

Model Studies in Heterogeneous Catalysis at the Microscopic Level: From the Structure and Composition of Surfaces to Reaction Kinetics

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Abstract

Heterogeneous catalysis is one of the fields of modern technology, in which a characterization of structural and chemical properties of solid surfaces at the microscopic level is of enormous importance. For a long time, such insights have been precluded by the complexity of most catalytically active materials. Recently, substantial progress has been made, however, toward a microscopic-level understanding of complex catalyst surfaces. We discuss the driving factors for these advancements, which are based on the development of new well-defined model systems as well as on advances in experimental technology and theory. Scrutinizing the example of planar model catalysts, we identify the process of linking structural and chemical information to microscopic reaction kinetics as a particular challenging aspect of today's work. We review the kinetic effects which may have an influence on the reaction kinetics on complex surfaces. As an example how structural and kinetic information can be correlated at the microscopic level we discuss the case of surface oxidation and oxygen induced restructuring of Pd nanoparticles as studied by molecular beam methods.

Keywords: Heterogeneous Catalysis, Supported Model Catalysts, Surface Reaction Kinetics, Nanoparticles, Oxide Surfaces

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Introduction

Heterogeneous catalysis is a key phenomenon in many fields of modern technology. Its economical impact is outstanding: Among the best known examples are applications in environmental chemistry¹, but heterogeneous catalysts play also a central role in the production of most chemicals and in emerging fields such as energy storage and conversion^{2,3}. In spite of its importance, today's understanding of many catalytic processes is, however, still poor at the microscopic level. The reason for this lack of knowledge is twofold: First, there is the *structural complexity* of most catalyst materials, which are often multi-component mixtures of oxides or combined oxide-metal systems. Secondly, there is the *chemical complexity* of the reaction system, which in many cases involves mixtures of multiple reactants, complex reaction pathways and numerous intermediates. Both aspects, chemical and structural complexity, are notoriously difficult to deal with in fundamental surface science studies. Consequently, most molecular-level information on catalytic phenomena has been obtained for very simple model reactions on single crystal surfaces. In spite of the fundamental importance of such studies, it is likely, however, that such studies provide an incomplete picture of heterogeneous catalysis, as the structural and chemical complexity are inherent properties of catalytic materials and processes: Often, catalytic properties are found to depend sensitively on structural parameters such as particle size or shape or chemical parameters such as the properties of the support or promoters. In catalyst development, these dependencies provide the possibility of empirically optimising properties in order to maximize selectivity and activity with respect to the desired reaction pathway. In a similar fashion, complex chemical environments are often an intrinsic property of catalytic processes. If we consider the car exhaust catalyst as an example, it is crucial to selectively remove specific poisonous traces from the exhaust gas in the presence of a mixture containing many other reactants. Consequently, a detailed understanding of possible interferences with other reactants is a critical issue. Similarly, in complex reaction networks, the interaction with by-products, intermediates and contaminations may lead to small changes in the energetics and kinetics, which, however, may be decisive for the selectivity of the catalyst under reaction conditions. It is one of the challenges of today's research to transfer the molecular and atomic level understanding, which has been achieved for simple reactions on simple surfaces to such more realistic surfaces and reaction conditions. In the following, we will briefly review some of the approaches that have been taken towards this aim.

Reaction Kinetics on Simple and Complex Surfaces: What is different?

To start with it is useful to remind oneself that catalysis is – by definition – a kinetic phenomenon. In applied catalysis, reaction kinetics is typically described using global terms such as *activity*, *selectivity* or *stability*^{2,3}. The activity quantifies the increase in reaction rate toward the desired product upon use of the catalytic material. In most cases, the global rate is the result of a more or less complex sequence

of microscopic steps with a different degree of rate control, and, besides the pure surface reaction kinetics, may also be influenced by other factors such as heat or mass transport. *Selectivity* is, in general, one of the most important characteristics, as it determines the nature and quantity of side products. From a kinetic point of view, selectivity is related to the ratio of reaction rates, which are determined by small differences in activation energy. As a result, investigations of selectivity are often a rather delicate issue, both from an experimental and from a theoretical point of view. For practical reactions, *stability* is a very important aspect. The stability of the catalyst is related to slow changes of the rate of one or more steps of the reaction network as a function of reaction time. Such changes may, for example, be the result of morphological changes or poisoning processes.

As a result, a microscopic-level understanding of the global reaction kinetics on a complex catalyst surface involves two issues: First, the global kinetics has to be disentangled into elementary steps, i.e. a microkinetic description of the reaction has to be developed. Such microkinetic descriptions have been developed for some simple reaction systems on single crystal surfaces (see ^{4, 5,6} and references therein). In the second step, we have to address the question why the microscopic reaction kinetics on a more complex surface should be different from the perfect single crystal case. In this paper, we mainly address the latter question.

