

## *Invited Review*

# Model Studies in Heterogeneous Catalysis. From Structure to Kinetics

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**Summary.** Heterogeneous catalysis is one of the fields of modern technology, where the application of complex inorganic materials is of enormous economical importance. For a long time, the chemical and structural complexity of catalyst materials has precluded detailed insights into chemical processes on catalyst surfaces. In the last decades, however, substantial progress has been made toward a microscopic-level understanding of reaction mechanisms and kinetics, mainly based on the development of new well-defined model systems and on advances in experimental technology and theory. Scrutinizing the example of supported model catalysts, we review some of these innovations in model catalysis. As a particular challenging aspect of today's work, we discuss the question how detailed structural information on the model systems can be linked to catalytic reaction kinetics at the microscopic level.

**Keywords.** Heterogeneous catalysis; Supported catalysts; Supported model catalysts; Palladium; Carbon monoxide; Nitrogen oxide; Methanol.

## Introduction

Heterogeneous catalysis is a key phenomenon in many fields of modern technology. Some of the best known examples are applications in environmental chemistry [1], but heterogeneous catalysts are also important in the production of most chemicals and in fields such as energy storage and conversion [2, 3]. Typical catalysts are highly complex materials such as *e.g.* multi-component mixtures of oxides or combined oxide-metal systems. The chemical and structural complexity of these materials is crucial: 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 promotor materials. In catalyst development, these dependencies provide the possibility of empirically optimizing structural and

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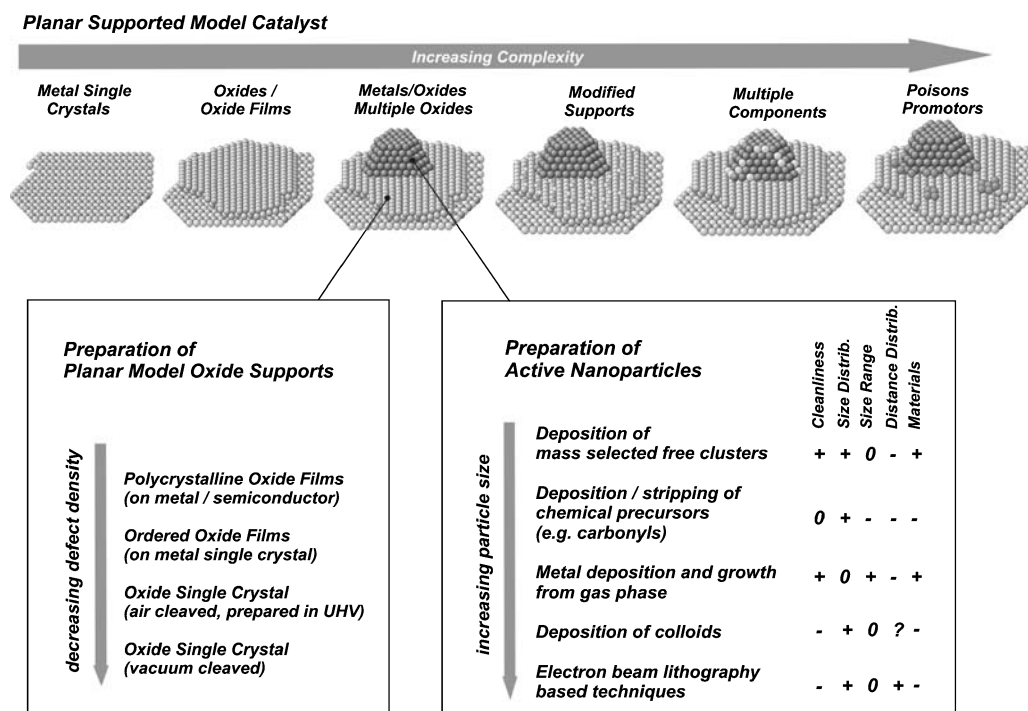
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chemical properties in order to maximize selectivity and activity with respect to the desired reaction pathway. From a fundamental research point of view, however, the resulting systems are inherently difficult to characterize at the microscopic level. As a result, the underlying chemical reaction kinetics is still poorly understood at the microscopic level. This problem is often referred to as the “complexity” or “materials gap” between surface science and catalysis [4, 5].

A fundamental understanding of reaction kinetics on a heterogeneous catalyst would require a direct link between the microscopic structure on the one side and the reaction kinetics on the other. In the last decade, major progress has been made towards this aim. Primarily, these achievements are the results of the development of model systems for heterogeneous catalysts and major developments in experimental technology and theory. Here, the principal advantage of model systems is that complex structural or chemical features of a catalyst surface can be introduced in a well-controlled fashion, simultaneously avoiding the vast complexity of the real system [6–9]. In a second step kinetic measurements have to be performed, which allow to identify the connection between structural features of the surface on the one side and their role in the reaction kinetics on the other. In this review, some approaches are discussed, in particular focussing on supported metal catalysts and on the specific kinetic phenomena occurring on these type of catalyst systems.

