

Catalyst Design: A Narrative Study on Nanocatalysis and Green catalysis

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Abstract: Catalysis represents a very essential aspect of chemical production and industrial growth and development. Thus, in contribution to the research efforts made towards transcending the challenges encountered by catalyst design practitioners, this review highlights some noteworthy benefits of inculcating nanotechnology (bottom-up approach) a front liner technique which have essentially facilitated present day advancements in catalysts design and promotion of green catalysis. This review takes into account the challenges and opportunities encountered at different levels in its application, taking into consideration the prospects of interplay of nanotechnology with Artificial intelligence (from the previous studies) in catalyst design, and further proposes options that will be effective towards maneuvering the challenges encountered in catalyst design and structuring.

Keywords: Catalyst, Green Chemistry, Nanocatalysis.

1. INTRODUCTION

Catalysts and Green Catalysis

Catalysts are substances (neither reactant nor product) that alters/controls the rate of a reaction (i.e. speeds up or slows down), lowers the activation energy (the minimum energy required for which atoms or molecules undergo a chemical transformation) thereby disrupting reaction spontaneity and is recovered chemically unchanged at the end of the process. In other words, a catalyst aside altering a chemical reactions' speed, is also energy conservative. Catalytic effect on chemical processes is necessary for achievement of peculiar results. This is a nature of catalysts termed selectivity – achievable by activation energy reduction. However, catalysis being an enabling technology has found essential role of application in numerous fields of study ranging from energy development, to environment and health, to agriculture, to industrial technology and so on. The rational design and synthesis of highly efficient 'green' catalysts has become of primal importance in the fields related to catalysts research [1]. Among three well-known catalysis categories (i.e. homogeneous, heterogeneous and enzymatic catalysis), enzymatic catalysis is the most efficient and greenest catalysis found in nature. With the growing need to mitigate environmental impact of exposure to harmful chemicals from chemical processes, Anasta and Warner [2] documented a dozen set of principles as the main philosophy that governs green chemistry. This development has been prompted owing to the emphatic growing energy demand against global uproar for environmental protection. Green chemistry emphasizes on making chemical processes work more like nature – i.e. environmentally benign and conservative, characteristically like enzymatic catalysis. Green chemistry encourages the utilization of these set of principles that encourages the mitigation and/or elimination of the use or generation of hazardous substances in the design, manufacture, and application of chemical products, with emphasis on hazard reduction as the performance criteria while designing new chemical processes.

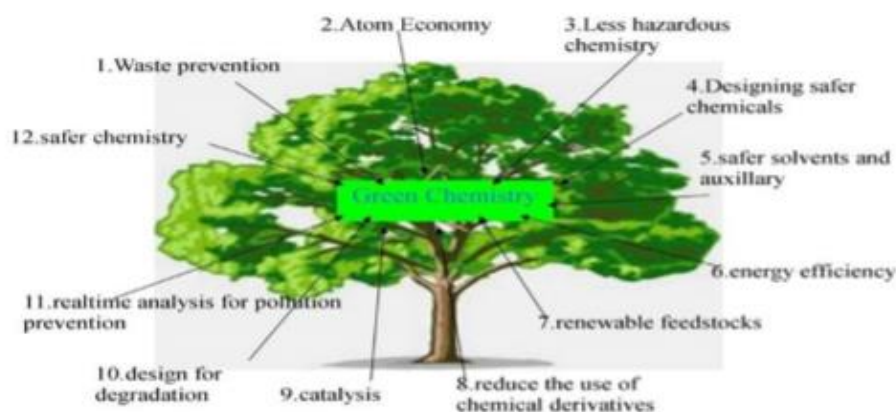


Figure 1. The Twelve Set Principles of Green Chemistry [2]

Catalysis is not only a means to make existing processes more efficient, but it also allows us to synthesize novel and unexplored molecules and materials, unlocking and enabling the technologies of the future [3]. Catalytic processes present a fundamental aspect in scientific and technological processes development – in creating safe and sustainable alternative processes. Therefore, structuring and creating perfect catalysts is one of the ideas and focuses of green technology in optimizing and economizing synthesis of pure materials. In fact, cutting across industrial production processes, its economic implications is cost efficiency – through development of value chain frameworks it has supported optimization activities to maximize output while lowering costs. However, catalytic technologies are critical to the current and future state of the energy sector, chemical processes and environmental industries from the research and development (R&D) stages all the way to experimental/pilot program design and implementation. Processes such as: crude oil, coal and natural gas conversion into fuels; emission control of CO and hydrocarbons; chemical feedstock (raw material) conversion; fuel cells electrochemical conversion; and a whole lot of biophysicochemical processes, etc., are a few of many common but notable processes that are highly dependent on catalyst for process optimization. There is need for development of advanced catalyst in order to:

1. Produce high value products with inexpensive raw materials;
2. Perform energy-efficient chemical conversion processes;
3. Impose stringent environmental regulations; and
4. Fabricate low-cost catalysts such as with reduction or replacement of precious metals.

