Abstract

The increasing demand of nanotechnology for its emerging applications in diverse area treasures the most dynamic and prevailing research area in the current field of science and technology. From the catalysis perspective, ‘nanocatalysis’ i.e. the study of catalysis in nanoscale regime plays significant role in the arena of chemical transformations. Fundamentally, nanoparticles have the dimension between 1-100 nm have gained much interest in scientific research and industrial fields for their improved catalytic activity. From the last few decades, several methodologies have been developed for the synthesis of different metal and metal oxide nanoparticles with controlled size, shape and morphology. Therefore, the present thesis aims at the development of Pd-based metal nanoparticles for their different environmental and energy related applications such as waste-water treatment and fuel cell reactions.

Pd-based metal nanoparticles have attracted great deal of attention because of their growing applications in various fields such as catalytic reforming, organic transformations, chemical synthesis, biological and energy related reactions etc. Considerable efforts have been given in the recent years to design and characterize the Pd-based nanoparticles. Bimetallic nanoparticles comprising of two different metals have finds more research interest in current days due to their enhanced catalytic activity compared to their monometallic counterparts which is attributed to the ensemble/synergistic effect. In recent years, various methods have been developed to synthesize different Pd-based alloy nanoparticles such as PdCu, PdNi, PdCo, PdFe, PdAu using different methods like electrodeposition, microemulsion, polyl, solvothermal/hydrothermal, mechanical alloying etc. Metal nanoparticles supported on suitable metal oxide structures have attracted attention for their stability, large surface area and high selectivity and surface permeability which results in improved catalytic activity. The choice of support plays a critical role for determining the catalytic activity of metal nanocatalysts. Cerium oxide (CeO₂) is widely investigated as support material in different areas because of their unique Ce⁴⁺/Ce³⁺ redox couple. Thus, the main goal of the present investigation is the development of Pd-based nanoparticles with complete structural characterization and to evaluate their catalytic activity for environmental and energy applications. A considerable amount of research is being
conducted on fuel cells as a clean, alternative energy source. Proton exchange membrane fuel cells (PEMFCs) are getting more attention due to their high energy density, convenient operations and friendly environmental characteristics. However the use of expensive and rarely available Pt electrocatalyst in PEMFCs made the researchers interested about the findings of alternative of Pt electrocatalyst. Eventually, the search for new materials for the Oxygen reduction reactions (ORR), a sluggish reaction that occurs in the cathode which requires high content of Pt is a major concern.

The contents of the thesis are broadly divided into six chapters. Chapter 1 includes the introduction part and Chapter 2 summarizes the details of experimental procedures, materials used and the characterization techniques. Chapter 3, Chapter 4 and Chapter 5 include the results and discussion of the present investigation. Conclusions and future scopes of this thesis are presented in Chapter 6.

Chapter 1: Introduction
A general introduction to nanotechnology, importance and their emerging applications in diverse areas are described in the chapter 1. The present chapter includes an overview on the use of nanoparticles in catalysis as well as the importance of various metallic nanoparticles along with suitable review of the existing literature. The advantages of bimetallic nanoparticles and supported catalysts are well elaborated. The present work mainly focused on the Pd-based metal nanoparticles with efficient catalytic activity. The key properties of Pd-based bimetallics and cerium oxide are discussed herein. The chapter comprises briefly the applications of metallic nanoparticles on different environmental and energy related application such as wastewater treatment, fuel cell reactions etc. Furthermore, the chapter describes extensive literature reviews on the applications of Pd-based nanoparticles for aqueous phase reduction reactions and electrocatalytic applications. At the end of this chapter, the final objectives for the present investigation are highlighted.

Chapter 2: Experimental
This chapter provides the details of the materials that are used in this entire work. All the experimental methods for the synthesis of nanoparticles and the reaction
procedures to evaluate the catalytic activities are described herein. Moreover, the present chapter also contains the details of the different analytical tools and techniques that have been used to characterize the synthesized nanoparticles.

**Chapter 3: Composition Dependent PdM (M = Cu, Co, Ni) Nanoparticles for Aqueous Phase Reduction Reactions**

Chapter 3 describes the synthesis and characterization of different composition of PdM (M = Cu, Co, Ni) nanoparticles for their activity toward aqueous phase reduction reactions such as reduction of nitroaromatics and hexavalent chromium at room temperature. This chapter is divided into three sections, viz., Section 3A, Section 3B and Section 3C as described below:

**Section 3A: Composition Dependent Pd\textsubscript{x}Cu\textsubscript{10-x} (x = 1, 2, 3) Nanoparticles for Reduction of Nitroaromatics and Hexavalent Chromium**