### Supported Model Catalysts. Preparation and Characterization

Since modern surface science emerged more than three decades ago, the understanding of heterogeneous catalysis has been one of the main driving forces for



**Fig. 1.** Development of supported model catalysts and comparison of the preparation techniques

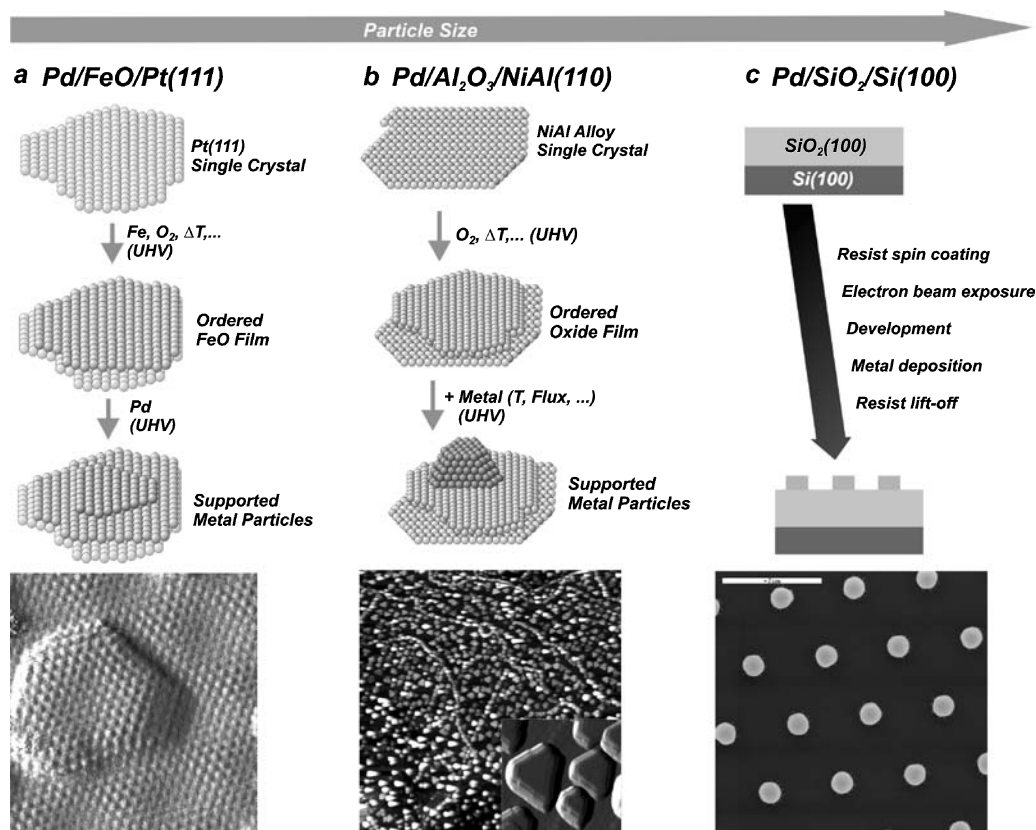
studies in this field. Over the years, the complexity of surfaces employed in experimental work has increased dramatically (see Fig. 1). Early studies mainly focussed on the chemistry of metal single crystal surfaces, providing important reference data on the reactivity of ideal surfaces and possible reaction mechanisms (see *e.g.* Refs. [10, 11]). Natural limitations arise with respect to the study of effects, which result from deviations from these ideal structures. Here, studies on stepped or defect-rich single crystals provide some insights. Unfortunately, these surfaces only poorly resemble the properties of real catalysts. The reason is that bulk metals are rarely used in catalysis. Most heterogeneous catalysts are based on metal oxides or oxide supported metal particles instead.

As a result, great efforts have been made to apply surface science methods to oxide surfaces. Here, one of the key issues is to obtain 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. One strategy to prepare planar oxide surfaces with low defect density is via cleavage of oxide single crystals (see Ref. [6] for an overview). Cleavage can be carried out in air with subsequent cleaning in ultrahigh vacuum (UHV), but lower defect densities are achieved, if cleavage is performed directly under UHV conditions. From an experimental point of view, the low electrical and thermal conductivity of bulk oxides represents a severe restriction, *e.g.* it leads to complication with respect to the application of electron spectroscopies, scanning tunneling microscopy (STM), and other experimental methods. Here, a solution is provided by the use of ultrathin oxide films on metallic supports. For these systems, however, substantial efforts have to be undertaken to develop suitable preparation procedures and to characterize structure, defects, and defect densities. Some experiments in this field have made use of polycrystalline oxides and oxide films (see *e.g.* Refs. [12–15]), which, however, are associated with high defect densities and poorly defined surface structures. In order to avoid these drawbacks, substantial efforts have been undertaken by various groups to prepare ordered oxide films on metallic supports. Today, a large number of recipes are available for the preparation of many different ordered oxide films including *e.g.*  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{MgO}$ ,  $\text{NiO}$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{FeO}$ , or  $\text{Fe}_3\text{O}_4$  and others (see *e.g.* Refs. [16–21] and refs. therein). Their preparation is typically based (a) on the direct oxidation of a metal (or semiconductor) single crystal, (b) on the oxidation of an alloy single crystal, or (c) on the deposition and oxidation of a metal on an inert substrate single crystal. Today, current research aims at the development of the next generation of model catalyst surfaces, including additional structural and chemical features such as modified [22] or mixed oxide systems [23], multiple component particles [24, 25] or poisons [26] and promoters.

Once the model support has been characterized, the next step in the development of a model catalyst 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 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. As a result, there is still no universal preparation method,

