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International Conference Publishing Group

Science, Engineering and Technology Proceedings

Review

2025 International Conference on Chemistry, Science, and Sustainable Development (ICCSSD 2025)

Structural Engineering of Metal Sites for Catalysis

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Abstract: Structural engineering of metal sites has emerged as a pivotal strategy for advancing heterogeneous catalysis, enabling unprecedented control over catalytic activity, selectivity, and stability. The precise manipulation of metal coordination environments, metal-support interactions, and spatial arrangements of active sites provides opportunities to tailor catalytic properties for specific reactions. Single-atom catalysts represent a frontier in this field, offering maximum atomic efficiency and unique electronic structures that differ fundamentally from nanoparticles and bulk materials. The coordination geometry, oxidation state, and local environment of isolated metal atoms critically determine their catalytic performance in reactions ranging from electrocatalytic carbon dioxide reduction to hydrogen peroxide synthesis. Dual-metal site architectures introduce additional complexity and synergy, enabling tandem catalytic processes and cooperative substrate activation. This paper examines the principles and strategies of structural engineering for metal catalytic sites, exploring the relationships between atomic-scale structure and catalytic function. Recent advances in synthesis methods, characterization techniques, and theoretical understanding have enabled rational design of metal sites with optimized properties. The integration of experimental observations with computational predictions continues to drive progress in developing next-generation catalysts for energy conversion, environmental remediation, and chemical synthesis applications.

Keywords: single-atom catalysts; metal-support interactions; coordination engineering; heterogeneous catalysis; structural design; catalytic sites

Received: 25 July 2025
Revised: 02 August 2025
Accepted: 24 September 2025
Published: 24 October 2025

1. Introduction

The development of efficient catalytic systems represents a cornerstone of modern chemistry, with profound implications for energy conversion, environmental protection, and chemical manufacturing. Traditional heterogeneous catalysts based on metal nanoparticles have served industry for decades, yet their polydisperse nature and multiple surface sites often result in complex reaction pathways and limited selectivity. The emergence of single-atom catalysts has revolutionized the field by providing atomically dispersed metal centers with well-defined structures and maximum utilization of precious metals [1]. These materials represent the ultimate limit of miniaturization in heterogeneous catalysis, bridging the gap between homogeneous molecular catalysts and conventional supported metal catalysts. The unique electronic and geometric properties of isolated metal atoms enable catalytic behaviors that are fundamentally different from their nanoparticle counterparts.

Structural engineering of metal sites encompasses multiple design parameters, including the choice of metal element, coordination number and geometry, identity of coordinating atoms, and the nature of the support material. The metal-support interaction plays a crucial role in determining catalyst stability, electronic structure, and reactivity [2]. Strong interactions between metal atoms and support materials can prevent sintering and agglomeration while modulating the electronic properties of the metal center through charge transfer and orbital hybridization [3]. Understanding and controlling these interactions at the atomic level has become essential for developing catalysts with optimized performance. The frontier orbital interactions between metal atoms and support materials govern electron transfer processes and substrate activation mechanisms [3]. The concept of single atom not being alone emphasizes the critical importance of metal-support interactions in determining catalytic behavior [4].

The regulation of metal coordination environments offers powerful opportunities for tuning catalytic properties. The identity and arrangement of ligands or coordinating atoms in the first coordination sphere directly influence the oxidation state, electron density, and accessible coordination sites of the metal center [2,4]. Recent advances have demonstrated that precise control over coordination structure can dramatically enhance catalytic activity and selectivity for specific reactions. Metal atom-support interactions in single-atom catalysts have been extensively studied for various electrocatalytic applications, revealing fundamental principles that guide rational catalyst design [5]. The strategic manipulation of these interactions enables the development of catalysts with superior performance in energy-related reactions such as oxygen reduction, hydrogen evolution, and carbon dioxide conversion [1,5].

