Applications of a high performance platinum nanocatalyst for the oxidation of alcohols in water†

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Nanoparticles of platinum (NP-Pt), have been synthesized by supporting high nuclearity anionic carbonyl cluster (Chini cluster) on a water soluble anion exchanger, and the performance of this material, **1**, as an oxidation catalyst for alcohols in water has been studied. The E-factor for the synthesis of NP-Pt by this method has been calculated and compared with that of other NP-Pt recently reported in the literature. With **1** as a catalyst, oxidations of a variety of primary and secondary alcohols by dioxygen are achieved and high turnover numbers and selectivities are obtained. The performances of **1** in the oxidation of benzyl alcohol and 1-phenylethanol are compared with those of three other platinum catalysts. These are platinum nanoparticles **2** prepared by the hydrogen reduction of $[PtCl_6]^{2-}$ supported on the same water soluble polymer, 5% Pt on carbon, and 5% Pt on alumina, designated as **3** and **4**, respectively. **1** has been found to be considerably more active than **2–4** and also other reported water soluble platinum nanocatalysts. After many turnovers (~1000 and ~165 for benzyl alcohol and 1-phenyl ethanol, respectively) partial deactivation (~ 40%) is observed, but the deactivated catalyst can be fully regenerated by treatment with dihydrogen. The TEM data of fresh, deactivated and regenerated **1** show a correlation between the particle size and activity. A mechanism consistent with this and other experimental observations including XPS data is proposed.

Introduction

Among many of the requirements of environmentally benign and economically viable chemical processes, the use of water rather than organic solvents is an important theme of current chemical research.[1–7] Apart from being totally non-hazardous, water is cheap, and a number of gasses have good solubility in water thereby making it possible to develop manufacturing processes where such a gas is one of the reactants. From a green point of view equally important is the development of *catalytic* oxidation processes with dioxygen (O_2) as the oxidant, rather than heavy metal based stoichiometric oxidants such as CrO_3, $KMnO_4$.[8–16] Besides obvious problems due to heavy metal toxicity, metal based oxidants have poor "atom utilisation" or "E-factor" indices as compared to the catalytic oxidation process.[4] Thus, in recent years, water soluble complexes and nanoparticles (NP) of noble metals have come under increasing investigation as potential catalysts for oxidation reactions.

To the best of our knowledge the recent report of Sheldon and co-workers first time highlighted the advantages of catalytic oxidation of alcohols in water, where a water-soluble palladium complex was used as a homogeneous catalyst for the oxidation of alcohol in water.[8a] Subsequently other catalytic systems based on soluble ruthenium complexes and NP of gold, palladium and platinum have been reported, but the range of alcohols that could be oxidised with these catalytic systems with high turnovers and long life time are limited.[17–20]

Notable improvements in catalytic performances have been reported recently where NP of platinum (NP-Pt) have been successfully used for the oxidation of a variety of alcohols in water by O_2.[11–13] These catalytic systems give moderate to excellent turnover numbers for the oxidation of a range of alcohols and are fully selective towards the oxidation of the alcoholic functionalities. The differences in the catalytic activities that cover a wide range of turnover numbers (TON) resulting from the different matrices used for the stabilisation of NP-Pt, as well as the differences in the synthetic methods of generating NP-Pt from high valent platinum salts.

Thus Wang *et al.* report a platinum nanocatalyst (Pt-GLY) prepared by the reduction of $H_2PtCl_6{\cdot}6H_2O$ with glycol, stabilising it with poly (N-vinyl-2-pyrrolidone) (PVP), and then removing glycol *via* dialysis.[13] The platinum nanocatalyst (ARP-Pt) reported by Yamada *et al.*[11] was prepared by supporting Zeise's salt on a functionalised amphiphilic resin and then reducing it with benzyl alcohol. The most active catalyst *n*Pt@*h*C (h*C* = hollow carbon) recently reported by Ng *et al.*[12] was made in a three step process: reaction of phenol with H_2PtCl_6 using TiO_2 as a photocatalyst followed by carbonization at 973K, and finally removal of TiO_2 by HF.

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The aforesaid recent reports clearly suggest that there is an urgent need for a high performance catalyst for the dioxygen assisted oxidation of alcohols in water. However, as has been pointed out recently for NP of gold, the "green" aspect of the synthetic method itself is an important consideration.[21] The environmental friendliness of different synthetic methods for NP-Pt may be quantified in terms of the amounts of reagents used and waste generated *i.e.*, an approximate E-factor.[4] Therefore an optimum balance between the E-factor of the synthetic method for NP-Pt and its performance as an oxidation catalyst is very important.

