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Quantitative kinetics for mechanisms in heterogeneous catalysis

The apparently magical property of some solids to accelerate chemical reactions under conditions where they are usually too slow to be observed, has captivated chemists since the early 1800s. Research has since revealed a rich world of new chemical phenomena occurring on surfaces and, two centuries later, our modern chemical industry relies on heterogeneous catalysis to guide reactions with high selectivity and reduced energy demands, making large-scale technical processes economically viable and sustainable.

Despite its importance and enormous effort, we still lack a fundamental understanding of the chemical mechanisms underlying heterogeneous catalysis. In gas phase chemistry, by contrast, such understanding has essentially been achieved, owing to the continuous development and refinement of electronic structure methods, rate theories and methods for making reaction rate measurements, which have been used to validate theory. For reactions on surfaces, we still face two important limitations: (i) the need to employ computational methods for periodic systems that scale favorably with system size, and (ii) the experimental difficulties to accurately measure the rates of elementary reactions in catalysis.

Over the past decade, significant experimental advances have enabled accurate measurements of elementary surface reaction rates in well-defined model systems. This has allowed theory and experiment to be meaningfully compared for the first time; a process of analysis that now routinely reveals fundamental reaction mechanisms in heterogeneous catalysis. In fact, theory can often reproduce rates of reactions on model catalysts with surprising (nearly quantitative) accuracy. Of course, this can only be achieved when one avoids certain pitfalls, some of which we illustrate below. The accumulating evidence coming from recent work shows that we are now within reach of quantitative chemical models of real catalysis.

Obtaining quantitative kinetics of surface reactions

Figure 1 shows experimental HD formation rates measured when a pulsed molecular beam of H_2 and D_2 (1:1) impinges on a platinum surface [1]. The desorbing HD molecules are detected with a combined laser ionization and ion imaging technique, which we refer to as velocity-resolved kinetics (VRK) [2-4]. This method provides flux profiles, equivalent to reaction rates, of surface reactions with unprecedented accuracy. Data is shown for a range of surface temperatures and for two surface facets, a nominally flat Pt(111) surface and a stepped Pt(332) surface. These measurements provide a test for theoretical models of surface reactions.

One such model relies on the principle of detailed balance, which states that adsorption and desorption probabilities are fundamentally equivalent in surface reactions. Using previously measured sticking probabilities on platinum [5], we determine the thermal adsorption rate constant. By multiplying this quantity with the equilibrium constant between gas phase H_2 and adsorbed H atoms – accounting for entropies of both species [1] – we can predict the thermal desorption rate constant.

Figure 1 shows a detailed-balance-based prediction of the second order HD formation rates using calibrated molecular beam fluxes [1]. The model, shown as solid and dashed lines for Pt(111) and Pt(332), agrees remarkably well with the ex-

