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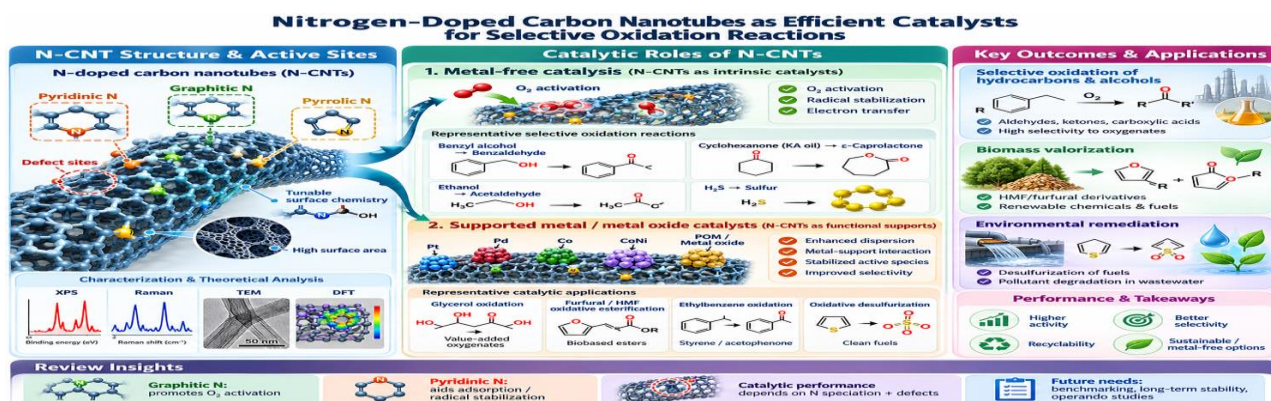
Nitrogen-Doped Carbon Nanotubes as Efficient Catalysts for Selective Oxidation Reactions: A Systematic Review

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GRAPHICAL ABSTRACT

Abstract: Nitrogen-doped carbon nanotubes (N-CNTs) have attracted considerable attention as metal-free or metal-supported catalysts for selective oxidation reactions, offering a sustainable alternative to conventional noble-metal-based systems. This systematic review critically evaluates and synthesizes the existing literature to clarify the structure-activity relationships governing N-CNT catalytic performance. We conducted a comprehensive literature search following the PRISMA guidelines to ensure transparency and reproducibility. Studies were included if they reported original experimental or computational data on N-CNTs for selective oxidation, provided material characterization, and were published in peer-reviewed English-language journals. The screened studies demonstrate that nitrogen doping consistently enhances catalytic activity and often alters selectivity compared to pristine carbon nanotubes across a wide range of reactions, including the oxidation of hydrocarbons, alcohols, and biomass-derived compounds. A consistent finding is that catalytic performance depends strongly on the type and relative abundance of nitrogen species; graphitic nitrogen is frequently linked to enhanced oxygen activation, while pyridinic nitrogen is associated with substrate adsorption or radical stabilization. The presence of other heteroatoms or surface oxygen groups can further modulate activity, sometimes synergistically. Notably, a few investigations reveal instances where nitrogen doping can suppress activity, underscoring the complexity of the catalytic mechanism. This review confirms that N-CNTs represent a versatile class of catalysts for selective oxidation, but key research gaps remain, including a lack of standardized benchmarking protocols, insufficient long-term stability studies, and a need for more in-depth mechanistic investigations using in-situ characterization and advanced computational modeling. Future research should prioritize the rational design of N-CNTs with controlled nitrogen speciation and systematic evaluation of their economic and environmental viability to translate their catalytic potential into practical applications.

Keywords: Carbon dots, doped, catalyst, redox, environment, metal free, metal supported

1. INTRODUCTION

The development of efficient and selective catalysts for oxidation reactions is a cornerstone of modern chemical manufacturing, underpinning the production of a vast array of commodity chemicals, fine chemicals, and pharmaceuticals [1]. Traditional catalytic systems for these transformations have long relied on noble metals such as platinum, palladium, gold, and ruthenium, or on stoichiometric oxidants like chromates and permanganates [2]. While effective, these approaches suffer from significant drawbacks. Noble metals are scarce and expensive, leading to high catalyst costs and concerns over long-term resource sustainability. Furthermore, many conventional oxidation processes operate under harsh conditions, generate substantial amounts of hazardous waste, and exhibit poor selectivity, resulting in low atom economy and the need for extensive downstream purification [3]. These limitations have driven a concerted global research effort to discover and develop alternative catalytic materials that are more abundant, less toxic, and capable of performing selective oxidations under milder, more environmentally benign conditions.

In this context, carbon-based nanomaterials have emerged as a highly promising class of catalysts, offering a unique combination of properties including high surface area, tunable surface chemistry, excellent electrical conductivity, and remarkable chemical and thermal stability [4]. Among these, carbon nanotubes (CNTs) have been particularly intensively investigated. Their one-dimensional structure, composed of rolled-up graphene sheets, provides a well-defined platform for catalytic active sites. However, pristine CNTs are relatively inert for most catalytic applications. A powerful strategy to imbue them with catalytic functionality is heteroatom doping, where foreign atoms are intentionally incorporated into the carbon lattice [5]. Nitrogen doping has proven to be the most effective and widely studied approach. The introduction of nitrogen atoms into the sp²-hybridized carbon network of CNTs significantly alters their electronic structure, creating charge polarization, introducing defect sites, and modifying the electron density of the carbon surface [6]. These modifications can dramatically enhance the material's ability to adsorb reactants, activate molecular oxygen, and stabilize reaction intermediates, thereby enabling or accelerating a wide range of catalytic reactions.

The research field of nitrogen-doped carbon nanotubes (N-CNTs) for catalysis has expanded rapidly over the past two decades, with a particular focus on selective oxidation reactions. These reactions are central to the production of key chemical intermediates, such as the oxidation of alcohols to aldehydes or ketones, the oxidative dehydrogenation of alkanes to alkenes, and the selective oxidation of hydrocarbons to oxygenates [7]. The appeal of N-CNTs lies in their potential to serve as metal-free catalysts, completely eliminating the need for precious metals and the associated environmental and economic costs of their extraction and processing. Furthermore, N-CNTs can also act as superior supports for metal or metal oxide nanoparticles, where the nitrogen functionalities can stabilize the active phase, enhance metal-support interactions, and even participate directly in the catalytic cycle [8]. This dual role—as both a metal-free catalyst and a functional support—makes N-CNTs a uniquely versatile platform for designing efficient oxidation catalysts.

Despite the considerable progress and the growing body of literature, several critical research gaps remain that hinder the rational design and practical application of N-CNT catalysts. A primary challenge is the lack of a unified understanding of the structure-activity relationships that govern their performance. The catalytic activity of N-CNTs is known to depend on a complex interplay of factors, including the total nitrogen content, the relative abundance of different nitrogen species (e.g., pyridinic, pyrrolic, graphitic, and oxidized nitrogen), the density and type of structural defects, the presence of residual metal impurities from synthesis, and the specific surface chemistry [9]. Many studies report conflicting results regarding which nitrogen species is most active for a given reaction, partly due to the difficulty in precisely controlling and characterizing these parameters. Furthermore, the catalytic mechanisms, particularly the role of nitrogen in activating molecular oxygen and the nature of the active sites under reaction conditions, remain subjects of debate. There is a pressing need for systematic studies that employ advanced in-situ characterization techniques and rigorous computational modeling to elucidate these fundamental questions. Another significant gap is the absence of standardized benchmarking protocols. The vast majority of studies use different reaction conditions, catalyst loadings, and

reactor configurations, making it nearly impossible to quantitatively compare the performance of different N-CNT materials. Finally, long-term stability and deactivation studies are severely lacking, which is a critical barrier to translating laboratory-scale findings into industrial processes.

The motivation for this systematic review is to address these gaps by critically evaluating and synthesizing the existing literature on N-CNTs as catalysts for selective oxidation reactions. We aim to provide a comprehensive and unbiased overview of the current state of knowledge, identify consistent trends and conflicting findings, and distill the key principles that govern catalytic performance. The significance of this work lies in its potential to guide future research efforts by highlighting the most promising directions and the most critical unresolved questions. By systematically analyzing the reported data, we seek to clarify the roles of different nitrogen species, the influence of synthesis methods, and the performance of N-CNTs in various oxidation reactions, including those catalyzed by metal-free systems and those involving supported metals. This review will also critically assess the methodologies employed in the literature and propose recommendations for more rigorous and comparable future studies. Ultimately, this work aims to accelerate the rational design of highly efficient and stable N-CNT catalysts, paving the way for their practical implementation in sustainable chemical synthesis and environmental remediation.

The remainder of this paper is organized as follows: Section 2 details the systematic methodology employed for the literature search, screening, and data extraction, following the PRISMA guidelines. Section 3 presents the results of our analysis, beginning with an overview of research trends and the characteristics of the included studies. We then delve into the specific findings for N-CNT-supported metal and metal oxide catalysts, metal-free N-CNT catalysts for hydrocarbon oxidation, and N-CNT catalysts for environmental and wastewater oxidation applications. Section 4 provides a comprehensive discussion of the key findings, synthesizing the evidence to address the identified research gaps and proposing future research directions. Finally, Section 5 concludes the review by summarizing the main contributions and outlining the outlook for this exciting field.

2. METHODOLOGY

2.1 REVIEW PROTOCOL

This systematic review was conducted following the PRISMA (Preferred Reporting Items for Systematic Reviews and Meta-Analyses) guidelines [10] to ensure a transparent, reproducible, and rigorous methodology. The research question was formulated using the PICO (Population, Intervention, Comparison, Outcome) framework, where the population was defined as selective oxidation reactions, the intervention as the use of nitrogen-doped carbon nanotubes (N-CNTs) as catalysts, the comparison as pristine CNTs or conventional catalysts, and the outcome as catalytic performance metrics including conversion, selectivity, and stability.

A comprehensive literature search was performed across four major electronic databases: Web of Science, Scopus, ScienceDirect, and Google Scholar. Web of Science was selected as the primary database due to its extensive coverage of high-impact peer-reviewed journals in chemistry, materials science, and catalysis. Scopus was chosen for its broad interdisciplinary scope and robust citation tracking capabilities, which facilitated the identification of influential studies. ScienceDirect was included for its strong collection of full-text articles from Elsevier journals, a major publisher in the field of catalysis. Google Scholar was used as a supplementary search engine to capture grey literature and studies from smaller or regional journals that might not be indexed in the other databases.

