Green Chemistry and Catalysis: A Review of Recent Advances

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Abstract: Green chemistry catalysis represents a transformative approach toward sustainable chemical synthesis by emphasizing efficiency, safety, and environmental responsibility. Central to this field is the development of catalytic systems that promote essential transformations such as reduction and oxidation while minimizing energy consumption and waste production. Catalytic reduction and oxidation reactions, often mediated by transition metals or metal-free catalysts, are critical in fine chemical and pharmaceutical production, enabling high selectivity and atom economy. Microwave-assisted synthesis has emerged as a powerful tool in green catalysis due to its ability to dramatically reduce reaction times and energy usage. This method enhances reaction kinetics and vields while aligning with the principles of green chemistry. Similarly, sonochemistry-utilizing ultrasonic waves to initiate or accelerate reactions-offers another eco-friendly alternative. Through acoustic cavitation, sonochemical techniques improve mass transfer and promote unique reaction pathways that are not easily achievable through conventional means. The choice of solvent plays a pivotal role in defining the green credentials of a catalytic process. Traditional volatile organic solvents are being increasingly replaced by greener alternatives such as water, supercritical fluids, and bio-based solvents. Among these, ionic liquids have attracted considerable attention due to their negligible vapor pressure, high thermal stability, and tunable physicochemical properties. These designer solvents not only enhance catalyst solubility and reusability but also contribute to more sustainable reaction conditions. Overall, advancements in green chemistry catalysis-spanning innovative reaction media, energy-efficient technologies, and selective catalytic processesare paving the way for a more environmentally benign chemical industry

Keywords: Green chemistry, Catalysis, renewable resources, catalytic processes, green synthesis, Eco-friendly, Biocatalysis, Heterogeneous catalysis, Photocatalysis, Sustainable development.

1. Introduction

Green chemistry, sometimes referred to as sustainable chemistry, is the creation of chemical products and procedures that minimize or completely do away with the use and production of hazardous substances ^[1]. Chemical products should be made to decompose into ecologically benign components after their intended use and not remain in the environment^[2].

A. Introduction to Green Chemistry and Its Application in *Pharmaceuticals*

The concept of green chemistry emerged in the early 1990s. Key milestones include the establishment of the Green Chemistry Institute in 1997 and the launch of the Royal Society of Chemistry's Green Chemistry journal in 1999^[3]. Green chemistry principles apply broadly across chemical disciplines-such as organic, inorganic, polymer, biochemical, and environmental chemistry- with the aim of promoting both environmental protection and economic efficiency. Core strategies include the use of catalysts (including biocatalysts), safer and renewable feedstocks like biomass, environmentally friendly solvents (e.g., water, ionic liquids, supercritical fluids), and innovative methods such as microwave assisted and photocatalytic reactions ^{[4].} Pharmaceutical Green Chemistry The pharmaceutical industry, being one of the most dynamic sectors in chemistry, is at the forefront of adopting greener technologies. It is shifting towards sustainable feedstocks, cleaner solvents, and ecofriendly production techniques to minimize environmental impact and reduce manufacturing costs. Green chemistry is increasingly viewed as a guiding principle-or a "Hippocratic oath"-for chemists, emphasizing the responsible use of resources and minimizing harm. By eliminating hazardous substances from processes, risks are significantly reduced or eliminated altogether. As summarized in the field's ethos, green chemistry is focused on minimizing waste, raw material use, risks, energy consumption, environmental harm, and cost^[5].

2. Principles

The twelve principles of green chemistry were introduced by Paul Anastas and John Warner of the EPA, as outlined in their 1998 book Green Chemistry: Theory and Practice. These principles emphasize minimizing or eliminating the use and generation of hazardous substances throughout the design, synthesis, and application of chemical products. The aim is to protect both human health and the environment. Among these guiding principles are ^[6] "Reducing Risk" and "Minimizing the Environmental Footprint." Historically, chemical industries have been associated with significant risks due to the use of harmful substances and the environmental impact of synthetic products, which often contributed to their negative perception. Factors such as excessive energy consumption, climate change, resource depletion, and environmental pollution have all added to the chemical sector's ecological footprint.^[7]

3. Catalysis

Catalysis serves as one of the essential foundations of green chemistry, which focuses on designing chemical processes and products that minimize or entirely avoid the use and generation of hazardous substances.

