

Promoting Carbon Dioxide Reduction via Operando Surface Reconstruction

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Commentary

It is of great significance to study the dynamic reconstruction effect in various heterogeneous catalytic reactions, such as electrocatalysis, thermal catalysis, including photocatalysis. So, the atomic or electronic structure change of the catalyst during the reaction processes should be deeply explored to understand the nature of the exact active sites [1-5]. Recently, we published a paper discussing the photocatalytic operando reconstruction on cobalt-based catalyst surface with a slight-oxidation state occurring. Based on a self-adaptive process, the unsaturated coordination state to optimize the structure of catalytic site in the surface reconstruction process, which was rarely seen in previous studies, especially for photocatalytic CO₂ reduction reaction. We found and demonstrated that in-situ CO₂ adsorption and coordinated activation on the reconstructed catalytic CoO_x sites lead to an unpredictable enhancement of catalytic activity and selectivity. The reconstructed catalytic sites generated in the testing condition were smart and flexible for accelerating the CO₂ reduction reaction in the practical testing environment. However, the original catalytic site Co-O (CoO and Co₃O₄) was fabricated with the post-thermal treatment performing an inefficient CO and H₂ evolution and rarely changed during the catalytic process. This type of operando reconstructed catalytic sites have impressively improved our understanding of the catalytic origin and nature.

Because the 3d orbital electrons of the transition metal (TM) with strong coordinative ability prefer to match the O 2p orbital, the coordination structure of catalytic centers

of transition metal-based materials (including sulfide, phosphates and selenides) are prone to be affected by oxygen adsorption. Besides, influenced by coordination atom O, these materials are also affected by suspension bonds of some active species under in-situ reaction conditions [6]. Taking cobalt based catalytic materials as an example, when bonded to oxygen or some defective traps present on the surface, such metastable catalytic sites CoO_x would be formed. By adapting to the environment, their thermodynamic catalytic mode was more flexible than that of the original sites, which gave them superior selectivity and self-regulation ability [7].

The surface reconstruction is always happening during the thermal- and electrochemical process. In **Figure 1a**, Guo et al. employed various characterization techniques and kinetic experiments to reveal the basic process in CO₂ hydrogenation. Specifically, surface reconstruction of ZnAl₂O₄ formed an amorphous ZnO layer, which dramatically improved the selectivity of CO₂ hydrogenation to synthesize methanol [8]. In **Figure 1b**, Zhang et al. used in-situ XRD to study the in-situ conversion mechanism involving Fe₂N transfer into iron carbide (Fe_xC_y) during CO₂ hydrogenation [9]. Besides, the structural evolution of Fe-based catalyst in the hydrogenation of CO₂ into hydrocarbon was systematically studied by combining various in-situ characterization techniques, as displayed in **Figure 1c** [10]. Sun et al. introduced the release of metal cations from NiFe-LDH nanosheets by solvation with an aprotic solvent to produce vacancy defects (**Figure 1d**) [11]. In situ Raman characterization was also used to investigate the surface reconstruction process of the electrocatalyst, and the process of locally transforming the crystalline Ni(OH)_x into

