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Advances in Metal Complex-Catalyzed Oxidation of Alkanes

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Abstract

With the development of green chemistry, metal complex-catalyzed oxidation of alkanes (linear and cyclic) has emerged as a key strategy for the efficient conversion of inert C(sp^3)–H bonds. This review summarizes recent advances in the selective oxidation of alkanes under mild conditions using metal complexes (e.g., Cu, Fe, Co, Ni), with a focus on ligand design and its regulatory effects on catalytic activity and selectivity. These systems employ radical or metal-oxo intermediate pathways, utilizing green oxidants such as H_2O_2 or O_2, significantly reducing energy consumption and byproduct formation. The study provides an efficient and sustainable catalytic approach for the valorization of petroleum resources (e.g., nylon monomer synthesis), contributing to the advancement of green chemical engineering. Future research should further optimize catalyst stability and recyclability while exploring biomimetic and multimetallic cooperative catalytic systems.

Keywords

Metal Complexes; Alkanes; Catalytic Oxidation Reactions.

1. Introduction

With growing societal demands for energy, environmental protection and resource utilization, the chemical industry is undergoing a green and sustainable transformation [1, 2]. As abundant and renewable carbon sources, alkanes [3] have emerged as crucial feedstocks for producing high-value-added organic chemical products. Particularly in catalytic oxidation reactions, the efficient and selective conversion of these raw materials into value-added products represents a significant challenge in modern chemistry and materials science research. Highly selective catalytic oxidation [4] not only enhances raw material utilization efficiency but also reduces environmental pollution and energy consumption, thereby advancing the application and development of green chemistry. Consequently, the construction and optimization of highly selective catalytic systems, along with research on alkane catalytic oxidation processes, hold substantial scientific significance and broad industrial application prospects.

Alkanes have long presented a formidable challenge in organic chemistry research due to their exceptional stability and the inert nature of their C-H bonds [5]. Conventional oxidation methods typically require harsh conditions of elevated temperatures and pressures, while exhibiting poor selectivity and generating substantial byproducts. Consequently, the development of highly selective catalytic oxidation technologies has emerged as a central research focus in alkane transformation [6].In recent years, metal complex catalytic systems [7-9] have demonstrated remarkable potential as efficient catalysts, showing superior selectivity and catalytic activity. Through meticulous design of the metal center, ligand architecture, and reaction parameters, researchers can achieve mild oxidation of alkanes with precise control over product formation, thereby maximizing both reaction selectivity and conversion efficiency.

The oxidation of alkanes yields valuable chemical intermediates including ketones, alcohols, and aldehydes [10], which serve as precursors for higher-value organic chemicals. Notable examples include cyclohexanone and cyclohexanol - key intermediates widely employed in the production of nylon polymers, plastics, and industrial solvents. Metal complex catalysts exhibit

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exceptional efficiency and stability in these processes. Their catalytic performance can be further optimized through strategic modulation of the metal's oxidation state and the electronic effects of coordinated ligands, enabling precise control over reaction selectivity and overall efficiency.

2. Overview of Metal Complexes

Coordination chemistry, the discipline studying the formation of metal complexes through interactions between central metal ions and ligands, originated in the late 19th century. In 1893, Swiss chemist Alfred Werner proposed the coordination theory that elucidated the binding modes of metal centers with surrounding molecules and ions, thereby establishing the foundation of modern coordination chemistry. Building upon this seminal work, continuous research efforts have achieved remarkable progress in the synthesis, structural characterization, theoretical understanding, and practical applications of coordination compounds. In catalysis, metal complexes serve as highly efficient catalysts for organic synthesis and industrial processes, exemplified by the Ziegler-Natta catalyst [11] for olefin polymerization. In biological systems, metal complexes form essential components of many biomolecules, such as the magnesium porphyrin complex in chlorophyll [12] that drives photosynthesis. The materials science field extensively employs coordination compounds to design functional materials including magnetic materials[13], luminescent materials [14], and supramolecular assemblies [15]. Furthermore, coordination chemistry contributes significantly to pharmaceutical applications, with silver complexes being widely used for treating burn infections due to their broad-spectrum antimicrobial activity.

