Operando Electronic Structure Engineering of Zhang–Rice Singlet Catalysts for Simultaneous Water Oxidation and Volatile Organic Compound Mitigation in Urban Transportation Microenvironments

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Abstract

The urban transportation microenvironment constitutes a pervasive and underexplored exposure landscape for volatile organic compounds (VOCs), with subways, buses, and taxis exhibiting distinct chemical fingerprints and adverse health outcomes. Simultaneously, electrochemical water oxidation driven by earth-abundant catalysts offers a pathway toward decentralized oxygen generation and coupled pollutant degradation, yet catalysts capable of performing both functions with high efficiency under realistic, fluctuating conditions remain elusive. This paper advances a systems-level framework for operando electronic structure engineering of Zhang–Rice singlet (ZRS) catalysts to achieve concurrent oxygen evolution reaction (OER) and VOC mineralization within vehicular microenvironments. The ZRS, a correlated quantum state arising from hole coupling between copper 3d and oxygen 2p orbitals, has recently been demonstrated as a powerful motif for triggering water oxidation under operando conditions. We argue that external stimuli such as applied bias, illumination, and humidity can dynamically modulate the ZRS formation energy and hole delocalization, thereby tuning both OER selectivity and the complete oxidation of aromatic and aliphatic VOCs. Moving beyond molecular-scale optimization, the article examines structural trade-offs embedded in the design of catalytic modules for integration across heterogeneous vehicle fleets—including energy supply architecture, real-time feedback control through environmental sensing, modular cartridge-based replacement systems, and communications protocols with vehicle climate control units. Detailed analysis addresses robustness against poisoning, thermal cycling, and mechanical vibration, as well as sustainability through reliance on copper-based oxides that circumvent critical raw material bottlenecks. Governance, fairness, and policy dimensions are explored from the perspective of differentiated exposure burdens across socioeconomic strata and the need for regulatory

frameworks that encourage equitable deployment of advanced catalytic air purification in both private and public transit. The study ultimately outlines a socio-technical roadmap in which operando electronic structure engineering converges with distributed infrastructure thinking to transform urban mobility into a site of active environmental remediation.

Keywords

operando spectroscopy, Zhang–Rice singlet, water oxidation, volatile organic compounds, urban transport, catalyst design, air quality governance, sustainable infrastructure.

1. Introduction

Urban transportation systems sustain the metabolic rhythms of modern cities but concurrently generate complex indoor atmospheric environments that have only recently attracted systematic scrutiny from the atmospheric chemistry and public health communities. Subway carriages, bus cabins, and taxi interiors encapsulate microcosms of street-level pollution, passenger-emitted bioeffluents, and materials off-gassing, producing volatile organic compound (VOC) mixtures whose composition and concentration profiles diverge sharply from those found in outdoor or indoor residential settings. Epidemiological investigations have associated short-term exposures in these microenvironments with oxidative stress, respiratory inflammation, and cardiovascular perturbations, underscoring the urgency of interventions that move beyond dilution ventilation toward active chemical conversion. In parallel, electrocatalytic water oxidation has matured into a cornerstone of renewable energy storage, with recent breakthroughs revealing that engineered quantum correlations in transition metal oxides—specifically the Zhang–Rice singlet state—can dramatically lower the kinetic barriers for the oxygen evolution reaction (OER). The confluence of these two domains creates a fertile interdisciplinary frontier: the design of catalytic systems that simultaneously split water to produce oxygen and completely mineralize VOCs into carbon dioxide and water, all within the constraints of moving vehicle platforms. This paper develops a systems-oriented perspective on operando electronic structure engineering of Zhang–Rice singlet catalysts for such dual-purpose remediation, treating the catalyst not as an isolated chemical entity but as a node embedded in a layered architecture of sensing, actuation, energy supply, and governance.

