Chapter 1

1. Introduction

1.1 Overview

Over the last 30 years, the synthesis of nanocrystals-crystalline particles ranging in size from 1 to 100 nm has been intensively pursued, not only for their fundamental scientific interest, but also for their many technological applications [1-5]. The physico-chemical properties of such nanoparticles neither correspond to those of the free atoms or molecules making up the particles nor to those of bulk solids with identical chemical composition, but are controlled by phenomena that have critical dimensions on the nanoscale. Such nanoparticles are also characterized by a large value of surface area to volume ratio, which signifies that a large fraction of atoms in nanoscale materials are exposed on the surface and thus can be involved in surface activities like catalytic reactions [1-13]. Among various nanomaterials, the development of metal and metal oxide nanoparticles are intensively studied for their applications not only in the field of catalysis but also in different areas like drug delivery, sensors, optoelectronics, magnetic devices, abatement of pollution, solid fuels, analytical applications etc [1-5,14-16]. The potential exploitation of nanoparticles based materials as catalyst precursors for organic synthesis as well as their effectiveness in biological and medical field is a challenge for the researchers. The overall performance of nanomaterials is dependent on the size, shape and textural parameters of the particles as well as the supporting materials on which these nanoparticles are stabilized [1-13]. Different types of 1D, 2D or 3D supporting materials have been employed to support nanoparticles including carbon nano tube, carbon nano fibres, graphene, silica, TiO₂, indium tin oxide, activated...
carbon, polymers, dendrimers, organic ligands, metal oxides, clay matrix etc [17-26]. In recent time, due to stringent and growing environmental regulations, there has also been increasing interest to employ ‘green’ procedure for synthesis of nanoparticles and applications. Thus, the use of environmentally benign, cheap, easily available, robust and strong support / stabilizer materials for the synthesis of metal nanoparticles and their utilization in different fields have contributed much towards the development of nanoscience and nanotechnology. Therefore, there is a great scope to develop supported nanoparticles of metals or metal oxides, which include their preparation, characterization and applications in different fields.

1.2 What are ‘Nanoparticles’?

Matter can be placed into broad categories according to size. Macroscopic matter is visible with the naked eye. Atoms and (most) molecules are microscopic with dimensions < 1 nm. Mesoscopic particles, such as bacteria and cells that have dimensions on the order of micron(s), can be observed with optical microscopes. Falling into the gap between the microscopic and the mesoscopic is another class of matter, the nanoscopic particles. The size of nanoparticles is compared to that of other “small” particles in Figure 1.1, where the bacterium is huge in comparison [27]. The term ‘nano’ is derived from the Greek word for ‘dwarf’, ‘nanos’, which means extremely small. This etymology and its placement on the metric scale (1 nm = 10^{-9} m), clearly demonstrated the size of nanoparticles. The nanoparticles are tiny dimensions objects not visible to our naked eye. For comparison, a single human hair is around 1,00,000 nm thick. Any objects with lateral dimensions less than 100 nm are typically termed nanoparticles.
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This classification is somewhat arbitrary, but it is largely established in the scientific literature.

1.3 What are Nanoscience and Nanotechnology?

‘Nanoscience’ is at the cutting edge of science. It is highly multidisciplinary and deals with all branches of science. Nanoscience is concerned with materials and systems whose structures and components exhibit novel and significantly improved physico-chemical properties, phenomena and processes compared to the behavior of their bulk materials, because of their small nanoscale size (0.1 to 100 nm).

The term ‘Nanotechnology’ refers to research and technological development which is associated with particles and materials of size range approximately 0.1 to 100 nm in any dimension (i.e. nanoscale). Nanotechnology involves the use of nanomaterials in various areas such as chemical and textiles industries, biotechnology, electronics, medicine to provide better and improved technologies to the society.
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1.4 A brief Historical Background

Although the concept of “Nano” is very recent, it was practised for different purposes in ancient time. Ancient civilizations produced and utilized colloidal metal nanoparticles. The preparation of these nanoparticles has a long and storied history dating back in the millennia. Colloidal gold and silver have been used since ancient Roman times to color glass of intense shades of yellow, red or mauve, depending on the concentration of the two metals. In the middle ages, colloidal gold was used for a diverse assortment of purpose including its use as a purported curative for a wide variety of disease [28]. The Roman added gold salts to their glass preparation, which was reduced to colloidal gold when the glass was annealed, producing transparent ruby-red glass. The red color strike as a result of the nucleation and growth of small metallic gold particles, whose optimum size for yielding a strong ruby color is 5-60 nm [29].

One of the earliest examples of colloidal metal nanoparticles used for aesthetic purpose is the famous Lycurgus cup of 4th century, presently in the British Museum [30]. This late Roman glass cage cup showed unusual optical effects displayed by the glass. In the transmitted light, the glass appears a deep wine-red, while in reflected light it is an opaque pea-green. Chemical analyses of the glass of the cup attributed this dichroic coloring of the surface plasmon resonance of the nanocrystals of an alloy of gold and silver (and probably Cu) dispersed throughout the glassy matrix [30-31].

