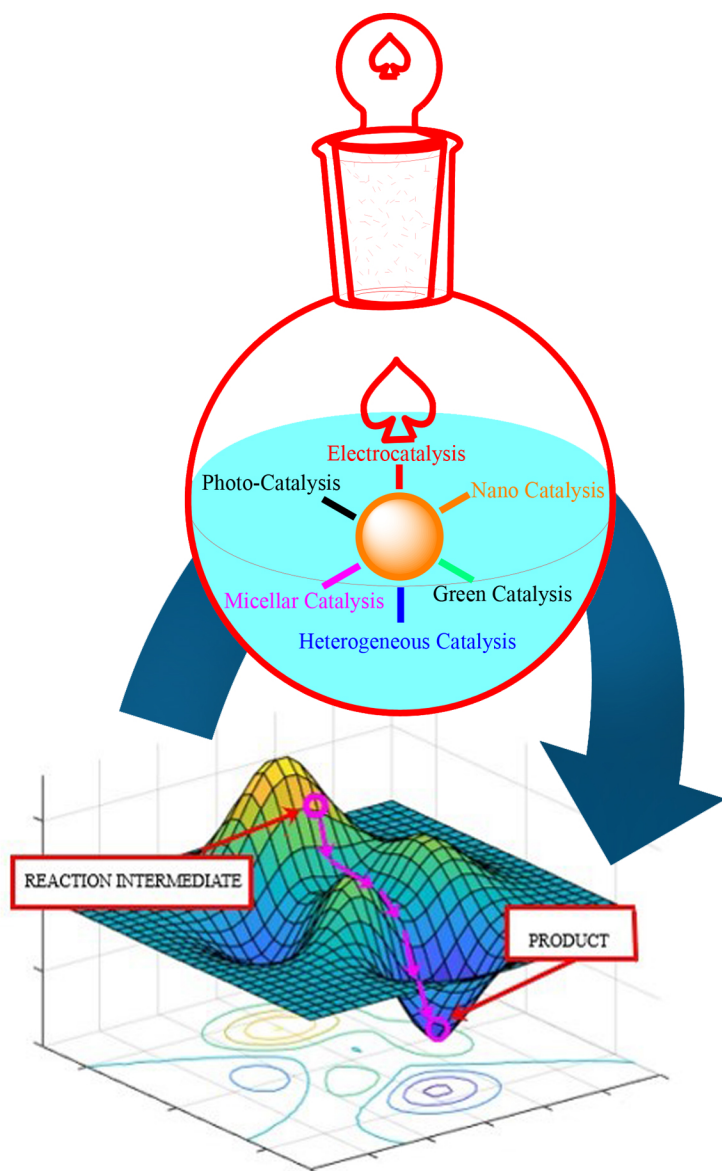


DIVERSE STRATEGIES FOR CATALYTIC REACTIONS



Editors:
Goutam Kumar Patra
Santosh Singh Thakur

Bentham Books

Catalysis: Current and Future Developments

(Volume 2)

Diverse Strategies for Catalytic Reactions

Edited by

Goutam Kumar Patra

&

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PREFACE

Catalysis is one of the basic fundamental as well as thrust research areas of chemical sciences which fascinate a wide range of academicians, researchers, chemical technologists and industries throughout the world. The field of catalysis is interdisciplinary by its nature and includes organic synthesis, coordination and organometallic chemistry, kinetics and mechanism, stereochemical concepts and material science, all at its very heart. In the past few decades, the commercially valuable products obtained via the diverse catalysts and catalytic processes have been gaining unprecedented prominence, which could be evidenced by increasingly large numbers of publications and patents. Innumerable organic, inorganic and biochemical reactions are facilitated by catalysis, and thus, it plays a crucial role in chemical sciences. The global catalyst market shows about 90% of all commercially produced bulk and fine chemicals, biochemical, synthetic and medicinal products involving homogeneous or heterogeneous catalysis at some stage in the chemical or biochemical process of their manufacture. In recent years, there has been tremendous growth in various types of subfields in catalysis, e.g., nanocatalysis, asymmetric or chiral catalysis, industrial catalysis, organocatalysis, photocatalysis, electrochemical catalysis, enzyme and biocatalysis, tandem catalysis, autocatalysis, induced catalysis and environmental catalysis. The quantitative requirement of the catalyst in a chemical process, from the stoichiometric amount to the catalytic amount and potential to change the equilibrium, excites the researcher to dream about a perpetual motion machine, a contradiction to the law of thermodynamics. Stereospecific catalysts not only accelerate the reaction rates but it also controls the absolute configuration of product, therefore, a deep insight into the kinetics and mechanism of catalysis is vital to get desired product conversion rates, turnover number, and frequency of the catalytic reaction processes. Therefore, catalysis development and understanding are crucial not only to the academics or basic microscopic level but to the industrial, technology or macroscopic level.

This book involves the most distinctive characteristics inclusive of catalysis and highlights many important topics and subfields/subdisciplines. The novel design, synthesis, development, reducing energy consumption and side products, atom economy and green chemistry approach of catalysis definitely would play a vital role in the diverse strategies for catalytic reactions.

We hope this book will serve as an excellent reference book for graduate students and researchers at all levels in both academic and industrial laboratories.

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CHAPTER 1

Recent Advances in Electrocatalysis**Goutam Kumar Patra^{1,*}, Amit Kumar Manna¹, Meman Sahu¹, Vanshika Sharma¹ and Santosh Singh Thakur¹**¹ Department of Chemistry, Guru Ghasidas Vishwavidyalaya, Bilaspur, Chhattisgarh, India

Abstract: In this chapter, we have briefly studied electrocatalysis. Electrocatalysis plays an important role in many synthetic procedures, such as biodiesel production, CO₂ reduction, O₂ evolution reaction, *etc.* Numerous electrocatalytic kinetic characteristics are discussed to fairly assess the efficiency of electrocatalysts, including overpotential (η), exchange current density (i_0) and Tafel slope (b). These variables are essential and provide valuable insight into the electrochemical reaction's process. Due to this, herein, we give a brief overview of these kinetic characteristics along with a review of different electrocatalysts for various reactions.

Keywords: Biodiesel production, Current density, Electrocatalysis, Electrocatalytic kinetics, Overpotential, Tafel slope.