but the method has to be chosen according to the specific structural feature to be investigated. Some current methods are briefly summarized in Fig. 1. The most common approach is metal deposition and growth from the gas phase (*physical vapor deposition*, PVD) [6, 21, 27]. The main advantages of PVD are its applicability to most materials, cleanliness of the samples prepared, and in addition, a broad range of particle sizes can be obtained by carefully controlling the preparation conditions. One inherent drawback is the fact that samples are characterized by a more or less broad distribution of particle sizes, instead of the desired monodisperse system. Moreover, the position and distance of the particles on the surface cannot be controlled externally, but in most cases is determined by the distribution of surface defects on the model support. Several approaches have been suggested to overcome these drawbacks. Most of these methods aim at the formation of aggregates of well-defined size, which are subsequently deposited on the surface. A rather straightforward approach is *chemical vapor deposition*, *i.e.* the preparation of complexes with well defined stoichiometry and sufficiently high vapour-pressure, which can be deposited on the surface *via* the gas phase (see *e.g.* Refs. [28, 29]). Here, the main restrictions are given by the availability of suitable precursors, the stability of the aggregates after stripping of the ligands, and the lack of control over the distribution of the active aggregates on the surface. A rather successful approach, which avoids contaminations due to incomplete removal of the ligand shell, is the *deposition of free clusters from the gas phase*. Such aggregates can be mass-selected and subsequently soft landed on the surface [30, 31]. In a unique fashion, this method allows atom-by-atom control over the aggregate size. Also, approaches without additional mass-selection have been tested [32]. The main drawback which remains is the fact that the distribution of the particles can only indirectly be controlled by the quality of the oxide surface *via* nucleation at defect sites. As a result, the particle distance distribution remains poorly defined. Recently, preparation methods have been developed, which aim at a simultaneous control over particle size and distance. Here, one possibility is the *deposition of colloidal metal particles*, the distance of which can be determined *via* their ligand shells. Not only the distance, but the individual position of each particle can be controlled by using lithographic preparation methods such as *colloidal lithography* [33] or *electron beam lithography* [34, 35]. The latter methods imply, however, the application of non-UHV techniques and, therefore, have an inherent tendency to introduce contaminations into the model system. In addition, they are not easily extendable to very small particles.

Figure 2 shows the preparation and microscopy images for a selection of typical model catalyst surfaces spanning a broad range of particle sizes. The Pd particles in Figs. 2a and 2b were prepared by metal vapor deposition and growth in UHV. Small aggregates of monoatomic height are obtained in case of a strong metal-support interaction, such as for Pd on an FeO film on Pt(111) (prepared by Meyer *et al.*, FHI Berlin [36]). In the more common case of relatively weak interaction of the metal with the oxide support, the formation of three dimensional particles is observed (such as for the growth of Pd on a Al<sub>2</sub>O<sub>3</sub> film, Fig. 2b, from Ref. [37]). For this and many other metal/oxide systems it has been shown that nucleation of the metal particles preferentially occurs at oxide defect sites. It is important to note that the type of defects, which are active for nucleation processes, can be chosen *via* the

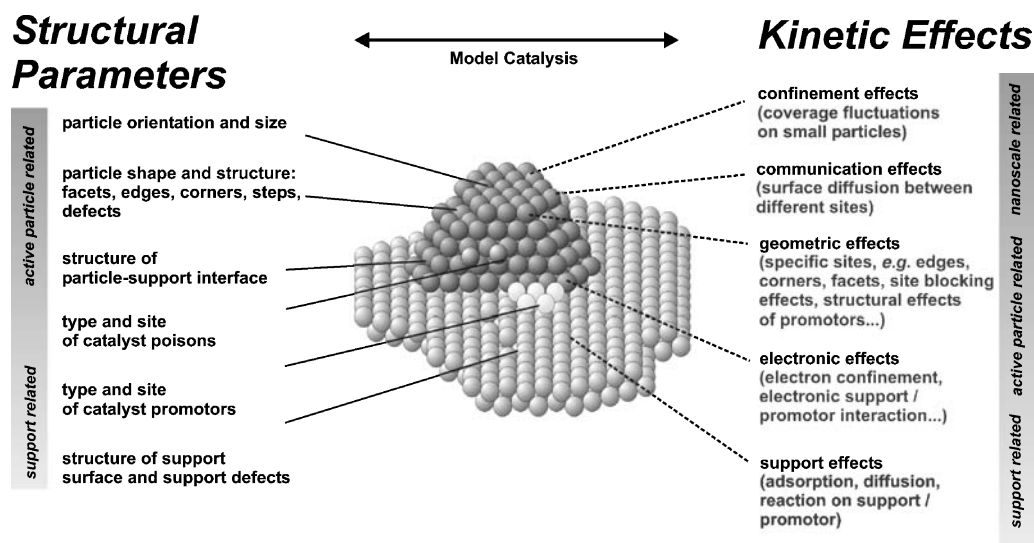


**Fig. 2.** Preparation methods for some Pd model catalysts of different size and structure: (a) two-dimensional Pd particles on a well ordered FeO film on Pt(111), STM image from Ref. [36]; (b) three-dimensional Pd particles on an ordered Al<sub>2</sub>O<sub>3</sub> film on NiAl(110), STM image from Ref. [37]; (c) lithographically prepared Pd model catalyst on a SiO<sub>2</sub> film, from Ref. [39]

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 [38] (particle size in Fig. 2b is 6 nm). For the preparation of larger particles, however, alternative preparation methods have to be used. In Fig. 2c, a Pd/SiO<sub>2</sub> model catalyst prepared by means of electron beam lithography is shown. The particles are characterized by a uniform size and shape and are located on a perfect hexagonal lattice (500 nm particle size, prepared by *Grant and Kasemo*, Chalmers University, Göteborg, Sweden [39, 40]). Today, lithographic preparation techniques are capable of producing metal aggregates with sizes down to approximately 10 nm.

