

Babeş-Bolyai University
Faculty of Chemistry and Chemical Engineering

Abstract of the Ph.D. Thesis

***ACTIVATION OF MOLECULAR NITROGEN AT
(BIO)INORGANIC CENTERS***

Ph.D. Student

Rami A. Doukeh

Scientific advisor:

Prof. Dr. Radu-Lucian Silaghi-Dumitrescu

Cluj-Napoca, 2026

CONTENTS OF THE DOCTORAL THESIS

1	INTRODUCTION	1
1.1.	The Role of Iron in N ₂ Activation: Insights from Enzymatic and Model Systems	1
1.2.	Exploring the Role of Non-Biological Transition Metals in Nitrogen Fixation Chemistry	4
1.3.	Innovations in Materials for Photocatalytic N ₂ Fixation	6
1.4.	Objectives, Scope, and Original Contributions of the Present Thesis	8
2	COMPUTATIONAL MODELING OF DINITROGEN ACTIVATION ON TRANSITION METAL CENTERS	11
2.1.	Effect of the coordination environment on the ability of iron to bind/activate N ₂ : a theoretical study with relevance to the nitrogenase mechanism	12
2.1.1.	Computational Setup for Fe–N ₂ models with Tunable Coordination Environments	12
2.1.2.	Energetic and Geometrical Properties of Octahedral Fe–N ₂ Models	14
2.1.2.1.	Energetics of octahedral Fe–N ₂ models	14
2.1.2.2.	Geometries of octahedral Fe–N ₂ models	16
2.1.3.	Molecular Orbital Analysis of Octahedral Fe–N ₂ Models	21
2.1.4.	N ₂ Binding Energies in octahedral Fe–N ₂ Models	23
2.1.5.	Tetrahedral Fe–N ₂ Models as Nitrogenase Mimics	25
2.1.6.	Dynamics calculations	27
2.2.	An iron-free nitrogenase? Computational estimation of the ability to bind/activate N ₂ in manganese and cobalt complexes	28
2.2.1.	Computational Setup for Mn–N ₂ and Co–N ₂ Complexes with Controlled Coordination Environments	28
2.2.2.	Energetic and Structural Features of Co and Mn–N ₂ models	30
2.2.3.	N–N Bond Activation and Orbital Interactions in Mn and Co models	34
2.2.4.	Energy Decomposition and Ligand Effects: Insights from ETS-NOCV and EDA-SBL	40
2.3.	Conclusions	43
3	CATALYTIC ACTIVATION OF MOLECULAR NITROGEN BY ENZYME-INSPIRED METAL-ORGANIC CATALYSTS	45
3.1.	Materials and Methods	46
3.1.1.	Materials	46
3.1.2.	Preparation of Zero-Valent Fe/Co/Ru Photocatalysts Supported on CNTs and g-C ₃ N ₄	47
3.1.3.	Preparation of electrode and Electrochemical measurement	48
3.1.4.	Photocatalytic NRR measurements	48
3.2.	Photocatalyst Characterization	52
3.3.	Results and discussion	53
3.3.1.	X-ray diffraction (XRD)	53
3.3.2.	SEM–EDS Analysis	57
3.3.3.	TGA-DTG Analysis:	62
3.3.4.	N ₂ adsorption–desorption isotherms	63

3.3.5.	UV–Vis diffuse reflectance spectra (DRS)	65
3.3.6.	X-ray photoelectron spectroscopy (XPS)	67
3.3.7.	Electron paramagnetic resonance (EPR)	69
3.3.8.	Electrochemical experiments	71
3.3.9.	Photocatalytic Efficiency of Nitrogen Reduction Reaction (NRR)	75
3.3.9.1.	Photocatalytic NRR Performance of Fe- and Co-Based Catalysts	75
3.3.9.2.	DFT rationalization of the experimental differences in activity with Fe vs. Co catalysts	81
3.3.9.3.	Photocatalytic NRR Performance of Ru-Based Catalysts	87
3.3.9.4.	DFT rationalization of the reactivity of the Ru catalysts	92
3.4.	Conclusions	102
4	General conclusions	103
5	List of scientific contributions	105
5.1.	Articles on which the thesis is based:	105
5.2.	Articles related to the topic of the thesis	105
5.3.	Contributions at scientific conferences	105
6	References	106
7	Appendix	119

1. INTRODUCTION

The activation of molecular nitrogen (N_2) remains a fundamental challenge due to the exceptional stability of the $\text{N}\equiv\text{N}$ bond [1,2]. This transformation is essential for ammonia production, a key compound in both chemical industry and emerging sustainable energy systems. In nature, nitrogenase enzymes achieve this process under mild conditions through iron–sulfur clusters that provide unique electronic environments for N_2 coordination and reduction (Figure 1) [3-6], inspiring the development of synthetic catalytic systems.

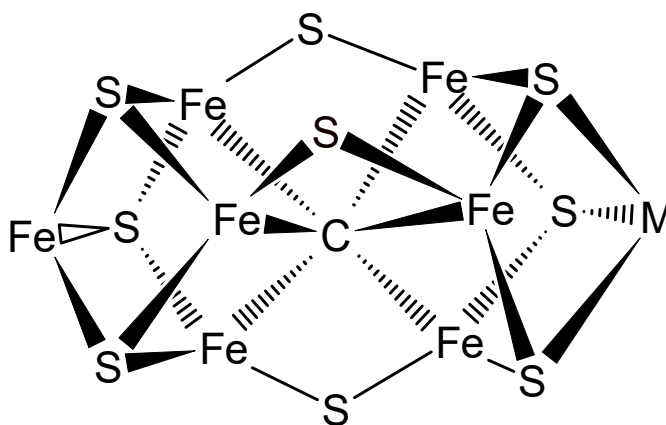


Figure 1. Structural models of nitrogenase cofactors [4]. “M” denotes Mo, V or Fe. The sulfur shown in grey may be replaced by other ligands, such as carbonate.

A central issue in nitrogen fixation is understanding the role of transition metals, particularly iron, in N_2 activation. While synthetic complexes indicate that low-valent metal centers favor N_2 binding through π -backdonation, biological nitrogenases often operate at higher oxidation states. This discrepancy raises important mechanistic questions regarding whether enzymatic systems follow pathways similar to synthetic models or rely on fundamentally different electronic structures. The involvement of hydride species and multi-electron/proton accumulation further complicates the mechanistic picture [4,7].

Significant progress has been made in designing transition metal complexes capable of activating dinitrogen, including systems based on Fe, Mo, Co, Ru, and Mn. Although these systems provide valuable insights into metal–nitrogen interactions, their catalytic efficiencies remain limited compared to biological systems. This highlights the need for improved understanding of the relationship between metal oxidation state, ligand environment, and electron transfer processes.

In parallel, heterogeneous photocatalytic approaches have emerged as promising alternatives for sustainable ammonia synthesis. Materials such as metal oxides, doped

semiconductors, and carbon-based supports (e.g., g-C₃N₄ and carbon nanotubes) offer tunable electronic properties and enhanced charge transfer capabilities. However, their performance is often restricted by low quantum efficiency, weak N₂ adsorption, and rapid charge recombination. Strategies such as heteroatom doping, defect engineering, and heterojunction formation have been proposed to address these limitations.

Despite these advances, the fundamental principles governing nitrogen activation remain only partially understood, particularly regarding the interplay between electronic structure and catalytic activity. Addressing these challenges is essential for the rational design of efficient catalysts.

The present thesis tackles these issues through a combined computational and experimental approach. Density functional theory (DFT) calculations are used to investigate the ability of transition metals (Fe, Mn, Co, Ru) to activate N₂, highlighting the importance of low-valent states and electron-rich environments. Based on these insights, nanostructured catalysts supported on carbon materials such as carbon nanotubes and g-C₃N₄ are synthesized and evaluated as photocatalysts under visible light.

A particular focus is placed on iron, cobalt and ruthenium-based systems supported on carbon materials, addressing a gap in current research. Overall, this work contributes to identifying key electronic factors governing N₂ activation and to the development of efficient catalytic systems, bridging theoretical understanding with experimental validation.

2. COMPUTATIONAL MODELING OF DINITROGEN ACTIVATION ON TRANSITION METAL CENTERS

This chapter presents a computational investigation of molecular nitrogen (N₂) activation at transition metal centers, with a primary focus on iron systems relevant to nitrogenase chemistry. The activation of N₂ under mild conditions remains a major challenge due to the stability of the N≡N bond, and understanding the role of metal centers, oxidation states, and ligand environments is essential for elucidating this process.

A density functional theory (DFT) approach was employed to examine the intrinsic ability of transition metals to bind and activate dinitrogen. Iron was selected as the main system of study due to its central role in nitrogenase enzymes, while manganese and cobalt were also considered for comparison. Simplified mononuclear complexes were used to allow systematic variation of structural and electronic parameters, including oxidation state, spin multiplicity, and ligand identity.

2.1. Effect of the coordination environment on the ability of iron to bind/activate N₂: a theoretical study with relevance to the nitrogenase mechanism

The models were based on complexes of the general form Fe(H₂O)₄(R)(N₂), in which the ligand R was varied to represent different electronic environments. The coordination geometry was defined such that N₂ occupies a position trans to the R ligand, enabling evaluation of ligand effects without direct interaction between R and N₂ (Figure 2) [8].