INTRODUCTION

The electrocatalysis process is a combination of catalysis and electrochemistry, where catalysis quickens a chemical reaction, while electrochemistry interconverts electrical and chemical energy. Electrocatalysis is a unique type of heterogeneous catalysis that involves interaction and electron exchange between reactants and an electrocatalyst, which is frequently the electrode or a component of the electrode since it achieves chemical transformation at an electrode surface [1]. In an overall electrocatalytic process, cathodic and anodic processes take place in two compartments that are partitioned by a membrane to prevent the mixing of the cathodic and anodic reaction products, as illustrated in Fig. (1). During this process, an external power source drives a non-spontaneous electron transfer reaction, converting the electrical energy into the chemical energy of the reaction products. Electrodes with electron-conducting phases that are joined by an ion-conducting phase make up the cathodic and anodic parts of the process (electrolyte medium).

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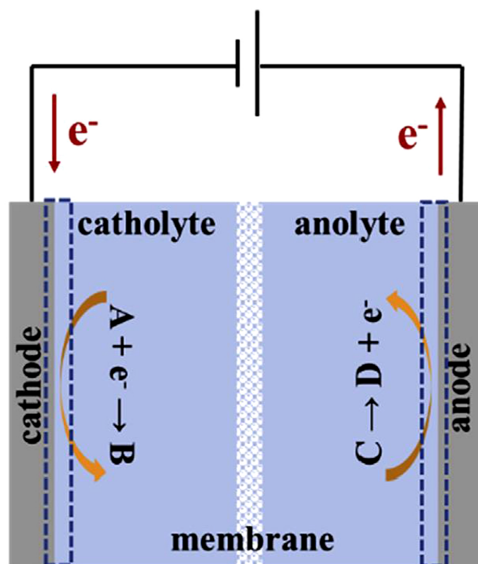


Fig. (1). Illustration of a conventional electrocatalytic system [2].

Electrocatalysts in nature comprise the hydrogenases that catalyse $2\text{H}^+ + 2e^- \rightleftharpoons \text{H}_2$, and CO-dehydrogenases, which catalyse $2\text{H}^+ + 2e^- + \text{CO}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$. Similar to this, nitrogenases use ATP to break down N_2 and protons into two equivalents of NH_3 and various amounts of H_2 . These fuel-forming reactions go forward swiftly, even when the enzymes function close to the equilibrium redox potentials of their separate processes. We aim to imitate the enzyme's high activity and energy efficiency when creating artificial homogeneous and heterogeneous catalysts. Although several of the most active electrocatalysts feature precious metals, the past decades have seen many researchers take up the challenge of developing comparably superior base metal catalysts, which, in addition to being more sustainable and economically producible, may be less susceptible to CO poisoning [3].

The activation energy in electrochemical processes is related to the potential, *i.e.*, voltage, at which a reaction occurs. Thus, electrocatalysts frequently change the potential at which oxidation and reduction processes are observed [4]. Alternatively, an electrocatalyst can be thought of as an agent that facilitates a specific chemical interaction at an electrode surface [5]. Given that electrochemical reactions occur when electrons are passed from one chemical species to another, favourable interactions at an electrode surface increase the likelihood of electrochemical transformations occurring, thus reducing the potential required to achieve these transformations [6].

Electrocatalysts can be evaluated according to three figures of merit: activity, stability and selectivity. The activity of electrocatalysts can be assessed quantitatively by understanding how much current density is generated and, therefore, how fast a reaction is taking place for a given applied potential. This relationship is described with the Tafel equation [4]. In assessing the stability of electrocatalysts, the ability of catalysts to withstand the potentials at which transformations are occurring is crucial. The selectivity of electrocatalysts refers to their preferential interaction with particular substrates and their generation of a single product [4]. Selectivity can be quantitatively assessed through a selectivity coefficient, which compares the response of the material to the desired analyte or substrate with the response to other interferents [7].

High activation barriers can be a problem in many electrochemical systems, including galvanic cells, fuel cells and several types of electrolytic cells. Heat is produced from the energy that was diverted to go beyond these activation barriers. This heat would typically only catalyse the reaction in most exothermic combustion reactions. This heat is a waste by-product that is lost to the system in a redox process. Low faradaic efficiency and high over-potentials are typical descriptions of the additional energy needed to overcome kinetic barriers. Each of the two electrodes in these devices as well as the corresponding half-cell, would need a unique, specialised electrocatalyst [8].

There are frequently significant kinetic barriers in half-reactions that include many steps, multiple electron transfers, and the evolution or consumption of gases in the course of their total chemical transformations. Moreover, there are frequently multiple possible reactions at an electrode's surface. For instance, the anode can oxidise water through a two-electrons-or-more process to hydrogen peroxide or a four-electron process to oxygen during the electrolysis of water. Either of the chemical pathways might be aided by the presence of an electrocatalyst.

ELECTROCATALYTIC KINETICS

An electrocatalyst is a catalyst that speeds up electrochemical reactions (charge-transfer reactions like Eqn (1)). It has two options: it can modify the electrode's surface or serve as the electrode itself. In general, the electrocatalyst's primary function is to help the electrode and reactant for transferring charges by adsorbing the reactant on its surface to create the adsorbed intermediate. Numerous electrocatalytic kinetic characteristics are used to fairly assess the efficiency of electrocatalysts, including overpotential (η), exchange current density (i_0) and Tafel slope (b). These variables are essential and can provide valuable insight into the electrochemical reaction's process. Due to this, we give a brief overview of

CHAPTER 2**Nano-Catalysis in the Selective Oxidation of Alcohols and Anilines****Ashok Raj Patel¹, Geetika Patel¹, Arti Srivastava¹, Bhaskar Sharma¹, Goutam Kumar Patra¹ and Subhash Banerjee^{1,*}**¹ *Department of Chemistry, Guru Ghasidas University, Bilaspur, Chhattisgarh, India***Abstract: Background:**

Recently, the development of eco-friendly and sustainable organic redox reactions has attracted considerable attention. In the classification of catalysis, the two categories, homogeneous and heterogeneous catalysis, have their own advantages and limitations. Thus, we need catalytic species that show properties like homogeneous and heterogeneous catalysts. Nano-catalysts fulfill the above requirements as it works as a “linker” between the homogeneous and heterogeneous catalysts. In past years, various heterogeneous nanomaterials have been used in different organic transformations as green catalysts due to their larger surface area and smaller size. Most importantly, nano-catalysts are the modern catalysts that promise green synthesis.

