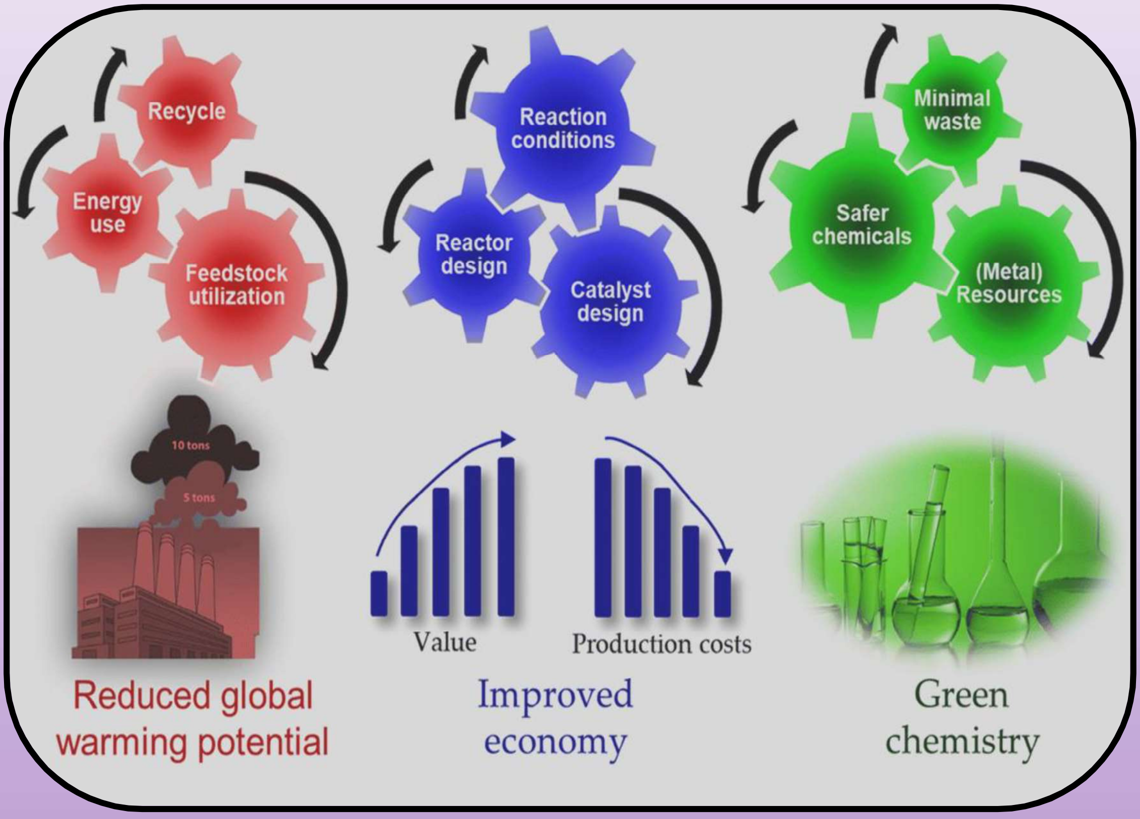
CHAPTER-1

INTRODUCTION



[1.1] General Introduction

Over the last century, catalysis was turn out to be a renowned phenomenon and became a hidden force for the up-gradation of our chemical industry. On the same basis, it is estimated that the maximum percentage of industrial chemical processes in the 21st century will have the involvement of catalytic reactions [1] For instance, the making of detergents, the fermentation of wine to vinegar, leavening of bread, etc. are all based on catalysis.

Catalysis is a phenomenon through which chemical processes are fastened with the help of minor quantities of the other substance, called a catalyst. Despite not changing the position of thermodynamic equilibrium, a perfect catalyst for any thermodynamically allowed reaction can enhance its rate. Most of the catalysts are in the solid or liquid phase, but the gaseous state may also exist. [2]

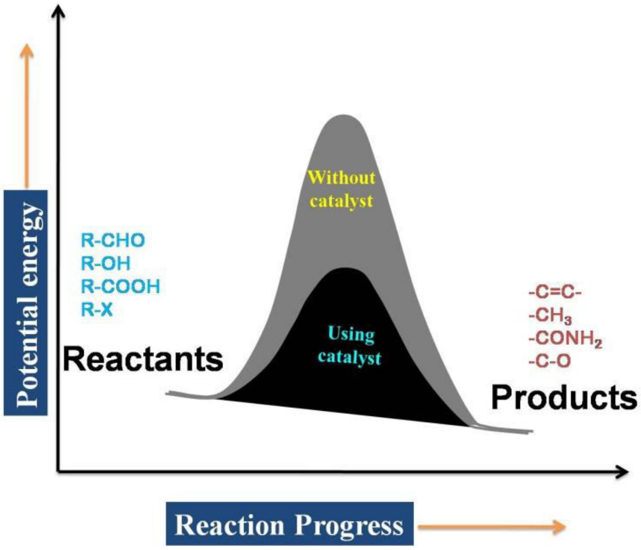


Figure 1 Schematic energy diagrams of simple catalytic and non-catalytic reaction pathways.

[1.2] A brief historical background

In the 1830s, the Swedish scientist Jons Jakob Berzelius was the first one to notice that catalyst itself being unchangeable may influence a reaction as an agent: "***Several bodies exercise on other bodies an action very different from chemical affinity. They produce decompositions of their elements and different recombination of these same elements, to which they remain indifferent***."

In reality, before Berzelius's discovery, the catalyst had been used in laboratories, for example, the Dutch chemist Martinus van Marum observed the dehydrogenation of alcohol on metal catalysts. However, the special unknown effect of metal other than a source of heat was first recognized by Berzelius and later he put forward the existence of a new force i.e. *catalytic force*. Around 30 years later, the British physicist and chemist Michael Faraday marked that the aforementioned effect takes place on the catalyst's surface. To prove his point, he showed that hydrogen and oxygen recombined with the help of Pt metal. At the end of the 18th century, the Riga-born German chemist Wilhelm Ostwald recognized that catalyst influences the rate of a reaction without affecting its outcome. By that time, although the molecular view of the matter had been accepted, but still the actual working ability of the catalyst was not completely known. [3-5]

