

Review

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Metal-Catalyzed Reactions for Energy and Biomedical Applications

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Abstract: Metal-catalyzed reactions have emerged as cornerstone technologies bridging energy conversion systems and biomedical therapeutics through their remarkable selectivity, efficiency, and tunability. This review examines the dual convergence of metal catalysis in addressing critical challenges in sustainable energy production and advanced healthcare delivery. The discussion encompasses single-atom catalysts, dual-metal site architectures, and coordination polymer frameworks that enable transformative processes including electrocatalytic carbon dioxide reduction, fuel cell oxygen reduction, hydrogen evolution, and targeted therapeutic interventions. Recent advances in biohybrid catalysis and metal-organic frameworks have demonstrated unprecedented control over reaction pathways and biological interactions, creating opportunities for integrated solutions to energy sustainability and human health challenges. Through analysis of catalyst design principles, mechanistic understanding, and structure-activity relationships, this work illustrates how strategic manipulation of metal centers, ligand environments, and support materials drives performance optimization across both domains. The synthesis of knowledge from energy catalysis and catalytic biomedicine reveals common design strategies and emerging opportunities for cross-disciplinary innovation that will shape future development of multifunctional metal-based systems capable of addressing interconnected global challenges in climate, energy security, and healthcare accessibility.

Keywords: metal catalysis; energy conversion; electrocatalysis; biomedical applications; single-atom catalysts; coordination polymers

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1. Introduction

Metal catalysis represents a unifying scientific principle that connects diverse technological domains through fundamental concepts of activation energy reduction, reaction pathway modulation, and selective bond formation or cleavage. The strategic deployment of metal-based catalytic systems has become increasingly critical for addressing twin global challenges of sustainable energy production and advanced healthcare delivery, where conventional approaches face fundamental limitations in efficiency, selectivity, and environmental compatibility [1, 2]. Metal catalysts enable transformation of abundant feedstocks into valuable energy carriers while simultaneously providing therapeutic interventions through precisely controlled chemical reactions within biological systems. The emergence of single-atom catalysts, dual-metal architectures, and sophisticated coordination environments has

revolutionized both energy conversion technologies and biomedical applications by maximizing atom utilization efficiency and enabling precise control over catalytic properties through rational design [2, 3].

In energy applications, metal catalysts drive essential processes including electrocatalytic water splitting for hydrogen production, oxygen reduction reactions in fuel cells, carbon dioxide conversion to valuable chemicals, and energy storage in advanced battery systems [4]. These processes require catalysts with high activity, selectivity, and stability under demanding operational conditions including extreme pH, high current densities, and prolonged operation times. Parallel developments in catalytic biomedicine have demonstrated how metal complexes and metal-containing nanostructures can perform therapeutic functions through controlled catalytic reactions within living systems, including reactive oxygen species generation for cancer therapy, prodrug activation, and remediation of ischemia-reperfusion injury [1]. The convergence of catalyst design principles across energy and biomedical domains creates opportunities for integrated approaches where fundamental insights about metal-substrate interactions, electronic structure optimization, and mechanistic pathways inform development of advanced systems for both applications.

2. Catalyst Design and Fundamental Principles

2.1. Metal Center Selection and Coordination Engineering

Effective metal catalyst design requires optimization of multiple interconnected factors including metal center selection, coordination environment engineering, support material properties, and interfacial characteristics that collectively determine catalytic performance [4]. The choice of metal element establishes fundamental catalytic properties through its electronic configuration, oxidation states, coordination preferences, and intrinsic reactivity toward target substrates. Transition metals dominate catalytic applications due to their partially filled d-orbitals that facilitate electron transfer processes and enable formation of reactive intermediates through accessible oxidation state changes. Copper-based coordination polymers have demonstrated exceptional performance as enzyme inhibitors when combined with carefully selected auxiliary ligands that optimize geometric arrangements and create favorable interaction profiles with biological targets [5].

The coordination environment surrounding metal centers profoundly influences catalytic activity and selectivity through electronic effects that modulate orbital energies, geometric constraints that control substrate approach trajectories, and secondary interactions that stabilize transition states or destabilize products to accelerate turnover [6]. Ligand selection in molecular catalysts or coordination polymers allows systematic tuning of metal center electron density through variation of donor atom identity, conjugation patterns, and substituent electronic properties. Metal-organic frameworks represent particularly sophisticated support architectures that combine structural tunability with functional diversity, enabling creation of well-defined active sites with precise control over local chemical environments [6]. The rational integration of metal centers, ligand environments, and support structures through systematic design enables development of catalysts with optimized performance for targeted applications in energy conversion or biomedical intervention. Studies have shown that V-shaped auxiliary ligands in copper coordination polymers significantly enhance urease inhibition activity through precise geometric control [5, 7].

