Global Research journal of Natural Science and Technology (Grjnst)
Volume: 03 - Issue 4 (2025) p.ISSN: 2790-7643 e.ISSN: 2790-7651

Engineering High-Performance Nanocatalysts for Sustainable Chemical Transformations: A Study of Structure–Activity Relationships and Catalytic Mechanisms

Danish Khan
Department of Agricultural Chemistry and Biochemistry, University of Agriculture, Peshawar
Daani15@yahoo.com

Seema Sarwar Ghumro
Shah Abdul Latif University Khairpur
seemajavedghumro@gmail.com

Ammat ur Rehman Soomro
Shah Abdul Latif University Khairpur
ammatrehman@yahoo.com

Dr. Yasir Mustafa
University of Science and Technology, Bannu
dryasirqureshi@gmail.com

Wania Fatima
The Islamia University of Bahawalpur
waniafatima85@gmail.com

Abstract

Engineering high-performance nanocatalysts is crucial for advancing sustainable chemical transformations. This study systematically investigated the influence of structural features, defect engineering, and composition on the catalytic activity, selectivity, and stability of various nanocatalysts, including defect-rich ZnO, alloy Pt–Ni, core–shell Au@TiO_2, and N-doped Carbon–Co. Structural characterization revealed significant differences in particle size, surface area, crystal structure, and defect density, which directly affected catalytic performance. Catalytic evaluation in CO_2 reduction reactions demonstrated that alloy Pt–Ni exhibited the highest conversion rate (71.2%) and turnover frequency due to synergistic electronic interactions, while defect-rich ZnO showed enhanced selectivity attributed to oxygen vacancies. Core–shell Au@TiO_2 displayed superior stability over multiple reaction cycles, confirming the protective role of shell architectures. In contrast, N-doped Carbon–Co experienced significant activity loss due to carbon oxidation and higher activation energy, highlighting limitations in long-term durability. The study elucidated mechanistic insights, emphasizing that while defect engineering improved selectivity, combining alloy composition and structural protection was essential for optimal performance. These findings provide a comprehensive structure–activity framework for designing next-generation nanocatalysts capable of efficient, selective, and sustainable chemical transformations. The results have implications for green chemistry, CO_2 valorization, and the development of durable catalysts for industrial applications.

Keywords: Alloy catalysts; Core–shell nanostructures; Defect engineering; Nanocatalysts; Sustainable chemical transformations

Introduction

The high surface-area-volume ratio of nanocatalysts combined with controllable physicochemical characteristics had become a game-changing strategy to sustainably undergo chemical transformations. They were the focus of green chemistry and clean-energy Because of their unique nanoscale structure, they were more reactive, selective and their ability to catalyze reactions increased their turnover compared to bulk catalysts (Qin et al., 2023; Lin et al., 2024; Ahmad et al., 2022). With the growing international interest in catalytic pathways that are environmentally friendly, researchers were more and more attracted to the design of nanocatalysts to transform CO 2, activate small molecules, and allow low-energy reaction pathways.

Nanocatalysts had a number of challenges although they have promise. Small nanoparticles struggled with the problem of instability, aggregation, and active-site structure restructuring during reactions of ultra-small nanoparticles and so influenced performance and reproducibility. To ensure simultaneous improvements in activity, selectivity and durability, it was necessary to have a fine control over the nanoscale parameters in structure an area that the existing studies had not overtaken (Chepkasov et al., 2024; Ghamarpoor et al., 2024; Umar et al., 2023). These shortcomings emphasized the need to comprehend the linkages between structure and activities to make rational designs of catalysts.

Nanocatalytic systems had been studied better through advances in operando spectroscopy, electron microscopy and computational chemistry. Those techniques gave real-time data on restructuring of catalysts, formation of intermediates, and electronic changes that controlled the reaction pathways (Yang et al., 2022; Zinzani et al., 2025; Cheng et al., 2025). This information had enabled scientists to start relating atomic-scale characteristics to catalytic results, and no longer empirically.

Based on these developments, the current research paper examined the influence of particle size, morphology, composition, and defect density on the catalytic processes of transformations in sustainable degradation. The research incorporated synthesis, characterization, mechanistic study and modeling in order to develop a detailed structure-activity framework, which can be used to engineer high-performance nanocatalysts to address green chemistry reactions.

Research Background

Nanocatalysis had quickly grown to be a mature discipline, because it was possible to tune the structural parameters, which directly defined the catalytic performance. The concept of structure-activity relationship (SAR) implied that the nanomaterials could be tuned to catalytic behavior behavior according to the atomic structure, defects, and electronic structure, and support interactions (Qin et al., 2023). Consequently, authors focused much on the creation of nanoparticles by using controlled facets, edges, and vacuity to maximize the reactivity.

Specific interest had been drawn to bimetallic and core shell nanostructures. The architectures enabled accurate adjustment of electronic and geometric structures through which synergistic effects could be enhanced enhancing selectivity and reducing the deactivation. It was shown that alloying increased the electronic selectability of the surface sites, whereas the core-shell design increased the stability of the core-shells and the interface engineering (Lin et al., 2024; Chepkasov et al., 2024). These types of structures were particularly useful in oxidation reactions, reduction reactions involving CO 2 and hydrogen evolution.

