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Advancements in Catalysts for Electrochemical Nitrate Reduction: A Sustainable Approach for Mitigating Nitrate Pollution: A Review

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Abstract

Nitrate pollution is of great importance in both the environmental and health contexts, necessitating the development of efficient mitigation strategies. This review provides a comprehensive analysis of the many catalysts employed in the electrochemical reduction of nitrate to ammonia, and presents a viable environmentally friendly approach to address the issue of nitrate pollution. Hence, the electrochemical transformation of nitrate to ammonia serves the dual purpose of addressing nitrate pollution in water bodies, and is a useful agricultural resource. This review examines a range of catalyst materials such as noble and non-noble metals, metal oxides, carbon-based materials, nitrogen-doped carbon species, metal complexes, and semiconductor photocatalysts. It evaluates catalytic efficiency, selectivity, stability, and overall process optimization. The performance of catalysts is influenced by various factors, including reaction conditions, catalyst structure, loading techniques, and electrode interfaces. Comparative analysis was performed to evaluate the catalytic activity, selectivity, Faradaic efficiency, current density, stability, and durability of the catalysts. This assessment offers significant perspectives on the structural, compositional, and electrochemical characteristics that affect the efficacy of these catalysts, thus informing future investigations and advancements in this domain. In addition to mitigating nitrate pollution, the electrochemical reduction of nitrate to ammonia is in line with sustainable agricultural methods, resource conservation, and the utilization of renewable energy resources. This study explores the factors that affect the catalytic efficiency, provides new opportunities to address nitrate pollution, and promotes the development of sustainable environmental solutions.

Keywords

Nitrate Pollution, Electrochemical Reduction, Ammonia, Sustainable Farming, Catalysts

1. Introduction

Nitrogen (N) pollution occurs when nitrates in the groundwater or surface water reach unhealthy concentrations. Nitrates, which consist of nitrogen and oxygen, are commonly employed as fertilizers in agriculture because they are essential for plant growth [1]. Nitrates cause severe environmental and human health problems if misused, or their excessive use leads to runoff, where the fertilizer is washed off into neighboring water bodies by precipitation [2]. Nitrates also originate from animal waste, namely manure, because of their large amounts of nitrogen molecules [3]. Industrial activities, such as the production of fertilizers, chemicals, and explosives, are also released into the environment through wastewater discharge or unintentional spills [4]. Nitrate pollution occurs when industrial effluents leak into waterways, thereby affecting the local water supply. It also originates from septic systems and municipal sewage treatment facilities [5]. Untreated nitrate-containing wastewater also affects nearby water sources, such as rivers and lakes, or seeps into the ground and contaminates it [6].

Nitrous oxide emissions are also caused by nitrate pollution, making climate change even more severe [7]. Nitrates are incredibly soluble, meaning they spread quickly across groundwater aquifers, threatening the access of populations to a vital source of drinking water [8]. This is a persistent problem for drinking water sources because they seep into the ground and remain there [9]. Nitrate pollution harms aquatic and terrestrial ecosystems and has been linked to shifts in plant community composition and, in worst cases, to the loss of entire species. It also lowers agricultural output by making land less fertile and lowering crop yields [10]. Sustainable farming strategies that maximize nutrient and use reduce adverse environmental effects while maintaining yields high [11]. Eutrophication caused by excessive nitrate in water promotes the rapid expansion of algae and other aquatic plants. As a result, aquatic ecology suffers, with biodiversity falling and dead zones of low or no oxygen created [12]. High levels of nitrate in drinking water cause methemoglobinemia, popularly known as blue baby syndrome, which is particularly dangerous for infants [13].

An increased risk of cancer and other health problems in adults has been associated with exposure to nitrate-contaminated drinking water [14]. Nitrate pollution costs a lot of money because it needs expensive treatment methods to remove nitrates from polluted water supplies [15]. Communities that rely on fisheries, tourism, and recreational activities are particularly vulnerable to the decline of aquatic ecosystems [16]. The illustration presented in **Figure 1** provides an overview of the different forms and origins of nitrate pollution. Nitrate pollution can originate from various sources, such as agricultural runoff, industrial emissions, and wastewater treatment facilities. In agriculture, this is often the result of excessive use of fertilizers and manure, which can lead to leaching of nitrates into groundwater and surface water. Urban areas also contribute to nitrate pollution through stormwater runoff and release of treated sewage. To ensure efficient environmental management and water quality preservation, it is essential to understand the various forms and sources of nitrate pollution.

Many countries have enforced strict limits on drinking water and surface water nitrate concentrations to protect people and ecosystems. It requires the combined efforts of government agencies, businesses, farmers, and communities to solve this problem [17]. The critical components for minimizing nitrate pollution and protecting water resources for future generations include sustainable farming practices [18], adequate wastewater treatment [19], better land management, and enhanced public awareness [20]. Protecting ecosystems, preserving biodiversity, and guaranteeing access to clean drinking water are some of the many benefits of taking preventive measures to reduce nitrate contamination [21]. The electrochemical conversion of nitrate to ammonia is a green method for addressing pollution problems [22]. Ammonia (NH_3) is a valuable resource that can potentially reduce nitrate contamination. This procedure efficiently eliminates nitrate from polluted water sources by electrochemically reducing it to NH_3, thereby lowering the risk of eutrophication and dead zones in aquatic environments [23]. There is less need to harvest more nitrogen resources for use in fertilizers and other uses because nitrogen compounds are recovered and recycled through the electrochemical reduction of nitrate. This method encourages the conservation of water resources and reduces the pressure on scarce and finite natural nitrogen supplies [24].

