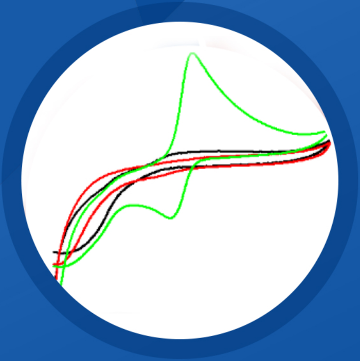
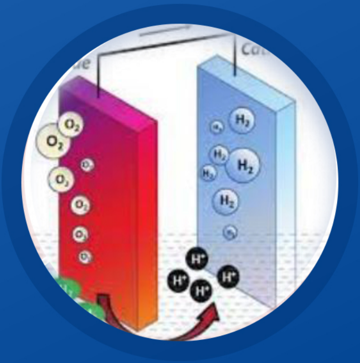
ADVANCED NANOCATALYSIS FOR ORGANIC SYNTHESIS AND ELECTROANALYSIS





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Advanced Nanocatalysis for Organic Synthesis and Electroanalysis

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PREFACE

To design and develop a green, sustainable and economical reaction is one of the major challenges in chemistry. Besides the traditional need for efficient and selective catalytic reactions, recent chemical synthesis strives for designing new and efficient catalytic systems with high rates of catalyst recovery. The initial papers in the field of nanocatalysis were published as early as 1941 on palladium and platinum nanoparticles as catalyst, which was prepared by reduction of the metal salts. This research of Rampino was evocative of the work of Prof. Paul Sabatier (Chemistry Nobel Prize in 1912), who discovered catalyzed hydrogenation using finely divided nickel particles prepared upon reduction of nickel oxide or hydroxide. Then, in 1987, Haruta *et al.* made another breakthrough in the field of nanocatalysis by reporting the catalytic activity of gold nanoparticles smaller than 5 nm towards oxidation of CO.

Inspired by the above initial discoveries of nanoparticles as catalyst, nanostructured materials have attracted the chemical community and are now recognized as efficient heterogeneous catalysts for various organic transformations and electroanalytical processes. Efficiency, selectivity and recyclability of nanocatalysts depend on their size, shape, composition and assembly, which further enhance the appeal of well-defined nanostructured materials as green and sustainable heterogeneous catalysts in a wide variety of organic transformations as well as electroanalytical processes. Role of nanocatalyst in organic synthesis and electroanalyses helps control the chemical reactions by varying their shape and size, chemical composition, dimensionality, *etc.* to improve the kinetics of the reaction. Several catalytic sites are explored due to variations in shape, size and composition of nanocatalysts because a specific site shows good selectivity towards a specific reaction pathway.

This book offers an exclusive link between the domains of nanocatalyst and their exploitation in organic syntheses as well as electrochemistry using nanotechnology-based catalysts and electrode structures, respectively. The book is aimed to prepare to deliver a quick and highly compiled knowledge which, in turn, is expected to promote further advances in the field of nanaocatalysis. Also, the book will open up new dimensions for designing novel nanocatalysts for unexplored chemical reactions important for academia and industries both. The topic chosen in the proposed book will be beneficial for a broad range of readers such as graduate, postgraduate, Ph.D. students, faculty members, research & development (R & D) personals, working in these areas as well.

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CHAPTER 1

Principles and Concepts of Nanocatalysis

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Abstract: Catalysis is one of the fundamental principles of the twelve principles of "Green Chemistry". Over the past few years, nanocatalysis has emerged as a growing field of catalysis in the construction, food, medical, pharmaceutical, energy, and water treatment sectors due to its high activity, selectivity, and productivity. Nanoparticles are different from their bulk counterparts and exhibit unique properties as compared to traditional catalysts, for example, simple and cheap approaches of production, good selectivity, high surface to volume ratio, high catalytic activity, ease of recovery, the possibility of being reused, enhanced mixing with reactants, easy separation, and presence of a large number of active sites. The nanoscale size (1nm = 10^{-9} m), shape, and remarkably large surface area to volume ratio impart inimitable properties to nanoparticles. This chapter presents the principles and concepts of nanocatalysis and discusses the inimitable structure and catalytic properties of monometallic nanoparticles and bimetallic nanomaterials, magnetic nanoparticles, nanocomposites, carbon-based nanomaterials, and nanophotocatalysts in various organic transformations.

Keywords: Bimetallic NPs, Carbon-based nanomaterials, Green chemistry, Magnetic NPs, Monometallic NPs, Nanocatalysis, Nanocomposites, Nanophotocatalysts.

INTRODUCTION

Catalysis

Humans are reliant on endless value-added chemicals and the associated chemical transformations to obtain advanced intermediates, pharmaceuticals, polymers, agrochemicals, natural products, fine chemicals, and bioactive molecules in drug and chemical industries. Among various pharmaceutical industries, the drug industry is the main industry to achieve a quality lifestyle since it generates value-

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added chemicals for battling infections/diseases. The significance of the drug industry is also highlighted in the "Covid-19" (Coronavirus Disease 2019) pandemic. The pharmaceutical and other sectors are generally dependent on chemical reactions in which a lot of chemical substances, catalyst/photocatalysts, energy (such as heat), and solvents are utilized, delivering an enormous amount of chemical waste and by-products [1 - 4]. Therefore, the innovative period of chemistry (especially medical chemistry) is shifting towards the path of inventive greener/sustainable technologies for the production of value-added chemicals, which essentially concentrate on environmental aspects [5 - 7]. "Catalysis" is a key technology and is located at the midpoint of numerous chemical transformations, which from a green and sustainable chemistry viewpoint need catalysts to accelerate transformations for maximum manufacturing chemical transformations [8, 9].

Green and Sustainable Catalysis

Chemical transformation can be designed in greener and eco-friendly ways by the development and attentive utilization of catalysts. Catalysts fulfill green chemistry aims in various languages of atom economy, elevated yields, low energy requirements, and ease of separation due to increased selectivity at minimal waste. As identified to all, the definite catalytic sites on the surface of catalysts perform a crucial character to regulate various chemical transformations. Traditionally, catalysts can be divided into two main types - heterogeneous and homogeneous [10 - 12]. Transition metals are usually utilised as homogeneous and heterogeneous catalysts in a majority of chemical reactions as they have variable oxidation states and good adsorption properties. On the one hand, heterogeneous catalysts are easy to recover, however, they have a few downsides. For example, in harsh environments, they need to be effective, the mass transportation issues, the susceptibility of metal leaching, and the reaction rate aredelimited because of their inadequate exterior area. In contrast, homogeneous catalysts with good solubility in reaction media are identified for their advanced catalytic activity and selectivity, but the isolation of costly metal-containing catalysts from the final compounds remains a central problem across chemical industries [13].

Disadvantages in homogeneous/heterogeneous catalysts demand innovative catalytic materials for disabling the boundaries related to both types. Due to their large surface area, NPs have originated to link "homogeneous (low loadings and good selectivity) and heterogeneous (recovery and recyclability) catalysis" processes. Both catalysis processes have specific benefits and undesirable properties (Fig. **1**). Nanocatalysts go beyond the boundaries of homogeneous and heterogeneous catalysts through nano-effects, which are completely unwritten yet.

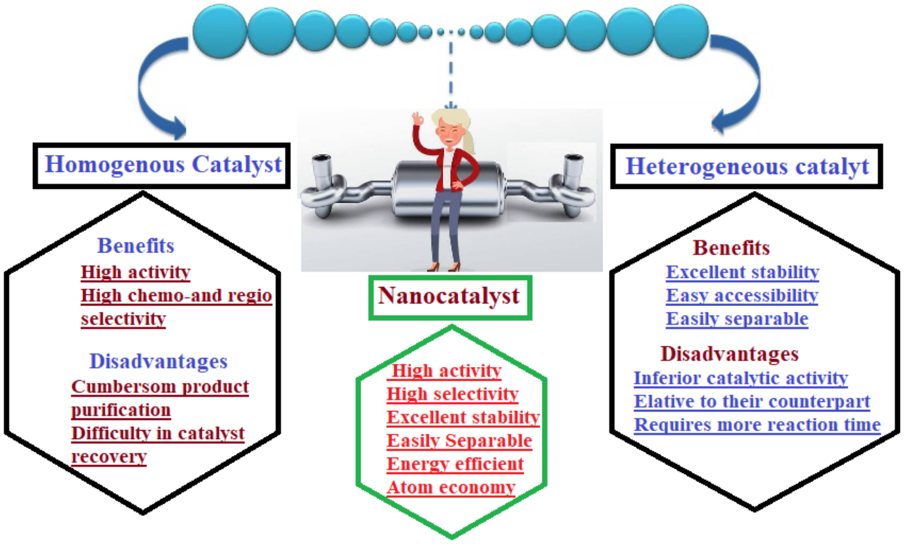

Fig. (1). Relative efficacy of homogeneous, heterogeneous, and nanocatalyst.

Nanocatalysis

In the growing field of catalysis, catalytic reactions and nanocatalysis have been intimately connected for a long time period and modern developments have made it far more stimulating. To advance eco-friendly chemical reactions having the goals of green chemistry, "Nanocatalysis" is an innovative Green Chemistry era [14, 15]. The prefix "nano" is taken from the Greek word 'Nanos' which means 'dwarf" and alludes to things of one billionth in size. Owing to the inimitable properties, "Nanomaterials" are considered to be the building blocks of the next generations of catalysis, especially because they meet the goals of green chemistry [16, 17].

Nanotechnology is the application of science to control matter at the atomic or molecular level. The words 'nanoscale' or 'nanostructured' substances (sub-micron moieties) are any solid that has a nanometer dimension ($1\text{nm} = 10^{-9}$ m). Unquestionably, the utilization of nanometer-sized solid particles in catalysis are eye-catching choices to traditional catalysts, for the reason that when the size of the "Nanomaterials" is reduced to a molecular level, the large surface-to-volume ratio is ominously improved and defects are introduced into these materials. NPS are identified to be much more efficient as a large part of active catalytic sites are provided to the reacting molecules, thus, raising its productivity manifold as compared to traditional catalysts.

CHAPTER 2

Nanocatalytic Carbon-Carbon Coupling Reactions

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Abstract: This chapter provides a brief overview of the general aspects and recent advances in the chemistry of carbon-carbon coupling reactions. Nanoclusters, their synthesis, stability, and catalytic performance in various C-C bond formation reactions are discussed. The interest in nanoparticles originates from the nanoscale size, shape, and large surface area to volume ratio, imparting exceptional surface properties compared to bulk catalysts. In recent years, many detailed investigations on nanocatalytic carbon-carbon coupling reactions have been documented. We tried to summarize some of the significant achievements in this flourishing field. Most of the nanocatalysts outlined in this chapter allow convenient and green synthetic pathways for the construction of carbon-carbon bonds.

Keywords: Bi-metallic, Bio-genic nanoparticles, Cross-coupling, Homocoupling, Multi-metallic, Nanocatalysis, Supported nanoparticles.

INTRODUCTION

The formation of carbon-carbon (C-C) bonds continues to be the vital synthetic paradigm in organic chemistry since its beginning in the 19th century [1]. "Coupling reaction," which conventionally referred to the transition metal-catalyzed reaction of an unsaturated organic halide electrophile with an organometallic nucleophile [2], is a comprehensive term today encompassing many advanced synthetic transformations. The very idea of $C(sp^2)$-$C(sp^2)$ coupling reactions emerged from the eminent observations in the 1940s by studying the unique ability of simple transition-metal salts to activate various organic compounds and allowing the formation of new bonds through homocoupling of Grignard reagents [3]; hence, marking the foundation of a new era in shaping chemical synthesis. Since then, C-C coupling reactions have been one of the vastly researched domains of study for organic chemists.

