

## In situ gas–surface interactions: approaching realistic conditions

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## FOREWORD

# *In situ* gas–surface interactions: approaching realistic conditions

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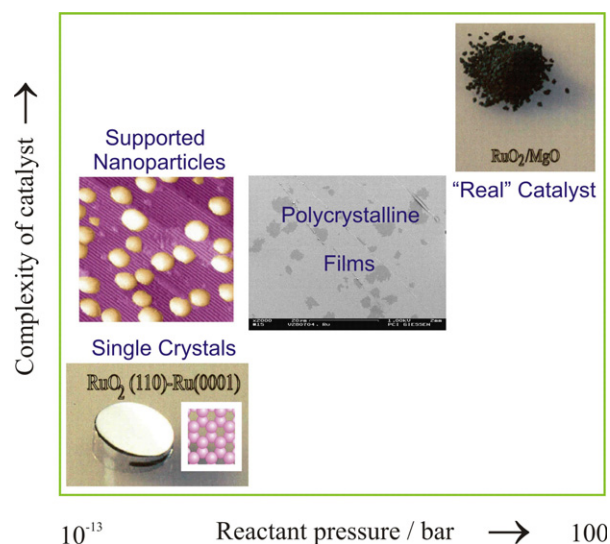
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This special issue is devoted to the application of *in situ* surface-sensitive techniques in the elucidation of catalysed reactions at (model) catalyst surfaces. Both reaction intermediates and the nature of the catalytically active phase are the targets of these investigations. *In situ* surface science techniques are also used to study the interaction of water with surfaces under realistic conditions.

Since 80% of all technical chemicals are manufactured by utilizing (heterogeneous) catalysis, scientific understanding and technological development of catalysis are of central practical importance in modern society [1]. Heterogeneously catalysed reactions take place at the gas/solid interface. Therefore one of the major topics in surface chemistry and physics is closely related to heterogeneous catalysis, with the aim of developing novel catalysts and to improve catalysts' performances on the basis of atomic scale based knowledge. Despite the economical and environmental rewards—if such a goal is achieved—and despite 40 years of intensive research, practical catalysis is still safely in a black box: the reactivity and selectivity of a catalyst are commercially still optimized on a trial and error basis, applying the high throughput screening approach.

The reason for this discrepancy between ambition and reality lies in the inherent complexity of the catalytic system, consisting of the working catalyst and the interaction of the catalyst with the reactant mixture. Practical (solid) catalysts consist of metal or oxide nanoparticles which are dispersed and stabilized on a support and which may be promoted by means of additives. These particles catalyse a reaction in pressures as high as 100 bar. Practical catalysis is in general considered to be far too complex for gaining atomic-scale understanding of the mechanism of the catalysed reaction of an industrial catalyst during its operation. Therefore it has been necessary to introduce idealization and simplification of both the catalyst and the reaction conditions. For structural simplicity, single crystals of transition metals or oxides are typically used to mimic the catalyst's active surface. To avoid interfering 'dirt' effects, ultrapure reactants are introduced in ultrahigh vacuum (pressures better than  $10^{-8}$  mbar) chamber systems. In order to gain an atomic-scale understanding of the reaction process, electron-based spectroscopic techniques, such as photoemission spectroscopy, LEED, etc, are applied, which need high vacuum environments due to the limited mean free path of the electrons. Simple model reactions, such as the CO oxidation reaction, have been chosen for trying to understand the microscopic reaction mechanism under these conditions. In this way, important, fundamental information on adsorption sites, dissociation processes and reaction pathways has been obtained over the past 40 years [2].

Nevertheless, the large differences between these simple UHV model systems and more real-world non-single-crystal surfaces exposed to high pressures often prevent extrapolation of this atomic-scale knowledge to more realistic situations: a materials and pressure gap (cf figure 1) is introduced [3].



**Figure 1.** Model catalysis and practical catalysis are separated by two gaps, i.e. the pressure gap and the materials gap. The pressure gap is introduced by well-defined reaction and preparation conditions in model catalysis when ultrahigh vacuum (UHV) conditions are used, while typical pressures in practical catalysis are as high as several 100 bar. The materials gap is introduced by the low structural complexity of the model catalyst. Typically, practical catalysts in heterogeneous catalysis are supported oxides or nanoparticles.

It is evident that the pressure gap is established by the use of ultrahigh vacuum (UHV) conditions to maintain well-defined reaction conditions. It is also clear that the materials gap is caused by oversimplifying the model catalyst as having single-crystal surfaces, by neglecting defects, by the simultaneous presence of various orientations on the catalyst's particle, and by communication between the various facets and by having support-particle interaction.

However, there is a third and extremely important issue which is devoted to the interaction of the catalyst with the reactant gas phase at elevated pressure and elevated temperatures [4, 5]. Under such conditions, the catalyst can easily undergo a chemical transformation into a surface compound, and the shape of a catalytic nanoparticle may change substantially. For instance, under typical reaction conditions for the oxidation of CO and other molecules the transition metal (TM) catalyst may be oxidized, while under more reducing reaction conditions the TM oxide surface formed may decompose to form metallic TM particles. Therefore, the interaction of the reactant gas mixture and the catalyst surface may have a dramatic influence on the catalytic properties of catalysts under reaction conditions. Consequently the application of *in situ* techniques is mandatory to identify the catalytically active state of the catalyst. At the moment, the nature of the active catalyst cannot be theoretically predicted without experimental input, or easily envisaged through studies at low temperatures under UHV conditions.

In recent years, a substantial effort has been directed to overcoming these obstacles in model catalysis [6]. At present, the technical development is rapid, and it is expected that a number of groups and laboratories (in particular emerging synchrotron ones) will actively promote the building of *in situ* instruments based on existing design as well as the invention of novel experimental *in situ* techniques. This special issue presents a collection of studies illustrating these efforts. The ultimate goal of these efforts is to allow transfer of the knowledge gained by model catalysis to practical catalysis.

