

Recent Developments in Revealing the Impact of Complex Metal Oxide Reconstruction on Catalysis

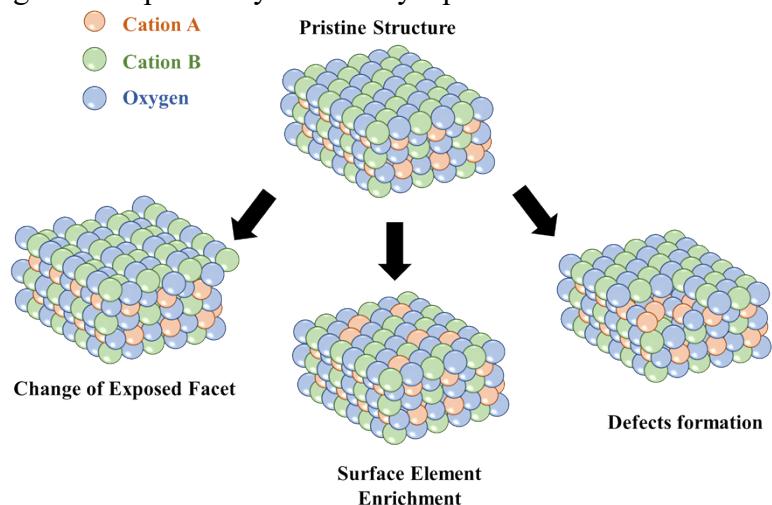
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Often, in catalysis, it is difficult to reconcile why catalysts with the same elemental composition present vastly different catalytic performance. When the catalysts under study are supported metal nanoparticles (NPs), one can pinpoint electronic and bonding properties that influence reaction intermediates by looking at the characteristics of the NP (e.g., size, facet exposed, shape). The advancement of *in situ* characterization techniques has enabled to capture dynamic changes of NPs during reactions, offering a more accurate depiction of active phases. For complex metal oxide catalysts, characterization of the top monolayer of the catalyst particle, beyond only characterizing the bulk, is needed to elucidate structure-performance relationships. Commonly, the interface where reactions occur experiences structural evolution. This results in surface composition that deviates from the stoichiometry present in the bulk phase, underscoring the need for top-surface sensitive characterization. When characterization of non-ideal surfaces is attained, differences in catalytic performance can be elucidated more accurately by gaining a detailed understanding of the topmost layer of catalyst particles.



Scheme 1 Surface reconstruction of complex metal oxide under different treatment conditions.

Surface reconstruction of complex metal oxides refers to the alterations of the topmost catalyst surface, relative to the bulk structure, following exposure to pretreatment or reaction conditions during heterogeneous catalysis.¹ This structural and electronic transformation may involve: 1) changes of the exposed crystallographic facets, 2) changes in chemical composition, such as the enrichment of specific elements; and, 3) morphological variations, including surface roughness and defects (as illustrated in **Scheme 1**). Beyond relaxation, surface reconstruction here also encompasses disruptions to the periodicity of the sublayers and changes to its stoichiometry. This change significantly influences the chemical properties of the catalyst surface, such as redox sites², acid/base pairs, hydroxyl groups,³ and surface defects. Surface reconstruction occurs due to the thermodynamic drive to lower the surface energy of the catalyst under the surrounding environment (e.g., temperature, chemical potential of species present). In addition to the treatment or reaction conditions, the extent of reconstruction also depends on the elements in the metal oxide structure. For instance, annealing ABO₃ perovskites (SrTiO₃, BaTiO₃, and BaZrO₃) at high temperatures (500 °C) in O₂ has very different impact on the A/B ratio at the surface (ranging from 0.9 to 2.5), depending on the identity of A and B.⁴ Metal oxide surface reconstruction under an electric field and exposure to acidic and alkaline media has recently gained increased attention in electrocatalysis, such as in the oxygen evolution reaction (OER);^{5, 6} however, in this Viewpoint we focus on the impact of surface reconstruction on thermal catalysis, a critical enduring research theme with ongoing challenges. We start showcasing approaches to characterize surface reconstruction at the topmost surface layer, such as low-energy ion scattering (LEIS), discussing advantages and limitations. Next, we connect characterization of surface reconstruction to site-specific kinetic analysis, enabled via steady-state isotopic transient kinetic analysis (SSITKA), and we express our viewpoint on building structure-performance relationships by deeply understanding reconstructed surfaces. Later, we comment on the potential of tuning surface reconstruction to enhance catalytic performance. Finally, we explore the interplay between surface reconstruction and the “intelligent behavior”.

1. Characterization of surface reconstruction: advances and challenges

Obtaining a clear understanding of surface reconstruction remains challenging despite significant advancements in modern characterization techniques. One challenge stems from the inherent complexity of complex metal oxides,⁷ including mixed valence of metal ions, complex coordination environments, defects (e.g., oxygen vacancies, step sites), interactions between different metal components, and acid or base sites with different strength and density. Another difficulty arises from the fact that the topmost layer comprises a small fraction of the overall solid particle composition, thus, bulk characterization techniques fail to reveal characteristics of the topmost catalyst surface. For instance, in the case of X-ray absorption spectroscopy (XAS), for a non-doped ABO₃ perovskite, the features of A or B at the very top-surface are overwhelmed by the bulk signal. Adding to this challenge, reconstruction can occur during pretreatment (e.g., oxidative/reductive atmospheres), during reactions or during characterization. Moreover, such a structural change can be reversible upon removal of the environmental conditions that promote the transformation; therefore, *in situ* characterization is preferred and *operando* characterization is ideal. *Ex situ* characterization can still be useful if other evidence suggests that the reversibility of reconstruction is negligible during *ex situ* sample transfer. By addressing (or mitigating) these challenges, a clearer understanding of surface reconstruction in complex metal oxides can be achieved.