### Reaction Kinetics on Supported Model Catalysts

The model catalysts described in the previous section allow to prepare surfaces with specific structural features of real catalysts in a well-controlled fashion, simultaneously avoiding the full complexity of the real surfaces. Some of these



**Fig. 3.** Structural parameters and kinetic effects on supported model catalysts

structural properties, which might play a role for reaction kinetics are summarized in Fig. 3. These factors include for example the size of the active particles, their orientation, shape, the presence of different facets, edges, corners, steps, and other defect sites, specific particle interface sites, poisons, promoters as well as the structure and defect structure of the support. These structural and chemical parameters can give rise to a variety of kinetic effects. Some of the most common types of kinetic phenomena, which may be responsible for the specific reactivity of real catalyst surfaces, are categorized in Fig. 3: (1) Firstly, there are effects related to the presence of the support, such as simple adsorption and diffusion processes [41–43], spillover phenomena [44], or chemical reactions directly involving the support (see *e.g.* Refs. [45–48]). (2) Secondly, a group of effects are related to the electronic structure of the active particle, which might be modified with respect to the perfect surface, *e.g.* due to the electron confinement in small metal particles or due to strong electronic interactions with the support or with promoters. The modified electronic properties can result in modified adsorption behavior and reactivity (see *e.g.* Ref. [49]). Often a specific role is attributed to interface sites between particle and support (see *e.g.* Ref. [50]). (3) In addition there can be effects, which are related to the geometric structure of the metal particles (see *e.g.* Ref. [6] and refs. therein). 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. It should be noted that the properties of these sites can in many cases not be simulated by the simple use of stepped or defect-rich single crystals and, therefore, represent an inherent property of particles in the nanometer size regime. In addition to these more obvious effects there might be more subtle kinetic phenomena, arising from the complexity of the surface without a direct modification of their adsorption properties. (4) Well-known examples are communication effects, which can result from coupling of small surface regions with different adsorption and reaction properties *via* surface diffusion. As a result, the reaction rate in the

coupled system may strongly differ from a simple superposition of the individual regions [7, 43, 51, 52]. (5) In addition, there are confinement phenomena, which arise from the mobility of the reactants which can be restricted by the limited particle size. These restrictions may include both surface or subsurface and bulk diffusion. One consequence of the reactant confinement are coverage fluctuations, which occur on small catalyst particles, and may have an influence on the reaction kinetics. We have recently shown that such noise induced effects may give rise to a macroscopically modified reaction kinetics [39].

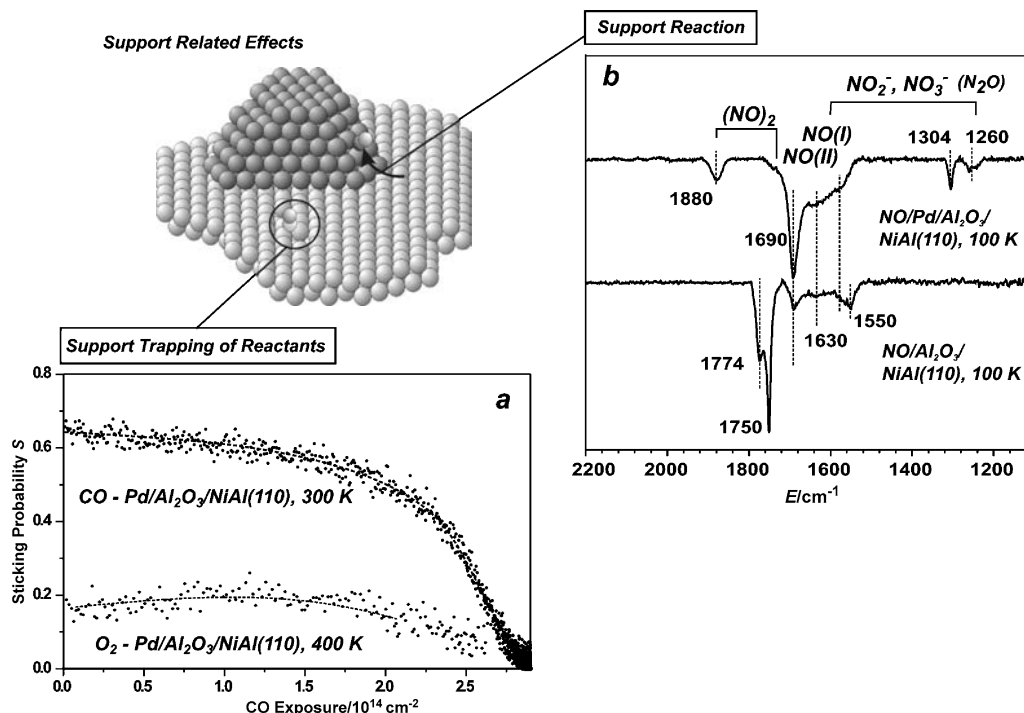
In the following sections, we will briefly review some of our previous work, showing how the individual effects discussed above can be identified by careful investigations of the reaction kinetics on structurally well-controlled catalyst surfaces. In most of the experiments, molecular beam methods are employed. Briefly, a molecular beam is a spatially and temporally defined flux of molecules. Molecular beams can be used in a broad range of experiments on surface reaction kinetics and dynamics and can provide detailed insights into the mechanisms and kinetics of reactions on complex surfaces. For a detailed introduction into the method we refer to the literature (see Refs. [53, 54] and refs. therein).

### Support Related Effects

We start by considering effects which are related to the support material. Here, we discuss two cases: (i) Trapping of reactants by the support and surface transport to the active particles, and (ii) chemical reactions occurring directly on the support.

(i) First we consider the case of weak interaction of the reactants with the support. Figure 4a shows an example, illustrating how a trapping and diffusion in a physisorbed or weakly chemisorbed state on the support may influence the adsorption kinetics of a Pd/Al<sub>2</sub>O<sub>3</sub> model catalyst. The traces display the total chemisorption probability on Pd for incident O<sub>2</sub> and CO beams [55]. It is found, that these probabilities are significantly higher than expected on the basis of the surface fraction covered by the metal. This observation indicates that most of the incident molecules which are adsorbed on the active Pd particles do not originate from direct impingement on the particle, but are initially trapped on the support and successively reach the Pd particles via surface diffusion.