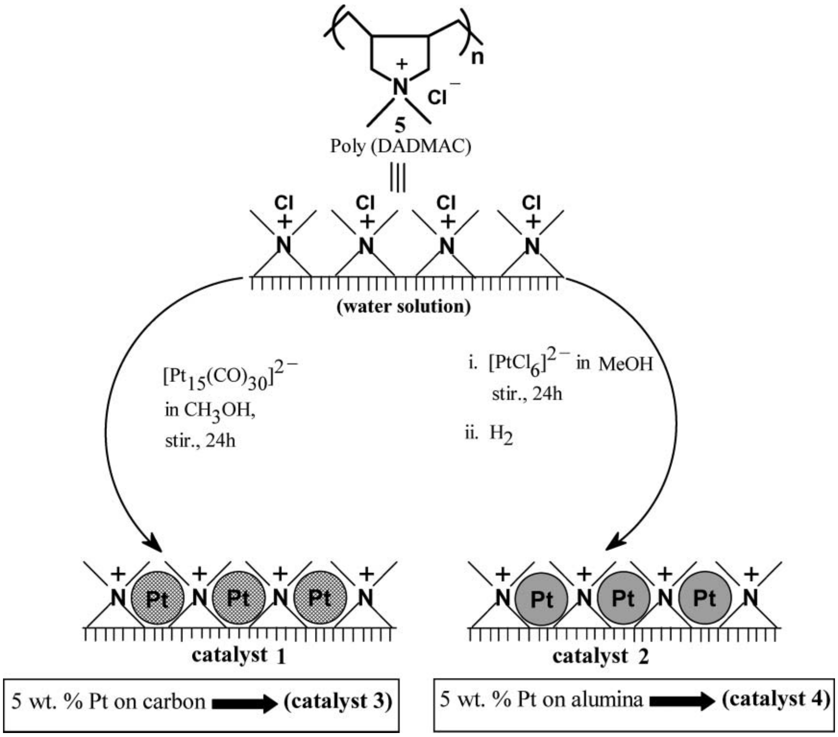
In addition to the above mentioned reports on the synthetic methodologies of NP-Pt, a few other preparative methods have also been reported.[22–27] We have shown that nanostructured platinum hydrogenation catalysts could be prepared by supporting Chini clusters of the general formula $[Pt_3(CO)_6]_n^{2-}$ on functionalised inorganic oxides as well as organic polymers.[28] Of special relevance in the present context is our recent finding, that a water soluble precursor for NP–Pt could easily be prepared by following the above general method using a water soluble polymer. Under hydrogenation conditions the CO ligands are lost and the resultant nanocatalyst has excellent activity and selectivity in hydrogenation reactions (Scheme 1). The recent reports on the remarkable performance of ARP-Pt,[11] Pt-GLY[13] and *n*Pt@*h*C[12] as oxidation catalysts in water, prompted us to investigate the performance of **1** in oxidation reactions. Interestingly we find that for alcohol oxidation reactions in water, **1** is more active than ARP-Pt and Pt-GLY. Moreover, **1** is also found to be more active than **2**, a nanocatalyst prepared by the hydrogen reduction of $[PtCl_6]^{2-}$ supported on **5** (see Scheme 1 below), and two commercial platinum catalysts, **3** and **4** (5% Pt on carbon and alumina, respectively).

Results and discussion

Nanocatalyst **1** is prepared by adding an aqueous solution of poly (diallyldimethylammoniumchloride) **5**, a commercially available water soluble polymer, to a methanolic solution of the preformed cluster, $[Pt_{15}(CO)_{30}]^{2-}$. The latter is prepared by reducing Na_2PtCl_6 under CO with methanol and sodium acetate according to the following equation.[28a,b,29]

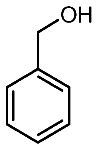
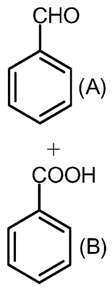
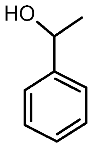
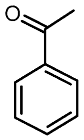
$$\begin{aligned}15\,Na_2PtCl_6 + 31\,NaOAc + 31\,MeOH + 30\,CO \rightarrow\\ Na_2[Pt_{15}(CO)_{30}] + 31\,AcOH + 31\,HCHO\\ + 31\,HCl + 59\,NaCl\end{aligned} \tag{1}$$

