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A Study on Nano Catalysis and Its Applications

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Abstract – This study has been attempted to know about the nanocatalysis and its applications. Catalysis is the process by which chemical reaction rates are altered by the addition of a substance (the catalyst) that is not itself changed during the chemical reaction. Catalysts are usually used so that chemical reactions can occur at temperatures and pressures low enough for producers to use economically priced equipment or to ensure that the rate of production of a desired product is greater than the rates of production of undesirable byproduct. Nanocatalysis has long become an important part of nanoscience. Nanoparticle can substitute conventional material and serve as active and stable heterogeneous catalysts or as support material for various catalytic groups.

Keywords: Catalysis, Nanocatalysis etc.

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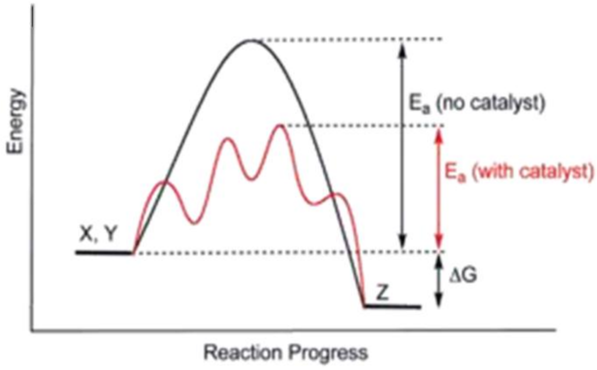
INTRODUCTION

In the absence of catalyst, variety of products i.e. medicines, fine chemicals, polymers, fibres, fuels, paints, lubricants, and a myriad of other value added products essential to humans, would not be feasible. Heterogeneous catalysis has received a remarkable amount of attention, both from a scientific and an industrial perspective. The production of most industrially important chemicals involves catalysis. Similarly, most biochemically significant process is catalysed. Research on catalysis is a major field in applied science and involves many areas of chemistry, notably organ metallic chemistry and material science. Catalysis is relevant to many aspects of environmental science for example, the catalytic converter into automobiles and the dynamics of the ozone hole. Many transition metals and transition metal complexes are used in catalysis as well. Catalysts called enzyme is important in biology. Many commercially important catalysts comprise catalytically active nano particles dispersed on high area oxide supports.

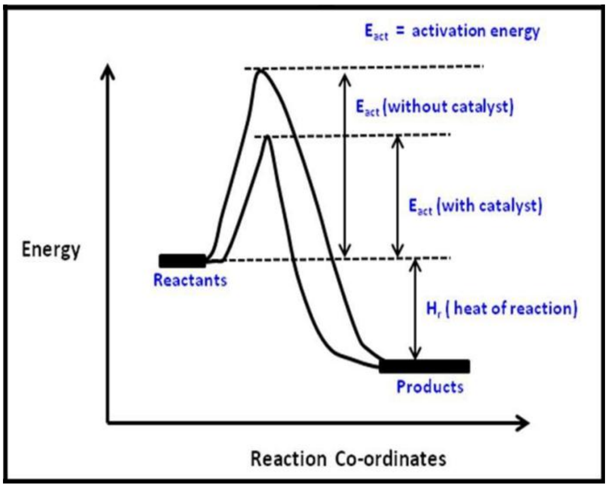
The catalyst increases the probability of interaction between the reactants by providing a localised surface, upon which the reactant molecules maybe located for sometimes. Catalysts open up alternative reaction pathway with reduced activation energy.



When a reaction is carried out without catalyst, very large activation energy (E) must be required for the reaction. But in the presence of a catalyst, molecules create a transitional state with a catalytic surface to reduce potential energy. An appropriate catalyst can therefore greatly increase the rate of the reaction.