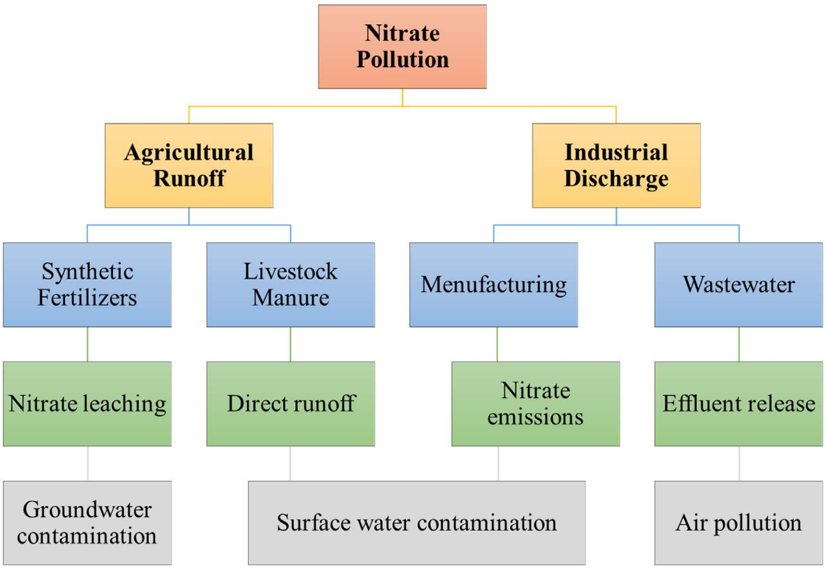

Figure 1. Types and sources of nitrate pollution.

Many types of fertilizers rely on NH_3 as the key ingredient. It is now possible to create NH_3-based fertilizers that are sustainable and ecologically friendly by electrochemically converting nitrate to ammonia [25]. Conventional NH_3 production techniques, such as the energy-intensive Haber-Bosch process, are linked to substantial greenhouse gas emissions and fossil fuel consumption. The carbon footprint of NH_3 manufacturing is further reduced by switching to electrochemical reduction, driven by renewable energy sources, such as solar or wind power. This strategy aligns with international initiatives to switch to greener energy sources and to aid in the fight against climate change [26]. The selective electrochemical conversion of nitrate to ammonia enables accurate management of nutrients [27]. More precise and efficient use of NH_3-based fertilizers means less waste and less chance of nitrate leaching into groundwater supplies [28].

Nitrate removal via electrochemical reduction in wastewater treatment plants is another promising approach. The treated wastewater is then safely discharged into water bodies or utilized for agricultural irrigation without nitrate contamination because of the conversion of nitrate to ammonia [29]. The electrochemical conversion of nitrate to ammonia is consistent with the principles of a circular economy, in which discarded materials are recycled into new goods. This procedure converts nitrate from waste products to marketable goods, thus encouraging the use of limited resources [30] [31].

Therefore, catalysts for the electrochemical reduction of nitrate to ammonia are discussed in depth in this review paper, which is essential because this reaction is key to reducing nitrate pollution. This review aims to help understand the parameters affecting catalytic efficiency, selectivity, stability, and overall process optimization by comprehensively analyzing various catalyst materials and their performance in this process. Various catalysts have been explored, including noble and non-noble metals, metal oxides, carbon-based materials, N-doped carbon species, metal complexes, and semiconductor photocatalysts.

This review also sheds light on the structural, compositional, and electrochemical features that influence the activity of these catalysts by clarifying their roles in the electrochemical reduction of nitrate. Several variables affect catalyst performance, including the reaction conditions, structure, loading tactics, and electrode interfaces. It provides a comparative analysis of the potential and limitations of various catalysts by analyzing their catalytic activity, selectivity, Faradaic efficiency, current density, stability, and durability. This study also provides valuable information that can guide future research and development in this important area of electrochemical reduction. This will open new ways to deal with nitrate pollution and move forward with sustainable environmental solutions by clearing problems, new trends, and future prospects.

2. Electrochemical Reaction and Its Significance

The electrochemical conversion of nitrate to ammonia is crucial because it significantly affects the environment and agriculture [32]. This reduces nitrate pollution in water and provides a sustainable source of ammonia for agriculture. It cleans water sources without polluting them, enhances water quality, and protects aquatic life and people using them [33]. It also helps produce sustainable NH_3-based fertilizers. It also reduces the usage of the energy-intensive and environmentally hazardous Haber-Bosch process for ammonia production [34]. This encourages resource efficiency, lowers waste production, and reduces the environmental damage caused by traditional trash treatment techniques [35]. The electrochemical conversion of nitrate to ammonia paves the way for the use of renewable energy sources such as wind and solar energy. The overall carbon footprint of NH_3 manufacturing is significantly decreased by utilizing clean and sustainable energy for electrochemical processes [36].

Research and development efforts on nitrate reduction catalysts and electrochemical systems have aided the evolution of electrocatalysis. Electrochemical methods are gaining popularity as effective and ecologically safe options for various chemical transformations [37]. It is also necessary to consider economic feasibility and large-scale implementation to ensure practical viability [38]. The electrochemical reduction of nitrate to ammonia is a revolutionary approach for sustainable agriculture and water purification. It is environmentally benign and generates useful NH_3 for fertilizer manufacturing [39]. A more sustainable future, where resource conservation, environmental preservation, and clean energy coexist for the benefit of people and the world, is achieved by embracing this technology [40].

2.1. Challenges and Considerations in the Electrochemical Reduction Process

Opportunities and difficulties are associated with the electrochemical conversion of nitrate to ammonia. Obtaining high selectivity for the desired NH_3 product was the main obstacle. Numerous competing routes are frequently present in electrochemical reactions, which may result in the generation of undesirable by-products. Researchers must design and optimize catalyst materials and electrode topologies to increase selectivity, boost overall efficiency, and ensure ammonia production with minimal side reactions [41]. Energy efficiency is another factor to be considered in electrochemical processes. Electrochemical cells require significant electrical energy to reduce nitrate [42].

Thus, it is critical to investigate ways to use less energy and to investigate renewable energy sources. Integrating renewable energy sources such as solar or wind energy significantly increases sustainability [43]. Another important factor in the electrochemical reduction process is scalability. Despite encouraging outcomes in laboratory settings, transferring the technology to large-scale applications requires overcoming engineering difficulties [44]. The stability and durability of catalysts and electrodes are essential, and the cost of the materials used in electrochemical cells and catalysts is a significant consideration for practical applications [45].