The Zhang–Rice singlet, a many-body quantum state first conceptualized to explain the electronic structure of cuprate superconductors, results from the strong hybridization of a copper 3d hole with an oxygen ligand hole, forming a localized spin-singlet entity that mediates charge transfer. Recent operando spectroscopic studies have established that a two-step oxidation pathway can deliberately form this singlet on the surface of copper-based oxides, triggering efficient OER with overpotentials that rival those of precious metal oxides. Yet the catalytic potential of the ZRS extends far beyond water splitting; the same delocalized hole character that activates lattice oxygen toward O–O bond formation can, in principle, activate organic substrates for deep oxidation. The critical challenge lies in engineering the electronic structure in real time under the dynamic conditions encountered aboard transportation vehicles—variable humidity, fluctuating VOC concentrations spanning several orders of magnitude, thermal swings, and the presence of co-adsorbed nitrogen and sulfur oxides. An operando approach, wherein the catalyst electronic structure is continuously monitored and modulated through external stimuli such as potential, photon flux, or temperature, becomes indispensable to maintain the ZRS in its optimally active configuration while avoiding deactivation pathways.

This article adopts a holistic, system-level lens that complements the rich body of molecular-level mechanistic investigations. We first deconstruct the Zhang–Rice singlet paradigm, emphasizing how its formation energetics, spectroscopic signatures, and reactivity fingerprints can be exploited for simultaneous OER and VOC oxidation. Subsequently, we analyze operando engineering strategies that leverage multimodal in-situ spectroscopy and autonomous feedback control to maintain the desired electronic configuration under transient conditions. The discussion then translates these principles to the urban transportation microenvironment, examining the architectural integration of catalytic modules into subway air handling units, bus HVAC systems, and compact taxi cabin purifiers. We devote substantial attention to structural trade-offs between performance, durability, form factor, and energy consumption, as well as to sustainability criteria that privilege earth-abundant copper-based materials. The latter sections address governance and equity, arguing that the deployment of advanced catalytic air quality technologies must be embedded within policy frameworks that recognize differentiated exposure burdens and mandate transparent performance verification. The paper concludes with a forward-looking synthesis that positions operando electronic structure engineering as a cornerstone of next-generation built-environment remediation.

2. The Zhang–Rice Singlet Paradigm in Catalytic Systems

The Zhang–Rice singlet represents a prototypical correlated electronic state in which the strong intra-atomic Coulomb repulsion on a copper site and the significant covalency of the copper-oxygen bond conspire to localize a hole symmetrically across one copper and four neighboring oxygen ions. In the canonical description derived from the three-band Hubbard model, the doped hole resides primarily in a linear combination of oxygen 2p orbitals surrounding the copper center, forming a spin singlet with the localized copper 3d hole. This state carries profound implications for surface catalysis, because the associated electron density redistribution weakens metal-oxygen bonds and lowers the energy barrier for the nucleophilic attack that initiates O–O bond formation. Furthermore, the partially delocalized nature of the hole imparts a high chemical potential for oxidation reactions, enabling the catalyst to abstract electrons from organic molecules with activation energies that are substantially lower than those encountered on conventional oxide surfaces. From a systems perspective, the ZRS motif therefore constitutes a building block whose electronic free energy landscape can be tuned by structural and environmental parameters, transforming a low-dimensional quantum phenomenon into a handle for macroscopic chemical conversion.

The identification of the ZRS in catalytic contexts relied on advances in high-resolution X-ray absorption spectroscopy and resonant inelastic X-ray scattering, which together can resolve the symmetry and energetic position of the singlet state relative to the Fermi level. In the landmark study by Peng et al., it was shown that a carefully orchestrated two-step oxidation—electrochemical oxidation followed by mild thermal annealing—generates a surface ZRS population in copper-based oxides that is directly correlated with OER activity [5]. Critically, the singlet formation was confirmed under operando conditions, meaning that the catalyst was probed while reacting in aqueous electrolyte at anodic potentials. This demonstration shattered the long-held assumption that ZRS physics was restricted to superconducting cuprates and opened the door to deliberate design of singlet-enhanced catalysts. Subsequent works have begun to explore how substitutional doping, oxygen vacancy engineering, and facet exposure modulate the ZRS formation energy, yet the field remains in its infancy with respect to harnessing the singlet for multi-electron oxidations beyond water.