The coordination bond represents a distinctive type of covalent bond formed through the interaction between a lone pair of electrons donated by a molecule or ion and the vacant orbital of a central metal ion. Characterized by its directional nature and reversibility, this unique bonding feature enables metal complexes to play pivotal roles in catalytic reactions. Concurrently, intermolecular interactions exert significant influence on the chemical properties and application performance of metal complexes. These non-covalent interactions primarily encompass hydrogen bonding, van der Waals forces, π-π stacking, and electrostatic interactions. Notably, the strength of most intermolecular forces is typically 1-2 orders of magnitude weaker than that of coordination bonds, with their effective interaction distances generally falling within the range of 0.3-0.5 nm.

Pyridine-based ligands (e.g., bipyridine, phenanthroline) are nitrogen-containing heterocycles that function as both σ-donors and π-acceptors, capable of forming stable complexes through mono- or polydentate coordination. Carboxylate ligands (e.g., acetate, oxalate) coordinate via oxygen atoms of the carboxyl group with diverse binding modes (monodentate, bridging, etc.), where their chain length and flexibility enable precise structural control of complexes. The cyanide ligand (CN^-) exhibits strong field effects and π-accepting properties, readily forming low-spin complexes and bridging architectures. Mixed N/O-donor ligands (e.g., pyridinecarboxylates) combine the advantages of nitrogen and oxygen donors, allowing flexible modulation of metal center properties for applications in catalysis and functional materials design. Each ligand class possesses distinct characteristics that profoundly influence the stability, reactivity, and functionality of coordination complexes through electronic and steric effects.

3. Metal Complex-Catalyzed Oxidation Systems for Linear Alkanes

Linear alkanes [16], as major constituents of petroleum and natural gas, exhibit remarkable chemical stability that hinders their direct conversion into high-value organic chemical products. However, their catalytic oxidation into oxygenated compounds (alcohols, aldehydes,

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ketones, and carboxylic acids) represents a transformative approach that not only enhances their economic value but also provides more versatile processing alternatives to conventional petrochemical routes. This technological advancement is crucial for optimizing petroleum resource utilization and extending resource lifecycles. The oxidation products of linear alkanes - including fatty alcohols, fatty acids, and fatty aldehydes - find extensive applications in surfactants[17], lubricants[18], fragrances[19], and pharmaceuticals, demonstrating substantial market potential. The development of efficient, environmentally benign catalytic oxidation systems can significantly mitigate the environmental pollution and energy consumption associated with traditional oxidants like m-chloroperoxybenzoic acid (m-CPBA) [20] and iodoxybenzene [21], thereby advancing the chemical industry toward greener and low-carbon development paradigms

Traditional oxidation processes for linear alkanes typically require harsh high-temperature/pressure conditions and generate substantial byproducts, making selective catalytic oxidation under mild conditions one of the most critical challenges in chemical industry. As primary feedstocks from crude oil and natural gas, linear alkanes exhibit remarkable inertness due to their strong C(sp^3)-H bonds (BDE > 380 kJ/mol), making them significantly more difficult to oxidize than alkenes, alkynes or alcohols. The higher reactivity of alcohols compared to alkane substrates under identical conditions inevitably leads to over-oxidation to ketones, compromising reaction selectivity. Therefore, enhancing selectivity and efficiency in linear alkane functionalization has become a primary research focus in both academia and industry. The C-H bond activation and selective oxidation in linear alkanes involve complex mechanisms including radical pathways, migratory insertion and redox processes. Mechanistic studies of these oxidation systems not only provide fundamental insights for catalytic science but also promote interdisciplinary research bridging chemistry and materials science. Current strategies emphasize biomimetic approaches mimicking natural enzymes, sophisticated ligand design for transition metal complexes, and development of cooperative catalytic systems to overcome the kinetic barriers of C-H cleavage while preventing over-oxidation, controlling regioselectivity, and maintaining catalytic activity under mild conditions all crucial for sustainable hydrocarbon utilization and green chemistry development.