CATALYTIC REACTIONS

In a thermodynamically feasible chemical reaction, when addition of a small amount a chemical substance increases the rate of attainment of chemical equilibrium but the substance itself does not undergo any chemical change, and then the reaction is called a catalytic reaction. The substance that enhances the reaction rate is called a catalyst. Catalysts work by providing alternative mechanism involving a different transition state of lower energy. Thereby, the activation energy of the catalytic reaction is lowered compared to the unanalyzed reaction as shown in Fig .



Catalytic reactions can be divided into two main types –

1) HETEROGENEOUS CATALYST

In heterogeneous catalytic reaction, the catalyst and the reactants are in different phases.Reactions of liquid or gases in the presence of solid catalysts are the typical examples.

An example is the Contact Process for manufacturing sulphuric acid, in which the sulphur dioxide and oxygen are passed over a solid vanadium oxide catalyst producing sulphur trioxide. Several hydrocarbon transformation reactions such as cracking, reforming, dehydrogenation, isomerization also fall in this category.

2) HOMOGENEOUS CATALYST

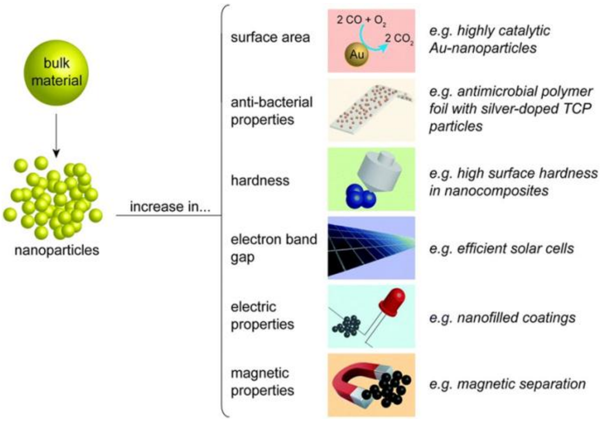
In a homogeneous catalytic reaction, the catalyst is in the same phase as the reactants. Typically, all the reactants and catalysts are either in one single liquid phase or gas phase. Most industrial homogeneous catalytic processes are carried out inliquid phase. Ester hydrolysis involving general acid-base catalysts, polyethylene production with organometallic catalysts and enzyme catalysed processes are some of the important examples of industrial homogeneous catalytic processes.

CHALLENGES FOR CATALYSIS

- Methods of synthesis and catalysis to convert product molecules and polymers back into useful starting materials
- Catalysts with long life and self-repairing capabilities
- New catalysts for the efficient conversion of biomass and unused by-products into useful raw materials

NANOCATALYSIS

Nanocatalysisis a process in which catalysis process use products of nanotechnology as a catalyst which is referred to as Nanocatalyst. **Nanocatalyst**- A catalyst composed of nanoparticles. Smaller than 100nm in at least one dimension Porous compounds having pore diameter not bigger than 100nm. Due to their small sizes, catalytic active nanoparticles have higher surface area and increased exposed active sites, and thereby improved contact areas with reactants, akin to those of homogeneous catalytic systems. At the same time nano structures catalyst can behave as heterogenous catalysts thus, they can also be easily separated from reaction mixture .In addition to their tunable catalytic activity and selectivity, often with activities close to homogeneous catalytic systems, the stability of nanocatalysts can be improved by tailoring the chemical and physical properties of nanomaterials by various synthetic methods. For example nanocatalysts with better activity, stability and selectivity can be designed and synthesized mearly by controlling the size, shape and morphology of nano materials.



Nanoparticles (NPs) find application in every field such as electronics, medicine and cosmetics. They are now evolving in the field of catalysis because their optical, electrical, mechanical and chemical properties are a function of their size, composition and structural order. This leads to new improved catalytic properties. Nanocatalysis has attained the form of a strategic field of science because it represents a new way to meet the challenges of energy and sustainability. Nanomaterials can be designed to control their size, shape, chemical composition and nature of the microenvironment surrounding the NPs and assembly structure for advanced applications. These materials can be a new class above the classical homogeneous and heterogeneous catalysts. Nanocatalysts are often considered as quasihomogeneous systems.