The applications of scientific and technological (S&T) processes finds its fundamental development in the study of catalyst. However, catalyst design has been incipient and nascent, thence, the need to structure and synthesize perfect catalysts that are environmentally compatible is very vital. In the attempt to design better performing catalysts, for a lifetime researchers and scientists have syndicated, consciously driving towards making this a feat through alteration of the surface structure and electronic state of catalysts materials which has in some cases (as will be later discussed in this review) been achievable by combining or blending parent catalysts with coordinate components thereby enhancing catalyst performance. From the onset of surface sciences to its earliest development, scientists and researchers have come to the awareness that surfaces of the same crystal could nonetheless possess different number of valence electrons as a result of differences in atomic arrangement and interactions/interplay. This difference can lead to variations in molecular adsorption and reactivity on different crystal faces [4, 5].

The design of chemical processes has evolved from the initial empirical techniques involving use of just stoichiometric reagents to the design of catalysts on a macro-scale basically through component regulation, size control, and morphology tailoring. However, in most recent times it has evolved into the precise regulation of the catalytic center coordination and electronic structures at the subatomic/atomic levels. However, the development of unconventional catalysts is inseparable from the bold innovations in strategic method of preparation, the technicality in methods of catalyst characterization, the repetitive renovations of the concept of catalysis, and the steady investigation and re-appraisal of the objective law of the

structure–activity relationship. On other considerations, aside from issues associated with environmental impact with respect to catalyst design, another challenge is the traditional research and development pattern (predominantly by trial and error) employed in catalyst synthesis [6, 7], which necessitates researchers and scientists to find potential target materials and synthesis paths based on anterior noesis, and to then experimentally optimize the synthesis conditions. The long development cycle and uncertainty of performance are speculative and hinder the discovery and application of new catalytic materials.

Types of Catalysts

Generally, catalysts are of two types, viz.: homogeneous catalysts and heterogeneous catalysts. Decades of successive research has shown that a greater percentage of researchers in the field of catalysis have based their studies more on heterogeneous catalysis more than homogeneous catalysis. Heterogeneous catalysts are easy and more advantageous to operate with than homogeneous catalysts for some reasons such as their operating range of temperature, method of recovery, waste management, etc. However, not all chemical processes will require heterogeneous catalysts. This unravels the need for further research into optimizing homogeneous catalytic processes. However, the characteristics of homogeneous and heterogeneous catalysts are found coherent in nanocatalysts; thence advantageously complementing for these characteristic deficiencies and even more.

This review paper takes a look at the involvement of nanotechnology (i.e. nanocatalysis) and artificial intelligence (two key areas of contemporary research), in advanced scientific and technological design and development of catalysts, including practical applications and implications in different fields and at different levels of study.

Nanocatalysis

Basically, nanocatalysts are materials with catalytic properties that functions in the atomic and subatomic levels. Catalysts classified as nano catalysts are composed primarily of particles sized (x) within the nanoscale (i.e., $1\text{ nm} \leq x \leq 100\text{ nm}$) or smaller than 100nm at least in one dimension – either externally or in terms of internal structures [8]. In recent pasts, nanocatalysis has gained wide acceptance by numerous researchers in different fields of application, on account of its advanced structural and electronic alteration (which influences change in absorbent strength or oxidation state), greater prospects for agglomeration – which distinguishes them their bulk forms. Their alternative characteristics and ability to operate at the atomic and subatomic levels is responsible for their higher activity, transcendence in selectivity and superior productivity. Alternative to traditional catalysts, their *larger surface areas from smaller particulate sizes* implies an extensive thinner surface is available for reaction, and therefore greater percentage of atoms are available and hence more valence electrons for bonding, greater opportunities for process control (such as pressure and volume management), including higher activity and better selectivity of nano catalysts [9, 10].

Because of nano size (high surface area) the contact between reactants and catalyst increases dramatically – the closer the surface areas of reactants and catalyst the more the phenomenon approaches homogeneity (or homogeneous catalysis), and on the other hand insolubility in the reaction solvent makes the catalyst heterogeneous and hence can be separated out easily from the reaction mixture – the farther apart the surface areas of reactants and catalyst the more the phenomenon tends towards heterogeneity (or heterogeneous catalysis) [11-16].

In modern times, catalytic materials have been structured and restructured into befitting conformations for application in various reactions processes. This phenomenon is termed catalysts restructuring. Catalysts restructuring is aimed at controlling chemical reactions by altering their kinetics using nanopatterning of the reaction centers. Nanopatterning is a nanotechnological process which involves fabricating a nanoscale pattern with at least a dimension below 100nm achievable by employing various non-photon or proximity mechanical techniques (such as nanoimprint lithography, Atomic Force Microscopy (AFM), Dip-Pen Nanolithography (DPN), etc.) which are essential tools for manipulating the individual atoms and molecules of a material in order to build complex advanced structures with atomic specifications. They're positively effective in terms of increased surface area to bulk volume ratio, consequent reduced cost implication and increased efficiency and productivity [17, 18]. Appropriate choice of the protecting/stabilizing agents is also a very important factor in nanocatalysis because these can alter the surface properties of the NPs, as it can modify the nature of active sites (morphology) and also the surface chemical environment (causing a steric effect and/or electronic effect) [19-22]. Selectivity and reactivity of the NPs has a critical importance as it can influence the course of a reaction which mainly depends on surface state of NPs. Thus, selectivity and reactivity of NPs depends on mainly two concerns i.e. control of

crystal structure and morphology, and control of surface composition [23-25]. Activity of NPs is the concern of surface structure, exposure of different crystallographic facets and increased number of edges, corners & faces [26, 27]. Thence, efficient control of morphology of the nanoparticles is becoming an interesting task all over the world in recent pasts. However, the selectivity of NPs can also be altered by controlling its intrinsic composition (an advantage over contemporary catalysts). Some examples of nanocatalysts are: Carbon nanotubes, Monometallic NPs (e.g. Al, Fe, Ag), Bimetallic NPs and Clusters, Metal oxides (e.g. ZnO, TiO₂, CeO₂, Fe₂O₂), Silica and Sulfide NPs, Nanowires, Nanocomposites, Nanoporous materials, clays [28- 31].

