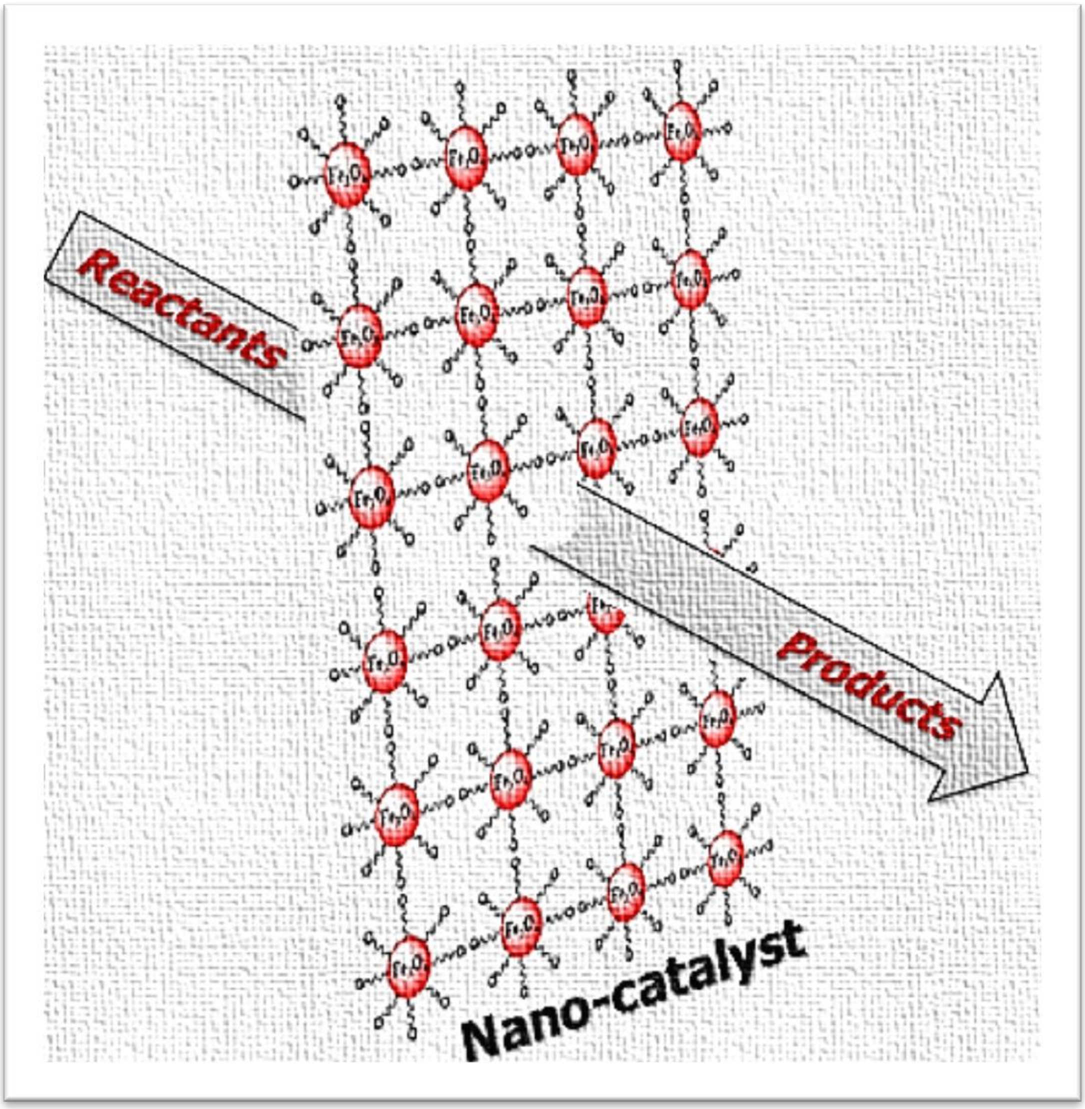
Chapter-1

Introduction



1.1 Introduction

Heterogeneous catalysis has received a remarkable amount of attention, both from a scientific and an industrial perspective. Global demand on catalysts was valued at US$29.5 billion in 2010 and will rise 5.8 percent per year.[1] The 2007 Nobel Prize in Chemistry was awarded to Prof. Ertl, who introduced surface science techniques to the field of heterogeneous catalysis. This lead to in depth understanding of chemical reactions taking place at the surfaces.[2,3] There is a need to develop catalyst for industrial and pharmaceutical important chemical reactions (like organic transformation reactions) an environmentally friendly manner.

1.1.1 Catalysis

The term catalyst was derived from the Greek 'kata'- meaning 'down', and 'lysis'– meaning 'to loosen' or 'to break'. The 'catalysis' was first invented in the 1830s by Berzelius,[4] along with other scientists[5] and founded the first experimental understanding of the role catalyst in the chemical reactions. The Oxford English dictionary describes a catalyst are:

> *"A substance that increases the rate of a chemical reaction*
>
> *without itself undergoing any permanent change."*

The catalyst significantly increases the probability of interaction between reactants by providing a localized surface, upon which the reactant molecules may be located for some time. However, the presence of a catalyst opens up the alternative reaction pathway with reduced activation energy. **Figure 1.1** is a schematic presentation of the role of catalyst in chemical transformation. In order for the reaction to proceed without catalyst very large activation energy (E) must be required for the reaction. However, in the presence of catalyst, a reactant molecule creates a transitional state with a catalytic surface to reduce potential energy. An appropriate catalyst can therefore greatly increase the rate of the reaction.[6] Catalysis can be divided into two categories: homogeneous catalysis -involving a catalyst that is in the same phase as the reactants; and heterogeneous catalysis –involving a catalyst in a different phase from the reactants.[6]

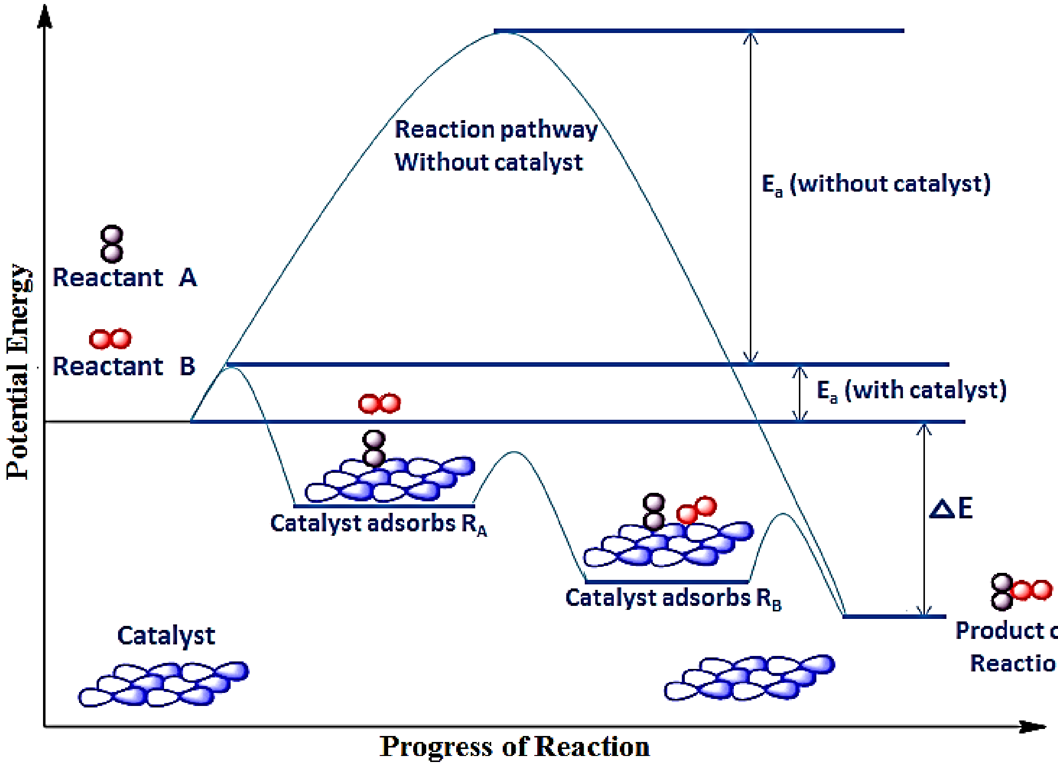


Figure 1.1 Schematic energy profile diagram of simple catalytic and non-catalytic reaction pathways.[6]

1.1.2 Nanocatalysis

On the other hand nanoparticles (NPs) find application in every field such as electronics, medicine and cosmetics. They are now evolving in the field of catalysis because their optical, electrical, mechanical and chemical properties are a function of their size, composition, and structural order. This leads to new improved catalytic properties. Nanocatalysis has attained the form of a strategic field of science because it represents a new way to meet the challenges of energy and sustainability. Nanomaterials can be designed to control their size, shape, chemical composition and nature of the microenvironment surrounding the NPs and assembly structure for advanced applications.[7] These materials can be a new class above the classical homogeneous and heterogeneous catalysts. Nanocatalysts are often considered as quasi-homogeneous systems.

More than 90,000 scientific publications appear on scifinder with the key word "nano-catalysis" in past years, which suggests an exponential growth in this field. NPs have a large surface area which makes possible new quantum mechanical effects.[8] A higher of surface area-to-volume ratios and active binding sites increased catalytic activity of NPs because more catalytic reactions can occur at the same time. The ultimate goal of nanocatalysis is to design catalysts with excellent activity, selectivity, stability, which, operates under environmentally benign conditions in the context of green chemistry (**Figure 1.2**).[9]

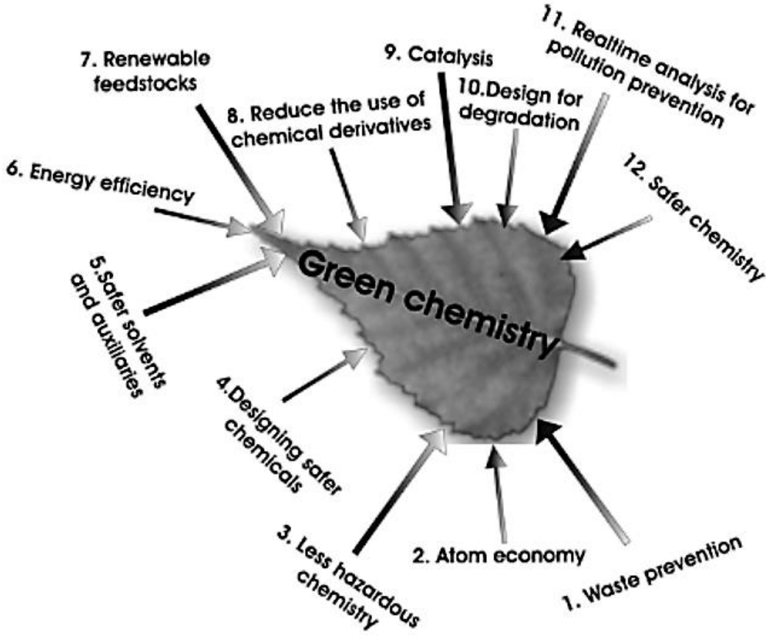


Figure 1.2 The 12 principles of green chemistry[9]

These characteristics can easily be achieved by tailoring the size, shape, composition, morphology, electronic structure, and chemical and thermal stability of the particular nanomaterial. There are quite a few excellent reviews on nanoparticle catalysis.[10] In this chapter, we will focus on some fundamental issues which affect the properties of a nanocatalyst. With a mention of synthesis and characterization of NPs we discuss the key focus of this chapter, that is, a variety of reactions and organic transformations using nanocatalysts.

