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Nano Technology: A Greener Tool of Organic Synthesis

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Abstract: Among the important and essential principles of Green Chemistry Catalysis is the most valuable one. Green chemistry is the application of a set of principles that eradicates or minimizes the use or formation of hazardous materials in the formulation, execution and utilization of chemical products and emphasizes vulnerability minimization as the desired quality while developing new synthetic protocols. In recent years, nanotechnology, specifically nanocatalysis has become an emerging field of science due to its higher activity, selectivity and productivity as compared to conventional catalysts. Due to the exclusive structural and electronic characteristics of the nano materials and the exceptionally large surface area to volume ratio impart unique catalytic properties to nano particles. In this article we will be discussing the latest advances in the field of nano-catalysis and surfactant mediated generation of Nano Pockets which have opened new ways to explore synthetic methodologies for generation of novel functional materials.

Index Terms - Green Chemistry, Atom Economy, Nano Catalysis, Aqueous Solution Organic Synthesis, Surfactant Combined Catalyst.

I. Introduction

During the last three centuries Chemical Science is being practiced as a tool for production of numerous functional materials which have made the human life smooth and prosperous. These inventions and discoveries include medicines and pharmaceuticals for improvement of human health and hygiene, fertilizers and pesticides for enhancement of food productivity, semiconductors and polymers for development of electronic devices and so on. But along with increase in chemical production the environmental issues also become prominent as the industrial wastes and bi-products started causing short term and long term harms to living ecosystem including human beings. In order to address this problem a new stream in the synthetic chemistry appeared which attempts to reorganize chemical knowledge and applies it to the creation, application and ultimate disposal of chemicals in a way that minimizes assimilation of materials in living system, exposure of living organisms, including humans, to poisonous materials and destruction of the ecosystem. But while attempting these modifications one has to be aware of the cost effectiveness and feasibility of the improvised chemical methodologies.

In one sense green chemistry is the most economical and efficient possible protocol of chemistry, where the cost calculation is inclusive of the potential hazards of society and nature due to exposure to the chemicals under consideration.

II. Importance Of Catalyst

New catalytic synthetic methods in organic chemistry that satisfy increasingly stringent environmental constraints are of great demand by the pharmaceutical and chemical industries [1]. In addition, novel catalytic procedures are necessary to produce the emerging classes of organic compounds that are becoming the targets of molecular and biomedical research. This interest in the diverse aspects of the catalysis of organic reactions for finer applications has been growing worldwide. Evolution and application of newer catalysts are in demand for application in the production of pharmaceuticals, agrochemicals and specialty chemicals such as perfumes and flavorings. Traditionally, high product selectivity has been the paramount concern rather than high production efficiency in judging the applicability of catalysts for organic synthesis. However, environmental concerns and challenge to achieve ecofriendly organic synthetic protocols are increasingly motivating the movement towards efficient catalytic alternatives to stoichiometric organic transformations. In 1998, Anastas and Warner [2] suggested a set of principles which governs the research and improvisation towards reducing and eliminating chemicals as well as chemical protocols with adverse ecological impacts. Therefore from a Green chemist's point of view catalytic reagents are always preferred as compared to the stoichiometric reagents as the atom economy is improved by using catalysts during a chemical reaction. Hence, application of catalysis can be utilized for development of greener and cleaner synthetic protocols which are economically as well as ecologically improved.[3] Although catalysts had been used during chemical synthesis from the year 1746, the catalysts used were usually derived from heavy metals in elemental form or their compounds. But the new scale of ecological sustainability rendered those catalysts unfit for green synthesis and search for new generation catalyst has become the most important area of interest for the researchers. Among the conventional catalysts the homogenous catalysts are usually more effective due to the close proximity and easy availability of reaction sites which is not possible in case of heterogeneous catalysts. But the difficult recovery of the homogeneous catalysts makes these catalysts less cost effective as compared to the heterogeneous ones [4]. Both the merits can be however achieved if Nano particles are employed as catalysts in organic synthetic protocols. The high surface to volume ratio ensures maximum contact area between the reactant and the catalyst where as the insolubility in organic solvents enhances the chance of recycling the catalyst [5-9].

