6.1.1 Introduction

The synthesis and characterization of metal nanoparticles have attracted great attention due to their potential applications in the field of electronics, opto-electronics, biosciences and catalysis [1-4]. The development of facile synthetic methods and choice of suitable support towards the synthesis of metal nanoparticles having uniform size and controllable preparation of nanocrystals with different shapes and exposed surfaces appear to be of key importance for the exploration of new research [1-6]. In recent years, intensive approaches have been devoted to the systematic control of the crystal shapes of metal nanoparticles [7-8]. For such nanoparticles synthesis, the synthetic routes and the supports play a vital role. Organic ligands are found to be one of the best supports for the synthesis of metal nanoparticles [9-11]. Ligands stabilized metal nanoparticles or nanoclusters are considered as important building blocks to construct nano-organised systems with different shape and size [9-12]. The ligands are choosen as stabilizer by considering their donor sites affinity towards nanoparticles and also structural suitability. The physico-chemical properties of metal nanoparticles can be tuned by variations in both the nature of the ligand and size of the metal core. For the preparation of metal nanoparticles with small sizes (< 2 nm), narrow size distributions and high stability, the use of various stabilizers such as amines [13-15], thiols [16-19] and phosphines [9-11] have been extensively studied. Phosphine stabilized metal nanoparticles are excellent building blocks possessing well organized metallic cores. Schmid et al. [20] reported the Ph₃P stabilized Au°- nanoparticles prepared by reduction.
Chapter 6  

Pt$^0$-nanoparticles and its applications

of Ph$_3$PAuCl with diborane. After the development of most convenient and versatile biphasic procedure [19], the synthesis of phosphine stabilized Au$^0$-nanoparticles (d ~ 1.5 nm) is further improved [9] by reduction of HAuCl$_4$ precursor with NaBH$_4$. Different types of biphosphine ligands are also reported [10,11] for the synthesis of Pd$^0$- and Au$^0$-nanoparticles having narrow size distribution and their catalytic applications. A numbers of mono and diphosphines as well as thiols stabilized metal nanoparticles were studied but metal nanoparticles particularly Pt$^0$-nanoparticles stabilized by tripodal phosphines and its chalcogen functionalized donor ligands have not been reported so far.

In this section, the elucidation of structural suitability and ligand donor site environment of tridentate phosphines ligands [CH$_3$C(CH$_2$PPh$_2$)$_3$; P$_3$] and their corresponding chalcogen i.e. tridentate ‘Sulfur’ functionalized ligands [CH$_3$C(CH$_2$P(S)Ph$_2$)$_3$; P$_3$S$_3$] for synthesis of Pt$^0$-nanoparticles having different sizes have been described.

6.1.2 Experimental

6.1.2.1 Synthesis of Pt$^0$-nanoparticles

The Pt$^0$-nanoparticles stabilized by phosphine and sulphur functionalized ligands were synthesized by following a slightly modified procedure reported by Hutchison et al. [9] [Scheme 6.1]. 10 ml aqueous solution of K$_2$PtCl$_4$ (2.42 mmol) and 15 ml of toluene solution of tetra-n-octylammonium bromide (TOAB) (160 mg, 0.293 mmol) were taken into a two necked round bottom flask and after vigorous stirring for about 45 min, the transfer of [PtCl$_4$]$^{2-}$ anion from aqueous layer to organic layer took place. The
Chapter 6  \textbf{Pt$^0$-nanoparticles and its applications}

Complete transfer was confirmed by the color changes that occurred in the two phases i.e. the initial pale yellow color of aqueous layer became completely colorless, while the organic phase turned into pale yellow. The ligand P$_3$ or P$_3$S$_3$ (0.253 mmol) in 10 ml toluene was added to the organic phase and the resulting mixture was stirred for about 1 h (stirring was done under nitrogen atm for P$_3$ since the ligand is air sensitive). In case of P$_3$, the organic phase became white and cloudy but for P$_3$S$_3$, no color change was observed. 10 ml aqueous solution of NaBH$_4$ (134 mg, 3.54 mmol) was then added slowly to the organic phase, the reaction started immediately and the organic phase turned into yellow brown and dark grey for P$_3$ and P$_3$S$_3$ ligands respectively. The reaction mixture was stirred for another 2 h at r.t. The organic phase was separated and washed with water and the solvent was removed in vacuo to yield the solid product. The washing of the crude solid was repeated until no free ligand or phase transfer catalyst was detected by TLC and $^1$H NMR spectroscopy. The synthesized Pt$^0$-nanoparticles were designated as Pt-1 and Pt-2 for P$_3$ and P$_3$S$_3$ ligands respectively.