1.2 Synthesis of nanoparticles

There are a large number of techniques available to synthesize NPs of different size and shape for catalytic application. These include various physical, chemical, biological and hybrid techniques as represented in **Figure 1.3**. Contrary to classic heterogeneous catalysts, NPs[11] are typically synthesized in a bottom-up approach from molecular precursors such as a metal salt, a stabilizer, and a reducing agent. The most interesting fact is that nanomaterial, can be designed to have different forms like clusters, powders, tubes, rods, wire, thin films etc.

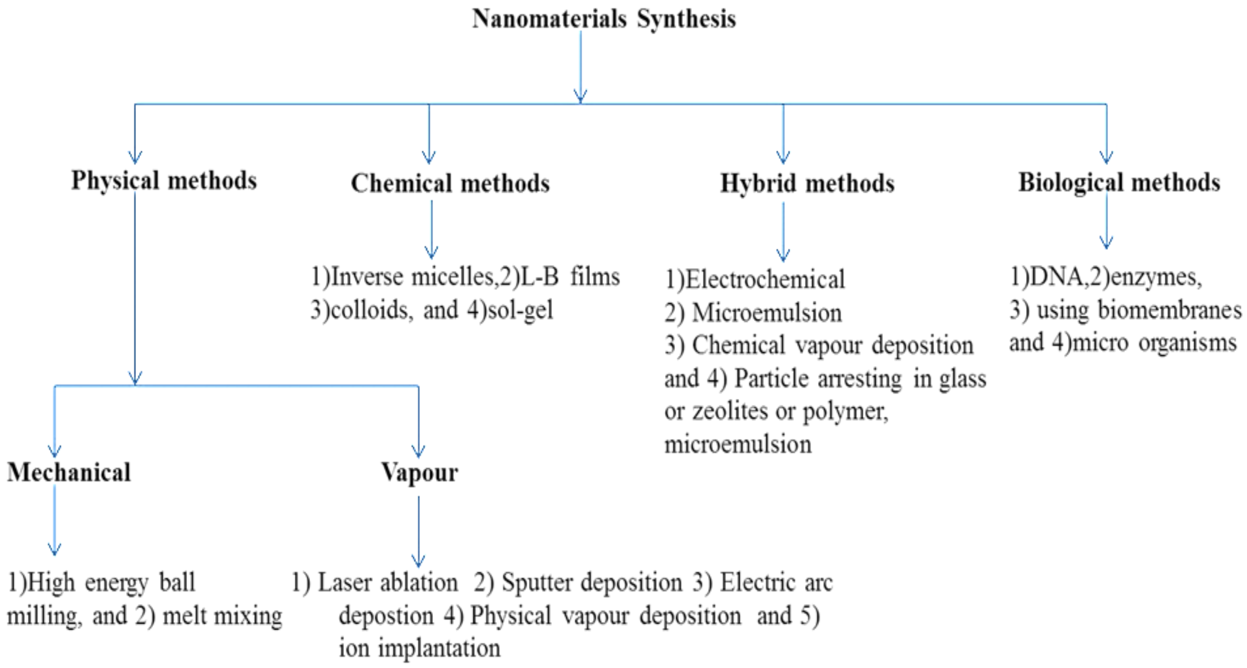


Figure 1.3 Various methods of synthesis of nanomaterials

1.2.1 Strategies for controlling the size and shape of nanoparticles

The size and shape of nanoparticles for catalytic studies can be controlled by colloidal solution-based methods. One of the approaches to synthesize NPs with various shapes like cubic and tetrahedral or octahedral, is to employ surface directing agents along with surface capping agent.

Surface directing agents such as alkali and organic salts of halides,[12] transition metal crystals, cations, and complexes such as Ag^+,[13] Fe^{3+},[14] Co^+,[15] $W(CO)_6$,[16] etc. are employed for this purpose. Some gas molecules such as H_2, O_2, CO, NO, etc. are also well known surface directing agents.[17]

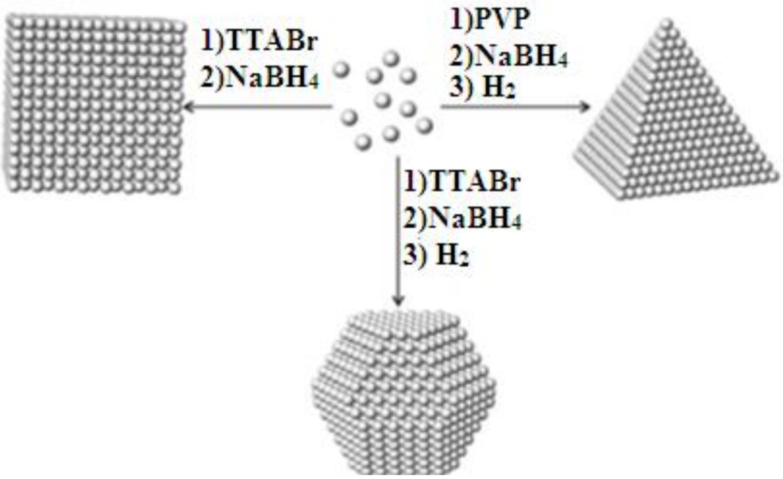


Figure 1.4 Schematics illustrate a generic synthetic procedure for preparing Pt nanoparticles with cube, octahedron and cuboctahedron shapes.[18]

For fcc crystals, {111} surfaces have the lowest surface free energies and thus are thermodynamically the most stable followed by {100} and then {110} surfaces. In the case of Pt group metal NPs, bromide ions present in the reaction solution produce cubic shapes by stabilizing {100}surfaces, whereas molecular hydrogen favors tetrahedral shapes with dominantly {111} surfaces. As shown in **Figure 1.4**, $NaBH_4$ reduction of aqueous solution of H_2PtCl_6 in the presence of tetradecylammonium bromide (TTABr) salt, produced Pt cubes. Here TTABr acts as both a surfactant and a surface-directing agent. Similarly, Ag^+ ions are known to favor cubic shapes when present in high concentrations and exclusively cuboctahedral shapes when present in trace amounts.[13]

1.2.2 Mesoporous materials and 2-D and 3-D nanocatalyst

A mesoporous material contains pores with diameters between 2 and 50 nm. Because of its high surface area, ordered pore structure, and large pore volume, mesoporous materials has been utilized widely as excellent catalyst and support in the field of heterogeneous catalysts.[19]

Colloidal metal NPs can be applied to two types of catalysts; 2-dimensional (2-D) and 3-dimensional (3-D) catalysts.[20] For decades, single crystals have been used for model studies of surfaces and catalysis, both as metal films and supports for metal particles. Langmuir–Blodgett technique is employed for 2-D catalysts wherein the self-assembled NPs get deposited on a substrate **(Figure 1.5)**.[18] The colloidal metal and alloy NPs are incorporated into the pores of mesoporous supports by methods such as a capillary induced inclusion method, (involving simple sonication in solution) and encapsulation.[21]

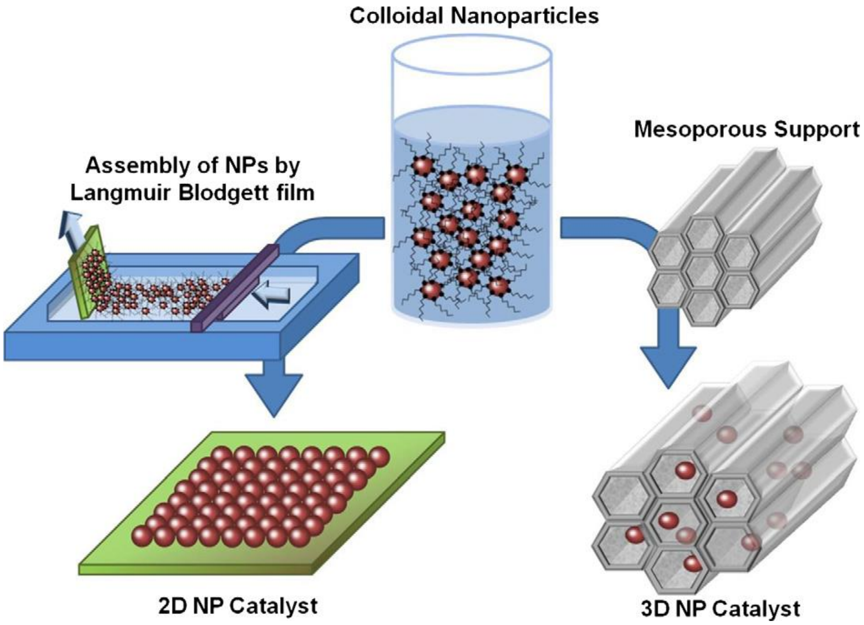


Figure 1.5 Schematic illustrations for preparation of colloidal nanopartcle-based 2D and 3D catalysts.[18]

1.3 Characterization of nanocatalyst

Some techniques that can be used to characterize nanomaterial catalysts given in **Table-1.1**

Table 1.1 Commonly used characterization techniques for nanomaterials

Techniques	Properties characterization
X-ray diffraction (**XRD**)	Crystal structure
Transmission electron microscopy (**TEM**)	Size, shape, and crystallinity
UV-vis-nIR Spectroscopy	Light absorption and scattering
X-ray photoelectron spectroscopy (**XPS**)	Chemical composition
Photoluminescence spectroscopy (**PL**)	Light emission
Chemisorption, physisorption (**BET**)	Surface area
Scanning electron microscopy (**SEM**)	Shape, and assembly structure
Scanning tunneling microscopy (**STM**)	Shape, size, and surface structure
Atomic force microscopy (**AFM**)	Shape, size, and work function
Ultraviolet photoelectron spectroscopy (**UPS**)	Electron valence band
X-ray emission spectroscopy (**XES**)	Electron band gap
Near-edge X-ray absorption fine structure (**NEXAFS**)	Chemical composition
Extended X-ray absorption fine structure (**EXAFS**)	Chemical composition and bonding environment
Small angle X-ray scattering (**SAXS**)	Characteristic distances of partially ordered nanomaterials
Energy dispersive X-ray analysis (**EDX**)	Chemical composition
Fourier transform infrared spectroscopy (**FT-IR**)/ Attenuated total reflection infrared spectroscopy(**ATR-IR**)	Surface functionalization, composition and conjugates.

