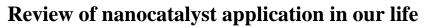
Kurdistan Regional Government-Iraq Ministry of Higher Education &Scientific research Salahaddin univesity-Erbil (SUE) College of science Department of chemistry



A Project Submitted to the Scientific Committee in the Chemistry Department in Partial Fulfilment of the Requirement for the Degree of Bacterial Science in Chemistry.

Prepared by:

Rana Bakhtyar Awla Ahmed

Supervised by:

Mr. Muhammed Haji

April2023

newroz2722

ramaddan1444



Acknowledgement

First and foremost, praises and thanks to God, the Almighty, for his showers of blessings throughout our research work to complete the research successfully, and thanks to my family who helped me to carry out this project successfully. Furthermore, we would like to express our sincere gratitude to my supervisor Mr.Muhammed Haji who helped me through this research with his endless support and the assistance of so many people whose names may not all be enumerated. Their contributions are sincerely appreciated and gratefully acknowledged.

List of Content

No	Title	Page
	Abstract	6
1.	Introduction	7-8
1.1.	Nanoparticle	9
1.2.	Factors affecting the catalytic properties of nanomaterial's	10-14
1.3.	Nanocatalyst	15-17
1.4.	Concept of nanocatalyst	17-18
2.	Different Methods of Nanocatalyst Synthesis	18-19
2.1.	Biological Approach for Nanocatalyst/Nanoparticle Synthesis	20-21
2.2.	Synthesis of green nanocatalysts	21-22
3.	Application of nanocatalyst	23-37
4.	Conclusion	37
5.	References	38-39

List of Figures

No	Content	Page
1.	Difference between homogeneous, heterogeneous and nano- catalysts	8
1.2.	The effect of gold nanoparticle size on catalytic ac tivity in the propene epoxidation reaction has been investigated, which shows that by reducing the size of gold nanoparticles, the yield of the product increases.	10
1.2.1.	The effect of nanoparticle distribution on the catalytic property in the oxidation reaction of carbon monoxide and its conversion to carbon dioxide (TOF in the vertical part is a standard diagram of catalyst activity).	11
1.2.2.	Relationship between angular and lateral surface atom fractions and catalytic activity of Pt nanoparticles in cubic, spherical, and quadrilateral structures.	12
1.2.3.	The effect of different oxide substrates on the catalyst activity of gold nanoparticles has been investigated and it is observed that in TiO_2 substrate, gold shows the most catalytic properties.	13
1.2.4	The structural changes are illustrated schematically.	14
1.3.	Major classes of size-sensitivity, which describe the relationships between NP size and turnover frequency for a given combination of reaction and NP catalyst. () negative size sensitivity; () positive size-sensitivity; () Mix of negative and positive sensitivity.	16
1.3.1.	Benefit of Nanocatalyst.	17
1.4.	Effect of intrinsic properties of nanomaterials on its catalytic activity.	18
2.	Two main methods of synthesizing nano-particles	19
2.1.	Method of nanoparticles synthesis	19
2.2.	Biological approach to nanoparticle synthesis	21
3.	Remediation of industrial wastewater using a nanocatalyst.	23
3.1.	Nanocatalyst in heavy metal remediation.	24
3.2.	Schematic representation of the main nanomaterials used as nanocatalysts in AOPs for the degradation of food dyes.	26

3.3.	The plausible photocatalytic mechanism for photocatalytic degradation of amaranth dye in the presence of Ag_2O nanoparticles decorated ZnO nanorod heterostructures under visible light irradiation.	27
3.4.	(a) Schematic design for the reduction of nitrobenzene with aqueous NaBH ₄ using nanocatalysts. (b) Classification of various nanocatalysts applied for the reduction of NAs to AAs.	27
	Schematic explanation for the reduction of 4-NP by NaBH ₄ catalyzed by Au nanocatalysts. (a) The reaction is driven rapidly in the absence of 4-NP. (b) The reaction rate is slower when the surface of Au nanocatalysts is decreased because of 4-NP binding resulting in the heterogeneous catalytic mechanism.	28
3.6.	Typical forms of sulfur compounds.	29
3.7.	The effect of pressure and temp. On the removal efficiency of sulfur compounds by HDS desulfurization.	30
3.8.	Nanocatalysts in AOPs and challenges for practical applications.	35
3.9.	Fabrication and catalytic-therapeutic schematics of sequential GFD NCs. a Synthetic procedure for $Fe_3O_4@DMSNs$ nanocatalysts and GODFe ₃ O ₄ @DMSNs nanocatalysts.	37

Abstract

Nanotechnology is no more new to the chemical community, daily development in this area have elevated it to the status of a decade-long buzzword. Catalysis is a key area of application in the nanoscience age, as all equipment and technologies are becoming smaller and more efficient. Nanocatalysts have emerged out with substantial characteristics concerning selectivity, activity, lifetime and recoverability. In this review article, we aim to compile information that has been published in the literature for the usage of nanosized catalysts in humankind's daily lives. Here, the primary uses of nanocatalysts are explored in detail, including their use in carbon nanotubes, energy storage, composite solid rocket propulsion, biodiesel synthesis, drug delivery, dye, and a number of other areas.

KEYWOED: Nanoparticle, Nanocatalyst, Green nanocatalyst, application.

1. Introduction

Nanotechnology has evolved as a highly technical research arena with potential applications in all spheres of life. The term "nano" has been derived from the Greek for "dwarf" (Arpita Roy et al, 2021). Nanoscience is the study of phenomena on a nanometer scale. Atoms are a few tenths of a nanometer in diameter and molecules are typically a few nanometers in size. The smallest structures humans have made have dimensions of a few nanometers and the smallest structures we will ever make will have the dimensions of a few nanometers. This is because as soon as a few atoms are placed next to each other, the resulting structure is a few nanometers in size. The smallest transistors, memory elements, light sources, motors, sensors, lasers, and pumps are all just a few nanometers in size like carbon nanotubes, grapheme etc (Shalini Chaturvedi et al,2011). Today nanotechnology plays an important role in industries and business. Due to the chemical and physical properties nanoscale materials in comparison to the macro and micro systems, they have opened up a new vision in application fields including optoelectronics, sensing, medicine and catalysis (Seyed mohammad vahdat et al,2013). Catalysis provides sustainable and cost-effective methods to transform raw materials into valuable chemicals. Thus, catalytic processes have long become essential to solving the energy and environmental challenges that we currently face around the globe. Catalysis can be broadly divided into homogeneous and heterogeneous catalysis. Homogeneous catalysis involves catalysts and reactants in the same phase. As homogeneous catalysts are generally soluble molecular or ionic compounds, they have more easily accessible active catalytic sites, and thus often exhibit good catalytic activity. Moreover, their structures and functional groups can easily be changed to result in chemo-regio-, and enantioselectivity. However, despite their many advantages and being widely used in industry, homogeneous catalysts do have some disadvantages, which is mainly to do with the fact that they are difficult to separate from the final products or reaction mixtures. Furthermore, even with the use of numerous techniques, such as chromatography, distillation, or extraction, the removal of trace amounts of residual catalytic species from the reaction mixture is always challenging in the case of homogeneous catalysis. This is an important issue that requires attention, given the fact that the presence of trace amounts of catalytic moieties, especially metallic ones, is strictly regulated in the commodity chemicals and pharmaceutical products, which are often produced using catalysts. All of these issues together, therefore, pose major hurdles for homogeneous catalysts, making many of them to have only limited applications. Some of these drawbacks of homogeneous catalysts can be overcome by supporting the homogeneous catalytic species on solid

support materials and producing their corresponding solid catalysts, known as heterogeneous catalysts. The general method used to create heterogeneous catalysts entails either immobilizing or attaching an active catalytic moiety to the solid support material. Heterogeneous catalysts frequently provide a number of benefits due to the physical attachment of the catalytic groups onto the solid support materials, including their simplicity in handling, effectiveness in recovery, increased stability and shelf-life, and reusability. However, because the reactants and the catalysts in heterogeneous catalysis must necessarily be in two different phases, the interaction between the reactant and the catalyst is reduced. Heterogeneous catalytic systems can reduce overall catalytic activity compared to homogeneous counterparts. This can be affected by possible leaching of active catalytic sites from solid support materials, such as the cleavage of covalent bonds between the catalytic groups and the solid support material, or the possible desorption of catalytic groups off the solid supporting material. Despite the smaller concentration of trace metals in heterogeneous catalytical systems, possible leached trace metals may still require separation from final products. To overcome some of the limitations associated with both homogeneous and heterogeneous catalysts, new catalytic systems were needed that could have the advantages of both homogeneous and heterogeneous catalytic systems, reactive activity should be accessible and effective to catalyze activity, selectivity, and yield, and enable catalyst separation. (Vivek Polshettiwar and Tewodros Asefa,2013). (Fig.1) exhibits to fundamental distinction in between homogeneous, heterogeneous and nano catalysts (Saurabh B. Somwanshi et al 2020).