III. Characteristics Of Nano Particles

Nanoparticles can be defined as the particles with a size within 100 nm in any of the dimensions. The recent development in nano-technology involves generation and stabilization of functionalized nano particles with enhanced catalytic properties [10, 11]. Various sophisticated instruments have been used to characterize the nanomaterials which includes nuclear magnetic resonance spectroscopy (NMR), infra red spectroscopy (IR), ultra-violet and visible spectroscopy (UV-Vis), transmission electron microscopy (TEM), scanning tunnelling microscopy (STM), X-ray diffraction (XRD), scanning electron microscopy (SEM) (Figure: 1), extended X-ray adsorption fine structure spectroscopy (EXAFS), energy dispersive X-ray spectrometer (EDS), X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), X-ray absorption near-edge spectroscopy (XANES), X-ray emission spectroscopy (XES), photoluminescence spectroscopy (PL), small angle X-ray scattering (SAXS), atomic force microscopy (AFM), , etc [12].

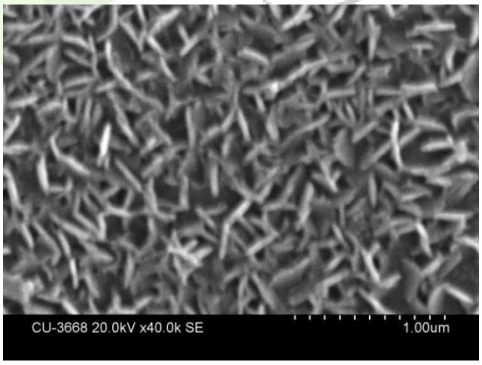


Figure 1: SEM Image of ZnO Nano Particle (Adopted from Ref. 12)

Synthesis of Nano Particles in either top-down or bottom-up method involves application of various polymers like polyvinyl pyrollidone (PVP), polyethylene glycol (PEG), poly(N-vinylisobutyramide) (PNVIBA); organic as well as inorganic ligands like amines, thiols, alcohols, phosphines; surfactants like tetraalkyl ammonium salts and long chain fatty acid salts. Symmetrical macromolecules like crown ethers as well as dendrimers are also often used as capping agents for newly synthesized nano particles. The proper choice of the stabilizing agent plays a crucial role in designing nano catalysts as the external morphology and structural features of the synthesized nano particles determines the stereo-electronic features of the nano catalyst and suitable modification of these characters makes the catalyst capable for catalysing a specific reaction. Thus, specificity and catalytic activity of Nano Particles depend on mainly two facets

(i) Control of crystal structure and morphology

(ii) Control of surface composition.

Along with the development in methodologies for synthesis of Nano particles with predefined morphology and composition numerous methods are also being invented to facilitate the easy recovery and enhanced reusability of the Nano particles being used as catalyst. The improved recovery techniques and consistent catalytic activity over several catalytic cycles have made the Nano particles a choice for industrial procedures [13].

As a part of this drive towards economic recovery of the catalysts the use of solid supported Nano particles are being promoted. In this method synthetic Nano particles are deposited on common and uncommon solid supports like silica, alumina, titanium clay, ceria or other oxides as well as carbon supports in various forms i.e. mesostructural silica [14], alumina membranes [15], carbon nano-tubes [16] to get heterogeneous systems which remain unaffected by organic solvents and reactants and can be recovered after reaction with almost intact catalytic activity.

Another latest concept of magnetically recoverable nanoparticles has quickly developed to further simplify the recovery process. In these cases, the catalytic activity relies on the surface of the magnetic particle itself, in a heterogeneous fashion. Many design features (Figure: 2) including the NPs size, the use of ligands or additives, or the use of hybrid structures have contributed to the development of the rich chemistry of magnetic Nano particles over the past few years [17].