The electrochemical reduction of nitrate to ammonia depends on the regulatory and policy considerations. This method requires extensive regulatory frameworks, water quality, ammonia production, and water treatment clearances for large-scale use [46]. Reducing regulatory barriers and promoting sustainable and innovative technologies require the engagement of decision makers and stakeholders. Researchers, enterprises, and water management authorities must collaborate to achieve scientific breakthroughs [47]. Researchers can learn about water treatment facilities and agricultural needs through collaborations. Collaboration makes electrochemical systems compatible with contemporary infrastructure and operating needs.

The electrochemical reduction of nitrate to ammonia requires ongoing research and innovation [48]. **Figure 2** shows a flowchart outlining the strategies and steps to improve the efficiency and selectivity of catalysts in electrochemical reduction processes for sustainable nitrate conversion. The flowchart shows the important elements for optimizing the reduction of nitrates, including catalyst design, operational parameters, and product selectivity. This guide will be useful for researchers and engineers seeking to develop more effective and eco-friendly nitrate conversion technologies.

2.2. Role of Catalysts in Enhancing the Efficiency and Selectivity of the Reaction

Catalysts convert nitrate to ammonia electrochemically, promoting selective synthesis and inhibiting unwanted by-products. The choice of catalyst material greatly influences the performance and reaction kinetics, with high activity and specific surface area accelerating reaction efficiency [49]. Catalysts with certain surface features and active sites enhance selectivity toward the target product while preventing unintended consequences and increasing energy efficiency. This makes the process economically and environmentally viable [50].

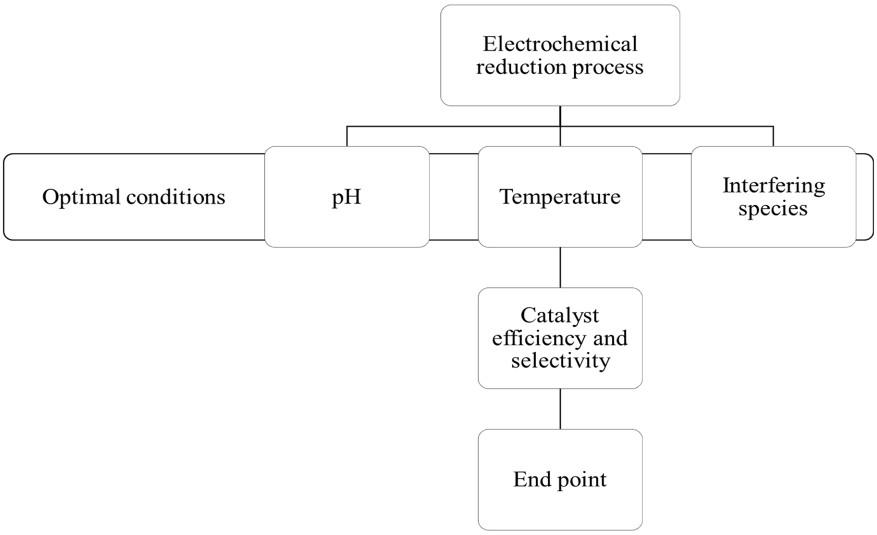

Figure 2. A flowchart for enhancement of catalyst efficiency and selectivity in electrochemical reduction for sustainable nitrate conversion.

The electrochemical reduction process runs continuously for a long time because of the capacity of the catalysts to maintain stability and endurance. For scalability and practical application of this technology in large-scale applications such as water treatment facilities and ammonia production for agriculture, it is essential to produce durable and long-lasting catalyst materials [51]. Research and development in catalyst design are crucial for maximizing the effectiveness and selectivity of electrochemical reduction of nitrate to ammonia. Customizing the catalyst quality, investigating new materials, and comprehending the underlying catalytic mechanisms are required to realize the full potential of this technology. Collaboration among researchers in electrochemistry, materials science, and catalysis is essential to enhance catalyst discovery and advance this sustainable and transformative process [52]. The electrochemical reduction of nitrate to ammonia using catalysts has the potential to be an effective and environmentally acceptable method for reducing nitrate pollution and promoting sustainable agriculture [53].

Catalysts are also incredibly adaptable and tailored to electrochemical processes and water compositions. Researchers have modified the reaction conditions based on the type of wastewater or contaminated water being treated because different catalyst materials demonstrate variable catalytic activity and selectivity degrees. This is significant because contaminants or interfering compounds in real-world water sources affect the effectiveness and selectivity of nitrate-reduction reactions [54]. Catalysts are also created to maximize the reaction at pH values and electrode potentials, improving electrochemical process control and efficiency. The electrochemical reduction of nitrate is customized to satisfy the requirements of various water treatment scenarios, agricultural practices, and energy requirements [55].

Catalysts help reduce the energy required for electrochemical reduction processes [56]. With the aid of catalysts, the nitrate reduction reaction occurs at lower applied potentials, which lowers the energy required to operate the electrochemical cell. This is crucial for large-scale applications because it directly affects the economically viable and environmentally sustainable potential of the process [57]. During nitrate reduction, the catalysts also aid in creating a stable intermediate, hydrazine (N_2H_4). N_2H_4 stores nitrogen atoms that are subsequently transformed into NH_3 and is essential for NH_3 synthesis. With increased hydrazine generation and stability, catalysts increase NH_3 yields and boost the overall effectiveness of the electrochemical reduction process [58].

