

Review



Design Principles and Structure-Activity Relationships of Single-Atom Catalysts for Low-Temperature VOCs Oxidation and Related Probe Reactions

Chang Sun, Zhiwei Huang, Haoran Liu, Jia Chen, Huazhen Shen, Xiaomin Wu, Huawang Zhao, Bihong Lv and Guohua Jing *

Department of Environmental Science & Engineering, College of Chemical Engineering, Huaqiao University, Xiamen 361021, China

* Correspondence: zhoujing@hqu.edu.cn

How To Cite: Sun, C.; Huang, Z.; Liu, H.; et al. Design Principles and Structure-Activity Relationships of Single-Atom Catalysts for Low-Temperature VOCs Oxidation and Related Probe Reactions. *Glob. Environ. Sci.* **2026**, 2(3), 312–345. <https://doi.org/10.53941/ges.2026.100021>

Publication History

Received: 10 March 2026

Revised: 19 April 2026

Accepted: 15 June 2026

Published: 13 August 2026

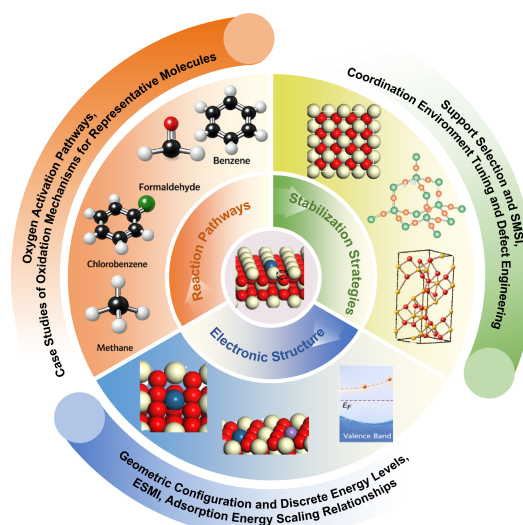
Keywords

single-atom catalyst;
VOC oxidation;
low-temperature catalysis;
oxygen vacancy;
defect-localized site

Highlights

- Design principles of single-atom catalysts for low-temperature VOC oxidation are summarized.
- Single-atom catalyst oxygen activation and intermediate transformation mechanisms over single-atom catalysts are discussed.
- Structure-activity relationships of single-atom catalysts in VOC oxidation are reviewed.
- Prospects and challenges for practical application of single-atom catalysts are proposed.

Abstract: Volatile organic compounds (VOCs) are key precursors of ozone and secondary organic aerosols and pose serious risks to human health. Consequently, stringent emission abatement is urgently required under realistic operating conditions such as low inlet concentrations, high gas hourly space velocities, and high humidity. Catalytic oxidation is widely regarded as one of the most competitive end-of-pipe technologies. However, low-temperature operation remains kinetically challenging. Oxygen activation is sluggish, reaction intermediates can bind strongly, and catalysts are prone to deactivation by water, chlorine/sulfur-containing species, and carbonaceous deposits. Single-atom catalysts (SACs) provide an atomic-level platform in which isolated metal centers exhibit unique electronic structures and metal-support interfacial chemistry. These features can fundamentally reshape oxygen activation and VOC oxidation pathways. This review summarizes recent advances in SACs for low-temperature VOC oxidation and discusses how anchoring motifs (M–O_x, M–N_x, and defect-localized sites), support redox properties, and microenvironmental factors (hydroxyls and hydrophilicity) synergistically regulate oxygen delivery (adsorbed oxygen vs lattice oxygen), intermediate evolution (formate/benzoate/carbonate species), and conversion stability. Finally, perspectives are provided on future design and application of single-atom catalysts.



1. Introduction

With the rapid pace of global industrialization and urbanization, atmospheric pollution has become a major bottleneck for sustainable societal development. Among diverse pollutants, volatile organic compounds (VOCs) are key precursors of ozone (O₃) and secondary organic aerosols (SOA); thus, controlling VOC emissions is pivotal for improving air quality and suppressing photochemical smog and haze formation [1–3]. Conventional physical absorption or thermal incineration is often limited by high energy consumption, potential secondary pollution, or insufficient removal efficiency. By contrast, catalytic oxidation—enabling complete conversion of VOCs into CO₂ and H₂O at substantially lower temperatures—is widely considered one of the most efficient and cost-effective abatement strategies [2,4,5].

Catalysts are the core component of catalytic oxidation technology. Owing to their excellent thermal stability, recyclability, and ease of separation, heterogeneous catalysts dominate industrial applications [6]. Nevertheless, widely used noble-metal nanoparticle catalysts (e.g., Pt and Pd) still face critical challenges. On the one hand, the scarcity and high cost of noble metals limit large-scale deployment [7–9]. On the other hand, noble-metal atoms buried inside conventional nanoparticles are inaccessible to reactants. As a result, atom utilization is intrinsically low (typically <20%), which not only wastes resources but also caps catalytic efficiency improvements [10–12]. Since H.S. Taylor proposed the concept of the fraction of active centers among exposed surface atoms [13], maximizing atom efficiency has remained a central objective in catalysis. The emergence of the single-atom catalyst (SAC) concept in 2011 offered a transformative route to address these challenges [14]. By dispersing the metal component as isolated atoms on supports, SACs can, in principle, achieve 100% atom utilization and dramatically reduce noble-metal usage [12,15]. However, the significance of SACs extends beyond maximizing atom efficiency. Reducing the metal size to the atomic limit fundamentally alters the electronic structure of active sites, which in turn governs their catalytic behavior. Specifically, the transition from nanoparticles to isolated atoms converts the continuous band structure of bulk metals into discrete energy levels, accompanied by pronounced quantum size effects. This transformation represents a shift from collective metallic behavior to localized electronic states that strongly interact with the support. As a result, catalytic properties become highly sensitive to the local coordination environment and to metal-support electronic coupling. This change directly influences key processes such as O₂ activation, VOC adsorption, and intermediate transformation. Therefore, atomic utilization, electronic-structure evolution, and catalytic performance are intrinsically linked in SAC systems.

Despite these advantages, deploying SACs under harsh VOC oxidation conditions—high temperature, the presence of water vapor, and complex feed compositions—remains challenging. The first issue is thermodynamic stability. Because surface free energy increases sharply at the atomic limit, isolated metal atoms exhibit a strong tendency to aggregate during thermal catalysis (especially under high-temperature oxidative atmospheres), readily sintering into nanoclusters or particles and thereby deactivating the catalyst [4,16,17]. Accordingly, a central design principle for SACs is to firmly anchor isolated atoms on supports via physical confinement and chemical bonding. A second challenge is electronic-state control. To stabilize isolated atoms, SACs commonly rely on coordination anchoring by surface heteroatoms (e.g., N, O, and S) or defect sites [16,18–22]. Such strong metal-support interactions (SMSI) are often accompanied by substantial charge transfer, rendering the metal center positively charged (oxidized) [23–25]. While higher oxidation states can favor adsorption of certain nucleophilic species, they may also diminish metallic character and abnormally increase the barriers of key elementary steps (e.g., C–H activation or O₂ dissociation) [25–27]. Campbell's concept of electronic metal-support interaction (EMSI) emphasizes that the support is not merely a dispersion medium but can profoundly modulate the chemistry of active sites via electronic perturbations (e.g., shifts in the *d*-band characteristics) [28]. Balancing the metal oxidation state and coordination environment is therefore a key challenge in SAC design.

For VOC catalytic oxidation—a complex reaction network involving multistep electron transfer and numerous intermediates—the structure–activity relationships of SACs are far more intricate than those of idealized model reactions. According to the bond-order conservation principle, adsorption energies of different intermediates at the same active site tend to follow linear scaling relationships (LSRs) [29]. This means that improving one elementary step may inadvertently worsen another. For SACs with only a single active center, it is often difficult to simultaneously optimize O₂ activation, VOC adsorption, and desorption of intermediates (e.g., CO and formate). These coupled constraints often limit low-temperature activity and kinetics [30–32]. In addition, existing studies frequently emphasize synthesis and characterization, whereas systematic and quantitative summaries linking atomic-scale structure to macroscopic catalytic performance remain insufficient.

In this context, this review aims to systematically summarize recent progress in single-atom catalysts for low-temperature catalytic oxidation of VOCs. It places particular emphasis on several key challenges that limit practical application, including atom instability, sluggish oxygen activation, deactivation by strongly adsorbed

intermediates, and poor resistance to poisoning under realistic conditions. Unlike previous reviews that mainly describe different catalyst systems, this work aims to build a clearer structure-activity-mechanism framework. Specifically, it links atomic-scale coordination environments and electronic structures with key catalytic functions such as oxygen activation, intermediate transformation, and resistance to deactivation. More importantly, recent literature suggests that the activity of SACs is governed by several strongly coupled factors rather than by the isolated metal center alone, including the coordination environment of the metal sites, the redox properties of the support, the strength of metal-support interactions, and the local microenvironment under realistic reaction conditions [33–36]. In this way, the review seeks to provide a mechanistic basis for understanding and overcoming these bottlenecks. We first discuss design principles, focusing on strategies to stabilize isolated atoms and tailor their electronic structures through strong metal-support interactions, coordination-environment engineering, and defect engineering of supports. These factors are closely related to suppressing atom migration and enhancing stability under thermal and hydrothermal conditions. We then analyze structure-activity relationships by combining operando/in situ characterization with theoretical calculations to elucidate microscopic mechanisms of oxygen activation and C–H bond cleavage on single-atom sites. It also highlights key descriptors and their trade-offs under linear scaling constraints, which are important for improving low-temperature O_2 activation and reducing site blocking by strongly adsorbed intermediates. In addition, particular attention is paid to recent studies showing that surface hydroxyls, hydrophilicity, and poisoning species such as H_2O and sulfur-containing compounds can critically alter reaction pathways, intermediate desorption, and long-term catalytic stability under realistic conditions [36,37]. Finally, we provide perspectives on key challenges for practical deployment, including water and sulfur tolerance, scalable synthesis at higher metal loadings, and multi-component cooperative catalysis, as well as catalyst performance under realistic high space velocity and complex feed conditions. This comprehensive overview is intended to deepen mechanistic understanding and to guide the rational development of efficient catalysts.

2. Design Principles and Stabilization Strategies

In SACs, the metal component is dispersed to the atomic limit, which maximizes atom utilization but also sharply increases surface free energy [5,8,15,32]. Under high-temperature VOC oxidation conditions, isolated metal atoms are thermodynamically unstable and tend to form nanoclusters via Ostwald ripening or particle migration and coalescence, leading to loss of active sites

[8,38,39]. Therefore, SAC design must address not only the construction of intrinsically active sites but also the realization of thermal and chemical stability of single atoms under harsh reaction environments.

2.1. Support Selection and SMSI

2.1.1. Reducible Oxide Supports

In heterogeneous catalysis, the support has traditionally been viewed as a passive scaffold for active components. However, when the supported metal is reduced to the single-atom regime, the role of the support changes fundamentally. For SACs, the support is not only a substrate for dispersing isolated atoms but also a ligand that dictates their electronic structure, geometric configuration, and reaction pathways [12,40]. In VOC catalytic oxidation, the support's acid-base properties, redox capability, and electronic coupling with the metal center directly impact low-temperature activity and resistance to poisoning. Reducible oxides (ROs) refer to oxides with multivalent cations and relatively mobile lattice oxygen, with typical examples including CeO_2 , TiO_2 , MnO_x , and Fe_2O_3 [9,41–43]. VOC oxidation on such supports often follows the Mars-van Krevelen (MvK) mechanism, where lattice oxygen directly participates in organic oxidation and gaseous oxygen subsequently replenishes oxygen vacancies. Introducing single-atom sites can markedly accelerate this redox cycle [29,44,45].

CeO_2 is among the most extensively studied supports for VOC catalytic oxidation. Its unique 4f electronic structure enables a low barrier for Ce^{3+}/Ce^{4+} interconversion, imparting excellent oxygen storage and release capacity (Oxygen Storage Capacity, OSC) [46–48]. When noble-metal single atoms (e.g., Pt and Pd) are supported on CeO_2 , pronounced electron transfer occurs across the interface. For instance, Pt/Pd single atoms tend to donate electrons to CeO_2 , forming positively charged $Pt^{\delta+}/Pd^{\delta+}$ species while reducing nearby Ce^{4+} to Ce^{3+} . This charge transfer not only stabilizes oxidized Pt species against over-oxidation or over-reduction, but also induces abundant interfacial oxygen vacancies (O_v) via the presence of Ce^{3+} at the interface (Figure 1a) [44,49–51]. These interfacial oxygen vacancies are key sites for O_2 activation, rapidly converting adsorbed O_2 into superoxide (O_2^-) or peroxide (O_2^{2-}) species to enable low-temperature VOC oxidation [52–54]. Nie et al. [44] reported that Pt single atoms preferentially substitute surface Ce sites, inducing adjacent Ce reduction (Ce^{4+} to Ce^{3+}) and O_v formation; this electronic perturbation significantly lowers the activation barrier of surface lattice oxygen, allowing lattice oxygen to participate in low-temperature CO and VOC oxidation. Duan et al. [25] dissected the electronic coupling between Ru single atoms and CeO_2 , showing that conventional preparation can produce overly oxidized Ru (Ru^{n+} , $n > 4$) that disfavors Cl^- desorption. By tailoring EMSI through controlled

thermal treatments, partial electron back-donation from the support to Ru can optimize the Ru electron density, enhancing chlorobenzene adsorption while promoting the Deacon process via interfacially activated lattice oxygen, thereby substantially improving chlorine tolerance. To address Ostwald-ripening-driven aggregation of single atoms at high temperature, the Datye group [16] discovered an atom-trapping mechanism on CeO₂: under high-temperature (>800 °C) oxidative conditions, surface reconstruction generates step sites that capture PtO₂ species, forming thermodynamically stable Pt–O–Ce bonds. This finding overturns the conventional view that high temperature necessarily accelerates sintering by leveraging CeO₂ surface reconstruction to suppress Pt agglomeration. Tang's group [55] proposed a dual nanospace confinement strategy using three-dimensionally ordered macroporous (3DOM) CeO₂ together with Ce-MOF-derived CeO₂ nanocages to precisely anchor Pt single atoms. Beyond physically blocking Pt migration and coalescence during high-temperature calcination, this architecture reconstructs the Pt coordination environment to create more active Pt–O₂ bonding motifs, significantly activating lattice oxygen adjacent to Pt and enhancing the redox capability. In benzene combustion, the catalyst delivered outstanding low-temperature performance with T₉₀ = 268 °C, 81 °C lower than that of a conventional impregnated Pt₁/CeO₂ catalyst.

TiO₂, a prototypical semiconductor oxide, is well known in photocatalysis and also performs strongly in thermal catalysis. In addition to abundant surface hydroxyls, different TiO₂ facets (e.g., anatase (101) and (001)) exhibit markedly different adsorption strengths and electronic modulation for single atoms. Theoretical calculations indicate that metal single atoms typically bind more strongly on high-energy TiO₂ facets (001) than on the thermodynamically stable (101) surface [56,57], enabling facet-dependent tuning of the coordination environment. Sun et al. [58] reported that a metastable Pt₁/TiO₂-MS can undergo a cycle of partial lattice-oxygen removal to generate vacancies followed by replenishment from external oxygen, which elongates Ti–O bonds, enhances oxygen mobility, lowers the H₂O dissociation barrier, and generates *OH in situ; isotope experiments further confirmed lattice-oxygen participation via an MvK pathway to promote C₆H₆ oxidation (T₉₀ ≈ 165 °C). Liu et al. [42] showed that Co single atoms doped into TiO₂ nanowires enable complete formaldehyde (HCHO) oxidation at room temperature, primarily by strengthening O₂ activation and generating surface active oxygen, thereby accelerating steps from adsorbed intermediates to deep oxidation. Wang et al. [59] found that, compared with TiO₂ (101), Pt₁/TiO₂(001) more readily forms and stabilizes undercoordinated, low-valent Pt^{δ+} under reaction atmospheres, while inducing coupled Ti³⁺–O_v defect motifs (Pt^{δ+}–O_v–Ti³⁺), enhancing interfacial acidity and O₂

activation (Figure 1b); consequently, Pt₁/TiO₂(001) exhibits much higher reactivity. Pt₁/TiO₂(001) shows onset activity at 350 °C and reaches 16.4% CH₄ conversion at 500 °C, whereas Pt₁/TiO₂(101) is nearly inactive in the same temperature window.

MnO_x, owing to its structural diversity and excellent low-temperature redox properties, is regarded as a promising alternative to noble-metal catalysts and an attractive support for anchoring single atoms. α-MnO₂ possesses a unique (2 × 2) tunnel structure that can accommodate and stabilize metal cations; for example, in α-MnO₂ (OMS-2), the tunnel architecture together with terminal-O coordination sites provides both geometric confinement and strong anchoring. Layered δ-MnO₂, in contrast, more readily forms defect sites via interlayer or cation vacancies [60,61]. Chen et al. [62] dispersed Ag single atoms on HMO surfaces, strengthening the involvement of both gaseous O₂ and lattice oxygen to facilitate deep oxidation of benzene; the same group further demonstrated that Na⁺ can also act as an effective isolated cationic site on MnO₂ for low-temperature HCHO removal, highlighting the structural tolerance and electronic buffering of MnO₂ toward isolated cations (Figure 1c) [63]. Hao et al. [43] anchored Pt single atoms on OMS-2 and achieved markedly enhanced benzene oxidation activity, indicating that the α-MnO₂ framework not only supplies anchoring motifs but also, via interfacial electronic coupling, strengthens single-atom control over oxygen-species formation and migration. Wang et al. [64] emphasized synergistic effects between Fe single atoms and defect-rich MnO₂ for molecular oxygen activation and reactive oxygen species (ROS) generation; embedding Cu single atoms into MnO₂ can form recyclable Cu^{II}/Cu^I and O_v-coupled motifs (Cu^I–O_v–Mn), maintaining O₂ activation and O–O bond scission capability [65].

2.1.2. Non-Reducible Oxide Supports

Unlike reducible oxides such as CeO₂ and TiO₂, nonreducible supports including Al₂O₃, SiO₂, and MgO generally do not derive their advantages in VOC catalytic oxidation from reversible lattice oxygen migration. Instead, their primary value lies in providing more robust anchoring sites and a tunable hydroxyl governed acid-base surface environment under high temperature and high humidity conditions, thereby stabilizing single atom species or highly dispersed metal entities and regulating reactant adsorption as well as the removal of key surface intermediates [66–68]. Because practical flue gas commonly contains water vapor together with sulfur and chlorine containing impurities, the chemical inertness and hydrothermal stability of nonreducible supports have made them increasingly important in application oriented VOC abatement studies, where they are particularly suitable as outer coating layers, inert frameworks, or isolation layers to achieve an integrated balance among

water tolerance, poisoning resistance, and sintering resistance [5,69–72].

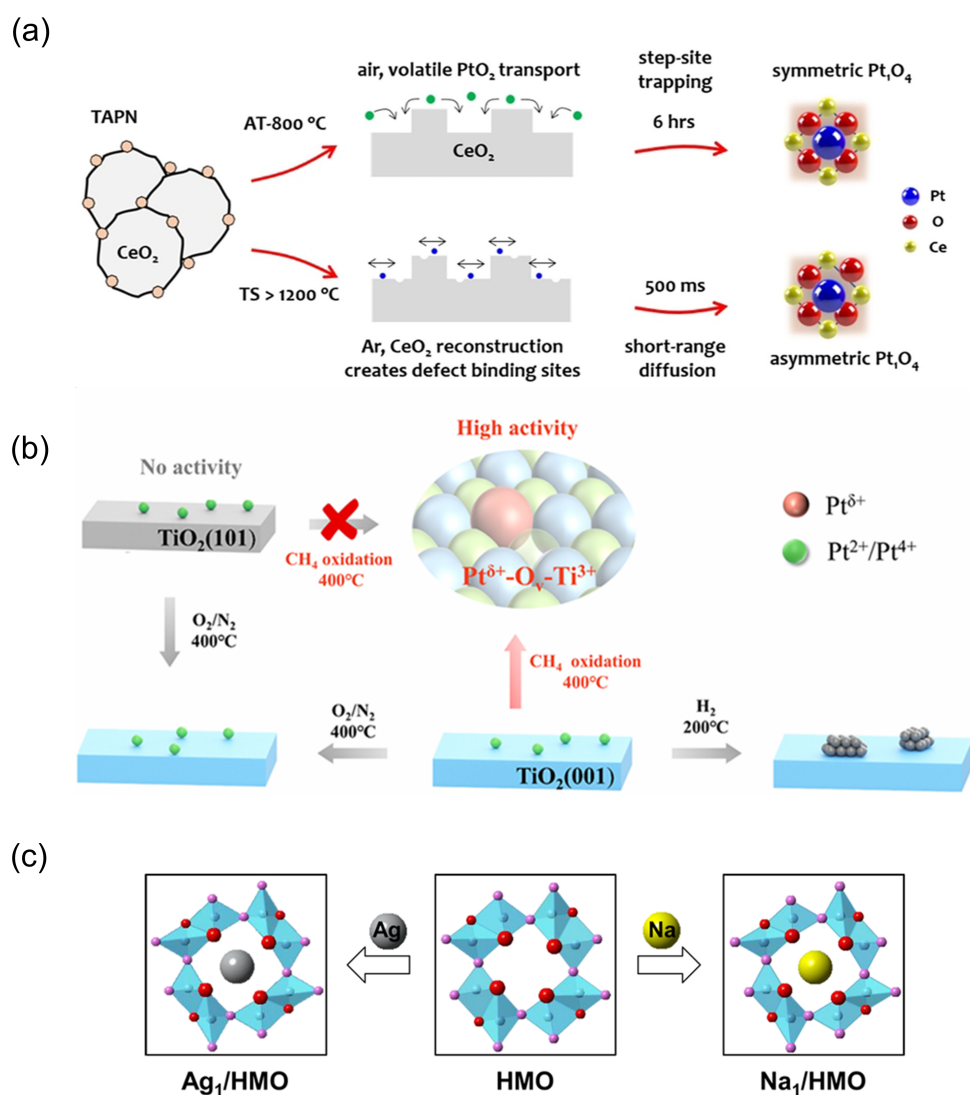


Figure 1. (a) Thermal-shock (TS) synthesis induces surface reconstruction of CeO_2 , resulting in the formation of an asymmetric (distorted square-planar) Pt_1O_4 coordination. Reprinted with permission from Ref. [50]; Copyright 2021 John Wiley and Sons. (b) Facet effects of TiO_2 stabilize undercoordinated Pt_1 species and couple with $\text{Ti}^{3+}-\text{O}_v$ defects. Reprinted with permission from Ref. [59]; Copyright 2025 American Chemical Society. (c) Local atomic environments of the catalytically active sites in HMO , Ag_1/HMO , and Na_1/HMO . Gray, red, pink and yellow balls represent Ag, O with sp^3 hybridization, O with sp^2 hybridization, and Na atoms, respectively. Blue octahedron is MnO_6 . Reprinted with permission from Ref. [63]; Copyright 2017 American Chemical Society.