As generally seen in the case of scientific development, the war became the sparking force for rapid progress in the application of catalysts. Roughly around in the 19th century, German chemistry altered gear when the ban was released on supply of natural Chile saltpeter, a key ingredient of dynamite. Primarily being imported from Chile, the substance was extorted from bird's droppings or guano. Munitions supply could be threatened by the shortage of saltpeter due to which their stakes were high and this prompted a key research exertion. Subsequently, a catalytic process to synthesize ammonia was swiftly established. It was then scaled up and for the first time before the epidemic of the First World War, Germany has set up the world's first nitrate plant. The whole project was initiated by three Nobel laureates –Fritz Haber, Wilhelm Ostwald, and Carl Bosch who are considered as the founding fathers of modern chemistry. Besides military purposes, later on, the non-military application of nitrogen found its way in important chemical processes in industry, such as fertilizer production. This became a changing point in agriculture and was proved to be a boon for humanity. [6]

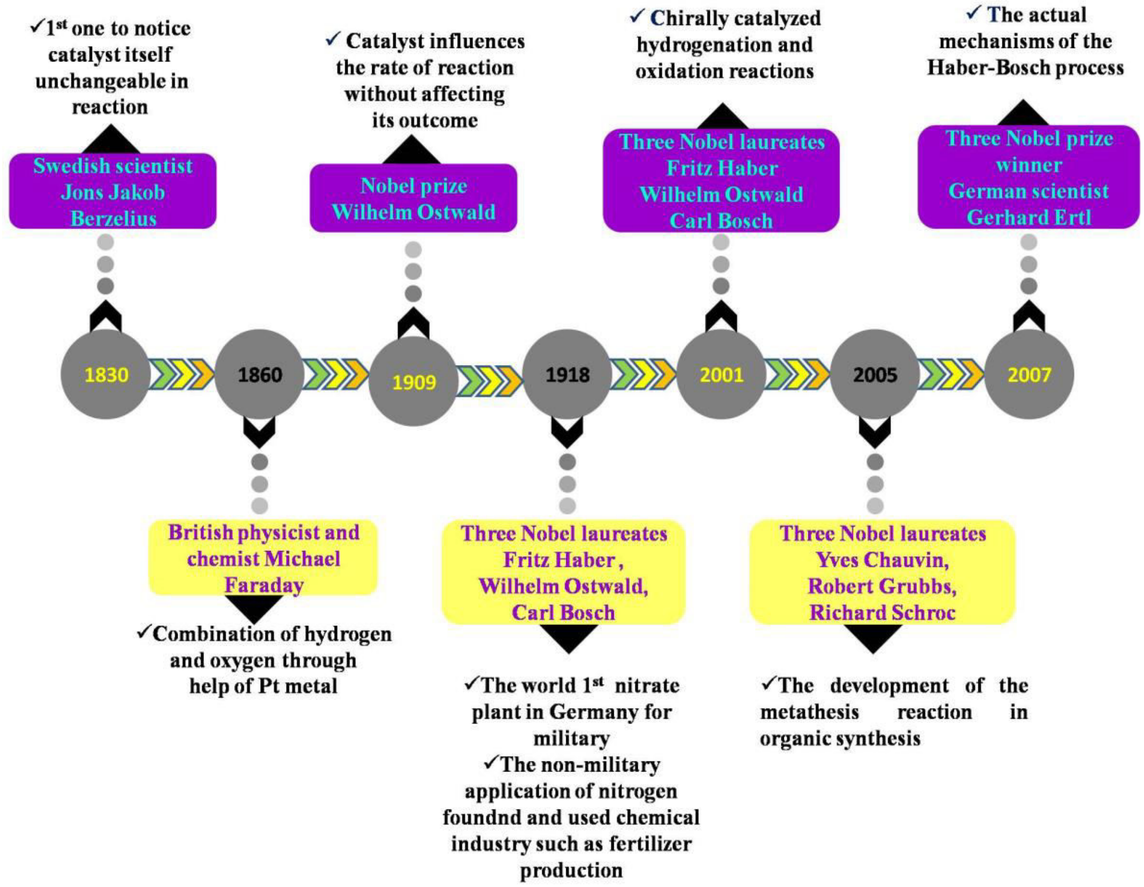


Figure 2 The historical development map of catalysts.

A German scientist Gerhard Ertl received the Nobel Prize in 2007 for straightening out the actual mechanisms of the Haber-Bosch process. During the 1960s, to investigate actual happenings on the surface of a catalyst, he started using the equipment used in the semiconductor industry. With the aid of the same advanced high-vacuum equipment, he was able to find out the individual layers of atoms and molecules on extremely pure surfaces. Taking help from a variety of harmonizing experiments, he developed a method, which could provide a complete picture of a catalytic reaction and found out to be a turning point in the understanding of catalyst action. [7]

Recent Nobel prizes have also rewarded new scientific discovery. Newly found catalysts i.e. metal-organic complex molecules are highly selective as comparable to the properties of enzymes. In 2001 William Knowles, Ryoji Noyori, and Barry Sharpless honored Nobel Prize for their chirally catalyzed hydrogenation and oxidation reactions. Yves Chauvin, Robert Grubbs, and Richard Schrock received the same honor for the development of the metathesis reaction in organic synthesis in 2005. This proves the enormous progress in the field of molecular homogeneous catalysis.

The advancement of catalytic processes proved to be an important transition in the chemical industry. In earlier decades of industrial growth, many industries showed that such processes are being also found in newly formed ecosystems i.e. land reclaimed from the sea, newly formed dunes, or an island from a volcanic eruption. The first species proved themselves the one for producing many seeds. By multiplying swiftly and scattering to new spots, such pioneering species survived in a complex environment. Just as locusts hardly care about the fields, similarly, factories are scrapping up raw materials and releasing residues without being thinking about the depletion of the earth or the trouble they are imposing on the eco-systems.

Over the last century, industry touched down roots, enlarged branches, and started to set up techniques that are more feasible. Inadequate natural resources were been replaced by manufactured chemical components. By making chemical processes more selective, catalysis is more economical in their use of materials. Giving an example, as we get to see in an oak-beech wood or a tropical rainforest, where maximum species are mutually supporting one another and the excreted products of one make available nutrients for another, similarly, this looks like an ecosystem that had developed in the direction of a complex biotope. Therefore, pure colonization gave an ideal basis for developing a close-knit rapport of the industrial ecosystem with its ambiance.

