MAKING KINETICS AT SURFACES A MORE EXACT SCIENCE

Introduction

Quantitative understanding of reactions at surfaces is essential for heterogeneous catalysis—an important cornerstone of modern society. Catalysis is about making chemical reactions possible at conditions where they would usually not occur. The catalyst accomplishes this by increasing the rate of chemical reactions and much effort in chemistry is spend on quantifying its action. The action of a catalyst is characterized by its activity and selectivity. Activity is the degree by which the desired product formation rate is increased, while selectivity reflects the degree by which the rate of unwanted side products is suppressed. These properties can be fully quantified when elementary rate constants of all underlying processes, like adsorption, diffusion, reaction and desorption are determined from experiment or theory. Today, catalyst discovery is increasingly transitioning into full in silico modelling, where elementary rate constants are predicted ab initio. For heterogeneous catalysis, this usually means using density functional theory (DFT) at the level of generalized gradient approximation (GGA) and transition state theory (TST) [1]. Unfortunately, the few experimental benchmarks available are enough to teach us that GGA-DFT based binding energies and reaction barriers are only accurate to within ±0.2 eV—far below chemical accuracy [2]. Furthermore, simplifying approximations are employed when TST rate constants are characterized, e.g., using harmonic and classical approximations for the evaluation of reactant and transition state entropies [3] or neglecting recrossing corrections. These theoretical methods, despite becoming a common practice for characterizing surface chemistry, uniformly lack validation from precise experiments. Given the fact that these untested methods are likely to influence our choice of the catalytic material for a given purpose, this situation remains highly unsatisfying.

The Velocity Resolved Kinetics (VRK) Technique

Transient rate measurements are very instructive to quantify chemical reactions at an elementary level. Therefore, tracking the rates (or concentration) as a function of reaction time is essential. Few years ago the Velocity Resolved Kinetics (VRK) method was developed, opening up the possibility to measure such data for surface reactions with extraordinary precision [4]. The idea behind VRK is to study transient rates of surface processes using a pump-probe scheme. Pulsed molecular beams deliver reactants to the catalytic surface held under ultrahigh vacuum (UHV)—see Fig. 1(a). One of the reactant beams has a temporal profile as short as 10 μs and initiates the reaction (pump-pulse). At the same time this reactant pulse dictates the temporal resolution of the experiment. A second reactant beam is temporally overlapped with the first reactant pulse at the surface or used as a dozer, which allows scaling of surface coverages. The desorbing products and reactants are ionized via multiphoton ionization (probe-pulse), while scanning the delay between the reaction-initiating molecule pulse and the laser pulse. Species selection is ensured by the ion’s time of flight (along z-axis, see Fig. 1b), which is determined by MCP detector gating with respect to the pulsed field extraction. The ion imaging detector is positioned parallel to the scattering plane (xy-plane, Fig. 1) and allows to map the in-plane velocity distribution of desorbing molecules. This is achieved either by spatial imaging or, with improved resolution, using velocity map imaging.

The knowledge of product velocities is essential for precise measurement of surface reaction rates. The simultaneous measurement of ionized product signal (particle densities) and their corresponding velocity enables the straightforward conversion of density to flux, the latter being equivalent to the surface reaction rate. From the instrument geometries and the velocity measurements, the reactant and product flight times (i.e. nozzle-surface, surface-laser and laser-detector) are easily subtracted from the beam-laser delay time to yield the absolute reaction time axis. VRK is thus a very direct method that provides transient kinetic traces—product flux vs. reaction time data. Such data remained elusive for many previous surface science techniques [6,7].

Taking Advantage of Reaction Dynamics

The ability to measure kinetic traces is a necessary requirement for the determination of elementary rates and reaction barriers, but often not sufficient to disentangle the processes dictating the magnitude of the observed rates. Here, experiments at varying coverages of reactants, varying concentration of catalytic active sites and isotope exchange experiments can be especially instructive. These simple kinetic “tricks” are well established and not specific for VRK experiments. However, the ability to investigate the reaction dynamics while measuring kinetics is unique to VRK [6,7] and can provide additional information about the reaction barriers and provide the complimentary information needed to investigate the mechanism of surface reactions.