Due to the complexity of surface reconstruction, a synergistic combination of different characterization techniques is needed to decipher its impact on catalysis. Several characterization techniques have been used to study the morphology, elemental composition, and bonding environment of the rearranged surface,⁸ including high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), X-ray photoelectron spectroscopy (XPS), UV Raman spectroscopy, and LEIS. In our work,^{4, 9-11} LEIS has been heavily employed to study surface composition. A crucial requirement for characterizing surface reconstruction is high spatial resolution, which is determined by the nature of the characterization probe. Typically, X-ray and UV lasers used for XPS and Raman spectroscopy have a penetration depth of several nanometers,¹² and ~ 1 nm in the best cases,^{7, 13, 14} which is deeper than a few top-surface monolayers. In contrast, LEIS characterization offers much higher surface sensitivity, probing only the topmost atomic layer of the sample. The penetration depth can be as low as ~ 0.3 nm,¹⁵ which avoids interference from bulk properties or overlooking monolayer-thick reconstruction. The full depth profile can extend to around 10 nm,¹⁶ thus making it possible to obtain a complete elemental distribution from top-surface monolayer to bulk phase. In a previous work, we showed that independent from the synthesis method and extent of surface reconstruction, for a set of SrTiO₃ (STO) samples, the composition of sublayers can be correlated with the composition of the topmost layer, suggesting that sublayer rearrangement occurs to stabilize top-surface reconstruction (**Fig. 1**).¹¹ Thus, XPS and Raman spectroscopy can still provide useful information regarding surface reconstruction, as the signal from a few monolayers below the surface can potentially reveal insights into features at the top-surface (**Fig. 1**).

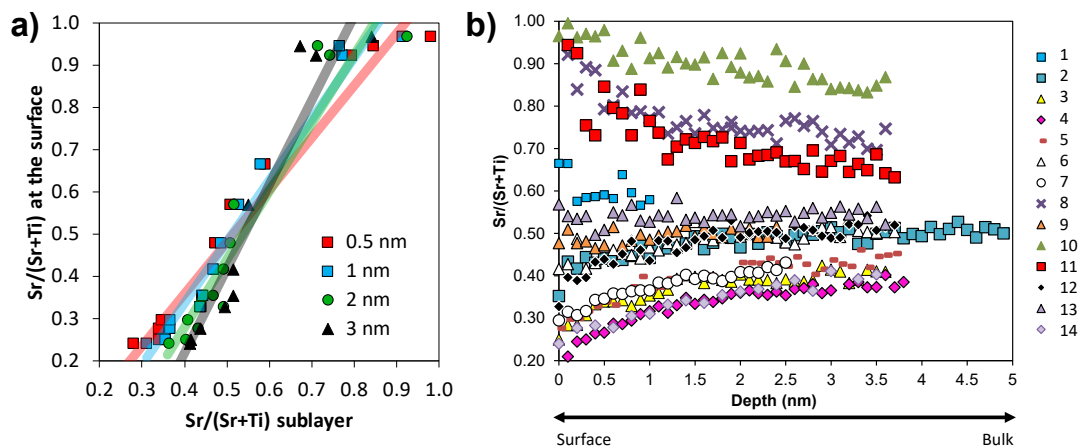


Fig. 1 LEIS characterization: **a)** Correlation between the concentration of Sr at the top-surface of the catalyst and the concentration at the subsurface at different probing depths for various STO samples. **b)** Surface and subsurface Sr concentration as a function of probing depth. The numbers in the legend refer to STO samples reconstructed differently (details in ref ¹¹). Reprinted with permission from ref ¹¹. Copyright 2018 American Chemical Society.

Despite the outstanding surface sensitivity of LEIS, this technique can present limitations distinguishing signals from metal elements with similar atomic weight and size (e.g., Sr and Zr in SrZrO₃) and the measurement still need to be applied under vacuum conditions after pretreatment, which could induce new reconstructions. To get complementary information, one can use probe molecules to indirectly titrate chemical properties (e.g., density of surface sites, acidity and basicity, affinity to reactants or products) of the surface. The interaction of probe molecules with

the surface is then monitored using techniques such as Fourier transform infrared (FTIR) spectroscopy, temperature-programmed reduction/oxidation/desorption, or microcalorimetry. Since acid and base centers play important roles in many catalytic transformations, probe molecules such as NH_3 , pyridine, CO_2 , SO_2 are commonly used to identify the types and strength of sites as well as their density. However, in most cases, the use of probe molecules is incapable of providing information under *operando* conditions, resulting in partial conclusions.

STEM is another powerful tool to characterize non-ideal surfaces. Defect sites, such as steps and corners, can be visualized. Further, their relative abundance can be correlated with catalytic kinetic studies. Moreover, STEM equipped with energy dispersive X-ray spectroscopy (EDX) or electron energy loss spectroscopy (EELS) capabilities can achieve elemental mapping along or perpendicular to the surface, offering complementary evidence to LEIS. Besides, atomic force microscopy (AFM) can provide 3D visual characterization of morphological changes occurring due to surface reconstruction,¹⁷ provided that the sample does not present an extremely irregular morphology. Other microscopy techniques, such as scanning tunneling microscopy (STM), are restricted to electrically conducting samples¹⁸. Therefore, the use of AFM and STM, requiring immobilized flat surfaces, is difficult for powder samples. It is worth noting that the advancement of *in situ* STEM and Environmental Transmission Electron Microscope (ETEM)¹⁹ allows observing catalyst surface changes under conditions closely resembling real operating scenarios. Surface reconstruction on TiO_2 ²⁰ and CeO_2 ²¹ has been visualized with ETEM under oxidative atmosphere. Recently, surface reconstruction of perovskites, $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ and $\text{Pr}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$, has been revealed by ETEM under high vacuum and in the presence of O_2 and H_2O ²². When characterizing reconstructed complex metal oxide surfaces via microscopy, finding the perfect orientation of powder samples for analysis can be extremely challenging, particularly for large metal oxide particles. Furthermore, it is possible that the information obtained is highly localized and is not representative of the entire catalyst particle. Despite these limitations, STEM can provide valuable input for constructing computational models for *ab initio* calculations that resemble (to the extent feasible) non-ideal surfaces. Density functional theory (DFT) can be used to provide insights into what is the main reaction pathway and what are the active sites, but the relevance of such input relies on a feedback loop with surface characterization and kinetic analysis, so that a congruent picture of the catalytic cycle is portrayed.

2. Deciphering active sites and intrinsic activity of reconstructed surfaces

In the field of heterogeneous catalysis, a fundamental goal is to decipher the relationship between structure and performance, which involves pinpointing the active sites and ascertaining their impact on the rate-determining step (RDS). In the context of surface reconstruction, the properties of the active sites can change and significantly impact catalytic performance. Polo-Garzon et al.⁹ tailored the surface termination of SrTiO_3 (STO) via thermal and chemical treatments to tune the selectivity between dehydration and dehydrogenation during the conversion of 2-propanol. Prolonged exposure to an oxidative atmosphere at high temperatures resulted in a Sr-enriched surface, which exhibited a high selectivity towards the dehydrogenation pathway, producing acetone. Conversely, a Ti-terminated surface, induced by acid etching, favored the dehydration of 2-propanol to propene. In this study, the nature of the sites post-reconstruction was qualitatively characterized using LEIS and FTIR. However, quantifying the exact number of active sites is a formidable challenge, albeit one that is crucial for a comprehensive kinetic analysis of the reaction.