The initial phase of development witnessed the utility of copper (Cu) as the sole metal for aryl-aryl bond formation, giving rise to the famous Cu mediated Glaser

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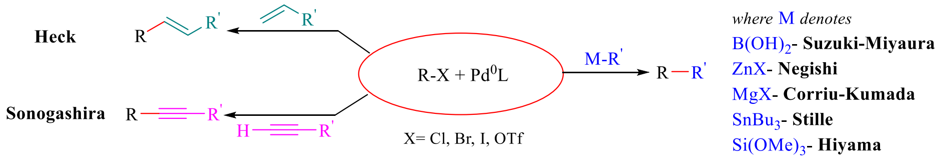
[4], Ullman homo-coupling [5], and Cadiot-Chodkiewicz [6] cross-coupling reactions. However, the introduction of palladium (Pd) catalysis revolutionized the field of organic synthesis. The chemistry of Pd in catalytic Wacker-type processes [7] inspired the researchers to exploit its activity in the reaction of carbon nucleophiles to construct C-C bonds. Accordingly, the classical cross-coupling reactions using olefin (Heck) [8], terminal alkyne (Sonogashira) [9], organozinc (Negishi) [10], organoboron (Suzuki-Miyaura) [11], organotin (Stille) [12], organosilicon (Hiyama) [13] or organomagnesium (Kumada-Corriu) [14] nucleophiles were devised (Scheme **1**). Apart from its phenomenal achievement in the construction of C-C bond, Pd catalysis gained popularity due to the mild conditions associated with the reactions along with its commendable tolerance towards different functional groups, high reactivity, and the diversity of organometallic reagents utilized in these reactions. These astonishing advances in the field of transition-metal catalyzed cross-coupling reaction [15, 16] have presented an ample number of synthetic alternatives for the construction of complex carbon frameworks of diversified interests and are conveniently extendable to large scale synthesis for the application in natural products, pharmaceuticals, material, and industrial processes and nanotechnology [17, 18].



Scheme (1). Pd catalyzed common cross-coupling reactions.

The past decades have seen numerous developments in homogeneous and heterogeneous metal-catalyzed cross-coupling strategies in organic as well as aqueous media [19]. However, the issue of recovery and reusability limits the practical utility of soluble homogeneous catalyst species. Those issues with homogeneous catalysis were addressed by their heterogenization on solid supports with high surface area [20]. While a majority of the solid-supported catalysts are known to follow heterogeneous pathways [21], yet under specific conditions, they are found to liberate highly active nanoparticle species into the reaction media [22], thereby acting as a pre-catalyst and enhancing the overall selectivity and performance in C-C coupling reactions. Hence, driving a necessary shift from conventional catalysis to nano-catalysis in the quest for an improved and advanced catalytic pathway [23]. The chemistry of metal particles at the nanoscale level (1-100 nm) has materialized as an interesting and promising field with increasing applications in industrial and chemical synthesis [24]. Owing to their properties between homogeneous and heterogeneous, these species have attracted great attention for the time being, and recently, much of their endeavors have been realised on carbon-carbon coupling reactions [25, 26].

Morphology Controlled Nanostructures for C-C Coupling Reactions

The concept behind the outstanding catalytic performance of nanocatalysts can be comprehended by accounting for the fundamental material properties of nanostructures on catalysis. The appropriate tunning of size, shape, and morphology of nanocatalyst allows the rational design of nanomaterials by a specific catalytic application [27]. Such catalytic dependence on the shape of nanomaterials has been significantly observed in C-C coupling reactions.

El-Sayed and co-workers prepared Pt nanoparticles (NPs) of different shapes namely, spherical, cubic, and tetrahedral as observed in Transmission electron microscopy (TEM) images, using the hydrogen reduction method [28]. When testing their catalytic activity in Suzuki cross-coupling reactions between iodobenzene and phenylboronic acid, they found that while moving from nearly spherical to cubic to tetrahedral Pt NPs, there is a surprising increase in their catalytic performance [29]. The tetrahedral NPs proved to be the most catalytically active followed by the spherical NPs while the cubic NPs showed the least catalytic activity with the highest activation energy. It was observed that tetrahedral Pt NPs can successfully catalyze the Suzuki reaction forming biphenyl, but itself transforms the shape from tetrahedral to spherical due to the high reaction temperature. When the recovered NPs are employed to catalyze the second cycle of the Suzuki reaction, a sharp reduction in the catalytic activity is observed. The reason behind such a difference in catalytic behavior is due to the difference in the number of catalytically active surface atoms on the nanomaterials. Tetrahedral NPs which are composed of facets have a large fraction of surface atoms on edges and corners compared to the cubic NPs, hence they are catalytically more active.

In a similar stroke, Zhang and co-workers [30] demonstrated a one-pot shape-selective synthesis of Pd-Rh nanocrystals of different shapes and morphologies namely hollow nanocubes (NC), nanoicosahedrons (NI), and nanotruncated octahedrons (NTO). The catalytic performance of the nanohybrids was evaluated in Suzuki cross-coupling reaction between aryl halides and phenylboronic acids. It was observed that Pd-Rh hollow NCs displayed the highest reactivity in comparison to other Pd-based solid nanocrystals, including Pd−Rh NIs, Pd−Rh NTOs, Pd−Rh NCs, Pd NCs, and commercial Pd/C, with both iodo and bromobenzene as the reactant (Fig. **1a**). The catalytic activities were also checked with Pd-Rh hollow NCs of varying Pd/Rh ratios, such as $Pd_{0.22}Rh_{0.78}$, $Pd_{0.32}Rh_{0.68}$, $Pd_{0.49}Rh_{0.51,}$ and $Pd_{0.68}Rh_{0.32,}$ however, no direct correlation was found (Fig. **1b**).

CHAPTER 3

Nanocatalysis in Aryl Carbon-Hetero Atom Coupling Reactions: Special Emphasis on Copper Free Protocols

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Abstract: Nanomaterials have emerged as a keystone of nanoscience and nanotechnology that cover a broad area in the field of research and development worldwide. A set of substances having at least one dimension less than around 100 nanometres are termed nanoscale materials. At such a range, these nanomaterials possess some unique optical, electrical, and magnetic properties; they have substantial impacts in electronics, medicine as well as various organic synthesis. A wide variety of nanoparticles, such as carbon-based/polymer-based/lipid-based/ceramic/metal-based, *etc*., are found depending on composition, size, chemical and physical properties, and morphology of nanoparticles. Metal nanoparticles have received special attraction for organic synthesis nowadays. Due to their stronger ability to transfer electrons, large surface area to volume ratio, easy recovery, and recyclability, metal nanoparticles have become an attractive alternative for both homogenous as well as heterogeneous catalysis in synthetic organic chemistry. The aryl-heteroatom bond formation in organic synthesis is very important as the molecules with the generality of this bond are of pharmaceutical, chemical, and biological interest. Synthesizing such molecules with metal nanoparticles has the advantage of high atom economy, easy recyclability, and reusability of the catalyst, which is far better than the conventional procedures that demand toxic ligands and tedious procedures. The use of copper-free metal nanoparticles for the synthesis of such moieties is a greener approach as copper has a toxic mechanism of action.

Keywords: Catalysis, Copper Free Protocols, Metal-Based Nanoparticles, N-arylation, O-arylation, S-arylation.

INTRODUCTION

The nature around us involves numerous spontaneous chemical processes such as photosynthesis, degradation, oxidation-reduction, *etc*. The presence of sunlight, air, moisture, and some other natural factors make these processes feasible.

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Perhaps, these processes mainly regulate the lives on this planet. However, these natural processes are not enough to standardize the life of every human being along with the other living organisms. Therefore, we are greatly dependent on synthetic procedures for mass production of most of the necessary commodities like medicines, groceries, fibres, *etc*. To enhance the productivities of the synthetic procedures, the catalyst must be used; in other words, catalysts play a vital role in the process of standardisation. Catalysts provide an alternative pathway for the reaction to occur easily by decreasing the activation energy. They have done it by exposing their surfaces, by physical interactions with the starting materials, by changing their physiologies, or by protecting the reactants in particular shapes and geometries. Though there exist different catalytic processes like homogenous, heterogeneous, photocatalytic, *etc*., we will only discuss nanocatalysis of aryl carbon hetero bond forming reaction. Moreover, as per literature, the construction of carbon-heteroatom bond is mostly accompanied by transition metal catalysts, among which copper assists as the leading domain. In this context, quite comprehensive literature is available on copper both in bulk as well as nano states [1]. As there is always a toxicity issue attached with copper, in this chapter, we have tried to cover the literature other than copper to highlight the cheap, less or nontoxic copper-free protocol to support environment, as well as green chemistry in the construction of carbon hetero atom bond.

NANOCATALYSIS: AN INTRODUCTORY OVERVIEW

The first reports published on nanocatalysis were in early 1941 based on poly(vinyl) alcohol-protected palladium and platinum nanoparticles (NPs) catalyzed hydrogenation reaction. The nanoparticles were prepared by the reduction of the metal salts by H_2 [2]. This work was very significantly inspired by the work of Paul Sabatier, which was a hydrogenation reaction catalysed by finely divided nickel particles prepared through the reduction of NiO_2 or $Ni(OH)_2$ by H_2.

Nanocatalysis revolutionized the chemical procedures for the synthesis of active molecular scaffolds in a far better way compared to the traditional procedures. The nanomaterial-based catalysts are heterogeneous type catalysts that are finely divided into smaller pieces with diameters between 1 and 100 nanometres (nm) [3]. As the particles' size decreases, more surface areas are exposed, which increases the catalytic activity. Moreover, nanoparticles can easily be separated and recycled [4].

The variety in shapes and geometry of the nanoparticles makes them a suitable partner for interaction with the starting reagents, which play a very significant factor in the enhancement of their catalytic activity. The nanocatalyst mainly combines the advantages of both homogeneous and heterogeneous catalysts and, therefore, can provide better selectivity, prominent efficiency, good to high stability, and easy recovery or recyclability. Moreover, specific reactivity can also be anticipated for nanoparticles that cannot be achieved with regular, bulk materials. From this point of view, since the 1990s, nanocatalysis has undoubtedly emerged as a vast domain that offers a wide range of properties that meet the demanding conditions for catalyst improvement [5].

Arylation Reaction

In the context of aryl carbon heteroatom bond-forming reaction, the arylation reactions play a vital role in demanding a better choice for its construction. Among all the arylation reactions, N-arylation, O-arylation, and S-arylation are common because the products obtained *via* these reactions possess a variety of important properties. For instance, N-Arylindoles are very much effective as antiestrogen, analgesic, antiallergic as well as effective against HIV-1 [6]. Similarly, diaryl ethers, which are O-arylation products, are present as an essential part of most of the natural and synthetic compounds having medicinal properties such as antibacterial, antibiotic, antifungal, antitumor, *etc*. [7]. Similar to that, S-arylated products also find tremendous applications in pharmaceutical industries as some of important drug molecules such as butoconazole (antifungal), Nelfinavir (anti HIV), Axitinib (anticancer) contain the aryl carbon sulphur bond in their core structures [8]. Some of the representative moieties are given in Fig. (**1**). Therefore, we have chosen this particular reaction for our discussion.

