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Green Catalysts – A Novel Approach Towards Sustainability

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Abstract

The production of most industrially important chemicals involves catalysis. Research in catalysis is a major field of chemical science. Catalysis is relevant to many aspects of environmental science. Catalytic reactions are preferred in environmentally friendly due to the reduced amount of waste hazardous. A catalyst works by providing an alternative reaction pathway to the reaction product. The rate of the reaction is increased as this alternative route has lower activation energy than the reaction route not mediated by the catalyst. Catalysis plays a very important role in the environmentally benign synthesis of new and existing chemicals. This paper describes the role of catalysts in the green synthesis of chemicals for a sustainable future and identifies those catalysts which will have beneficial economically as well as environmentally for chemical manufacturing.

Key Words Green catalysts, environment, green synthesis

Introduction

Catalysis is a key technology to achieve the objectives of sustainable green chemistry. Green catalysts are the catalysts which are ecofriendly, can be regenerated hence reused multiple times and thus minimize waste production during process. The chemical industry has always exploited catalysts to do reactions as near to ambient temperature as is practical, thus keeping energy usage and costs down. Today industry faces additional pressure to be cleaner and greener, which will require the development of new catalysts. The focus of catalyst research is now on finding catalysts that will enable industrial processes to be less polluting, operate with a better atom economy, produce purer products and last longer. Although we may think of the catalyst as lasting forever, this is never the case - all industrial catalysts have a finite lifetime, which makes the search for longer-lasting catalysts high on the industry's list of priorities. Green chemistry is an area of chemistry that focuses on the discovery and use of environmentally friendly chemicals and processes[1]. It is known as environmentally benign chemistry or sustainable chemistry. Green chemistry reduces toxicity, minimizes waste, saves energy, and cuts down on the depletion of natural resources, its mission is to design and implement pollution prevention technologies other than waste management[2,3]. Green chemistry is considered green because it is perceived to lower carbon emissions and create fewer pollutants [4].

Catalysis has played a significant role in reducing pollution in our environment. Catalysts have been applied in improving air quality by removal and emission control of NOx, reducing the use of Volatile Organic Compounds (VOCs), developing alternative catalytic technology to replace the use of chlorine or chlorine based intermediate in chemical synthesis and processes with waste minimization[5]. With catalysis, reactions can be more efficient and selective thereby eliminating large amounts of by-products and other waste

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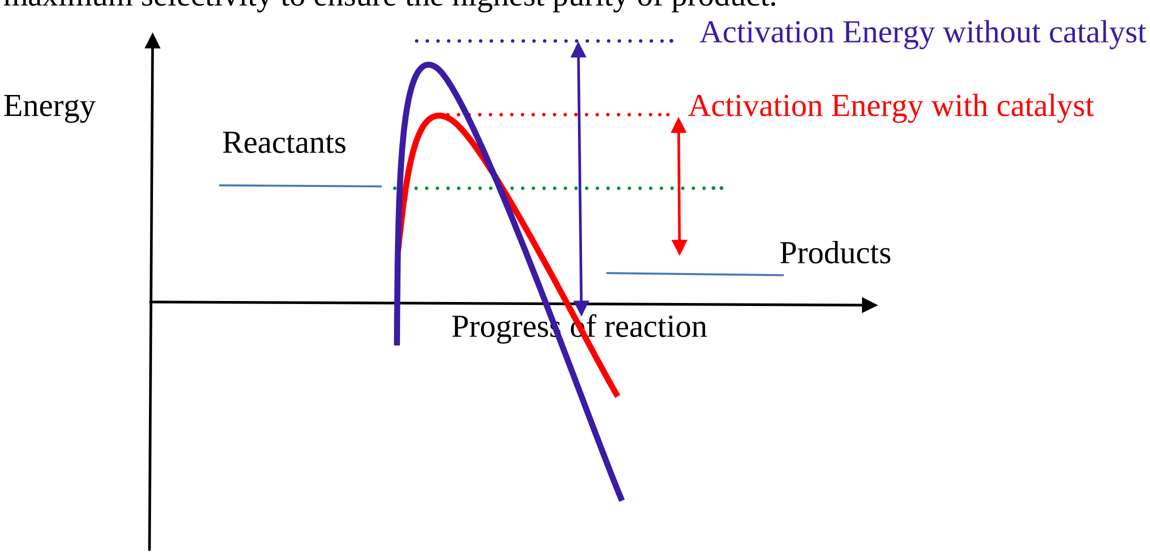
compounds[6]. At present, many industries have started to earnestly adopt green chemistry and other sustainable practices. The practice of green chemistry not only leads to environmental benefits but also economic and social benefits. The combination of the three benefits known as triple bottom line provides strong encouragement for businesses to develop sustainable products and processes.