Nowadays, less flexibility of small-scale manufacturing plants challenges our chemical industry. Here, comes the vital role of catalysis technology. By shifting attention towards the designing of small-integrated devices from developing processes in the large plants, performing a variety of tasks have become potential by using catalysts at precisely controlled conditions. This may help in bringing about the enhanced flexibility necessary for the stable industrial ecosystems for the future. [Fig. 3]

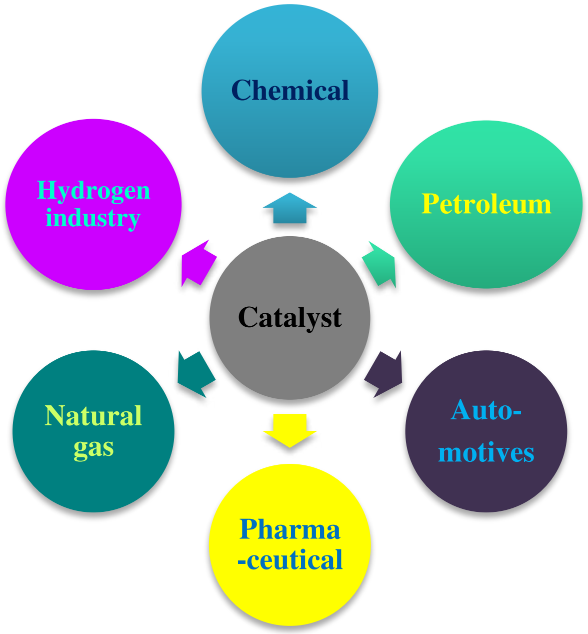


Figure 3 Potential application of Catalyst.

[1.3] Emerging materials on the industrial perspectives

Based on an industrial point of view, around 90% of chemical productive processes have catalyst playing as a key role like petroleum, chemical, and pharmaceutical industries producing several kinds of stuff starting from fuel and paint to drugs and cosmetics. Such an active role by catalysts signifies that they are indispensable for a healthy economy. Making alternative fuels by catalysts helps in the reduction of detrimental byproducts, maintaining the milieu hygienic and preventing future pollution. Though catalysts make up only a petite fraction of the total costs by the chemical industry their addition is substantial and the reason for the same is that they can be recyclable during the process. By such recyclable characteristics, although the production costing of products is about €1,000 billion worldwide, the actual outlay in catalysts is around 1% only. Such an intensify effect makes it attractive to invest in the progression of novel catalysts, keeping the chemical industry spirited.

Catalysis also helps in making numerous processes more eco-friendly. To clean up, our milieu has inbuilt monetary value, which is not figured out in the present cost-effective models. Additionally, the development of cleansing systems is an emergent profitable venture, extending from catalytic converters for automobile exhausts to potential photochemical systems through fuel cells. Overall, industrial activities that help accountable and tenable production have an exceptional growth prospective. For the accurate making of intermediate and fine chemical products, catalysis plays an imperative role by amplification in the selectivity of chemical processes.

Besides this, new intermediate stuffs are feasible only because of catalytically modified chemical routes. The more defined production of polymers brings it possible for superior tailoring properties of materials to their preferred use. Catalysts are helped out in fabricating drugs that are more precise proving in a variety of potentialities to the needs of a specific treatment. In the next forthcoming years, it is assumed that the chemical industries are going to face new challenges in terms of dwindling of fossil fuel together with alteration in surrounding weather patterns, which leads to stringent regulations on the use of hydrocarbons and their release into the environment. To fight against such the limitations of fossil feedstock in the future along with having progression of our economy, catalysis will assist us in the form of photocatalytic processes. Such processes may create sustainable forms of energy accessible, with catalytic devices serving as batteries for energy storage, for the hydrogen generation, or the alteration of biomass into conformable fuels.

[1.4] Fundamental aspects and contemporary scenario of the catalysts

Today’s society gets deeply influence by catalysis. Several areas where catalysis plays a foremost role are food, chemical, and energy production, petroleum industry, pharmaceuticals, and environmental protection. Cracking hydrothermal of crude oil, gasoline production, alkylations, polymerizations, epoxidation of ethylene, water-gas shift reaction, methanation, production of ammonia, sulfuric acid and many more are some of the largest processes based on heterogeneous catalysis. Apart from the industrial point of view, its influences are been seen economically. Proving the above statement, approximately 35% of the global GDP makes up from catalytic processes. In the USA, the gross national product (GNP) of fuels and chemicals produced with the use of catalysis is likely to be 17% and on average, it is the same with the industrial world. [8]

[1.5] Types of catalysts

Catalysts are of two types: Homogeneous and Heterogeneous catalysts. [9-16]

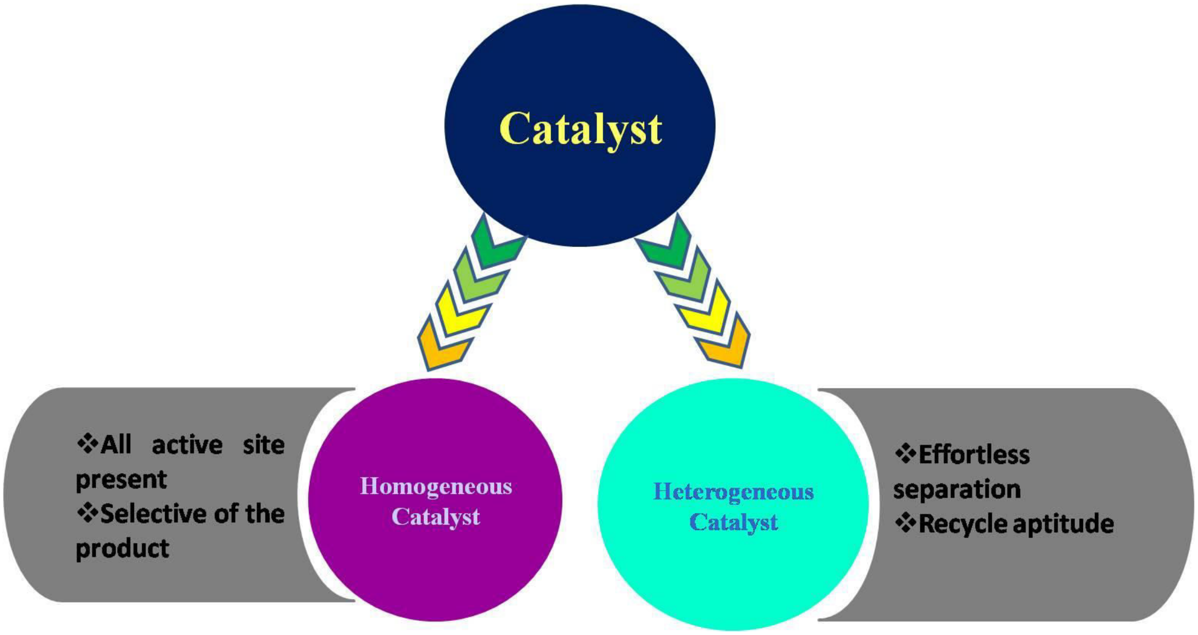


Figure 4 Classification of Catalyst.

