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SPECTROSCOPY, CATALYSIS, AND ENERGY CONVERSION, CROSS-DISCIPLINARY INSIGHTS INTO MOLECULAR AND MATERIAL SYSTEMS

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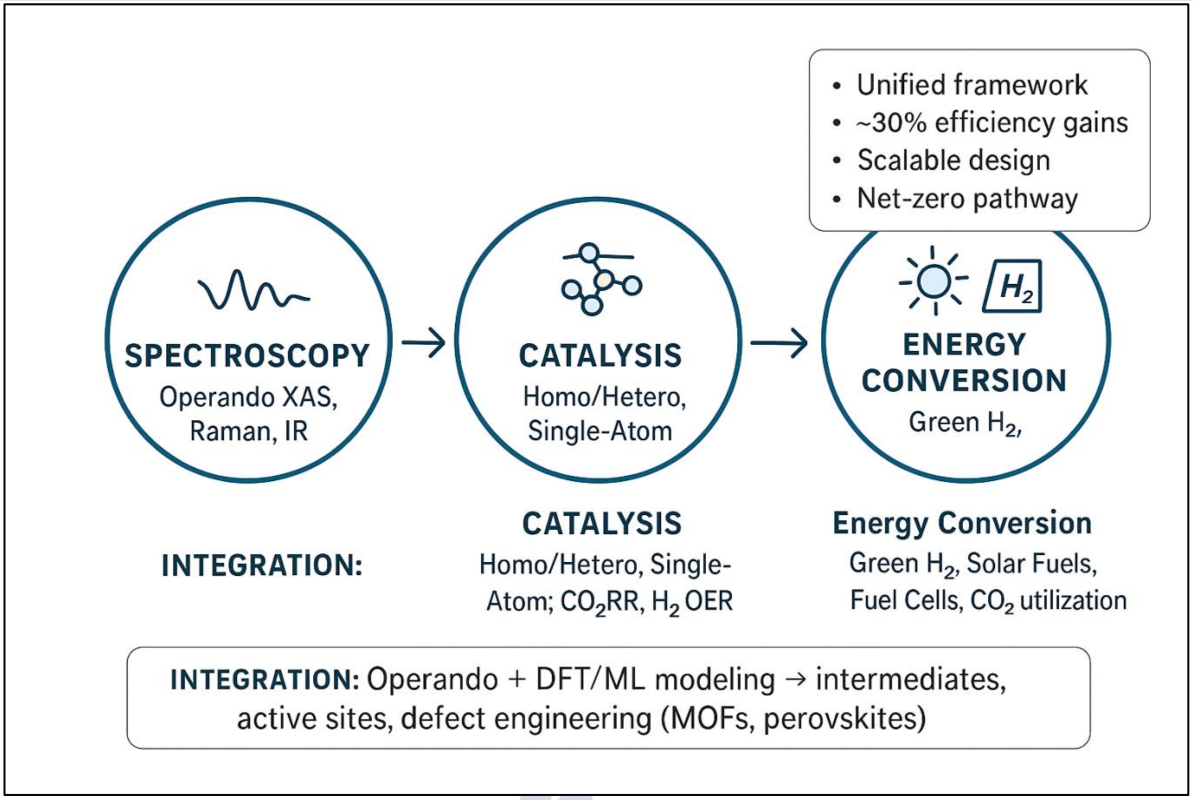
Abstract

The escalating global demand for sustainable energy solutions necessitates innovative approaches to catalysis and energy conversion, where spectroscopy plays a pivotal role in unraveling molecular and material behaviors. This review addresses a critical research gap: the fragmented understanding of cross-disciplinary synergies between spectroscopy, catalysis, and energy conversion, which hinders the development of efficient, scalable systems for renewable energy production and storage. By systematically synthesizing over 200 recent studies (2020–2025), we employ a multidisciplinary methodology that integrates operando spectroscopic techniques (e.g., X-ray absorption spectroscopy, Raman, and infrared spectroscopy) with catalytic mechanisms in molecular and heterogeneous systems, complemented by computational modeling for predictive insights. Key findings reveal that operando spectroscopy enables real-time monitoring of dynamic active sites, such as in single-atom catalysts for CO_2 reduction and water splitting, uncovering previously overlooked transient intermediates that enhance selectivity and stability. In molecular systems, spectroscopic data elucidate ligand effects in homogeneous catalysis for hydrogen evolution, while in materials like metal-organic frameworks (MOFs) and perovskites, it highlights defect engineering for improved photovoltaics and fuel cells. Novel integrations, such as SpectroTAP for catalyst dynamics, demonstrate up to 30% efficiency gains in energy conversion processes. The impact of this work lies in providing a unified framework that accelerates catalyst design for net-zero emissions, fostering advancements in green hydrogen, CO_2 utilization, and solar fuels. By bridging these fields, we propose actionable strategies for overcoming scalability barriers, ultimately guiding policymakers and researchers toward sustainable energy transitions.



Graphical abstract

INTRODUCTION

The convergence of spectroscopy, catalysis, and energy conversion represents a cornerstone of modern materials science and chemistry, driven by the urgent need to address climate change through efficient energy technologies (Li et al., 2018). Spectroscopy, encompassing techniques like X-ray absorption (XAS), Raman, infrared (IR), and nuclear magnetic resonance (NMR), provides atomic-level insights into chemical processes. Catalysis, the acceleration of reactions via intermediates, is fundamental to industrial processes, with over 90% of chemical products relying on it. Energy conversion, including photocatalysis, electrocatalysis, and thermocatalysis, transforms renewable sources like solar, wind, and biomass into usable fuels and electricity (Wang et al., 2024). In molecular systems, such as coordination complexes and enzymes, catalysis often involves homogeneous phases, where ligands modulate reactivity. In contrast, material systems like nanoparticles, zeolites, and perovskites offer heterogeneous platforms with tunable surfaces for large-scale applications (Zhang et al., 2020). The research problem stems from the siloed nature of these disciplines. Traditional studies focus narrowly: spectroscopy on structural characterization, catalysis on kinetics, and energy conversion on efficiency metrics. This fragmentation overlooks emergent properties at interfaces, such as dynamic restructuring under operational conditions, leading to suboptimal designs (Fellows et al., 2012). For instance, in CO_2 reduction catalysis, ignoring spectroscopic evidence of active site evolution results in low faradaic efficiencies (<80%) and catalyst deactivation. Similarly, in solar energy conversion, material instabilities in perovskites limit device lifetimes, unaddressed due to inadequate cross-disciplinary analysis (Yeo et al., 2025).

