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Surface Non-Ideality in Catalysts: Implications for Reaction Mechanisms and Design

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Description

Heterogeneous catalysis and electrocatalysis remain central to advancements in chemical and energy transformation processes. Over the past century, the understanding of binding and reactivity of surface-bound intermediates has been a fundamental challenge. Traditional models, such as those based on clean single-crystal surfaces and Langmuir isotherms, have often been adequate for many catalytic processes. However, the increasing complexity of modern catalysts, particularly in the form of nanoparticles, binary and ternary materials and irregular surfaces, calls for a re-evaluation of these assumptions. For a long time, catalysts were modeled as surfaces with idealized adsorption behaviors. The Langmuir isotherm, which assumes that adsorbates bind in a straightforward and ideal way, has been an effective model in many cases. It allows for simplified kinetic treatments and understanding of catalytic processes. The classic intuition suggests that non-ideal behavior-such as varying binding energies-does not significantly affect catalytic performance in many traditional catalysts, particularly those based on noble metals. However, modern catalysts, which often include small nanoparticles or irregular surfaces with diverse edge, corner and defect sites, have surfaces that are far from ideal. These sites can show increased reactivity and may change during a catalytic cycle or over time, making the assumptions of ideal adsorption less valid. Catalysts such as those composed of earth-abundant materials-oxides, chalcogenides, carbides and pnictides-further complicate the situation. These materials often exhibit complex surface structures that may differ significantly from their bulk counterparts and their surfaces can be amorphous or hydrous under catalytic conditions.

Surface diversity and non-ideality

One of the central intuitions in catalysis is the Sabatier Principle, which suggests that for efficient catalysis, surface intermediates should bind neither too strongly nor too weakly. This intuition, however, has been largely based on the assumption of ideal, uniform surfaces, which does not hold in the case of modern, complex catalysts. The surface diversity and non-ideality observed in modern catalysts-due to the varied nature of adsorption sites, material structures and electronic environments-render the traditional “Goldilocks” model insufficient for understanding reactivity.

Recent studies have shown that many catalysts are dynamic and non-ideal, exhibiting significant variation in their surface composition, structure and electronic states. Nanoscale gold catalysts, metal phosphide catalysts and electrosynthesis systems are just a few examples where this complexity plays a vital role in catalytic performance. These findings underscore the need to move beyond simplified models and account for the diversity and reactivity of real-world catalytic surfaces.

Analytical advances

The development of more advanced analytical tools has enabled a deeper understanding of surface non-ideality. These tools have revealed that many catalytic surfaces are far from uniform, with high levels of structural and compositional heterogeneity. This heterogeneity can include variations in stoichiometry, surface hydration, or the presence of strongly bound impurities, all of which can significantly influence catalytic behavior.

In addition, both theoretical and computational studies are increasingly focusing on surface heterogeneity and its effects on catalysis. These studies highlight the need to refine our understanding of the relationship between surface structure and reactivity. Non-ideal behavior, far from being an exception, is now recognized as a defining characteristic of many modern catalytic systems.

Conclusion

The complexity of modern heterogeneous catalysts necessitates a shift in our understanding of surface interactions. While the traditional models based on idealized surfaces have been successful in many cases, they fail to capture the nuances of modern catalysts, which exhibit significant surface diversity and dynamic reactivity. By recognizing the role of surface heterogeneity and non-ideality, researchers can develop more accurate models and design more efficient and robust catalytic systems. This perspective aims to raise awareness of these issues and their broader implications for the future of catalysis, emphasizing the need for new approaches that account for the complexities of real-world catalytic surfaces.