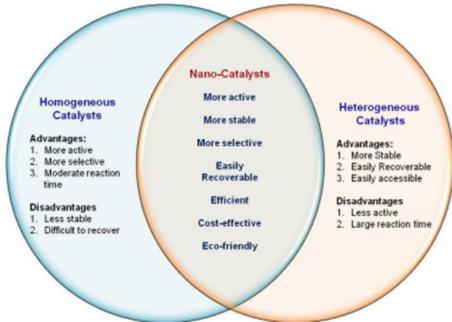


Fig.1 Difference between homogeneous, heterogeneous and nanocatalysts (Saurabh B. Somwanshi et al 2020).

1.1. Nanoparticle

Nanomaterials are those which have structured components with at least one dimension less than 100 nm. Materials that have one dimension in the nanoscale (and are extended in the other two dimensions) are layers, such as a thin films or surface coatings. Some of the features of computer chips come in this category. Materials that are nanoscale in two dimensions (and extended in one dimension) include nanowires and nanotubes. Materials that are nanoscale in three dimensions are particles, for example precipitates, colloids and quantum dots (tiny particles of semiconductor materials). Nanocrystalline materials, made up of nanometer-sized grains, also fall into this category. Some of these materials have been available for some time; others are genuinely new. Two principal factors cause the properties of nanomaterials to differ significantly from other materials: increased relative surface area, and quantum effects. These factors can change or enhance properties such as reactivity, strength and electrical characteristics. As a particle decreases in size, a greater proportion of atoms are found at the surface compared to those inside. For example, a particle of size 30 nm has 5% of its atoms on its surface, at 10 nm 20% of its atoms, and at 3 nm 50% of its atoms. Thus nanoparticles have a much greater surface area per unit mass compared with larger particles. As growth and catalytic chemical reactions occur at surfaces, this means that a given mass of material in nanoparticulate form will be much more reactive than the same mass of material made up of larger particles (Shalini Chaturvedi et al,2011).

Various sophisticated instruments have been used to characterize the nanomaterials to find out actual size, shape, surface structure, valency, chemical composition, electron band gap, bonding environment, light emission, absorption, scattering and diffraction properties which includes nuclear magnetic resonance spectroscopy (NMR), infra red spectroscopy (IR), ultra-violet and visible spectroscopy (UV-Vis), transmission electron microscopy (TEM), scanning tunnelling microscopy (STM), scanning electron microscopy (SEM), energy dispersive X-ray spectrometer (EDS), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), extended X-ray adsorption fine structure spectroscopy (EXAFS), X-ray absorption near-edge emission spectroscopy spectroscopy (XANES), X-ray (XES), photoluminescence spectroscopy (PL), small angle X-ray scattering (SAXS), atomic force microscopy (AFM), etc.(Santosh Bahadur Singh and Praveen Kumar Tandon, 2014).

1.2. Factors affecting the catalytic properties of nanomaterial's

Factors affecting the catalytic properties of nanomaterial's are:

- 1. The size of the nanoparticles.
- 2. The distribution of the nanoparticles.
- 3. The shape of the nanoparticles.
- 4. The preparation medium of the nanoparticles.
- 5. The reaction conditions
- 6. Structural effect

Nanoparticle size

In most cases, the smaller the nanoparticle size, the greater the catalytic properties (Figure1.2), but in some cases the catalytic properties do not increase with decreasing nanoparticle size. In the oxidation reaction of carbon monoxide using ruthenium nanoparticles in PVP substrate (PolyN-vinyl-2-pyrolidone), it has been shown that when ruthenium nanoparticles are 6nm in size, their catalytic activity is eight times that of 2 nm. It has also been proven that when gold nanoparticles with dimensions less than 5 nm are used, they show the highest activity and selectivity. Intermediate nanoparticles can have sizes in the range of less than 1 100 nm, but their greatest catalytic activity is observed when their size is around 1-10 nm. (Ehsan Kianfar,2020).

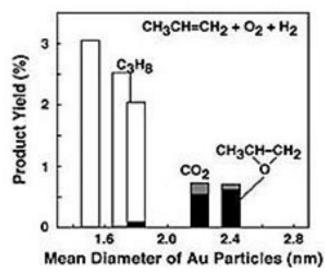


Fig 1.2 The effect of gold nanoparticle size on catalytic activity in the propene epoxidation reaction has been investigated, which shows that by reducing the size of gold nanoparticles, the yield of the product increases. (Ehsan Kianfar,2020).

Nanoparticles distributed

The spatial distribution of nanoparticles can also affect their catalytic properties. The higher the spatial distribution of the nanoparticles, the more catalytic properties increase as the number of surface atoms becomes available (Figure 1.2.1). In addition, it has been shown that the narrower the nanoparticle size distribution, the greater the catalyst activity. (Ehsan Kianfar,2020).

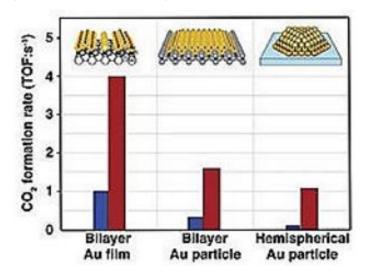


Fig 1.2.1 The effect of nanoparticle distribution on the catalytic property in the oxidation reaction of carbon monoxide and its conversion to carbon dioxide (TOF in the vertical part is a standard diagram of catalyst activity). (Ehsan Kianfar,2020).

The shape of nanoparticles

Considering the third factor, catalyst shape, Narayanan and El-Sayed showed that the distribution of the surface atoms in platinum nanoparticles strongly impacts the activity of the nanocatalyst system. For their study, they compared the ability of tetrahedral, cubic, and "near spherical" particles to catalyze the reaction of hexacyanoferrate (III) and thiosulfate ions and found that the catalytic activity correlates with the amount of atoms at corners and edges. Therefore, although having the same size, tetrahedral particles featuring a larger amount of edges and corners are considerably more active than spherical ones. (Sandro Olveira et al, 2014). Particles are said to have large curvatures when at the nanoscale, and their surface atoms are unstable. This effect is especially pronounced in non-spherical particles, particles that have many edge and corner locations, such as quadrilaterals, octagons, and cubes. In this case, as the surface-to-

volume ratio increases significantly, the nanomaterial's show more catalytic properties (Figure 1.2.2) this has been confirmed in most research studies using the X-ray diffraction technique and the observed efficiencies. It is worth mentioning that in the synthesis of colloidal nanoparticles by Bradley method (the most common method of synthesis of colloidal nanoparticles) by controlling the concentration ratio of nanoparticles to stabilizers or using different reluctant depending on the reaction, the desired shape can be synthesized. (Ehsan Kianfar,2020).

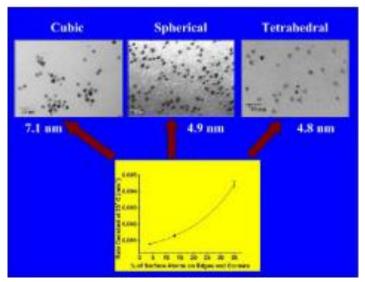


Fig 1.2.2 Relationship between angular and lateral surface atom fractions and catalytic activity of Pt nanoparticles in cubic, spherical, and quadrilateral structures. (Ehsan Kianfar,2020).

Nanoparticle preparation bed

Materials at the nanoscale have very high surface energy and tend to stick to each other. In most cases, nanoparticles are deposited on a substrate in different ways and then used in the reaction; The reason for this is that the substrate prevents the nanoparticles from accumulating and becoming socalled agglomerated, because when the nanoparticles accumulate, they become out of the nanoparticle state. The substrate traps nanoparticles on its surface through electrostatic and spatial interactions, reduces their surface energy, prevents their accumulation, and also stabilizes them. The effect that the substrate has on the catalytic properties of nanoparticles is different for different nanomaterial's and does not have a specific process and depending on the type of nanomaterial and the type of substrate used, the catalytic properties can be increased or decreased (Figure 1.2.3) .It has been shown that when ligand is used as a substrate in the preparation of nanocatalysts, the catalytic property decreases in most cases and when it is used as a substrate, the catalytic property increases in most cases. Various substrates – including polymers, dendrites, metal oxides, carbon nanotubes, and some ligands are used to make nanomaterial's, but polymer substrates are more common than others. The formation of nanoparticles in polymer substrates has been shown to increase the control of nanoparticles and can determine the state of nanoparticles on the surface, and in most cases increases the catalytic properties of nanomaterial's. Among polymeric substrates, PVP (PolyN-vinyl-2-pyrolidone) is the most commonly used substrate and is an inexpensive, linear polymer on which nanoparticles are uniformly dispersed. (Ehsan Kianfar,2020).