Typically, to estimate rates per site, rates of reactant consumption or product formation are measured per gram of catalyst and normalized by the density of adsorption sites on the catalyst. These adsorption sites are commonly assessed *in situ* but not *in operando* (sites are characterized before or after the reaction occurs, not while the reaction occurs) using characterization techniques such as pulse chemisorption, temperature-programmed protocols, FTIR, or adsorption microcalorimetry. These titration techniques can provide information on available adsorption sites, which are not necessarily the active sites under reaction conditions. Therefore, their use for characterization of active sites must be done with care. For example, NH₃-TPD is a widely implemented technique to characterize acid sites of varying strength (based on desorption temperature) and density. However, it can be challenging to distinguish and quantify the weak or medium-strength acid sites.²³ Moreover, this technique cannot precisely distinguish between Lewis and Brønsted acid sites, and desorption temperature is an indirect descriptor of adsorption strength. Lastly, there could be surface reconstruction induced during the TPD experiment, resulting in new surface properties. For instance, CO₂ is a commonly used probe molecule for basic site titration in TPD characterization; however, it can also act as an oxidative agent and potentially oxidize a reduced surface formed during pretreatment at high temperature. Similar limitations can exist for titration using other probe molecules. Thus, it is necessary to employ a combination of multiple characterization techniques to attain unbiased understanding of the reconstructed surface.

Adsorption microcalorimetry can reveal information regarding the dependence of adsorption energy with surface coverage of probe molecules. The variation of adsorption energy with surface coverage can imply the existence of adsorption sites with different strengths or the existence of “packing” effects as the surface gets more and more populated with adsorbates.²⁴ Surface reconstruction can directly affect the acid/base properties of the surface. FTIR spectroscopy during adsorption/desorption of probe molecules is a powerful technique for differentiating Lewis and Brønsted adsorption sites, as characteristic peaks arise from different vibrational modes of adsorbed probe molecules. The red or blue shifts of these peaks for similar types of sites can indicate changes in bonding strength. Additionally, site density can be determined by carefully measuring the integrated molar extinction coefficients using model catalysts with highly uniform active sites.²⁵ Nonetheless, this spectroscopic method requires samples with low light absorption properties, restricting the characterization of dark samples. Considering the above statements, a prudent strategy for site titration and quantification would involve combining two or more characterization methods. For example, one could use NH₃ TPD to quantify overall acid sites and then employ FTIR with probe molecules to differentiate site types.

Although titration of sites may provide useful information, if the conditions of titration are very different from those of the catalytic reaction, conclusions can be limited. For instance, the coverage of adsorbates generally decreases with increased temperature, even without considering the competitive adsorption of reactants and products. Foo *et al.*⁴ measured the FTIR spectra for pyridine (150 °C) and CO₂ (25 °C) adsorption over SrTiO₃, BaTiO₃, SrZrO₃, and BaZrO₃. It was found that in some cases the titratable surface sites can reduce to only 20-30 % if the adsorption temperature is increased to 300 °C. Consequently, normalizing the reaction rate based on site density measured at ambient conditions leads to an underestimation of turnover frequency (TOF) per active site. Accounting for competitive adsorption of reactants/products, the coverage of active sites by reactants could further decline. In an effort to titrate active sites under reaction conditions, one can introduce a poison agent with a strong affinity to acid or basic sites while the catalytic reaction proceeds at a steady state. For example, ammonia (NH₃), 6-di-tert-butylpyridine (DTBP),

and triphenylphosphine (TPP)²⁶ are often employed as base molecules for titration and the poisoning of acid sites, whereas carbon dioxide (CO₂) and sulfur dioxide (SO₂)²⁷ are predominantly utilized for covering basic sites. During steady-state catalytic conversion with unadulterated reactants, a switch to an identical feed containing a poisoning agent will provoke a drop of activity, followed by a gradual attainment of a new steady state, as depicted in **Fig. 2** for ethanol dehydrogenation to acetaldehyde. NH₃ binds to both Lewis and Brønsted acid sites, whereas DTBP selectively binds to Brønsted acid sites. The decrease in activity upon the introduction of NH₃ highlights the pivotal role of acid sites in ethanol dehydrogenation. The invariable reaction rate upon introduction of DTBP shows that Brønsted acid sites are not involved in the reaction, and rather, Lewis acid sites are. Adsorption microcalorimetry experiments were performed to assess the adsorption strength of NH₃. Although the presence of acid sites, where NH₃ adsorbs, is confirmed, caution must be taken when relating adsorption strength measured via *in situ* microcalorimetry to poisoning during the catalytic run. Information about the reversible adsorption of probe molecules on active sites can be obtained by repeating the microcalorimetry measurements with adsorption-desorption cycles. For fully reversible adsorption, not only the density of adsorption sites but the distribution of adsorption energy with surface coverage should be recovered. Besides, the chemical potential of species under the catalytic reaction can affect the reversible adsorption of the poisoning agent, further, the adsorption strength can be affected by competing adsorbates.

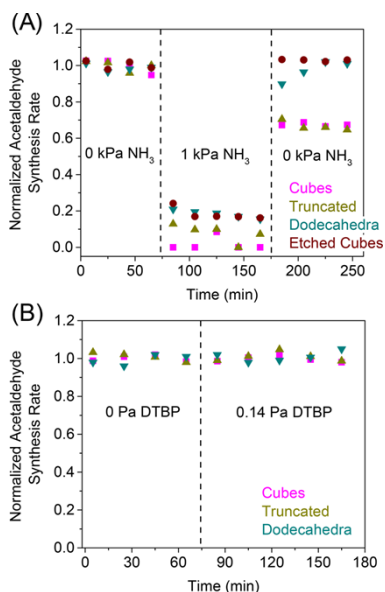


Fig. 2 Variation in the rate of ethanol dehydrogenation in the presence and absence of **a)** NH₃ and **b)** DTBP titrants, employed to ascertain the different reactivity of Lewis and Brønsted acid sites on STO with various shapes. Reprinted with permission from ref²⁷. Copyright 2018 American Chemical Society.

Correlating catalyst deactivation with the cumulative adsorption of the poison agent can provide the density of functional sites.²⁸ However, the accuracy of this type of titration heavily depends on the appropriate selection of an inert probe molecule that does not participate in the reaction and can fully occupy all active sites. Moreover, elucidating the real active sites is extremely challenging. The aforementioned spectroscopic methods do not directly provide information on the structure of the sites, and coordination environment. That is why,

complementary microscopy and X-ray based characterization (as discussed in section 1) are necessary.