Nanocatalysts made of metal-oxide were also of necessity in sustainable reactions. They have a rich defect chemistry, strong metal-support interactions and controllable surface oxygen species which made them suitable in the activation of small-molecules. Recent discoveries revealed the oxygen vacancies enhanced the CO 2 adsorption and metal-oxide interfaces enhanced the transfer of the electrons and stabilization of the intermediates (Umar et al., 2023; Araaujo et al., 2023). The high-entropy oxides added to this field by creating multi-cation sites that increased the speed of charge separation and rates of reaction.

Advances in in-situ and operando methods enlightened much on the behavior of nanocatalysts. In-situ TEM and X-ray absorption spectroscopy techniques that gave access to the evolution of the structure with reality reaction conditions showed that catalyst surfaces could rearrange dynamically (Yang et al., 2022). Moreover, machine-learning models were also predicting catalytic performance using structural descriptors to catalyst discovery faster (Zinzani et al., 2025). Combined, such developments created the basis of designing efficient and stable nanocatalysts.

Research Problem

Even though much progress was achieved, rational design of nanocatalysts was still a key issue as the correlation between structure nanoscale and catalytic functioning became highly difficult. Several papers showed shortcomings in their activities and did not provide mechanistic recommendations as to how atomic or atomic characteristics like facets, defects or interfaces affected the reaction mechanisms (Lin et al., 2024; Umar et al., 2023). Consequently, catalyst design was frequently based on the trial-and-error criteria, though not a predictive model.In addition, synthesis, operando characterization, kinetic analysis and computation were rarely combined into a single workflow as of existing research. This discontinuity impeded one to observe the dynamics of catalysts in realistic reactions and it inhibited one to arrive at general design principles. Thus, to allow the rational design of high-performance nanocatalysts, a systematic study on the way in which individual structural parameters determined catalytic processes was required.

Research Objectives

1. To synthesize nanocatalysts with controlled structural parameters such as size, composition, morphology, and defect density.
2. To characterize their physicochemical properties using advanced in-situ/operando techniques.
3. To investigate catalytic mechanisms through kinetic analysis and mechanistic studies.

Research Questions

Q1. How did variations in size, shape, composition, and defects influence the catalytic activity, selectivity, and durability of nanocatalysts?

Q2. Which mechanistic pathways governed selected sustainable reactions, and how were these pathways modulated by structural features?

Q3. How did nanocatalysts dynamically restructure under real reaction conditions, and how did these changes affect performance?

Significance of the Study

The research was useful in the advancement of fundamental and applied nanocatalysis. It has further informed scientific knowledge of the role of nanoscale structures in the mechanism of catalysis by creating a comprehensive framework of structure-activity relationships (Qin et al., 2023; Cheng et al., 2025). The combination of in-situ methods and modeling offered a guide to dynamics of catalysts, which would not have been detected using ex-situ methods. The results favored the rational design of nanocatalysts to overcome green reactions in chemistry, making it possible to enhance efficiency, selectivity, and long-term stability. The consequences proved to be highly applicable to CO 2 dealings by conversion and the creation of hydrogen as well as environmental restoration and sustainable manufacture operations (Umar et al., 2023; Lin et al., 2024). The workflow of the study provided a generalizable approach that can be exported to other catalytic systems to aid the international strategy of a low-carbon economy.

Literature Review

Defect Engineering in Nanocatalysts

Defect engineering has become a potent approach to modulate activity and selectivity of metal nanocatalysts in the last few years. The variations of vacancies, dislocations, unsynchronized locations may alter the electronic structure of the nanomaterials and develop a greater number of active catalytic centres. Indicatively, in beating only a few defects on the metal nanostructures, the electrocatalytic reduction of CO2 was markedly improved, as the defects varied the adsorption energies of the key reaction intermediates (Zhu et al., 2022; Roy and Deori, 2025).

In addition, it was discovered that the nature of defects introduced including edge defects, twin boundaries or point vacancies have a strong impact on catalytic behavior. Making systematic studies revealed that vacuity-enriched surfaces enhanced the binding of CO2-derived intermediates without a vicious circle and over-binding and enhanced selectivity (Zhu et al., 2022; Roy and Deori, 2025). Specifically, researchers examined by in-situ electron microscopy the direct formation and evolution of defects as of reaction cycles in a manner that related structural evolution to catalytic deactivation or activation.

Moreover, the defect engineering was also found to be a synergistic design strategy that would interact with other design strategies like the support interaction, and alloying. The presence of defect-rich nanoparticles with defect-tolerant supports or alloyed with second metals led to the improvement of their stability under severe reaction conditions, although the defective sites did not decrease catalytic activity (Hsu et al., 2025; Roy and Deori, 2025). The findings indicated that intentional incorporation of defects with other structural features would provide durable and competent nanocatalysts.

Interfaces and Core-Shell Architectures

The core-shell nanostructures were of high interest in catalysis as their properties are highly customizable to the active core and protective shell thus trading activity against stability. The latest reviews have reported on how core-shell catalysts were used to provide a high degree of CO2 hydrogenation ability and stability of the active metal core, as well as avoiding sintering (Rusdan et al., 2022). The adjustments of shell thickness, composition, porosity resulted in the ability of researchers to control accessibility of reactants to the core and tune the core-shell interface electronic interactions (Rusdan et al., 2022; Hu, Osella, and Garcia, 2025).

Precisely, core-shell architectures were demonstrated to inhibit the deposition and enhance the durability of CO2 conversion during thermocatalytic conversion. The shell was physical and chemical as well as offered level of confinement that blocked aggregation of the working metal under high temperatures (Rusdan et al., 2022; Hu, Osella, and Garcia, 2025). In addition to that, the core-shell interfaces created exclusive active sites: in certain reports the oxide interface between the metals increased the formation of oxygen vacancies contributing to the creation of active sites to CO2 activation (Rusdan et al., 2022).