A similar example is the use of the colloidal metal nanoparticles in stained glass windows in old European cathedrals. In the Middle Ages, colloidal gold was employed by artisans to produce bright red and purple colors in stained glass windows. For
example, the red and purple hues of the Rose Window of the Cathedral of Notre Dame are due to the presence of colloidal gold [32]. In 15th century brightly colored porcelain was prepared, containing silver and silver-copper alloy nanoparticles. The technique was developed in the Islamic world during 9th century and exploited the reducing atmosphere obtained heating dried genista up to 600 °C to obtain nanoparticles by reducing metal oxides or metal salts previously deposed on the ceramic piece from a vinegar solution [28, 33]. In the 17th century the glass coloring process was further refined by contriving “Purple of Cassius”, a precipitate of colloidal gold and stannic hydroxide they added to the base glass [28].

However, the first documented scientific investigation into the chemical synthesis of colloidal metal nanoparticles was reported by Michael Faraday in 1875 [34], who prepared gold colloids by reducing an aqueous solution of chloroaauric acid with phosphorous in the presence of carbon disulphide (CS₂) and obtained “ruby fluids” of dispersed gold particles [Figure 1.2]. He recognized the connection between the color and the size of the particles and also elucidated the mechanism of formation of gold particles from chloroaurate [AuCl₄⁻] solutions using phosphorous as a reducing agent. In 1957, Faraday presented during his lecture at royal society of London a purple color slide stating that “it contained gold reduced to extremely small particle which become diffused, produce a ruby red fluid”. Besides Faraday, the other pioneers were Thomas Graham, Marian Smoluchowsky, Richard Zsigmondy, Wilhelm and Wolfgang Ostwald [35]. The widespread interest of modern nanoscience and nanotechnology was began after a visionary lecture by the famous Physicist Richard P. Feynman, in 1959 at the
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annual meeting of American Physical Society held at The California Institute of Technology, USA by the vision, ‘There’s Plenty of Room at the Bottom’, and described the possibility of nanosized devices and related technologies. Feynman predicted that ‘It would be possible to put the 24 volumes of Encyclopaedia Brittanica on the head of a pin’.

![Figure 1.2 Michael Faraday’s colloidal gold suspension](image)

Object in nano dimension cannot be seen by naked eyes or even with a very high resolution optical microscope. Lack of sophisticated imaging instruments in early nineteenth century had restricted the development of the nanoscience in an infant stage. The modern development of nanoscience has been enabled by invention of electron microscopy that has revolutionized the imaging technique in the nano scale. These are scanning electron microscope (SEM) and transmittance electron microscope (TEM). Later on further development in this line like, atomic force microscope (AFM) and scanning tunneling microscope (STM) which are capable of imaging surface in atomic resolution. Binnig, Rohrer and Ruska (all from IBM, Zürich) were awarded Nobel Prize
in physics in 1986 for the invention of these two instruments, which practically opened the doors of the modern nanoworld.

1.5 Nanotechnology in nature

In nature, there are numerous examples of nanotechnology-based systems that are already highly optimized through millions of years of evolutionary development. A few examples are, in the photosynthesis process, the chloroplasts contain nanoscale molecular machinery arranged inside the stacked structures that convert light and carbon dioxide into biochemical energy. The inner ear of a frog has nanomechanical cantilevers that measure deflections as small as 3 nm due to sound. Geckos, a lizard, can climb walls and hang from ceilings with a single toe by using millions of its nano toe pads [9,36-39]. Animal cells are the perfect examples of busy multifunctional nanosystems, they are very tiny, a few nanometers in size, but they can store information, capable of replicating themselves, move around and also manufacture various substances needs by the organism. Therefore, cells can provide the blueprint for developing nanosystems that can work in atomic level. However, nature is very selective, despite all modern scientific progress, the degree of structuring, complexity and functionality that occurs in nature has not been reached yet.

1.6 Innovative properties of nanoparticles

The properties and behaviours of nanoparticles greatly change from that of the bulk materials. The color, melting point, conductivity of bulk material change when it is transformed into nano-dimension. For example, bulk gold melts at 1064 °C whereas
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gold nanoparticles of size around 2 nm melt below 500 °C. The properties which are responsible for such changes of nanomaterials are described below.

1.6.1 Surface-dependent particle properties

The main feature, which is considered one of the most important factors for changing the properties of nanoparticles, is the surface to volume ratio. In bulk materials, change of size doesn’t change the property. But, on reducing the size of materials to that of very small particles in the nanoscale then, most of the particles constituting the matter will be on the surface.

For particle of surface “a” and diameter “d” and volume “v”, the relations are:

\[ a = \pi d^2 \]
\[ v = \frac{\pi}{6} d^3 \]
\[ a = \frac{6}{d} \]

<table>
<thead>
<tr>
<th>Number of atoms</th>
<th>Atoms on the surface</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td>92 %</td>
</tr>
<tr>
<td>55</td>
<td>76 %</td>
</tr>
<tr>
<td>147</td>
<td>62 %</td>
</tr>
<tr>
<td>309</td>
<td>52 %</td>
</tr>
</tbody>
</table>

**Figure 1.3** Magic number cluster and number of atoms (%) on the surface.

Thus, surface increases with decrease in size. For example, a particle of size 1 nm, which consists of nearly 13 numbers of atoms, has about 92 % of atoms exposed on the surface [Figure 1.3]. Therefore, a large fraction of the atoms are exposed on the
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surface as a result of which the nanomaterials exhibit special properties such as higher chemical reactivity, high surface conductivity etc [2]. As the size of the particle increases, the numbers of atoms on the surface will decrease. The number of atoms constituting the different size particles [Figure 1.3] follows a certain sequence of number called “Magic Number” which exhibit relation with the surface atom.