In this section of the Chapter 3, we have discussed the synthesis of different compositions of Pd\textsubscript{x}Cu\textsubscript{10-x} (x=1, 2, 3) nanoparticles (NPs) i.e. Pd\textsubscript{1}Cu\textsubscript{9}, Pd\textsubscript{2}Cu\textsubscript{8}, Pd\textsubscript{3}Cu\textsubscript{7} and monometallic Pd and Cu via a modified hydrothermal route without adding any surfactant. The synthesized nanoparticles were characterized by different analytical and spectroscopic techniques for instance XRD, SEM/EDX, BET surface area, TEM, XPS etc. The catalytic activities were discussed for the aqueous reduction of nitroaromatics, such as, 4-nitrophenol and 4-nitroaniline; and reductive conversion of toxic Cr(VI) to less toxic Cr(III) at room temperature. Among the different compositions, Pd\textsubscript{1}Cu\textsubscript{9} NPs exhibited better catalytic activity for the reduction of 4-nitrophenol in terms of rate constant and reduction time. The effects of different parameters on the reduction reaction such as catalyst dosage and the concentration of reducing agent are also addressed. The catalytic activity for the reduction of 4-nitroaniline and the conversion of toxic Cr(VI) to less toxic Cr(III) over Pd\textsubscript{1}Cu\textsubscript{9} NPs are also included in this section. The catalyst shows high stability and good reusability for all the reactions. Thus, the investigation provides the development of very effective PdCu bimetallic nanoparticles for the application in waste-water treatment.
Section 3B: Synthesis, Characterization and Catalytic Evaluation of Pd$_x$Ni$_{10-x}$ (x=1, 2, 3) Nanoparticles for Reduction Reactions

Section 3B describes a facile strategy for one pot template free synthesis of bimetallic Pd$_x$Ni$_{10-x}$ (where x=1, 2, 3) alloy NPs. The synthetic procedure involves template free, economically feasible hydrothermal route with low palladium content. The synthesized NPs were characterized by different spectroscopic and analytic techniques such as powder XRD, SEM/EDX, BET-surface area analysis, TEM and XPS analysis etc. The Pd$_x$Ni$_{10-x}$ nanoparticles exhibited enhanced catalytic activity for the reduction of nitroaromatics in aqueous phase. The catalyst also exhibited remarkable catalytic activity towards reductive conversion of toxic Cr(VI) at room temperature. Structural and morphological characterizations reveal the formation of tiny alloy nanoparticles with a diameter range 3-4 nm. The catalyst has long-term stability for the aqueous phase reduction reactions as they showed very good recyclability and conversion for each reaction. Thus, the bimetallic Pd$_x$Ni$_{10-x}$ alloy nanoparticles are expected to be promising candidates for a wide variety of catalytic applications.

Section 3C: Pd$_x$Co$_{10-x}$ (x=1, 2, 3) Nanoparticles as Efficient Catalysts for Reduction of Various Nitroaromatics

In this section, we have discussed the synthesis of bimetallic Pd$_x$Co$_{10-x}$ (where x=1, 2, 3) nanoparticles by hydrothermal route. The structural and morphological analysis synthesized NPs were examined by different spectroscopic and analytic techniques. The Pd$_x$Co$_{10-x}$ nanoparticles exhibited significant catalytic activity for the reduction of different water pollutants such as nitroaniline, nitrophenols present in waste-water. The catalyst exhibited very good recyclability and conversion without any significant loss for the reduction reactions. Thus, the synthesized bimetallic PdCo nanoparticles are effective in the field of environmental applications.

Chapter 4: Synthesis, Characterization and Activity Studies of CeO$_2$; Pd/CeO$_2$ and PdM/CeO$_2$ (M = Cu, Co, Ni) Nanoparticles

Chapter 4 describes the synthesis and characterization of cerium oxide (CeO$_2$) nanoparticles using three different precursors as well as the Pd/CeO$_2$ and PdM/CeO$_2$ (M = Cu, Co, Ni) nanoparticles for different catalytic applications. Depending on the
synthesized material this chapter has been divided into three sections as described below:

**Section 4A: CeO₂ Nanoparticles and Their Radical Scavenging Activity**
This section contains the synthesis and characterization of different ceria (CeO₂) nanoparticles using ammonium oxalate, ammonium bicarbonate and sodium hydroxide as precipitants. Synthesized CeO₂ nanoparticles were characterized by thermogravimetric analysis, X-ray diffraction, Fourier-transform infrared spectorscopy and Raman spectroscopy, scanning electron microscopy, energy-dispersive X-ray analysis, transmission electron microscopy, Brunauer-Emmett-Teller surface area analyses and X-ray photoelectron spectroscopy etc. The characterization results reveal the formation of cubic phase of CeO₂ with particles sizes of 10 nm and a remarkably large BET surface area of 236.8 m²/g. To investigate the redox property of Ce⁴⁺/Ce³⁺ couple which has remarkable significance in catalysis we have carried out DPPH and hydroxyl radical scavenging activity that is to assess the antioxidant property of nanoceria by a simple *in-vitro* spectrophotometric approach.

