Superiority of Palladium Nano particles as hydrogenation catalysts over soluble and polystyrene anchored palladium complexes.

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Abstract

The search for more efficient catalytic systems that might combine the advantages of both homogeneous(catalyst modulation) and heterogeneous(catalyst recycling) catalysis is one of the most exciting challenges of modern chemistry. More recently with the advances of nanochemistry, it has been possible to prepare soluble analogues of heterogeneous catalysts. These nanoparticles are generally stabilized against aggregation into larger particles by electrostatic or steric protection. Herein we demonstrate the use of palladium nanoparticles as efficient catalysts for the hydrogenation of carbon-carbon double bonds and application of these catalysts to the selective hydrogenation of internal or terminal C=C bonds in unsaturated primary alcohols.

Keywords: nanoparticles, selective hydrogenation, agglomeration, particle size, turn over frequency.

1. Introduction:

Although a large number of investigations deal with palladium containing systems as catalysts for hydrogenation reactions[1-6], the study of catalytic activity of these palladium complexes anchored to polymers are relatively rare [7-10]. This may be due to poor chemical, thermal and mechanical properties of the selected polymeric materials and tendency of the metal to leave the support on prolonged use [11,12]. The field of nano catalysis has become active with numerous review articles published during the last decade[13-18]. Metal particles with nano sizes have been intensely investigated recently as they have application in various fields like optics, electronics, magnetic devices, photocatalysts, adsorbents and sensors. The small size of these particles makes them attractive in catalysis due to their large surface to volume ratio. Palladium nano particles stabilized with tetra alkyl ammonium salts [19], polyvinyl pyrollidine [20], dendrimers [21], chitosan [22] and cyclodextrin [23] have been reported in literatures. In most of these reports there has not been any detailed examination regarding size control of metal nanoparticles, the cause and effect of metal agglomeration during catalytic runs and whether the nanoparticles can be recycled with similar retention of catalytic behaviour. A detailed investigation is necessary to address these concerns and to understand the mechanism of nanocatalysis better. The present paper reports the use of tetrabutyl ammonium bromide stabilized palladium nanoparticles as efficient catalysts for olefnic hydrogenation reactions, their superiority over conventional soluble and polymer anchored varieties and finally the selective hydrogenation of unsaturated alcohols exhibited by this class of colloidal nanoparticles. TEM studies before and after hydrogenation reactions show marked changes in the average size and this is reflected in the catalytic activity of the nanoparticles upon recycling.

2. Experimental methods

2.1 Catalyst preparation:

Palladium nanoparticles were prepared from palladium chloride as per the following literature method [24]. A mixture of palladium chloride(101.5mg, 0.57 mmol) and n-Bu_4NBr (738mg,2.3mmol) was stirred under vacuum(0.1mbar) at 120^{O}C for 2 hours. The mixture was then placed under an argon atmosphere and n-Bu_3N (318mg, 1.72mmol) was added with the help of a syringe. After stirring the whole at 120^{O}C for an additional period of three hours, the mixture was cooled to room temperature and washed with diethyl ether(5mlx4). Drying the residue overnight under vacuum produced black crystalline powder (742mg),mpt:109-111^{O}C.

The soluble catalyst trans-$Pd(C_6H_5NH_2)_2Cl_2$ was prepared from palladium chloride by the method described earlier [25]. Aniline(1.5g) was added to a hydrochloric acid(100mL) solution of $PdCl_2$(1.0g). The solution was warmed gently for 30 minutes and the yellow crystals of the desired compound separated out on cooling. This was recrystallised from acetone. Anal: found C,40.2%; H, 3.8%; N,2.5%; Pd, 29.04%.

For the preparation of polystyrene bound palladium(II) complex,$(P_n\text{-}NH_2)_2PdCl_2$, where

Pn= polystyrene moiety, macroporous polystyrene crosslinked with divinyl benzene was first nitrated and then reduced to amines. The amines were then allowed to react with $PdCl_2$ to form the polymer anchored variety[25].