Homogenous catalysts:

A homogeneous catalytic reaction in which substrates for a reaction and the active components are been brought together in a single phase, especially in the liquid phase. Characteristic examples of the reactions catalyzed by homogeneous catalysts are as shown below.

In recent times, numerous catalyst designs have been instigated in the area of homogeneous catalysis especially by metal-based composite materials (metals, metal salts, or metal oxide nanoparticles). A metal-based composite material is found to be playing a consequential role in catalysis by elementary reactions for instance oxidative addition of reactants, reductive elimination of products, along with some various but well defined reshuffling of atom and chemical bonds in the metal’s coordination sphere. Although homogeneous catalysis has some unique characteristics like good accessibility to catalytically active sites, prominent selectivity of the products, etc. however, with incrementing public vigilance relating to ecological issues, heterogeneous catalysis has come out with much more paramount than homogeneous ones. Homogeneous catalysis are suffering from various obstacles like high cost, toxicity, corrosions, difficulty in separation from the reaction mixture and its recovery, recyclability, creation of huge solid waste, etc. and therefore, in today's environmentally cognizant and inexpensively pressured world this becomes incompatible for the industrial purpose. It is from acids to sophisticated transition metal complexes although they all have a great amount of catalytically active sites and usually has high activity and selectivity together with all the active sites are easily accessible, steric and electronic environment of the active site can be at least in principle varied extensively. The most important drawbacks of such catalysts are that they cannot hold out high temperatures and therefore difficulty in separating from the reaction mixture, as well as slow decomposition under the rigorous reaction conditions due to their comparatively low thermal and chemical stability. Therefore, they are having restricted applications in organic synthesis and industry as well. As a result, there is a great demand for heterogenizing such homogeneous metal complexes. [17-21]

- **Heterogeneous catalysis**

Heterogeneous catalysis consists of a system where active species (catalyst) and reactants are present in separate physical phases. For instance, the catalysts are present in solid-phase whereas, the reactants are in vapor and/or liquid phase. After playing an imperative role in organic transformations, they were found to have a major impact on not only the quality of human life but also on economic progress. Catalysis induces about more than 80% of the processes in the petroleum, petrochemical, fertilizers, and food industries [Fig. 5].On one side where heterogeneous catalysis is chosen for commodity materials, at the same point, on other side catalytic processes majorly involved in the bulk as well as fine chemicals manufacturing are homogenous, responsible for a hefty sum of side squander materials and imposing perilous impact on the ecosystem.

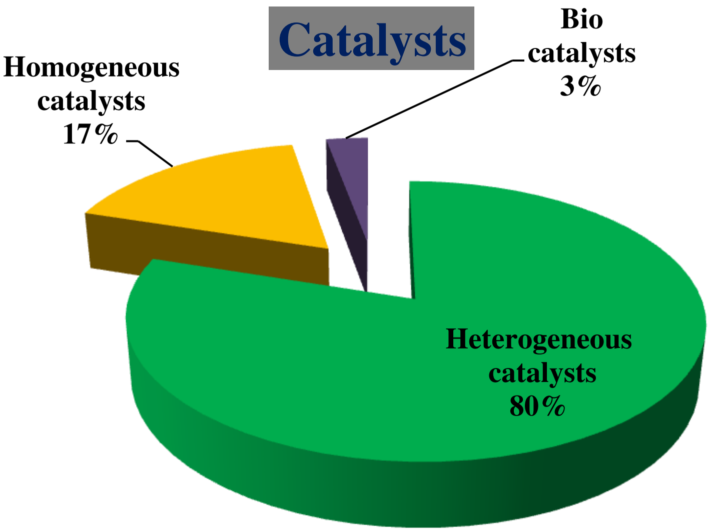


Figure 5 Catalytic process in chemical industry and heterogeneous catalyst compared with other catalytic processes.

Despite of having some inimitable properties, homogeneous catalyst faces major drawbacks like intricacy in separating the relatively pricey catalysts from the reaction mixture and the possible contamination of catalyst limits their application in industry. Efficient binding of these catalysts on supports possibly will conquer these disadvantages. [22] Seeing as the catalytic action takes place at particular sites on the solid support, often called as "**active sites**". However, the unvarying diffusion of metal catalysts is highly enviable for the remarkable enhancement of catalytic performance. The intrinsic characteristics of heterogeneous catalytic systems over their homogeneous analogs lie primarily in their effortless separation and recycle aptitudes. Numerous methods have been established for the binding of homogeneous transition metal complexes over solid support. Various solid supports such as organic polymers or inorganic solids like zeolites/molecular sieves, silica, alumina, other metal oxides, and carbon-based materials have been employed for the heterogenization of homogeneous catalysts.

Nowadays a tremendous number of researches focusing on heterogenization of homogeneous catalysts have the subject of an enormous number of research topics. Among them, an assortment number of researchers have deal with catalytic applications of various supported (like carbonaceous, zeolite, and ordered mesoporous molecular sieves) metal nanoparticle and/or metal complexes. Because of these, we present here a comprehensive summary of the transition metal nanoparticle supported on a carbonaceous solid support. [23-28]

[1.6] Metal and/or metal oxide nanoparticles

Along the way through the last 30-40 years, the preparation of nanocrystals-crystalline particles around 1 to 100 nm in the range has been pursued meticulously, aiming not only for their elementary scientific concern, but for their applications in technology as well. [29-33] Their physicochemical properties are not either matching with those of free atoms/molecules forming nanoparticles or those of bulk solids with interchangeable chemical composition, however, are restricted by phenomena having critical measurements on the nanoscale. They are substantiated by a large surface area to volume ratio, indicating a large number of atoms are exposed on the surface of nanomaterials and therefore can be engaged in surface reactions viz. catalytic reactions. [34-41]

