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Role of Bismuth Topological and Trivial Surface States in Molecular Adsorption

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Abstract

Topological materials have recently been proposed as a new class of catalysts, where robust surface states near the Fermi level are expected to influence adsorption and reactivity. In this paper, using first-principles calculations, we systematically investigate molecular adsorption on bismuth (Bi) slabs across a wide range of adsorbates, spanning both trivial and topological electronic regimes. We find that open-shell adsorbates strongly hybridize with both topological and trivial surface states, whereas closed-shell molecules mainly couple to bulk states. Although adsorption is primarily governed by conventional chemical bonding, we quantitatively assess how surface states modulate

binding energetics by comparing slabs (with surface states) to a monolayer. The COHP analysis further confirms that surface-state hybridization strongly reshapes the bonding and antibonding contributions near the Fermi level, thereby modulating adsorption energetics. This framework also qualitatively accounts for the distinct catalytic performance between bulk-like slabs and monolayer Bi. Overall, topological character appears to play a more indirect role, while a surface-state-centric perspective may provide a useful framework for understanding catalytic behavior.

Introduction

Topological materials^{1–7} have recently entered the catalysis field with a tantalizing premise: symmetry-protected surface or bulk states near the Fermi level may serve as unusually robust reservoirs for interfacial electron transfer, potentially stabilizing reaction intermediates and accelerating catalytic reaction kinetics.^{8–22} In the broadest view, this “topological catalysis” narrative proposes a catalytic lever distinct from conventional descriptors based on local coordination or *d*-band tuning, by emphasizing electronic structure features rooted in topology.^{23–25} Yet two key mechanistic questions remains unresolved: When an adsorbate binds, what happens to the surface states (topological or trivial) at the level of orbitals, hybridization, and chemical bonding? And, can one provably show that the topological state makes a significant (measurable) difference on catalytic processes?

These questions are difficult to address because, under realistic catalytic conditions, surface states do not exist in isolation but instead coexist with surface reconstruction, oxidation, and adsorbate-induced electronic rearrangement, all of which can strongly modify or obscure their signatures.²³ As a result, it remains unclear whether topology can still play a meaningful role in reactivity or whether its effects are largely overwhelmed by conventional chemical bonding. Resolving this issue therefore requires a platform in which (i) near-Fermi-level surface states are prominent and theoretically tractable, (ii) the same surface hosting these states also directly participates in adsorption and catalytic reactions, and (iii) the topological

character lies near a phase boundary and can be tuned with minimal changes to the chemical environment. Such a system enables catalytic trends to be directly linked to topological properties rather than to other chemical effects.

Bismuth offers a particularly suitable platform to investigate this problem. From a catalytic perspective, Bi-based electrodes are widely studied for selective electrochemical CO₂ reduction, ^{to formate} ~~often favoring formate production~~, because of their low toxicity, stability, and low cost.^{26,27} Atomically thin Bi derivatives, such as bismuthene, further enhance the sensitivity of catalytic behavior to surface electronic structure. Moreover, the strong difference in catalytic performance between thick Bi slabs and monolayers implies that the reactivity is highly surface sensitive and may be connected to the presence of topological or trivial surface states.²⁶ As we show in this paper, the Bi surface states can strongly modify the hybridization and bonding near the Fermi level, thereby reshaping the adsorption energetics of key reaction intermediates. From an electronic-structure perspective, elemental Bi hosts strong spin-orbit coupling and well-known metallic surface states whose details are highly surface- and structure-dependent.²⁸ Bi-based systems also sit close to topological phase boundaries and exhibit prominent near-Fermi surface-derived states, enabling comparisons between regimes with distinct surface-state character within a single material platform.^{29–31} Various approaches such as structure strain,^{32,33} Sb doping³⁴ or charge doping³⁵ are effectively to tune the topological character and surface states.

In this work, we use Bi as a model system to examine how surface states evolve during adsorption and whether topology leaves a measurable imprint on catalytic behavior. We show that (i) the chemically active states are the surface states themselves, making the distinction between topological and trivial surface states less important once adsorption occurs, even if the bulk topology remains intact; (ii) adsorption strongly reshapes these states through reconstruction and hybridization, which dominate the resulting electronic and bonding changes; and (iii) topology-related effects on reactivity are most likely to appear near critical regimes, where the surface electronic structure becomes highly sensitive to

adsorbates and external perturbations. By combining surface-state analysis with crystal orbital Hamilton population (COHP) bonding analysis, we further show that adsorption of open-shell adsorbates is generally influenced by hybridization between the adsorbates and Bi surface states, regardless of whether the states are topological or trivial. As a result, the overall adsorption differences between topological and trivial slabs remain relatively small. Nevertheless, several adsorbates, such as H^* and COOH^* , still exhibit noticeable deviations, indicating that topology-related surface-state effects can potentially influence some catalytic pathways and provide chemically measurable signatures. These results provide a chemically grounded picture of how surface states shape adsorption and catalytic behavior.

