

# **I. Introduction**

## **1.1 Introduction to Catalysis:**

The term catalysis was first used by Berzelius in 1836. The concept was used to identify a new entity capable of promoting chemical reaction by a 'catalytic contact'. The catalyst was seen as an important chemical that was added to the reaction to speed up the rate of reaction without being consumed or produced in the process. A chemical reaction takes place by lowering activation energy in going from reactants to the products. [1].

The phenomenon of catalysis has been extensively studied for nearly a century and half. Today, catalyst make possible about 90% of the chemical manufacturing processes globally. Consequently research on catalyzed reactions continues to increase at a very fast phase. Due to the immense contribution made by the catalysts to all the dimensions of the technological processes, catalytic science has grown as a separate branch of chemistry and reaction engineering and search for a new catalyst, for newer transformations and study the existing ones continues endlessly [1,2].

Catalyst started to play a major role on the chemical reaction since twentieth century. Currently more than 95 % industrial process utilizes catalyst to produce varieties of chemicals via a process that includes at least one catalytic step. In summary, catalysis nowadays plays a key role in the production of chemicals and materials [2].

### **Catalysis and Technology**

How important is catalysis? Our worldwide economy is based on the catalytic production of chemicals and fuels. Much of the food we eat is preprocessed catalytically and cloths we ware are made up of fabrics produced in catalytic process. Generally, almost all the chemical, fuels, polymers and fibers are manufactured by one or the other catalytic process [3]. Also various kinds of organic transformations and water treatment or purification processes are carried out with the help of catalyst only, without which the transformations are not feasible. Some of the applications of catalyst are enlisted in table 1.1.

**Table 1.1** Few applications of catalyst for organic transformation and water treatment

Catalyst	Applications	Referances
TiO <sub>2</sub> nanoparticles	Michael additions	<i>Adv. Synth. Catal.</i> 348 (2006) 867
TiO <sub>2</sub> nanoparticles	oxidation of sulfides to sulfones and sulfoxides	<i>J. Mol. Catal. A</i> 323 (2010) 59
MgO nanoparticles	Wadsworth–Emmons reactions	<i>J. Mol. Catal. A</i> 234 (2005) 25
MgO nanoparticles	synthesis of flavanones	<i>TetLett.</i> 46 (2005) 1369
MgO nanoparticles	Henry and Michael Reactions	<i>J. Am. Chem. Soc.</i> 127 (2005) 13171
ZnO nanoparticles	5-Substituted 1 <i>H</i> -tetrazoles	<i>Adv. Synth. Catal.</i> 347 (2005) 1212
Pd–Fe nanosphere	Sonogashira-, Heck-, and Ullmann-type coupling reactions	<i>J. Colloid. Inter. Sci.</i> 349 (2010) 613
Ni nanoparticles	Heck reaction	<i>Green Chem.</i> , 11 (2009) 1194
CuI Nanoparticles	C-N and C-O Cross Coupling	<i>J. Org. Chem.</i> 74 (2009) 7951
N-doped TiO <sub>2</sub>	Photodegradation of methyl parathion and dichlorvos	<i>Chem. Engg. J.</i> 172 (2011) 678
ZnO	Photocatalytic degradation of Metamitron	<i>Desalination</i> 249 (2009) 286

In fact, without catalysis no form of life could exist. The sustaining reactions of all life forms are catalyzed by the enzymes, the biological catalyst. They enable life processes to occur rapidly at ambient temperature and pressure. Enzymes are highly efficient, which can be manufactured in the order of  $10^2 - 10^3$  new molecules per second. Each enzyme contains an active sites or pockets having its own unusual geometry for binding to one specific kind of molecule.

### 1.1.1 Types of Catalysis

Catalysis is broadly classified into homogeneous catalysis and heterogeneous catalysis. A variety of homogeneous catalysts are known. Metal complexes, metal ions, organometallic complexes and organic molecules upto biocatalysts (enzymes, artificial enzymes, etc.) are used as catalyst in organic synthesis. Similarly heterogeneous catalysts, like Zeolites, metal oxides, heteropoly acids, heteropoly salts, clays, ion exchange resins, etc. are well known.

#### Homogeneous catalysis

Homogeneous catalysis can be defined as catalytic system in which the substrates for a reaction and the catalyst components are brought together in one phase most often the liquid phase [4-6].

Homogeneous catalysis involves use of organometallic complexes and non organometallic complexes [5]. A non organometallic complex involves use of general acid and base catalyst, Lewis acids – base catalyst, organic catalysts, enzymatic catalyst and co-ordination complexes catalyst etc.

Homogeneous catalysis has several advantages over the heterogeneous catalyst as follows

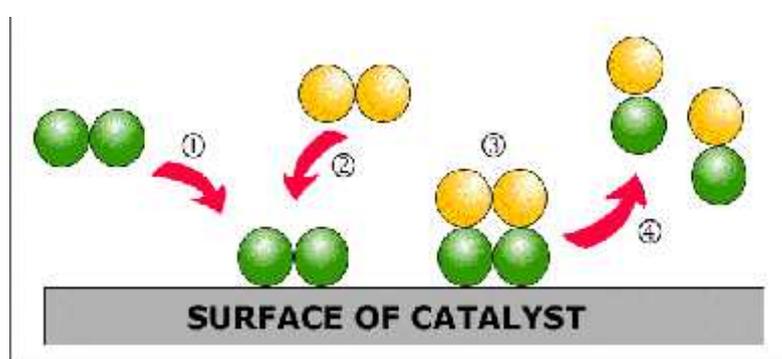
- I. Being soluble in same phase entire catalyst possesses active sites.
- II. Homogeneous catalysis allows the reactions to carry out at mild reaction conditions.
- III. The sensitivity to catalyst poisons is low.
- IV. Homogeneous catalysis is free of diffusion problems.
- V. The steric and electronic properties of catalysts can be varied.
- VI. Identification of the reaction mechanism is quite possible in case of homogeneous catalyst.

Furthermore, in the homogeneous catalysis it is possible to tune the chemo-, regio- and enantioselectivity of the catalyst. They have been widely used in a number of commercial applications.

However, the main problem associated with homogeneous catalysis was the difficulty in separation of catalyst from the final product [4-6]. Separation of trace amounts of catalyst from the end product is highly needful in the pharmaceutical industry since metal contamination is highly regulated. In spite of extensive and careful use of various techniques like distillation, chromatography or extraction, removal of trace amounts of catalyst have remained a challenge. This disadvantage of homogeneous catalyst was overcome by heterogeneous catalyst. The attractiveness of heterogeneous catalysis is mainly due to the ease of separation from the reaction products and recyclability of the catalyst.

