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Precision Surface Engineering of Functionalized Nanoparticles for Enhanced Catalytic Activity and Stability

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ABSTRACT: Nanoparticles (NPs) offer exceptional catalytic potential due to their high surface-area-to-volume ratios and tunable surface chemistries. However, limitations such as agglomeration, leaching, and poor selectivity hinder their broader application. This study investigates the role of surface functionalization in enhancing catalytic performance metrics, including activity, selectivity, and durability, across noble metal and metal oxide nanoparticles. Functionalized nanoparticles were synthesized via chemical reduction, sol–gel, and electrochemical methods, followed by ligand exchange, polymer grafting, and core–shell fabrication. Characterization tools TEM, XPS, TGA, and ICP-OES were employed to link surface features with performance. Catalytic activity was tested across model reactions, and key metrics such as turnover frequency (TOF), conversion efficiency, selectivity, and cycle stability were quantified. Results demonstrate that multidentate ligands, polymer brushes, and Janus morphologies significantly improve catalytic outcomes. AuNPs functionalized with tripodal phosphines achieved TOFs up to 2100 h^{-1}, while PdNPs with polymer brushes retained over 90% activity after 10 cycles. Correlation analyses confirmed that optimal ligand coverage (4.7–6.2 mg/m^2) reduces activation energy and enhances electron transfer. Structural and electronic stability were validated through TEM and XPS, and real-time spectroscopic data supported mechanistic interpretations. The study concludes that surface functionalization is a powerful strategy for engineering high-performance catalysts. It offers a design framework for linking structural features to functional outcomes, paving the way for intelligent, adaptive catalytic systems.

Keywords: Functionalized Nanoparticles, Surface Modification, Catalysis, Turnover Frequency, Stability, Ligand Engineering, Structure–Function Relationship

INTRODUCTION

The utilization of nanoparticles (NPs) in heterogeneous catalysis has garnered significant attention in recent decades due to their high surface-area-to-volume ratios, tunable physicochemical

properties, and size-dependent quantum effects. These characteristics position nanoparticles as promising candidates in a variety of catalytic processes ranging from hydrogenation and oxidation to complex carbon–carbon coupling reactions. However, despite their apparent advantages, unsupported nanoparticles frequently encounter critical challenges that hinder their deployment in industrial-scale catalysis. Key limitations include instability, aggregation, leaching, and limited reusability, all of which impact their catalytic efficacy and durability.

One of the foremost limitations of unsupported nanoparticles is their inherent instability under reaction conditions. The high surface energy of nanoscale materials often leads to spontaneous aggregation or sintering, especially in thermal or high-concentration environments, thereby diminishing the active surface area and, consequently, the catalytic activity (Patil, 2021). Additionally, the absence of a solid support matrix renders these nanoparticles particularly vulnerable to leaching, especially during liquid-phase reactions, where metal atoms may detach and dissolve into the reaction medium (Hock et al., 2021). This leaching not only reduces catalytic efficiency but also introduces contamination risks that complicate downstream purification. Moreover, unsupported nanoparticles typically lack the mechanical resilience necessary to endure prolonged operational stresses, thus limiting their viability in real-world catalytic applications (Bressi et al., 2023).

To address these drawbacks, surface functionalization has emerged as a pivotal strategy for modifying and stabilizing nanoparticles. Functionalization involves the deliberate attachment of organic or inorganic moieties onto the nanoparticle surface, thereby altering its charge distribution, hydrophilicity, steric profile, and electronic structure. This process enables the precise tuning of nanoparticle behavior within a catalytic system. For example, the incorporation of organic ligands can enhance colloidal stability by introducing steric hindrance or electrostatic repulsion, which mitigates aggregation (Chen & Rodionov, 2016). Additionally, certain ligands can modulate the electronic environment around the active site, effectively altering the adsorption energies of key reactants and intermediates, thus enhancing catalytic activity and selectivity. Such modifications are particularly influential in transition-metal-based nanoparticles, where ligand identity directly affects d-orbital occupancy and catalytic behavior (Fomenko et al., 2023).

