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Synthesis, Characterization and Catalytic Activity of Platinum Nanoparticles

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Abstract. The present work focuses on the synthesis and characterization of spherical, cubical and tetrahedral platinum nanoparticles. The catalytic activity in shape-dependency of Pt NPs is studied by comparing the catalytic activity of cubical Pt NPs (Pt cNPs) with tetrahedral (Pt tNPs). The Pt cNPs/Pt sNPs are synthesized by water-based process and Pt tNP is synthesized by hydrogen reduction method. The morphology of Pt colloidal particles was studied with the help of transmission electron microscopy (TEM). The reused catalyst of TEM images show modification in structure from cubical to spherical nanoparticles, imputed to the significant leaching susceptibility of Pt {100} surface facets. Tetrahedral Pt NPs are the most catalytically active, with a minimum activation energy of 12 kJ mol⁻¹. In contrast, cubic Pt NPs are the least catalytically active, with an uplifted activation energy of 23.4 kJ mol⁻¹. The reason is difference in amount of catalytically active surface atoms.

Keywords: Ascorbic acid (AA); Platinum cubical Nanoparticles (Pt cNPs); Platinum spherical Nanoparticles (Pt sNPs); Platinum tetrahedral Nanoparticles (Pt tNPs); Polyvinylpyrrolidone (PVP); Potassium bromide (KBr); Potassium chloride (KCl); Potassium hexacyanoferrate; Sodium thiosulfate.

INTRODUCTION

The field of nanocatalysis attracts the attention of researchers working in both catalysis and nanomaterials. Because of their high surface to volume ratio, nanoparticles have allowed surface scientists to increase the efficiency of their catalysts by reducing their size to the nanoscale level. Nanostructure science and technology is a broad and interdisciplinary area of research and development activity has been growing explosively worldwide in the past decades. Nanoscale materials are defined as a set of substances where at least one dimension is less than approximately 100 nanometers. Nanomaterials are of interest because at this scale, unique optical,¹ magnetic,² electrical³ and other properties emerge, with potential for great impacts in electronics⁴, medicine,⁵ and other fields. Nanomaterials have a much greater surface area to volume ratio than their conventional forms, which can lead to greater chemical reactivity and affect their strength. Porous nanostructured materials are solid networks having voids throughout the material.⁶ It can be classified depending on the diameter of their pores. According to the IUPAC, microporous (50 nm) materials are distinguished.⁷ Such porous materials were synthesized by various techniques such as chemical etching, sol-gel processing and template assisted techniques.⁸

Catalysis lies at the heart of countless chemical protocols, from academic research laboratories to the chemical industry. A variety of products, such as medicines, fine chemicals, polymers, fibers, fuels, paints, lubricants, and a myriad of other value added products essential to humans, would not be feasible in the absence of catalysts. Nanocatalysis is the emerging field in heterogeneous catalysis which can connect the homogeneous and heterogeneous catalysts and acts as greener catalysts/reagents in catalysis. Nanostructured materials have emerged as greener alternatives to conventional materials, as robust, high surface area heterogeneous catalysts⁹ and catalyst supports.¹⁰ The nano-sized particles increase the surface area of the active component of the catalyst, thereby enhancing the contact between reactants and catalyst dramatically and mimicking the homogeneous catalysts. However, their insolubility in reaction solvents renders them easily separable from the reaction mixture like

heterogeneous catalysts, which in turn makes the product isolation stage effortless. Also, the activity and selectivity of nanocatalysts can be manipulated by tailoring chemical and physical properties like size, shape and composition.

Platinum (Pt) is among the most widely used transition metals in organic synthesis. Development of high-performance Pt nanoparticles (Pt NPs) catalysts by the strategy of controlling the particle shape can be an effective way to improve the catalytic activity on a mass basis. While changing the particle size in nanoparticles (NPs), dramatic changes in reactivity and selectivity occur in catalytic reaction. For example, NPs in the size regimes of 1–10 nm are identical to the size of heterogeneous metal catalysts used as industrial catalysts. Considering the surface to volume ratio of a nanocrystal, the percentage of surface atoms of metal NPs as a function of size can be estimated. A metal atom can be surrounded by 12 atoms to become the completely shelled cluster with 13 atoms. To have n shelled atoms in an fcc structure, $10n^2 + 2$ atoms are needed for each shell, while $2n+1$ atoms on a sectional plane become a diameter of a crystal. Pt with an atomic diameter of 0.27 nm, has 92 % surface atoms when it becomes a particle with a diameter of 0.8 nm by adding one outer shell, then the surface ratios are abruptly decreased to 45 and 35% for the diameters of 3 and 4 nm, respectively. This indicates clearly that catalytic reactions undergo dramatic changes in the size ranges of less than 5 nm in terms of the surface area per a given size.