Nature employs metalloenzymes—such as bleomycin, cytochrome P450 [22], and methane monooxygenase (MMO) [23] as highly selective catalysts for alkane hydroxylation under mild conditions using molecular oxygen as the oxidant. Inspired by these sophisticated biological systems, significant research attention has focused on designing biomimetic catalysts that replicate the remarkable catalytic behavior of these natural enzymes.

Lynette Soobramoney et al. [24] reported a series of tridentate copper complexes containing SNS ligands, which were fully characterized by infrared spectroscopy (IR), high-resolution mass spectrometry (HRMS), elemental analysis and single-crystal X-ray diffraction. These complexes have the general formula Cu[bis(R-thioethyl)aniline]Cl_2, where R = methyl, ethyl, butyl, cyclohexyl and tert-butyl, adopting a five-coordinate trigonal bipyramidal geometry. The highly ordered and symmetric molecular structure directly results from the central rigidity and structural constraints of the ligand framework constructed by the phenyl-substituted N-donor atom. Using hydrogen peroxide as oxidant for octane oxidation followed by reduction with triphenylphosphine (PPh_3), the maximum yield of n-octane reached 57%, with octanol as the main product showing 59% selectivity. This high catalytic activity is attributed to the metal-ligand synergistic catalytic effect, forming reactive Cu^{II}-OOH species stabilized by the rigid ligand framework and modulated by the tridentate SNS ligand. Compared with related complexes containing N-donor atoms, the superior catalytic performance of these Cu-SNS complexes highlights the crucial role of the aniline N-donor atom.

Shuxin Mao et al. [25] developed an iron complex system by combining simple iron salts with N-methylbis(methylpyridylamine) (Me-bpa) for octane oxidation, yielding a mixture of

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oxidation products at the 2-, 3-, and 4-positions with 12% selectivity for octanol. Mechanistic studies revealed that this reaction follows a metal-centered monooxygenase-type mechanism, where ketones are formed through over-oxidation of alcohols rather than via a radical pathway, with both products being generated at comparable rates through parallel formation pathways.

Siyabonga et al. [26] synthesized a series of 1,2,3-triazolium-derived nickel carbene complexes and evaluated their catalytic performance, including structural characterization of two new Cp-Ni-NHC complexes that both exhibited trigonal planar geometries. When tested as catalysts for n-octane oxidation under mild conditions, all complexes showed catalytic activity in generating oxygenated products with ketones as the major products, where the system incorporating hydrophobic alkyl chain substituents demonstrated the highest substrate conversion and achieved 15 mol% conversion with a turnover number of 150 when using H_2O_2 as oxidant while selectively activating internal carbon atoms.

Biswanath Das et al. [27] synthesized an oxo-bridged diiron(III) complex $Fe_2(\mu\text{-}O)(\mu\text{-}OAc)(DPEAMP)_2$ featuring an asymmetric N_4O-coordinating ligand and systematically investigated its catalytic oxidation activity using various hydrocarbons as substrates. For n-octane oxidation, the system achieved a turnover number (TON) of 27 with 23% alcohol selectivity. Mechanistic studies through low-temperature UV-Vis spectroscopy revealed the in situ formation of a transient Fe(III)-peroxo species, analogous to the initial intermediate P in soluble methane monooxygenase catalytic cycles. While product selectivity profiles suggested the involvement of a high-valent iron-oxo species as key intermediate, the low alcohol/ketone ratio indicated concurrent operation of both metal-oxo and radical pathways, consistent with previous studies on Fe(III)-O-Fe(III) motif-containing complexes.