1.6.2 Size dependent particle properties

Many properties of nanoparticles are directly related to their small size. e.g. the melting point of bulk gold is 1064 °C, whereas 1.5 nm sized gold particles melt at about 500-600 °C, therefore, the melting point decreases dramatically as the particles size goes below 5 nm. Similarly, gold is inert in its bulk form, but if the diameter of the particles is reduced to a few nanometers, it acquires catalytic properties [40-43]. Even the color of the colloidal solution of metals changes depending on their size [Figure 1.4].

![Figure 1.4 Effect of particles size on the color of Ag nanoparticles.](image)
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1.6.3 Quantum effects

Nanoparticles having size below 2 nm in all coordinate are known as quantum dots due to the quantum confinement of the electrons [44]. If the electronic structure of nanoparticles is influenced directly by their size, the phenomena are called size-dependent quantum effects. These are due to the transition from an atom or molecule with defined energy levels to the dispersed bands of collective ensembles of atoms and finally of the bulk material. Examples are the shift of the plasmon resonance of gold nanoparticles and the size-dependent color and luminescence of semiconductor quantum dots [44].

1.6.4 Surface Plasmon Resonance (SPR) of nanoparticles

SPR is an optical phenomenon arising from the interaction between an electromagnetic wave and the ‘free’ electrons within the conduction band in a metal. The electric-field component of the incident light induces oscillation of the nanoparticle’s electron cloud [Figure 1.5]. As the wave front of the light passes, the electron density in the particle is polarized to one surface and oscillates in resonance with the light’s frequency causing a standing oscillation. The condition is determined from absorption and scattering spectroscopy and is found to depend on the shape, size, and dielectric constants of both the metal and the surrounding material [42,43]. The SPR peak for Au⁰-nanoparticles is positioned at ~ 520 nm, which is responsible for the ruby red color displayed by conventional gold colloids. Michael Faraday was the first person to observe this spectacular phenomenon [34]. The SPR spectra can be calculated by solving Maxwell’s equations. For spherical particles, Gustav Mie, a German
physicist, was the first to explain SPR by solving Maxwell’s equations in 1908 [42]. These days, one can still use the formulas derived by Mie to conveniently compute SPR spectra. Like gold, other metals also exhibited SPR spectra, e.g. for Ag°-nanoparticles SPR peak is appeared at ~ 400 nm.

Figure 1.5 Oscillation of a metal nanoparticle’s electron cloud with electromagnetic field.

1.7 Types of nanomaterials

Nanomaterials are of various types. Depending on the nature, dimension, shape, size and crystalline properties of nanomaterials, they are classified into following categories.

1.7.1 Carbon-based materials

These nanomaterials are composed mostly of carbon, most commonly taking the form of a hollow spheres, ellipsoids, or tubes. Spherical and ellipsoidal carbon nanomaterials are referred to as fullerenes, while cylindrical ones are called nanotubes. Carbon nanotubes belong to the fullerene family [9]. Carbon nanotubes can be considered to be extended fullerene and having diameter 1 to 10 nm. Carbon nanotubes are stronger than steel wires, can conduct thousand times more electricity and can bear
weight million times than their own weight [9]. Graphene, the two dimensional materials constitutes a new nanocarbon comprising layers of carbon atoms arranged in six-membered rings, became a hot topic of research recently. Graphene has extraordinary properties and used to make sensors, electrochemical devices and transistors [45,46]. These nanomaterials have many potential applications, including to improving films and coatings, to make stronger and lighter materials and in electronics.

1.7.2 Metal-based materials

These nanomaterials include quantum dots (e.g. CdSe, CdS, etc.), metals (e.g. Ni0, Cu0, Au0, Pt0 etc.) nanoparticles, metal oxides, such as TiO2, ZrO etc. A quantum dot is a closely packed semiconductor nanoparticles which sizes are generally below 2 nm in all coordinate. Quantum dots are particularly significant for optical applications due to their high extinction co-efficient [13]. Metal and metal oxide nanoparticles are widely used in the field of catalysis, electronics, biosciences etc [4-9].

1.7.3 Nano-composites materials

Nanocomposites materials are combined materials which have one or more dimensions in the nano range [35]. Clay, polymeric materials, graphite etc. are the examples of nanocomposites materials. Clay is widely available and relatively cheap nano-composites materials found in the market for commercial use. Nanosized clays are being used to products ranging from car parts to packaging materials to enhance mechanical, thermal and flame-retardant properties. Currently, carbon fibres and bundles of multi-walled carbon nanotubes are used in polymers to control or enhance conductivity, with applications such as antistatic packaging [47].
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1.7.4 Dendrimers

Dendrimers are spherical polymeric molecules, formed through a nanoscale hierarchical self-assembly process. The surface of dendrimer has numerous chain ends, which can be tailored to perform specific chemical functions. This property could also be useful for catalysis. Also, three-dimensional dendrimers can act as nanoscale carrier molecules and as such could be used in drug delivery. Environmental clean-up could be assisted by dendrimers as they can trap metal ions, which could then be filtered out of water with ultra-filtration techniques [9,39].

