

Theoretical catalysis

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THEORETICAL CATALYSIS

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INTRODUCTION

The ultimate aim of catalysis modelling theory is the a priori design of a catalyst for a proposed reaction. A second goal of theoretical catalysis is the development of a kinetics modelling approach based on first principle elementary reaction rate constant parameters.

The main conceptual limitations to be overcome are the complexity of the catalyst as well as the complexity of catalytic kinetics.

Issues are the mechanism of the reaction, the composition of the catalytic center under reaction conditions and transport of catalytic reaction intermediates through the catalytic system.

Nonetheless, impressive advances have been made. Essential to this progress has been the careful tuning of theoretical means with experiment.

An example is the design of a new zeolite catalyst for catalytic dewaxing [1]. Using graphical, geometric and steric modelling of the sites adopted by a guest molecule representative of the products and intermediates of a desired reaction proposals were made of templates to be used in zeolite synthesis. These templates control the shape of the zeolite micropores.

The main use of theoretical studies in catalytic kinetics has so far been the analysis of the reactivity of reaction intermediates.

The essence of catalysis is the concept of the catalytic reaction cycle. Knowledge on reaction intermediates, their transformations and the nature of the reactive catalyst center determine our level of molecular understanding of catalysis. The classical picture of catalysis by a surface has been provided by Langmuir [2]. He proposed a surface with a finite number of equal vacant sites. Adsorbates are supposed not to interact. Recent surface scientific investigations have convincingly demonstrated that the reality of the reactive surface is significantly more complex [3]. Generally the interactions between adsorbates cannot be ignored. The resulting ordering of adsorbates on a surface will strongly affect the rate of surface processes. A theoretical approach has to be capable of a detailed analysis of the lateral interaction effects

The reactivity of isolated atoms and atoms that are part of the overlayer may differ. During reaction significant surface reconstruction may occur.

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The concept of a catalytic reaction cycle implies that the microscopic picture of catalysis is a dynamic one (see Fig. 1).

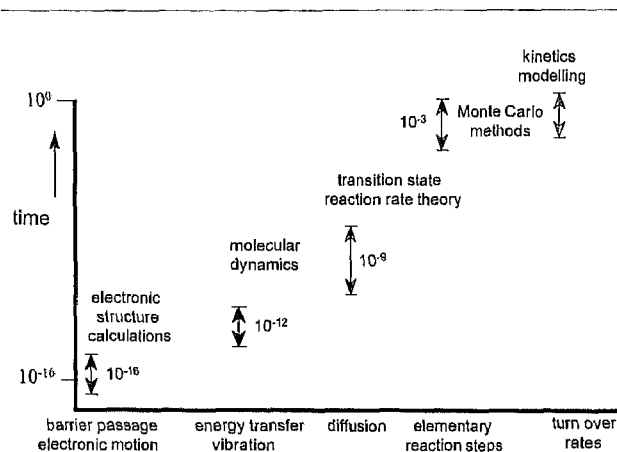


Figure 1
Timescales in kinetics.

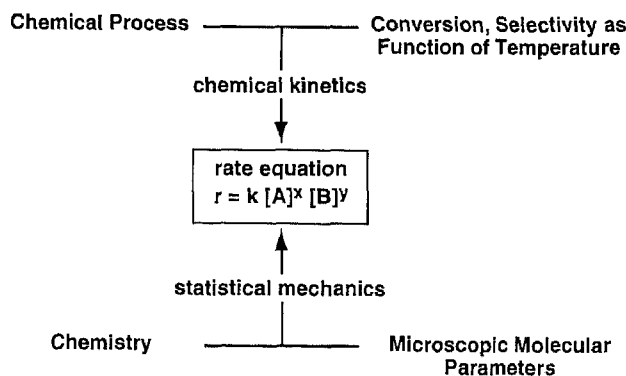


Figure 2
The relation between kinetic and molecular chemical parameters.

The timescale of a catalytic event is typically a microsecond or longer. However, surface atoms will rearrange on a picosecond time-scale, the same time-scale at which adsorbed molecules will equilibrate to the surface. On a time-scale varying between a nanosecond and a microsecond surface diffusion and reaction events can take place.

As illustrated in Fig. 1 each time regime requires a different theoretical treatment. It implies that a hierar-

chy of different methods has to be applied to reach the ultimate level appropriate for the timescale of overall catalytic kinetics.

Microscopic theory determines the kinetic parameters to be used in the macroscopic kinetic equations (see Fig. 2).

Quantum-chemical calculations provide information on the stability and dynamics of molecular intermediates of elementary reaction steps of the catalytic reaction cycle. Once one has formulated a molecular model of a reaction complex, transition state reaction rate theory can be used to compute reaction rate constants. This has been done successfully for several zeolite [4]- and metal-catalysed reactions [5].

STATUS OF THEORETICAL MODELLING THEORY

Quantum chemistry has traditionally contributed to experimental chemistry in two ways:

1. Interpretation of electronic and vibrational spectra
2. Formulation of reactivity rules.

Computed spectroscopic properties can be compared with experiment and hence the existence of the intermediate in the reaction is validated.

A similar approach can be followed to model the structure of a catalyst and compare its computed physical properties with experiment. The comparative approach of experiment and theory has become especially useful due to advances in the development of catalytic model systems and in-situ spectroscopic techniques.

