures (30–50 bar) and high catalyst loadings. The development of more active catalysts is therefore desirable for improving the utility of these oxidations. Platinumm nanoparticles prepared from K_2 [$PtCl_4$] 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.

Table 1: *Optimization of the Reaction Condition for Oxidizing Benzyl Alcohol to Benzaldehyde*[a].

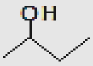
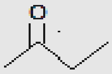
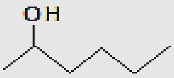
entry	solvent	catalyst	Additives[d]	conv%/yield%[e]
1	THF	Pt_s	-	Recovery
2	CH_2Cl_2	Pt_s	-	Recovery
3	CH_2Cl_2	Pt_s	CH_3COONa	Recovery
4	CH_2Cl_2	Pt_s[b]	-	Recovery
5	CH_2Cl_2	Pt_s[c]	-	Recovery
6	CH_2Cl_2	Pt_s[c]	Et_3N	Recovery
7	THF	Pt_n	-	88/75
8	CH_2Cl_2	Pt_n	-	87/82
9	CH_2Cl_2	Pt_n	Et_3N	66/70
10	CH_2Cl_2	Pt_n[c]	-	82/78
11	CH_2Cl_2	Pt_n	Py	Recovery
12	H_2O	Pt_n	-	Recovery
13	DMSO/H_2O(1:1)	Pt_n	-	10/8
14	CH_2Cl_2	5% Pt on Al_2O_3	-	Recovery
15	CH_2Cl_2	$K_2[PtCl_4]$	-	Recovery

a: 2 mmol benzyl alcohol, 2 mL solvent, room temperature, O_2 baloon pressure, run for 30 min; b: O_2 (20 bar pressure) in stainless steel reactor; c: O_2 (40 bar pressure); d: additives, 1 mmol was used; e: gas chromatographic analysis after isolation by flash chromatography.

Both the soluble variety K_2 [$PtCl_4$] and the nanoparticles suspended in organic solvents were subjected to oxidation of benzyl alcohol. Platinum nanoparticles were found to convert benzyl alcohol to benzaldehyde within 30 min of reaction. The soluble variety of platinum was also subjected to O_2 pressure (10–40 bar, Stainless steel autoclave fitted with pressure adaptor) to initiate the oxidation reaction. While the nanoparticles yield products at oxygen balloon pressure (1 bar) only substrate recovery was noted in case of K_2 [$PtCl_4$] used as catalyst. No additives were required in case of platinum nanoparticles 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 hours of catalytic reaction. Both tetrahydrofuran (THF) and dichloromethane (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. 5% Pt on Al_2O_3 (Merck product), $K_2[PtCl_4]$ as such are not viable catalysts for oxidation reaction under the existing conditions as no conversion was noticed even after 6 hours and almost 90% substrate recovery was observed using GC (Table 1).

Having optimized the reaction condition, the oxidation of other alcohols using Pt_n as catalyst under oxygen balloon pressure at room temperature was then examined. All the primary aromatic alcohols investigated gave excellent yields ranging from 80–90% and the products could be substantially purified by flash chromatography as indicated by ^{1}H NMR and GC analysis. The oxidation of secondary aliphatic alcohols was low and incomplete even after 4 hours of catalytic run. It is evident that as the chain length increases (run no 3–6, Table 2) % conversion as well as TOF decreases.

Table 2: *Substrate Scope in the Pt_n-Catalysed Oxidation of Alcohols in CH_2Cl_2 at Room Temperature.*

substrate	con%	time(min)	products	TOF(h^{-1})
1) 	96	30		648
2) 	79	30		592
3) 	90	30		620
4) 	84	60		290
5) 	60	60		210
6) 	54	60		170

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 (Figure 1).

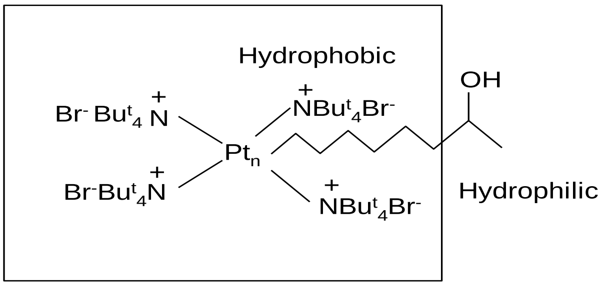


Fig-1

As the chain length increases, the –OH group moves away from the metal center and the rate of oxidation reduces to a considerable extent. Increasing the concentration of the Pt content 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.