To obtain surface residence time (τ), TOF, density of surface intermediates (N), and coverages under working conditions, and to overcome inherent challenges of site titration, one can employ SSITKA. In typical SSITKA experiments, streams of regular reactants and isotopically labeled reactants are switched while the reaction operates under steady-state conditions. The response of the system to the isotopic switch is monitored over time, and the resulting transient isotopic profiles offer valuable insights into reaction kinetics and mechanisms. Several comprehensive reviews have provided in-depth fundamental information and application examples of SSITKA.^{29, 30} A key advantage of SSITKA is that it allows to estimate TOF while circumventing the explicit experimental titration of surface sites. Thus, the general difficulty of identifying and titrating active sites is overcome.³¹ The concentration of reaction intermediates (N) can be estimated from τ and the rate per surface area. Surface coverage can be estimated from N and the binding site density. In particular, measuring intrinsic activity (TOF), independently from titration of available surface sites, creates a bridge with *ab initio* computations of surface reactivity. Our research group has conducted a series of studies focusing on the surface reconstruction of STO, employing a combination of the aforementioned techniques to determine real active sites and deconvolute the intrinsic activity of various sites and their density. Foo *et al.*⁴ investigated the surface reconstruction of SrTiO₃, BaTiO₃, SrZrO₃, and BaZrO₃ after oxidative treatment at 500-550 °C, revealing a clear enrichment of Sr and Ba on the top monolayer of SrTiO₃ and BaZrO₃ as evidenced by LEIS, and acid/base site titration. The increased basicity of the surface, upon surface reconstruction promoted isopropanol dehydrogenation to acetone (selectivity >65%) rather than dehydration to propene. FTIR spectroscopy and DFT simulations were able to identify the E_{1CB} pathway, involving weak Lewis acid and strong base sites, as the dominant path for isopropanol dehydrogenation. Further research²⁷ on STO nanoshapes with different exposed facets confirmed that the rate of ethanol dehydration strongly depended on the strength and distribution of acid-base pairs of the reconstructed catalyst, rather than the extent of the exposed surface facets, (001) or (110).

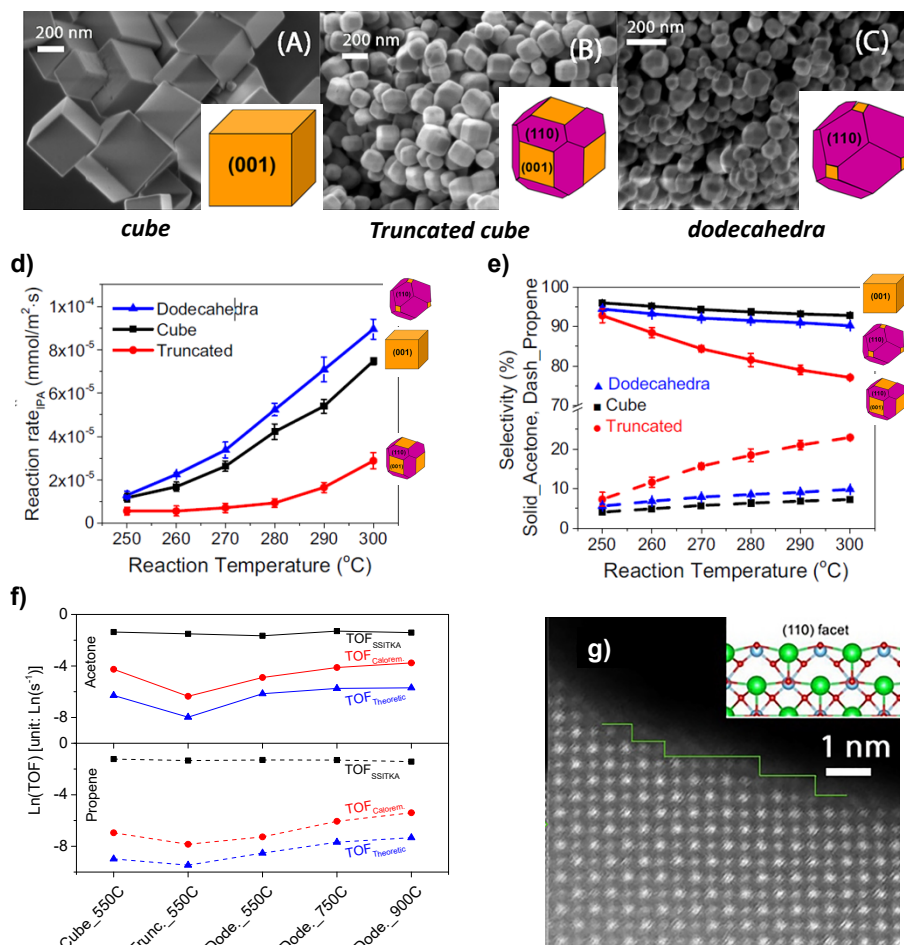


Fig. 3 STO nanoshapes: **a)** cube, **b)** truncated cube, **c)** dodecahedra. **d)** Isopropanol consumption rate and **e)** product selectivity (catalysts pretreated in O_2 at $550\text{ }^\circ\text{C}$). **f)** TOFs for isopropanol conversion over STO shapes after different pretreatment temperatures in O_2 (TOF measured via SSITKA, and calculated by estimating sites density via microcalorimetry ($TOF_{\text{Calorimetry}}$), and DFT ($TOF_{\text{Theoretic}}$)). **(g)** HAADF-STEM images of stepped sites formed on STO dodecahedra pretreated at $550\text{ }^\circ\text{C}$ in O_2 . Insert is the model of (1 1 0) facet (elements: Red, oxygen; Green, Sr; Blue, Ti). Reprinted with permission from ref.¹⁰. Copyright 2020 Elsevier Inc.

