



**FRITZ-HABER-INSTITUT**  
MAX-PLANCK-GESELLSCHAFT

## *Prof. Dr. Robert Schlögl*

Director



Our group is active at two locations namely in Berlin at the FHI and in Mülheim/Ruhr at the MPI CEC (Chemical Energy Conversion). This originates from the dual function of the director as member of the collegium at the FHI in Berlin and as founding director at the MPI CEC

### **Short Biography**

Robert Schlögl studied chemistry and completed his PhD on graphite intercalation compounds at the Ludwig Maximilians University in Munich (1982). After postdoctoral stays at Cambridge and Basle he carried out his habilitation under the supervision of Professor Ertl (Nobel Laureate) at Fritz Haber Institute in Berlin (1989). Later he accepted the call for a Full Professorship of Inorganic Chemistry at Frankfurt University. In 1994 he was appointed his current position as Director at the Fritz Haber Institute of the Max Planck Society in Berlin. In addition, in 2011 he was appointed Founding Director at the new Max Planck Institute for Chemical Energy Conversion in Mülheim a.d. Ruhr. He is an Honorary Professor at Technical University Berlin, Humboldt University Berlin, University Duisburg-Essen and Ruhr University Bochum. Robert Schlögl's research focuses primarily on the investigation of heterogeneous catalysts, with the aim to combine scientific with technical applicability as well as on the development of nanochemically-optimized materials for energy storage. The application of knowledge-based heterogeneous catalysis for large-scale chemical energy conversion summarizes his current research focus.

He is author of more than 1,000 publications, gave more than 450 invited talks and lectures and is registered inventor of more than 20 patent families. He is a Fellow of the Royal Society of Chemistry, Tetelman Fellow and member of numerous international organizations. His research activities have been recognized with several national and international awards.

[Curriculum vitae](#)

[Achievements in Research](#)

[Talks and Lectures](#)

Selected Talks:

- [Die Energiewende - Wunsch und Wirklichkeit \(PDF – 13 MB\)](#)
- [Chancen und Herausforderungen regenerativer Energie \(PPT – 33 MB\)](#)
- [CO<sub>2</sub> als Rohstoff \(PDF – 40 MB\)](#)

[List of Patents](#)

Contacts ▾



Prof. Dr. Robert Schlögl



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## Curriculum Vitae Prof. Dr. Robert Schlögl



Name: Robert Schlögl

Born: [REDACTED]

**Research Priorities: heterogeneous catalysis, nanochemically optimized materials for energy storage concepts, chemical energy conversion, energy conversion processes in nature**

Robert Schlögl is a chemist and catalysis researcher. His research focuses on heterogeneous catalysis and materials for energy storage concepts. With his work, he has contributed to a new understanding of catalytically active materials. More recently, he has been working on energy systems of the future and the complex challenges of the energy revolution.

### Academic and Professional Career

- since 2015 Honorary Professor at the Ruhr University Bochum, Germany
- since 2013 Honorary Professor at the University of Duisburg-Essen, Germany
- since 2011 Founding Director and Managing Director at the Max Planck Institute for Chemical Energy Conversion (MPI CEC), Mülheim an der Ruhr, Germany
- 2005 Fellow of the Royal Society of Chemistry, Cambridge, UK
- 2004 Tetelman Fellow, Yale University, USA
- 2001 Visiting Professorship at the Laboratoire des Matériaux, Surfaces et Procédés pour la Catalyse (L.M.S.P.C.), Université Louis Pasteur, Strasbourg, France
- since 1998 Honorary Professor at the Humboldt University Berlin, Germany
- since 1994 Honorary Professor at the Technical University Berlin, Germany
- since 1994 Director at the Fritz Haber Institute of the Max Planck Society, Berlin, Germany
- 1989 - 1994 C4 Professorship for inorganic chemistry at the University of Frankfurt/Main, Germany

1989	Habilitation at the Fritz Haber Institute of the Max Planck Society, Berlin, Germany
1984 - 1985	Postdoc at the Institute of Physics, Basel, Switzerland
1982 - 1983	Postdoc at the Institute of Physical Chemistry, Cambridge University, UK
1982	Doctorate at the Ludwig-Maximilians-University Munich, Germany
1979	Diploma in chemistry
1973 - 1978	Study of chemistry at the Ludwig-Maximilians-University Munich, Germany

### **Functions in Scientific Societies and Committees**

since 2020	Vice President of the German National Academy of Sciences Leopoldina
since 2020	Vice Chairman of the National Hydrogen Council, Germany
since 2018	Member of the Board of Trustees of the academy project "Energy Systems of the Future" (ESYS), supported by acatech – National Academy of Science and Engineering, the German National Academy of Sciences Leopoldina and the Union of the German Academies of Sciences and Humanities
since 2017	Co-Chair of the Carbon capture and utilisation (CCU) Working Group, Science Advice for Policy by European Academies (SAPEA)
2017	Member of the Supervisory Board of the Helmholtz-Zentrum Berlin für Materialien und Energie, Germany
since 2016	Chairman of the Advisory Board "Kopernikusprojekte" of the Federal Ministry of Education and Research Germany (BMBF)
since 2015	Member of the BMBF Hightech-Forum, Germany
2013 - 2017	Chairman of the Steering Committee of the academy project "Energy Systems of the Future" (ESYS), supported by acatech – National Academy of Science and Engineering, the German National Academy of Sciences Leopoldina and the Union of the German Academies of Sciences and Humanities
2012 - 2017	Head of Steering Committee of "Energy Systems for the Future", the academic advisory board to the German government
since 2010	Chair of the MPG Presidential Commission on Future Directions of Science, Germany
since 2010	Topical Network Leadership "Energy and Resources", acatech – National Academy of Science and Engineering, Germany
2010 - 2014	Member of the Scientific Advisory Board Leibnitz Institute for Catalysis, Rostock, Germany
since 2009	Member of the Editorial Board ChemCatChem

- since 2009 Member of the Advisory Board ChemSusChem
- 2008 - 2012 Member of the Advisory Board "Archiv zur Geschichte der Max-Planck-Gesellschaft", Germany
- 2007 - 2010 Chairman of Panel 4 "Chemistry and Materials Sciences" of the European Research Council (ERC)
- 2004 - 2006 Chairman of the Chemical Physical Technical (CPT) Section of the Max Planck Society, Germany
- 2003 - 2009 Member of the Editorial Board Catalysis Letters
- 2003 - 2009 Member of the Editorial Board Journal of Catalysis
- 1999 - 2005 Head of the Scientific Information Committee of the Max Planck Society, Germany
- 1999 - 2004 Chairman of the Awards Committee of the Berlin-Brandenburg Academy of Sciences and Humanities, Germany
- 1999 - 2003 Member of the Editorial Board of Physical Chemistry – Chemical Physics (PCCP)
- 1998 - 2002 Member of the Editorial Board of Applied Catalysis A
- 1996 - 2003 President of the German Catalysis Society (GECATS)
- 1996 - 2002 Head of the Catalysis Section of the Society for Chemical Engineering and Biotechnology (DECHEMA)
- 1995 - 2001 Member of the Advisory Board, Hahn Meitner Institute (HMI), Berlin, Germany
- Member of the Advisory Board of the German Catalysis Society (GEATS)
- Member of the Advisory Board of the European Federation of Catalysis Societies (EFCATS)
- Member of the Scientific Advisory Board of the Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung m.b.H. (BESSY)
- Member of the Advisory Board of the International Association of Catalysis Societies (IACS)

#### **Project Coordination, Membership in Collaborative Projects**

- since 2019 Participant in the DFG Cluster of Excellence EXC 2008: Unifying Systems in Catalysis „UniSysCat“
- since 2019 Participant in the DFG Cluster of Excellence EXC 2089: e-conversion
- since 2019 Participant in the DFG Cluster of Excellence EXC 2186: The Fuel Science Center – Adaptive Conversion Systems for Renewable Energy and Carbon Sources
- since 2018 DFG project "Transient High-Temperature Oxygen Evolution Reaction", Subproject of SPP 2080: "Catalysts and reactors under dynamic conditions for energy storage and conversion"

- since 2018 DFG project "Advanced TEM and in situ X-Ray Spectroscopy (B07)", Subproject of TRR 247: "Heterogeneous Oxidation Catalysis in the Liquid Phase – Mechanisms and Materials in Thermal, Electro-, and Photocatalysis"
- 2007 - 2018 Participant in the Cluster of Excellence EXC 314: „Unifying Concepts in Catalysis“
- 2007 - 2010 DFG project "Raman-Spektroskopie als diagnostisches Tool zur Bestimmung der Struktur-Reaktivitäts-Korrelation von Ruß unterschiedlicher Mikrostruktur"
- 2003 - 2008 DFG project "Mikroskopische Strukturbildung von Katalysatoroberflächen unter Realbedingungen", Subproject of SPP 1091: "Bridging the Gap between Ideal and Real Systems in Heterogeneous Catalysis"
- 2002 - 2008 DFG project "New tailored carbon nanofilaments for catalytic applications"
- 2001 - 2010 DFG Project "Oxidnitride des Zirconiums als Materialien und Modellverbindungen für die katalytische Aktivierung von Ammoniak"
- 2001 - 2006 DFG project "Nitridoxide und Nitridverbindungen als Materialien und Modellverbindungen für die katalytische Aktivierung von Stickstoff"
- 2000 - 2008 DFG project "Charakterisierung und Modifikation der aktiven Zentren für die heterogen katalysierte Partialoxidation von Methanol über Kupfer", Subproject of SPP 1091: "Bridging the Gap between Ideal and Real Systems in Heterogeneous Catalysis"
- 2000 - 2005 DFG project "Von Einkristallsystemen zu realen Katalysatoren am Beispiel der Hydrierung an Silber-Katalysatoren", Subproject of SPP 1091: "Bridging the Gap between Ideal and Real Systems in Heterogeneous Catalysis"
- 1999 - 2011 DFG project "Partialoxidation kleiner Kohlenwasserstoffmoleküle mit mikroskopischen Mengen von  $VxOy$  Katalysatorsystemen", Subprojects of SFB 546: "Structure, Dynamics and Reactivity of Aggregates of Transition Metal Oxides"

Involved in several EU projects, including CANAPE, ELCAT, TECHNOTUBES, GRAFOL

Cooperation with Boreskov Institute of Catalysis, Novosibirsk, Russia; EPFL, Schwitzerland; Cardiff University, U.K.; University of Messina, Catania, Italy; MIT, Boston, USA; University of Virginia, Charlottesville, USA; University of California, Berkeley, USA and others.