How catalysts work

A catalyst is defined as a substance that changes the velocity of a reaction without itself being changed in the process. It lowers the activation energy of the reaction but in so doing it is not consumed.A catalyst provides an alternative reaction pathway with lower activation energy than the no catalyzed reaction. The catalyzed reaction can involve several intermediates and transition state complexes, quite different from the one-step mechanism for the reaction in the absence of a catalyst. It is important to note that while the catalyst provides an easier path for reactant molecules to form a transition state, the catalyst also provides an easier path for the reverse reaction in which product molecules return via the transition state to reactant molecules. In this way the catalyst speeds up both forward and reverse reactions to the same extent and so the equilibrium constant remains the same as dictated by the thermodynamics. Many reactions are multi-step processes of which one will be the slow rate-controlling step, and it is this reaction that the catalyst must be active for. Additionally, many reactions are accompanied by the formation of side products, which may be useful but nevertheless need to be separated and therefore add to the costs of the process. Thus, industrial chemists are always looking for catalysts that will provide maximum selectivity to ensure the highest purity of product.



Heterogeneous and homogeneous catalysts

Two types of catalyst dominate in the chemical industry: heterogeneous and homogeneous catalysts. Heterogeneous catalysts are solids that catalyze the reactions between liquid or gaseous reactants. The catalytically active solid is typically coated onto a high surface area support to ensure the maximum exposure to the gas or liquid reaction mixture. These catalysts, usually transition metals and their compounds, are used in ca 85 per cent of industrial processes because they are easy to separate from the products at the end of the reaction. An important aspect of heterogeneous catalysis is the synthesis of active sites through attachment of metal complexes with a given chemical composition to the support surfaces [7]. A heterogeneous catalyst provides a lower energy path via a sequence that involves adsorption of reactant molecules upon an active site in the surface. The molecules become chemisorbed on the active site, their bonds are disrupted and rearrangements take place to form the activated complex; desorption then follows to release the product molecules into the gas, or liquid, phase. The active site is once again vacant to repeat the processHomogeneous catalysis is a single phase reaction commonly liquid/ liquid. The use of homogeneous catalysts has numerous advantages such as lowering of temperature of reactions and thereby saving energy. The lower temperature tends to provide greater specificity and fewer unwanted and perhaps undesirable by-products. Thus, these catalysts provide a totally benign synthesis, minimize energy cost and maximize yields and purity. One major disadvantage of the catalyst, however, is the need to separate and recover the catalyst.

Green Catalysts

Recently, growing attention is being directed towards the development of innovative catalytic systems with high performance from the point of environmentally greener processes, economicalefficiency and minimum consumption of resources. The application of catalysis to reduce toxicity and renewable energy systems, and efficiency makes it a central focus area for green chemistry research. Green Catalysis is a subtitle of green chemistry but the most important one and one of the urgently needed challenges facing engineers now is the design and use of environmentally benign catalysts. Green and sustainable catalyst should possess higher activity, higher selectivity, efficient recovery from reaction medium, durability or recyclability, cost effectiveness. In recent years the development of catalysts for processes to replace conventional ones has made a significant contribution to the reduction of environmental pollutants. Thus, there is an increasing interest on the topic of green catalysis recently. It not only includes developing new catalysts which can offer stable, highly effective catalytic performances, but considers the application of environmentally friendly catalyst preparations. Numerous studies have been focused on green catalysts.