\textbf{6.1.3 Results and discussion}

\textbf{6.1.3.1 Characterization of Pt$^0$-nanoparticles}

During the preparation of Pt$^0$-nanoparticles, addition of the ligand P$_3$ turns the organic layer into white and cloudy because of partial reduction of Pt (II) by trivalent phosphorous atom of ligand P$_3$. On the other hand, in case of ligand P$_3$S$_3$, no color change was observed in the organic layer and the partial reduction could not be possible due to presence of pentavalent phosphorous atom [Scheme 6.1]. Finally, reduction was carried out with NaBH$_4$ to generate Pt$^0$-nanoparticles.
Scheme 6.1 Synthesis of sulfur functionalized tripodal ligands and phosphine based ligands stabilized Pt⁰-nanoparticles.

6.1.3.1 FT-IR analysis

The presences of ligands on the surface of metal nanoparticles are determined by FT-IR study [13,21]. The IR spectra of ligands $P_3$ and $P_3S_3$ after and before stabilization give slightly different band assignments [Figure 6.1 (A) and (B)]. Some of the characteristic bands, e.g. in case of ligand $P_3$, sharp peak at 1433.8 cm⁻¹, ascribed to the P-C stretching vibration mode is shifted to 1437.0 cm⁻¹ and also the most characteristic νₚₛₛ bands of ligand $P_3S_3$ at 624.6 and 611.0 cm⁻¹ are shifted very marginally to 624.0 and 610.6 cm⁻¹ respectively. This gives the evidence that the ligands are grafted on the
Chapter 6  
Pt\(^0\)-nanoparticles and its applications

surface of Pt\(^0\)-nanoparticles through phosphorous and sulphur atom of ligands P\(_3\) and P\(_3\)S\(_3\) respectively.

![Image](image.png)

**Figure 6.1** FT-IR spectra of (A) ligand P\(_3\) and Pt-1 and (B) ligand P\(_3\) and Pt-2 nanocomposites

### 6.1.3.1.2 XPS analysis

In order to ascertain the chemical oxidation state as well as to ensure the complete reduction, the samples were characterized by XPS analysis. The binding energy of Pt 4f\(_{7/2}\) in the XPS spectra of P\(_3\) ligands stabilized Pt\(^0\)-nanoparticles (Pt-1) [Figure 6.2] and P\(_3\)S\(_3\) ligands stabilized Pt\(^0\)-nanoparticles (Pt-2) [Figure 6.3] was at 72.7 and 72.1 eV respectively which are slightly higher than those of the free platinum metal [22]. The corresponding Pt 4f\(_{5/2}\) peak for Pt-1 and Pt-2 appeared at 75.8 and 75.4 eV respectively. Although the energy shift for Pt-1 and Pt-2 is slightly higher than those of the free platinum metal, but it is much lower than that recorded for the potassium tetrachloroplatinate (K\(_2\)PtCl\(_4\)) in which platinum is in +2 valence state, i.e. \(\Delta E = 2.4\) with respect to Pt (0) [23]. It is also lower than the binding energy of the platinum oxides, PtO and PtO\(_2\), observed on partially oxidized nanoparticles [22,24]. The contribution at higher energy for Pt-1 and Pt-2 is attributed to the surface platinum.
atoms linked to the phosphorous (P₃ ligand) and sulphur (P₃S₃ ligand), which is expected to induce a positive charge on the metal surface and thereby increasing the binding energies of Pt [24].

![Figure 6.2 XPS spectra of Pt-1 nanocomposites](image1)

![Figure 6.3 XPS spectra of Pt-2 nanocomposites](image2)
6.1.3.1.3 FESEM-EDX analysis

FESEM-EDX analysis also substantiated the formation of Pt⁰-nanoparticles stabilized by ligands [Figure 6.4 (A) and (C)]. Furthermore, EDX analysis [Figure 6.4 (B) and (D)] indicates the presence of Pt on the surface. This gives the evidence that the ligands are grafted on the surface of Pt⁰-nanoparticles through phosphorous and sulphur atom of ligands P₃ and P₃S₃ respectively.

