TERM PROJECT

NANO STRUCTURED CATALYST IN HETEROGENOUS CATALYSIS

CHEMICAL REACTION ENGINEERING – II

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ABSTRACT:

As the world is at present confronting tremendous issues concerning the atmosphere, energy, and the environment, catalysis innovations have all the earmarks of being getting critical to energy, synthesis process, and environmental areas. Nanostructured catalysts have emerged as a pivotal advancement in heterogeneous catalysis, significantly enhancing reaction efficiency and selectivity. The high surface area-to-volume ratio characteristic of nanostructured materials facilitates increased active site availability, allowing for improved reactant interaction and conversion rates. Research areas such as Nanotoxicology, Nanomedicine, Nanoelectronics have a wide scope which make nanoparticle study crucial. Undoubtedly, the utilization of nanomaterials in catalysis and, all the more especially, inorganic nanoparticles has pulled in many research attempts over the globe to create imaginative and greener conventions. These nanoparticles can be used as the catalyst or as mediator and can encourage the reactant procedure in new medium such as, water. Besides, attributable to their little size and expanded surface area, nano-catalysts have obviously risen as offering an interesting candidate at the interface among homogeneous and heterogeneous catalysis, taking into consideration an expanded response rate. Along these lines, in this pursuit for ecofriendly and more affordable catalyst, nano-catalysis is turning into a significant field in science, which is applied broadly in the academics and industrial areas. This brief review principally centered around portraying the major comprehension of nano-catalysis, how remarkable catalytic property and other explicit properties of nanomaterials rely upon its size and structure at the nano level.

Introduction:-

Heterogeneous catalysis is quite prevalent in the chemical industry, and affects our everyday life in many ways. Over 90% of all chemical manufacturing is based or relies heavily on catalytic processes, and, by some estimates, catalysis contributes to approximately 35% of the world's gross domestic product (GDP).[1] Catalytic reactions are not only at the heart of the making of most chemicals and materials, including some of the polymers and composites found in so many modern products, but also play a

central role in energy applications old and new (in oil refining, biofuel production, and fuel cells, to name a few), in pollution control (to limit the emission of noxious gases from automobiles and stationary sources, to remove CO and odors from indoor air, to clean groundwaters), in medical applications (to make pharmaceuticals, in biosensors), and in food production (by aiding with the synthesis of fertilizers and pesticides, in oil hydrogenation, in other food processing).

As we all know that historically catalysis has been understood as a way to accelerate chemical reactions. And, this was the emphasis that Berzelius provided when he introduced the term in 1835.[2] Traditionally, heterogeneous catalysts have been made by using simple synthetic routes with limited control over the morphology and nature of the solids. For instance, in cases where expensive transition metals need to be dispersed onto cheap high-surface-area oxides, to enhance the surface-to-volume ratio of the active phase and reduce the cost of the catalyst, the latter are often impregnated with selected salts of the latter and then calcined. The consequence of this approach is that the resulting small metal particles produced display a wide distribution of sizes and shapes, with their corresponding array of surface ensembles. Different surface sites typically display significantly different catalytic activities, and the performance of the overall catalyst is determined by an average of all of those. It is not easy to control selectivity with such samples, in particular when subtle effects such as stereo or enantio selectivities are considered.

Fortunately, novel nanotechnologies have been developed in recent years to synthesize complex solids with well-defined characteristics, and those have already found applications in catalysis.[3,4] This shift toward an emphasis on reaction selectivity in catalysis has imposed new and stringent constrains on the requirements for the promotion of the desired reactions and the fulfillment of those requirements requires great control on the characteristics of the solids used as catalysts. The ability to produce samples with specific sizes or shapes, or to grow complex solid nanostructures, can be exploited to fulfill specific requirements in catalysis in terms of selectivity, as identified by molecular-level investigations on the reaction mechanisms. This synergy between the surface chemistry of catalysis and nanotechnology is still in its infancy, but has already led to many exciting developments, and promises to revolutionize chemical manufacturing.