1.8 Synthesis of nanomaterials

Several methodologies have been developed for the synthesis of metal nanoparticles. The first natural classification is into “top-down” and “bottom-up” synthetic strategies, which can also be considered as physical and chemical methods respectively [38-39, 48-50]. In the top-down approach materials of larger dimension are breakdown to nano dimension by means of mechanical force like grinding, milling etc. Photolithography, electron beam lithography, focused ion beams etc. are the techniques generally used in ‘top-down’ approach [38-39, 48-50]. But, the biggest problem with top-down approach is the imperfection of morphology of the nanostructure. In the ‘bottom-up’ approach, nanoparticles are constructed atom-by-atom or molecule-by-molecule. This approach also uses the principle of molecular recognition and self assembly. In this approach, nanosphere lithography, chemical, electrochemical, sonochemical, thermal and photochemical reduction techniques are used. Bottom-up approach promises a better chance to obtain nano-structures with less defects and more
homogeneous chemical composition. Lithography is one of the techniques used for construction of nanostructured materials but, it follows a hydride approach of bottom-up and top-down approach. In this technique growth of thin films is bottom-up whereas etching is top-down process.

Among the various nanomaterials, metal nanoparticles find special attention due to their unique properties and versatile application in various fields like catalysis, biology, electronics etc. Modern syntheses of metal nanoparticles are often inspired by the 150 year old method of Faraday [34] and the sustainable emerging as a design criterion in nanoparticles synthesis and applications start in mid 1990s, still there is scope for improvement in the methodologies employed for this purpose [51]. Some of chemical routes for preparation of metal nanoparticles are discussed below.

1.8.1 Wet chemical reduction of metal salt precursors

The first reproducible synthesis by this process was done by Turkevich and coworkers, who synthesized hydrophilic gold nanoparticles by the reduction of chloroauric acid with sodium citrate in a boiling aqueous solution [52]. The citrate appeared to work as a protective agent against coagulation by adsorption on the gold surfaces. According to the data from transmission electron microscopy, the synthesized nanoparticles were spherical, had a narrow size distribution and the average diameter of 20 ± 1.5 nm. This work was then refined in 1973 by Frens, who specified the effect of concentration ratio of citrate to gold salt on the resulting particle size ranging from 16 to 147 nm [53]. Later, the Turkevich method was used in the preparation of silver nanoparticles [54]. Citrate has been also used both as reducing agent and stabilizer by
Turkevich et al. to prepare palladium and platinum metallic particles [55,56]. They also proposed a mechanism for the stepwise formation of nanoparticles based on nucleation, growth and agglomeration. Now, the ‘wet chemical’ reduction has become the most common method for making metal nanoparticles, the schematic approach is shown by the following equation.

\[
\begin{align*}
    & \text{xA}^{n+} + \text{nxe}^{-} + \text{stabilizer} \\
    & \rightarrow \text{nM}^{0} (\text{cluster})
\end{align*}
\]

In this approach the reducing agent (e.g. hydrazine, sodium borohidride, hydrogen, alcohol etc.) is added with the metal precursor salt in the presence of stabilizing agents (e.g. porous materials, ligands or surfactants). The supports prevent the undesired agglomeration and formation of well dispersed metal nanoparticles. The actual size and shape of the metal nanoparticles depends on many factors, including the type of reducing agent, metal precursor, solvent, concentration, temperature and reaction time. Bönnemann et al. utilized long-chain tetraalkylammonium salts of hydridotriorgano-borate derivatives to generate nanoparticles of many transition metals [57]. Many metal nanoparticles, in particular of platinum group metals, have been synthesized through the reduction of metal salts with high boiling-point alcohols such as ethylene glycol. This method is known as the polyol process [58-60].

1.8.2 Microemulsions

Microemulsions can be described as homogeneous-like combinations of water, oils and / or surfactants [49,61-63]. The formation of reverse micelles was confirmed to be an interesting and environmentally friendly alternative to the preparation of metal
nanoparticles. Thus, a solid support is impregnated with a microemulsion containing a dissolved metal salt precursor and subsequently reduced with appropriate reducing agent. The microemulsion-support interaction can be enhanced by increasing the hydrophobicity of the support (e.g. silylation of hydroxy-rich surfaces), making it more chemically compatible with the microemulsion during the deposition step [62]. Wang et al. have reported an interesting approach of this methodology employing a water-liquid CO₂ (as oil phase) microemulsion stabilized by sodium bis(2-ethylhexyl)sulfosuccinate as surfactant and hexane [63]. In this way, Rh° and Pd-Rh nanoparticles with sizes ranging from 2 to 10 nm can be homogeneously deposited on the surface of multiwalled carbon nanotubes.

