Functional surfaces in heterogeneous catalysis – a short review

Dirk Rosenthal

Fritz-Haber-Institut der Max-Planck-Gesellschaft, D-14195 Berlin, Germany

* Corresponding author: e-mail dirkrose@fhi-berlin.mpg.de,

Abstract

A Heterogeneous catalysis and functional surfaces are intimately connected. Surface functionalities mediate the catalytic reactions. However, the surface must fulfil several requirements: adsorption of the reactants on the surface must be energetically favoured (but reversible), the surface functionalities must enhance the dissociation of chemical bonds in the reactant and the formation of new ones which will lead to the reaction's product(s), and finally the product(s) must be able to desorb and leave the surface. It was shown that for the ammonia synthesis on ruthenium single crystalline surfaces, both the geometric and electronic functionalities of step edges are crucial to dissociate nitrogen. Another well-investigated reaction is the catalytic oxidation of carbon monoxide over platinum and oxidized ruthenium. For both metals, the surface is dynamic, which leads to a change in its functionalities during reaction. These few examples of simple reactions already show the complexity of the necessary surface functionalities for heterogeneous catalysis and the problems connected with the understanding of rather simple reaction mechanisms.

The key objective in catalysis research consists in tailoring the geometric and electronic properties of catalysts depending on the target reactions. One attempt in this direction is the investigation of binary alloys and, more recently, of intermetallic compounds. Here the adsorption properties of the reactants could be drastically changed. A completely different way of changing adsorption properties also exists for semiconductor surfaces: the direct application of electric fields leads to a change of charge carriers near the surface – the electro-adsorptive effect.

Keywords: heterogeneous catalysis, dynamic catalyst, CO oxidation, ammonia synthesis

1. Introduction

Catalysis is often divided in two parts depending on the physical phases of the catalyst and the reactants. The industrially more important part is the case where catalyst and reactants have different physical phases: the heterogeneous catalysis. One simple reason for that is the easier removability of the solid catalyst from the gaseous or liquid reactants. The field of heterogeneous catalysis research is very broad reaching from nano-crystalline powders in industrial applications to surface science studies on solely one single crystal surface [1]. Although three-dimensional functionalities of catalysts could also influence the reaction behaviour (i.e. transport phenomena in zeolites) the main functionality is situated at the surface. The interface between the catalyst and the reactants is in general multifunctional: the reactants must adsorb, react and finally leave the surface as products. The adsorption and desorption can take place in principle at the whole catalyst surface, the places where the reactants have an energetically adsorption minimum are the adsorption sites. The first and at this time visionary description of the functional interface stems from Langmuir in 1922 [2]: "*In general, we should look upon the surface of a catalyst as consisting of a checkerboard in which some of the spaces are vacant, while others are filled with atoms or molecules.*" The places where the reaction itself occurs are named after Taylor [3] "active centres" or active sites. These sites are not necessarily the same. "*The identification and counting of active sites in heterogeneous catalysis became the ''Holy Grail'' of heterogeneous catalysis in 1925, and the situation remains the same today.*" is stated in the introduction of the handbook of heterogeneous catalysis [4]. A great step into this direction of "identification and counting" was the development of surface science. The application of ultra-high vacuum (UHV) and ideal single crystalline materials enable the usage of low-energy electrons and ions to probe the electronic and geometric properties of surfaces and adsorbates.

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With special surface sensitive experimental methods it is possible to really count sites of ideal single crystalline surfaces and identify their nature in adsorption. An ideal tool to "see" atoms is scanning tunneling microscopy. With this method Wintterlin and co-workers investigated the CO oxidation on platinum(111), one kind of the proposed checkerboards by Langmuir. They were able to measure reaction rates on an atomic scale resolution and reveal under their special conditions the rim of oxygen islands as the active centres of the reaction [5].