Participant of the European Network IDECAT "Catalysis for Sustainable Energy Production

Max Planck project ENERCHEM "Energy from renewable resources – an interdisciplinary approach by Chemists and Material Scientists to tackle questions of social relevance"

Co-initiator of the DFG priority program for catalysis research

Co-initiator of the DFG Excellence Cluster Catalysis Research

## Honours and Awarded Memberships

2020	Honorary Doctorate, University Darmstadt, Germany
2019	Ipatieff Lecture, Center for Catalysis and Surface Science (CCSS), USA
2019	Cultural Award, Eduard Rhein Foundation
since 2018	Honorary Professor, Boreskov Institute of Catalysis, Russia
since 2017	Distinguished Affiliated Professor, Technical University of Munich, Germany
2017	Ruhr Prize for Art and Science of the City of Mülheim a. d. Ruhr, Germany
2017	ENI Award Energy Transition
2016	Innovation Award, State of North Rhine-Westphalia, Germany
2015	Alwin Mittasch Prize, German Catalysis Society (GEATS)
2013	Max Planck Communitas Award
since 2011	Member of the German National Academy of Sciences Leopoldina
2010	DECHEMA Plaque in Titanium
since 2005	Fellow of the Royal Society of Chemistry, UK
since 1995	Member of the Berlin-Brandenburg Academy of Sciences and Humanities, Germany
1994	Otto Bayer Award, Bayer Science & Education Foundation
1989	Schunck Award for Innovative Materials

Member of acatech – National Academy of Science and Engineering, Germany

## Research Priorities

Robert Schlögl is a chemist and catalysis researcher. His research focuses on heterogeneous catalysis and materials for energy storage concepts. With his work, he has contributed to a new understanding of catalytically active materials. More recently, he has been working on energy systems of the future and the complex challenges of the energy revolution.

Robert Schlögl and his team are researching energy conversion processes in nature and the significance of catalysts within these processes. This concerns questions of the production, storage, and transport of energy. In nature, energy is stored through photosynthesis. During this process, carbon dioxide and water are converted into organic molecules such as sugar and oxygen. However, photosynthesis cannot be replicated using synthetic chemistry; the molecules involved are too sensitive.

Therefore, the scientists, led by Robert Schlögl, seek to understand the basic chemical reactions of these processes in order to use them for new energy systems. In individual

research projects, they are working, for example, on the conversion of light into electrical energy, storage materials for hydrogen, the catalytic splitting of water, and further development of fuel cells.

Catalysts play a significant role in all these processes. Without catalysts, for example, the storage of solar energy is not possible. His research aims to develop new, powerful catalysts while emphasizing the sustainability of the processes. Substances used as catalysts must be available and accessible on earth in sufficient quantities. He has also developed a process that could significantly reduce the chemical industry's energy consumption by using carbon nanomaterials. The chemical base material styrene can thus be produced in a more energy-efficient way than before.

In his research, Schlögl works on an interdisciplinary basis and combines scientific model studies with the high-performance systems of technical catalysis. He has developed new methods for observing dynamic phenomena at interfaces. This enables catalysts to be developed more effectively for industry.



# A Career in Catalysis: Robert Schlögl

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**ABSTRACT:** “Why?” is the question that initiates science. “Why?” is also the answer that maintains science. This interrogative adverb fuels the scientific career of Robert Schlögl. Robert is a dedicated solid-state chemist who has found his specialization in untangling the working principles of heterogeneous catalysts under realistic conditions. As such he combines the full complexity of real catalysts with tailor-made *operando* experiments to overcome pressure, material, and complexity gaps. His ability to quickly abstract the meaning of spectroscopic and microscopic data, his talent to ask the right question paired with curiosity, diligence, and creativity have made him a world-leading expert in heterogeneous catalysis and energy science. His scientific passion is focused on untangling chemical dynamics as well as working principles and understanding the important interplay of geometric and electronic structures in functional materials. Thereby his research interests involve ammonia and methanol synthesis, carbon materials in catalysis, hydrogenation, and dehydrogenation, selective oxidation, and the development of *operando* setups for microscopy and spectroscopy. He also has a strong commitment to society in scientifically accelerating the energy transition (“Energiewende”) in Europe, where he focuses on CO<sub>2</sub> utilization and hydrogen as an energy carrier. This is manifested in three recent large Germany-wide projects: *Carbon2Chem*, *CatLab*, and *TransHyDe*.

**KEYWORDS:** ammonia synthesis, carbon, selective oxidation, methanol synthesis, *operando* methods, energy transition

## Central elements in Robert Schlögl's scientific work

23 V 50.9415	42 Mo 95.94	6 C 12.011	46 Pd 106.42
29 Cu 63.546	47 Ag 107.8682		77 Ir 192.217

## 1. INTRODUCTION

The work of Robert Schlögl (Figure 1) aims to bridge the complexity gap in heterogeneous catalysis and untangle relevant processes that are involved in this technology. As such he deals with model systems, but with the intricacy required to guarantee the functionality of real catalysts.<sup>1</sup> The



Figure 1. Snapshot of a dynamic process—Robert Schlögl in motion.

focus of his interest is on reactions that are important for large-scale energy conversion and storage as well as the development of *in situ* and *operando* techniques.

Robert was born [REDACTED]. He studied chemistry at the Ludwig-Maximilians-Universität (LMU) in Munich, where he also received his doctorate in 1982. Stays abroad in Cambridge with Sir John Thomas and in Basel with Hans-Joachim Güntherodt led him to the border areas between chemistry and solid-state physics. Robert started his career in industry at Hoffmann-La Roche AG in Basel, where he studied the reproducible technical synthesis and function of the Lindlar catalyst for the selective hydrogenation of carbon triple bonds.<sup>2</sup> He then went to Berlin, where he completed his habilitation in the department of Gerhard Ertl at the Fritz-Haber-Institut (FHI) der Max-Planck-Gesellschaft (MPG) in 1989. He subsequently moved to the University of Frankfurt as Professor

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of Inorganic Chemistry. In 1994, Robert returned to the Fritz-Haber-Institut as the Director of the Department of Inorganic Chemistry. In addition, in 2011 he became Founding Director at the Max Planck Institute for Chemical Energy Conversion (CEC) in Mülheim a.d. Ruhr.

Robert is an enthusiastic and determined scientist with an incredible wealth of knowledge who tirelessly pursues new ideas and encourages his collaborators and colleagues to break new ground. He ensures a creative working atmosphere in the Inorganic Chemistry department, which is characterized by an open exchange of results, ideas, and concepts. The numerous project days in the form of workshops, which are often themed around an element (see graphic in the table of contents (TOC)), also contribute to lively discussions and good cooperation within the department and with cooperation partners. He aspires to contribute with his science to viable solutions for burning questions of our time. In the following sections, we provide an overview of his scientific work and social commitment without intending to be comprehensive.

## 2. AMMONIA SYNTHESIS

While Robert was working for his thesis on carbon intercalation compounds in the Institute of Inorganic Chemistry at the LMU in Munich, a group in the neighboring Institute of Physical Chemistry was investigating the interaction of nitrogen, hydrogen, and ammonia with clean single-crystal surfaces of iron, from which a model on the mechanism and kinetics of catalytic ammonia synthesis under surface science conditions was derived. With reduced conditions of real catalysis, a study on the surface properties of an industrial iron catalyst was performed, in which Robert became interested with his expertise in electron microscopy.<sup>3</sup>

**2.1. Iron Catalysts.** Here, the surface composition and topography of a BASF S6-10 catalyst were investigated by means of scanning Auger electron spectroscopy, scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS). After reduction, a network of particles with diameters between 10 and 50 nm was observed. An increase in the specific surface area was attributed to the "structural" promoter  $\text{Al}_2\text{O}_3$ . Fe, reduced to the metallic state, was uniformly covered by a K + O adlayer, which acted as an "electronic" promoter. These results were in full qualitative agreement with previous reports based on more indirect methods and served as justification for the conclusions on the mechanism of ammonia synthesis derived from the single-crystal studies.

This picture was confirmed and further refined by numerous studies during the subsequent years. These included X-ray diffraction (XRD), electron microscopy (EM), extended X-ray absorption fine structure (EXAFS), neutron diffraction, and others even at elevated pressures.<sup>4–8</sup>

**2.2. Ruthenium Catalysts.** Apart from the classical promoted iron catalyst, more recently, alternatively, Ru-based catalysts came into industrial use. The idea was to prepare systems in which Ru was exchanged into zeolites in order to obtain high dispersion. In this way a light purple solid was formed that was active in ammonia synthesis at atmospheric pressure. At 810 K the conversion was, however, much lower than that with the conventional iron catalyst, and slow deactivation took place due to agglomeration of the Ru particles. The latter are prevented from further sintering under the reducing conditions of catalysis by the framework of the zeolite.<sup>9</sup>

Controlled thermal activation under hydrogen converted the precursor into an active catalyst, which was stable against oxygen poisoning. Several nanometer-sized Ru particles were chemically bonded to the zeolite, which provides in the K-form an alkali promoter at the metal–zeolite interface.<sup>10</sup>

After further studies, also with single crystals, the present status and prospects for future development of this class of catalysts was outlined by Robert in an article entitled "Catalytic synthesis of ammonia—a 'never-ending' story?"<sup>11</sup>

**2.3. From Textbook Knowledge to a Future Energy Vector.** Today, the iron and ruthenium catalysts for ammonia synthesis have found entry in every catalysis textbook, while Robert's research interest in this reaction after the aforementioned article has focused toward the application of ammonia as a carbon-free hydrogen storage molecule in the context of chemical energy conversion.<sup>12,13</sup> He has worked on *operando* studies<sup>4</sup> and new synthesis methods for the iron catalyst.<sup>14</sup> Magnesioferrite ( $\text{MgFe}_2\text{O}_4$ )-derived mesoporous spinels of the general formula  $\text{MgFeM}^{3+}\text{O}_4$  with  $\text{M} = \text{Fe, Al, Ga}$  synthesized via a layered double-hydroxide (LDH) route surprisingly already show 27% of the catalytic activity of a fully optimized and multiply promoted industrial ammonia synthesis catalyst.<sup>14</sup> Thus, this is a promising candidate for a comparatively easy to prepare ammonia synthesis catalyst for which the influence of promoters and additives can be further studied. This work will be continued in the two large-scale research consortia *Carbon2Chem*<sup>15</sup> and *TransHyDe*. Robert is participating in the board of coordinators of the carbon capture and utilization (CCU) project *Carbon2Chem*, which started in 2016 and aims at converting steel mill offgases catalytically into valuable products.<sup>15</sup> He is also involved in coordinating the *TransHyDe* technology platform, in which implementation scenarios for hydrogen and various of its derivatives as future energy carriers are being researched, planned, designed, and demonstrated.

## 3. CARBON

Robert is known to everyone working in the field of carbon materials applied in catalysis as the author of the famous chapter *Carbons* in the *Handbook of Heterogenous Catalysis*, which comprises 70 pages and 534 references.<sup>16</sup> This comprehensive chapter provides both insight into the fundamentals of carbon and in-depth knowledge about the different carbon materials and their properties, also summarizing many of his groundbreaking achievements.