The amounts of the reagents used for the synthesis of **1** has been reported (see Experimental) and the E factor (amount of waste/amount of product) for the syntheses is 12.8 (see ESI†). As per convention, waste is defined as the amount of all reagents minus the weight of product, solvents are considered as reagents but water is not. On the basis of the reported synthetic details, the approximate E-factors for the other three nanocatalysts, *n*Pt@ *h*C, Pt-GLY and ARP-Pt have also been calculated and for the first two the values are found to be 30.9 and 12.7, respectively. The E factor for ARP-Pt is 4.4 and this has been calculated by summing two E-factors, one for Zeise's salt, $K[Pt(C_2H_4)Cl_3]$, and the other for the synthesis of the nanocatalyst. As shown in Scheme 1, the nanocatalyst **2** is synthesized by dihydrogen reduction of $[PtCl_6]^{2-}$ anchored on **5** in methanol with an E factor of 14.7. Studies on the catalytic performance of **2** in hydrogenation reactions have been reported by us and others.[27,28a] The particularly high E-factor of *n*Pt@*h*C arises because its synthesis involves the use of relatively large amounts of TiO_2 and hazardous HF as reactants. While



Scheme 1 Formulation of catalysts **1–4**.

Table 1 Comparative activity of different catalysts used in this work for the oxidation of benzyl alcohol and 1-phenylethanol[a]

Entries	Substrate	Product	Catalyst	Time (h)	% Conversion (A+B)	TON/TOF h^{-1}
1[b]			**1**	8	100 (2 (A) + 98 (B))	300/37.5
2[c]			**1**	8	100 (4 (A) + 96 (B))	300/37.5
3[d]			**1**	24	95 (5 (A) + 90 (B))	285/11.8
4[e]			**1**	8	56 (54 (A) + 2 (B))	840/105
5[f]			**1**	24	90 (12 (A) + 88 (B))	270/11.25
6[b]			**2**	8	74 (4 (A) + 70 (B))	222/27.75
7[b]			**3**	8	36 (4 (A) + 32 (B))	108/13.5
8[b]			**4**	8	66 (6 (A) + 60 (B))	198/24.75
9[g]			**ARP-Pt**	24	99 (0 (A) + 99 (B))	99/4.12
10[h]			**GLY-Pt**	24	100 (0 (A) + 100 (B))	20/0.83
11[b]			**1**	20	87	43.5/2.17
12[c]			**1**	20	84	42/2.1
13[d]			**1**	24	40	20/0.83
14[f]			**1**	24	48	24/1
15[b]			**2**	20	52	26/1.3
16[b]			**3**	20	32	16/0.8
17[b]			**4**	20	49	24.5/1.22
18[g]			**ARP-Pt**	24	82	16.4/0.68
19[h]			**GLY-Pt**	24	98.5	19.7/0.82
20[i]			**nPt@hc**	24	81	405/16.8

[a] Substrate/Catalyst molar ratio: for benzyl alcohol 300, for 1-phenyl ethanol 50, catalyst amount 100 mg, TON = mmole of product(s)/mmole of Pt; TOF = TON/Time, water 5 mL, temperature, 353 K. [b] O_2 as oxidant. [c] H_2O_2 as oxidant. [d] Air as oxidant. [e] Substrate/Catalyst molar ratio = 1500. [f] Reactions were carried out at 333 K temperature (under Uzomi's conditions, see reference 11 to compare the values). [g] From reference 11. [h] From reference 13. [i] From reference 12.

the calculated E factors are only indicative and not exact, it is clear that from an environmental point of view *n*Pt@*h*C is less desirable, though among all the nanocatalysts it is the most active.

