International Journal of Theoretical & Applied Sciences, 10(1): 300-307(2018)

ISSN No. (Print): 0975-1718
ISSN No. (Online): 2249-3247

Metallic Nanoparticles as Green-sustainable Catalyst: A Brief Outlook on Recent Progress

Vineeta Singh
Department of Chemistry, D.A.V. Post Graduate College,
(University of Lucknow), Lucknow, (Uttar Pradesh), India.

(Corresponding author: Vineeta Singh)
(Received 15 February, 2018, accepted 21 June, 2018)
(Published by Research Trend, Website: www.researchtrend.net)

ABSTRACT: Green nanoscience is the science useful for build clean technology by that one resolve scale back the potential risks of locale and furthermore advancement the human health conditions. The nanotechnology synthesizes new miniaturize at nanoscale level with excellent properties which can replace the classically existing low-quality macro-system by modern nanosystems. The most motive of developing new nanoproducts is to reinforce property and additionally to create them further environments friendly. In nanoscale materials (nanoparticles or NPs) having characteristic length within the nanometric range (1-100nm), properties of nanomaterials are entirely different from individual atoms/molecules or from bulk materials. For any catalyst, we wish to attain long life cycle, 100% property and low energy consumptions, and these properties is solely gained by dominant the scale, shape, electronic structure and chemical \thermal stability of chemical action particles. The nanoscale sized metallic nanoparticles (MNPs) which have an exceptionally large surface area to volume ratio. So MNPs are empowered with low energy consumption, high efficiency, selectivity, productivity, excellent recycling & recovery potential, an economical use and expanded catalytic capabilities ,these are help to reduce the global warming through any chemical process. NPs also minimize the chemical wastes, remediates wastes, as easy pollutants scavenger etc., all these factors thus resulted to fulfill modern requirement with an improved economy and safer (Eco-friendly) environment. This mini-review provides an inclusive study about metal nanoparticles (MNPs), its recent advancement and utilization as emerging green\clean catalysts in different fields.

Keywords: Green, Nanocatalysis, Metal-nanoparticles (MNPs), Eco-friendly, application.

INTRODUCTION

Catalysis plays a central role in chemical transformations and myriad chemical protocols and is studied in the field of elemental and industrial chemistry [1]. Catalysis is crucial due to the special abilities of the catalyst in fast chemical reactions by lowering the energy barrier of their transition states and via dominant reaction pathways for the selective synthesis of target products. The scope of nanocatalysis is increasingly expanding to meet the ever-increasing demands for sustainable processes with improved economic impact and reduced environmental conflict. Therefore, they can be made more economical, ecological and sustainable by using catalyst preparation protocols [2]. A nanocatalytic system enables fast and selective chemical transformations with excellent product yield coupled with easy catalyst separation and recovery. Waste and pollutant reduction, higher efficiency and higher catalyst revival rates are the key features of any catalyst intended to be part of green chemical processes.

Materials ranging in length from 1 to several hundred nanometers are referred to as nanoscale materials or nanoparticles (NPs) was coined to address this relatively new, burgeoning and exciting scientific field [2]. Therefore, the reactions related to nanocatalysts are associated with the exponential growth in chemical production, domestic energy generation, conversion and storage, and environmental protection [4]. As a result, its applications are diverse, ranging from environmental remediation with pollutant removal, power generation, and industrial to consumer and even therapeutic applications.

CHEMISTRY OF NANOPARTICLES

The chemistry of NPs/nanoparticles takes various forms including powder, crystal, and cluster formulations. Nanopowder is used to explain fine powder mixtures while ultrafine particle mixtures are defined as nanocrystals [3]. Clusters are further classified as nanoclusters when they require a sparse size distribution in the 1–10 nm range and at least 1 dimension.

Due to the nanometer size (large surface area), the contact area between the reactants and the catalyst increases dramatically. Metal nano-particles (MNPs) are used as catalysts due to their comparatively gigantic scattering/dispersion per unit volume or weight compared to bulk metal, which means that heterogeneous MNP catalysts usually work on metal surfaces. A variety of techniques are used to develop supports for industrial metal catalysts, which are often inorganic and are characterized by extremely distributed metals and bulky surface area. Metal particles are typically ensemble things, made up of more than one particle in a variety of shapes and dimensions.

