



REVIEW OF RESEARCH

ISSN: 2249-894X

IMPACT FACTOR : 5.2331(UIF)

VOLUME - 7 | ISSUE - 4 | JANUARY - 2018



Review Article METAL NANOPARTICLES AND CATALYSIS

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ABSTRACT :

The theme of nanoscience was stated, initially, by Nobel Laureate Physicist Richard Feynman, who delivered the lecture entitled "there is plenty of room at the bottom" at the California Institute of Technology in the annual meeting of the American Physical Society on December 29, 1959 [1, 2]. In his talk, Feynman considered the possibility of direct manipulation of individual atoms as a more powerful form of chemical molecules than those used at the time. He also suggested that it would be possible, in principle, to make nanoscale machines by arranging the atoms as per the desired and designing as well as synthesis of chemical molecules by manipulation. He pointed that the volumes of Britannica encyclopaedia would be put on the head of pin.

William McLellan constructed a small motor by hand using tweezers and a microscope in 1960. In 1974, the term "nano-technology" was first used by Norio Taniguchi, though it was not widely known earlier. In 1986, with inspirations of Feynman's ideas, K. E. Drexler independently used the term "nanotechnology" in his book "Engines of Creation: The Coming Era of Nanotechnology", which proposed the idea of a nanoscale "assembler" which would be able to build a copy of itself and of other items of arbitrary complexity with control of atoms. In 1986, Drexler also, co-founded Foresight Institute to help increase public awareness and understanding of nanotechnology concepts and implications.

KEYWORDS : *Chemical molecules, magnetic tools.*

INTRODUCTION:

1. Metal nanoparticles and catalysis

Metals as well as metal oxides in nano scale have been emerging materials in research direction to modernize the society in connection to the various fields such as catalysis, electronic devices, optical devices, magnetic tools, medicine, etc. It is well known that these particles in nano-scale dimensions are formed either by bottom-up or top-down approach; but as concerned to specific area such as opto-electronics, chemical transformation, the latter top-down approach is replaced by former one. Particularly, the bottom-up route for synthesis of NPs is one of the promising strategies due to its overriding advantages over other and also these particles would be efficient catalysts for the development of various chemical transformations and drug molecules from raw materials. Catalyst plays a dominant role in achieving a green environmental route, through, for example, the destruction of pollutants (as with the catalytic converters found on the exhaust systems of vehicles), the development of efficient industrial processes with higher product yields and fewer unwanted by-products, the generating clean energy using fuel cells. In addition to its contribution to further improvement in the quality of life and also for economic contribution, catalysts

are interesting in their own right: the subtle influence a catalyst has on reagents can completely change the overall outcome of a reaction. The complete understanding of mechanistic path in a catalytic reaction has improved considerably in recent years with isotopically labelled molecules, reaction rate determinations, the use of spectroscopic techniques, and much more reliable molecular orbital calculations. Transition metal NPs are easily prepared even in uniform nanometer size and their applications to catalysis successfully give the productive results as a fundamental research.

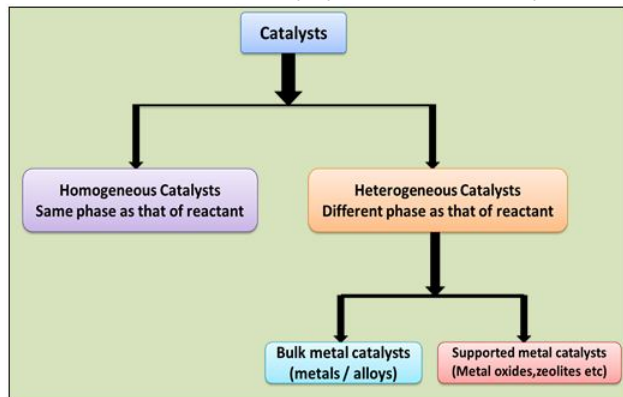
Catalysis

Catalysis is an important tool in chemical transformations. The Greek word 'catalysis' was coined by Berzelius in 1836, the prefix, 'cata' meaning down, and the verb 'lysis' meaning to split or break [3]. Catalysis-based research is a major field in applied science and involves many areas of chemistry, particularly materials science and organometallic chemistry. This process is relevant to many aspects of environmental science such as the degradation of toxic pollutants, catalytic converter in automobiles, etc and which is usually driven by a substance called as a catalyst.