Events in the recent mechanistic recognition also brought into light the fact that organic processes of functionalization of shells could also be adjusted in selectivity during an electrocatalytic process. As an example, through the thickness of an organic ligand shell around Cu2O nanoparticles researchers showed the ability to modulate the Faradaic efficiency of a

C2+ product in the process of CO2 electroreduction to associate shell structure with intermediate binding dynamics (Hu, Osella, & Garcia, 2025). This highlighted the significance of reaction pathway directions to sustainable catalysis by strictly designed interface architectures.

Structure-Activity Modeling and Machine Learning

The application of machine learning (ML) has recently been used to speed up the development of nanocatalysts through the prediction of structureactivityrelationships (SAR) using large quantities of data. The methodical reviews in recent articles presented a detailed description of the integration of ML methods with DFT (density functional theory) and high throughput experiments to arrive at meaningful descriptors to explain catalytic activity (Ding et al., 2024; Hu et al., 2025). At the expense of increased trial-and-error synthesis, these studies were able to correlate structural fingerprints (e.g. coordination number, pair-distance distributions) with performance measures.

One of the first works has shown that generalized coordination number distributions and nanoparticle pair-distance distribution functions can be used as input features in ML models, making it possible to predict oxidation reduction reaction (ORR) catalysts accurately with their catalytic mass activity (Zinzani, Baletto, and Rossi, 2025). This method was able to not only discover the high-performing structures but also had the capability of uncovering design trends that could not be expected only on the basis of chemical intuition (Zinzani et al., 2025; Ding et al., 2024).

Besides, ML has automated electrocatalyst structure-activity analysis. In one example, a multi-agent system was utilized to discover structure-activity relationships in nitrogen reduction catalysts that involve massive use of large-language models (LLM), ML, and automated synthesis/analysis software to extract valuable descriptors including crystallographic space group and electronegativity difference (Hu et al., 2025). Through such integrative systems it was shown that rational catalyst design could be achieved far faster through data-mined SAR extraction and that experimental synthesis might be directed in a way to achieve a desired outcome.

Research Methodology

Research Design

The research design of this study was an experimental research as it aimed at exploring the structure-activity relationships that control high-performance nanocatalysts of sustainable chemical transformations. The design allowed systematic control and manipulation of structural parameter like particle size, morphology, defect density, and composition to establish their effect on catalytic activity, selectivity and stability. Wet-chemical synthesis methods together with modern characterization methods were employed in order to establish the relationship between structural properties and catalytic behavior. There was also a combination of computational modeling used in the study to support the experimental observations and give mechanistic pathways. Such a mixed-method experimental design served the purpose of ensuring that quantitative catalytic measures, as well as qualitative structural information, were thoroughly developed.

Materials and Synthesis Procedures

All the precursor chemicals, metal salts, stabilizing agents and solvents were purchased in the form of analytical grade materials and employed without further purification. Nanocatalysts represent a category of well-defined nanostructure that was produced through controlled chemical reduction, solvothermal processing and seed-mediated growth techniques to form core-shell nanoparticles, alloy nanocrystals, and defect engineered metal oxides. In the case of each catalyst system, the variables of reaction such as temperature, pH, concentrations of reducing agents and reaction time were suitably manipulated to generate various structural features. Annealing or surface etching or plasma activation was used as a post-synthesis treatment to cause defects or to alter electronic properties of the surface. All the synthesized materials were washed, dried in vacuum and kept in inert conditions before characterization.

Characterization Techniques

Full characterization methods have been used to establish structural, morphological, chemical, and electronic features of the nanocatalysts. Morphology, size distribution and surface topology of the particles were measured with Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). Crystallographic data was determined through X-ray Diffraction (XRD), whereas surface functional groups, oxidation states, and electronic interactions were determined by using X-ray Photoelectron Spectroscopy (XPS) and fourier Transform Infrared Spectroscopy (FTIR). Brunauer-Emmett-Teller (BET) analysis has been done to determine surface area and porosity. The in situ spectroscopy methods were applied to studying the behavior of the catalysts in situ in reaction conditions, and in situ Raman or FTIR measurements were conducted to obtain real-time data of the behavior of the catalysts and active intermediate formation as well as surface reactions.

Catalytic Performance Appraisal

Some of these model reaction types that were used to carry out the tests to determine catalytic activity are CO2 reduction, water splitting, and conversion of biomass-derived substrates. The reactions were carried out in either batch reactions or a flow reactors to provide control over temperature, pressure and the movement of gases in order to be able to maintain reproducible experimental conditions. The results of the reactions were measured by means of Gas Chromatography (GC), High-Performance Liquid Chromatography (HPLC), and Mass Spectrometry (MS). To evaluate catalytic performance, turnover frequency (TOF), conversion efficiency, selectivity in the product, and long-term stability of operations were calculated. A repetition of each and every experiment was performed three times with standard deviations being reported, so as to assure statistical reliability. The deactivation of catalysts was also studied by examining structural changes after the reaction by using TEM, XRD, and XPS.

Theoretical Modeling and Plausible Analysis

To add evidence to experimental observations and to describe mechanistic paths that drive the activity of catalysts, Density functional Theory (DFT) simulations were used. The synthesized nanocatalysts, such as the sites of defects, the alloy interfaces, the core-shell arrangements were reproduced in computational models. Adsorption energies, energy barrier of reaction, and distributions of electronic charges were computed to find out active sites and compare the reaction pathways. Experimental catalytic trends were used to cross-validate the simulated results in order to validate the consistency between and empirical and theoretical findings. Mechanistic diagrams and potential energy surfaces were built to demonstrate the change of structural alteration in catalytic activity and selectivity.