Methods:

Selective oxidation of alcohols to carbonyl compounds is essential due to the wide applications of carbonyl compounds in pharmaceutical, agrochemical, fragrances, food industries, and electronic industries. Traditional methods for the synthesis of carbonyl compounds require a large number of oxidants; homogeneous catalysts, heavy metal catalysts, and precious metal supports are used. Further, aromatic azo compounds, composed of two phenyl groups interconnected by nitrogen-nitrogen double bonds, are well-known chromophores that have important applications in the synthesis of dyes, pigments, indicators, chemosensors, radical initiators, food additives, and therapeutic, diagnostic, and pro-drug agents as well as building blocks of various polymers and natural products. These compounds exhibited photophysical properties and significant applications in electronics and optics. Several methods have been developed for the preparation of aromatic azo compounds. Moreover, the selective oxidation of aniline is an important and useful organic reaction for the synthesis of oxygenated compound such as azoxybenzenes. Azoxybenzenes have attracted special importance as synthetically useful intermediates, precursors and employed as dyes, reducing agents, chemical stabilizers, and polymerization inhibitors, liquid crystals displays and thera-

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peutic medicines. Here, some green approaches have discussed for the preparation of azoxy compounds.

Conclusion:

This review focused on the recent green methods for the selective oxidation of alcohols to carbonyl compounds and direct oxidative azo-coupling of anilines to aromatic azo and azoxy compounds using heterogeneous nano-based catalysts.

Keywords: Direct oxidative aza-coupling, Heterogeneous catalysis, Nano-catalysts, Selective oxidation of alcohol.

INTRODUCTION

The term oxidation-reduction is very important in general chemistry, and can be defined in terms of oxidation as the *loss* and reduction as the *gain* of electrons simply. Other terms like “dehydrogenation”, “addition of oxygen”, and “loss of hydrogen” for oxidation and “hydrogenation”, “loss of oxygen”, and “addition of hydrogen” are used for reduction. However, it is not easy to use these terms in the context of organic chemistry. So, we need to use another term instead of classical definitions, such as oxidation is a *decrease* of *electron density* and reduction is an *increase* of *electron density* around the atom(s) involved [1]. In the 18th century, French chemist, A. Lavoisier introduced “The concept of oxidation states,” which derives from the oxygen-based dualistic system of chemistry [2], and the concept of oxidation number in chemistry is explained by other articles [3]. Another approach defines oxidation and reduction by comparing the “oxidation level” in the organic reactant(s) and product(s) by adding the total number of heteroatoms, π -bonds (triple bonds count as two), and rings. As a result, a higher number for the product assigns oxidation, whereas a lower number indicates reduction. One can also describe the oxidation as a decrease in hydrogen atoms or an increase in oxygen, nitrogen, or halogen atoms [4].

In addition, the IUPAC defines oxidation as a process wherein (I) an atom within a “molecular entity” loses electrons; (II) an atom within a “molecular entity” increases in oxidation state; or (III) an organic substrate either gains oxygen or loses hydrogen. Since, in organic chemistry, the cell potentials, free energy changes, or half-reactions involved in their redox reactions are seldom concerned, the evaluation of oxidation state changes is regardless here [5]. Another method called “ROLR (Right-Oxidation-Left-Reduction)” method may be used to define oxidation-reduction, in which mnemonic devices such as “OIL RIG” (Oxidation Is Loss of electrons; Reduction Is Gain of electrons) or “LEO says GER” (Loss of Electrons is Oxidation; Gain of Electrons is Reduction) are used as tools and this method may be helpful to understand of the relationship between electron flow

and change in oxidation number. Although the ROLR method provides a visual aspect and is a familiar and convenient method of tracking electron transfer in oxidation-reduction reactions, this method is useless after the development of confidence in understanding oxidation-reduction reactions clearly [6].

Recently, the development of eco-friendly and sustainable organic redox reactions has attracted considerable attention by minimizing the reaction conditions, avoiding chemical wastes, and using green catalysts [7]. According to principles of green chemistry, catalytic reagents are better than stoichiometric reagents as the catalytic reagents are applied in very small quantity quantities and may be reused while a large number of stoichiometric reagents are needed and can be used only one time [8]. In the classification of catalysis, the two categories, homogeneous and heterogeneous catalysis, have their advantages and limitations, so we need catalytic species that show properties like both homogeneous and heterogeneous catalysts. Nano-catalysts fulfill the above requirements as it works as a “linker” between the homogeneous and heterogeneous catalysts [9]. A short-time, specific and selective chemical conversion with good to excellent yields with easy recovery can be achieved by applying Nano-catalysts. Recyclability and reusability of catalyst are very important requirements of any catalyst to make it useful in industrial-level green synthetic methods [10]. In past years, various heterogeneous nanomaterials have been used in different organic transformations as green catalysts [11]. The larger surface area, size and morphology of nanomaterials affect the rate of reactions [12] and selectivity of the desired products [13]. Most importantly, nano-catalysts are the modern catalysts that promise green synthesis. Nanomaterials can be easily and efficiently prepared from various methods [14] using inexpensive starting materials and sustainable supporting materials [15] without using sophisticated instruments, and they are easily recoverable, highly efficient, and stable, termed “Green catalysts”.

OXIDATION OF ALCOHOL

Recently, carbonyl compounds have had numerous applications in pharmaceutical/agrochemical/fragrances/food/electronic industries [16]. In traditional methods for preparing carbonyl compounds, a large number of oxidants, homogeneous catalysts, heavy metal catalysts, and precious metal supports are used. The environmental issues such as toxicity, high cost, and potential danger in handling [17] were major issues associated with oxidants such as chromium-based reagents [18], MnO_2 [19], activated DMSO [20], hypervalent iodine [21], ruthenium [22], osmium(VIII) oxide [23], metals [24] or TEMPO [25], ammonium permanganate [26], and *tert*-butyl hydroperoxide [27], H_2O_2 [28], molecular oxygen [29], *etc.* The problems related to homogeneous catalysts,

Micellar Catalyst

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Abstract: Self-aggregates microenvironment affords a robust platform for synthesizing conventional and novel materials in aqueous media. Consequential enhanced the rate of reaction and reduced the barrier for organic solvents. A solvent is frequently asked to perform multiple tasks at once, such as ensuring contacts between substrates with different polarities, controlling heat transmission, and promoting the interaction that results in the ultimate transformation. Nature has chosen water as a solvent to carry out all types of chemical transformations, regardless of whether the substrates are soluble or not. Of course, surfactants resolve the various problems that arise from the interaction of insoluble substrates and reagents. The use of surfactants under micellar conditions represents one of the largest methods to achieve catalysis in water. To date, micellar systems are present in many areas, *e.g.*, medical science, nanoscience, organochemistry and industries of their vast application.