Morphology: - Morphology refers with the form, structure, and arrangement of materials on a microscopic scale. It involves studying how the size, shape, and

distribution of particles or grains within a material affect its properties and performancTe.
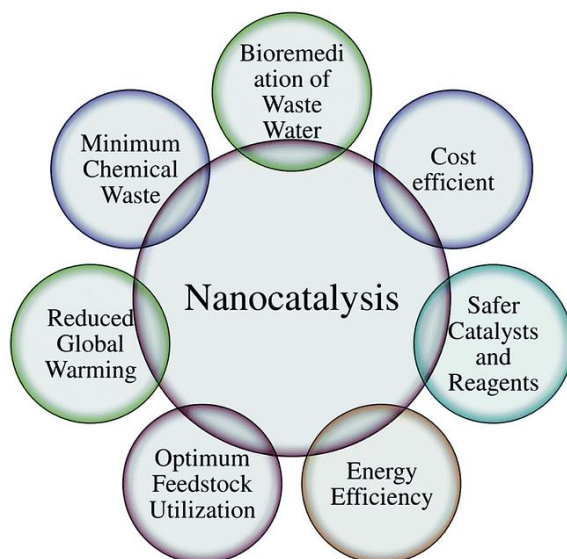

Figure 1: Schematic representation of advantages of nano structured catalyst

Development of Nanostructured Catalysts:-

As we have seen above that nanostructured catalysts have seen significant advancements in recent years. So for the development of Nanostructured catalysts we have various synthesis methods, such as colloidal synthesis, reverse micelle synthesis, sol-gel, electrochemical deposition, and template-assisted synthesis etc. to create catalysts with precise control over size, shape, and structure. These catalysts are used in applications like selective oxidation, biomass conversion, direct methane conversion, and water electrolysis.

Future Possible Fields of Inventions:

1. **Energy Storage:** Nanostructured catalysts can improve the efficiency of batteries, supercapacitors, and flow batteries.
2. **Energy Conversion:** They can enhance the performance of fuel cells and solar cells.
3. **Sustainable Fuel Production:** Nanostructured catalysts can be used in (photo)electrolysis to produce sustainable fuels.
4. **Environmental Remediation:** They can help in processes like CO2 reduction and pollution control.

5. **Medical Applications:** Nanostructured catalysts can be used in targeted drug delivery and diagnostics.

These advancements and applications show the potential of nanostructured catalysts to contribute significantly to various fields, making processes more efficient and sustainable.

1)Colloidal and reverse micelle nanoparticle synthesis: control of size

As mentioned above, many catalytic processes require the dispersion of metals as small nanoparticles onto a high-surface-area porous support. This dispersion is mainly required to optimize the amount of the surface of the expensive active phase exposed. Nevertheless, it has been learned over the years that the specific characteristics of those metal nanoparticles can also affect their catalytic performance.5 Fortunately, metal nanoparticles can now be made with quite narrow size distributions by using colloidal, reverse micelle, or dendrimer-based chemistry. In fact, nanoparticles made this way have already been tested for catalysis in solution, and even in electrochemical systems. Their extension to heterogeneous catalysis, however, has only been started, and only a handful of examples are available where a careful correlation between particle size and catalytic performance has been drawn. In one case provided by Somorjai and co-workers, the hydrogenation and hydrogenolysis of pyrrole on platinum catalysts were shown to shift from almost exclusive *n*-butylamine formation to the production of significant quantities of pyrrolidine as the nanoparticle size was lowered to ~1 nm in diameter6,7 Other examples from the same group include the hydrogenation of CO_2 over cobalt catalysts, the hydrogenation of cyclohexene crotonaldehyde and benzene and toluene and the ring opening of methylcyclopentane all on Pt/SBA-15, and the oxidation of carbon monoxide over ruthenium supported on a slicon wafer.

