Chapter-6
Summary, Conclusions and
Future scope
6. Summary and Future scope

6.1 Summary

This thesis describes the modification of naturally occurring montmorillonite clay by treatment with both mineral and organic acid to create a porous clay matrix with high surface area and pores in the nano domain. Nanoparticles of metals (Fe and Pd) have been generated into the nanopores of acid activated clay and characterized using powder XRD, SEM-EDX, HRTEM, XPS, VSM, H\textsubscript{2}-TPR, N\textsubscript{2}-sorption analysis etc. The synthesized metal nanoparticles were evaluated as heterogeneous catalyst in oxidation, hydrodechlorination and semihydrogenation reactions. Two heterogeneous Rh-catalyst were synthesized by functionalization of modified montmorillonite clay followed by immobilization with different N~O donor ligands and finally anchoring a Rh(I) carbonyl complex to it and catalytic activities have been undertaken. A brief summary of the work and general conclusions arrived at from the work are listed below.

Chapter 1

This is a introductory chapter where review of literature of nanoscience and nanotechnology, historical development, properties of nanomaterials and its importance in modern day to day life have been described. The different approaches for synthesis of nanomaterials, the role of different stabilizers/supports in the synthesis of nanoparticles and their potential application have been demonstrated. This chapter also deals with the review of literature regarding Rh complexes of N~O donor ligands
and their applications in homogeneous catalysis like carbonylation of methanol. Finally, the aims and objectives of the thesis are also outlined briefly.

Chapter 2

This chapter deals with the details procedure of different experiments like purification, modification and characterization of Montmorillonite clay matrix. The details experimental procedures for the synthesis of supported Pd and Fe nanoparticles and general procedures of catalytic reactions have also been illustrated. This chapter also describes the synthesis of Rh(I) complex and anchoring it to functionalized montmorillonite, its application as heterogeneous catalyst for carbonylation reactions. The different instrumental techniques adopted to characterize the different materials and catalytic reaction products are also described.

Chapter 3

This chapter discusses on green synthesis, characterization and catalytic activity of montmorillonite supported Pd-nanoparticles. This chapter is divided into two sections.

Section 3.1. This section discusses the acid activation of purified montmorillonite clay with HCl under controlled condition for generating high surface area and nanopores of desired sizes. The Pd nanoparticles of sizes 10-80 nm were generated by the reduction of $K_2[PdCl_4]$ impregnated on acid activated montmorillonite clay by incipient wetness impregnation technique. The reduction of the $PdCl_4$-montmorillonite clay composites were carried out using aqueous *Ocimum sacctum* leaf extract. The characterization of
activated montmorillonite clay and the Pd-montmorillonite nanocomposites (PdNP@AT-mont.) by standard analytical techniques like Powder X-ray diffraction (PXRD), FTIR, SEM-EDX with elemental mapping, NH$_3$-TPD, HRTEM, H$_2$-TPR, XPS, N$_2$ - sorption analysis have also been described. The synthesized PdNP@AT-mont. as a heterogeneous catalyst has been demonstrated in the hydrodechlorination of hazardous 4-Chlorophenol.

Section 3.2 This section discusses the acid activation of purified montmorillonite clay with HCl under controlled condition for generating high surface area and nanopores of desired sizes. The Pd nanoparticles were generated by the reduction of Pd(AcO)$_2$ impregnated on acid activated montmorillonite clay by incipient wetness impregnation technique. The reduction of the Pd-montmorillonite clay composites were carried out using microwave assisted polyol method. The characterization of activated montmorillonite clay and the Pd-montmorillonite nanocomposites (Pd$^0$@AT-mont.) by standard analytical techniques like Powder X-ray diffraction (PXRD), FTIR, SEM-EDX with elemental mapping, NH$_3$-TPD, HRTEM, H$_2$-TPR, XPS, N$_2$ - sorption analysis have also been described. The synthesized Pd$^0$@AT-mont. as a heterogeneous catalyst has been demonstrated in the semihydrogenation of aromatic alkynes.

Chapter 4

This chapter contains the description of synthesis, characterization and catalytic activity of montmorillonite supported Fe$_3$O$_4$ magnetic nanoparticles. It also discusses the generation of nanopores and stabilization of Fe$_3$O$_4$ magnetic
nanoparticles in the nanopores of modified montmorillonite clay. Fe$_3$O$_4$ magnetic nanoparticles have been synthesized by impregnation of FeCl$_3$.6H$_2$O into the nanopores of activated montmorillonite by incipient wetness impregnation technique followed by reduction with sodium borohydride. PXRD, SEM-EDX with elemental mapping, TEM, VSM, AAS, N$_2$-sorption, XPS analyses etc. were carried out to characterize the Fe$_3$O$_4$ magnetic montmorillonite clay nanocomposite (Fe$_3$O$_4$@AT-mont). The synthesized Fe$_3$O$_4$@AT-mont is used as efficient heterogeneous “green” catalysts in the Baeyer-Villiger oxidation of some cyclic and aromatic ketones to corresponding esters.

**Chapter 5**

This chapter describes the functionalization of modified montmorillonite clay thereby immobilizing it with different N−O donor ligands and finally anchored a Rh(I) carbonyl complex to it. The modification of montmorillonite clay was done by using an organic acid i.e. formic acid and its functionalization by 3-(aminopropyl) trimethoxy silane (APTMS). The material after each step are characterized by C, H, N elemental analysis, FT-IR, PXRD and N$_2$- sorption isotherm. This chapter also discusses the synthesis of Rh(I) dimer precursor complex [Rh(CO)$_2$Cl]$_2$.