Catalyst Recycling

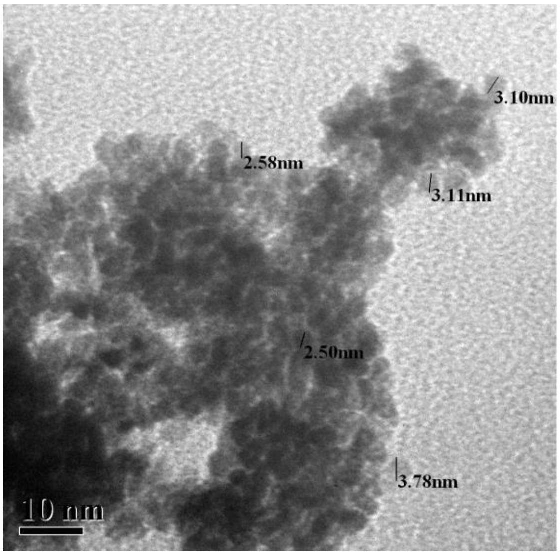
Separation of platinum nanoparticles from the system to study their recyclability nature was tedious as they tend to stick to the stirring bar and to the sides of the reaction vessel. The (%) conversion of substrate, butan-2-ol and (%) yield of product 2-butanone were determined based on gas chromatographic analysis and isolation of crude product by flash chromatography. After each run fresh substrate (0.1 mL, 1 mmol) was added keeping all other parameters same. When dichloromethane or tetrahydrofuran were used as solvents, the (%) conversion decreased to a considerable extent after first catalytic run. It is presumed that aggregation of platiunum nanoparticles to larger sizes leads to loss of active site for oxidation reaction. When common solvents were replaced by ionic liquids, (%)-conversion of substrate and yield of product remains almost constant even after four catalytic cycles (Table 3).

Table 3: *Recycling of the Pt-nano Catalytic System for Oxidation of Butan-2-ol at Room Temperature*[a].

Entry	**Solvent**[b]	**Conv%/yield%**	**Remarks**
run 1	CH_2Cl_2	90/87	Particles recovered for TEM analysis and recycling
recycling of run 1	CH_2Cl_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	-
run 3	$[bmim]PF_6$	74/70	-
run 4	$[bmim]BF_4$	70/66	-
Second cycle, run 4	-	67/64	-

a: all runs were conducted for 2h under oxygen filled in gas bag
b: 2 mL solvent used for runs 1, 2, 3 and 4.

Transmission electron microscopy 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 platinum particles on use and this is reflected in the increase in average size of recovered particles. Platinum particles freshly prepared from $K_2[PtCl_4]$ had on an average a diameter of 2.5±0.5 nm and this increased to around 10±1 nm at the end of the first cycle (Figure 2 and 3).



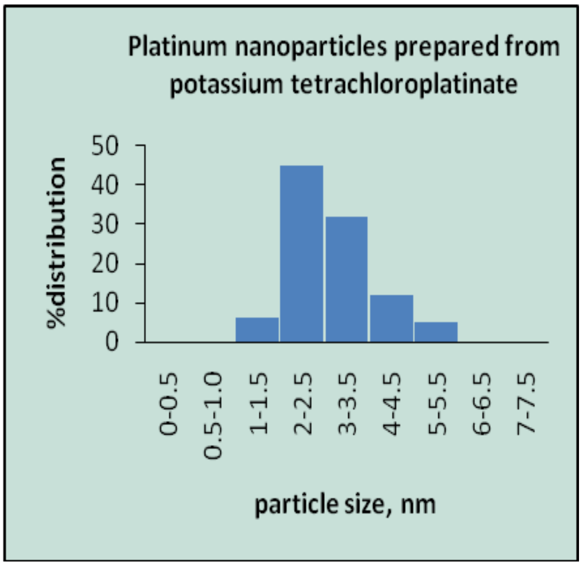
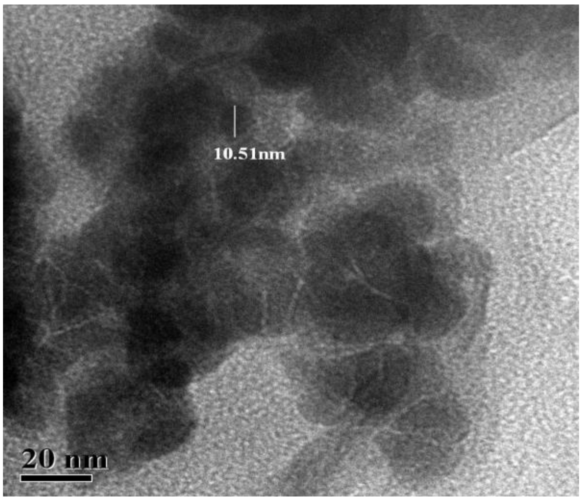


Fig. 2: *Platinum Nanoparticles Prepared from* $K_2[PtCl_4]$.