Among nonreducible supports, alumina represented by $\gamma\text{-Al}_2\text{O}_3$ is the most extensively investigated, as its surface enriched hydroxyl species and Lewis acid sites can provide reliable anchoring environments for metal species. Existing studies have shown that the alumina phase and the nature of surface hydroxyls can markedly influence low temperature activity and operational stability [73]. Wang et al. [74] systematically compared HCHO oxidation over Pt supported on $\gamma\text{-Al}_2\text{O}_3$, $\theta\text{-Al}_2\text{O}_3$, and $\alpha\text{-Al}_2\text{O}_3$, and, by correlating hydroxyl differences with multiple characterization results, analyzed changes in Pt dispersion and key surface processes. The results demonstrate that nonreducible supports can modulate

reaction pathways through regulation of hydroxyl networks and local coordination environments, thereby enabling efficient low temperature catalytic oxidation without relying on support reducibility. SiO_2 , as a more chemically inert nonreducible support, exhibits relatively weak metal support interactions, yet it can serve as an inert supporting phase to improve dispersion stability and mitigate the adverse impact of deleterious components on active sites [67,70,75]. Yang et al. [70] constructed a core shell catalyst using ordered mesoporous Pt/SiO_2 as the core and an ultrathin metal oxide shell, and by comparing MgO , ZnO , and MnO_x shells, found that the MnO_x coated sample maintained higher

benzene oxidation activity and long term stability in the presence of SO₂. The MnO_x shell reduced SO₂ adsorption and coverage on metallic Pt active sites via interfacial electronic effects, while its redispersion behavior under reaction conditions helped sustain an effective interface and active oxidation processes, thereby delivering sulfur resistant and anti-poisoning performance. MgO plays a more clearly defined role in nonreducible support systems, mainly through regulation by basic surface sites and buffering against deactivation [69,73]. On the one hand, the basic MgO surface can alter the interfacial behavior of acidic byproducts and chlorine containing species during chlorinated VOC oxidation, enhancing their adsorption and migration and thus lowering the probability of strong interaction and coverage on active metal sites or reducible phases [76]. On the other hand, MgO is often used as an outer component or coating layer in composite supports to introduce a layered architecture and functional allocation, where the inner component provides oxygen supply and redox cycling while the outer layer suppresses poison deposition and improves SO₂ tolerance [70]. Pan et al. [69] developed a MnO_x@CeO₂@MgO core shell structure for the synergistic removal of NO_x and chlorobenzene, and the MgO outer layer contributed to improved sulfur resistance and helped maintain the supply of active oxygen under reaction conditions.

2.1.3. Stability Derived from SMSI

The concept of strong metal-support interaction (SMSI) was first introduced by Tauster et al. in 1978 to describe the pronounced suppression of H₂ and CO adsorption after high-temperature reduction of noble metals supported on reducible oxides (e.g., TiO₂) [77–79]. This adsorption suppression does not arise from sintering of active sites, but rather from migration of suboxide species formed under reducing conditions, which generates an encapsulating overlayer on the metal surface and is accompanied by interfacial charge redistribution and altered adsorption properties [80,81]. In nanoparticle systems, SMSI typically manifests as support species migrating onto the metal particle surface. When the active component is reduced to single atoms, such coverage phenomena can become even more pronounced. Under high-temperature reductive or oxidative pretreatments, reducible-oxide lattices can reconstruct; suboxide species (e.g., TiO_{2-x} and CeO_{2-x}) may migrate to cover metal single atoms or the single atoms may embed into lattice interstices [38,82]. This structural rearrangement forms a physical barrier that effectively limits surface diffusion and prevents aggregation under high-temperature reaction conditions [16]. Liu et al. [83] reported that RuO₂ aggregates on Fe-containing spinel supports can undergo reverse Ostwald ripening into Ru single atoms upon high-temperature treatment; the essence is strong covalent

coupling between Fe sites and RuO₂ subunits together with interfacial charge-density reorganization to form Ru–O–(Fe/M) anchoring structures, which substantially increase migration barriers and enable thermally stable dispersion. Yang et al. [84] further showed in Pt₁/CoFe₂O₄ that Pt single atoms are clamped by the support via Pt–O–Fe bridges and exhibit charge transfer from Pt to the support; even after water treatment introduces H⁺ to weaken charge transfer and tune the Pt electronic state, the bridged anchoring motif remains intact, thereby balancing tunable electronics with structural stability. Li et al. [85] revealed that Ru₁/CeO₂ single atoms can occupy near-lattice surface positions to form Ru₁O₅ units; strong Ru–O–Ce bonding, together with Ce⁴⁺/Ce³⁺ conversion and defect reconstruction, provides embedded stabilization that suppresses evolution toward Ru–O–Ru aggregation pathways. While conventional SMSI is often associated with reductive atmospheres, recent studies show that analogous strong interactions can also arise under oxidative atmospheres, termed oxidative SMSI (O-SMSI) [80,86]. Under oxygen-rich conditions, metal single atoms on certain supports (e.g., hydroxyapatite and ZnO) can form stronger coordination bonds with support oxygen and may even induce specific peroxide-like surface species [87]. For example, in Pt/ZnO, high-temperature oxidation drives Zn migration toward Pt to form Pt–Zn interfacial alloy motifs; this O-SMSI effect substantially enhances selectivity in propane dehydrogenation and oxidation [88–90].

2.2. Coordination Environment Tuning and Defect Engineering

The active site of a single-atom catalyst is essentially the metal center together with its first coordination shell (M–X_n, X = O/N/S). This shell defines the metal valence state, *d*-orbital occupancy, and local charge distribution, thereby governing O₂/H₂O activation modes and VOC adsorption geometries [18–20,32,91,92]. Recent literature has further emphasized that the coordination environment should not be regarded merely as a structural descriptor, but as a primary factor determining the electronic structure of SACs and their ability to activate oxygen. In particular, M–O_x, M–N_x, and defect-bound configurations can induce markedly different charge polarization, orbital hybridization, and adsorption geometries of O₂-derived intermediates [33,34,36]. When oxide-supported single atoms adopt an asymmetric first coordination shell, the metal electron density can be regulated via ligand-field effects and interfacial charge redistribution, thereby introducing directional polarization at the active center. For instance, heteroligand-coordinated environments (e.g., M–O₃X₁ where X = S/N/Cl, or M–N₃O₁-like motifs at oxide interfaces) can alter the preference between end-on and side-on O₂ adsorption configurations and modulate the O–O activation barrier. By tuning the stability of *O₂[–]/^{*}OOH-type

intermediates, such motifs reinforce the coupled sequence of adsorption, activation, and desorption steps [18,20,93]. For VOC oxidation, such polarization effects often manifest as enhanced Lewis acidity and faster oxygen cycling, facilitating polarization/activation of aromatic π bonds and accelerating C–H bond cleavage [45,91,94]. On reducible oxides, single atoms are commonly anchored as M–O_x or M–O–support bridges at oxygen vacancies, step sites, or lattice-substitution sites, where stability arises from high bonding energies and geometric confinement [16,95–97]. Undercoordinated sites more readily generate high-valent M^{δ+} and lower the O₂ activation barrier, but also rely more strongly on anchoring to suppress metal migration; overcoordinated motifs improve thermal stability but may restrict neighboring adsorption of O₂/H₂O and formation of active oxygen. For example, in Pt₁/CeO₂, electron transfer from Pt to CeO₂ renders Pt positively charged and induces Ce⁴⁺ to Ce³⁺, creating interfacial Ov that participate in the MvK cycle and promote formation of O₂[−]/O₂^{2−} species [16,32,95,98]. This phenomenon is directly reflected in the oxidation of polar VOCs such as HCHO at room temperature [32,42]. Embedding Pt single atoms into lattice-defect sites can markedly enhance structural stability under reaction atmospheres while lowering VOC reaction barriers by strengthening lattice-oxygen mobility [94]. Similar coordination/defect synergies have also been exploited in Ir₁/CeO₂, Pt₁/MgO, and Pt₁/MnO_x for toluene oxidation, consistently yielding higher rates of active-oxygen generation and faster deep oxidation [45,99–102].

Beyond isolated oxygen vacancies, defect engineering in SAC systems has evolved toward regulating defect identity, spatial distribution, and concentration [55,103,104]. In VOC oxidation, the most prevalent motifs are metal–vacancy ensembles (M–O_v pairs) and dopant-induced defect structures, which extend electronic perturbations beyond the immediate coordination shell and promote O₂ activation and oxygen transport [55,94]. For instance, defect-confined Pt single atoms exhibit enhanced low-temperature VOC oxidation due to the simultaneous stabilization of isolated sites and promotion of reactive oxygen species generation [94], while dual-confinement strategies that enrich lattice oxygen around Pt centers further strengthen oxygen participation and catalytic efficiency [55]. These findings highlight that defect functionality arises from its coupling with the local coordination environment rather than from isolated vacancy sites alone.

In addition to anionic defects such as oxygen vacancies, reduced cation centers (e.g., Ce³⁺, Mn³⁺) and aliovalent dopants further modulate the electronic structure of the metal-support interface and the stability of reaction intermediates [104,105]. From the perspective of structure-activity relationships, these effects are closely related to the redox properties of the support, because the ease of vacancy formation, oxygen migration, and lattice-oxygen replenishment determines whether

adsorbed oxygen or lattice oxygen dominates the oxidation cycle. Recent studies on SACs have therefore increasingly treated support redox chemistry not as a background property of the carrier, but as a decisive factor controlling oxygen mobility and the balance between adsorbed and lattice oxygen participation [35]. Strong metal-support interactions in Pt single-atom catalysts have been shown to facilitate lattice oxygen activation and enable complete oxidation of low-concentration VOCs [105], while vacancy-rich Ir₁/CeO₂ systems demonstrate that defect-induced chemisorbed oxygen and interfacial redox coupling are critical for both activity and water resistance [99]. Together, these studies indicate that cooperative interactions among defect types lower the formation energy of reactive oxygen species and accelerate redox cycling.

Catalytic performance is highly sensitive to defect concentration. Insufficient defect density limits O₂/H₂O activation, whereas excessive defects may induce aggregation, structural instability, or nonproductive adsorption [99,105]. Consequently, an optimal defect density window is required to balance activity and stability. Cheng et al. [106] showed that oxygen-vacancy concentration and catalytic activity do not follow a simple monotonic relationship, but instead depend on achieving a suitable balance between vacancy generation, oxygen mobility, and redox cycling. Accordingly, such control can be achieved through strategies including aliovalent doping, defect confinement, and interface engineering, which enable precise tuning of defect populations and their interaction with single-atom sites [105,106].

Axial coordination and the second coordination sphere (hydroxyls, hydrogen bonding, and proton-transfer channels) can switch the rate-determining step. In a suitable interfacial microenvironment, water can dissociate more readily near single-atom sites to generate *OH and promote efficient cycling between lattice oxygen (O_{latt}) and adsorbed oxygen (O_{ads}), thereby enhancing low-temperature activity [32,58]. For Pt₁/TiO₂-MS, a vacancy-formation/oxygen-replenishment cycle elongates Ti–O bonds, increases oxygen mobility, and lowers the H₂O dissociation barrier; the in situ generated *OH markedly promotes low-temperature benzene oxidation [58]. Single-atom Co/MnO₂ has likewise been shown to accelerate stepwise oxidation of aromatic VOCs by promoting water dissociation to activate lattice oxygen [107]. When a second metal atom or aliovalent dopant is introduced, local charge coupling and oxygen-transport channels can be reconstructed, making active oxygen more labile and facilitating desorption/conversion of reaction intermediates [95,108]. Facet-dependent studies on TiO₂ further indicate that undercoordinated Pt₁ on high-energy TiO₂(001) exhibits stronger anchoring and more pronounced electronic polarization, enabling retention of isolated-atom character and high C–H activation capability under reaction conditions [59]. These findings

also highlight the importance of the local microenvironment around SAC sites. Surface hydroxyl groups, hydrophilicity, and hydrogen-bonding networks can either promote hydroxyl-assisted intermediate conversion or induce competitive adsorption of H₂O, depending on the local coordination and electronic structure. Under realistic conditions, such microenvironmental effects become particularly important because water and poisoning species may alter reaction pathways, impede intermediate desorption, and ultimately determine catalyst durability [36,37].

Beyond the regulation of defect identity and concentration, recent studies have further highlighted the dynamic and cooperative nature of defect-coordination coupling in SAC systems. In particular, it has been shown that composite defect environments, such as coupled oxygen vacancies and reduced cation centers, can dynamically participate in oxygen activation and redox cycling rather than acting as static anchoring sites. For example, recent studies demonstrate that interfacial oxygen vacancies can facilitate the formation and stabilization of superoxide and peroxide species, thereby lowering the barrier for O₂ activation and accelerating lattice oxygen replenishment cycles [109,110]. This further supports the view that the coordination environment of the metal center and the redox nature of the support should be considered together when evaluating SAC activity.

At the same time, defect-mediated electronic reconstruction at metal-support interfaces has been identified as a key factor governing catalytic performance under realistic conditions, especially in the presence of water and poisoning species. Recent reports show that optimized defect configurations can not only enhance oxygen mobility but also suppress competitive adsorption of H₂O and chlorine-containing intermediates, thereby improving catalyst durability [111,112]. Similarly, sulfur-containing species may poison the active interface by blocking oxygen activation sites or perturbing interfacial charge transfer, underscoring that resistance to poisoning is intimately associated with both the local electronic structure and the surrounding microenvironment. These findings suggest that defect engineering in SACs should be viewed as a dynamic, multi-parameter regulation strategy involving defect type, distribution, interfacial coupling, and microenvironmental regulation, rather than a simple increase in defect density.

3. From Geometric Structure to Electronic States

For conventional nanoparticle catalysts, multiple types of sites (steps, edges, and terraces) coexist on the surface, so the observed performance reflects a superposition of contributions from different sites, making it difficult to establish quantitative correlations between structural and activity/selectivity. In contrast, SACs

provide a clearer structural motif for resolving reaction pathways and rate-controlling steps at the atomic scale, because their active units are approximately single geometric configurations with isolated metal centers. For low-temperature VOC oxidation, this advantage is especially important because catalytic performance is controlled not by one isolated elementary step alone, but by the coupled balance among O₂ activation, VOC adsorption, intermediate conversion, product desorption, and active-site regeneration. Unlike the continuous band structure of bulk or nanometals, single atoms dispersed on supports and coupled via coordination and charge transfer exhibit markedly altered valence states, *d*-orbital occupancies, and local densities of states, often approaching discrete energy-level distributions [113–116]. Therefore, systematically clarifying how coordination number and coordinating-atom identity (geometric environment) and how metal-support charge transfer and orbital hybridization (electronic interactions) affect adsorption geometries, key transition-state barriers, and product desorption is central to explaining the activity enhancement and selectivity differences of SACs in low-temperature VOC oxidation. In Sections 3.1 and 3.2, a limited number of simpler reactions, such as CO oxidation or propane dehydrogenation, are discussed only as probe reactions to isolate general electronic and interfacial principles that are difficult to resolve directly in complex VOC reaction networks. They are not reviewed in parallel with VOC oxidation.

3.1. Geometric Configuration and Discrete Energy Levels

The most intuitive hallmark of SACs is the geometric isolation of their active centers. This isolation is not merely physical dispersion; it is accompanied by a discontinuous transition in physicochemical properties. This section discusses how energy-level discretization and local coordination geometry determine catalytic performance, with emphasis on their relevance to oxygen activation and intermediate conversion in VOC oxidation.

3.1.1. Physical Origin: From Continuous Bands to Discrete Energy Levels

On bulk metals or nanoparticles, metal-metal interactions lead to an approximately continuous band structure, and the distribution of states near the Fermi level can be described by classical band theory and concepts such as the *d*-band center [117]. When the metal size shrinks to the single-atom limit, M–M bonds are broken and electron localization is strongly enhanced, and the originally continuous *d*-band transforms into discrete molecular-orbital energy levels, rendering classical adsorption-activation models based on continuous bands inapplicable [118,119]. Kraushofer and Parkinson [118] emphasized that the real electronic structure of a single-atom site strongly depends on the

anchoring motif and the type of support defect. In the model system of Au single atoms on TiO₂(110), Au introduces spatially localized metal-induced gap states (MIGS) near the Fermi level, located below EF, which directly affect interfacial charge-transfer processes. Di Liberto et al. [120] noted that computational models for single-atom systems must explicitly account for local coordination and electron localization; otherwise, the key mechanism—coupling between discrete levels and reactant orbitals—cannot be properly captured. This discretization is not merely conceptual; it fundamentally changes adsorption geometries and activation kinetics. When electronic-structure reconstruction enables resonant hybridization between reactant frontier orbitals and specific localized states of the metal center, efficient charge transfer becomes concentrated through a small number of levels, leading to higher intrinsic activation efficiency [23,97,121]. Liu and Huang [122] compared O₂ activation on Pt single atoms and Pt₄ clusters supported on graphene, showing that Pt single atoms can promote O₂ activation via enhanced charge redistribution and electronic polarization. Such polarization effects are closely tied to anchoring groups and local charge states; pyridinic-N doping in graphene causes Pt to accumulate more positively polarized charge, shifting Pt *d*-character closer to the Fermi level and enhancing O₂ activation. Similarly, Tsounis et al. [123] modeled Pt single atoms anchored at graphene edges and showed that edge states provide highly localized density of states near EF that can be coupled with Pt 5d states. When Pt resides at a graphene step edge, its 5d-local DOS overlaps strongly with neighboring carbon orbitals, forming Pt- π hybridization distinct from that on basal-plane coordination sites (Figure 2a–c). Although these are probe systems, the implication for VOC oxidation is direct: isolated sites with localized frontier states can activate O₂ more efficiently than larger metallic ensembles, which is essential for sustaining low-temperature VOC oxidation.

3.1.2. Local Coordination Geometry

In the absence of M–M bonds, the thermodynamic stability of single-atom centers relies entirely on coordination bonds (M–L bonds) with surface atoms of the support [14,124,125]. Local coordination geometry—including ligand identity, coordination number (CN), bond length, and spatial symmetry—directly dictates ligand-field splitting and orbital-occupancy patterns of the metal center, thereby determining *d*-electron configuration, spin state, and reactivity [124,126,127]. Coordination number is a primary descriptor of SAC geometry and of the ‘optimal coordination’ for a given reaction [125]. Low coordination numbers (CN < 4) correspond to coordinatively unsaturated sites (CUS). Geometrically, low-CN sites are more open and impose less steric hindrance, enabling larger VOC molecules such as

toluene and chlorobenzene to approach the metal center and adopt favorable adsorption geometries [128,129]. Electronically, low coordination weakens metal–ligand bonding and reduces ligand-field stabilization energy (LFSE), often raising frontier-orbital energies toward the Fermi level [129,130]. Such high-lying *d* states more readily back-donate into antibonding orbitals of reactants, strengthening substrate activation [131,132]. Liu et al. [133] showed that coordination regulation of single Co atoms in Co–N/C catalysts strongly affected room-temperature HCHO oxidation, and that the more unsaturated Co sites generated at higher pyrolysis temperature were associated with markedly enhanced formaldehyde conversion. Wang et al. [134] demonstrated that lowering the N coordination number around Co from 4 to 2 enhances intrinsic catalytic activity because the low-coordination Co–N₂ motif provides more unoccupied 3d orbitals and more readily activates reactants (Figure 2d). This example is directly relevant to VOC oxidation because it shows that coordination unsaturation is not only a structural feature but also a kinetic handle for promoting O₂ activation and intermediate conversion under low-temperature conditions. Conversely, high coordination such as square-planar or octahedral environments, provides stronger thermodynamic stability and suppresses migration and aggregation under high-temperature VOC oxidation [124,135]. For example, Pt₁/Fe₂O₃ forms an octahedral Pt–O₆ coordination environment that sacrifices some intrinsic activity but confers exceptional anti-sintering stability, while the deficiency in adsorption-driven activation can be compensated by lattice-oxygen transport via an MvK mechanism [14].

Beyond coordination number, the spatial symmetry of the coordination environment determines the specific form of *d*-orbital splitting [126,127]. In canonical M–N–C catalysts, the metal atom typically occupies a defect site in the graphene plane to form a planar M–N₄ motif [136]. This configuration often drives the *d*_{*x*²–*y*²} orbital to higher energy due to in-plane head-on repulsion [113,137], whereas the *d*_{*z*²} orbital extends along the *z* direction and is more sensitive to out-of-plane displacement (Δz) and axial perturbations, frequently serving as the key channel for σ coupling and electron exchange with axial ligands [113]. Accordingly, during O₂ adsorption and activation, interactions between the metal *d*_{*z*²} orbital and O₂ frontier orbitals are often considered the dominant factor governing axial ligand binding and activation [138–140]. If large-radius heteroatoms are introduced or asymmetric defects are constructed, coordination asymmetry can induce geometric strain that shifts the metal center from a purely in-plane motif toward an out-of-plane configuration with axial-coordination participation, thereby creating single-atom sites that more readily activate substrates [20,141]. This effect is illustrated by Li’s asymmetric Cu–S₁N₃ motif [20]. Relative to symmetric

planar M-N₄ sites, the asymmetric motif shifts adsorbed intermediates away from a strict top configuration, introducing additional π interactions between O p orbitals and Cu d orbitals, and cooperatively leveraging $d_{x^2-y^2}$ orbitals, and tunes binding strength and reactivity through orbital redistribution (Figure 2e–j).

Although this is discussed as a probe example, its relevance to VOC oxidation is clear: coordination asymmetry provides a practical route to tune how

isolated sites bind and transform oxygen-containing intermediates, which is directly related to the conversion of formate-, benzoate-, or carbonate-like species during low-temperature VOC oxidation. Overall, although some of the above insights are derived from model systems, their implications for VOC oxidation are direct, because similar local electronic effects govern O₂ activation, C–H bond cleavage, and the stabilization or removal of oxygenated intermediates.