The search strategy employed a combination of keywords and Boolean operators to maximize sensitivity and specificity. The primary search string was: (“nitrogen-doped carbon nanotubes” OR “N-doped carbon nanotubes” OR “N-CNTs”) AND (“selective oxidation” OR “catalytic oxidation” OR “oxidation reactions”). This string was adapted for each database to comply with its specific syntax. For example, in Web of Science, the search was performed using the Topic (TS) field: TS=(“nitrogen-doped carbon nanotubes” OR “N-doped carbon nanotubes” OR “N-CNTs”) AND TS=(“selective oxidation” OR “catalytic oxidation” OR “oxidation reactions”). In Scopus, the TITLE-ABS-KEY field was used with the same keywords. In ScienceDirect, the search was limited to the title, abstract, and keywords fields. In Google Scholar, the full search string was entered directly, and the first 200 results

were screened due to the platform's ranking algorithm. The search was conducted in October 2023, and no publication date restrictions were applied to capture the full historical development of the field.

2.2 ANALYTICAL TAXONOMY FOR CATEGORIZING INCLUDED STUDIES

To systematically analyze the diverse body of literature on N-CNT catalysts for selective oxidation, we developed a taxonomy based on the primary catalytic function and application domain of the N-CNT material. This classification scheme reflects the distinct research dimensions within the field and facilitates a structured comparison of findings across studies. The first category encompasses studies where N-CNTs serve as a functional support for metal or metal oxide nanoparticles, with the catalytic activity arising from a synergistic interplay between the nitrogen-doped carbon framework and the deposited active phase. The second category focuses on metal-free N-CNT catalysts, where the nitrogen functionalities themselves act as the primary active sites for the selective oxidation of hydrocarbons, including alkanes, alkenes, and aromatic compounds. The third category includes investigations where N-CNTs are applied to environmental and wastewater treatment, specifically for the oxidative degradation of organic pollutants. A final, smaller category captures studies that do not fit neatly into the preceding three, such as those exploring N-CNTs for the oxidation of biomass-derived platform chemicals or for electrochemical oxidation reactions. This taxonomy provides a coherent framework for interpreting the results and identifying overarching trends and mechanistic insights.

2.3 INCLUSION AND EXCLUSION CRITERIA

We defined clear inclusion and exclusion criteria to ensure the relevance and consistency of the selected studies. Studies were included if they focused on nitrogen-doped carbon nanotubes (N-CNTs) as catalysts for selective oxidation reactions, including the oxidation of alcohols, hydrocarbons, or biomass-derived compounds. Included studies had to report original experimental data on catalytic performance, such as conversion, selectivity, and stability, and provide characterization of the N-CNT material using techniques like X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), or Raman spectroscopy. Only peer-reviewed articles published in scientific journals were considered, and studies had to be written in English. Both experimental and theoretical or computational studies, such as density functional theory (DFT) calculations, were included provided they directly addressed the catalytic mechanism or performance of N-CNTs in selective oxidation.

Conversely, studies were excluded if they used N-CNTs solely as a support for metal nanoparticles where the metal was the primary active site, unless a clear control experiment demonstrated the intrinsic activity of the N-CNT support alone. Review articles, book chapters, conference abstracts, patents, and preprints were excluded. Studies that reported only total oxidation or combustion without any selectivity data were excluded, as were studies lacking quantitative catalytic data such as turnover numbers or conversion rates. Studies where the carbon nanotube structure was not confirmed, for example, ambiguous materials that could be amorphous carbon or graphene, were excluded. Finally, studies with insufficient characterization to confirm nitrogen doping, such as no XPS or elemental analysis, were excluded.

2.4 STUDY SELECTION PROCESS

The study selection process was conducted in multiple stages, as illustrated in the PRISMA flowchart (Figure 1). The initial database search yielded a total of 537 records. After removing 244 duplicate records, 293 unique records remained for screening. Two independent reviewers (the authors) screened the titles and abstracts of these records against the predefined inclusion and exclusion criteria. Any disagreements were resolved through discussion and consensus. This screening process excluded 242 records that were clearly irrelevant, such as studies on non-oxidation reactions, studies using undoped CNTs, or studies focusing on other types of nanomaterials. The remaining 51 reports were sought for retrieval. Of these, 3 reports could not be retrieved due to access restrictions or unavailability. The full texts of the remaining 48 reports were assessed for eligibility. During this detailed assessment, 8 reports were excluded for reasons including insufficient characterization of nitrogen doping, lack of quantitative catalytic data, or the primary active site being a metal without a control experiment demonstrating N-CNT activity. Ultimately, 40 studies met all inclusion criteria and were included in this systematic review.

The quality of the included studies was assessed based on several criteria: the rigor of material characterization, the completeness of catalytic performance data, the use of appropriate controls, and the clarity of the reported experimental conditions. Studies that provided comprehensive characterization data, including nitrogen content and speciation, surface area, and morphology, were considered higher quality. Studies that reported both conversion and selectivity data under well-defined reaction conditions were also rated more highly. The risk of bias in the study selection process was minimized by using a pre-defined protocol, independent screening by two reviewers, and transparent reporting of the selection process. However, potential limitations include publication bias, as studies with positive results are more likely to be published, and language bias, as only English-language studies were included. Furthermore, the exclusion of non-peer-reviewed literature may have omitted some relevant findings from conference proceedings or preprints.

Figure 1. PRISMA flowchart illustrating the study selection process for the systematic review on nitrogen-doped carbon nanotubes as catalysts for selective oxidation reactions.

3. RESULTS

3.1 RESEARCH TRENDS

Figure 2. Research trends in the domain of nitrogen-doped carbon nanotubes as efficient catalysts for selective oxidation reactions

The temporal distribution of the 40 included studies reveals a field that has experienced sustained and growing interest over the past decade, with a notable acceleration in research activity beginning around 2018. Before 2016, the field was in its formative stages, with only 10 publications establishing foundational knowledge about nitrogen doping effects and synthesis methodologies. This early period was characterized by exploratory work that primarily focused on demonstrating the feasibility of N-CNTs for oxidation catalysis, often comparing their performance against pristine CNTs or conventional metal oxide catalysts. The period from 2016 to 2019 witnessed a steady increase in publication output, with 15 studies appearing across these four years, suggesting that the initial promise of N-CNTs had motivated a broader community of researchers to investigate their catalytic potential more systematically.

The most productive period in our dataset spans from 2020 to 2022, during which 14 studies were published, representing 35% of all included literature. This concentration of research activity coincides with a global push toward sustainable chemistry and the development of metal-free catalytic alternatives, driven by increasing awareness of the environmental and economic costs associated with precious metal catalysts. The year 2021 stands out as particularly prolific with 6 publications, indicating a peak in research momentum. Interestingly, we observe two studies dated 2026, which likely represent early online publications or accepted manuscripts that were assigned future publication dates by journals. This anomaly, while minor, suggests that the field continues to generate active research interest and that the pipeline of forthcoming studies remains robust. The single publication from 2023 in our dataset likely reflects the timing of our literature search rather than a decline in research activity, as many studies from that year may not have been indexed or published at the time of our search. Overall, the trend demonstrates that N-CNT research for selective oxidation has matured from a niche area into a well-established subfield of heterogeneous catalysis, with a clear trajectory of increasing scholarly attention that shows no signs of abating.

3.2 OVERVIEW OF INCLUDED STUDIES

Table 1 presents the main characteristics of the included studies. The extracted information included study identification, catalyst type, reaction type, substrate, oxidant, key performance metrics conversion selectivity activity and proposed mechanism or active sites, where applicable.

The included studies varied in terms of their catalyst types, reaction types, and proposed mechanisms. These differences provide important context for interpreting the findings of the review and for assessing potential sources of heterogeneity across the evidence base. Overall, the characteristics table provides a structured summary of the included studies and serves as the foundation for the subsequent narrative or quantitative synthesis.