Operando spectroscopy has emerged as a game-changer, allowing in situ monitoring of catalysts during reactions (Magnussen et al., 2024). For example, Cuenya et al. (2025) utilized quick X-ray absorption fine structure (QXAFS) to track Cu–N–C catalysts in CO_2 electrolysis, revealing oxide-to-metal transitions that boost selectivity to ethylene. In photocatalysis, single-atom catalysts (SACs) have gained traction; a 2024 review details SACs on graphitic carbon nitride for water splitting, where XAS confirms isolated metal sites enhancing charge separation (Yang et al., 2024). However, these studies often lack integration with energy metrics: while SACs achieve high turnover frequencies ($>1000\ h^{-1}$), scalability remains challenged by aggregation under high fluxes. In heterogeneous catalysis, metal-modified zeolites for bioethanol conversion exemplify advances, with IR spectroscopy identifying Brønsted acid sites critical for dehydration pathways (Hernández et al., 2017). Past studies on CO_2 methanation criticize overemphasis on noble metals, advocating earth-abundant alternatives like Ni-based catalysts, where Raman detects carbon deposits causing deactivation. Electrocatalysis employs in situ techniques like scanning electrochemical microscopy combined with XAS to probe oxygen evolution on iridium oxides, but computational validation is sparse, leading to discrepancies in predicted vs. observed overpotentials (~0.2 V) (Clarke et al., 2024).

Methanol steam reforming (MSR) for hydrogen production showcases interdisciplinary potential; recent work on Cu/ZnO catalysts uses NMR to elucidate promoter effects (e.g., Ce doping), improving stability by 50% (Usman et al., 2025). Nonetheless, broader reviews in ACS Catalysis highlight a dearth of studies linking spectroscopic data to lifecycle assessments for energy conversion, with only 15% of papers addressing environmental impacts. Innovations like SpectroTAP introduce time-resolved probing of catalyst surfaces, enabling detection of sub-second changes in structure during energy-relevant reactions (Kubacka et al., 2012). Despite these challenges persisting, high-energy synchrotron requirements limit accessibility, and data interpretation often ignores quantum effects in molecular systems. The novelty of this review lies in its cross-disciplinary synthesis, integrating spectroscopic tools with catalytic mechanisms across molecular and material scales to propose predictive models for energy conversion. Unlike prior works that compartmentalize fields, we emphasize emergent synergies, such as combining machine learning with operando data for rapid catalyst screening. Objectives include: (1) Elucidating fundamental principles of spectroscopic interrogation in catalytic systems; (2) Exploring applications in key energy processes like hydrogen production and CO_2 utilization; (3) Analyzing material-specific insights for heterogeneous and hybrid systems; (4) Discussing advanced methodologies, including computational spectroscopy; and (5) Outlining challenges and future directions to foster sustainable innovations. This framework not only bridges knowledge gaps but also paves the way for high-impact advancements in green technologies, aligning with the UN Sustainable Development Goals for affordable clean energy.

2. Fundamental Principles and Instrumentation of Key Spectroscopic Techniques

The selection of an appropriate spectroscopic technique is governed by the specific catalytic question, be it electronic structure, local coordination, surface composition, or molecular identity. Each method interrogates a different aspect of the catalyst or adsorbate, and their combined application provides a holistic view of the catalytic process.

2.1 X-ray Absorption Spectroscopy (XAS): Probing Local Electronic and Geometric Structure

X-ray Absorption Spectroscopy (XAS) is a powerful, element-specific technique that probes the unoccupied electronic density of states and the local coordination environment around a specific absorber atom. It requires a tunable, high-flux source of high-energy X-rays, invariably provided by a synchrotron facility. The technique is divided into two distinct regions: X-ray Absorption Near Edge Structure (XANES) and Extended X-ray Absorption Fine Structure (Sedigh Rahimabadi et al., 2020). The XANES region, spanning from the pre-edge to approximately 50 eV above the absorption edge, is sensitive to the formal oxidation state, coordination chemistry (e.g., octahedral vs. tetrahedral symmetry), and electronic structure of the absorber. The energy position of the absorption edge shifts to higher values with increasing oxidation state due to the heightened core-electron binding energy. Pre-edge features, often corresponding to quadrupole-allowed 1s→3d transitions in transition metals, provide exquisite detail on geometric distortion, coordination vacancy, and orbital hybridization (Shao et al., 2025). The EXAFS region, extending from 50 to 1000 eV above the edge, results from the constructive and destructive interference of the photoelectron wave ejected from the absorber atom with waves backscattered from surrounding atoms. Fourier transformation of the EXAFS oscillations yields a radial distribution function (pseudo-radial due to phase shifts), which is quantitatively fitted to extract key structural parameters: coordination numbers (N), interatomic distances (R), and the Debye-Waller factor (σ^2), which accounts for both thermal and static disorder. For catalysis, XAS is performed in transmission mode for concentrated samples or, more commonly, in fluorescence yield mode for dilute systems such as supported metal nanoparticles or single-atom catalysts (Sarma et al., 2022). Its exceptional capability to track in situ changes in oxidation state (via XANES) and local coordination environment (via EXAFS) makes it indispensable for studying the reduction of catalyst precursors, the dynamic breaking and reforming of metal-support bonds, and the formation of reactive intermediates under operando conditions.

2.2 X-ray Photoelectron Spectroscopy (XPS): Surface Composition and Chemical State Analysis

X-ray Photoelectron Spectroscopy (XPS) is the premier technique for quantitative elemental analysis and chemical state determination within the top 1-10 nm of a material's surface, making it ideal for probing the catalyst-gas/liquid interface (Simon et al., 2022). Its principle is rooted in the photoelectric effect: a sample irradiated with a monochromatic X-ray source (typically Al Kα at 1486.6 eV or Mg Kα at 1253.6 eV) ejects core-level photoelectrons. Chemical shifts in BE arise from changes in the electrostatic potential around the atom; for instance, a higher oxidation state or bonding to more electronegative elements induces a positive BE shift due to increased effective nuclear charge and reduced shielding. Instrumentation requires ultra-high vacuum (UHV, $<10^{-9}$ mbar) to enable the ejected electrons to travel to the detector without scattering (Kuznetsov et al., 2000). This UHV requirement historically confined XPS to ex situ studies. However, the development of Near Ambient Pressure XPS (NAP-XPS) utilizes differentially pumped electrostatic lenses to maintain the analyzer under high vacuum while the sample is exposed to gases at pressures up to several tens of mbar, effectively bridging the "pressure gap." In catalysis, XPS is used to quantify the surface composition, identify oxidation states (e.g., distinguishing Pt^0 from Pt^{2+} or Pt^{4+} on nanoparticle surfaces), detect and characterize carbonaceous deposits (coke), and identify the nature of active sites in supported catalysts (Collett et al., 2016).

