METAL NANOPARTICLES AS EMERGING CATALYST

Abstract

A set of principles which forgo the usage or production of harmful materials when producing, developing, synthesizing and using chemical substances is known as green chemistry. As a result, when developing new chemical processes or methods, green synthetic techniques consider hazard reduction as the primary consideration. All chemical processes begin with catalysis, hence nano catalysts with particle size dependent material engineering are very desirable for sustainable energy applicationsand green chemistry. Besides particle size, the nanostructured catalysts are extremely shape sensitive and can have a strong influence on catalytic efficiency by virtue of their morphological characteristics. Furthermore, nano catalysts are hailed as novel process candidates with expanding catalytic capabilities because of their enormous surface areas, remarkable recycling potential, and effective recovery features. As a result, nano-catalysts are employed in the synthesis of organic compounds as well as in other significant functionalization’s in the recapitulation of the manufacturingof numerous new types of chemical entities.

Keywords: Green Synthesis, Nano-Catalyst, Characterization, Catalysis, Catalytic Applications.

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I. INTRODUCTION

Nanotechnology is a branch of science which is developing currently and is covering wide range of technologies which are presently under advancement at nanoscale. Nanomaterials comprise substances of at least one dimension within the nanometer range, from 1 to 100 nm in diameter. These include nanofilaments, nanofibers and nanoplates[1].Nanoparticles reveals improved chemical and physical properties which are differ from free atoms or molecules and also from bulk solids making up the nanoparticles with same chemical composition. Due to size restrictions, the predominance of interfacial interactions and quantum effects, the behavior of the material at the nanoscale has frequently been identified as having very desirable qualities when compared to its behaviour at the macro scale. These novel and distinctive traits for nanomaterials, nanoparticles, or similar nanotechnologies will result in improved attributes such as catalysts, tunable photo activity, greater strength and many other intriguing features[2].It has a major role to play in developing innovative methods for the production of new products, replacing existing production facilities and reforming new constituents and chemicals with enriched execution resulting in reduced energy and material consumption and reduced environmental damage.

Catalysis is a highly studied and broadly investigated subject in the area of basic and Industrial chemistry. It also has a significant impact on the production of energy, industrial chemistry, and environmental correction with reference to the removal of toxins or pollutants from soil, water, and sediments. Currently, catalytic converters are used in 90% of chemical processes and over 60% of chemical products around the world. That scope will continue to grow in order to satisfy our increasing aspirations for sustainable procedures that have better economic impacts and fewer environmental problems[3]. In order to identify worthwhile uses for the pharmaceuticals and fine chemicals sectors, any reactants preferred by catalysts are given great attention. The development of green, sustainable, and affordable chemical processes continues to be a significant problem in chemistry. Additionally, there will be the ongoing requirement for effective and selective catalytic processes to convert raw materials into valuable compounds and crucial medications. But reducing waste and toxic materials, efficiency at the atomic level as well as a large number of catalysts coming back on line are also key challenges for greener chemistry. As they adhere to the green chemistry principle, nanostructure materials in this context serve as appealing components as heterogeneous catalysts for a variety of organic reactions. Researchers have significantly aided in the synthesis of well-defined nanomaterials over the last few years. By manipulating the structure and composition of active nanoparticles through interactions between catalytically active particle species as well as their support, these new approaches have facilitated a rational design and synthesis of highly efficient and selective nano structured catalysts. Further, metal nanoparticles are considered likely to be catalysts because of their relatively larger surface area for a given volume or weight unit and the fact that they have similar characteristics as bulk metals. Therefore, on metal surfaces, heterogeneous metal nano catalysts function as classical catalysts. The key to catalytic chemistry is the concept of catalyst design, in which metallics such as metals oxides, metal compounds and so forth are most potent for a number of fundamental reactions occurring in modern chemistry[4].The catalytic converter is significant because of its singular capacity to accelerate chemical reactions by lowering the energy barrier of their passage from one phase to another and by using regulated reaction paths to synthesize target products with selectivity[5]. By modifying the physical and chemical characteristics of nano catalysts, such as their size, shape, composition, and morphology, it is theoretically possible to change both their activity and selectivity.