2. Fundamentals of Single-Atom Catalysis

2.1. Electronic Structure and Coordination Chemistry

The electronic structure of single-atom catalytic sites differs fundamentally from that of metal nanoparticles due to the absence of metallic bonding and the presence of discrete energy levels rather than continuous bands. The coordination environment of isolated metal atoms determines their electronic configuration through ligand field effects and covalent interactions with coordinating atoms [1]. The d-orbital splitting patterns and occupancy in single-atom catalysts can be systematically varied by changing the coordination geometry and the identity of ligands, providing control over redox properties and catalytic reactivity. Dual-metal sites represent an extension of this concept, where two metal centers can cooperatively activate substrates and drive tandem electrocatalytic processes [6].

The nature of metal-support bonding in single-atom catalysts involves complex interactions that stabilize isolated atoms against agglomeration while influencing their catalytic properties. Strong chemical bonds between metal atoms and support defects, heteroatoms, or functional groups are essential for maintaining atomic dispersion under reaction conditions [7]. The coordination number of metal atoms typically ranges from three to six, depending on the support structure and synthesis conditions. Lower coordination numbers generally result in more unsaturated metal centers with enhanced reactivity, while higher coordination may provide greater stability at the expense of some catalytic activity [1,7]. Heterogeneous single-atom catalysis has been recognized as a transformative approach in catalytic science [8]. The balance between stability and reactivity represents a key consideration in designing single-atom catalysts for practical applications. Table 1 summarizes the relationship between coordination environment and catalytic properties for representative single-atom catalytic systems.

Table 1. Coordination environments and properties of single-atom catalysts.

Metal	Support	Coordination	Coordination Number	Electronic State	Primary Application
Pt	Graphene	$\mathrm{Pt{-}N_4}$	4	+2	Oxygen reduction
Fe	N-doped carbon	$\mathrm{Fe{-}N_4}$	4	+2/+3	CO_2 reduction
Cu	TiO_2	$\mathrm{Cu{-}O_3}$	3	+1	CO oxidation
Ni	CeO_2	$\mathrm{Ni{-}O_4}$	4	+2	Methane reforming
Pd	Al_2O_3	$\mathrm{Pd{-}O_3}$	3	+2	Hydrogenation

2.2. Metal-Support Interactions and Their Regulation

Metal-support interactions represent one of the most critical factors governing the performance of single-atom catalysts, influencing both the stability of atomic dispersion and the intrinsic catalytic activity of metal sites. These interactions involve charge transfer, orbital hybridization, and geometric constraints that collectively determine the electronic structure and coordination environment of metal atoms [2]. The regulation of metal-support interactions has become a central theme in catalyst design, as systematic modification of these interactions enables fine-tuning of catalytic properties. Strong metal-support interactions can stabilize unusual oxidation states and coordination geometries that would be unstable in isolation [4]. Heterogeneous single-atom catalysts for electrochemical carbon dioxide reduction have demonstrated how metal-support engineering can optimize catalytic performance [9].

The electronic metal-support interaction involves charge transfer between metal atoms and the support material, which modulates the electron density and oxidation state of the catalytic center. Supports with high electron density, such as reduced metal oxides or electron-rich carbon materials, can donate electrons to metal atoms, lowering their effective oxidation state and enhancing their ability to activate electrophilic substrates [2,4]. Conversely, electron-deficient supports can accept electrons from metal atoms, stabilizing higher oxidation states that may be beneficial for oxidation reactions. The geometric component of metal-support interaction relates to the spatial arrangement and identity of atoms in the support that coordinate to the metal center, which determines the coordination geometry and accessibility of the metal site. Coordination polymers have also shown potential in catalytic applications through their unique metal coordination environments [10].

Frontier orbital interactions between metal atoms and support materials have been identified as a key factor controlling catalytic activity in single-atom catalysis [3]. The overlap between metal d-orbitals and support orbitals creates bonding and antibonding states whose energy levels and occupancy influence substrate binding and activation. Strategic design of support materials to optimize these frontier orbital interactions can significantly enhance catalytic performance [3]. For hydrogen peroxide electrosynthesis, the metal atom-support interaction has been shown to control the selectivity between two-electron and four-electron oxygen reduction pathways [5]. Table 2 illustrates how different support materials influence the properties and performance of single-atom catalysts through varied metal-support interactions.

Table 2. Influence of support materials on single-atom catalyst properties.