Bao *et al.*¹⁰ studied isopropanol conversion over STO nanoshapes with different surface reconstruction (**Fig. 3a-c**). TOF (measured via SSITKA) for acetone and propene formation over all reconstructed STO nanoshapes was very similar (**Fig. 3f**), despite significant differences in reaction rate per surface area and selectivity (**Fig. 3d,e**). Then, the primary factor contributing to different reaction rates per surface area was the density of surface intermediates. Based on these observations, it was concluded that active sites with similar intrinsic activities form during STO surface reconstruction. TOF measured via SSITKA was significantly higher than $TOF_{\text{Calorimetry}}$ (estimated by normalizing rate by the density of binding sites, obtained through adsorption microcalorimetry) (**Fig. 3f**), evidencing that not all binding sites are active sites under reaction conditions. STEM images and DFT calculations suggested that the formed step sites (**Fig. 3g**) on the reconstructed surface were the most active, determining overall rates even though they accounted for less than 1.4% of surface coverage. In a previous work,¹¹ DFT calculations

confirmed that step-terminated Sr sites, as observed by HAADF-STEM, were the most active sites for CH₄ combustion over STO catalysts with various degrees of reconstruction. In summary, surface characterization, SSITKA and DFT calculations have proven complementary to deconvolute the contribution of active sites reactivity and density, helping to establish meaningful structure-performance relationships that account for surface reconstruction. **Table 1** summarizes typical experimental techniques used for characterizing surface reconstruction.

Table 1 Select characterization techniques for studying surface reconstruction.

Technique	Information	Advantages	Disadvantages
X-ray photoelectron spectroscopy (XPS)	<ul style="list-style-type: none"> - Elemental composition. - Valence of elements. 	<ul style="list-style-type: none"> - Near-surface characterization. - Composition and electronic information. 	<ul style="list-style-type: none"> - Not monolayer sensitive. - Not readily performed <i>in situ/operando</i>
Low-energy ion scattering (LEIS)	<ul style="list-style-type: none"> - Elemental composition. 	<ul style="list-style-type: none"> - Topmost layer characterization. 	<ul style="list-style-type: none"> - Hard to distinguish signals from metal elements with similar atomic weight and size. - Not readily performed <i>in situ/operando</i>
Scanning transmission electron microscopy (STEM)	<ul style="list-style-type: none"> - Surface structure. 	<ul style="list-style-type: none"> - Precise structure information. - Input for computational models. 	<ul style="list-style-type: none"> - Localized structural information. - Potential beam-induced reconstruction. - Not readily performed <i>in situ/operando</i>
Chemisorption/Temperature-programmed desorption (TPD)	<ul style="list-style-type: none"> - Density and binding strength of surface sites. 	<ul style="list-style-type: none"> - Easily accessible. - Accounts for interaction of selected molecule with the surface. 	<ul style="list-style-type: none"> - Potential conversion of probe molecule at high temperatures. - Potential reconstruction induced by probe molecule. - Not readily performed <i>in situ</i> - Not <i>operando</i>.
Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS)	<ul style="list-style-type: none"> - Type of adsorption sites. - Electronic environment of surface sites. 	<ul style="list-style-type: none"> - Relatively easy access. - Accounts for interaction of selected molecule with the surface. - Electronic information of surface sites. - Potential for <i>operando</i> measurement. 	<ul style="list-style-type: none"> - Unsuitable for opaque catalyst samples. - Potential reconstruction induced by probe molecules.
Microcalorimetry	<ul style="list-style-type: none"> - Density, distribution, and binding strength of surface sites. 	<ul style="list-style-type: none"> - Accounts for interaction of selected molecule with the surface. - Highly quantitative adsorption strength measurement. 	<ul style="list-style-type: none"> - Potential reconstruction induced by probe molecule. - No direct electronic information of the surface sites. - Not readily performed <i>in situ</i>

			- Not <i>operando</i> .
Steady-state isotopic transient kinetic analysis (SSITKA)	<ul style="list-style-type: none"> - Turnover frequency. - Density of intermediates. - Surface coverage. 	<ul style="list-style-type: none"> - Especially suited for <i>operando</i> measurement. - Measurement of intrinsic reactivity. 	<ul style="list-style-type: none"> - Need for costly isotopes. - No information on the electronic/bonding structure of the active sites. - Detection limit compromised for high temperature reactions (> ~600 °C).

3. Prediction of catalyst performance based on surface reconstruction

Relationships between catalyst reactivity and surface properties become more robust when the surface reconstruction of the catalyst is understood and taken into account. These relationships could potentially be utilized to predict trends in catalyst performance for sets of catalysts. A standing challenge is whether we can go beyond understanding the impact of surface reconstruction on catalysis and predict the occurrence of reconstruction for a broad set of catalysts. Predicting surface reconstruction is difficult due to the influence of several reconstruction drivers, e.g., temperature, oxidative/reductive atmosphere, and presence of adsorbates. Although there are some theory papers³²⁻³⁵ where DFT is used to elucidate the thermodynamic stability of different surface facets of complex metal oxides under varying environmental conditions, understanding the pathways for surface reconstruction remains elusive. Understanding why and how reconstruction occurs at the atomic level requires advancement in both *operando* experimental techniques and dynamic *ab initio* simulations. Understanding steps that determine the rate of surface reconstruction would help predict surface reconstruction and establish structure-performance relationships for catalysts. A massive computational challenge lies on the fact that sublayer reconstruction (up to a few nanometers deep) stabilizes the reconstruction of the top-layer. The length-scale of such computational model renders traditional *ab initio* computations time-prohibited. Due to the lack of in-depth studies of surface reconstruction, little is known on the implications of these reconstructions on the intrinsic activity of surface sites. Experimentally, a few insights regarding surface reconstruction have been collected in our work; for instance, generally oxidative treatment (> 500 °C) enriches A at the surface of perovskites, surface reconstruction stabilizes after 5 h for STO in O₂ treatment⁹, acid treatment with HNO₃ enriches Fe at the surface, whereas acid treatment with citric acid enriches La at the surface of LaFeO₃³⁶. However, gauging the susceptibility of a bulk composition to reconstruction is still in its infancy. For a determined elemental composition, Polo-Garzon *et al.*¹¹ showed via LEIS that the composition of the sublayers (close to the top-surface) can predict the composition of the very top layer (**Fig. 1**). In essence, it might be possible to develop generalized guidelines for predicting the top-surface reconstruction of perovskites based on near-surface information with resolution of a few monolayers. Such correlations would accelerate evaluating surface composition as a reactivity descriptor.

Exploring the relationship between surface reconstruction and catalytic performance leads to the following question: Can reactivity trends based on surface reconstruction be generalized for sets of reactions? To address this question, we compared the dependence of rates for methane combustion, and oxidative coupling of methane (OCM), on the surface composition of STO catalysts.³⁷ Results showed that the impact of surface reconstruction on reaction rates and

selectivity (to C₂ products during OCM) was general for these two reaction networks involving the activation of methane (**Fig. 4**). This finding highlighted the importance of understanding surface reconstruction to, at least qualitatively, predict trends in reactivity. Even though, CH₄ combustion and OCM have different reaction mechanisms, CH₄ activation is still a crucial energetic barrier to overcome, and that is why they share common trends with respect to the concentration of active sites (Sr-sites). There is considerable potential to predict the activity of perovskite-type catalysts based on their composition, particularly when surface reconstruction plays a role in active site formation. Additionally, catalysts with high activity obtained through tailored reconstruction can be implemented for other reactions with similar rate-determining steps, further expanding their potential application in various chemical processes.