Several classes of catalytic reactions stand to benefit substantially from nanoparticle surface modification. In particular, transformations such as Suzuki–Miyaura cross-coupling, selective hydrogenation, and oxidation reactions exhibit improved catalytic efficiencies when functionalized nanoparticles are employed (Verma et al., 2018). For instance, palladium nanoparticles, which are widely utilized in carbon–carbon bond formation, demonstrate increased stability and reusability when modified with appropriate ligands or polymer coatings. Functionalization strategies can also promote alternative reaction pathways, especially in systems where conventional routes are sluggish or non-selective. For example, the dehydrogenation of alcohols a reaction sensitive to both steric and electronic effects can be significantly enhanced through surface engineering (Viola et al., 2018).

Understanding the dominant degradation mechanisms in nanoparticle-based catalysis is critical to developing effective stabilization strategies. Leaching and sintering are the most prevalent forms

of degradation. Leaching involves the dissolution of surface atoms into the reaction medium, which is particularly problematic in aqueous or acidic environments, and is often exacerbated in unsupported systems. Sintering, on the other hand, results from particle coalescence under elevated temperatures or reactive atmospheres, leading to larger particle sizes and reduced surface area (Seth et al., 2023). Both mechanisms underscore the necessity of functionalizing the nanoparticle surface to introduce structural stability and resist degradation under operational conditions.

Ligand engineering is a subset of surface functionalization that focuses specifically on tailoring the chemical nature and configuration of ligands attached to nanoparticle surfaces. By selecting ligands with appropriate steric bulk, polarity, and binding strength, researchers can influence nanoparticle dispersibility, reactivity, and environmental stability. For instance, tripodal phosphine ligands have been shown to create robust surface bonds with noble metals such as gold and platinum, resulting in enhanced catalytic activity and reduced leaching (Kaźmierczak et al., 2021). Moreover, dynamic ligand exchange methods allow for adaptive functionalization, enabling the catalyst surface to reconfigure in response to changing reaction conditions (Chen & Rodionov, 2016). These strategies are increasingly applied in electrocatalysis and green chemistry contexts, where catalyst longevity and reusability are essential performance indicators (Vasileff et al., 2018).

In addition to ligand-based strategies, recent advances in interface engineering have contributed significantly to the optimization of nanoscale catalytic systems. Interface engineering refers to the deliberate design of interfacial zones between nanoparticle cores and surrounding environments be it solvents, supports, or reaction media to facilitate enhanced electron transfer, reactant diffusion, and product desorption. Modern techniques such as atomic layer deposition (ALD) and molecular beam epitaxy (MBE) have enabled researchers to create precise core–shell and heterostructure architectures that optimize these interfacial interactions (N. Zhang & Jiang, 2021). These approaches are particularly effective in applications such as CO2 reduction and oxygen evolution, where the catalytic performance is sensitive to electronic structure and charge mobility Myung et al., (2016). Emerging innovations include the integration of redox-active interfacial layers that can dynamically modulate catalyst behavior in situ, opening new avenues for responsive and adaptive catalytic systems (Irvine & Xie, 2019).

Taken together, the synthesis of functionalized nanoparticles represents a multifaceted strategy for overcoming the intrinsic limitations of conventional nanoparticle catalysts. Through careful design of surface chemistry, ligand architecture, and interfacial properties, it is possible to significantly enhance catalytic activity, selectivity, and durability. This study builds upon the aforementioned advances to systematically evaluate various functionalization strategies, focusing on their effects on key performance metrics such as turnover frequency, product selectivity, and operational stability. By establishing clear correlations between structural modifications and catalytic outcomes, this research aims to contribute to the rational design of next-generation nanoparticle catalysts for industrial and environmental applications.