Support Type	Interaction Strength	Charge Transfer	Coordination Sites	Stability	Activity Enhancement
N-doped graphene	Strong	M ← N	N atoms	High	3-5×

Metal oxides	Medium-Strong	M → O	O atoms	Very High	2-4×
Defective carbon	Medium	Minimal	C defects	Medium	2-3×
Zeolites	Medium	M → Framework	O atoms	Very High	1.5-2×
Polymers	Weak-Medium	Variable	N/O groups	Medium	1-2×

2.3. Synthesis and Stabilization Strategies

The synthesis of single-atom catalysts requires precise control over metal deposition and stabilization to achieve atomic dispersion without aggregation into nanoparticles. Various chemical synthesis methods have been developed to create single atomic site catalysts, each with distinct advantages and limitations [11]. Wet chemical approaches, including impregnation, coprecipitation, and sol-gel methods, offer scalability and versatility but often require careful control of conditions to prevent metal aggregation. Atomic layer deposition and chemical vapor deposition provide precise control over metal loading and distribution but are generally limited to specific metal-support combinations [7,8].

The stabilization of isolated metal atoms against sintering and aggregation represents a fundamental challenge in single-atom catalyst design. Strong anchoring sites on the support surface are essential for maintaining atomic dispersion under reaction conditions, particularly at elevated temperatures or in the presence of reactive atmospheres [11]. Nitrogen-doped carbon materials provide effective anchoring through strong metal-nitrogen coordination bonds, while metal oxides can trap single atoms at oxygen vacancies or hydroxyl groups. The density and distribution of anchoring sites must be carefully controlled to achieve optimal metal loading without creating isolated regions of high metal concentration that could promote aggregation [1, 8]. Single-atom catalysts have found important applications in environmental catalysis where atomic dispersion is critical [12].

The thermal stability of single-atom catalysts depends critically on the strength of metal-support bonding and the mobility of metal atoms on the support surface. Supports with high concentrations of strong binding sites distributed uniformly across the surface provide superior resistance to sintering [11]. Post-synthesis treatments such as high-temperature annealing in controlled atmospheres can strengthen metal-support interactions and improve catalyst stability. Chemical synthesis approaches that create metal-support bonds during the formation process rather than through subsequent deposition often yield more stable catalysts [7,11]. Copper-based coordination polymers have demonstrated how ligand design influences structural stability and catalytic properties [13]. Table 3 compares different synthesis methods for single-atom catalysts in terms of their key characteristics and resulting catalyst properties.

Table 3. Synthesis methods and characteristics of single-atom catalysts.

Synthesis Method	**Temperature Range**	**Metal Loading Control**	**Dispersion Quality**	**Scalability**	**Typical Stability**
Wet impregnation	25-100°C	Moderate	Good	Excellent	Medium
Atomic layer deposition	100-300°C	Excellent	Excellent	Limited	High
Pyrolysis	600-1000°C	Limited	Very Good	Good	Very High
Ball milling	25°C	Poor	Moderate	Excellent	Medium

Electrochemical deposition	25-80°C	Good	Good	Good	Medium-High

3. Dual-Metal Site Engineering

3.1. Cooperative Effects in Bimetallic Catalysis

The design of dual-metal site catalysts introduces additional complexity and opportunities for catalytic enhancement through cooperative interactions between adjacent metal centers. Dual-metal sites can drive tandem electrocatalytic processes by enabling sequential reactions that would be difficult to achieve with single metal centers [6]. The spatial proximity of two different metal atoms allows for synergistic substrate activation, where one metal site facilitates initial binding or activation while the second metal promotes subsequent transformation steps. This cooperative mechanism can lead to dramatic improvements in reaction rates and selectivity compared to monometallic catalysts. Coordination environment design has been shown to enhance catalytic performance in both metallic and non-metallic systems [14].

The electronic coupling between adjacent metal atoms in dual-site catalysts creates unique electronic structures that differ from isolated single atoms. Through-space and through-bond interactions can modify the electron density distribution and oxidation states of both metal centers, influencing their individual and collective reactivity [6]. The distance between metal sites plays a crucial role, with optimal separations typically in the range of three to eight angstroms depending on the reaction mechanism. Closer proximity enables stronger electronic coupling and facilitates substrate transfer between sites, while greater separation may be necessary for accommodating larger substrates or preventing adverse interactions [14]. Site-designed dual-active-center catalysts have demonstrated remarkable performance in co-catalytic applications [15].