**1.8.3 Impregnation**

This methodology involves the ‘wetting’ of the solid support with a solution containing the metal precursor. The common method of chemical impregnation is the so-called wetness impregnation. In this method, the metal nanoparticles precursor, which is normally a salt is dissolved in the minimum quantity of solvent. The resulting metal salt solution is then added to the porous support, filling its pores so that a thick paste is formed. The solvent is then removed in a rotary evaporator and the final solid is oven dried and subsequently calcined or reduced by appropriate reducing agent [58-60,64-65]. The metal nanoparticles obtained by this methodology are dispersed depending on the metal, support and loading of the final solid.
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1.8.4 Co-precipitation

The co-precipitation method involves the simultaneous precipitation of the metal and the support. In this way, the metal nanoparticles can be incorporated into the structure of various mesoporous materials, cellulose etc [66-68]. Yu et al. [67] reported the preparation of iron oxide nanoparticles on cellulose template synthesized by one step co-precipitation using NaOH-thiourea-urea aqueous solution, which have particle sizes around 5-100 nm and well dispersed in the cellulosic matrix. Bao and coworkers also reported a co-precipitation approach for the preparation of supported Ag\textsuperscript{0}-nanoparticles on silica [68]. The template-directed route comprises the capping of Ag\textsuperscript{+} cations in solution with dodecylamine, subsequent reduction to Ag metal using formaldehyde and eventual self-assembly of the material after addition of the silica source i.e. tetraethyl orthosilicate (TEOS).

1.8.5 Precipitation-deposition

This method was initially reported by Haruta et al. [40,69] and involves the dissolution of the metal precursor followed by adjustment of the pH (i.e. 5-10) to achieve a complete precipitation of the metal hydroxide (e.g. Au(OH)\textsubscript{3}), which is deposited on the surface of the support. The hydroxide formed is subsequently calcined and reduced to the elemental metal [69]. In general, these methodologies often provide a broad nanoparticles size distribution and it is difficult to tune the particle size for a particular application owing to a poor control of the nanoparticles size.
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1.8.6 Sol-gel processing

The sol-gel process is a wet-chemical technique that uses either a chemical solution (sol short for solution) or colloidal particles (sol for nanoscale particle) to produce an integrated network (gel). Metal alkoxides and metal chlorides are typical precursors. They undergo hydrolysis and polycondensation reactions to form a colloid, a system composed of nanoparticles dispersed in a solvent. The solvent was evaporated to form of an inorganic continuous network containing a liquid phase (gel). Formation of a metal oxide involves connecting the metal centers with oxo (M-O-M) or hydroxo (M-OH-M) bridges, therefore generating metal-oxo or metal-hydroxo polymers in solution. After a drying process, the liquid phase is removed from the gel. Then, a thermal treatment (calcination) may be performed in order to favor further polycondensation and enhance mechanical properties [70,71).

1.8.7 Electrochemical reduction

Electrochemical reduction is usually followed for the preparation of carbon nanotube supported metal nanoparticles. By varying the deposition potential, substrate and deposition time one can control the size and distribution of supported metal nanoparticles. This method for preparing mono- and bimetallic metal nanoparticles was developed by Reetz and his group since 1994 [72-75]. This method was also successfully applied in the preparation of a number of monometallic nanoparticle organosols and hydrosols, including Pd, Ni, Ag, Au etc [72-75]. Bimetallic alloys (e.g. Pd-Ni, Fe-Co and Fe-Ni) are accessible if two sacrificial metal anodes are used.
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simultaneously [74]. Recently, electrochemical and ‘wet chemical’ methods were combined to synthesize high surface area core / shell nanoparticles [75].

1.8.8 Thermal decomposition methods

Thermal decomposition reactions of organometallic compounds and metal surfactant complexes are typically performed in hot surfactant solutions to synthesize monodisperse nanoparticles of various materials [76]. Traditional thermolysis of metal salts in the absence of stabilizers generally produces nanoparticles with broad size distributions [77]. These results were found to be greatly improved when the thermolysis was performed in the presence of stabilizing polymers, such as PVP. Wostek-Wojciechowska et al. have reported the synthesis of Ru, Rh and Co nanoparticles using this technique by decomposition of organometallic precursor of these metals [78].

1.8.9 Chemical vapour deposition

Chemical vapour deposition is another promising route for the preparation of supported metal nanoparticles. This procedure involves the vaporization (sublimation) of metals and growth of the metal nanoparticles under high vacuum in the presence of an excess of stabilizing organic solvents (e.g. aromatic hydrocarbons, alkenes and tetrahydrofuran) and / or reducing agents (e.g. H₂) [79,80]. Chemical vapour deposition is claimed to allow the preparation of metal nanoparticles on a wide range of organic and inorganic supports under very mild conditions (< 50 °C) to afford highly active heterogeneous catalysts [80], thereby avoiding the formation of large agglomerated nanoparticles from other protocols.
1.9 Stabilizers or Supports for metal nanoparticles

Nanoparticles have a particular tendency to lower their very high surface energy, which is the origin of their thermodynamic instability. Bare nanoparticles tend to stabilize themselves either by adsorption of molecules from the surroundings or by lowering the surface area through coagulation and agglomeration. In order to avoid the later, nanoparticles have to be (kinetically) stabilized. Therefore, to retain shape and size of nanoparticles, there must be used some stabilizing agents or support. The main roles of stabilizers or supports are to prevent particles aggregation without passivating its surface. Depositing nanoparticles on porous solid supports is one of the most useful methods because it prevents the growth up to size of the pores and do not reduces its reactivity. Some of the important supports used for stabilization of metal nanoparticles are described below.