Specifically, we focus on the case of supported metal catalysts as an important class of catalytically active materials. It was recognized early on that a support does not only help to stabilize the high dispersion of the catalytically active metal, but that the particle size and support may have a drastic influence on the catalytic performance itself (see e.g. ⁷⁻⁹). Many different concepts have been put forward which can contribute to explain such effects, which may be briefly classified as follows (see Fig. 1):

- *Support Effects*: It is apparent that the kinetics are influenced by the support, if the reaction network directly involves elementary steps on the support. In practical applications, this is for example the case for NO_x storage components in automotive exhaust catalysts ¹⁰⁻¹². Alternatively, adsorption processes on the support and elementary steps on the active particle can be coupled via surface diffusion. In case of activated adsorption, such processes are well-known as *spillover* or *reverse-spillover* phenomena ^{13,14}, but also in the case of non-activated adsorption, surface diffusion between support and the active particle may have an effect on the kinetics (so called *capture zone effects*, e.g. ^{9,15,16}). In addition, there might be so-called *support interactions*, i.e. modifications of reaction and adsorption properties of the supported particles due to structural or electronic influences of the support (see e.g. the case of the *strong metal support interaction* for metals on reducible oxides, e.g. ¹⁷).
- *Electronic effects*: The electronic structure of a supported particle may differ from an extended metal surface, for example as a result of *electron confinement*, due to *lattice distortions* or due to *electronic influences of the support*. This type of effects is expected to be strong only for very

small particles (see e.g. ¹⁸). In addition, *promoters* located on the active particle may lead to a modification of the electronic structure of the active particle (e.g. ¹⁹). In a similar fashion, a specific role is often attributed to *interface sites* between particle and support, the specific properties of which may also be modified by local electronic effects ²⁰.

- *Geometric effects*: It is apparent that a metal particle exposes specific sites, such as particle edges or corners, which are not present on a perfect single crystal surface. Their density depends on the particle size and is substantial in the practically relevant size range of a few nanometers. These specific sites may exhibit specific activities with respect to a given reaction. In a series of studies, we have recently investigated the role of specific reactive sites on supported metal particles for the specific cases of NO dissociation and reduction ^{21,22} as well as for CH₃OH dissociation and dehydrogenation ^{23,24} on Pd model catalysts. In these studies information could be extracted on the activity and selectivity of specific sites on such particles, such as crystallite facets, edges or steps.

In addition to the before mentioned effects there may be phenomena, which arise without any direct modification of the adsorption properties of specific sites, but simply as a result of the small length scale of the structure elements of the catalyst surface (typically in the order of few nanometers). Among these effects are:

- *Communication effects*: Communication effects can result from coupling of small surface regions with different adsorption and reaction properties via fast surface diffusion. Such regions could for example be different facets of a crystalline particle or various defect sites. As a result, the reaction rate of the coupled system may strongly differ from a simple linear combination of the individual reaction rates ^{6,16}.
- *Confinement phenomena*: Modifications of the kinetics can arise as a result of the fact that the mobility of reactants is limited by structural barriers on the surface. Reactants, for example, may be confined to a small metal particle, with surface diffusion to other parts of the surface being inhibited. As a result, bulk diffusion, which is easily possible for some reactants such as hydrogen, may be restricted. Moreover, coverage fluctuations on sufficiently small catalyst particles may have an influence on the reaction kinetics ²⁵⁻²⁷.
- *Restructuring effects*: Adsorbate induced reconstructions or faceting are well-known effects on extended single crystal surfaces. On small particles, reactant induced restructuring is expected to represent an even more frequent and versatile phenomenon. Such restructuring effects may include changes of the particle equilibrium shape ²⁸, restructuring induced by bulk phase transformation (e.g. oxidation), adsorbate-induced disintegration of small particles ²⁹, or structural fluctuations of small clusters in the presence of reactants ³⁰.

Connecting Structure, Mechanism and Kinetics on Complex Surfaces

Despite these numerous ideas about the reactivity of supported catalyst systems, the actual number of examples, in which such effects have been directly linked to the kinetics of catalytic reactions at the microscopic level is very small. Some success towards this aim has only been possible recently^{6,9,31}.

Briefly, there have been three driving factors, which have mainly contributed to progress in this field recently (see Fig. 2): (i) the development of complex but well-defined model catalysts, (ii) the progress made with respect to the development of experimental methods in surface science and catalysis, and (iii) the rapid progress in theory.

The first point, i.e. the development of model catalyst surfaces, will be discussed in detail in the following section. Briefly, the most important point is that these model catalysts allow us to introduce certain aspects of complex surfaces, without having to deal with the full and, in many cases, hardly controllable complexity of the real system. Thus, the use of well defined model surfaces greatly simplifies the process of correlating structural and chemical properties on the one side and kinetic phenomena on the other.

There are several achievements which contribute to the second point, i.e. the developments of experimental techniques. First, there has been significant progress in different fields of microscopy, making available atomically-resolved structural information on the active state of the catalyst (for example by HR-TEM, high-resolution transmission electron microscopy, see e.g.¹⁹) or even on adsorbate layers during reactions (see e.g. fast STM, scanning tunnelling microscopy, e.g.³²). Moreover, significant progress has been made towards the development of in-situ spectroscopies, which allow investigations under reaction conditions and elevated pressures. Here, studies in the so-called “pressure gap” between the ultrahigh-vacuum (UHV) environment of surface science and the near-ambient pressure conditions of real heterogeneous catalysis are of special interest, in order to establish connections between these fields. Among the experimental methods which have been applied to obtain spectroscopic information at elevated pressure on model catalysts are for example sum-frequency generation (SFG,^{33,34} and refs. therein), polarisation-modulation IR reflection absorption spectroscopy (PM-IRAS,^{35,36}) or high-pressure XPS (X-ray photoelectron spectroscopy,³⁷). A final experimental aspect is the developments of methods, which allow detailed investigations of the reaction kinetics on model catalysts under well-controlled conditions. Here, the application of molecular beam (MB) methods opens up new possibilities with respect to a systematic and quantitative analysis of the kinetics. In our group we have recently applied this approach to a variety of model surfaces and reaction systems. An illustrative example is presented in the last section of this paper. For a complete overview we refer to several review articles on specific aspects of this approach^{31,38,39}.