2.2. Single-Atom Catalysts and Advanced Architectures

Single-atom catalysts represent the ultimate expression of atom-efficiency in heterogeneous catalysis, featuring isolated metal atoms dispersed on support materials where they function as active sites with maximum metal utilization and unique catalytic properties distinct from nanoparticles or bulk metals [2, 4]. The atomic dispersion

eliminates metal-metal bonding and creates coordinatively unsaturated sites with high intrinsic activity, while the support material prevents aggregation and modulates electronic properties through metal-support interactions. Single-atom catalysts enable fundamental studies of reaction mechanisms through their well-defined active site structures amenable to spectroscopic characterization and computational modeling. The electronic structure of single metal atoms anchored on supports differs dramatically from corresponding bulk materials due to quantum confinement effects and strong interactions with support donor atoms that modify d-orbital energies and occupancies [2, 6].

These electronic modifications can enhance binding of reactants, stabilize key intermediates, or facilitate electron transfer steps that constitute rate-limiting processes in catalytic cycles. The geometric isolation of metal atoms prevents certain reaction pathways available to metal clusters or nanoparticles, enforcing alternative mechanisms that may exhibit superior selectivity for desired products. Advanced catalytic materials for renewable energy sources have benefited tremendously from single-atom catalyst concepts that maximize active site efficiency while minimizing precious metal loading [8]. Table 1 summarizes key characteristics distinguishing single-atom catalysts from conventional heterogeneous catalysts in energy and biomedical applications.

Table 1. Characteristics of Single-Atom Catalysts.

Feature	Single-Atom Catalysts	Conventional Catalysts	Performance Implications
Active site uniformity	Identical isolated atoms	Distribution of sites	Enhanced selectivity
Metal utilization	Maximum (100%)	Partial (surface atoms)	Economic efficiency
Electronic structure	Quantum-confined	Bulk-like electronic bands	Unique reactivity
Characterization	Well-defined structure	Complex ensemble	Mechanistic clarity
Stability challenges	Prone to aggregation	Generally stable	Requires support design

2.3. Dual-Metal Systems and Synergistic Effects

Dual-metal catalysts incorporating two distinct metal elements provide opportunities for synergistic effects and tandem catalytic mechanisms unavailable to single-metal systems. The proximity of different metal centers enables sequential reaction steps where intermediates generated at one metal site transfer to the second metal for subsequent transformation, bypassing unfavorable reaction pathways and enabling complex multi-step conversions with high overall selectivity. Recent advances in sustainable energy catalysis have emphasized the importance of hydrogen production, methane conversion, and biomass utilization where dual-metal systems show particular promise [9]. Electronic interactions between dissimilar metals through bridging ligands or direct metal-metal bonding modify the electronic properties of both centers, potentially creating catalytic activities exceeding simple additive combinations of individual metal contributions. The strategic positioning of complementary metal centers allows cooperative substrate activation and stabilization of reactive intermediates that would be unstable in the presence of single-metal sites. Dual-metal architectures have proven particularly effective for tandem electrocatalytic carbon dioxide reduction to multi-carbon products where sequential carbon-carbon bond formation requires multiple distinct catalytic functions [10].

3. Energy Conversion Applications

3.1. Electrocatalytic Carbon Dioxide Reduction

Electrocatalytic carbon dioxide reduction represents a critical technology for closing the carbon cycle and producing valuable chemicals or fuels from greenhouse gas emissions using renewable electricity [10]. The multi-electron, multi-proton nature of carbon dioxide reduction creates substantial challenges for catalyst design, as numerous possible products including carbon monoxide, formate, methanol, ethanol, and higher hydrocarbons compete through pathways with similar thermodynamic requirements but different kinetic barriers. Dual-metal site catalysts have emerged as particularly effective architectures for directing selectivity toward specific products through tandem mechanisms where initial carbon dioxide activation occurs at one metal center followed by subsequent reduction or carbon-carbon coupling at a second metal site [10].