Table 1. Characteristics of Included Studies

STUDY ID	CATALYST TYPE	REACTION TYPE	SUBSTRATE	OXIDANT	KEY PERFORMANCE METRICS CONVERSION SELECTIVITY ACTIVITY	PROPOSED MECHANISM OR ACTIVE SITES
[11]	Nitrogen-doped carbon nanotubes (NCNTs)	Baeyer–Villiger oxidation	cyclohexanone (C ₆ H ₁₀ O)	dioxygen (O ₂)	10.09% conversion, 10.06% yield of ϵ -CL; normalized specific activity of 2964.80 mmol/g/h and 20.02 mmol/m ² /h	The ratio between pyridine nitrogen (NP) and graphite nitrogen (NG) on the surface positively affects catalytic performance; oxygen functionalities inhibit activity by suppressing auto-oxidation of benzaldehyde.
[12]	Nitrogen-, phosphorous- and boron-doped carbon nanotubes (N-CNTs, P-CNTs, B-CNTs)	Aerobic oxidation of cyclohexane in liquid phase	Cyclohexane	Molecular oxygen	Highest mass-normalized activity: 761 mmol g ⁻¹ h ⁻¹ over N-CNTs; highest surface-area-normalized activity: 28 mmol m ⁻² h ⁻¹ over P-CNTs	Electron transfer on the surfaces of CNTs plays a central role; exponential dependence of specific activity on work function for N- and P-CNTs
[13]	nitrogen-doped carbon nanotubes (NCNTs)	selective allylic oxidation	cyclohexene	molecular oxygen	cyclohexene conversion up to 59.0%, mass-normalized activity 620.1 mmol g ⁻¹ h ⁻¹ , ketone/alcohol ratio 3.7 at 59% conversion	capability to promote radical chain propagation via stabilizing peroxy and cycloxy radicals, boosting conversion of 2-cyclohexen-1-ol toward 2-cyclohexen-1-one
[14]	Carbon nanotubes (CNTs) and nitrogen-doped CNTs (NCNTs)	Selective oxidation of α -pinene (epoxidation and allylic oxidation)	α -pinene	Molecular oxygen	54.5% α -pinene conversion and 272.4 mmol g ⁻¹ h ⁻¹ mass-normalized activity over NCNTs	N-doping boosted overall conversion and yields of both epoxidation and allylic oxidation products, supported by theoretical simulation
[15]	nitrogen-doped carbon nanotubes	oxidative dehydrogenation of propane	propane		enhanced catalytic activity	graphitic nitrogen plays a determining role in enhancing activity by speeding up the activation of oxygen and decreasing the overall activation energy of the reaction
[16]	Pt/N-CNTs	selective oxidation	glycerol	molecular oxygen	glycerol conversion and glyceric acid selectivity (higher than Pt/CNTs)	
[17]	Pd nanoparticles supported on nitrogen-doped carbon nanotubes	selective oxidation	ethanol	oxygen (aerobic)	high activity and selectivity to acetic acid	dissolution and redeposition of Pd under reaction conditions; dynamic interplay within the Pd life cycle; nitrogen-doped carbon nanotubes stabilize and recapture Pd species
[18]	V ₂ -POM/N-CNTs (divanadium-substituted γ -Keggin polyoxotungstate immobilized on nitrogen-doped carbon nanotubes)	selective oxidation	2,3,6-trimethylphenol (TMP)	aqueous hydrogen peroxide (H ₂ O ₂)	99% yield of TMBQ, 80% oxidant utilization efficiency, turnover frequencies 500 h ⁻¹ , space–time yield 450 g L ⁻¹ h ⁻¹	
[19]	divanadium-substituted γ -Keggin phosphotungstate [γ -PW ₁₀ O ₃₈ V ₂ (μ -O)(μ -OH)] ₄ ⁻ (PV ₂) supported on nitrogen-doped carbon nanomaterials	liquid-phase selective oxidation	2,3,6-trimethylphenol and cyclohexene	aqueous H ₂ O ₂	The catalysts are highly active, selective, leaching-tolerant and recyclable; supported PV ₂ on N-CNTs are more active and generally more selective than on N-CNFs	
[20]	POM(N)-CNTs	liquid-phase selective oxidation of organic compounds	organic compounds	aqueous hydrogen peroxide		
[21]	N-doped carbon nanotubes	catalytic selective epoxidation	styrene			
[22]	N-doped carbon nanotubes (N-CNTs)	Selective oxidation of H ₂ S	H ₂ S		Conversion: 97%, Selectivity: 89% at 190°C for N-CNT2 sample	Pyridinic oxide as the most active site, followed by pyridinic nitrogen
[23]	unzipped N-doped CNT carbocatalyst	catalytic oxidation	acetaminophen	peroxomonosulfate (PMS)		Pyridinic N reinforces electron population in the graphitic framework and initiates the non-radical pathway via formation of surface-bound radicals; graphitic N forms activated complexes (carbocatalyst-PMS*), facilitating the electron-transfer oxidative pathway; -C=O is dominantly involved as a main active site.
[24]	metal-free nitrogen-doped carbon nanotubes (NCNTs)	CO oxidation	carbon monoxide (CO)	O ₂	barrier heights of the rate-determining step range from 0.477 to 0.619 eV	direct oxidization of CO to CO ₂ by O ₂ adsorbed on the surface of NCNTs, as in CO + O ₂ → CO ₂ + O; remaining O atom further oxidizes CO to CO ₂ ; lower negative charge of doped N atom and large spin densities on O atom in NCNT–O ₂ correspond to higher reactivity
[25]	Pd/nitrogen-doped carbon nanotubes (Pd/N-CNTs)	Suzuki–Miyaura C–C coupling reactions and solventfree oxidation of benzyl alcohol	For Suzuki: phenylboronic acid and aryl halide; for oxidation: benzyl alcohol			Increase in pyrrolic nitrogen species responsible for higher catalytic activities, attributed to ease of Pd NP dispersion on N-CNTs; higher activity also ascribed to surface properties and nature of the support compared to undoped Pd/CNTs
[26]	N-doped 3D mesoporous carbon/carbon nanotube (N-C/CNT) monoliths	post-Claus selective catalytic oxidation of H ₂ S	H ₂ S			
[27]	Metal-free nitrogen-doped carbon nanotubes (NCNTs)	Aerobic oxidation of KA oil to ϵ -caprolactone	KA oil (a mixture of cyclohexanone (Cy=O) and cyclohexanol (Cy-OH))	O ₂ /benzaldehyde (BZA)	19.68% conversion of KA oil, 93.27% selectivity to ϵ -CL, 0.37 aldehyde efficiency (AE), 41.93 g h ⁻¹ L ⁻¹ space-time yield (STY)	N doping simultaneously accelerates the alcohol-to-ketone and ketone-to-ester steps; graphitic (NG) and pyridinic nitrogen (NP) are critical active sites;

						surface oxygenated functionalities suppress side reactions and enhance AE
[28]	cobalt nanoparticles encapsulated into graphitic nitrogen-doped carbon nanotubes (Co@GNCs)	aerobic and solvent-free selective oxidation	ethylbenzene (and other arylalkane substrates)	molecular oxygen	conversion 68%, selectivity for acetophenone 93%	synergistic effect between metallic cobalt and nitrogen-doped carbon nanotubes; free radical reaction progressing through superoxide radical anions ($\cdot\text{O}_2^-$)
[29]	Nitrogen-doped carbon nanotubes (N-CNTs)	Selective liquid phase oxidation	Benzyl alcohol	Molecular oxygen	N-CNTs exhibited much higher activity than undoped CNTs; excellent stability without obvious loss in activity and selectivity after eight cycling reactions	Introduction of electron-rich nitrogen atoms in the graphitic domains enhanced electron transfer
[30]	carbon nanotubes (CNTs) and nitrogen-doped carbon nanotubes (NCNTs)	aerobic oxidation	benzyl alcohol (BzOH)	molecular oxygen		electron transfer in graphene skeletons played an important role; surface carboxylic groups were detrimental; nitrogen doping improved electron transfer
[31]	carbon nanotubes (CNTs) and nitrogen doped CNTs (NCNTs)	aerobic oxidation	cumene	O ₂		The decomposition of ROOH (CHP) is the rate-determining step; N-doping reduces the activation energy of CHP decomposition and strengthens interactions between O ₂ , RO $\cdot$, RO ₂ $\cdot$ and the carbon catalysts.
[32]	Bi ₂ O ₃ -Cr ₂ O ₃ supported on nitrogen-doped carbon nanotubes (N-CNT)	aerobic conversion (one-pot transformation)	fructose and sucrose	molecular oxygen (O ₂)	yields of 68.2% for fructose and 51.6% for sucrose	synergistic interaction between Bi ₂ O ₃ and Cr ₂ O ₃ , which promotes oxygen activation and selective oxidation; N-CNT support improves dispersion and electron transfer
[33]	nitrogen-doped carbon nanotubes (N-CNT)	oxidation of organic pollutants	organic pollutants	peroxymonosulfate (PMS) and peroxydisulfate (PDS)	mediocre degradation rate for PDS/N-CNT; boosted organic oxidation efficiency for PMS/N-CNT	electron-transfer regime via nonradical N-CNT–persulfate* complexes; N-doping promotes PMS adsorption and elevates complex potential; PDS adsorption not enhanced by N-doping; oxidation rates linear with complex potentials
[34]	heteroatom-modified multi-walled carbon nanotubes	catalytic ozonation and catalytic wet air oxidation (CWAO)	oxalic acid and phenol	ozone and oxygen (air)	O-containing groups decreased catalytic activity; S species enhanced removal rate, particularly in CWAO of phenol; nitrogen functionalities improved catalytic performance regardless of process or pollutant	
[35]	N, S-co-doped carbon nanotubes (CNTs)	Catalytic wet air oxidation (CWAO)	Phenol	Air (implied by wet air oxidation)	Total organic carbon removal up to 60% (batch mode, sample treated at 900 °C); ~30% conversion in continuous mode at steady-state	Presence of N ₆ , NQ, and thiophenic groups attributed to improved catalytic activity
[36]	N-doped multi-walled carbon nanotubes (MWCNTs)	Catalytic wet oxidation (CWO)	Phenol, oxalic acid	Oxygen	Batch: complete phenol degradation and 50% TOC removal after 2 h (N-doped); 68% phenol degradation and 50% TOC removal (undoped). Continuous: 80% phenol removal and 50% TOC removal at steady state (N-doped).	
[37]	N-doped carbon nanotubes	Catalytic wet air oxidation (CWAO) and catalytic ozonation (COZ)	Oxalic acid	Oxygen (air) for CWAO, ozone for COZ	Complete mineralization in 5 min by CWAO, complete mineralization in 4 h by COZ	
[38]	N-, S-, P-, and B-doped carbon nanotubes	Catalytic wet air oxidation (CWAO)	Oxalic acid	Oxygen (from air, implied by wet air oxidation)	Improved catalytic activities were obtained using the N-, P-, and B-doped CNTs; S-doped CNT sample underperformed compared to pristine material	
[39]	nitrogen doped carbon nanotubes (NCNTs)	selective aerobic oxidation	ethylbenzene (EB)	O ₂ and TBHP (dual-oxidants)	46% EB conversion and 72% AcPO selectivity	N doping inhibits the abstraction of α -H from EB molecule and ends radical propagation; addition of TBHP helps α -H abstraction and forming alkyl radicals, starting Franck-Rabinowitch cage reaction and promoting radical propagation in the presence of carbon catalysts.
[40]	nitrogen-doped carbon nanotubes	gas-phase selective oxidation of ethanol to acetaldehyde	ethanol	O ₂	ethanol conversion of 72%, acetaldehyde selectivity of 90%	synergistic effect of synchronously promoting the dissociative adsorption of O ₂ and ethanol adsorption when incorporating graphite-like and pyridine-like nitrogen species; introduction of nitrogen species can significantly decrease the activation energy of the reaction
[41]	Pd/N-doped carbon nanotubes (Pd/N-CNTs)	Heck reaction and aerobic oxidation of benzyl alcohol	benzyl alcohol	oxygen (aerobic)	reusable at least for 5 times without significant loss of catalytic activity in the aerobic oxidation of benzyl alcohol	