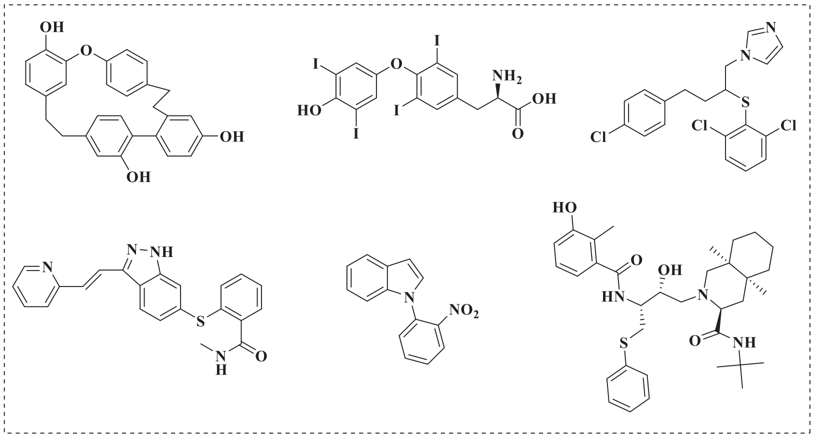

Fig. (1). Some biologically active aryl carbon hetero atom bond containing molecules.

CHAPTER 4

Organic Carbon-Heteroatom Cross-Coupling Reactions Mediated by Supported Transition Metal-Based Catalysts

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Abstract: Organic cross-coupling reactions have been broadly utilized in the synthesis of various organic products and valuable compounds. It is considered the backbone for the synthesis of various medicinally significant compounds. Although numerous organic compounds are made out of C-C bonds, however, the presence of heteroatoms, like nitrogen, oxygen and sulfur, makes them utilitarian. Conductive polymers and drugs often contain amine C-N bonds, and practically, the majority of natural products contain ether, ketone, or ester C-O bonds. Heterocyclic compounds containing C-N, C-O, or C-S bonds in the ring structure are found in all applications of chemistry. As a result of the developing significance of these cross-coupling reactions, the advancement of new extemporized strategies for the synthesis of such items has become the most elevated need for some researchers. Researchers are zeroing in on the advancement of green synthetic methods for the synthesis of such compounds. Catalysis is steadily overwhelming in the field of synthesis because of the expanding capacity to plan new materials with improved synergist exhibitions. Catalysis is proclaimed as a more up-to-date process that shows stability, durability, higher activity, and cost *via*bility analysis. High-yielding cross-coupling reactions using supported catalysts are also reported, resulting in the development of a large number of very effective catalysts for organic cross cross-coupling processes.. Heterogeneous catalysis has the advantage of easy separation and compared to homogeneous catalysis, product isolation requires less amount of the solvent. However, sometimes there may be a compromise in the selectivity process. This chapter contains a detailed discussion on different carbon-heteroatom cross-coupling reactions mediated by supported transition metal-based catalysts. The scope of these cross-coupling reactions in the pharmaceutical and industrial sectors has been investigated. Exceptional methodologies and significant advances accomplished in the field of carbon-heteroatom cross-coupling reactions have been talked about.

Keywords: Cross-coupling reaction, Green methodology, Heterogeneous catalyst, Pharmaceutical, Transition metals.

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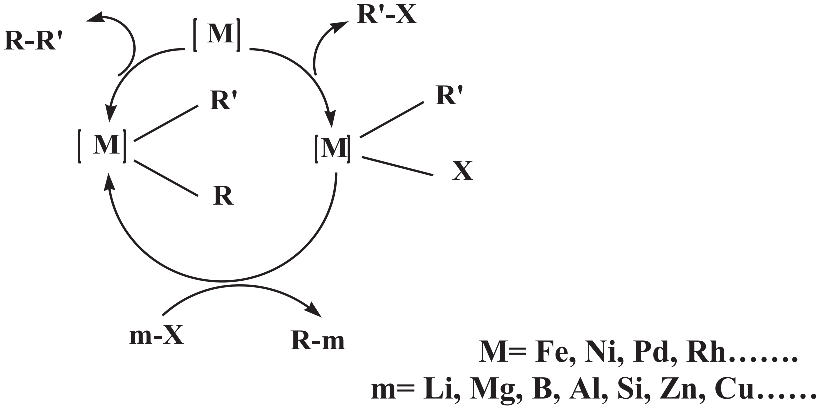
INTRODUCTION

Cross-coupling reaction involves a combination of an organometallic reagent (that generally contain a main group metal atom) with an organic electrophile in the presence of metal catalysts (group 8-10 metals) to accomplish a C–H, C–N, C–O, C–C, C–S, C–P, or C–M bond formation [1]. This was coined in early 1970s by Kumada, Kochi, Corriu, *etc*. and since then, many organometallic reagents have been developed which even revolutionized the field of organic cross coupling reactions. Examples of successful organometallic catalysts include many organoboron, organotin, organozinc, or organosilicon compounds. Various types of electrophiles and metal complexes have been successfully employed in these types of reactions, resulting in a plethora of synthetic methods for molecular assemblies [2]. Because of their milder reaction conditions and unique reactivity, a useful synthetic alternative compared to the conventional methods of synthesis has been provided to the researchers by the cross-coupling reactions [3]. Scheme **1** represents a general catalytic cycle for cross-coupling reactions.



Scheme (1). General catalytic cycle for cross-coupling reactions [4].

The reaction involves the reductive elimination of the organic substituents R and R' on a metal complex. The intermediate MR(R') is generally formed in a step two-step process. In the first step, oxidative addition of the organic halide (RX) to M gives MR(X). Subsequently, the second partner undergoes transmetallation with a source of R'. The final step is reductive elimination of the two coupling fragments to regenerate the catalyst and produce the organic product [5].

In cross-coupling reactions, two dissimilar chemical species are joined together to afford a single product. Some notable examples of cross-coupling reactions include:

- The Grignard reaction [6].
- Heck reaction [7].
- Sonogashira cross-coupling [8].
- Suzuki coupling [9].
- The Buchwald-Hartwig reaction [10].
- Kumada coupling reaction [11].

The function of many organometallic compounds is often derived from the presence of heteroatoms, such as nitrogen, oxygen, and sulfur, which are held by C–heteroatom bonds [12]. Drugs and conductive polymers frequently contain amine C–N bonds, and practically all regular items contain ether, ketone, or ester C–O bonds [13]. Heterocyclic mixtures containing C–N, C–O, or C–S bonds present in the ring structure, are found in different fields of chemistry [14]. In addition, valuable intermediates in blend frequently contain C–B or C–Si bonds that are subsequently changed over into C–C, C–O, or C–N bonds in the last products [15].

The primary focus of the chapter is mainly on cross-coupling reactions involving C-N, C-O, and C-S bond formation reactions supported by transition metal-based catalyst.

C–N BOND-FORMING CROSS-COUPLING REACTIONS

Because of their interesting and diverse biological activities, nitrogen-containing compounds often find important implications in many different fields and also as a synthetic precursor [16]. The construction of the C–N bonds of aromatic compounds is particularly important and proved to be challenging to medicinal chemists due to the involvement of harsh reaction conditions or the use of expensive catalysts in many cases [17]. Recently, some significant achievements have been made in C–N coupling reactions using metal complexes with new ligands under mild conditions in a cost-effective manner [18].

Herein, we have selected some prime literature reports for an elaborate discussion on the scope of C-N bond-forming reactions.

Copper (Cu)-Catalysed C–N Bond Formation

In recent years, considerable advancements have been achieved in C–N bond formation using various copper salts [19]. These reactions utilize a catalytic amount of copper in the presence of various ligands [20]. Some recent and interesting reports where various copper salts were used for C–N bond formation have been discussed in this section.

CHAPTER 5

Oxidation Reactions Using Nanomaterials as Heterogeneous Catalyst

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Abstract: Oxidation reactions play a pivotal role in chemical synthesis. Its wide range of industrial applications and processing, however, make use of corrosive chemicals and harsh reaction conditions, which create threats to the ecosystem, environment, and public health. Also, the traditional homogeneous catalysts used for this purpose get easily deactivated. Heterogeneous catalysts with various supports have been developed to achieve more environmentally benign conditions as well as to defeat other disadvantages of homogeneous catalysts. Nanomaterials, due to their large surface available to reactants and ease of separation, show promising applications in heterogeneous catalysis and lead towards a greener way of synthesis. The current chapter enlists the applications of nanocatalysts in the oxidation reactions of various organic molecules.

Keywords: Composite/hybrid nanoparticles, Heterogeneous catalyst, Metal-oxide, Nanomaterials, Oxidation.

INTRODUCTION

Oxidation reactions, being the heart of chemical synthesis, cover a large part of the area in the field of production of many industrially important compounds [1]. The oxidation process carries around 30% of the total production in chemical industries. For example, selective oxidation of alcohols and olefins produces epoxides, aldehydes, ketones, and carboxylic acids, which have significant applications and mechanistic interests in modern organic synthesis [2]. Acetophenone and 1-phenylethanol, which are one of the oxidation products of ethylbenzene, are used in the synthesis of a wide variety of drugs [3, 4]. Earlier, oxidation of organic compounds was done by adding stoichiometric amounts of strong oxidants such as permanganates, selenium oxide (SeO_2), chromium (IV) reagents, ruthenium (VIII) oxide, nitric acid, oxygen, and hydrogen peroxide, *etc*., however, the traditional homogeneous catalysts are not very useful as their

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recirculation is a fussy and time-consuming process [5]. Moreover, most of these chemicals are corrosive, toxic, unstable to the environment, and produce many undesired side products which result in less atom economy and create heavy metal waste [6].

Heterogeneous catalysis, on the other hand, in which reactants are in a different phase from the catalyst, solves most of the drawbacks of homogeneous catalysts. In most cases, the majority of heterogeneous catalysts are solid and reactants are either gas or liquid [7]. The new era of chemistry is more inclined towards finding new innovative techniques that concern the environment, safety, and human health [8 - 12]. Therefore, chemical synthesis and reactions are being explored based on eco-friendly concepts without affecting the quantity of products and quality of the reaction. Supported metal catalysts are one of the most widely used catalysts in various industrially important reactions which include oxidation, hydrogenation, dehydrogenation, Fischer-Tropsch, and ammonia synthesis [13]. Over the last decade, a considerable effort has been devoted to the field of nanoscience and nanotechnology due to its many specific characteristics especially high surface to volume ratio [14 - 18]. Nanomaterials, due to their special properties and novel characteristics in comparison to single-molecule and bulk materials, have gained tremendous attention since the last decade, especially in the field of catalysis [1]. They are highly selective, reactive, and stable; hence, extensively used in many oxidation reactions in recent times. The purpose of the chapter is to provide a brief overview of recent developments in oxidation reactions using various types of nanomaterials as heterogeneous catalysts.

Fig. (**1**) depicts the generalized representation of nanomaterials as a heterogeneous catalyst for different oxidation reactions.

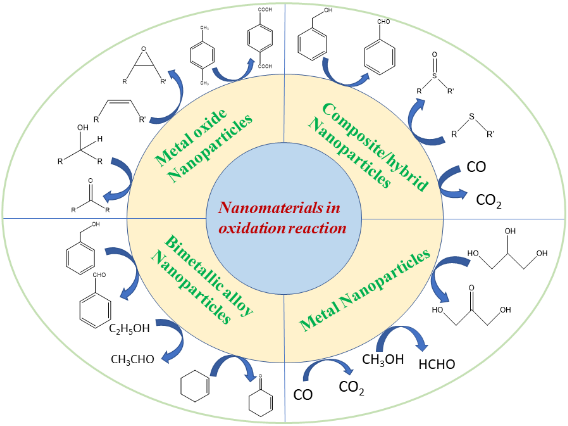

Fig. (1). Various types of nanomaterials as heterogeneous catalysts for oxidation reactions.