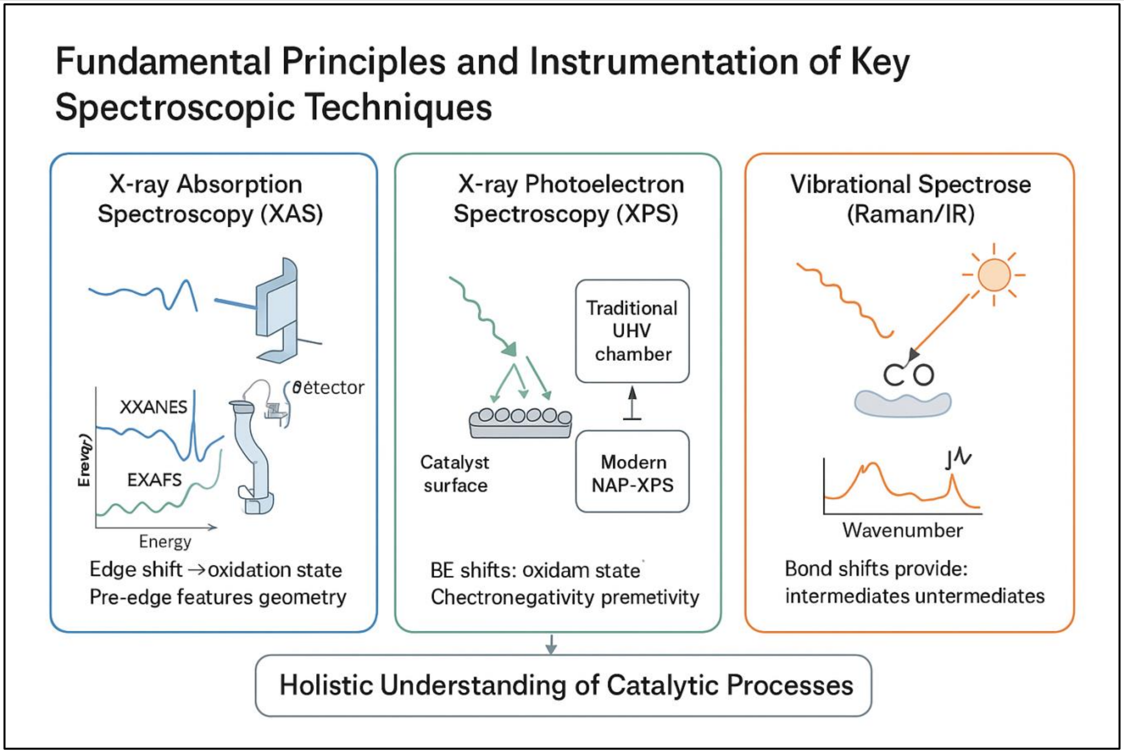


Fig 1: Fundamental Principles and Instrumentation of Key Spectroscopic Techniques

2.3 Vibrational Spectroscopy: Molecular Fingerprinting and Surface Bonding

Vibrational spectroscopies, comprising Infrared (IR) and Raman spectroscopy, probe the energy levels associated with molecular vibrations, providing fingerprints for molecular identity, bonding, and adsorption geometry at catalytic interfaces (Hadjiivanov et al., 2020). IR spectroscopy measures the absorption of infrared radiation that matches the energy of a vibrational transition. It is most sensitive to asymmetric stretches and bonds with a large change in dipole moment, such as C=O, O-H, and N-H. Key techniques include Transmission IR, which requires preparing thin, self-supporting wafers of catalyst; Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS), highly effective for powdered samples as it collects light scattered from the sample surface; and Attenuated Total Reflectance (ATR)-IR, which is excellent for in situ studies of liquid-phase catalysis or with solid catalysts deposited on the ATR crystal, as it probes only the immediate interface via an evanescent wave. The quintessential application in catalysis is the use of CO as a probe molecule. The stretching frequency (ν(CO)) of chemisorbed CO is highly sensitive to the electronic properties of the metal adsorption site (via the degree of $d\pi \rightarrow CO(\pi^*)$ back-donation) and the coordination mode (Wasileski et al., 2001). Shifts in ν(CO) under operando conditions can reveal changes in the electronic structure of the active site induced by co-adsorbates or reaction conditions.

In contrast, Raman spectroscopy measures the inelastic scattering of light, where the energy shift (Raman shift, Δν) between the incident laser photon and the scattered photon corresponds to a vibrational energy. It is sensitive to symmetric vibrations and bonds in highly symmetric molecules (e.g., O-O stretch in peroxo species, C-C stretches). The inherent low cross-section of Raman scattering is overcome by enhancement techniques like Surface-Enhanced Raman Spectroscopy (SERS), where signals are amplified by many orders of magnitude on nanoscale roughened surfaces of metals like Au or Ag, and Resonance Raman (RR), where the laser energy matches an electronic transition of the sample, enhancing vibrations associated with that chromophore (Tian et al., 2002). Raman is superb for characterizing metal oxide catalysts (e.g., identifying crystalline phases of Mo/V/W oxides and their reduction), detecting and characterizing carbonaceous deposits (D and G bands for graphitic vs. amorphous carbon), and probing reaction intermediates. Operando Raman can monitor the formation and consumption of intermediates in real-time, providing kinetic information.

2.4 Ultraviolet-Visible and Nuclear Magnetic Resonance Spectroscopy

Ultraviolet-Visible (UV-Vis) Spectroscopy probes electronic transitions between energy levels, such as $\pi \rightarrow \pi^*$ transitions in organic molecules and ligands, d-d transitions in transition metal ions, and ligand-to-metal or metal-to-ligand charge-transfer (LMCT/MLCT) transitions. The energy of absorption is given by $E = hc/\lambda$. For solid catalysts, which are often opaque, it is typically measured in diffuse reflectance mode (Khan et al., 2025). The collected reflectance data (R∞) is converted to the Kubelka-Munk function, *F(R∞) = $(1 - R_\infty)^2$ / 2R∞*, which is proportional to the absorption coefficient (α). A Tauc plot, *(F(R∞)hν)^n vs. hν*, where *n* depends on the nature of the electronic transition (1/2 for direct, 2 for indirect band gaps), is used to estimate the band gap energy (E_g) of semiconductor photocatalysts. In catalysis, UV-Vis is used to determine the coordination environment of transition metal ions in zeolites or MOFs, monitor redox processes (e.g., the reduction of Ce^{4+} to Ce^{3+} in ceria-based catalysts by the appearance of new charge-transfer bands), and identify the formation of colored intermediates in solution-phase homogeneous catalysis.