We explained the role of micelles and vesicles on the reactivity of nucleophiles towards the cleavage of the organophosphorus compounds. Recent developments include-application of micellar catalysis to complex single-phase and multiphase systems in which the surfactant plays multiple roles and interphase transport effects are often important. The distribution of the reagents between the aqueous phase and the micellar phase was described in terms of a simple pseudo-phase model (PPM). These quantitative treatments for the catalytic action of anionic reactants and the cationic micelles for cleaving the phosphate and thiophosphate ester improved an understanding of competitive counterion binding, the effects of reactive and inert solubilizates, functionalized surfactants, and the use of surfactant aggregates as reaction templates.

Keywords: Cationic micelles, Microemulsion, Phosphate ester, Pseudophase Model (PPM), Vesicles.

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INTRODUCTION

McBain, one of the top researchers at the turn of the 20th century, made a hypothesis on the development of molecular aggregates in an aqueous surfactant solution. McBain further underlined that, in such circumstances, surfactant aggregation can expose the peculiar solution properties of an aqueous surfactant solution over a critical surfactant concentration. This suggestion was met with two words by the meeting's moderator, "Nonsense" a well-known physical chemist: McBain." [1]. But today, everyone who is familiar with colloidal chemistry accepts the idea that surfactant molecules organise aggregation in aqueous fluids above a certain concentration of surfactant. Hydrophilic polar head groups and hydrophobic tails, which are typically extended chains of hydrocarbons, make up surfactants and lipids. While headgroups interact well with water when these molecules are disseminated in aqueous solutions, hydrophobic tails seek to avoid adverse interactions with polar water. As a result, "micelles," or aggregates of a particular size, begin to develop. J. W. McBain [2] coined the phrase for the first time to refer to a collection of soap molecules in 1913, and G. S. Hartley [3] advanced the first model of spherical micelles. According to Hartley's micelle model, the aggregate's shell is often made up of polar headgroups, and its inside is made up of hydrophobic moieties.

History of Micelle:

For generations, people have understood that a soapy solution can serve as a detergent. However, the composition of such solutions was not properly investigated until the early 20th century. James William McBain, who worked at the University of Bristol, carried out pioneering work in this field. He proposed the existence of "colloidal ions" as early as 1913 to account for the high electrolytic conductivity of sodium palmitate solutions. Micelles are the name given to these extremely mobile, naturally occurring clusters. G.S. Hartley, popularised this term in his famous work *Paraffin Chain Salts: A Study in Micelle Formation*. McBain, in 1913, first used the term micelle, now commonly known as a normal micelle, to describe the formation of molecular aggregates in an aqueous soap solution [1]. In the chemistry of surfaces by micelle in aqueous solutions, electrically charged atoms or lipid molecules organise themselves into micelles, which are loosely bonded aggregations that create a cluster of colloidal particles. Micelles consist of molecules containing two completely different regions that have opposite affinities against water. A typical micelle in water forms an aggregate with the hydrophilic "head" regions in contact with the surrounding solvent, impounding the hydrophobic single-tail regions in the micelle centre. Micelles are amphiphilic colloidal structures, with particle

diameters from 5 to 100 nm range. The micelles are of two types, 'normal micelles' (called micelles), which are formed by surfactant association in water or polar solvents, and 'reverse micelles', which are formed in nonpolar media [4].

MICELLE- “THE CHEMISTRY OF SURFACES”

Micelle Formation

Micelles function as emulsifiers, enabling the dissolution of substances that are often insoluble in water. Soap and detergents work by introducing their lengthy hydrophobic tails into the insoluble dirt (like oil) and surrounding the nonpolar particles with their hydrophilic heads. The micelle can then be removed by washing it away because its exterior is soluble in the solvent, which is typically polar. As water cannot remove the oil by itself, soap is used to remove greasy and waxy substances from plates. In soap water, micelles form on their own. This spontaneous organisation is caused by the molecule's amphipathic character, which implies that it has both hydrophilic (polar head groups) and hydrophobic regions (the long hydrophobic chain).

Micelles contain polar head groups that usually form the outside as the surface of micelles. They face the water because they are polar. The hydrophobic tails are inside and away from the water since they are nonpolar. The driving force for this arrangement is the hydrophobic interactions of the molecules. However, when the lipids form micelles, the hydrophobic tails interact with each other, and this interaction releases water from the hydrophobic tail, increasing the disorder of the system, and this increase in entropy is favourable. This overall hypothesis has been studied in varieties of studies [5 - 8]. The formation of micelles can be regarded thermodynamically as the formation of a new phase, with the critical surfactant concentration as saturation concentration. However, the resulting micelles do not form a continuous phase but are uniformly distributed throughout the aqueous environment, forming a “pseudophase”. On the basis of the pseudophase model of micelle formation, it can be considered that the variation in the c.m.c caused by various substances are variations in the actual solubility of the surfactant concentration [9]. Tanford was the first to formulate the thermodynamics of micelle formation [10]. His theory and its improvements, and also recent computer simulations based on these theories, are reasonably consistent with various experimental results for a wide range of materials. It is generally accepted that the aggregation number (N_{agg}) gradually changes with the surfactant concentration and other solvent conditions, such as the ionic strength and that N_{agg} have a certain distribution. The use of surfactants under micellar conditions is one of the easiest ways to obtain catalysis in water, as surfactants are very economical for their extensive everyday use in detergency. The major

Nanomagnetic Oxide: A Versatile Green Catalyst

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Abstract: In recent years, attempts to follow green protocol in organic synthesis have emerged along with the use of green solvent, solvent-free reaction conditions, the concept of multicomponent reactions and use of green catalysts. Fe₃O₄ is an oxide of iron called magnetite mineral; it is a ferromagnetic and strongly magnetic mineral on earth. It was the first mineral structure that was applied in X-ray. It is found that the nanomagnetic oxide shows an inverse spinel structure. Its unique properties, such as high Curie temperature, high spin polarization, and verwey transition, gains attention towards it. Nano-magnetic oxide is employed as a green catalyst. It can be synthesized by physical methods, microbial methods and wet chemical preparation methods. It demonstrates excellent catalysis in organic synthesis that gives a good yield; it enjoys an advantage over other catalysts as it is easily separable from the reaction mixtures using a bar magnet, and it is green & eco-friendly. It also shows wide applications in various fields, such as water treatment, biodiesel production, lithium-ion battery, and the biomedical field.

Keywords: Eco-friendly, Ferromagnetic, Green catalysts, Hetero catalyst, Nanomagnetic oxide, Organic synthesis, Recyclability.

