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A dynamic ion-transport channel: Interface-controlled bulk oxygen spillover redefines metal–support interactions

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In supported metal catalysts, the contact between metal nanoparticles and oxide supports extends far beyond simple physical juxtaposition. The support can modulate the electronic structure, geometric configuration, and adsorption properties of the metal, while the metal, in turn, can induce defect formation, localized reconstruction, and redox fluctuations within the support. For decades, spillover has been recognized as a pivotal mechanism linking metal active sites to support functionalities. Traditional spillover research, however, has focused almost exclusively on the migration of hydrogen, oxygen, or other reaction intermediates along the exposed surfaces of the catalyst. For oxide supports, direct atomic-scale evidence showing whether bulk lattice oxygen can bypass surface pathways and directly enter metal nanoparticles through the internal metal-support interface has remained elusive. To precisely tailor reaction pathways involving spillover, a profound understanding of the holistic spillover process-including atomic-resolution visualization-is urgently required.

Wang and co-workers have recently addressed this knowledge gap by reporting an "interface-controlled bulk oxygen spillover" phenomenon in the Ru/TiO_2 system.[1] Utilizing in situ environmental transmission electron microscopy (ETEM) to track the oxygen spillover process in a Ru/TiO_2 catalyst, the researchers dynamically observed oxygen species migrating from within three to five atomic layers below the rutile TiO_2 (r-TiO_2) surface into Ru nanoparticles via the internal Ru/TiO_2 interface. As illustrated in Figure 1, in stark contrast to the conventional surface-initiated pathway where oxidation propagates from the exterior of the nanoparticle inward (top-down), this newly uncovered process exhibits a distinctive "bottom-up" layer-by-layer oxidation mode, with each newly grown RuO_2 layer nucleating at the interior Ru/RuO_2 interface. Crucially, when the support is switched from rutile to anatase TiO_2 (a-TiO_2), no such bulk oxygen transport occurs. This stark contrast demonstrates that bulk oxygen spillover is not dictated solely by the reducibility of the support, but by interfacial structural compatibility together with oxygen-vacancy migration and oxygen chemical-potential gradients. Furthermore, analogous behavior in Ru/SnO_2 and Ir/r-TiO_2 suggests that this non-classical spillover may extend to selected supported-metal systems featuring epitaxial interfaces. Its operation during CO oxidation and N_2O decomposition was directly verified via ETEM. These findings underscore that rationally engineered metal-support interfaces are highly instrumental in activating bulk lattice oxygen to accelerate catalytic turnovers.

Spillover is conventionally defined as the migration of active species between distinct functional sites. In the classical paradigm of hydrogen spillover, for instance, H_2 dissociates on metal nanoparticles, and the resulting hydrogen species subsequently migrate onto the surface of the oxide support. By precisely controlling the distance between metal and acceptor nanoparticles, Karim et al. demonstrated that the rate and effective range of hydrogen spillover depend heavily on the nature of the support; migration is rapid on reducible TiO_2 surfaces but severely impeded on non-reducible Al_2O_3 surfaces.[2] While such studies firmly established the vital role of support surfaces in spillover processes, the fundamental spatial picture has remained confined to species diffusing along exposed surfaces.

Parallel to this, since Tauster et al. introduced the concept of Strong Metal-Support Interaction (SMSI),[3] reducible oxide supports have been known to profoundly alter the state of supported metals. Classical SMSI manifests primarily as the migration of support species onto the metal surface upon reductive treatment, leading to the partial encapsulation of metal nanoparticles and the concomitant suppression of H_2 and CO chemisorption. Within this traditional framework, mass transport occurs predominantly across the external surfaces of the metal and support, whereas the buried internal metal-support contact zone has routinely been viewed as a static, closed structural boundary inaccessible to reactants.

The work by Wang et al. fundamentally reshapes this conventional view. In $Ru/r\text{-}TiO_2$, the internal metal-support interface is not a static or occluded boundary, but functions as a dynamic gateway capable of driving oxygen ion transport. Sub-surface lattice oxygen from the support migrates via oxygen vacancies to the $Ru/r\text{-}TiO_2$ interface and subsequently feeds the interfacial nucleation and bottom-up growth of RuO_2. This implies that even if gas-phase reactants cannot directly access the bottom of the metal nanoparticle, the internal interface can continuously supply active oxygen to the metal from the underlying bulk support. Consequently, the support transcends its traditional role as a mere structural scaffold or electronic promoter, acting instead as a participant in the catalytic cycle by serving as a three-dimensional oxygen reservoir.