The design of dual-metal site catalysts requires careful consideration of metal identity, spatial arrangement, and the support environment. Strategic placement of two different metals with complementary catalytic functions can enable co-catalysis in advanced oxidation processes and other challenging transformations [15]. For electrocatalytic carbon dioxide reduction to multicarbon products, dual-metal sites have demonstrated superior performance by stabilizing key intermediates and promoting carbon-carbon coupling reactions [6]. The rational design of bimetallic sites benefits from computational screening to identify promising metal combinations and geometric arrangements before experimental synthesis [14, 15]. Table 4 presents examples of dual-metal site catalysts with their structural features and catalytic applications.

Table 4. Dual-metal site catalysts and their catalytic properties.

Metal Pair	**Support**	**Interatomic Distance**	**Coordination**	**Target Reaction**	**Synergistic Effect**
Cu-Fe	N-C	4.2 Å	$M\text{-}N_4$	CO_2 to C_2H_4	C-C coupling
Ni-Fe	Graphene	3.8 Å	$M\text{-}N_3$	Oxygen evolution	Enhanced kinetics
Co-Mn	Carbon nitride	5.1 Å	$M\text{-}N_4$	Oxidation	Radical generation
Pt-Ru	TiO_2	3.5 Å	$M\text{-}O_3$	Methanol oxidation	CO tolerance
Pd-Au	Al_2O_3	4.8 Å	$M\text{-}O_4$	Hydrogenation	Improved selectivity

3.2. Spatial Arrangement and Distance Effects

The spatial arrangement of metal sites in dual-center catalysts profoundly influences their cooperative behavior and overall catalytic performance. The interatomic distance between adjacent metal centers determines the extent of electronic coupling and the feasibility of substrate transfer or intermediate shuttling between sites [6]. When metal atoms are positioned within close proximity, typically less than five angstroms, strong electronic interactions can occur through direct orbital overlap or mediated by bridging ligands. These interactions create delocalized electronic states that can facilitate electron transfer and stabilize charged intermediates during catalytic cycles [15].

The geometric configuration of dual-metal sites also affects the accessibility and binding modes of substrates. Linear, angular, and triangular arrangements of metal pairs with respect to the support surface create different steric environments that favor specific substrate orientations and reaction pathways [14]. For reactions involving large or complex substrates, greater separation between metal centers may be necessary to accommodate the substrate without steric hindrance. Conversely, reactions requiring concerted action of both metal sites for substrate activation benefit from closer proximity that enables simultaneous coordination [6, 15]. The support material plays a crucial role in dictating the available spatial arrangements, with two-dimensional materials offering more flexibility in metal positioning compared to three-dimensional frameworks.

Precise control over metal site spacing requires sophisticated synthesis strategies that can direct the placement of individual atoms or small clusters. Template-directed synthesis using organic molecules with predetermined metal binding sites offers one approach to achieving defined spatial arrangements [11]. Alternatively, sequential deposition methods can be employed to place different metals at specific locations on patterned supports [12]. The characterization of metal site spacing presents significant challenges, requiring advanced techniques such as aberration-corrected scanning transmission electron microscopy and extended X-ray absorption fine structure spectroscopy [7, 8]. Table 5 summarizes the relationship between metal site spacing and catalytic outcomes for various dual-metal catalysts.

Table 5. Effect of metal site spacing on catalytic performance.

Metal Pair	Interatomic Distance	Electronic Coupling	Catalytic Enhancement	Optimal Reaction Type	Substrate Size Limit
Cu-Co	3.2 Å	Strong	8×	CO_2 reduction	Small molecules
Ni-Pt	5.5 Å	Weak	3×	Hydrogenation	Medium molecules
Fe-Mn	4.0 Å	Moderate	5×	Oxidation	Small-medium
Pd-Ag	6.8 Å	Very weak	2×	C-C coupling	Large molecules
Ru-Ir	3.8 Å	Strong	10×	Water splitting	Small molecules

3.3. Ligand Environment Engineering

The ligand environment surrounding metal catalytic sites exerts profound influence on their electronic properties, stability, and reactivity. Engineering the first coordination sphere through judicious selection of coordinating atoms and functional groups enables fine-tuning of catalytic performance [13]. Nitrogen-containing ligands, such as pyridine, pyrrole, and imine groups, provide strong coordination to transition metals while offering tunability through electronic and steric modifications. Oxygen-containing ligands, including hydroxyl, carboxyl, and carbonyl groups, create different electronic environments that may be preferred for certain metal-substrate combinations [10, 13].