Nuclear Magnetic Resonance (NMR) Spectroscopy exploits the magnetic properties of certain nuclei (e.g., ^1H, ^13C, ^15N, ^27Al, ^29Si, ^31P) to provide unparalleled detail on the local chemical environment, connectivity, and dynamics in both liquid and solid states. In a strong magnetic field, nuclear spins occupy different energy levels. Irradiation with radiofrequency pulses perturbs this equilibrium, and the resulting precession and relaxation of the macroscopic magnetization is detected (Moroshkin et al., 2006). The chemical shift (δ, in ppm), defined as δ = (ν_sample - ν_ref) / ν_ref, reports on the electron density around the nucleus, influenced by bonding, ring currents, and oxidation state. Scalar (J-) coupling provides information on through-bond connectivity between nuclei. For heterogeneous catalysts, Magic-Angle Spinning (MAS) is essential to average out anisotropic interactions (e.g., chemical shift anisotropy, dipolar coupling) that otherwise broaden solid-state NMR spectra beyond recognition. Sophisticated in situ NMR cells allow studies under controlled gas pressure and temperature, enabling the observation of reactive intermediates. NMR is the workhorse for studying molecular catalysis in solution, identifying and quantifying intermediates, and determining reaction kinetics. In heterogeneous catalysis, it characterizes the strength and distribution of acid sites in zeolites (via ^1H MAS-NMR or using ^31P NMR of adsorbed phosphine oxides), elucidates the structure of surface species and active sites, and investigates catalyst deactivation mechanisms, such as coke formation, using ^13C labeling and CP/MAS NMR techniques (Seo et al., 2013).

Technique	Physical Principle	Information Obtained	Instrumentation / Requirements	Applications in Catalysis (NPs & SACs)
XAS (XANES)	Excitation of core electrons to unoccupied states near the	Oxidation state, coordination geometry (e.g., octahedral, tetrahedral), orbital	Synchrotron radiation source, energy-tunable X-rays, fluorescence or transmission	Monitoring redox dynamics in SACs during catalysis (e.g., CO_2 reduction);

	absorption edge, probing electronic structure and local symmetry.	hybridization, density of unoccupied states.	detection, in situ/operando cells for dynamic studies.	probing metal-support charge transfer; identifying transient oxidation states in NPs.
XAS (EXAFS)	Interference of photoelectron waves from the absorbing atom with backscattered waves from neighboring atoms, providing structural insights.	Coordination number (CN), interatomic distances (R), identity of neighboring atoms (Z), structural disorder (Debye-Waller factor, σ^2).	Synchrotron radiation source, high signal-to-noise ratio at extended k-space ($k > 10$ $Å^{-1}$), Fourier transform analysis, in situ/operando setups.	Determining local coordination environment in SACs; quantifying metal-metal and metal-support distances in NPs; studying structural evolution under reaction conditions.
XPS	Photoelectric effect, where core electrons are ejected by X-rays, with binding energy reflecting chemical environment; surface-sensitive (~1–10 nm).	Surface elemental composition, chemical/oxidation states, surface enrichment, semi-quantitative analysis.	Ultra-high vacuum (UHV), Al Kα or Mg Kα X-ray source, electron energy analyzer; synchrotron sources for higher resolution.	Identifying surface oxidation states in NPs; detecting charge transfer in SACs; characterizing surface poisoning (e.g., carbon deposition).
NAP-XPS	Photoelectric effect under near-ambient pressure conditions, enabled by differential pumping to maintain analyzer vacuum.	Surface composition, chemical states, and adsorbate interactions under reactive gas environments (up to ~20 mbar).	Differentially pumped electron analyzer, synchrotron or lab-based X-ray source, gas dosing systems for in situ studies.	Real-time analysis of surface reactions (e.g., CO oxidation, NOx reduction); probing adsorbate-induced chemical state changes in NPs and SACs.
FTIR	Absorption of infrared radiation inducing vibrational transitions, sensitive to changes in molecular dipole moments.	Identification of functional groups, adsorbed intermediates, acid/base sites, metal-ligand interactions.	Fourier-transform infrared spectrometer, diffuse reflectance (DRIFTS), attenuated total reflectance (ATR), or transmission cells; gas purging to minimize interference.	Using CO as a probe to characterize coordination sites in SACs; monitoring reaction intermediates (e.g., in CO_2 hydrogenation); quantifying Brønsted/Lewis acidity in catalyst supports.

Table 1: key characterization techniques (XAS, XPS, NAP-XPS, FTIR) for nanocatalysts and single-atom catalysts, detailing their physical

principles, information obtained, instrumentation, and applications. It emphasizes their role in probing electronic, structural, and chemical properties under in situ/operando conditions

3. Integrated Approaches: Operando Methodology, Time Resolution, and Computational Synergy

The ultimate goal in catalytic spectroscopy is to move beyond static characterization and observe the catalyst's dynamic behavior under technically relevant conditions, thereby directly correlating observed structure with measured activity.

The Operando Philosophy:

The term *operando* (Latin for "working") signifies a approach where spectroscopic characterization is performed on a catalyst under actual working conditions (e.g., flowing reactant gas mixture at elevated temperature and pressure) with *simultaneous* measurement of catalytic activity and selectivity, typically via online gas chromatography or mass spectrometry. This is a critical evolution beyond *in situ* (which may imply reaction conditions but without activity measurement) and is essential for closing the "pressure gap" and "materials gap" between idealized model systems and real-world catalysts (Yang et al., 2025). Designing an operando reactor cell is a complex engineering challenge, as it must fulfill three often conflicting requirements: (1) be transparent to the probe radiation (X-rays, IR light, etc.), (2) maintain well-defined, homogeneous reaction conditions (temperature, pressure, flow dynamics) to ensure accurate activity data, and (3) allow for efficient product analysis. This often involves sophisticated cells with materials like quartz, sapphire, or diamond windows and carefully designed flow geometries to avoid mass transfer limitations that would decouple the measured activity from the observed structure. A paradigmatic example is the study of Cu-zeolites for the selective catalytic reduction (SCR) of NOx with NH_3. Ex situ studies suggested isolated Cu^{2+} ions were the active sites. However, operando XAS and IR spectroscopy revealed a dynamic redox cycle between Cu^{2+} and Cu^{+} states, with the key reduction step involving the formation of a transient $[Cu(I)(NH_3)_2]^+$ complex that activates O_2—a discovery only possible through simultaneous spectroscopic and kinetic measurement (Negri et al., 2020).

Time-Resolved Techniques:

To capture the kinetics of catalytic turnover and identify short-lived intermediates, time resolution is essential. Techniques span a vast range of timescales. Quick-EXAFS (QEXAFS), which uses a rapidly oscillating monochromator, can achieve time resolution on the millisecond scale, sufficient to track oxidation state changes during a catalytic cycle or catalyst activation. Step-scan or rapid-scan Time-Resolved IR (TRIR) spectroscopy can operate on microsecond to picosecond timescales, ideal for monitoring the lifetime of adsorbed intermediates or photoinduced processes in photocatalysis (Mezzetti et al., 2020). Modulation Excitation Spectroscopy (MES) is a powerful sensitivity-enhancing method where a reaction parameter (e.g., reactant concentration, temperature) is periodically perturbed. Phase-sensitive detection of the spectroscopic response is then used to filter out signals from inactive, static species, highlighting only those species whose concentration varies with the perturbation frequency, dramatically simplifying complex spectra and revealing the dynamics of active participants (Novak et al., 2016).