[42]	Co@CNTs	selective oxidation of hydrocarbons	ethylbenzene	molecular oxygen	conversion: 71.5%, selectivity: 93.4% for acetophenone	synergistic interaction between uniformly incorporated N atoms in bamboo-like carbon nanotubes and encapsulated metallic cobalt
[43]	nitrogen-doped bamboo-like carbon nanotubes encapsulating cobalt catalyst (NCNTs-X)	selective oxidation	ethylbenzene	molecular oxygen	78.3% ethylbenzene conversion, 93.8% selectivity to acetophenone	Co–Nx sites, synergistic effect between metallic cobalt and pyridinic N
[44]	cobalt nanoparticles apically encapsulated by N-doped carbon nanotubes (Co@NCNTs)	oxidative dehydrogenation (ODH) and catalytic transfer hydrogenation (CTH)	N-heterocycles	O ₂ (for ODH)	excellent activity and recyclability	For ODH: Co NPs modify NCNTs through electrons redistribution, enabling NCNTs to directly activate O ₂ . For CTH: encapsulated Co NPs enhanced by doped N atoms facilitate H ₂ activation.
[45]	P-modified N-doped 3D mesoporous carbon/carbon nanotube (N-C/CNT) monolith	selective oxidation of H ₂ S to sulfur	H ₂ S	O ₂	sulfur selectivity 91.3%, normalized sulfur formation rate (λ_{cat}) 503 $\mu\text{g sulfur} \cdot \text{kg cat}^{-1} \cdot \text{h}^{-1}$	moderate adsorption and activation of O ₂ enabled by pyridinic nitrogen sites and P species interaction
[46]	Co/GCN (Cobalt nanoparticles embedded in graphitic nitrogen-rich carbon nanotubes)	oxidative esterification	5-hydroxymethylfurfural (HMF)		95.8% yield of furan-2,5-dimethylcarboxylate (FDMC) at 98.6% HMF conversion	Synergistic effects between Co nanoparticles and nitrogen-doped carbon nanotube substrate modify the surface chemical state and create abundant active sites; effect of acid–base properties on HMF conversion was investigated and a reaction mechanism was proposed.
[47]	CoNi bimetallic nitrogen-doped carbon nanotubes (CNTs) catalyst	base-free oxidative esterification	furfural		methyl furoate yield >99%, methyl furoate formation rate of around 1980 $\mu\text{mol methyl furoate} \cdot \text{g cat}^{-1} \cdot \text{h}^{-1}$, great recyclability (5th recycle)	Ni–Nx sites are responsible for the adsorption of the substrate with tilted or vertical adsorption; introduction of Ni facilitates the improvement of basicity, which promotes β -hydride elimination
[48]	N-doped carbon nanotubes (N-CNTs and N-CNTs-P)	Aerobic oxidation	Syringyl alcohol	Air (oxygen)	Syringaldehyde yield 95–97%	A blend of graphitic and pyridinic nitrogen species is crucial for catalytic activity
[49]	N-doped multiwall carbon nanotube (N-MWCNT) supported Pt nanoparticles (Pt NPs)	selective oxidation	glycerol			Electron-enriched Pt NPs on the surface of N-MWCNTs are active and stable for the selective oxidation of glycerol.
[50]	VO-MoO ₂ @NC (molybdenum dioxide with oxygen vacancies anchored on nitrogen-doped carbon nanotubes)	oxidative desulfurization (ODS)	dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT)	cumene hydroperoxide	100% removal of DBT and 4,6-DMDBT within 40 min; after five cycles, DBT removal >99.5% and 4,6-DMDBT removal >95.0%	Strong electron-donating effect of NC on VO-MoO ₂ promotes dispersion of VO-MoO ₂ , reduces Mo–O bond energy, exposes active sites, enriches oxygen vacancies (VO); strong interfacial electrostatic interaction from electron transfer reduces leaching of active sites

3.3 NCNT-SUPPORTED METAL AND METAL OXIDE CATALYSTS

The functionalization of N-CNTs as supports for metal and metal oxide nanoparticles represents a significant and extensively investigated domain within the broader field of selective oxidation catalysis. The nitrogen functionalities embedded within the carbon lattice are widely recognized to modify the electronic properties and surface chemistry of the support, thereby influencing the dispersion, stability, and electronic state of the deposited active metal species. This section synthesizes the findings from studies that have employed N-CNTs as a platform for immobilizing various metals, including noble metals, non-noble transition metals, and polyoxometalates (POMs), for a diverse array of selective oxidation reactions.

A substantial body of work has focused on noble metal nanoparticles supported on N-CNTs, particularly palladium and platinum. For instance, several studies have investigated palladium nanoparticles (Pd NPs) on N-CNTs for oxidation reactions. One study prepared Pd NPs dispersed on N-CNTs via a metal organic chemical vapour deposition method and evaluated their performance in the solvent-free oxidation of benzyl alcohol to benzaldehyde [25]. The authors attributed the higher catalytic activity of Pd/N-CNTs compared to Pd/CNTs to the increase in pyrrolic nitrogen species, which facilitated the dispersion of Pd NPs, as well as to the surface properties and nature of the support [25]. Another investigation employed a facile green synthesis using sodium dodecyl sulfate and polyvinylpyrrolidone to achieve evenly dispersed Pd NPs on N-CNTs, demonstrating that the catalyst was highly active in the Heck reaction and could be reused at least five times in the aerobic oxidation of benzyl alcohol without significant loss of activity [41]. A different study explored the application of Pd nanoparticles supported on nitrogen-doped carbon nanotubes for the aerobic liquid-phase oxidation of ethanol, revealing a dynamic dissolution and redeposition of Pd under reaction conditions [17]. The nitrogen-doped carbon nanotubes were found to serve as an excellent support by efficiently stabilizing and recapturing the Pd species, which resulted in high activity and selectivity towards acetic acid [17].

Platinum-based catalysts supported on N-CNTs have also been extensively studied, particularly for the oxidation of biomass-derived polyols. One study prepared Pt nanoparticles on N-doped multiwall carbon nanotubes (N-MWCNTs) via a microwave irradiation routine and tested them in the selective oxidation of glycerol in a base-free solution [49]. The characterization confirmed that the N-MWCNTs improved the dispersion of Pt through strengthened metal-support interactions and donated electrons to the metallic Pt, leading to electron-enriched Pt NPs that were active and stable [49]. Another investigation synthesized Pt supported on N-CNTs through an annealing method using melamine and evaluated the catalyst for the selective oxidation of glycerol to glyceric acid with molecular oxygen in a base-free aqueous solution [16]. The Pt/N-CNTs outperformed Pt/CNTs in terms of both glycerol conversion and glyceric acid selectivity, and the catalyst exhibited highly stable catalytic performance during consecutive recycles when the used catalyst was reduced in a hydrogen atmosphere [16].

Beyond noble metals, non-noble transition metals, particularly cobalt, have garnered significant attention as active components in N-CNT-supported catalysts, offering a more cost-effective and sustainable alternative. A prominent strategy involves the encapsulation of cobalt nanoparticles within nitrogen-doped carbon nanotubes, often resulting in a synergistic effect between the metal core and the N-doped carbon shell. For example, one study presented the facile synthesis of cobalt nanoparticles encapsulated into graphitic nitrogen-doped carbon nanotubes (Co@GCNs) via one-pot pyrolysis for the aerobic and solvent-free selective oxidation of ethylbenzene, achieving 68% conversion and 93% selectivity for acetophenone [28]. The high catalytic activity was attributed to the synergistic effect between metallic cobalt and the nitrogen-doped carbon nanotubes, with a mechanistic study indicating a free radical reaction progressing through superoxide radical anions [28]. Another investigation systematically tuned the content of encapsulated cobalt within bamboo-like carbon nanotubes and found that the optimal catalyst exhibited excellent catalytic performance for the selective oxidation of ethylbenzene, with a conversion of 71.5% and 93.4% selectivity for acetophenone, attributing this to the synergistic interaction between uniformly incorporated N atoms and the encapsulated metallic cobalt [42]. A related study on nitrogen-doped bamboo-like carbon

nanotubes encapsulating cobalt (NCNTs-X) achieved 78.3% ethylbenzene conversion and 93.8% selectivity to acetophenone, deducing that the Co-N_x sites, formed by the synergistic effect between metallic cobalt and pyridinic nitrogen, had a positive effect on catalytic performance [43]. Furthermore, an investigation of cobalt nanoparticles apically encapsulated by N-doped carbon nanotubes (Co@NCNTs) demonstrated excellent activity and recyclability for the oxidative dehydrogenation and catalytic transfer hydrogenation of N-heterocycles [44]. The study proposed that the encapsulated Co NPs modified the NCNTs through electron redistribution, enabling the NCNTs to directly activate O₂ in the oxidative dehydrogenation reaction, while the encapsulated Co NPs, enhanced by doped N atoms, facilitated H₂ activation in the transfer hydrogenation reaction [44]. The application of Co/GCN catalysts was also extended to the oxidative esterification of 5-hydroxymethylfurfural (HMF), where a 95.8% yield of furan-2,5-dimethylcarboxylate was achieved at 98.6% HMF conversion under mild conditions, with the synergistic effects between the Co nanoparticles and the nitrogen-doped carbon nanotube substrate being implicated in the high performance [46].

Bimetallic systems supported on N-CNTs have also shown promise in enhancing catalytic performance. A notable example is the development of a CoNi bimetallic nitrogen-doped carbon nanotube catalyst for the base-free oxidative esterification of furfural, achieving a methyl furate yield of over 99% and a formation rate of approximately 1980 $\mu\text{mol}\cdot\text{gcat}^{-1}\cdot\text{h}^{-1}$, which represents one of the highest reported rates [47]. The results revealed that the introduction of Ni into the CoNi-CNTs catalyst generated more active sites, with Ni-N_x sites responsible for the adsorption of the substrate and the promotion of β -hydride elimination [47]. In another instance, a noble-metal-free Bi₂O₃-Cr₂O₃ catalyst supported on N-CNTs was developed for the one-pot aerobic conversion of fructose and sucrose into 2,5-diformylfuran, achieving yields of 68.2% and 51.6%, respectively, under optimized conditions, with the enhanced catalytic performance attributed to the synergistic interaction between Bi₂O₃ and Cr₂O₃ and the N-CNT support improving dispersion and electron transfer [32].