For comparative performance evaluation of catalysts **1–4**, ARP-Pt, Pt-GLY and *n*Pt@hC the oxidation of benzyl alcohol and 1-phenylethanol have been studied in detail. As can be seen from Table 1, highest turnover numbers and turnover frequencies (TON and TOF) are consistently obtained with **1**. The TONs of **1** are also higher than that of ARP-Pt and Pt-GLY. For the oxidation of benzyl alcohol in terms of turnover frequencies (TOF, h^{-1}), **1** is almost an order of magnitude or more active than both the reported catalysts (Entries 1, 9, and 10), while for 1-phenylethanol, its activity is ≥ 2.5 times of the other two reported catalysts (ARP-Pt and Pt-GLY) (Entries 11, 18, 19). As the temperature used by Yamada *et al.* was 60 °C, the TOFs of **1** for benzyl alcohol and 1-phenyl ethanol have also been measured at this temperature (Entries 5, 14). At 60°C for these two substrates **1** is ~2.5 and 1.5 times more active than ARP-Pt. As already mentioned, *n*Pt@hC is the most active among all the catalysts and gives a TOF of 16.8 (h^{-1}) for 1-phenyl ethanol oxidation but has not been studied for benzyl alcohol oxidation. For both the substrates, benzyl alcohol and 1-phenyl ethanol, instead of dioxygen, 30% hydrogen peroxide may also be used with comparable results (Table 1, Entries 2, 12). Also if air is used as the oxidant, a lowering in TON is observed, presumably due to dilution of dioxygen by N_2 (Table 1, Entries 3, 13).

Benzyl alcohol oxidation to benzoic acid obviously proceeds through the intermediate formation of benzaldehyde as confirmed by the time monitored concentration data of benzyl alcohol, benzaldehyde and benzoic acid (Fig. 1a). However, by increasing the substrate to catalyst concentration substantially (from 300:1 to 1500:1), benzaldehyde with TON > 800 and selectivity ~ 96% may be obtained (Table 1, Entry 4).

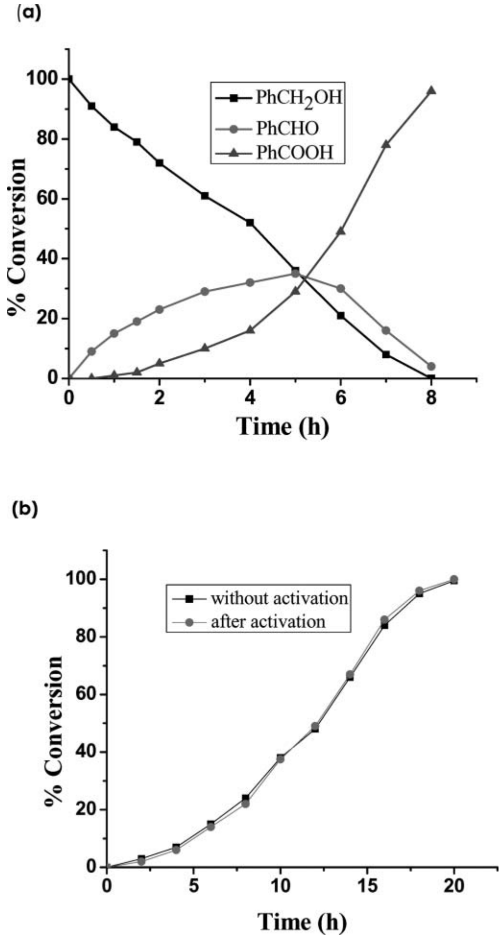


Fig. 1 **(a)** Time monitored conversion of benzyl alcohol to benzaldehyde and benzoic acid by **1** in water. **Reaction Conditions:** Catalyst (**1**) = 100 mg (5.4×10^{-3} mmol of Pt), benzyl alcohol = 175 mg (. Substrate to platinum molar ratio: 300). Solvent (water) = 5 mL, temperature = 353 K, O_2 = 1 atm., stirring speed = 900 rpm. **(b)** Comparative time monitored conversion of 1-phenylethanol to acetophenone by **1** in water with and without activation. **Reaction Conditions:** Catalyst (**1**) = 100 mg (5.4×10^{-3} mmol of Pt), 1-phenyl ethanol = 33 mg, (Substrate to platinum molar ratio: 50). Solvent (water) = 5 mL, temperature = 353 K, O_2 = 1 atm., stirring speed = 900 rpm.

The time monitored concentration profiles of 1-phenylethanol oxidation by using freshly prepared **1**, and activated **1** (**1** fully decarbonylated by heating under vacuum) as catalysts have been recorded (Fig. 1b). The concentration *vs.* time plots are practically identical and both catalysts show induction periods ~5 h. As reported for hydrogenation reactions in water, in oxidation reactions also the CO ligands are quickly (< 5 min) lost. This has been confirmed by carrying out a separate experiment and monitoring the disappearance of ν_{CO}. These observations are significant from a mechanistic point of view, as they show that the long induction time is independent of the time required for CO loss.