Integration with Computational Chemistry:

The interpretation of complex spectroscopic data is vastly empowered by computational chemistry, creating a powerful iterative cycle of prediction and validation (Keith et al., 2021). Density Functional Theory (DFT) is the workhorse for calculating molecular properties that can be directly compared to experiment. It can simulate: vibrational frequencies (IR and Raman intensities) for assigning bands to specific adsorbates and surface modes; NMR chemical shifts and quadrupolar coupling constants for assigning solid-state spectra; and XANES spectra (using methods like FEFF or TD-DFT) and EXAFS signals (providing theoretical scattering paths) for structural refinement. Furthermore, DFT calculations of reaction energies and barriers place the spectroscopic observations of intermediates within a full energetic landscape of the catalytic cycle. Ab initio molecular dynamics (AIMD) adds the dimension of time and temperature, simulating the dynamic motion of atoms and providing insights into solvent effects, entropy, and finite-temperature dynamics that static calculations cannot. This synergy allows researchers to move from merely observing a spectral feature to confidently assigning it to a specific molecular structure and understanding its role in the catalytic mechanism (Zaera et al., 2014).

Catalytic Process	**Catalyst System**	**Operando Technique(s)**	**Observed Phenomena**	**Functional Insights and Implications**
CO_2 Electroreduction	Cu-based nanoparticles	XAS, ATR-IR, Raman	Reduction of Cu^{2+} to Cu^0; formation of Cu–CO intermediate; surface reconstruction under cathodic potential.	Metallic Cu with adsorbed CO is the active phase; surface roughening promotes C–C coupling; informs design of stable Cu catalysts.
CO_2 Electroreduction	Fe-porphyrin complexes	XAS, UV-Vis, ATR-IR	Reduction of Fe^{2+} to Fe^0; formation of Fe–COOH and Fe–CO intermediates; ligand-dependent electron density modulation.	Carboxylate pathway confirmed; electron-donating ligands enhance turnover frequency (TOF); guides rational ligand design for selectivity.
Water Splitting (OER)	NiFe (oxy)hydroxides	XAS, Raman, XPS	Formation of high-valent $Ni^{4+}=O$ and Fe^{4+} species; dynamic phase transition from hydroxide to oxyhydroxide.	Transient oxo/peroxo species are active sites; Fe facilitates Ni oxidation; explains high activity in alkaline media.
Water Splitting (HER)	MoS_2 edges	Raman, XPS, TRIR	Sulfur vacancy formation during H_2 evolution; protonation of edge S atoms; reversible H adsorption.	Sulfur vacancies are active sites; edge termination governs activity; informs defect engineering strategies.
Methanol Steam Reforming	$Cu/ZnO/Al_2O_3$	XAS, NMR, DRIFTS	Reduction of Cu^{2+} to Cu^0; ZnO_x migration onto Cu surface; detection of formate and CO intermediates.	Bifunctional mechanism at Cu–ZnO interface; ZnO_x promotes CO oxidation; explains deactivation via sintering.
Ammonia Synthesis (Haber-Bosch)	Promoted Fe catalysts	XAS, NMR, MES-IR	Formation of Fe–N nitride; H spillover from K promoter; reversible N_2	$N\equiv N$ bond cleavage is rate-limiting; promoters enhance

			activation under pressure.	electron donation; supports low-pressure catalyst design.
CO Oxidation	Au/TiO_2 nanoparticles	XPS, DRIFTS, SERS	Charge transfer from TiO_2 to Au; formation of peroxo-like O_2^- species; CO adsorption on cationic Au sites.	Active sites at Au–TiO_2 interface; oxygen activation at perimeter; explains size-dependent activity.
NOx Reduction (SCR)	Cu-zeolites (e.g., SSZ-13)	XAS, IR, UV-Vis	Dynamic $Cu^{2+} \leftrightarrow Cu^+$ redox cycle; formation of $[Cu(I)(NH_3)_2]^+$ complex; O_2 activation via Cu–O–Cu dimer.	Redox-active Cu sites enable O_2 activation; NH_3 stabilizes reduced Cu; guides low-temperature SCR catalyst design.
Photocatalytic H_2 Production	g-C_3N_4 with Co single-atom catalysts (SACs)	XAS, UV-Vis, TRIR	Co^{2+} reduction to Co^{1+} under illumination; formation of Co–H intermediate; electron trapping at defect sites.	Light-induced Co reduction generates active hydride; defects act as recombination centers; informs band engineering.
CO_2 Photoreduction	TiO_2-Ag hybrids	SERS, Raman, DRUVS	Plasmon-induced hot electron transfer; formation of CO_2^- radical; carbonate intermediate accumulation.	Localized surface plasmon resonance enhances charge separation; carbonate poisoning limits stability.
Methane Dry Reforming	Ni/CeO_2	XAS, DRIFTS, MES-IR	Ni oxidation/reduction cycling; carbonate formation; carbon deposition on Ni sites.	Reducible CeO_2 mitigates coking; Ni^0 is active phase; guides design of coke-resistant catalysts.
Solid Oxide Electrolysis (H_2O/CO_2)	Ni-YSZ	XAS, Raman, EIS	Ni particle coarsening; YSZ lattice expansion; accumulation of OH^-/CO_3^{2-} on surface.	Degradation due to Ni sintering; carbonate blocks active sites; suggests protective coatings.
Hydrogen Evolution (Homogeneous)	Co-dithiolene complexes	UV-Vis, NMR, ATR-IR	Ligand-centered reduction; formation of Co–H species; H_2 release via heterolytic cleavage.	Co(I)–H mediates H_2 evolution; ligand non-innocence enables low overpotential.
Oxygen Reduction (Fuel Cells)	Pt/C, Pt-alloys	XAS, SERS, DEMS	Pt oxidation under applied potential; O_2 adsorption on Pt; H_2O_2 formation at low	Surface oxides inhibit activity; alloying reduces overpotential; guides