Of course this surface science model approach includes some draw-backs. One of these is immediately clear: surfaces of single crystals with their minimized surface area are not good real catalysts. In contrast one typical aim in real catalyst development is to produce catalyst materials with a high surface to mass aspect ratio. Often the active phases are nanoparticles and it is not always clear, whether these nanoparticles exhibit the surfaces investigated by surface science or other exposed surfaces, which are not investigated, play a major rule. Among others this discrepancy leads to the well known materials gap. The huge differences in the applied pressure regimes in surface science (UHV) and real catalysis (typically atmospheric pressure) represent another gap (pressure gap). One consequence could be that the single crystal cannot reach the (most) active catalytic state because of the low chemical potential of the reactants under UHV conditions (see section 2.2). Nevertheless is the surface science approach very useful especially in searching for the aforementioned holy grail – the elucidating and counting of active sites.

The scope of this short review is twofold: in Section 2 functionalities of catalytically active surfaces at the surface science level in simple catalytic reactions are shown and Section 3 introduces some attempts to tailor optimized catalysts.

2. Functional surfaces in simple reactions – ammonia synthesis and CO oxidation

2.1 Ammonia synthesis on ruthenium – the electronic and geometric factor

The typical catalyst for the ammonia synthesis with the Haber-Bosch process is promoted iron [6]. Another interesting catalyst is ruthenium [7], although its industrial importance is restricted by the higher costs. It is generally agreed that the ammonia catalyst must possess at least two important functionalities: at first, the activation energy for N_2 dissociation must be low and secondly, the residence time of the NH_x intermediates and products ($0 \leq x \leq 3$) must be short not to block surface sites. Theoreticians have shown that a more or less linear relationship exists between these quantities for N_2 and adsorbed N atoms in the case of ammonia synthesis [8]. Particular for nearly equal adsorption site geometries only the electronic differences of the catalysts play a role. This "Brønsted–Evans–Polanyi (BEP)
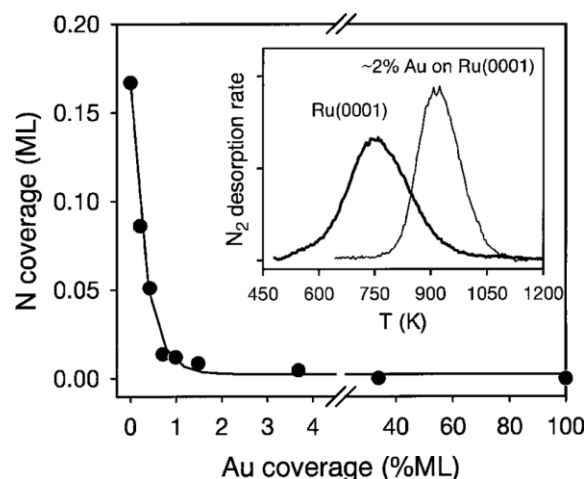

Fig. 1: The dependency of nitrogen atom coverage on small gold amounts on Ru(0001) after a fixed dose of N_2 (0.1 bar, 1 min, 500 K). The inset show temperature programmed desorption curves of N_2, the coverage of gold was approximately 0.02 ML (heating rate 4 K/s). (Reprinted from Dahl et al. [11] with permissions. Copyright 1999 by the American Physical Society.)

relation" [8] was proposed to be more general: the optimum catalyst for a reaction with a dissociation reaction as rate determining step has a minimal activation energy for the dissociation as well as a minimal binding energy of the dissociation products [9]. With this linear approximation the comparably easy accessible quantity of the dissociation-product binding energy enables the theoreticians to predict overall reaction rates for this type of catalytic reactions. Calculations for the dissociation of N_2 and the binding energy of atomic nitrogen yield iron and ruthenium as most active transition metal catalysts from the electronic point of view [10].