### Heterogeneous Catalysis

In heterogeneous catalysis, the phase of the catalyst is altogether different from that of the reactants. Phase here refers not only to solid, liquid or gas, but also immiscible liquids, e.g. oil and water. In general, in heterogeneous catalysis catalysts are mainly in solid phase while the great majority of reactants are gases or liquids [5]. Heterogeneous catalysis have supreme importance in many areas of the chemical and energy industries.



**Figure 1.1** Heterogeneous catalyzed reaction

The major advantage of the heterogeneous catalysis is the ease of separation of the product from reaction mixture and catalyst. The following steps are involve in heterogeneous catalysis (figure 1.1)

- i) Internal diffusion
- ii) External diffusion
- iii) Adsorption of reagents
- iv) Surface reactions
- v) Desorption of products

For solid heterogeneous catalysts, the surface area of the catalyst is vital as it determines the availability of catalytic sites. Hence it is essential to have surface areas of heterogeneous catalyst as high as possible for better efficiency. For example some mesoporous silicates have areas of 1000 m<sup>2</sup>/g. The most common approach to maximizing surface area is by the use of catalyst supports, which are the materials over which the catalysts are spread.

### **Photocatalysis**

In photocatalysis, light is absorbed by a catalyst and catalyst work under presence of light. The photocatalytic activity of the catalyst is depends on the ability of the catalyst to create electron–hole pairs, which generate free radicals (e.g. hydroxyl radicals: •OH)

### **Homogeneous Photocatalysis**

In homogeneous photocatalysis, the reactants and the photocatalyst exist in the same phase. The most commonly used homogeneous photocatalysts include, ozone, transition metal oxide and photo-Fenton systems (Fe<sup>+</sup> and Fe<sup>+</sup>/H<sub>2</sub>O<sub>2</sub>). The reactive species is the •OH which is used for different purposes. The mechanism of hydroxyl radical production photo-Fenton system is as follow



In photo-Fenton type processes, hydroxyl radicals are produced by photolysis of  $\text{H}_2\text{O}_2$ , and reduction of  $\text{Fe}^{3+}$  ions under UV light:



The efficiency of Fenton type processes is influenced by several operating parameters like concentration of hydrogen peroxide, pH and intensity of UV.

### Heterogeneous Photocatalysis

In heterogeneous catalysis, catalyst is a different phase from the reactants. Heterogeneous photocatalysis mainly includes water treatment and gaseous pollutant removal.

Most common heterogeneous photocatalysts are semiconductors. When light falls on these semiconductors, the electron present in the valence band jumps to the conduction band, a result of which is the generation of a positive hole. The recombination of the electron and the hole must be prevented as much as possible to increase the photocatalytic efficiency of the catalyst. Due to the generation of positive holes and electrons, oxidation-reduction reactions take place at the surface of semiconductors. In the oxidative reaction, the positive holes react with the moisture present on the surface and produce a hydroxyl radical.

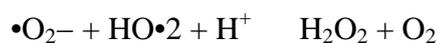
Oxidative reactions due to photocatalytic effect:



Here MO stands for metal oxide ---



The reductive reaction due to photocatalytic effect:



Both the oxidative and reductive reaction produces hydroxyl radicals. These hydroxyl radicals are very oxidative in nature [7].

### 1.1.2 Parameter to Measure Catalysis Performance

#### Turn over number or Turn over frequency

The catalysis performance is measured in terms of turn over number or turn over frequency [5]. The turn over number (TON) or turn over frequency (TOF) is defined as number of reactant molecule that reacts per unit site of catalyst per unit time for fixed set of reaction conditions (pressure, reactant concentration, time).

In general words

TON = No of molecules of given products / No. of. Active sites

TOF = No of molecules of given product / No. of. Active sites x time

Heterogeneous catalysis dominates chemical and petrochemical industry. Approximately 95% of all chemical processes use heterogeneous catalysts. Although the fundamental processes for refining petroleum and its conversion to basic building blocks are based on heterogeneous catalysts, many important value-added products are manufactured by homogeneous catalytic processes. **Table 1.2** shows some illustrative examples of few industrial processes and catalysts used for those processes [4].

**Table 1.2** some homogeneous and heterogeneous catalysts used in important industrial processes

Process	Typical Catalysts
<b>Petroleum Refining</b>	
Cracking	Pt/Re on alumina, Zeolites
Reforming (dehydrogenation)	Pt/Re/Ge/Sn on alumina
Hydrocracking	alumina, zeolites, Pt
Alkylation	H <sub>2</sub> SO <sub>4</sub> , HF

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Hydrodesulfurization	(Mo-Co) oxides, (Mo-Ni) oxides
Hydrodenitrogenation	(W-Ni) oxides
<b>Chemical Manufacturing</b>	
Natural Gas desulfurization	ZnO, Cu, Fe on activated C
Hydrogenations	Raney Ni, Raney Co, Pt, Rh
Ammonia synthesis	Promoted Fe
Methanol synthesis	Cu-ZnO
Dehydrogenation	Butadiene: Fe <sub>2</sub> O <sub>3</sub> , Pt/Re on alumina Styrene: Zn, Cr, Fe or Mn oxides
Oxidations	Ethylene oxide: Ag Nitric acid: Pt/Rh mesh/gauze Sulfuric acid: V <sub>2</sub> O <sub>5</sub> Maleic, phthalic anhydrides: V <sub>2</sub> O <sub>5</sub> Formaldehyde: Ag or Cu; Mo, Fe, V oxides Polymerizations Ziegler-Natta polypropylene: Al alkyls + TiCl <sub>3</sub> Dow single site polypropylene: Ti metallocene Phillips -- Chromium oxide on silica Polyethylene (low density): peroxides, peresters Polystyrene: benzoyl peroxide Urethanes: amines, organo-tin, phosphine oxides
Hydroformylation	Union Carbide/Hoechst/BASF: Rh/PPh <sub>3</sub> Exxon/BASF: HCo(CO) <sub>4</sub> Shell: HCo(CO) <sub>4</sub> (PR <sub>3</sub> ) (R = bulky alkyl)

Both these homogeneous and heterogeneous types of catalysis possess their own advantages and disadvantages as listed in **Table 1.3** below.

**Table 1.3** Homogeneous versus Heterogeneous catalysis

<b>Properties</b>	<b>Homogeneous</b>	<b>Heterogeneous</b>
Activity	High	Low
Selectivity	High	Poor
Catalyst Recycling	-	High
Catalyst Description	Low	-
TON	Poor	High
Quantity of catalyst	Low	High
Catalyst Modification	High	-
Reaction Temperature Required	Low	High
Reaction Mechanism	Well understood	Poorly understood

Heterogeneous catalysts have several advantages over the homogeneous counterparts. Thus a search for new and better heterogeneous catalyst has always remained an active area of research.

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### 1.1.3 Advantages of heterogeneous catalyst

There are many factors that affect the heterogeneous catalysis and effectiveness of a particular catalyst for a given reaction is likely to be the result of a combination of factors such as surface area, porosity, acidity-basicity, as well as the crystalline or amorphous nature of the material.