1.9.1 Polymers

Polymers are the most extensively used stabilizer for nanoparticles synthesis due to their stability, easy availability, low cost and excellent resistance agent for particle agglomeration. The size and shape of metal nanoparticles can be tuned by changing polymer concentration, polymer chain length and functionality on the polymer size chain. Chen et al. have synthesized very small Ru\(^{0}\)-nanoparticles of size around 1.7 nm by using ethylene glycol and Poly (N-vinyl-2-pyrrolidone) (PVP) [81]. Harpeness et al. have reported the direct reduction of RuCl\(_3\) by using microwave PVP as stabilizer [82]. Many other polymers have been used recently for stabilization of nanoparticles e. g. polyurea [83], polyacrylonitrile and / or polyacrylic acid [84], polysilane shell-cross-
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linked micelles [85], polysiloxane [86], oligosaccharides [87], \( \pi \)-conjugated conducting polypyrrole [88], chitosan [89], hyperbranched aromatic polyamides (aramids) [90] etc. Biopolymers and biomass related polymers such as cellulose have also been recently employed for the preparation of metal nanoparticles [91].

1.9.2 Dendrimers

Dendrimers are hyper branched macromolecules that are constructed around a core and are well defined by regular branching generation after generation [92-95]. Having shapes of molecular trees or cauliflowers, they become globular beyond low generations and thus behave as molecular boxes [94] that can entrap and stabilize metal nanoparticles, especially if they contain heteroatoms in their interiors [95,96-99]. The formation of nanoparticles stabilized by dendrimers was proposed in 1998 by three research groups Crooks [96,100], Tomalia [101,102] and Esumi [103-104]. The first two groups introduced the metal nanoparticles inside the dendrimers whereas the last one stabilized them at the dendrimer periphery. Dendrimer templates have allowed to exert a high degree of control over the size of catalytically active nanoparticles in the size below 3 nm [105,106]. Somorjai et al. and Amiridis et al. have reported a hydride process, where Rh\(^{\text{o}}\)-nanoparticles were synthesized in dendrimer templates followed by immobilization of porous supports like mesoporous silica and zirconium oxide [107,108]. The nanocomposites were found very efficient in alkenes hydrogenation.

1.9.3 Organic ligands

The introduction of ligands as nanoparticles stabilizers is of special interest, because it focuses on the precise molecular definition of the catalytic materials.
principle, this strategy potentially allows a good control of the molecular modulation in order to optimize the parameters that govern the efficiency in catalytic reactions, including enantioselective ones [109]. The ligands are chosen by considering their donor site affinity towards nanoparticles and their structural suitability. A large numbers of ligands such as amines [110], phosphines [22,109] and thiols [111] have been extensively used for stabilization of Au\textsuperscript{o}, Pd\textsuperscript{o}, Pt\textsuperscript{o} etc. nanoparticles. Fujihara and coworkers have introduced various BINAP ligands for stabilization of Au\textsuperscript{o} and Pd\textsuperscript{o}-nanoparticles. They also described the utilization of Pd\textsuperscript{o}-nanoparticles in different coupling reactions [22,109]. The biphasic (liquid-liquid) procedure has been extensively used for synthesis of various metal nanoparticles in organic medium utilizing different types of ligands like thiols, phosphines, amines, etc [112, 113]. The main advantage of above mentioned procedure is that, metal nanoparticles can be isolated as solid mass and that can be redispersed into appropriate solvents for further utilities.

1.9.4 Porous materials

A porous material is normally a solid that comprises an interconnected network of pores (voids). Many natural substances such as rocks, clays, biological tissues (e.g. bones) and synthetic materials including ceramics, metal oxides, carbonaceous materials and membranes can be considered as porous materials. A porous material is characterized by its porosity (e.g. macro, meso-, microporosity or combinations thereof) as well its textural and physical properties which are dependent on its constituents. The use of porous materials with defined pore sizes and characteristics as supports for nanoparticles allows the generation of specific adsorption sites, creating a partition
between the exterior and the interior pore structure [114]. Furthermore, by selecting and manipulating the textural properties of the porous support, it should be possible to control the size and shape of nanoparticles. A variety of porous materials have been used as the support materials for the controlled preparation of metal nanoparticles. Some of them are described below.

1.9.4.1 Carbonaceous materials

Carbon-related materials offer great advantages as supports because they have allowed the preparation of carbon nanostructures with well-defined porosities and high surface areas and also ease of modify their carbonaceous surfaces. Charcoal is a classic commercially available carbonaceous support for metal nanoparticles. Bönne mann applied his general synthetic method for synthesis of nanoparticles suspension on charcoal and used for a variety of catalytic reactions [115]. Activated carbons that are also suitable as support materials in catalytic processes need to be prepared and modify in order to obtain adequate surface area, porosity and pore size distribution for nanoparticles synthesis. Budarin et al. have recently reported the preparation of a wide range of supported metal nanoparticles on a novel family of mesoporous carbonaceous materials called Starbon prepared from controlled carbonization of mesoporous starch [69].