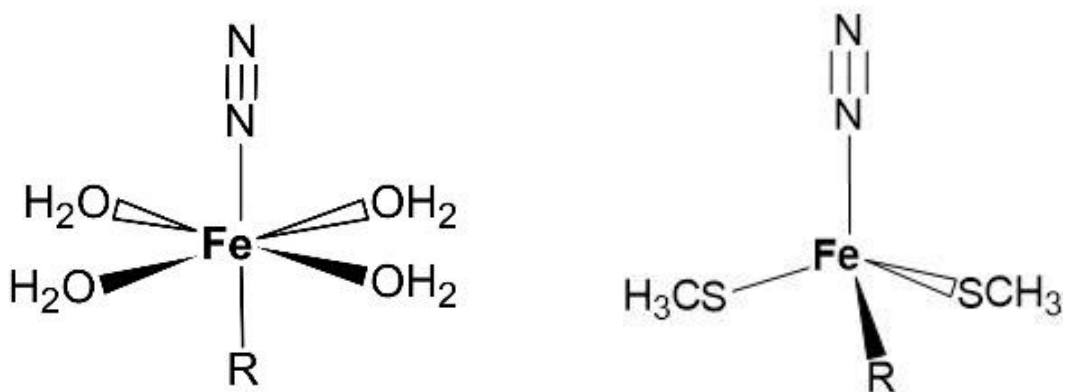


Figure 2. Structures of the Fe(H₂O)₄RN₂ octahedral and Fe(SCH₃)₂RN₂ tetrahedral (R = H₂O, OH⁻, CH₃⁻, CH₂²⁻, H₂S, H⁻) models employed in the present study.

The ligand set includes H₂O as a neutral reference, OH⁻ to represent deprotonated environments, H₂S as a softer donor ligand, and CH₃⁻ and CH₂²⁻ as strongly electron-donating carbon-based ligands. These ligands were selected to represent a range of coordination environments, from biologically relevant oxygen- and sulfur-based donors to highly electron-rich systems that approximate the influence of carbide ligands in nitrogenase active sites.

The computational setup involved variation of the formal oxidation state of iron from 0 to +3, with multiple spin states considered for each configuration. This allowed for a systematic exploration of the electronic factors that govern N₂ binding across different redox and spin conditions. The use of simplified mononuclear complexes enabled direct comparison between systems and facilitated identification of trends related to electronic structure and coordination environment.

In addition to octahedral systems, a selected set of tetrahedral models was also investigated in order to assess the effect of reduced coordination number and altered geometry on dinitrogen binding. These models provide further insight into how structural variations influence metal–ligand interactions and contribute to the overall ability of the metal center to interact with N₂.

Overall, this section establishes a computational framework for evaluating the role of coordination environment in dinitrogen activation. By systematically varying ligand identity, oxidation state, and coordination geometry, the study provides a structured basis for understanding how different electronic and structural factors influence the interaction between transition metal centers and molecular nitrogen.

This section presents a systematic computational summary of the energetic and structural properties of Fe–N₂ complexes, focusing on both octahedral and tetrahedral coordination environments. The study evaluates how oxidation state, spin configuration, and ligand type influence the interaction between iron centers and molecular nitrogen.

For the octahedral Fe–N₂ systems, the calculated relative energies indicate that spin state plays a crucial role in stabilizing the complexes. Low-spin configurations are generally preferred for Fe(0) systems with anionic ligands, while higher spin states become increasingly relevant for Fe(I) and Fe(II) species. The ligand environment also affects stability, with stronger electron-donating ligands contributing to more favorable energetic configurations.

From a geometrical perspective, the Fe–N and N–N bond distances provide insight into the extent of dinitrogen activation. The Fe–N distances typically fall within a narrow range, indicating stable coordination, while variations in the N–N bond length reflect different degrees of activation. In particular, slight elongation of the N–N bond compared to free N₂ suggests partial weakening of the triple bond upon coordination to the metal center.

The structural trends are further supported by molecular orbital considerations. As illustrated in Figure 3, the interaction between iron d orbitals and nitrogen π^* orbitals governs the bonding mechanism. The diagrams highlight the role of σ -donation from N₂ to the metal and π -backdonation from the metal to the antibonding orbitals of N₂, which collectively contribute to bond activation.

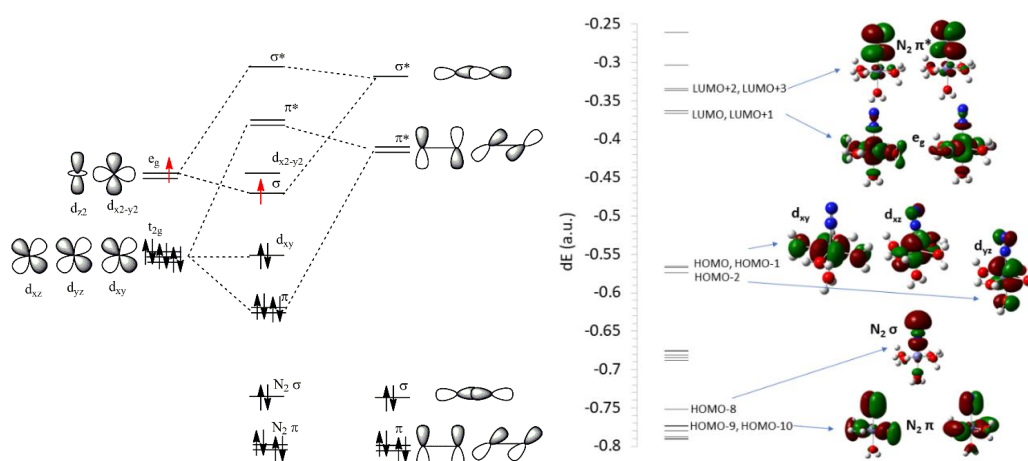


Figure 3. Left: molecular orbital diagram for the interaction of N₂ with octahedral S=0 Fe(II). Shown in red is the additional electron that would be added upon reduction to S=1/2 Fe(I). Right: Frontier orbitals of the S=0 [Fe(OH₂)₅N₂]²⁺ system (B3LYP/6-311+G**).

In Fe(I) systems, the interaction is more pronounced, leading to stronger metal–ligand bonding and increased activation of the N₂ molecule. In contrast, Fe(II) systems exhibit weaker interaction, particularly in the absence of strongly donating ligands. These differences are reflected in both bond distances and overall stability trends.

The energetic analysis of N₂ binding further confirms these observations. The interaction energies vary depending on both spin state and ligand type, with more favorable binding observed for electron-rich systems. The results indicate that Fe(0) and Fe(I) complexes are more effective in stabilizing coordinated N₂, while Fe(II) systems require specific ligand environments to achieve comparable interactions.

Dynamic behavior of selected systems was also investigated to assess their stability beyond optimized geometries. As shown in Figure 4, molecular dynamics simulations indicate that certain complexes may undergo structural changes under non-equilibrium conditions, including elongation or dissociation of the Fe–N₂ bond. These results suggest that while some configurations are stable at low temperature, their stability under realistic conditions may be limited.

Overall, the combined energetic and geometrical data provide a consistent description of Fe–N₂ interaction across different coordination environments. The results highlight the importance of electronic structure, ligand effects, and spin state in governing the binding and activation of molecular nitrogen.

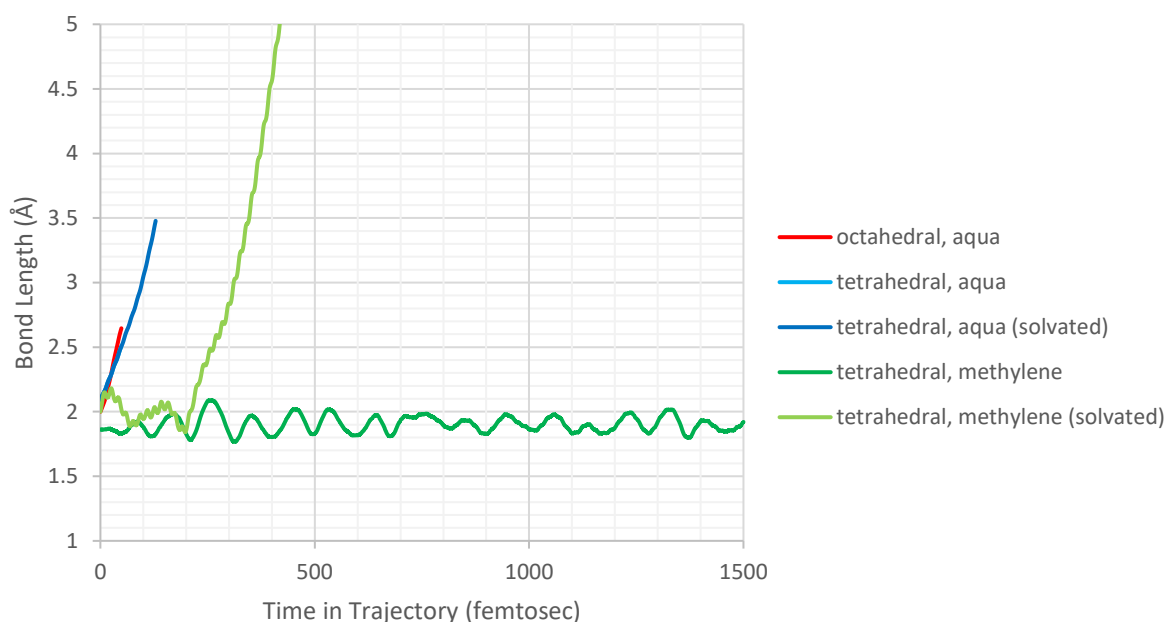


Figure 4. Dynamics of the Fe-N₂ bond in systems with water or CH₂²⁻ as ligand (octahedral aqua - Fe(H₂O)₅N₂, tetrahedral aqua Fe(SCH₃)₂(H₂O)N₂, tetrahedral methylene Fe(SCH₃)₂(CH₂)N₂, from B3LYP/6-311G(d,p) ADMP calculations.

2.2. An iron-free nitrogenase? Computational estimation of the ability to bind/activate N₂ in manganese and cobalt complexes

This section presents a comprehensive computational evaluation of the potential of manganese (Mn) and cobalt (Co) complexes to bind and activate molecular nitrogen, in comparison with iron-based systems that are known to be central to biological nitrogen fixation. The study aims to determine whether alternative transition metals can reproduce similar structural and electronic conditions required for N₂ activation within nitrogenase-like environments.

