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Editorial

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Taking a Nanoscale "Look" at Chemical Reactions on Surfaces

Guest Editorial for the Accounts of Chemical Research special issue on "Microscopic Insights into Surface Catalyzed Chemical Reactions"

Heterogeneously catalyzed reactions are among the most scientifically intriguing and technologically important chemical conversions and play a major role in the energy, petrochemical, pharmaceutical, and food industries. Practical catalysts generally contain multiple elements in a range of particle sizes supported on oxides, and their structure and composition change with reaction conditions. While the reaction pathways themselves are often highly complex, basic steps frequently dictate important parameters such as activity and selectivity. Rational design of effective catalysts requires a detailed knowledge of the molecular-level phenomena that control activity and selectivity like the relative rates of the elementary steps in the conversion sequence: adsorption, surface diffusion, surface reaction, and desorption. The rates of these steps depend, in turn, on the composition, electronic structure, and atomic scale structure of the catalyst. In order to design next generation catalysts for chemical conversion, control surface modifications, and begin to understand the complex workings of nature's own chemical converters such as enzymes, one must define the relevant structure−property−activity relationships. This requires combining knowledge of a system's local atomic-scale geometric and electronic structure with its chemical reactivity. This special issue addresses a selection of the most relevant state-of-the-art research activities in this research area with a focus on microscopic insights obtained mostly from scanning probe microscopies and outlines important future directions of the field.

The development of well-defined model systems enables a fundamental understanding of many important elementary steps in surface-catalyzed chemistry. The atomic-scale structure of the active sites in metal/oxide catalysts is hard, if not impossible, to characterize by conventional methods. In three Accounts, groups lead by Nilius, Weaver, and Schauermann describe their development of industrially relevant metal/oxide systems that are amenable to study by surface science and scanning probe methods. Stacchiola and Salmeron further demonstrate that high resolution scanning probe and surface science data can be gleaned from similar model systems at higher temperatures and pressures that mimic real operating conditions.

As illustrated by the majority of the Accounts in this issue, scanning probes have revolutionized many areas of science since their invention in the early 1980s, not least the fields of surface science and surface chemistry. The Account by Hines describes how the kinetics of complex processes like silicon etching can be understood by probing the atomic scale surface structures produced by etching. Furthermore, when studying surface *chemistry*, scanning probes have a great advantage over transmission electron microscopy in that fragile molecules and atoms as small as hydrogen can be directly visualized. Maier describes how complex hydrogen-bonded structures of water on metals can be understood using STM, and Altman writes about how noncontact AFM can be used to quantify the forces between molecules and surface reaction sites. Park describes how nanoscale diodes can be used to measure hot electrons produced by chemical reactions, which is interesting to contrast with Salmeron's discussion of inelastic tunneling into excited molecular vibrational states.

Looking forward, the ability to prepare complex chemical architectures on surfaces and probe their nanoscale structure and chemical properties opens up a new paradigm for nanoelectronics, photonics, or carbon-based technologies.

Barth describes a large body of work aimed at utilizing interfacial synthesis for the atomically precise fabrication of low-dimensional carbon-rich scaffolds and nanomaterials. Illustrating that scanning probes can both image structures and measure their electronic properties at the nanoscale, Lin and Zhu focus on surface-assisted C−C coupling reactions that enable, for example, tuning the electronic structure of graphene-like structures. Related metal−organic surface assemblies studied by Gutzler and Marbach offer model systems that can serve as a starting point to understand the complex action of metal atom sites in evolved catalysis by enzymes.

The ∼30 years since scanning probes were invented has seen the field move rapidly from imaging a limited range of surface structures and adsorbates to visualizing chemical reactions on catalytically relevant sites, understanding important surface modification processes, and tailoring molecular assemblies for complex functionality. Taken together, this collection of Accounts highlights some of the most recent advances in understanding and tailoring of surface chemical properties for a variety of applications.

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Notes

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