1.9.4.2 Clay minerals

Due to growing concern over environmental friendly materials, there has been increasing interest to employ environmentally benign, easily available and cheap supports for metal nanoparticles. Clay minerals are becoming one of the best substitutes
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for conventional supports as it is environmentally benign, very cheap and abundant in nature. Clay minerals have high surface area, absorptive and ion-exchange properties and they have been extensively exploited for catalytic applications through decades [116-119]. Clay minerals are made up of layered silicates. They are crystalline materials of very fine particle size ranging from 150 to less than 1 micron. There are two basic building blocks viz. tetrahedral silicates and octahedral aluminate layers, which are common to clay minerals. Brief classifications of different clay minerals are shown in the Table 1.1.

Table 1.1. A brief classification of different clay minerals.

<table>
<thead>
<tr>
<th>Type*</th>
<th>Name of the group</th>
<th>Common species</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 : 1</td>
<td>Kaolinite and Serpentine</td>
<td>Kaolinite, Halloysite, Chrysotile</td>
</tr>
<tr>
<td>2 : 1</td>
<td>Micas</td>
<td>Illite</td>
</tr>
<tr>
<td></td>
<td>Vermiculite</td>
<td>Vermiculite</td>
</tr>
<tr>
<td></td>
<td>Smectite</td>
<td>Montmorillonite, Beidellite, Nontronite, Saponite</td>
</tr>
<tr>
<td></td>
<td>Pyrophyllite and Talc</td>
<td>Pyrophyllite, Talc</td>
</tr>
<tr>
<td>2 : 1 : 1</td>
<td>Chlorite</td>
<td>Donbassite</td>
</tr>
</tbody>
</table>

* Silicates layer : Aluminate layer

Among the different clay minerals, montmorillonite is the most extensively studied smectite group of clays [116-123]. The high cation exchange capacity (CEC) and good swelling properties allow a wide variety of catalytically active forms of montmorillonite to be prepared. Montmorillonite is a hydrated 2 : 1 layered aluminosilicate of the smectite group [116-123]. It is composed of two tetrahedral silicate sheets which are bonded to either side of an octahedral aluminate sheet.
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Isomorphous substitution of Si$^{4+}$ and Al$^{3+}$ by other lower valence cations (e.g. Mg$^{2+}$) results in charge imbalance. This layer charge is balanced by hydrated exchangeable cations which occupy position between clay layers [Figure 1.6].

Figure 1.6 Structure of montmorillonite.

In the last few years, attempts have been made to incorporate metal nanoparticles into layered clay minerals of smectite group like montmorillonite, hectorite, saponite etc. by advantageously utilizing their intercalation chemistry [124-126]. Clays provide the same effect as that of zeolites for the synthesis of metal nanoparticles. However, the advantage of smectite group clays over zeolites is that their pore size can be tuned to suit a particular application under controlled conditions [121-123]. Metals clusters of 4-5 Å in size are formed and the microporous nature of such zero valent metal intercalated clay nanocomposites are also confirmed [59,124-126].
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Such metal clusters, supported on microporous materials, are expected to behave very differently from bulk metals and may exhibit unique catalytic activity, molecular selectivity and adsorption properties. Clay supported Pd⁰ and Pt⁰-nanoparticles are found to show excellent catalytic activity for hydrogenation in liquid phase [122-123]. Acid activated montmorillonite has attracted much attention of the chemists because of their applications in different types of catalytic reactions [127-130]. Acid activated montmorillonite are partially delaminated, exhibit higher specific surface area and contain micro- and mesopores with diameters of 0-10 nm. These nano range pores act as ‘host’ for *in situ* generation of various metal nanoparticles and also limit the growth of the particles upto desired range [131,132]. The specific surface area and the pore diameter as well as pore size distribution of montmorillonite can be varied by controlling the acid activation conditions [127-130].

1.9.4.3 Metal oxides

In general, metal oxides offer high thermal and chemical stabilities combined with a well-developed porous structure and high surface area (> 100 m²/g), meeting the requirements for most applications. They can also be easily prepared and further functionalized, adding value to their use as support or catalyst. Among the metal oxides, Si [133,134], Al [133-135], Ti [40,136], Ce [134,135] and Zr [108,137] oxides are the most extensively employed supports for various metal nanoparticles.

Paramagnetic oxides (e.g. Fe₃O₄) have recently emerged as new materials for the immobilization of metal nanoparticles with improved separation capabilities [138]. Well-distributed and stabilized supported Pd⁰ [138] and Rh⁰ [139] nanoparticles in the
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Magnetisable support surface (particle size in the 2-3 nm range) were found to be very active in the hydrogenation of cyclohexene and benzene. The most attractive feature of support is that the materials can be easily recovered and reused several times without a significant loss in catalytic activity.

1.10 Reactivities of supported metal nanoparticles

The supported metal nanoparticles have found wide range of applications in the fields of catalysis, biology, electronics, engineering etc. Herein, some of the catalytic activities of supported Cu\(^{\circ}\), Ni\(^{\circ}\) and Pt\(^{\circ}\)-nanoparticles are highlighted.