To ensure direct comparability, octahedral complexes of the general form M(H₂O)₄(R)(N₂), where M = Mn or Co, were constructed using the same modeling strategy applied for iron systems. The coordination framework isolates the electronic effects of the axial ligand and the N₂ molecule, allowing systematic evaluation of how ligand identity, oxidation state, and spin multiplicity influence the metal–nitrogen interaction. The representative structural arrangement of these models is shown in Figure 5, highlighting the octahedral coordination environment with four equatorial water ligands and axial positioning of both R and N₂ [9].

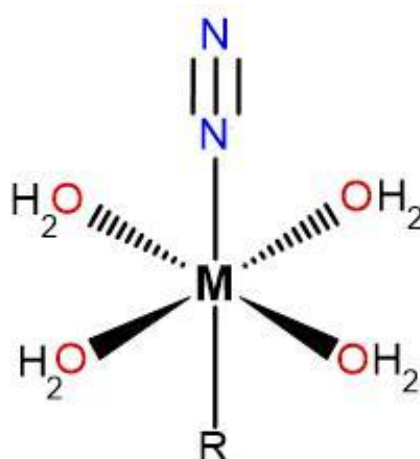


Figure 5. Structures of the $M(\text{H}_2\text{O})_4\text{RN}_2$ octahedral models employed in the present study ($M=\text{Co}, \text{Mn}$; $\text{R} = \text{H}_2\text{O}, \text{HO}^-, \text{CH}_2^{2-}, \text{H}_2\text{S}$).

A diverse ligand set was employed, including neutral (H_2O) and anionic donors (OH^- , H_2S), as well as strongly electron-donating carbon-based ligands (CH_3^- and CH_2^{2-}). This selection reflects both biologically relevant coordination environments and electronically extreme cases designed to probe the limits of N_2 activation. The oxidation states investigated span from 0 to +3, and multiple spin configurations were considered to capture the full range of accessible electronic structures for Mn and Co centers.

The computed energetic and structural data reveal that cobalt complexes generally exhibit unfavorable conditions for N_2 binding. The $\text{Co}-\text{N}_2$ bond distances are typically larger than the expected values for stable coordination, indicating weak interactions or even the absence of effective binding. This behavior is consistent across different spin states and ligand environments, suggesting that cobalt lacks the necessary electronic structure to efficiently engage in π -backdonation toward the antibonding orbitals of N_2 . In most cases, the interaction is dominated by weak electrostatic contributions rather than significant orbital overlap.

In contrast, manganese systems display slightly improved behavior, although they remain inferior to iron analogues. Structural and energetic parameters indicate that $\text{Mn}-\text{N}_2$ interactions can occur under certain conditions, particularly in the presence of strongly donating ligands and favorable spin states. In these cases, moderate elongation of the $\text{N}-\text{N}$ bond is observed, suggesting partial activation of dinitrogen. However, this effect is not consistent across all configurations and remains sensitive to both oxidation state and ligand environment.

The geometrical analysis shows that while $\text{Mn}-\text{N}$ distances can fall within a reasonable coordination range, the corresponding $\text{N}-\text{N}$ bond elongation is generally limited,

indicating that activation is incomplete. For cobalt systems, both the metal–nitrogen distances and the lack of significant N–N elongation confirm that effective activation is unlikely under the studied conditions.

Further insight into the nature of metal–nitrogen interaction is obtained through frontier molecular orbital analysis. The orbital representations presented in Figure 6 and Figure 7 illustrate the interaction between metal d orbitals and the π^* orbitals of N_2 . Compared to iron systems, both Mn and Co complexes exhibit reduced orbital overlap, particularly in the antibonding region of N_2 . This limited π -backdonation explains the weaker activation and the inability of these metals to significantly weaken the $N\equiv N$ triple bond.

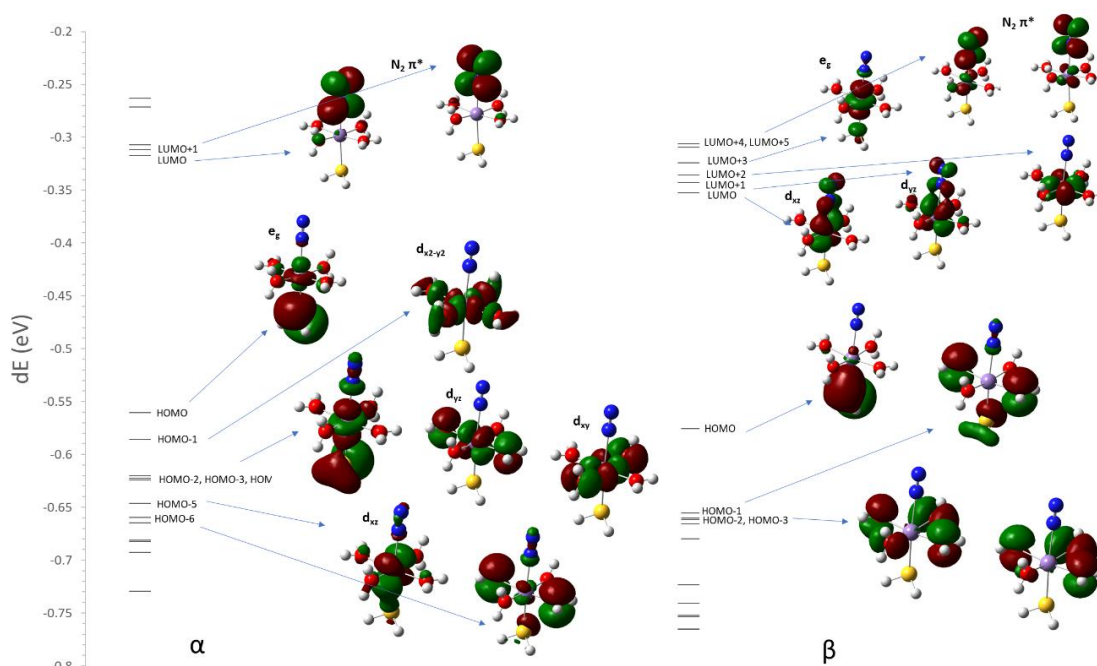


Figure 6. Frontier orbitals of the $S=5/2$ $[Mn(OH_2)_4(H_2S)N_2]^{2+}$ system (B3LYP/6-311+G**).

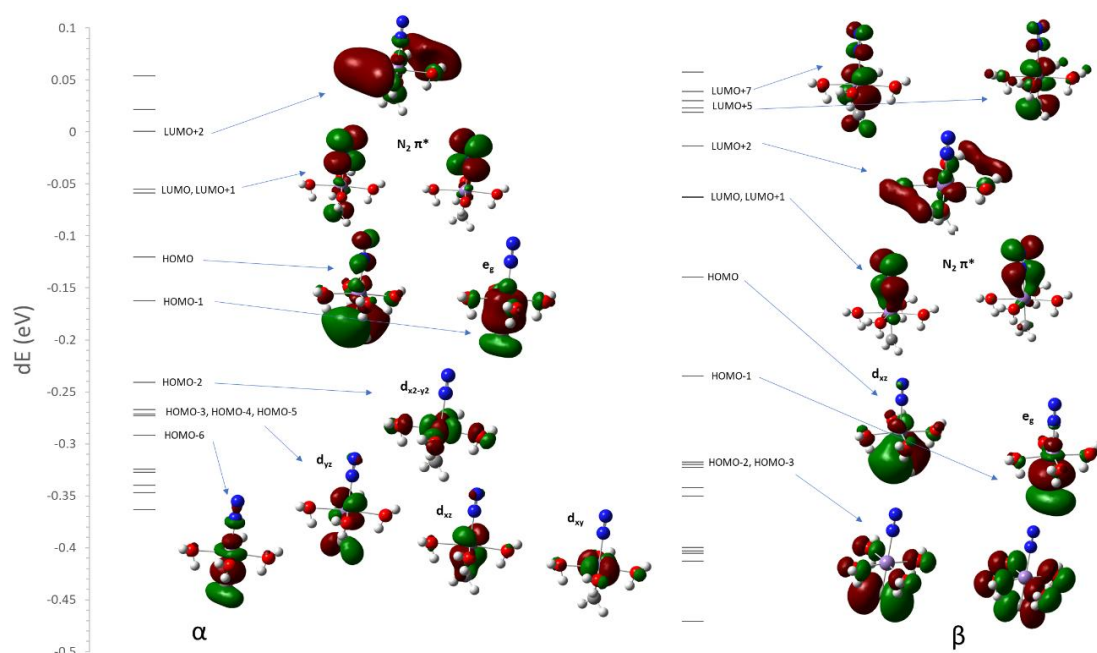


Figure 7. Frontier orbitals of the $S=5/2$ $[\text{Mn}(\text{OH}_2)_4(\text{CH}_2)\text{N}_2]^0$ system (B3LYP/6-311+G**).

The electronic structure analysis highlights that efficient N_2 activation requires not only sufficient electron density at the metal center but also appropriate orbital symmetry and energy matching. In Mn and Co systems, these conditions are only partially fulfilled. While manganese can, in some configurations, provide moderate backdonation, cobalt systems are generally less capable due to their electronic configuration and weaker interaction with N_2 orbitals.

Energy decomposition analysis further clarifies the contributions to the metal– N_2 interaction. The results indicate that electrostatic, orbital, and steric components vary significantly depending on the ligand environment. Carbon-based ligands enhance the orbital interaction component, leading to improved binding energies in certain Mn systems. However, even in these optimized cases, the overall stabilization remains lower than that observed for iron complexes, confirming the superior efficiency of iron in facilitating N_2 activation.