The final driving factor towards a molecular-level understanding of reaction kinetics on complex surfaces is the rapid advancement in the field of theory. The progress in theoretical calculations (mainly by means of density functional theory, DFT) is not discussed in further detail here and we

refer to some representative publications instead. Among the specific questions and achievements are for example the theoretical calculation of adsorption energies and activation barriers for elementary reactions such as the NO dissociation on simple low-index and stepped surfaces^{40,41}, the investigation of restructuring and oxidation processes of surfaces in reactant atmospheres⁴², the description of the interaction of reactants with large transition metal clusters⁴³, the structural analysis of complex model supports⁴⁴ or recent attempts to use ab-initio calculations of activation parameters in kinetic Monte-Carlo (KMC) studies⁴⁵.

The final goal behind the different approaches discussed is to combine the information on structure, composition, adsorption and kinetics on a model surface, which contains specific aspects of a real catalyst. The final result should be the development of advanced microkinetic models, which explicitly take into account the specific properties of the model surface in a realistic and microscopically appropriate fashion (see e.g.^{6,46,47} for some examples). These models should then serve as a link between the reaction kinetics on simple single crystal and real catalyst surfaces and should be capable of describing complex structure-activity dependencies.

On the Development of Model Catalysts

Parallel with the experimental developments in surface science, the complexity of model surfaces for heterogeneous catalysis has increased dramatically (see Fig. 3a). Early studies mainly focussed on the chemistry of metal single crystal surfaces, providing important reference data on the reactivity of ideal surfaces and possible reaction mechanisms (see e.g.^{48,49}). Subsequently, studies on stepped or defect-rich surfaces were performed in order to address effects, which result from deviations from these ideal structures. A big step toward more realistic model surfaces was the application of surface science methods to oxide surfaces. Here, one of the key issues is the control over the defect properties of the oxide surface, which in most cases have a major influence on the reactivity and the growth of metal deposits. Among the strategies to prepare planar oxide surfaces is the cleavage of oxide single crystals in air or in UHV (see e.g.⁹ for an overview) or, alternatively, the growth of ultrathin oxide films on metallic supports. From an experimental point of view, the latter methods circumvents the drawback of low electrical and thermal conductivity of bulk oxides (complicating the application of electron spectroscopies, STM and other experimental methods), but typically leads to higher defect densities. Today, a large number of recipes are available for the preparation of many different ordered oxide films including e.g. Al₂O₃, SiO₂, MgO, NiO, Cr₂O₃, FeO, or Fe₃O₄ and others (see e.g.⁵⁰⁻⁵⁵ and refs. therein). Their preparation is typically based on the direct oxidation of a metal, semiconductor or alloy single crystal or on the deposition and oxidation of a metal on an inert substrate.

After characterization of the model support, the next step is the preparation of the active particles. In most cases, these active particles are metal or oxide aggregates in the nanometer size range. Ideally, the model system is characterized by (i) a clean and contamination-free surface, (ii) a well-defined

size and structure of the active particles, and (iii) a well-defined spatial distribution of the active particles on the support. In addition, the preparation procedure should provide a maximum of control over these parameters and should be applicable to a broad range of materials. In practice, several preparation procedures have been developed, all of which, however, only partially fulfil the above criteria. Some current methods are summarized in Fig. 3a. The most common approach is metal deposition and growth from the gas phase (*physical vapour deposition, PVD*)^{9,55,56}. The main advantages of PVD are its applicability to most materials, cleanliness of the samples prepared, and a broad range of available particle sizes. One inherent drawback is the lacking control over particle size and distance distributions. A rather straightforward approach towards monodisperse particles is *chemical vapour deposition*, i.e. the deposition of complexes with well defined stoichiometry (see e.g.^{57,58}). Here, the main restrictions are the availability of suitable precursors as well as lacking stability and remaining contaminations after stripping of the ligands. A rather successful approach for the deposition of smaller monodisperse aggregates is the *deposition of free clusters from the gas phase*. Such aggregates can be mass-selected and subsequently soft landed on the surface [Heiz, 2004 #528]. Some limitations remain with respect to the distribution of the particles, which can only indirectly be controlled via nucleation at oxide defect sites. As a result, the particle distance distribution remains poorly defined. Currently, some efforts are made to develop preparation methods, aiming at a simultaneous control over particle size and distance. One possibility is the *deposition of colloidal metal particles* or *colloidal lithography*⁵⁹. The individual position of each particle can be controlled by the preparation via *electron beam lithography*⁶⁰. The latter methods imply, however, the application of non-UHV techniques and, therefore, have an inherent tendency to introduce contaminations.

Today, the above mentioned preparation methods are used to development the next generation of model catalyst surfaces, which including additional structural and chemical features such as modified⁶¹ or mixed⁶² and nanostructured⁶³ oxide systems, multiple component particles⁶⁴ or poisons and promoters.

In Fig. 3b, some examples are shown for supported model catalysts, previously used in kinetic studies performed in our group⁶⁵⁻⁶⁸. In two cases the Pd particles were prepared by PVD in UHV on ordered Al₂O₃ and Fe₃O₄ films respectively (^{65,68}, see also ⁶⁹). The Al₂O₃ film on NiAl(110) represents an example of an ordered oxide film prepared by simple oxidation of an alloy single crystal⁵⁰. It is very thin and characterized by a low defect density and high reproducibility of the preparation procedure. Its noteworthy that its atomic structure has only recently been solved in a combined work involving STM and DFT calculations⁴⁴. The Fe₃O₄, on the other hand, is prepared by stepwise deposition of metallic iron onto an inert substrate (Pt(111)), oxidation and annealing⁵⁴. Its thickness is variable and can be adjusted to the experimental requirements. In contrast to the Al₂O₃ support, the iron oxide

film typically shows a stronger interaction with adsorbates (e.g. CO) and represents a reducible system which can store and release oxygen.