1.4 Unique properties of nanoparticles and catalysis

Nanocatalysts with good activity, stability and selectivity can be designed by simple manipulation of their sizes, shapes and morphologies.[22] Tuning material properties is easy at the nanoscale, compared to macroscopic counterparts. The nanocatalytic systems are active for several such reasons:

1.4.1 High Surface area-to-volume ratio

Main advantage of the nano-size which favors the nanocataysts is the surface area to volume ratio. The available surface area of the active component of a nanocatalyst increases contact with the reactant molecules significantly. This enhanced interaction facilitates the heterogeneous catalytic system and helps to achieve a better reaction rate that mimics the homogeneous counterpart. Larger surface area increases the relative contribution of the surface energy so that the thermodynamic stability decreases with decreasing particle size.

1.4.2 Effect of size of nanocatalysts

Nanoparticles are not simply finely divided metals. In bulk metals, the large density of states at the Fermi level forms a conduction band of continuous energy levels. But as the particle size decreases, due to quantum confinement discrete energy levels are formed. It is a gradual change that occurs over a range of sizes. This phenomenon is called the size induced metal-insulator transition. For instance, it is reported that clusters of 13 atoms are non-metallic, while clusters of 309 atoms and larger show distinct bulk metal properties.[23] The consequences of metal-insulator transition are reflected as changes in electronic, optical and catalytic properties of NPs.[24] The fraction of surface atoms increases drastically with decreasing particle size. A nanoparticle of 1 nm would have ~ 76 % of the atoms on the surface; while a 3 nm nanoparticle will have only ~ 45%.[25] According to the literature, hydrogenation of small molecules such as pyrrole, crotonaldehyde,[26] furan[27] and methylcyclopentane[28] were reported to be of structure sensitive nature as seen in **Figure 1.6**. Dihydrofuran was produced by incomplete hydrogenation of the aromatic ring in presence of small NPs, while butanol resulted from hydrogenative ring opening of furan over larger NPs.[27a]

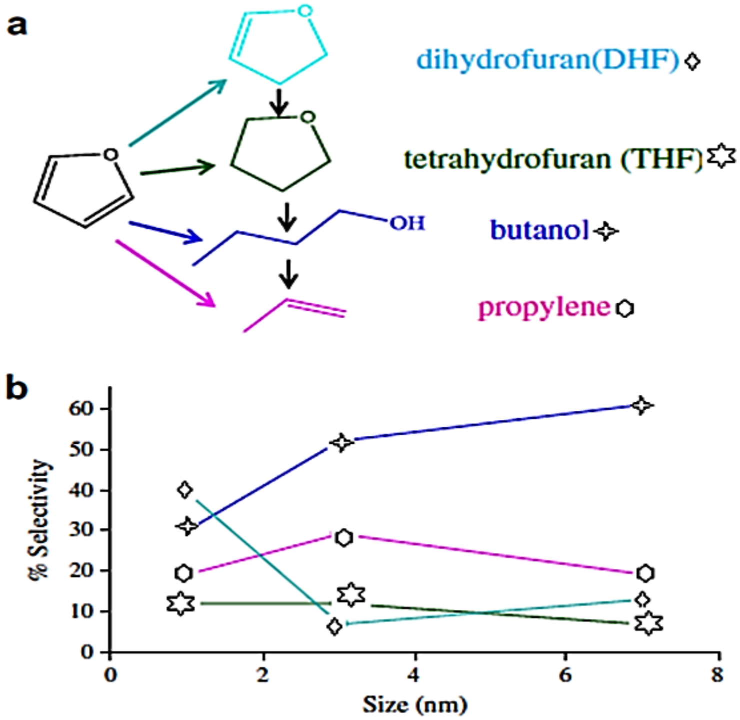


Figure1.6 Reaction scheme of furan hydrogenation showing successive hydrogenation steps (a). % Selectivity for different reaction products, colour coded as in (a) as a function Pt particle size (b).[18]

1.4.3 Shape and morphology

Shape dependent nanocatalysis has been extensively explored in the past two decades.[29] Since, it was first suggested in1996.[30] It has been reported that higher efficiency was found for NPs having more and sharper edges and corners.[29b,29c,31] the exposed crystallographic facets also affect the catalytic property of the NP. The arrangement of atoms on the surface strongly influences the adsorption of the reacting molecules and desorption of the products.[32] Thus, the morphology of the catalyst particle determined by the exposed crystal planes could substantially alter the catalytic property as well. This is termed as morphology-dependent nanocatalysis: an NP having an anisotropic shape can modify the performance of reaction by selectively exposing specific crystal facets.[33] Single-crystal studies have revealed that the exposed crystallographic plane has great influence on catalytic pathways and activities.

El-Sayed and co-workers used PtNPs with different shapes (tetrahedral, cubic and spherical)[34] as catalysts for electron transfer reactions.[35] The results of activation energy showed that the tetrahedral PtNPs were the most catalytically active, while cubic PtNPs were the least catalytically active. The spherical PtNPs had a moderate catalytic activity. Such a shape dependency was also observed in the case of the Suzuki reaction.[35] Narayanan and Al-Sayed[35] found that when they moved from nearly spherical PtNPs to tetrahedral PtNPs, catalytic activity improved. Tetrahedral PtNPs with (111) facets (as well as edges and corners) contain more active surface atoms than nearly spherical PtNPs with (100) and (111) facets.

Similar, shape-dependence was observed for methylcyclopentane/H_2 reaction over PtNPs **(Figure 1.7)**.[36] Hydrogenation of methylcyclopentane results in ring opening and a subsequent isomerization leads to various C6 isomers. Due to different surface crystallographic orientations, both activity and selectivity exhibited strong shape dependence. Similar shape dependence of surface reactivity was observed for benzene hydrogenation over Pt cubes and cuboctahedra.[33b]

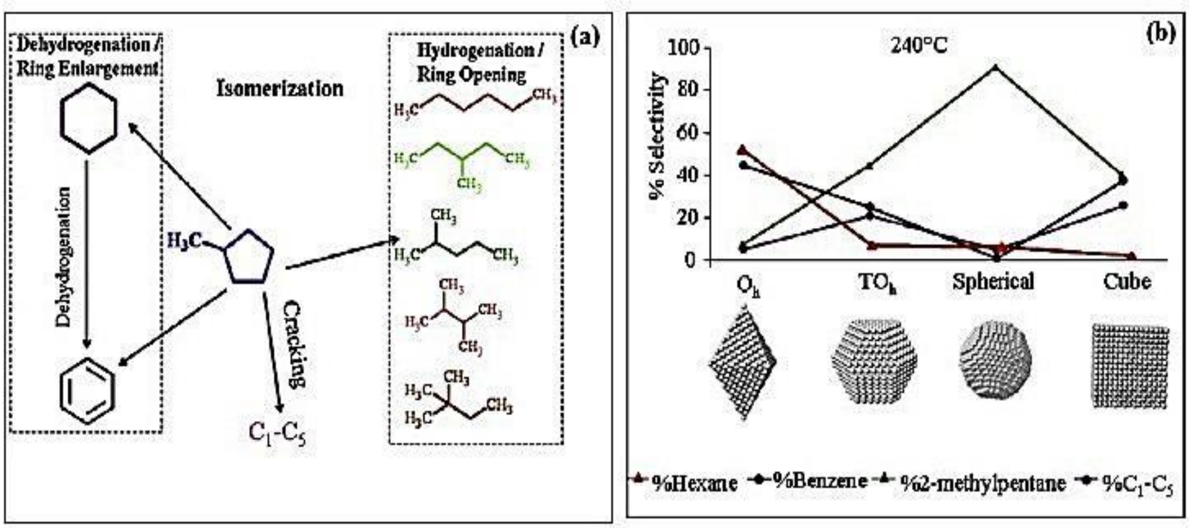


Figure 1.7 Reaction scheme of methylcyclopentane hydrogenation showing different reaction pathways and products (a). % Selectivity for different reaction products as a function of Pt nanoparticles shapes, (110) octahedron (Oh), truncated octahedron (TOh), sphere and (100) cube (b). Representative model atom clusters are also given.[18]

1.5 Advantages of nanoparticles as a catalyst

The properties and advantages of nanoparticles as catalysts can be summarized as follows.

(1) Heterogeneous nature,

(2) Improved efficiency under mild and environmentally friendly conditions (green chemistry),

(3) Higher surface area,

(4) Easy separation and recycling efficiency,

(5) Less fouling: less byproduct, easy work up,

(6) Possibility of Surface modification,

(7) Stability in organic solvents,

(8) Enhanced reactivity and selectivity

(9) Higher efficiency of NPs catalysts under mild conditions probably due to their good dispersion in solvent and three-dimensional rotational freedom.

1.6 Fundamental challenge for nanoparticle catalysis

Since NPs possess a large fraction of their atoms on the external surface, their surfaces are less stable compared to their bulk counterparts; under catalysis, their surface structures are dynamic due to the changing adsorbate–surface interactions. This can alter the reactivity of the nanocatalyst.[37] To overcome this challenge, it is necessary to terminate the particle growth and to stabilize the surface which can be done in various ways, such as immobilization or grafting onto inorganic supports and use of porous materials as matrix for particle growth.[38]

1.7 Nanocatalytic approaches: Role of stabilisers and ligands

A nanoparticle based catalytic system generally involves three components, i.e. metal core, stabilizer, and solvent. The metal core is the catalytic material with an activity and selectivity. The stabilizer protects the metal core against aggregation and controls its solubility. The role of the solvent is to offer a dispersion medium for both metal core and stabilizer. It serves as a carrier for transfer of reactant(s) to the metal core and product(s) away from the active site. The solubility of both the stabilizer and the reactant(s) in the solvent are therefore related to the final activity of the system. The symbiotic relation between metal core; stabilizer and solvent together constitutes an effective catalytic system.[10a] Some general approaches based on role offered by the metal, role of ligand and location of the ligand in catalytic applications of NPs, are represented in **Figure 1.8.**[39]

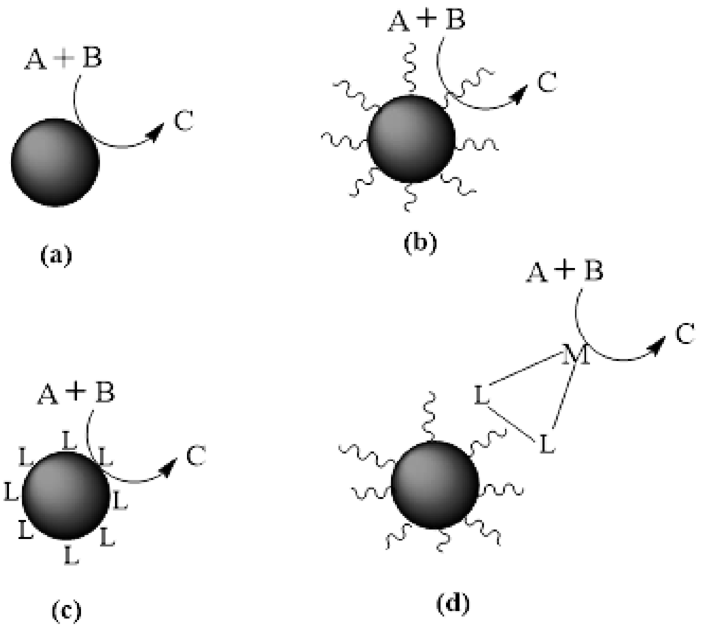


Figure 1.8 Catalysis with a) metal nanoparticles, b) metal nanoparticles capped with a protective shell, c) metal nanoparticles capped with ligands contributing to the catalytic activity, and d) metal nanoparticles with catalysts supported on the protective shell. Only in the last case the core material does not promote the reaction.[39]