The catalytic activity of **1** has been evaluated for the oxidation of other representative aliphatic and benzylic alcohols (Table 2). All primary alcohols are oxidized mainly to the acid while the secondary alcohols expectedly yield ketones. As mentioned earlier, in benzyl alcohol oxidation by increasing the substrate to catalyst concentration substantially, benzaldehyde with >95% selectivity may be obtained. Such a strategy may also work for the selective conversion of other primary alcohols to the corresponding aldehydes. Good TONs and TOFs are obtained in all the cases and no adverse effect due to olefinic functionalities are observed (Table 2, Entries 10, 12, 15). For substrates with such functionalities only the alcohol functionality is selectively oxidised. It may also be noted that as most of the reactions in Tables 1 and 2 were set to a fixed time, the TON and especially TOF given for the reactions that went to completion correspond to lower limits (Entries 1 and 2 in Table 1; entries 1 and 3 in Table 2).

The recycling and deactivation studies on **1** have been carried out under conditions where high turnovers are obtained per batch. As shown in Table 3, on recycling, partial deactivation of **1** is observed, from the first to the fifth batch the TONs drop from 300 to 183 and 44 to 26 for benzyl alcohol and 1-phenylethanol, respectively. The total turnovers over the five batches are 1150 and 165, respectively. This is to be contrasted with the reported data on recycling for ARP-Pt and Gly-Pt. For these two catalysts total turnovers ~80–90 over five batches were obtained but no deactivation was reported.

Interestingly and significantly, on treatment with dihydrogen (30 bar, 3 h, in water) the used **1** regains its original activity completely. This is evident from the conversion and TON data of the regenerated catalyst (Table 3, Entries 6, 12). The regenerated catalyst has been tested for more than one recycle for both the model substrates, benzyl alcohol and 1-phenyl ethanol. Its behaviour has been found to be identical to that of the fresh catalyst. As catalytic activity is very often found to be strongly correlated with the particle size, the TEM studies of the fresh, used and regenerated **1** have been performed (see Experimental). As reported in our earlier publications, freshly prepared **1** has CO-protected platinum nanoparticles within the size range of 2–8 nm with *ca.* 70% being within 3–5 nm.[28a,b] After five catalytic runs no small (≤6 nm) particles could be seen in the partially deactivated catalyst (Fig. 2a) which consists mainly of large particles (8–10 nm). However, the growth in particle size is reversible as the hydrogen treated regenerated catalyst shows a reduction in the particle size (Fig. 2b). The nanoparticle size measurements with the TEM facilities at our disposal (see Experimental) are approximate. However, the overall trend, that of an increase in the particle size in the used catalyst and a reduction of particle size in the regenerated catalyst, is unambiguous.

The X-ray photoemission spectra (Fig. 3) of fresh and used **1** have also been recorded. Freshly prepared **1** shows signals for the Pt 4*f* core levels with the binding energy (BE) of Pt $4f_{7/2}$ ~71.0 eV being very close to the literature reported value of the free cluster.[28a,d,30] The XPS signal of the five times used partially deactivated catalyst on deconvolution shows a strong peak at ~72.5 eV, and a much weaker one at ~71.0 eV. This indicates that the predominant oxidation state of platinum in the deactivated catalyst is +2.

Table 2 Aerobic oxidation of bezylic and aliphatic alcohols by catalyst **1**[a]