In the nanoscale regime, neither quantum chemistry nor the classical laws of physics hold. In materials where strong chemical bonding is present,delocalization of electrons can be extensive, and the extent ofdelocalization can vary with the size of the system. This effect, coupled with structural changes, can lead to different chemical and physical properties, depending on size. As for other properties, surface reactivity of nanoscale particles is thus highly size-dependent. Of particular importance forchemistry, surface energies and surface morphologies are also size dependent, and this can translate to enhanced intrinsic surface reactivity. Added to this are large surface areas for nanocrystalline powders and this can also affect their chemistry in substantial ways . Size reduction to the nanometer scale thus leads to particular intrinsic properties (quantum size effect) for the materials that render them very promising candidates for various applications, including catalysis. Such interest is well established in heterogeneous catalysis, but colloids are currently experiencing renewed interest to get well-defined nanocatalysts to increase selectivity.

EFFECT OF SIZE AND SHAPE ON CATALYSIS

EFFECT OF SIZE

In materials where there is a strong chemical bonding between them, delocalization of elelctrons can be extensive and this extend of delocalization varies depending on the size of the system. Hence surface reactivity of the nanoparticles is highly size dependent. In the early 1966, Boudart asked fundamental questions about the underlying between the article size and catalysis, such as how catalyst activity is affected by size in regime between atoms and bulk, whether some minimum bulk-like lattice is required for normal catalytic behaviour, and whether an intermediate ideal size exists for maximum catalytic activity. .These questions were extensively studied by somorjai’s group and found a solution although there is a tremendous variation in the relationship between size and its activity depending on the choice of the catalyst and choice of reaction. They have classified these relationships into three primary groups:-positive size-sensitivity reactions, negative size-sensitive reactions, and size insensitive reactions

- Positive size –sensitive reactions: are those reactions in which turnover frequency increases with decreasing particle size. The prototypical reactions for this group are methane activation. Here, dissociative bond cleavage via σ-bond activation is the rate limiting step.

- Negative size-sensitive reactions: are those for which the turnover frequency decreases with decrease in the particle size. The prototypical reaction for this group is dissociation of CO and N2, which require step-edge sites and contact with multiple atoms. Formation or dissociation of π-bond is often the rate-limiting step in this reaction.

- Size-insensitive reaction: for which there is no significant dependence of turnover frequency on the particle size. The prototypical size-insensitive reaction is hydrocarbon hydrogenation on transition metal catalysts, for which the rate limiting step is complimentary associative σ-bond formation.

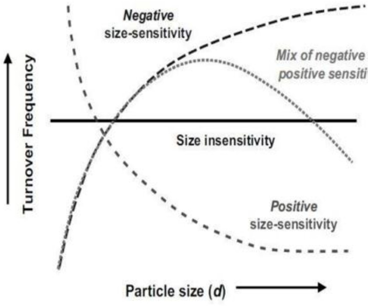


Figure 1.2 Major classes of size-sensitivity, which describe the relationships between NP size and turnover frequency for a given combination of reaction and NP catalyst. (------) negative size-sensitivity; (- - - -) positive size-sensitivity; (·······) Mix of negative and positive sensitivity.

Nanoparticles are not just simply finely divided metal. In bulk metals, the large density of states are at the fermi level and thus forms a conduction band of continuous energy levels. But as the size of the particle decreases, discrete energy levels are formed due to the quantum confinement. This shows that there is a gradual change that takes place with the change in the particle size. This phenomenon is known as size induced metal- insulator transition”. For instance, clusters of 13 atoms are considered to be non-metallic whereas those of 309 are considered to show metallic properties. The fraction of surface atoms thus increases with the decrease in the particle size.