1.8 Magnetically recoverable nanocatalysts

Conventional techniques such as filtration are not efficient for the isolation and recovery of nanocatalysts because of their nanosize. Magnetic NPs have emerged as a viable solution to this limitation. The insoluble and paramagnetic nature of Magnetic NPs easily facilitates efficient separation of the catalysts of the reaction mixture with an external magnet. This makes the nanocataysis protocol, practical and sustainable. Several magnetic materials have been used as supports for NPs, thus forming magnetically recoverable nanocatalysts.[40,10c]

1.9 Applications of nanocatalysis

Nanocatalysts have been used in a wide range of catalytic reactions such as hydrogenations, oxidations, C-C bond formation and photocatalysis (**Table 1.2**) as well as in novel applications in asymmetric synthesis and other reactions.[41] Furthermore, high turnover numbers (TONs) and turnover frequencies (TOFs) make nano catalysis very cost efficient.[41] In this section, we provide an overview of the applications of various metallic, nonmetallic, supported and unsupported nanomaterial used in a wide range of catalytic processes

1.9.1 Hydrogenation Reactions

Hydrogenation is an important chemical reaction used in the hydrogenation of carbon-carbon double, multiple bonds, carbonyls and nitrogen-containing bonds. Therefore, research focused on heterogeneous catalysis systems for hydrogenation reactions. Most of the transition metals NPs show hydrogenation ability, for example Ti, Zr, Nb and MnNPs.[42] Colloidal TiNPs are very efficient catalysts for the hydrogenation of titanium, zirconium sponges and nickel hydride battery alloy.[43] Other transition metal NPs such as Pd, Cu, Ag, Rh, Pt, Au, Ru, and Ni[44] showed higher catalytic activity than conventional supported metal catalysts in simple hydrogenation[45] as well as for the hydrogenation of C-C bonds. The activity trend of some metal NPs are Rh >Ru>Pt>Ir, which is similar to that observed in traditional heterogeneous catalysis.[46] Hydrogenation of the benzene ring attracted attention recently because it is challenging task. Januszkiewicz et al.[47] reported the first example of benzene hydrogenation by RuNP. The research focus is on the development of more stable and active NPs with high turnover numbers (TON) on benzene hydrogenation.[48] The Ir, Pt and Ru metal exhibit excellent activity for the hydrogenation of C-O bonds. Özkar and Finke synthesised IrNPs for catalysing the hydrogenation of acetones under ambient temperatures.[49] The temperature used for this reaction under traditional supported catalyst is between 100 to 300º C. The selectivity of reaction is about 95% in 2-hydroxyl propanol and TON is 16,400.

Nickel NPs have been found to efficiently catalyse the hydrogen-transfer reactions of a variety of functionalised and non-functionalised olefins using 2-propanol as the hydrogen donor.[50] The NPs have been shown to be highly chemoselective with high yields. The optimised reaction conditions **(Figure 1.9)** were applied to a variety of olefins. The reaction involved dihydride species, where the two hydrogen atoms of the donor become equivalent after being transferred to the metal to give the dihydride **(Figure 1.9)**.[51]

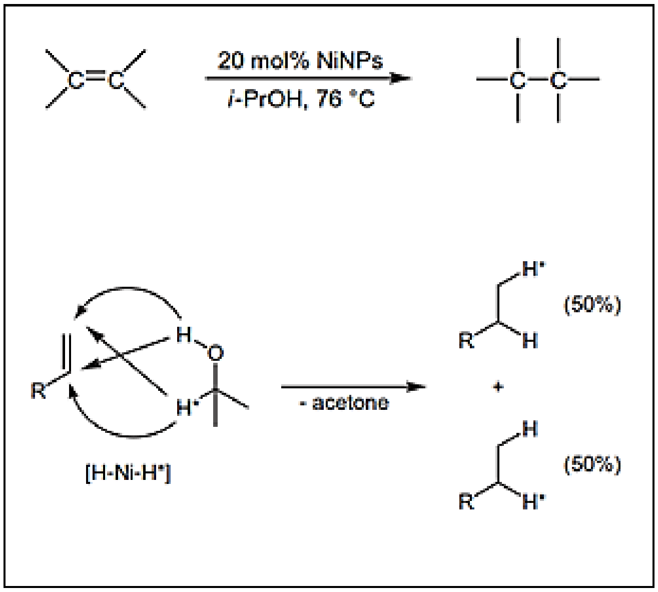


Figure 1.9 Proposed dihydride-type mechanisms for the transfer hydrogenation of olefins with isopropanol catalysed by NiNPs.

1.9.1.1 Magnetically recoverable nanocatalyst in hydrogenation

Magnetically Recoverable Platinum (Pt),[52] Rhodium (Rh),[53] Gold (Au)[54] Ruthenium (Ru) [55]and Palladium (Pd) based catalysts used for the various hydrogenation process. Pd metal has been paying much attention as a catalyst for hydrogenation reaction. Palladium on carbon (Pd/C), is a form of palladium that is commonly used for hydrogenation reactions in organic synthesis. Interestingly, this type of catalyst can be designed to a magnetically separable catalyst.[56]

Ying et al.[57]also reported the preparation of magnetically separable PdNPs supported on silica-coated Fe_2O_3NPs and catalyst employed in the hydrogenation of nitrobenzene **(Figure 1.10)**. Silica-coated Fe_2O_3NPs exhibited higher activities relative to those obtained with commercial Pd/C catalysts.

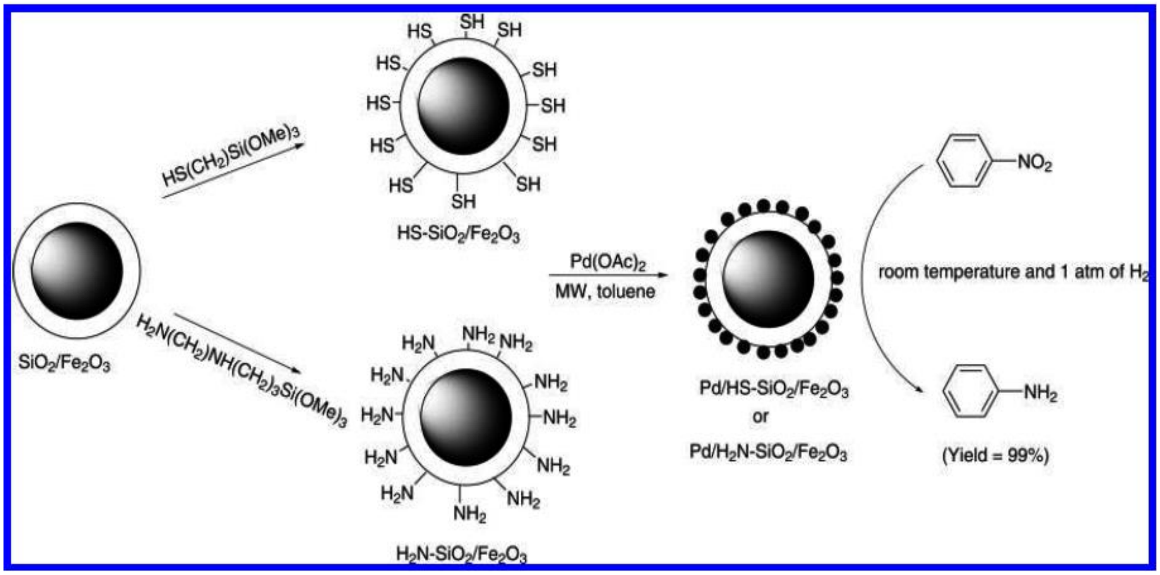


Figure 1.10 Synthesis and catalytic application of $Pd/SiO_2/Fe_2O_3$ magnetic nanocomposites.[57]

1.9.1.2 Asymmetric hydrogenation

Some of the homogeneous chiral Ru complexes are very active in asymmetric hydrogenations **(Figure 1.11**).[58] A magnetically recoverable chiral Ru complex was designed for the hydrogenation of a wide range of aromatic ketones to their corresponding secondary alcohols with high reactivity and enantioselectivity. Phosphonic acid was used to link the complex to the magnetite NPs. The enantiomeric excess (ee) values significantly higher than those of the parent homogeneous catalyst.

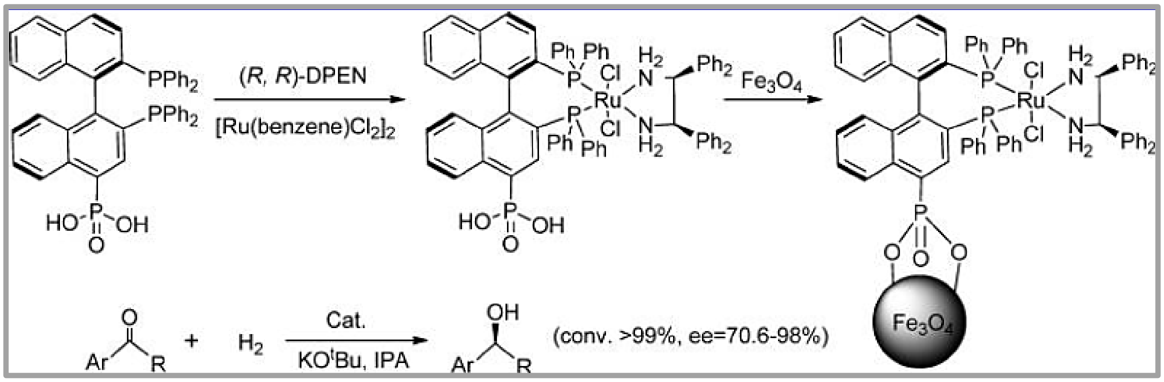


Figure 1.11 Magnetite chiral Ru catalyst for asymmetric hydrogenation of aromatic ketones.[58]

Conventional supported gold nanocatalysts have been capable of selective hydrogenation of α,β -unsaturated ketones to produce α,β -unsaturated alcohols, with side products of saturated ketones from C=C hydrogenation and saturated alcohols from further hydrogenation.[59] Instead[60] well-defined $Au_{25}(SR)_{18}$ nanoclusters have been used to attain chemoselective hydrogenation of the C=O bond in α,β -unsaturated ketones (or aldehydes) with 100% selectivity for α,β-unsaturated alcohols at room temperature or 0º C.[61] The low-coordinate Au atoms of $Au_{25}(SR)_{18}$ nanoclusters was expected to provide a favourable environment for the adsorption and dissociation of H_2 **(Figure 1.12)**. Surprisingly, a complete stereoselectivity could be achieved although the nanoclusters are non-chiral. The spatial environment of $Au_{25}(SR)_{18}$ seems to have a strong impact on the direction that this H atom attacks; the catalytic results indicate that the preferred direction is along the axial direction rather than the equatorial direction **(Figure 1.13)**. Consequently, the diastereoselective hydrogenation is a result of the three-dimensional restriction imposed by the $Au_{25}(SR)_{18}$ nanoclusters and of the activated geometry of the ketone as well.[60]