3. Common Catalysts Used in the Electrochemical Reduction of Nitrate to Ammonia

Catalysts are of paramount importance in the field of electrochemical reduction because they facilitate and expedite intended chemical reactions. **Figure 3** illustrates several aspects that can affect the performance and effectiveness of catalysts in this particular situation. It is crucial to acknowledge that the catalysts for

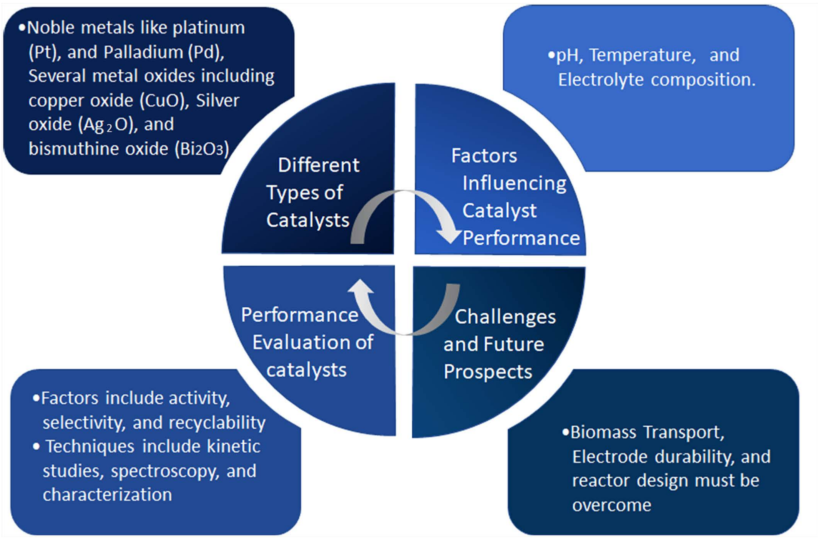

Figure 3. Schematic of common catalysts used for electrochemical reduction.

electrochemical reduction can be influenced by several factors, which can differ depending on the individual reaction, electrode material, and experimental settings. The investigation and enhancement of catalysts for electrochemical processes are currently prominent domains of research and advancement with the objective of enhancing the efficacy and specificity of electrochemical reactions.

The efficiency and selectivity of the electrochemical reduction of nitrate to ammonia have been improved using several common catalysts. Because of their high activity and stability, noble metals like platinum (Pt) and palladium (Pd) are commonly used to facilitate efficient nitrate reduction and ammonia synthesis [59]. Several metal oxides, including copper oxide (CuO), silver oxide (Ag_2O), and bismuth oxide (Bi_2O_3), show promise as catalysts for converting nitrate to ammonia because they can be designed to have desirable surface properties [60]. Conducting polymers such as polypyrrole (PPy) and polyaniline (PANI) are highly sought-after because of their adaptability and effective electron transport as catalysts for reducing reactions [61].

Nitrate reduction is an outstanding example of the catalytic activity and selectivity of transition metal complexes such as cobalt (Co), nickel (Ni), and iron (Fe) [62]. The increased catalytic performance is attributed to the high surface area and unique features of nanomaterials, such as metal nanoparticles, metal oxides, and other nanocatalysts [63]. Metal nanoparticles supported on conductive substrates or metal oxides integrated into conducting polymers are two examples of composite catalysts with diverse materials that display synergistic effects, further increasing total catalytic efficiency [64].

Carbon nanotubes (CNTs) and graphene, both made of carbon, have also been investigated as potential catalysts owing to their high electron mobility and advantageous surface properties [65]. Considerations such as the reaction conditions, desired selectivity, and cost-effectiveness are essential for determining the best catalyst. Catalyst development is continually being studied and optimized to improve the electrochemical reduction of nitrate to ammonia, facilitating more environmentally friendly ammonia production for agricultural purposes and allowing for more sustainable water treatment. Catalyst technology development holds great promise for sustainably reducing water pollution and increasing ammonia production [66].

3.1. Metal Catalysts (Noble Metal, Non-Noble Metals)

The electrochemical reduction of nitrate to ammonia is more efficient and selective when metal catalysts are used [67]. Many different metal catalysts have been studied, and it is clear that they exhibit unique characteristics and catalytic capabilities [68]. Because of their high activity and stability in electrocatalytic reactions, noble metal catalysts such as platinum (Pt) and palladium (Pd) are ideal for increasing nitrate reduction to ammonia while limiting the generation of undesirable by-products. Because of how long they last, they are excellent stimuli for real-world use [69]. Moreover, complexes of transition metals have shown vigorous catalytic activity in electrochemical nitrate reduction. These metals included copper (Cu), nickel (Ni), iron (Fe), and cobalt (Co). These metal complexes are appealing for efficient and selective nitrate reduction because of their ability to achieve remarkable selectivity for ammonia generation [70].

Nitrate is converted to NH_3 using metal-oxide catalysts including copper oxide (CuO), silver oxide (Ag_2O), and bismuth oxide (Bi_2O_3) [71]. The one-of-a-kind surface characteristics of these catalysts facilitate electron transport and boost the catalytic efficiency. In addition, metal nanoparticles and nanocatalysts are of interest because of their high surface areas and unusual characteristics [72]. Metal oxides integrated into carbon-based materials or metal nanoparticles supported on conductive substrates are two examples of nanomaterials that can boost catalytic efficiency and selectivity [73].

Considerations such as reaction conditions, desired product selectivity, and electrochemical system performance are key when deciding on a metal catalyst. Researchers are constantly investigating and optimizing metal catalysts to develop more effective, cost-effective, and sustainable techniques for electrochemical reduction of nitrate to ammonia. Taking advantage of the catalytic capabilities of metals, this technique has the potential to reduce nitrate pollution and increase the use of sustainable materials in NH_3 manufacturing [74]. Owing to their malleable nature, metallic catalysts have considerable potential for the conversion of nitrate to ammonia [75]. Increases in the reaction kinetics and selectivity have resulted from the use of novel metal catalysts featuring highly defined surface structures and active sites [76].

Metal catalysts can boost the performance of many electrochemical cell designs and electrode materials. Increasing the NH_3 production selectivity and decreasing unwanted reactions can be achieved by modifying the catalyst loading, shape, and composition [77]. However, issues such as catalyst stability, long-term performance, and possible poisoning effects must be resolved to make this technology helpful [78]. Scientists have consistently created novel catalyst designs and employed cutting-edge characterization techniques to better understand catalytic mechanisms and increase catalyst stability over time [79]. Electrochemical nitrate reduction using metal catalysts has the potential to significantly improve water pollution remediation and ammonia production processes while also being environmentally friendly. Responsible resource management and improved solutions to environmental concerns have been promoted by studying and optimizing metal catalysts [80].