This trapping/diffusion effect leads to a nominally enhanced flux of adsorbate molecules to the active particles, denoted as the “capture zone” effect [41–43]. Conceptually it is important to note the difference to “spillover” phenomena, describing the transport of active species formed on a first surface to a second surface, where it is not directly accessible [44]. Concerning the present experiment on model catalysts, it is noteworthy that by combination of scattering experiments, sticking probability measurements and structural investigations, the role of direct adsorption and “capture zone” contributions can be quantified exactly [55]. In general, it is found that the “capture zone” may strongly dominate the flux of adsorbates to the active particles, in particular at low reaction temperature (see *e.g.* Refs. [56–59]). In those cases in which the adsorption process has a substantial degree of rate-control, the capture zone must be considered in a microkinetic description of the reaction.



**Fig. 4.** Some examples for support related effects on model catalysts: (a) sticking coefficient measurements showing the effect of trapping and diffusion of  $\text{O}_2$  and  $\text{CO}$  molecules from the support to the active particles on a  $\text{Pd}/\text{Al}_2\text{O}_3$  model catalyst, from Ref. [55]; (b) surface IR spectra of the NO stretching frequency region, demonstrating the adsorption and decomposition of NO on a clean and Pd covered alumina model support, from Ref. [60]

(ii) In some cases the reactants may interact strongly with the support and a part of the reaction network may even take place on the support. Here, a prominent example are oxide storage compounds which may accumulate reaction intermediates such as oxygen or nitrogen oxide. An active field of research involving oxide storage compounds is NO removal in automotive exhaust catalysis (see *e.g.* Refs. [45–48]). As an example for the type of data available from a model study, surface IR spectra for the interaction of NO with an ordered  $\text{Al}_2\text{O}_3$  surface are displayed in Fig. 4b [60]. Upon exposure of the  $\text{Al}_2\text{O}_3$  thin film to NO, a complex reaction sequence is observed. It is found that the NO undergoes slow decomposition at low temperature, resulting in the formation of a variety of  $\text{N}_x\text{O}_y$  surface species, most likely including monomeric surface NO species, NO dimers, as well as surface nitrites and nitrates. The process involves strong structural transformations of the alumina support, resulting in a complete loss of its long-range order.

The most surprising effect, however, is observed if the analogous experiment is performed on a partially Pd-covered alumina film. In this case, the corresponding IR spectra at equivalent gas doses show nearly exclusively bands due to NO adsorbed on the Pd particles themselves. The characteristic bands, which are assigned to the decomposition of NO on the support, on the other hand, are strongly suppressed.



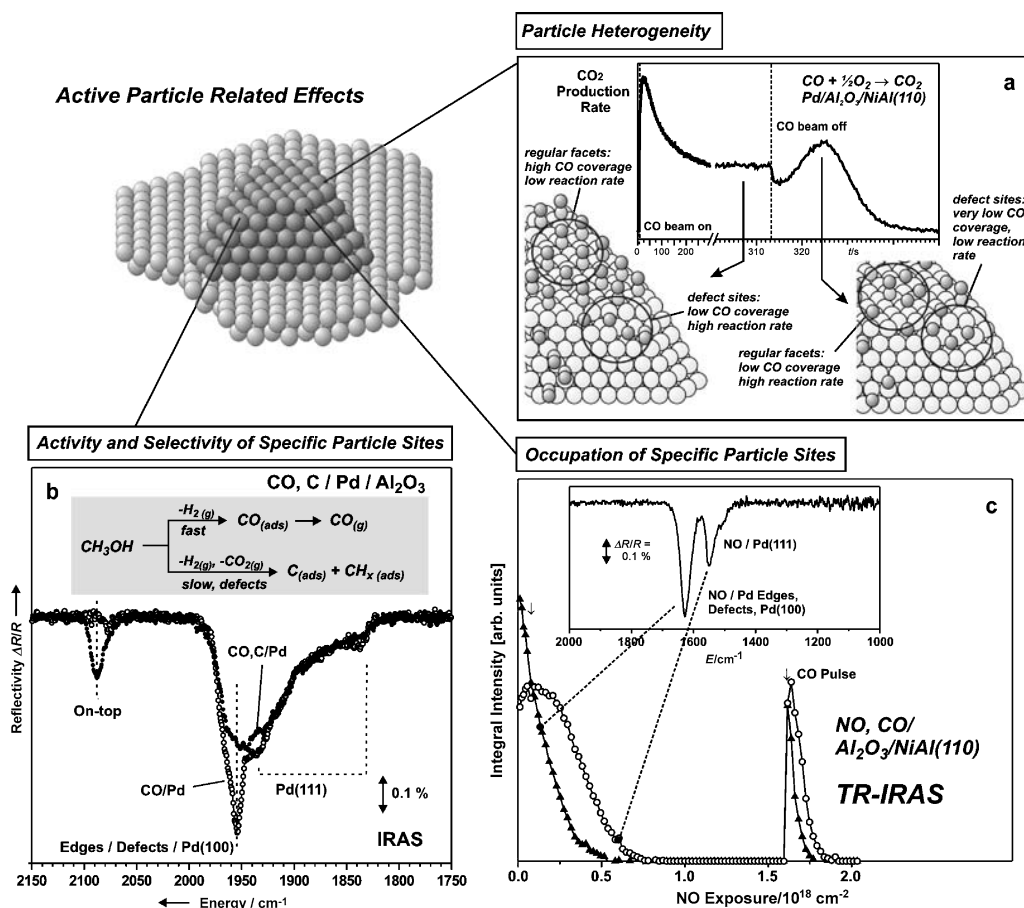
A possible explanation for this effect is related to the growth behavior of the metal particles (see previous discussion). The metal particles preferentially nucleate at oxide defects, thus effectively covering these irregularities. Defect-free oxide patches, on the other hand, remain uncovered. Thus, the suppressed reactivity of the partially Pd covered film indicates that the NO decomposition sequence is initiated at defect sites. Such a strongly enhanced activity of defect sites is a characteristic feature of oxide surfaces. As a result it is observed that in many cases the chemical reactivity of oxide surfaces is strongly dominated by the presence of defect sites.