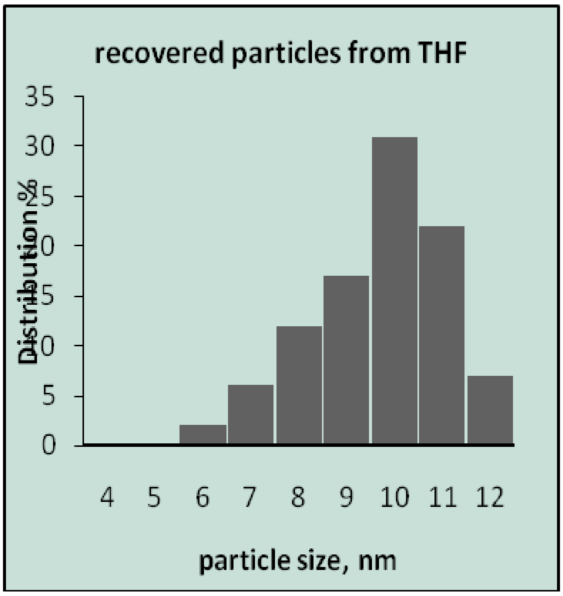


Fig. 3: *Platinum Nanoparticles Recovered from THF Solvent After* 1^{st} *Catalytic Cycle.*

Lower catalytic activity observed with the reused particles in dichloromethane solution is due to a lower amount of small sized nanoparticles present in active state in solution owing to aggregation into larger particles. ^{1}H NMR spectra of the recovered nanoparticles still show the presence of tetra-n-butyl ammonium bromide in their protective layer. To prevent agglomeration of platinum particles during oxidation reactions, 2 mL of the ionic liquid [bmim]OAc was added to the system keeping all other parameters same. At the end of 2 hours, the product mixture was extracted with diethylether and analyzed by GC (run 2, Table 3). Longer time period required when ionic liquids were used is due to lower solubility of oxygen in these types of solvents at room temperature. The first four oxidation cycles carried out with platinum based nanoparticles dispersed in the ionic liquid medium [bmim]OAc show that oxidation of butan-2-ol to Ketone is to the extent of 70% in all cases.TEM micrographs reveal the presence of platinum particles of average size distribution 3±0.5 nm after recovery from [bmim]OAc at the end of third cycle (Figure 4).

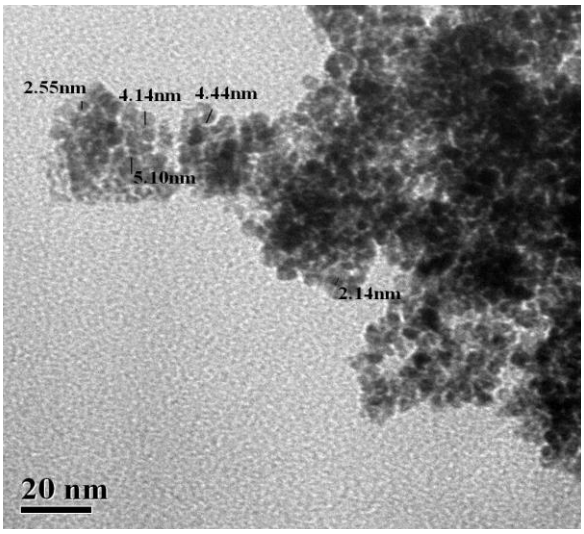


Fig 4: *Platinum Nanoparticles Recovered from [BMIM] OAc after* 3^{rd} *Catalytic Cycle.*

CONCLUSION

The findings demonstrate good catalytic activity of platinum nanoparticles compared to the soluble platinum complex. 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 like CH_2Cl_2 and THF are used. Recycling the nanoparticles becomes a cumbersome process then and shows reduced catalytic property. Dispersion of platinum nanoparticles in a room temperature ionic liquid prevents the phenomenon of agglomeration and retains their usual catalytic activity. The protocol followed supports green chemistry as use of hazardous, flammable organic chemicals have been limited and at the same time shows promise of commercial viability as far as organic synthesis of carbonyl compounds is concerned.

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