For both systems the formation of three dimensional particles is observed, which typically form well shaped crystallites in the size range of a few nanometers. These nanocrystallites preferentially expose low index facets (mainly (111) and (100) facets) the ratio of which may vary with the preparation conditions and support. For many metal/oxide systems it has been shown that nucleation of the metal particles preferentially occurs at oxide defect sites⁷⁰. It is important to note that the type of defects, which are active for the nucleation processes, can be chosen via the growth temperature. As a result, the particle density and size can be varied over a large range by choosing the appropriate growth conditions. Typically, particle sizes in the order of 1 to approximately 10 nm are easily accessible. Alternative preparation methods are available for the preparation of larger particles. The last example in Fig. 3b shows a Pd/SiO₂ model catalyst prepared by means of EBL. The particles are characterized by an uniform size and shape and are located on a perfect hexagonal lattice (500 nm particle size, prepared by A. Grant and B. Kasemo, Chalmers University, Göteborg, Sweden^{47,67}). Today, lithographic preparation techniques are capable of producing metal aggregates with sizes down to approximately 10 nm.

In summary, supported particle systems spanning a broad range of particle sizes and structures are available by combination of different preparation techniques. These systems can be characterized in detail with respect to their geometric and electronic structure as well as their adsorption systems using standard surface science techniques. The information provided serves as a basis for investigations of the reaction kinetics discussed in the following.

Kinetic Experiments on Complex Model Catalysts

In order to establish correlations between the structure of the model surfaces to the kinetic phenomena discussed above, detailed and quantitative studies of surface reaction kinetics are required. Molecular beam (MB) methods have established themselves among the major experimental tools to investigate the kinetics and dynamics of surface reactions under well-controlled conditions (see e.g.^{71,72}). Briefly, the main advantages of the MB approach are related to the single scattering characteristics of the experiment in which every molecule in the reactant beam interacts only once with the sample surface. This allows for example exact measurements of absolute reaction probabilities, very fast and precisely controlled transient experiments, and detailed studies of the adsorption or desorption dynamics. A more exhaustive discussion of this approach can be found in the literature⁷³. In our recent work, we have used MB techniques to address several of the kinetic effects on supported model catalysts discussed above. For example, the influence of particle defect sites on the kinetics of CO oxidation has been investigated by MB methods and time-resolved (TR) IRAS⁷⁴. The transient and steady-state data obtained have been utilized to develop microkinetic models, which explicitly take into account

the role of these defects⁴⁶. For the case of CH₃OH decomposition it was possible to assign specific selectivities for the two competing reaction pathways, i.e. C-H and the C-O bond scission, to different particle sites such as facets, edges and steps²³. In a different type of experiment, the distribution of local reaction rates over the particle surface has been measured by angle resolved detection of the CO₂ product. This approach has been used to derive information on the mobility of adsorbates under reaction conditions^{66,75}. Quantitative descriptions have been developed on the basis of diffusion-reaction models⁴⁷. Another example are fluctuation induced kinetic phenomena, which have been identified by transient experiments during CO oxidation on particles of different sizes, in combination with stochastic models⁶⁷. Finally, for the case of NO dissociation and reduction, the distribution of reactants over the different sites on the catalyst nanoparticles have been monitored by MB experiments in combination with TR-IRAS²¹. For a complete overview over these experiments we refer to a recent review article³¹.

In the following, we briefly illustrate the MB approach using a very recent example, which addresses the interaction of oxygen with supported metal nanoparticles. The interaction of oxygen with Pd surfaces has been controversially discussed in the literature for more than thirty years (see e.g.⁷⁶⁻⁸³). Different oxygen species have been observed including various chemisorbed structures, subsurface species, surface oxides and bulk oxides. Recently, significant progress has been made in this field with the structural analysis of surface oxide layers on Pd(111) and Pd(100)^{82,83}. Although surface oxidation processes have been shown to be related to changes in activity for CO oxidation⁸⁴, the role of the various oxygen species in the kinetics of oxidation reactions is not well understood at the microscopic level.

For the case of supported Pd particles two aspects are of particular importance: First, on real catalysts oxidation processes are often found to be related to structural changes including particle reshaping and growth. Secondly, the oxidation behaviour of small particles is expected to strongly differ from the behaviour of single crystal surfaces, partly due to modified energetics (e.g. due to low coordinated atoms and interaction with the support), partly due to reduced kinetic barriers, which often control the oxidation behaviour of single crystal surfaces⁸⁵. In order to investigate these processes, we have performed simple dosing and titration experiments on Pd particles (particle size approximately 4 nm) supported on Fe₃O₄/Pt(111) (see Fig. 4a, see also⁶⁸). The experimental setup involves two molecular CO beams of different intensity and an O₂ or ¹⁸O₂ beam. Isotopically labelled oxygen is used in order to reduce background effects and to identify oxygen exchange with the support.

Specific sequences of oxygen and CO pulses and temperature programmes are applied, to probe specific aspects of the interaction with oxygen. The experiment displayed in Fig. 4b is designed to identify oxygen-induced restructuring effects by using IR spectroscopy of adsorbed CO as a structural probe. The reaction sequence involves exposure to O₂, followed by CO treatment to ensure complete reduction of the surface. Subsequently, a CO IR spectrum is taken at 100 K and saturation coverage.