Consequently, the number of reactions involving micro catalysts has increased exponentially in environmental protection [6], chemical engineering [7],energy gathering[8] and conversion and storage [9].

This chapter begins by discussing the characteristics and uses of nano catalysts in order to shed light on the basic connections between the activity, selectivity, and recyclability of these materials and their compositions and architectures. Then, methods for creating supported metal nanoparticles with adjustable size, shape, and surface structure are outlined. Finally, new developments in nano catalysis in various organic transformations, energy conversions, and environmental remediation are discussed.

II. NANOCATALYST – SHAPE, SIZEAND SURFACE CHEMISTRY

Researchers have not come to an agreement on the exact definition of nanomaterials, however it is generally acknowledged that they are primarily distinguished by their small size, measured in nanometers. 100,000 times smaller than the diameter of a human hair, a nanometer is one millionth of a millimeter. Due to their small size, most nanoscale materials are invisible to the naked eye and even to conventional laboratory microscopes. Manufactured nanomaterials, which could have unique optical, magnetic, electrical, and other properties, are typically referred to as materials because they have been manufactured at such a small scale. These emerging features have the potential to have significant effects in many fields, including electronics, medicine and other fields.In comparison to molecules, atoms, or bulk goods, materials at this scale exhibit very diverse properties. In order to deal with this relatively new scientific discipline, the term "nanoscience" was created. Despite the fact that the concept of this scientific field is not new, modern research is constantly discovering new and beneficial uses for both the manufacturing sector and academia, which has found nanoscience to be a flourishing and exciting issue. Diverse uses are being discussed, including those for consumer products, the environment, and even medicine.

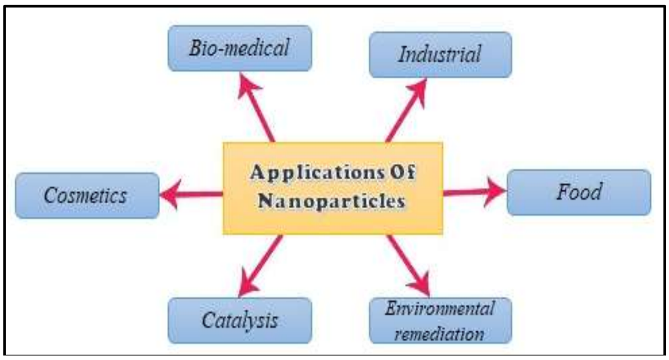


Figure 1: Various applications of Nanoparticles

There are numerous shapes that nanoparticles can adopt, such as powder, crystal, and cluster forms. Ultrafine particle mixes are referred to as nanocrystals, whereas mixtures of fine powder are referred to as nano powder. A cluster is said to be a nanocluster if it only has one dimension and a small size range of 1 to 10 nm. Heterogeneous metal nanoparticle catalysts are generally used on metal surfaces and are regarded to be likely candidates for catalysis due to the fact that they have a relatively high surface area per volume or weight unit when compared to bulk metal. Industrial metal catalysts are frequently inorganic, have a large surface area, and are characterized by widely dispersed metals. A variety of approaches are employed to generate and sustain these catalysts. Metal nanoparticles, which can take on a variety of shapes and sizes and have many particles, frequently work together. A few transition metals that are produced by spreading metal particles across inorganic surfaces include alumina, silica gel, and activated charcoal. There are a variety of factors that make them superior than metal powders, including consistent thermal performance, reduced cost, more surface area, and effective use of metal nanoparticles in the form of wide dispersion[10].