**3.1. Nanostructured Carbon Materials.** Carbon materials have always been a major topic in Robert's research. Actually, he already encountered them in his Ph.D. studies on graphite intercalation compounds supervised by Hanns-Peter Boehm at the LMU in Munich. In 2005, he investigated the reactivity of different carbon materials such as spark discharge soot, diesel engine soot under black smoking conditions, and carbon blacks toward oxidation.<sup>17</sup> This work revealed that the morphology of the different nanostructured carbon materials has a tremendous influence on the oxidation kinetics and that defective carbon structures are more easily oxidized.<sup>17</sup> When carbon nanotubes (CNTs) were identified as a promising carbon material for multiple applications, the characterization of commercially available nanostructured carbon materials became a major topic for Robert in 2009. His investigation of materials marketed as multiwalled CNTs proved that they differ in some cases fundamentally from the expected form of coaxially stacked single-wall CNTs.<sup>18</sup> Furthermore, his work

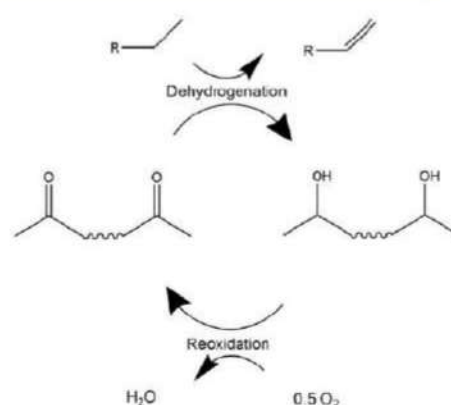
on CNTs covered the investigation of catalyst–support and catalyst–carbon interactions during the growth of single-walled CNTs by chemical vapor deposition over SiO<sub>2</sub>-supported metal-based catalysts. He showed in 2009 that crystalline metal nanoparticles are the active species in case of Ni and Fe, whereas Pd forms silicides under the reaction conditions. Additionally, his investigation demonstrated the high relevance of the support. For the Pd silicides and Au nanocrystals, the precursor decomposition was less efficient than for Ni and Fe, and the low adhesion of carbon on Au surfaces hindered nanotube nucleation.<sup>19</sup> The application of carbon-based materials as catalyst supports requires specific anchoring sites. Accordingly, the functionalization of carbon materials became another important topic for Robert. By treating oxidized carbon nanofibers with ammonia, he demonstrated that it is possible to tailor the properties of nitrogen-functionalized carbon materials to specific needs both in catalysis and in electronic devices.<sup>20</sup>

**3.2. Dehydrogenation and Oxidative Dehydrogenation.** In addition to carbon as a catalyst support, Robert and his co-workers investigated the application of carbon as a metal-free catalyst. They showed in 2001 that carbon nanofilaments and onionlike carbons have the potential to replace the potassium-promoted iron oxide catalyst applied in the dehydrogenation of ethylbenzene to styrene.<sup>21,22</sup>

Due to the high relevance of this reaction, they also investigated it over unpromoted iron oxide catalysts and provided an in-depth understanding of the underlying reactions.<sup>23</sup> This work was built on quite a number of fundamental studies on model systems, including single-crystalline iron oxide model catalyst films grown epitaxially onto Pt(111) substrates.<sup>24,25</sup> For the first time, the termination of a metal oxide was studied in detail. Two different surface terminations coexisting on single-crystalline  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>(0001) films, which were pretreated in high oxygen pressures, were observed by scanning tunneling microscopy (STM) and interpreted in collaboration with theory.<sup>26</sup> The concepts of these single-crystal studies were continued and enlarged<sup>27</sup> in the work of Hajo Freund at the FHI.<sup>28</sup>

Following previous work, the potential of oxidation-resistant ultradispersed diamond and onionlike carbon as a catalyst for the oxidative dehydrogenation (ODH) of alkanes was demonstrated in 2007.<sup>29,30</sup> It was found that sp<sup>2</sup>-hybridized carbon forms on the surface of the sp<sup>3</sup>-hybridized diamond during the pretreatment.<sup>29,30</sup> Again, a substantial improvement over the classical promoted iron oxide catalyst was achieved by carbocatalysis, as coke gasification with steam was no longer required to maintain high conversion over the ketonic C=O groups (Figure 2). In general, Robert's outstanding work on dehydrogenation reactions catalyzed by carbon materials significantly improved the understanding of the underlying reaction mechanisms<sup>31</sup> and the influence of heteroatoms on the selectivity of the ODH.<sup>32</sup> For example, phosphorus was found to significantly improve the ODH reaction of *n*-butane over CNTs.<sup>33</sup> Also, the influence of the purification of CNTs on the ODH reaction<sup>34</sup> and the potential of mesoporous carbon materials as ODH catalysts were demonstrated in detail.<sup>35</sup>

Additionally, Robert worked on carbon nitrides as potential catalysts in 2008, investigating a polymerization-like synthesis route and characterizing the obtained materials.<sup>37</sup> Again, metal-free catalysis using carbon and carbon nitrides as sustainable alternatives to conventional metal catalysts was



**Figure 2.** Oxidative dehydrogenation of alkanes over oxygen-functionalized metal-free carbon catalysts. Reproduced with permission from ref 36. Copyright 2010, John Wiley and Sons.

achieved.<sup>36</sup> He also studied the insertion of oxygen by sp<sup>2</sup>-hybridized carbon into acrolein<sup>38</sup> and the dehydrogenation of *n*-butane, emphasizing the role of the transformation from sp<sup>3</sup>- to sp<sup>2</sup>-hybridized carbon.<sup>39</sup> The most recent publication on this topic is a comprehensive review coauthored by the late Dang Sheng Su focusing on the potential of metal-free carbocatalysts in the field of liquid-phase reactions as well as its limitations, which appeared in 2016.<sup>40</sup>

**3.3. Metal Nanoparticles Supported on Carbon Materials.** In addition to the extensive work on metal-free catalysis, Robert and his co-workers also investigated the application of carbon materials as supports. For example, they demonstrated the significant influence of subsurface carbon on selectivity in the selective hydrogenation of alkynes to alkenes over a carbon-supported Pd catalyst.<sup>41</sup> Robert's in-depth knowledge about this reaction led to a minireview about the improvement of the selective hydrogenation of alkynes over Pd supported on different supports with respect to the ongoing subsurface chemistry.<sup>42</sup> He also worked on metal-based catalysts supported on carbon materials for the decomposition of ammonia into hydrogen and nitrogen.<sup>33,43</sup> The characterization results combined with the observed catalytic performance of Fe–Co alloy nanoparticles supported on CNTs showed that Fe in the alloy stabilized Co, in this way improving the durability of the catalysts via synergetic effects.<sup>33</sup> They also performed studies on CNT-supported Ru for the same reaction with the remarkable result that for Ru/CNT smaller particles do not lead to higher conversion.<sup>43</sup> Also, the investigation of the interaction of Pd with the pyridinic and graphitic nitrogen species in N-doped CNTs was a major contribution to obtain a deeper understanding of the metal–carbon support interaction in hydrogenation, CO oxidation, and the oxygen reduction reaction (ORR).<sup>44</sup> In the most recent publication in 2017 focusing on Pd on carbon as a selective hydrogenation catalyst, the capability of thermal treatments to tune the interfacial charge distribution between the metal and support was demonstrated, revealing that these electronic effects are strong enough to affect the performance of Pd nanoparticles as large as 5 nm.<sup>45</sup>

**3.4. Chemical Energy Conversion and Storage.** Finally, the growing importance of energy conversion and storage became an important topic for Robert. For example, the work on aminated graphene honeycombs as electrochemical storage

devices led to a novel electrode material for electrochemical applications.<sup>46</sup> Again, his work in this field also covers the application of high-surface carbon materials as a catalyst support, in this case for the oxygen evolution reaction (OER) over Ir.<sup>47</sup> His work on the IrO<sub>2</sub>-catalyzed OER resulted in a recent publication in *Nature*, improving the understanding of the reaction and linking thermal catalysis to electrocatalysis by taking charge accumulation in the catalyst into account (*vide infra*).<sup>48</sup> One of his most well known publications is a review on the role of chemistry to overcome the global energy challenge, presenting catalysis over carbon and carbon nitrides as a promising pathway for the production of chemicals with a focus on the ODH of unsaturated hydrocarbons and alkane activation, the ORR, and the photocatalytic production of hydrogen.<sup>49</sup>

#### 4. OXIDATION

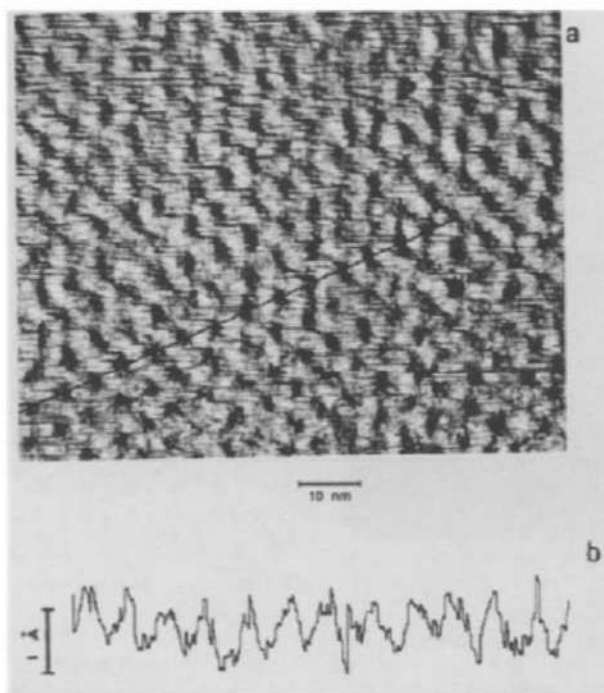
Robert was and is continuously interested in oxidation catalysis incited by the complexity of these reactions and the corresponding catalysts.<sup>1,50–52</sup> In the last 30 years, this work has included both metals, such as in particular Cu and Ag, and metal oxide systems, such as multimetal mixed or doped oxides and phosphates. From the reaction side, he has worked on the oxidation of carbon monoxide, oxygenates, and hydrocarbons, including the oxidative coupling of methane.<sup>51,53,54</sup> The longstanding, fruitful cooperation with BASF and the joint laboratory of BASF and the Technical University of Berlin (BasCat) in the field of selective oxidation has contributed to the fact that fundamental questions of the activation of C–H bonds and the oxygen molecule could be determined on high-performance catalysts emulating industrial systems.

A particular challenge in oxidation catalysis is the complex reaction network spanned by organic substrate molecules. These molecules can undergo a variety of parallel and consecutive reactions. The desired and undesired elementary steps include C–H activation, oxygen insertion in C–H and C–C bonds, and C–C cleavage. At the same time, these reactions are coupled with the network of molecular oxygen activation, which significantly influences the selectivity. In his research, Robert pursues the goal of achieving a fundamental understanding of the function of oxidation catalysts on the basis of physical principles while oversimplifications in terms of the models and mechanistic considerations are avoided. In this way, he intends to advance the development of selective oxidation catalysts on a rational basis. In particular, he considers the involvement of the kinetics of active site formation in the overall reaction kinetics to be important. This requires the study of the electronic and structural properties of both the bulk and surface under the working conditions of the catalyst.