The factors that play an important role in heterogeneous catalysis are listed follow:

- A. **Reduction in Dimension:** for a gas phase or solution phase reaction, the reacting molecules are free to move in three dimensional reaction volumes. In case of the heterogeneous catalysis, the dimensionality is reduced from 3-D to 2-D. Thus the effective encounter rates are greatly increased due to the constraints of the diffusing reacting molecules on the surface [8].
- B. **Increase local concentration on the surface:** Due to adsorption, there is always an increase in local concentration of the reactant molecules on the surface of the catalyst. Accordingly, the probability of the reactive encounter is highly increased. In case of the polyelectrolytic solid catalyst, due to the columbic interaction, there is an increased concentration (or activity) in proximity of the surface. This effect can be large –typically, when the average concentration is millimolar, the order of the magnitude of the local concentration next to the charged surface can be molar or more.
- C. **Surface area:** The increase in the surface area of the catalyst results in the increase in the rate of the reaction. This is not only due to the increase in the number of fruitful encounters on the surface but also due to the increase in the number of active sites available for the reaction. The surface area can be increased by number of methods for a variety of catalyst. It can be simply achieved by dispersing the catalyst over a high surface area material.
- D. **Easy work-up:** After the reaction, the product can be easily separated from catalyst by mere filtration or by centrifugation. This is not only easy isolation of the desired product but also switches off the reaction and removes any liable product in contact with the catalyst which may lead to unwanted side reactions. An excess of catalyst can be used to drive the reaction to completion. In many cases, the catalyst can be regenerated,

reactivated and reused, thus decreasing the cost of the process. Thus, the overall process creates less waste and the cost is reduced.

- E. **New or better selectivity:** An important motivation to investigate heterogeneous catalysis is the hope to improve upon the unsatisfactory performance of the soluble catalyst. Heterogeneous catalysts offer scope for a better selectivity. Impressive sensitivities can be obtained with the normal, acid treated, ion-exchanges and pillared variants of clays, as well as zeolites. This catalyst can offer the guest reactants highly structured microreactors that favor the formation of the single product.
- F. **Safe handling:** In a number of cases, immobilization of a reagent changes not only its chemical behavior, but also its properties such as its sensitivity to shock. Hazardous chemical can be controlled by deposition in electrostatic environment of a polyanion, such as anionic sheets of polysilicates. Alfred Noble domesticated wild nitroglycerine by affixing it onto kieselguhr diatomaceous earth and thus invented dynamite! Another example is HF adsorbed on polyvinyl pyridine [9].
- G. **Environmental viability:** Solid acid and base catalysts pose much less ecological problems than their soluble analogues, as the processes produce minimum waste.
- H. **Possibility to work in the continuous reaction mode:** The particle nature of the heterogeneous catalyst makes it possible to let the reactants flow through a bed continuously. This mode is used almost exclusively for the production of petrochemicals and bulk chemicals.

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## 1.2 Nanotechnology and Nanomaterials

The term 'Nanotechnology' is employed to study the materials or describe the creation and exploitation of materials with structural features, in between those of atoms and bulk materials, with at least one dimension in the nanometer range. Nanotechnology offers not just better products, but vastly improved manufacturing processes.

It covers fields from biology to material science, physics to chemistry, and includes development in a variety of specialties. Various applications of nanomaterials are enlisted below:

1. Gas storage applications
2. Ceramics and sensors
3. Batteries and fuel cells
4. Catalysis and electrolysis reactors
5. Various coatings such as, protective coatings of plastic surfaces, photo chromic coatings, automotive coatings, etc.
6. Electronics and laser displays
7. Thermal and scratch protection
8. Bioceramics, drug carriers
9. Magnetic nanoparticles for cancer treatment
10. In cosmetics, like sun screens

Most widely accepted definition of nanotechnology involved the following three characteristics:

1. Research and technology development at the atomic, molecular or macromolecular levels, in the range of approximately 1 - 100 nanometers.
2. Creating and using structures, devices and systems that have novel properties and functions because of their small and / or intermediate size.
3. Ability to control or manipulate on the atomic scale.

Nanoparticles consist of several tens or hundreds of atoms or molecules and may have different sizes and morphologies. These particles may be amorphous,

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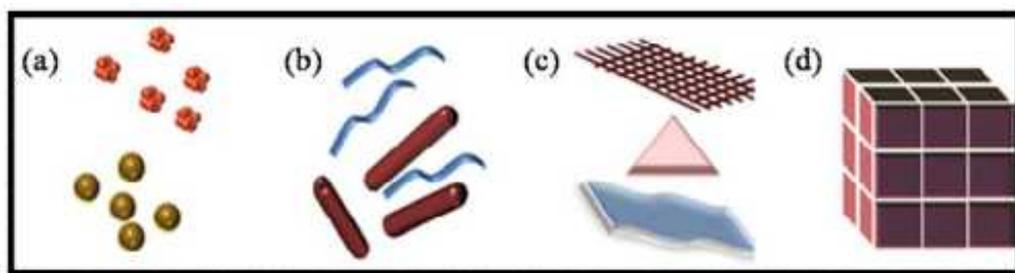
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crystalline, spherical, needle shaped, etc. Various types of nanoparticles are available commercially in the form of dry powders or liquid dispersions. Beginning of the twenty first century has witnessed a tremendous gain of scientific activity in the field of ‘Nanotechnology’ and ‘Nanoscience’. Areas producing the greatest revenue for nanoparticles are reportedly chemical-mechanical polishing, sunscreens, automotive and combustion catalyst supports, biolabelling, electro conductive coatings and optical fibers.

Nanochemistry is the growing research field in modern science that involves the synthesis and application of nanoparticles of different sizes and shapes. The terms ‘Nanotechnology’ and ‘Nanoscience’ are often used synonymously [10]. Nanoparticles are different from their bulk counterparts and exhibit unique optical, magnetic, electrical and other properties [5]. These properties have the potential for great impacts in electronics, medicine and other fields. The two main reasons behind different properties of nanomaterials at nanoscale are increased relative surface area and new quantum effects. 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. Also at the nano scale, quantum effects can become much more important in determining the material properties and characteristics, leading to novel optical, electrical and magnetic behaviors.