2.2 Catalyst characterization:

Elemental analysis(average of two concordant determinations) of the palladium chloride 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 ^{1}H NMR, ^{13}C NMR and FTIR studies which are in fact identical to the spectra of Bu_4NBr. Anal.:found C,53.88%; H, 10.78%; N, 3.86%; Pd, 6.76%; Br, 22.28%. ^{1}HNMR($CDCl_3$,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 multichannel Perkin Elmer machine at standard conditions. The value shown is the average of three determinations made against three blank samples. Strong evidence of the existence of nanoparticles in the studied sample comes from Transmission Electron Microscopy conducted on the colloidal particles suspended in acetonitrile.

Detailed analysis of the soluble and polymer anchored palladium(II) complexes used as hydrogenation catalysts here can be found in our earlier work[25]. The soluble palladium aniline complex, the polystyrene anchored variety and the palladium nanoparticles prepared from $PdCl_2$ are abbreviated as $Pd_{\mathbf{s}}$, $Pd_{\mathbf{p}}$ and $Pd_{\mathbf{n}}$ respectively throughout the text.

2.3 **Hydrogenation procedure**:

Hydrogenation of olefins was performed at atmospheric pressure at 25^{o}C in a closed 100 mL glass vessel equipped with a magnetic stirrer. Exactly 5 mL solution of colloidal Pd nanoparticles in methanol was fed into the glass reactor. Hydrogen gas was flowed several times to eliminate air and the catalyst was activated for 10 minutes with vigorous stirring. The reaction was started after the injection of 0.5mL of the substrate and hydrogen absorption was measured using a graduated gas reservoir. The intermediate samples were withdrawn from the reaction mixture at an interval of 10 minutes and analysed immediately by Gas Chromatography(Varian 3700) equipped with a carbowax capillary column and Flame ionization detector. Temperature programming was done in the range 60^0C -120^0C at the rate of 5^0C/min.

3. Results and Discussion

Both the soluble [trans-$Pd(C_6H_5NH_2)_2Cl_2$] and polystyrene supported complex of palladium(II) [P_n-(p-$C_6H_4NH_2)_2PdCl_2$] are active as hydrogenation catalysts so far as reduction of olefins are concerned. The catalysts are effective for normal pressure hydrogenation of Hex-1-ene, 1-octene, cyclohexene, isoprene and styrene used as substrates at room temperature. The temperature for normal pressure hydrogenation should invariably be below 30^0C in order to avoid slow decomposition of the soluble variety in hydrogen atmosphere. It has been observed that trans-$Pd(C_6H_5NH_2)_2Cl_2$ remain indefinitely stable at room temperature and does not show any decomposition even when heated in air at 100^0C. The solution of the complex in methanol is quite stable in air but suffers slow decomposition in presence of hydrogen. The rate of decomposition increased considerably with increase in hydrogen pressure and reaction temperature. The immobilized variety suspended in methanol is however stable under normal hydrogen pressure even at 100^0C. Palladium nanoparticles dispersed in methanol however show signs of agglomeration during the course of hydrogenation as revealed from the TEM pictures after catalyst recovery.

Alk-1-enes undergo simultaneous reduction and isomerization. The reaction product of Hex-1-ene in all cases was Hexane(major product) and Hex-2-ene(minor product). The reaction products of 1-octene with palladium complexes (Pd_s,Pd_p and Pd_n**)** were not only octane but also its isomers 2-octene and 3-octene. The catalytic activities in terms of turn over frequencies(TOFs, mole product/mole metal, hr^{-1}) and product distribution has been given in **Table-1**. Normal pressure hydrogenation of olefins with the three variety of catalysts show nearly quantitative transformation of the substrates into products. The initial rates of reduction as revealed from initial turn over numbers show that styrene and isoprene where the double bond is part of a delocalized system are reduced much more easily than alk-1-enes where the double bond is either single or non-conjugated. Palladium nanoparticles were found to be superior as far as hydrogenation of olefins is concerned followed by the polystyrene anchored palladium aniline complex and low rate of conversions were noticed for the soluble palladium aniline complex (**Fig. 1**).