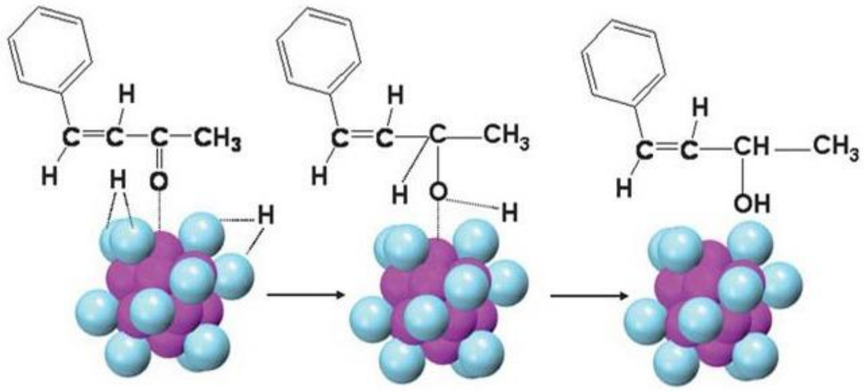


Figure 1.12 The proposed mechanisum of $Au_{25}(SR)_{18}$ nanocatalysts for the chemoselective hydrogenation of α,β-unsatureted alcohol(for clarity, only Au_{25} was shown; magenta: Au atom of the core, blue: Au atom of the shell. Thiolate ligands are omitted).[61]

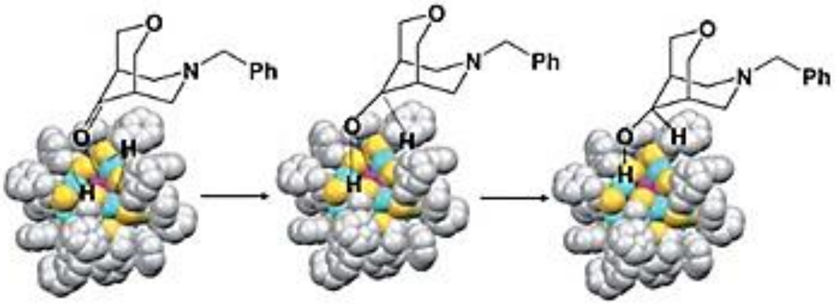


Figure 1.13 The proposed mechanism of sterioselective hydrogenation of bicyclic ketone on the $Au_{25}(SR)_{18}$ catalyst: the activation of C=O bond and H_2; H-atom addition to the activated C-O group in a particular direction, and the formation of the exo-alcohol isomer. Color labels: magenta for Au_{13} core atoms, blue for Au_{12} shell atom, yellow for S grey for $–CH_2CH_2Ph$.[60]

1.9.2 Oxidation Reactions

Oxidation reactions are important to the chemical industry because of their potential for producing a variety of chemicals. However, most of the known oxidation reactions are unacceptable with regard to waste generation and selectivity. Traditional methods using stoichiometric quantities of inorganic oxidants such as permanganates, chromium (VI) reagents, or N-chlorosuccinimide are not environmentally benign.[62] Because of growing environmental concerns, continuous efforts have been made in development of easily reusable and recoverable heterogeneous catalysts. In light of these concerns, the use of nanomaterials as a solid support for heterogeneously catalyzed oxidation reactions has highly effective.

Transition metals like Fe, Co, Ni, Cu, Ag and Au based catalysts are widely used in oxidation reactions in the industry. For example FeNPs can catalyze the oxidation of cyclooctane with acceptable activity under mild conditions (**Figure 1.14**).[63] Vukojevic et al. found that CuNPs (3–5 nm) were as reactive as commercialized Cu/ZnO catalyst in methanol synthesis.[64] The author claimed that the traditional catalyst requires a second component, like zinc, to be active.

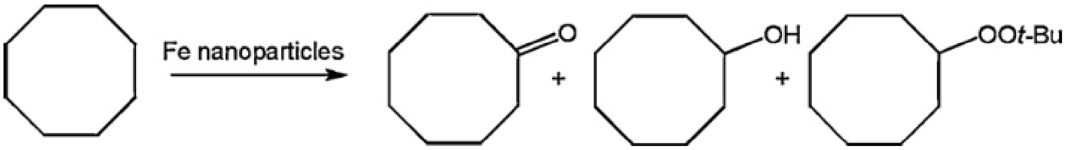


Figure 1.14 Oxidation of cyclooctane catalysed by Fe nanoparticles in reverse microemulsion.[63]

It was recently reported that 3 nm CuNPs also catalysed synthesis of methyl formate (MF) from methanol by carbonylation reaction in the absence of any base[65] with 100% selectivity (**Figure 1.15**). Commercially, this reaction is catalyzed by a CH_3ONa which is highly efficient but leads to inevitable problems such as by-product formation, corrosion and the possible deactivation of catalyst by H_2O and CO_2 impurities.

$$\mathbf{CO + CH_3OH \xrightarrow[\text{353-443 K, 0.3-3 MPa}]{\text{CuNPs}} HCOOCH_3}$$

Figure 1.15 Production of methyl formate from methanol carbonylation catalyzed by Cu nanoparticles.[65]

Epoxidation reaction catalysed by AgNPs is well known and widely applied in ethylene oxide production. AgNPs are superior catalysts relative to a conventional bulk Ag catalyst (**Figure 1.16**).[66] Now AuNPs is also used in oxidation reactions of carbon monoxide into carbon dioxide and glucose into gluconic acid.[67] Au and AgNPs can also effectively decompose $NaBH_4$ into H_2 and $NaBO_2$.[68] Haruta et al. was discovery that AuNPs catalyzed the CO oxidation.[69] The Pt/PdNPs catalysts that are currently used in cars for CO oxidation work only at temperatures above 200° C. Hence, most of CO pollution occurs in the initial minutes after starting the engine.[70] Clearly, the low temperature oxidation of CO by supported Au catalyst could solve this problem. The gas phase hexaauride clusters (Au^{6-}) of AuNPs particles are reported to catalyse the oxidation of CO to CO_2 in the presence of O_2.[71] The mechanism is shown **Figure 1.17**.

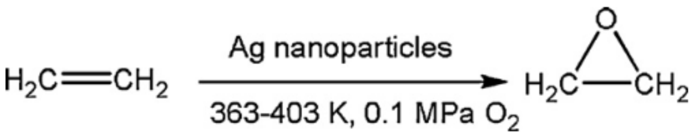


Figure 1.16 Epoxidation reaction of ethylene catalysed by Ag nanoparticles.[66]

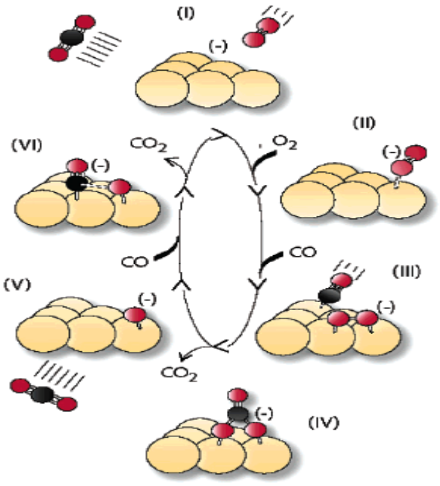


Figure 1.17 Proposed schematic mechanism of CO oxidation by Au_6^- cluster (I); the bare Au_6^-adsorbs molecular oxygen in the superoxo form (II) ; subsequent co-adsorption of CO may initially yield an $Au_6CO_3^-$ species (III), which rearranges to produce the very stable CO_3^-adsorbate (IV). Elimination of CO_2 yields the Au_6O^- form (V). Adsorption of a second CO yields the $Au_6CO_2^-$ (VI).[71]

The well-defined $Au_n(SR)_m$ nanoclusters offer a unique opportunity for oxidation of styrene also, in particular regarding how the electronic porperties and the core–shell structure of $Au_n(SR)_m$ nanoclusters influence their catalytic performance. Tsukuda and co-workers[72] immobilized $Au_{25}(SR)_{18}$ nanoclusters on a hydroxyapatite support for the selective oxidation of styrene in toluene (solvent). They achieved 100% conversion of styrene and 92% selectivity for the epoxide product.[73]

The use of magnetic nanomaterials as a solid support for heterogeneously catalyzed oxidation reactions has proven to be highly effective. Mizuno and colleagues developed a heterogeneous magnetic retrievable ruthenium hydroxide ($Ru(OH)_x$) catalyst.[74] This catalyst system was used to catalyze the aerobic oxidation of alcohols and amines, as well as the reduction of carbonyl compounds to alcohols (**Figure 1.18**). These systems are able to catalyze these reactions for a range of substrates in good yields and without requiring any additives. Another example is a Pd catalyst supported on dopamine-functionalized nanoferrite developed by Polshettiwar and Varma (**Figure 1.19**).[75] Dopamine was chosen as a linker on the basis of its ability to make octahedral geometry for oxygen-coordinated iron. These functionalized materials coated with Pd displayed high catalytic activity in the oxidation of olefins and alcohols.

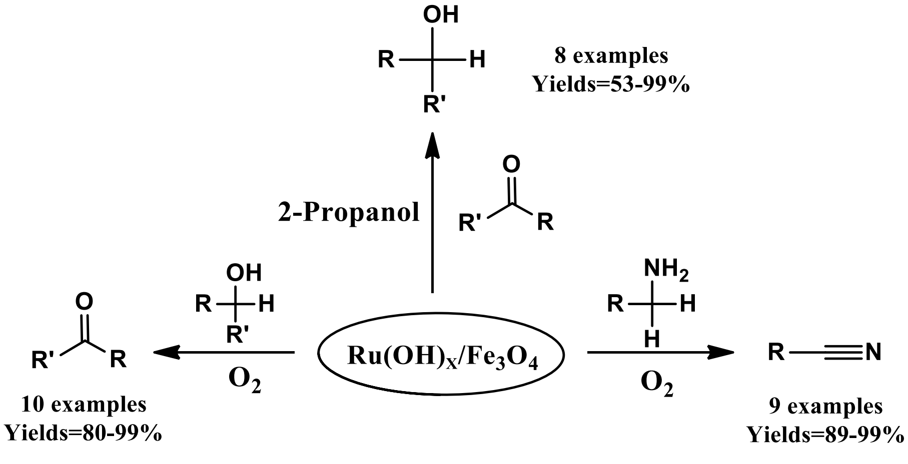


Figure 1.18 Ruthenium hydroxide (Ru(OH)x) catalyst supported on magnetic ferrites[74]

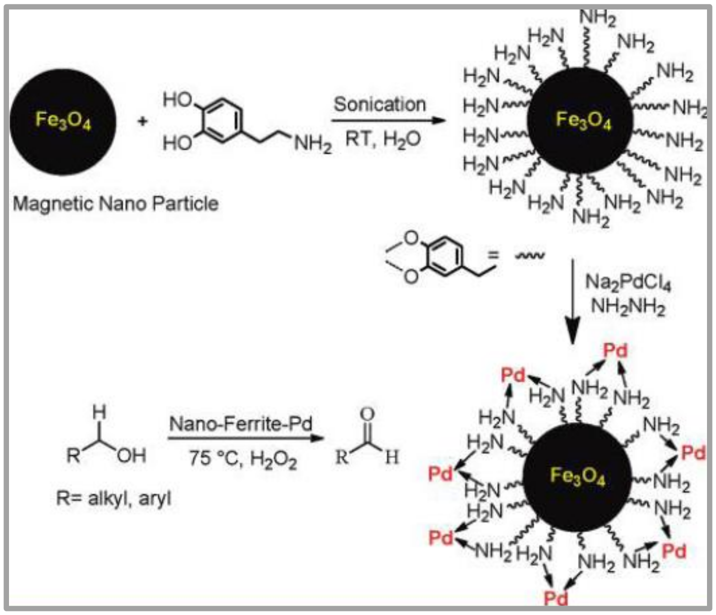


Figure 1.19 Pd Catalyst supported on dopamine-functionalized nanoferrite.[75]

1.9.3 C–C coupling reactions

Metal-catalyzed coupling reactions such as Heck, Negishi, Suzuki, Stille and Sonogashira are paramount importance in synthetic organic chemistry. This fact was recognized by the award of the 2010 Nobel Prize for Chemistry for C-C coupling reactions.[76] The C–C couplings offer an extremely convenient route to join large fragments of molecules in a controlled manner for designing convergent overall synthetic schemes. The resulting products have found numerous applications in the synthesis of natural products and drug compounds.

