Perspectives in Catalysis

From the century of the rate equation to the century of the rate constants: a revolution in catalytic kinetics and assisted catalyst design

M. Boudart

Departments of Chemical Engineering, Stanford University and University of California, Berkeley, CA, USA

Received 1 December 1999; accepted 18 January 2000

In the past, rate constants were extracted from rate equations obtained by fitting kinetic data. In the future, they will be calculated by computational chemistry or measured by surface science techniques. They will be used for the start-up of a microkinetic analysis in a combinatorial iteration for the development of optimized catalysts.

Keywords: rate constants for catalytic kinetics, assisted catalyst design

> "Catalysis is a kinetic phenomenon. The study of kinetics in catalysis started early in the 20th century in a phenomenological mode, then became linked to reaction mechanism in the 1920's, 1930's, and, finally, emerged as a systematized tool for process research and development in the 1940's and 1950's. It is currently going through a renaissance in surface science and organometallic chemistry. In the 1990's it will emerge as a predictive methodology for assisted catalyst design."

The above paragraph was written in 1991 and appeared one year later as the abstract of a paper in a book edited by John M. Thomas and Kirill I. Zamaraev. This book was part of a series devoted to Chemistry for the 21st Century, and was entitled *Perspectives in Catalysis* [1]. The purpose of this note is to acknowledge that there exists today a growing predictive methodology in assisted catalyst design, as anticipated in the abstract just mentioned.

Catalytic kinetics in the 20th century was dominated by the rate equation. It all started with two seminal papers by Bodenstein and co-workers. Both appeared in 1907. The first one dealt with the gas-phase reaction between H_2 and Br_2 to form HBr. The kinetic data were fitted to a strange equation for the rate v:

$$v = \frac{a[\mathrm{H_2}][\mathrm{Br_2}]^{1/2}}{1 + \{b[\mathrm{HBr}]/[\mathrm{Br_2}]\}}, \tag{1}$$

where [M] means the concentration of M and the parameters a and b do not depend on [M] [2]. It was especially bizarre because it showed that the product HBr was an inhibitor of the rate, although the overall reaction was clearly not limited by equilibrium.

The second paper [3] reported a surface-catalyzed reaction. It was the decomposition of gaseous SbH_3 into gaseous H_2 molecules and Sb atoms incorporated in the solid surface of antimony acting as a catalyst for the reaction. The rate equation was also unusual:

$$v = k[\mathrm{SbH_3}]^n, \tag{2}$$

with a non-integral exponent n equal to 0.55, 0.56, 0.63, and 0.65 at 0, 25, 50, and 75 °C, respectively.

In both cases, the rate equations (1) and (2) were obtained empirically by changing concentrations, temperature, and time. As it was, rate equations (1) and (2) for reactions that did not appear to be uni- or bimolecular had made their first appearance in the literature of chemical kinetics.

The explanation for equation (2) as proposed by Stock and Bodenstein remains in doubt [5], as is the case for the vast majority of heterogeneous catalytic rate equations. By contrast, a complete quantitative explanation of equation (1) was provided a few years *post facto*: the reaction is a free radical reaction, propagated by a closed, i.e., chain sequence of two elementary steps

$$\mathrm{H} + \mathrm{Br_2} \rightarrow \mathrm{HBr} + \mathrm{Br}$$
$$\mathrm{Br} + \mathrm{H_2} \rightleftharpoons \mathrm{HBr} + \mathrm{H}$$

with Br atoms in equilibrium with Br_2 molecules. The story of this first chain reaction has been told many times: it remains the classic example of chain reactions [4].

This brief historical account of the work of Bodenstein illustrates the kinetic approach during most of the 20th century studies of heterogeneous catalysis. First came the data, then the rate equation, and finally the fitting of the data into the rate equation by means of a hypothesized mechanism with rate constants chosen for the best fit [6]. The methodology for obtaining the rate equation from experimental data was systematized by Hougen and Watson [7]. It was practiced broadly in catalytic kinetics and its applications during the second part of the 20th century.

As time went on, more attention was paid to the physical meaning of the rate constants extracted from fitting data to a rate equation. Yet the new methodology of microkinetic analysis emerged only in the late 80's and early 90's, largely as a result of the pioneering work of Dumesic and coworkers [8,9] molecular modeling by Froment et al. [10].

Microanalysis starts with a meager data bank of guessed, estimated, or calculated rate constants for a putative sequence of elementary steps. A candidate catalyst is synthesized, characterized and tested under the best conditions, i.e., with another characterization *in situ*. Results suggest an improvement, and the cycle is iterated again, with improved results and a refined data bank.

The methodology is still in its infancy, but it looks promising. Note that there is no need for a rate equation: the kinetic program calculates activity, selectivity, under ideal or real process conditions. Computational chemistry, materials science and chemical reaction engineering help out in this *assisted catalyst design*. It is far from *a priori* design. But it is a new approach that will be perfected in the early part of the 21st century.