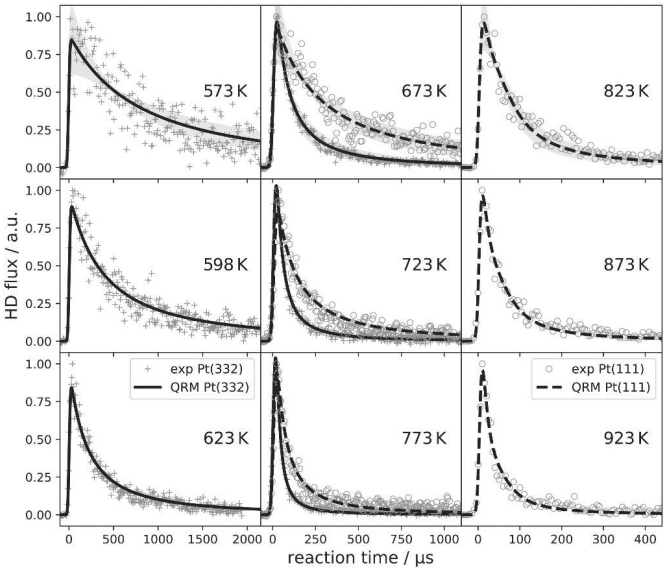

Fig. 1: Measured HD formation rates for Pt(111) (○) and Pt(332) (+) are compared with the results of a rate prediction (dashed and solid lines). The temperature dependence and the transient rate of the measurements are quantitatively captured by the model for both facets without adjustable parameters. The shaded regions of the top three panels indicate 2σ uncertainty, mainly associated with the absolute reactant flux measurement (~30%) and the equilibrium constant calculation. a.u. = arbitrary units. Reproduced from D. Borodin et al., Science, DOI: 10.1126/science.abq1414, 2022, AAAS.

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perimental data, when two important pitfalls commonly made in the past are avoided: First, adsorbed H atoms are highly delocalized on the platinum surface, and classical entropy models fail to capture this behavior, leading to disagreement with the VRK experiments [1]. Accurate reproduction of the data is achieved only when working with the quantum states of the adsorbed H atom by solving the H atom's Schrödinger equation on the surface. This approach provides an accurate treatment of the adsorbed H atoms' entropy accounting for quantum statistical effects and anharmonicity [1]. Second, we considered that four electronic spin states also contribute to the entropy of two adsorbed H atoms. These four states can be thought of as a nondegenerate singlet and a three-fold degenerate triplet, where only the singlet state leads to product formation, i.e., the singlet ground state of $H_{2(g)}$. Formation of the first excited triplet state of $H_{2(g)}$ is unlikely at the temperatures of our work and can be considered as effectively forbidden. This spin entropy effect reduces the rate of recombinative desorption by a factor of four compared to an alternative treatment where the electronic spin is ignored [1]. The high quality of VRK-derived reaction rates not only makes it possible to uncover these quantum effects in surface chemistry, it demonstrates how accurate the VRK method is in determining thermal rate constants in surface chemistry.

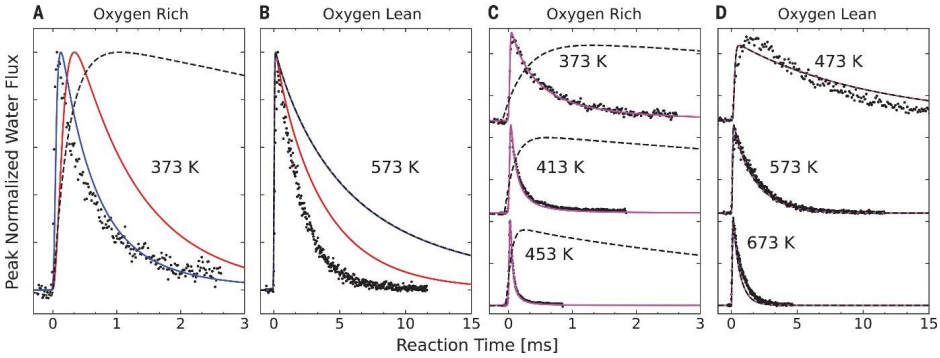

Fig. 2: Comparison of experimental and theoretical kinetic traces for water formation in hydrogen oxidation on Pd(332). Velocity-resolved kinetics results (black dots), TST microkinetic model based on RPBE (red line), PBE (blue line), and the optimized model (purple line). For PBE and the optimized model, results are also shown neglecting reactivity of the cooperatively bound O atoms at steps (dashed line). (A) $[O^*_{mean}]$ = 0.09 ML. (B) $[H^*]$ = 0.003 ML. (C) $[O^*_{mean}]$ = 0.09 ML. (D) $[H^*]$ = 0.026 (T = 473K), 0.003 (T = 573K), and 0.0007 ML (T = 673K). For (A) and (C), the H coverage is limited by the dose (0.002 ML) of the reaction initiating H_2 pulsed beam. For (B) and (D), the O-atom coverage is limited by the dose (0.001 ML) of the reaction-initiating O_2 pulsed beam. Reproduced from M. Schwarzer et al., Science, DOI: 10.1126/science.adk1334, 2024, AAAS.