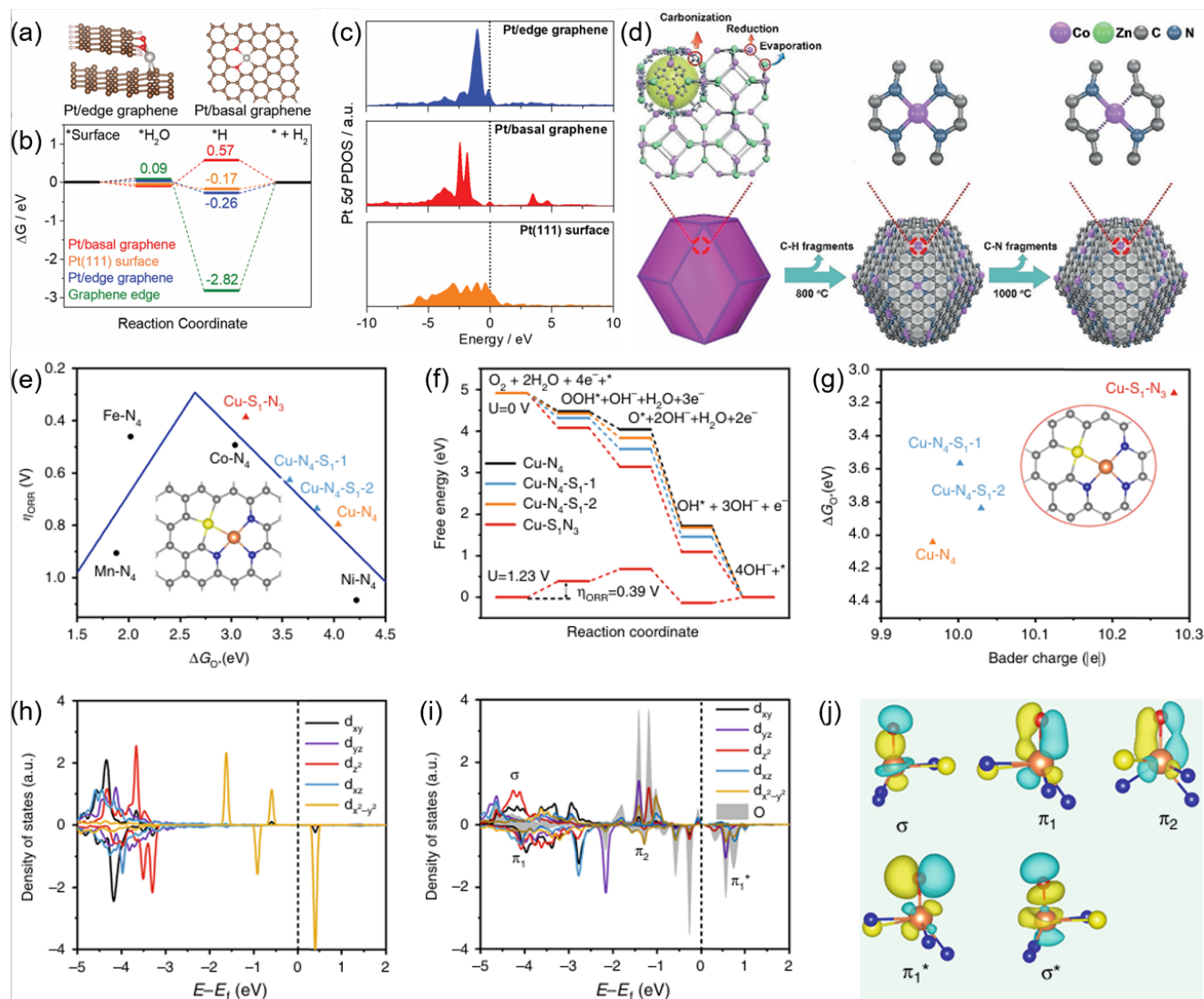


Figure 2. (a) Schematic illustration of a Pt single atom anchored at graphene edge versus basal-plane sites. (b) Comparison of free-energy changes (ΔG) for key reaction intermediates on different Pt configurations. (c) Pt 5d projected density of states (PDOS) for Pt/edge graphene, Pt/basal graphene, and a Pt(111) surface. Reprinted from Ref. [123]. (d) Schematic of site construction and coordination-environment evolution, including carbonization/reduction and the transformation between C–H and C–N fragments. Reprinted with permission from Ref. [134]; Copyright 2018 John Wiley and Sons. (e) Activity volcano plot using ΔG_{OH^*} as a descriptor, comparing the catalytic performance of various M-N_x sites and Cu-S₁N₃ (inset: representative asymmetric Cu coordination structure). (f) Free-energy reaction pathways on Cu sites with different coordination motifs (e.g., Cu-N₄ and Cu-N₄-S₁). (g) Correlation between ΔG_{OH^*} and Bader charge, together with representative site structures. (h) Orbital-resolved density of states of the d orbitals for representative sites. (i) Density-of-states variations associated with orbital redistribution and bonding interactions upon adsorption. (j) Spatial distributions of molecular orbitals relevant to key adsorbed intermediates. Gray, blue, orange and yellow balls denote C, N, Cu and S atoms, respectively. Reprinted from Ref. [20].

3.2. Electronic Structure and Electronic Metal-Support Interaction (EMSI)

At the single-atom scale, the physical boundary between metal and support becomes blurred: wavefunction overlap at the quantum-mechanical level merges the two into an integrated entity with distinct electronic characteristics. Understanding these electronic interactions—especially electronic metal-support interaction (EMSI)—is essential for elucidating how SACs break traditional scaling relationships and achieve high activity at low temperatures in VOC oxidation. This section analyzes the electronic origin of intrinsic activity from three angles: charge-transfer mechanisms, microscopic regulation within the *d*-band framework, and the coupling among spin state and orbital hybridization. Recent studies further indicate that metal-support interactions not only stabilize isolated atoms against migration and aggregation, but also regulate the binding strength of oxygenated intermediates and thus the balance between activation and turnover. In this sense, EMSI should be regarded as a central factor linking coordination environment, support redox behavior, and catalytic performance [33,35,36]. Where direct VOC evidence remains scarce, selected probe reactions are cited only to clarify the underlying electronic principle.

3.2.1. Charge-Transfer as the Origin of Reactive Electronic States

Charge transfer is the most direct manifestation of EMSI and plays a central role in defining the electronic state of single-atom sites. On reducible oxides such as CeO₂ and TiO₂, metal centers at single-atom sites commonly exhibit nonzero charge states ($M^{\delta+}/M^{\delta-}$), arising from interfacial charge redistribution rather than the near-zero valence typical of bulk metals or large particles [118,142–144]. This redistribution is governed by Fermi-level equilibration, work-function differences, and the participation of defects or localized electronic levels, and it can change with local coordination, oxygen-vacancy concentration, and adsorbates [28,144,145]. Therefore, under gaseous-O₂ supply conditions relevant to low-temperature VOC oxidation, the metal Bader charge or instantaneous oxidation state is a more informative reaction descriptor, because it can be correlated with O₂ adsorption geometries, activation depth, and the formation or regeneration of reactive oxygen species (O₂[−]/O₂^{2−}/O[•]).

Representative studies on Pt/CeO₂ systems have shown that interfacial charge redistribution stabilizes cationic Pt species while simultaneously generating Ce³⁺ and oxygen vacancies, thereby facilitating O₂ adsorption and activation [143,146,147]. For example, Daelman et al. [143] demonstrated that coulombic stabilization at the Pt–O–Ce interface can largely compensate the energetic penalty of Pt ionization, enabling stable Pt^{δ+} species. More specifically, the covalent contribution of the two Pt–O bonds is −1.93 eV, ionizing Pt to Pt⁺ costs 8.96 eV, and coulombic stabilization between interfacial Pt^{δ+}–O^{2−} and Ce–O ion pairs reach 9.73 eV, making the Pt⁰–to–Pt⁺ process only slightly endothermic. This result shows that the oxidation state of a single atom is a dynamic interfacial property rather than a fixed label. For VOC oxidation, the implication is direct: descriptors that link charge state to oxygen-species populations under reaction conditions are more meaningful than ex situ oxidation-state assignments alone. The same point is reinforced by the TiO₂ example in Figure 3a,b. Hoang et al. [148] reported that Pt atoms preferentially anchor at defect sites, with vacancy-bound configurations being ~2.3 eV more stable than regular lattice substitution. The coexistence of Pt⁴⁺/Pt²⁺ states, together with coordination flexibility, enables distinct reaction pathways: a low-barrier Eley-Rideal route (~0.2 eV) versus a significantly higher-barrier Langmuir-Hinshelwood pathway (~1.8 eV). Although this is a probe-reaction system, it is directly relevant to VOC oxidation because defect anchoring on TiO₂-like supports can simultaneously stabilize isolated Pt atoms and reshape the energetics of O₂ activation and interfacial oxidation steps.

Charge-transfer control of O₂ activation is also evident in Cu/CeO₂ and Au/CeO₂ systems. Kang et al. [149] showed that interfacial [Cu(I)O₂]₃[−] sites can form with pronounced charge redistribution, and that the deep O–O activation step proceeds with a barrier of 1.41 eV accompanied by a large change in adsorbate charge. Wang et al. [31] further showed that in Au/CeO₂ the Au Bader charge can oscillate from +0.40|e| to −0.56|e| during the reaction cycle, while O₂ binds strongly at defect sites and the effective redox barrier decreases to 0.65 eV. These results indicate that the interfacial charge state is a key descriptor governing oxygen activation and redox kinetics in single-atom catalysis. For low-temperature VOC oxidation, this is crucial because catalytic turnover depends on the continuous generation and replenishment of reactive oxygen species under fluctuating reaction environments.

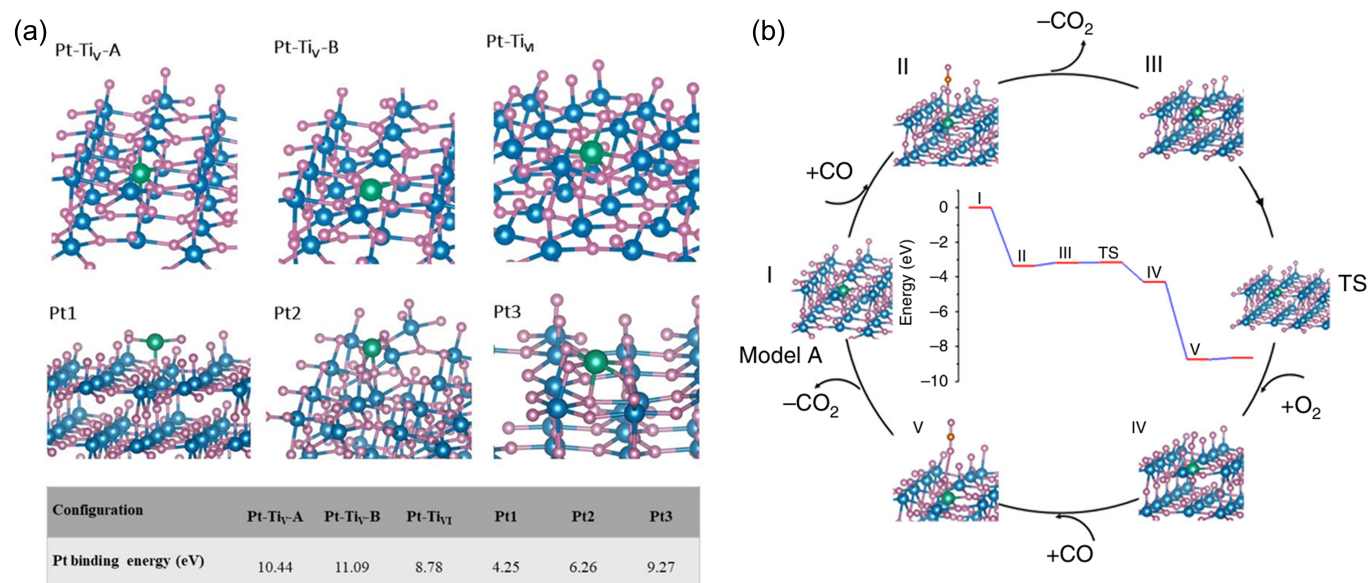


Figure 3. (a) Comparison of defect-anchoring sites and coordination configurations of Pt on TiO₂. (b) Reaction barriers for the CO oxidation cycle (Model A) on TiO₂. Adapted from Ref. [148].

3.2.2. *d*-Band-Center Theory and the Microscopic Essence of EMSI

Different from the classical SMSI picture that emphasizes encapsulation of active sites by suboxide overlayers, Campbell introduced the EMSI concept to describe intrinsic electronic interactions at metal-support interfaces, focusing on electronic perturbations, charge transfer, and energy-level hybridization upon contact [28]. The physical essence of EMSI is an electron-reconstruction process driven by equilibration of interfacial electronic chemical potentials. This includes not only substantial electron gain or loss between support and metal, but also redistribution and distortion of energy-level distributions induced by strong orbital interactions, ultimately reshaping the effective density of states near the Fermi level [150–152]. Within the adsorption-activation paradigm of heterogeneous catalysis, Nørskov's *d*-band model provides a useful starting point for correlating *d*-state energetics with adsorption strength. However, for SACs, *d*-states are often highly discrete and strongly hybridized with the first coordination shell and support defect states. As a result, EMSI in VOC oxidation should not be simplified to a single rigid shift of ϵ_d ; rather, it should be understood as a coordination- and support-dependent redistribution of spectral weight near the frontier orbitals that control O₂ activation, hydrocarbon adsorption, and intermediate removal. This broader view is especially important because low-temperature VOC oxidation is limited not by one adsorption event alone but

by the coupled balance among O₂ activation, VOC adsorption, and the removal of strongly bound oxygenated intermediates [128,144,153,154]. Charge redistribution also establishes interfacial dipoles and strong local electric fields. Quantitative analyses of vibrational Stark shifts using operando surface-enhanced infrared spectroscopy suggest field strengths on the order of 10⁹ V·m⁻¹, which are sufficient to substantially alter vibrational frequencies and adsorption geometries of polar adsorbates, providing spectroscopic evidence and physical mechanisms for oriented adsorption, bond polarization, and barrier lowering in polar-VOC reactions [150,155]. In a hemilabile model of Cu₁/CeO₂(111), Chen et al. [156] showed that the site can reversibly switch between open and closed coordination states, with corresponding changes in catalyst deformation energy, Cu *d*-state distribution, CO binding strength, and the energetics of CO–O₂ co-adsorption and O₂ dissociation (Figure 4). The open state provides stronger interaction with intermediates and a higher density of states near the Fermi level, whereas the closed state weakens product binding and facilitates turnover. Although Figure 4 is based on a probe-reaction framework, the mechanistic relevance to VOC oxidation is strong: low-temperature VOC oxidation also requires sufficiently strong activation of O₂ and the substrate, but sufficiently weak binding of oxygenated intermediates to prevent site blocking. In this sense, reversible coordination flexibility offers a concrete way to understand how SACs may partially resolve the strong-activation and weak-desorption trade-off in VOC oxidation.

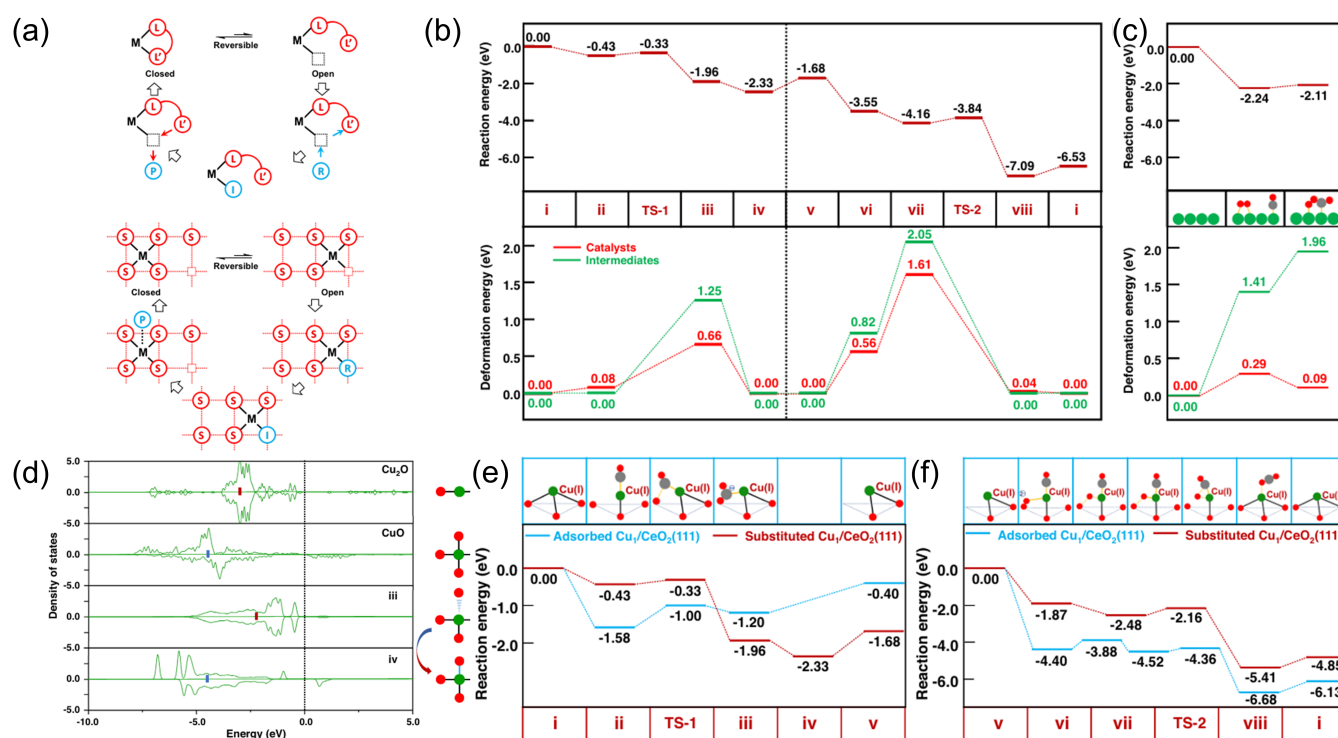


Figure 4. (a) Schematic of reversible open and closed coordination at the hemilabile Cu₁/CeO₂(111) site. (b) Reaction energetics of the CO oxidation pathway and catalyst deformation energy (ΔE_{def}). (c) Changes in reaction energy and ΔE_{def} between the open and closed states. (d) Comparison of Cu *d*-state density of states (d-DOS). (e) Comparison of CO binding strength between adsorbed-type Cu₁/CeO₂(111) and substituted-type sites. (f) Energetics of CO–O₂ co-adsorption and O₂ dissociation. Red, gray, and green circles denote O, C, and Cu atoms, respectively. Reprinted from Ref. [156].

3.2.3. Orbital Hybridization, Local Electric Fields and Spin-State Coupling

From a microscopic electronic-structure perspective, EMSI in SACs is better described as a density-of-states reconstruction rather than a simple rigid shift of ϵ_d [157,158]. After hybridization between discrete *d* orbitals of isolated metal atoms and the valence band or defect states of reducible oxides, metal *d* states can evolve from sharp atomic-like levels into broadened resonances, accompanied by coordination-dependent changes in electron distribution and spin polarization [28,153,159–162].

Within a Newns–Anderson picture, coupling between adsorbate frontier orbitals, such as O₂ π^* , and metal *d* or defect states yields bonding and antibonding resonances; π^* occupancy is jointly determined by the population of support electronic states and symmetry matching [149,157,160–162]. Therefore, charge density and spin density together determine the π^* filling threshold and the interconversion among reactive oxygen species (O₂[−]/O₂^{2−}/O*) [28,143,163]. Daelman et al. [143] used DFT and BOMD simulations to show that interfacial lattice distortions can shift oxygen-derived hybrid states to lower energy and promote charge transfer from Ce 4*f* states toward the central Pt site, highlighting the coupling between lattice dynamics and interfacial electronic structure.

Moreover, interfacial charge redistribution establishes local electric fields that polarize adsorbates [164], which thereby weakens key bonds (e.g., α -C–H and C–Cl) and thus enables lower-barrier bond scission. When combined with hemilability and reversible charge rearrangement, this coupling determines whether strong adsorption can be decoupled from catalyst poisoning [155,165–167]. This is particularly evident in the dynamic single-atom mechanism on Au/CeO₂: AIMD/NEB calculations by Wang et al. [31] show transient formation of Au⁺–CO and an increase in work function *W* from 4.8 to 5.1 eV; upon CO₂ desorption and Au occupation of oxygen vacancies, the Au Bader charge can decrease from +0.40 to −0.56, indicating that two electrons are transferred from CeO₂ and temporarily stored on the single atom. Subsequently, gaseous O₂ fills the vacancy with binding energy up to −1.51 eV to form peroxide O₂^{2−}, and the barrier for CO reaction with O₂^{2−} decreases to ~0.65 eV—charge redistribution and local electric fields jointly compress the oxygen-cycle bottleneck into the kinetics of single-atom detachment and reinsertion. Zhang et al. [168] reported that, after steam treatment, Pd₁/CeO₂ achieves complete HCHO conversion at about 30 °C (*r* = 100 $\mu\text{mol}\cdot\text{g}_{\text{Pd}}^{-1}\cdot\text{s}^{-1}$, E_a = 15.5 kJ·mol^{−1}). The underlying origin is steam-induced cooperative migration of Pd and CeO₂ to form a Ce₂O₃–Pd reverse interface, and orbital hybridization between Pd *d* states and defect/polaron-related states alters electron transfer. Pd₁ binding energies on CeO₂(111)

terraces/steps are $-2.15/-3.77$ eV with migration barriers of $0.14/1.45$ eV, while H_2O dissociation barriers are only $0.14/0.04$ eV, indicating that steam can trigger coordination opening/closing and defect reconstruction at low energetic cost (Figure 5). This example directly demonstrates that the electronic principles discussed above—orbital hybridization, local-field effects, and dynamic interfacial restructuring—are not confined to model reactions, but can govern catalytic

performance in practical low-temperature VOC oxidation. Overall, EMSI should therefore be viewed as a dynamic electronic coupling process in which charge transfer, electronic-structure reconstruction, and orbital hybridization collectively determine oxygen activation, intermediate conversion, and catalytic turnover in single-atom VOC oxidation.

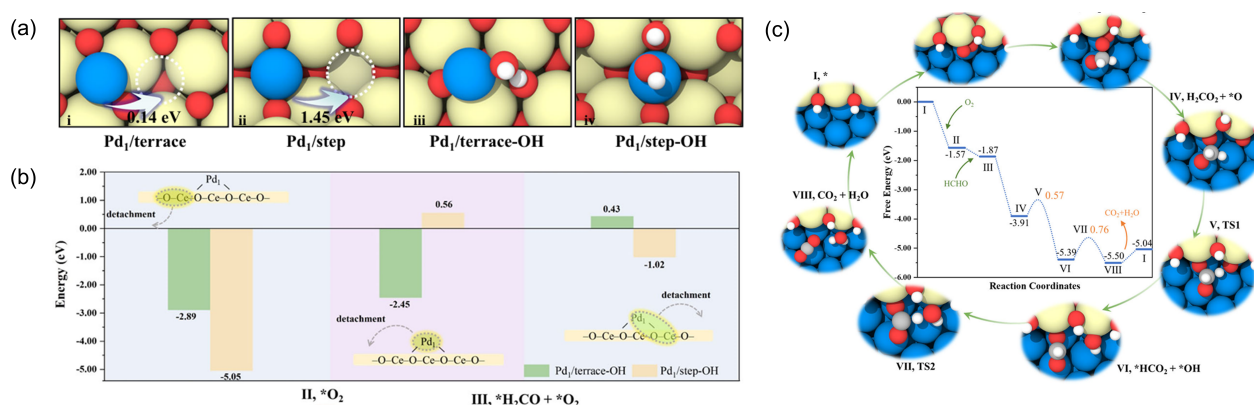


Figure 5. (a) Comparison of stable configurations and migration barriers of Pd₁ on CeO₂ terraces/steps and on hydroxylated surfaces. (b) Binding stability of Pd₁ at terrace/step sites and the associated detachment tendency. (c) Key intermediates and reaction barriers for HCHO oxidation at the Ce₂O₃–Pd reverse interface. Yellow, red, gray, white, and blue circles denote Ce, O, C, H and Pd atoms, respectively. Reprinted from Ref. [168].