Catalysis is not only a means to make existing processes more efficient, but it also allows us to synthesize novel and unexplored molecules and materials, enabling future advancements of current technologies in the future [3]. For example, in an interplay of nanotechnology and chemical catalysis, over a decade of study has experimentally shown that the idealized phenomenon that semi-conductor based NPs composed in colloidal quantum materials (such as Au, Ag, Cu, Fe, Pt, Pd, Rh, and Ru) have good light absorption properties and can be used as photocatalysts for energy conversion (solar energy to chemical energy) [32-35] and also the enhancement of photocatalytic processes through elemental doping [36-38]. The contributions of nanocatalysis towards achieving green catalysis is enabled by replacement of contemporary catalytic materials with nanomaterials in the vie for sustainable energy development. Furthermore, the ability to tune and tailor the electronic band structure of the nanoparticles by their characteristic properties (size, shape, and composition), coupled with their large surface to bulk volume ratio and their capacity to be utilized directly in solution or introduced in a matrix have prompted the exploration and discovery of various systems for artificial photosynthesis (water splitting technology), mostly, by separation of the two half-cell reactions. For example, the progress in synthesis and surface engineering of NCs gives a more vivid understanding of the general processes involved in light-induced catalytic reactions but more specifically in H₂ and O₂ generation (water splitting). Water splitting aims to utilize the energy absorbed by the nanocrystals (NCs), to produce hydrogen gas along with oxygen, directly by a redox reaction process (i.e. by reduction and oxidation of water, respectively). The hydrogen gas can then be reacted in a controlled manner with oxygen for the reformation of water in a fuel cell providing electricity, thus, elegantly resulting in a zero hydrogen emission cycle. This is essential for environmental sustainability because hydrogen, although not a greenhouse gas (GHG), has been found to have warming potential and classified as an indirect GHG because its chemical reactions can influence the abundance of the GHGs in the atmosphere. Alternatively, this photocatalytic technology will give allowance for a shift or transition from the potential polluting hydrogen production process to the not only desired renewable energy but environmentally friendly (solar to fuel) energy conversion. Despite photocatalysis technology having great potential for tackling the challenges of energy shortages as well as environmental pollution, improving the sunlight utilization efficiency and catalytic activity of photocatalytic nanomaterials constitutes the key problem restricting the large-scale application of photocatalytic technology. The cycle of photocatalysis can be classified under three processes step-wise [39]:

- Light Adsorption
- Charge Mobility
- Catalytic Reaction

However, these steps are influenced categorically by parameters such as:

- The composition and dimensions of the photocatalysts, that inherently determine their electronic and chemical properties, including the band offset and chemical stability, the over-potentials to the desired reactions as well as the reactivity and adsorption energy of the reagents to the catalytic site [40-42];
- The surface coating of the NCs which should provide sufficient distribution and passivate surface traps without interfering to the accessibility of the reagents to the reaction center [43-45]; and
- The environmental conditions should be tuned (which is near impossible) to provide chemical and colloidal stability and on the other hand, were found to significantly affect the measured quantum yields [46, 47].

Moreover, the tunability of the characteristic properties of nanoparticles permits and promotes the execution of systematic studies to reveal fundamental parameters influencing their performances and to decode their systemic pathways as well as mechanism of action. Nonetheless, the ambidexterity and tunability of nanomaterials make them attractive for tailoring solutions to specific industrial needs [48].

Classes of Nanocatalysts: Literature Review on Possible Challenges and Opportunities

A class of nanocatalysts called plasmonic catalysts have been known to possess good adsorption characteristics. Plasmonic catalysts are metal colloids (Au, Ag, Cu, Fe, Pt, Pd, Rh, and Ru), efficient catalysts prepared by reduction of metals through the mechanism of size and shape controlling; in other words referred to as metallic nanoparticles (MNPs). Plasmonic nanoparticles primarily from gold group metals have been utilized in the past as light absorbers enhancers but recently they were shown to act as direct light absorbers [35]. However, plasmonic energy transfer takes place through strong light absorption, intensive far-field light-scattering, near-field electromotive field strengthening, abundant hot carrier generation, plasmonic heating effects [29, 30]. Localized surface plasmon resonance (LSPR) excitation in plasmonic nanoparticles supports the acceleration and control of molecular transformations.

