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Editors

Operando Research in Heterogeneous Catalysis

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Preface

In modern society, catalysis is a crucial technology. Approximately 90% of all chemicals and materials we use are produced via catalysis. Furthermore, catalysis impacts around one-quarter of the world's gross domestic product. A catalyst is a chemical substance that affects the rate and selectivity of a chemical reaction without being part of its end products. The primary objectives of catalysis are to enhance the reaction rate and to yield the desired products with high selectivity and stability. Well-known examples of catalytic processes are the conversion of crude oil into gasoline and the conversion of toxic automotive exhaust gases into less harmful ones.

Due to its importance to society, heterogeneous catalysis has been studied extensively over the last 100 years. Much of our current knowledge, however, has been obtained under conditions that deviate significantly from those of practical catalysis. In the traditional surface-science approach to study heterogeneous catalysis, fundamental knowledge about the behaviour of catalysts has been obtained under (ultra)high vacuum conditions and on planar model catalysts. Many useful insights have been acquired in this way, and the important research performed in this field has been acknowledged by the Nobel Prize in Chemistry for Prof. Gerhard Ertl in 2007. The reason for the discrepancy between conditions in surface science and in practical catalysis stems from the fact that most measurement techniques, suitable for obtaining accurate results at the nanoscale, cannot perform under the typical working conditions of industrial catalysis (i.e. high pressures and high temperatures). Surface-sensitive techniques are usually limited to pressures below 10^{-5} mbar. Although there are cases, where the results obtained at low pressures can be extrapolated to industrial conditions, more and more examples are encountered where this “pressure gap” is found to be accompanied by fundamental changes in the reaction mechanisms and the structures of the active phase of the catalyst. The pressure gap seems to be the rule, rather than the exception. Therefore, the investigation of catalysis under more realistic (industrial) conditions, without compromising the sensitivity to the details on the atomic and molecular scale, inescapably forms the next arena in this research field, where major breakthroughs will be forced, both scientifically and in the technological application.

To bridge the pressure gap, the last decades have seen a tremendous effort in designing new instruments and adapting existing ones to be able to investigate catalysts in situ under industrially relevant conditions (i.e. atmospheric pressures and elevated temperatures). One approach is to build a set-up in which ultrahigh vacuum chambers are combined with high-pressure chambers, using differential pumping. With this approach, X-ray photoelectron spectroscopy (XPS), low-energy ion scattering (LEIS), and transmission electron microscopy (TEM) can operate in the mbar regime. Another approach is the use of micro- or nanoreactors that separate the high-pressure volume from the (ultra)high vacuum part via ultrathin walls of an inert material. Examples are TEM and X-ray microscopy.

Some surface-science techniques are able to bridge the pressure gap without facing major limitations, e.g. scanning probe microscopy (SPM), sum frequency generation (SFG) laser spectroscopy, polarization modulation infrared reflection absorption spectroscopy (PM-IRAS), ultraviolet Raman spectroscopy, surface X-ray diffraction (SXRD), X-ray absorption spectroscopy (XAS), and ellipso-microscopy. When combined, these techniques have the possibility to determine the detailed influence of the gas environment on the structure of model catalyst surfaces, to identify active sites for catalytic processes, and to elucidate the role of promoters, all by probing surfaces with (near)-atomic sensitivity under the high-pressure, high-temperature conditions of industrial catalysis.

This book discusses the topic of *operando* research in heterogeneous catalysis. Here, the term *operando* refers to not only monitoring the catalytic surface under industrial reaction conditions, but in addition to simultaneously monitoring the reactants and products. Thereby, the relationship between the morphological and/or chemical composition of the active phase of the catalyst and its activity and selectivity can be investigated. This book covers a wide range of measurement techniques and theoretical tools that are now emerging and that are able to bridge the pressure gap. In addition to describing how they measure or compute relevant properties of catalytic reactions on solid surfaces under industrially relevant conditions of atmospheric pressures and elevated temperatures, it also presents several of the exciting new insights on heterogeneous catalysis that have been obtained recently this way.