### Active Particle Related Effects

As a second group of effects, we investigate those phenomena which are directly related to the presence of specific adsorption sites on the particle. In particular we focus on the role of such sites on the kinetics of surface reactions.

From the geometrical structure of metal particles it is apparent that even the most regular particles will expose a variety of different reactive sites. Unfortunately, the identification of specific kinetic effects related to their presence turns out to be a severe problem in most cases. As an example, we focus on the oxidation of CO as one of the best understood model reactions on single crystal surfaces (see *e.g.* Ref. [61]). In Fig. 5a a transient kinetic effect for the CO oxidation on a supported model catalyst is illustrated. It was first observed by *Becker* and *Henry* on supported Pd particles and immediately related to the presence of defect sites [62, 63]: We start from steady-state conditions, at which the CO coverage on the particles is sufficiently high. If we now terminate the CO flux, the transient reaction rate is observed to decrease first, but then it is followed by a reaction rate maximum at a later time. As this transient kinetic effect cannot be described on the basis of a simple homogeneous surface model, it was attributed to the presence of defect or irregular sites. Recent investigations and simulations have shown that in particular those sites, which adsorb CO more weakly than the regular facets, are responsible for this phenomenon [64, 65]. The effect is easily explained: Briefly, the regular sites are largely blocked by CO under steady-state conditions, which has a strongly inhibiting effect on oxygen dissociation. As a result, the reaction preferentially occurs on defect-rich areas, which provide a channel for oxygen adsorption. After termination of the CO flux, the reaction stops on the defect-rich areas, whereas the decreasing CO coverage gives rise to an increasing reaction rate on the regular surface parts, leading to the evolution of the CO<sub>2</sub> peak.

The previous discussion shows that suitable transient experiments can in principle help to elucidate the influence of heterogeneity effects in kinetics. However, the more straightforward method would be a direct spectroscopic identification of the specific sites on the metal particles. Towards this aim, one possible strategy is again the use of probe molecules such as CO. As mentioned before, specific adsorption sites on nanoparticles can be identified by IR spectroscopy of adsorbed CO and comparison to suitable single crystal experiments and theoretical calculations [66]. An example is displayed in Fig. 5b, showing the CO stretching frequency region for CO adsorbed on Pd particles on Al<sub>2</sub>O<sub>3</sub>. The spectrum is



**Fig. 5.** Some effects related to the structure of active catalyst: (a) transient response to the modulation of the CO flux during CO oxidation on a Pd/Al<sub>2</sub>O<sub>3</sub> model catalyst, from Ref. [64]; (b) identification of specific adsorption sites on supported Pd particles by IR spectroscopy using CO as a test molecule, from Ref. [68]; (c) time-resolved IR spectroscopy during NO decomposition and reduction on a Pd/Al<sub>2</sub>O<sub>3</sub> model catalyst, providing information on the occupation of specific particle sites under reaction conditions, from Ref. [70]

characterized by a narrow feature around 1960 cm<sup>-1</sup> with a broad low-frequency shoulder. On the basis of the morphology of the particles and theoretical calculations, the narrow band can be assigned to CO adsorbed at defect and edge sites as well as to a small fraction of (100) facets on the Pd particles, whereas the majority of regular (111) facet sites gives rise to the broad shoulder [66] (At this point it should be noted that the intensities in surface IR reflection do not necessarily reflect the relative concentrations of the corresponding species, see *e.g.* Ref. [67] for a more detailed discussion). A surprising effect is observed if the surface of the Pd particles is partially covered by atomic carbon, generated by decomposition of methanol. The corresponding spectrum in Fig. 5b shows that the characteristic band assigned to the edge and defects sites is completely quenched and, instead, a new band at high frequency appears. From this observation, it was concluded that the C species preferentially occupy the step, defect, and (100) sites on the Pd particles [68].

Information on the catalytic activity of the two types of sites can now be obtained by measuring reaction rates, both on the pristine and on the partially carbon covered particles. As a model reaction, the methanol decomposition was chosen, which proceeds *via* two pathways, C–H bond scission leading to formation of CO and C–O bond scission resulting in the generation of adsorbed carbon and hydrocarbon species. The corresponding reaction rates were determined by means of time-resolved IR spectroscopy and isotopic-exchange experiments [68, 69]. It was found that C–H bond scission proceeds with similar kinetics both on the clean and on the partially carbon-blocked surface, whereas C–O bond scission is strongly decelerated on the partially C-covered particles. This observation shows that for C–H bond scission (dehydrogenation) there is no strong preference for specific sites, whereas C–O bond scission preferentially occurs at defect, edge, or (100) sites. Thus the selectivity of the reaction, *i.e.* the competition between both pathways, can be understood on the basis of the microscopic structure of the particles.