In addition, due to the well-defined and controlled physical and chemical features (size, shape, surface composition, morphology and orientation), the monometallic plasmonic catalysts (Ag and Au) exhibit plasmon-mediated chemical reaction (PMCR) transformations. PMCR is a process that makes use of nanostructure-based surface plasmons as mediators for redistribution and conversion of photon energy. This process facilitates chemical transformations by localizing photon, electronic and/or thermal energies. The noble MNPs such as Au, Ag and Cu demonstrate plasmonic resonance effect; that is collecting electron oscillations which resonates at the frequency of incident light. A phenomenon termed surface plasmon resonance (SPR). Catalytic activity of Ag NPs are easily tuned by the particle size, shape and temperature and these nanoparticles are active under mild conditions/ambient temperatures. Because of their low cost and relatively low toxicity, Ag NPs are preferred the most for photocatalytic reactions. In photocatalytic processes utilizes Ag NPs plasmonic catalysts with sunlight as a driving force in clean energy conversion, capable of producing fuels and chemicals by converting abundant natural resources and greenhouse gases. In 1986, first time Haruta *et al.* [49] reported the catalytic activity of gold (Au) nanoparticles in oxidation of carbon monoxide and hydrogen at low temperatures. After this reporting, a very old conventional idea about gold for its inertness towards chemical reaction has been completely changed and a new door to interesting applications of nanoscale materials in catalysis is opened. Studies shows that the interface confinement effect is strongly dependent on the metal substrate. For example, in a study it was discovered that the binding energy between the 2D FeO structure and metal substrate decreases in this sequence: Pt > Pd > Ru > Au > Cu > Ag [15]. The Pt surface exhibited the strongest confinement effect on FeO structure, while the Ag surface is weakest. The bonding of the substrate metal with Fe is critical to the interface confinement effect. The other prerequisite of a strong effect is that the metal should bind weakly with oxygen. Suggestions have been that further works could look for other substrates, such as carbon nanomaterials (CNM) or composite materials, which can act similarly to noble metals to confine the highly active oxide nanostructures.

Nano-confinement effects in CNTs offer opportunities for tuning the catalytic performance of metal NPs by modifying their surface structure and electronic properties without significantly changing the catalyst composition, bringing the intellectual design of catalysts from the molecular scale a step closer [1]. Also, catalysis by nanostructured carbon materials, especially CNTs, has received wide attention. For instance, Schloegl and researchers [50] demonstrated that the oxygen atoms on the defect sites of the outer surface of CNTs play a crucial role in the dehydrogenation of ethylbenzene. CNTs can be envisioned as graphene layers rolling up to form a well-defined tubular structure. The π electron density of the graphene layers shifts from the concave inner surface to the convex outer surface because of the curvature, resulting in an electron potential difference across the CNT walls [51, 52]. This endows CNTs with unique physico-chemical properties, distinct from other, conventional carbon materials. The electron potential difference between the concave and convex surfaces as a function of the CNT diameter, calculated from a simple model showed a potential difference as high as 0.20eV is estimated for a nanotube with a diameter of 1.36nm, causing a strong electric field in the nanospace from the study of Yu *et al.* [51]. Thus, if catalytic NPs are placed within such an environment, the nanospace not only exerts a physical restriction on them (and on the reactions they facilitate), but also provides a unique electronic microenvironment that modulates electron transfer processes [53-56]. Nano-sized carbon materials (NCMs), especially carbon nanotubes (CNTs) have attracted a lot of attention because of their unique physical and mechanical properties [57, 58]. CNTs have been used in many fields as field emission sources [59], electric nano-conductors [60], Li ion secondary batteries [40, 61], electric double-layer capacitors [62], fuel cells [63], and molecular sieves [64]. In addition, CNTs have been used to adsorb hydrogen [65] as a result of their high porosity, lightness, chemical and thermal stability, and are inexpensive to procure. Their unique tubular structure is favorable for hydrogen uptake [66]. 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 [67, 68]. According to the literature [69], the material characteristics of CNTs, governed by preparation procedures, significantly affect their hydrogen storage capability.

From the studies of Zhang *et al.* [70], an *in situ* high-resolution nuclear magnetic resonance (NMR) studies demonstrated that CNT channels can selectively absorb hydrophobic benzene relative to hydrophilic acetic acid and phenol molecules. Benzene tends to diffuse into the CNT channels, leading to locally higher concentration. Consequently, the rate of benzene conversion to phenol is enhanced 4 fold using a CNT-confined Re catalyst, relative to the same catalyst dispersed on the outer walls of the CNTs. This is not just because of local enrichment of benzene inside the CNT channels but also selective expulsion of hydrophilic phenol molecules [70]. CNT-based catalysts may thus find applications in high-pressure reactions such as the conversion of syngas to light olefins and ethylene glycol via C-C bond coupling, as well as low-pressure ammonia synthesis and some selective oxidations. Carbon nanotubes (CNTs) have exceptional mechanical properties, particularly high tensile strength and light weight. An obvious area of application would be in nanotube reinforced composites, with performance beyond current carbon fiber composites [71]. The surfaces of CNTs are smooth and relatively unreactive, thence they tend to slip through matrixes where they serve as catalysts.

Bi and Lu [72] reported the catalytic activity of nanoscale copper in production of hydrogen from formaldehyde at room temperature and also suggested a possible reaction pathway for this conversion. Copper has received more attention in organic synthesis due to its environmentally benign character, easy availability, and low cost. Sachin Sarode [73] presented an account of recent developments in C-C and C-heteroatom bond formation using Cu(O) nanocatalysts and the scopes of nanocatalysts. A number of outstanding catalytic systems have been developed in recent years, many organic reactions, such as formation of C (aryl)-C (aryl), C (aryl)-N, C (aryl) - O and C (aryl)-S, bonds as well as many other useful transformations involving carbon-carbon bond formation such as: Ullmann reaction: Ullmann coupling reactions of aryl iodide [74]; Suzuki reaction: Suzuki coupling reaction between aryl iodide and phenyl boronic acid [75]; Stille reaction: Cross coupling between aryl halides and organotin derivatives is known as Stille coupling [76]; Heck reaction: Coupling reaction between aryl halide and activated alkenes [77]; Sonogashira reaction: Sonogashira reaction of terminal alkynes with aryl halides [78]; Three-component condensation: Coupling reaction between aldehyde, amine, and alkyne using CuO nanoparticles [78]; Aniline from aryl halides in aqueous solution [79], etc.

