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Catalytic Paradigms: A Riddle and a Puzzle

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Can we design catalysts from first principles? This goal has been passionately sought after in the field of catalysis science. If we could, it would show that we really understand catalytic action. How far off are we from this goal?

Recent advances towards this goal build on the very fundamentals of catalysis science. There is Berzelius' classical[1] insight that a catalyst is not consumed in the reaction it induces. This perspective has the important implication that catalysis is a cyclical reaction event. So why are most catalytic reactions non-oscillatory?

We will explain how this apparent riddle is resolved by the science of complex systems.[2,3] The stationary or oscillatory nature of a reaction emerges from a combination of events having different lengths and timescales. Such events, as we will discuss below, are accompanied by changes of the catalyst (i.e., its surface in the case of a heterogeneous catalyst) and are induced by the reaction.

Ostwald's law, which states that a catalyst alters the rate of product formation but not the chemical equilibrium between the reactants and the products,[4] has been essential in many breakthroughs in catalysis research, especially in the first part of the previous century. While it provides the conditions for a reaction to proceed, it does not provide a recipe for the design of the optimum catalytic material.

Sabatier formulated a third paradigmatic law of catalysis,[5] one which actually helps the design process. Molecular reaction complexes formed from the catalyst and the reagent should be of intermediate stability. When the complex is too stable, the catalyst will become poisoned. When it is too unstable, the reaction will not proceed. This statement is an implicit invitation to formulate a theory of trends in catalyst activity as a function of catalyst composition.

For heterogeneous catalysis, which is the focus of this essay, such a theory has recently become available.[6] It is a practical one since quantum-chemical computational methods have become available to predict, for a catalytic reaction, the relative stabilities of reaction intermediates as a function of structure and composition of the catalyst's reaction center.

Such progress is an inspiring success for computational catalysis. The challenge that remains is to actually predict the state of the catalyst during the reaction. For a heterogeneous catalyst the adsorbate overlayer composition and structure of the catalytically reactive site may vary and depend on the type of reaction as well as on reaction conditions. Together with the stability of the reaction intermediate, it determines the overall catalytic reactivity of the catalyst.

The State of the Reactive Catalyst

Self-organization and self-assembly are fundamental processes which control the state of the catalyst at work. The interaction between adsorbates and surface atoms may lead to surface atom displacement and the reconstruction of the catalyst surface.[7] For instance a transition-metal surface may be converted into a surface compound, such as an oxide or carbide.

To be able to predict the state of the reacting catalyst, a theory about the dynamics of surface atom displacements and its relation with catalytic reaction events is needed. Clearly catalyst kinetics and catalyst surface states are interdependent. To predict the surface state of the reactive catalysts with ongoing kinetics, is one of the challenges of the current catalysis theory. It will extend currently available methods to compute thermodynamic stability and composition of an adsorbate-covered surface in equilibrium with a reactive gas or liquid.[8]

There is an interesting interplay between the processes at different lengths and timescales, and changes in the state of the catalyst surface. This interplay can be observed, for instance, in kinetic Monte Carlo (KMC) simulations[9] of the well-understood CO oxidation reaction on platinum surfaces. Ertl[10] observed and described the conditions under which it shows oscillatory reactivity. KMC simulations track reactive events of individual molecular and atomic movements on a grid defined by surface topology.

As a result of its particular nonlinear kinetics, the CO oxidation system can be considered physically, to be an excitable system. Such a system has an autocatalytic reaction step as well as an inhibiting one. Self-organized oscillatory behavior occurs when the driving force (the chemical affinity) of the reaction exceeds a particular value.

On a microscopic level, the reaction is autocatalytic with respect to the generation of surface vacancies. They are necessary for decomposition of O_2 into adsorbed O atoms, which react with CO to produce CO_2. Desorption of CO_2 increases the rate of O_2 dissociation, because it generates more surface vacancies than were present before reaction.

In contrast, the depletion of the surface of CO by CO_2 formation is also part of the inhibiting process. Adsorbed CO

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stabilizes the reactive surface. The desorption causes a change from a surface state of high reactivity to low reactivity, thus inhibiting the reaction because O_2 dissociation will only occur on the reactive surface.

Computed on a small grid with only a few reaction centers, self-organized oscillatory time dependence can be observed when reaction conditions are chosen properly. However, when the simulation is made more realistic (and complex) by choosing a simulation grid of increased size, the amplitude of these oscillations decreases and may even disappear. Since collisions of gas-phase particles with the surface are stochastic in time, there is then no correlation of the times at which nanoreaction cycles are locally initiated.

When long-range interactions are introduced, in this case, by diffusion, and these interactions exceed a particular strength, synchronization of the nanocycle events occurs and macroscopic spatiotemporal patterns can be observed. In the latter case, moving self-regenerating spirals or pulsing motions of locally different surface patches are generated. The local nanocycles can be compared with neurons, in the brain, which synchronize for brain activity.