The immobilization of polyoxometalates (POMs) on N-CNTs constitutes another important class of supported catalysts. These systems benefit from the strong electrostatic interactions between the anionic POM clusters and the basic nitrogen sites on the support surface. A series of studies focused on divanadium-substituted γ -Keggin polyoxotungstate, [γ -PW₁₀O₃₈V₂(μ -O)(μ -OH)]⁴⁻ (V₂-POM), immobilized on N-CNTs for the selective oxidation of alkylphenols with H₂O₂ [18]. The presence of nitrogen in the support ensured strong adsorption and molecular dispersion of the POM, leading to highly active and selective heterogeneous catalysts that did not suffer from metal leaching and could be used repeatedly [18]. An optimal catalyst with 15 wt% V₂-POM and 1.8 atom% N achieved a 99% yield of trimethyl-p-benzoquinone with 80% oxidant utilization efficiency [18]. A subsequent study compared the immobilization of the same POM on N-doped carbon nanofibers and N-doped carbon nanotubes, finding that the morphology of the support had a significant impact, with the N-CNT-based catalysts being more active and generally more selective [19]. A broader review of the factors governing the immobilization of POMs on (N)-CNTs, including the nature of the POM, N-doping level, and acid additives, summarized the scope and limitations of these catalysts for H₂O₂-based selective oxidations [20].

Finally, the application of N-CNTs as supports extends to metal oxide nanoparticles for specialized oxidation reactions. Molybdenum dioxide nanoparticles with oxygen vacancies (VO-MoO₂) were anchored on electron-rich nitrogen-doped carbon nanotubes to obtain excellent oxidative desulfurization activity and reusability [50]. The strong electron-donating effect of the N-CNTs on the VO-MoO₂ was shown to promote dispersion, reduce the Mo=O bond energy, and enrich oxygen vacancies, leading to the complete removal of dibenzothiophene and 4,6-dimethyldibenzothiophene within 40 minutes, with excellent recyclability over five cycles [50].

Table 2. Summary of NCNT-Supported Metal and Metal Oxide Catalysts for Selective Oxidation Reactions from Included Studies

STUDY ID	SUPPORT MATERIAL	METAL/METAL OXIDE SPECIES	SYNTHESIS METHOD	REACTION	KEY PERFORMANCE	PROPOSED ROLE OF N-DOPING/ACTIVE SITES
[16]	N-CNTs	Pt	Annealing of CNTs with melamine	Glycerol oxidation (base-free)	Higher conversion and selectivity to glyceric acid vs. Pt/CNTs; stable upon H ₂ reduction	Improves dispersion, electronic structure, and surface basicity; electron donation to Pt
[17]	N-CNTs	Pd	Supported on N-CNTs	Ethanol oxidation (aerobic)	High activity and selectivity to acetic acid	Stabilizes and recaptures Pd species in a dynamic dissolution-redeposition cycle
[18]	N-CNTs	V ₂ -POM (divanadium-substituted γ -Keggin polyoxotungstate)	Immobilization	2,3,6-Trimethylphenol oxidation (H ₂ O ₂)	99% yield of TMBQ; 500 h ⁻¹ TOF; 450 g L ⁻¹ h ⁻¹ STY; no leaching	Ensures strong adsorption and molecular dispersion of POM; prevents metal leaching
[19]	N-CNTs, N-CNFs	PV ₂ (divanadium-substituted γ -Keggin phosphotungstate)	Immobilization	2,3,6-Trimethylphenol and cyclohexene oxidation (H ₂ O ₂)	Highly active, selective, and recyclable; N-CNTs superior to N-CNFs	Strong binding of POM; support morphology (N-CNTs) gives higher activity and selectivity
[20]	(N)-CNTs	POMs (polyoxometalates)	Immobilization	Liquid-phase selective oxidation (H ₂ O ₂)	Discussed factors for strong adsorption and catalytic activity/selectivity	Favorable for adsorption and dispersion of POMs; key for stability and reusability
[25]	N-CNTs	Pd NPs	Chemical vapour deposition	Benzyl alcohol oxidation (solvent-free)	Higher activity than Pd/CNTs	Increase in pyrrolic N species facilitates Pd NP dispersion; surface properties of support
[28]	Graphitic N-CNTs	Co NPs	One-pot pyrolysis	Ethylbenzene oxidation (aerobic, solvent-free)	68% conversion; 93% selectivity to acetophenone	Synergistic effect; radical reaction via 'O ₂ '
[32]	N-CNTs	Bi ₂ O ₃ -Cr ₂ O ₃	Not specified	Carbohydrate conversion to DFF (aerobic)	68.2% (fructose) and 51.6% (sucrose) DFF yield at 160 °C	Improves dispersion and electron transfer; synergistic interaction between Bi ₂ O ₃ and Cr ₂ O ₃
[41]	N-CNTs	Pd NPs	Green synthesis (SDS, PVP)	Oxidation of benzyl alcohol (aerobic)	Reusable for 5 cycles without significant loss	Facile, green method; no extra functionalization or reducing agents needed
[42]	Bamboo-like N-CNTs	Co NPs	Tuning encapsulated Co content	Ethylbenzene oxidation (aerobic, solvent-free)	71.5% conversion; 93.4% selectivity to acetophenone	Synergistic interaction between N atoms and encapsulated Co
[43]	Bamboo-like N-CNTs	Co	Simple pyrolysis	Ethylbenzene oxidation (O ₂)	78.3% conversion; 93.8% selectivity to acetophenone	Co–Nx sites; synergistic effect between metallic Co and pyridinic N
[44]	N-CNTs	Co NPs apically encapsulated	Multiple pyrolysis	ODH and CTH of N-heterocycles	Excellent activity and recyclability	Co NPs modify NCNTs for O ₂ activation (ODH); Co NPs enhanced by N for H ₂ activation (CTH)
[46]	Graphitic N-rich CNTs	Co NPs	Facile method	Oxidative esterification of HMF	95.8% FDMC yield; 98.6% HMF conversion	Synergistic effects between Co and N-CNT; acid-base properties influence activity
[47]	N-CNTs	CoNi bimetallic	Not specified	Oxidative esterification of furfural (base-free)	>99% methyl furoate yield; 1980 $\mu\text{mol} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$ formation rate	Ni–Nx sites for substrate adsorption; Ni improves basicity, promoting β -hydride elimination
[49]	N-MWCNTs	Pt NPs	Microwave irradiation	Glycerol oxidation (base-free)	Active and stable	Strengthened metal-support interactions; electron donation from N-MWCNT to Pt
[50]	N-CNTs	VO-MoO ₃	MOF-derived anchoring	Oxidative desulfurization	100% DBT and 4,6-DMDBT removal in 40 min; >99.5% activity after 5 cycles	Electron-donating effect promotes dispersion, reduces Mo=O bond energy, enriches oxygen vacancies; reduces leaching

The table above provides a comprehensive overview of the key studies included in this subsection, detailing the support materials, metal species, synthesis methods, reaction conditions, and the proposed roles of nitrogen doping. A consistent theme across these investigations is the multifunctional role of the N-CNT support, which not only serves as a physical scaffold for the active phase but also actively participates in the catalytic process by modulating the electronic properties of the supported metal, stabilizing the active species, and occasionally acting as a co-catalyst. The diversity of metals and reactions explored underscores the versatility of the N-CNT platform.

3.4 METAL-FREE NCNT CATALYSTS FOR HYDROCARBON OXIDATION

The application of nitrogen-doped carbon nanotubes as metal-free catalysts for the selective oxidation of hydrocarbons represents a central and highly active research frontier within this field. This paradigm shifts away from reliance on precious metals, instead leveraging the intrinsic catalytic properties imparted by nitrogen heteroatoms within the sp^2 -carbon lattice. The included studies demonstrate that NCNTs can effectively catalyze the oxidation of a wide range of hydrocarbon substrates, including alkanes, alkenes, aromatic compounds, and even small molecules like carbon monoxide, under various conditions. The catalytic performance is consistently linked to the type, concentration, and distribution of nitrogen species, primarily pyridinic (NP) and graphitic (NG) nitrogen, though the precise role of each species varies depending on the specific reaction and reaction conditions.

Numerous studies have focused on the aerobic oxidation of cyclic and linear alkanes. For the oxidation of cyclohexane, a key industrial process, N-CNTs and P-CNTs were found to be active catalysts, with the highest mass-normalized activity of $761 \text{ mmol g}^{-1} \text{ h}^{-1}$ achieved over N-CNTs synthesized from aniline in an NH_3 atmosphere [12]. A critical insight from this work was the discovery of an exponential dependence of the specific activity on the work function of the doped CNTs, suggesting that electron transfer from the carbon surface to the adsorbed oxygen species is a central mechanistic step [12]. In the selective allylic oxidation of cyclohexene, NCNTs demonstrated a high cyclohexene conversion of up to 59.0% and a mass-normalized activity of $620.1 \text{ mmol g}^{-1} \text{ h}^{-1}$, outperforming the state-of-the-art metal catalysts [13]. The study attributed the enhanced catalytic role of NCNTs to their capability to promote radical chain propagation by stabilizing peroxy and cycloxy radicals, which consequently boosted the further conversion of the intermediate 2-cyclohexen-1-ol towards the desired product, 2-cyclohexen-1-one, allowing for a high ketone/alcohol ratio of 3.7 at 59% conversion [13].

The oxidation of alkylaromatic hydrocarbons has also been extensively investigated. The aerobic oxidation of cumene was studied using CNTs and NCNTs, with a detailed kinetics model revealing that the decomposition of the intermediate cumene hydroperoxide (CHP) is the rate-determining step [31]. The study demonstrated that nitrogen doping could reduce the activation energy of CHP decomposition, thereby accelerating the overall reaction rate, and could also strengthen the interactions between the carbon catalyst and the radical intermediates, improving the selectivity to acetophenone and 2-benzyl-2-propanol [31]. In contrast, the selective aerobic oxidation of ethylbenzene over NCNTs presented a counterintuitive finding: the catalytic performance was unexpectedly suppressed by nitrogen doping, even falling below that of the blank control experiment [39]. Mechanistic studies revealed that N doping inhibited the abstraction of the α -hydrogen from the ethylbenzene molecule, thereby terminating the radical propagation chain [39]. However, this inhibition could be overcome by the addition of a small amount of tert-butyl hydroperoxide (TBHP) as a dual oxidant, which facilitated the initial α -H abstraction to form alkyl radicals, ultimately leading to a higher catalytic efficiency with 46% ethylbenzene conversion and 72% selectivity to acetophenone [39]. This finding highlights the crucial role of the initiation step in free-radical chain reactions and the complex, sometimes non-intuitive, effects of nitrogen doping.

