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## The Surface Chemistry of Catalytic Reactions: Progress and Challenges

Chemistry at interfaces is ubiquitous in nature, yet our understanding of such processes still lags that of transformations occurring in homogeneous phases. This is not for lack of interest or effort; the problem is that interfaces are significantly more difficult to study than bulk samples. A new paradigm was advanced a few decades ago with the development of novel spectroscopies specifically designed to discriminate and isolate information from surfaces,<sup>1</sup> yet most of those require vacuum and are therefore not operational under the conditions relevant to many of the systems of interest. More recent advances have provided new avenues for the characterization of gas–solid and, in particular, liquid–solid interfaces,<sup>2</sup> but the struggle to develop a molecular-level description of the mechanisms and energetics of interfacial reactions continues. In this issue of *The Journal of Physical Chemistry Letters*, we include three Perspectives on surface phenomena associated with heterogeneous catalysis that exemplify both the progress made in this area and the challenges faced going forward.

Some of the most significant advances in the study of surface reactions in recent years come from theory. Over the years, experimentalists have been able to collect a reasonably large database for the energetics of simple adsorbates on well-defined (i.e., single-crystal) surfaces, mainly by using temperature-programmed desorption<sup>3</sup> but more recently also employing microcalorimetry,<sup>4</sup> and related experiments have yielded complementary information on activation energies of surface reactions.<sup>5</sup> Density functional theory (DFT) has now been refined to the point of being able to provide good estimates for binding energies and to favorably compare those to experimental values, but the calculation of kinetic data such as activation energies and other details of the potential energy surface has proven more elusive.<sup>6</sup> In his Perspective, Kroes provides a roadmap to build a database for barrier heights of reactions between small molecules and transition-metal surfaces.<sup>7</sup> As he reports, highly accurate reaction probabilities versus collision energies for those types of systems have been determined for only two systems, both involving molecular hydrogen and copper substrates, in calculations that use density functionals fitted to experimental molecular beam sticking probabilities. In the end, Kroes's discussion on the technical details associated with quantum mechanics calculation using either semiempirical density functional or first-principles theories indicates that the prospects for extending the number of activation barriers calculated to a similar levels of accuracy to include other systems, even the adsorption of H<sub>2</sub> on other transition-metal single-crystal surfaces, is still daunting.

The Perspective offered by Koper and co-workers<sup>8</sup> discusses the mechanistic details of the catalytic electrochemical reduction of carbon dioxide, a reaction that has gained considerable interest recently because of its potential as a way to store energy and reduce pollution.<sup>9,10</sup> The main challenges holding back the use of this process for practical applications are the high overpotentials associated with the CO<sub>2</sub> reduction

and the poor product selectivities displayed by most electrodes. The authors here focus on heterogeneous electrocatalysts, mainly based on copper solid surfaces or on immobilized metal complexes, and offer a comprehensive theoretical point of view of the mechanisms involved. They highlight the importance of negatively charged intermediates such as adsorbed CO<sub>2</sub><sup>•−</sup> radicals and (CO)<sub>2</sub><sup>−</sup> dimers in the formation of C<sub>1</sub> and C<sub>2</sub> products, which are especially sensitive to pH and solvent effects, and offer different strategies for the development of more efficient and selective electrocatalysts, including the alloying of different metals to optimize the adsorption energy of intermediates such as CO(ads) and to affect relative overpotentials and the tuning of pH and nonaqueous electrolytes to improve selectivity.

Finally, Thorne and co-workers provide an interesting discussion on the energetics at the interfaces between photoelectrodes and electrolytes in connection with photoelectrochemical processes.<sup>11</sup> Photoelectrochemistry promises to offer a direct route for solar energy storage<sup>12,13</sup> but only if the yields can be improved. The performance of photoelectrodes is limited by the efficiency with which the photoexcited charges are separated and by how fast the charges are transferred to the solution, and both of those are highly sensitive to the properties of the surfaces near the electrolyte. The authors chose hematite, one of the most promising materials for water splitting using solar energy,<sup>14</sup> as their platform to address the changes in energetics induced by surface modification and to expand on the consequences of those changes to the overall photoelectrochemical performance. They conclude that the great potential of hematite as a photoelectrode is limited by its poor inherent properties and that increasing its photovoltage, as needed for practical applications, requires a shift in the position of the band edge that is difficult to achieve because it involves changing the strong correlation between the hybridization of the Fe and O orbitals. Nevertheless, they argue that some general lessons can be derived from studies with this material, including the observation of a potential drop within the Helmholtz layer and the need to integrate catalytic functionality for oxygen and hydrogen evolution with the performance of the photoelectrodes. As in the other two Perspectives, the discussion in this third paper provides a nice overview of the state of the art but also raises many unresolved questions related to the chemistry on solid surfaces associated with important practical catalytic applications.

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## Notes

Views expressed in this editorial are those of the author and not necessarily the views of the ACS.

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