

approach to zero emission system due to CO<sub>2</sub> (produced in fermentation and combustion processes) sequestration in phototrophic algae cultivation systems and vinasse utilization in algal mixotrophic systems and to positive energy balance due to utilization of energy stored in sugarcane bagasse or lignin in the integrated topology. And from other hand the integrated biorefinery takes advantage of the numerous components in multicomponent feedstock producing several low-volume, but high-value, chemical biochemical or biological products increasing the general profitability and assuring the economic sustainability. The PSE, Process Integration, LCA, exergy and economic analysis tools were applied at all steps of integrated biorifiery design, integration and evaluation for selected case study.

## CHEMICAL KINETICS OF COMPLEX REACTIONS: DECODING THE FUTURE

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The 20<sup>th</sup> century was a time of great achievements in chemical kinetics: this period is characterized by the triumph of catalysis and the discovery of new reaction types such as chain and oscillating reactions. That is why some scientists exclaimed: "Everything has been done in the past, chemical kinetics has been completed". As is well known, the idea that "physics is completed" was expressed explicitly at the end of the 19<sup>th</sup> century on the very eve of the atomistic revolution, which completely changed this scientific discipline.

At present, we could hear a similar "fin-de-siècle" point of view regarding chemical kinetics. In 2000, Michel Boudart stated that "...the 21st century will be, for kinetics, the century of the rate constants..." [1]. However, in the same year, Boudart also stated something different: "A catalyst is a resilient self-assembly in space and time. A dead catalytic material comes to life by contact with reactants... a catalyst as a dead object in line with a fixed structure is a wrong model of the catalytic cycle" [2]. We agree with Boudart's second statement, but not with the first one: the knowledge of the rate constants alone is not sufficient in our opinion.

The concept of the "end of developments in chemical kinetics" appears to be one of the illusions that crop up from time to time in the history of science. As most illusions it is fueled by reality.

Three major advancements that were crucial for chemical kinetics during the last 50 years are:

1. the development of new analytical techniques that enable monitoring the chemical composition of multi-component reaction mixtures;
2. the development of a battery of new physical methods for catalyst characterization, enabling the determination of the structure of the catalyst surface and the surface intermediates. Recently, it has become possible to apply most of these techniques *operando*, *i.e.* during the reaction;

3. the increasing availability of powerful computational tools and techniques that enable solving complex kinetic models including hundreds of components and thousands of reactions.

It is difficult to overestimate the importance of these developments for decoding complex mechanisms of catalytic reactions, although it is clear that neither new physical methods nor recent and future advances in computer hard- and software are a panacea.

### **A new paradigm for decoding chemical complexity**

In 2008, Geoffrey Bond concluded that “Comprehensive measurement of kinetics is the only reliable way of accessing the transition state, and any mechanism derived from other information must be regarded as tentative until confirmed by the kinetics, and any that is not in harmony with them is unacceptable”[3]. This statement is exactly our point of view. But what to do?

Even as early as 1934, Nikolai Semenov stated that: “The classification of reactions by their kinetic regularities, even though this is much more complicated than Mendeleev’s classification of elements by their properties (the periodic law), nevertheless seems possible”[4]. Semenov’s program was “to repeat the evolution of chemistry from the kinetic aspect”. In heterogeneous catalysis, this is an even bigger challenge, which can be formulated as follows: “What is Z, *i.e.* the mysterious active catalyst site, and how does it work during a reaction?” In 2006, Jens Rostrup-Nielsen wrote: “The concept of the ‘active site’ has changed over the last 40 years. Although the Langmuir approach has been very efficient in establishing simplified reaction kinetics the assumptions behind it do not reflect the reality of catalysis.”[5]. There are many related questions, for example:

- Which surface intermediates are really formed during the catalytic reaction and which role does each of those intermediates play in catalysis?
- Which phase transformations and transitions occur on the catalyst surface during the reaction?
- Do the subsurface catalyst layer and the bulk of the catalyst play a role in catalysis?

The key words in all of these questions are “during the reaction”, *i.e.* operando studies.