![Figure 6.4](image)

**Figure 6.4** (A) SEM image and (B) EDX analysis of of Pt-1 nanocomposites; (C) SEM image and (D) EDX analysis of Pt-2 nanocomposites.

6.1.3.1.4 TEM and HRTEM analysis

The core size distributions of stabilized Pt⁰-nanoparticles were examined by TEM study [Figure 6.5 (A) and (B)]. The TEM images of both ligands P₃ and P₃S₃
Chapter 6  

Pt\(^{0}\)-nanoparticles and its applications  

stabilized Pt\(^{0}\)-nanoparticles (Pt-1 and Pt-2) showed that the particles are spherical in shape, well separated from each other and having narrow size distribution of particles 2-5 and 2-8 nm for Pt-1 and Pt-2 respectively.

The HRTEM images [Figure 6.6 (A) and 6.7 (A)] depict clearly the visible lattice fringes inside the nanoparticles and these fringes are continuously extended to the whole particles indicating the formation of crystalline Pt\(^{0}\)-nanoparticles. The corresponding selected area electron diffraction (SEAD) patterns of Pt\(^{0}\)-nanoparticles obtained by focussing the electron beam on the nanoparticles lying on the TEM grid are shown in Figure 6.6 (B) and 6.7 (B). SAED pattern, exhibited diffused rings indicating that the Pt\(^{0}\)-nanoparticles are of polycrystalline in structure.

The Pt contents in Pt-1 and Pt-2 as analyzed by ICP-AES, reveal the presence of about 0.6 wt % of Pt in both the samples.

![TEM images](image)

**Figure 6.5** TEM images of (A) Pt-1 and (B) Pt-2 nanocomposites respectively.
6.1.4 Conclusion

The effect of donor site environment of the ligands P$_3$ and P$_3$S$_3$ toward the stability of Pt$^{0}$-nanoparticles and their bonding capabilities are demonstrated. These ligands are found to be excellent stabilizer for Pt$^{0}$-nanoparticles having small core diameter (< 8 nm) and narrow size distribution. Furthermore, FT-IR and FESEM-EDX analysis confirm that the ligands are grafted on the surface of Pt$^{0}$-nanoparticles through
phosphorous and sulphur atom of ligands P$_3$ and P$_3$S$_3$ respectively. The stabilized Pt$^0$-nanoparticles are polycrystalline in nature. The work reported here points towards a new direction in the design of new ligands for the stabilization of metal nanoparticles having different shape and sizes.
Chapter 6  Pt\(^{0}\)-nanoparticles and its applications

Section 6.2  Catalytic application of Pt\(^{0}\)-nanoparticles stabilized by tripodal phosphine based ligands

6.2.1 Introduction

Chloroanilines (CAN) are important intermediate which find extensive applications in dyes, corrosion inhibitors and polymers. CAN are also used as curing agent for epoxy resins, as cross-linking agent in some polymer preparation and in urethane manufacture [25-28]. In pharmaceuticals, some CAN are used for the synthesis of tranquilizers (diazepam) and in the preparation of herbicides such as anilophos and N-isopropylamine [29,30]. Synthesis of haloaromatic amines using catalytic hydrogenation of halonitroaromatic compounds offers several advantages including the low cost of hydrogen, the ease of product separation and the advantage of nonpolluting process. Control of selectivity is the critical problem while carrying out hydrogenation of halonitroaromatics due to the tendency towards hydro-dehalogenation which cannot be avoided unless modifications are made in the process [31]. To avoid hydro-dehalogenation, one could either introduce suitable regulators to the reaction mixture such as acids, bases, sulphur, phosphorus [32-34] or modify the properties of the catalyst in a definite way like particle size and support [35-38] or use appropriate reaction conditions of temperature, pressure and so forth. The present work is an attempt to ascertain the suitable catalyst and process conditions for the hydrogenation of chloronitrobenzenes (CNB) to CAN with a view to obtaining reasonably high activity and selectivity with respect to the desired product by the utility of tripodal phosphine based ligands stabilized Pt\(^{0}\)-nanoparticles having different particle morphologies.
Chapter 6  
Pt⁰-nanoparticles and its applications