A particularly interesting size dependence of catalytic activity has been identified with gold catalysts, because bulk gold is often inert but gold nanoparticles can promote many reactions under mild conditions. Such effects have been reported for CO oxidation, for instance,where the maximum in activity seen with Au nanoparticles ~2–3 nm in diameter has been explained by a quantum effect related to their thickness on the surface.A separate study showed that the catalytic activity of gold nanoparticles toward the reduction of 4-nitrophenol decreases monotonically starting with nanoparticles 8

nm in diameter. The oxidation of ethylene glycol was also found to be optimum on carbon-supported gold nanoparticles ~7 nm in diameter.Particle size effects using colloidal-made catalysts have been reported in electrocatalysis as well.9

2)Sol–gel growth:

Additional catalytic engineering may be accomplished by addressing issues associated with the high-surface-area oxide supports often used in catalysis. Typically, an amorphous and highly porous solid, most often a silica or alumina powder, is used to disperse the active catalytic phase, the metal nanoparticles discussed above, for instance. The porous oxides traditionally used in catalysis have complex and ill-defined structures. If the sole role of such materials were to act as supports for the active phase, as they were originally conceived, a lack of control on their structural details would not be an issue. However, it has been determined that in many instances the support contributes to the performance of the catalyst, either because of its own surface functionalities or because of interactions with the active phase, which may create unique sites at the interface. The nature of the support can be controlled during its synthesis. Alternatively, additional functionality can be added after dispersion of the catalytic active phase. Perhaps the most common synthetic approach to grow additional oxide material on an existing catalyst is sol–gel chemistry. Sol–gel processes are based on a two-step solid growth, where a molecular precursor, such as tetraethyl orthosilicate (TEOS) for silica growth, is hydrolyzed in water so the individual units first polymerize to form colloidal particles that then aggregate to form a solid gel. Solvent removal and gel aging can be attained subsequently by heat treatments. The characteristics of the final product, in particular its porosity, may be controlled by adjusting a number of parameters during synthesis, including the pH of the solution, the stoichiometry of the reactants (in particular if mixed oxides are to be grown), the gelation temperature and time, and the choice of solvent. Although sol–gel chemistry has been available for some time already, it has nevertheless found some new and exciting applications in recent times in connection with catalyst preparations. In general, sol–gel synthesis can be used to make high-surface-area materials such as catalytic membranes and superacids, and mixed oxides or solids with metal active phases intimately interlaced in the oxide network. Sol–gel chemistry is also good to add thermal and mechanical stability, and can be used to prevent sintering in supported catalysts.

One approach for the preparation of thermally stable metal-based catalysts is by co-precipitation of the metal and the support in a one-step sol–gel process.This technique was first reported by Reetz and Dugal to stabilize a liquid-phase Pd-based 1,5-cyclooctadiene hydrogenation catalyst.An analogous procedure was used soon after to prepare encapsulated Pd–Au hydrogenation catalysts.Those authors did not check on the thermal stability of their samples, but it has been later shown that, in some instances, it is possible to prevent the agglomeration of the metal particles during surfactant removal this way.In one case, a modified sol–gel approach was designed for the preparation of low-temperature CO oxidation Au/SiO_2 and Au/CeO_2 catalysts where the metal nanoparticles were incorporated in what the authors characterized as an "open shell" of the oxide.Similar procedures were latter extended to the preparation of other supported catalysts, including samples made out of palladium nanoparticles dispersed in silica for the promotion of Suzuki coupling reactions,of platinum on ceria for the water-shift reaction,and of ruthenium on zirconia for ammonia decomposition.Unfortunately, no long-term stability studies have been carried out on these catalysts to check for their stability under realistic conditions.

Alternatively, the metal nanoparticles may be dispersed onto the high-surface-area support and then covered with additional material, grown by sol–gel chemistry, in order to anchor and to add thermal stability to those nanoparticles. Increased thermal and electrochemical stability has indeed been reported by using this technique, by growing silica layers *via* sol–gel chemistry, on Pt/zeolite three-way catalysts, on Pt catalysts dispersed on carbon supports, used for methane combustion and for cyclohexane decomposition,and on a Pt/Fe_2O_3 water-shift catalyst.This approach was also demonstrated by using a model catalyst based on silica beads decorated with Pt nanoparticles: the subsequent deposition of a mesoporous silica layer, used as a selective membrane, rendered the catalyst quite resistant against poisoning in H_2S containing streams. Other oxides can be added this way as well: in one example, titania was added to a Au/SiO_2 catalyst to create the unique interface sites believed to be responsible for low-temperature CO oxidation catalysis.