Results and Discussion

Electronic Topology of Bismuth and Slab Band Structures

Bismuth lies close to a $\mathbb{Z}_2$ topological phase boundary, such that modest structural perturbations can tune the trivial and topological ordering and alter the connectivity of surface states at high symmetry point.^{36,37} Fig. 1(a) summarizes the Bi atomic models used in this work. The Bi(111) structure is composed of buckled bilayers separated by a larger inter-bilayer spacing, which naturally produces surface-localized states on the outermost layers. Previous theoretical study showed that bulk Bi lies extremely close to a $\mathbb{Z}_2$ topological phase boundary and that its topological character is highly sensitive to lattice anisotropy: small variations of the structural ratio c/a can drive a band inversion and switch the $\mathbb{Z}_2$ invariant.^{36,37}

In this study, we use first-principles methods to explore how strain-tuned trivial and topological surface states influence molecular adsorption and catalytic behavior in Bi. Electronic structure calculations were performed within Kohn–Sham density-functional theory (DFT) using the Perdew–Burke–Ernzerhof (PBE) generalized-gradient approximation³⁸ with Grimme DFT-D3 van der Waals corrections.³⁹ Structural relaxations, adsorption calculations, and band-structure analyses were primarily carried out using QUANTUM ESPRESSO,^{40,41}

while electrochemical surface-charging calculations were performed using VASP.^{42–44} Bi(111) slabs were constructed from rhombohedral bulk Bi and separated by ^{How many Å?} sufficient vacuum to avoid spurious slab interactions. Adsorption geometries were optimized on multiple high-symmetry surface sites, and adsorption energies were evaluated from total-energy differences between the adsorbate–slab system, clean slab, and isolated molecule. Spin–orbit coupling was included using fully relativistic pseudopotentials from PseudoDojo⁴⁵ for single-point and band-structure calculations to accurately capture the Bi surface-state manifold near the Fermi level. Additional computational details, convergence parameters, slab constructions, and adsorption configurations are provided in the Supporting Information.⁴⁶

To model trivial and topological Bi slabs, we use the strain sensitivity of bulk Bi topology. We construct two representative slab structures: a *trivial* Bi slab using an in-plane 3% compressive strain, and a *topological* counterpart obtained by additionally applying a 3% tensile strain along the c direction relative to the trivial structure to mimic the c/a -driven topological switching. We also tested slabs with other strain values, which will be discussed later to assess the robustness of this comparison. The detailed structure and lattice parameters are provided in the Supporting Information.⁴⁶ The band structures of the trivial and topological 30-BL Bi slabs are shown in Fig. 1(b,c), with surface-localized states highlighted in red and bulk-like states in blue. The key difference appears near M, which is the surface projection of the bulk Brillouin zone high symmetry point, where a small gap controls the Z_2 character of Bi. In the trivial slab, the two surface states approach each other near M, but a small residual gap remains because the finite slab thickness allows hybridization between the two surfaces. This finite-size “crosstalk” effect is especially important in Bi because its surface states penetrate unusually deeply into the bulk.^{36,37} In contrast, the strained topological slab shows a different surface-state connectivity near M, consistent with a strain-induced change of the bulk Z_2 invariant. This strong finite-size effect is also useful for our later analysis, where comparisons between thicker slabs and monolayers help isolate surface-state contributions from other chemical effects as much as possible. Besides the different surface-state

connectivity, the overall band velocities remain comparable between the two slabs, indicating that strain does not strongly modify the global band dispersion. This further suggests that the direct chemical differences between the topological and trivial slabs are relatively small and therefore difficult to distinguish independently from surface-state effects.

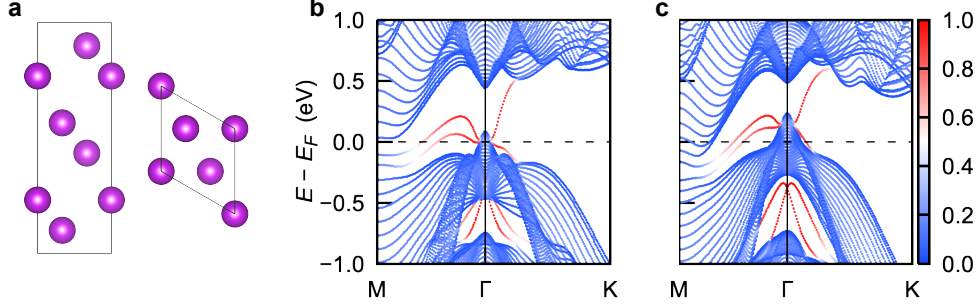


Figure 1: (a) The the side and top view of unit cell Bi. The 30-BL (b) trivial and (c) topological Bi slab band structure. The color-map red and blue highlight the surface and bulk domination.