METHOD

The synthesis, functionalization, and characterization of nanoparticles (NPs) form the basis for understanding their catalytic behavior. This chapter describes the methods employed in preparing functionalized noble metal and metal oxide nanoparticles, highlights the influence of different grafting strategies on surface coverage and catalytic accessibility, and details the characterization techniques used to correlate surface properties with catalytic performance.

Synthesis of Functionalized Nanoparticles

The selection of synthesis methods plays a crucial role in determining the morphology, crystallinity, and functional potential of nanoparticle catalysts. This study incorporates three principal techniques: chemical reduction, sol–gel synthesis, and electrochemical deposition. These approaches are selected based on the type of nanoparticle core noble metals or metal oxides and their compatibility with downstream functionalization strategies.

Chemical reduction is a widely adopted approach for synthesizing noble metal nanoparticles such as gold, palladium, and platinum. This method involves the reduction of metal precursors in solution using reducing agents under controlled conditions. The resulting nanoparticles are typically stabilized with capping agents or surfactants, which can later be exchanged or modified for specific functionalization. The method offers good control over particle size and monodispersity. Although the primary focus of Karadaghi et al. (2022) was on molybdenum-based systems, their work underscores the critical role of surface modifications in stabilizing active phases under mild reaction conditions, a principle applicable to noble metals as well.

Sol–gel synthesis is particularly suited for the fabrication of metal oxide nanoparticles such as TiO_2, CeO_2, and Fe_3O_4. This method involves hydrolysis and polycondensation reactions of metal alkoxides or salts, followed by aging and calcination processes. The sol–gel route enables precise control over porosity, crystallinity, and surface area. Jing et al., (2024) highlighted the importance of ligand evolution during sol–gel synthesis for catalytic selectivity enhancement, demonstrating that tailoring surface chemistry during synthesis is as crucial as post-synthetic modification.

Electrochemical deposition offers an effective means of producing noble metal coatings or particles on conductive substrates. This technique is particularly advantageous for applications requiring high catalyst-substrate adhesion and is conducive to preparing electrocatalysts. Demonstrated the use of electro-spark deposition to enhance the catalytic performance of NiTi electrodes through noble metal incorporation, indicating the broader relevance of deposition strategies for catalyst design(He et al., 2016).

Functionalization Strategies and Surface Grafting Techniques

Following synthesis, nanoparticles are subjected to functionalization via two principal strategies: ligand exchange and grafting-from polymerization. Each method offers distinct advantages and challenges in terms of surface coverage uniformity, ligand density, and catalytic site accessibility.

The ligand exchange technique involves replacing native surface ligands (e.g., citrate or CTAB) with functional ligands that can enhance catalytic properties. These ligands may include phosphines, amines, thiols, or carboxylates. While ligand exchange is relatively straightforward, it may result in heterogeneous surface coverage or introduce steric hindrance that limits access to active sites. (L. Zhang et al., 2018) illustrated how the selection of ligands affects hydrogen bonding networks and catalytic selectivity in palladium-based systems, confirming that surface chemistry dictates the interaction landscape for substrates and intermediates.

The grafting-from approach involves initiating polymerization directly from the nanoparticle surface. This method typically produces higher ligand densities and uniform coatings compared to grafting-to methods. Controlled radical polymerization techniques, such as atom transfer radical polymerization (ATRP) or reversible addition–fragmentation chain transfer (RAFT), are often used. Liu et al. (2018) demonstrated how grafted polymer layers could regulate the surface electronic structure of supported catalysts, thereby fine-tuning their reactivity and selectivity. This control is essential in balancing catalyst stability and active site accessibility.

In practice, both techniques are selected based on the desired surface architecture, the target reaction, and the solvent compatibility of the ligand system. Karadaghi et al., (2022) further showed that grafting methods influence both the spatial orientation and chemical interaction of the functionalized surface, thereby impacting catalytic outcomes.

Characterization of Functionalized Nanoparticles

Characterization techniques are employed to analyze the structural and chemical attributes of nanoparticles before and after functionalization. These tools are critical for establishing correlations between surface properties and catalytic behavior.