INTRODUCTION

Fe₃O₄ is one of the iron oxides which occurs as mineral magnetite in nature. It contains two irons of Fe³⁺ and Fe²⁺ oxidation states. Fe₃O₄ is formulated as FeO.Fe₂O₃ (Fig. 1), where FeO [Fe (ii)] oxide and Fe₂O₃ [Fe (iii)] oxide common chemical name is ferrous ferric oxide. It is found to be the most strongly magnetic mineral on earth [1], ferromagnetic, and its magnetized pieces are called lodestone.

The detailed structure of magnetite was first established in 1915. This is the first mineral structure that was applied in X-ray diffraction (Bragg 1915: Nishikav 1915).

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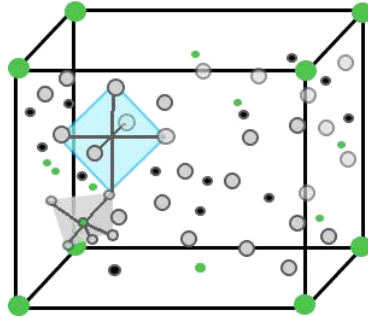


Fig. (1). Showing bonding in magnetite [2].

The structure was found to be inverse spinel (Hill *et al.*, 1979) [2]. The formula of magnetite is $[\text{Fe}^{3+}][\text{Fe}^{3+}, \text{Fe}^{2+}]\text{O}_4$. It shows 8 fcc unit cells, O^{2-} occupies fcc lattice points and iron occupies octahedral and tetrahedral voids. Fe^{2+} and a half Fe^{3+} occupied octahedral voids forming an octahedron and half Fe^{3+} occupied tetrahedral voids forming a tetrahedron. One tetrahedron and one adjacent octahedron sharing one oxygen atom shown in Fig. (2) [2].

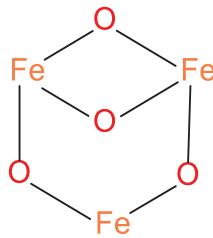


Fig. (2). Structure of Fe_3O_4 [2].

Magnetite has unique properties like high spin polarization, high Curie temperature and Verwey transition at 120 K [3 - 6]. It attracted the researcher and employed it with nanoparticles, its magnetic properties are influenced by the size and morphology of magnetite (Lin *et al.*, 2006, Song *et al.*, 2012) [7].

Various methods have been reported for the synthesis of Fe_3O_4 nanoparticles, like the physical methods [8, 9], microbial methods [10, 11], and wet chemical preparation methods [12, 13]. Nano Fe_3O_4 shows a wide application in different fields (biomedical application [14, 15], water treatment [16, 17], biodiesel production [18], Lithium-ion battery [19] and voltammetry sensing [20].

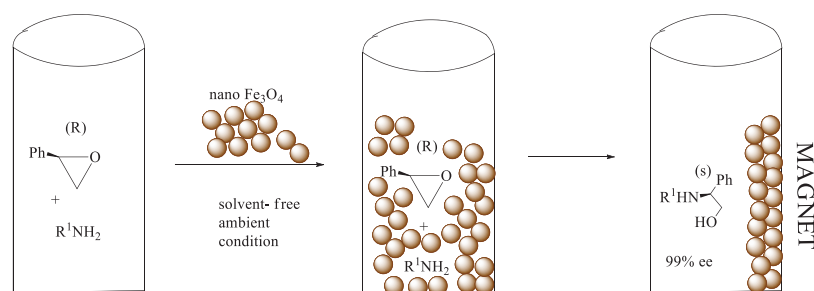
Reaction Catalyzed by Nano Fe₃O₄

Due to the unique properties of Nano Fe₃O₄, it finds applications as a catalyst in various reactions. There are many reactions catalyzed by Nano Fe₃O₄ in an environmentally friendly manner. Some of these are discussed as under:

1) Magnetic Nano Fe₃O₄ Catalyzed Solvent-Free Stereo and Regioselective aminolysis of Epoxides by amines; a Green Method for the Synthesis of β -Amino Alcohols.

A green protocol for the synthesis of β -amino alcohol using magnetic nano Fe₃O₄ as a heterogeneous catalyst under solvent-free conditions at ambient temperature was reported by Kumar *et al.* [21].

β -amino alcohol showed the importance in the field of medicine and was synthesized by heating epoxides with amine (excess) [22]. This method shows some disadvantages, such as poor efficiency and regioselectivity. To overcome the drawbacks, several methods have been employed by using a catalyst such as metal triflates, metal halides, and lewis acid [22 - 24]. These methods show some drawbacks in recycling, and recovery of catalysts. Magnetic nanoparticles are a greener heterogeneous catalyst that is magnetically separable and has attracted researchers [25]. Recently reported Friedel Craft reaction using nano Fe₃O₄ and CuFe₂O₄ as catalyst [26] which gives an idea of using nano Fe₃O₄ as a catalyst.



Scheme. (1). Diagrammatic representation of the reaction [21].

For the synthesis of β -amino alcohol, epoxide and anilines were treated in the presence of magnetic nano Fe₃O₄ as a catalyst under solvent-free and ambient temperature, which gives a yield of 99% shown in Scheme (1) [21].

A study on the ring opening of epoxide catalyzed by nano Fe₃O₄ was investigated using epoxide with a primary amine which gives trans products a good yield shown in Scheme (2).

CHAPTER 5

Advantages of Nanocatalysts on Knoevenagel Condensation

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Abstract: Nanocatalysts revolutionize organic chemistry for the conversion of various organic reactions to obtain a high yield, low hazard and stability. It plays an important role in the transformation of organic reactions due to its high surface area, small size, and low reaction time. Therefore, green methodology, both in the synthesis of nanocatalysts and organic transformation reactions, is an advanced technology, and findings promise results. Many scientists all over the world synthesised nanoparticles and used them as catalysts in Knoevenagel condensation. In this book chapter, we documented the synthesis and characterisation techniques of the homo/hetero metallic nanocatalyst and applied it in the Knoevenagel condensation reaction for its reusability and easy separation after a chemical reaction because, in organic chemistry, separation is a tedious job for finding pure compounds.

Keywords: Bimetallic Nanocatalysts, Characterisation, Green synthesis, Knoevenagel, Magnetic nanoparticles, Microwave, Organic Transformation.