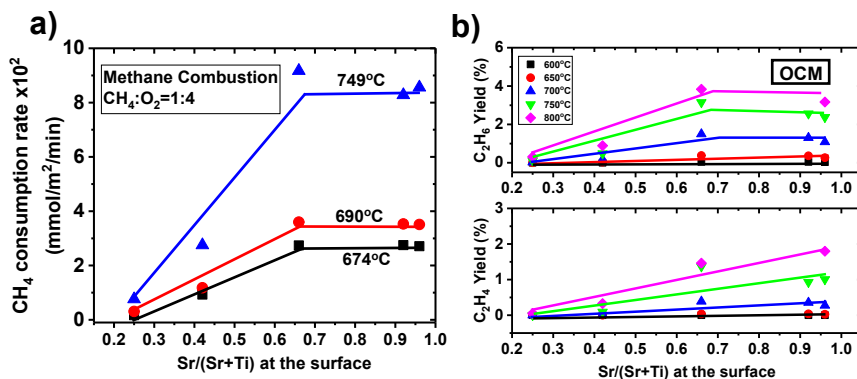


Fig. 4 Catalytic performance of reconstructed STO catalysts with various surface compositions for **a)** CH₄ combustion, and **b)** OCM. Reprinted with permission from ref ¹¹. Copyright 2018 American Chemical Society. Reprinted with permission from ref ³⁷. Copyright 2019 John Wiley and Sons.

The next inquiry is whether general trends in catalyst performance are elucidated when the surface reconstruction in a set of complex metal oxides, with different elemental composition, is studied. In our recent work,³⁶ catalytic methane combustion was studied over a series of perovskites, including Sr and La as A-site elements and Ti, Zr, Fe, In, Co, and Mn as B-site elements (i.e., SrTiO₃, SrZrO₃, SrFeO₃, LaFeO₃, LaInO₃, LaCoO₃, LaMnO₃). TOF for methane combustion ranged from 0.1 to 3.4 s⁻¹ at 625 °C. No correlation was found between TOF and *N* (**Fig. 5a**), evidencing the need to characterize these two kinetic parameters to properly guide catalyst optimization efforts. *N* was successfully correlated with the density of CO₂ adsorption sites (**Fig. 5b**), but the strength of CO₂ adsorption did not correlate with *N* or TOF. The heat of adsorption of CO₂ was the same for all perovskite samples. The results of the study undoubtedly show the impact of surface composition on TOF, *N* and rates per surface area. As shown in **Fig. 5c**, when studying the potential of boosting performance of the LaFeO₃ catalyst by tuning surface reconstruction, nitric acid treatment increased the surface exposure of B sites and induced a TOF increase of around 4-fold, reflecting on a 2-fold increase in the rate per surface area. However, increasing TOF came at the expense of a reduction in *N*, thus tampering the overall increase in the reaction rate. Reconstruction induced by citric acid created a pure La-dominant surface with high density of active intermediates, but TOF was low. All in all, a clear correlation between *N* and CO₂ adsorption sites was observed (**Fig. 5b**); in addition, TOF was clearly influenced by surface composition (**Fig. 5c**). However, it is still early to fully understand and rationally support general trends (**Fig. 5d**). Prediction of catalytic performance trends is still a monumental task, but understanding catalyst reconstruction greatly advances knowledge in that direction.

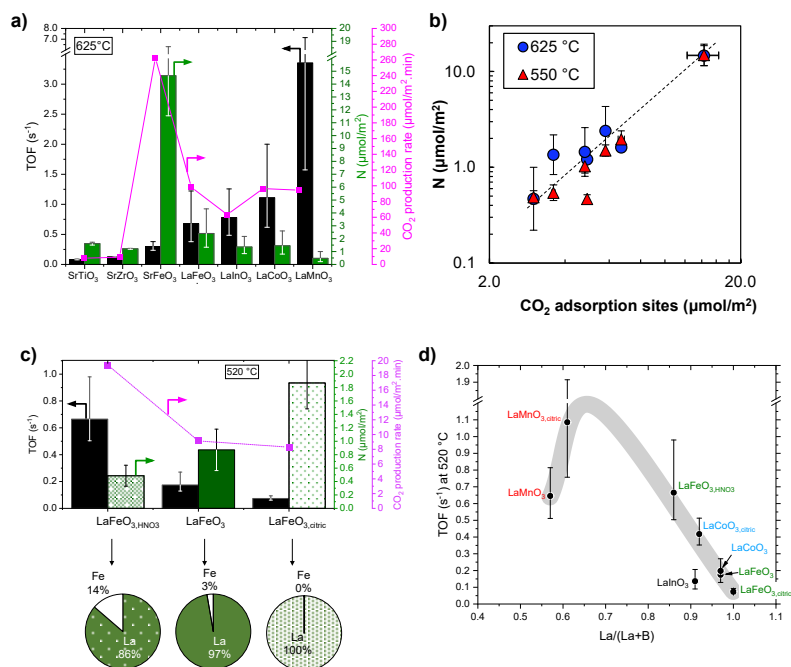


Fig. 5 a) Rates, TOF and N at 625 °C measured via SSITKA for CH₄ combustion over perovskites. b) Correlation between N and CO₂ adsorption sites (for catalysts in a). c) Rates, TOF and N at 520 °C measured via SSITKA for CH₄ combustion over reconstructed LaFeO₃ catalysts. d) TOF versus surface termination of La-perovskite catalysts for CH₄ combustion. Reprinted with permission from ref³⁶. Copyright 2022 American Chemical Society.