### 1.2.1 Type of nanomaterials

Nanomaterials are classified into zero dimensional, one dimensional, two dimensional and three dimensional nanomaterials based on number of dimensions that are present in the nanosize in the given materials ( Figure 1.2)



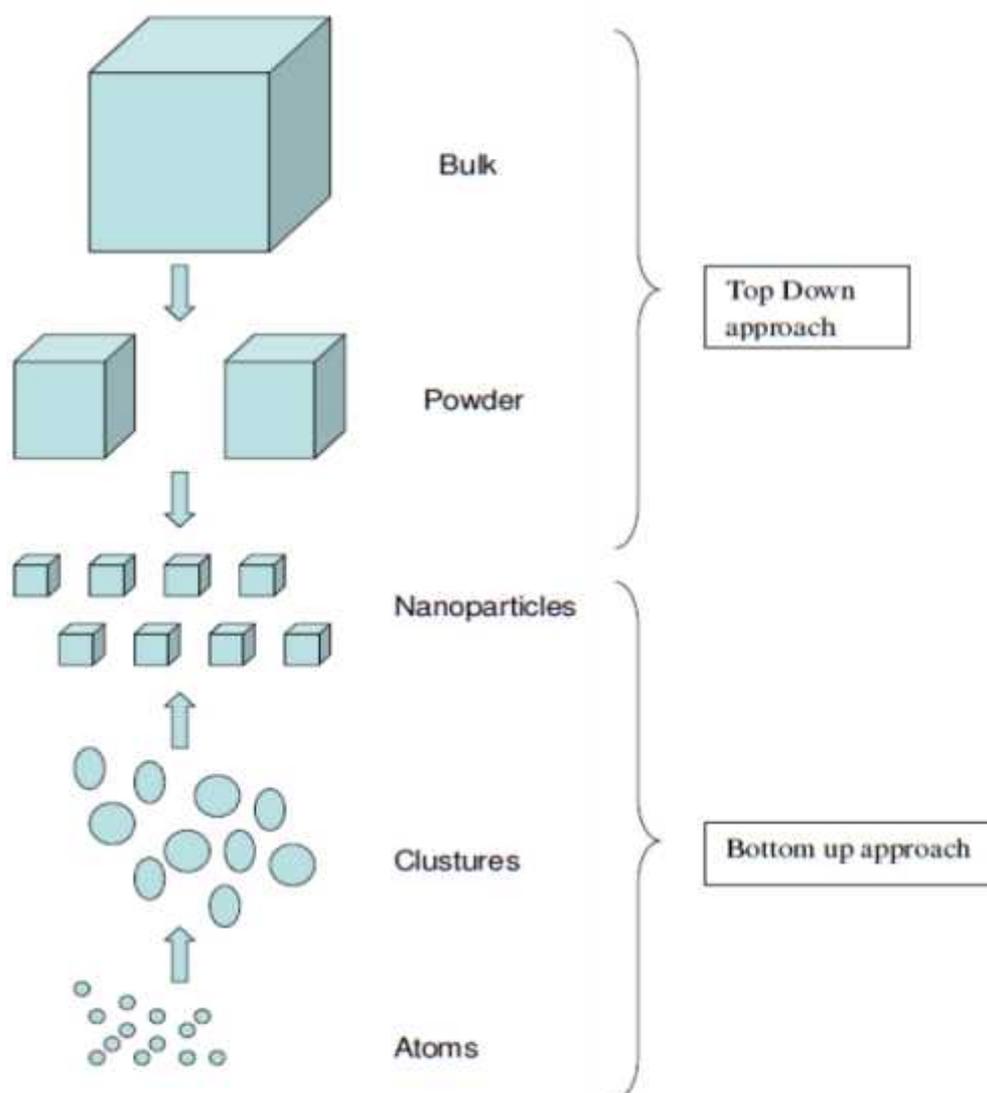
**Figure 1.2** -Classification of Nanomaterials

Various modulation dimensionalities are:

- (a) Zero (spheres, atomic clusters, filaments and cluster assemblies)
- (b) One ( nanofibers, wires, rods, multilayer's)
- (c) Two (films, plates, networks, ultrafine-grained over layers or buried layers)
- (d) Three ( nanocubes, nanophase materials consisting of equiaxed nanometer sized grains)

### 1.2.2 Synthesis of Nanomaterials

There are two main basic approaches for synthesis of nanoparticles namely top down approach and bottom up approach (Figure 1.3) [5]. The top-down or bottom-up approaches comprised of varieties of techniques. Synthesis and assembly strategies of nanoparticles mostly accommodate precursors from liquid, solid or gas phase; employ chemical or physical deposition approaches; and similarly rely on either chemical reactivity or physical compaction to integrate the nanostructure building blocks within the final material structure.



**Figure 1.3** Preparation approaches for nanomaterials

## **Top down approach**

In this approach bulk size material is converted into the anodize materials. In the Top-down approach a suitable starting material is taken and then it is modified into the desired shape. This approach mainly provides advantage of synthesizing material in bulk quantity however materials from this approach has irregularity in their shape size and have surface strain. This particular area of nanostructure formation has tremendous scope in the electronics industry. Some of the methods of top-down approach are as follows

### **1. Mechanical Methods:**

In this mechanical method large size material is grinded into the smaller size material with the help of rotating spheres. The shape and size of material is depends on the physical dimension of the rotating balls and kinetic energy of grinding is used for size reduction. This is simplest and most economical process among top down approach for nanoparticles synthesis. Ball milling is perhaps the simplest of them all.

Ball milling produces nanomaterials by mechanical attrition in which kinetic energy from a grinding medium is transferred to a material undergoing reduction.

### **2. Melt mixing:**

The melt mixing process finds favor in polymer industry due to its compatibility with current industrial compounding facilities. This process is economically favorable and benign as it eliminates use of solvents. In the melt mixing processes, polymer molecules gain increased mobility through an input of thermal energy and are mixed with the fillers mechanically.

### **3. Methods based on evaporation:**

In these methods nanostructures are deposited in the form of thin films, multilayers films or nanoparticles by evaporating the materials. Evaporation can be achieved by various methods like resistive heating, electron beam heating, laser heating, sputtering, etc. According to method of evaporation they are named as:

Laser vaporization (ablation), ionized cluster beam deposition, physical vapor deposition, Laser pyrolysis, sputter deposition, etc.

### **Chemical Vapor deposition**

It has been widely used for synthesis of carbon nanomaterials. In this technique, carbon nano tubes grow from the decomposition of hydrocarbons at temperature range of 500 to 1200 °C. They can grow on substrates such as carbon, quartz, silicon, etc or on floating fine catalyst particles, e.g. Fe, Ni, Co, etc from numerous hydrocarbons e.g. benzene, xylene, natural gas, acetylene.

### **Laser ablation technique**

It involves the use of laser beam to evaporate a target mixture of graphite and metal catalyst at high temperature about 1200 °C in a flow of controlled inert gas (argon) and pressure. The catalysts mainly used are Fe and Co. This in turn hampers its scale up potentials as compared to the CVD method.

### **Electric arc discharge**

The arc discharge method produces a number of carbon nanostructures such as fullerenes, whiskers, soot and highly graphitized carbon nanotubes from high temperature plasma that approaches 3700 °C. The nanoparticles produce with the help of DC arc discharge between two carbon electrodes, anode and the cathode in presence of noble gas (helium or argon) environment.