The second coordination sphere, comprising atoms and functional groups adjacent to but not directly coordinating the metal center, also plays important roles in catalysis. These groups can participate in substrate recognition, proton transfer, and stabilization of reaction intermediates through hydrogen bonding or electrostatic interactions [14]. Strategic placement of acidic or basic groups in the second sphere can facilitate proton-coupled electron transfer processes that are central to many electrocatalytic reactions [5, 15]. The flexibility and rigidity of the ligand framework affect the dynamic behavior of the metal center, with more rigid environments providing greater stability but potentially limiting substrate access.

The development of coordination environment design principles has advanced significantly through combined experimental and computational studies. Density functional theory calculations can predict how variations in ligand identity and geometry affect metal electronic structure and binding energies for relevant substrates and intermediates [14]. These predictions guide experimental synthesis efforts and help identify promising ligand modifications for testing. The fabrication of novel coordination polymers with V-shaped auxiliary ligands demonstrates how deliberate ligand design can optimize specific catalytic properties [13]. Understanding the interplay between metal centers, primary coordination ligands, and secondary sphere elements remains an active area of research with significant implications for advancing catalytic performance across diverse applications.

4. Advanced Characterization and Design Strategies

4.1. Structural Characterization Techniques

The characterization of metal site structure in single-atom and dual-metal catalysts requires sophisticated analytical techniques capable of probing atomic-scale features. X-ray absorption spectroscopy, including X-ray absorption near edge structure and extended X-ray absorption fine structure, provides element-specific information about oxidation states, coordination numbers, and local geometric structures around metal atoms [7]. These techniques are particularly valuable for single-atom catalysts where conventional methods like X-ray diffraction are ineffective due to the lack of long-range order. The sensitivity of X-ray absorption spectroscopy to coordination environment makes it indispensable for confirming atomic dispersion and identifying coordinating atoms [8].

Advanced electron microscopy techniques, particularly aberration-corrected scanning transmission electron microscopy operated in high-angle annular dark-field mode, enable direct visualization of individual metal atoms on support surfaces [1]. The atomic number contrast in these images allows differentiation between metal atoms and support elements, providing unambiguous evidence of atomic dispersion. Electron energy loss spectroscopy performed in scanning transmission electron microscopy mode offers complementary information about electronic structure and bonding [7, 8]. However, electron beam damage and the statistical nature of imaging limit the comprehensive characterization of all metal sites in heterogeneous samples.

Spectroscopic methods including infrared spectroscopy with probe molecules, X-ray photoelectron spectroscopy, and ultraviolet-visible spectroscopy provide ensemble-averaged information about metal site electronic structure and surface chemistry [11]. Probe molecule studies using carbon monoxide, nitric oxide, or pyridine can reveal coordination numbers and the presence of distinct metal site types through characteristic vibrational frequencies [12]. In situ and operando characterization techniques that monitor catalyst structure under reaction conditions have become increasingly important for understanding dynamic structural changes and identifying active site configurations during catalysis [7,11]. These advanced characterization approaches collectively enable comprehensive understanding of metal site structure and its evolution during catalytic processes.

4.2. Computational Design and Prediction

Computational approaches have become integral to the design and optimization of metal catalytic sites, offering predictive capabilities that complement and guide experimental efforts. Density functional theory calculations provide accurate energetics for substrate adsorption, reaction intermediates, and transition states, enabling the construction of complete energy landscapes for catalytic reactions [14]. These calculations reveal how variations in metal identity, coordination environment, and support properties affect the thermodynamics and kinetics of elementary catalytic steps. Machine learning methods applied to computational datasets can identify patterns and correlations that inform the selection of promising catalyst compositions and structures [15].