This was for example essential to understand the kinetic mechanism of CO oxidation on atomically flat and stepped Pt surfaces. Here, CO$_2$ was formed in two dynamical channels, where each had a different transient formation rate. This observation alone was in contrast to the “established” idea that different dynamic channels emerged as a consequence of post transition state dynamic rather than from different reactions at the surface. The VRK data was informative enough to disentangle an active-site specific mechanism for CO oxidation and to determine the elementary rate constant for this reaction at Pt(111)-terraces [4].
Robust Microkinetic Framework

While investigation of reaction dynamics helps to understand surface reaction mechanisms in some cases, such occurrences tend to be rare, as most reaction products thermalize with the catalyst prior to desorption. It is therefore important to have a solid basis upon which VRK data are modelled and analyzed. The seemingly simple example of thermal NH\textsubscript{3} desorption from Pt underlines the importance of a robust analysis framework [8].

From VRK experiments we found that NH\textsubscript{3} desorption from Pt(111) with 0.4\% step density experienced non-trivial kinetics, while the same experiment at highly stepped Pt(332) yields first-order rates as expected from a conventional desorption process. The desorption rate from Pt(332) is slower than from Pt(111), indicating a stronger NH\textsubscript{3} binding to steps. To explain the VRK data uniformly, the competition between NH\textsubscript{3} desorption and NH\textsubscript{3} diffusion from terraces to steps—exchange between the active sites of the catalyst—had to be modeled explicitly. Using a comprehensive diffusion-desorption model, elementary rate constants for site-to-site hopping and desorption were obtained from a global fit to the experimental data. We found that NH\textsubscript{3} diffusion barrier at (111)-terrace is unexpectedly high, taking almost 65\% of the binding energy, which led to a strong competition between diffusion and desorption. On Pt(332), where the step density was high, the exchange between steps and terraces was on a shorter timescale than the surface residence time, which resulted in a uniform population and first-order kinetics. On Pt(111), however, the distance between steps was too large to ensure fast exchange of all molecules between the active sites during their residence time. This circumstances explained the non-trivial desorption kinetics from Pt(111). At early desorption times we probe predominantly molecules that have never managed to reach the steps and, therefore desorbed from terraces, while at late desorption times we detected those which have interacted with steps and experienced an increased residence time at the surface.

The motivation for studying NH\textsubscript{3} desorption from Pt is due to its importance in the Ostwald process. In addition, the exchange between active sites is of special interest for this chemistry as it is well known that NH\textsubscript{3} oxidation on Pt is dominated by steps [8–9]. Based on the experimentally determined elementary rate constants we could easily predict the competition between diffusion and desorption at high temperature conditions typical for the industrial process. It turned out that under these conditions the desorption becomes increasingly important compared to diffusion, resulting in suppressed exchange between active sites. One apparent consequence of these findings is that mean field rate equations, frequently employed in heterogeneous catalysis, are not appropriate for modelling of reaction rates in the Ostwald process [8].

Benchmarking Elementary Rate Constants

It will not always be possible to extract all elementary rate constants from the experiment. This is why those constants, which can be determinedhave to be precise enough to improve ab initio methods for rate constants modelling. An obvious starting point can be the hydrogen atom recombination at Pt(111)—probably the simplest surface reaction [10].

The thermal rate constant for H-atom recombination at Pt(111) has previously been reported with large uncertainties, making a serious comparison to theory impossible. One of the challenges in past experiments, preventing a definitive conclusion about the magnitude of the rate constant, was the determination of the initial reactant concentration, which is essential for the determination of a second-order rate constant. Spatial ion imaging implemented for VRK experiment allowed us to overcome past limitations, by mapping the absolute spatial density profile of the incoming molecular beams with H\textsubscript{2} and D\textsubscript{2} as reactants. Using independently determined sticking probabilities we obtained the initial concentration of hydrogen atoms at the surface, and combined them with the transient HD, H\textsubscript{2} and D\textsubscript{2} formation rates generating the temperature dependent rate constants—see Fig. 2.

