

Review on Green Chemistry and Catalysis

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Abstract: *Green chemistry, also known as sustainable chemistry, refers to the development of chemical products and processes that minimize or exclude the operation and product of dangerous composites. They only use environmentally friendly chemicals and chemical procedures. It is erected on twelve principles that can be used to develop or reproduce motives, accoutrements, responses, and processes that are safer for mortal health and the terrain from the ground over. Green Chemistry decreases the environmental impact of chemical processes and technologies, as demonstrated in this composition. The thing of this exploration is to learn further about the part of catalysts in green chemical conflation for a further sustainable future. In the ecologically friendly conflation of novel and being composites, catalysis plays a critical part. Catalyzed processes bear lower energy to produce and produce smaller by-products, co-products, and other waste particulars, indicating increased effectiveness. Catalysts can be created in such a way that they aren't dangerous to the terrain. Catalysts come in a variety of shapes and sizes, and some of them have positive goods in the chemical assiduity.*

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I. INTRODUCTION

Green chemistry (sometimes referred to as sustainable chemistry) is the branch of chemistry that deals with the design and optimization of processes and products in order to lower, or remove altogether, the production and use of toxic substances. Green chemistry is not the same as environmental chemistry

The former focuses on the environmental impact of chemistry and the development of sustainable practices that are environment-friendly (such as a reduction in the consumption of non-renewable resources and strategies to control environmental pollution). The latter focuses on the effects that certain toxic or hazardous chemicals have on the environment

1.1 Principles

The twelve principles put forward by the American chemists Paul Anastas and John Warner in the year 1998 to lay the foundation for green chemistry are listed below.

- **Prevention of Waste:** Preventing the formation of waste products is always preferable to it's the clean-up of the waste once it is generated.
- **Atom Economy:** The synthetic processes and methods that are devices through green chemistry must always try to maximise the consumption and incorporation of all the raw materials into the final product. This must strictly be followed in order to minimise the waste generated by any process.
- **Avoiding the Generation of Hazardous Chemicals:** Reactions and processes that involve the synthesis of certain toxic substances that pose hazards to human health must be optimised in order to prevent the generation of such substances.
- **The Design of Safe Chemicals:** During the design of chemical products that accomplish a specific function, care must be taken to make the chemical as non-toxic to humans and the environment as possible.
- **Design of Safe Auxiliaries and Solvents:** The use of auxiliaries in processes must be avoided to the largest possible extent. Even in the circumstances where they absolutely need to be employed, they must be optimized to be as non-hazardous as possible.

- **Energy Efficiency:** The amount of energy consumed by the process must be minimized to the maximum possible extent.
- **Incorporation of Renewable Feedstock:** The use of renewable feedstock and renewable raw materials must be preferred over the use of non-renewable ones.
- **Reduction in the Generation of Derivatives:** The unnecessary use of derivatives must be minimized since they tend to require the use of additional reagents and chemicals, resulting in the generation of excess waste.
- **Incorporation of Catalysis:** In order to reduce the energy requirements of the chemical reactions in the process, the use of chemical catalysts and catalytic reagents must be advocated.
- **Designing the Chemicals for Degradation:** When designing a chemical product in order to serve a specific function, care must be taken during the design process to make sure that the chemical is not an environmental pollutant. This can be done by making sure that the chemical breaks down into non-toxic substances.
- **Incorporating Real-Time Analysis:** Processes and analytical methodologies must be developed to the point that they can offer real-time data for their monitoring. This can enable the involved parties to stop or control the process before toxic/dangerous substances are formed.