We deem that the new paradigm for decoding kinetic complexity will include two main constituents, *viz.* (i) advanced experimental kinetic tools and (ii) new mathematical tools.

### **Advanced experimental tools**

At first sight, paradoxically, catalysis provides a fast detour from reactant to product via a sequence of elementary steps and corresponding catalyst states. Certainly if combined with operando catalyst characterization, Temporal Analysis of Products (TAP) created in late 1980ies [6] will prove to be a unique technique due to the insignificant change of the catalyst composition during a kinetic measurement. The TAP–approach is presented as ‘chemical calculus’, a new theoretical and methodological framework of precise characterization of the solid material activity.

The three basic principles of the TAP–approach are:

1. Insignificant change of the solid material during a single-pulse experiment and controlled change during a series of pulses;
2. Well-defined Knudsen diffusion as a “measuring stick” for chemical reaction characterization;

3. Uniformity of the surface composition of the material across the active zone.

The first one can be considered as the main idea of 'chemical calculus'. The uniformity of the active material is achieved in Thin-Zone TAP-reactor (TZTR)-experiments.

The rigorous theory developed starting from the middle 1990ies [7-8] includes different methodologies, in particular the moment-based procedure and Y-procedure, i.e. an algorithm for the 'kinetically model free' reconstruction of non-steady-state reaction rates, gas concentrations and estimation of the surface coverages in the catalytic zone of TAP reactor.

Theoretical results of the TAP-approach have been illustrated by examples taken from the catalytic reactions of complete and partial oxidation. The current generation of TAP reactors, which operate at pressures well below atmospheric, can be considered as prototypes, and their operation needs to be extended into the domain of normal conditions, bridging the so-called pressure gap. In our opinion, the introduction of the "chemical calculus" technique into the researcher's routine is the main challenge in advanced kinetic studies.

Thus, with this approach, the "naive" definition by Berzelius (1835) of catalysis as a phenomenon that changes the composition of a reaction mixture, but leaves the catalyst unaltered, emerges again at a new level of understanding.

This approach combined with different operando techniques can provide answers to much debated questions, one of which is the question whether catalyst surfaces are "ideal" or "non-ideal", *i.e.* uniform or nonuniform.

Ideal models are based on the assumption of the classical mass-action law, *i.e.* these are models of the ideal adsorbed layer by Langmuir and Hougen and Watson. Non-ideal adsorbed-layer models are based on the ideas of the Soviet theoretical school (Temkin, Pyzhev Roginskii, Zel'dovich) [9-12] and account for different types of nonuniformity regarding thermodynamic and kinetic catalyst properties, in particular the dependence of the catalyst adsorption properties on its surface coverage. A vast amount of information on models of catalyst nonuniformity has been collected by Kiperman [15], see also [16].

Boudart has intensively popularized the achievements of the Soviet theoretical school, in particular in the United States. However, he also published a paper with the remarkable title "Classical catalytic kinetics: a placebo or the real thing?" [17], pointing out that: "Yet taking surface nonuniformity into account in catalytic kinetics has remained singular exception, except among the members of Temkin's school."

Ten years back, a discussion has re-ignited between two representatives of Temkin's catalyst science, Ostrovskii and Murzin. Ostrovskii demonstrated the constancy of molar heats of chemisorption over a wide range of surface coverages, based on available data on 40 metal-gas-systems [18] and concluded that "No surface heterogeneity reveals itself in catalysis and chemisorption on metals". He explained the "paradox of heterogeneous catalysis" formulated by Boudart [19] – inadequate models of nonuniform catalytic surfaces can be successfully used to describe kinetic data – as caused by the approximation of experimental data by sophisticated algebraic models, see also [20].

In reply to Ostrovskii's paper, Murzin stated that: "It can be thus concluded that surface heterogeneity manifests itself in catalysis and chemisorption. Despite the fact that the current catalytic engineering practice is very much limited to Langmuir-Hinshelwood kinetics based on concepts of ideal surfaces, there is a number of cases when such an

approach is not sufficient enough for the modeling of the kinetics of heterogeneous catalytic reactions” [21].