The concepts such as amplification, inhibition, synchronization, and self-organization, of excitable systems are part of nonlinear physics and the complex chemical systems theory[2]. They apply to a wide range of systems ranging from laser physics and biological evolutionary dynamics to stock market fluctuations.[11] In contrast to the steady-state condition, where the system is close to its entropy maximum (near chemical equilibrium), self-organized spatiotemporal processes operate near a state of minimum entropy (far from equilibrium) and hence, create order.[3]

The concept of excitable systems has also led to an important hypothesis regarding the origin of chirality in nature's molecules. Following the work of F. C. Frank,[12] the same mathematical expression used for synchronized excitable systems describes the amplification of the concentration fluctuations in an equimolar enantiomeric mixture, so that one of the enantiomers becomes enhanced. Soai et al.[13] even designed a reacting system, with an autocatalytic as well as an inhibitory reaction step, which showed such behavior.

Rutger van Santen obtained his doctorate in Theoretical Organic Chemistry at the University of Leiden, Netherlands in 1971. After a postdoctoral stay at SRI, Menlo Park California, he joined Shell Research in Amsterdam, and in 1988 Eindhoven University of Technology (TU/e) as a Professor of Catalysis. In 1991 he became the founding director of the Netherlands Research Institute of Catalysis. Currently he is professor at the Institute of Complex Molecular Systems of the TU/e. One of his international invited lectureships was as Karl Ziegler lecturer at the MPI für Kohlenforschung, Mülheim in 2000.

The Number of Active Surface Sites

Any macroscopic reaction will show steady-state behavior as long as its chemical driving force is not too large. Then at the microscopic level, the cyclic succession of catalytic reactions steps will lead to stochastic behavior, not temporal self-organization.

Even when the reaction is at a steady state, the important consequence of the self-assembled nature of the reactive surface state is that the number of reactive centers, to which the rate of the catalytic reaction is proportional, is not a well-defined constant. This phenomenon can be illustrated by changes in the surface state of a cobalt catalyst during the Fischer–Tropsch reaction, which transforms CO and H_2 into hydrocarbons.[14] STM analysis by Wilson et al.[15] showed large structural changes in the catalyst, changes which were induced by the reaction.

Adsorbed CO molecules or carbon atoms deposited at the surface during the reaction induce a transformation of the initially dense and reactive metal surfaces into surface structures which are less dense in metal atoms. This change causes the expulsion of surface metal atoms, thus resulting in the formation of step-edge sites.[7] On such step-edge sites, bond dissociation reactions will be fast.[10] The major challenge is to determine the actual concentration of such sites because it also depends on the ad-metal atom mobility, which may lead to a decrease in concentration of reactive sites.

In zeolite catalysis, an example of in situ generation of catalytically reactive centers is found the conversion of methanol into olefins.[16] The catalyst is a solid acid, but the catalytically reactive center is formed in situ by the reaction and consists of cationic carbonaceous molecular fragments which may agglomerate with time. The latter will lead to deactivation of the catalyst.

Such scenarios are general and illustrate the interplay between the formation of reactive catalyst sites and the onset of deactivation. For optimum catalyst performance catalyst-state reactivity and stability have to balance.

The situation is complex because even when averaged over many catalytic cycles, the surface-reactive state may remain disordered, as demonstrated for mixed oxide catalysts by Schögl et al.[17] It can be considered a catalytic puzzle in which different pieces have to match.

The process of surface reorganization, discussed in this section, is a self-assembly process. The state remains when the driving force of its formation is removed. This process is in contrast to the self-organized system of the previous section, wherein it changes back to its equilibrium state. The nonlinear physical events that underpin both phenomena will provide a rich field for further scientific endeavor.

Catalyst Design

The solution to catalyst design that satisfies the different criteria for catalyst optimization implies that working catalyst systems have a complex composition.

Complex self-organized systems may behave as though they have been designed with a goal. For instance, one may wonder whether the chance events of molecular biology would ever be able to design a complex functional enzyme such as the rotating molecular machine proton pump enzyme. Despite its complexity, this molecular machine has been the result of a high-probability evolutionary process.[18] Directed evolutionary methods have been used with great success in biological systems to design improved enzyme systems.[19,20] Manmade evolutionary catalytic systems have also been designed through mutation and adaptation, and theoretical methods for evolutionary dynamics have been developed for their description.[21]

The adaptive process that forms the reactive-surface state, in response to the reaction, stabilizes particular fluctuations in the surface structure. These fluctuations can be considered the analogue to mutations in biological systems. The catalytic practice to influence formation of the reactive surface state by the addition of promoting compounds can be viewed as an attempt to control the adaptation process.

In zeolite synthesis[22] the use of template molecules, which emulate the structure of reaction intermediates of a desirable catalytic reaction, biases the catalyst structure to favor the reaction by adaptation of its microcavities to the shape of a key reaction intermediate.

Methods borrowed from complexity science are an inspiration to future theories of catalytic systems design. The benefits, particularly to the theories of catalytic material synthesis, are something to look forward to.

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