The chemical composition of MNPs with remarkable dimensions allows their use as catalysts. Compared to bulk gold-containing catalysts, the higher scatter and the measured quantitative edge permeation ratio lead to higher yields. MNPs are also compatible with stereo selective synthesis. In recent years, MNPs have been increasingly studied in various contexts due to their catalytic properties, e.g. as wetting agents (surfactants) for water-soluble chemical compounds, resins, vesicles, etc. The reactions like Fischer-Tropsch isomerization and hydro-formylation, etc., which also include NPs such as Rh, Ru, Pt, Ir, Au and palladium as catalysts [5]. The size of the metal particles has a major impact on the catalytic activity of the metal, just like the use of gold NPs in the chemical process; their size is directly related to the activity and/or selectivity of the catalytic action. Gold NPs with diameters of less than ten nm are considered to be extremely active catalysts, while this activity decreases significantly with increasing diameter of Au and, moreover, almost disappears when the diameter is measured in microns [6]. MNPs are functionalized in different ways, as they generally show higher stability in solution than unfunctionalized gold-containing NPs. This is often because non-functionalized particles have less surface area and this lowered the capability for catalytical effects due to their tendency to aggregate during dissolution. Although the ligands usually used to avoid aggregations of NPs in solutions, they must have the consequence of the practicality stabilization MNPs. Nanocatalysts can also be functionalized by using polymers and oligomers. Catalytically acting NPs are generally deposited by cycling with chemical compound matrices; also upon solid supports [7]. The petro-organic compounds uses supported metal catalysts, particularly noble metals used to dissolve naphtha reformers. However, new techniques are currently being developed that utilize the electrostatic interaction forces of a multilayered polyelectrolyte through surface assimilation of metal ions (Ag+, Pt^{2+}) that is stable chemical catalytic aggregate [8,9].

MNPs are mainly described by their size; it follows that size is the real driver of their catalytic potency. Since the surface area of the metal particle is inversely proportional to square of the diameter NPs, the surface area increases with decreasing particle size of MNPs thus catalytic activity also, as all chemical reactions take place on the surface of the catalyst [10, 11]. In some chemical reactions, the reaction rate is also influenced by the size/amount of the catalytic particles. In these cases, the reactions can be slow-down by the reduced quantity of MNPs/ incresed the particle size of the nanocatalyst. Such as the noble metal nano-catalysts like platinum is mainly used for photochemical production of H_2 gas, it is ideal to use catalysts with particle size of diameters of three nm. The other size, larger or smaller, can hinder this chemical process [12]. The size of the catalyst particles also affected the selectivity of the reaction process. For example mono-ene is produced by the partial hydrogernation of cyclopentadiene, a size of two nm of platinum NPs is considered ideal. However, larger size particles can change the nature product of the reaction due to the steric effect of noble metal nano-particle [13].

Recently, few approaches have enabled the rational design and synthesis of high-energy and selective nano-structured catalysts by mapping the structure and composition of active nano-particles and by manipulating the interaction between catalytically active NPs species and their stabilizing agent. The design of MNPs as catalysts includes metal, metal oxide, metal complexes, etc. They are certainly the most vivid for several primeval chemical/ industrial processes in modern chemistry and different field as agriculture, biomedical, electrical, industrial, food processing so on (Fig. 1).

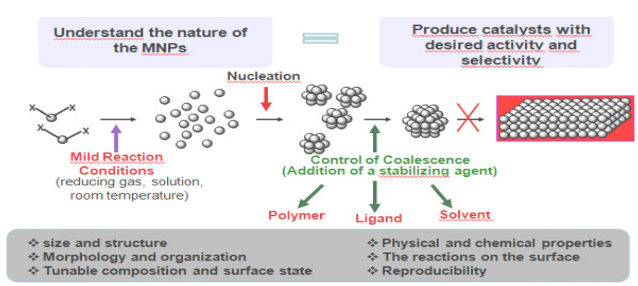

Fig. 1.

A. Synthesis of Nanoparticles

The synthesis of metallic nanoparticles is generally carried out in one of two ways; Top-down (physical) or bottom-up (chemical) technologies as shown in Fig. 2. A bottom-up approach is performed during a reverse maneuver, increasing the size of the precursor particles by exploiting chemical reactions to mix atomic or molecular species. The top down approach uses an external force/pressure on bulk materials to break down it into smaller components by means of mechanical, chemical or some other energy sources. Each of the approaches is applied in a variety of states, including solids, liquids, gases, and supercritical fluids or vacuum. Because of the size, the shape of the metal particles is the most important facet that needs to be modified to improve the performance of the application; it is also essentially dynamic facet that needs to be considered for the catalysis in any chemical process.