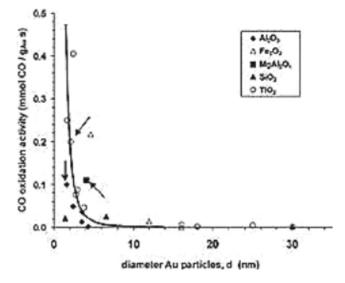


Fig 1.2.3 The effect of different oxide substrates on the catalyst activity of gold nanoparticles has been investigated and it is observed that in TiO_2 substrate, gold shows the most catalytic properties. (Ehsan Kianfar,2020).

Reaction conditions

Daniela de L. Martins et al. Heck reaction (reaction between an aryl halide with an allyl) between iodine benzene and styrene polymer by palladium nanoparticles in a Pt-PVP polyethylene substrate once under normal heating and once using They performed microwaves and observed that catalytic activity as well as selectivity to normal conditions (reflux) improved significantly when the reaction was performed under microwave conditions. The reason for this is that palladium nanoparticles absorb microwave waves and by absorbing these waves, heat transfer is accelerated and catalyst activity is increased. (Ehsan Kianfar,2020).

Structural effect

Important structural changes in the size and morphology occur during the preparation of nanocatalysts, but also when they are applied under certain conditions (e.g. during the course of a chemical reaction). The structural changes are illustrated schematically in (Figure 1.2.4) Materials have a higher specific surface when their particle size is reduced. To give an example, for a spherical dot of 1 µm across the volume, the surface-tovolume ratio is only 1%, but for a dot of 10 nm size it is 25%. The surfaceto-volume ratio reaches 100% when the solid is ca. 1 nm (sections of three atomic shells or less). The particle size reduction is often assisted by an enrichment in the surface defects (crystal edges, corners and faces). The effect on the catalyst performance also depends on how the accessible active sites are fitted into the porous structure and onto the surface of the support. Tuning the porosity characteristics of the support is an essential task in the design of functional catalysts. Porosity analysis not only provides data on the specific surface area $(m^2 g^{-1})$, pore sizes (nm) and volumes $(cm^3 g^{-1})$, but also on the pore morphology, topology and tortuosity (interconnection between the pores). (Rafael Luque and Pepijn Prinsen, 2019).

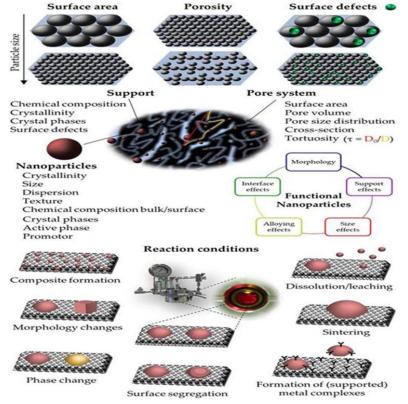


Figure 1.2.4. The structural changes are illustrated schematically. (Rafael Luque and Pepijn Prinsen, 2019).

1.3. Nanocatalyst

Catalysis is one of the pioneer applications of nanoparticles. Various elements and materials like I, iron, titanium dioxide, clays, and silica all have been used as catalysts in nanoscale for many years. But appropriate explanation of its tremendous catalytic behaviour showing by NPs still has not been fully understood. Unlike catalysts, nanocatalysts, due to their nanosize, have a larger surface area, allowing for better surface-volume interaction and, therefore, greater diffusion of reagents and products. Sometimes, to improve the efficiency of the process, these nanoparticles are dispersed on support, coupled, or doped with metals or adsorbents that have high porosity. The most commonly used support materials are zeolites, activated carbon, silicon film, and hybrid materials. Large surface area of nanoparticles has a straight forward positive effect on reaction rate and may also be a reasonable explanation of its catalytic activity. Structure and shape-based properties of any materials at its nanoscale size can also effect the catalytic activity of a material. The fine tuning of nanocatalysts, in terms of composition (bimetallic, core-shell type or use of supports), shape and size has accomplished greater selectivity. Thus the question here is how the physical properties of nanoparticles affect their catalytic properties, and how fabrication parameters can in turn affect those physical properties. By better understanding of these, a scientist can design nanocatalysts which are highly active, highly selective, and highly resilient. All these advantages will enable industrial chemical reactions to become more resource efficient, consume less energy, and produce less waste which help to counter the environmental impact caused by our reliance on chemical process. Nanoparticles are recognized as the most important industrial catalyst and have wider application ranging from chemical manufacturing to energy conversion and storage. Variable and particle-specific catalytic activity of nanoparticles is due to its heterogeneity and their individual differences in size and shape. (Santosh Bahadur Singh and Praveen Kumar Tandon ,2014). Although there is tremendous variation in the relationships between size and activity depending on the choice of catalyst and choice of reaction, these relationships are often broken into three primary groups: positive sizesensitivity reactions, negative size sensitivity reactions, and sizeinsensitive reactions. There is also a fourth category composed of reactions for which a local minima or maxima in activity exists at a particular NP size (Figure 1.3).

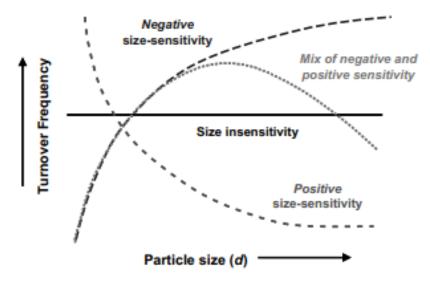


Figure 1.3. Major classes of size-sensitivity, which describe the relationships between NP size and turnover frequency for a given combination of reaction and NP catalyst. (-----) negative size sensitivity; (- - -) positive size-sensitivity; (.....) Mix of negative and positive sensitivity. (Karine Philippot and Philippe Serp,2012).

Positive size-sensitivity reactions are those for which turnover frequency increases with decreasing particle size. The prototypical reaction demonstrating positive size-sensitivity is methane activation. Dissociative bond cleavage via s-bond activation as the rate-limiting step is a common feature in reactions with positive size-sensitivity. Negative size-sensitivity reactions are those for which turnover frequency decreases with decreasing particle size. In this case, formation or dissociation of a p-bond is often the rate-limiting step. The prototypical reactions for this group are dissociation of CO and N₂ molecules, which each require step-edge sites and contact with multiple atoms. These sites do not always exist on very small NPs, in which step-edges approximate adatom sites. These reactions also sometimes fall into the fourth category of those with a local maximum in turnover frequency versus particle size because certain particle sizes geometrically favor the formation of these sorts of sites. The third type of reaction is the size-insensitive reaction, for which there is no significant dependence of turnover frequency on nanoparticle diameter. The prototypical size insensitive reaction is hydrocarbon hydrogenation on transition metal catalysts, for which the rate-limiting step is complementary associative s-bond formation. (Karine Philippot and Philippe Serp, 2012).

Nanostructured catalysts have been the subject of considerable academic and industrial research attention in recent times due to the numerous potential benefits that can accrue through their use (figure 1.3.1). (Santosh Bahadur Singh and Praveen Kumar Tandon ,2014).

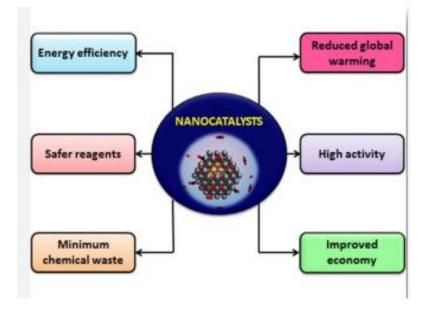


Fig 1.3.1. benefit of Nanocatalyst. (Ashu Chaudhary and Anshul Singh ,2017)

1.4. CONCEPT OF NANOCATALYSIS

Concept behind the nanocatalysis may be understood by considering the impact of the intrinsic properties of nanomaterials on catalysis. Intrinsic properties of nanomaterials that have a vital impact on their catalytic activity may be categorized as (i) quantities that are directly related to bond length, such as the mean lattice constant, atomic density, and binding energy. Lattice contraction in a nano-solid induces densification and surface relaxation., (ii) quantities that depend on the cohesive energy per discrete atom, such as self-organization growth; thermal stability; coulomb blockade; critical temperature for phase transitions, and evaporation in a nano-solid; and the activation energy for atomic dislocation, diffusion, and chemical reactions, (iii) properties that vary with the binding energy density in the relaxed continuum region such as the Hamiltonian that determine the entire band structure and related properties such as band gap, core level energy, photoabsorption, and photoemission and (iv) properties from the joint effect of the binding energy density and atomic cohesive

energy such as the mechanical strength Young's modulus, surface energy, surface stress, extensibility and compressibility of a nano-solid, as well as the magnetic performance of a ferromagnetic nano-solid. (Santosh Bahadur Singh and Praveen Kumar Tandon ,2014).