Using oxide/metal catalytic systems, we have illustrated an interface confinement effect and its application in some catalytic systems. Heterogeneous catalysts consisting of metal NPs supported on oxides have found important applications in reactions such as selective oxidations and hydrogenations. The role of the metal/oxide interfaces is crucial in these reactions. In particular, oxygen vacancies at these interfaces, and the interaction between the metals and their oxide supports, have been regarded as the most critical factors [80, 81]. These interfacial phenomena have often been explained by the concept of strong metal-support interaction introduced by Tauster *et al.* [82] in the late 1970s. In metal/oxide systems, it is hard to control the oxygen vacancies at the interface in a well-defined way and, moreover, the interfaces are buried under 3D metal NPs, making the nature of interfacial interaction difficult to control. We have deposited well-defined oxide nanostructures onto noble metal surfaces, and investigated the oxide/metal interface at the atomic and molecular level [83]. Although these so-called oxide/metal inverse catalysts were already studied. However, due to their potent photocatalytic activity, metal oxides (such as TiO₂) nanoparticles are utilized in water treatment.

Semiconductor NPs are another class of potential candidates as catalyst materials due to their wide band gap in the visible region, whose efficiency is determined by their structural parameters (size, shape, crystallinity, porosity, contact interface, and spatial distribution). A group of semiconductor materials with narrower band-gaps includes titanium dioxide. It can excite an electron from the valence band to the conduction band and absorb visible light. The electron causes a hole to form in the valence band and gives the conduction band a negative charge. It is possible for redox reactions to occur in liquid solutions [84]. Hence, to improve the photocatalytic performance of semiconductor is to expand the light response region and to enhance formation rate of electron-hole pairs. Band gap of Titania can be modified by doping with metal ions. Due to the antibacterial qualities of silver nanoparticles, the possibility of covering polyurethane foam with them to avoid bacterial contamination in water filters has also been investigated [85]. In addition, since the semiconductor nano photocatalysts have the drawback of rapid recombination of photogenerated electron-hole pairs, by preparation of nanocomposite photocatalysts the recombination of photogenerated electron-hole pairs can be delayed.

Nanocomposites photocatalysts as the name implies are metal/semiconductor nanocomposites (MS) NC prepared by coupling semiconductor nanostructures with MNPs. The preparation of nanocomposite catalysts presents one of the most effective methods to achieve high-performance photocatalysts because of the plasmo-induced resonance energy transfer. The origination of the photocatalytic aspects are by the improved charge separation at the M/SC interface and by increased absorption of visible light due to the surface plasmon resonance of metals. Therefore, decorating the semiconductors with MNPs reduces the band gap and makes the possibility of visible light irradiation for the generation of electron-hole pairs.

Supported metal nanoparticles (SMNPs) are used today in several application fields such as sensors, nanoelectronics, medical-technical applications, and in heterogeneous catalysis [86, 87]. Mainly hydrogenation (dehydrogenation), oxidation, automotive off-gas cleaning, and C-C coupling reactions run on such SMNP catalysts [88, 89, 90]. In general, SMNPs consist of metal nanoparticles (MNPs) from transition metal or noble metal pools that are deposited on high surface area supports (150–1200 m²/g). In general, the metal load of supported metal catalysts is generally in the range of 0.5 up to 10 wt% (even higher in rare cases). The activity of supported metal catalysts in heterogeneously catalyzed reactions is mainly determined by the shape and size of the metal species (i.e., MNPs) deposited onto the support, because only surface metal atoms might take part in a chemical reaction [87-92]. Heterogeneous catalyst performance is very sensitive to particle size, because the structure of the solid surface and the electronic properties may significantly change depending on the size of the MNPs [87, 91]. For example, the activation energy for CO dissociation and the heat of adsorption for CO alter with changing size of MNPs. These changing properties affect its performance in several CO-converting reactions like Fischer-Tropsch (FT) synthesis for the manufacture of hydrocarbons from gas synthesis. Supported Au-containing catalysts show similar size effects with respect to applied supports [93, 94]. Au nanoparticles on alumina smaller than 4nm showed complete conversion in ethylene glycol oxidation, but increasing nanoparticle diameter above 5nm led to substantial drop to roughly 40% conversion only [93].

Gawande *et al.* [95] reported the use of surface functionalized nano-magnetite supported nanoparticles in catalysis, green chemistry and pharmaceutically significant reactions. These nanoparticles act as bridge between heterogeneous and homogeneous catalysis. Magnetite-supported metal nanocatalysts have been successfully used in organic synthesis for a variety of important reactions [96, 97, 98, 99]. However, the use of magnetic nanoparticles as a catalyst support can also enable, in specific cases, easy and efficient separation of the catalysts from the reaction mixture with an external magnet [73], as well as in modifying their chemical structure thus assisting in chemical structure, helps in 3D structure due to movement of free electrons that can move in all directions due to their compatibility to the structure [100, 101].