Unfortunately, encapsulation of metal nanoparticles in a solid matrix, either during co-deposition or if encapsulation is added afterward, is known to often limit exposure of metal nanoparticles to the reactant, and consequently decrease catalytic activity.For instance, when a sol–gel silica layer was added to CO oxidation Au/TiO_2 catalysts, higher stability was indicated by retention of activity to higher temperatures than when using the naked catalyst, up to 975 K, but activity below 475 K was totally suppressed.It is also important to point out that porous solids prepared by sol–gel methods keep evolving over long periods of time, typically aging by forming additional network

bonds and closing up some pores. This means that additional treatments may be required to re-gain access to the surface of the embedded metal nanoparticles. The newly sol–gel deposited layer may, for instance, be partially etched, by using NaOH or another similar agent. However, such procedure may undo the added stabilization of the new silica layer. A novel surface-protected etching procedure was developed in our laboratory to prevent this problem, where a surfactant is used to inhibit silica etching at the outside surface and to promote pore opening.Significant thermal stability of the Pt nanoparticles was obtained without sacrificing catalytic performance, which could be reinstated after proper etching .It may even be possible to use organic growth-directing agents to define the directionality and/or shape of the pores of the newly deposited mesoporous material.

3)Electrochemical deposition:

Electrochemical deposition is a widely used method for preparing nano-structures catalysts, involving the reduction of metal ions onto a conductive substrate via an applied electric current. This process begins with the preparation of an electrolyte solution containing metal ions, followed by the cleaning and immersion of a conductive substrate into this solution. By applying a specific voltage, metal ions are reduced and deposited onto the substrate, forming nanoparticles. The size and morphology of these nanoparticles can be finely controlled by adjusting parameters such as current density, voltage, and deposition time. Post-deposition treatments, like annealing (a**nnealing** is a heat treatment process used to alter the physical and sometimes chemical properties of a material to increase its ductility and reduce its hardness, making it more workable), are often applied to enhance the catalytic properties of the nano catalysts. This method is highly valued for its precision and versatility in creating catalysts for various applications in heterogeneous catalysis.(Ref.10)

4)Template Assisted synthesis:

Template assisted synthesis is a method used to create nanocatalysts with precise control over their size, shape, and structure. This technique involves using a template, such as a porous material or scaffold, to guide the formation of nanoparticles. Nanoparticles are deposited into the pores of the template using methods like electrodeposition, chemical vapor deposition, or sol-gel techniques. After deposition, the template is removed, often through processes like calcination or dissolution, leaving

behind nanocatalysts with the desired morphology. This approach allows for the production of nanocatalysts for various applications, including catalysis, energy storage, and environmental remediation. (Ref.11)

5) Use of Directing Agents:

Heterogeneous catalysis may be further enhanced by developing materials with specific environments surrounding the catalytic active sites. In particular, the size and shape of the pores within the high-surface-area supports may be tailored to favor the access, adsorption, or formation of the desired molecules. Most traditional catalysts have been based on amorphous porous solids, and limited if any control is possible on the characteristics of the pores in such materials. However, the incorporation of zeolites to catalysis changed that. Zeolites are crystalline in nature, and display very specific pore structures. By choosing the appropriate materials, with pores of well-defined size and shape, it has been shown that, in some instances, the appropriate products can be selected.168 Perhaps the best example of this use of zeolites is in the selective production of para-xylene, a feedstock in polyester production, using the 10-member-ring ZSM-5 zeolite.Another well-known case of shape-selective catalysis involves the use of the 10-member-ring SAPO-11 zeolite to remove normal paraffins selectively from lubricating oils, leaving the branched paraffins behind. A more recent system is that of the selective acylation of toluene to para-ene to para-methylacetophenone with small-crystal-size zeolite beta.