Extending the ZRS paradigm to VOC oxidation requires a conceptual leap that is, however, grounded in well-established surface science principles. The complete mineralization of a representative aromatic VOC such as toluene involves the sequential transfer of 18 electrons from the carbon scaffold to the catalyst, a process that demands sustained oxidative power and resilience against carbonaceous deactivation. The ZRS, by virtue of its hole delocalization, can serve as a reservoir of strongly oxidizing equivalents that are replenished continuously by the anodic bias. Moreover, the lattice oxygen sites directly involved in the singlet are often the same sites that participate in Mars–van Krevelen oxidation cycles, whereby lattice oxygen is consumed in substrate oxidation and subsequently replenished by water or gas-phase oxygen. This mechanistic convergence suggests that a single ZRS-active surface can catalyze OER—generating molecular oxygen that improves cabin air quality—and simultaneously combust VOCs, provided the electronic structure is held in a window where both the OER intermediate binding energies and the organic substrate activation barriers are favorable. The key engineering question, then, is how to position the ZRS energy level dynamically to satisfy the divergent thermodynamic requirements of the two half-reactions, a challenge that demands an operando control paradigm.

3. Operando Engineering of Electronic Structure: Principles and Instrumentation

Operando electronic structure engineering denotes the capability to measure and actively adjust the electronic degrees of freedom of a catalyst while it performs its function, closing the loop between spectroscopic observation and control input. In the context of ZRS-based systems, the primary control handles include the electrochemical potential, which shifts the Fermi level and thereby modulates the occupancy of the singlet state; the photon flux and wavelength in photoelectrochemical configurations, which can photo-generate additional carriers and alter the hole distribution; and the local chemical environment, especially the partial pressure of water vapor, which influences the proton-coupled electron transfer steps that stabilize the singlet. A sophisticated operando platform integrates a miniaturized electrochemical or photoelectrochemical cell with hard X-ray or soft X-ray spectroscopy, often employing grazing-incidence geometries to enhance surface sensitivity. Key observables are the pre-edge features in the O K-edge and Cu L-edge X-ray absorption spectra that fingerprint the ZRS, as well as the resonant inelastic scattering profiles that discriminate between singlet and triplet excitations.

The translation of these laboratory capabilities into a transport-compatible module introduces formidable systems integration demands. High-brilliance synchrotron sources are obviously incompatible with on-vehicle deployment, yet emerging laboratory-based X-ray spectrometers, Raman probes, and impedance-based electronic structure sensors provide viable proxies for detecting changes in the ZRS population. The control architecture must accommodate a hierarchy of timescales: fast potentiostatic adjustments to counteract transient VOC spikes lasting seconds to minutes, slower thermal management to maintain the oxide in its optimal oxidation state over hours of operation, and long-term regeneration cycles that periodically restore the ZRS after accumulation of inactive surface phases. This multi-scale orchestration aligns with established frameworks for cyber-physical systems, wherein a supervisory controller receives inputs from an array of chemical sensors—metal-oxide semiconductor VOC sensors, humidity probes, and temperature thermistors—and modulates the catalyst potential, UV illumination intensity, and airflow across the catalytic bed.

A crucial trade-off emerges between the fidelity with which the ZRS state can be maintained and the energy overhead of the control system. High-fidelity, rapid-response potential

modulation requires a power supply with sufficient bandwidth and ripple tolerance, potentially drawing several watts from the vehicle's electrical system. While that load is modest compared to traction power, it becomes significant when aggregated across an entire subway fleet or taxi network and must be justified by the health and comfort benefits. The system architect must therefore balance the aggressiveness of the feedback loop against the energy budget, possibly adopting event-triggered control strategies that switch to a low-power baseline state when VOC concentrations fall below a threshold. Such strategies resemble the duty-cycling protocols used in wireless sensor networks and can reduce average power consumption by an order of magnitude without compromising peak remediation capacity.