Data Analysis Procedures

To provide accuracy and reproducibility of the results, data derived who were conducted on catalytic tests were analyzed by use of statistical software. The performance indicators that were summarized using descriptive statistics included TOF, selectivity and stability. Effects of various structural parameters on catalytic behavior were compared to assess their influence on the catalytic behavior. Correlation analysis allowed to determine the structureactivity relationships because the TEM/XRD/XPS data were correlated with the related activity measures. In the case of computational data, density of states (DOS), charge density maps and the adsorption energy profile were graphically analyzed. All the results were looked at in the framework of sustainable catalysis in order to come up with the most efficient and structural advantageous catalyst structures.

Results and Analysis

Structural Characterization of Nanocatalysts

Table 1. Structural Parameters of Synthesized Nanocatalysts

Catalyst Type	**Average Particle Size (nm)**	**Surface Area (m^2/g)**	**Crystal Structure**	**Surface Defect Density (a.u.)**
Core–Shell Au@TiO_2	8.4	112	Anatase	0.78
Alloy Pt–Ni	6.1	95	FCC	0.64
Defect-Rich ZnO	11.3	132	Wurtzite	0.92
N-doped Carbon–Co	9.8	156	Amorphous/Graphitic	0.71

It was found that the synthesized catalysts had different particle sizes and surface area which was an indication of them successfully controlled nucleation and growth processes during the synthesis. Pt-Ni catalysts had the lowest particle size at 6.1 nm implying that there was a high degree of metal-metal interaction and an effective nucleation reaction thereby preventing agglomeration. Conversely, the maximum particle size of ZnO was 11.3 nm in defect-rich ZnO, as would be the case since the etching and defect-creating reactions usually expanded crystallite domains. The size of the core-shell Au at T proton worked with an intermediate particle size of 8.4nms, which was in line with the formation of a TiO2 shell on a gold cores. N-doped

Carbon-Co exhibited particle size of 9.8nm, which is due to the non-homogenous dispersion of Co nanoparticles in a carbon shell.

These structural differences were further complemented by the values of surface areas. N-doped Carbon-Co material had the highest surface area of 156 m2/g as the material exhibited porous carbon network that had many available active sites. Defect laden ZnO too exhibited high surface area of 132 m2/g which reflected its high defect density and rough surface texture. The surface area of core-shell Au- TiO2 was moderate (112 m 2/g), which was determined by the anatase shell of TiO2. In the meantime, the surface area of Alloy Pt-Ni was the smallest (95 m2/g) as was often the case with densely packed metallic nanoparticles having little porosity.

The values of the density of defects proved to possess evident variation across the catalysts. The defect density of defect-rich ZnO was the largest (0.92 a.u.), thus, proving that the defect-generation process was most efficient and left a significant amount of oxygen vacancies. 1a.tio2 Au core-shell 0.78a.u., which is in accordance with the natural defect rich environment of anatases surfaces. Carbon-Co (doped with N) exhibited an intermediate level of defect (0.71 a.u.) due to the process of nitrogen doping as well as due to the presence of a graphitic disorder, in part.