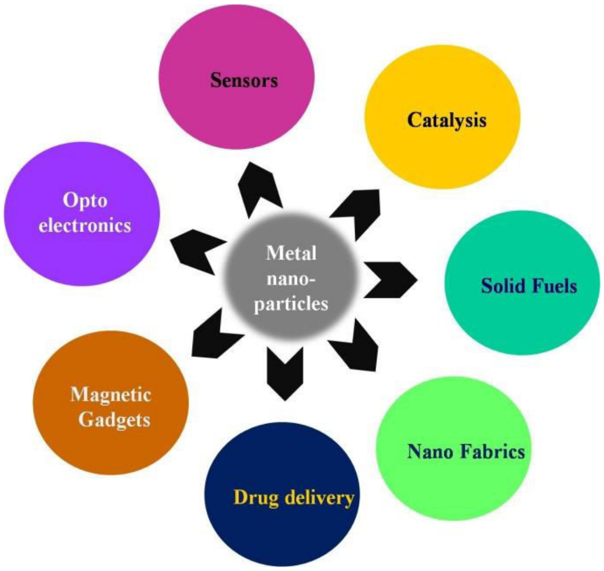


Figure 6 Potential application of Metal nanoparticles.

Amongst them, metal or metal oxide-based nanoparticles are extensively studied for their diverse applications in the field of catalysis, drug delivery agents, sensors, magnetic gadgets, solid fuels, optoelectronics, a dropdown of pollution, analytical applications and so on [Fig. 6]. The prospective utilization of metal and/or metal oxide-based nanomaterials as catalyst precursors for organic synthesis, in the biological and/or medical field, is nowadays a great challenge to scientific researchers. It has relied on the size, shape, and textural frameworks of the nanoparticles and the supported materials as well. The different kinds of supporting materials (viz. 1D, 2D or 3D) have been used to provide contented support to the nanoparticles such as silica, TiO_2, indium tin oxide, carbon nanotube (CNTs), carbon nanofibres, graphene, polymers, dendrimers, clay matrix, activated carbon, organic ligands, metal oxide, etc. [42-50] At present, owing to inflexible and emergent environmental regulations there has been enormous attention to set up a “green” method for the synthesis of nanoparticles and applications. Hence, the sturdy supporting materials (with inexpensive, easily accessible, strong and eco-friendly) for the preparation of metal nanoparticles and their exploitation in diverse fields have provided much attention towards the progression of nanoscience and nanotechnology. To put it briefly, there is an immense interest to establish supported nanoparticles of metals or metal oxides, which comprises their synthesis, characterization, and applications in various fields.

[1.7] Numerous solid supports

Generally, heterogeneous catalysts are employed in several industries particularly in petrochemical, agrochemical, bulk chemical and pharmaceutical sectors. Though, for their successful utilization, heterogeneous catalysts have to endure the conditions within the chemical reactor without wearing down or deterioration [51]. In recent times, numerous types of heterogeneous solid supports have been well established such as mesoporous titanosilicate, superparamagnetic mesoporous bi-metallic oxides, MCM-41 silica, nanocrystalline ceria-zirconia, heteropolyacids, chitosan hydrogel, acrylic resin immobilized lipase, IRMOF-3, and ZIF-8 [Fig. 7]. [52-55] However, these solid catalysts have been suffered from several detriments like low selectivity, elevated temperature, longer reaction time, and laborious work-up methods. The selectivity and activity of many heterogeneous catalysts permit for the preparation of high added-value chemicals from simple and economic substrates utilizing processes with high atom economy, diminishing the formation of residues and, therefore, with a minimum environmental impact.

However, the application of carbonaceous support based catalysts in diverse catalytic reactions has put on much effort owing to their static, non-hazardous, nonvolatile, high tensile strength, promising thermal stability, ease of recovery and recyclability which in turn is significant in adhering to sustainable chemistry protocol. Furthermore, as compared to inorganic solid supports, carbonaceous support with two-dimensional open pore network structures, elevated surface area and porosity, reusability, and heat stability provide a trustworthy and well-separated environment for the deposition of active constituents and interactive surfaces between the catalysts and reactants. One of the promising ways for enhancing the support properties of carbonaceous materials is through its surface modification.

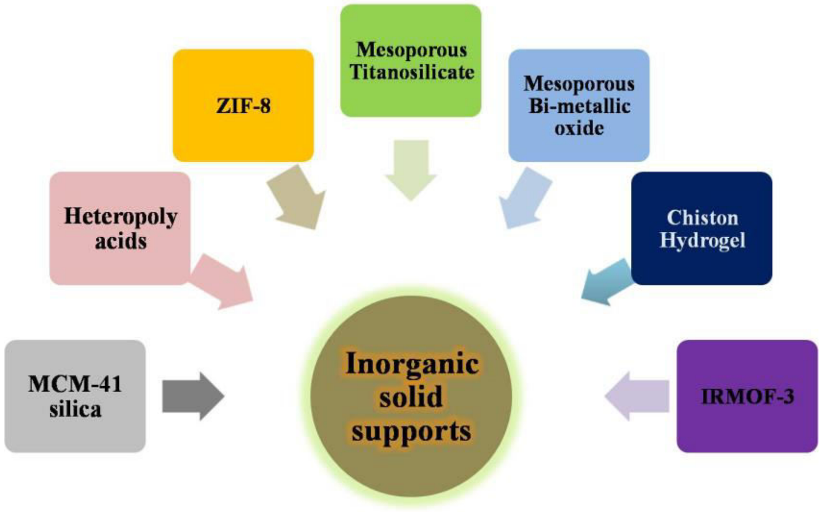


Figure 7 Different Inorganic solid supports.

[1.8] Advantages of carbonaceous materials as catalyst support

The heterogeneous catalysts supported by carbonaceous materials are leading to notable selectivity and drop down the cost of catalysts. When catalysts composed in this fashion normally would involve length scales extending from the atomic to the catalyst particle or pallet size, even though it can be a concern on the reactor that the catalyst is to be applied. Even though, the essential parameters i.e. activity and selectivity of heterogeneous catalysts supported by carbonaceous materials relies on the atomic structure of its potent site. The potent sites depend on the exterior of mesopores that comprises of an enormous network within a solid particle, with size extending from nanometers to centimeters. Normally, the potent site presides over the number of species to be bound and transformed on the surface of the catalyst. In carbonaceous supported materials, ease of accessing the potent site can be expanded by allocating the sites in a microscopically irregular fashion. Therefore, there are putting some efforts to increase the accessibility of the catalytic system in which the potent sites are centralized inside a region near to the exterior surface of the catalyst and form of a new structure called an eggshell catalyst or carbon nanocage.