Palladium is probably the most versatile metal in promoting C-C bond formation, compared to other transition-metal catalysts.[77] The difficulties in recycling of soluble palladium-based catalysts were widely overcome in the past by heterogenization of homogeneous palladium NPs on various solid supports **(Figure 1.20).**[77,78] Here, these systems and other salient evidences are explored concerning the hetero-geneity of NPs catalyzed C–C coupling reactions (**Table-1.2 & 1.3**).

PdNPs catalyzed C–C coupling reactions acting truly heterogeneously, even though this may be a result of a less extensive number of studies. El-Sayed and co-workers identified the importance of surface sites in the reaction[79] and the effect of Ostwald ripening on activity.[80] Both these factors specify the role of the PdNPs surface in C–C coupling reactions. A study using ionic liquids showed again that NPs play important role in the catalysis.[81]

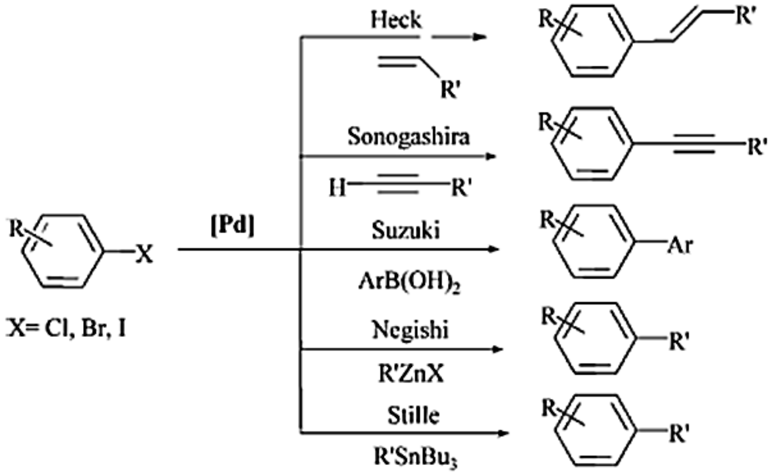
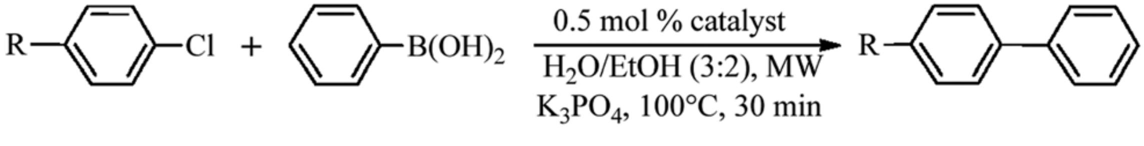


Figure 1.20 Selected C-C coupling reaction catalysed by supporting Pd metal nanoparticles.[77]

Cao and co-workers used Pd and Pd/Au alloy NPs for Suzuki coupling reactions under microwave (MW) irradiation **(Figure 1.21a)**.[82] They found that Pd/Au alloy NPs showed superior performance and recyclability in the coupling of aryl boronic acids with aryl bromides as well as aryl chlorides. The proposed mechanism is shown in **(Figure 1.21b)**.



R	yield (%)
Me	55
MeO	43

Figure 1.21a Suzuki cross-coupling reactions catalysed by Pd/AuNPs.[82]

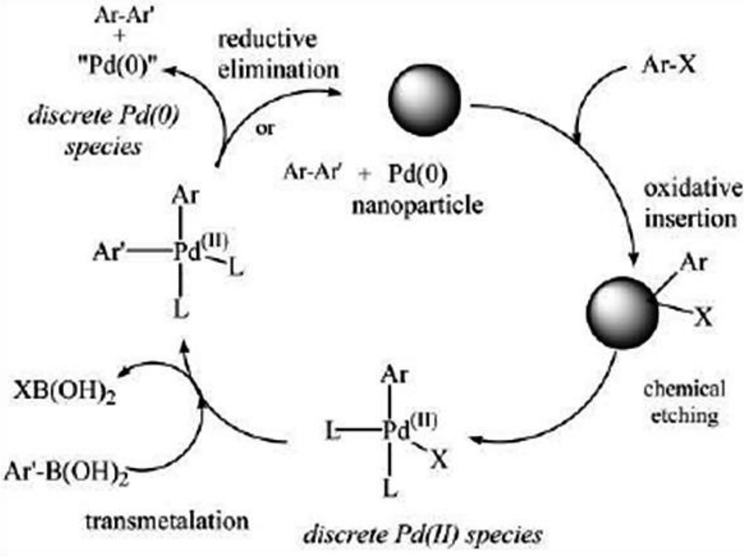


Figure1.21b Proposed mechanism of the Suzuki cross-coupling catalytic cycle.[83]

The Suzuki–Miyaura reaction involves the coupling of aryl halides with aryl boronic acids. Metallic PdNPs supported on alumina- and silica-based oxides[84] commercial magnetic NPs[85] and polymers including polyaniline nanofibers have been reported as highly active and reusable catalysts for this reaction. Budarin et al.[86] prepared highly active and reusable PdNPs on biopolymers for the cross-coupled product of bromobenzene within a few minutes of reaction **(Figure 1.22).** Sarkar et al.[87] reported aqueous nano-sized Pd as a highly efficient catalyst for Suzuki, Heck, Sonogashira, Stille and Hiyamacoupling.

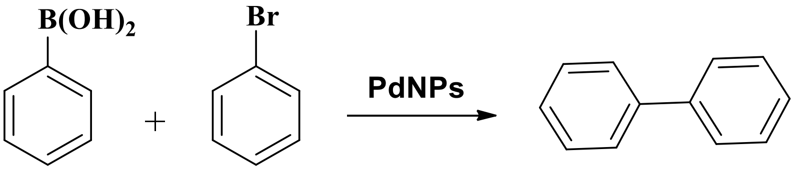


Figure 1.22 Suzuki coupling of bromobenzne and phenylboronic acid using Pd metal nanoparticles on expanded starch

Ranu et al.[88] report a PdNPs catalyzed C–H functionalization of aliphatic aldehyde by aryl halides leading to an easy route to alkyl–aryl ketone **(Figure 1.23a)**. Alkyl–aryl ketones are of much importance as useful intermediates in industries.[89] The reaction follows a similar reaction pathway as proposed by Xiao and co-workers,[90] as outlined in **Figure1.23b** in situ-generated PdNPs undergo oxidative addition followed by Heck coupling to provide an intermediate **A** with the insertion of aryl group at the **a**-position of the heteroatom. The intermediate **A** on **b**-hydride elimination followed by hydrolysis furnished the product, alkyl–aryl ketone.

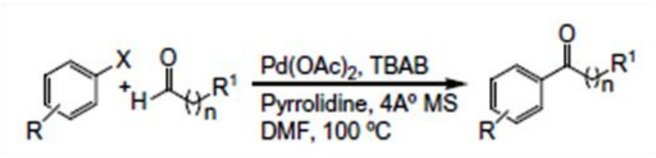


Figure 1.23a Direct acylation of aryl halides with aldehydes.

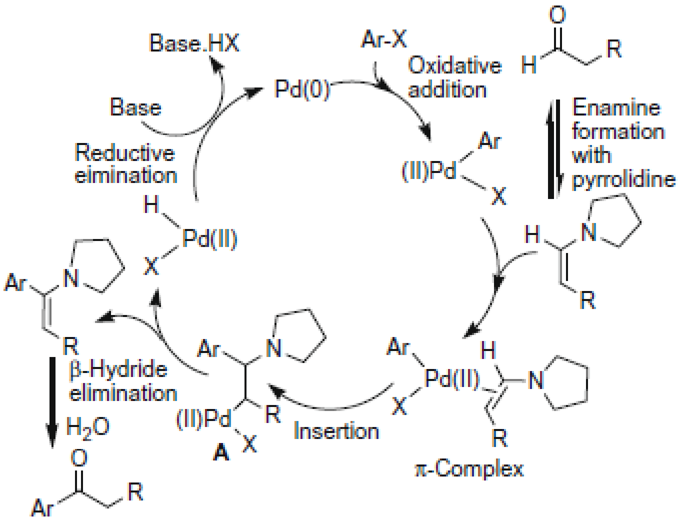


Figure 1.23b Probable mechanism of acylation reaction.[88]

1.9.3.1 Magnetic nanocatalysis for C-C coupling reaction

Gao and colleagues reported[91] the preparation of a Pd-N heterocyclic carbene that could be immobilized onto maghemite NPs to improve the solubility of nanocatalyst in organic solvents **(Figure 1.24a)**. By using Na_2CO_3 as the base in the presence of DMF, this catalyst provided nearly quantitative yields for electron-rich and electron-poor aryl iodides and bromides **(Figure 1.24b)**. This catalytic system was shown to be faster than an analogous polystyrene solid-phase system. This Pd/N-heterocyclic carbene complex could also be applied to the Heck and Sonogashira cross-coupling reaction.[91]

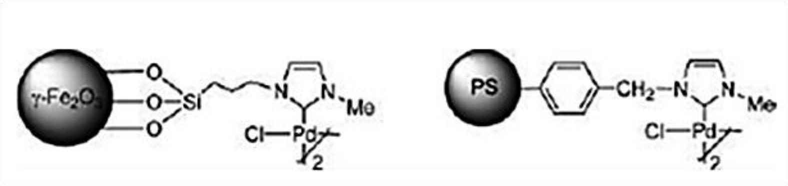
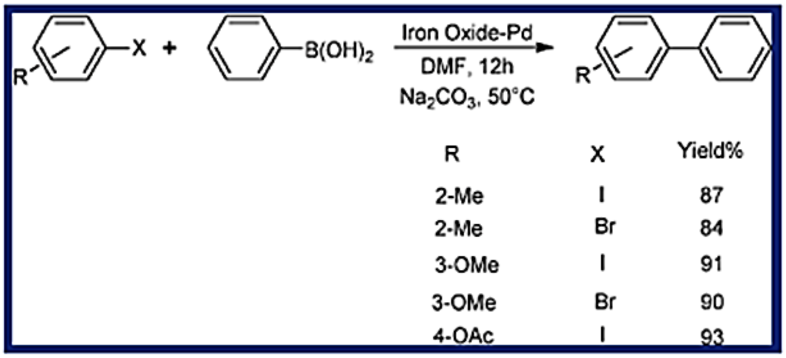


Figure 1.24a Pd-N-Heterocyclic carbene immobilized on magnetic nanoparticles and on polystyrene resins.[91]



R	X	Yield%
2-Me	I	87
2-Me	Br	84
3-OMe	I	91
3-OMe	Br	90
4-OAc	I	93

Figure 1.24b Maghemite nanoparticle-supported Suzuki cross-coupling reaction[91]

The Stille reaction has widespread use in organic synthesis.[91a,92] The first example of Stille reaction, catalyzed by heterogeneous Pd-SiO_2/Fe_3O_4 was provided by Jin and colleagues.[93] Some of the examples of magnetic nanosupported C-C coupling reactions, are given in **Table 1.2 and 1.3**.