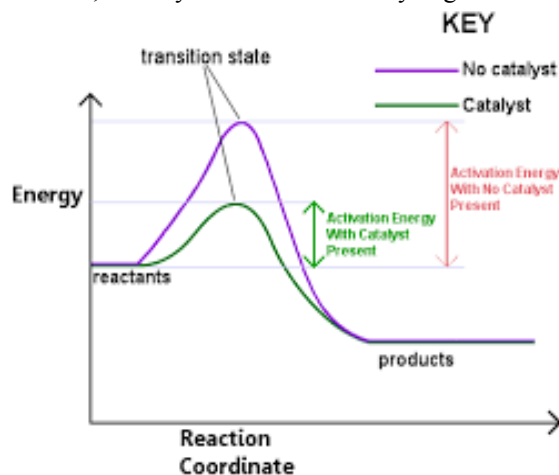
Incorporation of safe chemistry for the prevention of accidents: While designing chemical processes, it is important to make sure that the substances that are used in the processes are safe to use. This can help prevent certain workplace accidents, such as explosions and fires. Furthermore, this can help develop a safer environment for the process to take place in.

1.2 Catalysis

Chemical reaction, changes the rate of a chemical reaction, but remains unchanged itself after the chemical reaction has finished. This catalysis usually changes the rate of a reaction by speeding it up or lowering its temperature in a way that would not be possible without a catalyst. The term catalyst is also used outside of chemistry for anything that causes a change or reaction to happen.

A. Role of Catalysis

- A catalyst is a material that, without being consumed by the process, speeds up a chemical reaction or decreases the temperature or pressure required to initiate one.
- The addition of a catalyst to a reaction is known as catalysis.
- A catalyst is a material that influences, encourages, or speeds up the reaction of two or more components to produce an alternative end result.
- In industrial operations, including the production of food, catalysts are frequently utilized to maximize production rates and quantities.
- For example, if we have Pt metal as a catalyst for the reaction of hydrogen gas and ethene gas, then the Pt is a heterogeneous catalyst. However, an enzyme in solution catalyzing a solution phase



B. Solid Acids and Base as Catalysis

acid-base catalysis, acceleration of a chemical reaction by the addition of an acid or a base, the acid or base itself not being consumed in the reaction. The catalytic reaction may be acid-specific (acid catalysis), as in the case of decomposition of the sugar sucrose into glucose and fructose in sulfuric acid; or base-specific (base catalysis), as in the addition of hydrogen cyanide to aldehydes and ketones in the presence of sodium hydroxide. Many reactions are catalyzed by both acids and bases.

Processes catalyzed by acids and bases play a key role from economical and ecological point of view in chemical and petrochemical industry as well as refinery technology in the oil refining and in the manufacture of a wide variety of specialty chemicals such as pharmaceuticals, agrochemicals, flavors and fragrances. Few examples are hydrocracking, alkylation, catalytic cracking, isomerization, oligomerization, hydration/dehydration, esterification and hydrolysis and a variety of condensation reactions, to name but a few.

In most of these processes, traditional Brønsted acids (H_2SO_4 , HF, HCl, p-toluenesulfonic acid) or Lewis acids (AlCl_3 , ZnCl_2 , BF_3) in liquid-phase homogeneous systems or on inorganic supports in vapor phase systems are employed. Similarly, typical bases include NaOH, KOH, NaOMe and KOBut. Oil refining and petrochemical industries, use only catalytic amounts of these acids or bases, but not always, and the absolute quantities of waste generated are considerable owing to the enormous production volumes involved.

Their subsequent neutralization leads to the generation of inorganic salts which ultimately end up in aqueous waste streams. Whereas in fine and specialty chemical industries acids and bases are often used in stoichiometric quantities despite the fact that production are much smaller, for e.g. Friedel-Crafts acylations, volumes aldol and related condensations.⁶ Rising environmental concerns and stringent regulations have led to the widespread replacement of traditional Brønsted and Lewis acids with recyclable solid acids and bases.

C. Solid Acid Catalysis

Solid acids have been the subject of the most extensive and detailed studies of all heterogeneous catalysts

Definition Solid acid may be understood to be a solid on which the color of a basic indicator changes or a solid on which a base is chemically adsorbed or a solid acid

shows a tendency to donate a proton or to accept an electron pair. The number of these sites determines the total surface acidity while their structure (coordination, partial charge) is responsible for the acid strength.