Transmission Electron Microscopy (TEM) and High-Resolution TEM (HRTEM) provide detailed morphological and structural information at the nanoscale. These techniques allow visualization of nanoparticle shape, size distribution, and core–shell or heterostructure configurations. HRTEM is particularly useful for revealing lattice fringes and interface boundaries. Rafaïdeen et al., (2019) employed TEM and HRTEM to understand how surface modifications influenced catalyst stability and sintering resistance during reactions.

X-ray Photoelectron Spectroscopy (XPS) is used to analyze surface elemental composition and oxidation states. This technique is indispensable for confirming successful functionalization and for assessing how surface ligands affect the electronic environment of active sites. Huang et al., (2018) applied XPS to investigate the electronic interactions between ligands and metal centers, revealing significant shifts in binding energy that correlate with catalytic reactivity.

Atomic Force Microscopy (AFM) and Scanning Tunneling Microscopy (STM) are employed to map surface topography and measure local mechanical and electronic properties. These techniques enable the identification of ligand distribution and surface roughness, both of which influence diffusion and substrate binding. Zhang et al. (2018) demonstrated that variations in surface functional group density affected nanoparticle performance across catalytic cycles.

Catalytic performance testing involves exposing functionalized nanoparticles to model reactions under controlled temperature and pressure conditions. Parameters such as turnover frequency (TOF), product selectivity, and conversion rates are recorded. These values are then correlated with surface characteristics identified through structural techniques. Moiseeva et al., (2023) demonstrated this approach across various catalytic systems, showing that specific surface attributes such as ligand density or shell thickness correlate directly with enhanced performance metrics.

Temperature-Programmed Desorption (TPD) and Temperature-Programmed Reduction (TPR) techniques provide further insights into the thermal stability and reactive properties of catalysts. These analyses measure how strongly molecules adsorb to the catalyst surface or how readily the surface can be reduced. He et al. (2016) employed TPD and TPR to assess the desorption dynamics and redox behavior of surface-modified Ni-based catalysts, thereby elucidating the role of surface modification in tuning catalytic energetics.

Experimental Workflow and Data Integration

The methodology integrates synthesis, surface functionalization, and performance evaluation into a coherent workflow. Nanoparticles are first synthesized using appropriate chemical or physical methods, followed by ligand attachment or polymer grafting. These materials are then subjected to extensive characterization and evaluated in model catalytic reactions. Performance data are statistically analyzed to determine trends and validate hypotheses related to structure–function relationships.

In conclusion, the methodology is designed to elucidate the impact of surface functionalization on the catalytic behavior of nanoparticles. By combining controlled synthesis, strategic functionalization, and rigorous characterization, this framework enables a comprehensive understanding of how nanoscale engineering influences catalytic efficiency, selectivity, and durability.

RESULT AND DISCUSSION

This chapter presents and analyzes the experimental findings related to the catalytic performance of functionalized nanoparticles (NPs), including their turnover frequency (TOF), selectivity, structural correlations, stability across catalytic cycles, and mechanistic insights from microscopy

and spectroscopy. The results are categorized into four main sections, each corresponding to a specific facet of catalyst evaluation.

Catalyst Performance Overview

The evaluation of catalytic performance began with benchmarking TOF and product selectivity for functionalized versus unfunctionalized nanoparticles. The data consistently showed that functionalized NPs delivered higher TOF values and greater selectivity across reactions such as oxidation and hydrogenation.

For instance, AuNPs with multidentate phosphine ligands exhibited a TOF of 2100 h^{-1} and 88% selectivity, outperforming unfunctionalized analogs. This aligns with the findings of Albrahim et al. (2021), who observed that ligand-modified catalysts exhibit enhanced electrochemical reaction rates due to optimized ligand–substrate interactions. Similarly, PdNPs coated with polymer brushes (PVP-b-PEG) showed notable conversion rates and a 90% selectivity over 10 catalytic cycles.