INTRODUCTION

Currently, various organic transformation reactions are being developed by using nanocatalysts because the world is moving away from traditional techniques, and is primarily focusing on the environment and industrial aspects. Therefore, every component of the organic reaction is taken as an eco-friendly concept, like a solvent-free, nontoxic solvent (water), low synthetic cost of nanocatalyst, high yield, minimum reaction time, *etc* [1 - 4]. In synthetic organic transformation reactions, heterometallic catalysts play an essential role in separating the product from catalysts without loss of the yield of desired products, reusable of catalysts,

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high yield of product, *etc.* These also have a variety of applications in heterocyclic products of pharmaceutical chemistry [5 - 8]. This chapter investigates several organic reactions using traditional techniques like the catalyst, ultrasonic, microwave irradiation, *etc.* [9 - 16]. These techniques have advantages and disadvantages like expensive instruments, non-usable catalysts, low yield, separation, recyclable efficiency, *etc.* Therefore, scientists are moving towards using normal Ni, Pd-based catalysts for nanocatalysts for organic transformation reactions. The advantage of nanocatalysts is efficiently eliminating the above problems of traditional techniques. Moreover, nanocatalysts have several applications such as photocatalyst, catalyst, magnetic, sensor, photoluminescence and biological activity (antimicrobial, anticancer, and DNA binding) [17 - 25]. Therefore, the researchers are very much interested in nanocatalysts for use in different organic transformation reactions because of their small size (2-99 nm), high surface area, stability at room temperature, low cost, high yield, less toxic, easily separable from the reaction mixture (filtration or magnet), reusability, recyclability, eco-friendly and finally follow the green approach.

In Knoevenagel condensation, one modification has been introduced to the aldol condensation reaction; the derivatives of benzylidenemalonitrile (BMN) were the main product of the Knoevenagel condensation reaction and designated as Emil Knoevenagel. The aldehydes and active hydrogen-containing groups are essential requirements for the Knoevenagel reaction, and it is one of the powerful synthetic tools in heterocyclic compounds. The applications of the Knoevenagel reaction are carbon-carbon bond formation, synthesis of fine chemicals, hetero Diels-Alder reaction, anticoagulant, antibacterial, fungicidal and pesticidal [26 - 30]. The Knoevenagel condensation occurs mainly in the presence of base catalysts like pyridine, piperidine, ammonia and sodium ethoxide [31]. Some metal oxides also served as a catalyst in the Knoevenagel condensation, like ZrO_2 [32], TiO_2 [33, 34], Fe_3O_4 [35], NiO [36, 37] and CuO [38, 39].

Here, we have demonstrated the synthetic and characterisation stages of nanocatalysts as well as the development of the Knoevenagel reaction using different nanocatalysts.

Synthesis Technique of Nanocatalyst

The nanocatalyst can be synthesised by different methods like sol-gel, hydrothermal, glow discharge plasma, sonochemical, photochemical, thermal decomposition, chemical precipitation, oxidation irradiation, electrolysis, microwave irradiation, chemical vapour method, wet-chemical method, anti-solvent precipitation, and sonoelectrooxidation [40 - 45].

Characterisation of Nanocatalyst

The characterisation of nanoparticles is a significant feature of material study; without it, we can't be sure that nanoparticles will develop. To understand the material scientifically, the basic procedure is required. Methods for investigating the material properties and microscopic structures (such as mechanical, thermal, and density investigations) were comprised in the characterization technique. We discussed many characterisation techniques in this part like UV-visible spectroscopy (Fig 1a), Fourier Transform Infrared (FTIR) (Fig 1b), Transmission Electronic Microscopy (TEM) (Fig 1c), Scanning Electronic Microscopy (SEM) (Fig 1d), Powder X-ray Diffraction (P-XRD) (Fig 2a) and Zeta potential (Fig 2b) [46]. The conversation of organic transformation reaction is proven by the analysis of ^1H NMR spectroscopy.

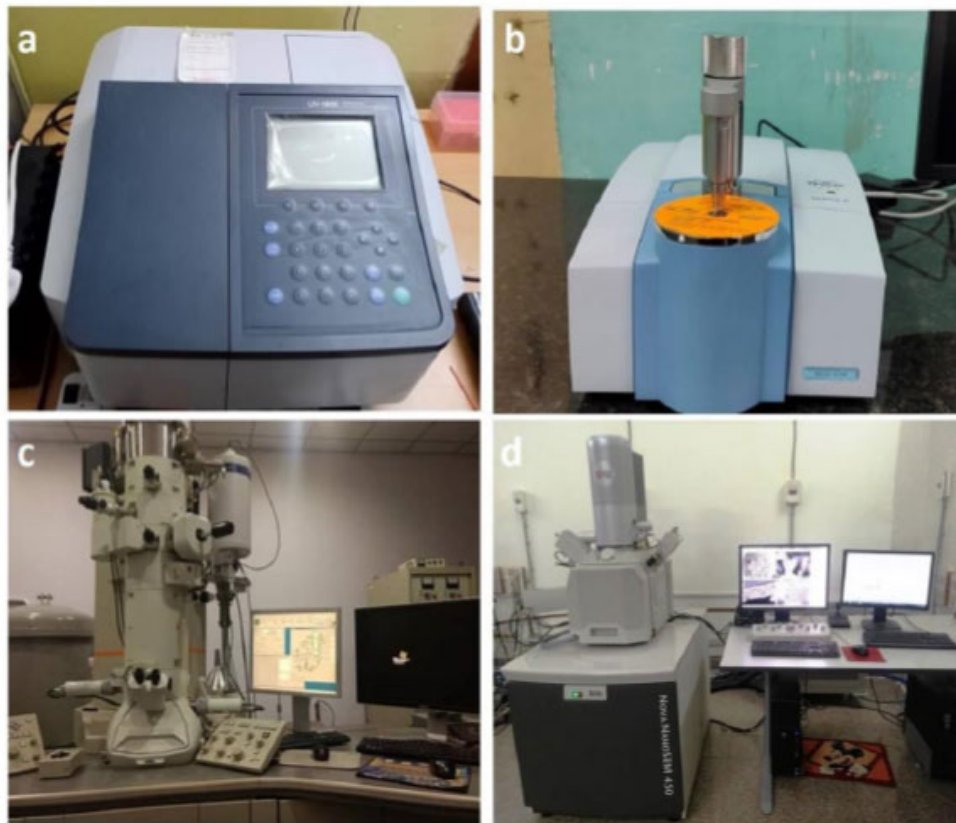


Fig. (1). A typical UV-Visible Spectroscopy (a), Fourier Transform Infrared (FTIR) Spectroscopy (b), Transmission Electron Microscopy (TEM) (c), Scanning Electron Microscopy (SEM) (d) [46].