3.3. Adsorption Energy Scaling Relationships

3.3.1. Bond-Order Conservation and the Sabatier Principle

The Sabatier principle states that catalytic rates are maximized when adsorption and desorption are balanced. If adsorption of a key intermediate is too weak, reactants cannot be effectively activated; if adsorption is too strong, desorption or subsequent conversion of intermediates and product precursors becomes sluggish and occupies active sites, thereby reducing the turnover frequency [169–171]. Quantitatively, this concept is often reflected by a volcano-type dependence of catalytic activity on adsorption free energy (or adsorption energy) [169]. In studies of VOC catalytic oxidation, density functional theory (DFT) and microkinetic modeling commonly treat the adsorption energies and reaction energetics of oxygenated intermediates on metal sites (e.g., O*, OH*, OOH*) and carbon-containing adsorbates (e.g., alkoxy/acyl species, surface formate/acetate) as key thermodynamic parameters. These quantities are used to link O₂ activation, C–H/C–C bond cleavage, and rate-controlling steps along the deep-oxidation network, thereby rationalizing or predicting activity trends [42,45,172]. For example, Ding et al. [173] combined DFT and microkinetics to analyze A-site regulation of La–Mn perovskites, showing that A-site tuning shifts the balance point between adsorption strength and reaction progression and consequently alters the relative rates of DOM formation, formate accumulation, and CO₂ production. This work exemplifies a typical strategy that optimizes the adsorption strength of oxygen-

containing species on the same class of surface sites. When oxygen-supply capability is enhanced to lower barriers associated with O₂ activation, the stability and coverage of OH-related species often increase simultaneously, which amplifies kinetic limitations associated with subsequent surface transformation and desorption. As a result, the system exhibits a classical Sabatier trade-off rather than a substantive break from linear scaling constraints. Zhang et al. [32] further demonstrated for single-atom Pt₁/CeO₂ that steam treatment or co-feeding water can establish a hydroxyl cycle, lower the barrier for formate removal, and promote the continuous conversion of DOM to formate and its subsequent deep oxidation, thereby maintaining O₂ activation capability while alleviating kinetic limitations induced by formate coverage. In steam-treated Pd₁/CeO₂, cooperative Pd–Ce migration generates a reverse interface, such that O₂ activation and deep-oxidation steps are distributed across distinct interfacial sites; this weakens the linear coupling of oxygenated-species binding strengths that typically holds on a single site and enables ultra-low-temperature HCHO oxidation [168]. In aromatic oxidation, oxygen vacancies in single-atom Pt/MgO enhance O₂ activation and increase the formation of reactive oxygen species; under humid conditions, the surface more readily generates *OH and radical-type active oxygen. Consequently, the kinetics shift from being governed solely by the binding strength of oxygenated intermediates to being jointly influenced by H₂O dissociation and hydroxyl regeneration. The resulting rate enhancement primarily arises because H₂O participation

introduces additional pathways for active-oxygen formation and conversion, reshaping the steady-state balance. Similarly, for single-atom Fe catalysts, the ability to sustain low-temperature HCHO removal under humid feeds is attributed to a hydroxyl cycle that accelerates downstream conversion of key oxygenated intermediates, thereby mitigating site-coverage effects associated with stabilized *OH [174].

Within the framework of linear scaling relations, when different intermediates bond to transition-metal surfaces through the same binding atom, their adsorption energies or adsorption free energies are often approximately linearly correlated. This correlation can be rationalized by bond-order conservation arguments and by the Newns–Anderson picture, in which hybridization between adsorbate frontier orbitals and metal *d* states leads to level renormalization and changes in bonding/antibonding occupation [175–178]. For VOC oxidation, a broadly relevant limitation originates from strong correlations among oxygenated intermediates. Thus, when alloying or support-induced electronic effects are used to lower the barrier for O₂ activation, *OH is frequently stabilized simultaneously and its site coverage increases, which in turn amplifies kinetic limitations associated with intermediate desorption and subsequent surface transformation [175,179]. For instance, A-site tuning of La–Mn perovskites adjusts the stability of oxygenated species on the same class of sites and moves the system toward an optimal adsorption regime, yet ultimately remains constrained by *OH-stabilization-induced site coverage and by limitations in formate removal [173]. In room-temperature HCHO oxidation over Pt₁/CeO₂, the water-mediated hydroxyl cycle partially weakens the dependence of formate removal on the binding strength of oxygenated species; even when OH species are relatively stable, improved hydroxyl regeneration and interfacial cooperation can reduce coverage effects and increase the steady-state reaction rate [32]. Overall, merely shifting key adsorption free energies toward the volcano optimum through electronic-structure tuning on a single site is often still limited by strong correlations among oxygenated intermediates, making further activity gains difficult [29,180,181]. More sustainable performance improvements typically rely on functional site partitioning, interfacial reconstruction, or microenvironment engineering, such that O₂ activation and deep-oxidation steps occur in different local environments, thereby relaxing the hard constraints imposed by strong correlations on the minimum achievable barriers and optimal free-energy allocation [182–185].

3.3.2. Single-Site Limitations of Single-Atom Catalysts

Compared with metal nanoparticles that provide multiple types of sites (steps, edges, terraces), the geometric isolation and site uniformity of SACs compress essentially all elementary steps of a multistep reaction onto

one metal atom, making competitive adsorption and site blockage more likely [118,186]. In such multistep reactions, the adsorption energies of key oxygenated intermediates (e.g., O*, *OH, *OOH) are often coupled through near-linear scaling relations on a given class of sites [177,186,187]. For low-temperature deep VOC oxidation, activating inert C–H or O=O bonds often require a more electrophilic or Lewis-acidic metal center to increase the probability of initial adsorption and activation; however, this simultaneously favors accumulation of strongly adsorbed oxygenated intermediates (carbonates, formates, carboxylates) and produced H₂O on the same site, leading to blockage and low-temperature deactivation [118,172,188].

An effective strategy to mitigate the intrinsic limitations of a single active site is to introduce a neighboring second center that can share functions such as O₂ activation, lattice-oxygen supply, and intermediate conversion [189,190]. Dual-atom catalysts (DACs) refer to catalysts in which two adjacent isolated metal sites, or two chemically distinct but neighboring active centers, jointly participate in the reaction [189,191]. Strictly speaking, they do not fall within the conventional definition of single-atom catalysis, because the active center is no longer a single isolated metal atom [190,191]. Nevertheless, introducing DAC or dual-site motifs is highly meaningful, because they represent a systematic extension motivated by the single-site limitations of SACs [192,193]. In particular, when catalytic functions are spatially partitioned between two coupled centers, DACs can, to some extent, relax the linear-correlation constraints that arise when multiple intermediates must bind to the same site, and reduce the risk that strongly adsorbed intermediates block the catalytic cycle [192,194,195]. Recent DAC studies and reviews have further emphasized that adjacent dual active sites can provide synergistic interactions, more flexible adsorption geometries, and cooperative reaction pathways, thereby optimizing adsorption/desorption energetics and, in some cases, partially breaking traditional scaling relationships. This emerging interest is not limited to one reaction family, but has been broadly discussed in recent DAC literature as a general route to lower activation barriers and improve both activity and selectivity in complex multistep reactions [196–199].

Taking a Pt–O–Ni bridged center as an example, Xu et al. [200] constructed a Pt–O–Ni bridged dual site on Pt₁Ni₁/TiO₂-NW. EXAFS and DFT + U verified the structural robustness of the bridged motif and showed that this dual site simultaneously lowers the barrier for benzene C–H activation while markedly enhancing O₂ adsorption/activation on the Ni side, thereby accelerating key steps for deep oxidation from phenolate toward benzoquinone (Figure 6). This result illustrates one of the central advantages of DACs over SACs: O₂ activation and hydrocarbon activation no longer need to be fully optimized on the same isolated site, but can be distributed across adjacent, electronically coupled centers. Ma et al. [41]

reported that a Pt–Co cooperative dual site in Pt₁Co₁/CeO₂ strengthens interfacial charge transfer and tunes metal valence states to promote cooperative O₂ activation. As a result, benzene binds more favorably on the dual site, and O₂ dissociation and sustained generation of active O* species are facilitated, enabling a more efficient deep-oxidation pathway. This type of heteronuclear dual-site configuration is particularly important because it expands the electronic design space beyond SACs: the two neighboring atoms need not play identical roles, and asymmetric charge distribution or orbital hybridization can be exploited to better match the distinct requirements of O₂ activation, VOC adsorption, and intermediate conversion. Chu et al. [108] emphasized in Pd₁V₁/CeO₂ that dual sites can regulate lattice-oxygen mobility and metal redox properties. By balancing the Pd/V redox character between overly active and overly inert regimes, the catalyst achieves optimized Pd/V redox behavior, enabling simultaneous toluene oxidation and NO_x conversion over a broad temperature range (90% conversion of NO_x and toluene at 238 °C and 230 °C, respectively, with an effective window >150 °C). This example suggests that DACs may outperform SACs particularly under conditions where the reaction requires simultaneous control of several coupled

processes, such as oxygen activation, redox cycling, and intermediate removal, which are difficult to optimize on one isolated center. Under photothermal coupling, Zhang et al. [201] proposed that Pt–Cu dual-atom pairs can promote intermediate activation in single-atom-based systems, making it easier to surmount key barriers during VOC oxidation under photothermal conditions and thereby improving turnover efficiency. More generally, DACs are expected to be especially advantageous over SACs when: (i) strong adsorption of intermediates causes site blocking on single isolated centers; (ii) O₂ activation and VOC activation require different local electronic environments; or (iii) multi-step oxidation pathways benefit from spatially adjacent but electronically coupled active sites. Under these conditions, DACs can retain much of the structural precision of SACs while introducing a level of cooperative reactivity that is inaccessible to strictly isolated sites. At the same time, this advantage is not unconditional: if the two metal centers are too strongly coupled, the system may evolve toward cluster-like behavior; if they are too far apart, the cooperative effect is weakened. Therefore, the superior performance of DACs depends critically on controlled inter-site distance, electronic coupling strength, and coordination environment [197,198].

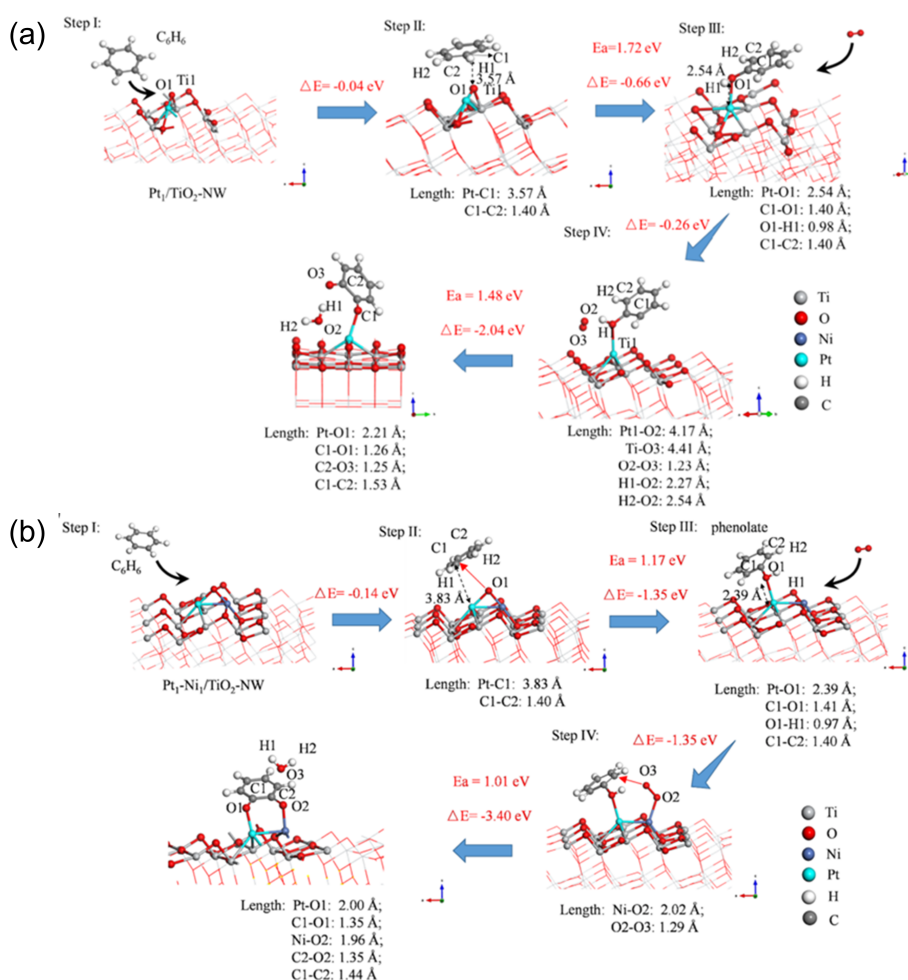


Figure 6. (a,b) Reaction pathway on Pt₁/TiO₂-NW and Pt₁-Ni₁/TiO₂-NW with the corresponding ΔE and E_a . Reprinted with permission from Ref. [200]; Copyright 2024 Elsevier.

4. In-Depth Mechanistic Analysis

Guided by the electronic-structure descriptors and scaling considerations discussed in Chapter 3, this chapter provides an in-depth mechanistic analysis of surface reactions. In heterogeneous catalysis, a deep mechanistic understanding of surface reactions is the foundation for rational catalyst design. For VOC catalytic oxidation, the reaction network is intrinsically complex, involving multielectron transfer, evolution of multiple intermediates, and coupling across multiphase interfaces. The emergence of single-atom catalysts, with isolated and uniform active sites, provides an ideal model system for interrogating such complexity at the atomic/molecular scale. Compared with conventional nanoparticle catalysts, the quantum size effects and metal-support electronic coupling of SACs profoundly alter adsorption geometries and activation barriers of reactants—especially O_2 and VOC molecules—thereby giving rise to distinct reaction pathways.

4.1. Oxygen Activation Pathways

4.1.1. Mars-van Krevelen (MvK) Mechanism: Lattice-Oxygen-Driven Redox Cycling

The MvK mechanism describes oxidation as a redox cycle in which support lattice oxygen participates directly: after interfacial activation, reactants consume lattice oxygen to generate oxygen vacancies, and gaseous O_2 subsequently reoxidizes the defect sites to refill vacancies and restore the lattice [202]. On reducible oxides such as CeO_2 , MnO_x , and Fe_2O_3 , low-temperature activity is often governed by interfacial lattice-oxygen mobility and the reoxidation rate of oxygen vacancies under reaction conditions, rather than solely by adsorbed oxygen coverage or total oxygen content [145,203,204]. From the perspectives of defect thermodynamics and diffusion kinetics, the oxygen-vacancy formation energy and oxygen-migration barrier jointly determine the kinetics of lattice-oxygen extraction and replenishment; thus, lowering the vacancy formation energy and/or enhancing oxygen mobility generally corresponds to faster oxygen cycling and lower reaction temperatures [204–206]. Single-atom motifs on reducible oxides (M_1 -O-support) can modify local charge distribution and bond strength, thereby influencing both the barrier for lattice-oxygen participation and the kinetics of defect reoxidation [49,207,208]. Using atom-trapped Pd_1/CeO_2 as an example, Zhang et al. [168] showed that the untreated sample is nearly inactive for HCHO oxidation at 30 °C, whereas steam treatment enables 100% conversion at 30 °C with a much lower apparent activation energy (15.5 kJ mol⁻¹). The O_2 reaction order reflects differences in O_2 activation; Pd/CeO_2 -AT is unable to effectively activate gaseous oxygen at low temperature and thus exhibits MvK behavior, where lattice oxygen serves as the active oxygen for HCHO oxidation and is subsequently replenished

slowly by gaseous oxygen. Free-energy calculations based on a Ce_2O_3 -Pd interfacial model indicate an O_2 adsorption free energy as low as -1.57 eV, and free-energy barriers of 0.57 and 0.76 eV for key H-transfer and final-state formation steps along the HCHO oxidation pathway. In Pt_1/CeO_2 , Wen et al. [209] combined ^{17}O solid-state NMR with DFT to identify a square-planar Pt_{LC} configuration embedded in the $CeO_2(111)$ surface formed via steam dispersion, using a high-coordination Pt_{HC} motif as reference. CO oxidation on Pt/CeO_2 typically follows an MvK route: adsorbed CO reacts with a neighboring bridged lattice oxygen to produce CO_2 and create an oxygen vacancy. DFT shows that Pt_{LC} has a CO adsorption energy of -2.09 eV and a barrier of only 0.10 eV for reaction with a neighboring bridged lattice oxygen, whereas Pt_{HC} binds CO more strongly (-2.75 eV) and requires a barrier of 1.10 eV to react with lattice oxygen.

4.1.2. Langmuir–Hinshelwood (L–H) Mechanism: Interfacial Attack by Adsorbed Oxygen Species

When lattice oxygen cannot migrate rapidly within the relevant temperature window—such as on inert supports (Al_2O_3 , SiO_2) or under low-temperature/high-GHSV conditions where vacancy refilling lags behind oxygen consumption—the Langmuir–Hinshelwood (L–H) mechanism typically dominates: both the organic substrate and gaseous O_2 (and its derivatives) participate as adsorbed species and undergo surface-coupled reactions en route to stepwise oxidation [210–212]. For SACs, the effectiveness of the L–H pathway often does not require complete O_2 dissociation on the metal site; rather, it hinges on stabilizing electrophilic molecular oxygen species (e.g., $*O_2^-$, $*O_2^{2-}$, $*OOH$) within an isolated coordination environment, and ensuring that these species are consumed and regenerated promptly after attacking C–H/C=C bonds or aromatic rings to avoid long-term site occupation [213–215]. Because geometric isolation limits bridging adsorption configurations and fast O–O scission pathways common on nanometal surfaces, SACs more often form terminal M–O–O motifs that retain the O–O bond, imparting higher electrophilic selectivity and helping lower the barrier for initial VOC conversion at low temperature [55,213].

Under L–H conditions, the rate limitation on SACs often arises from competitive adsorption and site saturation. For VOCs—especially aromatics and oxygenated VOCs—the substrate and O_2 must coadsorb and be activated at the same metal center, which can markedly reduce the surface coverage of O_2 (θ_{O_2}) [212,214,216]. Meanwhile, strongly adsorbed species generated during reaction, such as carbonates, carboxylates, and water, can accumulate on a single metal site and hinder rapid regeneration. In industrial hydrocarbon VOC oxidation systems exemplified by PdO/Al_2O_3 , such behavior has been systematically attributed to H_2O -induced accumulation of

surface hydroxyls and interfacial deactivation, requiring reduction/reoxidation protocols to restore the active phase [212,216]. Wang et al. [217] studied atomically dispersed Pt anchored on Ti-doped mesoporous silica SBA-15 for oxidation of benzene-series VOCs. By tracking intermediate evolution with in situ DRIFTS, they showed that aromatic substrates and gaseous O₂ (and derived adsorbed active oxygen species) co-participate in surface reactions consistent with an overall L–H pathway, and proposed sequential deep-oxidation routes for benzene and p-xylene (benzene → phenol → benzoquinone → maleic anhydride/acetic acid → CO₂ + H₂O; p-xylene → p-xylyl alcohol → p-xylyl aldehyde → terephthalic acid → maleic anhydride → CO₂ + H₂O), highlighting that adsorbed oxygen species, rather than rapid lattice-oxygen migration, drive surface coupling and consecutive oxidation. DFT yielded adsorption energies of $E_{adsC_6H_6} = -0.060$ eV, $E_{adsC_7H_8} = -0.066$ eV, and $E_{adsC_8H_{10}} = -0.073$ eV on Pt/Ti-SBA-15, indicating weak adsorption dominated by van der Waals interactions, with slightly stronger binding upon increasing methyl substitution. Zhang et al. [218] used in situ DRIFTS to determine that deep toluene oxidation on a confined PdAg@S-1 alloy site follows the L–H mechanism and emphasized that gaseous O₂, once adsorbed/activated on the alloy, directly participates as active oxygen species in surface oxidation (T₉₀ = 179 °C and complete conversion <180 °C). XPS further indicated electron transfer from Ag to Pd to form electron-enriched Pd sites, which is beneficial for coupling C–H activation with adsorption/activation of gaseous O₂.

4.1.3. Eley–Rideal (E–R) Mechanism: Direct Reaction between Gas-Phase Molecules and Adsorbed Surface Species

In addition to the MvK and L–H mechanisms, the Eley–Rideal (E–R) mechanism may also be involved in VOC oxidation over single-atom catalysts under some reaction conditions [219]. Unlike the L–H mechanism, which requires both reactants to be adsorbed on the surface, the E–R mechanism involves direct reaction between a gas-phase molecule and an adsorbed surface species [42]. This pathway may become relevant when co-adsorption is difficult because the number of available sites is limited, surface sites are occupied by H₂O or intermediates, or the lifetime of adsorbed species is short [41,55].

In SAC-catalyzed VOC oxidation, the reaction pathway is often affected by the balance between surface oxygen species and adsorbed VOC species [42,55]. When oxygen activation is slow, especially at low temperature, gas-phase O₂ may react directly with adsorbed intermediates on the surface [219]. In contrast, when reactive oxygen species are already present on the surface but VOC adsorption is weakened by water or by the isolated nature of the active sites, gas-phase VOC molecules may react directly with these pre-adsorbed

oxygen species [55]. Under such conditions, E–R-type steps may exist together with L–H steps [55,220]. Zhang et al. reported that Co single-atom catalysts showed excellent activity for room-temperature formaldehyde oxidation, and they linked this performance to efficient O₂ activation and fast conversion of surface intermediates [219]. Liu et al. [42] also found that Co single atoms on TiO₂ nanowires promoted the formation of superoxide species and lowered the barrier for intermediate conversion in HCHO oxidation. Chen et al. [220] showed by DFT that oxygen vacancies and surface hydroxyls on Pt₁/ZrO₂ can strengthen the co-adsorption and activation of HCHO and O₂, which further indicates that the local surface environment strongly affects how the oxidation pathway proceeds.

For aromatic VOCs, Ma et al. [221] reported that silica-assisted Pt₁/CeO₂ improved benzene oxidation under humid conditions by promoting H₂O and O₂ activation and by easing competitive adsorption of water on Pt sites. Han et al. [55] further showed that Pt single atoms with abundant lattice oxygen gave efficient VOC oxidation, again emphasizing the importance of rapid oxygen supply and oxygen transfer on the catalyst surface. Ma et al. [41] also prepared a Pt₁Co₁/CeO₂ bimetallic single-atom catalyst for benzene oxidation and found that the interaction between isolated Pt and Co sites improved both activity and stability. Likewise, Xu et al. [200] reported that a Pt₁–Ni₁/TiO₂ dual-single-atom catalyst showed enhanced benzene oxidation because the neighboring isolated metal atoms worked together to promote oxidation steps that are difficult on a single isolated site alone.

A similar view has also been suggested in toluene and chlorinated VOC oxidation. Wang et al. [99] reported that Ir₁/CeO₂ showed high activity, good stability, and strong water resistance for toluene oxidation, indicating that isolated metal sites on reducible oxides can maintain oxygen activation even when the surface environment is disturbed by reactants and water. Duan et al. [25] found that regulating the electronic metal-support interaction in Ru single-atom catalysts improved chlorobenzene oxidation by strengthening chlorobenzene and lattice-oxygen activation. Wu et al. [222] further showed that Ru single atoms supported on Sn-doped Silicalite-1 improved the removal of mixed VOCs by combining redox sites with acidic sites, which is important in feeds where adsorption competition is strong and the surface state changes continuously during reaction.

At present, however, direct experimental proof of the E–R mechanism in VOC oxidation over SACs is still limited [55,200]. Most available studies provide indirect support only, such as sustained activity under conditions that are not favorable for stable co-adsorption, rapid turnover of surface oxygen species or intermediates, and weaker dependence on VOC adsorption alone than expected for a pure L–H route [25,41]. Therefore, in this review, the E–R mechanism is better considered as a

possible supplementary pathway under specific conditions, rather than a generally dominant mechanism in all SAC-catalyzed VOC oxidation systems [99,220,222].

4.2. Case Studies of Oxidation Mechanisms for Representative Molecules

VOCs encompass alkanes, alkenes, aromatics, oxygenated derivatives (OVOCs), and chlorinated VOCs (CVOCs). Because functional groups differ, adsorption motifs, bond-cleavage sequences, and intermediate evolution on SAC surfaces also vary. This section focuses on four representative molecules—formaldehyde, light alkanes, benzene-series compounds, and chlorinated VOCs—to illustrate distinct mechanistic regimes in SAC-catalyzed oxidation.

