

# Chapter 7

## Outlook: Applicability of the methods to other systems

**Abstract** New approaches, combining experiments and theory, were suggested for the study of several aspects relevant to a fundamental understanding of heterogeneous catalysis and size dependence of the reaction rate, electronic properties and morphology of the support and of the particles. These methods, however, should not be limited to the particular case of CO oxidation on Pd supported particles. In this chapter, we briefly review the applicability of these techniques to other systems.

### 7.1 Diffusion under reaction conditions

The results suggest that AR experiments of the type presented in Chapter 4 can be quantitatively understood on the basis of RD models. The information on the distribution of reaction rates on the particle surface survives in spite of support scattering effects and diffuse local angle distributions of desorbing products. As a result, information on kinetic parameters such as surface diffusion rates as well as on the local reaction rates on supported nanoparticles can be extracted from a comparison of experiments to simulations.

It is apparent that a highly directed product desorption leads to a stronger asymmetry of the total CO<sub>2</sub> distribution. Therefore, a highly peaked local desorption is advantageous for the type of experiments discussed. However, the angle dependent effects can be easily detected even in the case of very diffuse local distributions of desorbing products ( $\cos^n$  with  $n = 1$ ) as were the case in our experiments. With respect to the applicability of the method, this result demonstrates that angle-dependent measurements of the type performed in this work should be feasible for many reaction systems, and do not require particularly narrow local angle distributions of desorbing products.

## 7.2 Diffusion and bistability

The results in Chapter 5 demonstrate that the global CO oxidation kinetics of a model catalyst, when its surface is exposed to reactant fluxes showing strong local variations, are similar to the kinetics observed on single crystal surfaces. This prediction holds even for very large particle sizes as a result of fast surface diffusion of  $\text{CO}_{\text{ad}}$ . With respect to microkinetic simulations, the behavior is well described by HoMF, under both transient and steady state. In spite of the single-crystal-like global kinetic behavior there may exist pronounced gradients in the coverage of one reactant and the local reaction rates. The analysis of these effects, which contain information on the surface mobility of the individual reactants, requires microkinetic simulations based on a detailed reaction–diffusion model.

The success of HF for the simulations, however, should not be taken as a general rule for other systems. It is mainly due to the influence of  $\Theta_{\text{CO}}$  on the RDS under all reaction conditions. Either it determines CO adsorption when it is the RDS; or it determines  $\text{O}_2$  adsorption (by inhibiting it) when this is the RDS. As  $\text{CO}_{\text{ad}}$  diffuses fast,  $\Theta_{\text{CO}}$  is equilibrated and farther effects due to the inhomogeneity of the flux distribution are canceled. Therefore, RD schemes should be used in any case to gain relevant informations on the diffusion of adsorbates under reaction conditions.

Another point is that the situation might be different in case of model catalysts based on well-oriented and faceted nanoparticles, as opposed to the polycrystalline particles used here. The distribution of the reactant fluxes onto differently oriented facets may give rise to changes in the global reaction rate. Moreover, edges at the facet boundaries may further complicate the situation [10]. Future experimental work on such structurally well-defined supported nanocrystallites, in combination with the simulation approaches presented here, may help to provide detailed insights into the reaction–diffusion coupling on supported catalysts and into related kinetic phenomena.

## 7.3 Bistability and stochastic phenomena

It is noteworthy that the results from Chapter 6 represents the first clear experimental evidence for a fluctuation-induced kinetic effect on a macroscopic catalyst surface. The results reported are expected to hold not only for the specific case studied, but universally for all reactions exhibiting similar kinetic multistabilities. In general, the frequency of fluctuation-induced transitions is expected to depend sensitively on modifications of the adsorption properties and on the presence of specific adsorption sites, with both effects naturally playing an increasing role with decreasing particle size. Finally, it should be pointed out that the presence of coverage fluctuations on nanoscale particles is expected to have an influence on the global reaction kinetics even in absence of kinetic phase transitions. Thus, general deviations from a deterministic description based on rate equations are predicted, although these effects can be subtle and may be difficult to identify experimentally.

As a final point concerning the origin of size and structure effects in heterogeneous catalysis, the present work supports the idea that in many cases it might not be possible

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to assign a kinetic phenomenon to a single geometric, electronic or confinement effect. Instead, we should expect a strong coupling between different effects, leading to synergistic or antisynergistic contributions once a specific property of a complex surface is modified. This point might be one of reasons for the difficulties to derive a quantitative understanding of reaction kinetics in heterogeneous catalysis. For future studies, it underlines the necessity to develop model systems and microkinetic descriptions, which do not only focus on a single structural or electronic effect, but simultaneously take into account multiple degrees of complexity.