The following topics will be discussed: the ReactorSTM and ReactorAFM (Chap. 1), Ambient-Pressure X-ray Photoelectron Spectroscopy (Chap. 2), Surface-Sensitive X-ray Diffraction Across the Pressure Gap (Chap. 3), X-ray Absorption and Emission Spectroscopy under Realistic Conditions (Chap. 4), *Operando* Transmission Electron Microscopy (Chap. 5), Planar Laser Induced Fluorescence Applied to Catalysis (Chap. 6), Ab Initio Thermodynamics and First-Principles Microkinetics for Surface Catalysis (Chap. 7), and Catalysis Engineering: From the Catalytic Material to the Catalytic Reactor (Chap. 8).

Most of all, this book illustrates that we are at the brink of a new and exciting era of surface science. Finally, after half a century of promise, the emerging new

experimental and theoretical tools are bringing this research field to a more complete level of understanding and to truly predictive power in the area of catalysis. This will prove necessary to progress towards one of the holy grails of catalysis research, namely to leave the traditional path of “educated trial and error” and to enable the direct development of “designer catalysts”.

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Contents

1	Live Observations of Catalysts Using High-Pressure Scanning Probe Microscopy	1
	Joost Frenken and Irene Groot	
1.1	Introduction	2
1.1.1	Why Working Conditions?	2
1.2	Scanning Tunneling Microscopy	3
1.3	High-Pressure SPM Instrumentation	6
1.3.1	Requirements for <i>Operando</i> SPM	7
1.3.2	Design of the ReactorSTM	8
1.3.3	Design of the ReactorAFM	12
1.3.4	Design of the Gas System	15
1.4	Catalytic Systems Investigated Under High-Pressure Conditions	16
1.4.1	CO Oxidation on Pt(110)	17
1.4.2	CO Oxidation on Pd(100)	18
1.4.3	NO Reduction on Pt(110)	20
1.4.4	Fischer-Tropsch Synthesis on Co(0001)	21
1.4.5	Hydrodesulfurization Reaction	24
1.4.6	Deacon Process for Chlorine Production	25
1.5	Conclusions and Outlook	27
	References	28
2	Ambient-Pressure X-ray Photoelectron Spectroscopy (APXPS)	31
	Osman Karshoğlu and Hendrik Bluhm	
2.1	Technique	31
2.1.1	Basics of XPS	31
2.1.2	Operating XPS at Elevated Pressure	33
2.1.3	Phenomena that Are Relevant to XPS Analysis of Catalysts Under Gas Ambient	41

2.2	Examples	49
2.2.1	CO Oxidation on Ru	49
2.2.2	CO Oxidation on Pd	50
2.2.3	Catalytic Oxidation of Small Organic Molecules	52
2.3	Summary	54
	References.	55
3	Surface-Sensitive X-ray Diffraction Across the Pressure Gap	59
	Andreas Stierle, Johan Gustafson and Edvin Lundgren	
3.1	Introduction	59
3.2	Surface-Sensitive X-ray Diffraction as in situ Tool.	60
3.2.1	Basics of Surface X-ray Diffraction.	61
3.2.2	X-ray Reflectivity and Grazing Incidence Diffraction	63
3.2.3	In situ and <i>Operando</i> Sample Environments.	64
3.3	In situ Near-Atmospheric-Pressure Oxidation of Transition Metal Surfaces and Nanoparticles.	66
3.3.1	Transition-Metal Low-Index Surfaces	67
3.3.2	Oxidation of Vicinal 4d Transition-Metal Surfaces.	70
3.3.3	Nanoparticle Oxidation Across the Pressure Gap: Pd, Rh and Pt Nanoparticles on MgO(100) and MgAl ₂ O ₄ (100)	71
3.4	In situ Catalytic Studies Using Batch Reactors.	73
3.4.1	CO Oxidation Over Pt	73
3.4.2	Ru.	74
3.4.3	CO Oxidation Over Rh.	76
3.4.4	Batch Reactor Studies of Nanoparticle Model Systems.	78
3.5	<i>Operando</i> Studies Under Flow Conditions.	78
3.5.1	CO Oxidation Over Pd(100).	78
3.5.2	CO Oxidation Over Rh(111).	80
3.5.3	CO Oxidation Over Stepped Surfaces.	80
3.5.4	Methane Oxidation Over Pd(100).	82
3.5.5	The Use of Large 2D Detectors in Combination with High X-ray Photon Energies.	82
	References.	84
4	From Spectator Species to Active Site Using X-ray Absorption and Emission Spectroscopy Under Realistic Conditions.	89
	Maarten Nachtegaal, Urs Hartfelder and Jeroen A. van Bokhoven	
4.1	Introduction	89
4.2	Transient X-ray Absorption Spectroscopy.	92
4.3	X-ray Emission Spectroscopy.	94
4.4	Examples	99
4.4.1	Carbon Monoxide Oxidation: Time-Resolved X-ray Absorption	99