Table 1.2 C-C coupling reactions catalysed by maganetic nanosupports

Reaction studied[(Ref.)]	**Particle composition**
Suzuki[94]	NHC-Pd/ polymer coated γ-Fe_2O_3
Heck[95]	Pd/NH_2-Fe_3O_4, Pd/ polypyrrole nanotubes
Suzuki, Heck[96]	Pd/DA-$NiFe_3O_4$
Suzuki, Heck,Sonogashira[97]	Pd/DA-α-Fe_3O_4, Pd/ Fe_3O_4, Pd/N-MCNPs
Sonogashira[98]	Pd/SiO_2-Fe_3O_4

1.9.4 Organocatalysis

Metal-free catalysts for the synthesis of organic molecules have recently attracted great attention.[99] Polshettiwar et al.[100] reported Paal–Knorr reaction catalyzed by glutathione-functionalized MNPs. The glutathione molecules were attached on MNPs through thiol groups. The catalyst displayed high activity for a wide variety of amines like aryl, alkyl, and heterocyclic (**Figure 1.25**). Remarkably, functionalized amines were selectively converted into the corresponding pyrroles, while preserving their functional groups (C=C bonds, esters, alcohols, ketones, etc.).

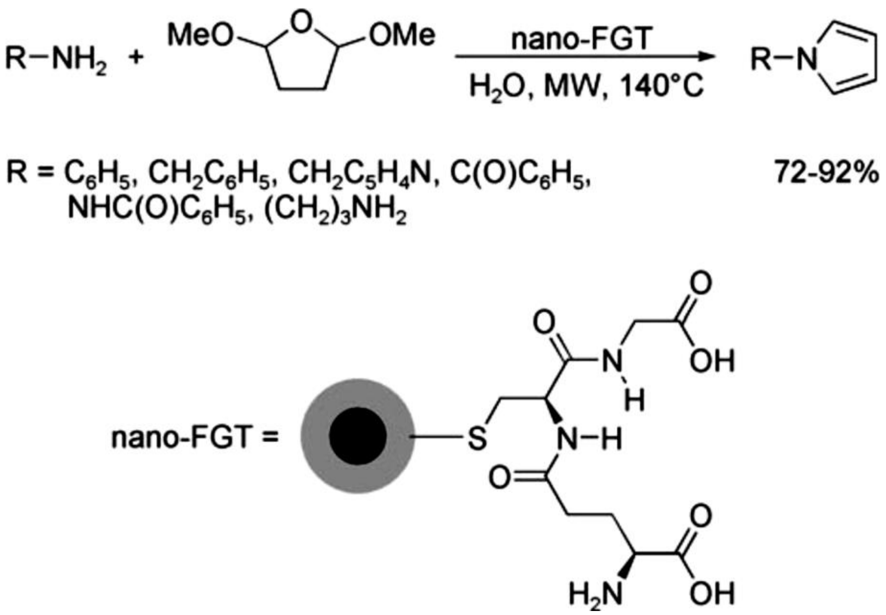


Figure 1.25 Nano-FGT-catalyzed Paal–Knorr reactions[100]

Another nano-organocatalyst was prepared with a magnetic cobalt core using “click” chemistry (**Figure 1.26**).[101] The CoNP-TEMPO showed high catalytic activity in the chemoselective oxidation of primary and secondary alcohols. The catalyst could be reused without any considerable loss in activity. The Magnetic nature of the catalyst provides facile isolation and recycling.

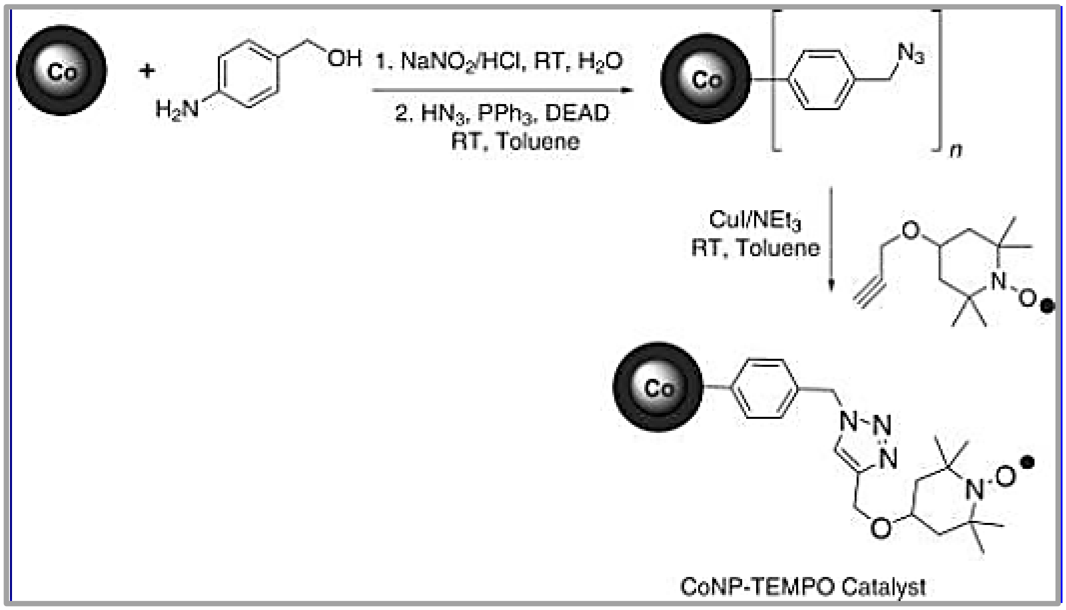


Figure 1.26 Synthesis of the magnetic CoNP-TEMPO catalyst system.[101]

Table 1.3 Some metal-nanoparticle-catalyzed reactions with references

Hydrogenations Reaction (Ref.)	**Oxidation Reaction(Ref.)**	**Coupling reactions(Ref.)**
Alkynes[102] Simple olefins and dienes[103] Aromatic Nitro Compounds[104] Arene rings[105] Arene rings of bibenzo-[18]crown-6[106] Methylacrylate[107] Allylic alcohols[108] Acrolein[109] N-isopropylacrylamide[108] Asymmetric hydrogenation [110] Cinnamaldehyd[111] Ketones, benzonitrile[112]	Cyclooctane[113] Dihydrogen[114] Aromatic amines[115] 1-Phenylethanol [116] Alkyl amines [117] CH_3OH[118] CO[119] Cyclohexane[120] Ethene and propene epoxidation[121] Glucose[122] Diol, glycerol, ethylene glycole[123] Oxalate[124]	Heck coupling [125] Suzuki coupling[126] Sonogashira coupling[127] Stille coupling[128] Negishi coupling[129] Kumada coupling[130] Dehydrohalogenation of arylhalides[131] Amination of aryl halides and sulfonates[132] Hydrosilylation[133] Coupling of silanes[134] [3+2] Cycloaddition[135]

1.9.5 Nanocatalysts in Miscellaneous Reactions

Nanoparticles have been reported to catalyze a wide range of related reactions with significant catalytic performance. The NPs can be modified with various functional groups to generate different types of catalytically active sites that can be employed in various reactions (**Table 1.4**).

Table 1.4 Miscellaneous reactions catalyzed by different NPs.

Reaction type(Ref.)	NPs/supported nanoparticls
Hydroformylation of 1-dodecene[136]	Rh(0)(Rhodium NPs)
Acylation[137]	Fe_3O_4-nanoparticle-supported4-N,N-dialkylaminopyridine catalyst
Transesterification[138]	Immobilization of amine on Nickel NPs
Dehalogenation[139]	Fe–Pd(2.4±0.5 nm), Pd (2.7 nm), Pd/Au (4nm Au, Pd surface coverage 71.2%), Pd (2.4 nm)
Phenyl-selenylation[140]	Cu (4.3±0.6 nm)
Aza-Michael reaction[141]	SiO_2@Cu (57 nm)
Monoallylation[142]	Pt (5–8 nm)
1,4-Addition of boronic acids[143]	Rh–Fe_2O_3(10 nm)
Polymerization[144]	Ag (10–20 nm)
Selective H–D exchange[145]	Pd (3.4±0.5 nm)
Phenylborylation[146]	Ir (3.5 nm)
Ullmann C–C coupling[147]	Pd and Cu-nanoparticle
Carba–Michael addition reaction[148]	Cu (50–60 nm)
cyanation reactions[149]	Pd(0)
Mannich reaction[150]	Cu-nanoparticle(18±2) nm)
Deoxygenation[151]	Ag NPs

Cycloaddition of terminal alkynes and azides[152]	CuNPs
C–N bond-forming reaction[153]	Fe (0)
Aldol reaction/hydrogenation[154]	Pd/Hydrotalcites
Oxidative cyclization of Schiffs' bases[155]	CuNPs
Synthesis of polyhydroquinoline derivatives via Hantzsch condensation[156]	NH_4OAc / Ni-NPs
cyclization of 2-(1-hydroxy-3-arylprop-2-ynyl)phenols[157]	AgNPs
azide–alkyne click reaction in water[158]	Cu@Fe NPs
Wittig-Type Olefination of Alcohols[159]	Nickel NPs
Homocoupling of aryl iodides [160]	Nickel(0) NPs
Knoevenagel reaction[161]	$CoFe_2O_4$NPs
Bis-Michael Addition[162]	Silica nanoparticle
Anti-Markovnikov addition[163]	Silica nanoparticle
One-step synthesis of 'privileged medicinal scaffolds', 2-amino-3,5-dicarbonitrile-6-sulfanylpyridines[164]	Silica NPs
N-Alkylation[165]	Fe_3O_4 NPs
Hydrochlorination of ethyne[166]	Activated carbon impregnation AuNPs

1.10 Environmental applications

In this section, an outline of the applications of various NPs in environmental challenges, including photo degradation of pollutants, biocatalysis and photocatalysis for clean energy applications is provided.