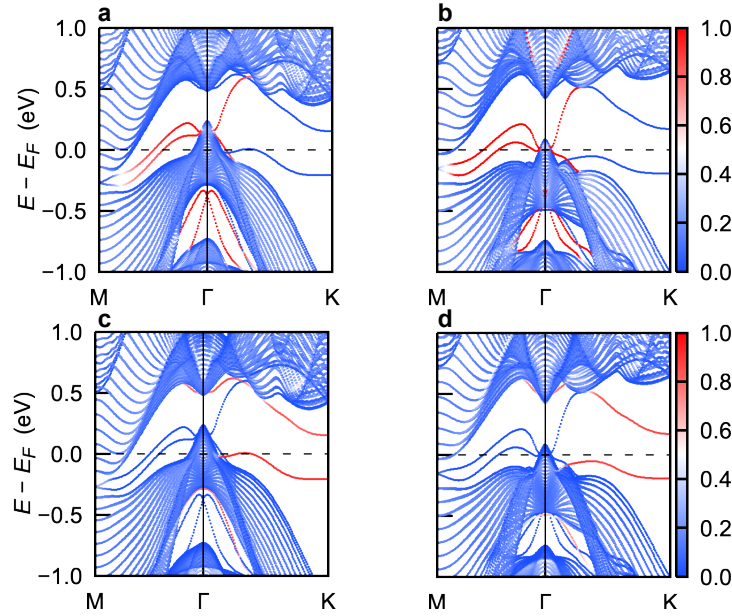


Figure 2: The (a) topological and (b) trivial band structure of Bi slab with H on top. The red-blue colormap indicates the relative dominance of surface (red) and bulk (blue) contributions. (c) and (d) The color-map red and blue highlight H atom and Bi atoms domination, respectively

Hybridization Between Adsorbates and Surface States

Having established the surface-state structure of the pristine slabs, we now examine how molecular adsorption perturbs this electronic manifold. In particular, we focus on how adsorbate states hybridize with surface states across different electronic regimes.

We begin with hydrogen as a minimal model system, as its single frontier state near the Fermi level provides a clean probe of how an adsorbate hybridizes with surface states without additional orbital complexity. Fig. 2 shows the projected band structures for a representative open-shell adsorbate (H) on topological and trivial slabs. In both regimes, H-derived states appear near E_F and hybridize with the surface-localized Bi bands on the adsorption side, leading to clear modifications of the surface-dominated dispersions. The corresponding atom-projected weights in Fig. 2(c,d) confirm that the states near the Fermi level acquire mixed H/Bi character, consistent with adsorption-driven orbital hybridization localized at the outermost bilayer. Importantly, the qualitative hybridization mechanism is similar in the trivial and topological slabs, motivating the central theme that local orbital alignment and bonding control adsorption more directly than the global topological classification. To further examine the role of topology, we also calculated the H adsorption energy under continuously varying strain across the trivial-to-topological transition of bulk Bi. As the strain increases and the system evolves toward the topological phase, the adsorption energy changes gradually rather than abruptly, indicating that the adsorption behavior evolves continuously across the topological phase transition. This trend, shown in the Supporting Information,⁴⁶ further supports the view that adsorption is governed primarily by continuous changes in the local surface electronic structure and hybridization, rather than by the topological classification alone.

para belongs to after-the-next

While H provides a representative example, we next examine how adsorption modifies Bi surface states more generally and which molecular features control the hybridization. A key factor is the presence of an unpaired electron: adsorbates (molecules or atoms) with a singly occupied state provide an open-shell frontier orbital that can strongly mix with Bi surface p