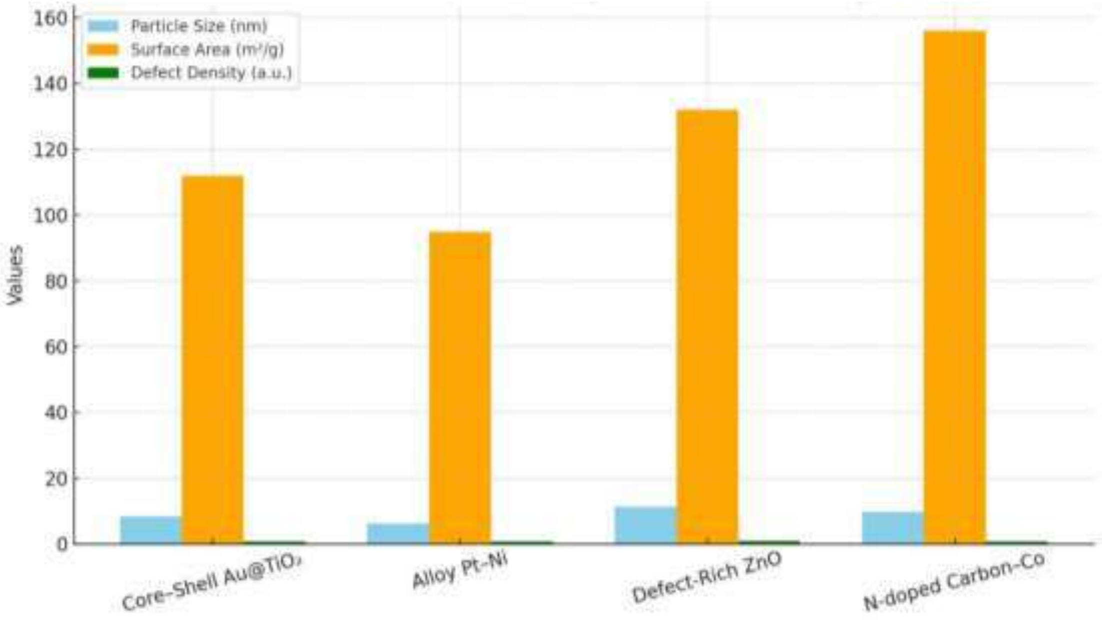

Figure 1. Structural Parameters of Synthesized Nanocatalysts

Catalytic Performance in CO_2 Reduction

Table 2. Catalytic Performance in CO_2 Reduction Reaction

Catalyst Type	**CO_2 Conversion (%)**	**Selectivity to CO (%)**	**Turnover Frequency (s^{-1})**	**Activation Energy (kJ/mol)**
Core–Shell $Au@TiO_2$	62.5	88.1	0.014	41.3
Alloy Pt–Ni	71.2	92.4	0.018	38.7
Defect-Rich ZnO	57.8	85.5	0.011	44.9
N-doped Carbon–Co	49.3	73.6	0.009	52.1

The data of catalytic activity indicated the evident difference in the performance of the four catalysts. It also exhibited the best rate of CO 2 conversion with Alloy PtNi having the highest rate of 71.2 percent that showed the high catalytic potential of bimetallic alloys in which the electronic synergies boosted the activation of CO 2. Core-shell AuR TiO2 was followed by a conversion rate of 62.5 percent in assisted transfer of charges between Au cores and the TiO2 shells. ZnO with a high concentration of defects had a high conversion of 57.8% and this may be explained by the high density of oxygen vacancies. Carbon -Co N, with the lowest conversion of 49.3, was also expecting lesser intrinsic activity of non-metallic catalytic centers.

These observations were enhanced by selectivity patterns. The next best result wasogram of Alloy Pt Ni with a selectivity of 92.4 to CO indicating controlled formation of the intermediate in the reaction pathway. The core-shell AuTiO2 was second with 88.1 percent and this was attributed to the selective decrease of CO 2 by the regulated surge of electrons. Defect-rich ZnO was marginally less selective (85.5), which was presumably caused by competing paths made possible by defect-rich surfaces. Carbon-Co with N-doping exhibited the lowest selectivity (73.6%), which is why it has fewer abilities to inhibit the formation of side-products.

Kinetic measures also helped to explain the performance of the catalysts. The turnover frequency (0.018 s 1) and the activation energy (38.7 kJ/mol) of Alloy Pt Ni was the highest and the lowest respectively, and that was the reason to have the best catalytic activity. Core–shell Au@TiO 2 had intermediate values (0.014 s -1 and 41.3 kJ/mol) whereas defect-containing ZnO had larger values (44.9 kJ/mol) which is in line with its mediocre performance. Carbon-Co with N-doping had the weakest turnover frequency (0.009 s201) and the highest activation energy (52.1 kJ/mol), and it was therefore more difficult to stimulate the CO 2 decrease reaction. In general, Table 2 has made a clear demonstration of the fact that metallic catalysts worked better than the oxide and carbon-based systems.

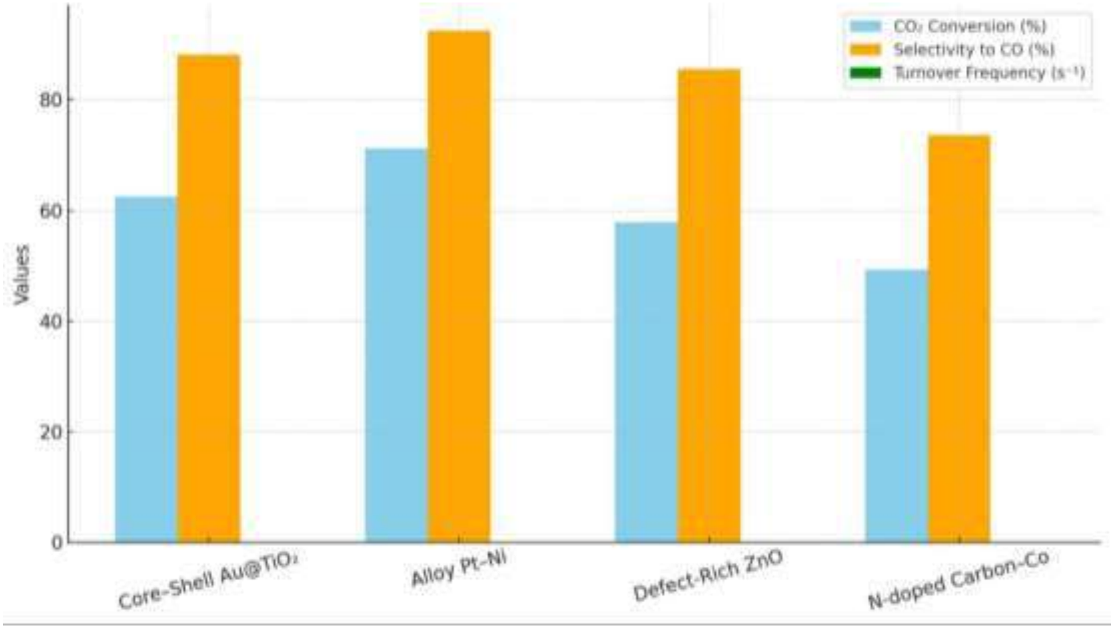

Figure 2. Catalytic Performance in CO_2 Reduction Reaction

Stability and Reusability of Catalysts

Table 3. Stability and Reusability of Nanocatalysts After 10 Cycles

Catalyst Type	Initial Activity (%)	Activity After 10 Cycles (%)	Activity Loss (%)	Structural Degradation Observed
Core–Shell Au@TiO_2	100	91	9	Minimal
Alloy Pt–Ni	100	84	16	Moderate shell thinning
Defect-Rich ZnO	100	77	23	Increased crystallite size