EFFECT OF SHAPE

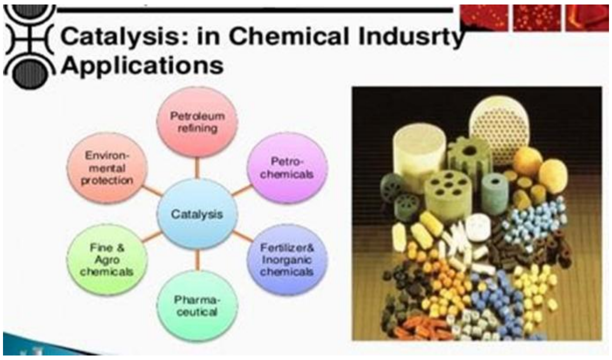
Shape dependent nanocatalysis has been extensively explored in the past two decades. It was first suggested in1996. It has been reported that NPs with more and sharper edges and corners have higher efficiency. It is therefore seen the size of the nanoparticles affects the reaction rate, selectivity and deactivation. The arrangement of atoms on the surface strongly influences the adsorption of the reacting molecules and desorption of the products. Thus, the morphology of the catalyst particle determined by the exposed crystal planes could substantially alter the catalytic property as well. This is termed as morphology- dependent Nanocatalysts: an NP having an anisotropic shape can modify the performance of reaction by selectivity exposing specific crystal facets. Experiments on a variety of catalysts have determined that the atomic arrangement of atoms on a surface has a significant effect on catalyst behaviour.

OBJECTIVES OF THE STUDY

The main objective of the study is to know about the nanocatalysis and its applications.

APPLICATIONS OF NANOCATALYSTS

In era of nanotechnology where size of every object is going to smaller and smaller with their enhanced properties; catalysts of nano size are also used in several chemical processes and beneficial for human being. In this section we are trying to collect all literature data on application of nanocatalysis reported within the last few years.


Catalysis: in Chemical Indusrty Applications

BIO DIESEL PRODUCTION

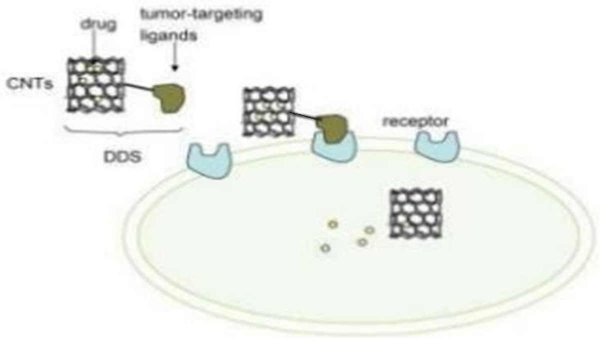
With the increase of environment protection consciousness and decrease of petroleum reserves, biodiesel, defined as the monoalkyl esters of fatty acids, has been the focus of a considerable amount of recent research as an alternative renewable fuel. More and more biodiesel is being used in many countries such as Germany, France, Italy, USA, Japan and so on. The general method for the preparation of biodiesel is trans esterification reaction of oil and alcohol with homogeneous catalyst. However, the homogeneous catalyst has many shortcomings, such as the difficulty in product isolation, requirement of large quantity of water and environmental pollution by the liquid wastes .A new trend in the preparation of biodiesel is to use ‘‘green’’ method based on heterogeneous catalyst

Heterogeneous catalytic methods are usually mass transfer resistant, time consuming and inefficient. Nanocatalysts have high specific surface and high catalysis activities, may solve the above problems. They have become the focus of recent research .It has been studied that the solid base nanocatalyst KF/CaO can be used for biodiesel production with yield of more than 96%. The high specific surface area and large pore size are favorable for contact between catalyst and substrates, which effectively improved efficiency of transesterification. Production of biodiesel from Chinese tallow seed oil has positive impact on the utilization of agricultural and forestry products.