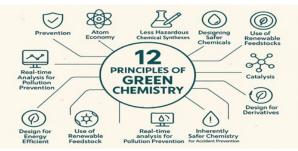


Fig. 1. Essential foundations of green chemistry

4. Solid Acids and Bases as Catalysts

Acid- and base-catalyzed reactions play a crucial role in industries such as oil refining, petrochemicals, and the manufacture specialty of chemicals-including pharmaceuticals, agrochemicals, and fragrances. Traditionally, these reactions have relied on homogeneous liquid-phase systems or supported inorganic materials in vapor-phase systems. Common Brønsted acids like sulfuric acid (H₂SO₄), hydrofluoric acid (HF), hydrochloric acid (HCl), and ptoluenesulfonic acid, along with Lewis acids such as aluminum chloride (AlCl₃), zinc chloride (ZnCl₂), and boron trifluoride (BF3), are frequently used. Likewise, typical base catalysts include sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium methoxide (NaOMe), and potassium tertbutoxide (KOBut).

5. Solid Acid Catalysis

Acid-catalyzed reactions represent one of the most significant areas within heterogeneous catalysis, with solid acid catalysts being widely used across various chemical processes. These include materials such as acidic clays, zeolites, supported heteropoly acids, and mixed metal oxides like silica–alumina and sulfated zirconia. Additionally, hybrid organic–inorganic catalysts—such as mesoporous oxides and organic ionexchange resins containing sulfonic acid functional groups are also employed. These solid acids offer high surface areas and strong acid sites, making them effective in numerous industrial applications.

6. Solid Base Catalysis

In contrast to acid catalysis, the use of solid base catalysts is relatively limited. This is likely because acid-catalyzed reactions dominate the production of a wide variety of chemical products. Nevertheless, several types of solid base materials have been explored, including basic zeolites, anionic clays, and mesoporous silica functionalized with organic base groups. Although fewer in number, these solid base catalysts are gaining attention for their reusability and potential applications in green chemistry^[10]

7. Catalytic Hydrogenation in Organic Synthesis

Catalytic hydrogenation, which involves the use of hydrogen gas and heterogeneous catalysts, is widely regarded as one of the most essential techniques in synthetic organic chemistry both at the laboratory and industrial scales. Hydrogen is considered the cleanest and most efficient reducing agent, and robust heterogeneous catalysts are commonly employed for this purpose. This method offers several significant advantages: (i) it has a broad range of applications and can selectively hydrogenate a variety of functional groups; (ii) it typically achieves high conversion rates under mild, liquid phase conditions; (iii) the extensive practical experience available enables chemists to effectively choose the appropriate catalyst for specific reactions.

8. Catalytic Oxidations

An essential industrial technology for converting chemical feedstocks such alkanes and alkenes into fine chemicals, epoxides, dioles, and alcohols is the oxidation reaction. The current use of stoichiometric oxidants, such as nitric acid, chromic acid and its derivatives, permanganate, osmium tetroxide, and hypochlorite, is incredibly effective; however, the stoichiometric component causes low atom efficiency, greater costs, and the creation of toxic waste. ^[11] One of the most crucial oxidation reactions is the epoxidation of alkenes, which produces epoxides and other essential compounds including alcohol and diols. Using H2O2 as an oxidant, bioinspired catalysts based on iron and manganese exhibit intriguing features among the several methods to accomplish such transformation.^[12-14]

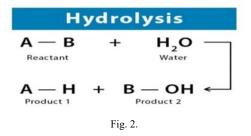
Table 1 Product containing oxidant		
Product	Feedstock	Oxidant/Product
Styrene	Benzene or Ethene	O2/L
Terepthalic acid	P-Xylene	O2/L
Ethene oxide	Ethene	O2/G
Adipic acid	Benzene	O2/L
Propene oxide	Propene	RO2H/L

9. Formation of Catalytic Carbon-Carbon Bonds

C-H bond metalations, in which a metal centre takes the place of a hydrogen atom, have transformed syntheses by lowering or doing away with the need for particular and constricting chemical functional groups. ^[15-17] The functionalised products of these metalations retain the organic reactants' carbon-based molecular structure. Techniques that simultaneously modify the carbon-based skeleton of organic compounds and add new functional groups could be used to exploit an even greater variety of starting materials. Such changes could, for instance, boost late-stage structural diversification during multistep syntheses or make natural resources containing structural components of the desired products available for chemical manufacture. These framework functionalisation events would be made possible by C–C bond metalations, in which a metal centre takes the place of a particular hydrocarbyl moiety.