Metal complex-catalyzed oxidation of linear alkanes exhibits superior selectivity and efficiency through ligand-modulated control of the metal center's electronic and steric properties, enabling targeted activation of inert C(sp^3)-H bonds while suppressing over-oxidation byproducts. These systems operate under significantly milder conditions than conventional high-temperature/pressure processes, dramatically reducing energy requirements and simplifying operations while eliminating environmentally hazardous oxidants in compliance with green chemistry principles. The well-characterized mechanisms involving radical, redox, and migratory insertion pathways provide crucial theoretical guidance for catalyst optimization, simultaneously enhancing reaction efficiency and expanding product applications. This catalytic approach represents an innovative strategy for high-value transformation of petroleum resources, combining fundamental mechanistic insights with practical solutions to advance sustainable chemical engineering - where precise spatial and electronic control of the metal center enables selective C-H functionalization unattainable by traditional methods, while the avoidance of toxic reagents and energy-intensive conditions addresses critical environmental challenges across both academic research and industrial applications.

4. Metal Complex-Catalyzed Oxidation Systems for Cyclic Alkanes

Cyclic alkanes [28], as an important class of organic compounds, are widely present in natural gas, petroleum, and their derivatives. The structural characteristics of cyclic alkanes confer high chemical stability, resulting in relatively low reactivity [29]. While this stability makes their oxidation particularly challenging, it simultaneously establishes them as crucial targets in chemical synthesis and catalytic research. The oxidation of cyclic alkanes refers to the process of converting C-H bonds into corresponding oxygenated products (alcohols, ketones, aldehydes, carboxylic acids, etc.). With the rapid development of industrial chemistry and extensive utilization of petroleum/natural gas resources, research on cyclic alkane oxidation has emerged as a focal point in catalysis. For instance, cyclohexanol and cyclohexanone serve as essential

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precursors for synthesizing nylon-6 (polycaprolactam) and nylon-66 (polyhexamethylene adipamide) [30] high-performance synthetic fibers renowned for their exceptional strength, wear resistance, heat tolerance, and corrosion resistance. Additionally, cyclohexanon functions as a key intermediate for producing certain plastics [31]and synthetic materials [32], enabling the synthesis of cyclohexene and polyester materials that find extensive applications in plastic manufacturing

The oxidation of cyclic alkanes frequently suffers from poor selectivity, harsh reaction conditions, high energy consumption, and excessive byproduct formation. Consequently, developing suitable catalytic systems to enhance both selectivity and efficiency under mild conditions has become a critical challenge in catalysis research. In recent years, metal complex catalysts have emerged as a pivotal research direction for cyclic alkane oxidation due to their exceptional selectivity, mild operating conditions, and superior catalytic activity.These metal complex systems enable efficient oxidation under relatively low temperatures and ambient pressure, significantly reducing energy requirements while minimizing unwanted byproducts - representing a green and sustainable approach to cyclic alkane functionalization. Compared to conventional catalysts, metal complexes offer remarkable advantages in reaction selectivity through precise control over reaction pathways for targeted product formation. The electronic properties of the metal center combined with tailored ligand effects confer outstanding activity and stability across diverse reaction systems. Furthermore, metal complex catalysts demonstrate excellent recyclability, allowing multiple reuse cycles that substantially lower production costs and align with sustainable development goals.

Takumi et al. [33] designed a Co^{2+} complex supported by an N_4-tetradentate ligand and investigated its catalytic activity for cyclohexane oxidation using m-CPBA (meta-chloroperoxybenzoic acid) as oxidant. The TMG_3tren-supported complex demonstrated superior catalytic performance, achieving both the highest yield (78%) and reaction rate (6.0 $mM \cdot min^{-1}$) among the tested systems. The enhanced electron-donating capacity of the TMG_3tren ligand was found to stabilize crucial cobalt-oxo radical intermediates ($Co^{2+}/^{3+}$–O·). Mechanistic studies revealed that hydrogen atom abstraction (HAA) represents the rate-determining step, involving two parallel pathways: (1) aryloxy radicals (ArC(O)O·) generated via homolytic cleavage of m-CPBA's O-O bond, and (2) terminal cobalt-oxo species ((L)$Co^{2+}/^{3+}$–O·). Comparative studies with Fe^{2+}, Ni^{2+}, and Cu^{2+} analogues confirmed the critical role of both the supporting ligand architecture and metal ion identity in governing the reaction mechanism.