## **4. Lithographic methods:**

Nanolithography is used during the fabrication of leading-edge semiconductor integrated circuits (nanocircuitry) or nanoelectromechanical systems (NEMS).

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**Bottom up Approach**

In this approach, material at atom or molecular level is tuned into the nanosize materials. The bottom up approaches to nanofabrication involves the addition of atoms or group of atoms. The variety of preparation methods are involved in bottom-up techniques, which allow good control onto scale dimension, even from atomic or molecular level. They are not as expensive as top-down approaches. Some of the methods of bottom-up approach are as follows

**1. Wet chemical methods:**

This method involves the precipitation of chemical compound in solution. This method can be classified into five major categories

**a) Colloidal methods:**

Solutions of the different ions are mixed under controlled temperature and pressure to form insoluble precipitates.

**b) Sol-gel processing:**

Sol-gel process consists of the chemical transformation of a liquid (the sol) into a gel state and with subsequent post treatment and transition into solid oxide material. The main benefits of sol-gel processing are the high purity and uniform nanostructure achievable at low temperatures.

**c) Water-oil microemulsion method:**

Synthesis of nanoparticles in the cavities produced in microemulsion is a widely used method. An advantage of this method is the biocompatibility and biodegradability of synthesized materials.

**d) Hydrothermal and Solvothermal synthesis:**

Solvothermal and hydrothermal approaches utilize solvent under elevated pressure and temperature above or below its critical point to increase the solubility of a solid and to speed up reaction between precursors.

**e) Chemical precipitation route:**

Chemical precipitation is a widely used approach for the preparation of nanoparticles. During the process of precipitation, nucleation is a key step of the precipitation process and a large number of small particles are generated. This process involve simultaneous occurrence of nucleation, growth, coarsening and agglomeration processes, hence careful control of the reaction conditions is required for the generation of monodisperse nanoparticles. The essential controlling factor of this method includes styles of precipitation reaction, pH, concentration, temperature, surfactants etc. All these factors must focus on the nucleation with only one burst formation of nuclei during the whole precipitation reactions [11].

### **1.2.3 Characterization of Nanomaterials**

Characterization provides means to have understanding and control over synthesis and applications of nanoparticles. Morphology, crystal structure and elemental composition identification via characterization is important to have understanding of nanomaterials. Common techniques for morphological analysis are Transmission electron microscopy (TEM), Scanning electron microscopy (SEM), Atomic force microscopy (AFM); Particle size analysis, dynamic light scattering (DLS), etc. Techniques used for chemical analysis are x-ray photoelectron spectroscopy (XPS), powder X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), ultraviolet-visible spectroscopy (UV-vis spectroscopy), Energy dispersive x-ray spectroscopy (EDX), Thermal analysis, Raman spectroscopy, Surface area measurement, Temperature programmed desorption (TPD), Inductively coupled plasma (ICP), etc. Some of the most commonly used techniques are described below.

#### **Transmission Electron Microscopy (TEM)**

Transmission electron microscopy (TEM) is one of the most important techniques for characterization of nanomaterials. It is useful to get size of the nanomaterials. It is a technique whereby a beam of electrons is transmitted through an ultra thin specimen, interacting with the specimen as it passes through. An image is formed from the interaction of the electrons transmitted through the specimen; the image is magnified and focused onto an imaging device, such as a fluorescent screen, on a layer of photographic film, or to be detected by a sensor such as a CCD camera. TEMs are capable of imaging at a significantly higher resolution than light microscopes. Apart from structural visualization TEM also can provide the information about melting point of nanoparticles and it can correlate the mechanical and electronic properties of Nanowires.

#### **Scanning electron microscopy (SEM)**

SEM is one of the most widely used techniques in characterization of nanomaterials and nanostructures. The resolution of the SEM is about a 3 nm and

the magnification power of instruments is over 300,000. The scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample.

### **Atomic force microscopy (AFM)**

The Atomic force microscopy (AFM) is a form of scanning probe microscope developed in the mid 1980s. It works by scanning an extremely fine probe on the end of a cantilever across the surface of a material, profiling the surface by measuring the deflection of the cantilever. This allows a 3D profile of the surface to be produced at magnifications over one million times, giving much more topographical information than optical or scanning electron microscopes. Its limitation is that the surface to be observed needs to be very flat or the tip will crash into the 'hills' as it is scanned [12].

### **X-Ray Diffraction**

XRD is a useful analytical technique for the determination of the crystal structure of solids, including lattice constants and geometry, identification of unknown materials, orientation of single crystals, preferred orientation of polycrystals, defects, stresses, etc. When an X-ray beam hits an atom, the electrons around the atom start to oscillate with the same frequency as the incoming beam. In almost all directions one will have destructive interference, and there is no resultant energy leaving the solid sample. However the atoms in a crystal are arranged in a regular pattern, and in a very few directions one will have constructive interference and there will be well defined X-ray beams leaving the sample at various directions. Hence, a diffracted beam may be described as a beam composed of a large number of scattered rays mutually reinforcing one another. A typical diffraction spectrum consists of a plot of reflected intensities versus the detector angle  $2\theta$  or  $\theta$  depending on the goniometer configuration [13] The beam diffracted by the crystalline phases in the specimen according to Bragg's law:

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$$= 2d \sin$$

Where  $d$  = spacing between atomic planes in the crystalline phase

= the X-ray wave length.

The intensity of the diffracted X-rays is measured as a function of the diffraction angle  $2\theta$  and the specimen's orientation. This diffraction pattern is a key to understand the specimen's crystalline phases and to measure its structural properties. The XRD is non-destructive method. XRD is also capable of measuring homogeneous and heterogeneous strain with the help of diffraction peak position. The crystallite size can be measured with XRD using the Scherrer's formula:

$$D = 0.9 \lambda / \Delta 2\theta \cos \theta$$

Where

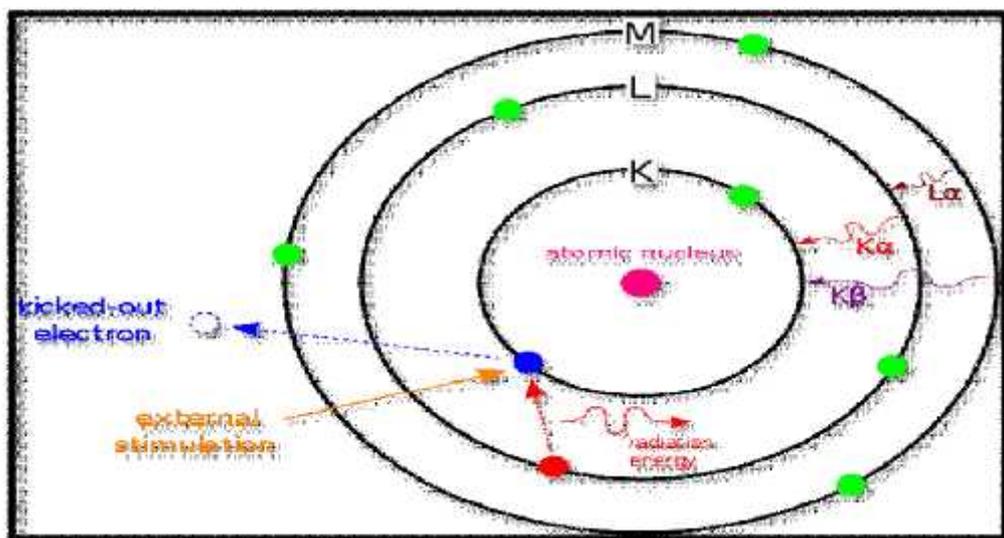
$\lambda$  is the X-ray wave length,

$\Delta 2\theta$  is the full width of height maximum of a diffraction peak,

$\theta$  is the diffraction angle.