As a third example for a site-specific effect, we choose NO decomposition on the same Pd model catalyst [70, 71]. This reaction is particularly interesting, as it allows to monitor the occupation of different sites on the Pd particles under reaction conditions. The inset in Fig. 5c shows an IR spectrum of NO adsorbed on the Pd particles of a Pd/Al<sub>2</sub>O<sub>3</sub> model catalyst. Two peaks are observed, which – in a similar fashion as in the case of CO adsorption – can be assigned to (a) NO adsorbed at particle edge, defect, and (100) sites (high frequency band, solid triangles in Fig. 5c) and (b) to NO adsorbed on the (111) facets (low frequency band, open circles in Fig. 5c). Again, this assignment is mainly based on comparisons with single crystal data [72]. The temporal behavior of both adsorption bands during NO dissociation can be monitored by time-resolved IR spectroscopy. As expected, the NO bands decrease as a function of time as the reaction products, atomic nitrogen and oxygen, are accumulated on the surface (Fig. 5c). It is found that, similar as in the case of adsorbed carbon, defect, edge, and (100) sites are occupied preferentially, before the (111) facets are blocked at a later time. A differentiation between the effect of oxygen and nitrogen is possible by application of an intense CO pulse, instantaneously removing adsorbed O *via* oxidation to CO<sub>2</sub> (see Fig. 5c). After O removal the NO adsorption capacity is partially recovered. The peak related to the defect and edge sites remains partially attenuated, however, indicating that a strongly bound atomic nitrogen species remains present in the vicinity of these sites. Surprisingly, a comparison of the NO dissociation activity of the clean and of the partially nitrogen covered particles shows pronounced differences. Although the microscopic origin of this effect is still under debate, the experimental results demonstrate that the catalytic activity of the active catalyst particles are critically controlled by the presence of atomic coadsorbates on their surface. These findings underline the central role of in-situ probes which are capable of monitoring the distribution of reactants and products over different sites of the catalyst surface under reaction conditions.

### Nanoscale Related Effects

Most effects discussed in the previous sections primarily depend on the modification of adsorption and reaction properties of individual sites. In addition, there might be

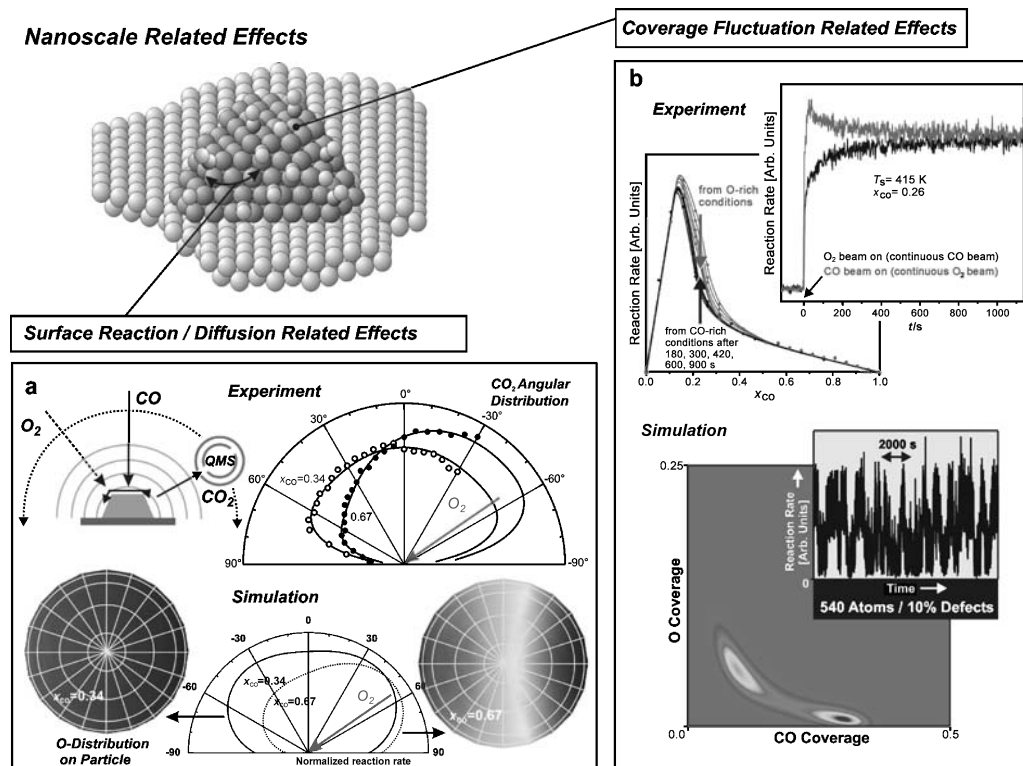
kinetic phenomena on catalyst surfaces, which solely arise from the fact that the surface exhibits a specific structure on a particular length scale (in most cases in the order of several nanometers). Here, we briefly review two phenomena which may occur on such nanostructured surfaces: (i) Effects due to reaction-diffusion coupling on heterogeneous surfaces, and (ii) coverage fluctuations on small active particles.

(i) The role of coupling of different surfaces region *via* surface diffusion has been theoretically investigated by *Zhdanov* and *Kasemo* [43, 51, 52]. The effect may be illustrated as follows: We consider two nanometer-sized surface areas with different adsorption or reaction behavior, such as *e.g.* particle facets with different sticking coefficients or activation barriers. The individual surfaces can be characterized by a well defined reaction rate as a function of reactant fluxes and surface temperature and the corresponding data may be obtained from single crystal experiments. If both systems are coupled *via* fast surface diffusion, however, strong modifications of the reaction behavior may occur. As a result the coupled system cannot be described as a simple linear combination of the individual surfaces.