A wide variety of solid acids include mixed oxides such as silica–alumina and sulfated zirconia, acidic clays, zeolites, supported heteropoly acids, organic ion exchange resins and hybrid organic–inorganic materials such as mesoporous oxides containing pendant organic sulfonic acid moieties and Nafion. Some of the processes employing solid acids are, catalytic Cracking (X and Y zeolites), paraffin Isomerization (chlorinated Pt-Ag), reforming (silica-alumina, noble metal support)

D. Solid Base Catalysis

In comparison to catalysis by solid acids, the applications of recyclable solid base catalysts are far fewer.

This is probably because acid-catalyzed reactions are much more common in the production of commodity chemicals. The main features of the reactions catalyzed by solid bases in contrast to solid acids are high activity and high selectivity; suppress undesired reactions, when used as supports, or as additives and high possibility of transforming the molecules resulting

in new products.

Definition

Solid changes or a solid on which an acid is chemically adsorbed or a solid base shows a tendency to accept a proton or to donate an electron pair

1.3 Catalytic Reductions

Selective catalytic reduction (SCR) refers to the reduction of nitrogen oxides (NO , NO_2 , N_2O) with oxygen and a selective inorganic or organic reducing agent. Nitrogen oxides (NO_x) are produced as tail gas in the industrial synthesis of nitric acid or in the exhaust emissions from lean-burn or gasoline engines

1.4 Enzyme Technology in Biocatalytic Reduction

Biocatalysis refers to the use of living (biological) systems or their parts to speed up (catalyze) chemical reactions. In biocatalytic processes, natural catalysts, such as enzymes, perform chemical transformations on organic compounds.

Enzymes are biocatalysts- the catalysts of life. A catalyst is defined as a substance that increases the velocity or rate of a chemical reaction without itself undergoing any change in the overall process.

Enzymes may be defined as biocatalysts synthesized by living cells. They are protein in nature, colloidal and thermolabile in character, and specific in their action.

In the laboratory, hydrolysis of proteins by a strong acid at 100 °C takes at least a couple of days. The same protein is fully digested by the enzymes in gastrointestinal tract at body temperature (37 °C) within a couple of hours. This remarkable difference in the chemical reactions taking place in the living system is exclusively due to enzymes. The very existence of life is unimaginable without the presence of enzymes.

1.5 Catalytic Oxidation

Catalytic oxidation is the process of using a catalyst to increase the rate of an oxidation reaction. Catalytic oxidation of methanol, for example, can be used to produce formaldehyde. Formaldehyde is an important industrial chemical used in many applications, such as adhesives and resins.

Catalytic reactions are important in many industries, such as the chemical industry, because they can help to produce chemicals more efficiently and with less pollution. Catalytic oxidation is just one type of catalytic reaction; there are many others, such as catalytic hydrogenation and catalytic dehydrogenation.

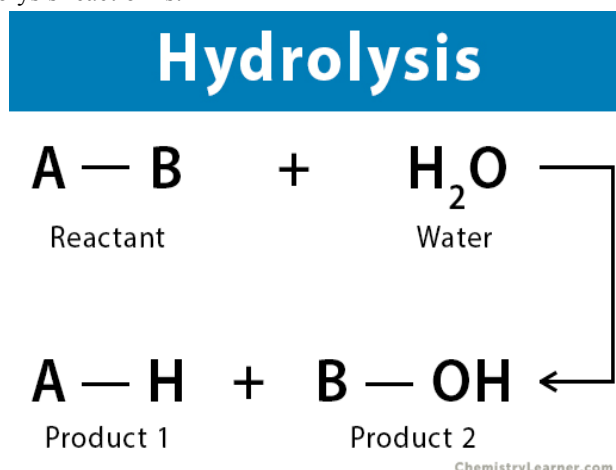
1.6 Catalytic Carbon–Carbon Bond Formation

Carbon–carbon bond formation is the key reaction for organic synthesis to construct the carbon framework of organic molecules. The review gives a selection of biocatalytic C–C-bond-forming reactions which have been investigated during the last 5 years and which have already been proven to be applicable for organic synthesis. In most cases, the reactions lead to products functionalized at the site of C–C-bond formation (e.g., α -hydroxy ketones, aminoalcohols, diols, 1,4-diketones, etc.) or allow to decorate aromatic and heteroaromatic molecules. Furthermore, examples for cyclization of (non)natural precursors leading to saturated carbocycles are given as well as the stereoselective cyclopropanation of olefins affording cyclopropanes. Although many tools are already available, recent research also makes it clear that nature provides an even broader set of enzymes to perform specific C–C coupling reactions. The possibilities are without limit; however, a big library of variants for different types of reactions is required to have the specific enzyme for a desired specific (stereoselective) reaction.