3.2. Properties and Activity of Copper (Cu) Catalysts

The electrochemical reduction of nitrate to ammonia, in which copper catalysts play a pivotal role, is just one example of why Cucatalysts have attracted significant attention [81]. It has been demonstrated that copper catalysts can effectively accelerate this crucial reaction. Their unique properties have made them a favorite among researchers and entrepreneurs [82]. Cu is an abundant and cost-effective metal, making it a practical choice for large-scale applications. Its wide availability contributes to the economic viability of Cu catalysts for the electrochemical reduction of nitrate to ammonia [83].

The electrocatalytic activity of copper is relatively high, and it is this activity that drives the nitrate to ammonia reaction. Efficient electron transport facilitates nitrate ion conversion at the cathode of the electrochemical cell, which is responsible for this ability [84]. The catalytic performance was enhanced by modifying the surface characteristics of the Cu catalysts. The surface area, crystallinity, and oxidation state are the characteristics that researchers manipulate to maximize the efficiency and selectivity of the catalyst in the nitrate reduction process [85]. The low price and high availability of Cu makes it a viable option for large-scale projects. Cu catalysts for electrochemical nitrate reduction are feasible because of their widespread availability [86].

Cu catalysts are highly stable during the reduction process, enabling their employment in a nonstop extended manner [87]. Although the pH, temperature, and competing species influence stability, scientists are working to find solutions [80]. The electrochemical reduction of nitrate to ammonia using copper catalysts is not unique to the water-purification industry [88]. Catalysts based on Cu have demonstrated promise in related processes, such as the electrocatalytic conversion of nitrogen-containing compounds, indicating their adaptability to sustainably manage the nitrogen cycle [89]. Studies have been conducted to enhance the long-term stability and endurance of Cu catalysts, making them more suitable for large-scale industrial applications [90].

Cu catalysts play a crucial role in the electrochemical reduction of nitrate. **Table 1** provides a concise summary of their critical characteristics and attributes to help researchers and practitioners understand and compare the various Cu catalysts for sustainable nitrate conversion applications. This table includes essential information regarding the catalyst composition, morphology, surface area, selectivity, and specific enhancements or modifications that contribute to their effectiveness in the nitrate reduction process.

Table 1. Key features of Cu catalysts for nitrate electrochemical reduction.

Features	Description
High electrocatalytic activity	Because of its exceptional electrocatalytic activity, Cu is crucial in converting nitrate to ammonia. Cu's superior electron-transfer properties are responsible for its extraordinary ability since it facilitates the reduction of nitrate ions to ammonia at the cathode of an electrochemical cell [86] [90] [91].
Tunability of surface properties	Scientists try to improve the efficiency of Cu catalysts by tweaking their surface properties. Several factors, including surface area, crystallinity, and oxidation state, are carefully controlled to maximize the efficiency and selectivity of the catalyst throughout the nitrate reduction process. Such improvements greatly boost the process's overall efficiency and open the door to future developments [92].
Catalyst stability	Cu catalysts exhibit good stability during the reduction process, allowing for continuous and long-term operation. However, stability is affected by factors such as pH, temperature, and the presence of interfering species, and ongoing research aims to improve catalyst durability [93].
Selectivity control	The selectivity of copper catalysts in the electrochemical reduction of nitrate is influenced by adjusting reaction conditions and surface properties. By carefully controlling the reaction parameters, researchers enhance the selectivity towards ammonia production, minimizing the formation of undesired by-products [94].
Nanomaterials and nanostructured catalysts	Cu nanoparticles and nanomaterials have demonstrated enhanced catalytic activity due to their high surface area and unique electronic properties. Nanostructured copper catalysts offer improved electron transfer and efficiency, leading to higher ammonia yields and reduced energy consumption [95].
Synergistic effects	Cu catalysts are combined with other materials, such as carbon-based nanomaterials or metal oxides, to create composite catalysts with synergistic effects. These composite materials often exhibit improved catalytic performance, providing opportunities for further optimization in nitrate reduction reactions [96].
Electrochemical response	Cu catalysts display distinctive electrochemical responses during nitrate reduction, allowing for facile monitoring and optimization of their catalytic performance through electrochemical techniques [97].

3.3. Gold Metal Catalyst

Gold (Au) metal is a catalyst for the electrochemical reduction of nitrate to ammonia owing to its unique properties and performance. Despite its noble nature, its catalytic activity makes it desirable [98]. Au catalysts improve electron transport and reduce nitrate to ammonia, thereby increasing the NH_3 yields. Researchers have regulated the size and shape of gold nanoparticles (AuNPs) for nitrate reduction for catalytic activity [99]. The electrochemical stability of Au catalysts ensures long-term performance [100]. Changing the support materials or ligands increases Au catalyst selectivity for certain reactions. They also improve NH_3 production while reducing unwanted by-products in the electrochemical reduction of nitrate, proving their selectivity in various catalytic processes [93] [101].

Au catalysts are energy-efficient and easy to integrate at neutral pH and low temperature. Au-based bimetallic or alloyed catalysts exhibit synergistic effects that increase catalytic activity and selectivity, allowing for improved electrochemical nitrate reduction to ammonia [102]. **Figure 4** shows a visual representation of the different properties and characteristics of the Au catalysts. The diagram shows various aspects of Au catalysts, such as their remarkable stability, catalytic activity, selectivity, and distinctive surface properties. This is a useful resource for understanding the complex nature of Au catalysts and their importance in catalysis and different industrial applications.

Investigations of the use of Au catalysts in ecologically benign chemical transformations have been conducted to increase awareness of the importance of these processes [103]. In keeping with green chemistry principles, they are useful for water purification and ammonia generation by lowering the nitrate levels [104]. Despite their outstanding effectiveness, the high prices of Au catalysts limit their widespread use. Optimized gold catalyst architectures are the focus of current research, as they identify cheaper alternatives that maintain the catalytic performance [105]. Catalytic operations involving Au metal catalysts include the electrochemical reduction of nitrate to ammonia and synthesis of organic compounds. Their unique qualities make them useful in many applications, including cleaning polluted environments, converting energy, and creating sensors. Au catalysts allow for the creation of environmentally friendly technologies that assist multiple sectors without negatively affecting the natural world [106] [107].