In an attempt to synthesize and efficient catalyst for hydrogenation of arenes, Hong Yang *et al.* [102] used metal catalyst support to contain the tethered complex Rh(N-P)/Pd-SiO₂ and Rh(N-N)/Pd-SiO₂, which showed better activities than the usual homogeneous catalysts used for this purpose[102]. However, immobilized catalysts are costly and have limited access. They have lower selectivity, and their activity reduces with reuse, and (metal) active species are subjected to leaching in solution [103]. The catalysts employed in the reactions in the fine chemical synthesis must be extremely selective and efficient in order to minimize wastage and make the process profitable. It is easier to separate heterogeneous catalysts from the reaction products. Sometimes, they do not even need to be separated at all. They are easy to recover and reuse. The combining abilities of both homogeneous and heterogeneous catalyst is a characteristic property of nanocatalysts and are sometimes referred to as quasi-homogeneous systems [73] – however, heterogeneous catalysis has gained wider acceptance for a good number of reasons [104-107].

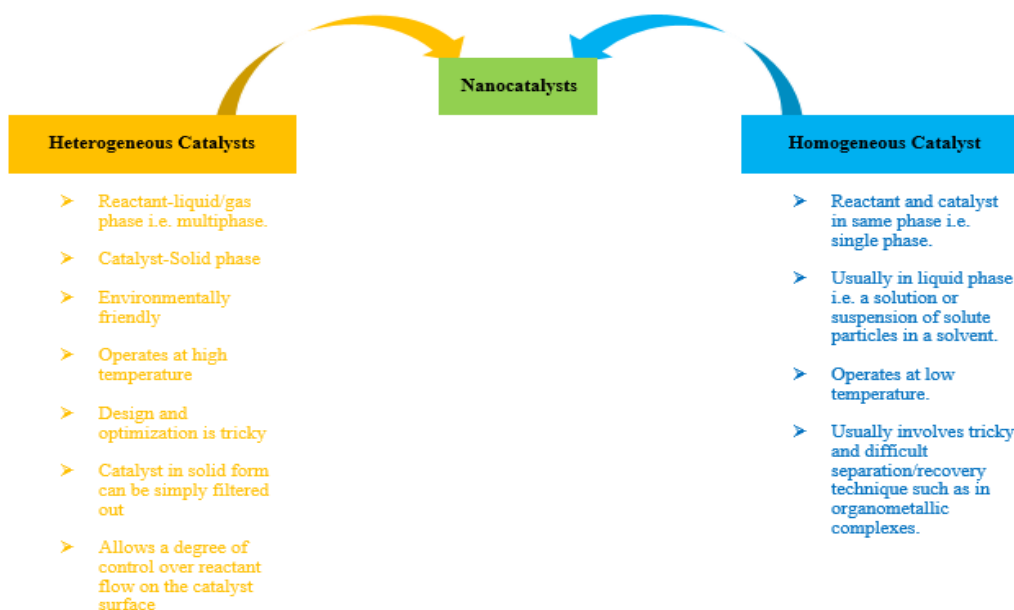


Figure 2: Shows nanocatalysts as an advantage over Heterogeneous and Homogeneous catalysts.

Nonetheless, moving from homogeneous to heterogeneous catalysis is a trend towards frugal economy – solves waste disposal problems while simplifying steps used in production such as recycling and neutralization. Heterogeneous catalysis is usually used to produce bulk chemicals, and noncatalytic organic synthesis is used in fine chemical synthesis [108].

Future progress in catalysis science is expected to bring about exciting progress not only in the design of novel nanostructured catalysts with high selectivity, activity, and durability, but also in the fundamental understanding of the elementary reaction mechanisms at the atomic level [109, 110]. Catalysts with high selectivity [111] and of low energy consumption (i.e., in mild processes) should be of particular importance in future catalytic research. As discussed by Somorjai *et al.* [112] in their recent work ‘the challenge of chemistry in the 21st century is to achieve 100% selectivity of the desired product molecule in multipath reactions (“green chemistry”) and develop renewable energy based processes’. Looking into the future of catalytic science, there are many huge challenges but they offer very exciting opportunities [113]. Tailoring catalysts at the atomic level will constitute the ultimate goal of catalysis research.

The controlled fabrication of nanomaterials of specific composition and structure is vital for catalytic applications. Despite the great success so far, there are still challenges in correlating the structures of nanomaterials with their catalytic properties, hindering rational design of catalytic active centers from first principles. The first major challenge is to synthesize identical nanostructures. Current accuracy in size control of NPs has reached the sub-nanometer level, but individual NP may still differ in the numbers of atoms they contain by hundreds or even thousands. Moreover, control of the surface structure and the distribution of defects remain extremely difficult. And while it is now easy to prepare various forms of CNTs, selective synthesis with precise control of the number of wall layers, metallic or semiconducting properties, and the amount or distribution of dopants such as N and B remains very difficult, yet is critical to the catalytic activity of nanotube-based materials. The second major challenge is to understand the dynamics of catalytic nanostructures. Catalysis is, in general, a dynamic process, which often occurs at high temperatures, under high pressures, and in the presence of a variety of reactants and products. Under such harsh conditions, NPs are expected to be ‘sensitive’, undergoing pronounced changes in their composition, structure and electronic state. These dynamic changes might, to some extent, be similar to those found in biological catalytic processes. It is of tremendous importance to correlate the static structures of active centers with their dynamic structures [1].

