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Combined experiment and theory approach in surface chemistry: Stairway to heaven?

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ABSTRACT

In this perspective we discuss how an intimate interaction of experiments with theory is able to deepen our insight into the catalytic reaction system on the molecular level. This strategy is illustrated by discussing various examples from our own research of surface chemistry and model catalysis. The particular examples were carefully chosen to balance the specific strength of both approaches – theory and experiment – and emphasize the benefit of this combined approach. We start with the determination of complex surface structures, where diffraction techniques in combination with theory are clear-cut. The promoter action of alkali metals in heterogeneous catalysis is rationalized with the apparent activity of chlorinated $TiO_2(110)$ in the oxidation of HCI: Even if we know all elementary reaction steps of a catalytic reaction mechanism, the overall kinetics may remain elusive and require the application kinetic Monte Carlo simulations. Catalysts are not always stable under reaction conditions and may chemically transform into RuO₂, a process which is hardly understood on the molecular level. Lastly we focus on electrochemical reactions. Here theory is clearly ahead since spectroscopic methods are not available to resolve the processes at the electrode surface.

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1. Introduction

One of the greatest scientific challenges in catalysis research is to achieve a molecular understanding of the underlying processes of a complex catalyzed reaction that culminates in the formulation of the reaction mechanism consisting of a complete sequence of elementary steps [1,2]. In the case of a heterogeneously catalyzed gas phase reaction the set of elementary reaction steps includes processes of adsorption, desorption, dissociation, recombination and diffusion of molecules and fragments on the catalyst's surface and how these steps are affected by promoters [3]. In order to gain atomic scale insight into a heterogeneously catalyzed reaction system one has to resort to model catalysis [2,4]. Proper model systems have to be designed with the lowest possible structural complexity, but still capturing the most important features of the catalyzed reaction system and thereby spurring a tight interaction between theory and experiment. The proper choice of the model system is dictated by the scientific question in mind.

With surface science methods applied to model catalysts of welldefined atomic structure, in particular single crystalline surfaces, we have access to the elementary steps. The whole battery of experimental

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http://dx.doi.org/10.1016/j.susc.2015.01.006 0039-6028/© 2015 Elsevier B.V. All rights reserved. surface science techniques can be applied and theory can be beneficially employed as soon as the surface structure of the model catalyst is known. We need to note that we use theory synonymously with computational chemistry, most of the time the density functional theory (DFT) in particular, throughout the paper. With spectroscopic and atomically-resolved imaging methods we can identify reaction intermediates on the model catalyst surface and with well-designed temperature programmed reaction experiments part of the involved activation barriers can be determined [5]. Theory, in turn, is able to provide activation barriers and the electronic structure, but also allows for the interpretation of experimental results such as scanning tunneling microscopy (STM) images and core level binding energy shifts. In the present perspective we discuss a few examples from our own research from the past two decades where experiment and theory go hand in hand to solve a specific scientific question in the context of surface chemistry and model catalysis.

The most important property of a surface is its atomic structure [6]. Without knowing the precise atomic structure, all other surface science investigations remain mostly elusive, theory in particular. However, the achievement of this starting point can be a true scientific challenge as discussed in chapter 2. Another important question in catalysis research concerns the action of promoters. The most notable ones are alkali metals whose promoting effect will be discussed in chapter 3.

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These additives are able to modify the internal bonds of reaction intermediates and the adsorption to catalyst surface [7]. A second example in chapter 4 focuses on the HCl oxidation (Deacon) process. We show that theory predicts activity of $TiO_2(110)$ when the bridging surface O atoms are replaced by chlorine. The question is whether this is a real effect or an artifact of standard DFT.

Even if all elementary reaction steps and the underlying energetics are known, the kinetics of the catalyzed reaction are still far from understood since the various elementary reaction steps intertwine in quite a complicated way resulting in the observed reaction kinetics [8]. Microkinetic simulations in the form of kinetic Monte Carlo simulations call for intimate collaboration between theory and experiments and will be the subject of chapter 5.

In all our considerations above we tacitly assume that the underlying catalyst does not change under reaction conditions. This is actually not the case as exemplified with the CO oxidation reaction over transition metal surfaces [9]. The chemical composition of the catalyst may change under reaction conditions: either only the surface composition or the chemical nature of the material is changed, such as in an oxidation reaction where the original metal surface transforms into a surface oxide or even a bulk oxide. This behavior has been extensively studied over the past decade, starting from clear-cut experiments [10]. In fact, this problem calls for ab-initio thermodynamics in heterogeneous gas phase catalysis, that is presented in chapter 6. The atomic details of the actual oxidation process of the Ru(0001) surface have only recently been explored by STM on the atomic scale [11]. These experiments allow for a deeper insight into the initial oxidation process of Ru(0001) but these studies also raise many questions which can be answered only by theory.

Similar to heterogeneous catalysis, fundamental insight into electrochemical processes is expected to be gained only if proper model systems with low structural complexity and under well-defined ultra pure reaction conditions are studied in the so-called surface science approach [12–14]. Currently basic understanding of electrocatalysis is pushed by ab-initio calculations [15–21], although a validation of the theoretical results by experiments is still required. In chapter 7 we will present results from ab-initio thermodynamics which deepen our understanding in the chlorine evolution reaction over $RuO_2(110)$ -based model electrodes and which motivate further experiments.