3.4. Graphene-Based Catalyst

Graphene, a two-dimensional carbon allotrope comprised of a hexagonal lattice of carbon atoms, has proven an interesting and flexible catalyst in recent years [108]. Due to its electrical, thermal, and mechanical properties, large surface area, and high conductivity, graphene is a promising catalytic material [109]. Because of its unique structure, graphene provides many active sites for surface reactions, making it an efficient catalyst. Functionalization and doping boost its selectivity and catalytic capabilities. Graphene's adaptability and catalytic power could revolutionise energy conversion, storage, environmental cleaning, and chemical synthesis [110]. Graphene is ideal for catalytic applications due to its properties. The catalyst's enormous surface area and two-dimensional structure allow more active sites to speed up catalytic processes [111].

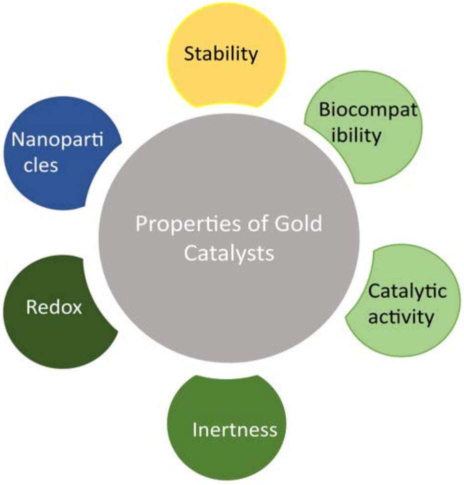

Figure 4. Illustration showing the different properties of gold (Au) catalyst.

The remarkable electrical conductivity of graphene allows for charge transfer, thereby improving the reaction speed and effectiveness. The mechanical strength of graphene makes it stable and durable in demanding catalytic environments, enabling its long-term catalytic performance. Functionalized and doped graphene can be customized for specific reactions to optimize catalytic activity and selectivity. Owing to its unique features, graphene has revolutionized several catalytic industries [112]. Graphene-based catalysts use the unique properties of graphene to improve the catalytic performance in numerous applications [113]. **Table 2** provides key information on the graphene-based catalysts that enhance their performance. It discusses graphene oxide (GO) and its reduced form, reduced graphene oxide (rGO), the impact of modification on the selectivity and activity, the advantages of nanocomposites, and the catalytic influence of heteroatom doping.

Graphene catalyst design requires structural and content analysis. A catalyst's surface area and flaws determine its catalytic ability [114]. Surface area and flaws affect active site density and catalyst reactivity. Shape and composition affect graphene catalyst performance. Recent attention has focused on graphene's electrochemical potential [111]. Due to its hexagonal lattice of sp^2 hybridised carbon atoms, graphene conducts electricity well. Electrochemical applications include graphene's excellent conductivity and fast electron transfer [115]. Many active sites in its two-dimensional structure and high surface area improve electrode-electrolyte interactions and provide effective charge storage and transmission in supercapacitors and batteries.

Owing to its mechanical strength and chemical stability, graphene lasts longer under electrochemical conditions [116]. The doping, functionalization, and

Table 2. Description, effects and advantages of graphene-based catalysts.

Graphene-based catalysts	Description	Effects and advantages
Graphene oxide (GO)	Active sites for catalysis are oxygen-containing functional groups.	Improves catalytic efficiency because of the presence of functional groups.
Reduced graphene oxide (rGO)	By removing oxygen groups, reducing GO results in an improvement in electrical conductivity and catalytic activity.	The electrical conductivity and catalytic activity are both improved.
Graphene nanocomposites	Hybrid structures are formed when graphene is combined with metals, metal oxides, or polymers, which increases catalytic activity.	Graphene's synergistic interaction with other materials improves their catalytic efficiency.
Nanoscale catalysts	Nanoparticle catalysts are dispersed and stabilized in a graphene matrix to reduce aggregate formation and increase activity.	Maintains catalytic efficiency and improves stability.
Heteroatom doping	New catalytic sites are created, and the electrical structure of graphene is altered when nitrogen, Sulphur, or boron are added.	Modifies surface interactions and charge transfer to enhance catalytic activity.

stacking of graphene can alter its properties. The unique features of graphene make it a viable electrochemical material for energy storage, sensors, and catalysis [117]. **Figure 5** shows the linear sweep voltammetry (LSV) curves of the graphene and CoO NC/graphene electrodes that reduced nitrate. The electrochemical nitrate reduction started at 0 V vs. the reversible hydrogen electrode (RHE) at both electrodes. Based on the current density studies, the CoO NC/graphene electrode was more active in the nitrate reduction reaction than the graphene electrode.

The synergistic effects of graphene and nitrate electroreduction catalysts improved the reduction efficiency and selectivity. Owing to its high electrical conductivity and large surface area, graphene enhances the catalytic properties of several nitrate reduction catalysts by promoting electron transport and nitrate adsorption [119]. In addition to effective electron flow, the graphene matrix has active sites for nitrate adsorption via several interactions. This interaction boosts catalytic activity by introducing additional nitrate species near the catalyst [120]. Graphene increases the stability and lifetime of nitrate-reduction catalysts. The strength and chemical resistance of graphene improve its electrochemical catalytic endurance. Tailoring the reaction environment by altering the composition and structure of graphene with a catalyst material may accelerate the reduction routes and reduce by-products [121]. In electrochemistry, graphene and nitrate electroreduction catalysts work effectively together, despite their physical differences. They boost catalytic efficiency and increase the conversion rates and selectivity for nitrogen gas and ammonium [122].