Noble Metal Supported Heterogeneous Catalyst for Oxidation and Oligomerization Reaction

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Abstract: Noble metals like platinum, gold, silver, rhodium, palladium and copper were used as catalysts and promoters in oligomerization hydrogenation, dehydrogenation, and oxidation reaction to get valuable chemicals, and green fuel without any harmful effect on the environment. Platinum, rhodium, palladium, copper, monometallic and bimetallic with reducible and non-reducible supported material zeolites, Si/Al, MCM-41 and Al₂O₃ show excellent activity toward conversion of reactants. Among noble metals, gold has shown low activity and high deactivation. The C₄ hydrocarbon formation was faster than C₆ during the oligomerization reaction over the metal catalyst at mild reaction conditions.

Keywords: Bimetallic, Catalysts, Hydrogenation, Metal complexes, Noble metals, Nanoparticles, Oligomerization, Oxidation, Supported material, Valuable chemicals.

INTRODUCTION

The demand for energy and valuable chemicals worldwide is increasing due to the increase in population as well as the modernization of the standard of living. Various methods are continuously introduced day by day to produce and fulfill the gap between the demand and supply of such kinds of valuable chemicals and green fuels without any harmful effect on the environment. The conversion of various hydrocarbons into precious chemicals to reduce waste and increase economic benefits is a safe and promising process [1]. The main routes of techniques to find out these requirements are broadly known as hydrogenation, thermal cracking, condensation, oxidation, photocatalysis, isomerization, oligomerization, polymerization, *etc* [2 - 4]. The oligomerization of olefins, ethylene, propane, isobutene, and dibromomethane was investigated by several

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authors [3 - 7]. Diesel fuel produced through the oligomerization of light olefins has several advantages, such as the absence of sulphur and aromatics if the conversion is properly carried out [3]. The oxidation of carbon monoxide (CO) and methanol was also studied by several authors to achieve the desired need for green fuel as well as valued chemicals [8 - 11]. The light and heavy hydrocarbon chemicals obtained from oxidation and oligomerization have been extensively used as necessary precursors to a wide range of industrial products, including motor fuels, lubricants, plasticizers, pharmaceuticals, dyes, resins, detergents, and additives [7, 12]. These methods are widely accepted in various industries like petroleum, oil, and pharmaceuticals. There are two types of catalysts, homogeneous and heterogeneous, in industries, which play a crucial part in the synthesis of these substances. The heterogeneous catalyst used in process industries is the utmost 80%, and the remaining is the homogeneous catalyst.

Homogeneous catalysts are generally organometallics types, while heterogeneous catalysts are noble metals, mixed oxides, zeolites, clays, *etc.* Heterogeneous catalysts are preferred over homogeneous catalysts because of their better stability and ease of recovery, lower cost of catalyst, scale-up industrially, and higher throughput [13 - 16]. Numerous solid catalysts or noble metals were applied in oxidation and oligomerization reactions. This noble metal scan is made use of either monometallic, bimetallic, or supported over solid materials like zeolites, mesoporous, MCM-41, activated carbon, *etc* [2 - 12]. However, many authors reported that the pore shape, size, and acidity affect the catalyst properties [3, 4, 12, 17]. The noble metals can be dispersed or loaded on solid materials (zeolites, Si/Al, MCM-41, Al₂O₃, *etc.*) by wet impregnation, impregnation precipitation, coprecipitation, and ion-exchange methods [17 - 19].

PHYSICAL AND CHEMICAL PROPERTIES OF VARIOUS NOBLE METALS

Noble metal, any of numerous metallic chemical elements which have high-quality oxidation resistance, even at excessive temperatures, generally is taken into consideration to encompass rhenium (Re), ruthenium (Ru), rhodium (Rh), palladium (Pd), silver (Ag), osmium (Os), iridium (Ir), platinum (Pt), gold (Au) and copper (Cu). Noble metals are regarded for their good stability, unusual splendid physical properties, and attractiveness. All these noble metals have a face-centered cubic (FCC) crystal structure. Their specific heat and thermal conductivity lie in the range of 0.03 – 0.09 cal /gm and 0.17 – 1.00 cal-cm/sec-cm² °C, respectively [20]. Some common useful characteristics like an atomic number, atomic weight, density, melting, and boiling are represented in Fig. (1).

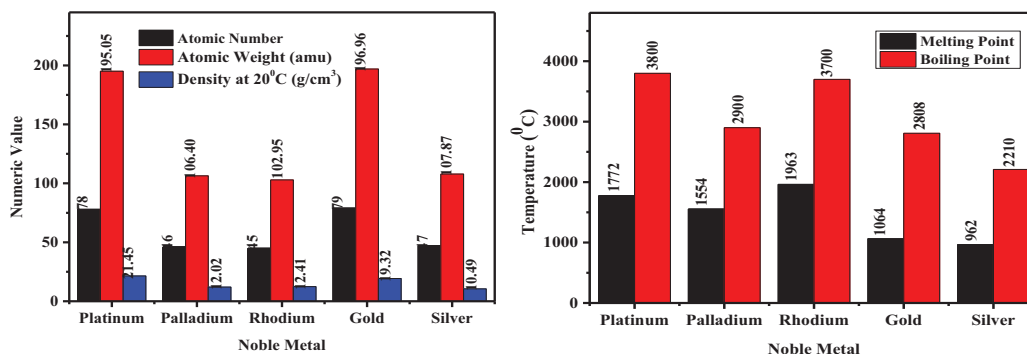


Fig. (1). Common characteristics of noble metals.

Platinum (Pt)

It has a high melting point, high heat resistance, high corrosion resistance, and unique catalytic properties. Pt and its group element are being used widely in many industrial fields, most notably as automobile exhaust catalysts, the high-tech manufacturing industry, and the handicraft industry. Pt nanoparticles are also recognized for their competence in catalytic chemical reactions, bio-sensing applications like the detection of cancerous cells, *etc.* It is a highly expensive, precious metal and constrained reservation significantly inspired the improvement of metallic restoration generation from secondary sources [21 - 23].

Palladium (Pd)

It is one of the noble metals of the six Pt group metals. It appeared to be silver-white metal in color. It is well known for its wide application in electrical equipment, dental materials, automobile industries, and catalytic reactions. Many researchers have reported in their research that it can trigger chemical reactions and can be employed with mixtures of noble metals, like Pt, Pd, and Rh, for oligomerization, dehalogenation, and oxidation reaction [24 - 27].