Overall, the results demonstrate that while manganese and cobalt complexes can exhibit limited interaction with molecular nitrogen, their ability to effectively bind and activate N_2 is significantly reduced compared to iron systems. Manganese shows partial potential under specific electronic and coordination conditions, whereas cobalt appears largely ineffective in promoting dinitrogen activation. These findings reinforce the unique role of iron in biological nitrogen fixation and suggest that alternative metal centers would require highly specialized environments to achieve comparable reactivity.

3. CATALYTIC ACTIVATION OF MOLECULAR NITROGEN BY ENZYME-INSPIRED METAL-ORGANIC CATALYSTS

This chapter presents the experimental extension of the theoretical insights, focusing on the synthesis, characterization, and catalytic evaluation of nanostructured materials designed for molecular nitrogen activation and reduction under mild conditions. The study is based on the premise that the electronic properties of transition metal centers and the nature of the support play a decisive role in facilitating N₂ activation.

3.1. Preparation and characterization of zero-valent Fe/Co/Ru photocatalysts supported on CNTs and g-C₃N₄

To this end, iron, cobalt, and ruthenium species were deposited onto carbon-based supports, namely multi-walled carbon nanotubes (CNTs) and graphitic carbon nitride (g-C₃N₄). These materials were selected due to their high surface area, conductivity, and ability to promote charge transfer processes. The catalyst preparation involved a two-step procedure consisting of impregnation of metal precursors followed by thermal treatment under hydrogen atmosphere, leading to the formation of zero-valent metal nanoparticles strongly anchored to the support [10].

Electrodes were prepared by immobilizing the catalysts onto glassy carbon surfaces using a chitosan-based binder. Electrochemical characterization was carried out in a standard three-electrode system, enabling evaluation of charge transfer behavior and catalytic response under controlled conditions.

Photocatalytic nitrogen reduction experiments were performed in a quartz reactor under visible-light irradiation. The reaction parameters, including pH, irradiation time, and catalyst loading, were controlled, while the system was purged with inert gas prior to irradiation to eliminate oxygen. These conditions allow consistent evaluation of catalytic performance toward nitrogen reduction.

Quantification of reaction products was conducted using spectrophotometric methods. Ammonia was determined via the indophenol blue method, hydrazine via the Watt–Chrisp method, and nitrate/nitrite via the Griess reaction [11-15].

The catalytic performance was evaluated using standard analytical expressions based on measured concentrations, solution volume, and catalyst mass, providing a consistent basis for comparison between systems.

The synthesized materials were comprehensively characterized using multiple analytical techniques. Structural properties were investigated by X-ray diffraction (XRD),

while morphology and elemental composition were analyzed using scanning electron microscopy (SEM) coupled with EDS. Thermal stability was assessed by thermogravimetric analysis (TGA-DTG), and textural properties were determined using nitrogen adsorption–desorption measurements (BET and BJH methods).

Additional characterization included UV–Vis diffuse reflectance spectroscopy (DRS) for optical properties, X-ray photoelectron spectroscopy (XPS) for surface chemistry, and electron spin resonance (ESR) for electronic structure analysis. These techniques provide a complete description of the structural and electronic features of the catalysts relevant to nitrogen reduction.

Overall, this chapter establishes an integrated experimental framework combining controlled synthesis, electrochemical and photocatalytic evaluation, quantitative product analysis, and advanced characterization, enabling the systematic investigation of nanostructured catalysts for molecular nitrogen activation.

3.2. Results and discussion

This section presents a comprehensive evaluation of the structural, morphological, compositional, optical, and electrochemical properties of the synthesized photocatalysts, providing a coherent understanding of their behavior in nitrogen reduction applications.

The structural properties of the prepared materials were first examined by X-ray diffraction analysis. The diffraction patterns, presented in Figure 8, confirm the successful formation of the carbon-based supports and the incorporation of transition metal species. Characteristic reflections corresponding to CNTs and g-C₃N₄ were clearly identified [16-20], while additional diffraction peaks indicate the presence of metallic phases associated with iron, cobalt, and ruthenium. The observed patterns demonstrate that the synthesis and thermal reduction processes led to the formation of well-defined crystalline structures, confirming the successful preparation of the catalysts.

The crystallite size and interplanar spacing were further evaluated using standard diffraction-based approaches, highlighting the influence of metal incorporation on the structural organization of the materials. The results indicate that the presence of metal nanoparticles induces modifications in the crystallographic features of both CNT and g-C₃N₄ supports, reflecting strong metal–support interactions.

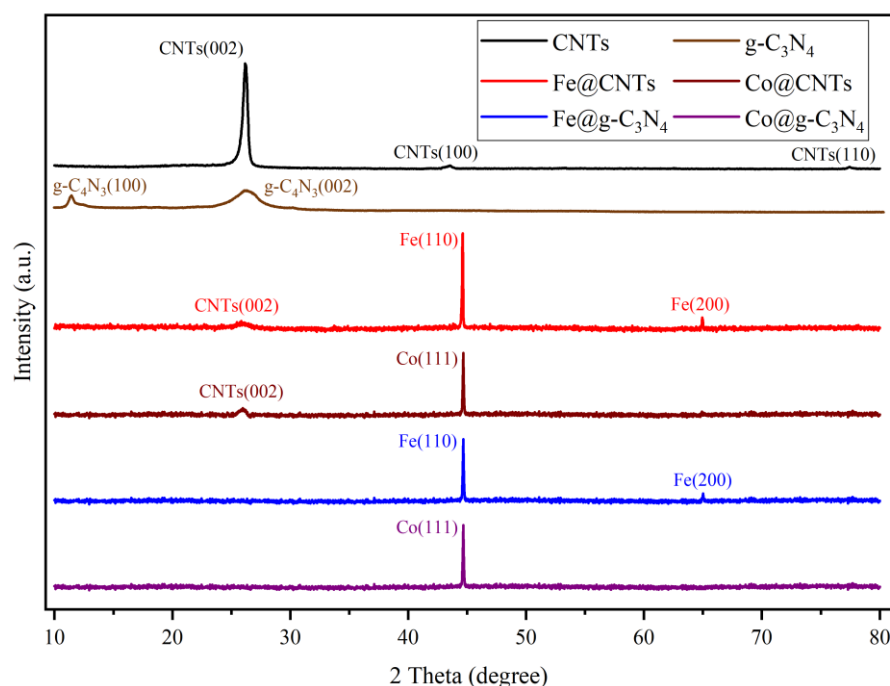


Figure 8. XRD patterns of CNTs, g-C₃N₄, Fe@CNTs, Co@CNTs, Fe@g-C₃N₄ and Co@g-C₃N₄.

Morphological analysis carried out by scanning electron microscopy revealed distinct structural features depending on the type of support. Carbon nanotube-based catalysts exhibit a three-dimensional interconnected network structure, while g-C₃N₄-based materials display layered, graphitic-like morphologies. The presence of spherical nanoparticles distributed across the support surface confirms the successful anchoring of metallic species. This morphology contributes to enhanced surface accessibility and facilitates reactant diffusion.

Elemental composition and distribution were investigated using energy-dispersive X-ray spectroscopy, confirming the presence of iron, cobalt, and ruthenium within the catalysts. The mapping results demonstrate that the metals are distributed throughout the support matrix, indicating effective incorporation during synthesis. Differences in elemental distribution between CNT and g-C₃N₄ systems suggest variations in metal dispersion and interaction with the support.

Thermal stability was evaluated using thermogravimetric analysis, revealing distinct decomposition behaviors for CNT- and g-C₃N₄-based catalysts. The observed weight loss profiles indicate that carbon nanotube-supported catalysts exhibit higher thermal resistance, while g-C₃N₄-based systems undergo structural transformations at elevated temperatures. These findings highlight the role of the support in determining the thermal behavior of the catalysts.

Textural properties were analyzed through nitrogen adsorption–desorption measurements. The obtained isotherms, shown in Figure 9, indicate the presence of mesoporous structures, characterized by typical hysteresis loops. The pore size distribution confirms that the materials possess well-defined mesoporosity [21-24], which is essential for enhancing mass transfer and providing accessible active sites. The specific surface area and pore volume were significantly influenced by both the type of support and the incorporation of metal nanoparticles.