1.7 Hydrolysis

Hydrolysis is a common form of a chemical reaction where water is mostly used to break down the chemical bonds that exists between a particular substance.

The general formula of a hydrolysis reaction is:



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1.8 Catalysis in Novel Reaction Media

New types of Lewis acids as water-compatible catalysts have been developed. Various metal salts were found to work as Lewis acid catalysts in aqueous media, and catalytic asymmetric aldol reactions in such media have been attained. Furthermore, Lewis acid-surfactant combined catalysts, which can be used for reactions in water without using any organic cosolvents, have been also developed. These investigations will contribute to reducing the use of harmful organic solvents and to develop efficient catalytic systems which cannot be realized in conventional organic solvents.

1.9 Microwave Assisted Synthesis

Microwave-assisted synthesis works on the basis of aligning dipoles of the material in an external field via the excitation produced by microwave electromagnetic radiations and is usually executed in combination with a known synthesis strategy.

A. Theoretical aspects of microwave dielectric heating

Here the term dielectric heating is used to represent the radiofrequency (RF) and microwave (MW) bands of the electromagnetic spectrum. RF heating is in the frequency range 1–200 MHz and MW from 300 MHz to 300 GHz. By international agreement, certain frequencies have been allocated for industrial use, in order to avoid interference with telecommunications. These are RF 13.56 and 27.12 MHz and MW 2450 and a band within the range 896–915 MHz

The half-power depth for water is about 12 mm at a frequency of 2450 MHz and 75 mm at 100 MHz. Penetration into foods is less than into water

B. Microwave-accelerated metal catalysis

Microwave-assisted catalytic pyrolysis is considered to be a promising technology for coal-staged conversion due to its high efficiency and selectivity. This work was undertaken to investigate the pyrolysis behavior and products quality of microwave-assisted pyrolysis of low rank coal catalyzed by metallic catalysts (K, Ca and Fe) with both dielectric response and catalytic effect via a microwave tube furnace. The mechanism of metallic catalysts on catalytic cracking tar under microwave radiation was also investigated. The dielectric properties and physicochemical structure of coal chars were characterized by a vector network analyzer, XRD, FT-IR, SEM, EDS, and Raman. The chemical structure characteristics of generated tars were determined by FT-IR and GC-MS. Results manifested that microwave interacted preferentially with metal catalysts by polarization and conductivity loss could efficiently induce the occurrence of catalytic pyrolysis reactions to generate high yield syngas ($\text{CO} + \text{H}_2$). Specifically, the dielectric loss factor of resultant chars was considerably improved with the introduction of metallic catalysts especial for Ca and Fe. Furthermore, it is found that metal catalysts dramatically enriched the amorphous carbon structure in produced chars whereas in favour of suppressing the trend of carbon graphitization. Additionally, the transformation of larger polycyclic aromatic compounds into lighter tar species was catalytically accelerated, resulting in the large proportion of single-ring aromatics in tar under the synergistic effect between microwave and metal catalysts.