To elucidate which functionality of the surface is responsible for the dissociation of N_2 Dahl et al. [11] conducted a very special experiment (figure 1). They pre-exposed a Ru(0001) surface with a small amount of gold. This amount of gold preferentially decorated the steps existing on every real single crystal surface [12]. Both the thus gold decorated and a gold-free surface exhibit very different adsorption/desorption behaviour for N_2. After exposition of equal N_2 amounts the concentration of atomic nitrogen was drastically higher at the Ru(0001) surface without gold. Additionally the desorption temperature for the gold decorated surface was higher by ~150 K (heating rate 4 K/s) in a temperature programmed desorption experiment with the same starting amount of atomic nitrogen. The explanation for these findings is that the step edges of Ru(0001) serves as catalytic sites with low activation energy barrier for N_2 dissociation. The step edge site density in the experiment was below 1% but the rate of N_2 dissociation was approximately lower than 9 orders of magnitude on the terrace sites compared with step edge sites. Hence a decisive difference must exist between a terrace site and a step edge site on Ru(0001): The local coordination of a N_2 molecule counts 4 ruthenium atoms at the ter
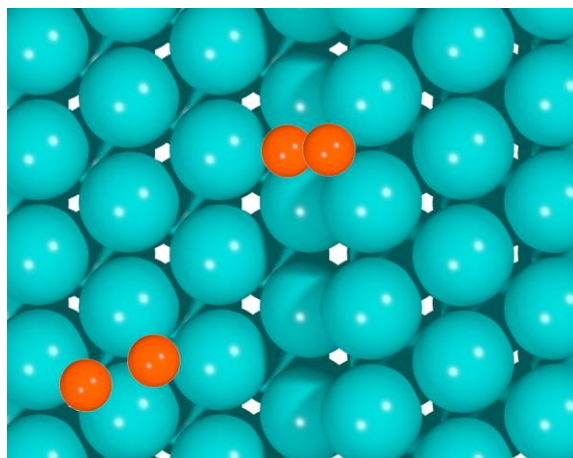
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Fig. 2: Geometric configurations during N_2 dissociation on a Ru(0001) terrace site (lower left) and on a step edge shows the surface functionalities (active sites): 5 ruthenium atoms at the step edge and 4 ruthenium atoms (one is shared) at the terrace.

race site but 5 ruthenium atoms at the step edge site. This geometric and local electronic variation makes such a huge difference in catalytic activity. Thus, the authors in [8] stated that these five-fold coordinated step edge sites are the active sites for the ammonia synthesis. A comparison of the coordination during N_2 dissociation on terrace and step edge sites is depicted in figure 2.

Interestingly this geometric effect is not in line with the initially introduced BEP relation. While the binding energy for atomic nitrogen is nearly equal at step edge sites and terrace sites the dissociation energy is strongly lowered at the step edge site with the fivefold geometry [11]. Therefore the trends given by the electronic properties of the transition metals are not the only decisive parameter for a good ammonia syntheses catalyst, local geometries are also very important. For further reading on ammonia syntheses the author refers to the corresponding chapter of Schlögl in the handbook of heterogenous catalysis [13].

2.2 CO oxidation – the dynamic catalyst

Another comparably simple reaction is the CO oxidation. No side reactions exist except CO dissociation and subsequently carbon enrichment at the surface (coking). The commercial use is more or less restricted to the removal of CO traces where CO represents a catalyst poison. For surface scientists this apparent simplicity makes the CO oxidation an object lesson to elucidate the reaction mechanism and identify the active sites. Two best investigated systems in surface science are the CO oxidation on platinum and on oxygenated ruthenium. The pioneering work of Gerhard Ertl (and co-workers) on CO oxidation over platinum single crystals was motivated by numerous reports on oscillating reaction rates at polycrystalline Pt catalysts (for an overview see Schüth et al. [14]). In the following the focus is set on the functionalities necessary of the platinum

surfaces during CO oxidation. The first idea of the reaction mechanism was a typical Langmuir-Hinshelwood kinetics: CO and O_2 adsorb on the platinum(111) surface, oxygen is dissociated and O atoms and CO molecules diffuse on the surface and finally reacts to the immediately desorbing CO_2. This simple reaction mechanism was found to be more complicated, adsorbed oxygen atoms forms islands and the reaction occurs on the perimeter of these islands only [5]. Both mechanisms leave no space for the necessary feedback for the oscillating rates, hence another reaction step has to be involved and again the picture is more complex.