The soluble catalyst could not be recycled for the reduction of olefins due to exhaustive decomposition of the complex to Pd(0). The yellow solution of the complex in methanol turned deep brown on stirring under hydrogen for 15 minutes and addition of substrates at this stage initiates hydrogen absorption at a maximum rate. At the end of the reaction period(approximately 60 mins) the black particles collected at the bottom of the reaction vessel show no catalytic activity with fresh addition of olefinic substrates. XPS studies on these particles show unambiguously the presence of Pd(0) which were believed to be formed during the course of hydrogenation reaction. The polymer anchored variety of the Palladium (II) complex appear to be superior so far as the number of successful substrate reductions are concerned. The deep brown materials obtained in this case after hydrogen activation were identical in catalytic activities and exhibited similar IR spectra to the corresponding ones left at the end of normal pressure hydrogenation reaction. IR spectra of deep brown materials collected before and after substrate reduction exhibit peaks in the region 3300-3400cm^{-1}(νNH$_2$),1630-1640 cm^{-1}(νNH), 1970-12980 cm^{-1}(νPdH), 450 cm^{-1}(νPdN) and 365cm^{-1}(ν PdCl). Analysis of the brown material (Pd:Cl, 1:1.22) and liberation of HCl during hydrogen activation strongly suggest partial replacement of Pd-Cl bond by Pd-H during the activation step. This brown material is believed to be the active species formed in situ and the rigid bond positions in the polystyrene matrix may be the reason that prevents its decomposition during the catalytic run. Subsequent use of the polymer anchored variety as hydrogenation catalyst with 1-octene as substrate do not show any decomposition of the materials to the elemental state. Most of the palladium from the brown material can however be extracted by heating with ethanolic solution of KCN for 24 hours. The residual material was then found to be catalytically inactive indicating the activity of the brown material to be due to Pd(II) complex only.

Table 1. Relative catalytic activity of Palladium complexes in methanol at 25^{O}C.
[Pd] =1.8x10^{-5} mol,[substrate]=3x10^{-3} mol, reaction time=60min.

Substrate	**Product(s)^a**	**Product distribution(%) in different systems**			**TOFs(h^{-1})^b**		
		Pd$_s$	**Pd$_p$**	**Pd$_n$**	**Pd$_s$**	**Pd$_p$**	**Pd$_n$**
Hex-1-ene	Hexane	84	88	88	232	472	970
	Hex-2-ene	15	10	10			
1-Octene	Octane	66	78	84	288	512	884
	2-Octene	22	12	10			
	3-Octene	10	10	05			
Styrene	Ethyl benzene	88	88	96	312	766	1083
Isoprene	2-methyl butane	84	89	95	480	506	982
Cyclohexene	Cyclohexane	90	92	92	298	222	516

a determined by Gas Chromatography using standards as reference.
b determined as mol product/mol metal per hour.