There are two situations where this methodology is highly successful:

- a. First principle calculations on organo-metallic complexes and clusters, representative of actual catalyst components or as models for catalyst surfaces.
- b. Molecular mechanics simulations of crystallographically well defined and three-dimensional extended systems, based on (semi) empirical or ab-initio two- or three body-potentials.

Ad a. Density Functional Theory electronic structure computations have become the method of choice for studies involving transition-metals [5, 6, 7]. However, also for the study of proton-transfer reactions DFT can be fruitfully applied [4d]. There is not only a need to compute the electronic structure and energy of a system accurately, but one also has to predict geometries.

The interaction energies can be typically computed with an accuracy of ~ 20 kJ/mol. Accurate electronic structure calculations cannot only be done on clusters but also on extended three dimensional systems or slabs, simulating the metal surface.

Techniques, as the Car-Parinello method, are becoming available to also perform geometry optimization in extended systems [8]. The complexity of the system to be studied is mainly limited by computational limitations.

Ad b. Solid state modelling allows for the rapid development and evaluation of structural models [9]. They can also be used to predict physical properties as vibrational spectra [10] or elasticity constants [11]. Very complex systems can be analyzed.

The main limitation to this approach is the availability of suitable two- or three-body potentials. Recently, potentials have become available obtained by fit procedures to cluster energies from ab-initio quantum chemical calculations [12]. Once classical two- or three-body potentials are available, statistical mechanical methods as Monte Carlo techniques and Molecular Dynamics can be applied to predict the distribution of molecular adsorption sites, free energies of adsorption, and diffusion constants. The accuracy of the predictions of course depends on the quality of the potentials.

There is a need for extension of the currently available potentials.

Docking techniques have been applied to locate guest molecules within a host matrix. Molecular Dynamics techniques can be applied to probe preferred guest locations [14].

Configurational biased grand canonical Monte Carlo techniques can be used to study the adsorption of linear alkanes as a function of temperature and concentration. This method is suitable to also study ordering and phase transitions within the adsorbed layers [15].

Related techniques are Molecular Dynamics applications to compute rates of diffusion [16].

Molecular dynamics approaches to compute diffusion rates are useful only as long as the activation barriers for diffusion are low ($\Delta E < 5$ kT). When activation barriers for a reaction become too large ($\Delta E > 5$ kT), the rate processes become too slow and molecular dynamics approaches cannot be used.

Now, techniques as the generalized Langevin method [17] or transition state reaction theory [18] have to be applied.

These techniques become useful when intra- and intermolecular energy exchange becomes fast compared to the overall rate of the kinetic event.

Due to the availability of transition state search routines in several quantum-chemical computer programs, first principle transition state reaction rates can now be computed from computed barrier height and vibrational frequencies [4, 5]. This implies that in principle all ingredients for the computation of the reaction rate based on an analysis of the full catalytic cycle are available.

Reaction energy diagrams representing the change in enthalpy of each successive elementary reaction step in the catalytic reaction cycle, provide useful information. Inspection of such diagrams may suggest candidates for rate limiting steps for which in consecutive studies the reaction rate constants can be computed.

First principle reaction energy diagrams of two heterogeneous catalytic reaction cycles [19] have recently become available: the oxidation of NH_3 by Cu and desulfurization of thiophene. Earlier reaction energy diagrams for homogeneous reactions were produced by Morokuma [20].

Different reaction energy diagrams are produced dependent on the mechanistic assumptions. This can be used to discriminate between different mechanisms.

To simulate the overall kinetics of a reaction it is essential to incorporate explicitly the change in the composition of the catalyst surface during reaction. The application of special statistical mechanical techniques is needed to study the "many" particle problems that appear in chemical kinetics of surface adlayers, that due to lateral interactions between the particles cannot be considered to be ideally mixed. This is especially important when surface reconstruction, island formation or ordering effects occur in the surface layers of the catalyst.

Monte Carlo techniques have been developed [21] to analyze the changes in pre-exponential factors that appear as a result in simulations that include such non-ideal behaviour.

Notwithstanding the current successes, there is still a need for further methodological development. Another related problem is the extension of the description of the catalytic reaction to the liquid phase.

Effective medium approaches are available that account for the polarization effects due to solvent media [22]. However, molecular details of the first and second coordination shell appear very important and have to be simulated in corresponding molecular models.

CONCLUSION

The main reason for the increasing relevance of model systems to simulate catalytic behaviour is their closeness to the chemical reality. This is due to the availability of computer systems allowing for large scale computing at reasonable cost.

One foresees that in the near future the size of transition metal clusters to be used in first-principle Density Functional Theory approaches will increase from the current limitation of ~20 metal atoms to ~100 metal atoms. A parallel development will be the possibility to do computations on slabs representing transition metal surfaces with increasing unit cell size. These developments are especially of importance to incorporate consequences of surface reconstruction and island formation into catalytic theory.

From a methodological quantum-chemical point of view there are still questions on the accuracy of predicted transition states and weak van der Waals bonding.

Improved and more extended sets of two-body and three-body potentials are needed for Molecular mechanics, Molecular Dynamics and Molecular Mechanics studies of structures, adsorption and diffusion. Transition state rate theory methods have to be extended to study activated diffusion as a function of concentration. Also quantum-dynamical corrections have to be developed for the many reactions that involve proton transfer. A combination of molecular dynamics and quantum-mechanical procedures will have to be used to extend catalysis theory from the gas-solid to the liquid-solid interphase.

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