According to Berzelius, the catalyst is a substance added to the reaction precursor to change the rate of reaction without being consumed or produced in the process. A catalyst is a substance which also changes the pathway or mechanism of a reaction without its involvement and often may appear in the rate determining step, but not in the overall stoichiometry of the reaction. A catalyst usually increases the rate of a reaction but is not itself consumed. Catalysts are widely used in nature, in industry, in the laboratory for conversions. It is generally estimated that they are contributing one-sixth of the value of all manufactured goods in developed countries. The catalytic activity and selectivity of catalyst depends on its composition and structure. The particle size, morphology are the key factors; which mostly affect the catalytic properties of catalyst. As the catalytic process occurs only on the surface of the catalyst, the high surface area with small size metal particles are favoured as catalyst [4].

Types of Catalysts

Catalysts are classified into two types basically such as heterogeneous and homogeneous depending on whether a catalyst exists in the same or different physical state as compared to reactant.



1) Homogeneous catalysts

Homogeneous catalysts are present in the same phase to that of reactants, and are often well defined; this normally means that they are present as solutes in liquid reaction mixtures. Generally homogeneous catalysts are dissolved in a solvent with the reactants. As per practical sense, homogeneous catalyst is promising because it is often highly selective towards the formation of a desired product. In large-scale industrial processes, these catalysts are preferred for exothermic reactions because these are easier to dissipate heat from a solution than from the solid bed of a heterogeneous catalyst. In principle, every homogeneous catalyst in solution is accessible to reagents, potentially leading to very effective activity. It should also be noted that the mechanism of homogeneous catalytic process is more accessible to detailed

investigation than that of heterogeneous one as species in solution are often easier to characterize than those on a solid surface and hence the kinetic interpretations are easier. The main disadvantage associated with homogeneous catalysts is its ease separation.

II) Heterogeneous catalysts

Heterogeneous catalysts are present in a different phase from the reagents. These are usually in solid forms that act on reactants in a liquid or gaseous reaction mixture. Heterogeneous catalyst is gaining increasing importance in the chemical conversions due to its definite technical advantages, which greatly enhance production processes, competitiveness and economics. For example, heterogeneous catalysts employed as main cracking catalysts in petroleum refinery, which is the largest process among the industrial chemical processes. The main advantage of the heterogeneous catalytic process is that it can be operated continuously in a reactor without interruption. As the catalyst is present in different phase from the reactants and products, the separation of the catalyst from the final reaction mass is also quite easy. Among various heterogeneous catalysts, metal-based systems are versatile and widely used for many organic transformations reactions like oxidation, hydrogenation and dehydrogenation, condensation, cracking, alkylation, isomerization, etc.

A heterogeneous catalyst has active centers, which are the atoms or crystal faces where the reaction actually occurs. Depending on the mechanism, the active sites may be either crystal edge with imperfect metal valence, or planar exposed metal surface, or complicated combination of the two. Nano-dimension heterogeneous catalysts are usually "supported," which means that the catalyst is dispersed or supported on another material that enhances its effectiveness in transformations. Supportive materials prevent or reduce agglomeration of the small particles and hence enhances more stability, exposing more surface area, thus catalysts have a higher specific activity (per gram) on a support. Sometimes the support is merely a surface on which the catalyst is spread to enhance the surface area. More often, the catalyst and support interact, also affecting the catalytic paths. Various types of supportive materials are used. These include alumina, zeolites or various kinds of activated carbon, silicon dioxide, titanium dioxide, calcium carbonate, barium sulphate, etc. Most of the heterogeneous catalysts used are in porous solids form. These catalysts usually consist of active species, promoters and supports. The overall activity and selectivity of the catalyst would be a combined effect of these components present in it. Catalytic reaction takes place when one or more of the reactants chemisorbed on the surface and get reacted. The activity and selectivity of a catalyst depends strongly on the structure and surface morphology.

Depending on the nature and form of an active component, the heterogeneous catalysts are sub-classified as follows:

(a) Bulk metal catalysts

Among the most important and widely used industrial catalysts, metals are catalyzing wide variety of transformations [3]. In the literature, the preparation and characterization of unsupported metals are reviewed [5]. In case of alloys, the introduction of a second metal may enhance the properties of the resultant catalytic system [6]. Relatively, the high densities of skeletal catalysts provide excellent settling characteristics compared to supported catalysts when used in slurry phase reactors.

(b) Supported metal catalysts

Multiphase catalysts are non-uniform solids at the molecular or crystalline level and usually consist of an active phase dispersed on a carrier support. Metals used in industrial catalysis are often expensive and hence they are predominantly used in a highly dispersed form on high surface area porous supports (e.g. metal oxides, zeolites, carbon or polymers). Naphtha reforming catalyst, which is rhenium-platinum supported on $\gamma\text{-Al}_2\text{O}_3$ is a classic example of this kind [7].