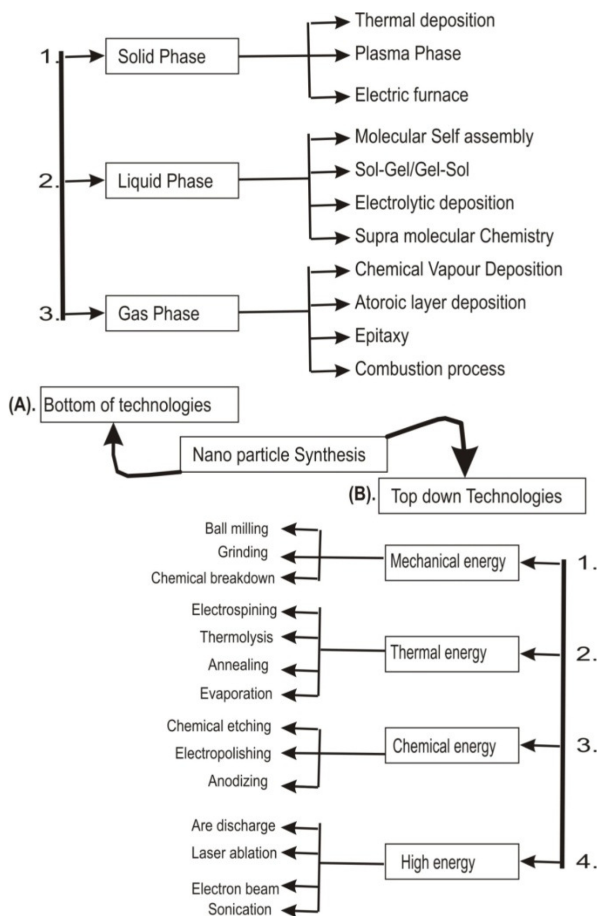

Fig. 2.

In the synthesis of MNPs with well-controlled size, it is specially generated by exploiting completely different stabilizing agents or protecting agents, i.e., ligands (thiols, phosphines, amines), surfactants (ammonium salts), polymers (polyvinyl alcohols, polyvinylpyrrolidone, block copolymers), dendrimers (polyamidoamines), ions, polyoxoanions, etc [26, 27]. The appropriate choice of protecting/stabilizing agents is an extremely important issue as they alter the surface properties of NPs by modifying the active sites (morphology) and the surface environment (steric and/or electronic effect). The selectivity and reactivity of NPs are of crucial importance, since they extremely affect the course of the reaction, which depends in particularly on the surface composition, structure, exposure, and morphology, and thus can be efficiently controlled.

B. Possibilities for the characterization of nano-particles

Nano-scale materials have unique properties that make them suitable for a wide variety of applications. It is important to have a thorough understanding of the nanoscale properties of metallic particles in order to know the nature of the active sites, which in turn facilitates the search and fitting of the key achievement sign. There are many techniques for characterizing nanoparticles, although none are ready to provide complete data on the materials studied (as in Table 1). Because of this, many techniques must be used to substantiate each sample in terms of scale, structure, shape, valence, chemical composition, etc. and chemical properties.

The common forms of MNPs characterization include transmission electron microscopy (TEM) and scan electron microscopy (SEM). Other common techniques include X-ray photoelectron spectroscopy (XPS), UV spectroscopy; atomic force microscopy, X-ray powder diffraction (XRD), Energy Dispersive X-ray (EDX) and dynamic light scattering (DLS).UV spectroscopy and Fourier transform infrared (FTIR) spectroscopy methods would be combined to study gold and palladium nanoparticles [14]. In contrast, silver nanoparticles would be studied by TEM, high-resolution TEM and selected area diffraction pattern (SAED) [15]. Finally, X-ray diffraction, SEM and FTIR would be combined to study magnetite, silver, zinc and gold nanoparticles [15-17], a solvent free ZnO nano-rods synthesis also reported [41].

Table 1: Some Selected techniques used for metal nanoparticles.

S. No.	Characterization techniques	Informations received
1.	Scanning electron microscopy (SEM)	Dimension size and Morphology of MNPs
2.	Transmission electron microscopy (TEM)	Size and Morphology of MNPs
3.	X-ray photoelectron spectroscopy (XPS)	Surface composition of supported MINPs
4.	UV-Vis spectrum	Configuration of colloidal MNPs (Plasmon band)
5.	X-ray diffraction (XRD)	Crystal structure and size , element composition
6.	Dynamic light scattering (DLS)	Size and size distribution of MNPs in solution
7.	Fourier transformed infrared spectroscopy (FTIR)	Dissimilar functional groups and mental- mental and/or mental-oxygen bond identification
8.	Energy Dispersive X-ray (EDX)	Element and distribution of MNPs
9.	Scanning tunneling microscope Raman Spectroscopy	Mass and Morphology of MNPs chemical structure, phase and morphology

CATALYTIC PROPERTIES OF SUPPORTED METAL NANO-PARTICLES (SMNPS)