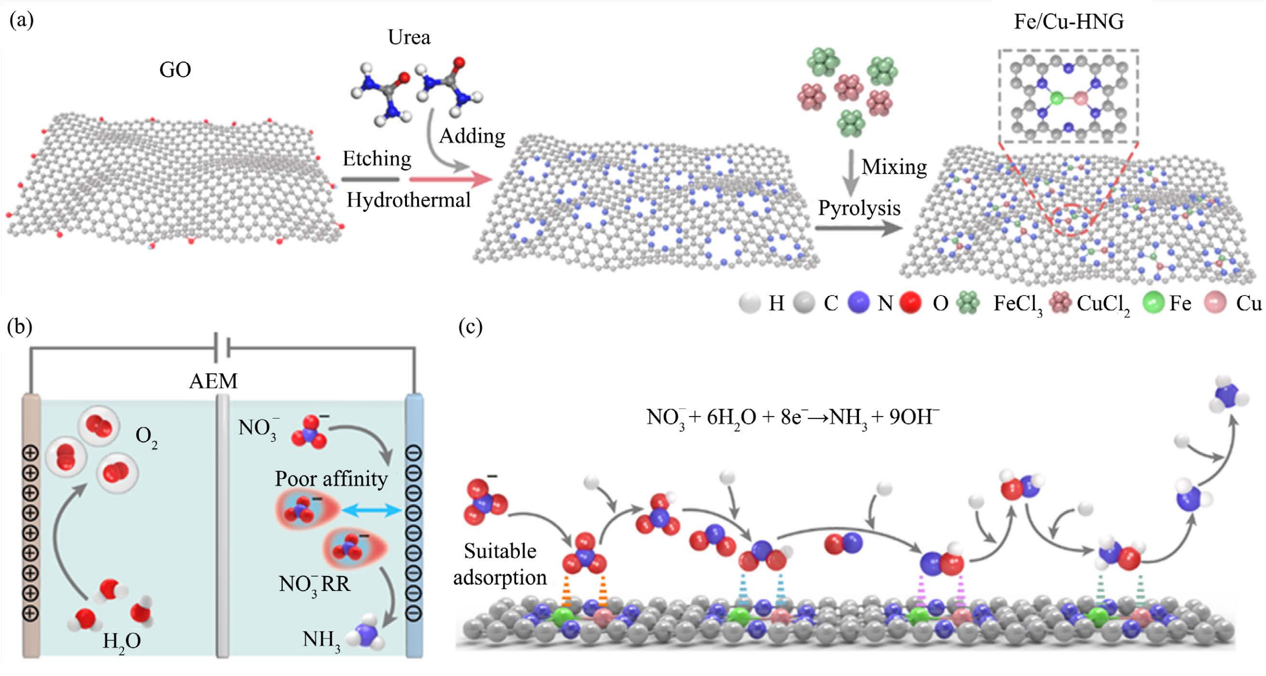

Figure 5. An illustration of the electrochemical nitrate reduction and the synthesis of Fe/Cu-HNG. (a) A diagrammatic representation of the catalyst's creation; (b) An electrochemical method for reducing nitrates; (c) Catalytic conversion steps from NO_3^- to NH_3 [118].

The reduction process was more efficient when graphene and nitrate electroreduction catalysts were used together. The high electrical conductivity and large surface area of graphene make it a suitable catalytic substrate [123]. Rapid electron transit from the electrode to the catalytic sites accelerates the reduction kinetics and reduces energy losses during electroreduction. The graphene matrix attaches to and stabilizes the catalytically active sites [124]. Graphene disperses and immobilizes nitrate electroreduction catalysts, preventing aggregation of the active species. Immobilization provides additional active sites for nitrate adsorption and reduction [125]. Graphene-enhanced nitrate electroreduction catalysts sustainably produce ammonia and control nitrogen [126].

4. Activated Carbon and Other Carbon Materials

Activated carbon (AC) is a low-cost catalyst material with several applications, including organic synthesis, wastewater treatment, and environmental remediation. Its large surface area and pore structure make it ideal for catalysis, accelerating processes, and providing active sites [127]. The simplicity of isolation and recycling makes it a promising candidate for heterogeneous catalysis [128]. Combining a porous structure and a high surface area improves its efficiency and longevity in driving a wide variety of chemical processes [129]. The electrochemical properties of a material dictate its ability to reduce nitrates. Materials with high surface areas, high conductivities, and controlled redox potentials have proven to be particularly effective.

These characteristics allow for rapid electron transit, enhanced selectivity toward the desired products, and active sites for nitrate adsorption and reactions. Using advanced materials with these characteristics has great potential for reducing water pollution and fostering sustainable water resource management [130]. AC catalysts exist in various forms with desirable and useful features. The versatility and promise of activated carbon in chemical processes has been demonstrated in metal-impregnated activated carbon, activated carbon composites, and other forms [131]. Different types of activated carbon catalysts exhibit different properties, as summarized in **Figure 6**.

The catalytic potential of the AC catalysts was tested by observing how well they promoted the designated processes and recording the resulting conversion rates and product yields [132]. Both internal and external parameters affect catalyst activity. These include catalyst surface area, pore size distribution, and surface functional groups. These parameters determine the routes and selectivity of the reactions by serving as the active sites for catalysis [133]. Catalytic reactions are sensitive to environmental conditions, such as temperature, pressure, and pH. It is also important to consider the type and amount of reactants, co-catalysts, and promoters used, as shown in **Figure 6**. The surface area, pore structure, active site distribution, functional groups, and metal content determine how well a catalyst catalyzes nitrate reduction [134].

4.1. Comparative Analysis of Different Catalysts

Catalysts made from Cu, Ag, Au, CuO-SnO_2 composites, and Pt-M alloys are commonly used in various fields for their effectiveness in reducing nitrate and producing nitrogen gas (N_2), carbon dioxide (CO_2), and water (H_2O), respectively. Cu-based catalysts are susceptible to corrosion, whereas silver-based catalysts are sensitive to sulfur compounds. Gold-based catalysts exhibit exceptional stabilities and selectivities. CuO-SnO_2 composites exhibit high water resistance and are used in environmental remediation and catalytic oxidation processes. Pt-M alloy catalysts have high efficiency and selectivity for water (H_2O) formation, making them commonly used in fuel cells for oxygen reduction (Table 3).