III. SYNTHESIS AND CHARACTERIZATION OF NANOPARTICLES

Various techniques are employed to produce various types of nanomaterials, depending on their composition. The "top-down" and "bottom-up" approaches are the two methods used most frequently to create nanomaterials. The top-down method applies pressure on bulk materials from the outside, eventually forcing them to disintegrate into smaller components utilizing mechanical, chemical, or other energy sources. However, because it is highly challenging to generate very small nanoparticles, this process does not produce nanomaterials that are uniformly formed and also consumes a lot of energy. In addition, the freshly produced nanoparticle forms suffer crystal loss due to this approach. In a bottom-up method, precursor particle size is increased by combining atomic or molecular species through chemical processes. This method aids in preventing the proliferation of undesirable particles by regulating the synthesis. This method is also cost-effective and environmentally beneficial. It should be noted that the top-down approach is viewed as a physical method and the bottom-up approach is a chemical one. In addition to liquid, solid, gas, supercritical fluids, and vacuum, both methods can be used in a variety of states. The end desired outcome and manufacturer must be considered while choosing between the two methods. When using catalysis as an example, it's crucial to take into account this element's dynamic character because changing the size and shape of the metal particles is the single most essential thing that can be done to improve application performance.

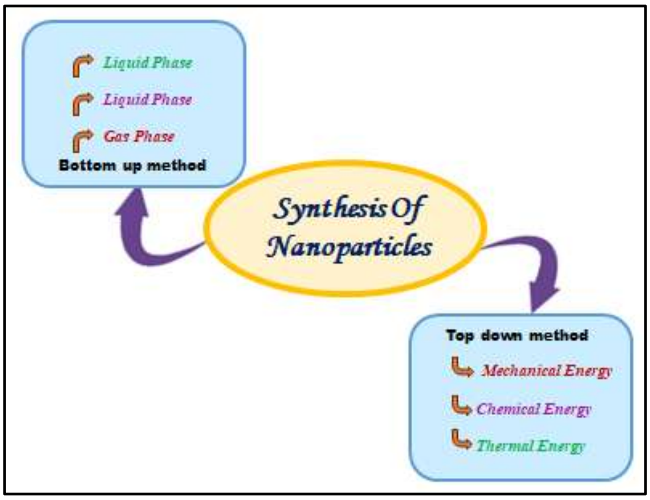


Figure 2: Schematic representation of Synthesis of Nanoparticles

Nanoscale materials have unique characteristics that make them appropriate for a wide range of appliances and make them a focus for a number of researches. To comprehend the nature of active sites and, in turn, to locate as well as adjust the key performance metrics, a thorough study of the characteristics of metal particles at the nanoscale level is necessary. Although there are numerous methods for characterizing nanoparticles, none of them can provide comprehensive details about the materials being studied. The size, structure, and catalytic qualities of each sample must therefore be classified using a variety of methodologies in order to comprehend them. The numerous analytical techniques used to characterize metal nanoparticles are described in Table 1.

Table 1: Some selected characterization techniques of metal nanoparticles

Sr. No.	Characterization techniques	Information obtained	Reference
1.	TEM -Transmission electron microscopy	Size and Morphology of Metal Nanoparticle's	[11]
2.	SEM - Scanning electron microscopy	Size and Morphology of Metal Nanoparticle's	[11]
3.	XRD- X-ray diffraction	Crystal structure, size and chemical composition	[12]
4.	DLS - Dynamic light scattering	Size and size distribution of MNPs in solution	[13]
5.	UV visible spectroscopy	Formation of colloidal MNPs (Plasmon band)	[14]
6.	XPS - X-ray photoelectron spectroscopy	Surface composition of supported MNPs	[15]
7.	FTIR- Fourier transformed infrared Spectroscopy	Different functional groups and metal - metal and/ormetal-oxygen bond identification	[16]
8.	EDX - Energy Dispersive X-ray	Element and distribution of MNPs	[17]

Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM) are frequently used techniques for describing MNPs [11]. Other procedure include powder X-ray Diffractometry (XRD)[12], Dynamic Light Scattering (DLS)[13], UV visible spectroscopy[14], atomic force microscopy, and X-ray photoelectron spectroscopy (XPS)[15]. As previously mentioned, gold and palladium nanoparticles would be examined using UV spectroscopy and Fourier transformed infrared (FTIR)[16] techniques. The investigation of silver nanoparticles, however, would include the use of TEM, high-resolution TEM, and selected area diffraction pattern (SAED).Lastly, a combination of X-ray diffraction, SEM, and FTIR would be used to evaluate magnetite, Ag, zinc, and Au nanoparticles[17-21].