Supported metal nano-particles (SMNPs) carry transition-metal MNPs or noble metal groups deposited on supports with large surface area (150–1200 m^2 /g). In general, the metal loading of the supported metal catalytic particle ranges from 0.5 to 10 wt% and MNPs typically have a size range of about 01 to 30 nm. Thus the SMNPs reveal chemical and physical properties intermediate between those of single metal atom and bulky metal particles size of more than 100 nm. In particular, the reactivity of the supported metal catalyst in heterogeneously catalyzed reactions is determined, by the size and shape of the metal species (MNPs) deposited (or distributed atomic monolayer) on the carrier (support) surface, whereby the surface metal atoms can only participate in the chemical reaction [18, 19]. Gold NPs on alumina (when used as a support) smaller than 4 nm (while 7-8 nm in size on carbon support) show complete conversion upon ethylene glycol oxidation, but as the diameter of gold NPs increases & when it exceeds 5 nm and falls up in the conversion of about 40 percent [20]. Therefore, nano-catalyst performance is very sensitive toward particle size and is also greatly affected by different types of supporters. Various oxidic supports such as alumina, silicas, titanias, ceria, zirconia etc. and a number of other carbon materials are typically used as supports for MNPs. Usually a support material must have strong a “Metal-Support interaction” , a high surface area and incidence of active sites that can contribute to the reaction process [29]. These supports are superior to the metal powders for several reasons, such as stable heat capacity, reduced price, larger surface area and effective use of MNPs within the wide dispersion style [30]. The SMNPs are used today as sensors, nano-electronics, medico-technical devices, drug delivery and heterogeneous catalysis [31, 42].

The catalytic properties of MNPs can be influenced by a second metal, the so-called bimetallic catalyst, whereby the addition of the second metal usually leads to alloys with completely different electronic and structural properties. Some examples are the formation of bimetallic “Pt- Ni”or Pt-bimetal SMNPs for electro catalytic applications [21] or “Au-Ni” SMNPs for steam reforming of hydrocarbons, Co-Mo and Ni-Mo bimetallic SMNPs for sulfur removal in refineries [20]. Bimetallics are a tremendously new and advanced area of nanocatalysis [22]. Au, Pd, Rh, Ru, Ni or Ag are the most commonly used MNPs/SMNPs for hydrogenation/dehydrogenation (fats and CO), oxidation and gas upgrading from automobile exhaust, fossil fuels purification and C-C coupling transformations [24, 25].

The structure and shape-dependent properties of any nanometer-sized material can affect the reactants mobility and product quality of a chemical reaction. Again, the standardization of nanocatalysts in specific shape and size for the synthesis of a desired product has achieved a remarkable additional property in MNPs as selectivity [32].

GREEN CATALYTIC USES OF METAL NANOPARTICLES (MNPS)

Nano-catalysis is a newly growing field and an important part of "sustainable technology and organic transformations" applicable to mostly all types of catalytic-chemical transformations [28]. Nano-catalysis is greatly effective in the chemical processing industry due to lower energy consumption, environmentally friendly behavior and especially also it’s improved economical considerations. For example, novel alumina-supported-NiO nano-catalysts are used in the assembling of syn-gas and bio-oil from pyrolysis of biomass.

The nano-catalysts improved the syngas standard by lowering the monoxide content in the syngas; it also reduced the tar content in the product [33]. Biomass energy covers about 15 percent of the total global energy needs; the organic materials namely; wood, crops, organic waste (animal manure, municipal waste, etc.) have been used for biomass energy production.

Biomass produced mostly through the method of photosynthesis; according to the study, around 720 tons of biomass is produced every year [34]. Three main types of reaction to convert bio-mass into fuel energy are combustion, pyrolysis and catalytic gasification process. The pyrolysis technique is the most popular among the alternative techniques to produce bio-Oil, which has high moisture content; long chain organic compounds and low carbon to hydrogen ratio make it difficult to burn. Therefore, mainly bio-fuels are not used directly as a fuel. Aravind [35] and Malik [36] studied the influence of nanocatalysts in the bio-oil to syngas conversion process and concluded that vast surface area nanoparticles are the simplest alternatives to typical catalysts to improve syngas performance. Due to its high boiling point, tar is an undesirable by-product of the corresponding quality in syngas production and therefore clogs the filter and the piping. Tar is also a catalyst poison [37].

There are two ways to manage the assembly of tar: one, interval treatment of the carburetor, and the other, treatment of hot gases in the carburetor. The second method is the cheapest, so it is used only in industry. Na, K and Ca nanocatalysts are used to treat wastewater with hot gases to reduce the amount of tar [38]. The catalytic reforming of tar using metal nano-catalysts is preferred because no additional energy is required and that is why nanocatalysts are called green catalysts.