6.2.2 Experimental

6.2.2.1 General procedure for hydrogenation reaction

1 mmol (157.5 mg) of CNB was dissolved in ethyl acetate (5 ml) and 20 mg of Pt⁰-nanoparticles was added in a 50 cm³ capacity of a high pressure reactor (Parr-4592, USA) fitted with a pressure control. The reaction vessel was purged with H₂ gas for about 5 min and then pressurized with H₂ gas up to 10 ± 1 bar at room temperature (25 °C). The reaction was carried out at temperature 45 ± 5 °C for a period of 1 h at 500 rpm. The yields of the product was analyzed by gas chromatography (Chemito 8510) using BP-20 Wide bore capillary column, 30 m x 0.53 mm id x 1.0 μm film thickness and hydrogen as carrier gas.

6.2.3 Results and discussion

6.2.3.1 Catalytic application of Pt⁰-nanoparticles in hydrogenation of chloronitrobenzene to chloroaniline

The tripodal phosphine based ligands stabilized Pt⁰-nanoparticles (Pt-1 and Pt-2) having different particle morphologies were tested as a catalyst precursors for organic transformations involving the aforementioned hydrogenation of CNB [Scheme 6.2]. First, the reaction conditions were optimized using p-CNBr as a substrate. After screening with different solvents and exploring the scope of pressure and temperature, it was found that the catalysts system is most efficient for hydrogenation of CNB in ethyl acetate as a solvent at hydrogen pressure 10 bar and temperature 45 °C. Using optimized reactions conditions, the efficiency of the catalysts Pt-1 and Pt-2 were studied for hydrogenation of CNB with different chlorine substituent sites (o-, m-, or p-CNBr)
Chapter 6  
Pt\textsuperscript{0}-nanoparticles and its applications

and the results are illustrated in Table 6.1. The results revealed that all the substrates produce hydrogenation products with very good yields and high selectivity with negligible C-Cl bond cleavage. A control reaction without the presence of catalyst did not show any catalytic activity, which indicates that Pt\textsuperscript{0} is the active catalytic site.

![Scheme 6.2 Hydrogenation of chloronitrobenzenes catalysed by Pt\textsuperscript{0}-nanoparticles](image)

**Table 6.1** Hydrogenation of different chlorine substituent CNB over Pt\textsuperscript{0}-nanoparticles catalysts

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Catalyst</th>
<th>Reaction Time (h)</th>
<th>Conv. (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>CAN</td>
<td>AN</td>
</tr>
<tr>
<td>1</td>
<td>p-CNB</td>
<td>Pt-1</td>
<td>1.0</td>
<td>91.0</td>
<td>98.6</td>
</tr>
<tr>
<td>2</td>
<td>p-CNB</td>
<td>Pt-2</td>
<td>1.0</td>
<td>96.7</td>
<td>99.3</td>
</tr>
<tr>
<td>3</td>
<td>o-CNB</td>
<td>Pt-1</td>
<td>1.0</td>
<td>89.9</td>
<td>98.4</td>
</tr>
<tr>
<td>4</td>
<td>o-CNB</td>
<td>Pt-2</td>
<td>1.0</td>
<td>94.4</td>
<td>98.0</td>
</tr>
<tr>
<td>5</td>
<td>m-CNB</td>
<td>Pt-1</td>
<td>1.0</td>
<td>91.4</td>
<td>99.6</td>
</tr>
<tr>
<td>6</td>
<td>m-CNB</td>
<td>Pt-2</td>
<td>1.0</td>
<td>97.3</td>
<td>99.2</td>
</tr>
</tbody>
</table>

**6.2.4 Conclusion**

The tripodal phosphine based ligands stabilized Pt\textsuperscript{0}-nanoparticles were evaluated as catalyst in hydrogenation of CNB with different chlorine substituent sites (o-, m-, or p-CNB) with high conversion 89.9-99.6 % and selectivity 98.0-99.6 %. The work reported here points toward a new direction in the design of new ligands for the
Chapter 6

Pt\(^0\)-nanoparticles and its applications

stabilization of metal nanoparticles having narrow size range and an alternative catalyst for hydrogenation of CNB reactions.
Chapter 6  
Pt\(^0\)-nanoparticles and its applications

6.3 References


Chapter 6  

Pt⁰-nanoparticles and its applications


Chapter 6  
Pt\textsuperscript{0}-nanoparticles and its applications