Summary

As stated in the introduction, the field of catalysis has a long and illustrious history already. Nevertheless, it is our belief that it still has much more new to contribute. In fact, with the incorporation of the new nanotechnologies briefly discussed in this review, heterogeneous catalysis has the potential to undergo a renaissance and to address many modern industrial processes not previously accessible to it. For one, it may be able to offer new creative solutions to issues associated with the harvesting, storage, and use of energy.(Ref.12)
The expansion of the range of applications of catalysis to industrial processes relies on our ability to develop new effective and selective catalysts. One interesting development in modern times has been the discovery of the activity and versatility of gold as catalyst when used in nanosize form. Such gold-based materials have proven

promising in many low-temperature oxidations39 and bond-forming reactions, but problems with stability need to be solved before they become useful in practical applications. Selective catalysts are also still required for the manufacturing of many fine chemicals. The selective partial oxidation of hydrocarbons, for instance, is still an unresolved and quite general challenge. Moreover, almost all modern pharmaceuticals rely on chiral compounds, so the addition of enantioselectivity to heterogeneous catalysts could offer a new approach to the production of high-value chemicals. High selectivity in catalysis requires great control over the design and manufacturing of the active sites in catalysts. This may now be possible to an extent not available before the recent growth experienced by the nanotechnology field.(Ref.13,14)

Having access to so many new types of nanoscaled solids offers the temptation to proceed with their indiscriminate test in catalysis. In fact, some of this is already going on: many synthetic groups develop new preparation techniques to make novel solids first, and search for possible applications afterward. Such a sequence of events may lead to an endless search with little reward, as the parameter space for the development of catalysts is vast and complex. Motivation may be obvious in some cases, as discussed above in terms of ways to increase catalyst stability or to carve specific catalytic sites in solid supports, but it is not as clear in others, such as when specific particle shapes are developed.

References:

1. J. N. Armor, *Catal. Today*, 2011, **163**, 3– 9
2. J. Berzelius, '*Jahres-Bericht über die Fortschritte der Physichen Wissenschaften*', H. Laupp, Tübingen, 1836
3. F. Zaera, *J. Phys. Chem. Lett.*, 2010, **1**, 621–627
4. I. Lee, M. A. Albiter, Q. Zhang, J. Ge, Y. Yin and F. Zaera, *Phys. Chem. Chem. Phys.*, 2011, **13**, 2449–2456

5. M. Boudart and G. Djéga-Mariadassou, in *'Kinetics of Heterogeneous Catalytic Reactions'*, ed. J. M. Prausnitz and L. Brewer, Princeton University Press, Princeton, N.J., 1984

6. H. J. Freund, *Chem.–Eur. J.*, 2010, **16**, 9384–9397

7. R. Narayanan and M. A. El-Sayed, *J. Phys. Chem. B*, 2005, **109**, 12663–12676

8. B. E. Hayden, D. Pletcher, M. E. Rendall and J.-P. Suchsland, *J. Phys. Chem. C*, 2007, **111**, 17044–17051

9. B. E. Hayden, D. Pletcher, J.-P. Suchsland and L. J. Williams, *Phys. Chem. Chem. Phys.*, 2009, **11**, 1564–1570

10. Tonelli D, Scavetta E, Gualandi I. Electrochemical Deposition of Nanomaterials for Electrochemical Sensing. Sensors. 2019; 19(5):1186. https://doi.org/10.3390/s19051186

11. W. W. Kaeding, C. Chu, L. B. Young, B. Weinstein and S. A. Butter, J. Catal., 1981, 67, 159–174.

12. Sisman. (2011). Template-Assisted Electrochemical Synthesis of Semiconductor Nanowires. InTech. doi: 10.5772/20551 H. Arakawa, M. Aresta, J. N. Armor, M. A. Barteau, E. J. Beckman, A. T. Bell, J. E. Bercaw, C. Creutz, E. Dinjus, D. A. Dixon, K. Domen, D. L. DuBois, J. Eckert, E. Fujita, D. H. Gibson, W. A. Goddard, D. W. Goodman, J. Keller, G. J. Kubas, H. H. Kung, J. E. Lyons, L. E. Manzer, T. J. Marks, K. Morokuma, K. M. Nicholas, R. Periana, L. Que, J. Rostrup-Nielson, W. M. H. Sachtler, L. D. Schmidt, A. Sen, G. A. Somorjai, P. C. Stair, B. R. Stults and W. Tumas, Chem. Rev., 2001, 101, 953–996

13. B. Pugin and H. U. Blaser, Top. Catal., 2010, 53, 953–962.

14. C. Cope´ret and J.-M. Basset, Adv. Synth. Catal., 2007, 349, 78–92.