Microkinetic analysis is the best guiding technique in the search for new or improved catalysts by combinatorial chemistry. The latter methodology has been practiced since the days of Mittasch at BASF during the development of the first catalyst for ammonia synthesis at the beginning of the 20th century [11]. The difference between the Mittasch approach and the new combinatorial technique is the new decisive impact of new technology: computers, information technology, robotics, and micro-manufacturing of reactors. The new package offers high-speed parallel synthesis, screening, and testing of a large number of catalysts.

A recent lead article in *Catalysis Letters* provides a detailed perspective of the rapidly burgeoning field of combinatorial chemistry with high-speed screening of homogeneous and heterogeneous catalysts [11]. The work of diverse groups actively working in combinatorial catalysis is discussed in some detail. What is not discussed is the startup: how to choose a target and how to guide the combinatorial enterprise. The choice of target will be made as it has been in the past: the scientist will propose the chemistry that will be submitted to an engineering feasibility analysis backed by a sound business plan. But once the target has been agreed upon, what will guide the thrust of the combinatorial program? It cannot be left to whim or chance.

To propose an answer to this question, I return to my opening statement: catalysis is a kinetic phenomenon. In their lucid discussion of the various aspects of combinatorial chemistry applied to catalysis, the authors of the perspective article [11] do not discuss any sort of guidance. I submit that the best guidance is provided by an iterative microkinetic analysis based on rate constants of the assumed elementary steps. The process is explained elsewhere [12]. Here is a simplistic example. The gas-phase reaction, taking place in the stratosphere, destroys ozone:

$$\mathrm{O} + \mathrm{O}_3 \rightarrow \mathrm{O}_2 + \mathrm{O}_2$$

Ozone destruction can be accelerated by a catalyst X, following a catalytic cycle

$$\begin{aligned} \mathrm{X} + \mathrm{O}_3 &\rightarrow \mathrm{XO} + \mathrm{O}_2 \\ \mathrm{XO} + \mathrm{O} &\rightarrow \mathrm{X} + \mathrm{O}_2 \end{aligned}$$

that sums up to the uncatalyzed reaction. This catalytic reaction, with NO as the gas-phase catalyst X, is a celebrated example first demonstrated by H.S. Johnston. It can be shown [13] that the highest rate of the catalytic cycle can be achieved with a value of $D(\mathrm{X–O})$, the bond dissociation energy of XO:

$$D(\mathrm{X–O}) = (1/2)\left[D(\mathrm{O–O_2}) + D(\mathrm{O–O})\right].$$

In words, as shown in [14], the catalytic "site" X should bind atomic oxygen with an energy just inbetween the binding energies of O with O_2 and with O. If so, both steps in the optimized catalytic cycle will have the same activation energy. The *kinetics-assisted catalyst design* consists of tampering with the binding energies of the active site or sites, so as to optimize activity or selectivity by changing values of the rate constants involved in the catalytic cycle. If the values of these rate constants can be guessed, estimated, or calculated, the *catalyst composition and structure* may be modified so as to change the relevant rate constants in an optimum way. Without kinetic guidance, to go through a combinatorial campaign is to play dice with high technology. But kinetic guidance can load the dice. This can be done with a knowledge of rate constants, without knowing or writing the rate equation. The design follows an iterative process guided by microkinetic analysis.

With the growing importance of combinatorial technologies in catalyst design, it appears that the 21st century will be, for kinetics, the century of the rate constants, as the rate equation recedes into the background, perhaps in a simplified form that helps in the understanding of the mechanism if and when necessary.

The urgent need for rate constants in heterogeneous catalytic cycles demands the support of surface science, the discovery of molecular heterogeneous catalysts, the study of model catalysts, and the characterization of catalysts in their working state. In turn, the scientific community and the federal agencies will regard heterogeneous catalysis as an increasingly important contributor to the science of chemical reactivity and to the competitiveness of chemical process industries.

In conclusion, I want to recall a profound statement by Harold S. Johnston, under the title *Reaction Kinetics as a Predictive Science*:

> "In some branches of science, one can *predict* new or different situations. Other branches of science are merely explanatory: one fact, one theory; two facts, two theories; etc. The stage is now set to illustrate that a laboratory reaction may be predicted by way of *elementary*

rate constants (my emphasis) measured in completely different systems" [14].

It has taken more than 30 years for kinetics and heterogeneous catalysis to reach the stage that enabled Johnston to predict and verify the catalytic role of NO in the destruction of stratospheric ozone. While kinetics-assisted design of catalysts may not be truly predictive, it is a guiding tool based on the *elementary rate constants* mentioned by Johnston. Thus, it seems to me very pertinent to dedicate my present essay to Harold Johnston at the occasion of his 80th birthday.

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