This selection is based on their complementary molecular features and catalytic challenges: formaldehyde, as

a typical oxygenated VOC, highlights the critical role of surface hydroxyls and low-temperature reaction pathways; light alkanes represent saturated hydrocarbons with strong C–H bonds, emphasizing the difficulty of initial bond activation; benzene-series compounds exemplify π -conjugated systems with high thermodynamic stability, requiring effective adsorption and ring activation; and chlorinated VOCs introduce halogen-related effects, including catalyst poisoning and Cl-mediated reaction pathways.

Together, these model systems span key bond types (C=O, C–H, C=C, and C–Cl) and mechanistic constraints, enabling a unified analysis of how single-atom catalysts regulate oxygen activation, intermediate evolution, and resistance to deactivation across different VOC classes. Table 1 provides a comparative summary of representative SACs reported for VOC oxidation.

Table 1. Comparative summary of reported single-atom catalysts for VOC oxidation.

VOCs	Catalysts	Coordination Environment	Reaction Condition	Representative Activity Metric	Ref.
HCHO	Co ₁ /N–C	Co–N _x	50 ppm HCHO + 20% O ₂ + N ₂ , total flow rate of 100 mL·min ^{−1} ; RH ≈ 25%	complete conversion at 25 °C; HCHO conversion > 90% within 120 h	[219]
HCHO	Pt ₁ /CeO ₂ -S	Pt ²⁺ –O–Ce; Pt ²⁺ –O _{latt} H interfacial motifs with lattice hydroxyls adjacent to Pt	400 ppm HCHO + 20 vol% O ₂ + N ₂ , total flow rate of 100 mL·min ^{−1}	Complete removal at 288 K; 55% conversion over 60 h at RH = 25%	[32]
HCHO	Pd/CeO ₂ -AT-S	Ce ₂ O ₃ –Pd domain interface	400 ppm HCHO + 20 vol% O ₂ + N ₂ , total flow rate of 50 mL·min ^{−1}	Complete conversion at 30 °C; ~50% conversion at 0 °C; 92% conversion maintained for 7 h	[168]
C ₃ H ₈	Pt ₁ –Nb ₁ /ATO	Pt ₁ –O–Nb ₁	1% C ₃ H ₈ + 20% O ₂ + N ₂ , total flow rate of 20 mL·min ^{−1}	T ₅₀ = 140 °C T ₉₀ = 192 °C	[223]
CH ₄	Pt ₁ /TiO ₂ (001)	Pt ^{δ+} –O _v –Ti ³⁺	1% CH ₄ + 20 vol% O ₂ + N ₂ , total flow rate of 20 mL·min ^{−1}	16.4% conversion at 500 °C	[59]
CH ₄	Pd ₁ O ₄ Ce ₂ /CeO ₂	Pd–O ₄ –Ce ₂	1% CH ₄ with air balance, total flow rate of 20 mL·min ^{−1}	T ₅₀ = 439 °C	[224]
C ₆ H ₆	0.5 wt% Pt ₁ @CeO ₂	Pt–O–Ce	2000 ppm C ₆ H ₆ with air balance, total flow rate of 200 mL·min ^{−1}	T ₅₀ = 186 °C T ₉₀ = 212 °C	[94]
C ₆ H ₆	0.3 wt% Pt ₁ /CeO ₂ @SiO ₂ -4	Pt–O–Si	2000 ppm C ₆ H ₆ with air balance, total flow rate of 200 mL·min ^{−1}	T ₅₀ = 160 °C T ₉₀ = 190 °C	[221]
C ₆ H ₆	Pt ₁ /TiO ₂ -MS	Pt ₁ –O–Ti on metastable TiO ₂ with metastable lattice oxygen	1000 ppm C ₆ H ₆ + 20 vol% O ₂ + N ₂ space velocity (SV) of 30,000 mL/(g·h)	T ₉₀ = 175 °C	[58]
CB	Ru ₁ /CeO ₂	Ru ₁ –O ₃ sites on CeO ₂ (111)	1000 ppm CB + 5 vol% H ₂ O + air, total flow rate of 100 mL·min ^{−1}	rate 0.83 mmol·g ^{−1} ·h ^{−1} , TOF 8.07 h ^{−1} ; no Cl ₂ formation	[225]
CB	4 RuCeO ₂ -AA	Ru–O–Ce	500 ppm CB, total flow rate of 25 mL·min ^{−1}	T ₅₀ = 185 °C T ₉₀ = 215 °C	[226]
o-DCB	0.5 Ru ₁ /MnO _x	Ru–O–Mn	100 ppm o-DCB + 10% O ₂ + N ₂ , total flow rate of 60 cm ³ ·min ^{−1}	T ₅₀ = 142.9 °C T ₉₀ = 175.6 °C	[227]

4.2.1. HCHO Oxidation: Surface-Hydroxyl-Driven Metal-Support Synergy

Room-temperature formaldehyde oxidation differs in nature from high-temperature combustion of most VOCs: the steady-state rate is governed more strongly by the supply and regeneration of surface hydroxyls than by rapid oxygen incorporation driven by high-coverage atomic oxygen [32]. In SAC systems, geometric isolation diminishes the probability of multi-metal-site cooperative oxygen activation, making hydroxyl motifs near the single atom, defect-associated hydroxyls, and their coupling with lattice oxygen key determinants of light-off temperature and long-term stability [32]. Recent studies repeatedly show that low-temperature activity does not correlate simply with higher oxygen-vacancy concentration; instead, it correlates more consistently with structural features that maintain a high steady-state hydroxyl coverage and enable rapid replenishment under reaction conditions [228,229].

At the molecular level, effective activation at room temperature often manifests as a coupled process of carbonyl polarization and nucleophilic addition: the metal single-atom site provides polarized adsorption of the HCHO carbonyl, while support hydroxyls or defect-associated hydroxyls supply a nucleophilic attack pathway toward the carbonyl carbon [32,230]. Zhang et al. [219] reported Co₁/N-C that achieves complete HCHO oxidation at 25 °C, with a pseudo-first-order rate constant $k \approx 0.102 \text{ s}^{-1}$ and stable operation for ~120 h, demonstrating sustained turnover without noble metals. Isotope experiments and DFT identified formate decomposition as the rate-determining step (0.75 eV), attributing performance to electronic back-donation modulation of formate at Co-N_x sites and accelerated oxidative decomposition kinetics. Regarding construction and participation of hydroxyl motifs, Zhang et al. [32] created lattice hydroxyl sites (O_{latt}H) near Pt²⁺ via steam treatment; complete HCHO removal was achieved at 288 K with an apparent activation energy of $\sim 14 \pm 2 \text{ kJ} \cdot \text{mol}^{-1}$, indicating that the low-temperature barrier is controlled by hydroxyl-involved elementary steps rather than by adsorption alone. More importantly, operando spectra at 303 K showed that, for untreated samples under O₂, the bands of DOM and formate change little over time, whereas after steam treatment, DOM formation and subsequent formate oxidation exhibit clearer dynamic coupling, evidencing that O_{latt}H participates in a continuous sequence from HCHO to formate and onward to deep oxidation. This work also showed that higher relative humidity improves steady-state conversion and long-term stability, maintaining 55% conversion over 60 h at RH $\approx$ 100%. Steam-triggered dynamic restructuring can likewise create new low-temperature active motifs in other SAC

systems; for atom-trapped Pd₁/CeO₂, Zhang et al. [168] found that steam treatment induces cooperative metal/support migration to form a Ce₂O₃-Pd nanodomain interface, enabling complete conversion at 30 °C ($r \approx 100 \mu\text{mol} \cdot \text{g}_{\text{Pd}}^{-1} \cdot \text{s}^{-1}$) and ~50% conversion even at 0 °C. DFT indicated a Pd₁ migration barrier of 1.45 eV on step sites; after H₂O dissociation to form OH, the migration barrier drops to 0.51 eV, and H₂O dissociation barriers on CeO₂ terraces and steps are as low as 0.14 eV and 0.04 eV, respectively. The authors emphasized that the reverse interface formed under steam provides an interfacial structure more favorable for O₂ activation and deep oxidation of intermediates, delivering appreciable stability under humid conditions (92% conversion maintained for 7 h in 10% H₂O). Beyond steam treatment, directed regulation of alkali metals or support hydroxyls has also been used to simultaneously address single-atom anchoring and hydroxyl steady-state coverage. In Pt-Na/nano-Al₂O₃, Zhang et al. [230] achieved complete room-temperature HCHO oxidation at an ultralow Pt loading (0.05 wt%) and showed that Na converts terminal hydroxyls on nano-Al₂O₃ into Na-Al doubly bridged hydroxyls, which serve as anchoring sites for atomically dispersed Pt. Anchored Pt can activate O₂ and H₂O to regenerate bridged hydroxyls and promote rapid reaction between formate and surface hydroxyls to produce CO₂ and H₂O, mitigating low-temperature deactivation from formate coverage. In the non-noble-metal direction, site geometry and coordination can directly tune the barrier of formate removal. Liu et al. [42] proposed that Co single atoms doped into TiO₂ nanowires promote O₂ to O₂²⁻ conversion and lower the barrier from DOM to formate, yielding an overall activity 13.3 higher than TiO₂ P25 (Figure 7a,b). For Fe_{SA}-N₅-C, humidity can markedly enhance low-temperature removal efficiency, reaching 85.8% at 25 °C and 75% RH and delivering 1.6× activity enhancement under 10% humid conditions [231]. Promoter modulation can also accelerate formate removal and improve low-temperature activity by altering electron donation and oxygen migration. In Pd-Ba/TiO₂, Chen et al. [232] identified Ba as an electron donor that increases electron density at Pd and its interface, strengthening O₂ activation and increasing the migration rate of chemisorbed oxygen. This electronic effect fundamentally shifts the pathway from formate accumulation toward efficient formate conversion. On Pd/TiO₂ without promoter, oxidative dehydrogenation of HCOO* faces a relatively high barrier (0.65 eV), whereas Ba lowers it to 0.42 eV by optimizing the interfacial redox potential, accelerating direct oxidation of HCOO* to CO₂ and H₂O and preventing low-temperature accumulation (blockage), thereby accounting for the excellent room-temperature HCHO oxidation activity and long-term stability of Pd-Ba/TiO₂.

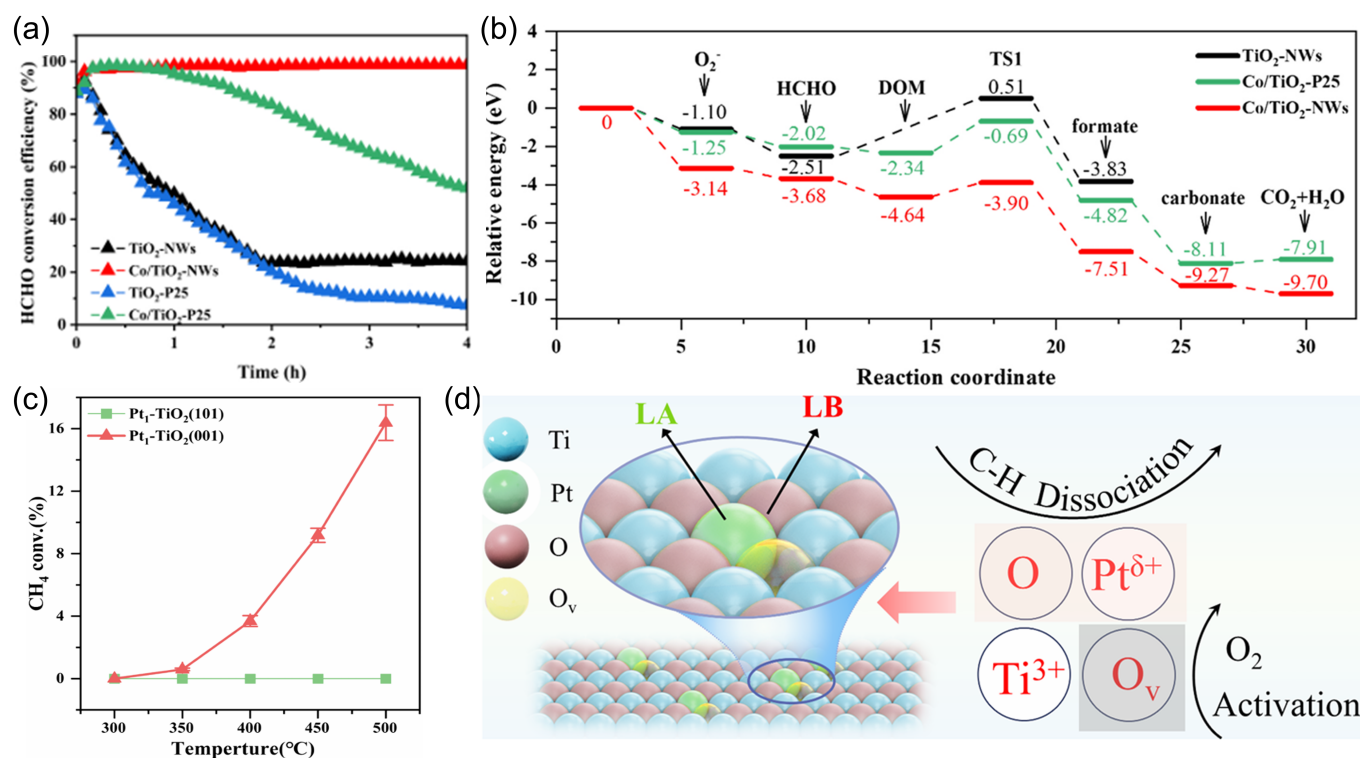


Figure 7. (a) Time-dependent HCHO conversion efficiency over different TiO₂-based catalysts. (b) DFT results for HCHO oxidation on different TiO₂-based catalysts. Reprinted with permission from Ref. [42]; Copyright 2024 Elsevier. (c) Catalytic activity of Pt₁-TiO₂. (d) Synergistic Lewis acid-base pairs of Pt^{δ+}-O_v-Ti³⁺ for enhanced methane oxidation. Reprinted with permission from Ref. [59]; Copyright 2025 American Chemical Society.

4.2.2. Short-Chain Alkane Oxidation: The First C–H Activation Step

Short-chain alkanes (CH₄–C₃H₈) possess nonpolar σ bonds, weak adsorption on oxide surfaces, and high sp³ C–H bond strengths. Their overall polarizability is low, and they lack lone pairs or π systems that could form strong, directional interactions with surfaces; as a result, they typically exhibit weak adsorption and difficult activation in the low-temperature regime [233]. Accordingly, both apparent kinetics and theoretical calculations widely identify the first C–H bond cleavage as the primary rate-controlling step [234–236]. This imposes two constraints on single-atom catalysts (SACs): on the one hand, the active center must effectively lower the barrier for the initial C–H scission; on the other hand, it must sustain a rapid catalytic cycle spanning oxygen activation, active-site regeneration, and intermediate desorption, so as to avoid competitive adsorption by stable surface species such as –OH, carbonates, and bicarbonates that can increase site coverage and induce low-temperature deactivation [212,235,237,238].

For SACs, the initial C–H scission can generally be classified into two limiting pathways: (i) interfacial heterolytic activation enabled by acid–base cooperativity, and (ii) radical-mediated homolytic activation [233,239–241]. In the heterolytic pathway, the isolated metal center acts as a Lewis-acid site, while adjacent support O₂⁻/OH⁻ species

or defect oxygen serve as Lewis/Brønsted-base sites. Together they form an interfacial acid–base pair that strongly polarizes the adsorbed C–H bond under geometric constraints, leading to separation of a proton and an alkyl fragment. In this process, H⁺ migrates to the basic oxygen site, whereas the alkyl moiety is stabilized at the metal center. This heterolytic route is often associated with reducible oxides, strongly polar M–O bonds, or interfacial structures exhibiting Lewis-acid/base-pair (or FLP-like) behavior on solid surfaces. Its advantage is that it can reduce the barrier of the first step at milder temperatures, thereby suppressing radical-chain side reactions [240,242,243]. In the homolytic pathway, radical-type interfacial oxygen species (e.g., O₂⁻/O[•], •OH, metal-oxygen radicals, or high-valent M=O species) abstract H[•] via hydrogen-atom transfer (HAT), cleaving the C–H bond to form an alkyl radical that subsequently undergoes consecutive oxidation [241,244]. This radical-mediated route is more likely to dominate at higher temperatures or on surfaces enriched with reactive oxygen species such as O₂⁻/O₂²⁻ and capable of fast redox cycling, and it is closely linked to a sustained supply of mobile lattice oxygen or highly reactive surface oxygen species [233,244]. Fang et al. [223] reported a current-assisted adjacent dual-atom Pt₁-Nb₁/ATO site for low-temperature propane combustion, achieving T₉₀ = 192 °C under current assistance (TOF@220 °C = 27.67 × 10⁻³ s⁻¹, E_a = 41.2 kJ·mol⁻¹). By deconvoluting thermal and non-

thermal contributions, they obtained an ECC of 74% and noted that noble-metal usage could be reduced by >80%. Wang et al. [59] found that the $\text{TiO}_2(001)$ facet can stabilize undercoordinated $\text{Pt}^{\delta+}$ species coupled with $\text{Ti}^{3+}\text{-O}_v$ motifs ($\text{Pt}^{\delta+}\text{-O}_v\text{-Ti}^{3+}$) under reaction conditions, whereas $\text{TiO}_2(101)$ tends to stabilize saturated $\text{Pt}\text{-O}$ coordination with limited activity. Such an undercoordinated, vacancy-coupled interfacial microenvironment can simultaneously promote C–H activation and oxygen cycling, leading to measurable CH_4 conversion and demonstrating that facet selection and defect coupling can shift the kinetic boundary of the first C–H step for the most inert alkane (Figure 7c,d). Tao et al. [224] reported a coordination-unsaturated single-atom Pd catalyst, $\text{Pd}_1\text{O}_4\text{Ce}_2/\text{CeO}_2$, constructed on CeO_2 via precursor pre-coordination, with the more saturated $\text{Pd}_1\text{O}_4\text{Ce}_3/\text{CeO}_2$ as a reference. In thermocatalytic complete oxidation of CH_4 , $\text{Pd}_1\text{O}_4\text{Ce}_2/\text{CeO}_2$ exhibits markedly enhanced low-temperature activity, with T_{50} lowered by 118 °C and an approximately eightfold increase in TOF at 400 °C. DFT and operando/in situ characterizations collectively indicate that the advantage originates from the coordination-unsaturated Pd single-atom site, which is more favorable for the first C–H scission of CH_4 and for reactive-oxygen supply, thereby accelerating the deep-oxidation process.

4.2.3. C_6H_6 Oxidation: Adsorption-Geometry Constraints, Ring-Opening Pathways, and Anti-Poisoning Mechanisms

Benzene, a prototypical aromatic hydrocarbon, possesses a highly stabilized π -conjugated system; thus, the initial activation step is not merely C–H cleavage but rather disruption of aromatic π -electron delocalization followed by ring opening [245–247]. On conventional metal nanoparticle surfaces (e.g., $\text{Pt}(111)$ or $\text{Pd}(111)$), benzene readily adopts a flat-lying, multi-point π -coordinated adsorption geometry. Although this can facilitate electron transfer and initial oxidation, it also increases surface coverage and polymerization probability, promoting formation of polycyclic aromatics/coke and causing site deactivation [248–250]. The geometric isolation and coordination constraints of SACs weaken such multi-point π adsorption; benzene is more likely to interact with the metal center via tilted η^1/η^2 configurations or a single-carbon end-on motif, reducing surface residence time and suppressing condensation—an important structural origin for the frequently observed improved coking resistance of SACs in aromatic oxidation [247,251–254].

Mechanistically, benzene is first converted into aromatic oxygenated intermediates such as phenolate and benzoquinone under the action of reactive oxygen species (electrophilic lattice oxygen O^- , superoxide O_2^- , hydroxyl-related oxygen, etc.). Subsequent C–C bond cleavage yields smaller oxygenated fragments

(maleate/acetate/alkoxide species), which are ultimately oxidized to CO_2 and H_2O . The most difficult requirement is to continuously supply sufficiently electrophilic oxygen species while preventing long-term coverage by strongly adsorbed carbonate/carboxylate species [245,255–257].

To address these challenges, several mechanistically guided routes have emerged in the past two years. The first route employs defect engineering on reducible oxides to confine and modify single atoms. Dong et al. [94] reported $\text{Pt}_1@\text{CeO}_2$ prepared by pyrolyzing an MOF precursor to precisely confine Pt single atoms at CeO_2 lattice defect sites. This catalyst exhibits outstanding low-temperature activity for deep benzene oxidation ($T_{90} = 212$ °C), far outperforming conventional impregnated nanocluster catalysts. In situ DRIFTS confirmed that benzene first chemisorbs at $\text{Pt}_1\text{-O-Ce}$ interfacial sites and rapidly evolves into oxygenated intermediates such as phenol and benzoquinone; these species are then oxidized by lattice oxygen (O_{latt}), generating oxygen vacancies. Bands of carboxylates and maleates show clearly reversible growth/decay with temperature and upon O_2 introduction. Lattice defect sites not only anchor Pt in a high-oxidation-state form ($\text{Pt}^{\delta+}$) via strong electronic interactions, but also markedly reduce the formation energy and migration barrier of neighboring oxygen atoms. Relative to pristine CeO_2 , introduction of Pt single atoms strengthens O_2 adsorption ($E_{\text{ads}} = -3.50$ eV) and significantly lowers the activation energy of the first C–H activation step, thereby alleviating the kinetic barrier for aromatic oxidation and ring opening. A second route uses dual-site division of labor to decouple adsorption energies and mitigate competitive adsorption. Hou et al. [258] reported $\text{Pd}_1\text{Co}_1/\text{Al}_2\text{O}_3$, where Co_1 preferentially governs formation and conversion of reactive oxygen species, whereas benzene preferentially adsorbs on Pd_1 , thereby reducing benzene–oxygen competition at a single metal center and avoiding single-site congestion. Notably, this catalyst remains active under sulfur-containing conditions, indicating that functional separation between oxygen-activation sites and aromatic-adsorption sites weakens sulfur poisoning. In $\text{Pt}_1\text{Co}_1/\text{CeO}_2$, Ma et al. [41] further showed that coexisting Pt and Co single atoms lower the benzene combustion temperature and improve water resistance: Pt promotes aromatic-ring activation and intermediate formation, while Co enhances reactive oxygen species and accelerates lattice-oxygen cycling, reducing the steady-state coverage and accumulation of carbonates and carboxylates. Water vapor can also play a critical role in benzene combustion. On the one hand, water competes for adsorption and increases hydroxyl coverage, weakening O_2 activation and aromatic adsorption; on the other hand, an appropriate amount of water can facilitate formation of -OH at defect sites and promote proton transfer, improving conversion of certain intermediates. Ma et al. [221] reported SiO_2 -assisted encapsulated Pt_1/CeO_2 ($\text{Pt}_1/\text{CeO}_2@\text{SiO}_2\text{-4}$) designed to

regulate interfacial H₂O behavior. Under 10 vol% H₂O, this catalyst still achieves T₉₀ ≈ 190 °C with long-term stability, substantially outperforming Pt₁/CeO₂. Structural characterization showed that the SiO₂ shell does not disrupt Pt single-atom dispersion: HAADF-STEM and EXAFS before and after reaction confirm the single-atom state, and CO-DRIFTS verify that Pt remains in a high oxidation state and is stably anchored on CeO₂. The key is that the Pt–O–Si interface reconstructs water-involved pathways: the SiO₂ layer weakens direct strong adsorption of H₂O at Pt sites without impeding O₂ diffusion to the interface. Water cooperatively promotes formation of *OOH-related active oxygen species, and *OOH acts as a new active intermediate that continuously drives low-temperature benzene oxidation.