C. Heterocyclic chemistry using microwave-assisted approaches

Principle of Microwave Heating

The basic principle behind the heating in microwave oven is due to the interaction of charged particle of the reaction material with electromagnetic wavelength of particular frequency. The phenomena of producing heat by electromagnetic irradiation are either by collision or by conduction, some time by both. Two basic principal mechanisms involve in the heating of material

1) Dipolar Polarization:

Dipolar polarisation is a process by which heat is generated in polar molecules. On exposure to an oscillating electromagnetic field of appropriate frequency, polar molecules try to follow the field and align themselves in phase with the field. Dipolar polarisation can generate heat by either one or both the following mechanisms:

1. Interaction between polar solvent molecules such as water, methanol and ethanol
2. Interaction between polar solute molecules such as ammonia and formic acid

2) Conduction mechanism:

The conduction mechanism generates heat through resistance to an electric current. The oscillating electromagnetic field generates an oscillation of electrons or ions in a conductor, resulting in an electric current. This current faces internal resistance, which heats the conductor. Microwave heating is different from conventional heating in many respects.

D. Microwave-assisted reductions

This chapter deals with the development of microwave-assisted reduction (MWAR) method as a rapid, selective, economic, efficient, and environmentally friendly synthesis method for organic and inorganic compounds. Without doubt, the fundamental aspects of microwave irradiation help to better understand the role of MW for the reduction of aldehydes, ketones, heterocyclic products, and aromatic and other types of organic compounds as well as inorganic materials, composites, nanoparticles, and catalysts. Moreover, several applications of the corresponding reduced material in different fields have been investigated.

E. Microwave-assisted multi-component reaction

Microwave-assisted (MWA) multicomponent reactions (MCRs) have successfully emerged as one of the useful tools in the synthesis of biologically relevant heterocycles. These reactions are strategically employed for the generation of a variety of heterocycles along with multiple point diversifications. Over the last few decades classical MCRs such as Ugi, Biginelli, etc. have witnessed enhanced yield and efficiency with microwave assistance. The highlights of MWA-MCRs are high yields, reduced reaction time, selectivity, atom economy and simpler purification techniques, such an approach can accelerate the drug discovery process. The present review focuses on the recent advances in MWA-MCRs and their mechanistic insights over the past decade and shed light on its advantage over the conventional approach.

F. Microwave-assisted solid-phase synthesis

Microwave-assisted peptide synthesis has become one of the most widely used tools by peptide chemists for the synthesis of both routine and difficult peptide sequences. Microwave technology significantly reduces the synthesis time while also improving the quality of the peptides produced. Microwave energy allows most amino acid couplings to be completed in just 5 min. The Fmoc removal can also be accelerated in the microwave decreasing the reaction time from at least 15 min to only 3 min in most cases. Common side reactions such as racemization and aspartimide formation are easily controllable with optimized methods that can be applied routinely. This protocol outlines the detailed procedure for performing both manual and automated microwave-assisted peptide synthesis of two difficult peptide sequences, ACP (65-74) and β -amyloid, in high purity and yield.

1.10 Sonochemistry

Sonochemistry is a branch of chemical research dealing with the chemical effects and applications of ultrasonic waves, i.e., sound at high frequencies that the human ear finds difficult to respond and eventually the human hearing threshold is reached, normally around 18–20kHz for adults.

Although the applications of ultrasound have long been known in both industry and academy, the “green” value of the non-hazardous acoustic radiation has been recognised by synthetic and environmental chemists only recently. The chemical and physical effects of ultrasound arise from the cavitation collapse which produce extreme conditions locally and thus induce the formation of chemical species not easily attained under conventional conditions, driving a particular radical reactivity. This rationale, accessible in a non-mathematical manner, anticipates the advantages of using this technology in a variety of processes that include milder reactions with improved yields and selectivities, easy generation of reactive species and catalysts or replacement of hazardous reagents. Sonication enables the rapid dispersion of solids, decomposition of organics including biological components, as well as the formation of porous materials and nanostructures. This review summarises how ultrasound can be harnessed to develop an alternative and mild chemistry, which parallels the ability of acoustic waves to induce homolytic bond cleavage.

Solvent-free Sonochemical Protocol

An ultrasound-assisted preparation of a series of ambient-temperature ionic liquids, 1-alkyl-3-methylimidazolium (AMIM) halides, which proceeds via efficient reaction of 1-methyl imidazole with alkyl halides/terminal dihalides under solvent-free conditions, is described.