**4.1. Metal–O Interaction and Catalytic Oxidation.** On single crystals and polycrystalline films of Cu and Ag, the reconstruction of metal surfaces under oxidation conditions was found in groundbreaking *in situ* and *operando* experiments. Time-resolved EXAFS spectroscopy combined with the detection of the catalytic turnover revealed that polycrystalline copper in the catalytic oxidation of methanol to formaldehyde is transformed into a defect structure in which oxygen is intercalated.<sup>55</sup> Thermal desorption and temperature-programmed reaction spectroscopy (TDS and TPRS, respectively) was applied to identify chemically inequivalent species of atomic oxygen in methanol oxidation over copper.<sup>56</sup> Atomic force microscopy (AFM), SEM, surface-sensitive X-ray

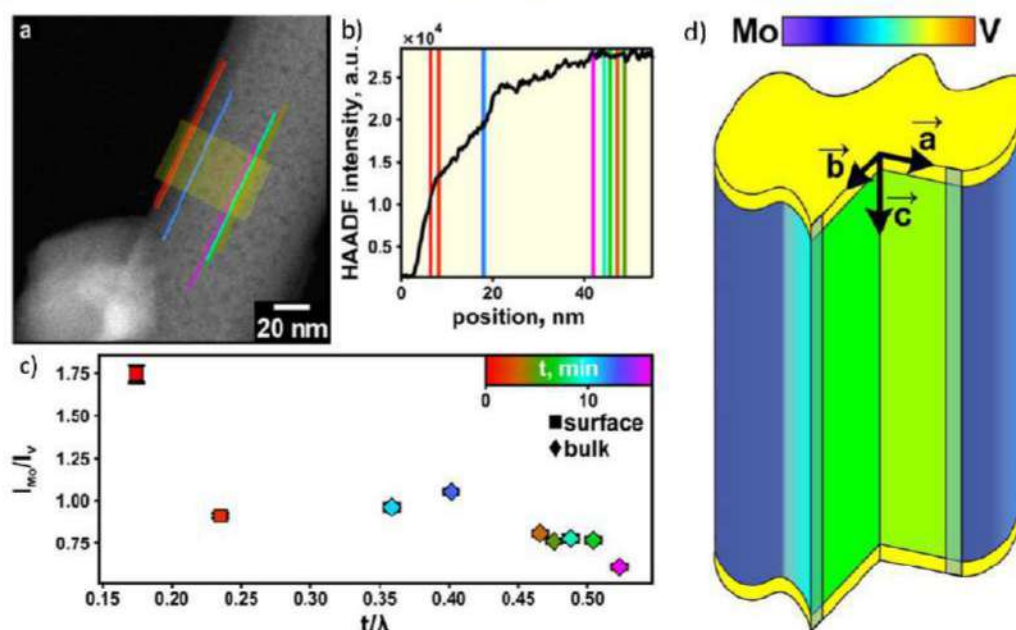
absorption spectroscopy (XAS),<sup>57</sup> core-level XPS, and ultraviolet photoelectron spectroscopy (UPS) displayed morphological changes of the bulk and the surface of copper and the presence of an oxygen-deficient copper(I) oxide phase under reaction conditions.<sup>56</sup>

Silver acts as a catalyst in many important industrial processes such as ethylene epoxidation and oxidation of methanol to formaldehyde. The interaction of silver with oxygen has been subject to numerous studies, in particular in Robert's collaboration with Xinhao Bao.<sup>58–63</sup> The role of nucleophilic and electrophilic oxygen species in oxidation reactions was discussed (*vide infra*).<sup>66</sup> By means of STM, reflection electron microscopy (REM), and reflection high-energy electron diffraction (RHEED), it was found that the interaction of oxygen with Ag(111) surfaces at atmospheric pressure and at temperatures >800 K leads to the activated formation of a new phase with long-range order exhibiting periodicities of about 70 Å in the [112] direction and 40 Å in the [1–10] direction, respectively, and a slight rotation by about 2° with respect to the substrate lattice (Figure 3).



**Figure 3.** (a) STM image (900 Å × 900 Å) of the reconstructed Ag(111) surface formed by exposing the bulk Ag(111) crystal to 1 bar O<sub>2</sub> at 900 K for 400 h. (b) Corrugation profile along the line marked in (a). Reproduced with permission from ref 58. Copyright 1993, Elsevier.

Photoelectron spectroscopic analysis has been further performed to study the oxygen species on the surface.<sup>61</sup> The formation of a strongly bound surface layer has been identified by an asymmetry of the Ag 3d<sub>5/2</sub> core-level peak at 367.3 eV and an O 1s peak at 529.0 eV (O<sub>s</sub>), with its interaction being different from that of atomic oxygen adsorbed on bulk Ag<sub>2</sub>O. The species is stable up to 900 K, in contrast to the binary silver oxides, and is relevant for high-temperature oxidation reactions catalyzed by Ag. In addition, oxygen was found to be dissolved in the bulk (O<sub>b</sub>), exhibiting an O 1s binding energy between 531 and 530 eV. The monolayer of silver-embedded



**Figure 4.** Mo/V integrated intensity ratio variations along the growth direction of orthorhombic  $(\text{Mo,V})\text{O}_x$ . (a) High-angle annular dark-field scanning transition electron microscopy (HAADF-STEM) image of orthorhombic  $(\text{Mo,V})\text{O}_x$ ; yellow highlighted area, area used to extract the HAADF-STEM intensity profile; colored lines, exact scan positions. (b) Intensity profile of the HAADF-STEM image: colored lines, exact scan positions. (c)  $I_{\text{Mo}}/I_{\text{V}}$  variation based on STEM–electron energy loss spectroscopy (EELS) measurements. The color code highlights the temporal order of STEM-EELS measurements. (d) Local compositional distribution in an orthorhombic  $(\text{Mo,V})\text{O}_x$  crystal: black arrows, crystallographic axes; color bar, degree of enrichment. Reproduced with permission from ref 71. Copyright 2020, American Chemical Society.

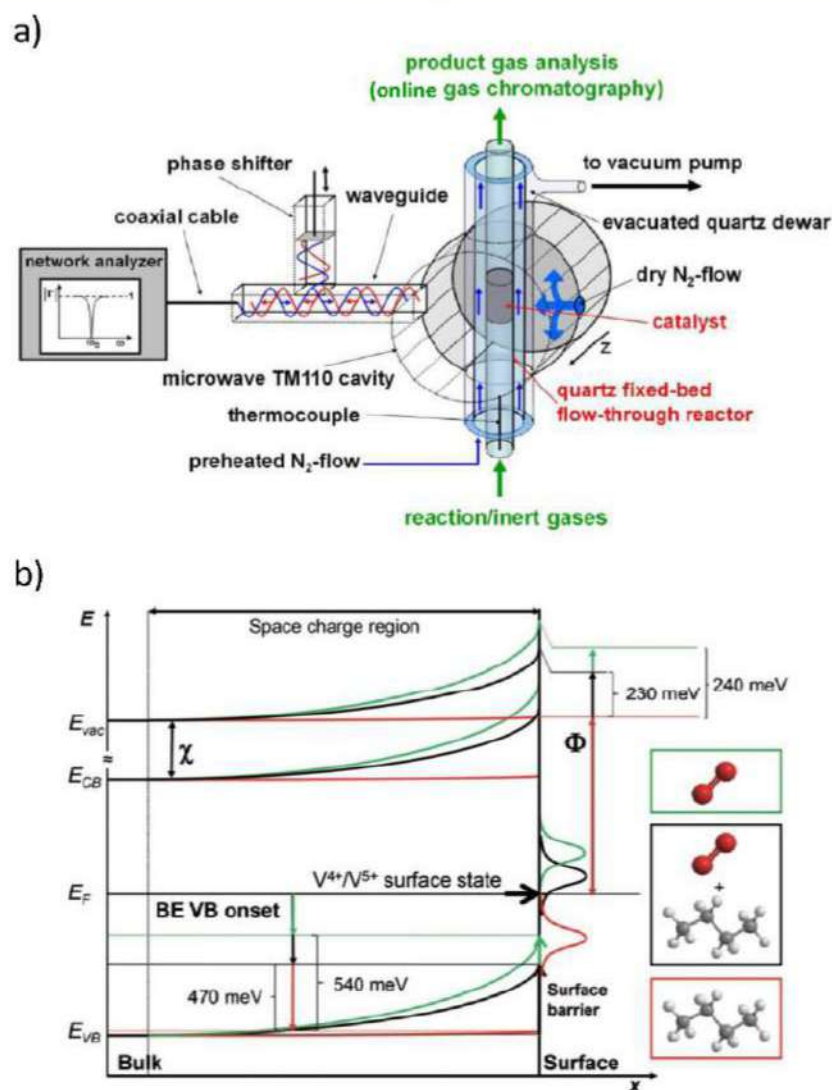
oxygen is in dynamic equilibrium with surface atomic oxygen segregated from the bulk at high temperature. The surface reaction processes such as methanol oxidation to formaldehyde<sup>59</sup> and oxidative coupling of methane<sup>62,67</sup> have been demonstrated to proceed through the  $\text{O}_\gamma$  species. The dynamics of the formation of the different atomic oxygen species has been later addressed by synchrotron-based near-ambient-pressure (NAP) XPS at temperatures relevant for industrial oxidation reactions, confirming their importance in oxidation reactions.<sup>68</sup>

**4.2. Structural Dynamics of Mixed Oxides.** Structural transformations and redox dynamics of heteropoly compounds,<sup>69</sup> vanadyl pyrosulfate  $(\text{V}^{\text{IV}}\text{O})_2\text{P}_2\text{O}_7$  (VPP),<sup>70</sup> and defective Mo-based oxides<sup>71</sup> were investigated by XRD and XAS techniques complemented by a broad spectrum of additional methods, including Raman, Fourier-transform infrared, and UV/vis spectroscopy, electron microscopy, and photoelectron spectroscopy. Heteropoly compounds exhibited a “living” and metastable nature under the reaction conditions, partially reversibly restructuring into crystalline  $\text{MoO}_3$  and other amorphous phases. Phase transformations of  $\text{MoO}_3$  between oxidized and reduced forms occur rapidly,<sup>72–75</sup> and the oxygen is bound quite strongly to the oxide.<sup>76</sup> To build on this work, various Mo-based phases, such as the “ $\text{Mo}_3\text{O}_{14}$ -type” structures or the so-called “M1” phase, were investigated that have significance as components in catalysts for the oxidation of methanol, acrolein, propene, and propane. The structural genesis of the  $\text{Mo}_3\text{O}_{14}$ -type phase from molecular precursors in solution, during thermal activation and under the reaction conditions, has an effect on the catalytic performance of the material, and the catalysis is related to the formation of nanocrystalline domains with  $\text{Mo}_3\text{O}_{14}$ -type and disordered structures.<sup>77–81</sup> *In situ* XAS was used to investigate reversible

changes in the  $(\text{Mo,V})_5\text{O}_{14}$  surface composition, which occur under severe conditions of methanol oxidation. The abundance of vanadium at the surface increases under the reaction conditions and reverts to its original value upon reoxidation, whereby a thermal effect can be excluded. With this pioneering work as inspiration, the surface dynamics of oxidation catalysts under reaction conditions of alkane oxidation were systematically investigated by means of NAP-XPS and XAS.<sup>82–86</sup>

The elucidation of local bulk and surface structures was tackled using high-resolution (HR) electron microscopy.<sup>71,87–89</sup> Scanning transmission electron microscopy coupled to electron energy loss spectroscopy (STEM-EELS) revealed variations in the composition not only between the bulk and surface but also among the termination layers of different surface facets (Figure 4).<sup>71</sup> An exciting and extremely difficult task for the future will be to elucidate the relationship between these local differences and the catalytic properties of the entire catalyst and thus to identify the nature of the actual active sites.