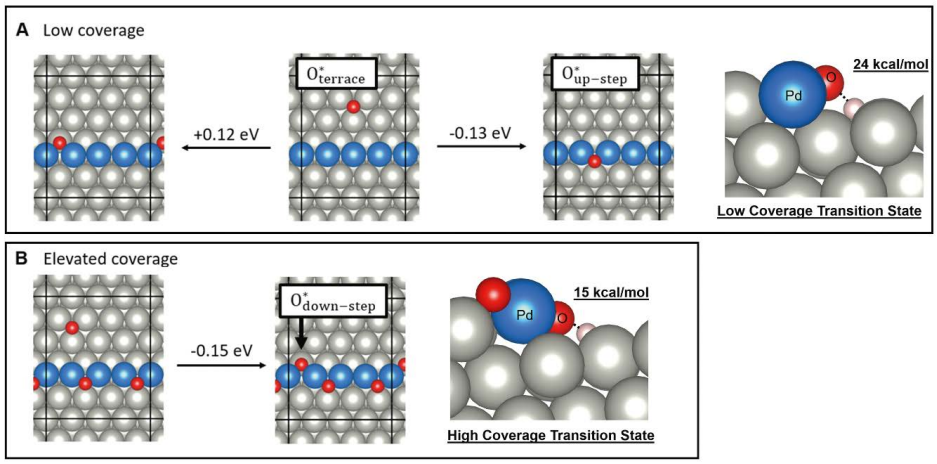

Fig. 3: Cooperative bonding of O atoms at Pd steps forms active configurations at elevated O-coverage. Panel A shows DFT predicted bonding of O atoms at Pd steps at low O-coverage and the resulting transition state for OH formation. At low coverage, reaction (3) is rate limiting. Panel B shows DFT predicted binding of O atoms in a zig-zag like structure where the O atom at the down-step site offers a new reactive configuration with a lower energy transition state. Under these conditions, reaction (5) becomes rate limiting. Reproduced from M. Schwarzer et al., Science, DOI: 10.1126/science.adk1334, 2024, AAAS.

The mechanism of hydrogen oxidation on palladium

Hydrogen oxidation on platinum group metals is considered a simple catalytic process, with only a few possible elementary reactions shown below.

$$O_{2(g)} + 2* \xrightarrow{k_1} 2\,O^* \qquad (1)$$

$$H_{2(g)} + 2* \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} 2\,H^* \qquad (2)$$

$$H^* + O^* \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} OH^* + * \qquad (3)$$

$$H^* + OH^* \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} H_2O^* + * \qquad (4)$$

$$2\,OH^* \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} H_2O^* + O^* \qquad (5)$$

$$H_2O^* \xrightarrow{k_6} H_2O_{(g)} + * \qquad (6)$$

However, Figure 2 illustrates the complexity of surface chemistry using the example of the hydrogen oxidation reaction on a palladium catalyst [6]. Here, water formation rates obtained with VRK are shown under oxygen-rich (panels A and C) and oxygen-lean (panels B and D) conditions. Under oxygen-rich conditions, water formation proceeds much faster than under oxygen-lean conditions, and increasing the oxygen coverage causes a change from pseudo first order kinetics to second order reaction kinetics [6].

These observations arise because the rate-limiting step changes with oxygen coverage. Under oxygen-lean conditions, OH^* formation limits the rate of water formation, as evidenced by the agreement between the experimentally determined activation energy of the rate-limiting step, 0.80 ± 0.01 eV, and the DFT-predicted barrier height for OH^* formation at steps [6]. However, at elevated oxygen coverage, adjacent step-bound oxygen atoms can cooperatively stabilize the transition state

for OH* formation, causing the subsequent OH* disproportionation reaction to form water to become rate-limiting [6]. See Figure 3.