Furthermore, because of the porous structure of carbonaceous materials, both the products and reactants proceed are frequently very small, however, the confined surface curve is very large, and mostly could persuade the rate of the reaction. Porous carbonaceous materials provide a very stretchy supports for the synthesis of heterogeneous catalysts. Hence, its physical and chemical properties can simply be modified to build up a large surface area for dispersing the active phase. It is assumed that suitable pore size allocation caused by carbon as the support could facilitate the dispersion of reactants and products back and forth of the surface, which in result possess an acid-base characteristic needed to present a better catalytic performance. In the meantime, the size of the carbon particle might also be established by mechanical and ecological aspects. Tiny particles of carbon can make a potentially unsafe dust. Therefore, it is expected to keep the particle size invariable and focusing on the optimization for the utmost yield, selectivity of the products, strength, and/or arrangement of these.

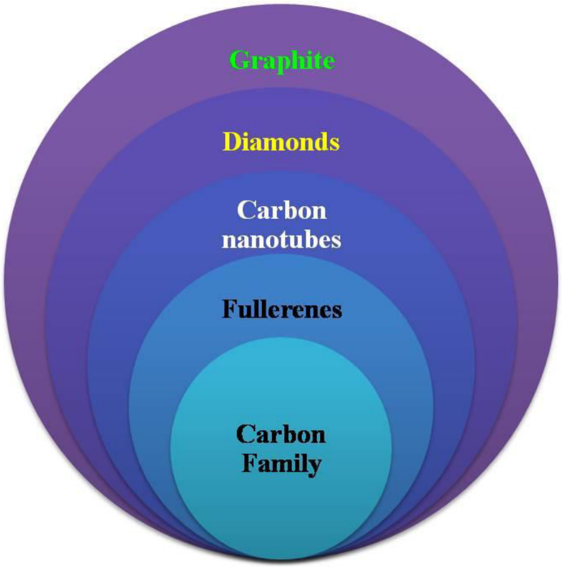


Figure 8 Members of Carbon family.

The prominent materials as fullerenes, diamonds, carbon nanotubes (CNTs), and graphite were regarded as members of the carbon family until the end of the 20th century [Fig. 8]. Owing to having some fundamental constraints of fullerene such as toxicity, high cost, etc., it was replaced with graphite and single-layer graphene with pioneering work of Brodie [56] and determining the role of Geim and Novoslow [57] together with the first segregation of 2D graphene by C. W. Bielawski [58] in 2004. Consequently, graphene, graphene oxide (GO), and/or reduced graphene oxide (rGO) has appended much deliberation as a catalyst or catalytic support by research group. They may perhaps resistance towards acidic and basic media, a stable structure at high temperature and pressure, alteration of chemical properties of the surface, organizes polarity and hydrophobicity, flexible pore structure that resulted in giving varying pore size required for different applications. Overall, one can articulate that carbonaceous supports are inexpensive than other conventional supports. The detailed study of graphene, graphene oxide (GO), and/or reduced graphene oxide (rGO) based materials has been discussed in chapter 2.

[1.9] Literature Survey

At present, many researchers are focusing on the metal or metal oxide nanoparticles decorated on carbonaceous materials as heterogeneous catalysts and employed proficiently in the various industrially important reactions. Gallegos-Suarez et al. [59] have synthesized supported ruthenium catalysts by incipient wetness impregnation technique using diverse carbon-based materials such as activated carbon (AC), high surface area graphite (HSAG), multi-walled carbon nanotubes (CNTs) and/or KL zeolite (KL). The role of the supports on the activity and selectivity of the catalysts viz. Ru/AC, Ru/HSAG, Ru/CNT and/or Ru/KL for the hydrogenolysis of glycerol was examined and giving excellent results. Among them, Ruthenium supported on activated carbon (Ru/AC) produces ethylene glycol as the key product. On the other hand, reduction of ruthenium generates Brønsted acid sites in Ru/KL, enhancing the selectivity toward 1,2-propanediol, whereas graphite and carbon nanotubes facilitate the formation of $Ru^{\delta-}$ species and favor in the production of methane and 1,2-propanediol. Mirza-Aghayan and co-workers [60] have prepared palladium oxide nanoparticles supported on graphene oxide (PdO NPs/GO) as a heterogeneous catalyst. It was brought into being an effective reductive system for a wide range of reduction processes comprising of reduction of various carbonyl compounds like aromatic aldehydes, ketones, and acyl chlorides to the corresponding methylene derivatives using triethyl silane (Et_3SiH) as a reducing agent. The desired products were got hold in good to outstanding yields under mild conditions. A room temperature copper-free Sonagashira cross-coupling reaction in ethanol catalyzed by palladium nanoparticles homogeneously immobilized on reduced graphene oxide (Pd NPs@rGO) has been reported by A. Mahanta and co-workers [61]. The catalyst offered exceptional catalytic activity towards the previously mentioned coupling reaction, was thoroughly characterized using different physicochemical techniques, and was recycled up to six times with keeping steady yield of the desired product. Ibrahim et al. [62] have demonstrated partial functionalization of reduced graphene oxide supported by N-containing p-phenylenediamine and benzidine molecules with the dispersion of Pd nanoparticles giving Pd/(RGO-PPD) and/or Pd/(RGO-BZD) catalysts and tested for Suzuki coupling reaction under ligand-free ambient conditions. These catalysts offered notable turnover frequencies (400,000 h^{-1}) monitored under the microwave-assisted Suzuki cross-coupling reaction with effortless subtraction from the reaction mixture. These catalysts show unique catalytic activity that surpasses the recital of Pd catalysts supported on other carbon-based supports. Raut et al. [63] have synthesized ruthenium ion supported on ionic liquid immobilized into graphene oxide (Ru@GOIL) catalyst and tested over reductive amination reaction of levulinic acid (LA) to make N-substituted pyrrolidones. The aforementioned catalyst was characterized using various analytical techniques such as FT-IR, XRD, XPS, TGA, FEG-SEM, TEM, and EXAFS. The as-prepared Ru@GOIL catalyst gave an enormous catalytic performance over the reductive amination reaction of LA bestowing good turnover frequency (TOF = 62 h^{-1}) value in contrast to other catalysts. Magnetic nanocomposite catalyst RGO/Fe_3O_4@C_{-N}-Co_3O_4 involving Co_3O_4 nanoparticles immobilized on magnetic N-doped graphene was synthesized by Z. Li and co-workers [64]. The dopant nitrogen can play a vital role and make strong interaction between Co_3O_4 nanoparticles and the support in the aforementioned catalyst. RGO/Fe_3O_4@C_{-N}-Co_3O_4 showed higher catalytic reactivity viz. 93.2% conversion of styrene and 88.4% selectivity to styrene oxide while compared with bulk Co_3O_4 and Co_3O_4 supported on N-free RGO/Fe3O4@C, owing to site-isolation, fine dispersion of Co_3O_4 nanoparticles and competently synergistic effect between Co_3O_4 and the magnetic support. Ruthenium nanoparticles (RuNPs) supported on reduced graphene oxide doped with N (NH_2-rGO) (Ru/NH_2-rGO) were synthesized by L. M. Martínez-Prieto and co-workers [65] and tested over selective hydrogenation of fatty acids to alcohols. Ru/NH_2-rGO catalyst has been characterized by HRTEM, XRD, Raman, and FT-IR techniques and examining the presence of N-dopant in the graphene sheet by XPS and ^{15}N solid-state MAS NMR spectral studies. This catalyst was very selective over carbonyl reduction reaction yielding 93% of the aliphatic alcohol at 99% conversion.