4.2.4. CVOCs Oxidation: Deacon Reaction and Halide Tolerance

In studies of noble metal single atom catalysts for the catalytic oxidation of chlorinated volatile organic compounds CVOCs, atomically isolated metal centers enable an unambiguous molecular level correlation between structural variables and catalytic response, allowing halogen tolerance to be elevated from phenomenological observations to mechanistically testable structure-activity relationships [247,259]. Existing evidence indicates that the key structural determinants governing CVOc oxidation performance include the composition and dynamic reversibility of the first coordination shell around the metal center, the geometric constraint imposed by the anchoring site together with the resulting local electronic structure, and the spatial cooperativity between the single atom site and the oxygen supply function and acidity of the support [247]. These factors jointly regulate the adsorption strength and apparent residence time of chlorinated species and HCl in the vicinity of the active center, thereby affecting active site regeneration, the interfacial propensity for HCl oxidation to Cl₂ and the associated side reactions, which ultimately manifest in light off behavior, CO₂ selectivity, the distribution of polychlorinated by products, and long-term stability [259,260].

From the perspective of single atom coordination, the coordination environment of a single atom site can modulate competitive adsorption of chlorinated components on the metal center, thereby influencing the fraction of available active sites and the steady state turnover efficiency. Bi et al. [261] reported a chlorine coordinated Pd single atom catalyst Pd@ZrO₂. Operando DRIFTS showed that formation of Pd₁–Cl species suppresses the preferential adsorption of dichloromethane on Pd sites, allowing more sites to participate in adsorption activation and deep oxidation of toluene and its intermediates, while maintaining good stability and water tolerance in the presence of dichloromethane and water

vapor. This work indicates that reversible Cl coordination in the first coordination shell does not necessarily lead to irreversible deactivation. Instead, by decreasing the apparent occupancy of chlorinated species at the active center and accelerating site regeneration, it can enhance resistance to chlorinated co feeds (Figure 8).

In terms of anchoring site effects, the geometric constraint and local electronic structure of the anchoring site can simultaneously regulate substrate activation and the desorption form of chlorinated species, thereby affecting the interfacial route for HCl oxidation to Cl₂ and determining the formation of polychlorinated by products [247,260]. Wang et al. [225] reported a Ru₁/CeO₂ single atom catalyst for chlorobenzene oxidation. Under 1000 ppm chlorobenzene in air containing 5 vol% water vapor, the reaction rate reached 0.83 mmol g^{−1} h^{−1} and the TOF was 8.07 h^{−1} at 200 °C, with high mineralization selectivity and negligible Cl₂ formation. In this system, Ru single atoms preferentially anchor at the O₃ hollow site on CeO₂(111) and are more stable at an intermediate oxygen vacancy concentration. Their stability is higher than that at the O top site, as reflected by a decrease of formation energy from 5.78 eV to 3.83 eV. In this anchoring configuration, the Cl related steps exhibit higher dissociation energy, which lowers the probability of further HCl oxidation to Cl₂ and concurrently suppresses the stepwise accumulation of polychlorinated by products.

With respect to metal support redox coupling, the coupling between single atom sites and oxygen supplying supports determines how the oxygen supply function responds to changes in the extent of surface chlorine accumulation under chlorinated conditions, thereby influencing the synergy between activity and long-term stability under strongly chlorinating environments. Sun et al. [227] reported an atomically dispersed Ru₁/MnO_x catalyst for low temperature o dichlorobenzene oxidation. At a WHSV of 36,000 cm³ g^{−1} h^{−1}, it achieved T₅₀ of 157 °C and T₉₀ of 180.5 °C, and maintained close to 90% conversion during continuous operation at 240 °C for 700 min. These results suggest that the synergy between the single atom activation center and the continuous flux of reactive oxygen species supplied by the support helps sustain an effective redox cycle during progressive surface chlorine accumulation, thereby mitigating the rapid deactivation commonly observed in chlorinated systems.

Under multicomponent conditions, spatial cooperativity between a single atom oxidation center and acidic sites can enhance the formation and desorption of HCl after dechlorination and reduce the probability of chlorinated by product formation [259]. Wu et al. [222] constructed a Sn doped Silicalite-1 confined Ru single atom catalyst. By creating tightly coupled redox and acidic sites, it achieved T₉₀ of 287 °C for toluene oxidation and T₉₀ of 361 °C for dichloromethane oxidation, while remaining stable for 100 h at 380 °C and effectively suppressing toxic chlorinated by products. Acidic sites

promote C–Cl bond cleavage and facilitate HCl formation and desorption, whereas adjacent single atom oxidation centers accelerate deep oxidation of dechlorinated intermediates, thereby reducing chlorine accumulation on the surface.

In addition, defect engineering combined with a high density of single atom sites can increase the number of active centers and strengthen oxygen supply, but the practical benefit depends on whether defects can maintain a reversible oxygen cycle under chlorinated conditions rather than being preferentially chlorinated [259]. Wang et al. [226] used ascorbic acid to induce surface defects on CeO₂,

enabling high loading of atomically dispersed Ru for chlorobenzene catalytic combustion. The Ru loading reached 2.4 wt%, achieving 90% chlorobenzene conversion at about 210 °C and showing no obvious deactivation over 20 h. This study indicates that defects play dual roles as anchoring sites for single atoms and as sources of oxygen vacancies. Only when the defect type and distribution balance anchoring stability with reversible oxygen supply under chlorinated atmospheres can a high density of single atom sites translate into steady state performance advantages.

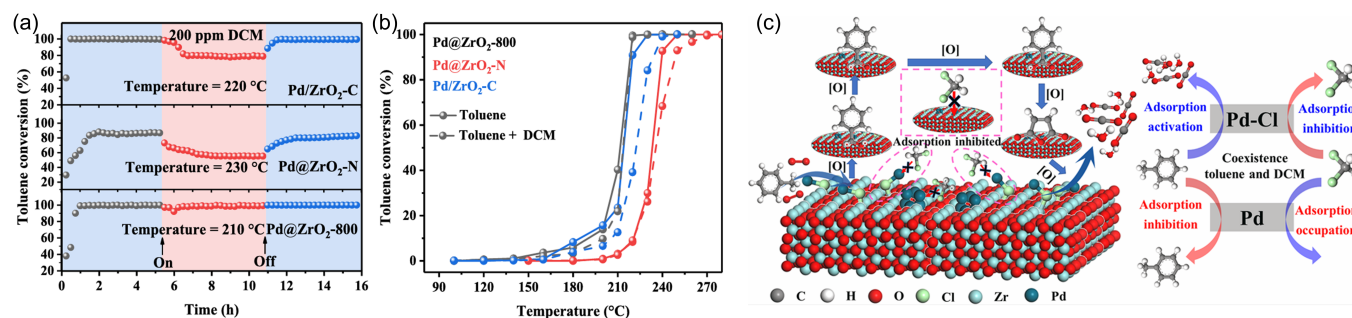


Figure 8. (a) Time-dependent toluene conversion with and without DCM over supported Pd catalysts. (b) Time-dependent toluene conversion with and without DCM over supported Pd catalysts. (c) Chlorine resistance mechanism of Pd@ZrO₂ catalysts with Pd₁-Cl species. Reprinted with permission from Ref. [261]; Copyright 2022 American Chemical Society.

5. Conclusions and Perspectives

5.1. Key Conclusions and Take-Home Messages

Single-atom catalysts (SACs) provide a powerful platform for low-temperature VOC oxidation by coupling atomic dispersion with tunable electronic structures. Beyond maximizing atom utilization, the defining feature of SACs lies in their ability to reconstruct oxygen activation pathways and reaction microenvironments through metal-support interfacial interactions.

From the collective studies reviewed here, several key take-home messages can be distilled:

- (1) Atomic dispersion alone is not sufficient; the catalytic performance of SACs is governed by interfacial electronic structure rather than simply isolated active sites. Coordination environment, charge state, and support coupling collectively determine O₂ activation and VOC conversion pathways.
- (2) There exists an intrinsic trade-off between stability and reactivity. Strong metal-support interactions and defect anchoring stabilize single atoms and promote oxygen cycling, but excessive charge transfer or over-coordination may suppress key elementary steps such as C–H activation and O₂ dissociation.
- (3) Low-temperature VOC oxidation is fundamentally constrained by coupled scaling relationships. The adsorption energies of O₂, VOC molecules, and intermediates cannot be independently optimized on

a single site, leading to a kinetic bottleneck where oxygen activation and intermediate removal compete.

- (4) The reaction microenvironment plays a decisive role under realistic conditions. Surface hydroxyls, water adsorption, and support redox properties jointly regulate oxygen supply pathways (adsorbed vs lattice oxygen) and intermediate evolution, particularly under humid and low-temperature conditions.

5.2. Design Principles Emerging from SAC Studies

Based on the above mechanistic understanding, several general design principles can be established:

- (1) Interfacial electronic structure engineering: tailoring metal-support charge transfer and orbital hybridization to balance O₂ activation and C–H bond activation.
- (2) Coordination environment optimization: regulating first-shell (M–O_x, M–N_x) and second-shell interactions (hydrogen bonding, hydroxyl networks) to modulate adsorption strength and reaction barriers.
- (3) Defect and oxygen-vacancy engineering: constructing supports with tunable oxygen mobility to sustain continuous oxygen supply while maintaining structural stability.
- (4) Microenvironment regulation (hydroxyl and hydrophilicity): designing catalysts that enable efficient OH generation and utilization, particularly under low-humidity or high-humidity conditions.
- (5) Beyond isolated sites: cooperative or multi-site design: introducing dual-site or proximity effects to

partially overcome linear scaling limitations and decouple key reaction steps.

5.3. Future Perspectives and Research Directions

Despite significant progress, several critical challenges remain for translating SACs into practical VOC abatement technologies:

- (1) Scalable synthesis and high metal loading: developing synthetic strategies that enable high-density single-atom dispersion without aggregation, while maintaining structural uniformity and reproducibility.
- (2) Stability under realistic conditions (humidity and poisons): designing catalysts that maintain activity under high humidity, sulfur/chlorine-containing species, and long-term operation, where dynamic restructuring and deactivation pathways must be understood and controlled.
- (3) Advanced in situ/operando characterization: establishing techniques capable of probing dynamic coordination structures, oxidation states, and oxygen species under reaction conditions, to bridge the gap between static characterization and working catalysts.
- (4) Mechanism-driven descriptor development: moving beyond qualitative descriptions toward quantitative descriptors (e.g., ΔG_0 , ΔG_{OH} , electronic-state metrics) tailored to VOC oxidation systems, enabling predictive catalyst design.
- (5) Industrial translation and reactor-level integration: evaluating SACs under realistic flow conditions (high GHSV, low concentrations, multicomponent feeds) and integrating catalyst design with reactor engineering to achieve practical deployment.

Overall, the future of SACs in VOC oxidation lies not only in achieving higher intrinsic activity, but in integrating atomic-scale design with reaction engineering and real-world operating conditions, thereby bridging the gap between fundamental catalysis and industrial application.

Author Contributions

C.S.: writing—original draft editing, visualization; Z.H.: writing—reviewing and editing, investigation; H.L.: visualization; J.C.: visualization; H.S.: visualization; X.W.: investigation; H.Z.: investigation; B.L.: investigation; G.J.: writing—reviewing and editing, conceptualization, methodology, supervision, project administration. All authors have read and agreed to the published version of the manuscript.

Funding

This work is supported by the Natural Science Foundation of Fujian Province of China (Grant No. 2025J01173). The authors declare no conflict of interest.

Institutional Review Board Statement

Not applicable.

Informed Consent Statement

Not applicable.

Data Availability Statement

Not applicable.

Conflicts of Interest

The authors declare no conflict of interest.

Use of AI and AI-Assisted Technologies

No AI tools were utilized for this paper.

References

1. Huang, R.-J.; Zhang, Y.; Bozzetti, C.; et al. High secondary aerosol contribution to particulate pollution during haze events in China. *Nature* **2014**, *514*, 218–222.
2. Kamal, M.S.; Razzak, S.A.; Hossain, M.M. Catalytic oxidation of volatile organic compounds (VOCs)—A review. *Atmos. Environ.* **2016**, *140*, 117–134.
3. He, C.; Cheng, J.; Zhang, X.; et al. Recent advances in the catalytic oxidation of volatile organic compounds: A review based on pollutant sorts and sources. *Chem. Rev.* **2019**, *119*, 4471–4568.
4. Li, J.; Lei, X.; Zhao, R.; et al. Catalytic oxidation removal of typical sinter flue gas volatile organic compounds by CoMn binary spinel via peroxy monosulfate wet scrubbing. *Sep. Purif. Technol.* **2025**, *363*, 132071.
5. Liu, J.; Burciaga, R.; Tang, S.; et al. Heterogeneous catalysis for the environment. *Innov. Mater.* **2024**, *2*, 100090.
6. Wang, P.; Ma, X.; Hao, X.; et al. Oxygen vacancy defect engineering to promote catalytic activity toward the oxidation of VOCs: A critical review. *Catal. Rev.* **2024**, *66*, 586–639.
7. Cheng, N.; Stambula, S.; Wang, D.; et al. Platinum single-atom and cluster catalysis of the hydrogen evolution reaction. *Nat. Commun.* **2016**, *7*, 13638.
8. Galushko, A.S.; Ananikov, V.P. Deactivation of single-atom catalysts by nanoparticles. *Angew. Chem. Int. Ed.* **2026**, *65*, e20712.
9. Lang, R.; Du, X.; Huang, Y.; et al. Single-atom catalysts based on the metal-oxide interaction. *Chem. Rev.* **2020**, *120*, 11986–12043.
10. Zhao, J.; Wang, Y.; Chen, Z.; et al. Recent advances in catalytic removal volatile organic compounds: Structure activity correlation, mechanism and application insights. *Sep. Purif. Technol.* **2025**, *378*, 134598.
11. Bond, G.C. The origins of particle size effects in heterogeneous catalysis. *Surf. Sci.* **1985**, *156*, 966–981.
12. Wang, A.; Li, J.; Zhang, T. Heterogeneous single-atom catalysis. *Nat. Rev. Chem.* **2018**, *2*, 65–81.

13. Taylor, H.S. A theory of the catalytic surface. *Proc. R. Soc. Lond. A* **1925**, *108*, 105–111.
14. Qiao, B.; Wang, A.; Yang, X.; et al. Single-atom catalysis of CO oxidation using Pt₁/FeO_x. *Nat. Chem.* **2011**, *3*, 634–641.
15. Yang, X.-F.; Wang, A.; Qiao, B.; et al. Single-atom catalysts: A new frontier in heterogeneous catalysis. *Acc. Chem. Res.* **2013**, *46*, 1740–1748.
16. Jones, J.; Xiong, H.; DeLaRiva, A.T.; et al. Thermally stable single-atom platinum-on-ceria catalysts via atom trapping. *Science* **2016**, *353*, 150–154.
17. Goodman, E.D.; Schwalbe, J.A.; Cargnello, M. Mechanistic understanding and the rational design of sinter-resistant heterogeneous catalysts. *ACS Catal.* **2017**, *7*, 7156–7173.
18. Chen, Y.; Ji, S.; Wang, Y.; et al. Isolated single iron atoms anchored on N-doped porous carbon as an efficient electrocatalyst for the oxygen reduction reaction. *Angew. Chem. Int. Ed.* **2017**, *56*, 6937–6941.
19. Wang, L.; Chen, M.-X.; Yan, Q.-Q.; et al. A sulfur-tethering synthesis strategy toward high-loading atomically dispersed noble metal catalysts. *Sci. Adv.* **2019**, *5*, eaax6322.
20. Shang, H.; Zhou, X.; Dong, J.; et al. Engineering unsymmetrically coordinated Cu-SiN₃ single atom sites with enhanced oxygen reduction activity. *Nat. Commun.* **2020**, *11*, 3049.
21. Babucci, M.; Sarac Oztuna, F.E.; Debeve, L.M.; et al. Atomically dispersed reduced graphene aerogel-supported iridium catalyst with an iridium loading of 14.8 wt%. *ACS Catal.* **2019**, *9*, 9905–9913.
22. Wan, J.; Chen, W.; Jia, C.; et al. Defect effects on TiO₂ nanosheets: Stabilizing single atomic site Au and promoting catalytic properties. *Adv. Mater.* **2018**, *30*, 1705369.
23. Liu, J.-C.; Wang, Y.-G.; Li, J. Toward rational design of oxide-supported single-atom catalysts: Atomic dispersion of gold on ceria. *J. Am. Chem. Soc.* **2017**, *139*, 6190–6199.
24. Bruix, A.; Lykhach, Y.; Matolínová, I.; et al. Maximum noble-metal efficiency in catalytic materials: Atomically dispersed surface platinum. *Angew. Chem. Int. Ed.* **2014**, *53*, 10525–10530.
25. Duan, X.; Niu, B.; Wang, Y.; et al. Regulating the electronic metal-support interaction of single-atom ruthenium catalysts for boosting chlorobenzene oxidation. *Environ. Sci. Technol.* **2025**, *59*, 7408–7418.
26. Jeong, H.; Shin, D.; Kim, B.-S.; et al. Controlling the oxidation state of Pt single atoms for maximizing catalytic activity. *Angew. Chem. Int. Ed.* **2020**, *59*, 20691–20696.
27. Yuan, L.; Hung, S.-F.; Tang, Z.-R.; et al. Dynamic evolution of atomically dispersed Cu species for CO₂ photoreduction to solar fuels. *ACS Catal.* **2019**, *9*, 4824–4833.
28. Campbell, C.T. Electronic perturbations. *Nat. Chem.* **2012**, *4*, 597–598.
29. Pérez-Ramírez, J.; López, N. Strategies to break linear scaling relationships. *Nat. Catal.* **2019**, *2*, 971–976.
30. Li, H.; Wang, L.; Dai, Y.; et al. Synergetic interaction between neighbouring platinum monomers in CO₂ hydrogenation. *Nat. Nanotechnol.* **2018**, *13*, 411–417.
31. Wang, Y.-G.; Mei, D.; Glezakou, V.-A.; et al. Dynamic formation of single-atom catalytic active sites on ceria-supported gold nanoparticles. *Nat. Commun.* **2015**, *6*, 6511.
32. Zhang, L.; Bao, Q.; Zhang, B.; et al. Distinct role of surface hydroxyls in single-atom Pt₁/CeO₂ catalyst for room-temperature formaldehyde oxidation: Acid–base versus redox. *JACS Au* **2022**, *2*, 1651–1660.
33. Perilli, D.; Breglia, R.; Valentin, C.D. Using coordination chemistry concepts to unravel electronic properties of SACs in bidimensional materials. *J. Phys. Chem. C* **2022**, *126*, 9615–9622.
34. Chowdhury, C.; Lovato, M.; Di Liberto, G.; et al. Predicting the HER activity of SACs on MXenes with simple features and interpretable machine learning models. *J. Mater. Chem. A* **2026**, *14*, 5349–5365.
35. Rasool, A.; Anis, I.; Bhat, S.A.; et al. Optimizing the NRR activity of single and double boron atom catalysts using a suitable support: A first principles investigation. *Phys. Chem. Chem. Phys.* **2023**, *25*, 22275–22285.
36. Hassan, A.; Dar, M.; Dar, M.A. Driving CO₂ conversion to C₁ and C₂ products on single-atom catalysts: Recent experimental and theoretical insights. *ACS Appl. Mater. Interfaces* **2025**, *17*, 53056–53080.
37. Amin, S.; Krishnamurthy, S.; Dar, M.A. Boosting the CO₂ reduction activity of Cu double-atom catalysts through coordination environment engineering. *Sustain. Energy Fuels* **2025**, *9*, 5589–5600.
38. Guan, X.; Han, R.; Asakura, H.; et al. Subsurface single-atom catalyst enabled by mechanochemical synthesis for oxidation chemistry. *Angew. Chem. Int. Ed.* **2024**, *63*, e202410457.
39. O'Connor, N.J.; Jonayat, A.S.M.; Janik, M.J.; et al. Interaction trends between single metal atoms and oxide supports identified with density functional theory and statistical learning. *Nat. Catal.* **2018**, *1*, 531–539.
40. Shi, H.; Yang, P.; Huang, L.; et al. Single-atom Pt-CeO₂/Co₃O₄ catalyst with ultra-low Pt loading and high performance for toluene removal. *J. Colloid Interface Sci.* **2023**, *641*, 972–980.
41. Ma, S.; Feng, C.; Dong, F.; et al. A Pt₁Co₁/CeO₂ bimetallic single-atom catalyst with a strong Pt-Co synergistic effect for efficient oxidation of benzene. *Appl. Catal. B* **2025**, *374*, 125369.
42. Liu, L.; Jing, G.; Xu, C.; et al. Exceptional formaldehyde oxidation at room temperature on Co single-atom functionalized TiO₂ nanowires via highly effective O₂ activation. *Appl. Catal. B* **2024**, *344*, 123634.
43. Hao, X.; Dai, L.; Deng, J.; et al. Nanotubular OMS-2 supported single-atom platinum catalysts highly active for benzene oxidation. *J. Phys. Chem. C* **2021**, *125*, 17696–17708.

