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Preface

Heterogeneous catalytic reactions are highly non-linear multilevel chemical reaction systems that are operated far from equilibrium. They are known to exhibit complex temporal and spatiotemporal behaviour that has been in the focus of research also in the general context of the dynamics of non-linear systems in other fields of natural and engineering sciences. In dependence on the experimental conditions including the design of the catalyst such phenomena originate at various levels of a catalytic system ranging from the nm-scale on single crystal surfaces up to the macroscopic scale of a packed bed supported catalyst. The intensive investigation of the dynamic aspects of heterogeneous catalysis during the past decades has yielded deep and fascinating insights into the details of the kinetics of the reactions on a microscopic level as well as into the complexity of real reaction–diffusion systems at elevated pressure on a macroscopic level. It is the aim of the present issue to summarize and evaluate most recent achievements and highlights in the field, to present new reaction systems of practical relevance and to discuss future perspectives.

Details of the structure sensitivity of kinetic oscillations during the $H_2 + O_2$ and $NO + H_2$ reactions as obtained on sharp tips prepared for field electron (FEM) and field ion microscopy (FIM) of a number of platinum group metals are presented and discussed by Gorodetskii et al. The authors identify on the nm-scale and under UHV-conditions drastically different feedback mechanisms at the heart of the observed spatiotemporal dynamics characteristic for the specific metal and the chosen reaction.

The reliability of the details of the kinetics of such reaction systems allow the design of almost quantitative mathematical models including the verification of the feedback mechanism based on lateral interactions between molecules adsorbed on the catalytic surface. This is documented in the contribution by R. Imbihl in the case of the $NO + H_2$ reaction on Rh(1 1 0) and in the paper by N.V. Peskov et al. in the case of the $N_2O + H_2$ and the $N_2O + CO$ reactions on a Ir(1 1 0) surface. The paper by R. Imbihl further demonstrates the success of recently developed surface science tools, e.g., scanning photoelectron microscopy (SPEM) that can provide information concerning the actual chemical composition of various surface structures, information that the photo-emission electron microscope (PEEM) could not provide. Higher resolution, a richer contrast and a decrease of the length scale on which spatiotemporal structures can be observed thanks to low energy electron microscopy (LEEM) and mirror electron microscopy (MEM), two recently developed methods of high potential for revealing further details of the development of spatiotemporal structures on catalytic surfaces.

The details of the kinetics obtained under UHV conditions and on single crystal metal surfaces have raised the question as to the relevance and applicability of the results under the conditions of real catalysis. A major challenge in current catalysis research therefore is directed towards bridging the pressure gap as well as the materials gap between UHV conditions and metal single crystal surfaces and real conditions, i.e., elevated pressures and complex materials like supported metal catalysts. Two papers demonstrate significant progress in the field. Results of the application of in situ high-pressure scanning tunnelling microscopy (STM) inside a flow reactor in the case of the CO oxidation on Pt(1 1 0) and Pd(1 0 0) are presented in the contribution by B.L.M. Hendriksen et al. The results demonstrate, e.g., that low pressure atomistic models like the (1×2) missing row structure observed under UHV conditions in the case of Pt(1 1 0) do not play a role in high pressure reaction rate oscillations. Further, the authors present results that contradict the up to now widely accepted Sales–Maple–Turner oxidation–reduction mechanism underlying the kinetic rate oscillations in the CO oxidation. Noah McMillan et al. report the formation of subsurface oxygen during the CO oxidation on Pt(1 0 0) and demonstrate for the first time its active role in the catalytic reaction and in spatiotemporal pattern formation at intermediate pressures. The results that have been obtained by ellipsomicroscopy for surface imaging (EMSI) are important for catalysts operated at higher pressures. The authors discuss new micro kinetic models that incorporate subsurface oxygen.

The formation of a plethora of spatiotemporal patterns under atmospheric pressure conditions on the macroscopic scale, namely on extended polycrystalline surfaces and on the level of the catalyst bed are discussed for a number of oxidation reactions in the contribution by D. Luss and M. Sheintuch. Due to the fact that the reactions over supported catalysts under normal conditions are usually non-isothermal, pattern formation can be recorded with IR cameras in

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fairly high resolution. The spatiotemporal pattern formation in such systems is strongly impacted by global interactions, inherent heterogeneities in the catalyst, transport coefficients and by coupling of different surface and subsurface kinetics. Patterns can be qualitatively simulated. Quantitative simulation requires reliable kinetic models like in the case of the formation of hot regions in a three-dimensional fixed bed reactor. The studies are of intrinsic academic interest as well as of practical importance, e.g., for developing a qualitative understanding of the formation of hot zones transversal to the flow direction in a catalytic reactor and as a consequence design criteria.

In recent years, many new oscillating heterogeneous catalytic systems have been discovered. As a guide to the readers the editors found it appropriate to summarize the known oscillatory catalytic systems in a table that appears as an appendix to this volume. Among these catalytic systems two reactions have attracted much interest, namely the environmentally important decomposition of nitrous oxide N_2O into the elements and the oxidation of CH_4 over metal catalysts. They are discussed in two papers. Th. Turek reviews experimental and modelling studies concerning kinetic oscillations during the catalytic decomposition of N_2O on Cu-ZSM-5 and Fe-ZSM-5 catalysts. The role of adsorbed nitrate in the assumed feedback mechanism could be confirmed by in situ FTIR spectroscopy in the case of the Cu-ZSM-5 catalyst while oscillations observed on Fe-ZSM-5 have yet to be explained. The oscillating oxidation of methane on nickel catalysts represents an interesting example of complex thermokinetic oscillations, where the oscillatory behaviour originates due to temperature variations, Ni/NiO phase transitions and the change of the selectivity of the process. The experimental data, concerning the observed oscillations over various metallic catalysts and possible feedback mechanisms, are discussed in the paper by Xunli Zhang et al.

Finally, we wish to thank all the authors for their high quality, thorough and state of the art contributions and the reviewers for their rapid and careful assistance. The two guest editors would like to acknowledge professor B.E. Nieuwenhuys for his kind suggestion to participate in the preparation of this issue and for his continued encouragement. We hope that the readers will find the papers informative and that more research activities will be stimulated in the exciting field of the dynamics of heterogeneous catalytic reactions.

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