The first IR spectrum shows the CO stretching frequency region on the Pd/Fe₃O₄/Pt(111) system immediately after preparation. On the basis of comparisons with reference data on single crystals (see discussion in ^{23,43}) and DFT cluster calculations ⁴³, three spectral regions can be identified and assigned: The band at 1990 cm⁻¹ can be attributed to bridge-bonded CO on Pd(100) facets, particle edges and defects such as steps. It shows a broad shoulder ranging down to around 1900 cm⁻¹, which contains contributions from CO on bridge and hollow sites, mainly on (111) terraces. The band around 2107 cm⁻¹ is attributed to CO in on-top adsorption geometry on particles edges, steps and on (111) facets. It is noteworthy that the band contains a high frequency shoulder around 2130 cm⁻¹, which may be tentatively attributed to Pd species in close contact with the support. The weak feature around 2210 cm⁻¹ is due to CO adsorption on the Fe₃O₄ film ⁸⁶.

It is important to note that neither extended annealing in UHV at 500 K nor annealing in oxygen atmosphere at temperatures up to 400 K (the O₂ flux is equivalent to an partial pressure of 10⁻⁶ mbar) leads to significant changes of the IR spectra in this region, indicating that no structural changes occur under such conditions. If the same oxygen treatment is performed at 500 K, however, drastic and irreversible changes of the spectrum are observed. Specifically, the features in the Pd induced regions become substantially sharper and the intensity ratio changes towards the low frequency component. These effects can be interpreted by an increase in particle size (larger terraces lead to sharper bands) and an increased fraction of (100) facets (contributing to the feature around 2000 cm⁻¹ only). These findings are consistent with first STM studies ⁶⁸.

It is noteworthy that the temperature and pressure conditions at which the restructuring is observed coincide with the conditions at which a partial oxidation of the Pd particles occurs. As discussed below the first step of oxidation involves the formation of a Pd interface oxide layer stabilized by the support ⁶⁸. It may be anticipated that among the Pd oxide species stabilized by the Fe₃O₄ support there are mobile entities, which facilitate the growth and reshaping processes.

In Fig. 4c, a typical pulsed CO titration experiment is displayed. This type of experiment allows an exact quantification of the oxygen uptake and release and provides detailed kinetic information on the oxidation kinetics, for example by variation of the delay times and the duration and intensity of CO and oxygen pulses. Here, we focus on some qualitative aspects only. The experiments are performed by first reducing the Pd particles using an extended pulse of CO. The reduced particles are exposed to a pulse of O₂ of exactly defined duration and flux. Subsequently, the oxygen is titrated by pulses of CO, simultaneously monitoring the CO₂ production rate. If the experiment is performed below the threshold temperature for oxide formation, the CO₂ release is fast, indicating a high reaction probability for CO with pre-chemisorbed oxygen on the Pd particles (compare ^{74,87}). If we cross the temperature threshold for oxidation, the initial reaction probability decreases, whereas the total amount of oxygen released increases drastically. Surprisingly, an analysis of the chemical state of Pd particles by means of photoelectron spectroscopy (PES) using synchrotron radiation showed that the

oxidation process preferentially starts at the particle/support interface rather than at the Pd/vacuum interface ⁶⁸. Only at more drastic oxidation conditions (around 600 K) the particles are nearly completely covered with a thin surface oxide layer. The decreasing reaction probability with increasing degree of surface oxidation indicates that the surface (or interface) oxide itself shows a low activity for CO oxidation. A more detailed analysis of the kinetics in fact reveals that the interface and surface oxides merely act as an oxygen reservoir ⁶⁸. A dynamic equilibrium between oxygen chemisorbed on the metallic Pd surface and oxygen incorporated into the interface and surface oxide is established. Via this mechanism, the supported particle system acquires a storage functionality which allows reversible uptake and release of relatively large amounts of oxygen.

Conclusions and Outlook

One of today's major challenges for fundamental studies in heterogeneous catalysis is the development of a microscopic understanding of reaction kinetics on complex catalyst surfaces. Substantial progress has been made towards this aim in the last years, mainly driven by three factors, i.e. (i) the development of model catalysts, which facilitate reactivity studies on well-defined, yet complex surfaces, (ii) rapid progress in the development of experimental methods providing detailed information on the kinetics and on structure and adsorption properties under reaction conditions, and (iii) substantial advances in theory, which allow a high-level treatment of the structural and mechanistic issues, even of relatively complex model surfaces. Many different preparation methods are available for different types of model catalysts, which all come with specific benefits and drawbacks. We have considered some typical examples for supported model catalysts on planar supports (Pd/Al₂O₃/NiAl(110), Pd/Fe₃O₄/Pt(111), Pd/SiO₂/Si(111)) and show that an analysis of these model systems using surface science techniques provides very detailed structural and chemical information on their geometric and electronic structure and on their adsorption properties. In a second step, this information can be correlated to specific kinetic phenomena. As an example for an experimental approach which can provide this correlation, we discuss molecular beam experiments on supported model catalysts. We scrutinize the specific example of the interaction of oxygen with Pd nanoparticles supported on Fe₃O₄/Pt(111). It is shown that under relatively mild conditions the Pd particles are subject to partial oxidation, starting via the formation of an interface oxide layer and proceeding via the formation of surface oxides. These thin oxide structures play an important role with respect to the catalytic properties of the surface: They serve as a reservoir for oxygen storage during catalytic reactions and they are related to restructuring and growth processes changing the dispersion and morphology of the active particles under reaction conditions.