Rhodium (Rh)

It is also a noble metal having a place in the Pt group of elements in the periodic table. It is obtained in a very low concentration in the Earth's crust. It has extensive use in the glass, chemical, and electronic industries, but its principal application is as an active catalyst material and various chemical reactions such as alkene oligomerization and oxidation [28].

Heterogeneous Catalysts for Photo-Oxidation

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Abstract: Photocatalysis is gaining momentum for the degradation of persistent pollutants apart from other applications, including wide-scale industrial use. Non-Hazardous, efficient, greener approach and reusable properties make photocatalyst potential molecules for field application. Heterogenous make available solid surface, absorb photoenergy and initiate redox process for target molecules. Modification of heterogenous catalysis and improvement of the process is continuously accessed for better performance. The current chapter deals with some important practical aspects and challenges with some important heterogeneous catalysts like TiO₂, ZnO, CdS, etc.

Keywords: Anatase, CB (Conduction Band), Catalysts, Heterogeneous catalysis, Heterocatalysts, Heterocatalytic property, Insulators, Metal-Organic Frameworks, Photocatalyst, Photooxidation, Semiconductors, SnO₂, TiO₂, VB (Valance Band), ZnO₂, CdS.

INTRODUCTION

The broad field of heterogeneous photocatalysis covers potential applications of pollution remediation, energy production, synthesis of chemicals and designing of materials. In recent years, the field of heterogeneous photocatalysis has drawn great interest due to its interdisciplinary convergence, including chemical synthesis, surface and material science, electrochemistry, spectroscopy, etc [1]. Homogeneous catalysis for photooxidation reactions explains the increasing rate effect of a catalyst present in a different phase with respect to reactants and products. Heterogeneous catalysis represents a class of catalysis where the catalyst occupies a different phase as compared to the reaction mixture. The area

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of heterogeneous catalysis has become more and more popular during the past few decades as efficient recovery of expensive catalysts is straightforward. Most of the processes of heterogeneous catalysis involve the application of solid phase catalysts where reactants are either in a liquid state or in a gaseous state.

Within the periodic table, almost each of the transition metals may act as a heterogeneous catalyst or as a promoter of catalyst because each of these has excellent capabilities of reaction rate enhancement effect with product selectivity at low cost.

Heterogeneous catalysis is gaining momentum, with a variety of studies opening new fields. The surfaces of a solid can act as a reaction site as it has the ability to make and break different kinds of bonds to the molecules present in its surroundings. Based on this fact, the occurrence of many chemical reactions catalyzed on solid surfaces can well be explained [2]. About 85% of chemical products are manufactured using catalytic processes. Historical impressions of such catalysis in the field of photooxidation begin to reflect around four decades back when the surface of semiconductor metal oxides and sulphides, mainly ZnO, TiO₂, WO₃, CdS *etc.*, were used as hetero-catalysts for processes like purification, photocatalytic transformation, decontamination, deodorization, etc. A typical heterogeneous metal catalyst consists of a promoter which is an active metal component. In some cases, the metal itself acts as an active ingredient, but such catalysts largely consist of precious metals and some base metals under a reducing environment [3]. Surface adsorption theory explains heterogeneous catalysis as a three-step mechanism. In the first and foremost step, as a result of the formation of bulk concentration of reactants around the solid catalyst surface, adsorptions of one or more reactants take place at the active sites of the surface of the solid phase catalyst. The active site is that particular area at the catalyst surface where more adsorption is feasible that may provide a reactive site. The second step involves the proceeding of reaction between reactants. The reactant gets bound to the catalyst surface when it comes to surface's close proximity. At this stage, simultaneous bond breaking and formation results in the dissociation of old bonds and the formation of new bonds resulting in the production of a new molecule. Most common solids that are incorporated as hetero-catalysts include metal, metal oxides and metal silicates, which are capable of maintaining a desired rate of reaction at economical reaction conditions giving a large-scale production. The classification of heterogeneous catalysts includes three categories (i) Conductors (Includes metals and alloys) (ii) Semiconductors (includes oxides and sulphides) and (iii) Insulators (includes metal oxides and solid acids or bases, e.g. clay, silica, alumina, zeolite and heteropolyacids) [4]. The hetero-catalytic property of conductors is attributed to various types of defects present over the surface of metals and alloys that include electronic defects, point defects and non-

stoichiometric defects. Combining the two phenomena, *i.e.*, heterogeneous photocatalysis and photoreaction, give results on expected lines in the environmental cleanup process.

The photocatalytic reactions based on redox processes involve the use of light energy to produce electron/hole pairs. These pairs are produced at an activated state and are capable of performing reduction and oxidation, resulting in a chemical reaction. During a typical photochemical reaction, the activation of a reactant or catalyst involves absorption of an appropriate wavelength of light radiation that is followed by electron-transfer processes performing coupled redox reactions. To achieve a sustainable outcome, the oxidation and reduction processes must occur one after another at the highest possible speed [5]. Photooxidation occurs as a result of consecutive chain processes producing free radicals after photon absorption that ultimately terminates with the loss of one or more electrons. The photocatalysts involved in photooxidation have their own merits and demerits. The semiconductors, when used as a photocatalyst, show enhanced activity when exposed to ultraviolet light; at the same time, these have been found to show weak absorption in the presence of visible light. In these ways, the photocatalytic efficiencies vary depending upon the light to which photocatalysts are exposed. The inefficient separation of charges at an excited state is another issue that adversely affects the potential of the photocatalyst. Therefore, to get maximum output during photocatalytic activity, the charge separation needs to be improved [6].

Homogeneous and Heterogeneous Photocatalysis

Heterogeneous catalysis represents a class where the catalyst occupies a different phase as compared to the reaction mixture. In homogeneous catalysis, the photocatalyst (in general, soluble molecular catalyst) and oxidation-reduction catalytic sites, all are in the same phase. The common homogeneous photocatalysts include transition-metal complexes as these contain suitable electronic band gaps with proper stability that is requisite for homogeneous photocatalysis [7].

In homogeneous catalysis, a single catalytic entity is capable of speeding up the reaction rate and decreasing reaction time [8]. The area of heterogeneous catalysis has become more and more popular during the past few decades as efficient recovery of expensive catalysts is straightforward. Most of the processes of heterogeneous catalysis involve the application of solid-phase semiconductor catalysts like TiO_2 is extensively utilized for the oxidation and degradation of pollutants. Semiconductors are primary light absorbers. The properties of semiconductors that make them ideal for extensive applications include easy

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