In other considerations, bimetallics represents an emerging and new field of nanocatalysis [114-116]. They are not only expecting to show combined properties of two distinct metals but also new properties and capabilities due to a synergy between the two metals. By precisely controlling the size, shape, spatial distribution, surface composition and electronic structure, and thermal and chemical stability of the individual nano components, it can be widely used in catalysis with newer properties and activity [100]. 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. However, it is noteworthy that catalysis is the very important part of green chemistry which encompasses other aspects of greencatalysis. Nanocatalysts are used in smaller amounts which is significant for optimization and cost reductions in chemical processes. Nanocatalysis adds greener to chemical process through:

- Higher activity which avoids drastic reaction conditions and increases energy efficiency
- Higher selectivity which reduces the by-products and allows performing chemical reactions in a specific manner with the least possible consumption of substances. This, in turn, improves atom economy and waste prevention
- Efficient recovery from reaction medium
- Durability or recyclability
- Cost-effectiveness.

Inconclusively, nanocatalysis has been broadly recognized for its successful application in different aspects amongst many more, including:

- Water purification and waste water treatment: to degrade contaminants under irradiation of light (Ag NPs and TiO₂ NPs) [34, 117-121];
- Biodiesel production: to increase transesterification efficiency (basically using metal oxide) [122-126];

- Fuel cell application: to improve the performance of fuel cells (CNT and Pt catalyst) [127-129];
- Drug delivery: for creating gels for drug delivery [130-133];
- Photocatalytic activity [34, 134-141];
- Composite solid rocket propellants: to enhance the propellant burning rate (e.g. nano aluminium) [142-146];
- Thin film solar cells [147-154];
- Environmental protection [155];
- Fuel production: to release oxygen gas which is critical process in energy storage [156-161];
- Alkanol oxidation [162-169];
- Nanotoxicology [170, 171];
- Hydrogen production for fuel cells [172, 173].

Prospects from an Interplay of Nanotechnology and AI in Enhancing Catalysis Design

It is undeniable that ML is already boosting computational chemical sciences and engineering, at different levels. Deliberate efforts have been geared towards building nanocomputers and chips for the implementation of AI paradigms in different scopes [174-176]. These pioneering efforts call for a real convergence of nanotechnology and AI in high performance computers enabled by nanocomputing devices including those based on biomaterials. Emphasis have been largely on the potential impact of using AI tools whilst applying nanotechnology in the context of biomedical research and clinical applications. Today's information technologies deal with big data, fast real time complex analysis and computations, security and encryption methods, high performance, multimodal and ubiquitous sensors, closed-loop interaction with complex systems, etc. In vie to bridge the gap that exists between nanotechnology and AI, a more effective interaction between brains and machines and has factually provided a means for advancement of empirical processes in catalysts design. Nanotechnology research is concerned with bottom-up building in tackling catalysts design challenges (i.e., an approach that begins with individual components (micro level) and builds up to the highest conceptual level (micro level)), while AI research ordinarily provides a top-down approach to tackling catalyst design challenges (i.e., an approach that begins with the highest conceptual level (macro level) and breaks down to the simplest conceptual levels (micro level)). The combination of these two disciplines will lead to solutions for many complex problems that require multiple description levels and interactions [177]. While, many NPs (such as ceramics, metals) are natural occurring and spontaneous, the novel NPs (such as quantum dot, Au graded NPs) can be synthesized arbitrarily by adopting AI techniques [178-180]. Convergence between AI and Nanotechnology can shape the path for various technological developments and a large variety of disciplines [181, 182]. The article by Kohlstedt and Schatz [35] revealed that computational frameworks being utilized in predicting the structure–property relationships in materials and devices, including ML techniques, placing significant focus on the concept of organic photovoltaic cells. Terahertz (THz) spectroscopy has emerged over the last few decades as a technique that can provide powerful insights into the electrical properties of catalytic materials [183]. Terahertz (THz) spectroscopy is an optical technique that averts physical contact with the material being analyzed – a phenomenal development advantageous when dealing with ensembles of nanocatalysts. The obvious trends in computational and ML techniques (such as the availability of THz spectroscopic data) proffer new chances for more accurate and efficient extraction of parameters for material characterization. This advancements may surmount some of the extrema of the less complex models in use today; however, these models are reliable for apprehending the fundamental characteristics of nanomaterials and the functionalities in devices. Such development has been valuable in the successful designing of the energy conversion in solar systems (materials and devices). However, complex numerical models are improbable to completely replace well thought-out visceral descriptions [35]. Although, attempts have been made to improve the resolution and the ability to manipulate atoms in recent pasts. However, the microscope signal's interpretation is still a challenge – of which AI (ML precisely) is viewed as a cognitive approach adoptable in addressing. The major challenge is that a great number of the tip-sample interactions are not easy to grasp and are contingent upon parameters. AI can be beneficial in solving problems of this sort [184]. Inconclusively, nanotechnology is the future of small scale that needs AI to enhance its data analytics for collecting information, more accurate predictions and can provide a power rational to more decisive results [185].