10. Hydrolysis

The process of hydrolysis a typical type of chemical reaction is hydrolysis, in which the chemical bonds between a given substance are primarily broken by water.^[18]



11. Renewable Raw Materials as Chemicals

Petrochemicals get their name from the fact that the chemical industry has relied on natural gas and crude oil (petroleum) as basic raw materials for the past 70 years or so. However, this might not be the case for very long. The transition from fossil fuels to renewable agricultural raw materials is poised to bring about a new revolution in the chemical industry. From a distance, the Cargill production facility in Blair, Nebraska, resembles a medium-sized petrochemical plant or a small oil refinery. But upon closer examination, it turns out to be a maize-processing facility; a biorefinery that produces lactic acid, ethanol, and high-fructose corn syrup, among other things According to James R. Stoppert, a senior executive at Cargill, carbon is the foundation of the chemical business, and whether the carbon was fixed two million years ago or six months ago makes no difference. ^[19] One significant finding of the 1972 Club of Rome Report was the need to transition from nonrenewable fossil fuels to renewable basic materials, such as triglycerides and carbohydrates made from biomass.^[20]

Table 2			
Average market price of raw material			
Raw material	Average world market price		
Crude oil	0.175(0.400)		
Coal	0.035		
Corn	0.080		
Wheat straw	0.020		
Sugar	0.180		
Ethanol	0.400		
Ethylene	0.400		

12. Microwave Assistant Sythesis

Microwave chemistry is the application of microwave radiation to chemical processes. The development of microwave synthesis, a major breakthrough in synthetic chemistry techniques, has revolutionized chemical synthesis. [21]

A. Mechanisms of Microwave Heating

Since different materials react differently to microwave radiation, not all of them can be heated by microwaves. Materials can be broadly categorized into the following groups based on how they react to microwaves: ^[22]

(1) Materials that are microwave-transparent, such as sulphur(2) Materials like copper that reflect microwaves (3)Substances like water that absorb microwaves.

Dipolar polarization, conduction, mechanism, and interfacial polarization are the three primary mechanisms that heat microwave-absorbing materials, which are crucial for microwave chemistry ^[23]

B. The Main Advantages of Microwave Assisted Organic Synthesis are

- 1. Faster reaction
- 2. Better yield and higher purity
- 3. Energy saving

13. Application

- 1. Pure chemicals, less by products, and faster reactions
- 2. Rapid synthesis reduces solvent evaporation
- 3. Higher temperatures (super heating in sealed vessels)
- 4. Complete control over reaction parameters
- 5. Easy access to high pressure performance^[24]

14. Theortical Aspects of Microwave Dielectric Heating

It was known from these early days those foods with a highwater content would heat up quickly in a microwave cavity because water molecules efficiently convert microwave energy into thermal energy at microwave frequencies. Therefore, the benefits of microwave dielectric heating for drying were realized in the 1950s and 1960s, along with the development of large-scale applicators for the food processing sector; DuPont, for instance, constructed large-scale facilities for drying nylon based on microwave technology ^[25]

15. Heterocyclic Chemistry Using Microwave – Assisted Approaches

Microwave heating has emerged as a powerful technique to promote a variety of chemical reactions. Microwave reactions under solvent-free conditions are attractive in offering reduced pollution and offer low cost together with simplicity in processing and handling. The recent introduction of singlemode technology assures safe and reproducible experimental procedures and microwave synthesis has gained acceptance and popularity among the synthetic chemist community. The growing number of publications in microwave-assisted synthesis includes virtually all types of chemical reactions such as additions, cycloadditions, substitutions, eliminations, fragmentations etc. ^[26]

16. Microwave Assisted Reductions

In synthesis, reductions of organic functional groups are essential. However, due to the severe conditions required, their applicability is frequently limited and incompatible with the synthesis of sensitive goods. High temperatures and lengthy reaction durations are typical, and many reactions suffer from the production of byproducts, just like many other kinds of transformations in organic chemistry. Therefore, it is crucial to upgrade the current reduction schemes to include quicker, more selective, cost-effective, and environmentally friendly processes. In this regard, it has been demonstrated that the use of microwave heating significantly improves a wide range of synthetic processes. ^[27-30]

17. Heterogeneous Catalysis in Organic

Metal-organic frameworks (MOFs) are crystalline materials composed of metal ions, typically transition metals, connected by organic ligands. These materials offer several advantages, including a large surface area, high metal content, and versatility in designing active sites, making them promising candidates for novel catalysts. This review provides a comprehensive overview of MOFs' catalytic applications, particularly focusing on their structural evolution for catalyst development. It discusses various catalytic processes, including the condensation reactions of multiple organic components. The review specifically highlights MOFs' roles in C-C and C-X (S, N, O) bond formation, which leads to the synthesis of more complex compounds. Additionally, the review addresses the stability and reusability of MOFs, comparing their performance to that of other homogeneous and heterogeneous catalysts ^[31-32]