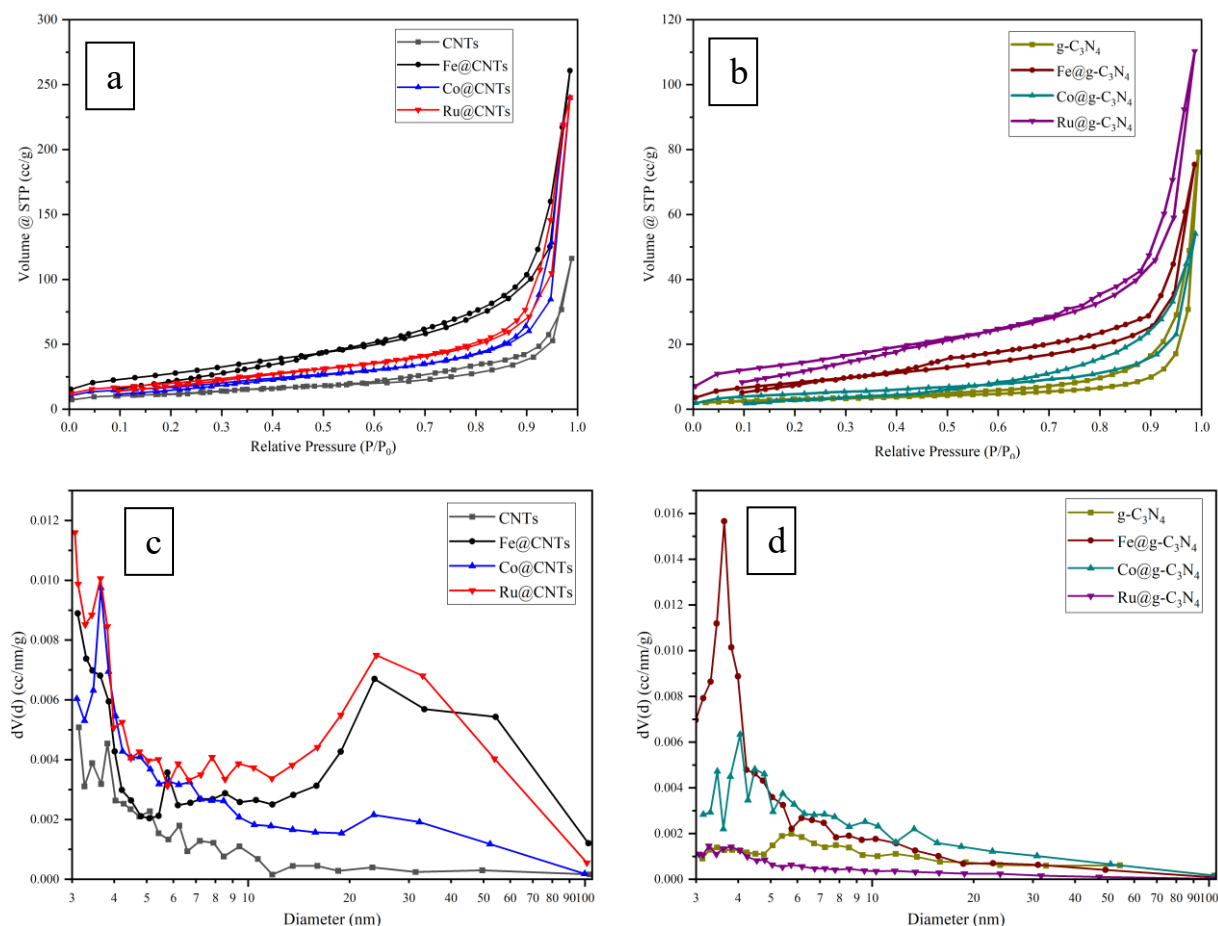


Figure 9. (a, b) N₂ adsorption-desorption isotherms and (c, d) pore size distribution curves.

The optical properties of the catalysts were investigated using UV–Vis diffuse reflectance spectroscopy. The results demonstrate that CNT-based catalysts exhibit broader light absorption across the UV, visible, and near-infrared regions, while g-C₃N₄-based materials show strong absorption in the UV region with limited extension into the visible range. These differences are attributed to the electronic structure of the supports and their interaction with the metal nanoparticles, influencing their photocatalytic performance.

Surface chemical states and electronic structures were analyzed using X-ray photoelectron spectroscopy. The spectra presented in Figure 10 confirm the presence of zero-

valent metal species, indicating the effective reduction of metal precursors during synthesis. Additionally, signals corresponding to carbon, nitrogen, and oxygen species provide further evidence of the structural integrity of the supports and the interaction between metal nanoparticles and the support matrix [25-30].

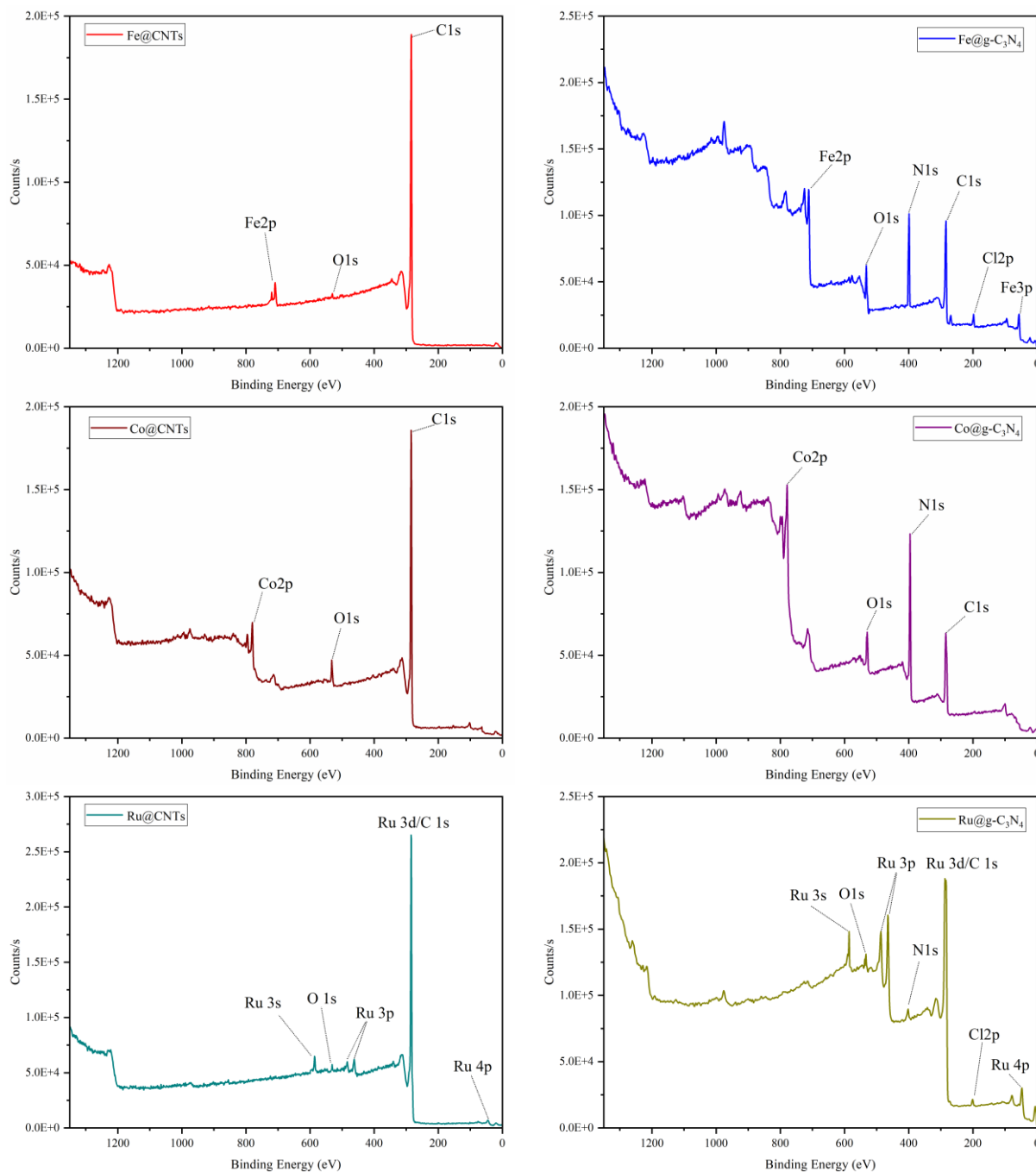


Figure 10. X-ray photoelectron spectrum surveys scan for photocatalysts.

Electron paramagnetic resonance analysis provided additional insight into the electronic environment of the catalysts. The observed signals suggest the presence of paramagnetic species and highlight differences in the electronic structure between iron-,

cobalt-, and ruthenium-based systems. These findings support the conclusions obtained from XPS analysis regarding the electronic properties of the catalysts.

The electrochemical performance of the catalysts toward nitrogen reduction was evaluated using linear sweep voltammetry under controlled conditions. The results indicate that nitrogen-saturated conditions lead to enhanced current response compared to inert conditions, confirming the catalytic activity of the materials toward nitrogen reduction.

Furthermore, the comparison of electrochemical behavior across different catalysts highlights the influence of both the metal type and the support structure on catalytic performance. The observed trends suggest that the interaction between metal nanoparticles and conductive supports plays a crucial role in facilitating electron transfer processes and promoting nitrogen activation.

Overall, the results presented in this section demonstrate that the synthesized catalysts exhibit well-defined structural, morphological, and electronic properties, which collectively contribute to their performance in nitrogen reduction reactions. The combination of high surface area, controlled porosity, efficient light absorption, and favorable electronic structure establishes these materials as promising candidates for catalytic nitrogen activation under mild conditions.

3.3. Photocatalytic NRR Performance of Fe- and Co-Based Catalysts

The photocatalytic nitrogen reduction performance of the synthesized catalysts was systematically evaluated under controlled irradiation conditions, highlighting significant differences between Fe- and Co-based systems. The results demonstrate that catalytic activity is strongly dependent on both the nature of the metal center and the support structure.

Under standard reaction conditions (pH = 5.5, 4 h irradiation), Fe-based catalysts exhibited significantly higher ammonia production compared to Co-based systems. As illustrated in Figure 11, Fe@CNTs achieved an ammonia yield of approximately 660.31 $\mu\text{mol g}^{-1}$, increasing to 721.1 $\mu\text{mol g}^{-1}$ under optimized conditions, while Fe@g-C₃N₄ reached 258.27 $\mu\text{mol g}^{-1}$. In contrast, Co@CNTs showed substantially lower activity, with ammonia yields in the range of 21.33–165 $\mu\text{mol g}^{-1}$, whereas Co@g-C₃N₄ exhibited negligible ammonia production, instead favoring the formation of nitrate species.

The effect of pH further confirmed the superiority of Fe-based systems. At pH = 3, ammonia production increased by approximately 14.6% for Fe@CNTs and 45% for Fe@g-C₃N₄, indicating that acidic conditions enhance proton availability and facilitate the nitrogen reduction pathway. Co-based catalysts also showed some improvement under acidic

conditions; however, their overall activity remained significantly lower due to competing hydrogen evolution reactions (HER).