**4.3. Electronic Structure of Mixed Oxides.** In combination with the semiconductor properties of successful oxidation catalysts, such as vanadyl pyrosulfate  $(\text{V}^{\text{IV}}\text{O})_2\text{P}_2\text{O}_7$  (VPP)<sup>90</sup> and the Mo–V–Te–Nb mixed oxide with an “M1” structure,<sup>91</sup> this surface layer may be the key to understanding the mode of action of selective oxidation catalysts. In Robert’s working group, the development of methods for determining the electronic structure of oxidation catalysts under operating conditions has been advanced in recent years. In addition to synchrotron-based high-pressure photoelectron spectroscopy, particular mention should be made here of the contactless measurement of the conductivity of semiconducting catalysts. The contact-free microwave perturbation technique (MCPT) is based on the principle that the electric and magnetic field distribution inside a microwave cavity is



**Figure 5.** (a) Schematic representation of the *operando* MCPT setup. (b) Schematic band diagram of vanadyl pyrophosphate with experimentally obtained values for the binding energy (BE) shifts of the valence band (VB) onset and of the work function  $\Phi$  measured in *n*-butane/helium (red), *n*-butane/oxygen (black), and oxygen/helium (green).  $E_{VB}$  = valence band onset,  $E_F$  = Fermi level,  $E_{CB}$  = conduction band minimum,  $E_{vac}$  = vacuum level,  $X$  = electron affinity. Figure 5b is reproduced with permission from ref 90. Copyright 2015, John Wiley and Sons.

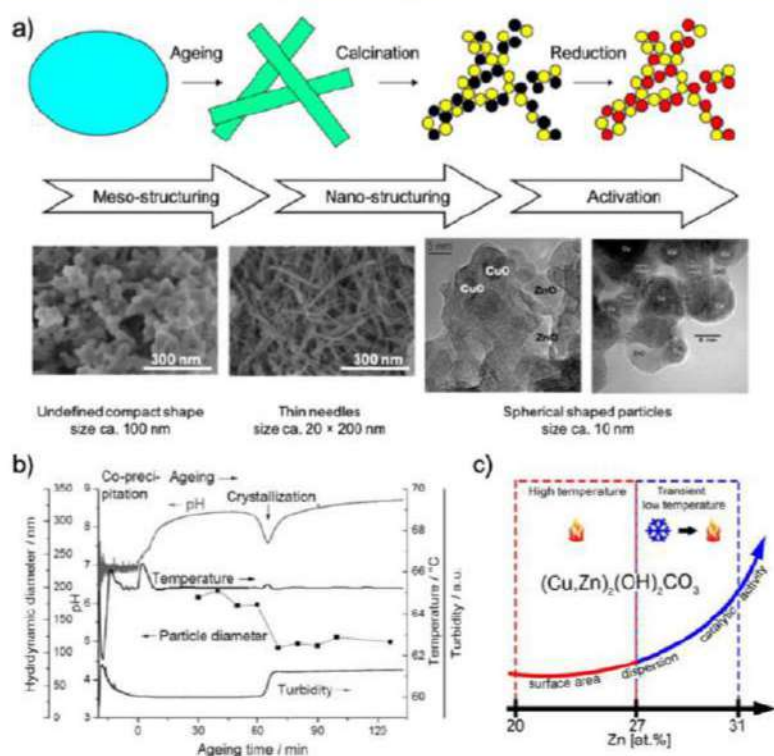
modified by a dielectric sample. An apparatus for measuring the influence of reaction conditions on conductivity while simultaneously determining the performance of the catalyst was developed by Maik Eichelbaum et al. (Figure 5a).<sup>92</sup>

The analysis of the electronic structure in the presence of the reacting molecules by using NAP-XPS and the measurement of the conductivity under realistic reaction conditions revealed band bending, which causes a shift of the band gap states with respect to the rigid Fermi level and thus affects the filling of these states with electrons (Figure 5b).<sup>90</sup> The catalyst behaves like a gas sensor, as the electrical conductivity varies with the filling of the band gap states pinned to the Fermi level. The band bending creates a barrier for the charge transfer toward adsorbed oxygen and limits the reduction and, hence, the abundance of activated oxygen species on the catalyst surface. High selectivity thus requires the interplay of local sites characterized by specific molecular structure and responsible for the adsorption of the reacting molecules and the collective semiconducting properties of the bulk phase, which acts as a

support for the termination layer providing the adsorption sites.<sup>52</sup>

## 5. METHANOL SYNTHESIS

Robert's achievements in the field of catalytic methanol synthesis are an example for the difficulty to classify his work as either fundamental or applied research. It is both, and his interest has always been in the fundamentals of applied and useful processes without the need for a clear distinction. This holistic view is also expressed in his interpretation of the famous citation of Max Planck that "insight must precede application", which he often uses to end his presentations. The conversion of synthesis gas to methanol is not only a research topic with (still) many exciting fundamental open questions but also an economically highly important industrial process for the production of a commodity chemical. Many of the most visible results of Robert's group in the field of methanol synthesis originate from joint research projects that were



**Figure 6.** (a) Schematic representation of the industrial Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst synthesis with the amorphous coprecipitation product (blue), the crystalline (Cu,Zn)CO<sub>3</sub>(OH)<sub>2</sub> precursor (green), and the thermal steps including decomposition into CuO (black) and ZnO (yellow) with final activation by the formation of Cu nanoparticles (red). The electron microscope images show the microstructural evolution during these steps.<sup>94</sup> (b) Coprecipitation and ageing are of special importance for the success of the synthesis and can be controlled by automatized synthesis workstations that monitor the relevant parameters.<sup>94</sup> (c) Scheme showing how the interplay of these parameters, such as temperature and composition of the metal salt solution, is the key to control important properties such as the Cu dispersion.<sup>99</sup> Figure 6a,b is reproduced with permission from ref 94. Copyright 2013, John Wiley and Sons. Figure 6c is reproduced with permission from ref 99. Copyright 2019, Elsevier.

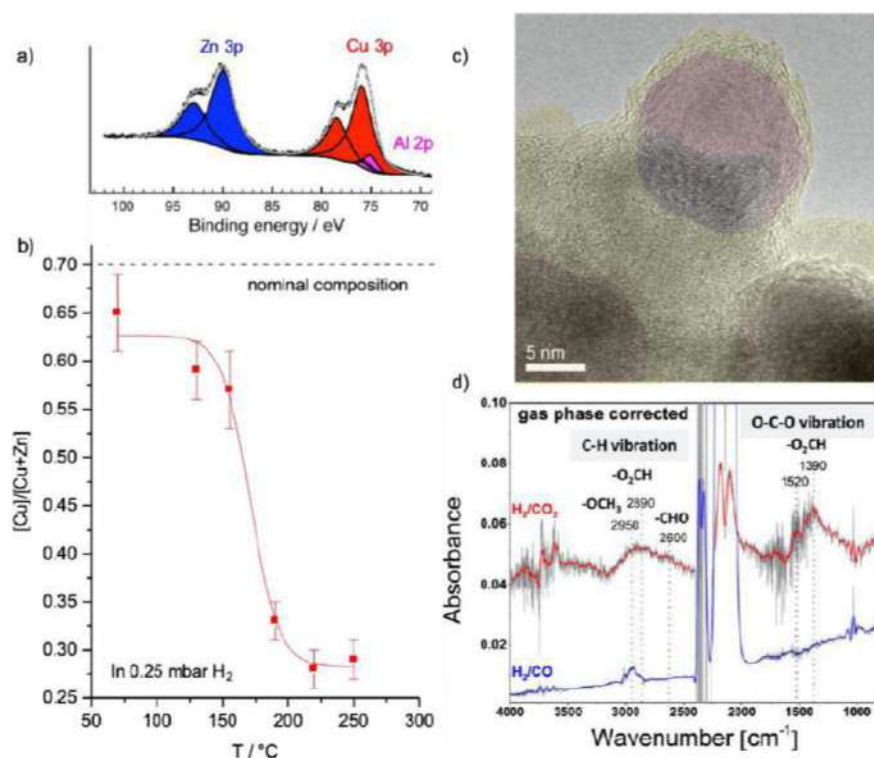
coinitiated by him and industry, in particular with the former Süd-Chemie AG from his home region of Bavaria in southern Germany.

Importantly, as methanol synthesis includes the hydrogenation of CO<sub>2</sub> to give a possible liquid fuel and energy storage molecule, it is currently considered as a potential pillar in CO<sub>2</sub> recycling. Both goals—efficient use of resources in industry and, currently with increasing weight, future sustainable energy scenarios—contribute to Robert's motivation to understanding the long-debated fundamentals of the catalytic formation of methanol on the industrially employed Cu/ZnO-type catalyst. Complementary to many other research groups who worked on the identification of the active site or the reaction mechanism using surface science models, Robert chose to approach these open questions, in accordance with the name he chose for his research Department in Berlin, by studying the fundamentals of the real catalyst's inorganic chemistry, including its synthesis, and facing its full complexity.