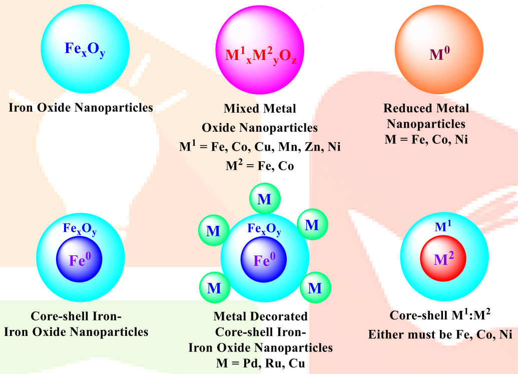


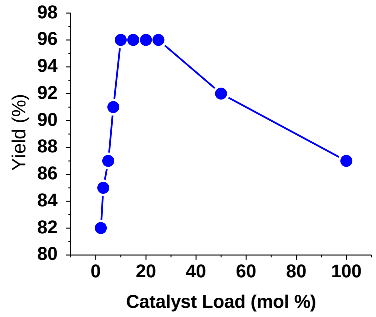
Figure 2: Different Types of Metallic Nano Particles

IV. Nano Catalysis In Organic Synthesis

Catalysis is the most versatile and abundant utility of the new group of the synthesized Nano particles. The use of nano scale particles of aluminum, iron oxide, titanium oxide, clays are well known from the time well prior to the discovery of Nano particles. However the mechanistic explanation of the amazing catalytic activity of such nano particles was not explored in details. The catalytic activity of the Nano particles can be mainly attributed to the large surface-volume ratio of the Nano particles with a considerable weight on the stereo-electronic modification of the surface to enhance the specificity and activity of the catalyst. Therefore a better understanding of the catalytic details is necessary to develop more active, selective and resilient Nano catalysts [18]. Nanoparticles are recognized as the most important industrial catalyst and have wider application ranging from chemical manufacturing to energy conversion and storage.

V. Homogenous And Heterogeneous Nano Catalysis

Catalysis is one of the pioneer applications of nanoparticles. Nano-catalyst in homogeneous system typically means a solution or suspension of nanoparticles in a solvent. But in homogeneous nanocatalysis (catalyst which is in a same phase to the reactants), it is a must to consider how to prevent its aggregation when designing a nano-catalyst for use in a solution. Nanoparticles have a special characteristic to aggregate and will clump together to form larger particles, if it is not prevented properly, nanoparticles lose their large surface area and other benefits. The catalyst load optimization study is often carried out to determine the optimum load of the catalyst. Though initial increase in the catalyst load can enhance the rate, often a drop in the reaction rate is observed (Graph: 1) after the catalyst concentration crosses a certain limit. This drop can be attributed to self-aggregation of the nano-particles [12].



Graph 1: Catalyst load optimization study (Adopted from Ref. 12)

Polymer-based stabilization of nano-particles to prevent its aggregation is recognized as most effective way to stabilize nanoparticles in solution. Long chain molecules make it impossible for the nanoparticles to come in contact to aggregate or clump together to form larger particles [19].

Research to investigate the catalytic potential of various nano-particle-support systems has attracted more attention of scientific community nowadays. Recent examples include copper, ruthenium; rhodium, silver, palladium, iron, gold, zinc, nickel and platinum nanoparticles along with the corresponding metal oxides. Although the details mechanistic course of such Nano particle catalysed reactions cannot be always understood properly but some attempts (Figure 3) are made to rationalize the catalytic activity of the Nano particles [12].