Although theoretically well described, the identification of this type of “communication effects” turns out to be extremely difficult. An important prerequisite would be techniques that allow measurements of local reaction rates on different parts or facets of catalyst particles. Towards this aim, we have recently started to explore the combination of molecular beam methods and angular resolved detection of products [73, 74]. The essential idea behind the experiment is that for some reactions, such as *e.g.* the CO oxidation on most noble metal surfaces, the desorption of the products is extremely fast on the timescale of diffusion and, therefore, the angular distribution of desorbing products may contain information on the local reaction site or facet where the molecule has been formed. A typical experiment is illustrated in Fig. 6a. We use an oxygen beam in an asymmetric set-up, such that a part of the particle surface is exposed to a direct O<sub>2</sub> flux, whereas other parts are shadowed. For CO oxidation under steady state conditions, the desorbing CO<sub>2</sub> flux is detected in an angular-resolved fashion. In case of fast oxygen diffusion, there is equilibration of the local oxygen coverage over the complete particle surface, leading to a symmetric angular distribution of CO<sub>2</sub>. In case of slow oxygen surface diffusion on the timescale of the oxygen surface residence time, however, an oxygen gradient is established over the particle surface, resulting in an asymmetric CO<sub>2</sub> production.

Some representative experiments on a lithographically prepared Pd/SiO<sub>2</sub> model catalyst are shown in Fig. 6a. It is observed that the angular distribution changes as a function of the CO/O<sub>2</sub> ratio, which controls the oxygen surface coverage and, therefore, the oxygen residence time. By comparison with microkinetic models, these experiments do not only allow the measurement of surface diffusion rates under reaction conditions [40]. Moreover, it is possible to directly extract local reaction rates on different parts of the particle surface.

(ii) As a last effect we consider the role of coverage fluctuations on nanoparticles. In catalysis, noise-induced effects are rarely discussed, mainly because of the lack of experimental evidence for such effects. Theoretically, fluctuation induced kinetic effects have been predicted by several groups (see *e.g.* Refs. [75–77]). In order to illustrate the origin of these phenomena, we consider a conventional microkinetic description of a catalytic reaction by a set of deterministic



**Fig. 6.** Some kinetic effects arising from the nanostructured nature of model catalyst surfaces: (a) investigation of reaction-diffusion coupling on supported nanoparticles by angular-resolved detection of desorbing products during CO oxidation on lithographically prepared Pd model catalyst; by comparison with simulations (bottom panel), information on the surface mobility of adsorbates under reaction conditions is obtained, from Ref. [74]; (b) coverage fluctuations on small supported particles lead to the disappearance of kinetic bistabilities which are observed during CO oxidation on Pd model catalysts; the lower panel shows a simulation of the probability distribution of the CO and O coverage and temporal development of the reaction rate on a single particle, from Ref. [39]

rate equations. The use of kinetic rate equations implies per definition the existence of well-defined surface coverages. For sufficiently small particles, however, spontaneous coverage fluctuations become increasingly large leading to deviations from the deterministic approach.

Similar as for the kinetic effects discussed previously, the experimental verification of noise induced phenomena turns out to be difficult. Direct experimental observations of noise-induced effects during CO oxidation on Pt field emitter tips were performed by *Suchorski et al.* [78, 79]. Stimulated by these experiments, we have again performed particle size dependent measurements of the transient CO oxidation behavior on Pd model catalysts [39]. The simulation in the lower panel of Fig. 6b shows what is expected theoretically: At sufficiently low temperature the CO oxidation on Pd exhibits a kinetic bistability similar as many other simple surface reactions [80, 81]. The two kinetic states are characterized by high oxygen and low CO coverage and *vice versa* and in a kinetic measurement it is possible to arbitrarily switch between both regimes. With decreasing particle size, however,

the amplitude of coverage fluctuations increases and finally leads to spontaneous transitions between the two regimes. As a result, any macroscopic bistability is expected to vanish with decreasing particle size. The experiments shown in the upper panel of Fig. 6b confirm the theoretical model. Sufficiently large particles show perfect bistable behaviour, whereas for small Pd particles the bistability effects vanish as a function of time.

Finally, it should be noted that not only the particle size is critical for the effect discussed. In fact, the adsorption properties and defect densities of the particles have a large influence on the steady-state conditions established and, therefore, on the exact behavior of the noise-induced phenomena as well [39]. This interrelation between different kinetic effects indicates a further difficulty in reaction kinetics on complex surfaces: In addition to the various individual effects discussed in this work, there may be cooperative or anti-cooperative contributions which may further complicate a description at the microscopic level.

## Conclusions

We have reviewed recent model studies in heterogeneous catalysis, particularly focussing on the connection between structural properties of catalyst surfaces on the one side and kinetic phenomena occurring on these systems on the other.

Different methods for the preparation of supported model catalysts are discussed, including their particular advantages and disadvantages. Still, no universal approach to preparation exists, but the numerous preparation methods available provide access to a broad range of surface structures. Their common key feature is that complex surface properties of real catalysts can be introduced in a well-controlled fashion, without the necessity to deal with the full complexity of the real catalyst surface.

Combined with detailed kinetic experiments, the well-controlled model catalyst surfaces provide access to a variety of kinetic phenomena on complex catalyst surfaces. We review experiments on a broad spectrum of effects including (a) *the role of the support material*, which may modify the reaction kinetics via adsorption and surface transport of reactants, *via* direct participation in the reaction sequence, or *via* modification of the adsorption or reaction properties of the active particles, (b) *the role of the active particles*, on which, due to geometric or electronic reasons, different adsorption and reaction sites coexist, differing with respect to their catalytic activity and selectivity, and (c) *the role of nanoscale kinetic effects*, originating from diffusion or fluctuation effects on surfaces with complex structure. One main advantage of the model catalyst approach is the fact that the microkinetic models derived are based on quantitative experimental data obtained on surfaces with a controllable degree of complexity and thus provide experimentally based insights into the origins of kinetic phenomena on catalyst surfaces at the microscopic level.

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