Shape also plays a key role in catalyst activity. Surface atoms of NPs have elevated surface energies, and the atoms at their edges and corners have even more surface energies, especially with three-dimensional particles. Therefore, these atoms, and in turn the NPs as a whole, are highly reactive. Based on the literature survey, the present study focuses on the synthesis and characterization of spherical and cubical platinum nanoparticles. The synthesised Pt NPs are characterized by TEM analysis. From the result, it confirms that the catalytic activity and selectivity not only depends on the size of NPs but also on their shape with a profound effect on catalytic activity, selectivity and even catalyst stability.

MATERIALS AND METHODS

Potassium chloride was purchased from Merck. Sodium tetrachloroplatinate, Ascorbic acid, Polyvinyl pyrrolidone, Potassium bromide were procured from Sigma-Aldrich. Double distilled deionised water was used as a solvent for the synthesis.

Synthesis of Cubical Pt Nanoparticles (Pt CNPS)

The Pt cNPs were incorporated by adding wet solution of Na_2PtCl_4 into the moist solution of AA, PVP, KBr and KCl. A wet solution 7.0mL containing AA, PVP, KBr and KCl was kept in a bottle (vial) and foreheated to 90°C in oil bath under magnetic stirrer for about 15 min. Afterwards, a wet solution of 2.0mL containing Na_2PtCl_4 was added along with a pipette. Then, the reaction was allowed to continue at 100°C for about 2.5h to bestow Pt cNPs. Finally, the Pt cNPs were collected by means of centrifugation and the collected Pt cNPs were washed several times with water in order to remove excess PVP, and then again redispersed in water.

Synthesis of Spherical Pt Nanoparticles (PT SNPS)

The Pt sNPs were incorporated by adding wet solution of Na_2PtCl_4 into the moist solution of AA and PVP in agreement with slight modification. A wet solution 7.0mL containing AA and PVP was kept in a bottle (vial) and foreheated to 90°C in an oil bath under magnetic stirrer. In the meantime, a wet solution of 2.0mL containing Na_2PtCl_4 was added along with a pipette. Then, the reaction was allowed to continue at 100°C for 2.5h to get Pt sNPs and the Pt sNPs were separated from the reaction mixture by means of centrifugation. And, finally the collected Pt sNPs were washed several times with water to remove excess PVP, and then again redispersed in water.

Synthesis of Tetrahedral Pt Nanoparticles (PT SNPS)

The PVP stabilized Pt nanoparticles were fabricated using the H_2 reduction method. Na_2PtCl_6 is used as a precursor and PVP as the stabilizing agent for the synthesis of Pt sNPs. A three-necked flask containing 500mL furnished with a gas trap was used for the preparation. 300 mL of doubly deionized water, 2mL of 0.03M Na_2PtCl_6 , and 0.35g of stabilizer was added to the flask. After some time interval, the solution was thoroughly mixed and the noble gas of argon was bubbled for 15min and then hydrogen gas was bubbled for 3 min. Subsequently, the flask was then closed, enfolded in aluminum foil, and stored in the dark place for about one day (24h). The product

obtained in colloidal solution was lightest brown. A drop of the colloidal solution was placed onto a carbon grid and then allowed to evaporate in air.

Study on the Catalytic Activity

The catalysts used in the reaction are PVP capped platinum nanoparticles with presiding tetrahedral shape and PVP stabilized platinum nanoparticles with presiding cubic shape. Three mL of the platinum nanoparticles, 100 μ L of 0.03M potassium hexacyanoferrate, and 200 μ L of 0.2M sodium thiosulfate were mixed together for a total volume of 3.4mL. The hexacyanoferrate (II) ions absorb at 420nm, and the progress of the reaction can be watched by the disappearance of the hexacyanoferrate (II) peak over time.