1.10.1 Photocatalysis

The treatment of industrial waste waters for removing organic pollutants by heterogeneous photocatalysis has developed as an advanced technique.[167] Recently, metal NPs were reported as effective photocatalysts under ambient temperature with visible light illumination.[168] This can be attained by increasing the optical path of photons leading to a higher absorption rate of NPs in the presence of a local electrical field.[169] Hence, the interest for the photocatalytic degradation of dyes by using NPs has developed. The widespread use of nanomaterial like semiconductor metal oxides increases the possibility due to their excellent properties such as ferroelectricity, high temperature stability, superconductivity, semiconductivity, ferromagnetism, piezoelectricity and catalytic activity.[170] NPs such as WS_2, CdS, ZnO, SnO_2,TiO_2, AgS, ZrO_2, MOS_2, ZnS, WO_3, and $SrTiO_3$ have been identified as photocatalysts for the degradation of numerous synthetic dyes and organic contaminants. Although any pure metal and its alloy NPs are also used as photocatalst like Ag,[171] Fe-Ni[172] etc. the photocatalytic activity of TiO_2 NPs is well recognized. Again, the combination with MNPs allows a simple recovery of such well dispersed TiO_2 particles.[173] TiO_2 NPs immobilized on various magnetic supports such as ferrites, magnetite, Fe_3O_4-SiO_2 have been used for photodegradation various dyes like[174] methylene blue,[175] rhodamine B[176] and methyl orange (MO).[177]

1.10.2 Nanobiocatalyst

Nanobiocatalysis, in which enzymes are incorporated into nanostructured materials, has developed as a fast growing area. Enzymes are versatile macromolecular biocatalysts.[178] However, their widespread application is hampered by inherent disadvantages, including cost, availability and recycling. To improve the reusability of enzymatic systems a wide range of inorganic materials are used as a support. Nanostructures, including NPs, nanofibers, carbon nanotubes and nanoporous media, have shown great efficiency in the manipulation of the nanoscale environment of the enzyme and magnetic NPs have the additional advantage of stability and separation.[179]

In literature, the first reports of the entrapment of enzymes in magnetic materials for heterogeneous nanobiocatalysis were described by Reetz et al. in 1998.[179,180] The activity of the biocatalyst was investigated for the esterification and also tested as an enantioselective catalyst in the kinetic resolution of racemic 2-pentylamine **(Figure 1.27)**. The ee obtained in the resolution was 97-99%.[181] Another such example is magnetically immobilized lipase, which was used to produce biodiesel fuels from soybean oil.[182] Magnetic Fe_3O_4 NPs treated with (3-aminopropyl) triethoxysilane were used as immobilization material. Lipase was covalently bound to the amino-functionalized MNPs by using glutaraldehyde as a coupling reagent with the activity recovery up to 70% and the enzyme binding efficiency of 84%. Similar immobilization of lipase on magnetic nanocomposites (hierarchically ordered porous functionalized magnetic nanocomposites) is demonstrated in **Figure 1.28**. The resulting nanobiocatalysis has been utilized for hydrolysis reaction.[183] Similarly horseradish peroxidase entrapped on magnetite-containing spherical silica NPs,[184] was reported by a reverse-micelle technique. The present progress of nanobiocatalysis has demonstrated the advantages of nanobiocatalytic approaches and their bright future as a fusion of nanotechnology and biocatalysis.

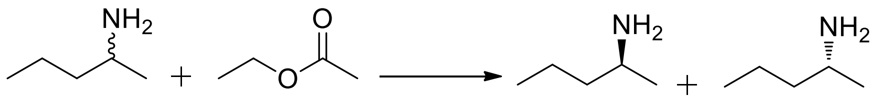


Figure 1.27 Racemic resolution of 2-Pentylamine using a biocatalyst based on candicaantartica entrapped on magnetite containing a methyl-/ propyltrimethoxyorthosilane gel.[180]

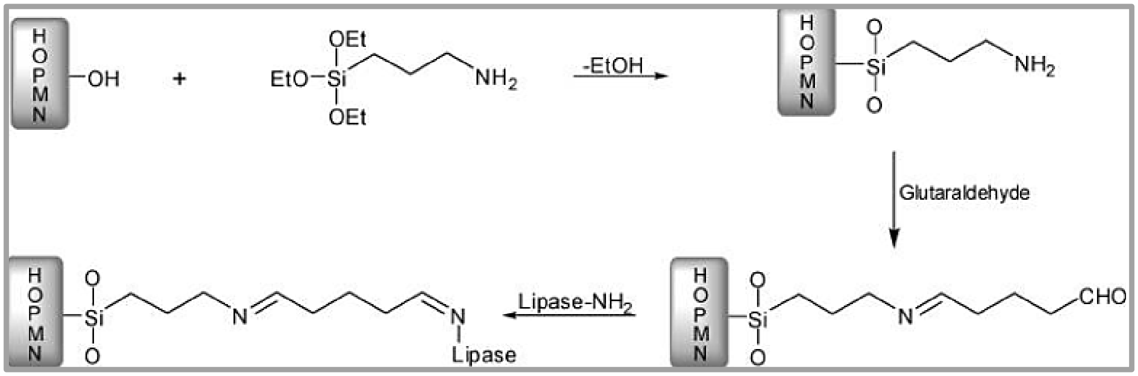


Figure 1.28 Immobilization of Lipase on the Novel Hierarchically Ordered Porous Magnetic Nanocomposites.[182]

1.10.3 Nanocatalysts for Clean Energy Applications

Today the world is on the verge of an energy crisis Hence alternative technologies that can provide replacement for existing fossil fuel-based energy system is highly required. The concept of green chemistry is also involved in the progress of sustainable energy technologies such as H_2 and fuel cells.[185] These technologies depend mostly on catalysis for energy harvesting and nanocatalysis have been extensively used for the H_2 storage, H_2 generation, and in energy conversion.[186] O_2 and H_2 react with each other to release its stored chemical potential and procedure the water.

Water is considered as the ideal source for H_2 production; however, this process is a highly energy intensive process. Water splitting in the presence of a photocatalyst (e.g. TaON, TiO_2, and $LaTiO_2N$) has been studied extensively as a potential method to supply renewable H_2. Heterogeneous photocatalysis TiO_2 is extensively used for water splitting (**Figure 1.29**).[186,187] The two challenging problems in TiO_2 photocatalysis are i) the necessity of near-UV light because of its relatively high band gap and ii) the relatively low quantum efficiencies because of quick electron–hole pair combination. The issues that affect the photocatalytic efficiencies of TiO_2 include the surface area, size, morphology, and phase of the particles.[188] For example, the nanotubular architecture allows for more efficient absorption of incident photons as well as decreased bulk recombination.

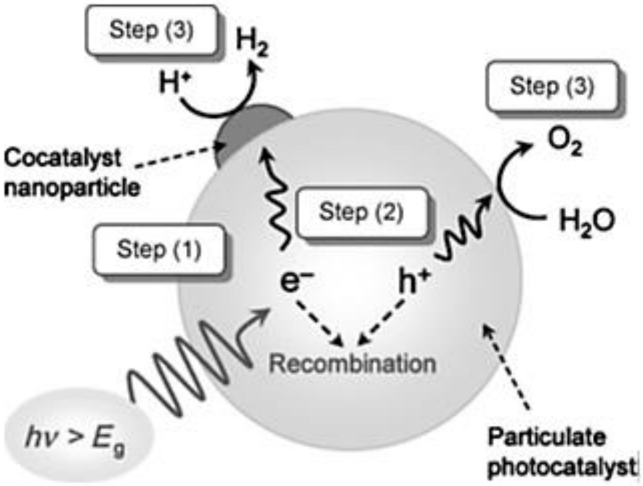


Figure 1.29 Processes involved in the photocatalytic overall water splitting reaction on a heterogeneous photocatalyst[189]

1.11 Aim and outline

Catalysis is of vital significance for the development of the world by providing a sustainable way to transform raw materials into valuable chemicals in an efficient, cost-effective and environmentally benign manner. While nanotechnology has several applications, the use of nanomaterials as catalysts has attracted great attention.

This thesis provides an extensive overview of the applications of nanocatalysts in a wide range of catalytic processes and numerous synthetically significant reactions including: oxidation, reduction and transesterification reactions. It also discusses the use of nanomaterials in some emerging areas such as environmental applications for degradation of dye from water.

There has been an increasing recent trend of the use of magnetically separable nanomaterial for the reason of their facile separation, high selectivity, stability and activity.

Chapter-1 Designing an efficient and cost-effective catalyst is a subject to extensive research. The chapter describes a new fast growing area of catalysis viz., metal nanocatalysis. In the nano size regime, metals show a perceptible change in their electrical, optical, and catalytic properties, which allows them to act as catalysts in various electron transfer processes as well as organic transformations. Metal nanoparticle (NP) catalysts exhibit superior reactivity and selectivity compared to their bulk counterparts. Additional advantages include easy synthesis and separation, tunable size and shape as well as improved efficiency under mild and environmentally benign conditions in the context of green chemistry. These systems offer efficient protocols for sustainable and environmentally friendly future, leading to the development of active and selective materials for a wide variety of applications.

Chapter-2 This chapter is devoted to the synthesis, characterization and catalytic application of nickel nanoparticles. The application part is divided into three subparts.

Part-1 Catalytic application of Nickel Nanoparticles (NiNPs) in transesterification of primary esters

Part-2 Catalytic application of Nickel Nanoparticles (NiNPs) in transesterification of *Aloe vera* seed oil and other oils

Part-3 Catalytic applications of Nickel Nanoparticles (NiNPs) electron transfer reactions

Chapter-3 This chapter discusses magnetically separable core/shell Iron oxide@Nickel nanoparticles: Synthesis, characterisation and catalytic application. The application part is divided into two subparts

Part-1 Catalytic application magnetically separable core/shell Iron oxide@Nickel nanoparticles in chemoselective reduction of nitroaromatics

Part-2 Catalytic application magnetically separable core/shell Iron oxide@Nickel nanoparticles in degradation of azo dyes

Chapter-4 Discusses the synthesis and characterization of magnetically recoverable L-3,4-dihydroxy phenylalanine (L-DOPA) immobilized based nanocatalyst. The catalyst was exhibited aldol reaction of several aldehydes with acetone to achieve β-hydroxy carbonyl compounds in good yields at room temperature. The chapter title is Nanoparticle-supported and magnetically recoverable L-DOPA: Novel catalyst for the Room temperature aldol reaction

Chapter-5 Magnetically recoverable copper based nanocatalyst was prepared from inexpensive starting materials and used for oxidation of benzylic alcohols. The chapter title is Nanoparticle-supported and magnetically recoverable organic–inorganic hybrid copper (II) nanocatalyst: a selective and sustainable oxidation protocol

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