Therefore, Scherrer's formula may produce crystallite size different from the true particle size.

### Energy dispersive X-ray spectroscopy (EDX)



**Figure 1.4-** Schematic representation of EDS principle

Energy-dispersive X-ray spectroscopy (EDS or EDX or EDAX) is an analytical technique used for the elemental analysis or chemical characterization of

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a sample. This characterization technique is based on the fundamental principle that each element has a unique atomic structure allowing X-rays that are characteristic of an element's atomic structure. To stimulate the emission of characteristic X-rays from a specimen, a high energy beam of charged particles such as electrons or protons, or a beam of X-rays, is focused into the sample being studied. The incident beam may excite an electron in an inner shell (K-shell), ejecting it from the shell while creating an electron hole where the electron was. An electron from an outer, higher-energy shell then fills the hole, and the difference in energy between the higher-energy shell and the lower energy shell may be released in the form of an X-ray (Figure 1.4). The energy of the X-rays emitted from a specimen can be measured by an energy-dispersive spectrometer. As the energy of the X-rays is characteristic of the difference in energy between the two shells, and of the atomic structure of the element from which they were emitted, this allows the elemental composition of the specimen to be measured [14].

### **Fourier Transform - Infrared spectroscopy (FT-IR)**

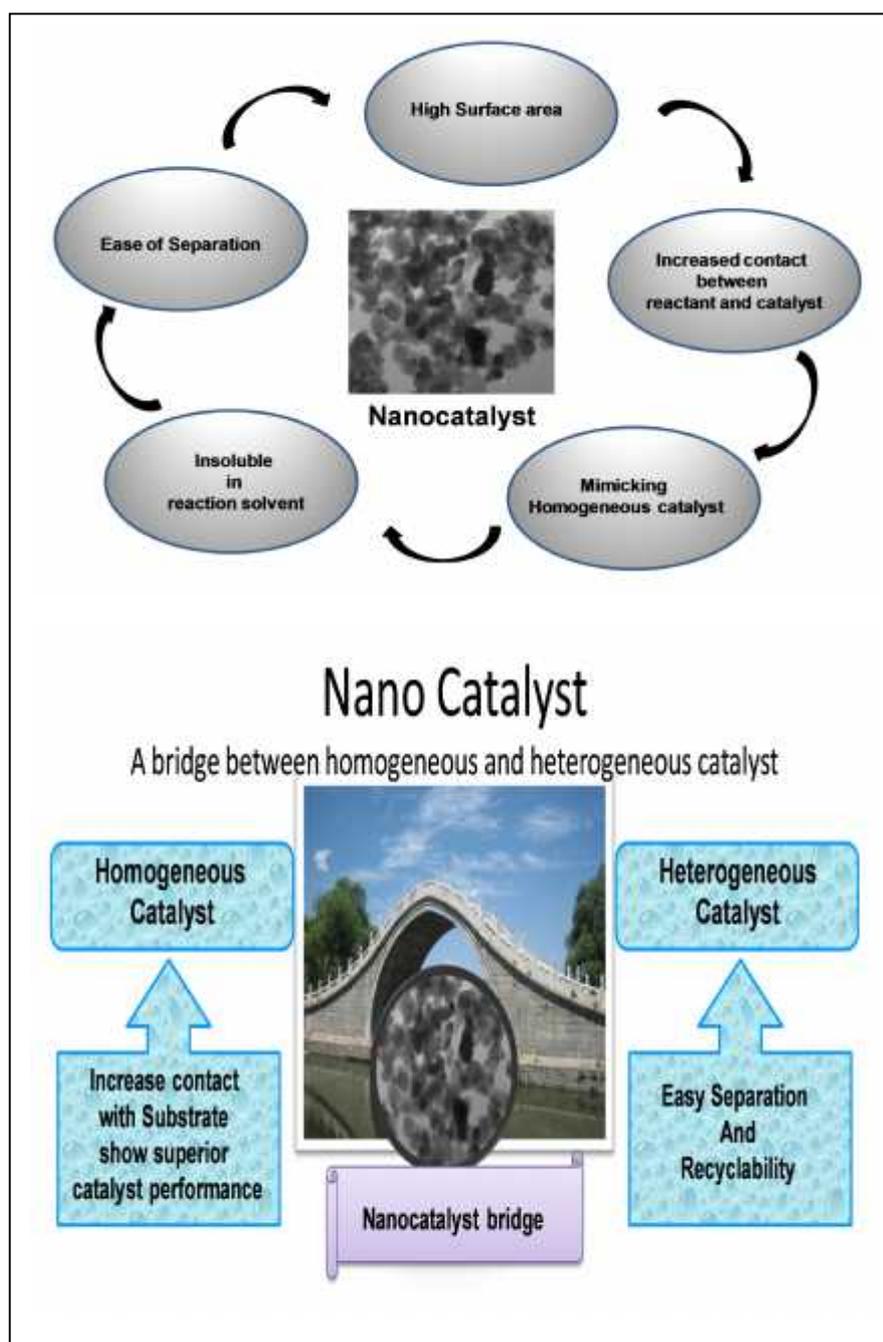
Infrared spectroscopy has is useful technique for qualitative analysis of the material. An infrared spectrum represents a fingerprint of a sample with absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms making up the material. Because each different material is a unique combination of atoms, no two compounds produce the exact same infrared spectrum. Therefore, infrared spectroscopy can result in a positive identification (qualitative analysis) of every different kind of material.

### **Particle size analysis**

Particle size analysis is used to characterize the size distribution of particles in a given sample. Particle size analysis can be applied to solid materials, suspensions, emulsions and even aerosols. There are many different methods employed to measure particle size. One basic problem in particle size analysis is characterizing particles using just one number. Most particle sizing techniques aim report particle size distributions on a two dimensional graph (that is particle size on

the x-axis and quantity of material on the y-axis). This technique can be used to get approximate idea about the size of the nanomaterials synthesized.