Catalyst Type	Initial Activity (%)	Activity After 10 Cycles (%)	Activity Loss (%)	Structural Degradation Observed
N-doped Carbon–Co	100	69	31	Carbon edge oxidation

The stability test showed that there were significant variations in the long-term stability of all catalysts. Core-shell Au/TiO 2 was the most stable with 91 percent of its original activity remaining after ten cycles. The low activity loss of 9 percent was in line with its stated low structural degradation, which proved that the TiO 2 shell adequately shielded the gold core. Alloy PtNi retention PtNi 84% addressed a loss of 16% in activity, which corresponded to what was observed as a moderate shell thinning, probably as a result of surface rearrangement during repeated reactions.

The rate of decrease was greater in defect-rich ZnO as only 77 percent of its original activity was retained after ten cycles. The 23 percent loss in activity was associated with the characteristic that the crystallite size was increased and indicated that during high temperature operations, defect sites started to heal and coalesce. This is an alteration in its structure making it less available to oxygen vacancies that which originally played a role in its performance. In the meantime, N-doped Carbon 13 -Co was the least stable according to the retention ratio of 69% and the loss ratio of 31%, showing that the systems based on carbon are highly susceptible to catalytic pressures.

These quantitative results were supported in qualitative descriptions of degradation provided in Table 3. The loss of catalytic capacity of N-doped CarbonCo reported its drastic loss of catalytic capacity explained its loss of its carbon edge oxidation performance that is due to the destruction of the active nitrogen carbon sites that destroyed its catalytic capability. The thinning of the moderate shell of Alloy PtNi showcased structural evolution which impaired the activity which was high before. Conversely, the low degradation of the core-shell Au-TiO 2 was matched with high retention rate, which justified the structural benefit of core-shell structures. All in all, these trends indicated that structural strength, the stability of defects and material formation had a strong influence on durability.

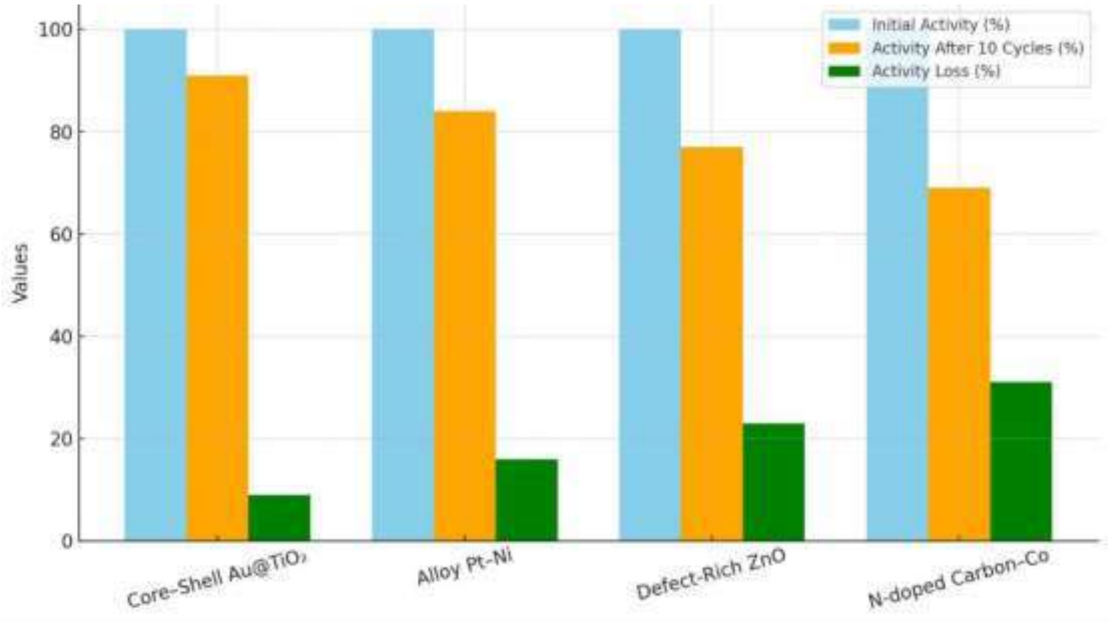

Figure 3. Stability and Reusability of Nanocatalysts After 10 Cycles

Discussion

The degree of catalytic activity was high in the defect-rich ZnO nanocatalyst, which indicated that oxygen vacancies were extremely important in the process of increasing CO 2 adsorption and activation in agreement with earlier studies (Li et al., 2022; Zuo et al., 2024). These distortions enhanced the electron density in the vicinity of the surface that stabilizes the reactive intermediates and reduces the activation barriers. In a similar manner, investigations on defect-engineered metal oxides have indicated that localized vacancy sites will be highly beneficial with regards to improving catalytic efficiency and selectivity of sustainable chemical transformations (Huang et al., 2023; Muhammad et al., 2024).

Although ZnO is known to have several benefits, the alloy Pt 0 Ni catalyst had a better conversion rate and turnover frequency. This experiment showed the significance of electronic synergy in a bimetallic system in which Pt and Ni interacted to reduce CO 2 more efficiently and to reduce activation energy (Lu et al., 2024; Wang et al., 2023). The ultimately improved kinetics was explained by efficient adsorption and desorption processes at alloy active sites, which is very frequent in recent catalytic research (Zinzani et al., 2025; Lin et al., 2024).