Instrumentation Techniques

The morphology of Pt colloidal particles were studied by means of transmission electron microscopy (TEM). Tecnai™ G2 spirit microscope operating at an accelerating voltage of 200kV was used to propose the morphology and size of the particles. The TEM samples were prepared by dispersing the material in ethanol by ultrasonication and dried onto a copper grid.

RESULTS AND DISCUSSION

The characterization of the platinum nanoparticles and the detailed study on the shape and catalytic activity are reported in this section.

Transmission Electron Microscopy (TEM)

For Cubical Platinum Nanoparticles (PT CNPS)

By water-based process, the Pt cNPs are prepared which involves injection of Pt²⁺ into a wet solution of ascorbic acid (AA) at 90°C along with Br⁻ and Cl⁻ ions which serves as a capping agents and polyvinylpyrrolidone (PVP) acting as a stabilizer. The halide species decrease the rate of reduction of the Pt²⁺ ions while capping with {100} facets of Pt cNPs. A cubic structure of Pt cNPs with an edge length of 12 nm, 5 nm and surfaces covered by {100} facets is obtained from the TEM images Figure.1 (a) and (b). The high crystallinity of Pt cNPs was obtained from the SAED pattern Figure.1 (c).

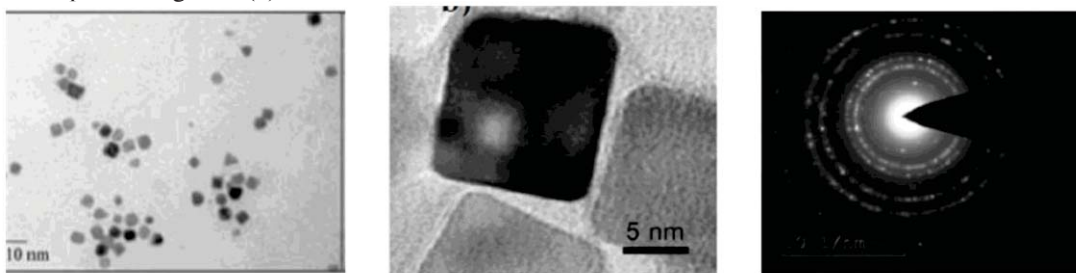


FIGURE 1. TEM image of: (a) and (b) Pt cNPs (Platinum cubical nanoparticles) and SAED pattern of: (c) Pt cNPs (Platinum cubical nanoparticles)

For Spherical Platinum Nanoparticles (PT SNPS)

The preparation of Pt sNPs was done by the reduction of Na₂PtCl₄ with AA in the aqueous solution of PVP. The stabilization, prevention and agglomeration by PVP was done by reducing Pt²⁺ ions with ascorbic acid to give Pt sNPs. TEM images clearly portrays that well-dispersed Pt NPs with particle sizes of 3-4 nm are obtained Figure.2 (a) and (b). The SAED pattern reveals that the Pt sNPs are crystalline in nature. Figure.2 (c).

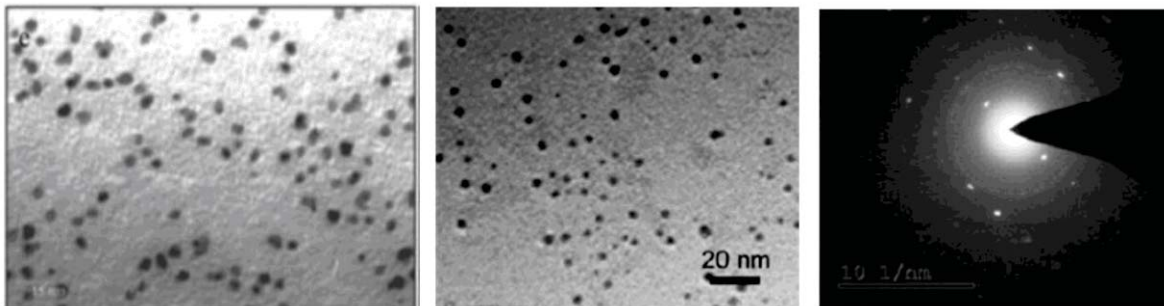


FIGURE 2. TEM image of: (a) and (b) Pt sNPs (Platinum spherical nanoparticles) and SAED pattern of: (c) Pt sNPs (Platinum spherical nanoparticles)

TEM images of reused catalyst show change in structure from cubical to spherical nanoparticles, attributed to the significant leaching susceptibility of Pt {100} surface facets.