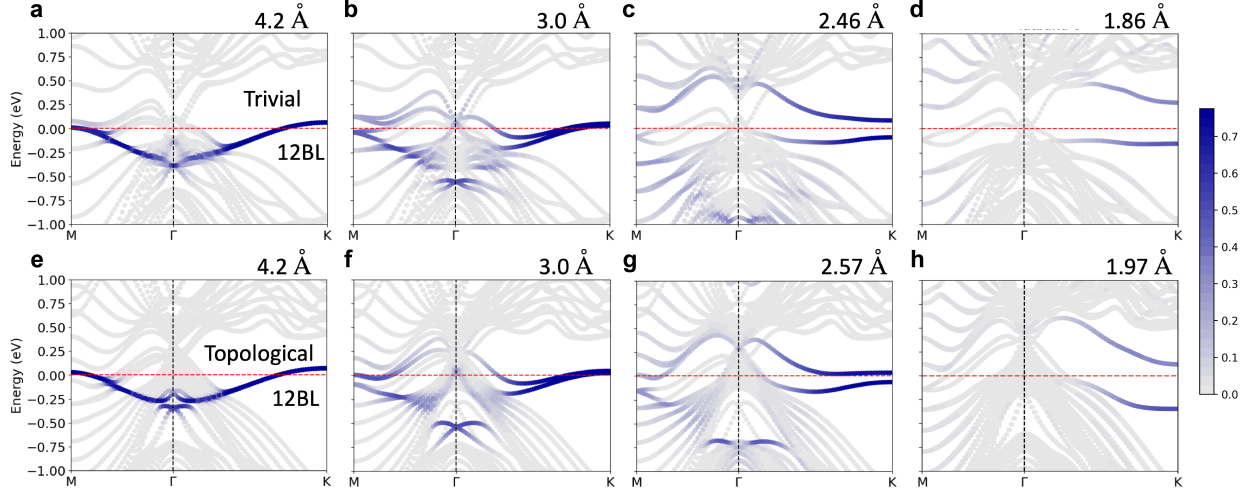


Figure 3: Band structures of hydrogen atom at different distances from the Bi slab, ranging from far from the surface to near the equilibrium adsorption position. (a-d) Trivial; (e-h) topological. The blue color indicates the relative dominance of the H atom (blue) and Bi (gray) contributions.

states near the Fermi level.

As the hydrogen atom approaches the Bi slab, its electronic states increasingly hybridize with the surface states of the slab (Fig. 3), regardless of whether the system is in the trivial or topological phase. This hybridization predominantly affects the top surface, where the H atom is adsorbed, leading to a clear modification and energy shift of the corresponding surface states. As a consequence, the spectral weight associated with the top surface becomes strongly mixed with the H-derived states, while the bottom surface states remain comparatively less perturbed. This effect is particularly evident in the trivial case, where the bottom surface states are more clearly resolved once the top surface states hybridize with hydrogen and shift away in energy. Overall, the adsorption of hydrogen induces an asymmetric modification of the surface electronic structure, effectively decoupling the top and bottom surface contributions.

While hydrogen illustrates the basic hybridization mechanism, it remains unclear whether this behavior is specific to a simple adsorbate or reflects a more general trend across different chemical species. We therefore extend this analysis to a broader set of adsorbates. This trend is general as shown in Fig. 4. For the open-shell adsorbates in panels (a)–(g) (CH_3O , $\dots$, N),

the singly occupied state hybridizes primarily with the top-surface states on trivial Bi slab. The blue color highlights the bottom-surface contribution, and we observe that because the top-surface bands are strongly perturbed by adsorption, the bottom-surface bands remain essentially intact and stay closed at the M point. The hybridization between atoms with topological Bi slab are shown in the Supporting Information, where similar trend is observed.

In contrast, for the closed-shell molecules in panels (h)–(l) (H_2O , $\dots$, CO_2), there is no open shell state near Fermi to hybridize with the top surface state. Then the top surface state still hybridize with the bottom one and opens the gap at M. This indicates that the Bi surface states can selectively interact with the open shell state in the molecule and potentially affect the chemical and catalytic process.

While the band-structure analysis reveals how adsorption modifies the electronic states, it does not directly quantify the underlying chemical bonding. To establish a more explicit connection between hybridization and bond formation, we analyze the Bi–adsorbate interaction using the COHP. The associated chemical-bonding picture is further quantified by the COHP analysis in Fig. 5, which decomposes the Bi–adsorbate interaction into energy-resolved bonding and antibonding contributions reconstructed from the first-principles electronic structure.^{47–49} For open-shell adsorbates carrying an unpaired electron (e.g., H, OH, and COH), the COHP exhibits a distinct **antibonding contribution** pinned near E_F . with only an antibond populate, the adsorbate would not bind. remark on the deeper bulk state that forms a bond Because these states are partially occupied, they contribute directly to the net bond order and indicate that the frontier (singly occupied) adsorbate-derived level hybridizes strongly with Bi surface states, producing a near- E_F antibonding component that is populated under adsorption. In contrast, for a closed-shell adsorbate such as CO, the COHP intensity at E_F is strongly reduced: the interaction is dominated by filled bonding states well below E_F and unoccupied antibonding states above it, consistent with weaker involvement of a singly occupied frontier level in the Bi-adsorbate coupling. We next examine whether these effects translate into measurable differences in adsorption energetics.