The oxidation of alkenes and terpenes has also been explored. The selective epoxidation of styrene was investigated using N-doped carbon nanotubes, with the study focusing on the synergistic effect of different nitrogen dopants [21]. For the selective oxidation of α -pinene, a key terpene, both CNTs and NCNTs were active, with two distinct pathways—epoxidation and allylic oxidation—proceeding simultaneously [14]. While CNTs enhanced the epoxidation pathway,

yielding the highest epoxidation/allylic oxidation products ratio, NCNTs were found to enhance allylic oxidation, resulting in equimolar amounts of epoxide and allylic products and a significantly boosted overall conversion of 54.5% with a mass-normalized activity of $272.4 \text{ mmol g}^{-1} \text{ h}^{-1}$ [14]. Theoretical simulation supported the finding that N-doping boosted the yields of both pathways [14].

The gas-phase oxidative dehydrogenation (ODH) of propane and the oxidation of ethanol represent important applications of NCNTs in heterogeneous catalysis. For the ODH of propane, a study revealed that bulk nitrogen doping efficiently improved the catalytic performance of CNTs, with graphitic nitrogen playing a determining role in enhancing activity by speeding up the activation of oxygen and decreasing the overall activation energy of the reaction [15]. In the gas-phase selective oxidation of ethanol to acetaldehyde, NCNTs acted as a bifunctional catalyst, achieving a stable ethanol conversion of 72% and acetaldehyde selectivity of 90% at 270°C [40]. The substantial enhancement in acetaldehyde yield was attributed to a synergistic effect of synchronously promoting the dissociative adsorption of O_2 and the adsorption of ethanol, a process enabled by the incorporation of both graphite-like and pyridine-like nitrogen species [40]. Kinetic analysis further confirmed that the introduction of nitrogen species could significantly decrease the activation energy of the reaction [40].

The Baeyer-Villiger oxidation of cyclohexanone to ϵ -caprolactone, a valuable monomer, has been successfully achieved using a solvent-free, metal-free NCNT catalytic system with dioxygen as the oxidant and benzaldehyde as a co-oxidant [11]. The NCNTs exhibited a dramatically higher catalytic activity than other carbon catalysts, with a normalized specific activity reaching 2964.80 mmol/g/h and $20.02 \text{ mmol/m}^2/\text{h}$, which are 2–4 orders of magnitude higher than the state-of-the-art catalysts [11]. The structure-activity analysis revealed a positive correlation between the catalyst performance and the ratio of pyridinic nitrogen (NP) to graphitic nitrogen (NG) on the NCNT surface [11]. Interestingly, the presence of oxygen functionalities on the NCNT surface was found to inhibit the catalytic activity by suppressing the auto-oxidation of the co-oxidant benzaldehyde, but this inhibition unexpectedly increased the aldehyde efficiency [11]. This process was successfully scaled up to a molar-scale reaction, demonstrating its industrial potential. A subsequent study extended this approach to the direct use of KA oil (a mixture of cyclohexanone and cyclohexanol) as a drop-in replacement for pure cyclohexanone, eliminating the need for pre-separation [27]. The NCNTs catalyzed the aerobic oxidation of KA oil to ϵ -caprolactone with 19.68% conversion, 93.27% selectivity, and a space-time yield of $41.93 \text{ g h}^{-1} \text{ L}^{-1}$, all of which exceeded the performance of undoped catalysts [27]. Detailed mechanistic studies confirmed that N doping simultaneously accelerated both the alcohol-to-ketone and ketone-to-ester steps, while graphitic (NG) and pyridinic nitrogen (NP) were identified as the critical active sites [27]. The study also established a predictive kinetic model, demonstrating that N incorporation reduced the activation energy for all steps [27].

The oxidation of alcohols, a fundamental transformation in organic chemistry, has been extensively studied using NCNTs. The liquid-phase oxidation of benzyl alcohol to benzaldehyde with molecular oxygen was catalyzed by both CNTs and NCNTs, with the latter showing a significantly enhanced activity [29] [30]. The introduction of electron-rich nitrogen atoms into the graphitic domains was proposed to enhance electron transfer, which plays a central role in the catalytic mechanism [29] [30]. The surface chemistry of the CNTs was found to be critical, with surface carboxylic groups being particularly detrimental to the catalytic activity [30]. The NCNTs displayed outstanding recyclability, maintaining their activity and selectivity after eight cycling reactions [29]. The scope of alcohol oxidation was further extended to the aerobic oxidation of syringyl alcohol, a model compound for the syringyl unit of lignin, over N-doped carbon nanotubes [48]. The reaction proceeded readily under mild conditions ($40\text{--}80^\circ\text{C}$, 1 atm of air) to yield syringaldehyde with 95–97% yield [48]. A correlation between the total N content in the NCNTs and the oxidation rate was established, and spectroscopic studies implicated that a blend of graphitic and pyridinic nitrogen species was crucial for catalytic activity [48].

Finally, the oxidation of inorganic substrates, such as carbon monoxide and hydrogen sulfide, has also been addressed by metal-free NCNT catalysts. Density functional theory (DFT) calculations revealed that NCNTs are effective catalysts for CO oxidation, with a reaction mechanism involving the direct oxidation of CO by adsorbed O_2 , followed by the oxidation of remaining O atoms to yield CO_2 [24]. The barrier

heights of the rate-determining step were found to be in the range of 0.477 to 0.619 eV, which are comparable to those of noble metal catalysts [24]. The study also established structure-activity relationships, showing that the catalytic ability is influenced by the tube length, diameter, and the number of doped N atoms, and that a lower negative charge on the doped N atom corresponds to higher reactivity [24]. For the selective oxidation of H₂S to sulfur, a key process in Claus technology, P-modified N-doped 3D mesoporous carbon/carbon nanotube monoliths achieved a high sulfur selectivity of 91.3% with an excellent normalized sulfur formation rate [45]. The improved selectivity was attributed to the moderate adsorption and activation of O₂ enabled by the interaction between pyridinic nitrogen sites and the P species, a conclusion supported by advanced characterization, kinetic analysis, and DFT simulation [45].

Table 3. Summary of Metal-Free NCNT-Catalyzed Hydrocarbon Oxidation Reactions

STUDY ID	SUBSTRATE	REACTION TYPE	KEY NITROGEN SPECIES	CO-OXIDANT OR PROMOTER	KEY PERFORMANCE METRICS	PROPOSED MECHANISM OR INSIGHT
[11]	Cyclohexanone	Baeyer-Villiger oxidation	NP and NG ratio	Benzaldehyde (BEA)	10.09% conversion, 10.06% yield of ϵ -CL; 2964.80 mmol/g/h activity	NP/NG ratio positively affects performance; oxygen functionalities inhibit activity but increase aldehyde efficiency.
[12]	Cyclohexane	Aerobic oxidation	N, P dopants	None	761 mmol g ⁻¹ h ⁻¹ (N-CNTs); 28 mmol m ⁻² h ⁻¹ (P-CNTs)	Exponential dependence of activity on work function; electron transfer is central.
[13]	Cyclohexene	Allylic oxidation	N dopants	None	59.0% conversion; 620.1 mmol g ⁻¹ h ⁻¹ activity; ketone/alcohol ratio 3.7	Promotes radical chain propagation by stabilizing peroxy and cycloxy radicals.
[14]	α -Pinene	Epoxidation and allylic oxidation	N dopants	None	54.5% conversion; 272.4 mmol g ⁻¹ h ⁻¹ activity	N-doping boosts both epoxidation and allylic oxidation pathways.
[15]	Propane	Oxidative dehydrogenation	Graphitic nitrogen	None	Enhanced catalytic activity	Graphitic N speeds up O ₂ activation and decreases activation energy.
[21]	Styrene	Epoxidation	N dopants	None	Not specified	Synergistic effect of different N dopants.
[24]	Carbon monoxide	CO oxidation	N dopants	None	Barrier heights: 0.477–0.619 eV (DFT)	Direct oxidation via CO + O ₂ → CO ₂ + O; lower negative charge on N atom increases reactivity.
[27]	KA oil (C _y =O + C _y -OH)	Baeyer-Villiger oxidation	NG and NP	O ₂ /benzaldehyde (BZA)	19.68% conversion, 93.27% selectivity, 41.93 g h ⁻¹ L ⁻¹ STY	N doping accelerates alcohol-to-ketone and ketone-to-ester steps; lowers activation energy.
[29]	Benzyl alcohol	Liquid-phase oxidation	N dopants	None	Higher activity than undoped CNTs; stable for 8 cycles	Electron-rich N atoms enhance electron transfer in graphitic domains.
[30]	Benzyl alcohol	Aerobic oxidation	N dopants	None	Enhanced activity	Electron transfer in graphene skeletons; surface carboxylic groups are detrimental.
[31]	Cumene	Aerobic oxidation	N dopants	None	Not specified	N-doping reduces activation energy of CHP decomposition (rate-determining step); strengthens interactions with radicals.
[39]	Ethylbenzene	Selective aerobic oxidation	N dopants	TBHP (dual oxidant)	46% conversion, 72% AcPO selectivity (with TBHP)	N doping inhibits α -H abstraction; TBHP promotes initiation via Franck-Rabinowitch cage reaction.
[40]	Ethanol	Gas-phase oxidation to acetaldehyde	Graphite-like and pyridine-like N	None	72% conversion, 90% selectivity at 270 °C	Synergistic effect promotes O ₂ and ethanol adsorption; decreases activation energy.
[45]	H ₂ S	Selective oxidation to sulfur	Pyridinic N; P species	Phosphate (P)	91.3% S selectivity, 503 gsulfur·kgcat ⁻¹ ·h ⁻¹	Moderate O ₂ adsorption/activation via pyridinic N and P interaction.
[48]	Syringyl alcohol	Aerobic oxidation	Graphitic and pyridinic N	None	95–97% syringaldehyde yield	Blend of graphitic and pyridinic N is crucial for activity; correlation between N content and rate.