4. Simultaneous Water Oxidation and VOC Abatement: Mechanistic Synergies

Simultaneous water oxidation and VOC abatement on a single catalytic surface is not merely the co-location of two independent reactions; it involves a network of coupled elementary steps whose net thermodynamic and kinetic outcomes depend sensitively on the coverage of reactive intermediates. The OER on copper-based ZRS oxides proceeds through the lattice oxygen mechanism, wherein surface lattice oxygen atoms are oxidized to form O–O bonds, generating molecular oxygen and leaving behind oxygen vacancies that are subsequently re-filled by water oxidation. In the presence of VOCs, the same lattice oxygen can be intercepted by an organic molecule before the O–O coupling step, leading to insertion of oxygen into the C–H or C–C bonds and initiating cascading oxidation. This competition can either enhance or suppress the overall rates, depending on the relative adsorption strengths and the rate of vacancy regeneration. Operando spectroscopy combined with product analysis has revealed that under mildly anodic conditions, the presence of benzene derivatives can actually enhance the OER faradaic efficiency because the organic molecules scavenge reactive oxygen species that would otherwise recombine to peroxide intermediates, thereby reducing the overpotential.

From a systems standpoint, the synergy creates an opportunity to implement a single-unit catalytic reactor that delivers two environmental services: replenishment of oxygen and removal of VOCs. In a subway carriage, where occupancy density periodically spikes, the oxygen demand and the VOC emission from cleaning agents, personal care products, and building materials are often correlated. A catalyst that co-optimizes both functions can therefore provide demand-responsive air revitalization without requiring separate sorbent beds or photocatalytic modules. However, realizing this synergy demands precise control of the operating point: too anodic a potential favors oxygen evolution but may over-oxidize the surface and quench the ZRS, while too cathodic a potential suppresses OER and may leave partially oxidized VOC intermediates that desorb as hazardous carbonyls. A dynamic potential waveform that oscillates between a ZRS-stabilizing potential and a deep oxidation pulse could resolve this conundrum, effectively time-sharing the surface between the two reaction manifolds.

The dual-function operation also introduces nuanced long-term stability considerations. Oxygen evolution continuously replenishes lattice oxygen, which helps sustain the Mars–van Krevelen cycle for VOC oxidation, but it also generates oxygen bubbles that may mechanically disrupt the catalyst layer if not efficiently disengaged. The incorporation of hierarchical porosity and hydrophilic/hydrophobic patterning at the mesoscale, informed by computational fluid dynamics simulations, can mitigate this issue by facilitating bubble detachment while maintaining sufficient VOC mass transfer. Such design choices constitute system-level decisions that link catalyst morphology, reactor engineering, and vehicle vibration spectra—a helicopter might experience lower-frequency vibrations that promote

bubble coalescence, whereas a subway train undergoes high-frequency oscillations that could assist bubble removal.

5. Translation to Urban Transportation Microenvironments

The urban transportation microenvironment is a highly heterogeneous exposure chamber characterized by rapid fluctuations in pollutant concentrations, temperature, and relative humidity. A recent comprehensive study of subway, bus, and taxi environments in Beijing quantified VOC species including aromatics, alkanes, aldehydes, and chlorinated compounds, revealing distinct source profiles: subway cabins were enriched in cleaning-derived chlorinated species and brake wear-related aromatics, buses exhibited elevated levels of combustion-related VOCs due to engine proximity and boarding-induced cabin pressurization, and taxis showed high peak concentrations of interior trim off-gassing compounds [9]. Short-term health effect modeling in that work indicated that exposure to specific VOC mixtures was associated with increased odds of throat irritation and pulmonary function decrements, providing a concrete epidemiological rationale for on-board remediation.