METAL NANOPARTICLES AS CATALYST

The use of metal nanoparticles (NPs) as a catalyst in chemical transformations is promising due to their surface activation and thereby brings selectivity and efficiency to heterogeneous catalytic system [8,9]. Particularly, transition-metal NPs are bunches containing from a few to several thousand atoms, stabilized by surfactants, ligands, dendrimers, polymers or protecting their surfaces or supported by oxides. Their sizes vary between 1-100 nm or higher than it, but the most active form in catalysis are only one or a few nanometer in diameter [10]. This approach is also similar to homogeneous catalyst, because there is a full continuum between small metal clusters and large metal clusters, the latter being also called colloids, sols or NPs. NPs are also well soluble in regular solvents and can often be characterized as molecular compounds by spectroscopic techniques such as NMR, infrared, UV– visible spectroscopy and cyclic voltammetry. The size and shape of the metal NP catalysts are key aspects of the catalytic steps and molecular mechanisms involving the NP surfaces in catalytic reactions are much more difficult to elucidate, however, than those of monometallic catalysts. NPs themselves can also be used as catalysts in homogeneous systems or alternatively they can be heterogenized by fixation onto a heterogeneous support such as silica, alumina, or other oxides or carbon nanotubes. Thus, metal NPs in catalysis field involves both the homogeneous and heterogeneous catalytic systems, and these systems are sometimes therefore called “semi- heterogeneous” [8-10].

Among these, metal NPs as a heterogeneous catalyst has attracted in all kinds of catalytic reactions, because these systems are selective, efficient, recyclable and thus meet the modern requirements in catalysis. Applications are already numerous, and the use of these catalysts in industry will obviously considerably expand in the coming years. The stabilization of metal NPs is one of the challenges associated with the system. However, with various ways such as electrostatic, steric, electrosteric (combination of steric and electrostatic) or by ligands or by supportive materials [10-14], one can enhance the stability of metal NPs. In view of the catalyst recycling, NP catalysts are often immobilized or grafted onto inorganic or organic supports [10-14].

Importance of supported metal nanoparticles in chemical transformations

Supported metal NPs are promising systems for various catalytic chemical transformations. As concerned to catalytic applications, the supported metal NPs have several overriding advantages over elemental or bare metal NPs. This is due to well dispersion of the active catalytic centres, recyclable, good accelerability and stability for longer period. Support is an important component in heterogeneous catalysis. The various supportive materials include metal oxides, polymers, ligands, carbon based materials, zeolites, etc.

Metal NPs loaded on an inert support used as catalyst for hydrogenation reactions, oxidation-reduction reactions, condensation reactions, coupling reactions, etc. By anchoring the metal NPs on a solid surface, structurally organized catalytically active sites are fabricated. These systems exhibit higher activity and selectivity than their homogeneous counterparts with structurally disorganized active sites. In unsupported form, the atoms present on the surface will only be taking part in the catalysis and remaining atoms present inside the bulk of the unsupported system cannot take part in the reaction, since these atomic or molecular species remain inaccessible. In order to overcome this problem, the active materials are often loaded on a support surface. Catalysts anchored to inorganic or organic supports are sufficiently different in their physiochemical aspects when compared to other support materials like polymers or others [15,16].

Following are the important features of the supportive materials:

- ✓ Supports provide best dispersion of the active component, good stability and accelerability. Hence, a porous or mesoporous material which has high surface area is preferred as a support. The porous nature of the support may also control the overall conversion through transport of the reactant and the product molecules.

- ✓ The support reduces the amount of the active component needed and increases the effective surface area of the catalyst.
- ✓ The support holds on its surface the microcrystalline particles of the active component and prevents its sintering. Hence metal-support interactions are an important in supported catalysis.
- ✓ The support may interact with the active component deposited on it and form a new complex which may have better catalytic activity and selectivity than that of the bare catalyst.

CONCLUSION

As the catalytic process occurs only on the surface of the catalyst, the high surface area with small size metal particles are favoured as catalyst.

Nano-dimension heterogeneous catalysts are usually supported, which means that the catalyst is dispersed or supported on another material that enhances its effectiveness in transformations.

The use of metal nanoparticles as a catalyst in chemical transformations is promising due to their surface activation and thereby brings selectivity and efficiency to heterogeneous catalytic system.

The size and shape of the metal NP catalysts are key aspects of the catalytic steps and molecular mechanisms involving the NP surfaces in catalytic reactions are much more difficult to elucidate, however, than those of monometallic catalysts.

Metal NPs loaded on an inert support used as catalyst for hydrogenation reactions, oxidation-reduction reactions, condensation reactions, coupling reactions, etc. By anchoring the metal NPs on a solid surface, structurally organized catalytically active sites are fabricated.

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