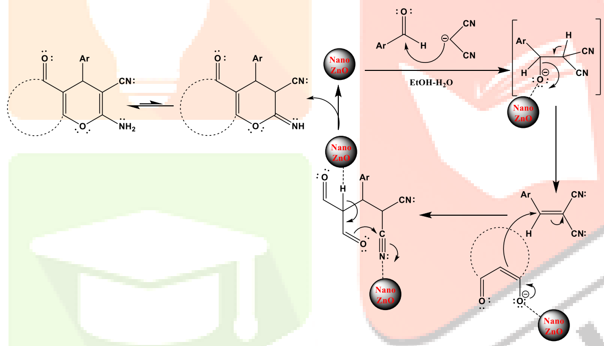
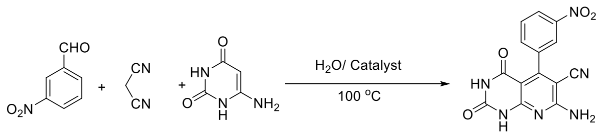


Figure 3: Mechanism of formation of 4H-pyrans catalysed by nano crystalline ZnO (Adopted from Ref. 12)

VI. Chemistry Of Nano Pockets: Surfactant

Catalysis Surfactant Combined Catalysts are often being employed now a day to overcome the problems of carrying out organic reactions in aqueous medium. Surfactants helps is dissolving organic reactants in the aqueous medium by forming micelles where the hydrophilic heads are present in the outer surface and hydrophobic tails are oriented towards the core. Often along with surfactant other catalysts like acids and bases are required to promote the reaction. To overcome this problem of the application of combination of catalysts a new variety of catalyst has emerged. These catalysts are capable of performing acid-base reaction along with the expression of standard surfactant phenomena [20].

This novel methodology of Lewis Acid/Base-Surfactant combined catalyst was employed while standardizing the following synthesis (Scheme 1).



Scheme 1: Synthesis of pyridopyrimidines (Adopted from Ref. 20)

The catalyst optimization study of this reaction revealed that Lewis base-surfactant-combined catalyst (LBSC) showed a better catalytic activity as compared to Lewis base or Surfactant alone (Table 1).

Table 1: Catalyst Optimization Study (Adopted from Ref. 20)

Entry	Catalyst	Reaction Time	Yield (%)
1	Triethylamine	4 hr.	58
2	Triethylamine/SDS	3 hr.	70
3	TEOA	2 hr.	85

TEOA is a sterically hindered neutral organic base and especially useful for inhibition of the formation of unwanted side products. This new type of catalyst, "Lewis base-surfactant-combined catalyst (LBSC)" would act both as a catalyst to activate the substrate molecules and as a surfactant to form colloidal particles. The reaction driving force in the micelles working as "Nano Pockets" may be related to the hydrophobic force which compresses the reactants together in a highly compact arrangement of complexes together within a restricted hydrophobic domain.

VII. Future Applications Of Nano Catalyst

Concept of nanocatalysis is known since the 1950s when the term nanotechnology was not even introduced [21, 22]. In 1986, first time Haruta et al. [23] reported the catalytic activity of gold (Au) nanoparticles in oxidation of carbon monoxide and hydrogen at low temperatures. After this reporting, a very old conventional idea about gold for its inertness towards chemical reaction has been completely changed and a new door to interesting applications of nanoscale materials in catalysis is opened.

Traditional heterogeneous catalyst systems have two main demerits in contrast to their homogeneous counterparts is (i) the reduced surface area that is accessible to reactant molecules, thereby limiting their catalytic activities [24] and (ii) leading to an unnecessarily high consumption of expensive catalyst materials [25]. Nano-scaled catalytic materials can solve these problems by increasing the surface to volume ratio. These specifications are the base of present status of nanocatalysis. Advances in nanocatalysis in past few years with present day's developments open a new vision for nanocatalysis and its future aspects such as inspired design, synthesis and formulation of industrially and biologically important safe catalysts.

VIII. Conclusion

Nanocatalysis plays a crucial role in both the academic as well as industrial research. Industrial impact of nanocatalysis is clearly reflected by the increasing number of nanocatalysis related patents, products and products in the market. Size and shape controlled preparation of metal nanoparticles are very promising for greener and cleaner heterogeneous catalytic protocols. On the basis of detailed understanding of morphological effects of the nanoparticles and their interactions with stabilizing agents, today we could be optimistic that chemists are on the era of a Green Revolution in Chemistry.

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