Translating ZRS catalytic reactors into these environments requires careful matching of reactor scale to pollutant loading and vehicle characteristics. For a subway carriage, the ventilation system already moves large volumes of air, typically on the order of thousands of cubic meters per hour, which suggests an in-duct catalytic module downstream of the main air handler. The module must present a low pressure drop to avoid excessive fan energy penalties, yet provide sufficient contact time for deep VOC oxidation—a classic throughput-versus-conversion trade-off that can be navigated through monolithic catalyst supports with high open frontal area and thin catalytic coatings. In contrast, a taxi cabin, with a volume of only a few cubic meters and a ventilation rate an order of magnitude lower, can accommodate a compact, stand-alone purifier integrated into the parcel shelf or center console, where the catalyst is embedded in a recirculation loop and illuminated by low-power UV LEDs to drive photoelectrochemical ZRS activation. Buses occupy an intermediate position, often already equipped with rooftop HVAC units that can be retrofitted with catalyst-coated heat exchanger fins, enabling waste heat recovery to thermally assist the oxidation kinetics.

The heterogeneity across vehicle types creates a system-of-systems integration challenge: a metropolitan transit authority must maintain a fleet of catalytic modules with varying form factors, lifetimes, and monitoring requirements. Standardizing the electrochemical core—the ZRS catalyst composition and the potentiostatic control electronics—while modularizing the housing to fit different duct geometries and airflow rates can contain the logistical complexity. Such modularization echoes the design philosophy of automobile oxygen sensors, where a universal sensing element is packaged into diverse vehicle-specific configurations, and has proven highly successful in achieving economies of scale. Moreover, a unified communication protocol, perhaps built on vehicle-area-network standards, would allow central fleet management systems to aggregate performance data, predict maintenance cycles, and push firmware updates that refine the potential waveform in response to seasonal VOC profile shifts.

6. System Architecture and Integration with Vehicular Microenvironments

The proposed system architecture comprises four functional layers: the catalytic reaction layer, where the ZRS-active coating interacts with the air stream; the sensing and actuation layer, consisting of VOC sensors, humidity and temperature probes, and reference electrodes that measure the catalyst's open-circuit potential as a proxy for surface oxidation state; the local

control layer, a microcontroller executing real-time optimization of the applied potential and, where applicable, the illumination intensity; and the supervisory layer, which interfaces with the vehicle's climate control module and telematic units to coordinate operation with passenger occupancy, outdoor air quality, and energy availability. Each layer embodies its own design tensions. For example, the catalytic layer must balance high surface area for reaction with mechanical robustness against vibration and thermal expansion. Nanostructured copper oxide films grown on porous metallic foams have demonstrated excellent adhesion and conductivity, but the long-term stability against delamination under thousands of kilometers of road vibration remains a subject of active investigation. Encapsulation strategies using atomic layer deposition of ultrathin alumina or titania overlayers can passivate dissolution-prone sites without blocking access to the ZRS-active centers, provided the overlayer thickness is kept below the tunneling length for electron transfer.

The sensing layer must be capable of detecting tens of VOCs at parts-per-billion concentrations with response times of seconds, a specification that currently exceeds the capabilities of low-cost metal-oxide sensors. Hybrid sensor arrays that combine a few broadband photoionization detectors with an array of semi-selective chemiresistors and a recurrent neural network for pattern recognition have shown promise in resolving benzene, toluene, formaldehyde, and acetaldehyde under interferent-laden conditions. The computational load of such inference can be offloaded to the vehicle's central computing unit or to an edge processor on the catalyst module, leveraging advances in tiny machine learning. The actuation command—the target potential—is then computed by a model predictive controller that embeds a reduced-order kinetic model of the ZRS catalyst, enabling anticipatory adjustment rather than pure reactive feedback. This closes the loop between the electronic structure and the macroscopic air quality, realizing the operando vision in a realistic cyber-physical implementation.

The supervisory layer introduces systemic considerations that transcend the individual vehicle. Transit authorities can pool data from hundreds of catalyst-equipped buses and subway cars to create spatiotemporal maps of in-cabin VOC concentrations, which in turn can inform ventilation strategies at station platforms and depots. Such data, when anonymized and aggregated, have the potential to serve as a new modality for urban air quality monitoring, complementing fixed monitoring stations. However, this prospect raises privacy and data governance questions that must be addressed from the outset. The same connectivity used for performance optimization could be misconstrued as surveillance if vehicle locations are not properly anonymized. Architectural decisions such as on-module data aggregation before transmission and differential privacy protocols are therefore not ancillary technical details but integral components of a trustworthy system design. The system architect must therefore possess a transdisciplinary fluency that spans materials science, embedded systems, and information governance.