Studies such as those by Zhu et al., (2018) have emphasized that core–shell and Janus architectures can improve reactivity through synergistic or interfacial effects. In this work, Pt Janus nanoparticles reached a TOF of 1800 h^{-1}, demonstrating the benefit of structural asymmetry.

Established performance benchmarks, such as those reported by Lai et al., (2018) for Pd-based C–C coupling, were used as reference points. Our functionalized PdNPs consistently met or exceeded these standards. Further, as Wei et al. (2023) noted, decreasing NP size increases surface-to-volume ratio and TOF; our smaller 2–5 nm Pt and Au catalysts confirmed this trend.

Structure–Function Correlation

The relationship between nanoparticle surface modifications and catalytic activity was investigated by measuring ligand coverage, nanoparticle size, activation energy, and electronic properties.

Table 2 below shows that ligand coverage (measured via TGA) between 4.7–6.2 mg/m^2 correlates with increased TOF and reduced apparent activation energies (43–52 kJ/mol). This supports Risch et al., (2017), who theorized that optimal ligand density promotes electron transfer without excessive steric hindrance.

X-ray photoelectron spectroscopy (XPS) revealed shifts in binding energies for functionalized catalysts, indicative of changes in electron density. As discussed by Ali et al., (2024), such shifts correlate with ligand–metal interactions and catalytic reactivity. Our results showed that AuNPs with denser ligand coatings had larger XPS shifts, suggesting stronger ligand-induced electronic modulation.

However, TGA-based ligand quantifications displayed some inconsistencies, likely due to variation in NP morphology and ligand thermal stability an observation aligned with Guzman-Juarez et al., (2022), who recommended cross-validation with FTIR or XPS data for robust ligand assessment.

Catalyst Stability Across Cycles

Catalyst durability was assessed over multiple reaction cycles. Table 3 summarizes TOF retention, morphological integrity, and leaching values.

PdNPs with polymer brushes retained 91.2% activity after 10 cycles, with a minor particle growth (+6.5%) observed via TEM and 2 ppm metal detected by ICP-OES. NiOx with an SiO_2 shell showed 88.8% retention and <1 ppm leaching, confirming the anti-sintering protection afforded by inorganic coatings. These results echo the work of Wang et al. (2023), who showed Janus and core–shell particles outperform uncoated systems in multiphase catalysis.

Leaching and regeneration were quantified using ICP and supported by XPS. Lai et al. (2018) have shown that polymer shells often outperform inorganic ones in reusability but may offer less structural protection. Our findings confirm this balance, as polymer-coated PdNPs showed better reusability, while inorganic-coated NiOx offered stronger leach resistance.

Morphologies such as Janus structures (PtNP-05) showed exceptional retention and reusability over four cycles due to interfacial stabilization. Vega et al., (2019) similarly observed prolonged activity in Janus catalysts designed for phase-specific catalysis.

Visual and Mechanistic Evidence

Transmission electron microscopy (TEM) was employed to monitor particle morphology before and after catalysis. TEM images revealed that NiOx-03 particles maintained size integrity (<8% change), while PdNP-02 exhibited minor sintering. These visual confirmations are consistent with Albrahim et al. (2021), who used in situ TEM to study particle changes in real time.

Changes in ligand shell morphology were confirmed by high-resolution TEM and AFM. In the case of chitosan-functionalized Fe_3O_4, the shell thickness and morphology were altered after reaction, possibly due to thermal or solvent interactions.

Janus nanoparticles showed evidence of interface-specific catalytic activity. As Lai et al. (2018) highlighted, Janus NPs engage differently at water–oil interfaces, facilitating localized catalytic enhancement. Our PtNP-05 exhibited differential behavior when positioned at multiphase boundaries, confirming directional reactivity.

In situ spectroscopy further validated the functionalization effects. Operando XAS and XPS indicated electronic transitions in Au and Pd NPs during catalysis. These results align with studies by Risch et al. (2022), which confirm that real-time spectroscopic methods can trace catalytic mechanism shifts upon surface modification.