Zeolite catalyst

zeolite-catalyzed reactions in organic synthesis include Friedel-Crafts alkylation and acylation and other electrophilic aromatic substitutions, additions and eliminations, cyclization, rearrangements and isomerization, and condensations. Electrophilic Aromatic Substitutions Friedel-Crafts alkylation are widely used in both the bulk and fine chemical industries. For example, ethylbenzene (the raw material for styrene manufacture) is manufactured by alkylation of benzene with ethylene. The original process, developed in the 1940s, involved traditional homogeneous catalysis by $AlCl_3$. This process was superseded by one employing a heterogeneous catalyst consisting of H_3PO_4 or BF_3 immobilized on a support (UOP process). This system is highly corrosive and, because of the enormous production volumes involved, generates substantial amounts of acidic waste.

A major breakthrough in FC alkylation technology was achieved in 1980 with the application of the medium pore zeolite, H-ZSM-5, as a stable recyclable catalyst for ethylbenzene manufacture (Mobil-Badger process). An added benefit of this process is the suppression of polyalkylation owing to the shape selective properties of the catalyst. This process marked the beginning of an era of intensive research, which continues to this day, on the application of zeolites in the manufacture of petrochemicals and, more recently, fine chemicals. Zeolite-based processes have gradually displaced conventional ones, involving supported H_3PO_4 or $AlCl_3$ as catalysts, in the manufacture of cumene, the raw material for phenol production.

Biocatalysts

Biocatalysts have many attractive features in the context of green chemistry: mild reaction conditions (physiological pH and temperature), an environmentally compatible catalyst (an enzyme) and solvent (often water) combined with high activities and chemo-, regio- and stereoselectivities in multifunctional molecules. Furthermore, the use of enzymes generally circumvents the need for functional group activation and avoids protection and deportation steps required in traditional organic syntheses.

The time is ripe for the widespread application of biocatalysts in industrial organic synthesis[8] and according to a recent estimate[9] more than 130 processes have been commercialized. Advances in recombinant DNA techniques have made it, in principle, possible to produce virtually any enzyme for a commercially acceptable price. Advances in protein engineering have made it possible, using techniques such as site directed mutagenesis and in vitro evolution, to manipulate enzymes such that they exhibit the desired substrate specificity, activity, stability, pH profile, etc.[10]. Furthermore, the development of effective immobilization techniques has paved the way for optimizing the performance and recovery and recycling of enzymes. An illustrative example of the benefits to be gained by replacing conventional chemistry by biocatalysts is provided by the manufacture of 6-aminopenicillanic acid (6-APA), a key raw material for semi-synthetic penicillin and cephalosporin antibiotics, by hydrolysis of penicillin G [11]. The glycolic acid is readily available from acid-catalyzed carbonylation of formaldehyde. Traditionally, glyoxylic acid was produced by nitric acid oxidation of acetaldehyde or glyoxal, processes with high E factors, and more recently by ozonolysis of maleic anhydride. The key enzyme in the above process is an oxidase which utilizes dioxygen as the oxidant, producing one equivalent of hydrogen peroxide, without the need for cofactor regeneration.

Enzyme Catalysts

Enzyme catalysts are not only in biochemical reactions in biological systems but are also having impact on the complex organic synthesis of bioactive molecules. One of the remarkable properties of enzyme catalyst is selectivity. They are regioselective, which means that they can discriminate among several identical groups within the same molecule. For instance, in the acylation of pyridine group of castanosermine, an anticancer agent for the treatment of Acquired Immune Deficiency Syndrome (AIDS), the four secondary hydroxyl groups of similar reactivity would all undergo acylation under normal conditions with acyl chloride. In contrast, the enzyme catalyst subtilisin (used in anhydrous, pyridine)

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acylated only the C-I hydroxyl group[12]. Enzyme catalysts are also chemo selectivei.e. they can select among groups of similar reactivity but of different chemical nature, for instance the catalysts show a preference towards the acylation of a primary hydroxyl group over a primary amino group during the acylation of adenosine[13]. Enzyme catalysis is both in aqueous and non-aqueous applicable solvents including supercritical fluid[14,15]. The disadvantages of enzyme catalysts include; high cost, instability to high temperature (>250oC) and the difficulty in recovering them for re-use. A lot of researches have been conducted on enzymatic catalysts[21] in recent years, due to harmless nature of these catalysts to both human health and the environment and their potential for displacing more hazardous catalysts, the use of enzyme catalysts is one of the goals of green chemistry.