The combined structural and chemical information can be used as an experimental data base for microkinetic descriptions, which explicitly take into account specific kinetic phenomena on complex

surfaces. At least for some simple kinetic phenomena, such model approaches have successfully been developed.

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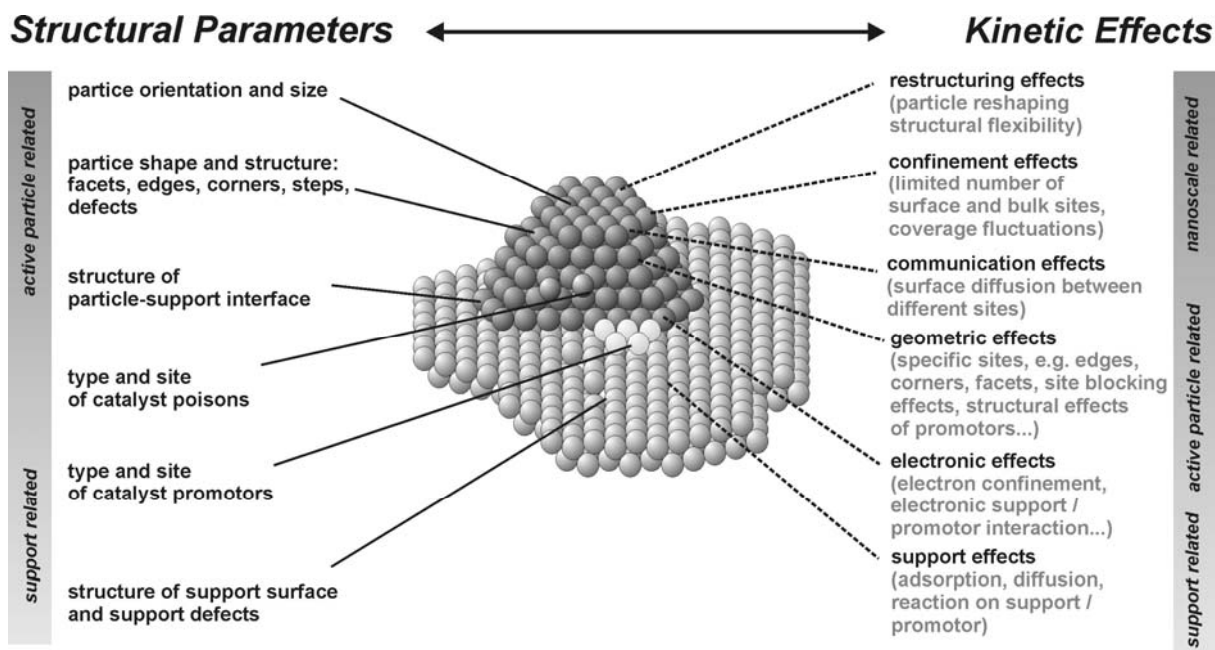


Fig. 1: Structural properties and classification of kinetic phenomena on supported catalysts,⁸⁸.