**5.1. Synthesis of the Cu/ZnO Catalyst.** Robert became interested in the late 1990s in the chemistry of Cu/ZnO catalysts for methanol synthesis and methanol steam reforming, and already in the first paper from the early 2000s,<sup>93</sup> he and his team recognized the crucial role of microstructure in this catalyst, which cannot be easily captured in surface science model materials. Therefore, the industrial synthesis of the catalyst has been carefully deciphered by his group (Figure 6a),<sup>94</sup> which was an endeavor of many years but finally laid the foundation for a Cu/ZnO/(Al<sub>2</sub>O<sub>3</sub>) materials

basis comprised of uniform high-performance catalysts with a homogeneous microstructure. This materials basis was the key for the establishment of structure–activity relationships. The breakthrough for the synthetic control was an understanding of the pH-controlled coprecipitation<sup>95</sup> (Figure 6b) and the bottom-up formation chemistry of the Cu-rich crystalline (Cu,Zn)CO<sub>3</sub>(OH)<sub>2</sub> precursor,<sup>96,97</sup> which contains the precursor species for the Cu and ZnO nanoparticles in a single phase-pure solid solution. With this prerequisite, the thermal treatment of the precursor leads to a top-down decomposition<sup>98</sup> of each precursor crystal into a highly interdispersed porous aggregate of Cu and ZnO nanoparticles. This synthetic principle has been employed for the optimization of the (Cu,Zn)CO<sub>3</sub>(OH)<sub>2</sub> precursor based synthesis<sup>99</sup> (Figure 6c) but has also been transferred over the years to other mixed (Cu,Zn)-hydroxy-carbonate compounds,<sup>100</sup> to formates<sup>101</sup> and oxalates,<sup>102</sup> and also to completely different supported metal catalysts: for example, for dry reforming of methane,<sup>103</sup> selective hydrogenation,<sup>104</sup> and more recently also ammonia synthesis<sup>14</sup> and methanation.<sup>105</sup>

**5.2. Structural Dynamics: Strong Cu–ZnO Interaction.** Robert recognized early in his career that working catalysts are not static<sup>1</sup> and regarded Cu/ZnO as a prototype catalyst for this insight. He always promoted the progress of *in situ*, *quasi in situ*, and *operando* experimentation in his research environment (*vide infra*), and consequently, FHI's Department of Inorganic Chemistry was the ideal place to study the dynamics of industrial-type methanol synthesis catalysts. With



**Figure 7.** (a) *In situ* NAP-XPS core level spectra of a Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst obtained in high resolution at the ISIS beamline at BESSY II in Berlin.<sup>125</sup> (b) Inversion of the surface composition ratio Cu:Zn as the catalyst is reduced and activated by surface decoration of the Cu particles with partially reduced ZnO<sub>x</sub> species.<sup>108</sup> (c) HR-TEM image of the catalyst surface microstructure after self-assembled formation of the porous ZnO<sub>x</sub> film. (d) The resulting surface chemistry can be studied by *in situ* IR spectroscopy under reaction conditions of 30 bar and 250 °C.<sup>116</sup> Figure 7b is reproduced with permission from ref 108. Copyright 2012, The American Association for the Advancement of Science. Figure 7d is reproduced with permission from ref 116. Copyright 2019, American Chemical Society.

a combination of XAS,<sup>106,107</sup> NAP-XPS (Figure 7a,b),<sup>108</sup> XRD,<sup>106</sup> neutron diffraction,<sup>109</sup> MCPT,<sup>110,111</sup> and vibrational spectroscopy<sup>112</sup> with high resolution transmission electron microscopy (HR-TEM)<sup>113–115</sup> (Figure 7c) and, recently, thermal analysis<sup>116</sup> (Figure 7d)—all applied *in situ* or *operando* on samples from the aforementioned materials basis representing the industrial catalyst—the partial reduction of ZnO leading to surface decoration of the Cu particles with a porous film of ZnO<sub>x</sub> ( $0 < x < 2$ )<sup>112–114</sup> and finally to (surface) alloy formation<sup>108,117</sup> could be studied in great detail despite the high complexity of the catalytic material.<sup>117</sup> These dynamics turn the working catalyst into an “inverse structure” with ZnO<sub>x</sub>–Cu site ensembles being present not only at a static perimeter and have important consequences for the adsorption properties, in particular the activation of the formate intermediate, which as a result of combining experiment and theory in a fruitful collaboration with Jens K. Nørskov and his co-workers was shown to be efficient on the reduced Zn sites.<sup>108,118</sup> These results have been important contributions to our current understanding of the industrial methanol synthesis catalyst and demonstrate how the fundamental concepts of strong metal–support interactions and Cu–Zn synergy developed in model catalysis<sup>119</sup> are validated for the applied reaction conditions and in real high-performance catalysts.

**5.3. Search for the Active Site in CO<sub>2</sub> Hydrogenation to Methanol.** Another important piece of the puzzle of the active site in industrial Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts was the finding that another fundamental observation made in surface

science, namely the different reactivities of different surface terminations,<sup>120</sup> was also highly relevant in industrial catalysts, where this structure dependence became manifest in a very special form. Deviations from the ideal bulk structure of copper in these catalysts has been a major research topic in Robert’s group since the beginning of their work in this field. An early working hypothesis that paved the way to a consistent picture was that Cu lattice strain contributes to the high activity of the industrial catalysts in methanol synthesis and methanol steam reforming.<sup>121–123</sup> Later, the benefit of HR-TEM with strict avoidance of air contact of the activated catalysts led to a more complete analysis of the microstructure in the Cu component of the catalyst<sup>115</sup> and the group could refine the view on its relevance by the inclusion of planar structural defects. Such defects, stacking faults and twinning boundaries, were observed to terminate at the surface of the nanoparticles, causing a change in surface faceting even for relatively large particles with diameters above 10 nm and low surface curvature that were found in the industrial catalyst.<sup>108</sup> These interruptions of the surface facets give rise to lines of more open or stepped surfaces. The aforementioned surface science studies and theoretical calculations inspired the hypothesis that these features are candidates for the active site of methanol synthesis. Strong experimental support was found in a linear correlation between the stacking fault probability in a series of Cu/ZnO catalysts, determined by integral diffraction methods,<sup>124</sup> with their intrinsic activity, i.e. the Cu surface area normalized activity.<sup>108</sup> Importantly, *in situ* neutron diffraction was able to show that these defects that are anchored in the bulk of the Cu



particles were stable under the reaction conditions and were not easily annealed.<sup>109</sup>

Altogether, the work of Robert and his co-workers of the last two decades has helped to reveal the three principles of success of the industrial Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> methanol synthesis catalyst:<sup>125</sup>

- (1) the unique microstructure of the porous Cu/ZnO aggregates with high interdispersion and a large interface area resulting from the precursor chemistry during catalyst synthesis
- (2) the dynamic surface promotion by partially reduced Zn species that decorate the Cu surface and create new promoted sites that make it more oxophilic for the activation of the formate intermediate
- (3) the high activity of structural defects in the Cu particles that give rise to undercoordinated surface atoms.

**5.4. Methanol Synthesis for Chemical Energy Conversion.** More recently, Robert and his team at the MPI CEC have been working on employing the fundamental knowledge of applied Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts for their utilization in CO<sub>2</sub> capture and utilization processes in terms of chemical energy conversion.<sup>126</sup> He has always advocated the key role of chemistry in the energy challenge<sup>49</sup> and considered methanol synthesis, e.g. from industrial sources,<sup>127</sup> an attractive way to recycle CO<sub>2</sub> with the help of regenerative energy sources in the context of a “solar refinery”.<sup>128</sup> The commercial Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst was found to be generally stable and to be capable of dealing with the required dynamics of the conditions when it is coupled to volatile regenerative energy.<sup>129</sup> The conversion of steel mill exhaust gases has also been described recently<sup>130</sup> with a focus on the reversibility of catalyst poisoning.<sup>131</sup> These very new results exemplarily show that there still are open questions and important problems, but the starting position for young researchers entering this field today to tackle these challenges is promising—also as a result of the contributions of Robert and his team. Thanks to his work, the complex Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst is today among the best-studied industrial catalytic materials.

## 6. OPERANDO X-RAY SPECTROSCOPY AND OPERANDO ELECTRON MICROSCOPY

Since 1980 the scientific interests of Robert have involved the description of the local geometric<sup>132</sup> and electronic structures<sup>133</sup> of complex solids as well as the description of the surface states by X-ray spectroscopy<sup>134,135</sup> by itself and in combination with electron microscopy.<sup>3</sup>

These early publications show that X-ray spectroscopy and electron microscopy techniques have been a constant companion throughout his scientific career. Although he started working on understanding the structural interplay of complex solids 40 years ago, retrieving detailed insights into the geometric and electronic structure of functional materials and understanding their chemistry are still key questions in his current research.

The working structures of a real catalyst can be quite complex and differ from pristine structures that are traditionally obtained from electron microscopy and X-ray spectroscopy measurements under vacuum. Catalysts respond structurally to changes in the chemical potential. These so-called chemical dynamics can be reversible or irreversible.<sup>136</sup> In addition, the presence of a reaction gas mixture at elevated temperature might induce the formation of metastable states at the catalyst

surface. Capturing these structures and dynamics, requires sophisticated *operando* analysis, which is conducted simultaneously with the catalytic reaction. Since the concentration of spatially separated active sites at the surface is not necessarily very high, surface-sensitive techniques, which can be applied under the reaction conditions, are needed to study active catalyst surfaces. In addition, heterogeneous catalysis is a multiscale phenomenon<sup>136,137</sup> and analytical methods are needed that can bridge the scales and allow the investigation of catalyst particles with sufficient spatial resolution.

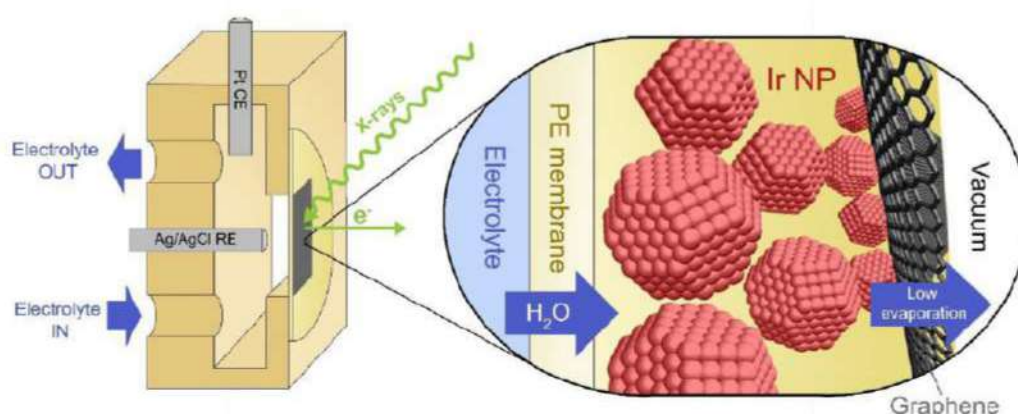
As the director of the Department of Inorganic Chemistry of the Fritz-Haber-Institut and the director of the Department of Heterogeneous Reactions of the Max-Planck-Institut of Chemical Energy Conversion, Robert has strongly promoted the development and application of *operando* X-ray spectroscopy and *operando* electron microscopy.

