

Chapter 1

Heterogeneous catalysis

Abstract Many industrial processes in chemical industry resort on catalysis. Heterogeneous catalysis is the most practical method as separation processes are avoided by keeping catalysts and products in different phases. Its economical impact is therefore outstanding in environmental chemistry [1] or energy storage and conversion [2], for examples.

Most heterogeneous catalysts consist of expensive transition metals like Pt or Pd. Reducing the quantity of metal employed has then a large economical interest. Powders or finely dispersed particles are therefore preferred to bulk materials. However, this morphological change has deep implications for the electronic structure of the metals and for its catalytic properties. Added to the so-called size effects, the complexity of practical catalysts also comes from their historical empirical design, which often led to complex mixtures including small quantities of promoters.

Yet a fundamental understanding of the reactions at the atomic scale would certainly lead to a better understanding of heterogeneous catalysis. A rational design would also be preferable. However, the added complexity of composition and of the structure of practical catalysts prevent fundamental sciences from a direct approach. And not only the catalysts are complex systems but the reaction itself is usually complex as well.

In this chapter, we introduce kinetics and review size effects. We then propose an approach, which could lead to some fundamental understanding of heterogeneous catalysis.

1.1 Kinetics

The overall rate of heterogeneous catalytic reactions, or activity, can usually be described by simple differential equations. However, such depiction of the reaction hardly reflects its true mechanism. Reactions usually occur through elementary steps. Each one can be considered a chemical reaction in itself, having its own kinetics and degree of control over the overall rate. Rational catalyst design would therefore consist in influencing each of the elementary steps toward the desired products. However, due to the complexity of heterogeneous reactions, the elementary steps are experimentally difficult to assign. Practical catalysts are thus often designed empirically, leading to an even higher degree of complexity. Moreover, the activity may also be influenced by factors such as mass transport and temperature [2–4]. Another point, which is relevant practically, is the

stability of catalysts. Stability is related to slow changes of the rate of one or more elementary steps of the reaction network as a function of time by mechanisms such as poisoning, fouling and sintering [5].

Consequently, a fundamental understanding of heterogeneous catalytic reactions at a molecular level faces the added complexities of the reaction mechanism, the catalyst surface, composition and morphology and the different timescales at which relevant phenomena occur. Such an understanding should arise from a gradual and controlled approach, the goal of which being a rational design of new catalysts.

Surface science studies consist in studying the reaction on a uniform single crystal surface. This first step allows to identify the elementary steps experimentally [6–8] and to create microkinetic models of the reaction [9–12, and Refs. therein]. Then, the surface is complicated gradually and tends to resemble practical catalysts. The influence of each degree of complexity on the overall reaction has to be addressed at the molecular level. However, surface science still faces many difficulties. Indeed, the simplified models are likely to react very differently from real catalysts as the catalytic behavior is usually an inherent property of the complexity of catalysts: Often, catalytic properties are found to depend sensitively on structural parameters such as the particle size or shape or chemical parameters such as the properties of the support or promoters. Similarly, not only the complexity of the material is often required for good performances of the catalyst, but the complex reaction network is also intended. Here, a good example is the automotive exhaust systems, where hydrocarbons, carbon monoxide and nitrogen oxides should be selectively removed in the presence of other reactants. The challenge of today's research is therefore to transfer the knowledge acquired on simple surfaces for simple reactions to more realistic systems.

1.2 Size effects

Heterogeneous catalysis often relies on expensive transition metals. Hence, there is an economical interest in using as low as possible metal quantities. Size is therefore a critical parameter. However, using metal particles instead of bulk material can affect the rate and mechanism of a reaction. Added to the genuine size effects, it is likely that properties of surface atoms vary from bulk properties as well as from surface atoms in a perfect single-crystal environment, would it only be due to lowered coordination numbers [13–15]. Let us now review what can be theoretically expected on supported catalysts.

1.2.1 Genuine size effects

Confinement phenomena A structural barrier can induce modifications of the kinetics by limiting the mobility of the reactants. With an inhibition of diffusion to other parts of the surface, the reactants are confined to small particles. This may result in modifications of bulk diffusion, which may be either restricted (e.g., for H on Pt [16]) or enhanced, leading to incomplete reduction of the metal [17].

Fluctuations Fluctuations are a general phenomenon in physics and chemistry [18–20].

The intensity of fluctuations vanish rapidly with increasing particle size. However, they can have a large impact on the activity of small particles for bistable reactions [21] or even induce bistability in deterministically monostable reactions [22].

1.2.2 Geometric effects

Particles expose different crystalline facets. These facets usually behave differently toward the reaction. Surface diffusion then allows communications between the different facets, leading to possible farther complications of the reaction network. Decreasing the particle size increases the dispersion, so that surface-related effects are stronger on small particles. Among geometric effects, one can discriminate:

Restructuring Small particles are likely farther from thermodynamical equilibrium than bulk material. Adsorbate-induced reshaping toward the Wulff shape or adsorbate-induced restructuring is enhanced on small particles [23–25]. Stronger deviations in the crystal structure have also been reported [13, 26].

Communication Experiments on single crystals have shown that reaction properties vary with the crystalline facet. And particles inherently expose different facets. However, the reaction rate on particles can be dramatically different from the mere superposition of the kinetics of the individual facets [27].

Defect density Another implication of faceting is the exposure of specific sites such as edges, steps and kinks. These defects have a different number of neighboring atoms, and therefore different electronic environments from the terraces. They can induce an increase or a decrease of the activity [14, and Refs. therein]. The influence of steps, in particular, can be systematically investigated on single crystals with low Miller indices [28]. A controlled sputtering of single-crystal surfaces can also increase the defect density and lead to systematic experiments.