18. Heterocyclic Synthesis in Water

Heterocyclic compounds containing nitrogen and oxygen are fundamental to many structurally and pharmaceutically active organic molecules due to their wide range of applications in everyday life. These heterocycles are key components in numerous marketed drugs, and the pharmaceutical industry heavily depends on them. They are crucial in drug design and discovery and are found across various scientific and technological fields. ^[33] Some heterocycles occur naturally, while others can be synthesized in the lab. Given their significance, various methods have been developed for producing versatile heterocycles used in agrochemicals, pharmaceuticals, petrochemicals, and medicinal products. Initially, little attention was paid to the environmental impact of these synthetic processes. However, with the advent of green chemistry, the focus shifted toward minimizing toxic waste and improving reaction outcomes. Numerous eco-friendly approaches, including catalysis, solvent-free methods, green solvents, multicomponent reactions (MCRs), heterogeneous reagents, photocatalysis, and irradiation techniques (e.g., microwave, ultrasound, visible light), have been developed to avoid harmful metal catalysts, waste generation, harsh conditions, and toxic solvents. This review article concentrates on sonochemical methods for synthesizing a variety of heterocycles. Sonochemistry investigates how ultrasonic radiation affects chemical systems and its application in chemical transformations. Ultrasound was first discovered in 1794 by Italian physiologist Lazzaro Spallanzani, who observed echolocation in bats, and later in 1917, Langevin invented the hydrophone, a sonar system. The first technological use of ultrasound was in submarine detection during World War^[34].

19. Solvent-Free Reactions

Acoustic waves within the human hearing range (20 Hz to 20 kHz) are referred to as "sonic" waves, while waves below and above these frequencies are known as "infrasound" and "ultrasound" (US), respectively. These waves serve as the foundation for various applications in science and technology and are further divided into "power US" (20 kHz to 1 MHz) and "high-frequency US" (above 1 MHz), based on their use either as an energy source or in low-intensity therapeutic and diagnostic applications. There is a growing body of scientific literature highlighting how power US can replace traditional heating and stirring methods for chemical reactions, particularly in organic reactions, polymerization, and the synthesis of inorganic nanostructures. Several reviews have been published on various aspects of sonochemistry, including organic transformations, catalysis, polymer science, surface modification, and the design and scaling of US reactors. ^[35] However, to date, no comprehensive review has specifically focused on the use of environmentally friendly solvents in sonochemical synthesis, even though combining these two sustainable approaches offers significant benefits. The review categorizes these studies based on the solvent used and the type of chemical reaction described, critically discussing the advantages and challenges associated with using ultrasound as an energy source, based on literature up to early 2016. Reactions performed in mixtures of volatile organic solvents and green solvents are not included [36]

20. Reactions in Organic Solvents

There are three types of sonochemical reactions: homogeneous sonochemistry (occurring in liquids), heterogeneous sonochemistry (involving liquid-liquid or solidliquid systems), and sonocatalysis (the use of ultrasound to accelerate chemical reactions through catalysis). Sonoluminescence results from the same cavitation effects that drive homogeneous sonochemistry. The use of ultrasound to enhance chemical reactions has proven valuable in mixed-phase synthesis, biomedical applications. Since cavitation can only occur in liquids, chemical reactions cannot be initiated by ultrasonic irradiation of solids or solid-gas systems. Ultrasound has been shown to significantly increase chemical reactivity in various systems, sometimes by up to a million times, acting as a powerful tool to activate heterogeneous catalysts. In liquidsolid reactions, ultrasound can break solid materials into smaller pieces, exposing fresh active surfaces through microjet pitting from cavitation near the surfaces and by fragmenting solids through cavitation collapse^[37]



21. Heterocylic Functionalization

The importance of chemistry and material science cannot be overstated, and this underlines the ongoing efforts to develop new synthetic methods for their production. Growing awareness of the need to protect natural resources and optimize energy use has driven both private and public sectors to pursue environmentally sustainable processes. One promising approach involves ultrasound (US)-assisted heterocyclization reactions of functionalized substrates, enabling the synthesis of highly functionalized heterocycles from easily available starting materials under mild and selective conditions [38] This process, known as sonochemistry, enhances chemical reactivity through acoustic cavitation, which accelerates reactions. US irradiation significantly reduces reaction times and offers advantages such as simple procedures, high yields, improved selectivity, and cleaner reactions, making it a valuable tool in synthetic organic chemistry ^[39]

22. Organometallic Reactions

This chapter aims to provide a critical introduction to the nature and origins of the chemical effects of ultrasound, with a focus on organo-transition metal sonochemistry as a case study. It will not be exhaustive, as recent comprehensive reviews on both organometallic sonochemistry and the synthetic applications of ultrasound have been published, and a full monograph on the chemical, physical, and biological effects of ultrasound is in progress. The chemical and biological effects of ultrasound were first documented by Loomis over 50 years ago. Within 15 years of Loomis' work, ultrasound found widespread industrial applications, such as welding, soldering, dispersion, emulsification, disinfection, refining, cleaning, extraction, mineral flotation, and degassing liquids. However, its use in the chemical community was initially limited.^[40]

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