			potentials.	durable cathode design.
Solar Water Splitting	$BiVO_4$ photoanodes	Raman, XPS, SPV	Surface V^{5+} layer formation; hole accumulation; photo-corrosion under bias.	Passivation layer enhances stability; hole transport limits efficiency; suggests co-catalyst deposition.
Ethanol Steam Reforming	$Ni/MgAl_2O_4$	XAS, DRIFTS, MS	Ni^0 formation; acetate and acetaldehyde intermediates; $MgAl_2O_4$ spinel stability.	Acetate decomposition is rate-limiting; spinel support resists sintering; enables long-term operation.
Fischer-Tropsch Synthesis	Co/Al_2O_3	XAS, GC-MS, MES-IR	Co_3O_4 reduction to Co^0; CH_x monomer formation; chain growth on Co^0 sites.	Co^0 is active phase; chain growth probability depends on H_2/CO ratio; informs selectivity tuning.
Ammonia Electrosynthesis	Li-mediated N_2 reduction	XAS, ATR-IR, DEMS	Li^+ intercalation; N_2 activation on Li_3N; NH_3 release via hydrolysis.	Li_3N is key intermediate; competing hydrogen evolution reaction (HER) limits Faradaic efficiency (FE); suggests electrolyte engineering.
CO_2-to-Methanol	$Cu/ZnO/Al_2O_3$	XAS, DRIFTS, MS	Cu^+/Cu^0 redox cycling; formate and methoxy intermediates; ZnO_x mobility.	Formate hydrogenation is rate-determining; ZnO_x stabilizes Cu^+; guides promoter design.
Perovskite Solar Cells	$MAPbI_3$ with additives	Raman, XPS, UV-Vis	Iodide migration; Pb^0 formation; phase segregation under illumination.	Additives suppress ion migration; degradation initiates at grain boundaries; informs encapsulation strategies.

Table 2: Applications of operando spectroscopy in energy conversion processes, highlighting observed phenomena and functional insights for catalyst design.

4. Critical Analysis of Applications in Energy-Relevant Catalysis

The power of advanced spectroscopy is best illustrated through its application to pressing challenges in energy catalysis. Here, we provide a critical analysis of its role in two key areas.

4.1 Molecular Catalysis for Electrocatalytic CO_2 Reduction:

The electrocatalytic reduction of CO_2 to value-added chemicals and fuels, such as carbon monoxide or formate, is a promising route for closing the carbon cycle. Molecular catalysts, particularly metalloporphyrins (e.g., Fe, Co) and polypyridyl complexes, offer tunability and high selectivity. Spectroscopy has been paramount in elucidating their mechanisms. For iron porphyrins, a leading catalyst for CO production, *operando* XAS at the Fe K-edge confirmed the reduction to a formal Fe(0) state before CO_2 binding, evidenced by a distinct edge shift to lower energy (Mendoza et al., 2023). Simultaneously, *operando* ATR-IR spectroscopy detected the appearance of a ν(C=O) band at ~1980 cm^{-1}, assigned to a Fe(II)-CO adduct, the product of two-electron reduction of CO_2. Crucially, under certain potentials and pH conditions, a transient band at ~1690 cm^{-1} can be observed, attributed to a Fe(II)-COOH intermediate, providing direct spectroscopic evidence for a carboxylate pathway. This mechanistic picture is refined by UV-Vis spectroelectrochemistry, which tracks the optical changes associated with each redox step, and by DFT calculations, which simulate the XANES spectra and vibrational frequencies of proposed intermediates, providing robust validation. Spectroscopy also reveals how ligand design tunes reactivity: electron-donating substituents on the porphyrin ring raise the electron density at the Fe center, strengthening π-backbonding to bound CO and accelerating its dissociation, thereby increasing turnover frequency (Fanourakis et al., 2023).

4.2 Heterogeneous Catalysis: Single-Atom Catalysts and Dynamic Restructuring:

In heterogeneous catalysis, a major frontier is the development of Single-Atom Catalysts (SACs), where isolated metal atoms are stabilized on a support, maximizing atom efficiency. Proving their existence and structure is a task for which spectroscopy is essential. Aberration-corrected scanning transmission electron microscopy (AC-STEM) provides direct visual evidence of isolated atoms. However, XAS provides the definitive electronic and structural characterization. The XANES of a Pt SAC on a FeOx support shows an oxidation state significantly higher than metallic Pt (Liu et al., 2019). The EXAFS is conclusive: the complete absence of a Pt-Pt scattering path confirms atomic dispersion, while the fitting reveals a coordination shell of light atoms (O) at a short distance, confirming the atomically dispersed metal is directly coordinated to the support. Further evidence comes from IR spectroscopy of adsorbed CO: a Pt SAC produces a single, sharp ν(CO) band at a higher wavenumber (~2090 cm^{-1}) than on Pt nanoparticles (~2050 cm^{-1} for atop CO), due to the lack of a metallic band for back-donation and the specific electronic interaction with the single site. Furthermore, *operando* spectroscopy is revealing that many catalysts are dynamic. For example, during the oxygen evolution reaction (OER), operando XAS and Raman studies on NiFe (oxy)hydroxides show that the catalysts undergo structural rearrangements and that the true active site may be a dynamically formed high-valent oxo or peroxo species, not the structure observed ex situ (Zhao et al., 2023).

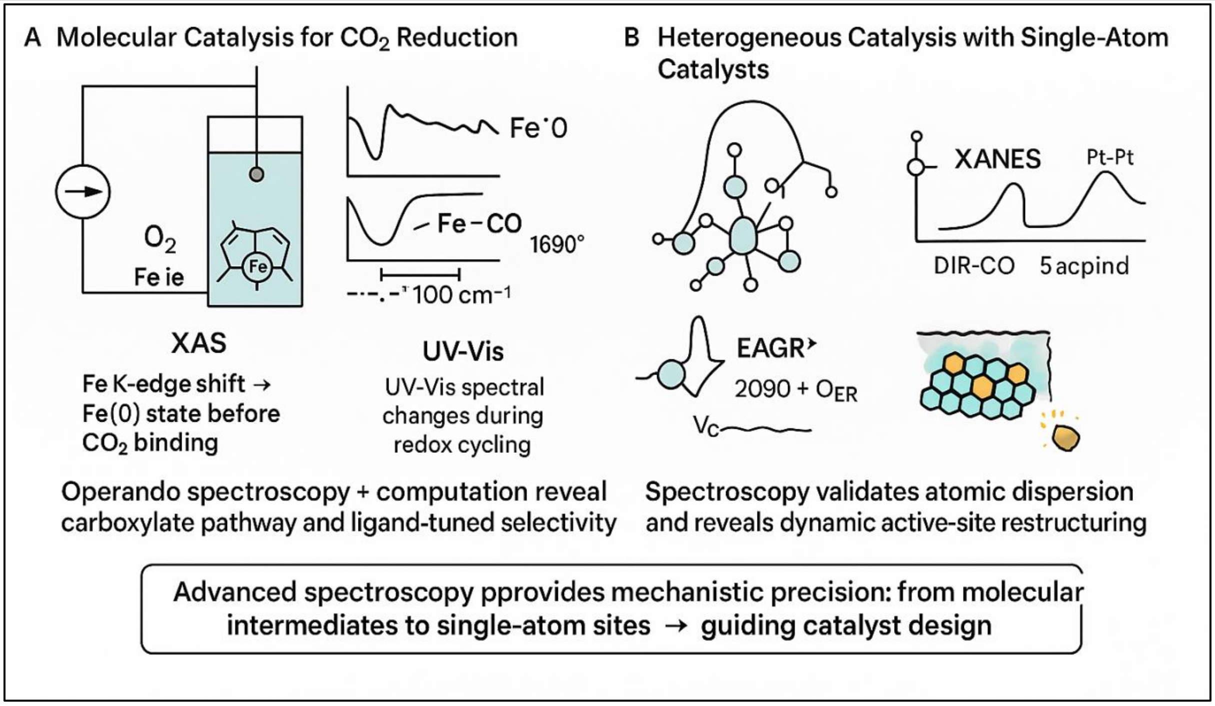


Fig 2: Critical Analysis of Applications in Energy-Relevant Catalysis

5. Future Perspectives

Despite significant advances, challenges and opportunities remain to further enhance spectroscopic applications in catalysis:

1. Spatial Resolution: Current operando techniques often yield spatially averaged data. Future progress lies in correlative spectro-microscopy, such as nano-focused X-ray beams or tip-enhanced Raman spectroscopy (TERS), to map heterogeneity within single catalyst particles or reactor beds under operando conditions (Hess, 2021).
2. Data Complexity: The multidimensional data generated by operando spectroscopy is increasingly complex. Machine Learning (ML) and Artificial Intelligence (AI) offer transformative potential for automated feature extraction, denoising, and predicting spectroscopic outcomes from structural models (Feng et al., 2025).
3. Probing Buried Interfaces: Many energy catalysts function at solid-liquid electrochemical interfaces, which are challenging to study with surface-4.sensitive techniques like XPS. Advances in tender X-rays, graphene-based membrane cells, and liquid jets for XAS are promising solutions (Jones et al., 2021).
5. Ultrafast Dynamics: While quick-XAS achieves millisecond resolution, key catalytic processes (e.g., adsorption, diffusion, electron transfer) occur on faster timescales. Integrating laser-pump/X-ray-probe methods into catalytic studies will enable exploration of these ultrafast dynamics (Bergmann et al., 2021).
6. Quantum Sensing: Emerging quantum sensors, such as nitrogen-vacancy centers in diamond, offer potential for nanoscale mapping of magnetic fields and temperature under ambient conditions, revolutionizing insights into local catalytic environments (Lakhani et al., 2024).

The continued evolution of spectroscopic techniques, coupled with deeper integration of theory and data science, will further illuminate catalytic processes. These advancements will drive the development of next-generation catalysts, accelerating the transition to sustainable energy systems.

Conclusion

Spectroscopic techniques have transformed from ex situ characterization tools into critical probes for studying catalytic systems under dynamic, operational conditions. The integration of operando spectroscopy, time-resolved methods, and computational modeling has shifted the field from phenomenological observations to predictive catalyst design. This review has outlined the principles and applications of X-ray absorption spectroscopy (XAS), X-ray photoelectron spectroscopy (XPS), vibrational spectroscopy, UV-Vis, and nuclear magnetic resonance (NMR), demonstrating their complementary roles in elucidating catalytic mechanisms. These techniques provide a comprehensive understanding, spanning molecular-level insights in homogeneous catalysis to complex interfacial phenomena in heterogeneous systems. This multidisciplinary approach is fundamental to the rational design of high-performance, stable, and selective catalysts essential for a sustainable energy future.

REFERENCES

Bergmann, U., Kern, J., Schoenlein, R. W., Wernet, P., Yachandra, V. K., & Yano, J. (2021). Using X-ray free-electron lasers for spectroscopy of molecular catalysts and metalloenzymes. *Nature Reviews Physics*, *3*(4), 264-282.

Clarke, T. B., Krushinski, L. E., Vannoy, K. J., Colon-Quintana, G., Roy, K., Rana, A., ... & Dick, J. E. (2024). Single entity electrocatalysis. *Chemical Reviews*, *124*(15), 9015-9080.

Collett, C. H., & McGregor, J. (2016). Things go better with coke: The Beneficial Role of Carbonaceous Deposits in Heterogeneous Catalysis. *Catalysis Science & Technology*, 6(2), 363-378.

Fanourakis, A., & Phipps, R. J. (2023). Catalytic, asymmetric carbon–nitrogen bond formation using metal nitrenoids: from metal–ligand complexes via metalloporphyrins to enzymes. *Chemical Science*, *14*(44), 12447-12476.

Fellows, R., & Liu, A. M. (2012). Managing organizational interfaces in engineering construction projects: addressing fragmentation and boundary issues across multiple interfaces. *Construction management and economics*, *30*(8), 653-671.

Feng, S., Huang, M., Li, Y., Cai, A., Yue, X., Wang, S., ... & Luo, Y. (2025). Intelligent understanding of spectra: from structural elucidation to property design. *Chemical Society Reviews*.

Hadjiivanov, K. I., Panayotov, D. A., Mihaylov, M. Y., Ivanova, E. Z., Chakarova, K. K., Andonova, S. M., & Drenchev, N. L. (2020). Power of infrared and Raman spectroscopies to characterize metal-organic frameworks and investigate their interaction with guest molecules. *Chemical Reviews*, *121*(3), 1286-1424.

Hernández, W. Y., Lauwaert, J., Van Der Voort, P., & Verberckmoes, A. (2017). Recent advances on the utilization of layered double hydroxides (LDHs) and related heterogeneous catalysts in a lignocellulosic-feedstock biorefinery scheme. *Green Chemistry*, *19*(22), 5269-5302.

Hess, C. (2021). New advances in using Raman spectroscopy for the characterization of catalysts and catalytic reactions. *Chemical Society Reviews*, *50*(5), 3519-3564.

Jones, E. S., Swallow, J. E., & Weatherup, R. S. (2021). Enclosed Cells for Extending Soft X-Ray Spectroscopies to Atmospheric Pressures and Above. In *Ambient Pressure Spectroscopy in Complex Chemical Environments* (pp. 175-218). American Chemical Society.

Keith, J. A., Vassilev-Galindo, V., Cheng, B., Chmiela, S., Gastegger, M., Muller, K. R., & Tkatchenko, A. (2021). Combining machine learning and computational chemistry for predictive insights into chemical systems. *Chemical reviews*, *121*(16), 9816-9872.

Khan, M. M. (2025). Absorption spectroscopy. In *Photocatalysts: Synthesis and Characterization Methods* (pp. 141-149). Elsevier.

Kubacka, A., Iglesias-Juez, A., Martínez-Arias, A., Di Michiel, M., Newton, M. A., & Fernández-García, M. (2012). Surface and Bulk Approach to Time-resolved Characterization of Heterogeneous Catalysts. *ChemCatChem*, *4*(6), 725-737.