1.2.3 Electronic effects

Decreasing the number of atoms per particle can have a large impact on the electronic structure of metals [29]. The band structure on a large ensemble of atoms is accurately described by a continuum. However, as the number of atoms decreases, the levels become more discrete and the gap between the levels may become appreciable with respect to kT . The particles then might lose their metallic properties [14].

1.2.4 Support effects

So far, we considered the particles as isolated reactors on an inert surface. However, the presence of the support can also have an effect on the catalytic properties, be it involved in the reaction network or not. The support to model and practical catalysts usually is an oxide surface. Such a support often provides control over dispersion and size of the active metal and also helps to stabilize it [30].

Diffusion Diffusion of reactants at the support surface can have in principle two effects. The capture zone effect, when the adsorbate flux is increased by trapping on the active particles [30–33]. Or non-activated diffusion of the reactants from particle to particle. In the latter case, the particles do not behave like isolated reactors any more. It is noteworthy that, even where adsorption of the reactants to the support is weak, an additional flux can come from molecules bouncing at the support and scattered in direction of the particles.

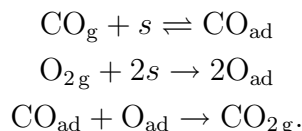
Metal bonding with the support Ionic or covalent bonding of the metal to the support is expected for the metallic atoms directly in contact with the support. The proportion of these atoms increases as particle size decreases. And therefore the influence of such atoms on the reaction increases with decreasing particle size [14,34].

Active support The support can also be directly implied in the reaction network. Adsorption processes may be facilitated on the support and coupled with reaction on the active metal by diffusion (spillover) [35,36]. Or an active support may be deliberately chosen, such as for example reducible oxide surfaces for car exhaust systems [37–39].

The size effects described here can occur simultaneously and affect the activity as well as the selectivity of catalytic reactions in different directions. Thus, if these effects are well known and understood in principle, experimental evidences are usually difficult to find. It is therefore of a fundamental interest to find suitable methods to investigate the size behavior of supported particles. Moreover, it is often reported that particles of a certain reduced diameter exhibit better selectivity or activity. Whereas the understanding for such behavior is generally poor, a control of the size of heterogeneous catalysts remains of practical interest.

1.3 CO oxidation

The reaction used throughout this dissertation is CO oxidation on Pd supported catalysts. CO oxidation is the first success of surface science in the elucidation of elementary steps of a reaction network [6]. It is therefore widely used in surface science and only the most critical knowledge about the reaction is given in this section. The reaction follows a Langmuir-Hinshelwood (LH) mechanism with adsorption of CO, dissociative adsorption of O₂ [40] and fast reaction to CO₂ at the surface,



Yet, this reaction exhibits peculiar features such as a kinetic bistability and an oscillatory behavior [41–44] under certain conditions (also see [45] for a review on kinetic oscillations). CO₂ produced interacts only weakly with the surface and desorbs immediately after its

formation [46]. O_{ad} does not desorb for temperatures lower than 700–800 K [47, 48], whereas CO_{ad} desorption starts around 200 K [49, 50, and Refs. therein]. And CO_{ad} diffuses fast at the surface of close-packed surfaces [51].

1.4 Organization of the dissertation

1.4.1 Experimental perspective

Due to experimental difficulties, diffusion on systems relevant to heterogeneous catalysis is usually studied experimentally in the low coverage limit. Whereas reactions are usually performed in the high coverage limit. Chapter 4 proposes a new technique to study diffusion under reaction conditions utilizing angle resolved mass spectrometry.

Fluctuations are a general phenomenon in chemistry. Many heterogeneous catalysts consist of dispersed small metal aggregates, where fluctuations are expected to have a major influence on the activity. However, a study on a realistic ensemble of particles is exposed to experimental difficulties as this phenomenon occurs at the scale of single particles. Fluctuations on a bistable system should result in even higher discrepancies with the deterministic limits. Indeed, the global equilibrium is then an average of the different stable states. Here again, few experimental studies have been performed, which could show the existence and the influence of kinetic fluctuations. Chapter 6 proposes experiments in which fluctuations are observed, although for farther characterizations, modeling is required. The combination of experiments and modeling also allows to investigate the effect of the defect density on fluctuations.

Therefore (i) diffusion under reaction conditions (Chapter 4), (ii) the interplay between diffusion and kinetic bistability (Chapter 5) and (iii) the effect of spontaneous fluctuations on a kinetic bistability (Chapter 6) are investigated experimentally.

1.4.2 Theoretical perspective

Modeling and simulations provide another point of view on the experiments. Modeling and experiments should therefore be regarded as complementary techniques to achieve a fundamental understanding of reactions. Malchow and Schimansky [52] gives an overall perspective to the theoretical part of this work: A mathematical description of a non-equilibrium bistable system must include (i) the chemical reactions (ii) diffusion and (iii) a noise source of stochastic origin.

Let us now consider this statement in regard of size effects: For a system small enough, the diffusion lengths of all the reactants at the timescale of their surface residence time exceeds the size of the system. In that case, diffusion is negligible. But effects related to spontaneous fluctuations may then dominate the activity. Conversely, the intensity of spontaneous fluctuations vanish rapidly with increasing system size. Therefore, for a system large enough, fluctuations are negligible but diffusion may play a role in the activity.

Diffusion is studied in the limit of a large system size in Chapter 4. Chapter 5 investigates the interplay between diffusion and bistability in the limit of a large system size.

On the basis of the knowledge acquired then, fluctuations are studied in Chapter 6 on a large range of system sizes. We therefore propose an exhaustive theoretical study of the reaction, as defined by Ref. [52].