### 1.2.4 Catalysis by Nanomaterials



**Figure 1.5-** Nanocatalysis A bridge between Homogeneous and heterogeneous catalysis.

Nanoparticles have emerged as sustainable alternatives to conventional materials, which provide high surface area to catalysts and catalyst supports. The

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nano-sized particles increase active surface area of the catalyst, thereby enhancing the contact between reactants and catalyst 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 nano-catalyst can be manipulated by tailoring chemical and physical properties like size, shape, composition and morphology [15]. Thus it shows that nanocatalysts behave like the homogeneous catalyst and heterogeneous catalyst and play a role of bridge between the conventional catalytic systems (See Figure 1.5).

Nanoparticles give high efficiency at high conversion rate under mild reaction conditions. This is the most prominent advantage of the nanoparticles (NP) catalyst. The high efficiency of the NP system relies mainly on the approach to the metal core, including the screening of the metal, the size of the particle, and the structure of the surface. The most significant merits are energy and time saving and waste reducing. In a word, it improves reaction efficiency. Although there are very few examples of such efforts at present, more attention is being paid to this aspect since it represents the future of green chemistry [16].

### 1.2.5 Applications of Nanomaterials in Catalysis



**Figure 1.6** Application of Nanomaterials in various field.

Applications of nanomaterials incorporated in this thesis are mainly for A) photocatalytic degradation of organic molecules such as pesticide and dyes and B) for organic transformations.

#### **A) Photocatalytic degradation.**

Nanomaterials are widely used in photocatalytic degradation processes. Photocatalysis is a greener methodology for the treatment of pollutants with light energy. The process of photocatalysis is photo-oxidative decomposition of organic pollutants and thereby purification of wastewater. [17] Photodegradation process involves direct UV excitation or photosensitization of the catalyst surface. This process of light irradiation of surface of catalyst promotes the electron from the valence band into the conduction band (CB) of the catalyst. As a consequence of irradiation, photogenerated positive holes and excited electrons are produced. These electrons and positive holes are responsible for generation of hydroxyl radical and super oxide radical. The photooxidation process occurs by reacting hydroxyl radical and super oxide radical with organic matter [18].

Some of the catalysts used in the photocatalytic degradation processes are enlisted in table 1.4:

**Table 1.4** Few applications of catalyst used for photocatalytic treatment

Catalyst	Degradation of Dyes/Pesticides	Referances
TiO <sub>2</sub>	Dichlorvos	19
Metalloporphirins/TiO <sub>2</sub>	Atrazine	20
TiO <sub>2</sub>	Atrazine	21
TiO <sub>2</sub>	Acephate	22
V <sup>5+</sup> , Mo <sup>6+</sup> , Th <sup>4+</sup> / TiO <sub>2</sub>	Chlorpyrifos	23
TiO <sub>2</sub> and ZnO	Methyl Parathion	24
BiPO <sub>4</sub>	Methyl orange	25
Zinc Ferrite	Rhodamine B	26
MgO/ SnO <sub>2</sub>	Chlorophenol and Textile colorant	27
MgO/TiO <sub>2</sub>	Eosin Y	28

### B) Organic transformations.

Nanomaterials played an important role in heterogeneous catalysis due to their large surface area, concentration of under coordinated surface sites and their potential for dispersion on the surface of an oxide or other support. Nanomaterials can achieve higher catalytic activity when compared to bulk particles, and also higher selectivity which is an important issue in the development of greener synthesis methods. Maximum chemical processes like alkylation, hydrogenation, dehydrogenation, dehydration, condensation and coupling reactions were carried out by transition metal or metal oxide catalyst. In recent years, the interests in catalytic properties of transition metal nanoparticles have grown tremendously. The catalytic activity of transition metals is mainly decided by their 'd' orbital properties. Mainly according to their catalytic behavior, the frequently encountered metals in catalysis can be divided into five categories: (1) Ti, Zr, Nb, Mn, V, Cr, Mo and W; (2) Fe, Co and Ni; (3) Cu, Ag and Au; (4) Ru, Rh, Pt and Ir; (5) Pd.

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**1) Catalysis by nanoparticles****a) Catalysis by Ti, Zr, Nb, Mn, V, Cr, Mo and W nanoparticles**

These elements are relatively inexpensive as compared to other transition metals which make their choice as catalyst. They are useful in hydrogenation reaction. For example, Ti, Zr, Nb and Mn nanoparticles for hydrogenation reaction [29]. Colloidal Ti nanoparticles were most efficient catalysts among various metals for the hydrogenation of titanium and zirconium sponges as well as for nickel hydride battery alloy [30]. Ti NP were also found to be effective catalyst for various McMurry coupling reactions of benzophenone, benzaldehyde and acetophenone to give desired products in good yield and selectivity [31].

The oxides of Mn, V, Cr and Mo are used in the selective oxidation and epoxidation of alkanes. The TiO<sub>2</sub> nanoparticles have used as an excellent Photo catalyst, which is capable of producing H<sub>2</sub> from water and degrading some environmental pollutants in the presence of UV light [32].

**b) Catalysis by Nanoparticles of Fe, Co and Ni**

Fe, Co and Ni metals are cheap elements and available in abundant. Their nanoparticles are found to be a good catalyst for hydrogenation, hydrosilation, C–C coupling and oxidation reactions. Ni nanoparticles were found to be highly efficient for selective reduction of nitro benzaldehyde. Diels alder reaction to form C-C bond was effectively carried out in presence of Ni nanoparticles. [33]

Similarly Co nanoparticles were useful in hydrogenation of , unsaturated carbonyl compound and shown a good selectivity and efficiency. For over a decade's Fe, Co nanoparticles were the good catalyst for Fischer –Tropsch synthesis of CO hydrogenation [34]. Fe nanoparticles have shown a good catalytic activity in hydrosilylation and hydroformylation reaction [35].

**c) Catalysis by Cu, Ag and Au nanoparticles**

Copper, silver, and gold nanoparticles are very good catalyst for redox reactions. Copper nanoparticles are essentially a good catalyst for methanol synthesis by CO hydrogenation, C-C bond formation via coupling reactions and

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various condensation reactions [33]. C-N, C-C, C-O and C-S bond formation reactions were extremely studied by using cuprous oxide and cupric oxide nanoparticles [35]. Gold nanoparticles are used in oxidation of CO gas is a relatively milder reaction [36]. Epoxidation of ethene has been successfully carried out by Ag nanoparticles [37].

Silver and gold nanoparticles have even performed as good catalyst for selective oxidation, reduction and C-C bond formation reactions. Ag nanoparticles showed good activity in oxidative coupling of phenol, synthesis of unsaturated carbonyl compounds from alcohol condensation. [38] Gold nanoparticles also showed a good activity in coupling reactions of C-C and C-N bond formation. [39].