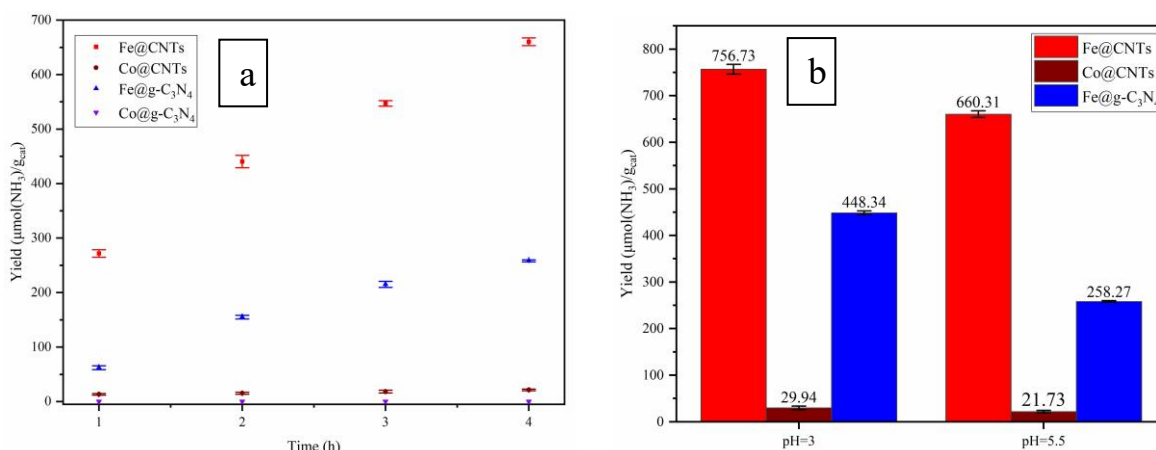


Figure 11. (a) Ammonia yield versus time at pH 5.5, (b) Ammonia yield versus of pH after 4 h by Fe⁰@CNTs and Fe⁰@g-C₃N₄

Hydrazine (N₂H₄) was identified as an intermediate in the reaction pathway, with yields ranging between 3.25 and 46.45 μmol g⁻¹, depending on the catalyst and support. The relatively low hydrazine concentration compared to ammonia suggests its rapid conversion, supporting a reaction mechanism involving stepwise hydrogenation of N₂. Additionally, recyclability tests demonstrated that Fe@CNTs maintained relatively high activity over multiple cycles, although a gradual decrease in ammonia yield (up to ~37–44%) was observed, indicating partial deactivation.

To rationalize these experimental observations, density functional theory (DFT) calculations were employed, focusing on the intrinsic differences between Fe and Co active centers. The computational models, represented schematically in Figure 12, explore the interaction of N₂ and its hydrogenated intermediates with transition metal centers under different coordination environments.

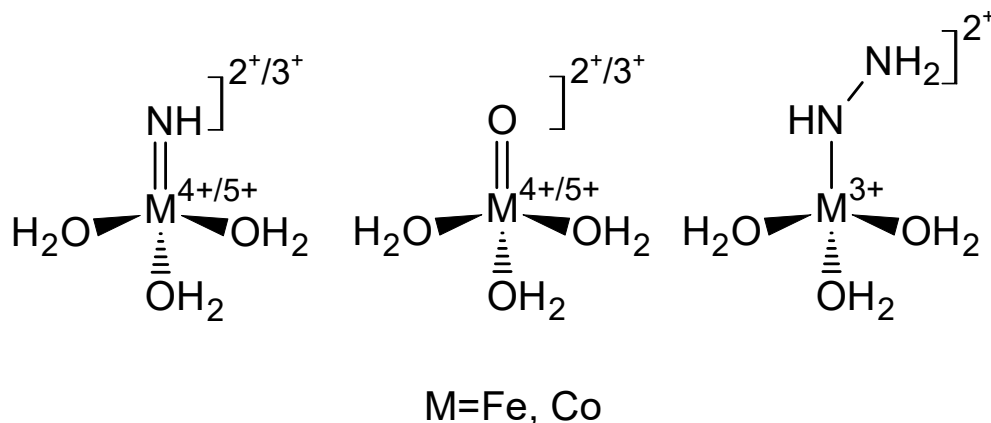


Figure 12. Structures subjected to DFT geometry optimizations.

The DFT results reveal that iron centers exhibit a stronger ability to facilitate N₂ activation due to their electronic configuration and favorable d-orbital occupation. In particular, Fe sites promote effective electron donation into the antibonding orbitals of the N≡N bond, weakening the triple bond and lowering the activation barrier for subsequent hydrogenation steps. This behavior is consistent with the higher catalytic activity observed experimentally.

In contrast, cobalt-based systems display a less favorable electronic structure for N₂ activation. As summarized in Table 1, the electronic population analysis indicates a lower electron density transfer toward nitrogen in Co systems compared to Fe analogues. This reduced electron donation limits the weakening of the N≡N bond and favors alternative pathways, such as nitrate formation, rather than ammonia synthesis.

Table 1. Populations of metal d orbitals and nitrogen p orbitals as deduced from Mulliken analyses of DFT-optimized geometries in [Fe/Co⁴⁺-NH²⁻]²⁺ models. Formally empty orbitals are shown in **bold**.

Element	orbital	Fe(IV)=NH S=1		Co(IV)=NH S=3/2	
		α	β	α	β
Fe/Co	11D0+12D0+13D0	0.98	0.09	0.84	0.50
	11D+1+12D+1+13D+1	0.99	0.77	0.98	0.23
	11D-1+12D-1+13D-1	0.97	0.10	0.99	0.86
	11D+2+12D+2+13D+2	0.99	0.11	0.99	0.65
	11D-2+12D-2+13D-2	0.95	0.24	0.71	0.45
N	6PX+7PX+8PX	0.07	0.96	0.86	0.26
	6PY+7PY+8PY	0.57	0.68	0.69	0.31
	6PZ+7PZ+8PY	0.07	0.94	0.62	0.54
		Fe(IV)=NH S=2		Co(IV)=NH S=5/2	
		α	β	α	β
Fe/Co	11D0+12D0+13D0	0.97	0.15	1.00	0.11
	11D+1+12D+1+13D+1	1.01	0.41	1.00	0.79
	11D-1+12D-1+13D-1	0.99	0.15	1.00	0.80
	11D+2+12D+2+13D+2	0.99	0.13	1.00	0.24
	11D-2+12D-2+13D-2	1.00	0.24	1.00	0.24
N	6PX+7PX+8PX	0.96	0.40	0.98	0.04
	6PY+7PY+8PY	0.22	0.76	0.98	0.04
	6PZ+7PZ+8PY	0.45	0.67	0.66	0.58

Furthermore, DFT calculations suggest that the N–N bond cleavage process is energetically more accessible in Fe-based intermediates, particularly in hydrazine-like

species. The energy profiles indicate that elongation and eventual cleavage of the N–N bond require lower energy in Fe systems compared to Co systems, supporting a more efficient reduction pathway toward ammonia. In contrast, cobalt systems tend to stabilize intermediates with partial oxidation character, which may redirect the reaction toward side products.

The analysis of spin states and coordination environments further supports these conclusions. Iron complexes exhibit electronic configurations that favor stronger interaction with nitrogen orbitals, while cobalt complexes show reduced orbital overlap and weaker activation capability. These differences at the electronic level directly translate into the observed catalytic behavior.

Overall, the combined experimental and computational results clearly demonstrate that Fe-based catalysts outperform Co-based systems in photocatalytic nitrogen reduction. This enhanced performance arises from the more favorable electronic structure of iron, which enables efficient N₂ activation, lower energy barriers for intermediate transformations, and a reaction pathway that selectively leads to ammonia formation.

3.4. Photocatalytic NRR Performance of Ru-Based Catalysts

The photocatalytic nitrogen reduction behavior of Ru-based catalysts reveals a distinct mechanistic pathway compared to Fe- and Co-based systems, characterized by moderate ammonia production and a stronger tendency toward competing oxidation reactions.

As shown in Figure 13, ammonia formation over Ru@CNTs increases progressively with reaction time, reaching a value of approximately $183.22 \pm 3.74 \mu\text{mol g}^{-1}$ after 4 h. Under similar conditions, Ru@g-C₃N₄ exhibits lower activity, with ammonia yields around $150.42 \pm 4.44 \mu\text{mol g}^{-1}$. The enhanced performance of Ru@CNTs is attributed to its higher specific surface area and improved light absorption properties, which facilitate charge separation and increase the availability of active sites.

Despite this improvement, the overall ammonia yields remain significantly lower than those obtained with Fe-based catalysts, indicating intrinsic limitations of Ru centers in promoting efficient nitrogen reduction. This behavior is further influenced by the competitive hydrogen evolution reaction (HER), particularly in g-C₃N₄-supported systems, where proton reduction dominates over N₂ activation.

The influence of pH confirms the proton-coupled nature of the reaction. A decrease in pH leads to a moderate increase in ammonia production, consistent with enhanced proton

availability. However, this effect is less pronounced than in Fe-based systems, suggesting that proton transfer is not the rate-limiting step in Ru-catalyzed NRR.

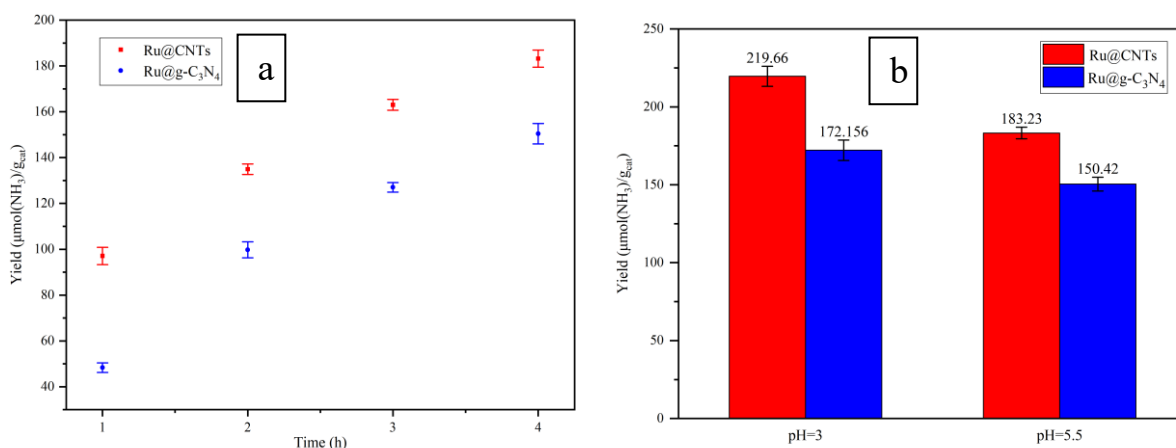


Figure 13. (a) Ammonia yield versus time at pH 5.5, (b) Ammonia yield versus of pH after 4 h by Ru@CNTs and Ru@g-C₃N₄.