Table 1: Functionalized NP Catalysts – Performance Overview

Material_ID	Core	Size (nm)	Functionalization_Type	TOF (h^{-1})	Conversion (%)	Selectivity (%)	Cycles	Leaching (ppm)
AuNP-01	Au	5	Multidentate ligand	2100	95	88	5	<1
PdNP-02	Pd	3	Polymer brush	1300	85	90	10	2
NiOx-03	NiO	8	Inorganic shell	850	78	84	6	<1
Fe3O4-04	Fe_3O_4	12	Bio-functionalization	670	60	92	8	1.5
PtNP-05	Pt	2	Janus	1800	91	86	4	1

Table 2: Structure–Function Parameters

Sample_ID	Ligand_Coverage (mg/m²)	NP_Size (nm)	TOF (h^{-1})	Activation Energy (kJ/mol)	XPS_Binding_Shift (eV)	TGA_Weight_Loss (%)
AuNP-01	6.2	5.0	2100	45	0.7	12.5
PdNP-02	4.7	3.0	1300	52	0.5	14.1
PtNP-05	5.5	2.0	1800	43	0.8	10.8

Table 3: Catalyst Stability Across Cycles

Catalyst_ID	Initial_TOF (h^{-1})	TOF_After_10_Cycles	Activity_Retention (%)	TEM_Size_Change (%)	ICP_Leaching (ppm)
PdNP-02	1300	1185	91.2	+6.5	2.0
NiOx-03	850	755	88.8	+7.8	<1.0
Fe3O4-04	670	600	89.6	+4.3	1.5

The results presented in this study highlight the multifaceted role of surface functionalization in optimizing the catalytic performance of nanoparticles (NPs). Functional groups, ligand structures, and surface architectures collectively define the local environment of active sites, influencing activity, selectivity, and durability. This discussion interprets the experimental findings within the broader context of nanoparticle surface science, examining mechanistic underpinnings, trade-offs in design, and convergence with computational models, while identifying future directions for responsive catalyst systems.

Functional groups play a pivotal role in shaping the microenvironments surrounding catalytic centers. These modifications modulate electronic distribution and adsorption behavior, affecting how reactants interact with the catalytic surface and the nature of the transition state. Wu et al., (2020) demonstrated that in platinum-group-metal high-entropy-alloy nanoparticles, strategically placed surface functional groups enhanced catalytic performance by modifying the local reaction microenvironment. This modification stabilized transition states and promoted specific adsorption geometries, effectively lowering the activation energy barrier. Our findings support this mechanism, as seen in the lower activation energies recorded for Au and Pt nanoparticles with optimized ligand coverage. The interaction of ligands with surface atoms can stabilize intermediate species or direct reactants toward energetically favorable pathways.

In metal oxide systems, surface functionalization also introduces point defects or modifies redox behavior through donor–acceptor characteristics. These effects alter the surface energy landscape and catalytic reactivity. Additionally, the steric environment introduced by functional groups influences adsorption–desorption kinetics. For example, the shell thickness in chitosan-functionalized Fe_3O_4 NPs affected the accessibility and release of reactants and products during catalysis, as observed from post-reaction TEM and XPS data.

However, the benefits of surface functionalization must be weighed against its limitations. One of the primary trade-offs is the risk of excessive surface coverage, which can restrict access to active sites due to steric hindrance. As highlighted by Sun et al., (2019), while functional ligands may promote desired selectivity through defect mediation, dense ligand shells can inhibit substrate diffusion and increase energetic barriers. Our structure–function analysis indicates that beyond a certain ligand coverage threshold (e.g., >6.5 mg/m^2), catalytic turnover frequency (TOF) plateaus or decreases, suggesting that an optimal balance must be struck. Overfunctionalization may also limit nanoparticle mobility and flexibility during catalytic cycling, diminishing reusability and dynamic adaptability.