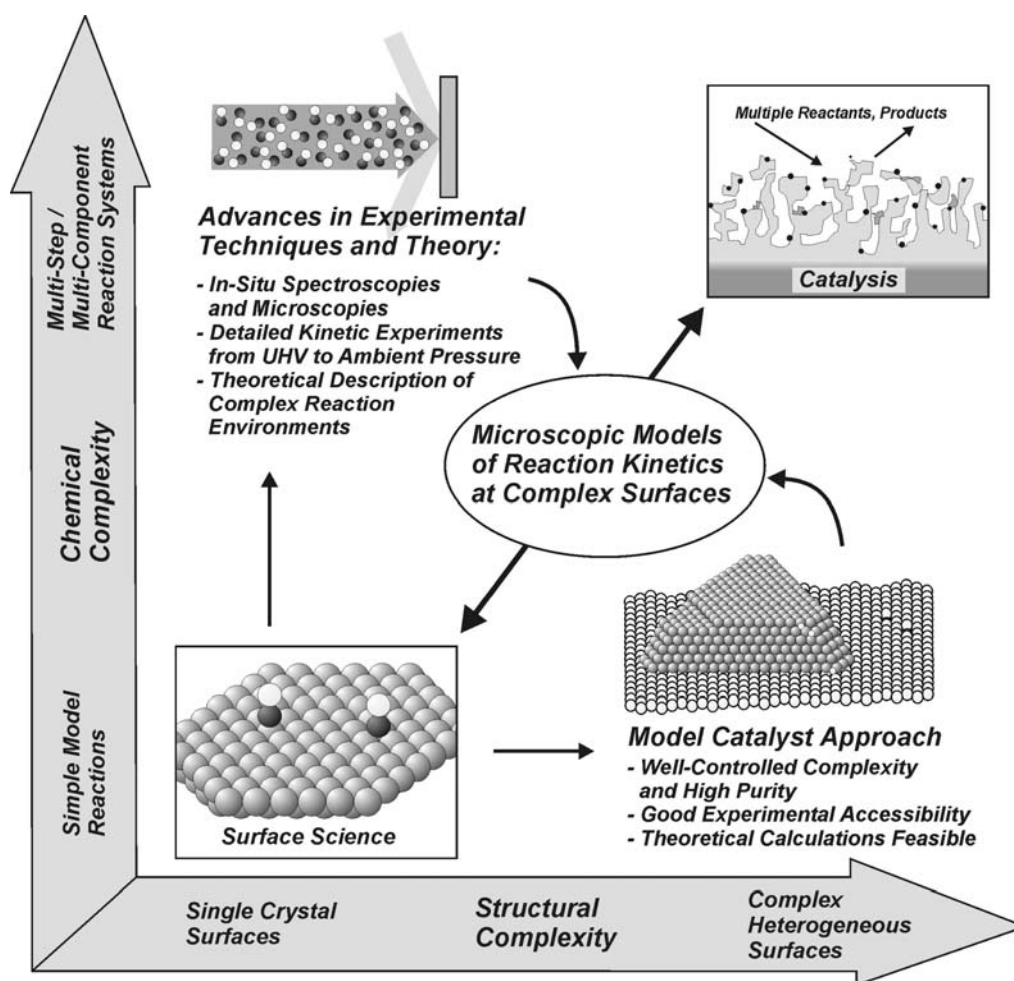
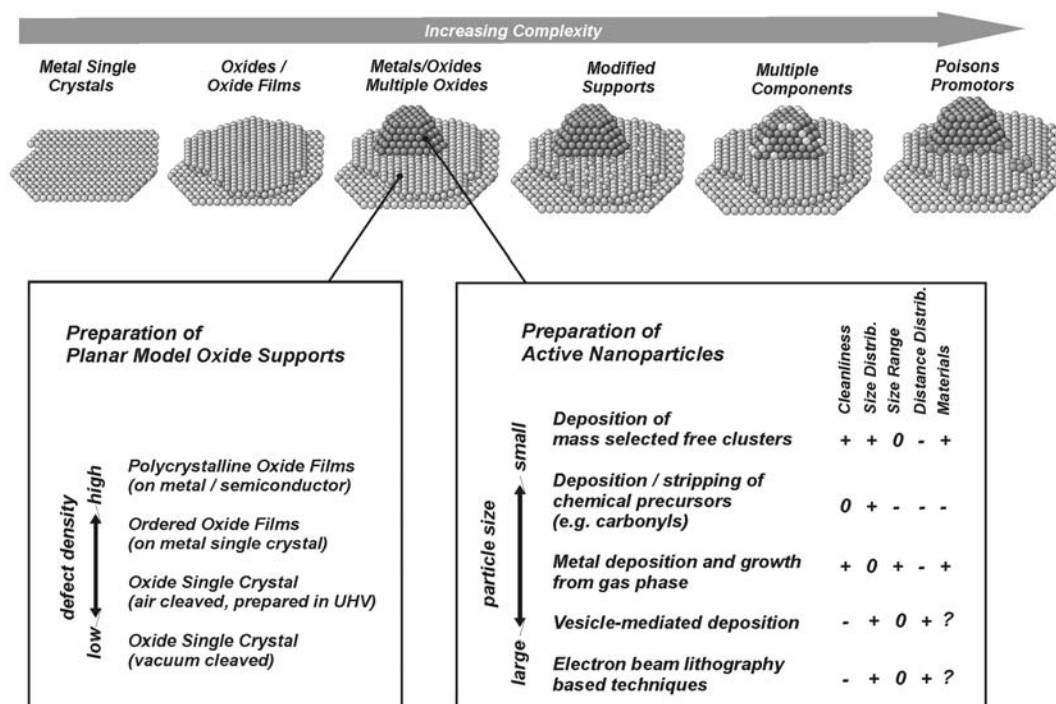


Fig. 2: Experimental and theoretical strategies aiming at an understanding of reaction kinetics on complex surfaces at the microscopic level, adapted from³¹.

a Preparation of Planar Supported Model Catalyst



b Specific Examples

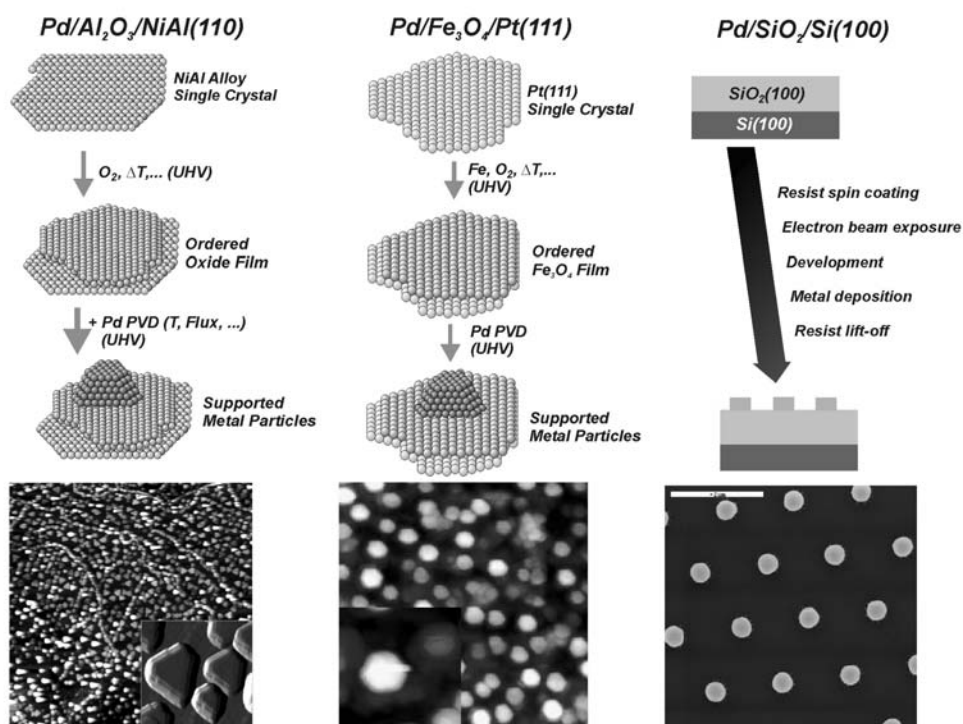
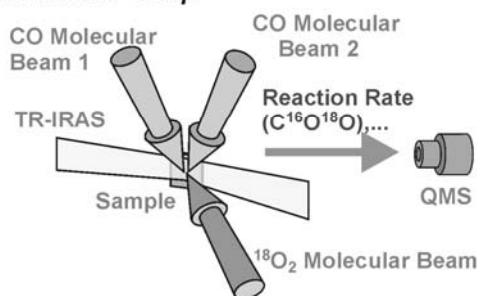