IN DRUG DELIVERY

Many different types of drug delivery systems are currently available. Within the family ofnanomaterials,carbon nanotubes(CNT) have emerged as a new alternative and efficient tool for transporting and translocating therapeutic molecules. CNT can be functionalised with bioactivepeptides, proteins,nucleic acidsand drugs, and used to deliver their cargos to cells and organs. Because functionalised CNT display low toxicity and are not immunogenic, such systems hold great potential in the field of nanobiotechnology andnanomedicine.

.Typically, carbon nanotubes (CNTs) have a feature of endohedral filling of 2–10 nm in diameter leading to encapsulation of small molecules. Accordingly, CNTs may be suitable for bio-applications in biorecognition and drug delivery systems.



IN ENVIRONMENT PROTECTION

Current concerns and challenges in SR-AOTs, including (i) need of heterogeneous activation of sulfate salts using transition metal oxides, (ii) nanoscaling of the metal oxide catalysts for high catalytic activity and promising properties with respect to leaching, and (iii) easy removal and recovery of the catalytic materials after their applications for water and wastewater treatments.

Fe-Co mixed oxide nanocatalysts for the heterogeneous activation of peroxymono-sulfate

(PMS) to generate SRs targeting the decomposition of 2,4-dichlorophenol was introduced.

Ferromagnetic CoFe2O4 composites formed by thermal oxidation of a mixed phase of Fe and Co exhibited significant implications for the efficient and environmentally friendly activation of PMS, including:

(i) The cobalt species in CoFe2O4 are of Co(II), unlike Co3O4 showing some detrimental effects of Co(III) on the PMS activation,

(ii) CoFe2O4 possesses suppressed Co leaching properties due to strong Fe-Co interactions (i.e., Fe-Co linkages), and

(iii) Fe-Co catalysts in form of CoFe2O4 are easier to recover due to the unique ferromagnetic nature of CoFe2O4.

IN FUEL

Gas to liquids (GTL) process is considered as an alternative process to produce liquid fuels from natural gas due to high oil price. GTL process consists of synthesis gas production, Applications of nano-catalyst in new era 319 Fischer–Tropsch synthesis, and product workupNi catalyst supported on nano-particles of ZrO2 could be highly active and stable for CRM(, carbon dioxide reforming of methane). nano-sized Ni–Ce–ZrO2 catalyst could be active and stable in CRM.Ni/MgO–Al2O3 catalyst exhibited the highest activity as well as stability among supported Ni catalysts. As a result, the Ni/MgO– Al2O3 catalyst pre-calcined at 800 C exhibits the highest coke resistance due to the smallest Ni crystallite size and SMSI, resulting in the highest catalytic activity and stability. Thus, the Ni/MgO–Al2O3 catalyst will be a promising catalyst in CSCRM (combined steam and carbon dioxide reforming of methane) for the GTL process.

CONCLUSIONS

The replacement of carbon black with carbon nanostructures has led to significant changes in the catalytic layer of a direct methanol fuel cell. The arrangement of carbon nanoparticles at the anode and cathode differs significantly, which prevents the formation of small or closed pores (aggregates) in the catalytic layer of fuel cells. The high surface area and high number of mesopores in ordered mesoporous carbons and carbon gels allow high diffusivity and good reactant flux. Thus, catalysts supported on these materials show higher catalytic activity than the same catalysts supported on carbon black. Among new carbon-based materials, nanotubes are the most investigated catalyst support for low-temperature fuel cells. The highly crystalline structure of CNTs provides high conductivity, surface area and porosity, resulting in exceptional diffusivity. Moreover, CNTs and CNFs have a positive effect on catalyst structure, yielding higher catalytic activity and stability than carbon black. On the other hand, few studies have been conducted on carbon nanohorns, nanocoils and fibers as Pt catalyst supports. Technologically significant nanomaterials come in many shapes, sizes and structures. Nanomaterials range from small molecules to complex composites and mixtures. Depending upon the spatial dimensions of the system and properties under investigation, molecular modeling of nanomaterials can be accomplished. This review illustrates a variety of modeling techniques through recent applications.

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