Nano catalysts

Nanomaterials have structured components with at least one dimension less than 100 nm. Nanomaterial is expected to be fruitful area for green chemistry catalysis due to the increasing ability to design in nano state and the high surface areas found in nano materials. Employing green chemistry principles for the production of nanoparticles can lead to a great reduction in waste generation, less hazardous chemical syntheses, and an inherently safer chemistry[16]. Materials reduced to the nanoscale can show different properties compared to what they exhibit on a macroscale, enabling unique applications. For instance, stable materials turn combustible (aluminum); solids turn into liquids at room temperature (gold); insulators become conductors (silicon). A material such as gold,

The nano sized particles increase the exposed surface area of the active component of the catalyst, thereby enhancing the contact between reactants and catalyst dramatically and mimicking the homogeneous catalysts. However, their insolubility in reaction solvents renders them easily separable from the reaction mixture like heterogeneous catalysts, which in turn makes the product isolation stage effortless. Also, the activity and selectivity of nano-catalyst can be manipulated by tailoring chemical and physical properties like size, shape, composition and morphology[17]. In the emerging regime of nano-catalysis the synergetic effect of the nanosized catalyst is known to be important for the overall performance, where global processes such as the transport of the reactant atoms to the catalyst could play an important role in the overall reaction kinetics[18]. Nanotechnology can step in a big way in lowering the cost and hence become more effective than recent techniques for the removal of pollutants from water in the long run. In this perspective nanoparticles can be used as potent sorbents as separation media, as catalysts for photochemical destruction of contaminants; nanosized zerovalent iron used for the removal of metals and organic compounds from water[16]. Advances in nanoscale science and engineering suggest that many of the current problems involving water quality could be resolved or diminished by using nano sorbents, nano catalysts, bioactive nanoparticles, nanostructured catalytic membranes, nanotubes[16]. Nanomaterial properties desirable for water and wastewater applications include high surface area for adsorption, high activity for (photo)catalysis, antimicrobial properties for disinfection and biofouling control, superparamagnetic for particle separation, and other unique optical and electronic properties that find use in novel treatment processes and sensors for water quality monitoring[19]. Nanosized metal oxides, including nanosized ferric oxides, manganese oxides, aluminum oxides, titanium oxides, magnesium oxides and cerium oxides, are classified as the promising ones for wastewater treatment systems[20]. Consequently, the catalysts that are prepared by methods of nanotechnology used in advanced oxidation processes are of particular interest because of their environmentally friendly features.

AluminiumPhosphate Based Molecular Sieves

The prospects of aluminium phosphate based molecular sieves are as microporous catalyst and an absorbent material. Initially, they were discovered as a neutral aluminium phosphate (AlPO4)n framework [22] but later Si, other metals (such as Be, Mg, Ti, Mn, Cr, Fe, Co, and Zn) and other elements (such as Li, B, Ga, Ge, and As) have subsequently been incorporated into the AlPO4 framework; these substitutions give additional applications for the catalyst. Some of the applications include: catalytic dewaxing, hydro-cracking, methanol conversion and toluene alkylation.

Conclusion

Catalysis has come a long way and has served industry well in enabling many reactions to be done which, otherwise, would have been uneconomic or even impossible. Today chemists are faced with new challenges as concerns for the environment and scarcity of resources motivates them to look for greener processes. Catalysis plays a very important role in environmental benign synthesis of chemicals. Substitution of conventional synthetic pathway with environmental benign synthetic pathway can help to curb a lot of by-products, co-products, potential wastes and pollutants. The potential for catalyst to be used for environmentally benign synthesis is seen in the reduction of series of steps that usually occur during conventional synthesis. The applications of catalysts in chemical synthesis can play an important role in designing environmentally safer technologies and in the production of safer chemicals.

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