#### **d) Catalysis by Ru, Rh, Pt and Ir nanoparticles**

The nanoparticles of rhodium, ruthenium, platinum and iridium have shown a good catalytic activity for hydrogenation reactions. The effectiveness of their reduction magnitude is  $Rh > Ru > Pt > Ir$ . Ru, Ir and Pt gave effective reduction of carbonyl compound under milder reaction conditions [40]. Platinum and Ruthenium nanoparticles are capable to catalyze some oxidation reactions [41]. Platinum nanoparticles effectively oxidize various activated and non activated alcoholic compounds under mild reaction conditions [42]. Ruthenium nanoparticles effectively carried out oxidation of cyclo-octane into various oxidation products like cyclo-octanone and cyclooctanol. Ruthenium and Platinum nanoparticles have brought reduction of N=O bond into the  $NH_2$  group under mild reaction conditions [43].

#### **e) Catalysis by Palladium nanoparticles**

Palladium nanoparticles have played excellent catalytic role in hydrogenation, dehydrogenation and C-C bond formation reactions. Pd nanoparticles bring about selective reduction of unsaturated carbonyl compounds. Several coupling reactions like Heck, Sonogashira, Suzuki coupling reactions and C-S, C-N, C-O bond formation reactions have been effectively catalyzed by Pd nanoparticles [34].

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## 2) Catalysis by nano metal oxides

Metal oxides play a very important role in many areas of Chemistry, Physics, and Materials science. Metal oxides are a form of important class of heterogeneous catalyst. Metal oxides show high level of chemo-selectivity, environmental compatibility, simplicity of operation and availability at low cost. They exhibit metallic, semiconductor, or insulator character due to the different in electronic structure. The variety of attributes of oxides enable the wide applications in the fabrication of microelectronic circuits, sensors, piezoelectric devices, fuel cells, coatings against corrosion, and as catalysts.

Almost all catalysts involve an oxide as active phase, promoter or support, which allows the active components to disperse on. In the chemical and petrochemical industries, products worth billions of dollars are generated every year through processes that use oxide and metal/oxide catalysts. The three key features essential for their application as adsorbents or catalysts are

- (i) the coordination environment of surface atoms,
- (ii) the redox properties, and
- (iii) the oxidation state at surface layers

Compared to the metallic state, the oxides of early transition metals are generally paid more attention as they can effectively catalyze many useful reactions in traditional heterogeneous catalysis. For instance, the oxides of Mn, V, Cr and Mo are extensively used in the selective oxidation of alkanes.

In the field of photo catalysis,  $\text{TiO}_2$  is widely recognized as an excellent catalyst that is capable of producing hydroxyl and superoxide radical from water and degrading some environmental pollutants in the presence of UV light. In a simple classification, oxides having only s or p electrons in their valence orbital's tend to be more effective for acid/base catalysis, while those having d or f outer electrons find a wider range of uses [44,45].

Surface of metal oxides exhibit both Lewis acid and Lewis base character. This is the characteristic of many metal oxides, especially  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{ZnO}$ , etc., and they are excellent adsorbents for a wide variety of organic compounds and they also increase reactivity of the reactants. Nanocrystalline metal oxides have shown to

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exhibit high chemical reactivities toward a variety of adsorbates, including acid gases, chlorocarbons, and polar organics including carbonyl compounds, insecticides, and chemical warfare agents (and surrogates). These high reactivities are due to high surface areas combined with unusually reactive morphologies [46-48]. High yield, selectivity and recyclability have been reported for a variety of nanocatalyst based organic reactions. [49]

Some of the most commonly and widely used nano metal oxides either as a catalyst support or directly as a catalysts are described below.

### 1) Cerium oxide

Ceria ( $\text{CeO}_2$ ) is an oxide with important applications in areas of catalysis, electrochemistry, photochemistry and materials science. In its most stable phase, bulk  $\text{CeO}_2$  adopts a fluorite-type crystal. One of the most interesting properties of ceria is its ability to undergo a facile conversion between “+4” and “+3” formal oxidation states. Because of this, ceria is a key component in catalysts commonly used to reduce the emissions of  $\text{CO}$ ,  $\text{NO}_x$ , and hydrocarbons from automobile exhaust. [50]

### 2) Titanium oxide ( $\text{TiO}_2$ )

Titanium dioxide ( $\text{TiO}_2$ ) is one of the most prominent oxide materials for performing various kinds of industrial applications related to catalysis among which the selective reduction of  $\text{NO}_x$  in stationary sources [51,52] photocatalysis for pollutant elimination [53] and organic synthesis[54], appear as rather important.

### 3) Zinc oxide ( $\text{ZnO}$ )

Zinc oxide presents the wurtzite structure and displays a high covalent Zn-O bond.  $\text{ZnO}$  is a wide band gap semiconductor extensively studied due to its intrinsic properties but with a limited industrial use as a UV-blocker in sun lotions, [55] and as a catalyst or photocatalyst [56].

### 4) Magnesium oxides

In its bulk state,  $\text{MgO}$  is a highly ionic compound and was a wide band gap (~ 7 eV) insulator. For several industrial applications  $\text{MgO}$  is doped with small amounts of a

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transition metal. Such doping can induce structural transformations and be used to stabilize MgO nanoparticles that expose (110) or (111) faces. [27, 28] Among heterogeneous basic catalysts, nano-MgO is a stable, non-volatile, non-hygroscopic, odorless, and white crystalline solid.

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### 1.3 Objectives of the current research work

In the survey of literature, we found that at present there are plenty of methods available for the synthesis of various nanomaterials, especially metal oxides. The work reported in the present thesis covers various investigations carried out using different nano metal oxides and metal. They include certain industrially as well as environmentally important reactions such as coupling, reduction, cycloaddition and photodegradation reactions.

In present research plan the objectives involved:

- Preparation of different nano-sized materials by methods reported in the literature.
- Modification of already existing methods so as to achieve synthesis of nanoparticles more efficiently.
- Characterization of prepared materials in terms of their bulk as well as surface properties.
- Test their catalytic activity for the different reactions

The various schemes carried out by using synthesized nanocatalysts are as follows:

1. Synthesis of nano  $\text{TiO}_2$  and its application to photodegradation of dichlorvos in water
2. Synthesis of nano  $\text{MgO/ZnO}$  and its application to photodegradation of methyl orange and rhodamine B in water
3. Synthesis and Characterization of Nano  $\text{CeO}_2$  for synthesis of - aminophosphonates under ultrasonication
4. Nano  $\text{CeO}_2$  catalyzed O, N arylation with 4 nitrochlorobenzene
5. Synthesis and Characterization of nano  $\text{Pd/CeO}_2$  for reduction of nitro compounds
6. Synthesis and Characterization of  $\text{ZnO/Co}_3\text{O}_4$  for synthesis of 5-substituted 1H-Tetrazole

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