In these days and age, the development of an ecological and sustainable synthetic methodology stays behind a challenge cater-cornered to the world. To address this prevailing challenge, hereby we present the work in this thesis for developing varied metal nanoparticles (MNPs) anchored onto carbonaceous supports with their applications in sustainable chemical processes. We have synthesized newfangled vanadium, iron, nickel, copper, zinc and niobium metal and/or metal oxide-based nanoparticles (MNPs) embedded onto carbonaceous [reduced graphene oxide (rGO) or activated carbon (AC)] supports viz. MNPs@rGO and/or MNPs@AC. The as-synthesized catalysts have been substantiated by various physicochemical techniques such as ICP-OES, elemental analysis, (FT-IR, Raman) spectral studies, BET, field emission scanning electron micrographs (FE-SEMs), high-resolution transmission electron microscope (HRTEMs), X-ray photoelectron microscope (XPS), thermal analysis and X-ray powder diffraction (XRD) patterns. To attain the strategic goal of this work, the catalytic aptitudes of the as-synthesized catalysts have been tested over diverse industrially imperative organic transformations such as hydrogenolysis, Biginelli coupling, Knoevenagel condensation (C-C formation), Henry and Aldol condensation reaction and Henry-Michael addition reactions. The impact of various parameters influencing catalytic activity such as mole ratio, catalyst amount, varying reducing agents and/or active methylene compounds, temperature, time, solvents, derivatives have also been monitored. Besides this, to check the aptitude for recyclability, the aforementioned catalysts could be effortlessly recycled by centrifugation after each run and reused several times without momentous loss of their catalytic activity.

[1.10] References

[1] Catalysis, selected applications, Ed. B. Viswanathan, Narosa publishing house, New Delhi, (2009).

[2] I. Chorkendorff, J.W. Niemantsverdriet. Concepts of modern catalysis and kinetics, WILRY-VCH GmbH and Co. KGaA. (2003).

[3] J. J. Berzelius *Jahresbericht über die Fortschritte der physischen Wissenschaften*, **15,** 237 (1836).

[4] A. D. McNaught, A.Wilkinson, *IUPAC Compendium of Chemical Terminology, 2nd ed. Blackwell Scientific Publications*, Oxford (1997).

[5] J.M. Thomas, W.J. Thomas, *Principles and Practice of Heterogeneous Catalysis*, VCH Verlagsgesellschaft, Weinheim (1997)

[6] O. J. Van Houten, *J. Chem. Educ*., **79**, 146 (2002).

[7] G. Ertl, H. Kneozinger, J. Weitkamp (eds.), *Environmental Catalysis*, Wiley-VCH, Weinheim, (1999).

[8] I. Chorkendorff, J.W. Niemantsverdriet, *Concepts of Modern Catalysis and Kinetics,* Wiley-VCH, Weinheim (2003).

[9] C. N. Satterfield, *Heterogeneous Catalysis in Practice*, McGraw Hill Book Comp., New York, (1980).

[10] D. L. Trimm, *Design of Industrial Catalysts*, Elsevier, Amsterdam, (1980).

[11] J. M. Thomas, R. M. Lambert (eds.), *Characterization of Heterogeneous Catalysts*,Wiley, Chichester, (1980).

[12] R. Pearce, W. R. Patterson (eds.), *Catalysis and Chemical Processes*, John Wiley, New York, (1981).

[13] B. L. Shapiro (ed.), *Heterogeneous Catalysis*, Texas A & M Press, College Station, (1984).

[14] B. E. Leach (ed.), *Applied Industrial Catalysis*, Vol. 1, 2, 3, Academic Press, New York, (1983 – 1984).

[15] G. Parshall, *Homogeneous Catalysis*, Wiley, New York, (1985).

[16] J. R. Anderson, K. C. Pratt, *Introduction to Characterization and Testing of Catalysts*, Academic Press, New York, (1985).

[17] A. Nakamura, M. Tsulsui, *Principles and applications of Homogeneous catalysis,* Wiley, New York, (1980).

[18] C. Masters, *Homogeneous transition metal catalysis,* Chapman and HallLondon, New York, (1981).

[19] G. H. Olive, S. Olive, *Coordination and catalysis,* Verlag Chemie, New York, (1977).

[20] R. S. Nyholm, *Proc. 3rd Internat. Congr. Catalysis,* North-Holland Publ. Co, Amsterdam, (1965).

[21] K. Wilson, J. H. Clark, *Pure Appl. Chem.*, 2000, **72**, 1313.

[22] J. H. Clark, D. J. Macquarrie, *Org. Process Res. Dev*. **1**, 149 (1997).

[23] C. E. Song, *Annu. Rep. Prog. Chem., Sect. C*, **101**, 143, (2005)

[24] C. E. Song, S.-G. Lee, *Chem. Rev.,* **19**, 3495 (2002).

[25] D. E. De Vos, M. Dams, B. F. Sels, P. A. Jacobs, *Chem. Rev*. **102**, 3615 (2002).