AP-XPS had already been applied in the 1980s,<sup>138</sup> but just the use of synchrotron radiation as an excitation source in the soft X-ray range and the implementation of electrostatic lens systems in the setups enabled the breakthrough of this technique in the *operando* study of heterogeneous catalytic processes at the beginning of this century.<sup>139</sup> Currently, almost every synchrotron radiation facility of the world in the soft energy range has a dedicated AP-XPS beamline in its portfolio and the demand is still increasing.<sup>140</sup> The fact that the kinetic energy of the emitted photoelectrons is related to the photon energy enables the optimization of the surface sensitivity of the measurement. This technique, codeveloped by Robert in collaboration with the group of Miquel Salmeron in Berkeley,<sup>141</sup> enables the study of structure–function relations from the millibar range in backfilling experiments to 1 bar experiments in closed cells.

*In situ* SEM is capable of capturing processes that occur during the interaction of a solid with a gaseous or liquid environment. In addition, the sensitivity of SEM to changes in the work function renders it into a powerful tool to study surface reactions.<sup>142,143</sup> Similarly to backfilling XPS experiments, this technique is limited in pressure to a few millibars. While *operando* SEM can visualize changes of the surface that occur during the catalytic reaction on the macro and micro scale, it has difficulty in explaining localized effects on the nano scale. However, this is important, as the majority of heterogeneous catalytic systems are nanomaterials. In order to resolve the response of nanoparticles during the catalytic reaction, different TEM techniques have been developed that rely on *quasi in situ* TEM,<sup>144–146</sup> environmental TEM (ETEM), and dedicated gas cell TEM holders that are based on microelectromechanical systems (MEMS).<sup>147</sup> Due to electron–gas interactions ETEM is limited in pressure to a few millibars. MEMS-based TEM holders can exceed atmospheric pressure and these gas cell TEM holders are commercially available. The concept of using MEMS-based TEM holders for *operando* TEM investigations of heterogeneous catalysts in thermal gas-phase reactions was introduced previously by Vendelbo et al.<sup>148</sup>

Hereinafter, Robert's significant contributions to the development of *operando* X-ray spectroscopy and *operando* electron microscopy, which delivered important insights into the evolution of structures and chemistry of heterogeneous catalysts under the reaction conditions, are presented.

**6.1. Operando X-ray Spectroscopy in the Soft Energy Range.** **6.1.1. Solid/Gas-Phase Interfaces.** The application of *operando* X-ray spectroscopy has provided new insights into



**Figure 8.** Schematic drawing of the electrochemical cell working with a confined electrolyte. Adapted with permission from ref 157. Copyright 2019, American Chemical Society.

the function of heterogeneous catalysts. Robert used this technique to investigate the economically relevant ethylene epoxidation over silver. It turned out that the species, which was expected to be active in this reaction, is not an atomic adsorbed oxygen species as discussed in the literature but an oxygen atom of adsorbed  $\text{SO}_4$  moieties that are present as an impurity of the silver catalyst or of the ethylene gained from crude oil.<sup>149</sup> In other systems the team around Robert demonstrated the significance of subsurface species for heterogeneous catalytic reactions by AP-XPS as well. The methanol oxidation to formaldehyde over copper is correlated to the formation of subsurface oxygen during the reaction.<sup>150</sup> The CO oxidation over Au nanoparticles supported on  $\text{TiO}_2$  is characterized by the reduction of  $\text{TiO}_2$  and formation of an ionic Au species. The formation of three phase boundaries ( $\text{TiO}_x$ ,  $\text{Au}^+$ , CO) is directly linked to the activity. Complementary TEM studies showed that an overlayer of reduced  $\text{TiO}_2$  is formed under the reaction conditions, and density functional theory (DFT) calculations confirmed that the formation of ionic Au is related to a strong metal–support interaction.<sup>151</sup> Furthermore, Robert investigated hydrogenation reactions by AP-XPS. In selective hydrogenation reactions the formation of subsurface carbon species was demonstrated. The formation of a surface Pd–C phase was detected during the selective hydrogenation of alkynes to alkenes, which controls the selectivity of the reaction.<sup>152</sup>

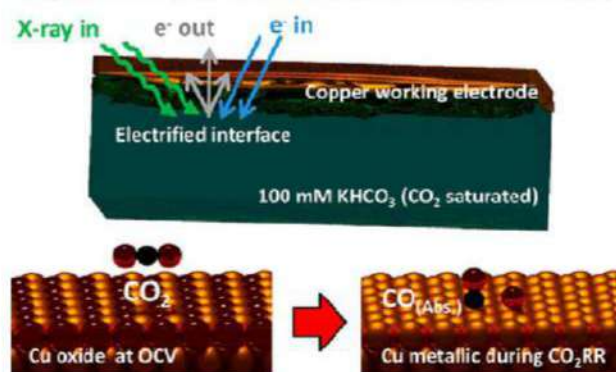
**6.1.2. Electrochemistry.** Renewable energies are becoming more important for the energy supply of mankind. One challenge in this context is the energy storage, which can be solved on a large scale just by chemical means. Devices such as electrolyzers use electrical energy provided by solar cells or wind wheels to split water into oxygen and hydrogen. The latter will be bonded in molecules such as methanol or ammonia, which can be catalytically decomposed when the stored energy will be used: e.g., to operate a fuel cell. In order to study electrochemical processes by AP-XPS, the development of dedicated electrochemical cells is necessary. In Robert's group, first approaches were developed to investigate the OER over noble-metal-based anodes in acidic electrolytes by using a proton exchange membrane (PEM). This approach has the disadvantage that just water vapor is in contact with the catalyst, since the water is evaporating when it diffuses through the membrane to the other side covered with the anode material. In any event, this type of electrochemical cell already

delivered interesting results on the electronic structure of Pt anodes and  $\text{IrO}_x$  anodes during the OER.<sup>153,154</sup> It was found that amorphous  $\text{IrO}_x$  is more active in the OER in comparison to the crystalline rutile  $\text{IrO}_2$ . A chemical electron microscopy analysis revealed that the amorphous  $\text{IrO}_x$  phase is composed of Hollandite motifs.<sup>155</sup> When the voltage at the anode is increased in the OER range, a feature at around 529 eV at the oxygen K-edge increases in intensity. Its strength shows a correlation to the applied voltage and to the oxygen partial pressure measured by a mass spectrometer.<sup>153</sup> This feature is interpreted as an  $\text{O}^-$  species. Under the conditions of the oxygen evolution reaction an increase in the potential does not result in further oxidation of  $\text{Ir}^{4+}$  in  $\text{IrO}_2$  to  $\text{Ir}^{5+}$  but rather in the oxidation of surface lattice oxygen  $\text{O}^{2-}$  to  $\text{O}^-$  due to the hybridization of the electron orbitals.

The nature of the oxygen species observed during the OER was studied in more detail in liquid water.<sup>156</sup> To enable this investigation, a layer of graphene was transferred on the  $\text{IrO}_x$  nanoparticles deposited on the PEM. The graphene membrane confines the water between the membrane and the graphene, which results in the formation of a liquid layer of water, as shown in Figure 8.<sup>157</sup> The combination of molecular dynamics calculations and X-ray absorption tracking experiments revealed that the OER is characterized by the deprotonation of the  $\mu_1\text{-OH}$  group.

Recently, Robert took part in the development of a reaction cell, which enables combined studies of *operando* X-ray spectroscopy and SEM. The cell was used to study  $\text{CO}_2$  reduction over a copper electrode. The Cu electrode is deposited on a 100 nm  $\text{Si}_3\text{N}_4$  membrane to measure the bulk properties by the detection of the fluorescence signal, and it was also used to measure the X-ray absorption signal in the total electron-yield (TEY) mode using the cell shown in Figure 8.<sup>158</sup> The Cu electrode was in the metallic state during the  $\text{CO}_2$  reduction reaction, whereas Cu oxide is formed in the open circle potential mode, as shown in Figure 9.

The next example highlights not only the potential of correlative X-ray spectroscopy and SEM for energy science but also the complementarity of X-ray spectroscopy and SEM. Similarly to X-ray spectroscopy, SEM *operando* measurements are not limited to closed-cell designs and liquid-phase reactions. The surface sensitivity of SEM can be also used to deliver valuable insights into the evolution of surface structures induced by thermal gas-phase reactions. As can be seen below,

CO<sub>2</sub>RR revealed by *Operando* spectroscopy/microscopy

**Figure 9.** Schematic drawing of Cu electrodes used in CO<sub>2</sub> reduction investigated by X-ray absorption spectroscopy (in the fluorescence mode) and scanning electron microscopy using the same cell. Reproduced with permission from ref 158. Copyright 2020, American Chemical Society.

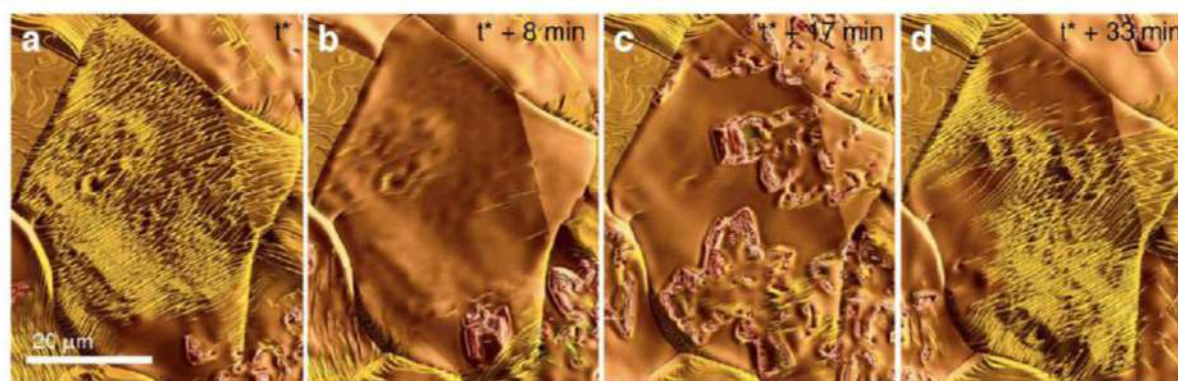
different gas-phase reactions are used in Robert's department to exploit the benefits of SEM and TEM analyses. With these techniques structural changes and transformations that occur during the prevailing time of a catalytic reaction can be visualized.

**6.2. Operando Electron Microscopy (OEM).** Within Robert's department, a commercially available *in situ* SEM was modified with a home-built laser heating stage. Its surface sensitivity was, for instance, used to visualize and to understand the growth of graphene on metallic supports.<sup>143,159–161</sup> In addition, spatiotemporal dynamics were detected in real time that occur during the NO<sub>2</sub> hydrogenation on platinum.<sup>142</sup> The occurrence of these spatiotemporal dynamics was found to be grain-dependent and showed the propagation of reaction fronts that arose from monolayers of adsorbed molecular species as well as the spillover of reactive species. They were further interpreted as the initiation of the reactive behavior. The study also demonstrated that spatially resolved reactivity patterns at surfaces can occur under conditions that exceed ultrahigh vacuum (UHV).