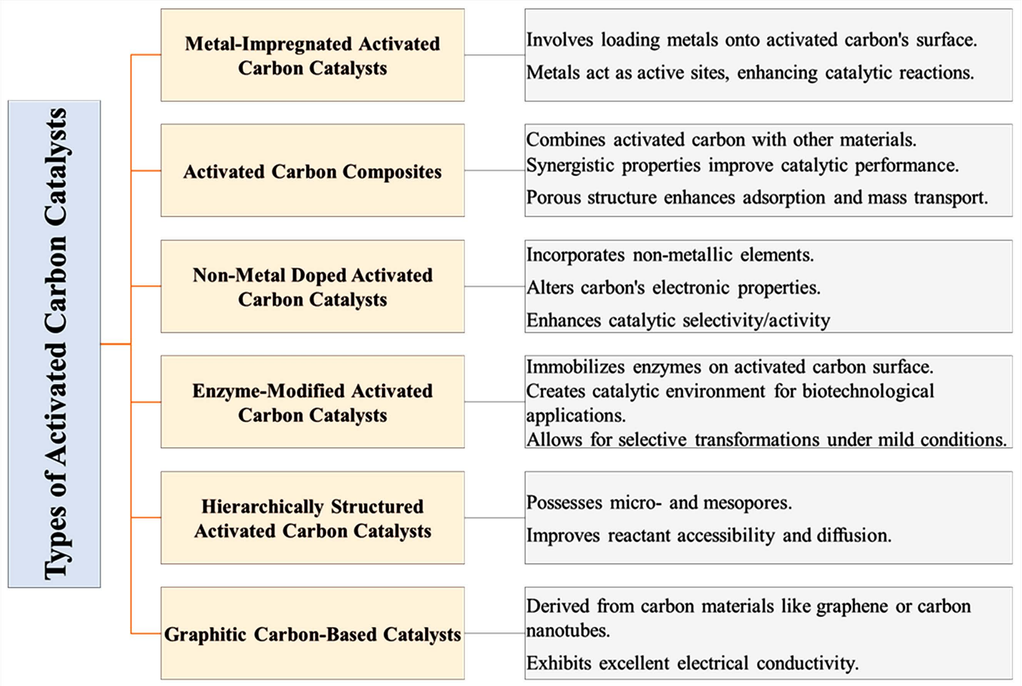

Figure 6. Overview of different types of activated carbon catalysts and their characteristics.

Table 3. Comparative analysis of different catalysts for nitrate reduction.

Catalyst	Composition	Selectivity	Efficiency	Stability	Applications
Copper catalyst	Cu-based	High for N_2	Moderate to high	Susceptible to corrosion	Water treatment, denitrification
Silver catalyst	Ag-based	High for N_2	Moderate to high	Sensitive to sulfur	Antibacterial coatings, sensing
Gold catalyst	Au-based	Varies by type	Moderate to high	Highly stable	Organic synthesis, fuel cells, sensors
CuO-SnO_2 catalyst	CuO-SnO2 composite	High for CO_2	High	Water-resistant	Environmental remediation, catalytic oxidation
Pt-M alloy catalyst	Pt-M (M = Pd, Fe, Ni)	High for H_2O	High	Relatively stable	Fuel cells, oxygen reduction

4.2. Potential Applications and Future Directions for Research

The development of new catalyst materials for the electrochemical reduction of nitrate to ammonia offers promising prospects in various fields of study. In sophisticated wastewater treatment systems, catalysts can be used to degrade nitrate contaminants and generate ammonia. Water pollution and resource depletion can be addressed permanently using this method. NH_3 can be used as a nitrogen fertilizer in agriculture, increasing crop yields while decreasing the negative effects of conventional nitrogen fertilizers on the environment [83]. When paired with renewable energy sources such as sunlight and wind, these catalysts might power an electrochemical system that stores and uses NH_3 as a carbon-neutral energy source. Furthermore, the manufacturing and distribution of NH_3 can be altered by introducing decentralized ammonia production units fuelled by locally accessible renewable energy sources. It positively affects the local economy, environment, and energy independence [135].

There are several potential directions for future research in this field. To achieve this goal, in-depth studies on the catalytic mechanisms of novel materials such as MOFs, two-dimensional materials, and catalysts found naturally on Earth are necessary. Designing multifunctional catalysts that can facilitate nitrate reduction while minimizing by-product generation and withstanding severe working conditions is an interesting problem [136]. Real-world applications also require an in-depth understanding of the catalyst stability over time and under changing reaction conditions. Accelerating catalyst discovery and optimization through the prediction of catalytic behavior and the identification of interesting candidates from a broad pool of prospective materials is possible through the integration of machine learning and computational approaches. Finally, it is crucial to determine the overall sustainability of innovative catalyst materials by considering their environmental effects and life cycle assessments in the context of their application pathways [137].

5. Conclusion

The investigation of catalyst materials for the electrochemical reduction of nitrate to ammonia holds significant promise for addressing environmental and agricultural challenges, and its progress is rapidly advancing. The interconnection between the catalytic activity, selectivity, stability, and reaction processes has been demonstrated through investigations of various types of catalysts. Numerous studies have demonstrated that the efficacy and proficiency of the nitrate reduction procedure are significantly influenced by the specific compositions of the catalysts employed in the process. The examination of contemporary advancements such as the integration of nanotechnology, hybrid systems, and earth-abundant materials indicates a promising trajectory towards the creation of durable and efficient catalysts. The implications of this area of research are extensive, as they find extensive use in various domains such as wastewater treatment, renewable energy storage, and fertilizer production. The significance of NH_3 production is growing owing to the escalating demand for agriculture and industry on a global scale. Therefore, exploring innovative catalyst materials, driven by the original concepts and a deep understanding of their mechanisms, has the potential to facilitate a more environmentally friendly approach to NH_3 synthesis. Recent developments in this domain have been moving forward satisfactorily and have the potential to initiate a new era marked by eco-friendly and financially feasible nitrogen fertilizer production.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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