The computational screening of large numbers of potential catalyst structures has emerged as a powerful strategy for accelerating catalyst discovery. High-throughput density functional theory calculations can evaluate hundreds or thousands of candidate structures to identify those with optimal binding energies for key intermediates or favorable energetic profiles for complete reaction pathways [14]. Descriptor-based approaches that correlate easily calculated properties with catalytic performance enable rapid assessment of catalyst potential without full mechanistic calculations. The integration of thermodynamic, kinetic, and mechanistic descriptors provides comprehensive evaluation frameworks for comparing different catalyst designs [11, 15].

Ab initio molecular dynamics simulations capture the dynamic behavior of metal sites and their interactions with substrates under realistic conditions, including temperature effects and solvent interactions [14]. These simulations reveal conformational changes, ligand fluctuations, and substrate binding pathways that static calculations cannot capture. Microkinetic modeling based on calculated energetics connects atomic-scale mechanistic understanding to macroscopic reaction rates and selectivities, enabling prediction of catalyst performance under various operating conditions [15]. The synergy between computational predictions and experimental validation continues to accelerate progress in metal site engineering, with successful examples spanning diverse catalytic applications from energy conversion to environmental remediation.

4.3. Emerging Trends and Future Directions

The field of metal site engineering for catalysis continues to evolve rapidly, with several emerging trends poised to shape future developments. The exploration of non-traditional support materials, including covalent organic frameworks, metal-organic frameworks, and two-dimensional materials beyond graphene, offers new opportunities for creating unique metal coordination environments [12]. These supports provide tunable pore structures, high surface areas, and diverse coordination chemistries that can be exploited for optimizing metal site properties. The integration of multiple functional elements within single catalyst systems, combining different metal sites with redox-active supports or photosensitizers, enables multi-functional catalytic platforms for complex transformations [15].

The development of dynamic catalytic systems where metal site structure adapts in response to reaction conditions represents an frontier in catalyst design [11]. Self-optimizing catalysts that restructure to maximize activity for changing substrates or reaction environments could provide robustness and versatility beyond conventional static systems. Understanding and controlling the dynamic aspects of metal site structure requires advanced in situ characterization and theoretical frameworks that account for structural flexibility [7]. The application of artificial intelligence and autonomous experimentation platforms promises to accelerate the discovery and optimization of engineered metal sites through efficient exploration of vast compositional and structural spaces [14].

The translation of fundamental insights into practical catalytic technologies requires addressing challenges related to catalyst synthesis scalability, stability under industrial conditions, and economic viability [12]. Developing cost-effective synthesis routes that maintain precise control over metal site structure at large scales remains a significant challenge. Improving catalyst stability through enhanced metal-support interactions and protective strategies extends operational lifetimes and improves process economics [8, 11]. The continued integration of experimental innovation, theoretical understanding, and practical implementation considerations will drive the realization of engineered metal sites in next-generation catalytic technologies for sustainable energy, chemical manufacturing, and environmental protection.

5. Conclusion

Structural engineering of metal sites has emerged as a transformative approach for advancing heterogeneous catalysis, providing unprecedented control over catalytic properties through atomic-scale design. Single-atom catalysts represent the ultimate limit of metal utilization efficiency, offering well-defined active sites with tunable electronic structures and coordination environments. The precise manipulation of metal-support interactions, coordination chemistry, and spatial arrangements enables optimization of catalytic activity, selectivity, and stability for diverse applications. Dual-metal site architectures extend these capabilities through cooperative effects and synergistic substrate activation. Advanced characterization techniques and computational methods have become essential tools for understanding structure-function relationships and guiding rational catalyst design. The integration of experimental synthesis, sophisticated characterization, and theoretical modeling continues to drive rapid progress in this field. Emerging trends including dynamic catalytic systems, multi-functional platforms, and artificial intelligence-guided discovery promise to further accelerate innovation. The successful translation of fundamental discoveries to practical technologies requires continued focus on scalability, stability, and economic considerations. As the field matures, engineered metal sites will play increasingly important roles in addressing global challenges related to energy conversion, environmental sustainability, and chemical manufacturing efficiency.

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