METAL OXIDE NANOPARTICLES IN THE OXIDATION REACTION

The application of metal oxide nanoparticles (NPs) in the field of catalysis has become a substantial research area during the last decades. Transition metal oxide nanoparticles have been extensively used as a catalyst for the oxidation of alcohols, alkenes, sulfides, and olefins towards the synthesis of various organic compounds. Traditionally, permanganate and dichromate were used as oxidizing agents, but they are costly, toxic, and produce a large quantity of waste [19 - 21]. A considerable effort has been devoted to the field of nanoscience and nanotechnology to reduce the disadvantages of traditional methods making the use of metal and metal oxide nanoparticles [22, 23]. Molybdenum oxide (MoO_x), amongst the transition metal oxides, has drawn a significant research interest. MoO_2 NPs can be used as an efficient catalyst in the epoxidation of olefins [24]. Also, it has been utilized in cracking and reforming hydrocarbon compounds as a catalyst [25, 26]. In this regard, to enhance the overall efficiency of the catalyst, the oxide nanoparticles were structurally or electronically modified by doping them with transition metals. As shown in Fig. (**2a**), hydrothermally synthesized Fe doped MoO_2 for epoxidation of olefins was developed [27]. Generally, most of the molybdenum (VI) complexes having organic ligands act as homogeneous catalysts [28, 29], besides a few other reports [30]. Partial oxidation of liquid hydrocarbons e.g., n-dodecane at 850 ºC and 1 atm by MoO_2 NPs (Fig. **2b, c**), has been developed using molybdenum trioxide as starting material [31]. Another interesting piece of work was carried out by Shokouhimehr and co-workers. They developed magnetically separable MoO_2 NPs which show excellent performance for epoxidation reaction in carbon tetrachloride (CCl_4) [32].

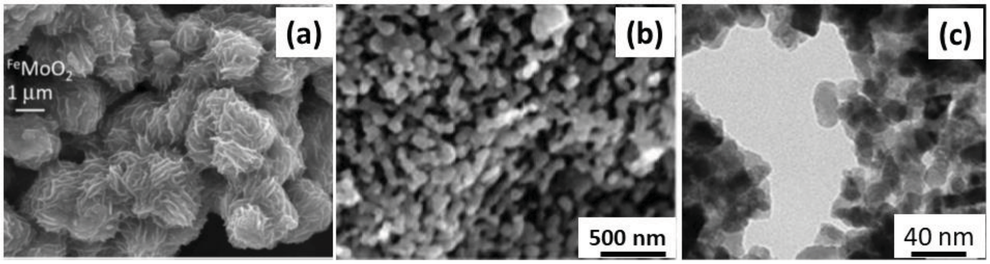

Fig. (2). SEM image of **(a)** hydrothermally synthesized Fe doped MoO_2. Reprinted with permission from ref [27]. Copyright 2016 Springer. **(b)** SEM, **(c)** TEM images of MoO_2 NPs used in partial oxidation of liquid hydrocarbons Reprinted with permission from ref [31]. Copyright 2010 American Institute of Aeronautics and Astronautics.

TiO_2 NPs, a well-known photocatalyst has also attracted worldwide interest due to their potential use in solar cell, photodegradation of inorganic and organic wastes *etc*. [33 - 35]. Selective photocatalytic oxidation of benzyl alcohol and its derivatives to their carbonyl products with 99% selectivity by TiO_2 NPs under

CHAPTER 6

Nanocatalysis for Reduction/Hydrogenation Reactions

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Abstract: Heterogeneous nanocatalyst demonstrate excellent catalytic activity for the hydrogenation/reduction of nitro-aromatics, carbonyls, alkenes/alkynes in the presence of different reductants such as $NaBH_4$ and H_2 using various solvents such as ethanol, methanol, dioxane, THF, and water, as green solvents. Earth-abundant coordinating elements such as Pd, Pt, Fe, Cu, Co, Ag, Au, and Ni, elementary synthesis, short time reactions, high selectivity, mild reaction conditions, and reusability of nanocatalyst for at least 4-5 cycles without any loss in catalytic activity, are some priorities for the hydrogenation reactions using nanocatalyst.

Keywords: Alkenes, Alkynes, Bimetallic, Carbonyls, Hydrogenation, Nano-catalyst, Nitro aromatics, Reducing agents, Reduction.

INTRODUCTION

Hydrogenation and reduction of compounds are important chemical reactions in organic synthesis as well as industries. The use of heterogeneous metal catalysts has been the most versatile and dynamic process for these reactions. It was about 100 years ago when Paul Sabatier hydrogenated alkenes efficiently over Ni metal catalysts [1]. Since then, the use of these solid catalysts has multiplied thousand times. The heterogeneous metal catalysis owns a broad scope, besides Ni, Pd, and Pt, we now have several cheap metals to catalyse the hydrogen-ation/reduction reactions. A wide variety of multifunctional molecules are reduced by this method, and numerous value-added products can be obtained in high yield in a short time, with chemo and/or regioselective control.

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Recently, the emphasis is on the development of sustainable, eco-friendly methods, utilizing metallic nanoparticles as a catalyst in these reactions, which can curb chemical waste generation with more safety, recyclability, and high-atom efficiency [2]. Moreover, the utility of monometallic catalysts has been surpassed by bimetallic and multimetallic nanocatalysts. The addition of another metal might induce surface-electronic structure reconfiguration, which generates diverse interaction between hydrogen and reactants in turnover cycles, leading to high catalytic activity [3].

In this chapter, we have featured numerous methods for hydrogenation/ reduction reactions using several reusable nanocatalysts [4, 5]. The simplest method of preparation of nanocatalyst follows the scheme, where metal precursors are mixed with polymer stabilizers and reduced by using chemical agents such as H_2, $NaBH_{4,}$ glycerol, amines, *etc*., to achieve different surface morphologies [6]. The novel structured mono, bi, or mixed nanoparticles, mostly obtained from Pt, Ru, Au, Pd, Fe, Cu, Co, and Ag, are mainly employed for reduction and hydrogenation catalysis of olefins, nitroaromatics, and carbonyls [7].

Material scientists are continuously designing different types of routes to obtain different nanoparticles with distinguishing specifications. Novel structured catalysts, such as nanometal clusters, particles with uniform but particular designs (*e.g*., octahedral, tetrahedral, cubic, rhombic), as well as bimetallic or multimetallic nanoparticles with disciplined structures (*e.g*., alloy, core–-shell, cluster-in-cluster, layer-by-layer),core-shell are generally found with improved catalytic activities as compared to traditional catalysts [3]. Different shapes of nanocatalysts can be obtained with different types of polymer and control over the rate of kinetic reduction of metal in the solvent [8].

REDUCTION/ HYDROGENATION OF NITRO COMPOUNDS

The reduction of nitro compounds is the most simplistic route to produce amino derivatives, which are important intermediates for producing nitrogen compounds, useful in pharmaceuticals, agriculture, polymers, dyes, cosmetic industries, *etc*. Some nitroaromatics are a serious threat to the environment. However, after reduction into amino aryls, they become harmless (Fig. **1**). The previously used catalytic methods had harsh conditions and expensive reagents to obtain products in high yield. The modern use of nano catalytic systems has minimized the use of catalyst, is eco-friendly with low cost and providing excellent yield and a high rate of conversion. We have tabulated Table **1**, the efficient reduction of nitro compounds to anilines using a variety of nanocatalysts. These catalysts can be recycled many times with high stability and no leaching up to many cycles. Suitably designing the catalyst structure and their wise selection has been successful in improving the reduction power, sustainability, and recoverability of the nanocatalyst. The use of cheap transition metals as nanocatalysts has enhanced the use of the catalytic system for the reduction of nitro compounds.

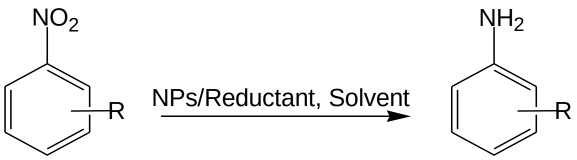

Fig. (1). Reduction of nitro compounds.

Table 1. Reduction/hydrogenation of nitro compounds.

Catalyst	Morphological Features	Solvent	Reductant	Reaction Condition	Yield	Refs.
Cu(0)NP	Metallic copper in the cubic phase.	Alcohols, ethers, and amines as Proton donor	Glycerol	130 °C for 1h 10 mol % of catalyst and 2 eq of KOH	93%	[9]
PdCu@ MWCNT	Face-centered cubic (fcc) 4.78 ± 0.43 nm.	1 ml of water: methanol mixture (7:3),	$NaBH_4$	r.t. 10 min.	99%	[10]
CuNPs	Mean size 10.2 ± 3.0 nm, roundish shape	Glycerol, KOH,	Glycerol	130 °C, 5 h.	99%	[11]
Co/N-SiC				r.t., 1 atm		[12]
Fe-Ni catalyst (Fe-Ag-ATP-CA beads)	Mean size 1.6 nm	Methanol	$NaBH_4$	r.t.	99%	[13]
Pd@MOF-1	Mean size 1–2 nm	Ethanol	H_2	2 h, r.t.	98%	[14]
(Co-DABCO-TPA@C-800)	Mean size from <5 nm to 30 nm.	t-BuOH, THF/H_2O	Aldehyde	40 bar H_2, 120 °C	80%- 90%	[15]
Pd@TPAPOP-1	External Surface Area (164 m^2/g)	EtOH	H_2	r.t.	85%- 95%	[16]
Pd@CTF	Mean size of Pd 5.34 nm	EtOH/ H_2O	NH_4COOH	25 °C	85%- 99%	[17]
Fe_3O_4-MWCNTs@PEI-Ag.	Mean size is 60 nm	Water	$NaBH_4$	70 °C-90 °C	70%-90%	[18]
Fe_3O_4/NH_2/Ru	Diameter 2.1 nm	Ethanol	$NaBH_4$	30 °C, 40 min.	90%	[19]

CHAPTER 7

Recent Trends in Metal Nanoparticles (MNPs) Catalyzed Synthesis of Aza- and Oxa-Heterocycles

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Abstract: Most of the currently marketed and approved drugs possess nitrogen and oxygen-containing heterocycles in their scaffolds. The importance of metal nanoparticles (MNPs) catalyzed synthesis of such aza- and oxa-heterocycles should not be underestimated due to their versatile applications. Previously, we reported the decennary update on MNPs catalyzed synthesis of *N*- and *O*-containing heterocycles reported during 2010-2019. In the present work, attempts have been made to summarize the prospects to highlight those promising MNPs of worthy catalytic potential reported during the year, 2020. The present compilation shall provide the new thought processes to address the unmet synthetic needs for the construction of nitrogen and oxygen-containing heterocyclic scaffolds.

Keywords: Catalysis, Heterocycles, Metal nanoparticles, Nanocatalysis.

INTRODUCTION

The medicinal importance of heterocyclic scaffolds should not be underestimated due to their wide spectrum of biological activities against pathogenic mycobacterial [1 - 7], bacterial [8] fungal [9], and viral strains [10]. Among the United States food and drug administration (USFDA) approved drugs, nitrogen [11] and oxygen [12] containing heterocycles ranked among the predominant heterocycles. Organic synthetic chemistry has been considered as the bottleneck for the transformation of drug discovery through new avenues such as C-C, C-heteroatom bond formation, and C-H activation [13]. To achieve the synthesis of these scaffolds, the enriched medicinal chemists' synthetic armory or toolbox [14] can be easily constructed using the green chemistry protocols such as reaction in water [15], ionic liquids [16 - 18], and nanoparticles (NPs) [19, 20].