IV. CATALYTIC APPLICATIONS OF METAL NANOPARTICLES

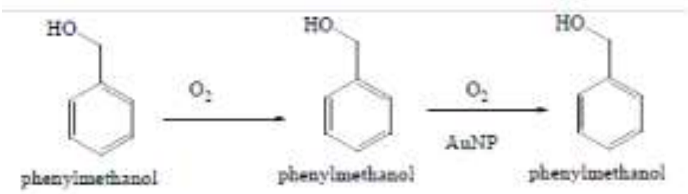
"Sustainable technology and organic transformations" is a subject that is constantly growing and is applicable to almost all catalytic organic transformations. Nano catalysis is a key element in these transformations [22]. The use of catalysts has a great deal to do with chemical technology. In order to take into account economic and environmental considerations, it is especially important for a small number of catalysts with considerable activity. As indicated in Table 2, a variety of nano catalysts, including magnetic nano catalysts, nano mixed metal oxides, core-shell nano catalysts, nano-supported catalysts, and nano catalysts based on grapheme, have been employed in catalytic applications[23]. Due to their low preparation costs, superior activity, exceptional selectivity, high stability, effective recovery, and outstanding recyclability, magnetic nano catalysts stand out in this group of reusable nano catalysts.

Table 2: Different types of nano catalyst and their applications

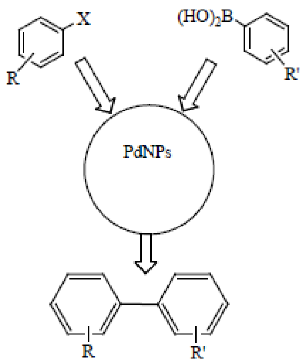
Sr. No	Nanomaterials	Size	Shape	Applications	Reference
01	CuO	200-500 nm	Microspheres, nano sheets, nano wires	Investigations were made into the nanomaterials' catalytic activity towards oxygen evolution. CuO microsphere material and CuO nanowire both had the best catalytic current densities between 1.10 and 1.40 V and the lowest over potential for water oxidation, respectively.	[24]
02	Carbon Nano tubes (CNTs)	-	Coiled in shape	Additionally, mixed catalysts showed increased oxygen reduction reaction activity. To ease mass transit and the transfer of electrons and protons, CCNTs have an unusual property that allowed them to build a multidimensional network.	[25]
03	Au–Pt nanomaterials	5-10nm	Cage bell structures	Compared to their solid counterparts, proton exchange membrane fuel cells have more surface area, which results in catalytic activity in the direction of oxygen reduction. Nano-channels in the Pt shell provide access to the interior surface areas. There is an electronic coupling effect between the Pt shell and the inner-positioned Au core.	[26]
04	Graphene oxide (GO)and Carbon	-	Multi-wall Carbon nano tubes	In the presence of graphene oxide and other functionalized carbon-based nanomaterials, the catalytic activity of cyt C can be enhanced up to 78 times and 2.5 times, respectively.	[27]
05	ZnO nanoparticles	10nm	Sheet, particle & spindle	Investigated photocatalytic degradation and antibacterial activities.	[28]
01	Zinc oxide (ZnO)	100nm	Nanorods, wires andparticles	The oxidative breakdown of butane is shape dependent. Butane might be fully converted into carbon oxides (COx) in this way. As opposed to nanoparticles, ZnO nanowires and nanorods produced better carbon balance and COx selectivity.	[29]
03	Strontium (II)-added ZnAl2O4 nanomaterials	2-5 m	Spinel structure	Strontium addition reduces grain size while enhancing the ability of zinc aluminate to selectively oxidize alcohols.	[30]
07	Graphite Oxide	50-500 nm	Flakes	for the goal of heating water for a variety of potential thermal, thermochemical, and mechanical purposes.	[31]