In contrast to the smooth Pt(111) surface the more open Pt(110) and Pt(100) surfaces tend to reconstruct to minimize their surface energy. CO adsorption, however, leads to the removal of the reconstruction, the driving force behind is again the lower surface energy of the hence created CO-covered Pt(110) or Pt(100) surfaces [15, 16]. Additionally these surfaces have a different sticking probability for oxygen and this is finally the reason for the reaction activity oscillations: the reconstructed and non-reconstructed surfaces possess different activities in the CO oxidation. Only under CO oxidation conditions especially on the Pt(110) surface not only the reconstruction and its lifting is observed but also micro faceting. This requires a very strong materials transport and in this context the possibility of oxygen incorporated into the platinum bulk, so-called subsurface oxygen, is discussed [17]. (For an overview on oscillatory reaction kinetics an extensive review by Imbihl and Ertl [18] is recommended.)

The picture of the working catalyst for the CO oxidation over oxygenated ruthenium becomes even more complex because in contrast to platinum ruthenium can be oxidised. It forms a stable oxide (RuO_2), can incorporate subsurface oxygen and in between exist a so-called transient surface oxide (TSO). Ruthenium as catalyst in the CO oxidation was the prime example for the already mentioned pressure gap. While it shows the lowest activity under UHV conditions [19]; it is a very potent catalyst at high pressures [20]. The reason is the unattainability of the higher oxidized states at low pressures. Several surface functionalities were discussed as the active sites: the "checkerboard-like" (1x1) oxygen covered Ru(0001)[20, 21], the coordinatively unsaturated Ru atoms in the RuO_2(110) surface (Ru cus-sites) [22] and subsurface oxygen/TSO [19, 23]. Recent first-principle kinetic Monte Carlo calculations by Reuter and Scheffler [24] on the RuO_2(110) surface nicely show that the application of realistic temperatures and pressures leads to the result of auto-poisoning in a wide range of oxygen and CO pressures. This gives evidence to the fact that a completely oxygen covered ideal RuO_2(110) surface is in fact catalytically completely inactive. Indeed recent experiments on the CO oxidation on crystalline RuO_2 reveal a very long induction period of hours until the reaction starts [25, 26]. Additionally the catalyst crystallites change their habit after this induction period; i.e. a strong dependency of the catalyst shape and oxidation state on the chemical potential of the
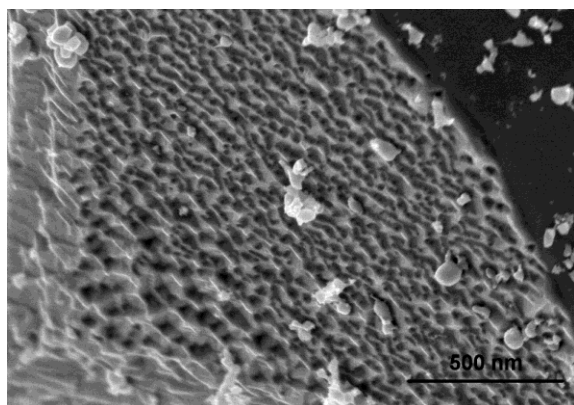
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Fig. 3: Scanning electron micrograph of a heavily faceted $RuO_2(111)$ surface after CO oxidation in the mbar range under oxygen rich feed conditions (CO/O_2 ratio = 1:2). The catalyst was diluted by BN.
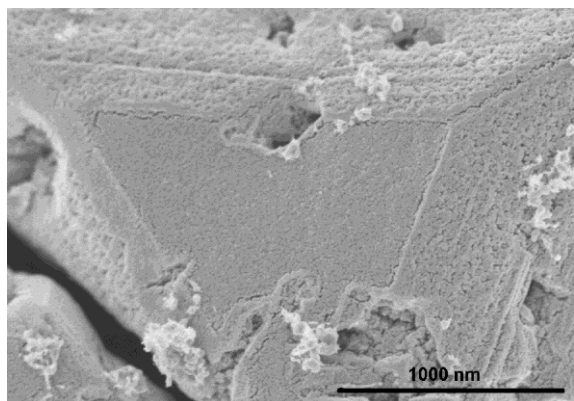