This catalytic reaction also includes steam reforming, hydro-cracking and hydraulic reforming. In the Fischer-Tropsch (FT) synthesis of green diesel, nano-catalysts composed of metallic elements like Fe and Co with a size of 10–15 nm are used in slurry reactors to improve the yield of high molecular weight waxes. These waxes are then hydro-cracked to produce green diesel, a very important method of converting the nanopetro-oil feedstock such as coal and biomass into clean/green diesel that could be used as green-fuel. It can be reported that the use of nano-catalysts drastically reduces the expenses of this method [39].

Fischer-Tropsch (FT) synthesis created an ultra-clean, high-quality, low-aromatic, zero-sulfur fuel. The raw material mainly consists of the mixture of linear and branched hydrocarbons. The two types of techniques are used for FT synthesis; however, levitated bubble column techniques are gaining additional interest due to their low pressure and stable temperature. In general, FT synthesis follows the distribution mechanism of ASP; however, this distribution does non-selective in this case. Later the new Fischer-Tropsch catalysts are developed; the novel FT nano-catalyst contain atomic number 27 (Cobalt) on porous silica is more selective for C_{10}–C_{20} hydrocarbons (diesel). MNPs are also used in fuel industry for reaction enhancement such as selective-hydrogenation, paraffin-hydrogenation, solvent-reforming and hydride-sulfurization, etc., few of the main units where nano-catalysts are used in oil refineries. Industrially, SMNPs catalysts are applied FT synthesis of hydrocarbons over Co, Fe, Ni, Ru transition metals. The monolayer hexane-thiol, protected with size of 1.5 nm palladium nano-particles are used to improve the energy consumption of the catalytic combustion of the JP 10 activation fuel. These nano-particles can also reduce the ignition temperature up to 240° C some of the fuels.

Hydrogen gas can be used in fuel cells to generate green energy; now the maximum 95 percent of the hydrogen is produced by partial oxidation and steam reforming of hydrocarbons. Both oxidation and steam reforming produce carbon dioxide, which is a major component of global warming. Catalytic reforming of green bio-fuels such as ethanol can be an environmentally friendly way to produce hydrogen gas. Ethanol is often available with high water content; the water and other impurities found in ethanol deactivate conventional catalysts. Nicolas *et al.*, [40] worked on the design of nano-catalysts for the production of hydrogen gas using ethanol and concluded that the alumina-supported rhodium metal nano-catalyst provides the highest yield of hydrogen gas with much better protection against water. The rhodium catalyst creates a split between carbon and hydrogen and this can be the main reason for the C-C bond cleavage. Hydrogen has an efficiency of 50-60% in the fuel cell, while only 20-25% of the fuel is converted into usable energy in the combustion diesel engine. Among all nano-catalysts, many forms such as magnetic nano-catalysts, nano-mixed metal oxides, core-shell nano-catalysts, nano-supported catalysts, and graphene-based nano-catalysts are used in various catalytic applications. Carbon supports to promote easy catalyst recovery from reaction systems. The recent trends use magnetic supports to recover the nano-catalysts from the catalytic reaction media. Magnetic separations can be an extremely cheap and fast tool for simple isolation with several advantages over alternative chemical and physical methods. Magnetic nano-catalysts feature in these re-usable nano-catalyst kits with their low capture price, wonderful reactivity, great selectivity, high stability, inexpensive recovery, and reasonable recyclability. Nano-particles are the emerging catalyst and find further applications which ranging from chemical manufacturing to energy conversion, storage and environmental remediation etc. (Fig. 3 and 4). Subsequently, the usual MNPs increase the selectivity and reactivity of the catalyst, resulting in lower energy consumption and high yield performance. In general, most chemical reactions take place on the surface of the catalyst and therefore the activity of the nano-catalyts increases with decreasing particle size of MNPs, also related reaction rate/speed.

The faster reactions are caused by the incessant decrease in the size of the metal nano-particle catalysts, while the increase in the size of the catalyst can decrease the reaction rate. Nano-catalysts indirectly help to reduce global warming by lowering the activation energy for each catalytic method/process with less poisoning magnitude. They further minimizing chemical wastes in the reaction processes; all of these factors resulted an improved economical and a safer ecological atmosphere.

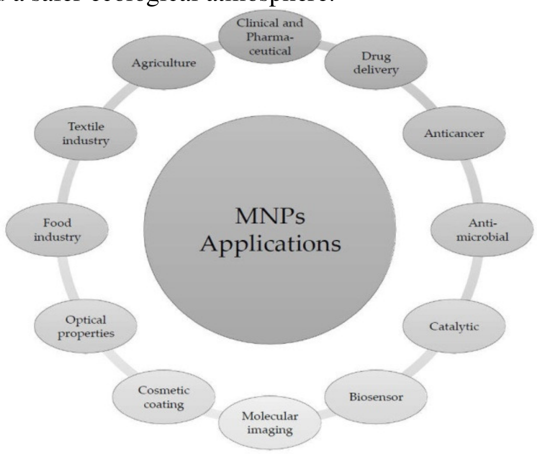

Fig. 3.