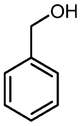
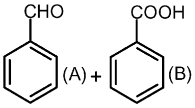
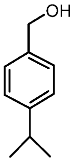
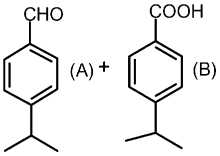
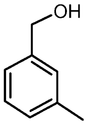
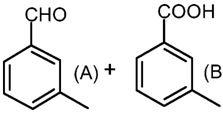
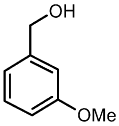
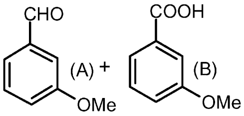
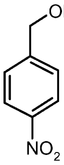
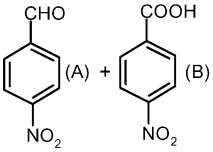
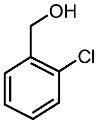
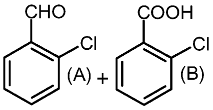
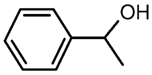
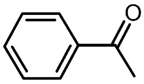
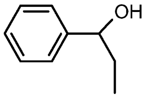
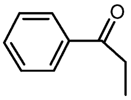
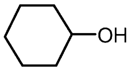
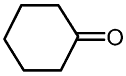
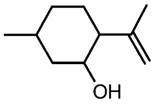
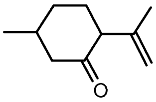
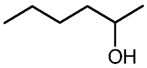
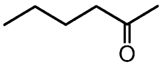
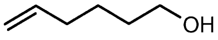
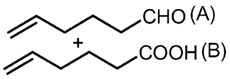
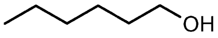
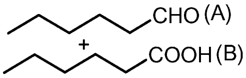
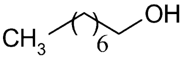
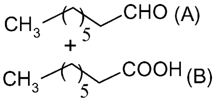
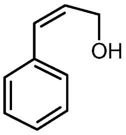
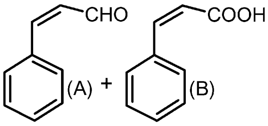
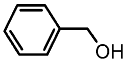
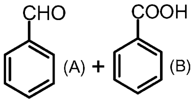
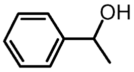
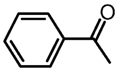
Entries	Substrate	Product	Time (h)	% Conversion (A + B)	TON (TOF^{-h})
1			8	100 (2(A) + 98(B))	300 (37.5)
2			8	89 (2(A) + 87(B))	267 (33.3)
3			8	100 (5(A) + 95(B))	300 (37.5)
4			8	92 (12(A) + 80(B))	276 (34.5)
5			8	72 (7(A) + 65(B))	72 (9)
6			8	65 (8(A) + 57(B))	65 (8.1)
7			20	87 (100)	43.5 (2.17)
8			20	83 (100)	41.5(2.07)
9			20	82 (100)	41 (2.05)
10			20	75 (100)	37.5 (1.87)
11			20	83 (100)	41.5 (2.07)
12			20	100 (2(A) + 98(B))	100 (5)
13			20	100 (4(A) + 96(B))	100 (5)

Table 2 *(Contd.)*

Entries	Substrate	Product	Time (h)	% Conversion (A + B)	TON (TOF^{-h})
14			20	95 (5(A) + 90(B))	95 (4.75)
15			20	99 (90(A) + 9(B))	99 (4.95)

[a] Substrate/Catalyst molar ratio: for benzyl alcohol 300, for 1-phenyl ethanol and 2° alcohols 50, for aliphatic primary alcohols 100, catalyst amount 100 mg (5.4×10^{-3} mmol of Pt), TON = mmole of product(s)/mmole of Pt; TOF = TON/Time, water 5 mL, temperature, 353 K. O_2 = 1 atm., stirring speed = 900 rpm. Entries 5, 6: solid substrates were dissolved in ethyl acetate and with a Substrate/Catalyst molar ratio of 100.

Table 3 Recycling data for the oxidation of benzyl alcohol and 1-phenylethanol by catalyst **1**[a]

Entries	Substrate	Product	No. of cycle	% Conversion (TON)	TTON over five cycles
1			1	100 (300)	1149
2			2	81 (243)	
3			3	73 (219)	
4			4	68 (204)	
5			5	61 (183)	
6[b]			Regenerated	99 (297)	
7			1	87 (43.5)	165.5
8			2	74 (37)	
9			3	60 (30)	
10			4	59 (29.5)	
11			5	51 (25.5)	
12[b]			Regenerated	91 (45.5)	

[a] Catalyst (**1**) = 100 mg (5.4×10^{-3} mmol of Pt); Substrate to platinum molar ratio, 50 for 1-phenyl ethanol and 300 for benzyl alcohol; solvent (water) = 5 mL; temperature = 353 K; O_2 = 1 atm with vigorous stirring (900 rpm); reaction time, 20 h for 1-phenyl ethanol and 8 h for benzyl alcohol. (TTON = total turnover number). [b] Regeneration of used catalyst (5 runs) by keeping it under 30 bar of hydrogen pressure for 3 h in water.