The comparison between experimental findings and theoretical predictions provides valuable insights but also highlights existing gaps. Density functional theory (DFT) serves as a reliable tool for estimating reaction energetics and surface configurations; however, Martí et al., (2023) reported discrepancies between DFT-predicted and experimentally observed TOF values in nanoparticle-based artificial photosynthesis. These differences were attributed to factors such as inter-particle coupling, dynamic restructuring, and solvent interactions conditions often not captured in idealized computational models. Our study also observed enhanced TOF and selectivity in Janus and core–shell systems beyond DFT-predicted values, suggesting that complex, real-time interactions play a substantial role in catalysis. As such, experimental validation remains essential to supplement and refine theoretical models.

Emerging trends in nanoparticle catalysis point toward the development of dynamic, stimulus-responsive systems capable of real-time surface adaptation. Such systems could modify their electronic or structural properties in situ to maintain catalytic efficiency under fluctuating reaction conditions. In situ monitoring techniques including environmental transmission electron microscopy (ETEM) and surface-enhanced resonance Raman scattering (SERS) are proving invaluable for capturing transient phenomena and morphological evolution during catalysis. These methods enable unprecedented temporal resolution in observing catalyst behavior, as also seen in Albrahim et al., (2021).

Furthermore, integration of machine learning with DFT calculations is being explored to predict how nanoparticle surfaces evolve and perform under dynamic conditions. By learning from extensive datasets, predictive models can suggest optimal combinations of core compositions, ligand types, and surface modifications. This synergy between computation and experimentation is poised to accelerate the rational design of next-generation catalysts.

In conclusion, the targeted functionalization of nanoparticles whether through ligands, polymers, or core–shell structures fundamentally transforms their catalytic behavior by engineering their surface properties. The effectiveness of such strategies lies in balancing ligand density, maintaining

active site accessibility, and ensuring structural stability. As mechanistic understanding deepens and real-time monitoring advances, the field is moving toward the realization of intelligent catalysts that adaptively respond to complex chemical environments. This trajectory holds promise for more efficient, selective, and durable catalytic systems tailored for both industrial and environmental applications.

CONCLUSION

This study presents a comprehensive evaluation of how surface functionalization strategies influence the catalytic performance of nanoparticles (NPs), particularly in the domains of activity, selectivity, and stability. Through a systematic combination of synthetic, structural, and performance analyses, the research demonstrates that functionalized nanoparticles can be precisely engineered to meet specific catalytic objectives.

Key findings show that functionalization whether via ligands, polymer brushes, inorganic shells, or Janus architectures significantly enhances turnover frequency (TOF), conversion efficiency, and product selectivity. Multidentate ligands on AuNPs and polymer brushes on PdNPs not only improved catalytic rates but also promoted durability across multiple cycles. The introduction of core–shell and Janus morphologies further revealed the role of interface asymmetry and interfacial protection in enabling reusability and stability, as evidenced by high retention of TOF and reduced metal leaching.

Structure–function analyses confirmed that optimal ligand coverage (e.g., 4.7–6.2 mg/m²) directly correlates with reduced activation energy and improved TOF, supporting theoretical models on microenvironment tuning. Visual and spectroscopic techniques such as TEM, XPS, and in situ operando analysis validated the morphological stability and electronic modulation induced by surface functionalization.

This research contributes a performance-guided framework that links nanoparticle surface design to catalytic function. It provides both experimental benchmarks and mechanistic insights, contributing to the rational development of next-generation catalysts. Moreover, by integrating real-time observations and literature-supported trends, the study offers strategies for overcoming limitations such as overfunctionalization and catalyst degradation.

Future research should focus on dynamic surface modulation systems capable of self-adjusting in response to reaction environments. The incorporation of machine learning with high-throughput screening and in situ characterization may further accelerate the identification of optimal functionalization strategies. Such advancements are expected to drive innovation in sustainable catalysis for chemical manufacturing, environmental remediation, and energy applications.

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