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SCOPE AND APPLICATIONS OF NPS IN SYNTHESIS OF HETEROCYCLES

Nowadays, the avenue for the growth of nanotechnology has opened several new vistas in synthetic chemistry, peculiarly in the arena of synthesis of novel biodynamic heterocycles [21]. To catalyze the organic transformations, the catalytic assistance of MNPs has emerged as sustainable alternatives to conventional materials, as robust, high surface-area containing heterogeneous catalysts with the potential of extendable recyclability [22]. MNPs have attained significant importance in green chemistry developments in benign aqueous reaction media for the construction of heterocycles [23]. Despite some potential hazards [24], MNPs still have greater triumph in the field of material chemistry with the positive spirit of versatile reactions to catalyze the synthetic transformations. Plasmodic gold NPs (AuNPs) have also emerged as important NPs in the field of advanced energy, environmental and biomedical applications [25].

Recently, we have reviewed the synthesis of *N*- and *O*-containing heterocyclic scaffolds catalyzed by MNPs for the decade of 2010 to the end of 2019 [26]. In the present work, we have presented the most recent trends of MNPs catalyzed synthesis of aza and oxa-heterocyclic scaffolds reported by several research groups during 2020 (Fig. **1**), which shall impart the inherent intuitions to the readers to design the synthetic strategy of desired heterocyclic scaffolds using NPs in catalytic amount along with the mechanistic insights of MNPs.

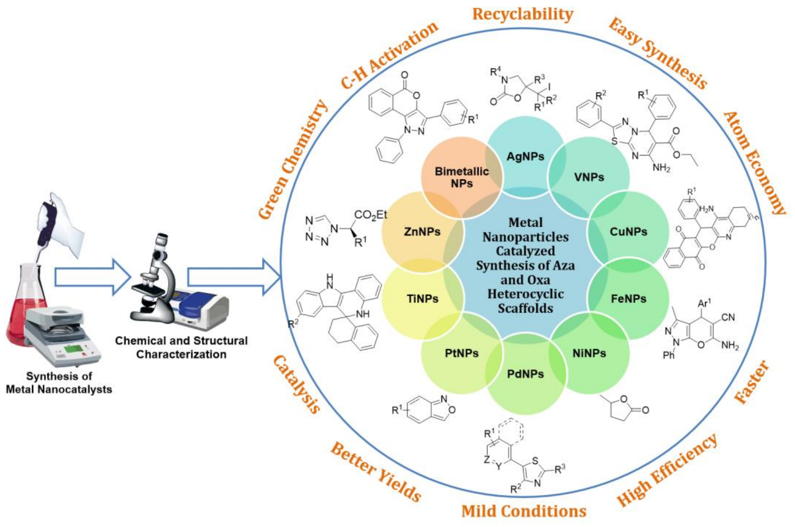
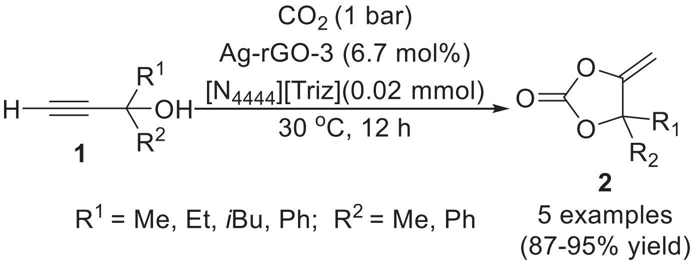


Fig. (1). Schematic representation of NPs with their catalytic applications in the synthesis of aza and oxa heterocycles.

AgNPs Catalyzed Synthesis of Heterocycles

Differently shaped silver nanoparticles (AgNPs) have been recognized in several forms such as cubic, rods, wires, bars, pyramidal, prisms, flower-shaped, and spherical due to their unique morphological properties [27]. Zhang *et al.* have performed carboxylative cyclization of propargylic alcohols (**1**) with CO_2 under atmospheric pressure using silver (0) nanoparticles [(Ag-rGO)] as catalyst and tetra butyl ammonium triazolide $[N_{4444}]$[Triz] (0.02 mmol) at 30 ºC for 12 h (Scheme **1**) [28]. Ag-rGO has been prepared from the reduction of graphene oxide and $AgNO_3$ and has been characterized by X-ray diffraction (XRD), energy-dispersive XRD (EDX), scanning electron microscopy (SEM), transition electron microscopy (TEM), Fourier-transform infrared (FT-IR), and X-ray photoelectron spectroscopy (XPS). Ag-rGO catalysts show good stability and can be reused up to at least five times without obvious activity loss and integrity of the catalysts. An increase in the yield of **2** has been found while increasing the loading of AgNPs on rGO. However, a further increase in catalytic loading of AgNPs leads to severe aggregations of AgNPs.



Scheme (1). Carboxylative cyclization of propargylic alcohols with CO_2 under atmospheric pressure catalyzed by silver (0) NPs (Ag-rGO).

Ghosh *et al.* have performed carbonylative cyclization of allylamines (**3**) to form cyclic carbamates (**4**) using highly reactive organic nanomaterials like AgNPs decorated covalent organic framework (COF) such as Ag@TpTta or Ag@TpPa-1 in the presence of *N*-iodosuccinimide (NIS) at 25 ºC for 16 h without using any solvent (Scheme **2**) [29]. AgNPs architecture COFs (Ag@TpPa-1 and Ag@TpTta) were synthesized by decorating AgNPs on the exterior surfaces of TpPa-1 and TpTta, wherein TpTta has been prepared by the treatment of 4,4′,4″-(1,3,5-triazine-2,4,6-triyl)-trianiline with 1,3,5-triformyl phloroglucinol and TpPa-1 has been synthesized from trifluoroacetic acid and phloroglucinol. The nanoparticles have been characterized using field emission SEM (FE-SEM), high-resolution transition electron microscopy (UHR-TEM), thermogravimetry analysis (TGA), Brunner-Emmett-Teller analysis (BET), 1H and 13C NMR,

CHAPTER 8

Nanomaterials-Based Photocatalytic Reactions

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Abstract: Mounting energy demand and alternatives to its non-renewable sources have led to an interest in the arena of photocatalysis. This field has emerged as a promising greener solution to environmental glitches. Nanomaterials are known to be potential semiconductors because they exhibit unique chemical and physical properties. Henceforth, the search and development of nanomaterial photocatalyst is in full swing and also need of the hour. Nanomaterials such as metal oxides, sulfides, and nitrides have cropped up as efficient photocatalysts to meet up energy demands by catalysing a variety of reactions. In this article, we have discussed different types of nanomaterials and their might to display various photocatalytic reactions.

Keywords: Band gap, Green, Nanomaterials, Photocatalyst, Semiconductor, Sustainable.

INTRODUCTION

The major universal concern at present is environmental pollution and global warming leading to a life-threatening crisis. The scientific community has the huge responsibility of finding and giving greener and sustainable solutions for the factors responsible for this catastrophe. One such remedy to this foreseen tragedy is a technique called photocatalysis which uses light as the clean energy source for catalysing various reactions with the help of a catalyst known as photocatalyst [1]. These photocatalysts are substances that can absorb light and modify the rate of photoreaction without being consumed. Among various substances, semiconducting nanomaterials are known to be good and efficient photocatalysts compared to their bulk counterparts. This change of property of a material in the nanoscale is because of the easy tunability of the bandgap due to the quantum confinement effect [2]. A wide range of nanomaterials has been developed for photocatalysis which includes various metal oxides [3], chalcogenides [4], nitrides, while a few are carbon and metal-organic framework based [5]. Also, several types of bimetallic nanoparticles, both bare and supported [6, 7], are employed as photo-

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catalysts for organic conversions. However, photocatalysis is not just limited to organic conversions, but many processes like dye degradation [8], Cr(VI) reduction [9] for waste water treatment, water splitting reaction for hydrogen and oxygen evolution [10], CO_2 reduction [11], *etc*. are also demonstrating good efficacy and getting tremendous attention in photocatalytic research.

In this chapter, we will discuss the fundamental theories and mechanism of photocatalysis, properties making nanomaterial reliable and excellent photocatalyst, and also an overview of the nano photocatalysts that have been designed and developed so far for this purpose (Fig. **1**).

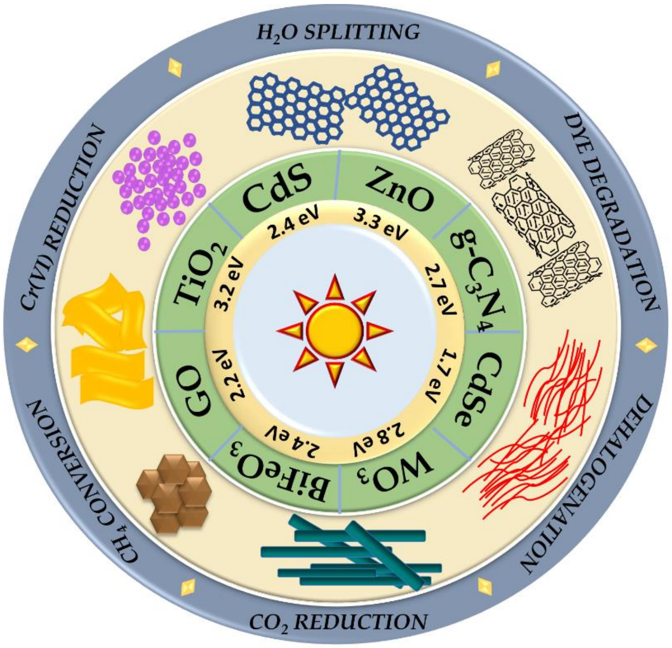

Fig. (1). Schematic representation showing various nanomaterials with different bandgaps used for a variety of photocatalytic reactions.

NANO-PHOTOCATALYST

Photocatalysts are the materials that act as a catalyst for various chemical conversions when light is irradiated on them. As mentioned, this interesting property of photocatalyst is due to its semiconducting property. This is where the role of nanomaterials comes to play. When a bulk substance is reduced to the nanoscale, the energy levels become discrete as a result of which the bandgap of the material increases. All this is feasible because of the confinement of electrons in the nanomaterial which helps in electron transfer between the valence band and conduction band. This fascinating property leads to the conversion of an insulator to a semiconductor. Another property that is crucial for an effective photocatalyst is the possession of a large surface area. More the surface area available, more will be the light absorbed for enhanced photocatalysis. The motive is to inhibit recombination of charge carriers to increase photocatalytic performance [2].

The utmost important entity to focus on while synthesizing a semiconductor photocatalyst is the bandgap. A high bandgap results in absorbing the ultra-violet (UV) light rather than visible light energy and also as observed the majority of the reported photocatalyst ensure the same. UV light comprises only 4% of the solar spectrum compared to visible light with 45%. Moreover, the inherent health hazards of UV exposure are also a matter of concern, and expensive quartz reactors are needed to deal with it.

Nano-photocatalyst can be of varied types concerning their composition, size, bandgap, morphology, and electronic structure which can be tuned according to the need [12]. A plethora of nanomaterials has been synthesized to date to serve as a photocatalyst. Transition metal-based oxides and sulfides like TiO_2, ZnO [13], CuS, ZnS [14], CdS [12]; carbonaceous materials like graphite, reduced graphene oxide (rGO), carbon nanotubes [15]; oxyhalides like BiOX (X = Cl, Br and I) [16]; bimetallic nanoparticles such as AuAg, AuPd, PtAu; and a composite or a hybrid of noble metals [17] with the mentioned compounds serves as potential photocatalyst.