4.4.2	Adsorption of Carbon Monoxide: High Energy Resolution XAS Spectra	101
4.4.3	Adsorption of Carbon Monoxide: Valence-to-Core RIXS	102
4.4.4	Time-Resolved X-ray Emission: Catalytically Active and Spectator Species	103
4.5	Conclusions	107
	References.	108
5	Development of <i>Operando</i> Transmission Electron Microscopy.	111
	Patricia Jane Kooyman	
5.1	Introduction	111
5.2	Aperture-Based Systems	112
5.3	Windowed Cell Systems	116
5.4	Towards <i>Operando</i> Catalysis	123
5.5	Conclusion and Outlook	128
	References.	128
6	Planar Laser Induced Fluorescence Applied to Catalysis.	131
	Johan Zetterberg, Sara Blomberg, Jianfeng Zhou, Johan Gustafson and Edvin Lundgren	
6.1	Introduction	132
6.2	Experimental.	133
6.2.1	Laser Set-Up and Laser Sheet	133
6.2.2	Reactor, Gas System, and Samples	133
6.2.3	LIF-General Considerations.	134
6.3	CO ₂ Imaging	136
6.3.1	One Sample: CO ₂ Imaging Above a Pd(100) Single Crystal.	137
6.3.2	Two Samples	139
6.3.3	Three Tubes	141
6.4	CO Imaging	142
6.4.1	CO Imaging Above a Pd(110) Single Crystal	143
6.5	NH ₃ Imaging	145
6.5.1	NH ₃ Oxidation Above a Ag/Al ₂ O ₃ Powder Catalyst.	145
6.6	Summary	147
	References.	148
7	Ab Initio Thermodynamics and First-Principles Microkinetics for Surface Catalysis.	151
	Karsten Reuter	
7.1	Introduction	151
7.2	(Constrained) Ab Initio Thermodynamics.	154
7.2.1	Methodology.	154
7.2.2	Oxide Formation at (Near-)Ambient Conditions	158

7.2.3	Constrained Thermodynamics: Approximate Structure and Composition Under Reaction Conditions	161
7.3	First-Principles Microkinetics	165
7.3.1	Methodology	165
7.3.2	The First-Principles Input	169
7.3.3	Surface Morphological Transitions in Near-Ambient Catalysis	172
7.3.4	Catalytic Activity from First Principles	177
7.3.5	Mass Transfer Limitations Under Near-Ambient Conditions	180
7.4	Conclusions and Outlook	183
	References	184
8	Catalysis Engineering: From the Catalytic Material to the Catalytic Reactor	189
	Stefano Rebughini, Mauro Bracconi, Alberto Cuoci and Matteo Maestri	
8.1	Introduction	190
8.2	Intrinsic Versus Observed Reaction Rate	192
8.2.1	Residence Time Distribution (RTD)	192
8.2.2	Interaction Between Chemical Rates and Transport Rates	195
8.2.3	External Transport Effects	196
8.2.4	Internal Transport Effects	198
8.2.5	Temperature Dependence of the Observed Reaction Rate	202
8.3	Computational Fluid Dynamics of Gas-Solid Catalytic Reactors	203
8.3.1	Multiscale Modeling	203
8.3.2	Governing Equations	204
8.3.3	Coupling CFD and Mean-Field Microkinetic Modeling	207
8.3.4	Coupling CFD and Kinetic Monte Carlo Simulations	208
8.4	Case Study: Detailed Analysis of a Spectroscopic Cell Reactor	210
8.4.1	Reactor Geometry and Operating Conditions	210
8.4.2	Reactor Analysis: Residence Time Distribution	211
8.4.3	Reactor Analysis: Species Concentration and Temperature Fields	213
8.5	Summary and Outlook	215
	References	217
	Index	219

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