08	Covalent Organic Frameworks (COF)	1 m	-	COF-102 and COF-103 are activated to measure the adsorption of gases. Measurements of Argon Adsorption for COF-102 at Low Pressure (0-760mTorr).	[32]
10	BiVO4 nanoparticles	-	nanoparticles	Investigation of antibacterial and photocatalytic degradation.	[33]

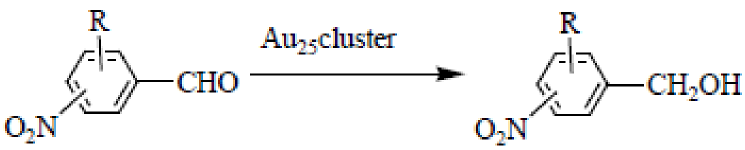
Any material's shape- and structure-dependent characteristics can have an impact on a material's reactant mobility at the nanoscale scale. Additionally, the calibration of a nano catalyst for synthesis in a certain shape and size has produced more notable selectivity [34-36]. Understanding the applications of nano catalysts will enable researchers to construct and design nano catalysts that are extremely dynamic, intensively specialized, and extremely robust. These themes will help modern synthetic reactions become more resource-efficient, consume less energy, and generate less waste, all of which serve to lessen the ecological effect brought on by our dependence on the synthesis process. A nanoparticle is believed to be the most important catalyst currently available. It can be used for a variety of processes, including chemical synthesis and energy conversion and storage[37-39].In addition, different metal nanoparticles are employed in organic synthesis in a variety of reactions, some of which are summarized here[40-51].



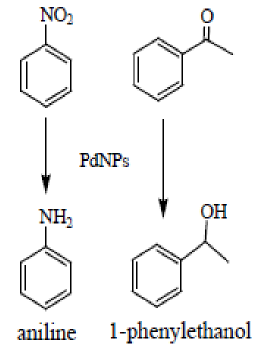
Scheme 1: Selective oxidation of benzyl alcohol using AuNP



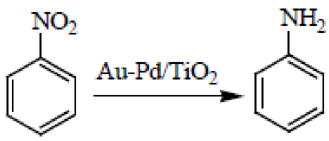
Scheme 2: Synthesis of biaryls using PdNPs



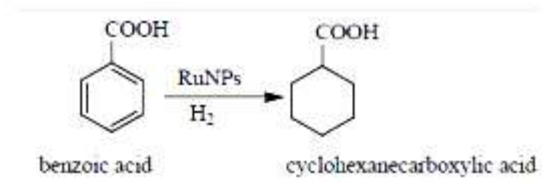
Scheme 3: Selective reduction using Au nano cluster



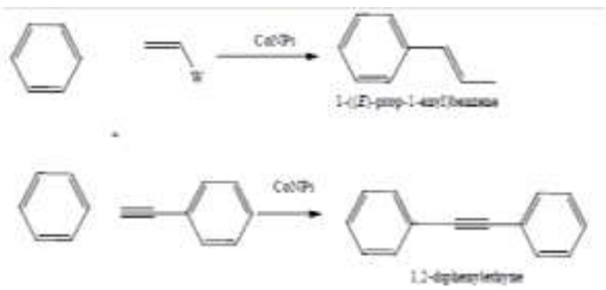
Scheme 4: Synthesis of Aniline and 1-phenyl ethanol using PdNPs



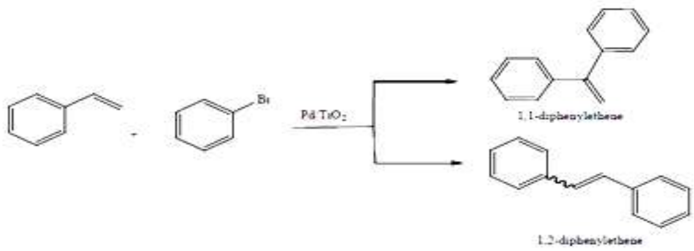
Scheme 5: Synthesis of Aniline using Au-Pd/TiO_2NPs