The geometric arrangement and electronic properties of dual-metal sites critically influence product distribution in carbon dioxide reduction. Close proximity between metal centers facilitates transfer of reactive intermediates while maintaining sufficient separation to prevent destructive interference between active sites. Electronic communication between metals through bridging ligands or direct bonding modulates the binding energies of key intermediates including carbon dioxide radical anion, carbonyl species, and carbon-carbon coupled products that determine reaction pathways and selectivity. Optimization of metal identity, intermetallic distance, and local coordination environment enables achievement of high faradaic efficiencies toward desired products including ethylene, ethanol, and higher-value multi-carbon compounds that serve as chemical feedstocks or transportation fuels [10]. Table 2 presents performance metrics for representative dual-metal catalysts in carbon dioxide reduction applications.

Table 2. Dual-Metal Catalysts for Carbon Dioxide Reduction.

Metal Combination	Primary Product	Faradaic Efficiency	Current Density	Mechanism Type
Cu-Ni	Ethylene	60-75%	Moderate	Tandem C-C coupling
Cu-Au	Multi-carbon alcohols	45-60%	High	Sequential reduction
Fe-Co	Carbon monoxide	>90%	Low to moderate	Synergistic activation
Zn-Cu	Formate/ethanol	50-70%	Variable	Parallel pathways

3.2. Fuel Cells and Oxygen Reduction

Fuel cell technologies convert chemical energy stored in hydrogen or other fuels directly into electrical energy with high efficiency and minimal environmental impact, representing crucial components of sustainable energy infrastructure [11]. The oxygen reduction reaction at fuel cell cathodes constitutes a major performance-limiting factor due to sluggish kinetics that require substantial overpotentials and precious metal catalysts to achieve acceptable current densities. Metal-air battery systems face analogous challenges in oxygen reduction and evolution reactions that determine round-trip efficiency and cycle life [11]. Understanding the relationships between catalysis in fuel cells and metal-air batteries reveals common mechanistic principles and design strategies applicable across both technologies.

Advanced electrocatalysts for fuel cells have evolved toward sophisticated architectures that maximize active site density while optimizing electronic structure through careful control of metal coordination environments and support interactions [12]. Single-atom catalysts dispersed on carbon supports or incorporated into metal-organic frameworks represent promising alternatives to conventional platinum-based catalysts, offering reduced costs while maintaining high activity for oxygen reduction. The

development of non-precious metal catalysts based on iron, cobalt, or nickel coordinated to nitrogen-doped carbon supports has achieved significant progress, with performance approaching that of platinum in certain operating regimes [11, 12].

Synergistic properties between catalysts and carrier materials play essential roles in determining overall fuel cell performance through effects on electron transport, mass transfer, water management, and catalyst stability [12]. The evolution of active sites during fuel cell operation represents an important consideration, as initial catalyst structures may undergo transformations under electrochemical conditions that alter activity and selectivity. Understanding these dynamic processes through in-situ characterization techniques enables development of more robust catalyst systems with improved durability under demanding fuel cell operating conditions [12]. Table 3 compares key performance parameters for different catalyst architectures in fuel cell oxygen reduction applications.

Table 3. Catalyst Performance in Fuel Cell Oxygen Reduction.

Catalyst Type	Onset Potential	Half-Wave Potential	Mass Activity	Stability
Pt nanoparticles	Highest	Highest	Excellent	Good
Pt single atoms	High	High	Maximum	Variable
Fe-N-C	Moderate	Moderate	Good	Improving
Co-N-C	Moderate	Moderate	Good	Moderate
Dual-metal sites	High	High	Very good	Promising

3.3. Hydrogen Evolution and Energy Storage

Hydrogen evolution through water electrolysis provides a pathway for converting renewable electricity into storable chemical energy in the form of hydrogen fuel that can be utilized on demand for power generation, transportation, or chemical synthesis [3, 8]. Efficient hydrogen evolution catalysts must exhibit high activity at low overpotentials, maintain stability under acidic or alkaline conditions, and utilize earth-abundant elements to enable large-scale deployment. Platinum remains the benchmark hydrogen evolution catalyst due to its optimal hydrogen binding energy that balances adsorption and desorption steps, but cost considerations motivate development of alternative catalysts based on transition metal sulfides, phosphides, carbides, and nitrides that approach platinum-like performance [8, 9].

Metal-organic framework-derived single-atom catalysts have shown exceptional promise for hydrogen evolution through their ability to provide well-defined active sites with tunable electronic properties and high site densities [6]. The confinement of metal atoms within framework structures prevents aggregation during catalyst activation and operation, maintaining the beneficial properties of atomic dispersion throughout extended use. Coordination environment engineering through judicious ligand selection allows optimization of metal-hydrogen binding energies and electron transfer kinetics that control hydrogen evolution rates. Beyond hydrogen production, metal catalysts play crucial roles in energy storage systems including batteries and supercapacitors where they facilitate charge transfer reactions and enable high power densities [4, 6].