Isolating Surface-State Contributions to Adsorption Energetics

To disentangle the role of surface states from conventional chemical bonding, we compare adsorption on thick Bi slabs with that on a single bilayer (1 BL). The monolayer retains a similar local bonding environment but lacks the extended surface-state manifold present in thicker slabs, providing a useful reference system in which surface-state contributions are minimized. It is worth noting that monolayer Bi itself was predicted to be a two-dimensional topological material with edge states,^{50,51} however, these edge states are spatially distinct from the surface adsorption region considered in this work and therefore are not expected to play a significant role in the adsorption processes discussed here. We therefore use the monolayer not as a quantitative thickness limit, but as an idealized surface-state-free reference that isolates the effect of the additional slab-derived electronic channel. By contrasting adsorption energies between these two limits, we can isolate how the presence of surface-localized states modulates binding, independent of the underlying chemical interaction. This comparison therefore allows us to assess whether surface states play a decisive or secondary role in determining adsorption energetics.

We quantified how slab surface states modulate adsorption by analyzing binding energies through three derived metrics: (i) the *trivial-slab effect* relative to the monolayer,

$$\Delta E_{\text{triv}} = E_{\text{bind}}(\text{trivial slab}) - E_{\text{bind}}(\text{monolayer}), \quad (1)$$

(ii) the *topological-slab effect* relative to the monolayer,

$$\Delta E_{\text{topo}} = E_{\text{bind}}(\text{topological slab}) - E_{\text{bind}}(\text{monolayer}), \quad (2)$$

and (iii) the *topological-trivial contrast*,

$$\Delta E_{\text{topo.-triv.}} = E_{\text{bind}}(\text{topological slab}) - E_{\text{bind}}(\text{trivial slab}). \quad (3)$$

As shown in Fig. 6(a), the open shell adsorbates (left) exhibit a substantially larger variation in ΔE_{triv} than that of the close shell, suggesting that surface states can modulate adsorption energetics for open shell adsorbates. Fig. 6(b) shows that the variation difference between ΔE_{topo} between the open shell and close shell adsorbates are slightly less significant than that of the ΔE_{topo} in Fig. 6(a). When comparing the topological and trivial thick slabs directly in Fig. 6(c), we find that (with the exception of H and COOH) the remaining molecules exhibit comparable adsorption energies in the two regimes. Together, these results indicate that in general (across distinct species), the adsorption is influenced more by the presence of surface-localized states and their availability for orbital hybridization than by the global topological character (topological vs trivial) of the slab.

To further quantify this trend, we performed statistical analyses summarized in the Supporting Information.⁴⁶ We find that adsorption energies on both trivial and topological slabs show substantially larger molecule-to-molecule variability for open-shell adsorbates, while the direct difference between topological and trivial slabs is comparatively small.

These results show that the presence of surface states enhances the sensitivity of adsorption to the adsorbate electronic character, particularly for open-shell species, whereas the distinction between topological and trivial slabs plays a more secondary role. Overall, the adsorption behavior does not follow a simple universal trend across all adsorbates, but instead shows strong system-specific variations dominated by local orbital hybridization and bonding details.

Our results further provide a microscopic rationale for the experimentally observed degradation of catalytic performance with increasing Bi slab thickness.²⁶ Under experimentally relevant conditions without externally applied strain, thick Bi slabs are generally expected to remain in the trivial regime. Experimentally, the CO₂ reduction activity decreases substantially as the Bi thickness increases from monolayer to bulk-like slabs, which is consistent with our calculations showing that thick Bi slabs bind key intermediates such as COOH* and COHO* more weakly than the monolayer ~~case~~ (red columns in Fig. 6a). Within our