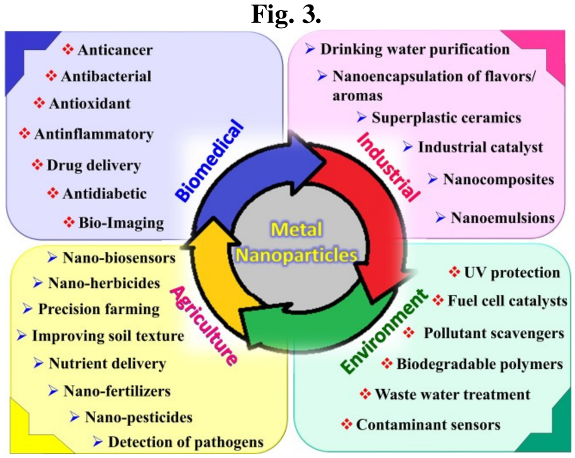

Fig. 4. Uses of MNPs In Different Fields.

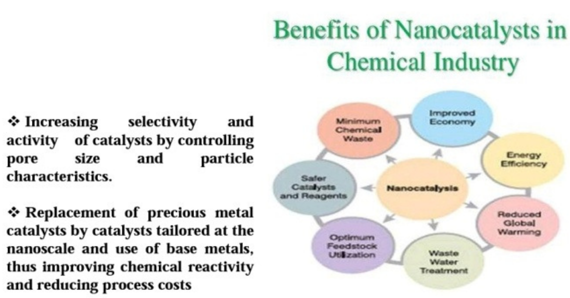

Fig. 5.

CONCLUSIONS AND FUTURE SCOPE

Metallic nanomateials, a vast new and emerging type of nanoparticls of the matters, have provocative prospects in the fields of microelectronics, optoelectronics, and sensors, especially in catalytic fields because of their excellent electrical, optical, magnetic and thermionic properties. Recent advances are created in governing metal particle morphology, size, and synthetic methodology. Previous analysis demonstrates that synthetic approaches and changes into chemical and oxidation-reduction environments may result in control over the ultimate form and morphology of NPs. Exploitation of the oxide carriers to synthesize stable MNPs has environment friendly implications because of the very fact that MNPs have distinctive properties as compared to bulk or isolated atoms (Fig. 5). Once these MNPs intervened successfully with the support, they'll stabilize the surface and should generate Lewis sites that will in turn bound reactants and may catalyze certain or selected catalytic reactions. However, their interaction degree depends upon the sort of support applied. Therefore, MNPs have diverse and new environmentally friendly applications. In-sight of this, extremely unsaturated systems are thought to be superior as they provide larger range of active surface for metal-nanoparticle sites that will permit efficient interactions between the support and active phases. The power to stabilize and management of other alternatives of MNPs (such as metallic element Pd, Rh, Pt, etc.) would be a wonderful advancement in its current potential, which now permitting the ideas and reactions with homogenized nano-catalysts to be employed in a heterogeneous context. However, the commercial application is proscribed by their activity and selectivity properties. Stability and durability of supported MNPs have good implications for productivity in catalyzed reactions. The various analyses conferred crucial the role of supported MNPs in numerous reactions happening, either in liquid or gas phase, still as their associated catalytic processes. The utilization of green nano-catalyst for the synthesis of variety of processes have many advantages such as shortened reaction time, high yield, inexpensive chemicals usage, easy work-up procedure and very selective in nature. Employment of nano-materials in catalysis has an inspiration for researchers makes to an attempt over globe to invent more resourceful and greener conventions. More pharmaceutical engineering are often accustomed with MNPs formulated drugs design which will target specific organs or cells within the body like caner/tumor cell, and enhances the effectiveness of medical care. Nanomaterials can even be value-added to cloths, food processing, refinery processing, cement industry etc., to form them stronger, eco-friendly, long-lasting and however light-weighted. Besides, as a result of their micron molecular size and an expanded surface area build them extremely helpful in electronically cleaning-up to bind with and neutralize micro-contaminants in environmental remediation devices.

Future analysis could address the creation of bi-functional or multifunctional MNPs, which can have implications for existing reactions or maybe new outputs. Investigation of bio-inspired efforts within the synthesis of nanomaterial's and its catalytic application in recoverability, biodegradability and bioremediation etc. are the forthcoming fields of MNPs/Nano-catalysts. There are more, rational approaches have to compelled to be puzzled out in the future for sequencing multi-functionalities, in the direction of developing a novel, attractive, more cost-effective and eco-friendly, nanostructure metal nanoparticles with the abundant exceptional catalytic applications.