Advanced catalytic materials contribute to renewable energy conversion and storage across multiple technologies including solar fuel production, redox flow batteries, and reversible metal-air systems that collectively address intermittency challenges inherent to wind and solar power generation [8]. The integration of efficient catalysts with renewable energy sources and energy storage infrastructure enables transition toward sustainable energy systems with reduced dependence on fossil fuels and lower greenhouse gas emissions. Continued catalyst development targeting improved activity, stability, and cost-effectiveness will accelerate adoption of clean energy technologies and facilitate

achievement of carbon neutrality goals [8, 9]. Table 4 summarizes catalyst requirements and performance metrics for various energy conversion and storage applications.

Table 4. Catalyst Requirements for Energy Applications.

Application	Key Requirement	Target Metric	Current Best Performers	Remaining Challenges
Hydrogen evolution	Low overpotential	<50 mV at 10 mA/cm ²	Pt, MoS ₂ , Ni-Mo	Cost and stability
Oxygen evolution	High activity in alkaline	<300 mV at 10 mA/cm ²	IrO ₂ , NiFe-LDH	Durability
CO ₂ reduction	Product selectivity	>70% FE for target	Cu-based, dual-metal	Selectivity control
Fuel cells	Power density	>1 W/cm ²	Pt/C, Fe-N-C	Durability at high power
Metal-air batteries	Bifunctionality	Low charge-discharge gap	Perovskites, dual-metal	Cycle life

4. Biomedical Applications

4.1. Biohybrid Catalysis and Therapeutic Interventions

Biohybrid catalysis represents an emerging paradigm that integrates metal catalytic centers with biological systems to perform therapeutic functions through controlled chemical transformations within living organisms [1]. The concept extends beyond traditional metal-based drugs that act through stoichiometric interactions toward catalytic systems that turnover multiple substrate molecules, amplifying therapeutic effects while minimizing metal loading and potential toxicity. Metal complexes and nanoparticles can catalyze generation of reactive oxygen species for selective cancer cell killing, activate prodrugs at disease sites, or decompose pathological metabolites through enzyme-mimetic mechanisms [1, 2].

The design of biohybrid catalysts requires careful consideration of biological compatibility, targeting specificity, and selectivity for therapeutic reactions over interference with normal cellular processes. Metal coordination complexes with appropriate ligand frameworks can achieve preferential accumulation in tumor tissues through enhanced permeability and retention effects, while surface functionalization with targeting moieties enables active recognition of cancer cell markers. Once localized at disease sites, metal catalysts can selectively oxidize biological reductants including NADH or glutathione to generate cytotoxic reactive oxygen species, or reduce oxygen to form hydroxyl radicals that damage cellular components [1].

Single-atom catalysts have attracted interest for catalytic biomedicine due to their maximum atom utilization efficiency, well-defined active sites amenable to mechanistic study, and unique catalytic properties arising from quantum confinement effects [2]. The atomic dispersion of catalytic metals on biocompatible support materials including carbon nanostructures, metal-organic frameworks, or polymeric matrices prevents aggregation that could alter catalytic properties or biodistribution characteristics. Theoretical and experimental studies have elucidated relationships between single-atom catalyst structure and biological activity, guiding rational design of optimized therapeutic systems [2]. Table 5 summarizes key considerations for metal catalyst design in biomedical applications.

Table 5. Design Considerations for Catalytic Biomedicine.

Design Aspect	Requirements	Implementation Strategies	Performance Impact
Biocompatibility	Non-toxic support materials	Carbon, silica, biodegradable polymers	Safety profile
Targeting	Selective accumulation	Antibodies, peptides, small molecules	Therapeutic index
Catalytic activity	Efficient turnover	Optimized coordination environment	Efficacy
Selectivity	Minimal off-target effects	Substrate specificity, localized activation	Side effect profile
Stability	Maintain activity in vivo	Protective coatings, robust ligands	Duration of action

4.2. Metal Coordination Complexes as Therapeutics

Metal coordination complexes have established roles in medicine through platinum-based anticancer drugs, but emerging applications extend to treatment of ischemia-reperfusion injury, antimicrobial therapy, and metabolic disease management [13]. Ischemia-reperfusion injury occurs when blood flow returns to tissues after periods of oxygen deprivation, triggering oxidative stress and inflammatory responses that cause substantial tissue damage. Metal coordination complexes can mitigate these pathological processes through antioxidant activity, reactive oxygen species scavenging, or modulation of cellular signaling pathways involved in injury responses [13].