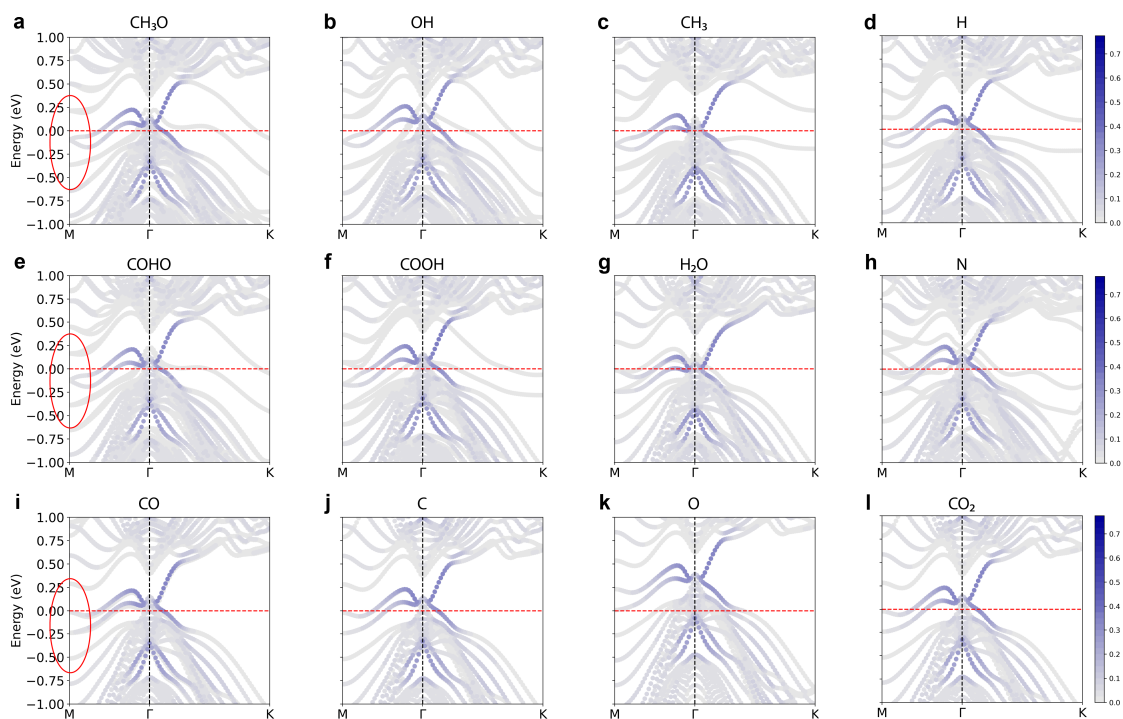


Figure 4: Projected band structures of the trivial Bi slab (12 BL) with various molecule or atoms adsorption. The blue color indicates the relative dominance of bottom surface (blue) and bulk (gray) contributions.

framework, the more localized surface states in thicker slabs promote antibonding contributions near the Fermi level, making adsorption less favorable and reducing stabilization of important intermediates. [invert after "This can": be accompanied by an increased barrier to the first reduction step of CO₂ \(by BEP principle\), and](#) [This can](#) hinder subsequent reaction steps and lower the overall catalytic activity. In contrast, monolayer lack these surface states and therefore support more favorable adsorption. [These results suggest that the key role of surface states is to mediate hybridization between the adsorbates and the Bi surface, thereby reshaping adsorption and catalytic behavior.](#) [We should remind the reader that most of the adsorption is controlled by bulk states. It would be good to show where those states are in the band structures.](#)

Although the overall adsorption differences between the topological and trivial slabs are generally small, [we still identify several notable outliers, particularly H* and COOH*, as shown in Figure 6\(c\).](#) In these cases, the topological slab binds both intermediates more strongly than the trivial slab. Such changes may alter the CO₂RR reaction pathway by stabilizing H* and COOH*, potentially suppressing the formation of COHO* while enhancing the competing hydrogen evolution reaction (HER). These adsorbate-specific deviations

[What I miss in this discussion is whether or not the orbital origin of the triv and topo states is any different. If they are the same orbitals, then the difference can be more due to strain than states being topo. If they are different orbitals, then it is a principally different bond type, which is more interesting.](#)

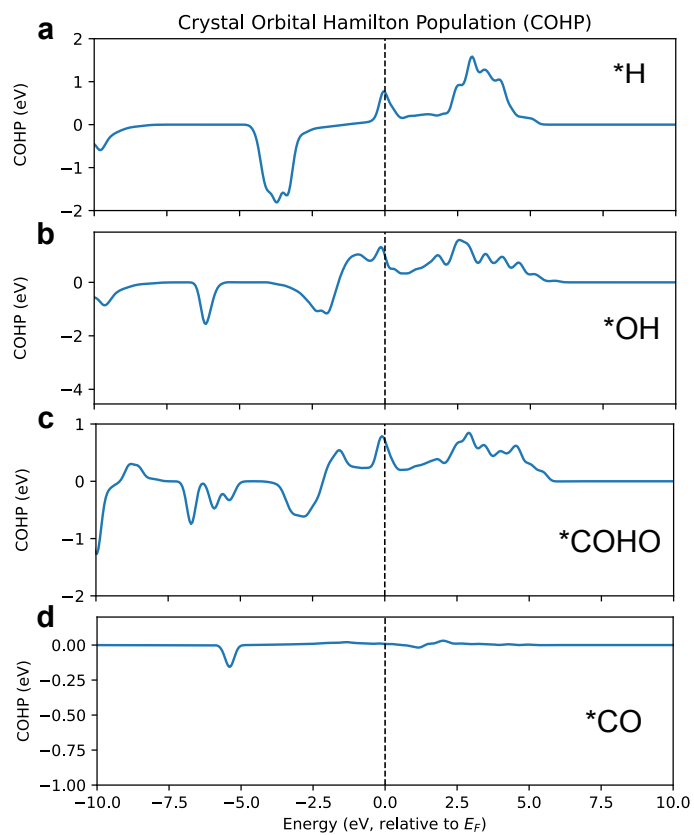


Figure 5: The COHP analysis for the H, OH, COHO, CO molecules adsorbed on Bi slab.

outline the area on these plots corresponding to interaction with the surface states.
Ideally, accompany these by projected DOS plots showing individual orbital contributions of Bi to these interactions.