Ab initio kinetics involving DFT input to transition state theory (TST) has been used to develop a microkinetic model for the hydrogen oxidation reaction on Pd catalysts [6]. The kinetic model's predictions are only weakly sensitive to the choice of functional—both RPBE and PBE functional inputs reproduce the experimental data, see Figure 2A and B. The dashed line shows a variant of the kinetic model that neglects reactivity of the cooperatively bound oxygen atoms at steps, resulting in an unrealistically slow water formation rate under oxygen-rich conditions, while leaving the rate under oxygen-lean conditions unchanged. This confirms that cooperative O atom reactivity at steps is important only at elevated oxygen coverage. Furthermore, slight adjustments to the DFT-derived energies yield excellent agreement between the kinetic model and the experiment for all oxygen coverages and surface temperatures [6]; see the magenta lines in panels 2C and D.

This reaction is a remarkable example, as it shows how atomic-scale adsorbate structures can dramatically increase the activity of a catalyst. These so-called "active configurations" differ from active sites as they can only form under reacting conditions. We speculate that this type of behavior is common in high temperature and high-pressure conditions of typical heterogeneous catalysis.

Conclusion and outlook

These two examples of VRK experiments provide quantitative kinetics of surface reactions, and when compared with theoretical models, yield valuable insights into the fundamental principles of heterogeneous catalysis. The examples discussed above highlight the critical role of quantum effects and active adsorbate configurations in surface reactivity. Beyond these cases, VRK has been applied to a wide range of systems [2, 7-16] and recent methodological advances, particularly the implementation of laser ionization at high repetition rates [3], have significantly enhanced sensitivity and experimental reach. These developments establish VRK as a powerful tool for bridging experiment and theory. For example, the goal of experimentally deriving reaction barrier heights with chemical accuracy for on-surface reactions is now within reach. The high sensitivity of high repetition rate VRK allows measurements to be made at very low reactant surface concentrations—the "isolated reactant limit"; under such conditions comparison to theory is straightforward. This contrasts to the complex behavior exhibited by the hydrogen oxidation example presented above. In the future, the method will be applied to increasingly complex and realistic catalysts. We are already able to use ab initio kinetics methods to reproduce accurate experiments on model catalysts. Looking ahead, continued progress using VRK in combination with theory promises to advance our understanding of the complex phenomena that govern real-world heterogeneous catalysis.

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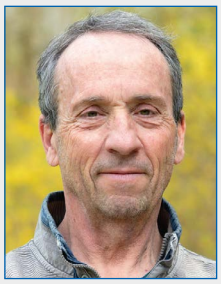
QUOTES

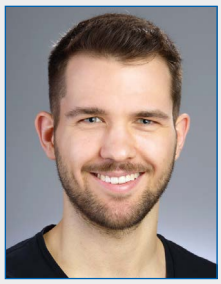
"If they can do it, I can probably manage it too."

Katharina Kohse-Höinghaus, in „Lives in Chemistry"



Prof. Dr. Alec Wodtke

I was born in 1959 in Salt Lake City, Utah, USA. I received my education through the public school system of Utah and California. I did my bachelor's studies at the University of Utah and my doctoral work at UC Berkeley. This was followed by 2 years of research in Göttingen between 1986 and 1988, where I also met my wife Liesel. In 1988 I went to UC Santa Barbara, where I taught and researched as a professor for over 22 years until I was appointed Max Planck Director and Professor at the University of Göttingen in 2010. At the Max Planck Institute and the University of Göttingen, I and my colleagues are researching surface chemistry and heterogeneous catalysis.



Mr. Florian Nitz

I was born in 1999 in Duderstadt, Germany. I studied chemistry at the Georg-August University of Göttingen with support of the German Academic Scholarship Foundation and received my master's degree in 2023. Since 2023, I am a PhD student in the research group of Prof. Dr. Alec Wodtke at the University of Göttingen. My work focuses on experimental and theoretical methods to study reaction kinetics on model catalyst surfaces, aiming to elucidate reaction mechanisms relevant to heterogeneous catalysis.

Wilhelm-Jost-Gedächtnisvorlesung

The Marvels of Thermodynamics: Or When Iron Man Meets Captain Planetary Boundary

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