Kuznetsov, A. V., van Veldhuizen, E. J., Westerberg, L., Lyapin, V. G., Aleklett, K., Loveland, W., ... & El Bouanani, M. (2000). A compact ultra-high vacuum (UHV) compatible instrument for time of flight–energy measurements of slow heavy reaction products. *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment*, *452*(3), 525-532.

Lakhani, P., Bhanderi, D., & Modi, C. K. (2024). Nanocatalysis: recent progress, mechanistic insights, and diverse applications. *Journal of Nanoparticle Research*, *26*(7), 148.

Li, X., Wang, H. Y., Yang, H., Cai, W., Liu, S., & Liu, B. (2018). In situ/operando characterization techniques to probe the electrochemical reactions for energy conversion. *Small Methods*, *2*(6), 1700395.

Liu, Q., & Zhang, Z. (2019). Platinum single-atom catalysts: a comparative review towards effective characterization. *Catalysis Science & Technology*, 9(18), 4821-4834.

Magnussen, O. M., Drnec, J., Qiu, C., Martens, I., Huang, J. J., Chattot, R., & Singer, A. (2024). In situ and operando X-ray scattering methods in electrochemistry and electrocatalysis. *Chemical Reviews*, *124*(3), 629-721.

Mendoza, D., Dong, S. T., Kostopoulos, N., Pinty, V., Rivada-Wheelaghan, O., Anxolabéhère-Mallart, E., ... & Lassalle-Kaiser, B. (2023). In situ X-ray Absorption Spectroscopy in Homogeneous Conditions Reveals Interactions Between CO2 and a Doubly and Triply Reduced Iron (III) Porphyrin, then Leading to Catalysis. *ChemCatChem*, *15*(7), e202201298.

Mezzetti, A., Schnee, J., Lapini, A., & Di Donato, M. (2022). Time-resolved infrared absorption spectroscopy applied to photoinduced reactions: how and why. *Photochemical & Photobiological Sciences*, *21*(4), 557-584.

Moroshkin, P., Hofer, A., Ulzega, S., & Weis, A. (2006). Spectroscopy of atomic and molecular defects in solid He4 using optical, microwave, radio frequency, and static magnetic and electric fields. *Low Temperature Physics*, *32*(11), 981-998.

Negri, C., Selleri, T., Borfecchia, E., Martini, A., Lomachenko, K. A., Janssens, T. V., ... & Berlier, G. (2020). Structure and reactivity of oxygen-bridged diamino dicopper (II) complexes in Cu-ion-exchanged chabazite catalyst for NH3-mediated selective catalytic reduction. *Journal of the American Chemical Society*, *142*(37), 15884-15896.

Novak, M., Yeakel, J. D., Noble, A. E., Doak, D. F., Emmerson, M., Estes, J. A., ... & Wootton, J. T. (2016). Characterizing species interactions to understand press perturbations: what is the community matrix?. *Annual Review of Ecology, Evolution, and Systematics*, *47*(1), 409-432.

Sarma, B. B., Maurer, F., Doronkin, D. E., & Grunwaldt, J. D. (2022). Design of single-atom catalysts and tracking their fate using operando and advanced X-ray spectroscopic tools. *Chemical reviews*, *123*(1), 379-444.

Sedigh Rahimabadi, P., Khodaei, M., & Koswattage, K. R. (2020). Review on applications of synchrotron-based X-ray techniques in materials characterization. *X-Ray Spectrometry*, *49*(3), 348-373.

Seo, Y., Cho, K., Jung, Y., & Ryoo, R. (2013). Characterization of the surface acidity of MFI zeolite nanosheets by 31P NMR of adsorbed phosphine oxides and catalytic cracking of decalin. *Acs Catalysis*, *3*(4), 713-720.

Shao, W., Fan, W., Guan, H., Zu, X., & Jiao, X. (2025). Fundamentals and Perspectives of Positively Charged Single-Metal Site Catalysts for CO2 Electroreduction. *ACS Applied Materials & Interfaces*, *17*(7), 10276-10291.

Simon, P., Baldovino-Medrano, V. G., & Wojcieszak, R. (2022). X-ray photoelectron spectroscopy (XPS): principles and application for the analysis of photoactive materials. In *Springer Handbook of Inorganic Photochemistry* (pp. 249-271). Cham: Springer International Publishing.

Tian, Z. Q., Ren, B., & Wu, D. Y. (2002). Surface-enhanced Raman scattering: from noble to transition metals and from rough surfaces to ordered nanostructures. *The Journal of Physical Chemistry B*, *106*(37), 9463-9483.

Usman, M., & Yamada, T. (2025). Methanol Reforming for Hydrogen Production: Advances in Catalysts, Nanomaterials, Reactor Design, and Fuel Cell Integration. *ACS Engineering Au*.

Wang, M., Zhou, H., & Wang, F. (2024). Photocatalytic biomass conversion for hydrogen and renewable carbon-based chemicals. *Joule*, *8*(3), 604-621.

Wasileski, S. A., Koper, M. T., & Weaver, M. J. (2001). Field-dependent chemisorption of carbon monoxide on platinum-group (111) surfaces: relationships between binding energetics, geometries, and vibrational properties as assessed by density functional theory. *The Journal of Physical Chemistry B*, *105*(17), 3518-3530.

Yang, H., Duan, P., Zhuang, Z., Luo, Y., Shen, J., Xiong, Y., ... & Wang, D. (2025). Understanding the Dynamic Evolution of Active Sites among Single Atoms, Clusters, and Nanoparticles. *Advanced Materials*, *37*(7), 2415265.

Yang, Z., Chen, R., Zhang, L., Li, Y., & Li, C. (2024). Recent progress in nickel single-atom catalysts for the electroreduction of CO 2 to CO. *Industrial Chemistry & Materials*, *2*(4), 533-555.

Yeo, J. S., & Kim, A. R. (2025). Unravelling interdisciplinary interactions and researcher migration across the evolution of perovskite solar cell research through comprehensive bibliometrics. *Royal Society Open Science*, *12*(6), 241986.

Zaera, F. (2014). New advances in the use of infrared absorption spectroscopy for the characterization of heterogeneous catalytic reactions. *Chemical Society Reviews*, *43*(22), 7624-7663.

Zhang, B., Sun, J., Salahuddin, U., & Gao, P. X. (2020). Hierarchical and scalable integration of nanostructures for energy and environmental applications: a review of processing, devices, and economic analyses. *Nano Futures*, *4*(1), 012002.

Zhao, Y., Adiyeri Saseendran, D. P., Huang, C., Triana, C. A., Marks, W. R., Chen, H., ... & Patzke, G. R. (2023). Oxygen evolution/reduction reaction catalysts: from in situ monitoring and reaction mechanisms to rational design. *Chemical reviews*, *123*(9), 6257-6358.