Unfortunately, the intrinsic uncertainty in DFT calculated desorption barriers prevented a meaningful comparison to experiments. To surmount these uncertainties we employed an exact TST formulation, where the dividing surface is placed at very large separation from the surface. With the principle of detailed balance it can be shown that this choice of the dividing plane results in thermal sticking coefficients as the recrossing correction [11]. The recombination rate of the Detailed Balance Rate Model (DBRM) is given as:

\[ k_d(T) = \langle S \rangle \cdot \frac{k_B T}{2 m} \cdot \frac{Q_{H^2}}{Q_{H_2}} \exp \left( \frac{E_0}{k_B T} \right). \]

The advantage of DBRM is that most parameters can now be replaced by experimental values—H\textsubscript{2} dissociative binding energy \( E_0 \), the partition function of gas phase molecule \( Q_{H_2} \) and thermal sticking coefficient \( \langle S \rangle \). These parameters are available from complimentary experiments. The only remaining is the partition function of the adsorbed hydrogen atom. In fact, the combination of accurate experimental rate constants and the DBRM framework provided the unique opportunity to directly test the established approximations for adsorbate partition functions. The most widely applied approach for the description of partition functions is the Harmonic Approximation (HA), where the adsorbates degrees of freedom are described as harmonic oscillators. Another approach that is considered to be very accurate is the Complete Potential Energy Sampling (CPES) [3]—a classical partition function with full in-plane potential energy surface (PES). Unfortunately, neither HA nor CPES were able to describe the experimental rate constants within one order of magnitude—see Fig. 2.

The CPES method is unable to describe the strong delocalization of H-atoms, expected from Heisenberg’s uncertainty principle. As a result CPES strongly underestimates the adsorbate entropy, which results in a factor of five error for the rate constant even at 1000 K. The nuclear quantum effects are easily included in the partition function by explicit counting of the H/Pt(111) eigenstates determined from the solution of the nuclear Schrödinger equation on the DFT calculated PES. The determined adsorbate partition functions were insensitive to the choice of the PES from different exchange-correlation functional, indicating that the partition function is accurate [10].

![Figure 2: Experimental and theoretical rate constants for hydrogen atom recombination at Pt(111). Rate constants (lower inset) are obtained from VRK, Temperature Programmed Desorption data are from Ref. [12] (upper inset). The lines are the DBRMs. The CRM is based on the CPES partition function while QRM includes nuclear and electron spin quantum effects in the partition function for H\textsuperscript{+}.

Temperature/K

<table>
<thead>
<tr>
<th>Rate Constant</th>
<th>Experiment (VRK)</th>
<th>CRM</th>
<th>DBRM</th>
<th>QRM</th>
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The inclusion of nuclear quantum effects have cured the experiment-theory mismatch only partially. It provided an accurate temperature dependence, which HA and CPES could not capture. However, the rate constants remained off by a factor of four. We assigned this contribution to the missing electronic partition function accounting for the electron spin of H-atoms. So far electronic partition functions have been uniformly ignored in modelling reactions at metal surfaces. This is certainly done with the idea that the electron spin of the adsorbate is “blurred” when binding to metals. However, the spin degeneracy of a gas phase H-atoms electronic ground state cannot vanish in the adsorbate-metal system as a whole. The fact that only one out of the four spin states correlates to the electronic ground state of H₂ (singlet) leads to a four times smaller thermal rate constant. It is interesting to realize that, while nuclear quantum effects are quite specific to reactions involving hydrogen, quantum effects associated with electronic spin are likely to be important for many other reactions at metal surfaces.

**Conclusion and Future Challenges**

So far, VRK work has predominantly focused on quantifying adsorption, diffusion and desorption. This is necessary in order to understand surface reactions at an elementary level. In many ways, quantifying elementary rates is like building pyramids, where the basis has to be strong enough in order to proceed to higher levels.

Furthermore it is important to realize that the beautiful idea of an elementary rate constant, i.e., universally applicable building blocks for kinetic mechanisms, also has limitations. Especially for surface reactions, where high reactant coverages may be present, the applicability of rate constants obtained at low coverages is limited. It is therefore essential to understand elementary rates, not just as a combination of two random parameters—activation energy and prefactor—but at the level of the basic interaction energies determining their magnitude. Only when we understand the dependencies and changes of the energy landscape, for example due to adsorbate-adsorbate interactions, will we be able to make accurate predictions in surface chemistry. The analysis of accurate rate data, such as those provided by VRK, using a solid microkinetic framework and the DBRM is certainly a big step in the right direction.

Also the VRK technique itself offers room for improvements. One example is the limitation of conventional VRK when it comes to non-stationary catalysts. So far, VRK was employed on simple model catalysts, where between two pump-probe cycles the catalyst returned to its initial state. However, a real catalyst will tend to change under operational conditions and methods able to track the changes of transient rates are desired. VRK improvements are underway that will make the technique applicable to more advanced materials and challenging non-stationary phenomena in catalysis. Some first attempts in this context have been successful [13] promising a bright future for surface reaction kinetics research.

**References**