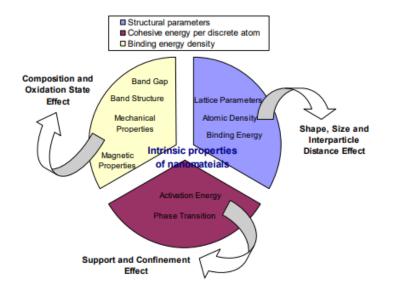


Fig 1.4. Effect of intrinsic properties of nanomaterials on its catalytic activity. (Santosh Bahadur Singh and Praveen Kumar Tandon ,2014).

2. Different Methods of Nanocatalyst Synthesis

Generally, there are two techniques for nanocatalyst synthesis: top-down and bottom-up (figure 2), (Sahar M. Abd Zaid, 2022). In the first method, the bulk material is broken down into smaller nanosized particles. Various metallic nanoparticles are composed of top-down methods such as etching, sputtering, and laser ablation. On the other hand, the bottom-up method involves joining a molecule by a molecule, atom by atom, and clusters by cluster. In this method, single molecules are explored to form a complex structure of nanoscale size. Various methods that use bottom-up techniques include supercritical fluid synthesis, plasma or flame spraying synthesis, laser pyrolysis, molecular condensation, the sol-gel process, chemical reduction, and green synthesis (Figure 2.1). In this technique, physicochemical reactions occur that may affect the properties of nanoparticles, and the nanoparticles are collected from smaller units. Therefore, both techniques are controlled by kinetic processes, which regulate the size and shapes of the synthesized nanoparticles. (Arpita Roy et al ,2021).

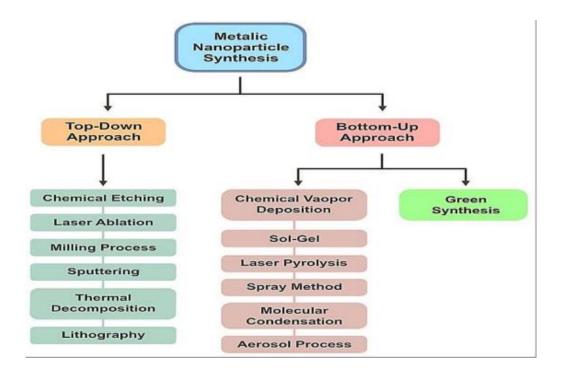


Fig2. Two main methods of synthesizing nano-particles. (Sahar M. Abd Zaid,2022).

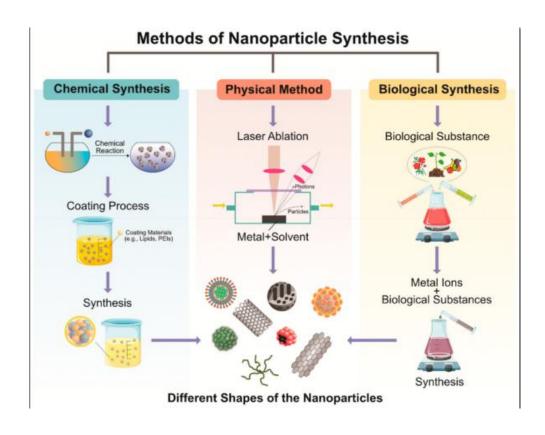


Fig.2.1 Method of nanoparticles synthesis.(Arpita Roy et al ,2021).

2.1. Biological Approach for Nanocatalyst/Nanoparticle Synthesis

The biological method is preferred over the other two conventional methods (top-down and bottom-up) as it is a green method, environmentally friendly, and does not require a higher energy consumption. Nanoparticles obtained through the biological approach have a greater specific surface area, increase the rate of catalysis, and have metal salt and improved enzymes. Hence the main objective in the synthesis of nanoparticles using a biological approach is to utilize cheap resources and facilitate a continuous production of nanoparticles. Biological sources that are used for nanoparticle synthesis provide a simple method and easy increase in biomass, ensuring a uniform particle size, as well as multiplication. The use of microbes is one of the most prominent methods among the biological approaches of nanoparticle synthesis. It utilizes different biological sources such as bacteria, fungi, and algae (Figure 2.2). Bacteria are the most commonly found organism in our biosphere. Under optimal conditions such as pH, temperature, and pressure, bacteria show the capability to synthesize various nanoparticles. The ability of bacterial cells to survive and proliferate under extreme climatic conditions make them the most ideal organisms for nanoparticle synthesis. They can reproduce and multiply even under high metal concentrations, which may be due to particular resistance mechanisms. Example, Parikh et al. reported the synthesis of silver nanoparticles using a bacterial strain, i.e., Morganella sp., which was isolated from an insect midgut. When exposed Synthesized crystalline silver nitrate, Morganella to sp. silver nanoparticles extracellularly. The nanoparticles produced by microorganisms have important uses in the biological field such as bioleaching, biocorrosion, biomineralization, and bioremediation. In addition to bacteria, fungi and algae are two other green sources that are capable of synthesizing nanoparticles. Fungi have an outstanding ability for the synthesis of various bioactive compounds that have potential for numerous applications. They are widely used as reducing and stabilizing agents and can be easily grown on a large scale for the production of nanoparticles with controlled shape and size. Various fungal species such as Fusarium oxysporum, Asperigillus oryzae, Verticillium luteoalbum, Alternata alternata, and Collitotrichum sp. Were utilized for nanoparticles synthesis. However, some of the drawbacks of using fungi include laborious and more costly downstream processes. Mukherjee et al. reported the production of gold nanoparticles by Verticillium sp. Where the intracellular gold nanoparticles were located on the mycelial surface. Similarly, algae have the ability to synthesize various bioactive compounds, pigments, and proteins, which help in the reduction of salts and act as capping agents in the synthesis mechanism. They are present in various environments such as marine water and freshwater. They are classified into macroalgae and microalgae and are used for various commercial purposes. They possess various advantages such as less toxicity, requiring low temperature for synthesis. Mata et al. reported a reduction of Au (III) to Au (0) using the biomass of the brown alga Fucus vesiculosus, and the synthesized nanoparticles were spherical. (Arpita Roy et al, 2021).

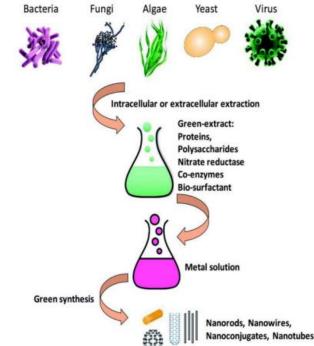


Fig2.2 Biological approach to nanoparticle synthesis. (Arpita Roy et al,2021).

2.2. Synthesis of green nanocatalysts

Green chemistry is generally accepted as "the design, development, and implementation of chemical processes and products to reduce or eliminate substances hazardous to human health and the environment". The idea of performing this kind of chemistry is gaining prominence amongst the players in the chemical industry, as today's major challenges are to achieve sustainable production processes, having lower energy consumption and less environmental impact. Additionally, greener production processes might also prove to be economically beneficial for the companies. (Sandro Olveira et al ,2014).

2.2.1. Silica nanoparticles

Silica nanoparticles that are mild and environmentally benign have been used as catalysts for synthesis of highly substituted pyridines. These catalysts retained most of their catalytic activity after being reused three times. Silica colloids and nanoparticles can be easily synthesized using the Stoeber synthesis method and redispersed in water which is an environmentally friendly solvent. Environmentally friendly silica nanoparticles have been used as catalysts for the synthesis of thioethers, thioesters, vinylthioethers, and thio-Michael adducts (Radha Narayanan ,2012).

2.2.2 Platinum nanoparticles

can be synthesized using a variety of green methods such as the hydrogen reduction method in water as solvent, ethanol reduction method in an ethanol-water mixture in which the ethanol can be rotovaped, and several other green methods. Monodisperse green platinum nanoparticles were synthesized by using glucose as the reducing agent and starch as the stabilizer. This synthesis method is simple, environmentally friendly, highly reproducible, and easy to scale up. These nanocatalysts were tested for reduction and oxidation reactions and were found to have high catalytic activity. Monodisperse platinum nanoparticles that are stabilized with ionic liquids have been used as catalysts for four-electron reduction of dioxygen to water. (Radha Narayanan ,2012).

2.2.3 Nickel-platinum nanoparticles

Bimetallic nanoparticles have been synthesized using the ethanol reduction method, hydrogen reduction method, and other green methods. Nickel encapsulated by Pt (NiPt) has been synthesized using a green colloidal method. Platinum nanoparticles are very expensive as electrocatalysts so the remedy for this is to reduce the cost by the synthesis of NiPt bimetallic nanoparticles. (Radha Narayanan ,2012).