4. Potential of noble-metal-free complex metal oxides catalysts

As previously discussed, combining SSITKA and DFT methods offers valuable insights into the activity and density of active sites, presenting intriguing avenues for catalyst development. Noble metal-supported catalysts have been extensively employed in industrial and environmental catalysis (e.g., (de)hydrogenation, reforming, oxidation, and NO_x treatment), as their unique electronic structure provides superior catalytic activity. However, limitations such as scarcity and increasing costs have motivated research to design highly active noble metal catalysts with low loading, such as single-atom or cluster catalysts, or to develop noble-metal-free catalysts with comparable performance. In our recent study,³⁸ we studied the impact of thermal aging and sulfur exposure of a commercial Pd/CeO₂-ZrO₂ catalyst on catalytic methane combustion. SSITKA revealed a TOF of 0.76 s⁻¹ (at 375 °C) and N of 0.04 μmol/m² for the fresh catalyst. Interestingly, the high-temperature aged (HTA) sample experienced a significant loss in intrinsic activity (TOF = 0.04 s⁻¹) but a substantial increase in the density of surface intermediates (N = 0.36 μmol/m²). When the catalyst was high-temperature aged and treated in sulfur (HTA+S), the density of surface intermediates decreased, compared to HTA, but the sulfur treatment generated new sites with improved TOF (0.11 s⁻¹) (Fig. 6a). HTA and HTA+S samples exhibited similar conversion of methane despite having different surface areas, TOF and N ; thus, highlighting the importance of discerning intrinsic kinetic parameters to guide the design of superior catalysts. In our recent study, the intrinsically most active noble-metal-free perovskite catalysts have TOFs of ~1 s⁻¹ at 520 °C (Fig. 6b).³⁶ The fresh commercial Pd/CeO₂-ZrO₂ catalyst presents a similar TOF at a temperature ~150 °C lower (reaction conducted at 375 °C). However, the intrinsic activity of the Pd-catalysts decreases to TOF ≤ 0.1 s⁻¹ when the catalyst is aged (Fig. 6a). TOF of noble-metal-free perovskite

catalysts lags behind that of “fresh” noble metal catalysts; however, noble-metal-free perovskite catalysts gain attention if the stability of noble-metal catalysts is subpar when exposed to harsh pretreatment or reaction conditions (**Fig. 6b**). Studies evaluating the intrinsic reactivity of the active sites on the reconstructed surface of complex metal oxides after aging and sulfur treatment are currently lacking in the literature, and they would educate the potential performance of complex metal oxide catalyst under conditions of practical relevance. In addition, beyond TOF, the density of active sites plays a crucial role on catalyst performance, and binding sites may become active sites depending upon reaction conditions and reaction mechanisms enabled. Our research has shown that surface reconstruction can be harnessed to increase the reaction rates per surface area (~ 2 -fold)³⁶ of the best performing noble-metal-free perovskite catalysts, bringing them a step closer to competitive implementation.

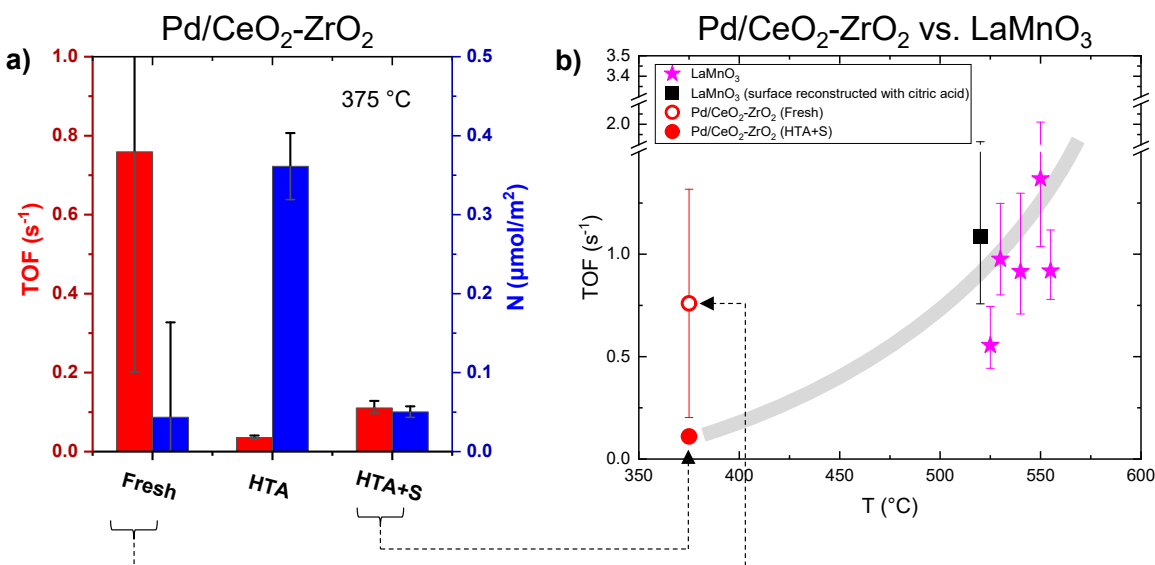
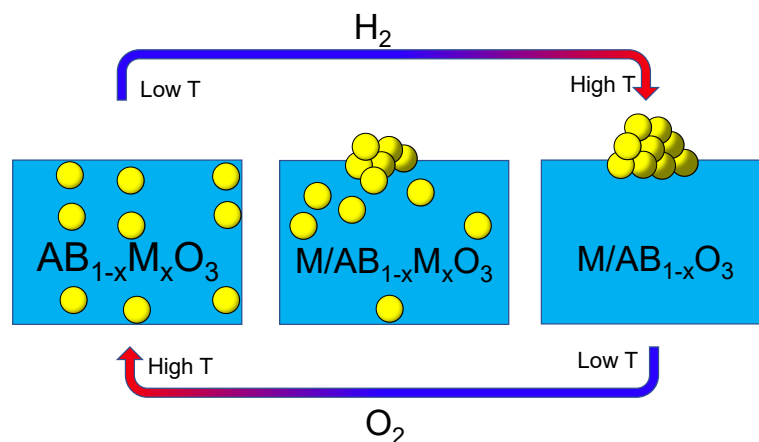


Fig. 6 CH₄ combustion over a benchmark noble-metal catalyst (Pd/CeO₂-ZrO₂) and noble-metal-free LaMnO₃. TOF and *N* for CO₂ production were measured via SSITKA. **a)** TOF and *N* for the fresh Pd/CeO₂-ZrO₂ catalyst (“Fresh”), after high-temperature aging (“HTA”), and after high-temperature and sulfur aging (“HTA+S”). **b)** TOF for LaMnO₃ with two different reconstructed surfaces, and comparison with TOF of Pd/CeO₂-ZrO₂. Reprinted with permission from ref³⁸. Copyright 2022 Elsevier Inc. Reprinted with permission from ref³⁶. Copyright 2022 American Chemical Society.

