



Account/Revue

# Evolution of heterogeneous catalytic reactions kinetics with time<sup>☆</sup>



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## ABSTRACT

An overview of development of heterogeneous catalytic kinetic concepts is presented. An emphasis is made on the application of mechanistically sound models, which are needed as a part of the understanding of catalytic reactions on a molecular level as well as of the design and the intensification of chemical processes. Such models should include among other parameters the size and geometry of reacting molecules, size of nanoclusters and deactivation as a part of the reaction mechanism.

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Catalysis by its very definition is a kinetic process; thus reliable kinetic models describing the rate of catalytic reactions are a vital part of any catalytic research either focused on the understanding of reactions on a molecular level or on more engineering aspects such as design and intensification of chemical processes [1–10].

It is even possible to say that reaction kinetics is the translation of our understanding of the chemical processes into a mathematical rate expression. The tradition of kinetic modelling is very long. For practical purposes in the past, power-law models have been used, although their applicability is limited as they do not predict reaction rates, concentration and temperature dependences outside the range of the studied experimental conditions.

Mechanistic models based on the knowledge of elementary processes (adsorption, desorption, surface reactions) provide reliable extrapolation outside the studied interval, making a particular reaction intellectually better understood.

Quite a number of textbooks on catalysis and chemical engineering contain “ready-to-use” equations, while few

[6,11] go in more depth on the principles of derivation of kinetic equations, using for example a theory of complex reactions [10,11].

The current trend is to utilize the so-called microkinetic approach [4,9] bringing physicochemical understanding of elementary steps into kinetic modelling, which helps dramatically in case of complex multistep reactions. Without such analysis, which in fact dates back to the development of the first computer programs for numerical data fitting of kinetic data in the 1970s, parameter estimation becomes extremely challenging, not resulting in reliable values of parameters.

Even if there is a long tradition in kinetic modelling in current-day catalytic research, one could see a clear decline in the utilization of the kinetic approach, mostly because it is time consuming. The second reason is that in the recent years many new experimental and theoretical tools have appeared, including various characterization methods and computer programs for quantum chemical calculations. Kinetic research, which used to be one of the few or maybe the only one method available, is not in fashion anymore. As a result, very often developed mechanistic concepts, based for example on spectroscopy and density functional calculations, are not tested against available kinetic data.

<sup>☆</sup> Thematic issue dedicated to François Garin.

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Certainly kinetic modelling cannot be a final proof of any mechanism, as particular kinetic models could correspond not to a single mechanism. However, kinetic analysis can be used to differentiate between rival mechanisms and eliminate incorrect mechanistic proposals.

The latter approach is particularly lacking in organic catalysis when rather complicated mechanisms with one or several catalytic cycles and a myriad of catalytic species are proposed without any derivation of kinetic equations and even qualitative analysis of the reaction kinetics.

Besides this obvious need for more widespread kinetic analysis of complex reactions, there are also some other areas where kinetic studies could essentially contribute, addressing the current needs of research in heterogeneous catalysis. Such contribution should be based on the present-day understanding of catalytic chemistry. Let us consider in detail few particular issues.

First is the size and geometry of reacting molecules. For very many years, in kinetic modelling, simple or rather simple kinetic models were based on the so-called Langmuir–Hinshelwood and Eley–Rideal mechanisms assuming one adsorbed site for the reactants, independently of their complexity and size.

In catalytic reactions involving organic molecules, the size of the latter can be ca. 0.5–1 nm, which means that the multi-centered nature of adsorption and differences in size of the reacting species should be taken into account in kinetic modelling. Few examples from the literature where such approach was considered could be mentioned [12–20]. Moreover, in kinetic models for catalytic reactions involving complex organic molecules with different functional groups, the mode of adsorption, requiring different numbers of catalytic sites, is important and should be reflected in kinetic modelling [1].

Such reactant sizes as mentioned above are in fact in the same range as the size of nanoclusters, imposing a severe restriction on the number of adsorbed molecules per cluster, as only few molecules could be adsorbed on the surface. Theoretical analysis of such cases was reported [21].

Even if it was realized a very long time ago [22] that the activity in the cluster size domain of 2–20 nm could be dependent on cluster size, incorporation of the cluster size in kinetic equations giving a quantitative explanation of structure sensitivity has started to be applied in kinetics research only very recently [23–34].

Another important issue worth mentioning in this short overview is the explosion of research devoted to transformations of (ligno)cellulosic biomass. Although some reactions of biomass processing are similar to those used in conventional refining and chemical industries such as hydrogenation or oxidation, there are also fundamental differences associated with the large number of functional groups (hydroxyls) present in biomass.

Apparently there would be a need for studying in the future kinetics of such reactions as aqueous phase reforming, catalytic pyrolysis, hydrolysis of poly- and oligosaccharides, ketonization, decarboxylation, aldol condensation, dehydration, etc. In some cases, for example aqueous phase reforming, kinetic modelling can be very

challenging, since quite a number of intermediates and products are formed. A recent paper on kinetic modelling [35] of this reaction represents a first attempt, which was however substantially limited only to gas-phase products.

Kinetic analysis of such complex reactions would require a special attention towards selectivity, which should be properly analyzed. Such analysis (for example one product vs. another one, selectivity vs. conversion) can significantly help in constructing the correct reaction network as well as diminishing the number of parameters to be determined by data fitting. Some computer programs could even nowadays have a possibility to combine differential ( $dc/dt$ ) equations with algebraic ones (i.e. selectivity vs. conversion).

Another complication in studying lignocellulosic feedstock is the presence of impurities, which can vary depending on the feedstock type and origin.

Typically deactivation is incorporated in the kinetic modelling of continuous processes in oil refining and other process industries through a time-dependent catalyst activity factor, even if time is not a true variable. Deactivation, however, should be considered as a part of the reaction mechanism and there are already examples of this approach available in the literature [36,37].

It should be also mentioned that heterogeneous catalysts can undergo transformations during catalytic reactions (changes in morphology, phase transformations, sintering, etc.). Such changes are yet to be considered in kinetic analysis, even if there are already some examples when for example sintering is quantitatively described [38].

Kinetic analysis discussed above was mainly related to catalysis by supported metals. Oxide catalysts have recently been considered as a modern alternative to noble-metal catalysts, leading to different selectivity behavior compared to noble-metals, for example in ring opening of methylcyclopentane [39–41]. Such difference can be ascribed to different compartment and should be then properly reflected in reaction kinetics.

Few final words could be related to methodological aspects of kinetic measurements in catalysis.

First experimental data that are thought to be important and relevant should be collected in the broad range of parameters followed by regression analysis, estimation of rate constants, and evaluation of the model adequacy.

Among the tools which appeared rather recently, one should mention micro-(micro-structured, microchannel) reactors with the size of channels typically ca. 10  $\mu\text{m}$ –2 mm, allowing to conduct reactions in a small scale. Microreactors can easily provide short residence time, provide or remove the heat and allow sufficient mass transfer. Such reactors are also suitable for acquisition of kinetic data for gas–solid catalytic reactions, as illustrated recently [42,43], even if there are still challenges associated with the deposition of catalytic layers in microreactors.

In this short account, it was not possible to consider in detail all aspects of catalytic kinetics and thus only few topics were selected, mainly reflecting the personal view and experience of the author.

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