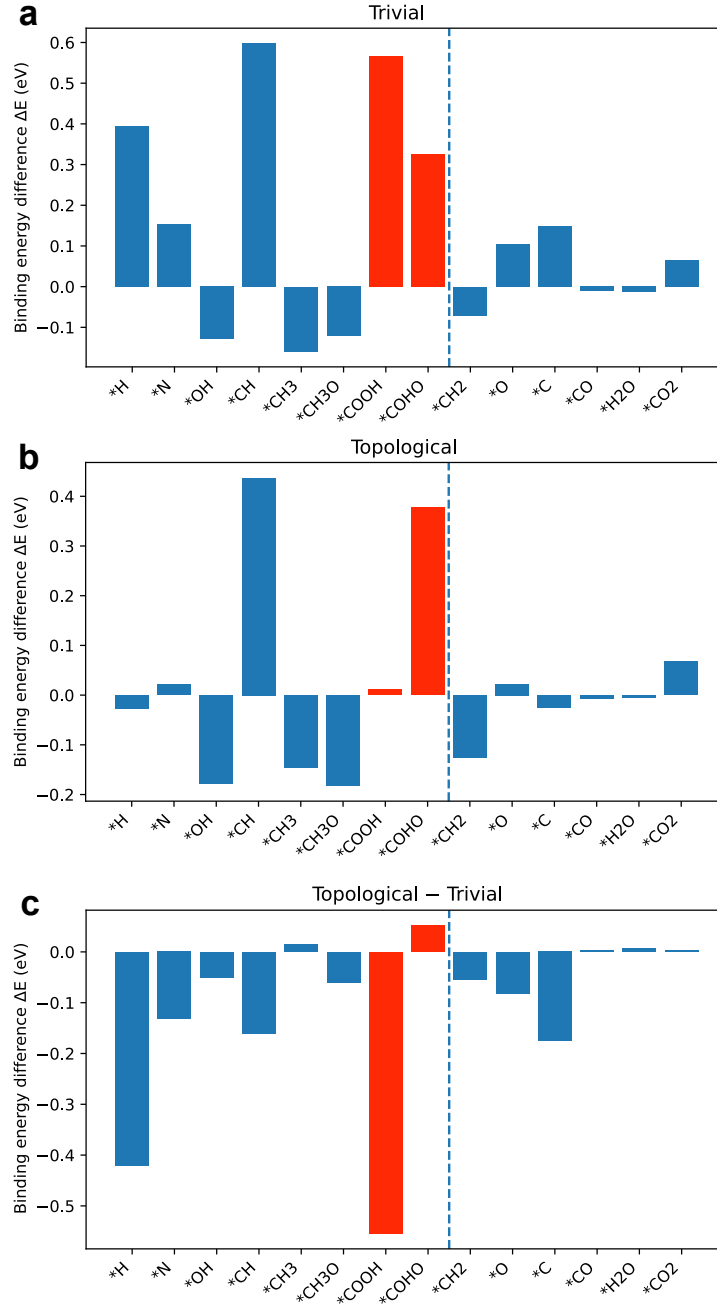


Figure 6: The binding energy difference between the monolayer (1 BL) and trivial (a); topological (b) bulk (12 BL) for different molecules or atoms. (c) The binding energy difference between topological and trivial Bi slab. The red color highlight the median product *COHO, *COOH in CO₂ reduction reaction.

therefore provide a potentially observable experimental signature of topology-related surface-state effects, even though the overall adsorption trends between topological and trivial slabs remain relatively similar.

Robustness under Surface Charging

To verify that the adsorption-induced modifications discussed above are not simply a consequence of what do you mean? You did not charge the slab so far. electrostatic charging, we examine the response of Bi surface states under an applied electrochemical bias. This provides a baseline for comparison and allows us to distinguish intrinsic adsorption effects from purely electrostatic perturbations.