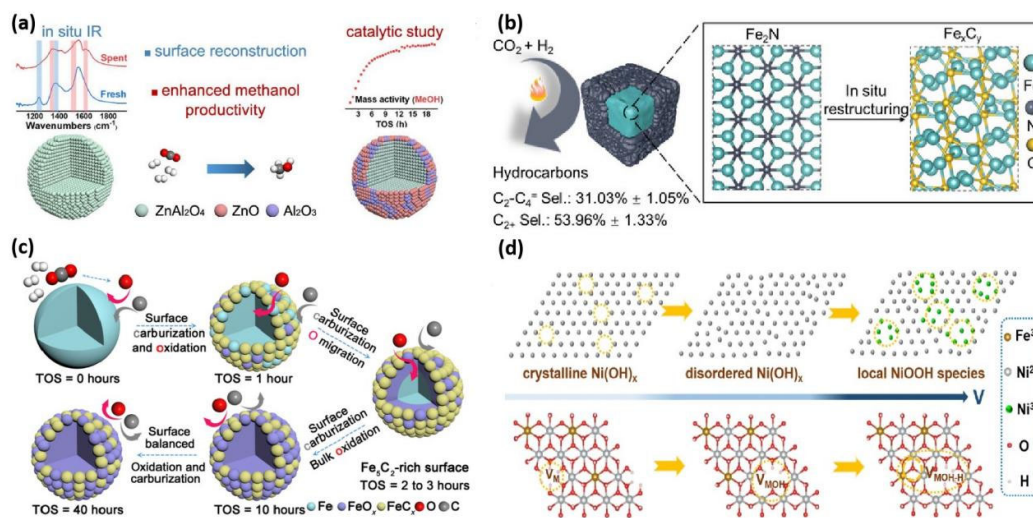


Figure 1. Some typical applications of in-situ reconstruction: (a) The reaction-driven surface reconstruction of ZnAl₂O₄ spinel for methanol production; Copyright 2021 Elsevier. (b) The in-situ restructuring of Fe₂N into iron carbides for thermal catalytic hydrogenation of CO₂; Copyright 2021 Wiley. (c) Schematic diagram of the evolution of iron species during CO₂ hydrogenation; Copyright 2022 AAAS. (d) Local conversion of crystalline Ni(OH)_x species to their disordered or defective status and eventually to NiOOH during the OER process. Copyright 2021 Wiley.

disordered or defective Ni(OH)_x, and subsequently into highly oxidized NiOOH with the increase of voltage. The slightly partial oxidation of transition metal-based photocatalysts due to oxygen adsorption may create disordered TMO_x clusters on the surface or asymmetric catalytic sites on the unsaturated surface.

The co-catalytic clusters formed in the testing process have not been systematically studied in photocatalysis until our recent publication. It is urgent to reveal the internal relationship between the structure and property of the reconstructed surface structure from the perspective of micro-structure dynamics. Pre-operando Raman characterizations were used to observe the changes of the active site. The structural modifications of the active site could result in the adsorption peak shift of CO₂. Simultaneously, CO appeared when cobalt and oxygen bonded with each other, which also verified that the formation of the new sites in the catalytic process strengthened the activated adsorption of CO₂ molecule. So, at the beginning of dynamic reconstruction, CO was not actually generated, but with the formation of sites on the metallic Co nanoparticles, the dynamic structure of the reconstructed catalytic site was self-regulated and optimized under the operando conditions, bringing about the gradually improved performance [6].

The O2p orbital can regulate the electronic structure of the Co 3d orbital, which was generally considered as a key step in CO₂

catalysis. In our article, it was strongly proved by calculation that CoO_x clusters formed in an adaptive environment can increase CO₂ adsorption energy and reduce CO desorption energy, making the reaction proceed in a feasible direction for CO₂ reduction. Catalysts with formed surface CoO_x clusters of unsaturated coordination have the lowest energy barrier in the rate-determination step. Thus, Co-O_x reconstructed sites can reduce the barrier energy and promote the activity and selectivity of CO₂ reduction. Compared with the Co-O_x strong bond formed by heat treatment of strong bond, the dynamic structure of the reconstructive surface sites has better performance. Our finding strongly confirmed that, the impact of environmental factors on the catalyst in the catalytic process should be considered, which is the most essential and must be considered in the study of real catalytic mechanism.

How to dynamically adjust the specific coordination behavior of the site and optimize the structure of the site will become the research focus in the field of catalysis as well as materials science. So, the operando technique has become an indispensable method to study the nature and properties of surface structure[12]. The surface of metal oxides is more complex than that of metal materials, which has led to a very limited understanding of the surface reconstruction of metal oxides [13]. However, with the development of in-situ characterization techniques (such as near-atmospheric X-ray photoelectron spectroscopy, near-atmospheric scanning tunneling microscope, environmental scanning electron

microscopy, etc.) those operando techniques are suitable for the practical conditions for the catalyst surface transformation process. The complexity of the catalyst itself is understood much better. And as the material synthesis techniques advance, precisely tuning the surface of the materials (such as nano-size, morphology, crystal surface exposure, etc.) [14-17] can be achieved. More commonly than previously thought, considering the crystal facets or reaction substrates, original bond breaking due to the coverage of species adsorbed that leads to the evolution of catalyst surface structure occurs broadly. The operando generated cluster-type active sites tend to bridge the gap between heterogeneous and homogeneous catalysis. Thus, a deeper understanding of the surface composition and structure of metal oxides was obtained, and the development of catalyst synthesis method was also promoted [18].

Conclusion

In a weak redox environment, some oxygen substances or active species will inevitably be adsorbed, resulting in in-situ reconstructed catalyst surface, during the preparation, storage, and reaction of catalysts. By using a wider range of operando characterization, we intend to take the opportunity to explore the fundamental mechanism of in situ reconstruction in detail. Through this paper, we hope to provide new research ideas and directions for researchers in the field of photocatalysis.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Figure 2: Results of chronopotentiometry experiments under electrolyte flow ($Q = 1.5 \text{ mL} \cdot \text{s}^{-1}$) for $i = 11 \text{ mA}$, 37.5 mA and 75 mA (from left to right). Chart (a) to (c) represent the overpotential due to surface coverage, while (d) to (f) represent the deduced free surface.