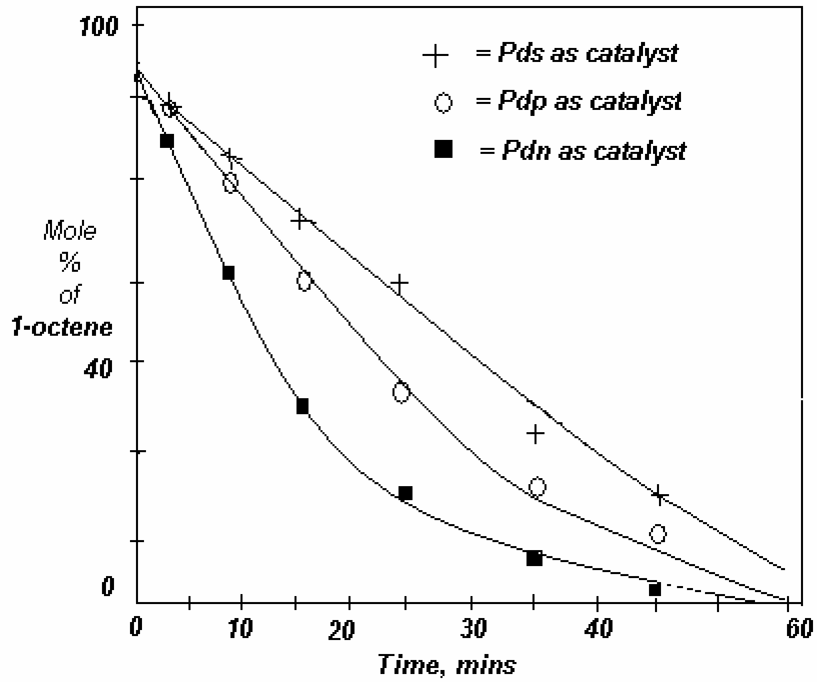

Fig.1 Normal pressure hydrogenation of 1-octene in methanol

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.. 1-octene and Hex-1-ene were reduced to the extent of 40% only and the major products were the saturated hydrocarbons with practically no isomerisation recorded(Gas Chromatography) under similar conditions as maintained for the freshly used particles. The turn over numbers(h^{-1}) calculated for the recycled colloidal nanoparticles show significant decrease in their catalytic activity(**Table 2**). Transmission Electron microscopy of the nanoparticles collected after the first hydrogenation reaction and the reused particles(after second catalytic reduction) show significant differences as far as average particle size distribution is concerned (**Fig.2**). Micrographs reveal considerable aggregation of the palladium particles on use as hydrogenation catalysts and this is reflected in the increase in average size of the particles. Palladium particles prepared from $PdCl_2$ had on an average a diameter of 4.1 ±0.98 nm. The particles collected after first cycle had average Pd size 8.1 nm with very narrow size distribution and standard deviation of 0.3. The average size of these palladium particles increased to 17.1 nm at the end of the second cycle. Lower catalytic activity observed with the reused particles in solution is due to a lower amount of palladium nanoparticles present in solution owing to aggregation and precipitation of larger particles. Poisoining of the active sites of these nanoparticles by the product mixture(saturated and isomerised hydrocarbons) could also be a reason of decreased catalytic activity. Hydrogenation of 1-octene with addition of octane (2.0 mmol) as substrate was next performed under similar conditions. As seen by GC results, presence of octane in the reaction mixture do not inhibit the catalytic hydrogenation process and reduction of 1-octene was almost quantitative as noted before. Surface poisoning of the palladium particles by the hydrogenated products has therefore been ruled out.

Table 2. Relative activity of recycled Palladium catalysts for normal pressure hydrogenation of Hex-1-ene and 1-octene in methanol.

Substrates used	Product composition	Product distribution(%) using			TON(h^{-1})		
		Pd_s	Pd_p	Pd_n	Pd_s	Pd_p	Pd_n
Hex-1-ene	Hexane	Recovery	82	42		447	316
	Hex-2-ene		12	05			
1-Octene	Octane	Recovery	70	48		503	328
	Oct-2-ene		15	05			
	Oct-3-ene		10	- -			
1-Octene[a]	Octane[a]		62	10		461	64.4
	Oct-2-ene		14	- -			
	Oct-3-ene		05	- -			

[a] Reaction performed with palladium complexes collected after second cycle.