We will conclude this perspective in section 8 with a critical assessment of the combined theory/experiment approach and its future prospects.

2. Metal induced (3 \times 1) reconstructions on the (111) surfaces of Si and Ge

The most fundamental and essential property of a material is its precise atomic structure. Knowing the precise crystal structure of a material all other properties can be determined by ab-initio calculations, at least in principle, and subsequently compared with experiments. Unfortunately, ab initio structure determination by theory-only has shown to be not reliable so that experiments, in particular diffraction experiments, are required. This general statement has been proven to be equally valid for surface structure determination: As soon as the surface structure becomes complex, theory alone is only of minor use. Predictions made by theory have been in most cases wrong and misleading, both due to limited accuracy of the computational theory methods and the vast chemical space, even if progress has been made in tackling both limitations. But also results from a single experimental technique are mostly not conclusive. In fact, the whole battery of surface science techniques is required to solve a complex surface structure. This is particularly true for semiconductor surfaces, exhibiting far reaching reconstructions, i.e. great deviations from the atomic structure of bulktruncated surfaces.

Many elemental and III–V compound semiconductors crystallize into diamond and zinc blende structure, respectively, which emphasizes the importance of the sp³ hybridization in the bond formation [22]. At bulk-truncated surfaces of a pure semiconductor not all of the sp³ bonds can be saturated due to missing binding partners. Therefore, unpaired sp³-type dangling bonds are inevitably present at bulk-truncated semiconductor surfaces that raise the surface energy prohibitively high. For instance, the bulk-truncated Si(111) surface exposes one dangling bonds at the surface, the semiconductor surfaces undergo far-reaching reconstructions without imposing too much strain in the surface region. The most prominent reconstruction is certainly the (7 × 7) structure of Si(111) [23].

An alternative route to minimize the number of dangling bonds at a semiconductor surface is the deposition of for example monovalent atoms such as hydrogen, alkali metals (AM) or silver (Ag) atoms. Indeed adsorption of hydrogen is able to stabilize the bulk-truncated Si(111)-(1 × 1) surface [24]. However, as soon as larger monovalent atoms other than H are deposited, also the adsorbate-covered Si(111) surface exhibits far-reaching reconstructions into the bulk still with a relatively small surface unit cell. Ag and AM adsorption on Si(111) and Ge(111), for instance, lead to $(\sqrt{3} \times \sqrt{3})R30^{\circ}$ or (3×1) reconstructions [25] depending on the actual metal coverage, whose atomic structure determination has represented a true scientific challenge, requiring the employment of a variety of experimental surface sensitive techniques in combination with first principles theoretical methods such as DFT calculations [6].

In this chapter we will concentrate on the metal induced (3×1) reconstruction of Si(111). This type of reconstruction exhibits unusual chemical [26] and electronic [27] properties in that the Si(111)- (3×1) -Na surface is less reactive against oxidation than the pure Si(111) surface and its surface-state band gap is with 1 eV extraordinarily large. Although the surface unit cell is quite small, the structure determination took more than 10 years. After the surface coverage of the metal deposit was determined to be 1/3 monolayer (ML) in a combined experiment/theory study [28], two promising and reasonable models for the surface structures were left in the literature both of which were supported by theory [28,29] and both of which turned out to be finally wrong. These are the Seiwatz model [28] and the extended Pandey model [29] (cf. Fig. 1a,b). The Seiwatz model is characterized by fivefold rings of Si atoms which form a kind of π -bonded chains as also found for the Si(111)- (2×1) [30]. The extended Pandey model consists of a sevenfold ring carrying the π -bonded chain in combination with a five and a six-member ring of Si considering Figure 2. An intuitive notation is therefore 567567 model and 500500 model for the extended Pandey and the Seiwatz model, respectively.

None of these models have been confirmed by a crystallographic technique such as LEED or SXRD [31]. It is fair to say that a surface structure is only considered to be solved if the proposed model is consistent with corresponding experimental diffraction data.

A general problem of structure determination using diffraction techniques is however the so-called multiple local minimum problem. The atomic geometry of a surface structure is found by optimizing the agreement between calculated and experimental diffraction data – quantified by a reliability factor *r* – starting from a proposed structure model and varying the structural parameters. For the metal induced (3×1) reconstruction of Si(111), the following observation by Fan and Ignatiev was to overcome this ambiguousness problem. The LEED IV data for Si(111)-(3 \times 1) and also for Ge(111)-(3 \times 1) were practically independent of the deposited monovalent metal. Therefore, the LEED data are not determined by the metal atoms themselves but rather by the metal-induced surface reconstruction only; we do not need to determine the adsorption site of the metal. Furthermore, we expect that the Ge(111)- (3×1) and the Si(111)- (3×1) reconstruction due to the chemical similarity of Si and Ge should be very much alike and the atomic coordinates may just be scaled by the unit cell dimensions [22,32]. If the experimental diffraction data of both Ge(111)-(3 \times 1) and Si(111)-(3 \times 1) can be fitted with the same

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