**Section 4B: Pd/CeO₂ Nanoparticles for Room Temperature Chemo-selective Reduction of Nitroaromatics**
Synthesis of Pd/CeO₂ nanoparticles via two step modified hydrothermal route and their structural properties and catalytic activity are discussed herein. The synthesized nanoparticles performed remarkable catalytic activity toward the chemoselective reduction of different nitroaromatics at room temperature with efficient yields. A kinetic study explains that the reaction follows pseudo-first order kinetics. The catalyst is found to remain active without any significant loss after several reaction cycles. Thus, the present investigation suggests a simple, economically feasible chemical route to synthesize very active, reusable, environmentally friendly cerium oxide stabilized Pd nanoparticles for the reduction of nitroaromatics at room temperature.

**Section 4C: Synthesis and Characterization of PdM/CeO₂ (M= Cu, Co, Ni) Nanoparticles and Their Catalytic Evaluation**
This section describes the complete characterization of PdM/CeO₂ (M= Cu, Co, Ni) nanoparticles along with their catalytic activity. A series of porous CeO₂ stabilized
PdCu nanoparticles are synthesized by a modified hydrothermal method and applied for catalytic reductive degradation of organic dyes. Catalytic studies show that the synthesized nanoparticles can efficiently reduce model azo dyes, methyl orange (MO) and congo red (CR) with good recyclability. Among various PdCu compositions, Pd$_1$Cu$_9$/CeO$_2$ exhibits superior catalytic activity toward reductive degradation of MO and CR at room temperature. Thus, Pd$_1$Ni$_9$/CeO$_2$ and Pd$_1$Co$_9$/CeO$_2$ nanoparticles were also synthesized, characterized and investigated their activity for the reduction of nitroanilines. Hence, PdM/CeO$_2$ (M= Cu, Co, Ni) can be accepted as potential component for the application in wastewater treatment.

Chapter 5: PdM/C (M = Cu, Ni, Co) Nanoparticles for Electrochemical Oxygen Reduction and Oxygen Evolution Reactions
This chapter describes the synthesis and characterization of carbon (Vulcan XC-72R) supported PdM (M = Cu, Ni, Co) nanocatalysts and their applications for the oxygen reduction reaction in fuel cells. The chapter has been divided into three sections, viz., Section 5A, Section 5B and Section 5C as described below:

Section 5A: Tuning the Electrocatalytic Activity of PdCu/C Nanoparticles toward Oxygen Reduction and Oxygen Evolution Reactions
Section 5A includes the complete synthesis, characterization of composition dependent PdCu/C nanoparticles for oxygen reduction reaction (ORR), a sluggish reaction occurs at the cathode of a fuel cell that requires high Pt-content electrocatalyst. They exhibited enhanced catalytic activity for ORR compared to the commercially available Pd/C and Pt/C nanocatalysts. Furthermore, the catalysts are also very active for oxygen evolution reactions (OER). The morphological and the structural propertied of the synthesized nanoparticles were investigated by powder XRD, BET surface area, EDX, ICP-OES, TEM and HRTEM and XPS analysis etc. Thus, the present work reports a new way for enhancing the catalytic activity of Pd-based nanoparticles alloyed with low cost transition metal Cu towards ORR in alkaline medium.
Section 5B: Composition Dependent Electrocatalytic Activity of PdNi/C Nanoparticles

This section continues with the synthesis and complete characterization of three different compositions of PdNi/C NPs, viz., Pd$_3$Ni/C, PdNi/C and PdNi$_3$/C and investigated their electrocatalytic activity for oxygen reduction reaction (ORR). The Pd$_3$Ni/C exhibited enhanced electrocatalytic activity toward ORR giving the electron transfer number 4.1 suggesting that the reaction proceeds by 4e⁻ pathway. The electrocatalytic activity of Pd$_3$Ni/C NPs is also evaluated for oxygen evolution reaction (OER). Thus, the synthesized carbon supported bimetallic PdNi nanoparticles can be accepted as a potential candidate for the application of fuel cell reactions.

Section 5C: Synthesis and Characterization of PdCo/C Nanocatalysts and Their Electrochemical Activity

Section 5C continues with the solvothermal synthesis of PdCo/C NPs with three different compositions. The oxygen reduction and oxygen evolution reaction activities of the synthesized PdCo/C NPs are also addressed herein. As in the previous section, the ORR activity is found to be improved with the high content of Pd that is for Pd$_3$Co/C, we have also conducted OER activity. The mass specific activities are highly impressive and the catalyst is found to be quite stable after 1000 cycle. The results are compared with the commercially available Pd/C and Pt/C nanocatalysts.

Chapter 6: Conclusions and future scopes

This chapter describes the overall conclusions and also the summary of the major findings of the experiments with the significance of the work. The future scopes of the present investigation are also highlighted in this chapter.