Fundamentals and Mechanism of Photocatalysis

Photocatalysis, in simpler words, is the harvesting of light energy for various chemical conversions. It is a type of advanced oxidation process where an eco-friendly technique based on the formation of reactive oxygen species for pollutant degradation is responsible. Photocatalyst on exposure to light of the desired wavelength generates electron-hole pair. The light energy *i.e.*, photons absorbed by the semiconductor photocatalyst promotes an electron from the valence band (VB) to the conduction band (CB) leaving behind a hole in the former (Fig. **2**). These generated electrons reduce the acceptor molecule and the respective holes oxidise the donor molecule which further produces free radicals. Reactive species with one unpaired electron are very short-lived and therefore readily and effortlessly reacts with many chemical species to initiate the desired secondary reactions which are otherwise arduous to carry out. Parameters like charge recombination rate, visible light absorption, and unsuitable band gap can seldom act as limitations to the photocatalytic process [2, 12, 18].

CHAPTER 9

Multicomponent Reactions Using Nanocatalysts

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Abstract: This chapter intends to deliver a wide variety of multicomponent reactions (MCRs) using nanomaterials as a catalyst to produce value-added chemicals *via* sustainable and environmentally benign protocols. MCRs provide the inherent creation of several bonds in one operation. This chapter deals with the efficacy of nanomaterials for extensive organic reactions ranging from the traditional carbon-heteroatom bond forming reactions to further contemporary transformations. These employed include various varieties such as magnetic nanoparticles (MNPs), core-shell nanoparticles, carbon-based nanocatalyst (CBN), graphene supported nanoparticles and nanocomposite, *etc*. These nanocatalysts could act as a reusable catalyst for the sustainable synthesis of the different heterocyclic compounds. Their intriguing and designable properties and impressive catalytic selectivity open a wide corridor to synthesize diverse heterocycles with maximum molecular complexities. A new era will be highly devoted to achieve skillfullness in the nanoworld with the technological, industrial, and scientific fields.

Keywords: Heterocyclic compounds, Multicomponent reactions, Nanocatalyst.

INTRODUCTION

Multicomponent reactions are a set of prominent processes that thrust for synthetic competence, in which more than two reactions are employed in a reaction to generate a novel compound using a high number of new bond and enormous functionalities [1 - 8] (Fig. **1**). MCRs are idyllically appropriate for the creation of combinatorial libraries inspired from the privileged structures of natural molecules prone to demonstrate biological activity [9 - 13]. Modern synthetic strategies involve organic transformation and conversions in such a logical manner that leads to the building of complex molecular structures [14]. This cascade reaction affords the construction of several bonds during a single operation. MCRs give better economic benefits by producing fewer wastes [15].

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Fundamentally in multicomponent reactions more than two reactants are combined in a single step either sequential (cascade) or simultaneously (domino) without changing the reaction medium or isolating the intermediate.

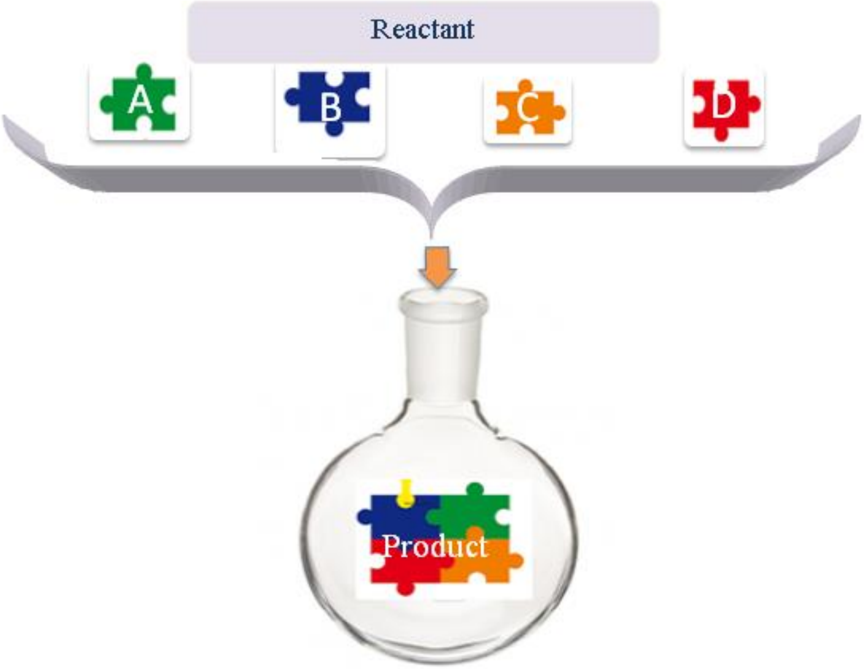

Fig. (1). Synthesis of the product *via* multicomponent reaction.

MCRs are seen as synthetic protocols advancing numerous fields such as organic, natural product synthesis, combinatorial, heterocyclic agro, polymer, pharmaceutical chemistry. It is a powerful tool for the construction of various biologically active heterocyclic compounds such as nucleic acid, plant alkaloids, anthocyanins and flavones as well as in heam, chlorophyll, and some protein, vitamin, hormones contain aromatic heterocyclic system. It has enormous potential for the design of new drugs which are used as an antitumor, antibacterial, anticancer, antirheumatic, and antiasthmatic [16 - 19].

Currently, MCRs are considered to be the foremost in terms of the green approach due to their minimalism, cost-effectiveness, high atom economy and efficiency of bond formation, waste avoidance, effortless implementation, reagents, solvents, energy and time saving as well as avoidance of complex purification method [20, 21]. Over the past year, the main challenges of these reactions are to develop organic transformations that are less contaminating in terms of resource, operational simplicity, clean and green, health, and environmental safety. Since its origin, the field of sustainable chemistry has been exclusively planned to congregate such challenges in synthetic transformations.

Classical chemical transformations for the organic synthesis of MCRs usually involve catalysts (homogeneous and/or heterogeneous), harmful/toxic organic solvents, a nasty working environment like elevated temperature and pressure [22]. Inventive efforts are on finding new methodology based on the specific and suitable catalytic system. Considering the significant features of sustainable chemistry, the utilization of nanomaterials as a catalyst in multicomponent reactions is attracting more attention due to their high efficiency under an eco-friendly reaction environment [23]. Nanoparticles have appeared as green substitutes to conventional substances owing to their unique chemical qualities like catalytic activity, enhanced mixing with reactants, easy separation, and physical properties like photoemission, electrical or heat conductivities and also exhibited novel characteristics of quantum size effects [24 - 26]. Nanocatalyst can be effortlessly recycled during organic transformations for numerous cycles without loss of its reactivity. Compared to regular catalysis, nanocatalysis has assured inimitable rewards [27, 28]. Several types of nanocatalyst are used for the encouragement of multi-component reactions (Fig. **2**).

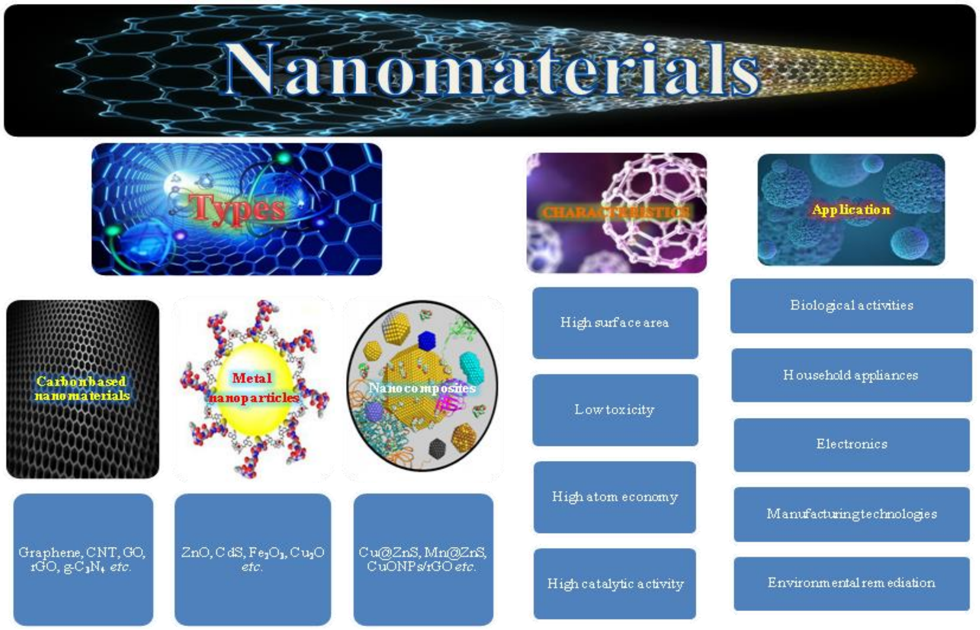

Fig. (2). Types of catalytic nanomaterials and their properties.

CHAPTER 10

Synthesis of Heterocycles Involving Nanomaterials as Heterogeneous Catalysts

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Abstract: Heterocycles are the most significant class of organic compounds comprising a wide range of biological and pharmacological activities. In particular, nitrogen and oxygen heterocycles are the important core structures, frequently found in a large number of natural products and medicinally important molecules. Consequently, great efforts have been made to develop direct methodologies for the synthesis of these heterocycles including nanomaterial-catalyzed approaches. In this chapter, we summarize the important synthetic methodologies for the synthesis of nitrogen and oxygen-containing heterocycles involving nanomaterial catalyzed reactions. The catalytic activity and the advantages of a variety of nanomaterials are described to understand their importance as heterogeneous catalysts towards the synthesis of various heterocyclic compounds.

Keywords: Heterogeneous catalysis, Nanocatalysts, Nanomaterials, Nitrogen heterocycles, Oxygen heterocycles.

INTRODUCTION

Heterocyclic compounds are the largest class of organic compounds that exhibit a variety of interesting pharmacological activities. Among the different classes of heterocycles, nitrogen and oxygen heterocycles are part of various natural products and compounds of biological significance [1]. Consequently, considerable effort has been devoted to the development of synthetic methodologies for these heterocycles, especially the five- and six-membered nitrogen and oxygen heterocyclic compounds [2, 3]. Some of the well-known examples of medicinally important heterocycles include ciprofloxacin **1**, which is a wide spectrum antibiotic drug used for the treatment of respiratory tract infections and urinary tract infections [4], and the antibacterial drug sulfamethox-

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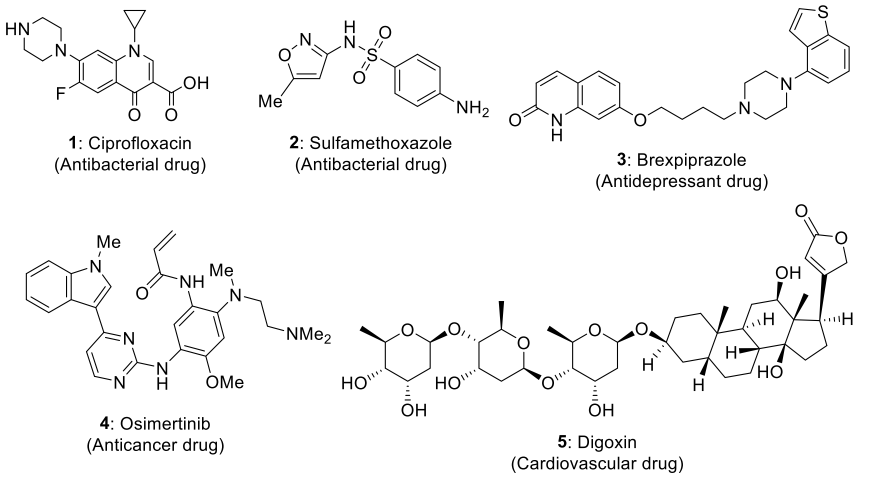
azole **2**, which is used to treat urinary tract infections in patients with a kidney transplant (Fig. **1**) [5].