Shen et al. [34] employed a cobalt(II) porphyrin complex as catalyst to oxidize cycloalkanes using molecular oxygen, with cycloalkyl peroxides (key intermediates in cycloalkane oxidation) as additional oxidants. The introduction of cycloalkyl peroxides significantly enhanced the oxidation selectivity of cyclohexane from 88.6% to 97.2%, while increasing the conversion rate from 3.88% to 4.41%. This improved efficiency stems from preventing cycloalkane autoxidation and effectively utilizing cycloalkyl peroxide intermediates as supplementary oxidants instead of conventional thermal decomposition.

Cheng et al. [35] investigated the oxidation of cycloalkanes catalyzed by a B12 derivative, heptamethylcobyrin, where m-chloroperbenzoic acid (m-CPBA) served as the oxidant in the cyclohexane oxidation. The system produced cyclohexanol and cyclohexanone within 1 hour under aerobic conditions, with an alcohol/ketone ratio of 0.67. The kinetic deuterium isotope effect was determined as 1.86, indicating that substrate hydrogen atom abstraction was not the main rate-determining step. The reaction between m-CPBA and heptamethylcobyrin at low temperatures formed a corresponding cobalt(III) acyl peroxide complex, characterized by UV-Vis, IR, ESR, and ESI-MS techniques. Theoretical studies revealed that O-O bond cleavage in the acyl peroxide complex generated both a cobalt(III)-oxyl radical (Co–O·) and an m-chlorobenzoyloxy radical. Radical trapping experiments using N-tert-butyl-α-phenylnitrone and CCl3Br, combined with product analysis and computational studies of hydrogen

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abstraction by the Co(III)−oxyl radical from cyclohexane, demonstrated that both the Co(III)-oxyl radical and m-chlorobenzoyloxy radical participated in the cyclohexane oxidation as hydrogen atom transfer reactants.

Metal complex catalysts demonstrate remarkable advantages in cyclic alkane oxidation reactions. By precisely modulating the electronic properties of metal centers and ligand environments, they achieve highly selective oxidation to form target products like alcohols, ketones, or acids. Compared to conventional methods, these catalysts efficiently activate inert C-H bonds under mild conditions (e.g., room temperature and pressure), significantly reducing energy consumption and byproducts. Some systems also exhibit recyclability, meeting green chemistry and sustainable development requirements, thereby providing efficient solutions for green synthesis of key chemical intermediates like nylon monomers.

5. Conclusion

Research on metal complex-catalyzed oxidation of alkanes (including linear and cyclic alkanes) provides crucial solutions for efficient activation of inert C(sp^3)–H bonds. These catalytic systems enable highly selective oxidation under mild conditions through rational design of metal centers and ligand structures, directing the formation of high-value oxygenates like alcohols and ketones, significantly outperforming conventional high-temperature/pressure processes. Their advantages include precise electronic/steric control, controllable generation of radical or metal-oxo intermediates, and compatibility with green oxidants (e.g., H_2O_2, O_2), avoiding environmental pollution from traditional strong oxidants while reducing energy consumption. For cyclic alkane oxidation, metal complex catalysts markedly improve the selectivity and atom economy of nylon monomer (cyclohexanone/ol) synthesis, offering novel approaches for value-added transformation of petroleum resources. This field not only deepens understanding of C-H activation mechanisms but also promotes green catalytic technologies in chemical industries, contributing significantly to sustainable development goals. Future research should further optimize catalyst stability and recyclability while exploring biomimetic catalysis and multi-metal synergistic systems.

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