3. Application of Nanocatalyst

3.1. Nanocatalysts in Dye Degradation

Due to the increasing population and use of dye in textiles, food, and other industries, the release of untreated waste into the water bodies is contaminating the environment at a rapid rate, due to which there is a growing demand for newer and more efficient technologies for the removal of these substances from the environment. Nanosized materials can be used to detoxify harmful organic and inorganic chemicals from the environment due to their ultrafine size, high aspect ratio, and interaction-dominating characteristics. Nanoparticles have generated a lot of interest due to their numerous uses in disciplines such as catalysts, detection, and environmental cleanup, such as the adsorption and degradation of different pollutants from liquid medium (figure 3). (Arpita Roy et al,2021).

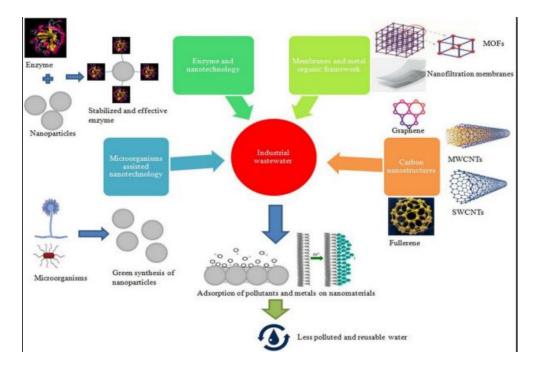


Figure 3. Remediation of industrial wastewater using a nanocatalyst. (Arpita Roy et al,2021).

3.2. Nanocatalysts in Heavy Metal Remediation

Heavy metals are detrimental contaminants that are toxic both in soluble and elemental forms. Diverse activities, including the development of industries, absurd waste management, defective landfill operations, and manufacturing and mining, lead to increased contamination of metals in soil and water. The traditional method for heavy metal removal includes reverse osmosis, chemical precipitation, ion exchange filtration, evaporation, and membrane technology. However, the cost of these methods is occasionally higher; therefore, a cost-efficient and environmentally friendly method is of prime importance. Various microbial-derived nanocatalysts have been reported to show remediated heavy metals (Figure 3.1). (Arpita Roy et al,2021).

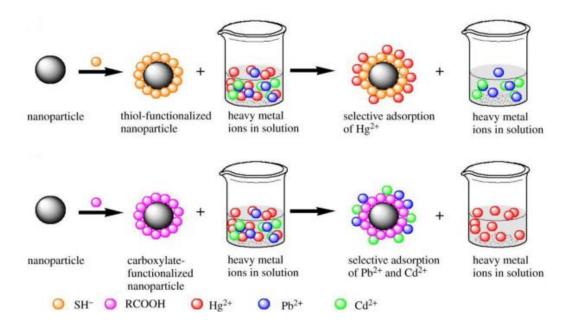


Figure 3.1. Nanocatalyst in heavy metal remediation. (Arpita Roy et al,2021).

3.3. Nano-TiO₂ catalyst in dye electrochemical treatment

Electrochemical technology is receiving more and more attention, for its success in removing colour without the production of a secondary pollutant and due to its convenience and simplicity. The exact mechanisms, which occur during the electrolysis, are complicated and not entirely clear. Based on the intermediate products and radicals that can be determined in the electrolysis, such as O_3 , H_2O_2 , Cl_2 , O_2 , OH, ClO- and other oxidants, it is postulated that organic pollutants could be oxidised directly or indirectly. It is herewith reported that the presence of a catalyst in the electrical field can enhance the treatment efficiency. Chen WG (Chen WG and Zhu, 1998) has used metal dioxide to remove three types of organic pollutants, phenol, phenylamine and di-mephthalate from wastewater. The presence of H_2O_2 and OH was verified during the electrolytical catalysis process. The results showed that the removal efficiency depended on the reactive

intermediate yield in the system. Organic pollutants were effectively removed by increasing the H_2O_2 yield. The removal of xenobiotic compounds, such as chlorophenols and pesticides, from municipal and industrial wastewater is very important because of their toxicity and their bioaccumulation tendency. Among the several methods proposed, photodegradation catalysed by suspending inorganic semiconductors (i.e TiO₂) has lately received wide attention because this process leads to non-toxic final products and shows high degradation efficiency. The TiO₂ electrode has been used to degrade 4-chlorophenol and dyes. (Yangming Lei et al ,2005).

3.4. Application of Nanocatalysts in Photocatalytic Processes for the Treatment of Food Dyes

The use of food additives (such as dyes, which improve the appearance of the products) has become more prominent, due to the rapid population growth and the increase in demand for beverages and processed foods. The dyes are usually found in effluents that are discharged into the environment without previous treatment; this promotes mass contamination and alters the aquatic environment. In recent years, advanced oxidation processes (AOPs) have proven to be effective technologies used for wastewater treatment through the destruction of the total organic content of toxic contaminants, including food dyes. Dyes are complex unsaturated aromatic compounds that exhibit good color, intensity, and solubility. Scotter classified food dyes into six groups according to their chemical structures: Azo (monoazo, diazo, and triazo), triarylmethane, azopyrazolone, xanthene, quinoline, and indigoid. (Figure 3.2) shows several of the different known structures of nanocatalysts that can mediate the degradation of food dyes.(Jennifer María Navia-Mendoza et al , 2021).

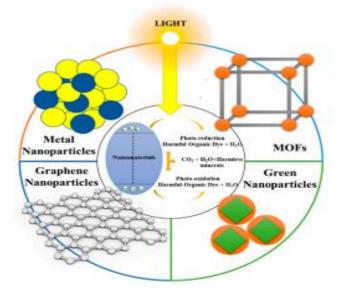


Figure 3.2 Schematic representation of the main nanomaterials used as nanocatalysts in AOPs for the degradation of food dyes. (Jennifer María Navia-Mendoza et al , 2021).

Oxide-based nanocatalysts are inorganic types that are generally prepared with metals and non-metals, which are widely used for the removal of hazardous pollutants from wastewater. They are characterized by high BET surface area, lower solubility, minimal environmental impact, and absence of secondary pollutants. Metal oxide nanocatalysts are classified into three generations: the first generation is composed of a single com- ponent, such as TiO₂ and ZnO; the second generation is composed of multiple components in a suspension, e.g., WO₃/NiWO₄, BiOI/ZnTiO₂; and finally, the third generation is formed by photocatalysts immobilized on solid substrates (FTO/WO₃ -ZnO, Steel/TiO₂ - WO₃). There are three natural states of the nanocatalyst, anatase, rutile, and brookite, with anatase being the best nano-photocatalyst, and is usually effective in degrading anionic, cationic dyes, and dyes with different chromophore groups. Through reaction photogenerated photocatalytic processes (Figure 3.3), electron/hole pairs actively participate in the chemical reac- tions for he generation of superoxide radicals and oxidizing agents, which are responsible for the degradation of the dye. Photocatalytic activity was measured by the degradation of Amaranth dye under visible light irradiation, exhibiting a photocatalytic yield of about 94% in 30 min. These heterostructures showed a synergistic effect, which was more effi- cient than pure ZnO nanowires and Ag₂O NPs separately, even presenting higher activity under visible light irradiation than commercially available photocatalysts, such as Merck ZnO, TiO₂-P25, and TiO₂-PC-50.

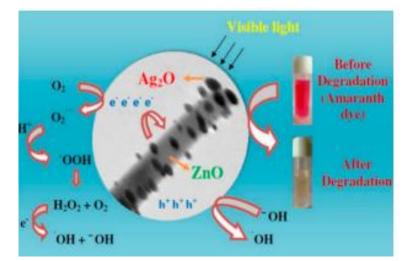


Figure 3.3 The plausible photocatalytic mechanism for photocatalytic degradation of amaranth dye in the presence of Ag_2O nanoparticles decorated ZnO nanorod heterostructures under visible light irradiation. (Jennifer María Navia-Mendoza et al , 2021).

3.5. Nanocatalyst-Assisted NaBH₄ Reduction of Nitroaromatics in Water

The reduction of nitroaromatics (NAs) is a common and facile route to produce aminoaromatics (AAs), which are very significant intermediates for the synthesis of several nitrogen-containing compounds, such as agrochemicals, pharmaceuticals, polymers, dyes, pesticides, and cosmetics.Several toxic NAs are responsible for serious environmental pollutions.However, they can be transformed into AAs, that is, nitrophenol (NP) conversion into harmless aminophenols (AP), which are potential intermediates for accessing pharmaceuticals and dyes via the reduction process (Figure 3.4).

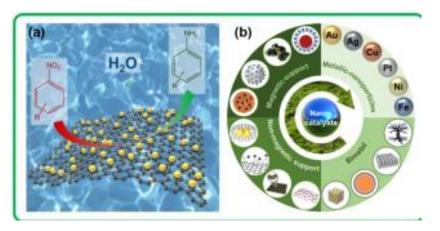


Figure 3.4 (a) Schematic design for the reduction of nitrobenzene with aqueous $NaBH_4$ using nanocatalysts. (b) Classification of various nanocatalysts applied for the reduction of NAs to AAs. (Kaiqiang Zhang et al, 2019).