The first six studies in this issue [7–12] concentrate on the effect on single-crystal surfaces using realistic gas pressures. These studies show that although the pressure in itself has a significant influence on the surface, the temperature of the sample governs compound formation which completely transforms the properties of the surface. The examples presented here of changing catalyst surfaces are the formation of surface oxides under reaction conditions and the formation of subsurface species in oxidation and hydrogenation reactions.

The next two papers [13, 14] increase the complexity of the system studied by focusing on nanoparticles on model substrate oxides as these are exposed to high pressures and temperatures.

One section in this special issue is devoted to theory [15–17]. For theoretical studies to be ‘*in situ*’ or to be ‘under operando’ means that these calculations include practical issues such as the interaction of the reacting gas mixture with the catalyst’s surface over a wide pressure range, introducing quasi-thermal equilibrium between gas mixture and catalyst surface in terms of the chemical potential. This includes also the chemical stability of the catalyst particle under varying conditions of reaction, such as the chemical potential of oxygen. For instance, metal surfaces may oxidize under oxidizing reaction conditions, forming surface oxides.

An extremely important issue which so far has not been discussed to much extent in the surface chemistry/physics literature, at least not under realistic conditions, is related to the interaction of water with various kinds of surfaces, including metal, oxide and biomaterial surfaces, at higher water pressures. These interaction systems are important not only to biology and electrochemistry in general, but also for heterogeneous catalysis, where water is a well-known poison of catalytic reactions. Two such studies are presented here [18, 19].

In this special issue we have tried to illustrate the importance of approaching realistic conditions in catalysis related surface science research. Our aim is to provide a solid backbone for those scientists entering the emerging and dynamic field of surface chemistry and physics.

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## References

- [1] Ertl G, Knözinger H and Weitkamp J (ed) 1997 *Handbook of Heterogeneous Catalysis* (Weinheim: VCH)
- [2] Ertl G and Freund H-J 1999 *Phys. Today* **52** 32
- [3] Ertl G 1990 *Angew. Chem. Int. Edn Engl.* **29** 1219
- [4] Schlögl R and Abd Hamid S B 2004 *Angew. Chem. Int. Edn Engl.* **43** 1628
- [5] Somorjai G A 1996 *Chem. Rev.* **96** 1223
- [6] Stierle A and Moelenbrok A 2007 Novel *in situ* probes for nano catalysis *MRS Bull.* **32**
- [7] Ellinger C, Stierle A, Robinson I K, Nefedov A and Dosch H 2008 Atmospheric pressure oxidation of Pt(111) *J. Phys.: Condens. Matter* **20** 184013
- [8] Barbier A, Stierle A, Finocchi F and Jupille J 2008 Stability and stoichiometry of (polar) oxide surfaces for varying oxygen chemical potential *J. Phys.: Condens. Matter* **20** 184014
- [9] Weaver J F, Kan H H and Shumbera R B 2008 Growth and properties of high-concentration phases of atomic oxygen on platinum single-crystal surfaces *J. Phys.: Condens. Matter* **20** 184015
- [10] Vass E, Hävecker M, Zafeiratos S, Teschner D, Knop-Gericke A and Schlögl R 2008 The role of carbon species in heterogeneous catalytic processes: an *in situ* soft x-ray photoelectron spectroscopy study *J. Phys.: Condens. Matter* **20** 184016
- [11] Assman J, Narhkede V, Breuer N, Muhler M, Seitsonen A P, Knapp M, Crihan D, Farkas A, Mellau G and Over H 2008 Heterogeneous oxidation catalysis on ruthenium: bridging the pressure and materials gaps and beyond *J. Phys.: Condens. Matter* **20** 184017

- [12] Westerström R, Wang J G, Ackermann M D, Gustafson J, Resta A, Mikkelsen A, Andersen J N, Lundgren E, Balmes O, Torrelles X, Frenken J W M and Hammer B Structure and reactivity of a model catalyst alloy under realistic conditions 2008 *J. Phys.: Condens. Matter* **20** 184018
- [13] Rupprechter G and Weilach C 2008 Spectroscopic studies of surface–gas interactions and catalyst restructuring at ambient pressure: mind the gap! *J. Phys.: Condens. Matter* **20** 184019
- [14] Evans M and Tromp M 2008 Interaction of small gas phase molecules with alumina supported rhodium nanoparticles: an *in situ* spectroscopic study *J. Phys.: Condens. Matter* **20** 184020
- [15] Stampfl C, Soon A, Piccinin S, Shi H and Zhang H 2008 Bridging the temperature and pressure gaps: close-packed transition metal surfaces in an oxygen environment *J. Phys.: Condens. Matter* **20** 184021
- [16] Li W-X 2008 Oxidation of platinum surfaces and reaction with carbon monoxide *J. Phys.: Condens. Matter* **20** 184022
- [17] Seriani N and Mittendorfer F 2008 Platinum-group and noble metals under oxidizing conditions *J. Phys.: Condens. Matter* **20** 184023
- [18] Ketteler G, Ashby P, Mun B S, Ratera I, Bluhm H, Kasemo B and Salmeron M 2008 *In situ* photoelectron spectroscopy study of water absorption on model biomaterial surfaces *J. Phys.: Condens. Matter* **20** 184024
- [19] Yamamoto S, Bluhm H, Andersson K, Ketteler G, Ogasawara H, Salmeron M and Nilsson A 2008 *In situ* x-ray photoelectron spectroscopy studies of water on metals and oxides at ambient conditions *J. Phys.: Condens. Matter* **20** 184025