REFERENCES

[1]. Hemalatha, K., Madhumitha, G., and Kajbafvala, A. (2013). Function of nanocatalyst in chemistry of organic compds revolution; an overview, *J. of nanomaterials*, Hindawi publishing corporation, **I**: 23, Article ID341015.

[2]. Nouailhat A. (2010). An introduction to nanoscience and nanotechnology, New York; Wiley, 101002/9780470610954

[3]. Polshettiwar, V., and Varma, R S. (2010). Green catalysis by nano-catalysis. *Green Chem.*, **12**: 743-754.

[4]. Liu, H., Guan, J., Mu, X., Wang, X., and Chen X. (2016). Nanocatal. Encycl., *Phys. Org. Chem.*, 1-75.

[5]. Somorjai, G., and Borodko, Y. (2001). Res. in nanosciences: Great opportunity for catalysis in science. *Catalysis letters.*, **76**(1-2): 1-5.

[6]. Haruta, M., and Date, M. (2001). Advances in the catalysis of Au nanoparticles, *Applied catalysis: A General,* **222**(1):2253–337.

[7]. Brayner, R., Viau, G., and Bozon-Verduraz, F. (2002). Liquid-phase hydrogenation of hexadiene on metallic colloidal nanoparticles on supports via coordination capture by bifunctional organic molecules. *J. of molecular catalysis; A Chemical,* **182**: 227-238.

[8]. Toshima, N., Shiraishi, Y., and Teranishi, T. (2001). Effects of additional metal ions on catalysis on polymer-stabilized metal nanoclusters. *Journal of Molecular catalysis ;A chemical*, **177**(1): 139-147.

[9]. Dai, J., and Bruening, M. L. (2002). Catalytic nanoparticles formed by reduction of metal ions in multilayered polyelectrolyte films. *Nano Letters*, **2**(5): 497-501.

[10]. Pileni, M. (1997). Nano-siezed particles made in colloidal assemblies. *Langmuir,* **13**(13): 3266-3276.

[11]. Fu, X., Wang, Y., Wu, N., Gui, L., and Tang, Y. (2002). Shape selective preparation and properties of oxalate-stabilized Pt colloid. *Langmuir*, **18**(12): 4619-4624.

[12]. Toshima, N., Kuriyana, M., Yamada, Y., and Hirai, H. (1981). Colloidal platinum catalyst for light induced hydrogen evolution from water; A particle size effect. *Chemistry Letters*, **10**(6): 793-796.

[13]. Hirai, H., Chawanya, H., and Toshima N. (1985). Colloidal palladium protected with poly (N-vinyl-2-pyrrolidone) for selective hydrogenation of cyclopentadiene. Reactive polymers, Ion exchangers, *Sorbents,* **3**(2): 127-141.

[14]. Srivastava, S. K., Yamada, R., Ogino, C., and Kondo, A. (2013). Biogenic synthesis and characterization of gold NPs by *E. coli* K12 and its heterogeneous catalysis in degradation of 4-nitrophenol. *Nanoscale research letters,* **8**(1): 70-77.

[15]. Petla, R. K., Vivekanandhan, S., Mishra, M., Mohanty, A. K., and Satynarayana, N. (2012). Soyabean (*Glycine max*) leaf extract based green synthesis of palladium NPs. *J. of biomaterials and nano-biotechnology*, **3**: 14-19.

[16]. Lee, J. H., Ahn, K., Kim, S. M., Jeon, K. S., Lee, J. S., and Yu, I. J. (2012). Continuous 3-days exposure assessment of workplace manufacturing silver NPs. *J. of Nanoparticle Research*, **14**(9): 1-10

[17]. Yang, H., Wang, Y., Huang, H., Gell, L., Lehtovaana, L., and Malola, S. (2013). All-thiol stabilized Ag-44, and Au-12, Ag-32 nanoparticles with single crystal structure. *Nature communications*, **4**: 2422-2427.

[18]. An, K., and Somorjai, G. A. (2012). Size and shape control of MNPs for reaction selectivity in catalysis. *Chem. Cat. Chem.*, **4**(10).

[19]. Cuenya, B. R. (2010). Synthesis and catalytic properties of MNPs, size, shape, support, composition and oxidation state effects, *Thin solid Films*, **518**(12): 3127-3150.

[20]. Haruta, M., and Date, M. (2001). Advances in the catalysis of Au NPs. *Applied catalysis A; General*, **222**(1): 427-437.

[21]. Cui, C., Gan, L., and Li, H. H. (2012). Octahedral Pt-Ni nanoparticles catalyst ; exceptional oxygen reduction activity by tuning the alloy particle surface composition. *Nano Letters*, **12**(11): 5885-5889.