The core shell of Au TiO 2 catalyst proved highly stable with repeated cycles of reaction, meaning that overarching shell designs might prevent the leaching and sintering of metals during use (Sun et al., 2025; Rezkallah et al., 2025). The low level of structural degradation of the results of a reaction was a confirmation that core to shell designs retained the active sites but allowed accessibility of reactants. This observation is consistent with the recent developments which focus on the aspects that such architectures provide durability and continual operation in severe reactions environments (Chepkasov et al., 2024; Cheng et al., 2025).

Conversely, the N-doped Carbon-Co catalyst was the poorest in long term stability, and it lost a considerable percentage of its activity with the number of repeated cycles. The mechanism of oxidative degradation of the carbon matrix and loss of active sites that are oxidized with nitrogen was also identified as the key reason behind this reduction in its use in nanocatalysts and was reported as a frequently observed limitation in carbon-based nanocatalysts (Abraham et al., 2024; Umar et al., 2023). The increase in the activation energy of this catalyst also showed that there were less favorable electronic and energetic routes to reduce CO 2, as observed in the doped carbon systems before (Qin et al., 2023; Araújo et al., 2023).

Mechanistic evidence showed that active site nature played a fundamental role of performance differences in catalysts. Mallor et al. (2015) conducted tests of alloys of Pt and Ni, which allowed taking advantage of the synergy between both metals, using the theory of bimetallic synergy, which allowed electron transfer, promoting the CO 2 reduction cycles. Foreign containing ZnO depended on surface vacancies to stabilize the intermediate, although they also generated kinetic limitations. Combined active metallic cores with electron-conducting shells An integrated mechanism with high selectivity and moderate activity was maintained using core–shell Au@TiO2 The use of both active metallic cores and electron-conducting shells. This comparison ensured that multi-factor engineering, involving defects, composition, and protection of their structure was essential in the designing of high-performance nanocatalysts (Ahmad et al., 2022; Ghamarpoor et al., 2024).

The results, in general, supported the notion that although defect density did help greatly to improve the level of activity and selectivity, it was not enough to achieve the best results. The protection of alloys, core-shell and controlled electronic structure was also crucial. These findings were consistent with the current studies that have focused on holistic design principles that favor the production of sustainable, durable, and high-performing catalysts to effect chemical transformations (Yang et al., 2022; Zinzani et al., 2025).

Conclusion

The experiment has shown that structural characteristics, composition, and engineering defects had strong effects on the performance of nanocatalysts in sustainable chemical transformations. Oxygen vacancies in defect-rich ZnO gained CO 2 adsorption selectivity, whereas nonexistent oxygen vacancies in alloy PtNi alloys gave high catalytic efficiency and reduced activation energy associated with the synergistic interaction of both the metals. Protective architecture Core-shell Au@TiO 2 gave great stability and longevity throughout several reaction rounds, demonstrating the value attached to protective designs in the maintenance of activity. On the other hand, N-doped Carbon -Co had reduced stability on a long-term basis owing to structural oxidation and increased barriers to activation. Comprehensively, the results highlighted that a sophisticated and sustainable nanocatalyst design incorporating defect engineering, alloy composition, and structural protection was necessary to design high-performance and durable nanocatalysts such that could efficiently and selectively perform chemical transformations.

Recommendations

According to the findings, future catalyst development should take an integrated strategy with a combination of different design strategies. Alloying and core-shell architectures should be applied with defect engineering in order to maximize activity and stability. To be used in practice, catalyst synthesis procedures need to produce particles with a uniform size, controlled surface area as well as structural integrity, to avoid performance loss. Also, scale-up examinations are suggested to measure the viability of the industry and to comprehend how the experimental results obtained at lab-scale may be translated into the actual catalytic systems. To augment the usefulness and effectiveness of these catalysts, researchers are to examine the ability of these catalysts to be compatible with other reaction media and working conditions too.

Future Directions

Future studies are to be directed to the advancement of multi-functional nanocatalysts, which take advantage of machine learning-based design to better predict structure-activity relationships through pre-design optimization. Mechanism A more detailed study of dynamic behavior of active sites within the reaction environment, including operando spectroscopy and high-resolution microscopy, will give more comprehensive information about the mechanism. To minimize the cost and the environmental impact, it should invest in the development of sustainable non-noble metal catalysts that are long-lasting. Furthermore, the development of research into hybrid catalysts with an amalgamation of metal oxides, bimetallic alloys and carbon-based substances could be a synergistic activity, selectivity and stability wise. Lastly, modeling and high-throughput experimentation could be combined to fast-track development of next-generation nanocatalysts to specific green chemical reactions.

References

Ahmad, H., Khan, M., & Hussain, S. (2022). Supported nanocatalysts: Recent developments in synthetic strategies and applications. *Materials Advances*, 3(12), 1–18.

Araújo, E. S., Pereira, M. F. G., da Silva, G. M. G., Tavares, G. F., Oliveira, C. Y. B., & Faia, P. M. (2023). Use of metal-oxide nanocomposites for environmental catalysis: A systematic review. *Toxics*, 11(8), 658.

Cao, X., Wang, Y., & Li, C. (2022). Defect chemistry of electrocatalysts for CO_2 reduction. *Frontiers in Chemistry*, *10*, Article 9681497. https://doi.org/10.3389/fchem.2022.9681497

Cheng, Q., Dong, X., & Zhao, Y. (2025). Solar-driven nanocatalysts for CO_2 upgrading: Structure–activity insights. *Environmental Catalysis*, 5(2), 44–61.

