Chapter 7 Summary, Conclusions and Future scope

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7.1 Summary

This thesis describes the modification of naturally occurring montmorillonite by activating with mineral acids to create a porous clay matrix with pores in the nano dimension. Nanoparticles of metals (Cu\textsuperscript{0}, Ni\textsuperscript{0} and Pt\textsuperscript{0}) have been generated in the nanopores of activated clay matrix and characterized using powder XRD, SEM-EDX, HRTEM, XPS, N\textsubscript{2}-absorption analysis etc. Bottom-up fabrication of self-assembly Pt\textsuperscript{0}-nanoclusters by stabilizing with phosphine based organic ligands and their characterizations are also reported. The catalytic activities of supported metal nanoparticles in oxidation of some important aromatic alcohols to corresponding carbonyl compounds, hydrogenation of some aromatic carbonyl compounds to corresponding alcohols, hydrogenation of chloronitrobenzenes to chloroanilines and four component Hantzsch condensation reaction of aldehydes, dimedone, ethyl acetoacetate and ammonium acetate to yield polyhydroquinoline are described. A brief summary of the work and general conclusions arrived at from the work are presented.

Chapter 1: This chapter describes the basic concept, development and importance of nanoscience and nanotechnology. The different properties, types, synthesis methodologies and applications of metal nanoparticles are also demonstrated. The roles of different supports / stabilizers used for stabilization of nanoparticles are also described. Finally, the aims of the thesis are outlined briefly.
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Chapter 2: In this chapter the details procedure of different experiments like purification, modification and characterization of montmorillonite clay matrix are described. This also includes the procedures for functionalization of a phosphine based ligands. The different instrumental techniques adopted to characterize the different materials and catalytic reaction products have also been demonstrated in the chapter.

Chapter 3: This chapter deals with modification of montmorillonite to generate matrix of high surface area with pores in nano domain. The synthesized Cu⁰-nanoparticles and their characterization with different standard analytical techniques like UV-Visible spectroscopy, Powder XRD, FT-IR, SEM-EDX, HRTEM, N₂ adsorption, XPS analysis etc. have also been demonstrated. The applications of the Cu⁰-nanoparticles as catalyst in the oxidation of some important aromatic alcohols to corresponding carbonyl compounds have been described. The recyclability of the catalysts for several runs are also described.

Chapter 4: This chapter discusses the synthesis of Ni⁰-nanoparticles supported on nanopores of modified montmorillonite and their characterization with different standard analytical techniques like UV-Visible spectroscopy, Powder XRD, SEM-EDX, HRTEM, N₂ adsorption, XPS analysis etc. The utilization of Ni⁰-nanoparticles as efficient catalysts for transfer hydrogenation of acetophenone to 1-phenylethanol, hydrogenation of chloronitrobenzenes to chloroanilines and four component Hantzsch condensation reaction of aldehydes, dimedone, ethyl acetoacetate and ammonium acetate to yield polyhydroquinoline derivatives are described. The recyclability of the catalysts for several runs are also described.
Chapter 5: This chapter discusses the in situ generation of Pt⁰-nanoparticles into the nanopores of acid activated montmorillonite and their catalytic activity in hydrogenation of chloronitrobenzenes to chloroanilines and transfer hydrogenation of some aromatic carbonyl compounds to corresponding alcohols. The characterization of Pt⁰-nanoparticles by Powder XRD, FESEM-EDX, HRTEM, N₂ adsorption, XPS etc. analyses are also described. The recyclability of the catalysts for several runs are also described.

Chapter 6: In this chapter the synthesis of Pt⁰-nanoparticles stabilized by tripodal phosphine based ligands and their characterization with different standard analytical techniques like FT-IR, FESEM-EDX, HRTEM, XPS analysis etc. are described. The utilization of Pt⁰-nanoparticles as efficient catalysts for hydrogenation of chloronitrobenzenes to chloroanilines reactions is described.