The most design-relevant finding of this study is the pronounced divergence of bulk oxygen spillover across different TiO_2 polymorphs. In $Ru/r\text{-}TiO_2$, the RuO_2 formed upon oxidation establishes an excellent structural match with the rutile TiO_2 substrate, creating a well-aligned, continuous pathway for oxygen migration. In addition, r-TiO_2 exhibits lower subsurface oxygen-vacancy migration barriers and preferentially stabilizes surface vacancies, whereas a-TiO_2 shows higher barriers and favors subsurface vacancy trapping. A substantial lattice mismatch also exists between RuO_2 and anatase TiO_2. As a result, $Ru/a\text{-}TiO_2$ undergoes typical external surface oxidation, with no observable interfacial bulk oxygen transport.

In other words, oxygen vacancies supply the transport vehicles, the redox chemical potential gradient provides the driving force, and an epitaxially matched interface serves as the gateway for ion transport across the solid-solid phase boundary. This picture is supported by the reversible compression of the topmost r-TiO_2 layers, calculated oxygen-diffusion barriers of 0.7-1.5 eV, and the suppression of bottom-up oxidation after local interfacial collapse. These three elements therefore act cooperatively. Thus, the metal-support interface can be conceptualized as an ionic transport valve whose state is determined by vacancy dynamics, chemical potential, and structural compatibility. During CO oxidation, iBOT supplies and replenishes oxygen in RuO_2, whereas the Mars-van Krevelen mechanism describes the subsequent consumption of RuO_2 lattice oxygen by CO, as confirmed by isotope labeling.

Earlier in situ studies revealed dynamic Au/TiO_2 reorientation and metal-support coupling under redox conditions.[4] More directly, a previous study from Wang's group showed that epitaxial matching selects interface-initiated self-adaptive oxidation or surface oxidation in Pd/CeO_2, Ni/MgO, and Ru/CeO_2.[5] This established the interface as a regulator of where nanoparticle oxidation nucleates. The present Ru/TiO_2 study advances substantially by identifying where oxygen originates and how it moves: oxygen from three to five TiO_2 subsurface layers crosses a vacancy-mediated buried-interface channel with reversible lattice strain. By linking this non-local flux to chemical-potential gradients, CO oxidation, and N_2O decomposition, it extends interface engineering from oxidation-pathway selection to bulk oxygen transport and catalytic cycling.

The primary contribution of this work lies in the spatial expansion of the spillover paradigm. While traditional spillover emphasizes species migrating

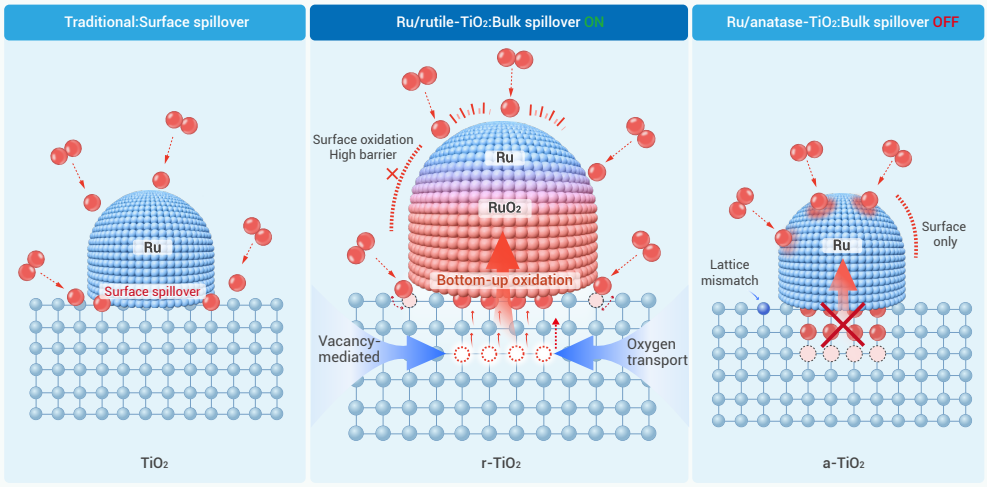


Figure 1. Shifting paradigms from surface oxygen spillover to interface-controlled bulk oxygen transport. (black circle, oxygen vacancy)