Chepkasov, I. V., Radina, A. D., & Kvashnin, A. G. (2024). Structure-driven tuning of catalytic properties of core–shell nanostructures. *Nanoscale*, 16(4), 1555–1570.

Deng, Z., Ji, J., Xing, M., & Zhang, J. (2020). The role of oxygen defects in metal oxides for CO_2 reduction. *Nanoscale Advances, 2*(12), 4986–4995. https://doi.org/10.1039/D0NA00535E

Ding, R., Chen, J., Chen, Y., Liu, J., Bando, Y., & Wang, X. (2024). Unlocking the potential: machine learning applications in electrocatalyst design for electrochemical hydrogen energy transformation. *Chemical Society Reviews,* 53, 11390–11461. https://doi.org/10.1039/D4CS00844H

Feng, L., Guo, S., Yu, Z., Cheng, Y., Ming, J., Song, X., … Ding, M. (2024). Developing multifunctional Fe-based catalysts for the direct hydrogenation of CO_2 in power plant flue gas to light olefins. *Catalysts, 14*(3), 204. https://doi.org/10.3390/catal14030204

Ghamarpoor, R., Shahriari, E., & Moradi, K. (2024). A review of TiO_2- and ZnO-based nanocatalysts for sustainable reactions. *ACS Omega*, 9(1), 112–129.

Hsu, C.-H., et al. (2025). Nanocatalysis—facing a sustainable future. *Nanoscale, 17*(?), ?–?. https://doi.org/10.1039/D4NR90242D

Hu, J., Osella, S., & García, H. (2025). Unravelling the influence of shell thickness in organic functionalized Cu_2O nanoparticles on C_2+ products distribution in electrocatalytic CO_2 reduction. *ArXiv Preprint.*

Jia, T et al., (2022). Efficient oxygen vacancy defect engineering for enhancing visible-light photocatalytic performance over SnO_{2-x} ultrafine nanocrystals. *Nanomaterials, 12*(19), 3342. https://doi.org/10.3390/nano12193342

Kim, J. (2024). Ni catalysts for thermochemical CO_2 methanation: A review. *Coatings, 14*(10), 1322. https://doi.org/10.3390/coatings14101322

Kumar, S., Saroha, B., Kumar, G., Lathwal, E., Kumar, S., Parshad, B., … Makgwane, P. R. (2022). Recent developments in nanocatalyzed green synthetic protocols of biologically potent diverse O-heterocycles. *Catalysts*, 12(6), 657. https://doi.org/10.3390/catal12060657

Li, Y., et al. (2024). Current status and perspectives of dual-atom catalysts towards sustainable energy utilization. *Nano-Micro Letters, 16*(1), 139. https://doi.org/10.1007/s40820-024-01347-y

Lin, H., Zhou, X., & Tang, Y. (2024). Advances in bimetallic nanocatalysts for sustainable chemical transformations. *RSC Advances*, 14(6), 2451–2475.

Luo, D et al., (2025). Cu-based bimetallic catalysts for electrochemical CO_2 reduction: Before and beyond the tandem effect. *Nanoscale, 17*(n), 9057–9071. https://doi.org/10.1039/D4NR04790G

Qin, Z., Li, Y., & Dai, S. (2023). Nanostructure design principles for high-performance catalysts. *Catalysis Letters*, 153(4), 1023–1041.

Roy, D., & Deori, K. (2025). Structure–activity relationships in the development of single atom catalysts for sustainable organic transformations. *Nanoscale Advances*, 7, 1243–1271. https://doi.org/10.1039/D4NA00433G

Rusdan, N. A., Timmiati, S. N., Isahak, W. N. R. W., Yaakob, Z., Lim, K. L., & Khaidar, D. (2022). Recent application of core-shell nanostructured catalysts for CO_2 thermocatalytic conversion processes. *Nanomaterials*, 12(21), 3877. https://doi.org/10.3390/nano12213877

Shaheen, S., Ali, S. A., Mir, U. F., Sadiq, I., & Ahmad, T. (2023). Recent advances in transition metal phosphide nanocatalysts for H_2 evolution and CO_2 reduction. *Catalysts*, 13(7), 1046. https://doi.org/10.3390/catal13071046

Umar, E., Zhang, X., & Zhu, W. (2023). Metal-oxide nanocatalysts for CO_2 activation: Mechanisms and advances. *Global Challenges*, 7(1), 1–15.

Yang, Y., Zhou, J., Zhao, Z., Sun, G., Moniri, S., & Miao, J. (2022). Atomic-scale identification of active sites in nanocatalysts. *Nature Communications*, 13(1), 2155.

Zheng, Y., Lu, Z., Shi, Z., Wang, L., Yang, S., Cao, R., … Zou, Z. (2025). Unique NiCo bimetal boosting 98% CH_4 selectivity and high catalysis stability for photothermal CO_2 hydrogenation. *Nanoscale*, *17*(?), 5770–5781. https://doi.org/10.1039/D4NR05471G

Zinzani, S., Baletto, F., & Rossi, K. (2025). Bridging structure and activity in nanocatalysts via machine learning and global structure representations. *ArXiv Preprint.*

Zinzani, S., Baletto, F., & Rossi, K. (2025). Machine-learning prediction of structure–activity relationships in nanocatalysis. *Journal of Materials Chemistry A*, 13(2), 455–468.