We model the electrified interface by introducing a net surface charge ΔN_e within an implicit electrolyte environment, which stabilizes the system via a compensating counter-charge. In practice, we perform self-consistent calculations over a range of electron-rich and hole-rich conditions while keeping the atomic structure fixed, thereby isolating the electronic response of the surface states.

reference which figures in SI. State here what potential range was explored. Why did you go so far in the cathodic but so little in the anodic? Also, in the SI figures, state whether it is SHE or RHE reference

The corresponding electrode potential is obtained from the work function $\Phi = V_{\text{vac}} - E_F$ and converted to the standard hydrogen electrode scale.⁵² Across the explored potential window, the surface-localized bands remain clearly identifiable in both trivial and topological slabs (See Supporting Information). Charging primarily induces an energy shift of the surface-state manifold relative to bulk states, with minimal change in their dispersion or character, consistent with an adiabatic evolution under bias.

you may discuss the contrast with the surface charging result we had for Bi₂Te₃ in <https://pubs.acs.org/doi/10.1021/acs.jpcclett.4c00064>

This behavior contrasts sharply with the adsorption-induced effects discussed above. While electrochemical charging preserves the structure of the surface-state manifold, adsorption, particularly for open-shell adsorbates, leads to strong hybridization, asymmetric modification of top and bottom surface states, and in some cases a closing of the finite-size gap at the M point.

These results serve as a crosscheck that the band-structure changes observed upon adsorption are not driven by simple charge transfer, but instead arise from genuine orbital

hybridization. At the same time, the resilience of Bi surface states under bias implies that they remain electronically accessible under realistic electrochemical conditions, supporting their potential role in catalytic processes.

Conclusion

In summary, Bi provides a particularly suitable model system for disentangling the role of topological surface states in catalysis. Its near-Fermi-level surface states are both prominent and theoretically tractable, while the same Bi surfaces are directly relevant to catalytic reactions such as CO₂RR. In addition, bulk Bi lies close to a strain-tunable topological phase boundary, allowing comparisons between trivial and topological regimes with only minimal changes to the underlying chemical environment. This combination makes Bi an ideal platform for separating topology-related effects from conventional chemical bonding contributions during adsorption and catalysis.

The molecular adsorption on bismuth reshapes the near-Fermi-level electronic structure through orbital hybridization and surface reconstruction. contrast twice in the sentence. rephrase. In contrast, electrochemical charging largely preserves the surface-state dispersion and produces mainly rigid energy shifts, whereas adsorption induces stronger perturbations, including band reconstruction and breaking the coupling between the top and bottom surface states. In this regime, the chemically active states are the surface states themselves, and the distinction between topological and trivial surface states becomes effectively blurred in practice, even though the bulk topological character remains formally preserved.

This molecular adsorption behavior depends on the electronic character of the adsorbate. Open-shell species have frontier states near the Fermi level and couple strongly and selectively to the surface manifold, while closed-shell molecules interact more weakly and more symmetrically. Because adsorption itself substantially reshapes the surface states through hybridization, the modified surface electronic structure can in turn feed back into the ad-

sorption energetics. COHP analysis supports this picture by showing that surface-state hybridization strongly modifies the balance between bonding and antibonding contributions near the Fermi level.

Comparisons between slabs and monolayers further confirm that surface states can modulate adsorption energetics, with a more pronounced effect for open-shell adsorbates. However, adsorption remains primarily controlled by local orbital alignment and bonding, with surface states providing an additional hybridization channel. how do you know? you did not study binding upon charging. The same trends persist under electrochemical bias, indicating relevance under realistic conditions. This picture is consistent with the experimental trend that increasing Bi slab thickness is accompanied by reduced catalytic performance. Our results show that stronger surface-state hybridization in thicker slabs introduces additional antibonding contributions, making adsorption of key intermediates such as COOH* and COHO* less energetically favorable. At the same time, certain adsorbates, particularly H* and COOH*, still show measurable differences between topological and trivial slabs. These selective deviations may serve as experimentally accessible signatures of topology-related surface-state effects on competing reaction pathways such as CO₂RR and HER. Such effects are likely to be most pronounced near topological phase transition critical point, where the electronic structure is highly sensitive and competing chemical contributions can be more clearly separated. In this limit, adsorption becomes more selective toward species whose frontier orbitals couple strongly to the surface states, such as open-shell adsorbates, and may be further tuned by external factors such as bias or strain that enhance or suppress specific reaction pathways.

More broadly, our findings provide a practical framework for understanding and searching for topological catalysts. Rather than treating topology itself as a direct catalytic mechanism, this is not a quantity you are describing. also, topology is not a mechanism. this sentence is very wrong. our results indicate that the key quantity is how surface states participate in adsorption-driven hybridization and bonding. This perspective connects topological electronic structure with conventional surface chemistry, and may help guide the design of catalytic materials in which surface-state hybridization can be selectively controlled through adsorbates, strain,

dimensionality, or external bias.

Acknowledgement

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