1: Ciprofloxacin (Antibacterial drug)

2: Sulfamethoxazole (Antibacterial drug)

3: Brexpiprazole (Antidepressant drug)

4: Osimertinib (Anticancer drug)

5: Digoxin (Cardiovascular drug)

Fig. (1). Representative examples of biologically active heterocycles.

Furthermore, brexipiprazole **3** is an example of antipsychotic drug used for the treatment of the major depressive disorder (MDD) [6] and osimertinib **4** is widely used for the treatment of non-small cell lung cancer [7]. The oxygen heterocycle digoxin **5** is an effective drug for the treatment of irregular heartbeats and heart failure [8].

Numerous conventional methods are available in the literature for the synthesis of these biologically relevant heterocycles and some of the downsides of many of these approaches involve expensive catalysts, harsh reaction conditions, toxic solvent, high temperature, and multistep synthetic sequence. Consequently, in recent years, synthetic chemists are paying more attention to the development of greener strategies involving nanocatalysts for the synthesis of these valuable heterocycles [9]. This chapter summarizes the heterogeneous nanomaterial catalyzed synthesis of various heterocyclic compounds.

SYNTHESIS OF NITROGEN HETEROCYCLES

A variety of nanomaterials have been extensively used as heterogeneous catalysts to access various nitrogen heterocycles. In this section, we describe heterogeneous nanocatalyzed strategies for the synthesis of five- and six-membered nitrogen heterocycles.

Synthesis of Five-Membered Nitrogen Heterocycles

2H-Indazoles

Recently, Pathak and co-workers developed a nanocomposite CuO@CB [6] involving CuO nanoparticles immobilized on cucurbit[6]uril, which showed effective catalytic activity for the synthesis of a series of 2*H*-indazoles **8** starting from 2-bromobenzaldehydes **6**, primary amines **7**, and sodium azide under base- and ligand-free conditions in high yields (Fig. **2**) [10]. It was observed that the nanocatalyst was an air-stable green powder and reusable up to five runs with no remarkable loss of catalytic property.

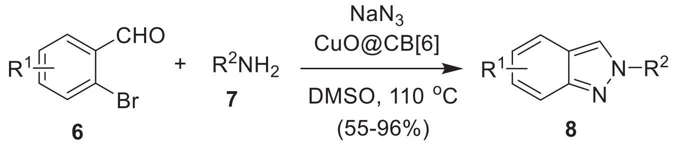


Fig. (2). Copper nanoparticles-catalyzed synthesis of 2*H*-indazoles.

An ultrasonic-mediated one-pot, the three-component reaction between 2-bromobenzaldehydes **9**, primary amines **10**, and tetrabutylammonium azide (TBAA) **11** was established for the synthesis of 2*H*-indazole derivatives **12** in good to excellent yields (Fig. **3**) [11]. The reaction was achieved using copper-doped silica cuprous sulphate (CDSCS) as a heterogeneous nanocatalyst and was reused for several sequential runs without any significant loss in catalytic activity.

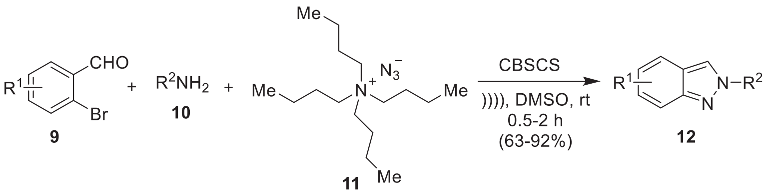


Fig. (3). Copper-doped silica cuprous sulphate-catalyzed ultrasonic-mediated synthesis of 2*H*-indazoles..

Imidazoles and Benzimidazoles

Aberi and co-workers established a one-pot approach for the synthesis of 2,4,5-triarylimidazoles **16** *via* a three-component reaction of benzil **13** or benzoin **14**, aryl aldehydes **15**, and ammonium acetate under mild conditions (Fig. **4**) [12]. The Mo^{IV}-salen complex was found to be an efficient and reusable nanocatalyst to access the desired products in high yields.

CHAPTER 11

Role of Nanocatalyst in Electrochemical Sensing of Heavy Metal Ions

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Abstract: This book chapter introduces the based nanocatalysts-based electrochemical sensors for the detection of heavy metal ions (HMIs) from their different sources. A serious challenge in the field of detection of HMIs is the innovation of simple and fast electrochemical sensor techniques with the potential ability to detect at low concentrations. The electrochemical sensors for the assay of heavy metal ions were designed and developed by many researchers in the past. To achieve repeatability, reproducibility, and stability, the fabrication of electrodes for electrochemical sensing applications has been given much emphasis in recent days. The selectivity of the modified electrode towards the detection of transition metal ions (Cd^{2+}, Zn^{2+}, Co^{2+}, Fe^{2+}, Mn^{2+}, Ni^{2+}, and Ag^{+}) was investigated by many researchers and was discussed in this chapter. In addition, the applications of 3 dimensional (3-D) nanomaterials and functionalized nanomaterials of metal and metal oxides supported on graphene, graphene oxide, and carbon nanotubes as nanocatalysts have been presented in this chapter. The modified and functionalized electrodes are anticipated to play a decent role in the latest electrochemical sensing of HMIs to demonstrate quantum confinement effects.

Keywords: Electrochemical sensor, Electrodes, Functionalization, Heavy metal ions, Nanocatalyst.

INTRODUCTION

Nowdays, with the advancement in the industrial, mining, and agricultural activities, a large amount of heavy metal ions were released into the environment,

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causing serious global problems. Heavy metals are chemical elements with a specific gravity that is at least 5 times the specific gravity of water. They are toxic or poisonous even at low concentrations [1]. The most common heavy metals, such as chromium (Cr), zinc (Zn), cadmium (Cd), copper (Cu), mercury (Hg), and nickel (Ni) are recognized as a great threat [2] in the earth due to their toxicity and even in small concentration, they seriously affect human beings [3].

The movement and toxicity of heavy metal ions are based on their speciations in terrestrial and aquatic environments, especially interactions with the solid fractions such as various (hydro) oxides [4] clay minerals, organic matters, and microorganisms. These biotic and abiotic constituents are naturally interacting to form varieties of compounds, composites and complexes by the physicochemical processes such as adsorption, coating, co-precipitation, *etc*. [5]. The mining activities by man have introduced these heavy metals into the environment during the extraction of different metals from different sources [6].

HEAVY METAL DETECTION

In the environment, heavy metals can remain for decades or centuries due to their non-biodegradability [7]. They are dispersed throughout the environment by several natural processes such as volcanic eruptions, anthropogenic activities, bacterial activities, industrial processes, an agricultural activities [8]. Heavy metals will normally cause acute diseases such as nausea, vomiting, diarrhea, or allergy after their entry into the human body. They can also cause chronic diseases, such as cancers, lung disease, stroke, Alzheimer's, diabetes, kidney problem, or nerve-related damages and even death [9]. In the human body, these heavy metals are believed to destroy the macromolecules and disrupt their cellular functions [10]. The detection and determination of these heavy metal ions in the soil, food, and water are very significant and therefore, serious efforts have been made in this direction by the researchers. Therefore, a sensitive and selective methodology for the detection of heavy metal ions is the need of the hour. World Health Organization (WHO) and the Centre for Disease Control (CDC) have declared heavy metals as the prominent species to be monitored and have a set of permissible limits as per the environmental quality standards (EQS) [11]. Therefore, a quick, extremely sensitive and efficient tracking of heavy metal ions from all types of samples is highly desirable. The most conventional methods applied for the detection of trace metals at lower concentrations include atomic absorption spectroscopy (AAS), inductively coupled plasma/atomic emission spectrometry (ICP-AES), neutron activation analysis (NAA), ion chromatography ultraviolet-visible spectroscopy (IC-UV-vis), inductively coupled plasma-mass spectroscopy (ICP-MS), microprobes (MP) and X-ray fluorescence spectroscopy (XFS) [12, 13]. Although, all these methods have been being proved to be sensitive and selective, but laborious and time-consuming pretreatment process and expensive analytical instrumentation remain their major drawbacks [3]. In addition to, application of the optical chemical sensors (OCSs) by utilizing electromagnetic (EM) radiation generated an analytical signal which exhibits great potential for the detection of heavy metals ions. But, OCS has also some limitations such as time-consuming sample preparation procedures, being costly, with no portability for the applications in the field [14].

For these reasons, material scientists have been researching for many years to develop a rapid, cheap, and eco-friendly technique to trace heavy metal ions . At present, electrochemical sensors have been proved to be a better alternative to conventional methods, in terms of samples handing, separation, and detection of heavy metal ions [15]. Electrochemical stripping analysis has been used as a powerful technique for a long time to trace metals and now it is the most sensitive electro-analytical technique for the analysis of trace metals in the environmental, clinical, and industrial samples [16]. The process of electrochemical sensing relies on the electrocatalytic oxidation of preconcentrated target analyte on the surface of a specially designed electrode [17].

ELECTROCHEMICAL SENSOR

Electrochemical sensors are very much useful in chemistry and medicine to detect and determine the presence of chemical species. Electrochemical sensors are special type of sensors in which the electrode acts as a transducer element and provides quantitative information about analyte chemical species. Electrochemical sensing has gained significance as a promising analytical tool with applications in the fields of energy, medicine, environment, and pharmaceutical industry [18]. Electrochemical sensors were found to exhibit superior sensitivity and selectivity during the quantitative evaluation of analyte species, in addition to their ability to undergo functionalization [19]. The chapter will only focus and discuss the electrochemical sensing activities for heavy metal ions. Electrochemical sensors are operated by reacting with the chemical solutions and by producing an electrical signal. A sensor transforms electrochemical information into an applicable qualitative or quantitative signal. The reactions which occur at the interface of the surface of an electrode between the recognition element, and the target/binding analyte generate an electrical double layer and thus this potential is measured after transforming these chemical reactions into this measurable electrochemical signal by a recognition element, and a transducer of the sensor (Fig. **1**). An electrochemical sensor mainly consists of two main components, one is a chemical recognition system which is responsible for recognizing the analyte species and the other one is a physicochemical transducer that converts chemical interactions into electrical signals that could be detected and displayed easily by

CHAPTER 12

Fundamentals and Advances in Transition Metal Oxide-Based Nano-Electrocatalyst for OER

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Abstract: Oxygen evolution reaction (OER) is the anodic reaction in the overall water splitting process. The four electron-proton reaction is thermodynamically non-spontaneous and kinetically slow. Hence, the need for an electrocatalyst is urgently required to achieve faster kinetics for OER and to enhance the rate of overall water-splitting reaction. The chapter discusses the fundamentals; which include mechanisms of OER, the characteristic features as well as kinetic performance parameters of OER electrocatalyst and advances in nano-electrocatalysis; which includes recent developments in TMO based electrocatalyst, strategies for improving the performance of an electrocatalyst; catalyst other than TMOs. The present discussion offers profound insight and interest on catalysts in oxygen evolution reactions.

Keywords: Electrocatalyst, Nano-catalyst, Overpotential, Oxygen evolution reaction, Transition metal oxides, Water splitting process.

