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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