To elucidate the origin of this behavior, density functional theory (DFT) calculations were performed on octahedral Ru–N₂ model complexes, as illustrated in Figure 14. These models allow for a detailed analysis of N₂ activation through structural and electronic descriptors.

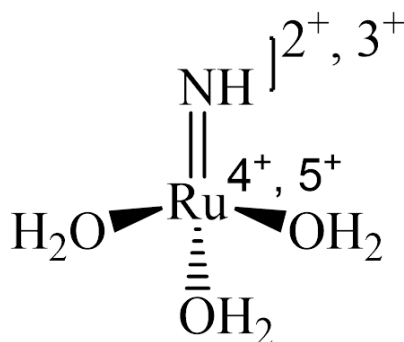


Figure 14. High-valent Ru models examined in the present study.

The structural parameters indicate that the N–N bond length in Ru complexes remains close to that of free N₂ (≈1.10–1.16 Å), with only slight elongation observed depending on the ligand environment and oxidation state. Correspondingly, the Ru–N bond distances (≈2.0–2.2 Å) suggest relatively weak coordination of the N₂ molecule to the metal center. These values reflect limited activation of the N≡N bond, consistent with the moderate catalytic activity observed experimentally.

Further insight is obtained from Mulliken population analysis, presented in Table 2, which reveals only partial electron transfer from Ru d-orbitals to the nitrogen π^* orbitals. The electronic populations indicate that the occupation of antibonding orbitals remains insufficient to induce significant weakening of the N–N bond. This limited back-donation contrasts sharply with Fe-based systems, where stronger electron transfer facilitates bond activation and subsequent hydrogenation steps.

Additionally, the analysis of orbital contributions shows that Ru complexes predominantly maintain a low-spin configuration, resulting in reduced orbital overlap with the nitrogen molecule. This electronic structure restricts the ability of Ru centers to effectively destabilize the $\text{N}\equiv\text{N}$ bond, thereby increasing the energetic barrier for N–N cleavage.

From a mechanistic perspective, these findings suggest that Ru-based catalysts favor associative pathways involving weakly activated N_2 intermediates, rather than direct dissociation. As a consequence, the reaction proceeds through slower hydrogenation steps, limiting the overall rate of ammonia formation. At the same time, the relatively weak activation of nitrogen facilitates competing pathways, including oxidation processes and hydrogen evolution, which further reduce selectivity toward ammonia.

Overall, the combined experimental and theoretical results demonstrate that, although Ru@CNTs exhibit improved performance compared to Ru@g- C_3N_4 due to structural and optical advantages, the intrinsic electronic properties of Ru limit its efficiency in photocatalytic nitrogen reduction. The weak N_2 activation, as evidenced by minimal N–N bond elongation and limited electron transfer, explains the lower ammonia yields and highlights the critical role of electronic structure in determining catalytic performance.

Table 2. Populations of metal d orbitals and nitrogen p orbitals as deduced from Mulliken analyses of DFT-optimized geometries in $[\text{Ru}^{5+}\text{NH}^{2-}]^{3+}$ models. Formally empty orbitals are shown in **bold**.

		Ru(V)=NH S=1/2				Fe(V)=NH S=1/2				Co(V)=NH S=0	
		α	β			α	β			α	β
Ru	7D0+8D0	0.96	0.11	Fe	7D0+8D0	0.99	0.16	Co	7D0+8D0	0.87	0.87
	7D+1+8D+1	1.00	0.99		7D+1+8D+1	1.00	0.24		7D+1+8D+1	0.86	0.86
	7D-1+8D-1	0.75	0.40		7D-1+8D-1	0.98	0.18		7D-1+8D-1	0.64	0.64
	7D+2+8D+2	0.39	0.35		7D+2+8D+2	0.44	0.24		7D+2+8D+2	0.43	0.43
	7D-2+8D-2	0.78	0.40		7D-2+8D-2	1.00	0.96		7D-2+8D-2	0.89	0.89
N	4PX+5PX	0.25	0.73	N	4PX+5PX	0.02	0.98	N	4PX+5PX	0.32	0.32
	4PY+5PY	0.67	0.68		4PY+5PY	0.40	0.80		4PY+5PY	0.54	0.54
	4PZ+5PZ	0.30	0.70		4PZ+5PZ	0.31	0.84		4PZ+5PZ	0.74	0.74
		Ru(V)=NH S=3/2				Fe(V)=NH S=3/2				Co(V)=NH S=1	
		α	β			α	β			α	β
Ru	7D0+8D0	0.96	0.12	Fe	7D0+8D0	1.01	0.19	Co	7D0+8D0	1.01	0.23
	7D+1+8D+1	1.00	0.03		7D+1+8D+1	1.00	0.19		7D+1+8D+1	1.00	0.89
	7D-1+8D-1	1.01	0.70		7D-1+8D-1	1.00	0.19		7D-1+8D-1	1.00	0.23
	7D+2+8D+2	0.44	0.36		7D+2+8D+2	1.01	0.18		7D+2+8D+2	1.01	0.38
	7D-2+8D-2	0.84	0.53		7D-2+8D-2	1.01	0.19		7D-2+8D-2	1.00	0.33
N	4PX+5PX	0.19	0.55	N	4PX+5PX	0.01	0.91	N	4PX+5PX	0.01	0.95
	4PY+5PY	0.69	0.67		4PY+5PY	0.01	0.91		4PY+5PY	0.14	0.87
	4PZ+5PZ	0.98	0.34		4PZ+5PZ	0.76	0.75		4PZ+5PZ	0.62	0.76
		Ru(V)=NH S=5/2				Fe(V)=NH S=5/2				Co(V)=NH S=2	
		α	β			α	β			α	β
Ru	7D0+8D0	0.96	0.12		7D-1+8D-1	1.01	0.18	Co	7D0+8D0	1.00	0.29
	7D+1+8D+1	1.00	0.02		7D+2+8D+2	1.01	0.14		7D+1+8D+1	1.01	0.51
	7D-1+8D-1	1.01	0.80		7D-2+8D-2	1.00	0.23		7D-1+8D-1	1.01	0.38
	7D+2+8D+2	0.41	0.36		4PX+5PX	1.01	0.20		7D+2+8D+2	1.01	0.23
	7D-2+8D-2	1.02	0.32		4PY+5PY	1.00	0.18		7D-2+8D-2	1.01	0.65
N	4PX+5PX	0.98	0.04	N	4PZ+5PZ	0.86	0.24	N	4PX+5PX	0.98	0.03
	4PY+5PY	0.69	0.63		4PY+5PY	0.09	0.79		4PY+5PY	0.12	0.77
	4PZ+5PZ	0.98	0.21		4PZ+5PZ	0.62	0.56		4PZ+5PZ	0.67	0.74

4. GENERAL CONCLUSIONS

This thesis presents an integrated computational–experimental study on nitrogen activation using metalloprotein-inspired catalysts, aiming to identify the key electronic and structural factors governing N₂ activation and reduction.

DFT calculations demonstrated that efficient N₂ activation is strongly dependent on the metal oxidation state and ligand environment. Low-valent metal centers, particularly M(0) and M(I), were identified as the most effective due to their ability to donate electron density into the antibonding orbitals of N₂. Among the investigated metals (Fe, Mn, Co, and Ru), iron exhibited the most favorable electronic characteristics, enabling stronger activation of the N≡N bond. Additionally, electron-rich carbon-based ligands, especially those with carbanion character, were shown to significantly enhance metal-to-ligand back-donation. However, even in optimal coordination environments, Fe(II)–N₂ interactions remain transient, highlighting the importance of low-valent iron species in catalysis.

Based on these insights, nanostructured catalysts consisting of low-valent metal nanoparticles supported on carbon materials (CNTs and g-C₃N₄) were synthesized and evaluated for photocatalytic nitrogen reduction. The experimental results demonstrated that Fe⁰@CNTs exhibit the highest efficiency for ammonia production, due to their high surface area, improved charge transfer, and strong interaction with N₂.

In contrast, cobalt-based catalysts showed lower selectivity toward ammonia, favoring instead nitrogen oxyanion formation. This behavior is consistent with DFT results, which indicate weaker N₂ activation and higher susceptibility of nitrogen intermediates to nucleophilic attack. Similarly, Ru-based systems exhibited moderate activity but a greater tendency toward nitrogen oxidation pathways, leading to increased nitrate formation, as supported by their electronic structure.

Overall, the combined results demonstrate that iron-based catalysts are the most efficient for selective nitrogen reduction to ammonia. Catalytic performance is governed by the accessibility of low-valent metal states, effective metal-to-N₂ back-donation, and the presence of electron-rich ligands. These findings provide a clear structure–activity relationship and a rational basis for the design of advanced catalysts for sustainable ammonia production.