The deactivation of **1** is clearly not due to metal leaching as estimation of Pt before and after the each batch shows no observable loss of metal. A likely mechanism that takes into account all the experimental observations is shown in Scheme 2.

The catalytic cycle that involves species of the type **1**, **6**, **7** and **8** is the generally accepted mechanism for the oxidation of alcohols with Pt-catalysts.[31] As indicated in Scheme 2, the deactivation of the catalyst is due to over oxidation, *i.e.*, "Pt–O–Pt" bridge formation which leads to the growth of platinum oxide lattice and a concomitant increase in the size of the NPs. This is consistent with the TEM and XPS data. As the concentration of water is considerably more than that of the alcohol, the equilibrium between **6** and **9** is expected to lie more towards the latter. The induction period of ~5h mentioned earlier probably results from the time taken for the build up of enough **6** under unfavorable equilibrium conditions.

Conclusion

In conclusion synthesis of NP-Pt through the anchoring high nuclearity platinum carbonyl cluster on a water soluble polymer has an approximate E-factor of 12.8. By using either dioxygen or hydrogen peroxide the NP-Pt obtained this way can selectively oxidise a wide variety of alcohols with high turnovers and selectivities. After many turnovers there is partial deactivation accompanied by an increase in the particle sizes, but the deactivated catalyst can be fully regenerated by treatment with dihydrogen and this is accompanied by a reduction in the particle

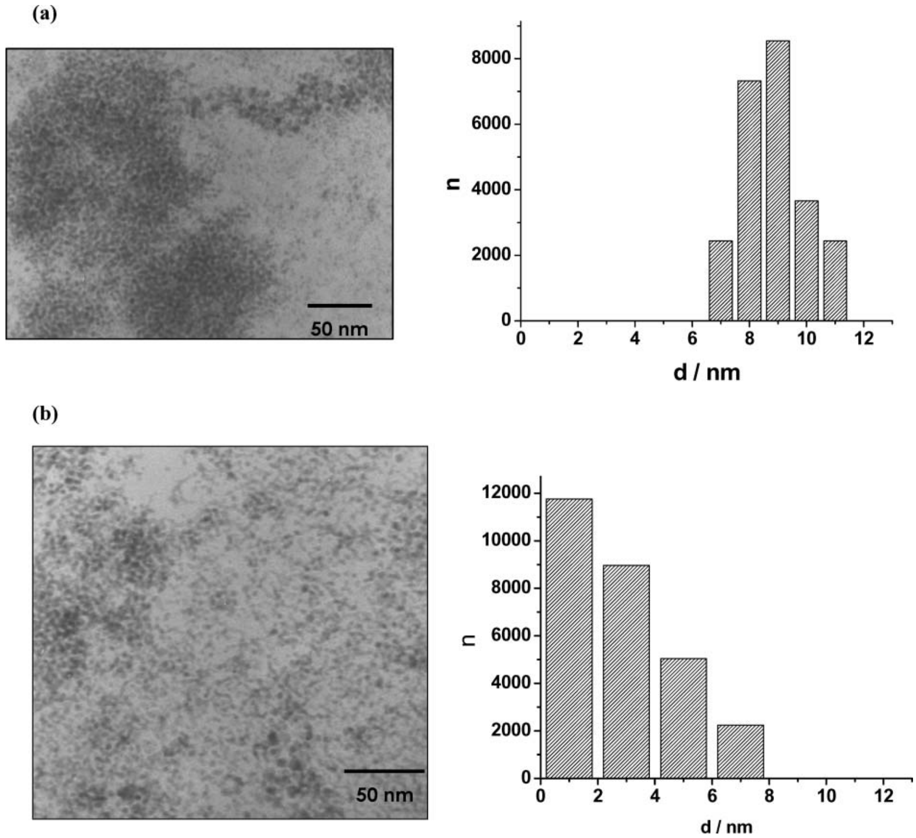


Fig. 2 **(a)** TEM picture and histogram of catalyst **1** after five runs. **(b)** TEM picture and histogram of used **1** from **(a)** after treatment with H_2 (30 bar) for 3 h.