1.10.1 Copper (Cu\(^{\circ}\)) nanoparticles

Supported Cu\(^{\circ}\)-nanoparticles have been prepared on a range of supports and shown activity in various catalytic processes. Supported Cu\(^{\circ}\)-nanoparticles catalyzed reactions provide the advantage of high atom efficiency, simplified isolation of product, and easy recovery and recyclability of the catalyst. Cu nanoclusters (typically 2-4 nm) supported on Al\(_2\)O\(_3\) films were employed in the reduction of NO [140]. Aziridination and cyclopropanation reactions are other interesting catalytic applications of Cu\(^{\circ}\)-nanoparticles [141]. Cu\(^{\circ}\)-nanoparticles supported on various supports were employed in the synthesis of 1,2,3-triazole by coupling of azides and terminal alkynes [142]. Recently, supported Cu\(^{\circ}\)-nanoparticles were reported to activate the water gas shift reaction. The reaction involves water splitting after reacting with CO to give CO\(_2\) and hydrogen [143]. Like Cu\(^{\circ}\)-nanoparticles, CuO nanoparticles are also quite stable and cheap. Very recently, CuO nanoparticles joined the catalyst family for organic synthesis. There are numbers of reactions such as C-N cross coupling of amines [144],
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synthesis of propargylamines [145], synthesis of quinazolines [146] etc. are catalyzed by supported CuO nanoparticles. Also resin immobilized Cu\(^0\) and CuO nanoparticles have been reported as highly active and selective catalyst in the oxidation of alcohols [147].

1.10.2 Nickel (Ni\(^0\)-) nanoparticles

Recently, attempts were made to stabilize Ni\(^0\)-nanoparticles into different supports such as carbon nano tube, carbon nano fibres, graphene, silica, TiO\(_2\), indium tin oxide and inorganic clay in order to construct new composite materials [10,37]. When nickel is prepared as very small and well dispersed on such support, it can be a highly active catalyst in a wide range of organic transformation reactions including hydrogenations of substituted chloronitrobenzene, transfer hydrogenation, semi hydrogenation, synthesis of Hantzsch polyhydroquinoline etc [132,148-149]. There are large numbers of literature report of metallic Ni\(^0\)-nanoparticles having size range 1 to 10 nm and well dispersed on different supports [148-150]. Reforming of methane with carbon dioxide catalyzed by Ni\(^0\)-nanoparticles has received increasing attention for more than a decade. This reaction directly converts two low-value greenhouse gases into a valuable synthesis gas, which can be used in chemical energy transmission systems or utilized in the Fisher-Tropsch synthesis to produce liquid hydrocarbons [150]. Other reactions such as chemo-selective oxidative coupling of thiols, Heck coupling reactions, hydrogenation of olefins etc. are also catalyzed by Ni\(^0\)-nanoparticles and well reported in the literature [132,151,152].
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1.10.3 Platinum (Pt\textsuperscript{0}) nanoparticles

Platinum group metals are well known for its very rich chemistry. Platinum is an invaluable catalyst due to its superb performance as an industrial catalyst for applications that range from methanol oxidation in fuel-cell technology to three-way automobile catalytic conversion. Thus, the preparation of supported metallic Pt\textsuperscript{0}-nanoparticles on different supports has been extensively investigated and employed in different organic transformation reactions such as hydrogenation reaction, transfer hydrogenation, oxygen reduction, allylation of aldehydes, CO oxidation etc [152-159]. Some important examples of hydrogenation reactions are hydrogenation of ethene, cyclohexene, benzene etc [156], hydrogenation of carbonyl compounds to alcohols [122], hydrogenation of chloronitrobenzene to chloroaniline [153-155], hydrogenation of azo bonds in methyl red [158], hydrogenation of toluene [159], Pyrrole hydrogenation [160], hydrogenation of citral to geraniol and nerol [161] etc. Oxidation is another important reaction catalyzed by Pt\textsuperscript{0}-nanoparticles using O\textsubscript{2} or air as oxidant, examples are alcohols to aldehydes [162], aerobic oxidation of hydroquinone derivatives [163], methanol electro-oxidation [164] etc. Somorjai [160] has reported that when platinum supported on mesoporous silica as ultrafine particles with size as small as 1 nm, it exhibits surprisingly high activities for pyrrole hydrogenations.

1.11 Aim and objectives of the Thesis

The literature survey presented here reveals that the syntheses as well as the applications of supported metal nanoparticles, particularly platinum group metals have aroused much interest and importance in recent time. The utilization of environmentally
benign, cheap and easily available supports / stabilizers for the synthesis of metal nanoparticles proceeded promisingly in context of ‘green’ chemistry. It is therefore important to synthesize and characterize supported metal nanoparticles and to determine their reactivities in organic transformation reactions. The specific objectives of the thesis are:

- Development of nanopores on the surface of montmorillonite by executing controlled acid activation and *in situ* generation of metal (Cu\textsuperscript{0}, Ni\textsuperscript{0}, Pt\textsuperscript{0}) nanoparticles into the well-tuned nanopores of modified montmorillonite.
- Development of methods for Bottom-Up fabrication of Self-Assembly Pt\textsuperscript{0}-nanoclusters by protecting / stabilizing with suitable phosphine based organic ligands.
- Evaluation of catalytic efficacy of metal nanocomposites for various organic transformation reactions like transfer hydrogenations, selective hydrogenations, synthesis of Hantzsch polyhydroquinoline, oxidations etc.
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