[22]. Mortensen, P. M., Grunwaldt, J. D., Jensen, P. A., Knudsen, K. G., and Jensen, A.D. (2011). A review of catalytic upgrading of bio-oil to engine fuels. *Applied catalysis A ; General*, **407**(1): 01-19.

[23]. Dingsheng, W., and Yadong, L. (2011). Bimetallic nanocrystals; liquid phase synthesis and catalytic applications. *Adv. Mater.*, **23**: 1044-1060.

[24]. White, R. J., Luque, R., Budarin, V. L., Clark, J. H., and Macquarrie, D. J. (2009). Supported metal NPs on porous materials; Method and applications. *Chemical society reviews*, **38**(2): 481-494.

[25]. Jia, C. J., and Schuth, F. (2011). Colloidal metal NPs as component of designed catalyst. *Physical chemistry-chemical physics,* **13**(7): 2457-2487.

[26]. Yan, K., Liao, J., Wua, X., and Xie, X. (2013). A noble metal free Cu-catalyst derived from hydrotalcite for highly efficient hydrogenation of biomass derived furfural and levulinic acid. *RSC Adv.*, **03**: 3853-3856.

[27]. Chaudhari, R. G., and Paria, S. (2012). Core/Shell nanoparticles, synthesis, mechanism, characterization and appl. *Chem. Rev.*, **112**: 2373-2433.
[28]. Gawande, M. B. (2014). Sustainable nano-catalysts for organo-synthetic applications. *Org. Chem. Curr. Res.*, **3**: 1000e137.
[29]. Kasta, P., and Friedricha, M. (2016).Strong metal-support interaction and alloying in Pd/ZnO catalysis for CO oxidation. *Catalysis Today,* **260**: 21-30.
[30]. Alshammari, A. S., Chi, L., Chen, X., Bagabas, A., Kramer, D., Alromaeh, A., and Jiang, Z. (2015). Visible-light photocatalysis on C-doped ZnO derived from polymer assisted pyrolysis. *RSC Adv.*, **5:** 27690-27698.
[31]. Prieto, G., Zecevic, J., Friedrich, H., and De Jongh, P. E. (2013).Towards stable catalyst by controlling collective properties of supported MNPs. *Nature materials*, **12**(1): 34-39.
[32]. Sadjadi, S., Majid, M. H., and Malmir, M. (2018). Pd (0) NPs immobilized on cyclodextrine-nanosponge-decorated Fe_2O_3@SiO_2 core-shell hollow sphere; an efficient catalyst for C-C coupling reactions. *J. Taiwan Inst. Chem. Engg.,* **86**: 240-251.
[33]. Akia, M., Yazdani, F., Motaee, E., and Han, D., Arandiyan, H. (2014). A review on conversion of biomass to bio-fuel by nanocatalysts. *Biofuel Res. Journal*, **1**(1): 16-25.
[34]. Luo, Z., and Zhou, J. (2012). Thermal conversion of biomass, *Handbook on climate change*, Mitigation, New York; Springer: 1001-1042.
[35]. Aravind, P., and De Jong, W. (2012). Evaluation of high temperature gas cleaning options for biomass gasification product for gas for solid oxide fuel cells. *Progress in combustion science*, **38**(6): 737-764.
[36]. Malik, P., and Sangwan, A. (2012). Nanotechnology; A tool for improving efficiency of bio-energy. *Journal of Engg. and Applied Sciences,* **01**: 37-49.
[37]. Asadullah, M. (2014). Barriers of commercial power generation using biomass gasification gas; A review. *Renewable and sustainable energy reviews,* **29**: 201-215.
[38]. Nziou, A., Stanmore, B., and Sharrock, P. (2013). A review of catalyst for gasification of biomass char; with some references to coal. *Energy,* **58**: 305-317.
[39]. Hutchings, G., Polshettiwar, V., and Asefa, T. (2013). Nanocatalysis; Synthesis and application, New York; John Wiley & Sons.
[40]. Bion, N., Dupreze, D., and Epron, F. (2012). Design of nanocatalysts for green hydrogen production from bio-ethanol, *Chem. Sus. Chem.,* **05**(1): 76-84.
[41]. Anand, K., Verghese, S., and Kurian, T. (2014). Synthesis of ZnO nano-rods through Mechano-chemical route; a solvent free approach. *International Journal of Theoretical and Applied Sciences,* **06**(01): 87-93.
[42]. Manchanda, S., Rokade, M., Saroan, M., and Saroan, M. (2016). Suitability of carbon nano-tubes as drug carrier. *International Journal of Theoretical and Applied Sciences,* **08**(02): 50-53.