References

1. Fryzuk, M.D. Activation and functionalization of molecular nitrogen by metal complexes. *The Chemical Record* **2003**, 3, 2-11, doi:<https://doi.org/10.1002/tcr.10044>.
2. Shaver, M.P.; Fryzuk, M.D. Activation of Molecular Nitrogen: Coordination, Cleavage and Functionalization of N₂ Mediated By Metal Complexes. *Advanced Synthesis & Catalysis* **2003**, 345, 1061-1076, doi:<https://doi.org/10.1002/adsc.200303081>.
3. Artz, J.H.; Zadvornyy, O.A.; Mulder, D.W.; King, P.W.; Peters, J.W. Chapter Eight - Structural Characterization of Poised States in the Oxygen Sensitive Hydrogenases and Nitrogenases. In *Methods in Enzymology*, David, S.S., Ed.; Academic Press: 2017; Volume 595, pp. 213-259.
4. Harris, D.F.; Lukoyanov, D.A.; Kallas, H.; Trncik, C.; Yang, Z.-Y.; Compton, P.; Kelleher, N.; Einsle, O.; Dean, D.R.; Hoffman, B.M.; et al. Mo-, V-, and Fe-Nitrogenases Use a Universal Eight-Electron Reductive-Elimination Mechanism To Achieve N₂ Reduction. *Biochemistry* **2019**, 58, 3293-3301, doi:10.1021/acs.biochem.9b00468.
5. MacLeod, K.C.; Holland, P.L. Recent developments in the homogeneous reduction of dinitrogen by molybdenum and iron. *Nature Chemistry* **2013**, 5, 559-565, doi:10.1038/nchem.1620.
6. Holland, P.L. Introduction: Reactivity of Nitrogen from the Ground to the Atmosphere. *Chemical Reviews* **2020**, 120, 4919-4920, doi:10.1021/acs.chemrev.0c00361.
7. Harris, D.F.; Lukoyanov, D.A.; Shaw, S.; Compton, P.; Tokmina-Lukaszewska, M.; Bothner, B.; Kelleher, N.; Dean, D.R.; Hoffman, B.M.; Seefeldt, L.C. Mechanism of N₂ Reduction Catalyzed by Fe-Nitrogenase Involves Reductive Elimination of H₂. *Biochemistry* **2018**, 57, 701-710, doi:10.1021/acs.biochem.7b01142.
8. Doukeh, R.; Crăciun, D.; Lupan, A.; Brânzanic, A.M.V.; Silaghi-Dumitrescu, R. Effect of the coordination environment on the ability of iron to bind/activate N₂: A theoretical study with relevance to the nitrogenase mechanism. *Polyhedron* **2023**, 243, 116571, doi:<https://doi.org/10.1016/j.poly.2023.116571>.
9. Doukeh, R.; Craciun, D.; Lehene, M.; Branzanic, A.M.V.; Lupan, A.; Silaghi-Dumitrescu, R. An iron-free nitrogenase? Computational estimation of the ability to bind/activate N₂ in manganese and cobalt complexes. *Journal Of Coordination Chemistry* **2024**, 77, 1597-1606, doi:10.1080/00958972.2024.2372812.
10. Doukeh, R.; Lehene, M.; Zagrean-Tuza, C.; Mot, A.C.; Silaghi-Dumitrescu, R.; Sarosi, C.; Fort, C.I.; Turdean, G.L.; Pandeale, M.; Borodi, G.; et al. Catalytic Activation of Molecular Nitrogen by Enzyme-Inspired Metal-Organic Catalysts. *Journal Of Physical Chemistry C* **2025**, 129, 20517-20533, doi:10.1021/acs.jpcc.5c05271.
11. Qiao, H.; Han, Y.; Hao, R.; Xu, L.; Ma, J.; Wen, B.; Hu, J.; Huang, H. Boosting nitrogen adsorption for photocatalytic ammonia production via tuning electron distribution using zero valent iron as medium. *Separation and Purification Technology* **2024**, 330, 125304, doi:<https://doi.org/10.1016/j.seppur.2023.125304>.
12. Chu, K.; Li, Q.-q.; Cheng, Y.-h.; Liu, Y.-p. Efficient Electrocatalytic Nitrogen Fixation on FeMoO₄ Nanorods. *ACS Applied Materials & Interfaces* **2020**, 12, 11789-11796, doi:10.1021/acsami.0c00860.
13. Tzollas, N.; Zachariadis, G.; Anthemidis, A.; Stratis, J. A new approach to indophenol blue method for determination of ammonium in geothermal waters with high mineral content. *Anal. Chem* **2010**, 90, 115-126, doi:10.1080/03067310902962528.
14. Song, P.; Wang, H.; Kang, L.; Ran, B.; Song, H.; Wang, R. Electrochemical nitrogen reduction to ammonia at ambient conditions on nitrogen and phosphorus co-doped porous carbon. *Chemical Communications* **2019**, 55, 687-690, doi:10.1039/C8CC09256G.
15. Kafle, B.P. Chapter 5 - Application of UV-VIS spectrophotometry for chemical analysis. In *Chemical Analysis and Material Characterization by Spectrophotometry*, Kafle, B.P., Ed.; Elsevier: 2020; pp. 79-145.

16. Soleimani, H.; Baig, M.K.; Yahya, N.; Khodapanah, L.; Sabet, M.; Demiral, B.M.R.; Burda, M. Impact of carbon nanotubes based nanofluid on oil recovery efficiency using core flooding. *Results in Physics* **2018**, *9*, 39-48, doi:<https://doi.org/10.1016/j.rinp.2018.01.072>.
17. Ramoraswi, N.O.; Ndungu, P.G. Photo-Catalytic Properties of TiO₂ Supported on MWCNTs, SBA-15 and Silica-Coated MWCNTs Nanocomposites. *Nanoscale Research Letters* **2015**, *10*, 427, doi:10.1186/s11671-015-1137-3.
18. Sun, J.; Maimaiti, H.; Bao, J.; Feng, L.; Zhao, X. Photoelectrocatalytic degradation of wastewater and simultaneous synthesis of NH₃ on Fe-CNTs-supported octahedral Cu₂O composite nanocatalysts. *International Journal of Hydrogen Energy* **2024**, *51*, 104-118, doi:<https://doi.org/10.1016/j.ijhydene.2023.08.069>.
19. Soleimani, H. Synthesis of Carbon Nanotubes for Oil-water Interfacial Tension Reduction. *Oil & Gas Research* **2015**, *1*, doi:10.4172/2472-0518.1000104.
20. Das, R.; Abd Hamid, S.B.; Ali, M.; Yongzhi, W. Carbon Nanotubes Characterization by X-ray Powder Diffraction – A Review. *Current Nanoscience* **2015**, *11*, doi:10.2174/1573413710666140818210043.
21. Thommes, M.; Kaneko, K.; Neimark, A.V.; Olivier, J.P.; Rodriguez-Reinoso, F.; Rouquerol, J.; Sing, K.S.W. Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report). **2015**, *87*, 1051-1069, doi:10.1515/pac-2014-1117.
22. Yang, Y.; Zhang, J.; Xu, L.; Li, P.; Liu, Y.; Dang, W. Pore Structure and Fractal Characteristics of Deep Shale: A Case Study from Permian Shanxi Formation Shale, from the Ordos Basin. *ACS Omega* **2022**, *7*, 9229-9243, doi:10.1021/acsomega.1c05779.
23. Chen, K.; Zhang, T.; Chen, X.; He, Y.; Liang, X. Model construction of micro-pores in shale: A case study of Silurian Longmaxi Formation shale in Dianqianbei area, SW China. *Petroleum Exploration and Development* **2018**, *45*, 412-421, doi:[https://doi.org/10.1016/S1876-3804\(18\)30046-6](https://doi.org/10.1016/S1876-3804(18)30046-6).
24. Asefa, T.; Dubovoy, V. 9.09 - Ordered Mesoporous/Nanoporous Inorganic Materials via Self-Assembly. In *Comprehensive Supramolecular Chemistry II*, Atwood, J.L., Ed.; Elsevier: Oxford, 2017; pp. 157-192.
25. He, X.; Wu, Z.; Xue, Y.; Gao, Z.; Yang, X. Fabrication of interlayer β -CD/g-C₃N₄@MoS₂ for highly enhanced photodegradation of glyphosate under simulated sunlight irradiation. *RSC Advances* **2019**, *9*, 4635-4643, doi:10.1039/C8RA10190F.
26. Dong, F.; Zhao, Z.; Xiong, T.; Ni, Z.; Zhang, W.; Sun, Y.; Ho, W.-K. In Situ Construction of g-C₃N₄/g-C₃N₄ Metal-Free Heterojunction for Enhanced Visible-Light Photocatalysis. *ACS Applied Materials & Interfaces* **2013**, *5*, 11392-11401, doi:10.1021/am403653a.
27. Dong, Q.; Wang, H.; Ji, S.; Wang, X.; Mo, Z.; Linkov, V.; Wang, R. Molten-Salt Media Synthesis of N-Doped Carbon Tubes Containing Encapsulated Co Nanoparticles as a Bifunctional Air Cathode for Zinc-Air Batteries. *Chemistry – A European Journal* **2020**, *26*, 10752-10758, doi:<https://doi.org/10.1002/chem.201905268>.
28. Okpalugo, T.I.T.; Papakonstantinou, P.; Murphy, H.; McLaughlin, J.; Brown, N.M.D. High resolution XPS characterization of chemical functionalised MWCNTs and SWCNTs. *Carbon* **2005**, *43*, 153-161, doi:<https://doi.org/10.1016/j.carbon.2004.08.033>.
29. Sun, M.; Zou, L.; Wang, P.; Fan, X.; Pan, Z.; Liu, Y.; Song, C. Nano valent zero iron (NZVI) immobilized CNTs hollow fiber membrane for flow-through heterogeneous Fenton process. *Journal of Environmental Chemical Engineering* **2022**, *10*, 107806, doi:<https://doi.org/10.1016/j.jece.2022.107806>.
30. Navidfar, A.; Bulut, O.; Baytak, T.; Iskender, H.; Trabzon, L. Boosted viscoelastic and dynamic mechanical behavior of binary nanocarbon based polyurethane hybrid nanocomposite foams. *Journal of Composite Materials* **2022**, *56*, 2907-2920, doi:10.1177/00219983221107964.