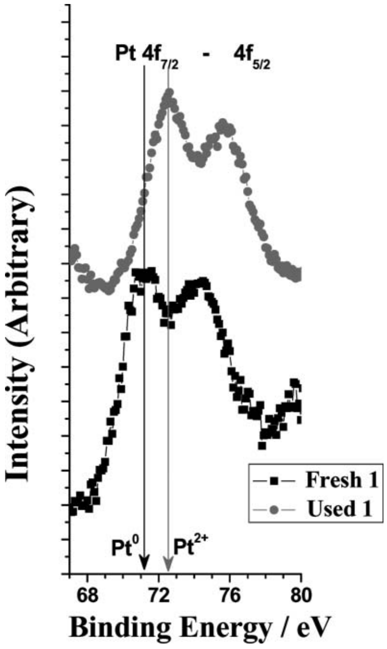
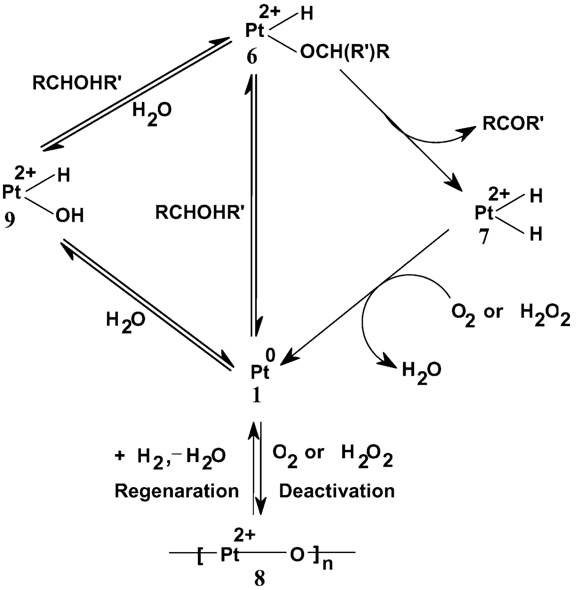


Fig. 3 XPS spectra of fresh and used catalyst **1**.



Scheme 2 Probable mechanistic pathway for the aerobic oxidation of alcohols by catalyst **1**.

size. These and other experimental observations are consistent with the generally accepted mechanism for platinum catalysed oxidation of alcohols.

Experimental

General methods

Methanol was dried over Mg-turnings/iodine and distilled under nitrogen prior to use. $^1H/^{13}C$ NMR spectra were recorded on a 400 MHz Varian spectrometer. TEM experiments were performed using a Philips 1200 EX at 120 kV. The histograms of TEM images were constructed manually from hard copies using the software ImageJ (http://rsbweb.nih.gov/ij/). The TEM pictures were scanned, saved as JPG files and opened by ImageJ program. After enlarging them substantially, sizes of fifty particles were measured manually for each picture and the histograms were obtained by using 'Origin' software.

UV-vis-NIR measurements were performed on a Perkin Elmer lamda-950 spectrophotometer. FT-IR spectra were taken on a Nicolet spectrophotometer with samples prepared as KBr pellets. All the samples were analysed by gas chromatographic technique with FID detector (Shimadzu GC-14A gas chromatograph) using a capillary column (CBP20 – M-25 – 025). The bulk platinum content of fresh and used **1** was determined using 8440 Plasma Lab ICP-AES instrument.

Poly(diallyldimethylammoniumchloride) (polyDADMAC, low molecular weight), 20 wt% solution in water, sodium hexachloroplatinate, and catalysts **3** and **4** were purchased from Aldrich, Germany and used as received. Carbon monoxide was supplied by BOC, India.

Synthesis of 1 and 2

Syntheses of **1** and **2** were carried out according to the reported procedures[28a] with the modification that methanol (10 gm) was used as the solvent.

Experimental protocol for the aerobic oxidation of alcohols in water using 1

A mixture of **1** {100 mg, (5.4×10^{-3} mmol of effective platinum)} and respective alcohols (amount of alcohol varies as shown in Table 2) were taken in 3 mL of water. The mixture was stirred at 80 °C under a steady flow of oxygen gas at atmospheric pressure (The specific reaction time has been mentioned in Table 2). After cooling the reaction mixture was extracted with ethyl acetate (5 × 1 mL). The extract was dried over magnesium sulfate and analysed by GC or proton NMR. The aqueous catalyst solution was reused subsequently. Similar experimental procedures were followed for the catalysis using all other catalysts (**2–4**).

For the reactivation of the used catalyst, an aqueous solution of used **1** was kept under 30 bar of hydrogen pressure for 3 h and then used as the regenerated catalyst.

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