along surface planes from one site to another, bulk oxygen spillover demonstrates that subsurface layers deep within the support actively participate in mass transport. Consequently, the "effective reaction zone" of a catalyst is no longer confined to its exposed surface area; it extends to previously deemed inaccessible internal interfaces and sub-surface lattices.

Secondly, this study expands the functional definition of metal-support interactions. Beyond electronic transfer, nanoparticle stabilization, support encapsulation, or alterations in chemisorption, SMSI can now be understood as the interfacial control over selective, trans-phase ionic migration. From this perspective, the interface functions simultaneously as a catalytically active structure and a mass-transport manifold.

Thirdly, this work introduces a fresh set of design variables for catalyst engineering. Historically, the optimization of supported catalysts focused on metal identity, particle size, loading, support surface area, and oxygen vacancy density. These new insights dictate that we must also consider the lattice matching, interfacial orientation, defect continuity, and local strain adaptability between the support and the in situ-formed metal oxide phases during reactions. Manipulating these factors offers an unprecedented avenue to deliberately open or close transport channels for bulk support species into the active phase.

Nevertheless, several key questions warrant deeper exploration. First, the gas pressures and reactor scales characteristic of *in situ* environmental electron microscopy differ fundamentally from industrial fixed-bed conditions. Although the authors provided ambient-pressure experiments and isotopic evidence, it remains vital to quantitatively determine the exact contribution of bulk oxygen spillover to the overall reaction rate under real-world industrial operations. Second, although similar behavior was observed on multiple r-TiO_2 facets, under 1 bar air, and in Ru/SnO_2 and Ir/r-TiO_2, atomic-scale evidence remains limited to nanoscale particles and a small number of epitaxial metal-oxide interfaces; whether variations in particle size, interfacial orientation, and defect concentration alter or shut down these oxygen migration pathways remain to be elucidated. Finally, while epitaxial matching accelerates oxygen transport, excessive interfacial binding or overly rapid metal oxidation may alter the intrinsic properties of the active sites. Therefore, an optimal balance likely exists between the oxygen transport flux and the stability of the active phase.

Looking forward, integrating in situ microscopy with spatially resolved spectroscopy, transient isotope kinetics, and multiscale computational modeling will be essential to establish quantitative correlations among interfacial structures, oxygen fluxes, and catalytic rates. Ultimately, by leveraging facet-selective synthesis, epitaxial growth, defect gradient tuning, and interfacial strain engineering, researchers can transition from relying on the spontaneous, reaction-induced restructuring of materials to proactively designing targeted ion migration pathways.

Whether bulk lattice oxygen directly participates in supported metal catalysis has long been inferred primarily through indirect kinetic evidence. The "bottom-up" oxidation process discovered in the Ru/rutile-TiO_2 system offers direct, atomic-scale dynamic evidence of oxygen from the top three to five sub-surface layers crossing the buried interface to form RuO_2. More importantly, the vivid contrast between the rutile and anatase forms reveals that bulk oxygen migration is not an intrinsic property of all reducible supports, but a cooperative phenomenon dictated by oxygen vacancy migration, chemical potential gradients, and interfacial structural compatibility and adaptability.

This breakthrough transitions the metal-support interface from a traditional boundary for electronic tuning into a highly designable channel for ion transport. Future paradigms in supported catalyst design should expand beyond simply maximizing defect densities or strengthening generic interactions. Instead, the focus should shift toward engineering structurally continuous, dynamically stable interfaces endowed with precise ion-transport capabilities-adding a new dimension to our understanding and design of oxidation catalysis.

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AUTHOR CONTRIBUTIONS

Q. W. Li wrote the draft and helped draw the figure. K.T. Chen, J. J. Long, C. Rao helped polish the language. L. J. Han, Q. H. Zhou, Y. B. Zhang supervised and revised the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.