Fig. 4: Scanning electron micrograph of a heavily roughened $RuO_2(111)$ surface upon bulk reduction after CO oxidation in the mbar range under stoichiometric feed conditions (CO/O_2 ratio = 2:1). The catalyst was diluted by BN.

CO and O_2 reaction mixture could be observed. In figure 3 and 4 two examples of heavily faceted and reduced $RuO_2(111)$ surfaces under net-oxidizing and net-reducing conditions, respectively, are shown. Under oxygen rich feed conditions only the apical surfaces tends to facet, the lateral facets remain smooth. In contrast, under stoichiometric and reducing conditions at first the apical surfaces become rough while the lateral surfaces remain smooth for longer times.

The thus disturbed crystallites did not show the induction period in a subsequent run under the same conditions. The occurrence of these very different functional surfaces with very different active sites and the possibility of auto-poisoning lead to the idea that in the case of oxygenated ruthenium not the existence of active sites is crucial under elevated pressures, but the existence of defects to reactively overturn the auto-poisoning. These defects can be grain boundaries, steps, but also the interplay between different oxidation states. In the case of the well-defined RuO_2 particles these defects must be generated under reac-

tion conditions. Within this predictive picture on oxygenated ruthenium two different kinds of surface functionalities exist: the active sites where without auto-poisoning the reaction takes place and the active sites which are necessary to reactively disturb the auto-poisoning.

3. Tailoring of functional surfaces

In the focus of the fundamental research into catalysts stands the question whether an existing catalyst could be optimized and how. The principle answers are to change the electronic and/or geometric properties in the right way. As mentioned in section 2.1 the best suited transition metal catalysts for the ammonia synthesis are ruthenium, (osmium) and iron. Fortunately the catalysts are not necessarily restricted to transition metals in the periodic system alone; alloying of two metals is a smart possibility of expanding the periodic system. The bulk alloy of cobalt and molybdenum (CoMo), which itself binds nitrogen too weakly or too strongly, respectively, was shown by theory to possess the right medium nitrogen binding energy to exhibit higher activity as ruthenium in ammonia syntheses [27]. The reaction activity in the corresponding volcano plot in figure 5 describes a maximum while the binding energy of nitrogen atoms is varied. The underlying reason for this behaviour of the reaction activity here is the already in section 2.1 mentioned BEP relation of the binding energy of nitrogen atoms with the activation energy for N_2 dissociation.

The concept of changing the electronic properties by alloying was already well known. Transition metals deposited as thin overlayer on other metals [28] could alter their mean of the valence band and even chemically bind to the
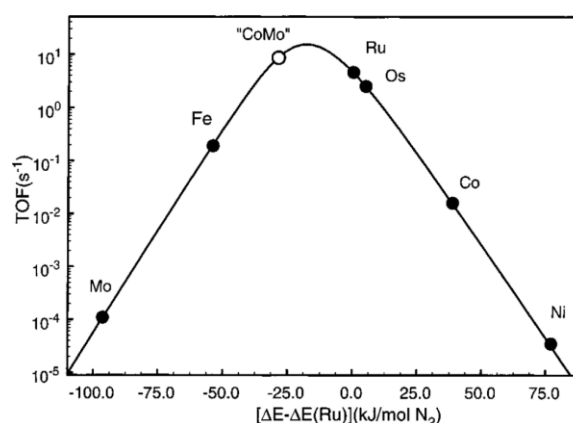