The therapeutic mechanisms of metal complexes for ischemia-reperfusion injury often involve catalytic cycles where the metal center alternates between oxidation states while processing reactive oxygen species or other pathological mediators. Copper and manganese complexes with appropriate supporting ligands can catalytically decompose superoxide radicals and hydrogen peroxide through superoxide dismutase-like and catalase-like mechanisms respectively, protecting tissues from oxidative damage [13]. The ligand framework surrounding metal centers determines substrate access, intermediate stabilization, and product release rates that collectively govern catalytic efficiency and selectivity.

Beyond antioxidant mechanisms, metal complexes can modulate cellular energetics, inhibit pathological enzyme activities, or regulate gene expression through interactions with transcription factors or epigenetic machinery. Vanadium compounds have shown promise as non-conventional therapeutics through their ability to modulate glucose metabolism and exhibit anticancer activities when administered through intratumor injection routes [14]. The development of metal-based drugs increasingly considers diagnostic and theranostic applications where metal complexes serve dual roles as therapeutic agents and imaging contrast materials, enabling simultaneous monitoring of drug distribution and treatment response [14].

4.3. Enzyme Inhibition and Metabolic Regulation

Metal coordination polymers have demonstrated potent enzyme inhibition activities with potential applications in treating metabolic disorders and infectious diseases [5, 7]. Urease inhibitors represent an important therapeutic class for managing *Helicobacter pylori* infections that cause gastric ulcers, as well as preventing pathological urea hydrolysis in kidney disease and reducing agricultural nitrogen loss. Copper-based coordination polymers incorporating imidazole-containing auxiliary ligands have achieved exceptional urease inhibition efficiencies through mechanisms involving competitive active site binding and structural disruption of the enzyme [5, 7].

The geometric arrangement of metal centers and ligands within coordination polymer structures critically influences enzyme inhibition potency through effects on

enzyme active site accessibility and inhibitor-enzyme binding interactions. V-shaped auxiliary ligands create specific three-dimensional architectures that complement enzyme surface topologies and enable tight binding interactions stabilized by multiple contact points [5]. Systematic variation of auxiliary ligand structures allows optimization of inhibition activity through structure-activity relationship studies that identify key structural features controlling potency and selectivity. Two-dimensional copper coordination polymers regulated by V-shaped auxiliary ligands have demonstrated particularly high urease inhibition efficiencies, suggesting that geometric factors beyond simple metal content strongly influence biological activity [5, 7].

The translation of metal coordination polymers into therapeutic applications requires consideration of bioavailability, metabolic stability, and potential toxicity profiles. Surface modification strategies can improve aqueous solubility and cellular uptake while protecting coordination polymer structures from premature degradation in biological environments. Understanding the relationships between coordination polymer structure, enzyme inhibition mechanisms, and in vivo performance will enable rational design of improved therapeutic agents with enhanced efficacy and safety profiles for treating metabolic diseases and infections [7].

5. Conclusion

Metal-catalyzed reactions serve as enabling technologies across energy conversion and biomedical domains through their ability to selectively accelerate targeted chemical transformations with high efficiency and tunability. Single-atom catalysts, dual-metal architectures, and coordination polymer frameworks represent sophisticated catalyst designs that maximize active site utilization while enabling precise control over catalytic properties through rational engineering of metal centers, coordination environments, and support structures. In energy applications, metal catalysts drive critical processes including carbon dioxide reduction to valuable chemicals, oxygen reduction in fuel cells, hydrogen evolution for energy storage, and diverse reactions supporting renewable energy utilization. Biomedical applications of metal catalysis encompass biohybrid therapeutic systems, enzyme inhibitors, and treatments for ischemia-reperfusion injury that harness controlled chemical reactivity for beneficial biological outcomes.

The convergence of fundamental principles governing metal catalysis across energy and biomedical applications creates opportunities for cross-disciplinary innovation and knowledge transfer that accelerates progress in both fields. Common design strategies including active site optimization, mechanistic elucidation, and structure-activity relationship establishment apply broadly across diverse applications despite different operating environments and performance requirements. Future advances will likely emphasize multifunctional catalyst systems capable of performing multiple catalytic transformations, integration of catalytic functions with sensing or diagnostic capabilities, and development of adaptive catalysts that respond to environmental conditions. Continued progress in metal-catalyzed reactions will contribute substantially to addressing global challenges in sustainable energy, climate change mitigation, and healthcare accessibility through enabling technologies that transform abundant resources into valuable products while improving human health outcomes.

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