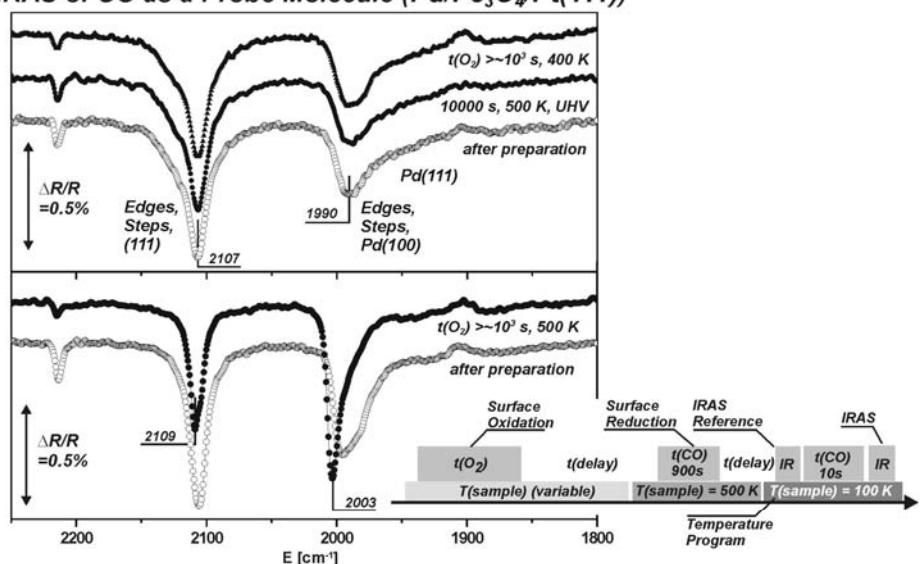
Fig. 3: (a) Development of supported model catalysts and comparison of some preparation techniques, adapted from ⁸⁸; (b) examples for the preparation of specific model catalysts (from left to right): (i) Pd particles (6 nm) grown by physical vapour deposition of on an ordered Al₂O₃ film on NiAl(110), STM image from from ⁶⁵; (ii) Pd particles (4 nm) prepared by PVD on an ordered Fe₃O₄ film on Pt(111), STM image from from ⁶⁸; large Pd particles (500 nm) prepared by EBL on SiO₂/Si(111), scanning electron microscopy (SEM) image from ⁶⁷.

Kinetic Molecular Beam Experiments on Supported Model Catalysts

a Experimental Setup



b IRAS of CO as a Probe Molecule (Pd/Fe₃O₄/Pt(111))



c Pulsed Molecular Beam Titration of Adsorbed Oxygen (Pd/Fe₃O₄/Pt(111))

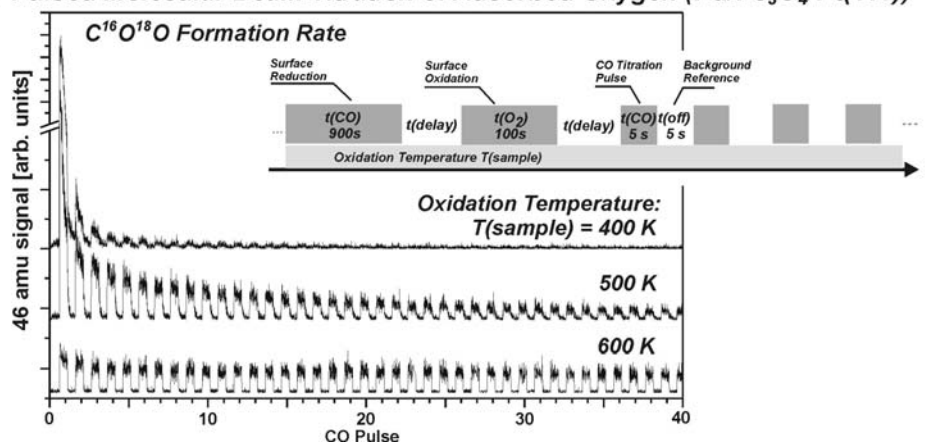


Fig. 4: Combined molecular beam / IRAS experiments showing oxygen-induced restructuring and surface oxidation of Pd nanoparticles on Fe₃O₄/Pt(111). (a) Schematic representation of the experimental setup. (b) Restructuring and growth of Pd particles upon heating in UHV and in O₂ atmosphere, monitored using IRAS of adsorbed CO as a structural probe. The inset shows the experimental sequence used to prepare the systems. (c) Pulsed CO titration experiments showing the uptake and release of oxygen at temperatures below the threshold of surface/interface oxide formation (400 K) and above the threshold (500 – 600 K). The inset indicates the experimental procedure applied.