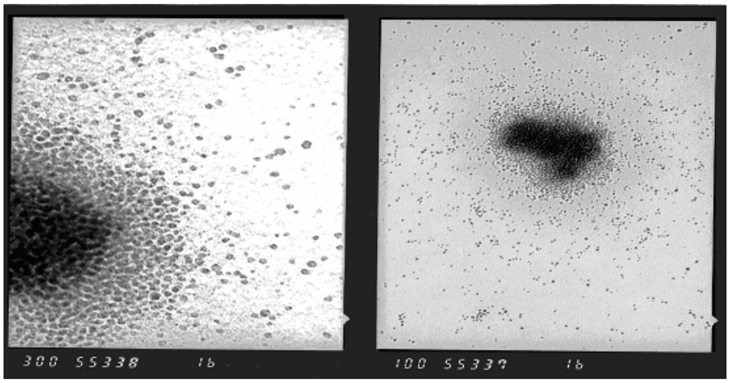

Fig.2a TEM pictures of palladium nanoparticles prepared from $PdCl_2$

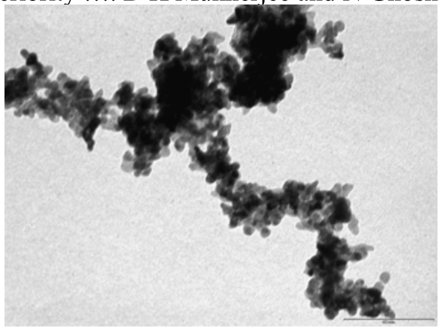

Fig.2b Particles collected after Hydrogenation of 1-octene in methanol

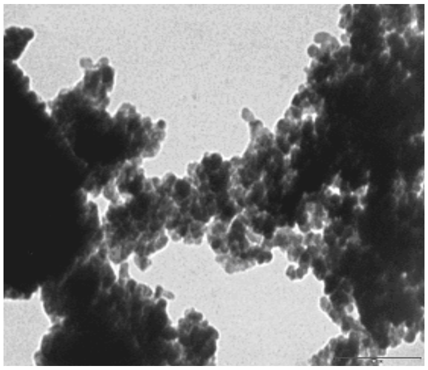

Fig.2c TEM image of the nanoparticles after the second cycle

Selective hydrogenation of unsaturated alcohols trans-Hex-2-ene-1ol and Hex-5-ene-1-ol in butan-2-ol was next performed using the present class of colloidal nanoparticles to investigate their field of application. The kinetics of the reaction was followed by GC analysis of samples taken at regular intervals of time. The results of the normal pressure hydrogenation of the mixture of two unsaturated alcohols at room temperature has been shown in **Fig.3**.