7. Sustainability, Robustness, and Lifecycle Considerations

Sustainability in catalyst-driven air purification is a multi-dimensional concept that extends beyond the operational energy efficiency to encompass raw material extraction, manufacturing impacts, and end-of-life recycling. Copper-based ZRS catalysts offer an inherent advantage over the iridium and ruthenium oxide catalysts that dominate acidic OER because copper is approximately ten thousand times more abundant in the Earth's crust and benefits from an established recycling infrastructure. However, the advanced synthesis methods required to generate the ZRS state—typically involving controlled calcination under

specific gas atmospheres and electrochemical conditioning—may temporarily draw upon reagents and energy sources that erode the net environmental benefit if not properly optimized. Lifecycle assessment studies of analogous layered oxide catalysts indicate that the use-phase emissions avoidance—in this case, the health and productivity gains from reduced VOC exposure—can outweigh the embodied energy by one to two orders of magnitude, provided the catalyst operates for at least several thousand hours. Targeted research on ZRS catalyst durability under realistic cycling conditions is therefore a high-priority knowledge gap.

Robustness encompasses both chemical resilience to poisoning and mechanical resilience to the vibrational and thermal stresses of vehicular service. VOCs themselves can cause reversible and irreversible deactivation. Reversible deactivation occurs when partially oxidized intermediates accumulate on the surface, blocking active sites; periodic potential pulses to brief oxidizing potentials can strip these adsorbates. Irreversible deactivation is more insidious, arising from sulfur dioxide adsorption that converts surface copper sites to inactive copper sulfates, or from silicone-derived volatile methylsiloxanes that deposit silica layers. In urban transportation, both sulfur species from lubricants and siloxanes from personal care products are ubiquitous, so catalyst formulations must incorporate sulfur-tolerant promoters—ceria or zinc oxide—that preferentially bind sulfur and can be periodically regenerated by thermal or chemical treatment. From a system perspective, robustness can be enhanced by designing the module for easy catalytic core replacement, akin to an oil filter, which transforms the catalyst from a permanent asset into a consumable with a defined service interval. Such a design choice, while increasing material throughput, may paradoxically lower lifecycle environmental impact by ensuring that the catalyst always operates near its peak efficiency and avoiding the energy waste of driving a degraded surface.

Fairness considerations enter the lifecycle discussion through the differential capacity of socioeconomic groups to access and maintain advanced cabin air purification systems. Luxury private vehicles may incorporate ZRS-based purifiers as premium options long before they become standard in public transit. Consequently, those who rely on subways and buses—often lower-income commuters—could continue to bear a disproportionate burden of VOC exposure. Correcting this equity imbalance requires that public procurement policies explicitly incentivize the early adoption of advanced air purification technologies in mass transit, potentially through subsidies, technology mandates in concession contracts, or inclusion in green bond frameworks for transit authority capital projects. The fairness dimension also intersects with international supply chains; if cobalt, a common dopant to stabilize ZRS oxides, is sourced from artisanal mines with poor labor conditions, the local environmental health benefits may come at the cost of distant social harm. Governance frameworks must therefore address the full value chain, echoing the principles of responsible research and innovation [13].

8. Governance, Fairness, and Policy Dimensions

The deployment of operando ZRS catalyst systems within urban transportation implicates multiple levels of governance, from technology-specific standards set by transportation authorities to broader public health and data protection regulations. Existing indoor air quality guidelines, such as those promulgated by the World Health Organization, provide concentration thresholds for a limited set of VOCs and particulate matter but were largely developed for residential and office environments and do not account for the unique exposure dynamics of commuting. Regulators are beginning to recognize the commuter microenvironment as a distinct category, yet enforceable limits for in-vehicle VOC

concentrations remain absent in most jurisdictions. The availability of active catalytic remediation technology creates a policy window: if continuous catalytic VOC removal can be demonstrated at scale, regulators may move from a purely ventilation-based paradigm to a performance-based standard that mandates a minimum clean air delivery rate for specific pollutants, analogous to the evolution of automotive emission standards.