Ultrasound irradiation (USI), by virtue of cavitation collapse, is able to conduct diverse organic reactions with outstanding outcomes in terms of reaction rates, yields, and selectivities. On another note, solvent-free synthesis has received considerable attention owing to the rising concern for the effect of solvents on the environment. USI combined with no solvent conditions leads to eco-friendly synthetic conditions together with considerable improved selectivity, cleaner reactions, higher yields and purities, and reduction of reaction times. This chapter includes material illustrating up-to-date developments on US-assisted solvent-free synthesis of heterocyclic compounds. To be more precise, the chapter consists of two parts

Heterogeneous Catalysis in Organic

Heterogeneous catalysis typically involves solid phase catalysts and gas phase reactants. In this case, there is a cycle of molecular adsorption, reaction, and desorption occurring at the catalyst surface. Thermodynamics, mass transfer, and heat transfer influence the rate (kinetics) of reaction.

Heterocyclic Synthesis in Water

Environmental and economic pressures have been forcing the chemical community to search for more efficient ways of performing chemical transformations. In this context, extraordinary attention has been paid to organic reactions in water in the past decade and research and development in this area are still increasing exponentially. Water as a solvent is not only inexpensive and environmentally benign, but also gives completely new reactivity. Many of organic reactions carried out in aqueous media occur quickly with excellent yields. Reactions previously thought to be impossible to conduct in water are truly realized today.

Quinazolin-4(3H)-ones are an important class of fused heterocycles with an array of biological activities such as inhibition of humane erythrocyte purine nucleoside phosphorylase and poly(ADP-ribose) polymerase treatment of diabetes and obesity, antagonist, anti-tumor, anti-inflammatory, insecticidal and anti-microbial activity. They are also important building-blocks in total synthesis of natural products and are the constituents of some isolated naturally occurring alkaloids. Quinazolin-4(3H)-one derivatives were previously prepared by thermolysis of 3-arylideneamine-1,2,3-benzotriazine-4-ones in paraffin oil at 300 °C or condensation of aryl, alkyl and heteroaryl aldehydes in refluxing ethanol in the presence of CuCl but these methods are suffering from high-temperature reaction, low yield, long-reaction time as well as not being environmentally green. As Deep eutectic solvents (DES) were introduced as an alternative to ionic liquids (IL) to overcome the 18 drawbacks of IL solvents. However, some authors consider them to be a subclass of ILs. In contrast, 19 other authors emphasize that these are by their nature independent, different groups of substances. 20 Thus, the question arises: Which solvent group should DESs belong to? Maybe a new class should be added to the existing ones. The aim of this work is to attach Solvents and Ionic Liquids Solvent-free Reactions part of our interests in the synthesis of quinazolinones and due to the present awareness of applying environmentally benign strategies in organic synthesis, in this communication we report the I₂/KI mediated oxidative cyclocondensation of o-aminobenzamide with various aldehydes for preparation of quinazolin-4(3H)-ones in ethanol-water (method A) or boiling water (method B). Initially, a solution of I₂/KI was prepared by dissolving specified molecular iodine in a saturated aqueous solution of potassium iodide. We were delighted to find that exposure of o-aminobenzamide with aromatic aldehydes on stirring

Solvent-Free Reactions

In the case of solid-liquid mixtures, the reaction implies either solubilization of solid in the liquid phase or adsorption of liquid on the solid surface as an interfacial reaction.

Reactions in Organic Solvents

Organic solvents are used by everyone in most of their daily activities starting right from the disinfectant treatment to the removal of tough grease stains. The perfumes or cologne we use, laundry detergents which are used to keep clothes fresh and clean, all these products contain those ingredients called as Organic solvents.

Solvents and Ionic Liquids

Deep eutectic solvents (DES) were introduced as an alternative to ionic liquids (IL) to overcome the drawbacks of IL solvents. However, some authors consider them to be a subclass of ILs. In contrast, other authors emphasize that these are by their nature independent, different groups of substances. Thus, the question arises: Which solvent group should DESs belong to? Maybe a new class should be added to the existing ones

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