44. Nie, L.; Mei, D.; Xiong, H.; et al. Activation of surface lattice oxygen in single-atom Pt/CeO₂ for low-temperature CO oxidation. *Science* **2017**, *358*, 1419–1423.
45. Zhao, S.; Wen, Y.; Liu, X.; et al. Formation of active oxygen species on single-atom Pt catalyst and promoted catalytic oxidation of toluene. *Nano Res.* **2020**, *13*, 1544–1551.
46. Su, H.; Chai, J.; Guan, Z.; et al. Tuning the f band for enhanced surface redox in strained rare earth oxides. *J. Am. Chem. Soc.* **2025**, *147*, 40196–40204.
47. Capdevila-Cortada, M.; Vilé, G.; Teschner, D.; et al. Reactivity descriptors for ceria in catalysis. *Appl. Catal. B* **2016**, *197*, 299–312.
48. Wang, X.; Hu, J.; Lu, T.; et al. Importing atomic rare-earth sites to activate lattice oxygen of spinel oxides for electrocatalytic oxygen evolution. *Angew. Chem. Int. Ed.* **2025**, *64*, e202415306.
49. Tan, W.; Xie, S.; Le, D.; et al. Fine-tuned local coordination environment of Pt single atoms on ceria controls catalytic reactivity. *Nat. Commun.* **2022**, *13*, 7070.
50. Jiang, D.; Yao, Y.; Li, T.; et al. Tailoring the local environment of platinum in single-atom Pt₁/CeO₂ catalysts for robust low-temperature CO oxidation. *Angew. Chem. Int. Ed.* **2021**, *60*, 26054–26062.
51. Jiang, D.; Wan, G.; García-Vargas, C.E.; et al. Elucidation of the active sites in single-atom Pd₁/CeO₂ catalysts for low-temperature CO oxidation. *ACS Catal.* **2020**, *10*, 11356–11364.
52. Schilling, C.; Ganduglia-Pirovano, M.V.; Hess, C. Experimental and theoretical study on the nature of adsorbed oxygen species on shaped ceria nanoparticles. *J. Phys. Chem. Lett.* **2018**, *9*, 6593–6598.
53. Chakarova, K.; Drenchev, N.; Mihaylov, M.; et al. Interaction of O₂ with reduced ceria nanoparticles at 100–400 K: Fast oxidation of Ce³⁺ ions and dissolved H₂. *Catalysts* **2024**, *14*, 45.
54. Xing, Y.; Wang, C.; Li, D.; et al. Solution plasma processing single-atom Au₁ on CeO₂ nanosheet for low temperature photo-enhanced Mars–van Krevelen CO oxidation. *Adv. Funct. Mater.* **2022**, *32*, 2207694.
55. Han, W.; Ling, W.; Gao, P.; et al. Engineering Pt single atom catalyst with abundant lattice oxygen by dual nanospace confinement strategy for the efficient catalytic elimination of VOCs. *Appl. Catal. B* **2024**, *345*, 123687.
56. Wang, T.; Qiu, S.; Dai, Z.; et al. Exploration of TiO₂ as substrates for single metal catalysts: A DFT study. *Appl. Surf. Sci.* **2020**, *533*, 147362.
57. Lazzeri, M.; Vittadini, A.; Selloni, A. Structure and energetics of stoichiometric TiO₂ anatase surfaces. *Phys. Rev. B* **2001**, *63*, 155409.
58. Sun, S.; Liu, S.; Cao, J.; et al. Metastable Pt₁/TiO₂ catalyst for activating H₂O to enhanced C₆H₆ oxidation under humid condition. *Appl. Catal. B* **2025**, *367*, 125125.
59. Wang, Q.; Gu, Q.; Wang, A.; et al. Crystal facet enhanced dynamic stability and reactivity of undercoordinated Pt₁-TiO₂ single atom species for methane oxidation. *J. Phys. Chem. Lett.* **2025**, *16*, 5887–5896.
60. Jia, J.; Zhang, P.; Chen, L. Catalytic decomposition of gaseous ozone over manganese dioxides with different crystal structures. *Appl. Catal. B* **2016**, *189*, 210–218.
61. Yang, W.; Su, Z. a.; Xu, Z.; et al. Comparative study of α -, β -, γ - And δ -MnO₂ on toluene oxidation: Oxygen vacancies and reaction intermediates. *Appl. Catal. B* **2020**, *260*, 118150.
62. Chen, Y.; Huang, Z.; Zhou, M.; et al. Single silver adatoms on nanostructured manganese oxide surfaces: Boosting oxygen activation for benzene abatement. *Environ. Sci. Technol.* **2017**, *51*, 2304–2311.
63. Chen, Y.; Gao, J.; Huang, Z.; et al. Sodium rivals silver as single-atom active centers for catalyzing abatement of formaldehyde. *Environ. Sci. Technol.* **2017**, *51*, 7084–7090.
64. Wang, Y.; Zhang, J.; Zhang, Y.; et al. Single Fe atom-anchored manganese dioxide for efficient removal of volatile organic compounds in refrigerator. *Nano Res.* **2024**, *17*, 3927–3933.
65. Wang, Y.; Wang, M.; Jin, X.; et al. Cyclable Cu I -O_v-Mn sites accelerate O₂ activation to enhance photo-driven catalytic oxidation performance. *Appl. Catal. B* **2024**, *353*, 124110.
66. Zhang, Q.; Zhang, S.; Wu, Y. Research advances in volatile organic compounds catalytic removal using CeO₂-based catalysts. *J. Environ. Chem. Eng.* **2025**, *13*, 119033.
67. Meng, F.; Tang, X.; Kadja, G.T.M.; et al. A systematic review with improving activity and stability in VOCs elimination by oxidation of noble metals: Starting from active sites. *Sep. Purif. Technol.* **2025**, *354*, 129222.
68. Wang, D.; Yuan, C.; Yang, C.; et al. Recent advances in catalytic removal volatile organic compounds over metal–organic framework–derived catalysts: A review. *Sep. Purif. Technol.* **2023**, *326*, 124765.
69. Pan, H.; Chen, Z.; Feng, X.; et al. Sulfur-resistant mechanism of MnO_x@CeO₂@MgO core-shell catalyst in simultaneous removal of NO_x and chlorobenzene. *Appl. Catal. B* **2025**, *362*, 124761.
70. Yang, D.; Dong, F.; Han, W.; et al. Significant enhanced SO₂ resistance of Pt/SiO₂ catalysts by building the ultrathin metal oxide shell for benzene catalytic combustion. *ACS Appl. Mater. Interfaces* **2023**, *15*, 42541–42556.
71. Zhang, X.; Zhang, X.; Liang, C.; et al. Flowerlike structured Cu promoted MnO_x catalysts for VOC oxidation: Enhanced water vapor resistance in simulated coal-fired flue gas. *Fuel* **2025**, *399*, 135668.
72. Li, J.; Chen, J.; Zeng, J.; et al. Tuning the crystallinity of the MnO_x catalysts to promote toluene catalytic oxidation. *Environ. Technol.* **2025**, *46*, 98–110.
73. Weng, X.; Shi, B.; Liu, A.; et al. Highly dispersed Pd/modified-Al₂O₃ catalyst on complete oxidation of toluene: Role of basic sites and mechanism insight. *Appl. Surf. Sci.* **2019**, *497*, 143747.

74. Wang, J.; Wang, C.; Chen, X.; et al. The performance and mechanism of HCHO oxidation on Pt/Al₂O₃ catalysts: The effect of alumina crystalline phase and surface hydroxyls. *Appl. Catal. B* **2024**, *357*, 124342.
75. Yang, D.; Dong, F.; Wang, J.; et al. Constructing a core-shell Pt@MnO_x/SiO₂ catalyst for benzene catalytic combustion with excellent SO₂ resistance: New insights into active sites. *Environ. Sci. Nano* **2024**, *11*, 1926–1947.
76. Li, J.; Feng, J.; Liu, F.; et al. Enhanced antichlorine poisoning of CaCO₃-modified MnO₂ catalyst for catalytic combustion of chlorobenzene. *J. Environ. Chem. Eng.* **2025**, *13*, 115038.
77. Tauster, S.J.; Fung, S.C.; Garten, R.L. Strong metal-support interactions. Group 8 noble metals supported on titanium dioxide. *J. Am. Chem. Soc.* **1978**, *100*, 170–175.
78. Monai, M.; Jenkinson, K.; Melcherts, A.E.M.; et al. Restructuring of titanium oxide overlayers over nickel nanoparticles during catalysis. *Science* **2023**, *380*, 644–651.
79. Tang, H.; Su, Y.; Zhang, B.; et al. Classical strong metal-support interactions between gold nanoparticles and titanium dioxide. *Sci. Adv.* **2017**, *3*, e1700231.
80. Liu, S.; Qi, H.; Zhou, J.; et al. Encapsulation of platinum by titania under an oxidative atmosphere: Contrary to classical strong metal-support interactions. *ACS Catal.* **2021**, *11*, 6081–6090.
81. Du, E.; Yang, J.; Huai, L.; et al. Quantifying interface-dependent active sites induced by strong metal-support interactions on Au/TiO₂ in 2,5-bis(hydroxymethyl)furan oxidation. *ACS Catal.* **2025**, *15*, 54–62.
82. Xie, S.; Liu, L.; Lu, Y.; et al. Pt atomic single-layer catalyst embedded in defect-enriched ceria for efficient CO oxidation. *J. Am. Chem. Soc.* **2022**, *144*, 21255–21266.
83. Liu, K.; Zhao, X.; Ren, G.; et al. Strong metal-support interaction promoted scalable production of thermally stable single-atom catalysts. *Nat. Commun.* **2020**, *11*, 1263.
84. Yang, J.; Huang, Y.; Qi, H.; et al. Modulating the strong metal-support interaction of single-atom catalysts via vicinal structure decoration. *Nat. Commun.* **2022**, *13*, 4244.
85. Li, Y.; Qin, T.; Wei, Y.; et al. A single site ruthenium catalyst for robust soot oxidation without platinum or palladium. *Nat. Commun.* **2023**, *14*, 7149.
86. Tang, M.; Li, S.; Chen, S.; et al. Facet-dependent oxidative strong metal-support interactions of palladium-TiO₂ determined by in situ transmission electron microscopy. *Angew. Chem. Int. Ed.* **2021**, *60*, 22339–22344.
87. Tang, H.; Su, Y.; Guo, Y.; et al. Oxidative strong metal-support interactions (OMSI) of supported platinum-group metal catalysts. *Chem. Sci.* **2018**, *9*, 6679–6684.
88. Ingale, P.; Knemeyer, K.; Preikschat, P.; et al. Design of PtZn nanoalloy catalysts for propane dehydrogenation through interface tailoring via atomic layer deposition. *Catal. Sci. Technol.* **2021**, *11*, 484–493.
89. Wei, P.; Chen, S.; Luo, R.; et al. Stable and homogeneous intermetallic alloys by atomic gas-migration for propane dehydrogenation. *Nat. Commun.* **2024**, *15*, 8157.
90. Arroyo-Ramírez, L.; Chen, C.; Cargnello, M.; et al. Supported platinum–zinc oxide core–shell nanoparticle catalysts for methanol steam reforming. *J. Mater. Chem. A* **2014**, *2*, 19509–19514.
91. Ran, L.; Li, Z.; Ran, B.; et al. Engineering single-atom active sites on covalent organic frameworks for boosting CO₂ photoreduction. *J. Am. Chem. Soc.* **2022**, *144*, 17097–17109.
92. Jiang, R.; Li, L.; Sheng, T.; et al. Edge-site engineering of atomically dispersed Fe–N₄ by selective C–N bond cleavage for enhanced oxygen reduction reaction activities. *J. Am. Chem. Soc.* **2018**, *140*, 11594–11598.
93. Zhang, J.; Zhao, Y.; Chen, C.; et al. Tuning the coordination environment in single-atom catalysts to achieve highly efficient oxygen reduction reactions. *J. Am. Chem. Soc.* **2019**, *141*, 20118–20126.
94. Dong, F.; Meng, Y.; Ling, W.; et al. Single atomic Pt confined into lattice defect sites for low-temperature catalytic oxidation of VOCs. *Appl. Catal. B* **2024**, *346*, 123779.
95. Tao, Q.; Song, J.; Sun, N.; et al. Boosting the activity of single-atom Pt₁/CeO₂ via Co doping for low-temperature catalytic oxidation of CO. *Inorg. Chem.* **2022**, *61*, 11932–11938.
96. Maurer, F.; Jelic, J.; Wang, J.; et al. Tracking the formation, fate and consequence for catalytic activity of Pt single sites on CeO₂. *Nat. Catal.* **2020**, *3*, 824–833.
97. DeRita, L.; Resasco, J.; Dai, S.; et al. Structural evolution of atomically dispersed Pt catalysts dictates reactivity. *Nat. Mater.* **2019**, *18*, 746–751.
98. Tan, W.; Xie, S.; Cai, Y.; et al. Transformation of highly stable Pt single sites on defect engineered ceria into robust Pt clusters for vehicle emission control. *Environ. Sci. Technol.* **2021**, *55*, 12607–12618.
99. Wang, Z.; Zhou, X.; Wang, G.; et al. High-performance Ir₁/CeO₂ single-atom catalyst for the oxidation of toluene. *Inorg. Chem.* **2024**, *63*, 7241–7254.
100. Zhang, H.; Sui, S.; Zheng, X.; et al. One-pot synthesis of atomically dispersed Pt on MnO₂ for efficient catalytic decomposition of toluene at low temperatures. *Appl. Catal. B* **2019**, *257*, 117878.
101. Wang, Y.; Dai, J.; Wang, M.; et al. Enhanced toluene oxidation by photothermal synergetic catalysis on manganese oxide embedded with Pt single-atoms. *J. Colloid Interface Sci.* **2023**, *636*, 577–587.
102. Yang, W.; Zhao, X.; Wang, Y.; et al. Atomically dispersed Ag on δ-MnO₂ via cation vacancy trapping for toluene catalytic oxidation. *Catal. Sci. Technol.* **2022**, *12*, 5932–5941.
103. Zheng, Y.; Fu, K.; Yu, Z.; et al. Oxygen vacancies in a catalyst for VOCs oxidation: Synthesis, characterization, and catalytic effects. *J. Mater. Chem. A* **2022**, *10*, 14171–14186.

104. Zhang, H.; Wang, Z.; Lin, H.; et al. Catalytic oxidation of volatile organic compounds over supported noble metal and single atom catalysts: A review. *J. Environ. Sci.* **2025**, *155*, 858–888.
105. Tang, T.; Zhao, S.; Liu, Y.; et al. Metal-support interaction in supported Pt single-atom catalyst promotes lattice oxygen activation to achieve complete oxidation of acetone at low concentrations. *J. Hazard. Mater.* **2024**, *480*, 135839.
106. Cheng, H.; Wang, Y.; Jin, Y.; et al. Oxygen vacancy engineering through equivalent and aliovalent doping on LaCoO₃. *Sep. Purif. Technol.* **2024**, *351*, 128078.
107. Jiang, M.; Yan, D.; Lv, X.; et al. Recognition of water-dissociation effect toward lattice oxygen activation on single-atom Co catalyst in toluene oxidation. *Appl. Catal. B* **2022**, *319*, 121962.
108. Chu, P.; Zhang, L.; Wang, Z.; et al. Regulation lattice oxygen mobility via dual single atoms for simultaneously enhancing VOC oxidation and NO_x reduction. *Environ. Sci. Technol.* **2024**, *58*, 17475–17484.
109. Barman, N.; Majumder, C.; Thapa, R. Electronic and energy descriptors for SACs as tri-functional catalysts towards urea formation and unveiling the C–N coupling mechanism. *Chem. Sci.* **2026**, *17*, 2169–2182.
110. Bhat, S.S.; Rasool, A.; Dar, M.A. Single-atom-functionalized covalent organic frameworks for efficient CO₂ conversion: Electronic structure insights from first-principles simulations. *J. Phys. Chem. C* **2025**, *129*, 17512–17518.
111. Belew, A.A.; Meshesha, D.S.; Assege, M.A.; et al. Recent progress of single-atom catalysts (SACs) for the advanced oxidation of organic compounds: A comprehensive review on metal-specific performance and mechanisms. *Mater. Today Sustain.* **2026**, *34*, 101335.
112. Khanam, R.; Rasool, A.; Dar, M.A. Unraveling the mechanism of oxygen electrocatalysis on transition metal-free single-atom-doped holey graphyne. *ChemPhysChem* **2025**, *26*, e202500167.
113. Wang, Y.; Liang, Y.; Bo, T.; et al. Orbital dependence in single-atom electrocatalytic reactions. *J. Phys. Chem. Lett.* **2022**, *13*, 5969–5976.
114. Greiner, M.T.; Jones, T.E.; Beeg, S.; et al. Free-atom-like *d* states in single-atom alloy catalysts. *Nat. Chem.* **2018**, *10*, 1008–1015.
115. Shi, Y.; Ma, Z.-R.; Xiao, Y.-Y.; et al. Electronic metal-support interaction modulates single-atom platinum catalysis for hydrogen evolution reaction. *Nat. Commun.* **2021**, *12*, 3021.
116. Wang, L.; Wang, H.; Lu, J. Local chemical environment effect in single-atom catalysis. *Chem Catal.* **2023**, *3*, 100492.
117. Liu, L.; Corma, A. Metal catalysts for heterogeneous catalysis: From single atoms to nanoclusters and nanoparticles. *Chem. Rev.* **2018**, *118*, 4981–5079.
118. Kraushofer, F.; Parkinson, G.S. Single-atom catalysis: Insights from model systems. *Chem. Rev.* **2022**, *122*, 14911–14939.
119. Giulimondi, V.; Mitchell, S.; Pérez-Ramírez, J. Challenges and opportunities in engineering the electronic structure of single-atom catalysts. *ACS Catal.* **2023**, *13*, 2981–2997.
120. Di Liberto, G.; Pacchioni, G. Key ingredients for the modeling of single-atom electrocatalysts. *ChemElectroChem* **2024**, *11*, e202400476.
121. Lu, Y.; Wang, J.; Yu, L.; et al. Identification of the active complex for CO oxidation over single-atom Ir-on-MgAl₂O₄ catalysts. *Nat. Catal.* **2019**, *2*, 149–156.
122. Liu, S.; Huang, S. Theoretical insights into the activation of O₂ by Pt single atom and Pt₄ nanocluster on functionalized graphene support: Critical role of Pt positive polarized charges. *Carbon* **2017**, *115*, 11–17.
123. Tsounis, C.; Subhash, B.; Kumar, P.V.; et al. Pt single atom electrocatalysts at graphene edges for efficient alkaline hydrogen evolution. *Adv. Funct. Mater.* **2022**, *32*, 2203067.
124. Li, J.; Chen, C.; Xu, L.; et al. Challenges and perspectives of single-atom-based catalysts for electrochemical reactions. *JACS Au* **2023**, *3*, 736–755.
125. Wang, J.; Li, Z.; Wu, Y.; et al. Fabrication of single-atom catalysts with precise structure and high metal loading. *Adv. Mater.* **2018**, *30*, 1801649.
126. Bethe, H. Termaufspaltung in kristallen. *Ann. Phys.* **1929**, *395*, 133–208.
127. Wu, B.; Chen, Z.; Ye, Y.; et al. Symmetry breaking of single-atom catalysts in heterogeneous electrocatalysis: Reactivity and configuration. *Chem. Soc. Rev.* **2026**, *55*, 114–143.
128. Hammer, B.; Nørskov, J.K. Theoretical surface science and catalysis—Calculations and concepts. *Adv. Catal.* **2000**, *45*, 71–129.
129. Nørskov, J.K.; Abild-Pedersen, F.; Studt, F.; et al. Density functional theory in surface chemistry and catalysis. *Proc. Natl. Acad. Sci. USA* **2011**, *108*, 937–943.
130. Chen, W.; Qian, G.; Wang, H.; et al. Rationalizing the *d*-band model from theory to practice in catalyst design. *J. Am. Chem. Soc.* **2025**, *147*, 46729–46744.
131. Blyholder, G. Molecular orbital view of chemisorbed carbon monoxide. *J. Phys. Chem.* **1964**, *68*, 2772–2777.
132. Patra, A.; Peng, H.; Sun, J.; et al. Rethinking CO adsorption on transition-metal surfaces: Effect of density-driven self-interaction errors. *Phys. Rev. B* **2019**, *100*, 035442.
133. Liu, J.; Liang, K.; Yao, D.; et al. Modulating the coordination of single Co atoms to trigger the catalytic oxidation of formaldehyde at room temperature. *Inorg. Chem.* **2023**, *62*, 4003–4010.
134. Wang, X.; Chen, Z.; Zhao, X.; et al. Regulation of coordination number over single Co sites: Triggering the

- efficient electroreduction of CO₂. *Angew. Chem.* **2018**, *57*, 1944–1948.
135. Rafsanjani-Abbasi, A.; Buchner, F.; Lewis, F.J.; et al. Digging its own site: Linear coordination stabilizes a Pt₁/Fe₂O₃ single-atom catalyst. *ACS Nano* **2024**, *18*, 26920–26927.
 136. Zhao, T.; Wang, J.; Wei, Y.; et al. From lab-scale to industrialization: Atomically M–N–C catalysts for the oxygen reduction reaction. *Energy Environ. Sci.* **2025**, *18*, 3462–3501.
 137. Zhong, X.; Huang, Y.; Cai, J.; et al. Axial fluorine coordination boosts the activity and durability of Fe single-atom catalysts in room-temperature Na–S batteries. *Chem. Sci.* **2025**, *16*, 18821–18831.
 138. Zhang, T.; Han, X.; Liu, H.; et al. Site-specific axial oxygen coordinated FeN₄ active sites for highly selective electroreduction of carbon dioxide. *Adv. Funct. Mater.* **2022**, *32*, 2111446.
 139. Chen, S.; Luo, T.; Li, X.; et al. Identification of the highly active Co–N₄ coordination motif for selective oxygen reduction to hydrogen peroxide. *J. Am. Chem. Soc.* **2022**, *144*, 14505–14516.
 140. Liu, K.; Fu, J.; Lin, Y.; et al. Insights into the activity of single-atom Fe–N–C catalysts for oxygen reduction reaction. *Nat. Commun.* **2022**, *13*, 2075.
 141. Chi, K.; Wu, Y.; Wang, X.; et al. Single atom catalysts with out-of-plane coordination structure on conjugated covalent organic frameworks. *Small* **2022**, *18*, e2203966.
 142. Mitchell, S.; Pérez-Ramírez, J. Single atom catalysis: A decade of stunning progress and the promise for a bright future. *Nat. Commun.* **2020**, *11*, 4302.
 143. Daelman, N.; Capdevila-Cortada, M.; López, N. Dynamic charge and oxidation state of Pt/CeO₂ single-atom catalysts. *Nat. Mater.* **2019**, *18*, 1215–1221.
 144. Sang, K.; Zuo, J.; Zhang, X.; et al. Towards a molecular understanding of the electronic metal-support interaction (EMSI) in heterogeneous catalysis. *Green Energy Environ.* **2023**, *8*, 619–625.
 145. Han, Z.-K.; Liu, W.; Gao, Y. Advancing the understanding of oxygen vacancies in ceria: Insights into their formation, behavior, and catalytic roles. *JACS Au* **2025**, *5*, 1549–1569.
 146. Wang, Q.; Yeung, K.L.; Banares, M.A. Ceria and its related materials for VOC catalytic combustion: A review. *Catal. Today* **2020**, *356*, 141–154.
 147. Zhao, Y.; Teng, B.; Wen, X.-D.; et al. Superoxide and peroxide species on CeO₂(111), and their oxidation roles. *J. Phys. Chem. C* **2012**, *116*, 15986–15991.
 148. Hoang, S.; Guo, Y.; Binder, A.J.; et al. Activating low-temperature diesel oxidation by single-atom Pt on TiO₂ nanowire array. *Nat. Commun.* **2020**, *11*, 1062.
 149. Kang, L.; Wang, B.; Bing, Q.; et al. Adsorption and activation of molecular oxygen over atomic copper(I/II) site on ceria. *Nat. Commun.* **2020**, *11*, 4008.
 150. Binniger, T. Electronic metal-support interactions in vacuum vs. Electrolyte. *Nat. Commun.* **2020**, *11*, 1471.
 151. Jackson, C.; Smith, G.T.; Inwood, D.W.; et al. Electronic metal-support interaction enhanced oxygen reduction activity and stability of boron carbide supported platinum. *Nat. Commun.* **2017**, *8*, 15802.
 152. Binniger, T.; Schmidt, T.J.; Kramer, D. Capacitive electronic metal-support interactions: Outer surface charging of supported catalyst particles. *Phys. Rev. B* **2017**, *96*, 165405.
 153. Leybo, D.; Etim, U.J.; Monai, M.; et al. Metal-support interactions in metal oxide-supported atomic, cluster, and nanoparticle catalysis. *Chem. Soc. Rev.* **2024**, *53*, 10450–10490.
 154. Beck, A.; Huang, X.; Artiglia, L.; et al. The dynamics of overlayer formation on catalyst nanoparticles and strong metal-support interaction. *Nat. Commun.* **2020**, *11*, 3220.
 155. Delley, M.F.; Nichols, E.M.; Mayer, J.M. Interfacial acid–base equilibria and electric fields concurrently probed by in situ surface-enhanced infrared spectroscopy. *J. Am. Chem. Soc.* **2021**, *143*, 10778–10792.
 156. Chen, Z.; Liu, Z.; Xu, X. Dynamic evolution of the active center driven by hemilabile coordination in Cu/CeO₂ single-atom catalyst. *Nat. Commun.* **2023**, *14*, 2512.
 157. News, D.M. Self-consistent model of hydrogen chemisorption. *Phys. Rev.* **1969**, *178*, 1123–1135.
 158. Wang, S.; Pillai, H.S.; Xin, H. Bayesian learning of chemisorption for bridging the complexity of electronic descriptors. *Nat. Commun.* **2020**, *11*, 6132.
 159. Liu, P.; Zheng, N. Coordination chemistry of atomically dispersed catalysts. *Natl. Sci. Rev.* **2018**, *5*, 636–638.
 160. Qin, R.; Liu, K.; Wu, Q.; et al. Surface coordination chemistry of atomically dispersed metal catalysts. *Chem. Rev.* **2020**, *120*, 11810–11899.
 161. Rosen, A.S.; Vijay, S.; Persson, K.A. Free-atom-like *d* states beyond the dilute limit of single-atom alloys. *Chem. Sci.* **2023**, *14*, 1503–1511.
 162. Franchini, C.; Reticcioli, M.; Setvin, M.; et al. Polarons in materials. *Nat. Rev. Mater.* **2021**, *6*, 560–586.
 163. Reticcioli, M.; Setvin, M.; Hao, X.; et al. Polaron-driven surface reconstructions. *Phys. Rev. X* **2017**, *7*, 031053.
 164. Liu, K.; Li, Y.; Guo, L.; et al. Heralding the electrification era of catalysts: A highly practical current-assisted catalytic strategy. *Innovation* **2025**, *6*, 100804.
 165. Ciampi, S.; Darwish, N.; Aitken, H.M.; et al. Harnessing electrostatic catalysis in single molecule, electrochemical and chemical systems: A rapidly growing experimental tool box. *Chem. Soc. Rev.* **2018**, *47*, 5146–5164.
 166. Shaik, S.; Mandal, D.; Ramanan, R. Oriented electric fields as future smart reagents in chemistry. *Nat. Chem.* **2016**, *8*, 1091–1098.