5. Interplay of surface reconstruction and “intelligent behavior”

Surface reconstruction of the perovskite structure and the inclusion of metal dopants can be harnessed to unlock avenues for catalyst design. When the complex metal oxide structure contains a dopant metal, surface reconstruction can be accompanied by an “intelligent” catalyst behavior^{39, 40}, where dopants undergo exsolution (sinter) and dissolution by switching between reducing and oxidizing atmospheres, respectively (**Scheme 2**).



Scheme 2 “Intelligent behavior” in M-doped ABO_3 perovskite.

Recently, we studied the co-existence of surface reconstruction and the “intelligent behavior” of Ni- and Cu-doped STO, where the Ni and Cu cations diffuse into the bulk phase under an oxidative atmosphere, and exsolve in the metallic state after reductive treatment at high temperatures (≥ 550 °C).⁴¹ Characterization of surface composition of the reconstructed catalysts was performed via *ex situ* XPS. As mentioned above, XPS is not as sensitive as LEIS to the topmost layer composition due to its penetration depth of several nanometers. However, for the catalysts studied, the extent of surface reconstruction included near-surface reconstruction, such that XPS can still provide meaningful insights into the composition of the reconstructed surface. As illustrated in **Fig. 1** for STO samples, subsurface composition correlates with top-surface composition. Characterization revealed that the diffused Ni and Cu cations occupy the B-site of the structure, which is accompanied by the enrichment of Sr (A-site) at the surface (**Fig. 7**). Careful understanding of surface reconstruction and the intelligent behavior opens a gateway to multifunctional catalyst design. As shown in **Fig. 7a,b**, one can manipulate the bonding coordination of the supported metal (cationic versus metallic), its availability (diffused versus exsolved), and the acid/base properties of the sites surrounding the supported metal (by controlling the segregation of the A and B cations). Understanding the non-ideal structures of the operating catalysts provides clear explanation for catalytic performance, as illustrated for CH_4 combustion over Ni-STO (**Fig. 7c**), where exsolved metallic Ni presents the lowest onset temperature for CH_4 combustion, but rates decrease as Ni becomes positively charged and later diffuses into the bulk.

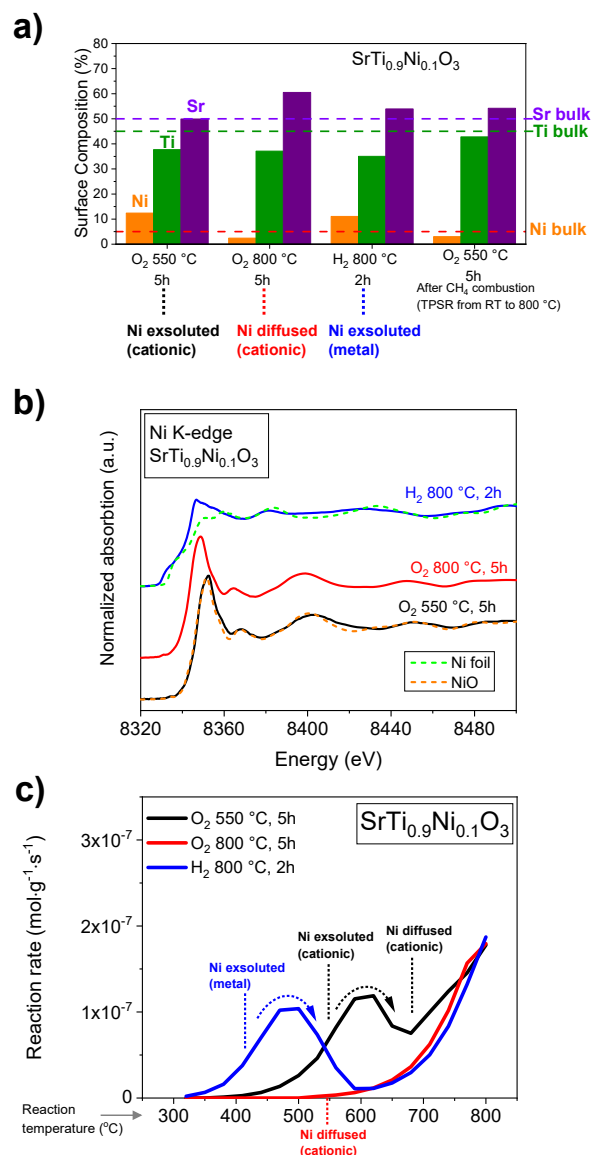


Fig. 7 a) Surface composition via XPS after O_2 and H_2 treatment of Ni-doped STO (TPSR= temperature-programmed surface reaction). Cationic and metal electronic state are determined via XANES. **b)** Fourier transform magnitudes of k^2 -weighted XANES spectra of Ni-doped STO after H_2 and O_2 treatment. **c)** Methane combustion over Ni-doped STO after different pretreatments. Reprinted with permission from ref⁴¹. Copyright 2022 Elsevier Inc.

6. Outlook

Catalysis occurs at the surface and studying catalysts as a bulk structure limits drawing meaningful guidelines for catalyst design. Establishing structure-performance relationships in catalysis demands looking at the very top monolayer of the catalyst surface to understand the bonding and electronic properties of the active sites. These properties can drastically change when the catalyst is exposed to different conditions and atmospheres. However, we have shown that

subsurface reconstruction plays a role in stabilizing top-surface reconstruction. The role that the bulk plays in enabling or limiting reconstruction is still uncertain, and advance computational approaches will play a key role in this endeavor. Key techniques to characterize the surface reconstruction of complex metal oxides with top-surface sensitivity include LEIS, STEM, probe molecule chemisorption coupled with DRIFTS and microcalorimetry. Combination of these techniques can give an accurate description of morphology, composition, and chemical properties of the reconstructed surface. Although *operando* characterization is ideal, current developments allow for *ex situ* and *in situ* characterization in most cases. These *ex situ* and *in situ* characterizations can be cleverly employed to provide useful insights into the catalytic system. However, the development of *operando* tools to characterize reconstruction under reaction conditions will shed unique insights into the reconstruction dynamics. Moreover, isotopic transient kinetic analysis and *ab initio* simulations can educate on the impact of surface reconstruction on catalysis. Beyond understanding the surface reconstruction of complex metal oxide catalysts, controlling it to rationally design superior catalysts is an exciting goal. It has been proven that some of the active sites on reconstructed complex oxide surfaces can have comparable intrinsic reactivity as noble metal nanoparticles, giving hope to design non-noble metal catalysts with superior performance. How far we can boost catalyst performance by careful design of reconstructed catalyst surfaces is yet to be known.

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Notes

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