INTRODUCTION

The beauty of the earth is kept alive only through sustainable development. So that, it is desirable to utilize energy properly. As the energy demand is increasing day by day, we must search for alternative renewable energy resources rather than depending on limited resources like fossil fuels. These widely used fuels such as coal, petroleum, natural gas, *etc*., are not only limited, but they aren't eco-friendly also. Around these years, many ideas have been proposed for achieving the simplest, reliable, and efficient energy conversion systems which include fuel cells, alkaline water electrolysis, metal-air batteries, *etc*. In all these systems, oxygen evolution reaction (OER) plays a major role along with oxygen reduction reaction (ORR) or hydrogen evolution reaction (HER). OER is simply an electrochemical process in which molecular oxygen is evolved. The electrolysis of water is a highly significant reaction as a means of clean hydrogen production.

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These reactions occur in a two-electrode system of which oxygen reduction reaction (ORR) or hydrogen evolution reaction (HER) takes place at the cathode, whereas oxygen evolution reaction (OER) takes place at the anode. OER is pH-dependent and occurs *via* different routes in acidic/basic/neutral environments.

The equilibrium half-cell potentials at standard conditions for OER are shown as follows [1];

$$4OH^- \leftrightarrow 2\,H_2O_{(l)} + O_{2(g)} + 4e^- \qquad E° = 0.404\text{ V (alkaline solution)} \qquad \textbf{(1)}$$

$$2H_2O_{(l)} \leftrightarrow 4H^+ + O_{2(g)} + 4e^- \qquad E° = 1.230\text{ V (acidic/neutral solution)} \qquad \textbf{(2)}$$

The equilibrium half-cell potentials at standard conditions for HER and ORR are [2, 3];

$$\text{HER: } 2H^+_{(aq)} + 2e \leftrightarrow H_{2(g)} \qquad E° = 0.000\text{ V } (vs\text{ SHE}) \qquad \textbf{(3)}$$

$$\text{OER: } O_{2(g)} + H_2O_{(l)} + 2e \leftrightarrow HO_2^- + OH^- \qquad E° = 0.695\text{ V } (vs\text{ SHE}) \qquad \textbf{(4)}$$

From this, it is evident that OER involves the transfer of four electrons as well as four protons [4]. Whereas at the cathode, HER is a two-electron transfer reaction *i.e.* evolution of a single oxygen molecule involves several single-electron/proton transfer steps. Both the reactions are slow in kinetics, especially OER as it involves four electron-proton coupled transfers and also the higher overpotential requirement to overcome the energy barrier associated with each step. While considering the practical application of this reaction, this overpotential has resulted in a huge loss of energy and hence a catalyst is urgently required to lower the activation barrier for the oxygen evolution reaction.

An ideal OER catalyst includes low overpotential, high conductivity, large surface area, active surface sites, high stability, and large earth-earth abundance metal-based catalysts like RuO_2 and IrO_2 show excellent electrocatalytic activity on OER. They are known as benchmark electrocatalysts for OER and are applicable for a wide range of pH conditions [5]. However, being costly and meagerly available, we can't use these catalysts on a large scale. Recently, numerous alternatives have been discovered. Oxides and non-oxides of other transition metals, organometallics, non-metal compounds like carbon nanotube, *etc.* show great results on electrocatalysis. Among these, transition metal oxide (TMO) based electrocatalysts have a supreme position in OER catalysis.

There are wide varieties of transition metals and their oxides. Besides, they are abundant to mostly first-row transition elements [5]. Flexibility towards alloying, doping, and nanoparticle synthesis makes them very special. Certain oxides of iron, nickel, and cobalt have been reported to act as efficient OER catalysts in alkaline media. While corrosion of these materials leaves a negative impact. This issue is found to be rectified by alloying those metals with other transition metals. For example, iron can be alloyed with Cu, Mo, Ni, Zn and/or Co, which enhances the corrosion resistivity of iron-based catalysts [5]. While discussing the application of nano-science in electrocatalyst, nanoparticles of lithium-induced $NiFeO_x$ are a great example [6]. This nano-electrocatalyst has shown higher activity as well as stability than the benchmark electrocatalysts in alkaline medium. Nano-electrocatalysts are very much effective than the normal catalysts typically due to their small size (10-80 nm), achieving a very large catalytic surface area [7]. Also, they show exceptionally different properties which they did not possess at their macroscopic stages. Considering all these, we can expect a wide range of applications of these transition metal-oxide based nano-electrocatalyst in OER. The chapter mainly discusses the mechanism of TMO based OER, features of a nano-electrocatalyst for the reaction, kinetic parameters used to express the catalytic efficiency, developments in TMO based catalytic system and catalysts other than TMOs, which are significant for OER.

FUNDAMENTALS OF OER

Thermodynamically, OER is an uphill reaction with slow kinetics and hence hard to achieve. Theoretically, evolution happens at 1.23 V. But practically occurs at a higher potential. The difference between theoretical and actual potential values is called overpotential [8]. OER is a complex four electron/four proton transfer reaction, that requires higher overpotential and hence acts as the bottleneck of overall water electrolysis. TMO's constitute the most active, stable and low cost electrocatalysts for enhancing the kinetics of OER from different chemical environments. They are efficient and hence widely used in alkaline water electrolytes. Among the different metal hydroxides, the highly conductive KOH solution is the most common electrolyte in use. Acid electrolytes, due to the highest molar conductivity of protons, could minimize voltage loss at high current density and also offer lower resistance. Mainly, noble metals such as Ir, Ru, and their oxides are well known for their catalytic activity for application in acid electrolytes. Compared to acid and alkaline electrolytes, OER reaction follows slower kinetics in neutral environment due to the low conductivity and the lower concentration of proton and hydroxyl ions.

Electrocatalytic OER reaction is pH-dependent. The starting material in an acidic medium is water. Whereas, OER from alkaline as well as neutral medium initiates with hydroxide ions. The mechanisms of OER from acidic, basic as well as. The mechanisms of OER from acidic, basic as well as the neutral environments are evidenced from many research publications. The general mechanism of OER from

CHAPTER 13

Need and Scope of Nanocatalysis for Synthesis and Sensing

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Abstract: The process of functionalization of nanomaterials with functional groups, molecules, or biomolecules significantly influences the performance of nanomaterials and nanoparticles and enables them to act efficiently in the design and fabrication of nanocatalysts and electrochemical sensors which can be applied in different fields for the detection of analytes such as biomarkers, contaminants, preservatives *etc*. Nanocatalysis is indispensable in the real sense for its benefits that come from both the homogenous and heterogeneous catalysts, such as greater efficiency, stability, an recyclability. Due to the unique properties of nanomaterial-based catalysts, nanocatalysts exhibit extraordinary potential applications in various sectors, like cosmetics, energy, power, petroleum, drug delivery, fuels, biomedicine, and herbal drug synthesis. This book chapter discusses the need for nanocatalysis and its scope, focusing on synthesis and sensing properties of varieties of nano-catalytic materials for multifunctional applications.

Keywords: Nanocatalysis, Nano-catalytic materials, Nanoscience, Scope, Synthesis.

INTRODUCTION

Nanoscience is considered the central science among the natural science disciplines in the 21st century. Recently, several publications have been released on the areas of nanotechnology; this may show the presence of great research interest in the field. Besides, nanomaterials have tremendous potential in several

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smart superhydrophobic applications. Smart food packaging and bacteria detection, drug delivery at a specific area of the human body, and blood purification, as an antibacterial agent and superhydrophobic properties in the textiles industries, and as sterilization and light-transmission controlling glasses [1].

At the pinnacle of the 19th century, besides the expansion of nanoscience, nanocatalysis has emerged as one of the dominant topics at the border between homogeneous and heterogeneous catalysis. This is also reported to be a novel solution that can answer the active conditions for catalyst development (Fig. **1**). The nanocatalysts have valuable potential as homogenous and heterogeneous catalysts. The efficiency, stability, selectivity, and simple regeneration/recycling properties are the countable merits of the nanocatalysts. The nanocatalyst also gives improved activity different from regular, non-nano materials; this is due to the nano dimensional properties [2].

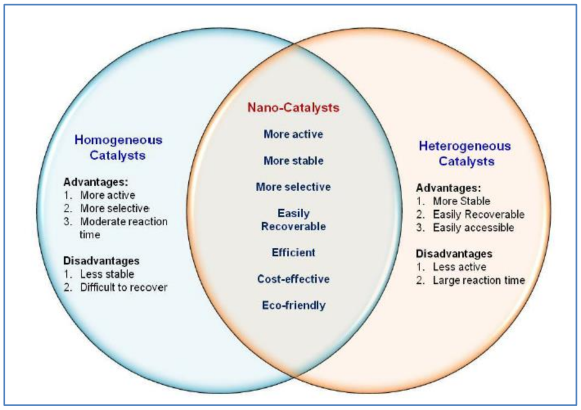

Fig. (1). A schematic showing the differences among the homogeneous, heterogeneous, and nano-catalysts [4].

Catalysis has a crucial purpose for the advancement of the chemical industry. The efficient use of natural resources and diminishing the contamination in the advancement of industrial technology is the countable use of catalysis. Since the last century, catalysis has gained the base of the mass making of the chemicals and varieties of petrochemical products. Catalysis has displayed some new difficulties and occasions as a consequence of the advancement in the field of nanotechnology. Recently, some achievements have been accomplished as per the earlier reports concerning metal-based nanomaterials as heterogeneous catalysts.

Catalysts have crucial catalytic properties and selectivity for particular reactions. The coupling, redox, and electrochemical reactions are countable catalytic chemical reactions that occur by nanocatalysts [3].

NANOCATALYSIS

Nanoparticles as catalysts are one of the principal nanomaterials. In the last decades, several nanosized materials such as titanium dioxide, zinc oxide, iron oxides, aluminum, and silica have been employed as a catalyst. The large surface active sites of nanoparticles have an honest and helpful consequence on the reaction rate. The geometry/structure and morphology-dependent properties of materials at their nanoscale crystallite size can affect the reactant progress of a material. Therefore, optimizing the structure, shape and size of the nanocatalyst during the synthesis should also be taken into consideration [4].

The concept of applying nanoparticles (NPs) for varieties of applications has been found in history for many centuries. The Lycurgus Cup, basically a dichroic glass of gold and silver NPs, exhibited opaque green when viewed from the outside and glowing red when seen from the inside. Similarly, the Damascus saber blades, used during the period between 300 BCE and 1700 CE, were found to exhibit excellent strength, toughness, and resistance to shattering, as they contained carbon nanotubes and cementite nanowires. Iron NPs were applied as a nanocatalyst for a very old Haber-Bosch process for the synthesis of ammonia. At the beginning of the 20th century, Ostwald experimented to increase the surface area of a catalyst for surface-dependent catalysis. Nowadays, a large number of nanomaterials have been utilized in the industries for varieties of synthetic processes of broad commercial applications [5].

The nanoparticles of metal or metal oxides or mixed oxides have a proven record of serving either as stable heterogeneous catalysts or as support materials for various industrially important processes. Similarly, nanostructured catalysts can also serve as heterogeneous catalysts; in which case, separation of catalysts from the reaction mixtures is much easier. In addition, highly active and stable nanocatalysts can be fabricated and functionalized in various ways in order to control the sizes, shapes, and morphologies of nanomaterials effectively [5]. The homogeneous catalysts were employed to a set of limited industrial processes. But, heterogeneous catalysts were found to be employed extensively in the industry due to their advanced features such as ease of separation and recovery as well as their capacity to withstand severe reaction conditions. These heterogeneous catalysts exhibit lower efficiency than their homogeneous counterparts, possibly due to limited diffusion and decreased active sites [6]. The application of NPs has gained significant momentum in the recent past, especially in global environmental problems, which could be attributed to their enhanced catalysis via increased surface area to volume (SAR) ratio [7].

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