167. Léonard, N.G.; Dhaoui, R.; Chantarojsiri, T.; et al. Electric fields in catalysis: From enzymes to molecular catalysts. *ACS Catal.* **2021**, *11*, 10923–10932.
168. Zhang, L.; Wan, S.; Du, C.; et al. Generating active metal/oxide reverse interfaces through coordinated migration of single atoms. *Nat. Commun.* **2024**, *15*, 1234.
169. Ooka, H.; Huang, J.; Exner, K.S. The Sabatier principle in electrocatalysis: Basics, limitations, and extensions. *Front. Energy Res.* **2021**, *9*, 654460.
170. Mao, Y.; Chen, J.; Wang, H.; et al. Catalyst screening: Refinement of the origin of the volcano curve and its implication in heterogeneous catalysis. *Chin. J. Catal.* **2015**, *36*, 1596–1605.
171. Quaino, P.; Juarez, F.; Santos, E.; et al. Volcano plots in hydrogen electrocatalysis—Uses and abuses. *Beilstein J. Nanotechnol.* **2014**, *5*, 846–854.
172. Guo, Y.; Wen, M.; Li, G.; et al. Recent advances in VOC elimination by catalytic oxidation technology onto various nanoparticles catalysts: A critical review. *Appl. Catal. B* **2021**, *281*, 119447.
173. Ding, J.; Liu, J.; Yang, Y.; et al. Understanding a-site tuning effect on formaldehyde catalytic oxidation over La-Mn perovskite catalysts. *J. Hazard. Mater.* **2022**, *422*, 126931.
174. Liu, Z.; Wei, J.; Zhang, G.; et al. Excellent room temperature catalytic activity for formaldehyde oxidation on a single-atom iron catalyst in a moist atmosphere. *J. Mater. Chem. A* **2023**, *11*, 1978–1990.
175. Zhao, Z.-J.; Liu, S.; Zha, S.; et al. Theory-guided design of catalytic materials using scaling relationships and reactivity descriptors. *Nat. Rev. Mater.* **2019**, *4*, 792–804.
176. Anderson, P.W. Localized magnetic states in metals. *Phys. Rev.* **1961**, *124*, 41–53.
177. Abild-Pedersen, F.; Greeley, J.; Studt, F.; et al. Scaling properties of adsorption energies for hydrogen-containing molecules on transition-metal surfaces. *Phys. Rev. Lett.* **2007**, *99*, 016105.
178. Hammer, B.; Nørskov, J.K. Electronic factors determining the reactivity of metal surfaces. *Surf. Sci.* **1995**, *343*, 211–220.
179. Khorshidi, A.; Violet, J.; Hashemi, J.; et al. How strain can break the scaling relations of catalysis. *Nat. Catal.* **2018**, *1*, 263–268.
180. Nørskov, J.K.; Rossmeisl, J.; Logadottir, A.; et al. Origin of the overpotential for oxygen reduction at a fuel-cell cathode. *J. Phys. Chem. B* **2004**, *108*, 17886–17892.
181. Ivanistsev, V.; Cepitis, R.; Rossmeisl, J.; et al. Twenty years after: Scaling relations in oxygen electrocatalysis and beyond. *Chem. Soc. Rev.* **2025**, *54*, 10956–10976.
182. Xu, S.; Feng, S.; Yu, Y.; et al. Dual-site segmentally synergistic catalysis mechanism: Boosting CoFeSx nanocluster for sustainable water oxidation. *Nat. Commun.* **2024**, *15*, 1720.
183. Du, K.; Zhang, L.; Shan, J.; et al. Interface engineering breaks both stability and activity limits of RuO₂ for sustainable water oxidation. *Nat. Commun.* **2022**, *13*, 5448.
184. Gao, S.; Wang, L.; Kang, X.; et al. Interface engineering towards overall water electrolysis over NiCo₂O₄/NiMo hybrid catalysts. *Catal. Sci. Technol.* **2024**, *14*, 1349–1358.
185. Cepitis, R.; Ivaništšev, V.; Rossmeisl, J.; et al. Bypassing the scaling relations in oxygen electrocatalysis with geometry-adaptive catalysts. *Catal. Sci. Technol.* **2024**, *14*, 2105–2113.
186. Liu, S.; Chen, Y.; Chen, C.; et al. From single-atom catalysis to dual-atom catalysis: A comprehensive review of their application in advanced oxidation processes. *Sep. Purif. Technol.* **2024**, *351*, 127989.
187. Fang, C.; Zhou, J.; Zhang, L.; et al. Synergy of dual-atom catalysts deviated from the scaling relationship for oxygen evolution reaction. *Nat. Commun.* **2023**, *14*, 4449.
188. Shen, Q.; Lu, Z.; Bi, F.; et al. Effect of actual working conditions on catalyst structure and activity for oxidation of volatile organic compounds: A review. *Fuel* **2023**, *343*, 128012.
189. Zhang, N.; Zhang, X.; Kang, Y.; et al. A supported Pd₂ dual-atom site catalyst for efficient electrochemical CO₂ reduction. *Angew. Chem. Int. Ed.* **2021**, *60*, 13388–13393.
190. Zhou, X.; Han, K.; Li, K.; et al. Dual-site single-atom catalysts with high performance for three-way catalysis. *Adv. Mater.* **2022**, *34*, e2201859.
191. Sun, H.; Li, L.; Li, X.; et al. Dual-atom catalysts for the hydrogen evolution reaction. *ACS Appl. Energy Mater.* **2025**, *8*, 3276–3293.
192. Jiang, X.; Chen, C.; Chen, J.; et al. Atomically dispersed dual-atom catalysts: A new rising star in environmental remediation. *Sci. of Total Environ.* **2024**, *912*, 169142.
193. Zhang, C.; Dai, Y.; Sun, Q.; et al. Strategy to weaken the oxygen adsorption on single-atom catalysts towards oxygen-involved reactions. *Mater. Today Adv.* **2022**, *16*, 100280.
194. Sun, Q.; Yue, X.; Yu, L.; et al. Well-defined Co₂ dual-atom catalyst breaks scaling relations of oxygen reduction reaction. *J. Am. Chem. Soc.* **2024**, *146*, 35295–35304.
195. Ouyang, Y.; Shi, L.; Bai, X.; et al. Breaking scaling relations for efficient CO₂ electrochemical reduction through dual-atom catalysts. *Chem. Sci.* **2020**, *11*, 1807–1813.
196. Zheng, X.; Yang, J.; Wang, D. Advanced dual-atom catalysts for efficient oxygen evolution reaction. *EES Catal.* **2023**, *1*, 665–676.
197. Rasool, A.; Dar, M.A. Multistep screening of transition-metal-based homonuclear double-atom catalysts to unravel the electronic origin of their activity and selectivity challenges for nitrogen reduction. *Catal. Sci. Technol.* **2024**, *14*, 5687–5698.
198. Jafarzadeh, M.; Daasbjerg, K. Rational design of heterogeneous dual-atom catalysts for CO₂ electroreduction reactions. *ACS Appl. Energy Mater.* **2023**, *6*, 6851–6882.

199. Rasool, A.; Khanam, R.; Masood, K.; et al. Atomically dispersed Fe–TM pairs on g-C₆N₆: A comparative theoretical insight into heteronuclear dual-atom catalysts for N₂ reduction to form ammonia and urea. *J. Mater. Chem. A* **2026**, *14*, 10988–10999.
200. Xu, C.; Liu, L.; Zhang, X.; et al. Enhanced catalytic oxidation of benzene through the synergistic Pt–Ni bimetallic single-atom catalyst. *Chem. Eng. J.* **2024**, *480*, 148361.
201. Zhang, Y.; Song, X.; Chen, Z.; et al. Pt–Cu dual-atom pairs-triggering intermediate activation on single-atom catalysts for enhanced photothermal catalytic VOCs oxidation in cooking oil fumes. *J. Hazard. Mater.* **2026**, *501*, 140740.
202. Mars, P.; van Krevelen, D.W. Oxidations carried out by means of vanadium oxide catalysts. *Chem. Eng. Sci.* **1954**, *3*, 41–59.
203. An, Y.; Chen, S.-Y.; Zhou, L.; et al. Sintering resistance of Pd single atoms on steam-modified ceria: Deciphering the role of hydroxyl groups. *J. Mater. Chem. A* **2023**, *11*, 21285–21292.
204. Zhou, H.; Su, W.; Xing, Y.; et al. Progress of catalytic oxidation of VOCs by manganese-based catalysts. *Fuel* **2024**, *366*, 131305.
205. Luo, S.; Zhao, X.; Qu, Y.; et al. Insights into the full cycling of oxygen in VOCs oxidation on α -MnO₂: A NAP-XPS study. *Appl. Surf. Sci.* **2023**, *634*, 157506.
206. Zhang, J.; Zhang, L.; Cheng, Y.; et al. Construction of oxygen vacancies in δ -MnO₂ for promoting low-temperature toluene oxidation. *Fuel* **2023**, *332*, 126104.
207. Zhang, Z.; Tian, J.; Lu, Y.; et al. Memory-dictated dynamics of single-atom Pt on CeO₂ for CO oxidation. *Nat. Commun.* **2023**, *14*, 2664.
208. Gan, L.; Ye, P.; Wu, Q.; et al. Surface lattice oxygen activation and oxygen vacancies formation in Cu-doped CeO₂ for boosting catalytic oxidation of toluene. *Appl. Surf. Sci.* **2025**, *710*, 163999.
209. Wen, Y.; Wang, F.; Zhu, J.; et al. Revealing the structure-activity relationship of Pt₁/CeO₂ with ¹⁷O solid-state NMR spectroscopy and DFT calculations. *Nat. Commun.* **2025**, *16*, 3537.
210. Langmuir, I. The mechanism of the catalytic action of platinum in the reactions 2Co + O₂ = 2Co₂ and 2H₂ + O₂ = 2H₂O. *Trans. Faraday Soc.* **1922**, *17*, 621–654.
211. Kiani, D.; Wachs, I.E. Practical considerations for understanding surface reaction mechanisms involved in heterogeneous catalysis. *ACS Catal.* **2024**, *14*, 16770–16784.
212. Xu, T.; Shen, M.; Shen, G.; et al. On the deactivation and regeneration mechanisms of Pd/ θ -Al₂O₃ catalysts for propane oxidation. *J. Catal.* **2025**, *451*, 116380.
213. Wang, Z.; Zhong, W.; Jiang, J.; et al. Decoupling analysis of O₂ adsorption on Metal–N–C single-atom catalysts via data-driven descriptors. *J. Phys. Chem. Lett.* **2023**, *14*, 4760–4765.
214. Liu, L.; Yung, K.-F.; Yang, H.; et al. Emerging single-atom catalysts in the detection and purification of contaminated gases. *Chem. Sci.* **2024**, *15*, 6285–6313.
215. Jiang, Z.; Wang, Y.; Chen, C.; et al. Progress and challenge of functional single-atom catalysts for the catalytic oxidation of volatile organic compounds. *Chin. Chem. Lett.* **2024**, *35*, 109400.
216. Wang, L.; Huang, C.; Gao, Z.; et al. Recent research on the anti-poisoning catalysts in the catalytic oxidation of VOCs: A review. *Catalysts* **2025**, *15*, 234.
217. Wang, L.; Liu, W.; Song, S.; et al. Promotional effects of atomically dispersed Pt on titanium-doped SBA-15 for efficient low-temperature oxidation of benzene derivatives. *J. Environ. Chem. Eng.* **2025**, *13*, 116378.
218. Zhang, Q.; Li, G.; Liu, W.; et al. Constructing highly active zeolite encapsulated PdAg alloy catalysts for typical VOCs deep oxidation: The role of electron-structure interaction. *Appl. Catal. B* **2024**, *352*, 124051.
219. Zhang, H.; Guo, G.; Wang, Z.; et al. Superior performance of formaldehyde complete oxidation at ambient temperature over Co single-atom catalysts. *Appl. Catal. B* **2023**, *333*, 122774.
220. Chen, Y.; Zhang, S.; Yang, X. Interfacial adsorption and catalysis of single-atom Pt-loaded ZrO₂ surfaces for enhancing formaldehyde oxidation. *Surf. Interfaces* **2024**, *52*, 104871.
221. Ma, S.; Dong, F.; Wu, S.; et al. Silica-assisted Pt₁/CeO₂ single-atom catalyst for enhancing the catalytic combustion performance of VOCs by inducing H₂O activation. *Appl. Catal. B* **2024**, *354*, 124152.
222. Wu, L.; Deng, J.; Liu, Y.; et al. Enhanced removal efficiency of multicomponent VOCs over the Sn-doped Silicalite-1-supported Ru single-atom catalysts by constructing tightly coupled redox and acidic sites. *Appl. Catal. B* **2024**, *351*, 123910.
223. Fang, Y.; Han, X.; Liu, K.; et al. Current-assisted dual-atom catalyst sequentially boosts low-temperature propane combustion through atomic relay. *Nat. Chem.* **2026**, *18*, 445–456.
224. Tao, S.; Rao, C.; He, F.; et al. Single-atom Pd₁O₄Ce₂/CeO₂ catalyst with unique local fields for methane-catalyzed combustion. *J. Colloid Interface Sci.* **2025**, *685*, 1184–1194.
225. Wang, Y.; Liu, Z.; Wei, Y.; et al. Significant inhibition of secondary pollution in the catalytic oxidation of chloroaromatics over a bifunctional Ru₁/CeO₂ single-atom catalyst. *J. Mater. Chem. A* **2024**, *12*, 2949–2958.
226. Wang, M.; Jia, Z.; Ji, X.; et al. Highly levels of atomically dispersed Ru atom on CeO₂ from defects designing for promoted catalytic oxidation of chlorobenzene. *Sep. Purif. Technol.* **2025**, *362*, 131936.
227. Sun, T.; Zhou, X.; Li, X.; et al. Chlorine poisoning-resistant atomically dispersed Ru for low-temperature o-dichlorobenzene oxidation. *Appl. Catal. B* **2025**, *366*, 125035.

228. Zhong, Z.; Chen, M.; Huang, X.; et al. Design and synthesis of Pt/TiO₂ catalyst with abundant surface hydroxyl for formaldehyde oxidation. *J. Hazard. Mater.* **2025**, *487*, 137302.
229. Chen, L.; Li, K.; Xue, T.; et al. Efficient and durable oxidation removal of formaldehyde over layered double hydroxide catalysts at room temperature. *Environ. Sci. Technol.* **2024**, *58*, 10378–10387.
230. Zhang, Z.; He, G.; Li, Y.; et al. Effect of hydroxyl groups on metal anchoring and formaldehyde oxidation performance of Pt/Al₂O₃. *Environ. Sci. Technol.* **2022**, *56*, 10916–10924.
231. Liu, S.; Li, C.; Zachman, M.J.; et al. Atomically dispersed iron sites with a nitrogen–carbon coating as highly active and durable oxygen reduction catalysts for fuel cells. *Nat. Energy* **2022**, *7*, 652–663.
232. Chen, X.; Qin, Q.; Wang, J.; et al. Strong interaction between promoter and metal in Pd–Ba/TiO₂ catalysts for formaldehyde oxidation. *J. Colloid Interface Sci.* **2025**, *678*, 520–531.
233. Ge, S.; Wang, A.; Guo, Y.; et al. Supported noble metal catalysts for complete propane oxidation: Structure–activity relationships and reaction mechanisms. *Chem. Synth.* **2026**, *6*, 8.
234. Zhang, F.; Han, D.; Mantzaras, J.; et al. Surface kinetics and pressure dependence of propane oxidation over platinum. *Proc. Combust. Inst.* **2024**, *40*, 105228.
235. Zhao, H.; Liu, L.; Hao, Y.-D.; et al. Mediating the competitive adsorption of propane and oxygen via Pt–Sulfate synergy for enhanced propane combustion. *ACS Catal.* **2025**, *15*, 21054–21065.
236. Karatok, M. Activation of propane on Ag–PdO (101) model surfaces. *Turk. J. Chem.* **2025**, *49*, 609–615.
237. Ge, S.; Chen, Y.; Tang, X.; et al. Preformed Pt nanoparticles supported on nanoshaped CeO₂ for total propane oxidation. *ACS Appl. Nano Mater.* **2023**, *6*, 15073–15084.
238. Wang, S.-W.; He, Z.-H.; Tian, Y.; et al. Metal nitride-terminated metal oxides efficiently catalyzing CO₂ oxidative dehydrogenation of propane. *ACS Catal.* **2026**, *16*, 2375–2385.
239. Yang, X.; Li, X.; Huang, Y. Single-atom catalysis: A promising avenue for precisely controlling reaction pathways. *Front. Chem. Sci. Eng.* **2024**, *18*, 79.
240. Jing, Y.; Wang, Y. Heterolytic dissociation of H₂ and bond activation: Spotting new opportunities from a unified view. *Chem Catal.* **2023**, *3*, 100515.
241. Wang, Y.; Hu, P.; Yang, J.; et al. C–H bond activation in light alkanes: A theoretical perspective. *Chem. Soc. Rev.* **2021**, *50*, 4299–4358.
242. Li, J.; Li, G.; Tsang, S.C.E. Heterogeneous frustrated Lewis pair catalysts: Rational structure design and mechanistic elucidation based on intrinsic properties of supports. *Acc. Chem. Res.* **2025**, *58*, 555–569.
243. Fang, Y.; He, Y.; Liu, K.; et al. Synergistic ceria facets and Mo-engineered acidity in Pt/CeO₂ catalysts driving superior low-temperature propane combustion. *J. Rare Earths* **2025**. <https://doi.org/10.1016/j.jre.2025.12.017>.
244. Zhang, Z.; Kang, R.; Yi, X.; et al. Migration roles of different oxygen species over Cu/CeO₂ for propane and soot combustion. *Sep. Purif. Technol.* **2024**, *349*, 127820.
245. Tabakova, T. State of the art and challenges in complete benzene oxidation: A review. *Molecules* **2024**, *29*, 5484.
246. Song, S.; Zhang, S.; Zhang, X.; et al. Advances in catalytic oxidation of volatile organic compounds over Pd-Supported catalysts: Recent trends and challenges. *Front. Mater.* **2020**, *7*, 595667.
247. Zhang, L.; Xue, L.; Lin, B.; et al. Noble metal single-atom catalysts for the catalytic oxidation of volatile organic compounds. *ChemSusChem* **2022**, *15*, e202200356.
248. Ullah, L.; Munsif, S.; Cao, L.; et al. Hydrogen Co-Combustion of aromatic volatile organic compounds over Pd/Al₂O₃ catalyst. *Catalysts* **2024**, *14*, 563.
249. Gunton, A.L.; Jenkins, S.J. Chemical softness in aromatic adsorption: Benzene, nitrobenzene and anisole on Pt{111}. *J. Phys. Chem. A* **2024**, *128*, 6296–6304.
250. Morin, C.; Simon, D.; Sautet, P. Chemisorption of benzene on Pt(111), Pd(111), and Rh(111) metal surfaces: A structural and vibrational comparison from first principles. *J. Phys. Chem. B* **2004**, *108*, 5653–5665.
251. Sarma, B.B.; Maurer, F.; Doronkin, D.E.; et al. Design of single-atom catalysts and tracking their fate using operando and advanced X-ray spectroscopic tools. *Chem. Rev.* **2023**, *123*, 379–444.
252. Wang, S.; Wang, L.; Zhou, X.; et al. Design principles of single-atom catalysts anchored over porous materials for green catalysis and conversion. *Nano Res.* **2025**, *18*, 94907137.
253. Yu, X.; Deng, J.; Liu, Y.; et al. Single-atom catalysts: Preparation and applications in environmental catalysis. *Catalysts* **2022**, *12*, 1239.
254. Song, Y.; Liu, T.; Feng, W.; et al. Atomically dispersed Ru species induced by strong metal–support interaction for electrochemical methane reforming. *J. Am. Chem. Soc.* **2024**, *146*, 31825–31835.
255. Vu, G.H.T.; Phan, T.T.; Nguyen, T.H.; et al. A theoretical study of the oxidation of benzene by manganese oxide clusters: Formation of quinone intermediates. *Phys. Chem. Chem. Phys.* **2024**, *26*, 18629–18648.
256. Wu, Y.; Wang, A.; Zhang, Q.; et al. Regulation of oxygen vacancies in MnCO₃-based catalysts by thermally inducing for efficiently catalytic benzene combustion. *Sep. Purif. Technol.* **2025**, *354*, 128897.
257. Guo, H.; Guo, T.; Zhao, M.; et al. Improving benzene catalytic oxidation on Ag/Co₃O₄ by regulating the chemical states of Co and Ag. *J. Environ. Sci.* **2024**, *143*, 201–212.

258. Hou, Z.; Dai, L.; Liu, Y.; et al. Highly efficient and enhanced sulfur resistance supported bimetallic single-atom palladium-cobalt catalysts for benzene oxidation. *Appl. Catal. B* **2021**, *285*, 119844.
259. Jia, H.; Xing, Y.; Zhang, L.; et al. Progress of catalytic oxidation of typical chlorinated volatile organic compounds (CVOCs): A review. *Sci. of Total Environ.* **2023**, *865*, 161063.
260. Hevia, M.A.G.; Amrute, A.P.; Schmidt, T.; et al. Transient mechanistic study of the gas-phase HCl oxidation to Cl₂ on bulk and supported RuO₂ catalysts. *J. Catal.* **2010**, *276*, 141–151.
261. Bi, F.; Zhao, Z.; Yang, Y.; et al. Chlorine-coordinated Pd single atom enhanced the chlorine resistance for volatile organic compound degradation: Mechanism study. *Environ. Sci. Technol.* **2022**, *56*, 17321–17330.