Such performance-based regulations would need to define standardized test cycles that replicate real-world driving and passenger usage patterns, with well-specified protocols for introducing VOC mixtures representative of each vehicle class. The development of these protocols is a system-level endeavor that should engage environmental health scientists, metrologists, vehicle manufacturers, and catalyst engineers. Crucially, regulation must grapple with verification and compliance in the field, not just in laboratory type-approval tests. This need reinforces the importance of the sensing and connectivity architecture described earlier, which can provide tamper-resistant, time-stamped performance logs. However, the mandatory installation of connected monitoring systems raises civil liberties concerns; policy design must strike a delicate balance between public health assurance and personal privacy, perhaps by requiring that performance data be streamed only to an independent auditing body and not to vehicle manufacturers or transit agencies in an identifiable form.

The fairness lens reveals that the health benefits of VOC mitigation are not uniformly distributed. Subway riders, who typically experience longer commutes and higher passenger densities, stand to gain substantially from catalyst retrofits, yet subway systems are often operated by cash-strapped public authorities that defer capital investments. Policy instruments such as municipal green bonds, public-private partnerships for air quality infrastructure, and health-impact-driven cost-benefit analyses that monetize avoided asthma exacerbations and lost workdays can strengthen the investment case. Furthermore, the design of catalyst replacement schemes—whether subsidized through fare-box revenue or general taxation—must ensure that cost burdens do not fall regressively on the most vulnerable populations. A just transition framework for in-vehicle air quality would explicitly consider the distribution of both benefits and costs across income quintiles and racial groups, informed by transportation equity metrics that have been developed in the context of fare policies and service cuts. The convergence of environmental justice and technology governance thus becomes a critical axis along which operando catalytic systems must be evaluated.

9. Conclusion

Operando electronic structure engineering of Zhang–Rice singlet catalysts represents a conceptual and practical frontier that bridges condensed matter physics, catalysis, and urban environmental engineering. By leveraging the correlated hole dynamics of the ZRS state, it becomes feasible to design a single catalytic surface that simultaneously evolves oxygen from water and mineralizes a broad spectrum of volatile organic compounds, thereby transforming vehicle cabins from passive containers of polluted air into active remediation nodes. Realizing this vision, however, demands more than incremental advances in catalyst synthesis and characterization; it calls for a system-level integration that marries materials architecture with embedded control, sensor fusion, mechanical robustness, and a governance framework attuned to equity and sustainability.

The architectural analysis presented herein underscores the importance of multi-layered design: the catalytic layer must balance surface area with vibration tolerance, the sensing and actuation layer must execute fast potential modulation informed by reduced-order kinetic models, and the supervisory layer must align operational goals with fleet-level data

aggregation and privacy norms. Throughout this hierarchy, trade-offs between performance, energy consumption, and cost are unavoidable and must be navigated with the same rigor applied to molecular design. The sustainability narrative is encouraging, as copper-based oxides can circumvent critical raw material supply risks while delivering competitive activity, yet lifecycle impacts must be verified under realistic service conditions including poisoning, thermal cycling, and maintenance cycles.

The deployment of ZRS catalytic systems in urban transportation microenvironments stands to reconfigure the relationship between mobility and public health. If embedded within policy frameworks that mandate performance-based clean air delivery and enforce equitable access, these technologies could substantially reduce the commuting-related burden of respiratory and cardiovascular disease. Conversely, an ungoverned rollout could widen existing environmental health disparities, locking in a two-tier reality of clean private travel and polluted public transit. The scholastic and policy communities are therefore confronted with the task of co-developing the technical and institutional scaffolding for operando catalytic air purification, a task that demands interdisciplinary collaboration across materials science, electrical engineering, data science, public health, and sociology. The Zhang–Rice singlet, a quantum state once confined to the esoteric world of high-temperature superconductivity, may thus emerge as an unlikely protagonist in the making of more breathable, just, and sustainable cities.

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