[26] N. E. Leadbeater, M. Marco, *Chem. Rev*. **102**, 3217 (2002).

[27] B. Kodicherla, P. Perumgani, C. M. R. Mandapati, *Appl. Catal. A: Gen*., **483**, 110 (2014).

[28] K. C. Gupta, A. K. Sutar, C.-C. Lin, *Coord. Chem. Rev.,* **253**, 1926 (2009).

[29] G. Schmid, *Nanoparticles: From Theory to Application*, Wiley-VCH, Weinheim, (2004).

[30] K. J. Klabunde, *Nanoscale Materials in Chemistry*, Wiley-Interscience, New York, (2001).

[31] J. H. Fendler, *Nanoparticles and Nanostructured Films*, Wiley-VCH, Weinheim, (1998).

[32] B. Zhou, S. Hermans, G. A. Somorjai, *Nanostructure science and technology*, Springer, (2004).

[33] D. L. Feldheim, C. A. Foss, *Metal nanoparticles: Synthesis, characterization and application*, Jr (Eds.), CRC Press, New York, (2002).

[34] G. Cao, *Nanostractures and nanomaterials: Synthesis, properties and Application*, Pub: Imperial College Press, (2004).

[35] H. Brune, A. Grunwald, W. Grunwald, H. Hofmann, H. Krug, P. Janich, W. Rathgeber, G. Schmid, U. Simon, *Nanotechnology assessment and perspectives*, Pub: Springer, (2006).

[36] P. M. Ajayan, L. S. Schadler, P. V. Braun, *Nanocomposite science and technology*, Pub: Willy-VHC GmbH & Co. KGaA, (2004).

[37] C. P. Poole Jr., F. J. Owens, *Introduction to Nanotechnology*, Pub: Willy-Interscience, (2003).

[38] J. M. Campelo, D. Luna, R. Luque, J. M. Marinas, A. A. Romero, *Chem. Sus. Chem*, **2**, 18 (2009).

[39] H. Bönnemann, W. Brijoux, R. Brinkmann, M. Feyer, W. Hofstadt, G. Khelashvili, N. Matoussevitch, K. Nagabhushana, *Nanostructured transition metarials*, , The Strem Chemiker, Vol. XXI, No. 1, (2004).

[40] F. Schröder, D. Esken, M. Cokoja, M. W. E. van den Berg, O. I. Lebedev, G. V. Tendeloo, B. Walaszek, G. Buntkowsky, H. H. Limbach, B. Chaudret, R. A. Fischer, *J. Am. Chem. Soc.***130**, 6119 (2008).

[41] T. Tsukatani, H. Fujihara, *Langmuir*, **21**, 12093 (2005).

[42] N. Mahata, A. F. Cunha, J. J. M. Orfao, J. L. Figueiredo, *Appl. Catal. A: Gen.* **2008,** 351, 204-209.

[43] Z. Libor, Q. Zhang, *Mater. Chem. and Phys.* **2009**, 114, 902-907

[44] X. Meng, H. Cheng, S. Fujita, Y. Hao, Y. Shang, Y. Yu, S. Cai, F. Zhao, M. Arai, *J. Catal.*, **269**, 131 (2010).

[45] K. Nouneh, M. Oyama, R. Diaz, M. Abd-Lefdil, *J. Alloys and Compounds*, **509**, 5882 (2011).

[46] D. H. Chen, C. H. Hsieh, *J. Mater. Chem.*, **12,** 2412 (2002)**.**

[47] M. Tamura, H. Fujihara, *J. Am. Chem. Soc.*,**125**, 15742 (2003).

[48] V. K. Sharma, R. A. Yngard, Y. Lin, Adv. *Coll. and Inter. Sci.*, **145**, 83 (2009).

[49] N. Aihara, K. Torigoe, K. Esumi, *Langmuir*, **14**, 4945 (1998).

[50] C. W. Chiu, P. D. Hong, J. J. Lin, *Langmuir*, **27**, 11690 (2011).

[51] D. Varade, K. Haraguchi, *J. Mater. Chem.* **22,** 17649 (2012).

[52] K. H. J. Buschow, R. W. Cahn, M. C. Flemings, B. llschner, E. J. Kramer, S. Mahajan, P. Veyssiere, *Encyclopedia of Materials: Science and Technology*, 1st Edn., Elsevier, Pergamon, (2001).

[53] F. Guo, Inorg. Chem. Commun., **101**, 87 (2019).

[54] Z. Gao, J. Zhou, F. Cui, Y. Zhu, Z. Hua, J. Shi, *Dalt. Trans*., **39**, 11132 (2010).

[55] B. Karmakar, B. Chowdhury, J. Banerji, *Catal. Commun*., **11**, 601 (2010).

[56] F. Shang, J. Sun, S. Wu, Y. Yang, Q. Kan J. Guan, *Micropor. Mesopor. Mater.*,**134**, 44 (2010).

[57] B. C. Brodie, Philos. *Trans. R. Soc. London*, **149**, 249 (1859).

[58] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, *Science*, **306**, 666 (2004).

[59] D. R. Dreyer, S. Park, C. W. Bielawski, R. S. Ruoff, *Chem. Soc. Rev*., **39**, 228 (2010).

[60] E. Gallegos-Suarez, A. Guerrero-Ruiz, I. Rodriguez-Ramos, A. Arcoya, *Chemi Engi. J* **262,** 326 (2015).

[61] M. Mirza-Aghayan, M. Kalantari, R. Boukherroub, *Appl. Organometal. Chem.*, 4837 (2019).

[62] A. Mahanta, N. Hussain, M. R. Das, A. J. thakur, U. Bora, *Appl Organometal Chem*, 3679 (2017).

[63] Amr Awad Ibrahim, Andrew Lin, Mina Shawky Adly, M. Samy El-Shall, *.J Catal.* **385**, 194 (2020).

[64] A. B. Raut, V. S. Shende, T. Sasaki, B. M. Bhanage*, J Catal* **383**, 206 (2020).

[65] Z. Lia, S. Wu, C. Yang, Y. Ma, X. Fu, L. Peng, J. Guan, Q. Kan, *Mole. Catal.* **432**, 267 (2017) .

[66] L. M. Martinez-Prieto, M. Puche, C. Cerezo-Navarrete, B. Chaudret*, J Catal*. **377**, 429 (2019).