We consider this issue to be open and its solution hampered by lack of direct measurements of catalyst characteristics such as surface composition and thermodynamic properties during the course of the reaction. Time will tell whether this discussion will be as significant as the long and famous controversy between Berthollet and Proust about the law of definite proportions, see e.g. [22]. In the end, we will know whether nonuniformity is similar to phlogiston, see e.g. [23] or indeed a useful concept. And, who knows, maybe the explanation of relationships between the ideal model and a model that takes into account nonuniformity, is non-trivial. As Richard Feynman put it: “... two schools of thought exist. One will say that it is really simple, ... but that there is a little complication ... Then there is another school of thought, which has only one representative, myself, which says no, the thing may be complicated and become simple only through the complications”[24].

In our opinion, even now the ideal models of complex reactions based on the mass-action law have to be analyzed first. Why? One could say: “because of Occam’s razor”, see e.g. [25]. More precisely formulated, the theory of complex chemical reactions that allows decoding the chemical complexity – or at least its first version – can be constructed only based on the assumption of a simple (ideal) dependence of the elementary reactions. Later, the rigorous non-ideal models may or may not be constructed, e.g. using the Marcelin-de Donder formalism of non-ideal potentials, see [16].

### **New mathematical tools. Chemical kinetics and mathematics**

There has been a long tradition of tension and misunderstanding between chemists and mathematicians. The expression “it is a typical chemical stupidity” is sometimes attributed to David Hilbert, one of the greatest mathematicians of the 20<sup>th</sup> century. Famous character Sherlock Holmes expressed his point of view as: “Well, I gave my mind a thorough rest by plunging into a chemical analysis”. Read in its context, it is clear that this phrase does not imply any deprecation of chemistry, because the next line is: “One of our greatest statesmen has said that a change of work is the best rest. So it is. When I had succeeded in dissolving the hydrocarbon which I was at work at, I came back to our problem...” (from Chapter 10 of “The Sign of Four”, the second book by Sir Arthur Conan Doyle featuring Sherlock Holmes, published in 1890).

From the other side, Auguste Comte, not a chemist but a well-known philosopher of the 19<sup>th</sup> century and founder of sociology said: “If mathematical analysis should ever hold a prominent place in chemistry – an aberration which is happily almost impossible – it would occasion a rapid and widespread degeneration of that science” [26].

Then again, the great mathematician James Sylvester, after having become acquainted with the records of Frankland’s “Lecture Notes for Chemical Students” [27], wrote: “The more I study Dr. Frankland’s wonderfully beautiful little treatise the more deeply I become impressed with the harmony or homology... which exists between the chemical and algebraical theories. In traveling my eye up and down the illustrated pages of “the Notes”, I feel as Aladdin must have done in walking in the garden where every tree was laden with precious stones, or like Caspar Hauser when first brought out of his dark cellar to contemplate the glittering heavens on a starry night. There is an untold treasure of hoarded algebraical wealth potentially contained in the results achieved by the patient and long continued labor of our unconscious and unsuspected chemical fellow-workers” [28].

We hope that such misunderstanding belongs to the past or that at least the situation has improved. In fact, there are many examples of the fruitful collaboration between chemists and mathematicians.

We believe that the interaction of physicochemical and mathematical ideas in the area of chemical kinetics can be much more than just successful illustrations of mutual support. The most important within chemical kinetics is that new problems, which are interesting from a mathematical point of view, have been and will be formulated. There are many unsolved problems in the theory of "chemical calculus". The theory of nonlinear kinetic problems is very far from being completed. For example, the problem of the analysis of nonlinear steady-state kinetic models for multi-route mechanisms has not been solved yet. To some extent, the same holds for the relationships between the structure of detailed mechanisms and complex kinetic behavior such as hysteresis, oscillations, etc. Even in the classical linear models, there may be many as yet undiscovered properties. For example, recently surprising and previously unknown properties have been found of very simple kinetic models, *viz.* coincidences and time invariants, which have already been verified experimentally [29-39]. These discoveries are an indication of a "new wave" of interesting results, a possibility of chemico-mathematical synthesis already felt by Sylvester. We hope that Sylvester's intuition finally will be realized.

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