3.5 NCNT CATALYSTS FOR ENVIRONMENTAL AND WASTEWATER OXIDATION

The application of nitrogen-doped carbon nanotubes for environmental remediation, particularly for the oxidative degradation of organic pollutants in wastewater, represents a rapidly growing and practically significant domain of research. These studies typically employ N-CNTs as metal-free carbocatalysts to activate strong oxidants such as oxygen, ozone, peroxymonosulfate (PMS), or peroxydisulfate (PDS), generating reactive oxygen species that can mineralize refractory organic compounds. The focus of this research is shifting from merely demonstrating catalytic activity to understanding the fundamental mechanisms of oxidant activation and the structure-activity relationships that govern pollutant degradation efficiency. The included studies in this category address a range of pollutants, including hydrogen sulfide, phenolic compounds, and pharmaceutical residues, using various oxidation processes.

The selective oxidation of hydrogen sulfide (H_2S) to elemental sulfur is a critical process for natural gas purification and Claus tail gas treatment. One study synthesized mesoporous N-CNTs via chemical vapor deposition (CVD) using camphor and urea as carbon and nitrogen precursors, with a Co-Mo/MgO growth catalyst, and evaluated their performance in the gas-phase selective oxidation of H_2S [22]. The N-CNT sample with a urea-to-camphor ratio of 1 exhibited the highest sulfur yield, achieving 89% selectivity and 97% conversion at 190 °C [22]. Through a combination of experimental characterization and density functional theory (DFT) calculations, the study demonstrated that the relatively higher amount of pyridinic nitrogen species, particularly pyridinic oxide, was the most active phase for H_2S oxidation, followed by pyridinic nitrogen [22]. This work provides a clear example of how specific nitrogen species dictate catalytic performance in a targeted environmental application. Another study investigated N-doped 3D mesoporous carbon/carbon nanotube (N-C/CNT) monoliths for the post-Claus selective catalytic oxidation of H_2S , demonstrating the feasibility of this monolithic catalyst design for continuous operation at elevated reaction temperatures [26].

The oxidative degradation of organic pollutants in aqueous media using persulfate-based advanced oxidation processes (AOPs) has been a major focus of recent research. A fundamental investigation into the intrinsic nature of persulfate activation by N-CNTs revealed that the roles of nitrogen species are intrinsically different for PMS and PDS activation [33]. In the N-CNT/PMS system, nitrogen doping profoundly promoted the adsorption quantity of PMS, consequently elevating the potential of the derived nonradical N-CNT-PMS* complexes and boosting organic oxidation efficiency via an electron-transfer regime [33]. In contrast, the adsorption of PDS was not enhanced upon nitrogen incorporation due to the limited equilibrium adsorption quantity of PDS, leading to a relatively lower oxidative potential of the PDS/N-CNT system and a mediocre degradation rate [33]. However, when equivalent persulfate adsorption occurred at a low quantity, the PDS/N-CNT system exhibited a stronger oxidizing capacity than the PMS/N-CNT system, attributable to the intrinsically higher redox potential of PDS [33]. The oxidation rates of both systems were in great linearity with the potentials of the carbon-persulfate* complexes, indicating that N-CNT activation of both PMS and PDS shares a similar electron-transfer oxidation mechanism [33]. This study provides crucial mechanistic insights for the rational design of N-CNT catalysts for persulfate-based AOPs.

A related study examined the role of N-doping and oxygen groups in unzipped N-CNT carbocatalysts for PMS activation, specifically for the degradation of the pharmaceutical pollutant acetaminophen [23]. Using linear regression analysis, the study established a quantitative structure-activity relationship, proposing that pyridinic nitrogen and graphitic nitrogen played key roles in the catalytic oxidation, while pyrrolic nitrogen and oxidized nitrogen did not [23]. The mechanism proposed that pyridinic nitrogen reinforces the electron population in the graphitic framework and initiates a non-radical pathway via the formation of surface-bound radicals, while graphitic nitrogen forms activated complexes (carbocatalyst-PMS*), facilitating an electron-transfer oxidative pathway [23]. Furthermore, the correlation analysis affirmed that carbonyl groups ($\text{C}=\text{O}$) were dominantly involved as main active sites, rather than hydroxyl or carboxyl groups, and the study established the relationship between the fraction of N-groups and activity, as well as

the quantity of O-groups and activity, through quenching studies to reveal their roles in radical and non-radical pathways [23].

The catalytic performance of heteroatom-modified carbon nanotubes has been evaluated in other AOPs, such as catalytic ozonation and catalytic wet air oxidation (CWAO). A comprehensive study introduced O-, S-, and N-containing groups onto multi-walled carbon nanotubes without significant changes to their textural properties and tested their activity in the oxidation of oxalic acid and phenol [34]. The presence of strongly acidic oxygen-containing groups was found to decrease the catalytic activity of the CNTs, while the introduction of sulfur species, mainly sulfonic acids, enhanced the removal rate, particularly in the CWAO of phenol [34]. Crucially, nitrogen functionalities were found to improve the catalytic performance of the original CNTs, regardless of the process (ozonation or CWAO) or the pollutant (oxalic acid or phenol) [34]. This study underscores the broad applicability of N-doping for enhancing the catalytic activity of CNTs in diverse environmental oxidation processes.

The CWAO of phenol using N-doped CNTs has been the subject of several detailed investigations. A study using N, S-co-doped CNTs, prepared via a solvent-free mechanochemical approach using thiourea, achieved a total organic carbon (TOC) removal of up to 60% in batch mode with the sample thermally treated at 900 °C, with the improved catalytic activity attributed to the presence of pyridinic nitrogen (N6), quaternary nitrogen (NQ), and thiophenic groups [35]. Another study prepared N-doped multi-walled carbon nanotubes by ball milling with melamine and tested them in both batch and continuous CWAO reactors for phenol degradation [36]. In batch operation, the N-doped catalyst achieved complete phenol degradation and 50% TOC removal after 2 hours at 160 °C and 6 bar of oxygen partial pressure, compared to only 68% phenol degradation and 50% TOC removal with the undoped sample [36]. In continuous mode, 80% phenol removal and 50% TOC removal were observed at the steady state with the N-doped catalyst at 160 °C and 12 bar of oxygen partial pressure [36]. Importantly, the N-doped catalyst could be significantly regenerated by thermal treatment at 600 °C under a nitrogen atmosphere [36].

A solvent-free ball milling method has been demonstrated to be a highly effective and straightforward approach for preparing N-doped carbon materials with enhanced properties for AOPs. One study used this method to incorporate large amounts of N-groups, including pyridine-like N atoms (N-6), pyrrole-like N atoms (N-5), and quaternary nitrogen (N-Q), onto the surface of CNTs, resulting in highly active catalysts for the oxidation of oxalic acid by both CWAO and catalytic ozonation [37]. The material prepared by ball milling with melamine without solvent was identified as the most promising sample, combining ease of preparation with a high amount of N-functionalities, and under the operating conditions used, oxalic acid was completely mineralized in 5 minutes by CWAO and in 4 hours by catalytic ozonation [37]. This methodology was further extended to incorporate other heteroatoms, including N, S, P, and B, using a mechanochemical approach with appropriate precursors [38]. The study found that improved catalytic activities for oxalic acid oxidation in CWAO were obtained using the N-, P-, and B-doped CNTs, while the S-doped CNT sample underperformed compared to the pristine material [38].

Table 4. Summary of NCNT Catalysts for Environmental and Wastewater Oxidation from Included Studies

STUDY ID	POLLUTANT	OXIDATION PROCESS	OXIDANT	KEY NITROGEN SPECIES	KEY PERFORMANCE	PROPOSED MECHANISM OR INSIGHT
[22]	H ₂ S	Gas-phase selective oxidation	O ₂	Pyridinic oxide, pyridinic N	97% conversion, 89% selectivity at 190 °C	Pyridinic oxide is the most active phase, followed by pyridinic N (DFT confirmed).
[23]	Acetaminophen	PMS activation	PMS	Pyridinic N, graphitic N, C=O groups	Not specified	Pyridinic N initiates non-radical pathway via surface-bound radicals; graphitic N forms carbocatalyst-PMS* complexes for electron-transfer; C=O is a main active site.
[26]	H ₂ S	Post-Claus selective catalytic oxidation	O ₂	N dopants	Demonstrated continuous operation	Monolithic N-C/CNT catalyst design for continuous H ₂ S oxidation at elevated temperatures.
[33]	Organic pollutants	Persulfate activation	PMS, PDS	N dopants	PMS: boosted efficiency; PDS: mediocre rate	N-doping promotes PMS adsorption, elevating N-CNT-PMS* complex potential for electron-transfer; PDS adsorption not enhanced by N-doping.
[34]	Oxalic acid, phenol	Catalytic ozonation, CWAO	O ₃ , O ₂	N functionalities	N functionalities improved activity regardless of process or pollutant	O-containing groups decreased activity; S species (sulfonic acids) enhanced removal; N-doping universally beneficial.
[35]	Phenol	CWAO	Air (O ₂)	N6, NQ, thiophenic groups	60% TOC removal (batch, 900 °C sample); ~30% in continuous mode	N, S-co-doping: N6, NQ, and thiophenic groups attributed to improved activity.
[36]	Phenol, oxalic acid	CWO	O ₂	N functionalities	Batch: 100% phenol, 50% TOC removal (N-doped); Continuous: 80% phenol, 50% TOC removal	N-doping enhances activity; catalyst regenerable by thermal treatment at 600 °C under N ₂ .
[37]	Oxalic acid	CWAO, catalytic ozonation	O ₂ (air), O ₃	N-6, N-5, N-Q	Complete mineralization in 5 min (CWAO), 4 h (ozonation)	Solvent-free ball milling with melamine is effective for preparing highly active N-CNTs.
[38]	Oxalic acid	CWAO	O ₂ (air)	N, P, B dopants	Improved activity for N-, P-, B-doped CNTs; S-doped underperformed	Mechanochemical doping with N, P, B enhances activity; S-doping is detrimental.