Monometal nanocatalysts used in NaBH₄ reduction of NAs, generally, noble- and transition metal NPs such as palladium (Pd), platinum (Pt), ruthenium (Ru), and silver (Ag), are synthesized and directly employed as nanocatalysts in the hydrogenation of various NAs using aqueous NaBH₄ as the reductant. Mahmoud et al. concluded, while reducing 4-NP, that the reaction yield is a function of free surface area of the NPs. In this study, the mechanism of 4-NP reduction by Au nanocatalysts was investigated using NaBH₄ in solution. The reduction process can be achieved either on the NP surface following the heterogeneous mechanisms or by the leached atoms or ions from the NPs (homogeneous mechanism) in the solution. Considering the plasmonic effect of Au NPs and measuring the dependence of the reaction yields on the surface area of the nanocatalyst by the adsorption isotherm of binding 4-NP and the changes of the plasmonic extinction band position of the NPs during the reactions, the researchers concluded that it is the surface heterogeneous-type mechanism and not the homogeneous path by the leached atoms in the solution (Figure 3.5) that is involved. (Kaiqiang Zhang et al, 2019).

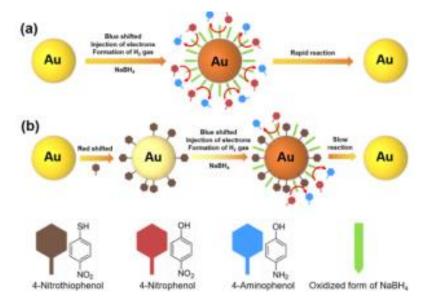


Figure 3.5 Schematic explanation for the reduction of 4-NP by NaBH₄ catalyzed by Au nanocatalysts. (a) The reaction is driven rapidly in the absence of 4-NP. (b) The reaction rate is slower when the surface of Au nanocatalysts is decreased because of 4-NP binding resulting in the heterogeneous catalytic mechanism. (Kaiqiang Zhang et al , 2019)

3.6. Nano-catalyst Applications in Kerosene Desulfurization

Kerosene is a clear, thin liquid, one of the petroleum products, It is obtained from the fractional distillation of crude oil between 150-275°C with a combination of carbon chains that contains between 6 and 16 carbon atoms per molecule, Sulfur is the 3rd abundant component after carbon and hydrogen in oil. The appearance of sulfur compounds in petroleum productions creates erosion in refinery equipment and poisoning of downstream catalysts, Moreover emissions SOx from engines cause serious environmental pollution such as respiratory diseases and acidic rain. Typical forms of sulfur compounds are summarized in (Figure 3.6). (Sahar M. Abd Zaid et al ,2022).

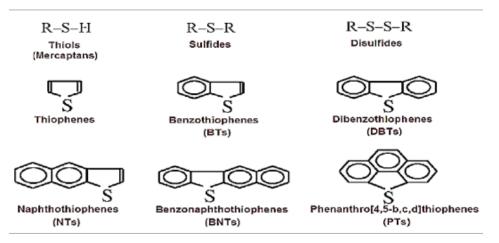


Figure 3.6 Typical forms of sulfur compounds. (Sahar M. Abd Zaid et al ,2022).

The desulfurization of kerosene was investigated using several technologies include* Hydrodesulfurization (HDS) is a well-known desulfurization process. It can handle a variety of liquid fractionation streams, from low to high boiling fractions. The mixture is forced to flow through a catalytic bed of metal oxides (usually cobalt or molybdenum oxides on various metal carriers), which aids in the formation of hydrogen sulphide (H₂S) by allowing hydrogen to react with sulphur. A multitude of variables influences HDS performance, including operating parameters like pressure, catalyst type, temperature, and reactor design. In (Figure 3.7) the researchers studied two main factors, pressure and temperature, and their effect on the efficiency and performance of the HDS process and can be seen that increasing pressure and increasing temperatures improves the efficiency of the removal process. (Sahar M. Abd Zaid et al ,2022).

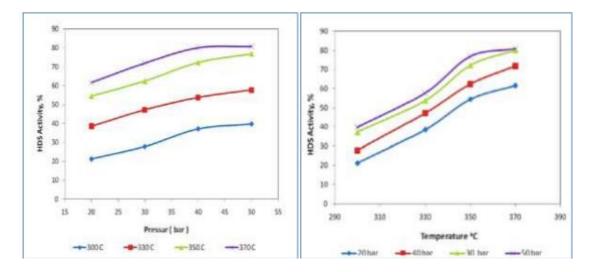


Figure 3.7 The effect of pressure and temp. On the removal efficiency of sulfur compounds by HDS desulfurization. (Sahar M. Abd Zaid et al ,2022).

*Adsorption Desulfurization (ODS), An adsorption technique is commonly designed to provide selective sulfur compound elimination, work at ambient conditions with no difficulty of process control, attain high sulfur removal from fuel oils at a reasonable cost, and easiness of restoration with low chemicals and operating power, contrary to the HDS process. Adsorption happens when a gas or liquid accumulates on the absorbent material's surface in a succession of phases. The adsorption mechanism is generally divided into four phases: (1) bulk diffusion, (2) film spread, or external mass propagation (diffusion across the boundary layer from the bulk fluid to the adsorbent (solid) surface), (3) Adsorbent pore propagation (intraparticle propagation): propagation from the adsorbent's outer surface into its pores. (4) Adsorption between the active sites of the adsorbent (physical and/or chemical contact).

*Catalytic Oxidation Desulfurization (CODS), This process has been considered the most promising method because of its mild operation conditions, and in comparison, to the HDS, it has a higher selectivity in removing aromatic sulfur compounds. Early studies on the CODS technique were conducted utilizing (NO2) as an oxidizing agent and methanol as solvent. From that on, other oxidizers have been tested like H_2O_2 , HNO₃, N₂O, NaClO, NaClO₂, NaBrO, and PhIO. The oxidizer gives O₂ atoms to the S–compounds to generate sulfones or sulfoxides. Among all the oxidants mentioned, H_2O_2 has been the best candidate. Is characterized by low cost, environmentally friendly, and availability. The major drawback of utilizing H_2O_2 is the slow rate of reaction. (Sahar M. Abd Zaid et al ,2022).

3.7. Hydrogen Energy Carrier

Nano-sized carbon materials (NCMs), especially carbon nanotubes (CNTs) have attracted a lot of attention because of their unique physical and mechanical properties. CNTs have been used in many fields as field emission sources, electric nano-conductors, Li ion secondary batteries, electric double-layer capacitors, fuel cells, and molecular sieves, electric nanoconductors. Due to its high porosity, light weight, structural stability, and non-expensive development, CNTs have recently been used to adsorb hydrogen. Their unique tubular structure is favorable for hydrogen uptake. Hydrogen, owing to its high energy content and non-polluting nature, is considered as an ideal energy carrier which may be widely utilized in the near future. According to the literature, the material characteristics of CNTs, governed by preparation procedures, significantly affect their hydrogen storage capability. Chang et al. (2008) studied, a novel NCMs preparation method utilizing the Metal Dusting (MD) process which is developed. Moreover, the possibility of using the produced CNTs as a hydrogen storage material, which has not been explored in the literature. The effects of acid post-treatment on the microstructure and hydrogen storage performance of the CNTs are also evaluated. The as-prepared multi-wall CNTs produced at 600C show a hydrogen discharge capacity of 57 mAh/g; which was measured; using an electrochemical method under room temperature and pressure. It was found that the post acid treatment in boiling nitric acid solution for 4 h can effectively remove metal particles and deposited amorphous carbon from the as-prepared CNTs. (Shalini Chaturvedi et al ,2012).

3.8. Water purification

The use of silver (Ag) nanocatalysts in water purification is a popular strategy as this catalyst is highly efficient in controlling microbes in water. Additionally,Ag-supported catalysts are reusable.Besides Ag nanocatalyst, the combination of Al_2O_3 and carbon like low acidity, high mechanical strength and presence of meso pores in carbon coverage in alumina (CCA) are also helpful for designing highly active AgCCA catalystis also used for water purification. This combination of nanomaterials possesses low acidity, high mechanical strength and contains mesopores, which are essential for the water purification process. (Shalini Chaturvedi et al ,2012).

3.9. Bio diesel production

The combustion of fossil fuels produces many harmful gases that negatively affect the environment. Additionally, the reduction in petroleum reserves has prompted scientists to search for alternative renewable fuels .Biofuel is the monoalkyl esters of fatty acids, regarded to be a promising alternative renewable fuel. Many countries such as Germany, Japan, France, Italy, and the USA are currently replacing petroleum fuel with biofuel. Recently, biofuels have been prepared using the "green" method based on heterogeneous catalysts .Heterogeneous catalytic methods have certain disadvantages: they are typically resistant to mass transfer, timeconsuming, and inefficient. These shortcomings can be overcome with the development of nanocatalysts, which possess high specific surfaces and have greater catalysis abilities. Scientists have reported that the use of solid base nanocatalyst KF/CaO in biodiesel production yielded more than 96% of biofuel. An X-ray diffraction (XRD) analysis revealed that this nanocatalyst has a large specific surface area and pore size that effectively improved transesterification efficiency. (Dr.priyom bose, ph.d, 2021).