For Tetrahedral Platinum Nanoparticles (PT TNPS)

The catalysts used in the reaction are PVP capped platinum nanoparticles with presiding tetrahedral shape and PVP stabilized platinum nanoparticles with presiding cubic shape. The most catalytically active tetrahedral Pt NPs is obtained with minimum activation energy of 10kJ mol^{-1} . A large fraction of the surface atoms on edges and corners of tetrahedral Pt NPs are composed of {111} facets. The well dispersed Pt tNPs with particle sizes of 3-4 nm are obtained from the TEM images Figure.3.

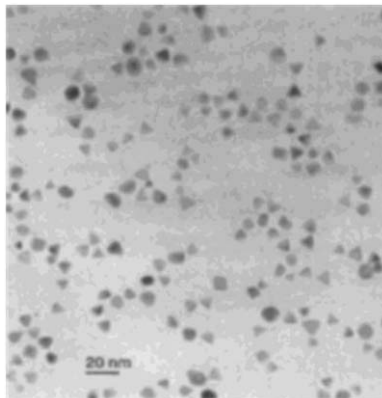


FIGURE 3. TEM image of Pt tNPs (Platinum tetrahedral nanoparticles)

The best two reason for using Tetrahedral nanoparticles as a part of my work is they have {111} facets which they are known to be the most catalytically active and they themselves are most sensitive to shape changes. They can be easily be reconstructed under chemical perturbations as they have sharp corners and edges with least surface energy. As a result, it leads to large shape changes which could be easily detected by TEM. Cubic shaped nanoparticles with their {100} facets is also considered when it is compared in addition. The edges and corners of tetrahedral particles are not as sharply pointed because the {100} facets are not as catalytically active, they probably will not be as sensitive to shape changes as the tetrahedral particles.

Studies on the Effect of the Catalytic Reaction

The catalysts used in the reaction are PVP capped platinum nanoparticles with presiding tetrahedral shape and PVP stabilized platinum nanoparticles with presiding cubic shape. $100\ \mu\text{L}$ of $0.03\ \text{M}$ potassium hexacyanoferrate and $200\ \mu\text{L}$ of $0.2\ \text{M}$ sodium thiosulfate were mixed together for a total volume of $3.4\ \text{mL}$. The hexacyanoferrate (II) ions absorb at $420\ \text{nm}$, and the progress of the reaction can be watched by the disappearance of the hexacyanoferrate (II) peak over time. The first cycle of the reaction was completed by the complete disappearance of the hexacyanoferrate (II) peak. For, beginning the second cycle of the reaction, $2\ \mu\text{L}$ of $2\ \text{M}$ potassium hexacyanoferrate

and 2 μL of 2M sodium thiosulfate was added to the mixture at that time a new total volume of 3.404 mL is obtained as a result, there is very little difference in the concentration of the nanoparticles during the second cycle compared to the first cycle. So, it is made very possible to compare the stability of the nanoparticles before the first cycle, after the first cycle and after the second cycle (Figure 4).

