Catalyst Design

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Linear Energy Relations and the Computational Design of Selective Hydrogenation/Dehydrogenation Catalysts**

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Over the past century, the development of efficient processes for converting fossil resources into a broad range of chemicals, materials, and fuels could undoubtedly be considered one of the most important scientific developments. The vast majority of chemicals are produced based on catalysis technologies, and essentially all transportation fuels are refined through a number of catalytic processes.[1] One such important catalytic process is the Haber–Bosch ammonia synthesis,[2] which through its use in the production of artificial fertilizer helps providing food for approximately half of the world's population.[3] This process has been suggested in a "millennium essay" in *Nature* to be the single most important discovery of the past century.[3] Like many other processes, the ammonia synthesis relies heavily on fossil resources, since the hydrogen consumed in the synthesis reaction is primarily obtained from natural gas (through the also-catalytic steam-reforming and water–gas shift processes).

It is clear today that as a consequence of our reliance on fossil resources, the pressure on the environment has drastically increased. Even the best available processes do not completely avoid undesirable byproducts, and a range of catalytic technologies have therefore been developed to diminish the associated problems, for example three-way catalysts for gasoline-powered vehicles and the selective catalytic reduction of nitric oxide in fossil-fuel-based power plants. The continuously increasing use of fossil resources also directly contributes to the increasing carbon dioxide levels in the atmosphere. It is becoming more and more evident that our consumption, during the course of a few centuries, of the fossilized carbon resources deposited during the course of tens of millions of years may have a dramatic impact on the global climate. Therefore there is currently a significant push towards reducing the dependence on fossil carbon resources. This calls for the development of a range of new and improved catalytic processes, and especially for sustainable catalytic technologies. These future technologies with a lower environmental impact will require a large number of new catalysts and processes, and a special focus will be on designing catalysts that are significantly more selective than those known today. Our ability to meet this challenge may well determine whether we can sustain high living standards in the industrialized part of the world and whether living standards can be significantly improved in the developing countries.

The catalytic properties of an active site on a catalyst are completely determined by the local electronic structure, and it is therefore a goal in itself to become able to understand and "design" the local electronic structure of the active sites by changing the catalytic materials structure and composition. During the course of the past few decades the understanding of why a given material can act as a good catalyst for a given reaction has drastically improved. The improvement has been achieved through the close integration of experimental and theoretical methods in surface science.[4] The number of possible atomic arrangements that one must investigate and understand in order to find a new and highly selective catalyst for a complex chemical reaction is, however, enormous, and the detailed atomic-level understanding of catalytic systems that have been found to work therefore by no means guarantee that an alternative good catalyst can be determined easily. The major part of the design challenge—the inversion of insight—therefore still exists: How can we, instead of deriving the catalytic properties from known materials structure and composition, derive appropriate materials and their structures and compositions only from the knowledge of the desired catalytic properties and perhaps the relevant working conditions (see Scheme 1)?[5]

The objective of atomic-scale design through engineering of the electronic structure is not limited to catalytic materials. It is a general challenge in materials science, chemistry, physics, and molecular biology, and extensive progress has been achieved in some research areas, for example, new molecules for homogeneous catalysis[6] and materials for

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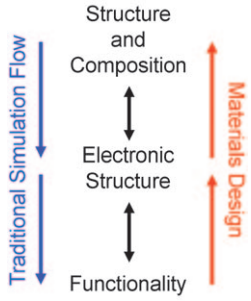

Scheme 1. Illustration of the work flow in traditional electronic structure simulations of materials properties and the inversion of this work flow required to carry out materials design using electronic structure simulations.

hydrogen storage,[7] batteries,[8] and photo-absorption.[9] The catalytic reactions at surfaces may be particularly well-suited for electronic structure engineering, since the link between the atomic-scale properties and the macroscopic functionality is relatively well understood.[5] This understanding has come about to a large extent through the theoretical description of surface reactions, which has been considerably sharpened by the availability of a broad range of quantitative experimental surface science studies of surface adsorption and reaction properties.[10]

Trends in the adsorption properties of transition-metal surfaces can be thought of in terms of the so-called d-band model.[11] According to the simplest version of this model, the adsorbate–surface interaction for a given adsorbate is linear in the position of the energy center of the d-electron band of the metal surface. This leads to linear scaling relations between the adsorption energies of different adsorbates.[12] Since the transition-state structures over different metals tend to be rather similar, there is also often a linear correlation between the adsorption energies of the transition states and the position of the underlying d-band center. This results in a linear correlation between the adsorption energy of a given adsorbate and its associated transition state, which underlies the wealth of studies of Brønsted–Evans–Polanyi relations on transition-metal surfaces and their implications for catalytic kinetics.[13] One way of inverting the catalyst-design problem is to derive descriptors for the catalytic properties from the basis of the underlying linear energy relations,[14] and the determination of accurate and reliable linear energy relations thus has central importance for computational catalyst design.

In a recent paper by Loffreda et al. scaling relations with unprecedented accuracy are presented for a reaction network of unprecedented complexity, and involving relatively large organic molecules.[15] It is shown that these scaling relations are accurate enough to address the selectivity for the hydrogenation of unsaturated aldehydes over Pt(111). That such an intricate property as the selectivity between so very similar hydrogenation reactions of such complex organic molecules can be treated reliably provides great hope for the future computational design of selective hydrogenation and dehydrogenation catalysts for complex hydrocarbons, which is a field of large industrial relevance.[16] That it has already now been possible in a number of simple cases to tailor surfaces with improved catalytic properties on the basis of insight and DFT calculations provides hope that this avenue may eventually become a versatile design strategy for finding good catalysts for more-complex reactions.

A number of challenges, however, must be overcome. Going beyond transition-metal catalysts may provide a considerable challenge from a theoretical point of view. From detailed comparisons between theory and experiment it is known that DFT works reasonably well for simple molecules on transition metals, but it may be less suitable for other types of catalytic systems such as strongly correlated oxides.[17] The observation that scaling relations also exist for adsorbates over oxides, nitrides, and sulfides lends hope that descriptor-based catalyst design eventually can be extended to these classes of materials.[18] For many adsorbates it is also essential to treat the van der Waals interactions[19] better than what is commonly done at the current level of theory. The recent progress of theory suggests this may soon become a realistic possibility.[20] It will also be necessary to establish a significantly improved description of electrocatalytic and photocatalytic processes, especially if we aim to harvest and store energy from sunlight on a scale that is relevant compared to the global consumption of energy. For new catalysts, high activity and selectivity can be necessary requirements, but other factors such as receptiveness to promoters, stability against poisons, long-term durability, low constituent costs, absence of even minute amounts of side products, and low cost of production can be important as well. These factors can perhaps be calculated or simulated to some extent, but in the end, experimental tests carried out at realistic reaction conditions will very likely always remain central in the development of new technical catalysts. While the experimental methods, however, usually tend to become more expensive with time, computational methods will continue to become cheaper as the computers become faster and our algorithms are improved. This alone seems to suggest that computational methods for the design and discovery of catalysts hold some promise for the future.

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