3.10. Photocatalytic Decolorization

Large amounts of textile dye (e.g., malachite green dye, methylene blue, azo dyes, etc.) effluents are often discharged into water bodies without processing, negatively affecting aquatic ecosystems. For example, marine organisms are affected by the coloration of the dye effluents, the toxic substances present in the dye-containing wastewater, enhancement of the chemical oxygen demand (COD), and biochemical oxygen demand (BOD) level. Coloration in the water bodies inhibits the penetration of the sun's rays and, hence, the photosynthetic activity of aquatic flora is affected. Many conventional processes, such as ozonation, incineration, and adsorption on solid phases, which have been introduced to process dye effluents, have certain limitations. However, a new method called heterogeneous photocatalysis, which utilizes nanocatalysts (e.g., ZnO, Nb₂O₅, and TiO₂), is a powerful alternative that can degrade harmfulorganic dye contaminants. (Dr.priyom bose, ph.d, 2021). Among the mentioned nanocatalysts, TiO₂ nanotubes are most favorable because of their high catalytic efficiency, high chemical stability, costeffectiveness, and toxicity. Another advantage of this nanotube is that it can be recycled and reapplied in many photodegradation cycles. According to new research, TiO₂ nanotubes could maintain 80% activity even after ten cycles of reaction.

3.11. In drug delivery

Drug designing at the nanoscale has been studied extensively and is by far, the most advanced technology in the area of nanoparticle applications because of its potential advantages such as the possibility to modify properties like solubility, drug release profiles, diffusivity, bioavailability and immunogenicity. This, can consequently lead to the improvement and development of convenient administration routes, lower toxicity, fewer side effects, improved biodistribution and extended drug life cycle.(Jayanta Kumar Patra et al., 2018). Carbon nanomaterials are of great interest in applications for biological fields. Typically, carbon nanotubes (CNTs) have a feature of endohedral filling of 2–10 nm in diameter leading to encapsulation of small molecules. Accordingly, CNTs may be suitable for bio-applications in biorecognition and drug delivery systems. Oh et al. (2010) reported the fabrication of carbonized polypyrrole nanoparticles (CPyNs) with controlled diameters and their textural properties, and are potential for use as imaging probes and drug carriers due to their porosity, magnetic property and biocompatibility. The guest molecule loading of CPyNs was conducted with pyrene as a typical hydrophobic dye and the guest molecule-releasing test was performed with ibuprofen as a common hydrophobia drug. Their magnetic property provided the selective separation and targeting of the nanoparticle, while their smaller size and amine surface modification provided an improved sustained property. These advantages open the way to use in fields such as biomaterials science, including bioimaging and magnetic induced drug carriers. (Shalini Chaturvedi et al ,2012).

3.12. Photo catalytic degradation of Azo dyes

Liu et al. (2005a,b) examined the photocatalytic degradation of three azo dyes, acid orange 7 (AO7), procion red MX-5B (MX-5B) and reactive black 5 (RB5) using a new type of nitrogen-doped TiO₂ nanocrystals. These newly developed doped titania nanocatalysts demonstrated high reactivity under visible light ($\lambda > 390$ nm), allowing more efficient usage of solar light. Experiments were conducted to compare the photocatalytic activities of nitrogen-doped TiO₂ nanocatalysts and commercially available Degussa P25 powder using both UV illumination and solar light; result shown that nitrogen-doped TiO₂ after calcination had the highest photocatalytic activity among all three catalysts tested, with 95% of AO7 decolorized in 1 h under UV illumination. The doped TiO₂ also exhibited substantial photocatalytic activity under direct sunlight irradiation; with 70% of the dye color removed in 1 h and complete decolorization within 3h. Degussa P25 did not cause detectable dye decolorization under identical experimental conditions using solar light. The decrease of total organic carbon (TOC) and evolution of inorganic sulfateSO₄^{2–}ions in dye solutions were measured to monitor the dye mineralization process. (Shalini Chaturvedi et al ,2012).

3.13. In solid rocket propellants

The use of aluminum particles of sub-micrometer size in the combustion of composite solid propellants has gained recent attention. Several facets of this application have been reported, such as production, thermal decomposition in combination with ammonium perchlorate (AP), surface coating of aluminum particles, ignition and oxidation or combustion of aluminum particles including bimodal blends of micrometer and submicrometer sized particles, aluminized composite propellants, and collection of aluminum agglomerates formed during the combustion of aluminized propellants. Jayaraman et al. (2009) studied nano-aluminum particles of 50 nm size are added to composite solid propellants based on ammonium perchlorate and hydroxyl-terminated poly-butadiene binder has gained much attention. This is because aluminum nanoparticles could plateau the burning rate trends. Scientists have stated that replacing micro-aluminum with nano-aluminum has enhanced the propellant burning rate by around 100%. (Shalini Chaturvedi et al ,2012).

3.14. Waste water treatment

Halogenated organic compounds (HOCs) are among the most widely distributed water pollutants in industrialized countries. HOCs are mostly hazardous and toxic compounds which have very often a high persistence and may cause serious health problems such as cancer or mutagenic damage. Therefore, a complete destruction of these compounds is aspired or even mandatory. Nanosized palladium catalysts are used in wastewater treatment, either cyclic batch or continuous flow-through reactor. (Shalini Chaturvedi et al ,2012). Many conventional methods such as activated sludge processes, waste stabilization ponds, sequencing batch reactors, membrane filtration methods, coagulation-flocculation, adsorption, etc., have been studied to remove chemical oxygen demand (COD) and inorganic contaminants. However, hazardous contaminants were observed in the effluents of treated wastewater using conventional treatment processes. This poses a severe threat to the environment and requires serious efforts to solve the problem. The hazardous contaminants that were

even observed in the effluents of treated wastewater using conventional treatment processes include organic pollutants, pathogens, heavy metals, pharmaceuticals, endocrine disrupting chemicals, and many other persistent organics. To conquer the deficiencies of conventional treatment technologies and for the reduction of significant pharmaceuticals, the coupling of AOPs must be established because these complex pollutants could not be removed completely by conventional treatment technologies. To conclude, this method is for efficient elimination of pharmaceuticals and safe discharge of hospital wastewater yet challenging. Advanced oxidation processes can be defined as the processes and technologies which involve the generation of active species such as hydroxyl radicals (•OH) which act as efficient oxidants to decompose pollutants in wastewater treatment. Hydroxyl radicals are very reactive and non-selective species that are proficient in rapidly degrading a wide range of organic compounds. AOPs, including catalytic ozonation processes, radiation-based AOPs, ultrasound, electro-catalytic oxidation, Fenton etc., were found to be highly for the treatment of reclaimant organic contaminants. efficient Nanocatalysts in AOPs and their challenges for practical application are shown in (Figure 3.8). (ShaliniChaturvedi et al ,2012).

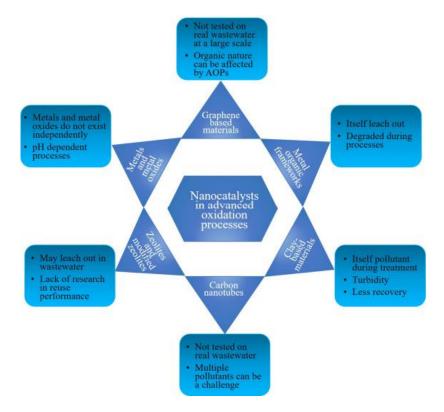


Figure 3.8 Nanocatalysts in AOPs and challenges for practical applications.