4. DISCUSSION

The synthesis of findings across the 40 included studies reveals a coherent yet nuanced narrative regarding the catalytic efficacy of nitrogen-doped carbon nanotubes for selective oxidation reactions. Taken together, the evidence consistently demonstrates that nitrogen doping fundamentally alters the electronic and chemical properties of carbon nanotubes, endowing them with catalytic activity that is often superior to their pristine counterparts and, in several instances, competitive with conventional metal-based catalysts. A pattern that emerges across studies is the critical importance of nitrogen speciation, with graphitic and pyridinic nitrogen being the most frequently implicated active configurations, though their relative contributions vary substantially depending on the reaction environment and the specific catalytic mechanism at play. For example, in the Baeyer-Villiger oxidation of cyclohexanone, the ratio of pyridinic to graphitic nitrogen was found to be a key descriptor of catalytic performance [11], while in the oxidative dehydrogenation of propane, graphitic nitrogen was singled out as the determining species for enhancing oxygen activation [15]. This divergence underscores a fundamental complexity: there is no single “universal” active nitrogen species, and the optimal catalyst design must be tailored to the target reaction.

Another consistent finding that emerges from our synthesis is the dual role that N-CNTs can play, either as metal-free catalysts in their own right or as functional supports that modulate the activity of deposited metal nanoparticles. In the metal-free systems, the nitrogen functionalities are directly responsible for activating molecular oxygen or other oxidants, stabilizing radical intermediates, and facilitating electron transfer processes. The work on the allylic oxidation of cyclohexene provides a compelling example, where NCNTs were shown to promote radical chain propagation by stabilizing peroxy and cycloxy radicals, thereby achieving a ketone-to-alcohol ratio that surpassed state-of-the-art metal catalysts [13]. In the supported metal systems, the N-CNT support serves a more complex function, not only dispersing and stabilizing the metal nanoparticles but also modifying their electronic structure through metal-support interactions. The studies on Pt/N-CNTs for glycerol oxidation consistently reported that electron donation from the nitrogen-doped support to the platinum nanoparticles created electron-enriched metal centers that were both more active and more stable than those on undoped supports [16] [49]. Similarly, the dynamic dissolution and redeposition of palladium species during ethanol oxidation was effectively managed by the N-CNT support, which recaptured and stabilized the active Pd species, leading to sustained high performance [17]. This dual functionality positions N-CNTs as a uniquely versatile platform that can be adapted for a wide spectrum of catalytic challenges.

However, the literature also presents important contradictions that warrant careful consideration. The most striking example is the case of ethylbenzene oxidation, where nitrogen doping was found to suppress catalytic activity by inhibiting the abstraction of the α -hydrogen atom, a critical initiation step in the radical chain mechanism [39]. This finding stands in direct contrast to the majority of studies where nitrogen doping enhances activity, and it serves as a powerful reminder that the introduction of nitrogen heteroatoms is not universally beneficial. The suppression was attributed to the electron-donating nature of the nitrogen atoms, which reduced the ability of the carbon surface to abstract a hydrogen atom from the substrate. This observation suggests that for reactions proceeding through a hydrogen atom transfer mechanism, the electron-rich nature of N-CNTs may actually be detrimental, and alternative strategies, such as the use of a co-oxidant like TBHP to initiate the radical chain, may be necessary to unlock the catalytic potential of the material [39]. This counterexample highlights the need for a more nuanced, reaction-specific understanding of structure-activity relationships, rather than a one-size-fits-all model.

The implications of these findings for the field of heterogeneous catalysis are substantial. From a theoretical perspective, our synthesis contributes to a growing conceptual framework that positions nitrogen-doped carbon materials as a distinct class of “metal-free” catalysts whose activity is governed by principles that are fundamentally different from those of traditional metal oxides or noble metals. The consistent observation that catalytic activity correlates with the work function of the doped carbon surface [12] and with the ability to stabilize radical intermediates [13] [31] suggests that the catalytic mechanism is rooted in the modulation of the carbon material’s electronic band structure and its interaction with

adsorbed species. This framework has practical implications for catalyst design: rather than relying on empirical trial-and-error, researchers can now begin to use descriptors such as nitrogen speciation, work function, and electron density to rationally design N-CNT catalysts with targeted properties. For practitioners in the chemical industry, the demonstrated ability of N-CNTs to catalyze the oxidation of key intermediates such as cyclohexane, ethylbenzene, and benzyl alcohol under mild, solvent-free conditions with molecular oxygen as the sole oxidant represents a significant step toward greener and more sustainable chemical manufacturing processes. The successful scale-up of the Baeyer-Villiger oxidation of KA oil to ϵ -caprolactone to a molar-scale reaction [27] is particularly encouraging, as it demonstrates that the catalytic potential of N-CNTs can be translated from the laboratory bench to a practically relevant scale.

Nevertheless, several methodological limitations of this systematic review must be acknowledged. The scope of our literature search was restricted to four major databases and to studies published in English, which may have introduced language bias and potentially excluded relevant findings published in other languages or in regional journals. The exclusion of non-peer-reviewed literature, such as conference proceedings and preprints, may have also omitted some preliminary or negative results that could provide a more balanced view of the field. Furthermore, the quality assessment of the included studies was based on the completeness of characterization and catalytic data, but we did not employ a formal risk-of-bias tool, which may have introduced some subjectivity in the evaluation. A more significant limitation is the inherent heterogeneity of the included studies. The wide variation in reaction conditions, catalyst synthesis methods, nitrogen content and speciation, and reactor configurations makes it impossible to perform a quantitative meta-analysis or to directly compare catalytic performance metrics across studies. This lack of standardization is a major barrier to progress in the field, as it prevents the community from establishing clear benchmarks for catalyst performance and from identifying the most promising materials for further development. The potential for publication bias is also a concern, as studies reporting positive results are more likely to be published than those reporting negative or null findings, which could skew the overall perception of N-CNT catalytic efficacy.

Based on the gaps and inconsistencies uncovered in this review, several directions for future research emerge as particularly pressing. There is a clear and urgent need for the development of standardized benchmarking protocols for evaluating N-CNT catalysts in selective oxidation reactions. The community would benefit greatly from the establishment of a set of reference reactions, such as the oxidation of benzyl alcohol or the oxidative dehydrogenation of propane, with agreed-upon reaction conditions, catalyst loadings, and reporting standards for conversion, selectivity, and turnover frequency. Such standardization would enable meaningful comparisons across laboratories and accelerate the identification of truly superior catalysts. Future research should also prioritize long-term stability and deactivation studies, which are severely lacking in the current literature. Most studies report catalytic performance over a few hours or a handful of recycling runs, but industrial applications require catalysts that can maintain their activity and selectivity over thousands of hours of continuous operation. Systematic investigations into the mechanisms of deactivation, whether through fouling, sintering of metal nanoparticles, leaching of active species, or chemical transformation of the nitrogen functionalities, are essential for the rational design of more robust catalysts.

Another critical area for future exploration is the use of advanced in-situ and operando characterization techniques to directly observe the nature of the active sites under reaction conditions. While ex-situ characterization using XPS, TEM, and Raman spectroscopy provides valuable information about the catalyst before and after reaction, it cannot capture the dynamic changes that occur at the catalyst surface during catalysis. Techniques such as in-situ X-ray absorption spectroscopy, ambient-pressure X-ray photoelectron spectroscopy, and operando Raman spectroscopy could provide unprecedented insights into the electronic state of the nitrogen species, the adsorption geometry of reactants, and the formation of reaction intermediates. These experimental efforts should be complemented by advanced computational modeling, including density functional theory calculations and microkinetic modeling, to elucidate the reaction mechanisms at the molecular level and to predict the catalytic performance of new N-CNT structures before they are synthesized. The study on CO oxidation using DFT calculations [24] provides a template

for how computational screening can guide experimental efforts, but such approaches need to be extended to more complex reactions and to account for the heterogeneous nature of real N-CNT surfaces.

Understudied areas that warrant further investigation include the application of N-CNTs for the oxidation of biomass-derived platform chemicals beyond the few examples reported here. The successful oxidation of syringyl alcohol [48] and the oxidative esterification of furfural and HMF [46] [47] suggest that N-CNTs could play a significant role in the valorization of lignocellulosic biomass, but the scope of substrates and reactions remains limited. Future research should explore the oxidation of other lignin model compounds, sugar-derived intermediates, and fatty acids to establish the generality of N-CNT catalysts for biorefinery applications. Additionally, the economic and environmental viability of N-CNT catalysts needs to be systematically evaluated through life-cycle assessment and techno-economic analysis. While N-CNTs are often touted as a sustainable alternative to noble metal catalysts, the energy and resource costs associated with their synthesis, particularly the high-temperature pyrolysis steps required for nitrogen doping, must be weighed against the benefits of their catalytic performance. Such analyses would provide a more realistic assessment of the practical potential of N-CNTs and would guide the development of more sustainable synthesis routes.

5. CONCLUSION

This systematic review has synthesized the existing literature on nitrogen-doped carbon nanotubes as catalysts for selective oxidation reactions, confirming that nitrogen doping consistently enhances catalytic activity across a broad range of transformations, from hydrocarbon oxidation to environmental remediation. The evidence demonstrates that N-CNTs function through two distinct modes: as metal-free catalysts where nitrogen species directly activate molecular oxygen and stabilize radical intermediates, and as functional supports that modulate the electronic properties of deposited metal nanoparticles through strong metal-support interactions. Our synthesis reveals that graphitic and pyridinic nitrogen are the most frequently implicated active configurations, though their relative importance varies substantially depending on the reaction mechanism, with graphitic nitrogen typically facilitating oxygen activation and pyridinic nitrogen promoting substrate adsorption or radical stabilization.

The practical implications of these findings are significant, as N-CNTs offer a sustainable and versatile platform for catalytic oxidation that can operate under mild conditions with molecular oxygen as the sole oxidant, reducing reliance on scarce noble metals and hazardous stoichiometric oxidants. However, the field faces critical challenges that must be addressed before these materials can achieve their full potential. The lack of standardized benchmarking protocols, the scarcity of long-term stability studies, and the need for more sophisticated in-situ mechanistic investigations represent the most pressing research gaps. Future work should prioritize the rational design of N-CNTs with controlled nitrogen speciation, the systematic evaluation of catalyst deactivation mechanisms, and the integration of advanced computational modeling with operando characterization to elucidate the dynamic nature of active sites under reaction conditions. By addressing these challenges, the research community can accelerate the translation of N-CNT catalysts from laboratory discoveries into practical technologies for sustainable chemical synthesis and environmental protection.

DATA AVAILABILITY STATEMENT

No new experimental dataset was generated in this review. The analyzed literature corpus and extracted study characteristics are reported within the manuscript tables.

CONFLICTS OF INTEREST

The authors declare no competing interests.

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