Fig. 5: Volcano curve of the activity in ammonia synthesis for different transition metals and the hypothetical alloy CoMo in dependency of the binding energy of atomic nitrogen compared to ruthenium. The synthesis conditions were 400 °C at 50 bar and a gas composition of $H_2:N_2$ = 3:1 containing 5% NH_3. (Reprinted from [27] with permission. Copyright 2001 American Chemical Society.)

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metal substrate. An impressive proof was the difference of the desorption temperature maximum of CO: for palladium on Ta(110) the difference to Pd(100) amounts 235 K towards lower temperatures [29]. However, bimetallic overlayer and bulk alloys typically exhibit strong segregation phenomena (e.g. [30]) or leaching processes leading to deactivation. However, the strong binding of the first monolayer in the bimetallic surfaces [28] could be conserved in several bimetallic systems (especially with palladium), called intermetallic compounds [31]. One example is the intermetallic compound PdGa which posses extraordinary high selectivity and long-term stability in the semi-hydrogenation of acetylene [32].

A very important field in catalyst development is the search for chemical promoters. In ammonia synthesis e.g. potassium (for iron) and barium (for ruthenium) are used and their effect on the reaction was investigated theoretically [8]. Another way to introduce promotion is the application of electrochemical transport: "*Electrochemical promotion is due to the current or potential-controlled electrocatalytic (Faradaic) introduction of promoting species (e.g. $O^{\delta-}$, $Na^{\delta+}$) from the solid electrolyte to the catalyst/gas interface where an, overall neutral, double layer is formed. The density of this double layer (and the field strength in it) varies as the applied potential is varied and this affects both the work function of the surface and the chemisorptive bond strength of reactants and intermediates, thus causing dramatic and reversible alterations in catalytic rate.*" (cited from p.1912 in [33]). The electrochemical promotion allows in particular the control of surface functionalities *in situ*, i.e. the optimization of the catalyst directly under reaction conditions.

Another direct way to control the adsorption properties, in this case of semiconductors, was already proposed in 1958 by Th. Wolkenstein [34]: In the field of semiconductors two kinds of chemisorption are divided: strong (charged) and weak (neutral) chemisorption [35]. The amount and hence the strength of the binding energy of the strongly chemisorbed species could be controlled by the application of an external field [34, 35]. This electroadsorptive effect (EAE) was theoretically expanded to ZnO

field-effect sensors by Geistlinger [36] and experimentally shown by Hoenig and Lane [37]: the conductivity of a ZnO sensor could be enhanced or suppressed by applying a negative or positive voltage, respectively. Recently the theory of gas sensing and the EAE was renewed and comprehensively presented [38]. The electronic processes in the bulk of the semiconductor, particular the drawback of drift effects, were analysed in detail [39]. With the advances in miniaturisation of sensors and hence the applicability of typical low battery voltages it should be possible to investigate the EAE in heterogeneous catalysis.

4. Summary

In this short review was shown that functionalities of surfaces in heterogeneous catalysis could be manifold. It ranges from the "simple checkerboard-like" Pt(111) surface over steps in the ammonia synthesis and the surface dynamic of the more rough Pt(110) and (100) surface to the bulk dynamic of oxygenated ruthenium catalysts in the CO oxidation. The identification of these functionalities was only possible by the application of the surface science approach. Advances in theory nowadays enable to predict suitable catalysts, while new, stable intermetallic compounds may serve as playground for expanding the electronic properties of the elements in the periodic system to bimetallic catalysts. The direct, *in situ* influence of the surface electronic properties by electrochemical promotion or the electro adsorptive effect will generate new insights into surface functionalities in heterogeneous catalysis.

Acknowledgements

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