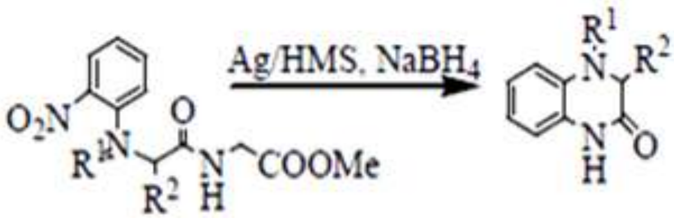
Scheme 6: Synthesis of Cyclohexane carboxylic acid using RuNPs



Scheme 7: Synthesis of 1-((E)-prop-1-enyl) benzene and 1,2-diphenylethyne using CoNPs



Scheme 8: Synthesis of 1,1-diphenyletane and 1,2-diphenylethane using Pd/TiO_2NPs



Scheme 9: Synthesis of Dihydroquinoxalinone Derivatives and Amine-substituted MCR Scaffolds

Scheme 10: Reduction of Methylene Blue dye

V. FUTURE OPPORTUNITIES AND DIFFICULTIES

The creation of nanomaterials on an industrial scale has a significant impact on the conventional chemical industry and its supporting production industries due to developments in the science behind their synthesis and the expansion of their varied application fields. Due to their exceptional electrical, optical, magnetic, and thermal capabilities, metallic nanomaterials, a novel and growing type of nanomaterial, have intriguing prospects in the domains of optoelectronics, microelectronics, and sensors, predominantly in catalytic areas. Additionally, it is exceedingly challenging to achieve large-scale industrial manufacturing of metallic nanoparticles. Hence, there is still much work to be done before the industrial manufacturing and associated applications are realized. In addition, there are several issues that need to be resolved. The first issue is how to industrialize the mass production of metallic nanoparticles, which is just one of many issues that are listed below. Second, in order to create and synthesize suitable catalysts for usage in diverse reactions and other processes, it is crucial to build innovative nanoscale structures and compositions. The future applications of nano catalysts include research into bio-inspired attempts at nanomaterial synthesis and their catalytic use in recoverability, biodegradability, and bioremediation. Future advancements could improve the numerous catalytic uses of nanomaterials. Additionally, it is increasingly important to actively investigate the uses of metallic nanomaterials in other disciplines and to increase the sophistication and breadth of such uses in the fields of materials science, chemistry, biology, physics, and some related ones.

VI. CONCLUSION

This study's objective is to assemble the literature on the application of nanomaterials in organic synthesis and other catalytic features. It must go without saying that accurate citations and a thorough review of the literature are essential for researchers looking for pertinent data, ground-breaking concepts, and advancement on any issue. On the other hand, results that have been published employing nanomaterials show the extensive synthetic capacity of the stated catalysts and the high level of interest in this area among researchers. Short reaction times, high yields, the use of affordable chemicals, ease of work-up procedures, and highly targeted reactions are just a few benefits of using green nano catalyst for the synthesis of a range of organic compounds. Supported metal nanoparticles and other non-metal based nano composites have also emerged as new and innovative sustainable catalysts for upcoming research projects, and these nano catalysts are much superior to conventional catalyst. Supported nano catalysts have a wide surface area and are employed for a variety of organic and inorganic transformations, such as oxidation, reduction, coupling reactions, and the creation of molecules of biological significance. Such nano catalysts could be helpful in the large-scale production of bulk and fine compounds due to their great efficiency. For the majority of reactions, it is simple to remove the used catalyst from the reaction mixture and to re-use it without significantly altering its catalytic activity. Additionally, medications that specifically target organs or cells in the body, including cancer cells, can be created using nanotechnology, increasing the efficacy of treatment. To make cement, textiles, and other materials stronger and lighter, nanomaterials can also be introduced. They are very useful in electronics because to their size, and they can also be employed to bind with and neutralize contaminants in the environment during environmental remediation or clean-up. There is still a need to investigate and create new nano catalysts with greater properties. This chapter offers a thorough grasp of organic processes that are catalyzed with the help of nanoparticles and nano catalysts that are safe for the environment.

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