Chapter 7: This chapter summarizes the interesting results of the research activities carried out and recommends future scope of work.

7.2 Conclusions

(i) Naturally occurring montmorillonite was modified by activation with mineral acid under controlled condition to achieve high surface area, pore volume and pore size size distribution in the nano domain. The pores act as “Host” for nanoparticles formation and also to control size by limiting the growth of the particles up to sizes of the pores.

(ii) Cu⁰-nanoparticles of size 1-10 nm were synthesized into the nanopores by impregnating with Cu(CH₃COO)₂ into the pores of acid activated montmorillonite
followed by NaBH₄ reduction. Electron microscopy as well as other analytical
techniques confirms the formation of Cu⁰-nanoparticles. The synthesized Cu⁰-
nanoparticles exhibit fcc crystal lattice form and single crystallinity.

(iii) The synthesized supported Cu⁰-nanoparticles were found excellent catalytic activity in oxidation of some important aromatic alcohols to corresponding carbonyl compounds with very good conversion and selectivity. The used catalyst were recovered and found active for several runs without significant loss of activity.

(iv) Ni⁰-nanoparticles of size 2-8 nm were synthesized into the nanopores by impregnating with Ni(CH₃COO)₂ into the pores of acid activated montmorillonite followed by polyol reduction. Electron microscopy as well as other analytical techniques confirms the formation of Ni⁰-nanoparticles. The synthesized Ni⁰-nanoparticles are polycrystalline and crystallized in fcc crystal lattice system. These nanoparticles demonstrated high catalytic activities in transfer hydrogenation of acetophenone to 1-phenylethanol, hydrogenation of chloronitrobenzenes to chloroanilines and four component Hantzsch condensation reaction of aldehydes, dimedone, ethyl acetoacetate and ammonium acetate to yield polyhydroquinoline derivatives. Further, the nanocatalysts were reused for new batch of reactions without significant loss of their activity.

(v) The nanopores of acid activated montmorillonite provided the space for Pt⁰-
nanoparticles formation and limited their growth upto desired size range. The Pt⁰-nanoparticles were spherical in shape and size in the range 0-10 nm. These
nanoparticles demonstrated high catalytic activity in hydrogenation of chloronitrobenzenes to chloroanilines and transfer hydrogenation of some aromatic carbonyl compounds to corresponding alcohols with good to excellent yields and high selectivity. Further, the nanocatalysts were reused for new batch of reactions without significant loss of their activity.

(vi) The effect of donor site environment of tripodal phosphine based 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. The Pt$^0$-nanoparticles show excellent catalytic activities for hydrogenation of chloronitrobenzenes to chloroanilines reactions which are widely used in organic synthesis.

7.3 Future scope

Although, in the recent time, there are considerable advancements in the field of nanoscience and nanotechnology particularly in synthesis and utilization of various metal nanoparticles, but the field is still thirsty and there is a high scope of scientific research. Some of the future scopes of investigations are highlighted below:

(i) The acid activated montmorillonite acts as an environmentally benign, cheap, easily available and robust support for Cu$^0$, Ni$^0$ and Pt$^0$-nanoparticles. Therefore, such clay matrix may be used as supports for other metals such as Fe, Co, Sn, In, Os etc.
(ii) There is a high scope to design a set of new and novel ligands system for the stabilization of different metal nanoparticles having narrow size range, which may give a new direction in the area of synthesis and utilization of metal nanoparticles.

(iii) Due to robust character of Cu\(^{0}\)-nanocatalyst supported on acid activated montmorillonite as well as environmentally friendly reaction conditions make it attractive for the large scale synthesis of biologically active molecules, important drug intermediates, etc. and also may be used as catalyst precursors for other important organic reactions such as A\(^3\) coupling, C-H activation etc.

(iv) The operational simplicity and robustness of modified montmorillonite supported Ni\(^{0}\)- and Pt\(^{0}\)-nanoparticles provide great promise towards further useful applications in other nickel and platinum promoted transformations in the future.