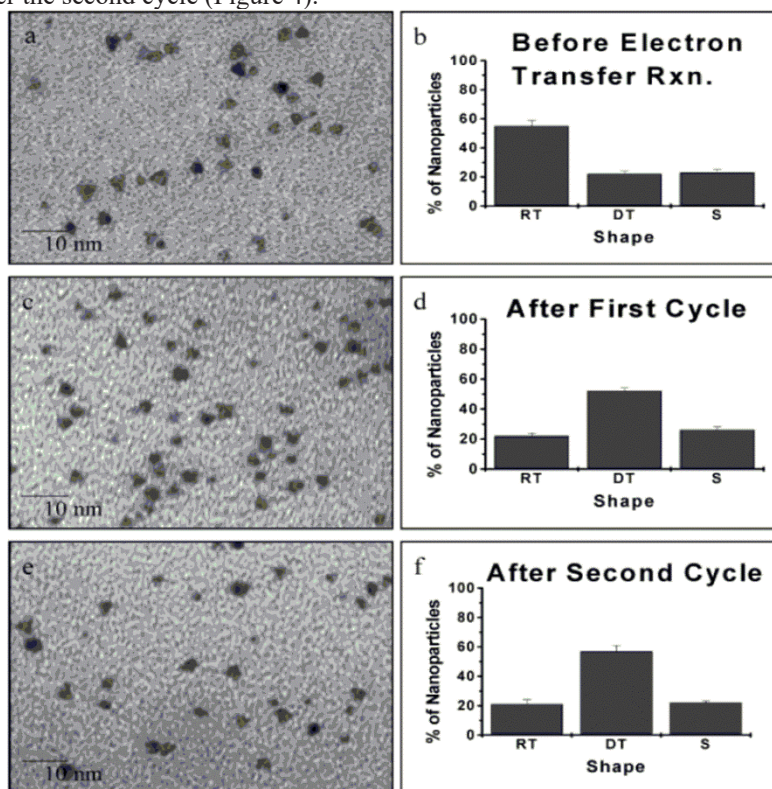


FIGURE 4. TEM image and shape distribution graph of dominant tetrahedral PVP-Pt nanoparticles before electron-transfer reaction (a-b), after first cycle (c-d) and after second cycle (e-f) [(RT regular tetrahedral, DT distorted tetrahedral, and S spherical)].

From the study, it has been found that the nanoparticles decrease slightly in size after the first and second cycle of the electron-transfer reaction between hexacyanoferrate (II) ions and thiosulfate ions which is catalyzed by spherical PVP-Pt nanoparticles. The decrease of nanoparticle size in the presence of hexacyanoferrate (II) ions alone but their size in the presence of thiosulfate ions is also maintained by the nanoparticles. This is mainly due to the reaction between hexacyanoferrate (II) ions and the surface Pt atoms of the nanoparticle which results to form cyanide complexes. The mechanism involves thiosulfate ions binding to the nanoparticle surface followed by the reaction with hexacyanoferrate (II) ions via collisional methods.

The addition of Hexacyanoferrate (II) ions itself has the capability to change the tetrahedral and the cubic shapes much more effectively than the ions present in the reaction mixture. This examination supports the work that the thiosulfate is adsorbed on the nanoparticle and is giving more protection from the direct hexacyanoferrate attack on the surface platinum atoms. The thiosulfate protects the particle surface by capping it as well as by reacting with the hexacyanoferrate (II) ions entering the surface. The catalysis mechanism must thus involve the reaction of hexacyanoferrate (II) ions in solution with the adsorbed thiosulfate species.

CONCLUSION

The present investigation deals about the synthesis and characterization of platinum nanoparticles by water-based process and hydrogen reduction method. The investigation is mainly focussed on the shape-dependency in catalytic activity of spherical, cubical and tetrahedral platinum nanoparticles. The morphology of Pt colloidal particles was studied by means of transmission electron microscopy (TEM). Besides capping the {100} facets of Pt cNPs/Pt sNPs, the halide species decrease the rate of reduction of the Pt^{2+} ions. TEM images of the Pt cNPs/ Pt sNPs

indicate a cubic/spherical structure with an edge length of 12 nm and particle sizes of 3-4 nm with surfaces covered by {100} facets. The SAED pattern reveals that the Pt cNPs /Pt sNPs are highly crystalline. The slight decrease in yield on reuse is attributed to the shape sensitivity of Pt{100} facets, which further leads to structural change from cubic to spherical.

Our results also demonstrate that using the same capping material, the same salt, the same temperature, and the same solvent with slight modification produces tetrahedral shape of Pt nanoparticles. The most catalytically active nanoparticle was the tetrahedral Pt NPs, with minimum activation energy of 10kJ mol⁻¹. Similarly, the least catalytically active nanoparticles was found to be cubic Pt NPs, with an elevated activation energy of 24.4 kJ mol⁻¹. The reason is difference in amount of catalytically active surface atoms. A change in the shape distribution with dominant tetrahedral or cubic nanoparticles occurs with the change occurring faster for the tetrahedral particles during the catalysis reaction. The result clearly indicates that the tetrahedral nanoparticles, with sharper edges and corners, are more sensitive and more liable to changes in shape during nanocatalysis than the cubic particles. It also, implements that the addition of Hexacyanoferrate (II) ions itself has the capability to change the tetrahedral and the cubic shapes much more effectively than the ions present in the reaction mixture. Exposure to the other reactant, thiosulfate ions, is believed to cap and protect the nanoparticles against dissolving their surface platinum atoms on the corners and edges by the hexacyanoferrate (III) ions. Thus, the nanoparticles proposed in this study may shed some light on future application.

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