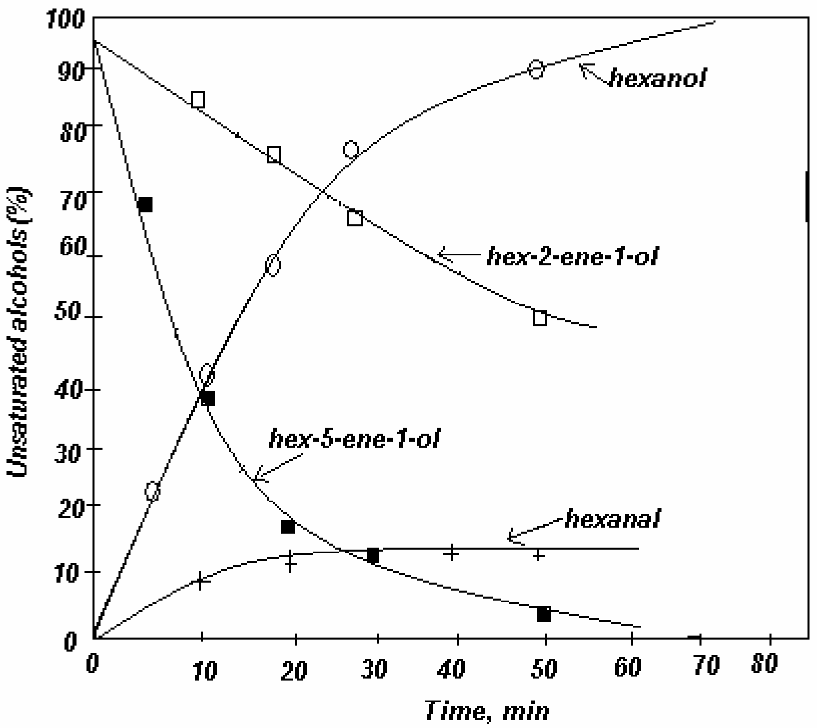

Fig.3 Hydrogenation of unsaturated alcohols by Pd-nano particles

Hydrogenation occurs with formation of hexanol as major product accompanied by small amounts of hexanal and hexane. Analysis of the reaction mixture at intervals of 10 minutes clearly shows that hex-5-ene-1-ol is reduced at a much faster rate compared to trans-hex-2-ene-1-ol where the olefinic bond is close to the polar group. It is presumed that this increase in activity for external double bond hydrogenation as compared to the internal double bond 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, it was believed that the polar hydroxyl group remains in the hydrophilic solvent media while the hydrophobic tail of the substrates extends through the hydrophobic layer and reaches the surface of the nano catalyst. Under this situation the terminal double bond which is situated at a greater distance from the polar hydroxyl group will reach the metallic surface first and therefore hydrogenated much more easily than the internal double bond. The competitive hydrogenation of the two unsaturated alcohols was also studied using soluble palladium aniline complex and the polystyrene anchored variety. In both the cases, simultaneous reduction of both the bonds take place with no preferential hydrogenation of either the internal or the terminal double bond. The ligands around the metal atom in these cases cannot create a favourable geometry which will preferentially bind either the internal or the terminal double bond resulting in no selective hydrogenation.

Conclusion

Catalytic activity of palladium is higher in Pd_n compared to Pd_s and Pd_p. The result corresponded to the nano size and highly dispersed state of the particles. Though the rate of hydrogenation of olefins is much higher using the nano catalyst, it suffers from the serious drawback of aggregation and precipitation from the reaction system. Recycling the nanoparticles is a tedious process and shows reduced catalytic property. Efforts are therefore made to disperse these particles in a medium which will suppress the phenomenon of aggregation and maintain the catalytic activity of the regenerated forms.

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References

1. G. W. Parshall, Application and Chemistry of catalyst by soluble transition metal complexes, Wiley-inter science, New York,(1980)227.
2. Y. I. Yermakov, Catal Rev., 13(1976)77.
3. D. Ducca, L.F. Leotta, G. Degnell, J. Catal,,154(1995)69.
4. D. K. Mukherjee, B. K. Palit, C.R. Saha, Indian J. Chem., 31(1992)243.
5. P. K. Santra, C.R. Saha, J. Mol. Catal.,39(1987)279.
6. T. Suji, Palladium reagents and catalysts: Innovations in Org synthesis, wiley, Chichester, 1995.
7. N. L. Holy, J. Org. Chem, 44(1979)239.
8. E. Baralt, N. L. Holy, J. Org. Chem, 49(1984)2626.
9. S. M. Islam, A.Bose, B. K. Palit, C.R. Saha, J. Catal., 173(1998)268.
10. D. K. Mukherjee, S.M. Islam, B.K. Palit, C.R. Saha, J. Mol. Catal.,124(1997)5.

11. F. R. Hartley, Supported Metal complexes, Reidel, Dordrechet, (1985).
12. C. U. Pittmann, S. K. Wu, S.E. Jacobson, J. Catal., 44(1976)87.
13. D.G. Duff, A. Baiker, Stud. Surf. Sci. Catal., 91(1995)505.
14. H. Bonnemann, R. Richards, Synth. Met Organomet Inorg. Chem., 10(2002)209.
15. M. Kralik, A. Biffis, J. Mol. Catal. A: Chem., 177(2001)113.
16. J. M. Thomas, R. Raja, Chem Rec,1(2001)448.
17. R. Narayanan, M.A. El-Sayed, J. Am. Chem. Soc., 125(2003)8340.
18. V. Chechik, R. M. Crooks, J. Am. Chem. Soc., 122(2000)1243.
19. M.T. Reetz, R. Breinbauer, K. Wanninger, Tetrahedron Lett., 26(1996)4499.
20. Y. Li, X. M. Hong, D. M. Collard, M. A. El-Sayed, Org. Lett., 2(2000)2385.
21. Y. Li, M.A. El-Sayed, J. Phys Chem. B, 105(2001)8938.
22. M.Adlin, M.A. Baker, K.Y. Liew, J. Ismail, J. Mol. Catal. A:Chemical, 212(2004)141
23. L. Strimbu, J. Liu, A. E. Kaifer, Langmuir, 19(2003)483.
24. M.T. Reetz, M. Maase, Advanced Materials, 9(1999)11.
25 D. K. Mukherjee, Indian J. Chem., 42B(2003)346.