3.15. Tumor-selective catalytic nanomedicine by nanocatalyst delivery

Chemotherapy, the most conventional modality for cancer therapy, suffers from severe side effects on account of the low bioavailability and tumortherapeutic specificity. A number of physical therapeutic modalities, such as radiation1, ultrasound, photoacoustic/photothermal or microwave therapies, are capable of positioning the therapeutic sites by imagingguidance, but these strategies may also cause severe damages to surrounding normal tissues and/or induce undesired tumor metastasis. To focused achieve more and tumor-specific a therapy, tumor microenvironment (TME) has been broadly exploited recently, in which the cellular metabolism, biosynthetic intermediates and physical environment are prominently different from those in normal tissues. TMEresponsive drug releasing and diagnostic imaging have been extensively developed, however the introduction of toxic anticancer agents would still induce undesired distribution to normal organisms and damage these tissues subsequently. Hence, it is here conceived that, if the intrinsic substances in the TME, which are naturally non-toxic and biocompatible, could be in situ transformed into toxic agents against tumors with significant therapeutic efficacy based on the specific features of TME, under the stimuli of intratumor-delivered non-toxic agent (s) or procatalyst(s), the tumor therapy will be realized without or with minimized harmful side effects. Tumor therapy can only trigger the therapeutic process within tumorous tissues, achieving high therapeutic efficacy and minimal damage to normal tissues and/or organs. Synthetic reactions can be used to determine the optimal therapeutic process, based on the available nanocatalysts. Ferromagnetic nanoparticles (y-Fe₂O₃ or Fe₃O₄ NPs) have been revealed to perform dual enzyme-like activity both in vitro and in vivo in a pH-dependent manner. These iron oxide nanoparticles (IONPs) could catalytically decompose H₂O₂ into non-toxic H₂O and O₂ under neutral pH condition, presenting catalase-like activity. More interestingly, they could disproportionate H₂O₂ into highly toxic reactive oxygen species (ROS) - hydroxyl radicals (·OH), displaying peroxidaselike activity under acidic condition. Therefore, IONPs are considered as potential tumor-therapeutic nanozymes because such a site-specific generation of the hydroxyl radicals could induce the apoptosis and death of cancer cells under the mildly acidic microenvironment of tumor, leaving the normal cells unharmed. However, the intracellular H₂O₂ level in tumor cells is too low for IONPs to generate high enough amount of hydroxyl

radicals to produce satisfactory catalytic performance even under the catalysis of Fe₃O₄ NPs. Therefore, a strategy to elevate the intratumoral H_2O_2 level is to be developed. The design and fabrication of the sequential nanocatalyst are illustrated in (Fig 3.9). GOD, (size: 6.0 nm × 5.2 nm × 7.7 nm) and synthetic ultrasmall Fe₃O₄ NPs (size: 2 nm), were successively integrated into the large mesopores (~40 nm) of dendritic mesoporous silica nanoparticles (DMSNs) to form a composite nanocatalyst for sequential catalytic reactions directly within the tumor tissue, designated as GOD-Fe3O4@DMSNs nanocatalysts (GFD NCs). (Minfeng Huo et al, 2017).

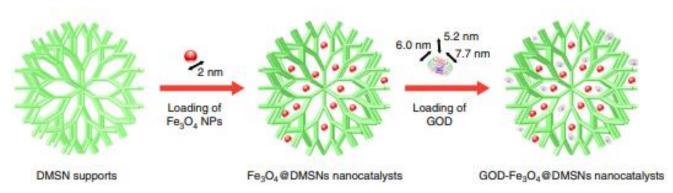


Fig 3.9 Fabrication and catalytic-therapeutic schematics of sequential GFD NCs. a Synthetic procedure for $Fe_3O_4@DMSNs$ nanocatalysts and GODFe₃O₄@DMSNs nanocatalysts. (Minfeng Huo et al, 2017).

Conclusion

In the last ten years, both homogeneous and heterogeneous catalysis have experienced tremendous growth in the field of nanocatalysis (the use of nanoparticles to catalyze reactions). Since they have a higher surface-tovolume ratio than bulk materials, hence they are striking materials to be used as catalysts. These nanocatalysts are used in many chemical reactions to increase the reaction rate and product efficiency. Nanomaterials provide various applications such as dye degradation, heavy metal remediation, photocatalytic decolorization, drug delivery, Tumor-selective catalytic nanomedicine and biological activity etc,. Nanotoxicity should also be taken into account because it can occasionally have a negative impact on both human and animal health. Regulation and laws can be implemented to address this, and researchers must collaborate on multidisciplinary studies across a range of medical sciences, nanomedicine, nanotechnology, and biomedical engineering sectors.

References

Roy, A., Elzaki, A., Tirth, V., Kajoak, S., Osman, H., Algahtani, A., Islam, S., Faizo, N.L., Khandaker, M.U., Islam, M.N., Emran, T.B. and Bilal, M. (2021). Biological Synthesis of Nanocatalysts and Their Applications. *Catalysts*, [online] 11(12), p.1494. Available at: https://www.mdpi.com/2073-4344/11/12/1494.

Somwanshi, S.B., Somvanshi, S.B. and Kharat, P.B. (2020). Nanocatalyst: A Brief Review on Synthesis to Applications. *Journal of Physics: Conference Series*, 1644(1), p.012046.

Santosh Bahadur Singh and Praveen Kumar Tandon (2014), "Catalysis: A Brief Review on Nano-Catalyst.", Journal of Energy and Chemical Engineering, Vol. 2 Iss. 3, PP. 106-115.

Abd Zaid, S., AbdulRazak, A. and Abid, M. (2022). A Review of Nanocatalyst Applications in Kerosene Desulfurization Techniques. *Journal of Applied Sciences and Nanotechnology*, 2(2), pp.86–102.

Kianfar E, (2020). Importance & Applications of Nanotechnology, MedDocs Publishers. Vol. 5, Chapter 4, pp. 22-25.

Philippe Serp and Philippot, K. (2012b). *Nanomaterials in Catalysis*. John Wiley & Sons.

Narayanan, R. (2012). Synthesis of green nanocatalysts and industrially important green reactions. *Green Chemistry Letters and Reviews*, 5(4), pp.707–725.

Chaudhary, A. (2017). Nano Catalysts: A Newfangled Gem in the Catalytic World. *Recent Advances in Petrochemical Science*, 3(5).

Chaturvedi, S., Dave, P.N. and Shah, N.K. (2012). Applications of nanocatalyst in new era. *Journal of Saudi Chemical Society*, [online] 16(3), pp.307–325.

Zhang, K., Suh, J.M., Choi, J.-W., Jang, H.W., Shokouhimehr, M. and Varma, R.S. (2019). Recent Advances in the Nanocatalyst-Assisted NaBH4 Reduction of Nitroaromatics in Water. *ACS Omega*, 4(1), pp.483–495.

Masood, Z., Ikhlaq, A., Akram, A., Qazi, U.Y., Rizvi, O.S., Javaid, R., Alazmi, A., Madkour, M. and Qi, F. (2022). Application of Nanocatalysts in Advanced Oxidation Processes for Wastewater Purification: Challenges and Future Prospects. *Catalysts*, [online] 12(7), p.741. Available at:

https://www.mdpi.com/2073-4344/12/7/741/htm [Accessed 20 Aug. 2022].

Navia-Mendoza, J.M., Filho, O.A.E., Zambrano-Intriago, L.A., Maddela, N.R., Duarte, M.M.M.B., Quiroz-Fernández, L.S., Baquerizo-Crespo, R.J. and Rodríguez-Díaz, J.M. (2021). Advances in the Application of Nanocatalysts in Photocatalytic Processes for the Treatment of Food Dyes: A Review. *Sustainability*, [online] 13(21), p.11676. Available at: https://www.mdpi.com/2071-1050/13/21/11676/htm [Accessed 20 Apr. 2022].

Vivek Polshettiwar and Asefa, T. (2013). Nanocatalysis. John Wiley & Sons.

VAHDAT, S.M., RAZ, S.G. and BAGHERY, S. (2014). Application of nano SnO2 as a green and recyclable catalyst for the synthesis of 2-aryl or alkylbenzoxazole derivatives under ambient temperature. Journal of Chemical Sciences, 126(3), pp.579–585.

Patra, J.K., Das, G., Fraceto, L.F., Campos, E.V.R., Rodriguez-Torres, M. del P., Acosta-Torres, L.S., Diaz-Torres, L.A., Grillo, R., Swamy, M.K., Sharma, S., Habtemariam, S. and Shin, H.-S. (2018). Nano based drug delivery systems: recent developments and future prospects. Journal of Nanobiotechnology, [online] 16(1).

bose, Dr.P. (2021). How are Nanocatalysts Used for Environmental Applications? [online] AZoNano.com. Available at: https://www.azonano.com/article.aspx?ArticleID=5881.

Luque, R. and Prinsen, P. (2019). Nanoparticle design and characterization for catalytic applications in sustainable chemistry. Croydon, UK: Royal Society of Chemistry.

Lei, Y., Shen, Z., Chen, X., Jia, J. and Wang, W. (2006). Preparation and application of nano-TiO2 catalyst in dye electrochemical treatmen, Water SA, Vol. 32 No. 2, pp.205-210.

Olveira, S., Forster, S.P. and Seeger, S. (2014a). Nanocatalysis: Academic Discipline and Industrial Realities. Journal of Nanotechnology, 2014, pp.1–19.

Huo, M., Wang, L., Chen, Y. and Shi, J. (2017). Tumor-selective catalytic nanomedicine by nanocatalyst delivery. Nature Communications, [online] 8(1), p.357. Available at: https://www.nature.com/articles/s41467-017-00424-8#Fig1 [Accessed 27 Oct. 2020].