AI assists in the cognitive design of nanoparticles – predict the properties and behaviors of nanomaterials thereby facilitating the discovery of novel materials with improved characteristics, which is crucial for development and functionality optimization of high-performance materials. These AI-driven simulations and models provide insights into molecular interactions, facilitating in the design of catalysts [186-188] and even go as far as carryout toxicological predictions on nanocatalytic materials [189]. AI-driven robots and automated laboratory equipment can assist in the synthesis of nanoparticles with precise sizes, shapes, and compositions. AI is also used to analyze and characterize nanoparticulates, ensuring their quality, selectivity, distribution and consistency [190, 191].

The use of AI algorithms in predicting the behavior of nanomaterials based on their atomistic features (such as morphology, orientation, size) is the canonical and most significant attribute of AI and nanotechnology in catalyst design. This helps researchers identify novel materials with specific desired characteristics, such as exceptional strength, conductivity, activity and reactivity [189]. AI can create predictive models for complex chemical reactions, enabling researchers to anticipate the outcomes of reactions and optimize reaction conditions. As earlier pointed out, this gives less room for trial-and-error experimentation and hence encourages progressive research. AI-driven models simulate molecular interactions, predict material properties with high accuracy and optimize nanosystems, accelerating the design of novel nanomaterials and structures [189].

AI can analyze vast datasets of Nanochemistry research, identifying trends, and correlations and uncovering hidden patterns that may not be apparent through traditional methods from experimental and theoretical & computational nanochemistry data. This can aid in the development of new theories and hypotheses. This datadriven approach can accelerate the identification of promising nanocatalysts and their applications [192].

Nanotechnology in many ways has been able to elucidate AI. Nanotechnology and AI are two (of many elite) prolific frontiers spearheading scientific and technological explorations and development that have both synergistically and independently, which over the years made remarkable progress in various important fields of application of which catalysts design is of key to this study [193, 194]. Prior to ML models having the ability to characterize novel catalysts through correlations between structure and performance, various sophisticated intelligent machines and instruments have been modeled to characterize nanocatalytic materials with the deliberate attempt to unveil accurately characteristics such as: actual particulate size, shape, surface structure, valency, chemical composition, electron band gap, bonding environment, light emission, absorption, scattering and diffraction properties, etc., of catalytic nanomaterials [195-199].

The overall catalyst performance can be described with its most intrinsic characteristics known, thereby enabling a better understanding on how catalyst efficiency can be improved with specific chemical enhancements [200]. Despite this framework being already studied and designed, its practical application is still restricted by the lack of databases with significant description of catalysts – their synthesis through output performance, limit the overall applicability of the models [201].

As a particle decreases in size, a greater proportion of atoms are found at the surface compared to those inside. 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 [202-206]. An automated robotic system will be crucial to handling nanoparticulated catalysts.

Summary, Conclusion and Recommendations

The traditional ways of catalysts discovery and synthesis come with a lot of challenges (such as: the cost inefficiencies and high energy demands, the uncertainty of the large unexplored chemical space, challenges of repeated experimental trials, the uncertainty of a successful discovery, environmental implication of catalyst utilization and so on). Recovery of catalysts from the system is one of the most important characteristics of any catalyst before being acceptable for green chemical manufacturing processes in industry. In order to transcend the hurdles of catalysis and achieve green catalysis, nanocatalysis offers numerous prospects because of their characteristic nano size, the contact between reactants and catalyst increases dramatically, larger surface-to-volume ratio, small size, and varied shapes of nanomaterials are highly beneficial to catalytic reactions, enabling better yield of products by using less energy and minimizing waste production, protecting the environment from various harmful aspects of industrial processes. Also, by using catalytic reagents, one can reduce the temperature of a transformation, reduce reagent-based waste and enhance the selectivity of a reaction that potentially avoids

the unwanted side reactions leading to a green technology. Characteristic properties of nano catalysts is that they have combined advantages of both the homogeneous and heterogeneous catalytic systems, nano catalytic systems allows the rapid, selective chemical transformations with excellent product yield coupled with the ease of catalyst separation and recovery. However, their catalytic properties depends on their surface structure, composition of nanoparticles, reaction intermediates, adsorbate, oxidation states. The earliest studies of this article points out that the rational and clear-cut reasons why nanocatalysts are better substitutes to contemporary catalysts. However, there are various methods of synthesis of nanocatalysts viz.: sol-gel method, micro emulsification, high energy ball milling, hydrothermal processing, micellar formation, chemical vapor deposition, and so on, of which practically, sol-gel and micellar formation are the most efficient methods for the synthesis of nanocatalysts. However, one characteristic challenge encountered is that some of the methods of synthesis become tiresome and ineffectual as a result of multiple reiterations to get the intended result.

All of these developments have been advantageous to advancements in the discovery and implementation of cognitive intuitions principal to the exposure of some less intricate and obscure concepts that have advanced the field of study.

AI conjugated with nanotechnology could champion the beginning of new research and perfection of catalysts design. The brainchild behind achieving green catalysis is largely fueled by the involvement of nanotechnology and co-involvement of artificial intelligence.

Finally, a conjugation of AI and nanotechnology from the studies has shown that it offers great prospects for achieving the dozen set of objectives of green chemistry pointed out at the beginning of this review. AI in conjugation with nanosciences represents two cutting-edge techniques that are essential to the future of catalyst design.

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