The immobilization of N−O donor ligand i.e. quinoline-2- carboxylic acid and quinoline-8- carboxylic acid to the APTMS functionalized mont. thereby obtaining two different composites. And finally to these composites the dimer precursor complex [Rh(CO)$_2$Cl]$_2$ is anchored resulting two different catalyst. They are then
characterized using PXRD, N$_2$- sorption isotherm, FT-IR spectroscopy and solid state NMR (\(^{13}\)C & \(^{29}\)Si). The catalytic application of the synthesized composites is used in the carbonylation of Methanol to Acetic acid.

Chapter 6

It summarizes the interesting findings of the research activities carried out.

6.2 Conclusions

1) Montmorillonite was extracted from Gujrat mined bentonite clay and was modified by activation with both mineral and organic acid under controlled condition to achieve high surface area and generate nanopores in the matrix. The pores act as “Host” for nanoparticles and also controlling the size by limiting the growth of the particles up to the sizes of the pores.

2) Pd nanoparticles were synthesized into the nanopores by impregnating with K$_2$[PdCl$_4$] and Pd(AcO)$_2$ trimer, into the pores of the acid activated mont. followed by aqueous Ocimum sanctum leaf extract and microwave assisted glycerol reduction respectively. Electron microscopy as well as other analytical techniques confirms the formation of Pd-nanoparticles. The synthesized Pd-nanoparticles are crystallized in fcc crystal lattice form and monocrystalline in nature.

3) The synthesized montmorillonite supported Pd-nanoparticles reduced by aqueous Ocimum sanctum leaf extract were found to be a good heterogeneous catalyst in hydrodechlorination of hazardous 4-chlorophenol with very good conversion and selectivity. The microwave assisted polyl reduced Pd-nanoparticles exhibit a
very good catalytic activity in the semihydrogenation of phenylacetylene with 98% selectivity. Both the catalysts were recovered and recycled for several runs without significant loss of activity.

4) Fe₃O₄ magnetic nanoparticles of size around 10 nm were generated in-situ into the nanopores of activated mont. by impregnating with FeCl₃·6H₂O followed by NaBH₄ reduction. Electron microscopy as well as other analytical techniques confirms the formation of Fe₃O₄ magnetic nanoparticles. The synthesized nanoparticles crystallized in fcc crystal lattice system.

5) The synthesized Fe₃O₄ magnetic nanoparticles were found to be very efficient heterogeneous catalyst in the Baeyer-Villiger oxidation of cyclic and aromatic ketones under mild and solvent free conditions with a conversion of up to 98% and good selectivity. The catalyst was recycled up to 4 th run and found active without significant loss in activity.

6) Two heterogeneous Rh-catalyst were synthesized by functionalization of modified montmorillonite clay followed by immobilization with different N–O donor ligands and finally anchoring a Rh(I) carbonyl complex to it. ²⁹Si NMR, FT-IR and other analytical techniques confirms from the functionalization to anchoring of the complexes.

7) The synthesized Rh- catalysts are used in the carbonylation of Methanol to Acetic acid. The carbonylation reaction has been carried out under different reaction condition by altering initial CO pressure 10, 15 and 20 bar at ~ 25 °C and higher turnover frequency (TOF) in the range 649 - 1172 h⁻¹ were obtained compared
to commercial Monsanto’s species \([\text{Rh(CO)}_2\text{I}_2]\) (TOF = ~ 464 - 1000 h\(^{-1}\)) under similar reaction conditions. The main advantage of these catalyst is that they are heterogeneous in nature and can be recovered by simple filtration. Another important advantage is that it has 100 % selectivity towards the formation of acetic acid.

6.3 Future scope

In recent years, due to stringent and growing environmental regulations, the use of montmorillonite as a support/stabilizer in the synthesis of metal nanoparticles, as solid acid in catalysis etc. will attract much importance because of its environmental friendly nature. For the synthesis of nanoparticles of controlled size and morphology, high selectivity in reaction etc., there is a high scope in scientific research. Moreover, the use of first row transition metal like Fe to replace noble metals in catalysis will attract considerable interest because of its different advantages like good catalytic activity, easy to use, cheap, magnetically recoverable etc. There is also scope in the further use of the heterogeneous Rh catalyst in larger scale as it gives single product and is reusable. Some of the future scopes of investigations are highlighted below:

1) Due to high stability and efficient recyclablity of the Pd and Fe\(_3\)O\(_4\) nanoparticles supported on activated montmorillonite clay, the possibility as an alternative catalyst in place of homogeneous metal complexes may be explored in different important organic reactions.
2) The synthesis process of Pd-nanoparticles supported on AT-mont. using glycerol as reducing agent may be used for synthesizing different shape selective nanoparticles by altering the glycerol : water ratio, temperature and time.

3) The acid activated montmorillonite clay may be used as support for synthesis of metal nanoparticles of various precious and non precious metals, at the same time as a solid acid catalyst.

4) The rhodium complexes containing N~O and chalcogen functionalized phosphine donor ligands may find application as catalyst for other reactions such as hydroformylation, hydrogenation etc.