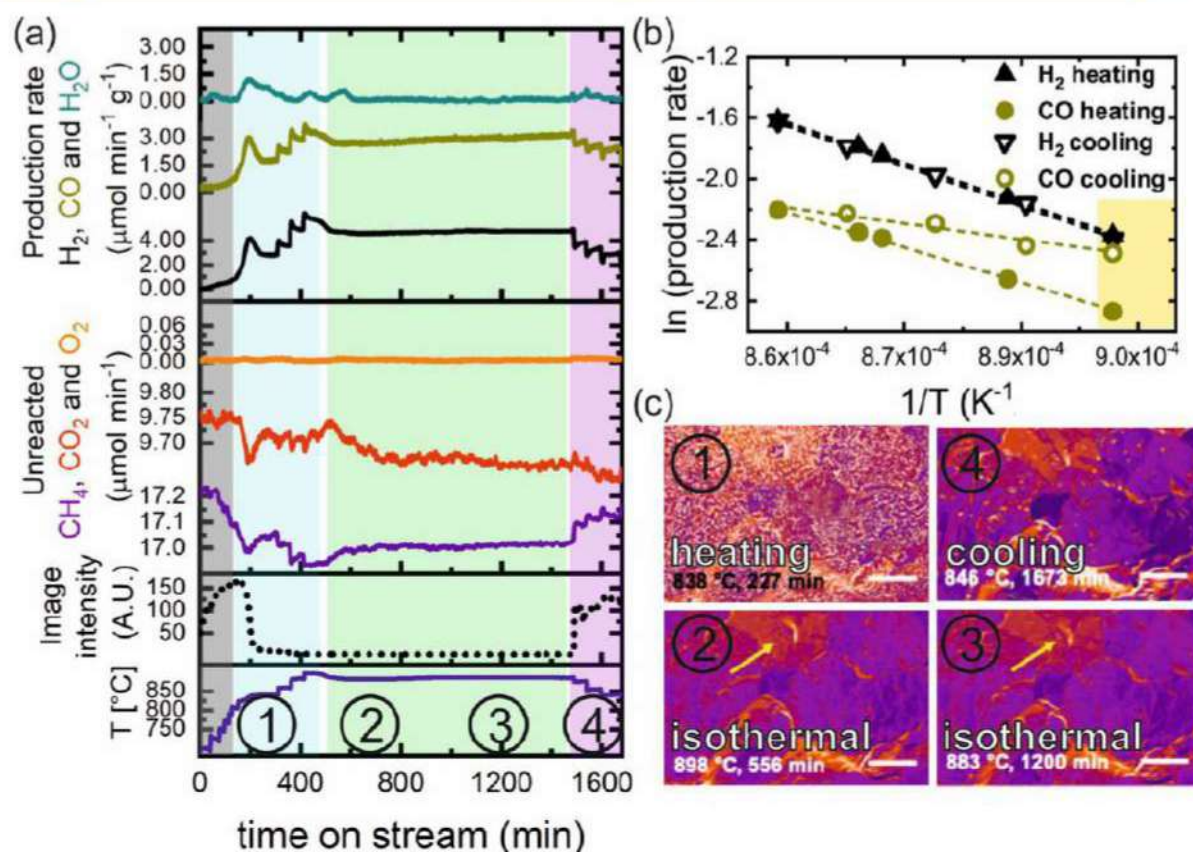
Furthermore, *in situ* SEM enabled Robert to gain insights into the reaction-induced surface dynamics of Cu during hydrogen oxidation.<sup>162</sup> In a comparative study that combined

*in situ* SEM imaging, *in situ* X-ray microscopy, and spectroscopy with HR-TEM, it was found that the transition from the metal to the stable cuprite phase does not take place directly. Instead, a transition region occurred with an increasing chemical potential of oxygen. This transition region is characterized by the coexistence of three spatially separated and interconverting surface phases. These states can be assigned to metallic Cu, O adsorbed species, and the oxide phase (Figure 10), which could be best described as the occurrence of "frustrated" phase transitions. In brief, the system aims to undergo a phase transition. However, the energy barrier needed for this phase transition is too high to be surmounted under the applied conditions.

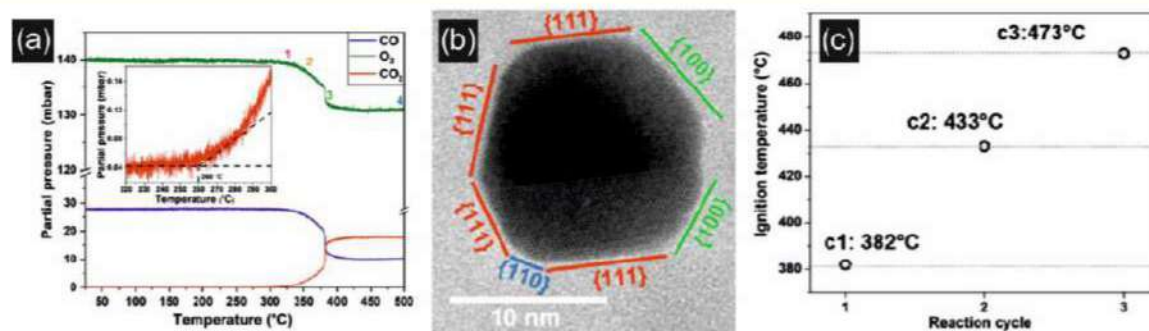
Using the capabilities of this SEM, Robert was interested in how oxide–metal phase transitions influence the production of synthesis gas over Ni catalysts. The key for the success of this study was the implementation of a special quartz tube reactor that enables contamination-free surface imaging and the detection of conversion.<sup>163</sup> This renders these SEM measurements into an *operando* approach. It was found that the transition from surface oxide species to the metallic state initiated the catalytic reaction (Figure 11a). A detailed analysis of the reaction traces suggested that the initial reaction mechanism relates more to partial oxidation of methane (POM) than to dry reforming of methane (DRM). The reaction mechanism started to change toward DRM after long-term measurements. A comparison of the activation energies ( $E_a$ ) for the production of H<sub>2</sub> and CO during heating and cooling indicated that the  $E_a$  values for the production of H<sub>2</sub> remained constant, while the  $E_a$  value for the CO production decreases during cooling (Figure 11b). This observation implies that during cooling the production of CO is favored and suggests that different reaction pathways are present. They depend on the (sub)surface state of the catalyst which seem to control the selectivity. The behavior could be explained by the occurrence of chemical dynamics. Reversible oxide–metal phase transitions initiated and stopped the reaction, while irreversible surface transformations that were observed in the long-term treatment led to a change in the reactivity. The assignment of surface transformations was further corroborated by the shape and position of the surface oxides that reappeared after cooling, which were different and more localized in comparison to the shape and spatial distribution of the initial surface oxides (Figure 11c).



**Figure 10.** *In situ* SEM investigation of Cu in a hydrogen and oxygen containing atmosphere at pressures of 0.2–0.5 mbar. (a–d) Time sequence of morphological changes at 700 °C in a gas mixture of 4% O<sub>2</sub> in H<sub>2</sub>. The different stages of a redox cycle are indicated by colors. Reproduced with permission from ref 162. Copyright 2020, Springer Nature. Reused under Creative Commons CC-BY4.0.



**Figure 11.** Production of synthesis gas over Ni catalysts as revealed from *operando* SEM analysis at a pressure of 2.46 mbar. (a) Correlation of reaction traces and image intensity. (b) Arrhenius plot for H<sub>2</sub> and CO production during heating and cooling. (c) Reversible and irreversible surface changes. Adapted with permission from ref 163. Copyright 2020, Elsevier.



**Figure 12.** *Operando* TEM investigation of CO oxidation over Pt nanoparticles at a pressure of 700 mbar. (a) Reaction traces of the first catalytic cycle. (b) Faceted nanoparticle after the second cycle. (c) Increase in the ignition temperature during temperature cycling. Reproduced with permission from ref 165.

Recently, Robert's department developed a home-built gas feed and analysis setup that is compatible with commercially available gas cell TEM holders for *operando* TEM.<sup>164</sup> CO oxidation over Pt nanoparticles was used to prove the concept.<sup>164,165</sup> It was found that the reaction lights off at 260 °C (Figure 12a). In addition, the combination of imaging, electron diffraction, online conversion detection, and catalytic cycling allowed disentangling the different contributions of chemical dynamics. As long as changes in the gas phase exist, i.e. as long as the chemical potential of the gas phase changes, irreversible transformations occurred. These transformations could be best described by surface faceting which led to the

exposure of low-index surfaces (Figure 12b) and during cycling to deactivation (Figure 12c). At high and constant conversion, partially reversible changes were spotted by electron diffraction analysis. These bulk changes could be explained by the concept of a frustrated phase transition and were considered important for maintaining high catalytic activity during CO oxidation.

## 7. SOCIAL COMMITMENT

While Robert is receiving ample praise from renowned colleagues in his own discipline, his achievements reach far beyond the field of catalysis. An interdisciplinary approach is indispensable to provide practical solutions to the highly

complex problems confronting modern societies, ranging from crisis management in the midst of a raging pandemic to addressing long-term challenges such as worldwide hunger and global warming. By their highly selective nature, identifying academy members among leading active researchers in their respective disciplines, leading institutions such as Leopoldina, the German National Academy of Sciences, BBAW, the Berlin-Brandenburg Academy of Sciences, and acatech, the German Academy of Technical Sciences are guarantors of the high quality of expertise which they conflate into policy advice.

This is the environment in which Robert has been leaving an impressive mark over the course of the past decade. Encounters with him, and the ensuing collaborations, are without doubt among the most inspiring and rewarding experiences for everybody working at the interface of research and science-based policy advice. He was also behind the inception of the German national academies' joint project "ESYS—Energy Systems of the Future", which is the leading scientific endeavor accompanying the energy transition in Germany, and served as the chairman of its steering committee from 2013 to 2017. Furthermore, he contributed to a Leopoldina ad-hoc statement on German climate policy published in 2019 and coordinated an ESYS ad-hoc statement on European climate policy published in 2020.

As a partner in collaborative projects, Robert is extremely generous in sharing his expertise and in his commitment to get the work done and also in his tolerance of team members who do not display the same level of dedication. He is also a role model for any researcher working at the science–policy interface. Correspondingly, in 2020 he was elected to the position of one of Leopoldina's Vice Presidents and was chosen to become Deputy Chairman of the National Hydrogen Council. There could hardly be a better choice for both of these positions. These responsibilities are vivid testimony to his untiring devotion to translating his research on issues of energy conversion, storage, and transport into practical use. His colleagues, friends, and admirers are very grateful to constantly be inspired and driven to ever greater heights of effort by his incredible dynamism and vehemence.

## 8. SUMMARY AND OUTLOOK

In conclusion, Robert Schlögl has generated outstanding achievements in heterogeneous catalysis. His contributions to ammonia and methanol synthesis, carbon materials in catalysis, selective oxidation, and the development of *operando* techniques have led to a significant knowledge enhancement in the field. In addition to his scientific contributions, he has also a great personality with excellent mentoring skills of young scientists. His commitment to society involves not only public discussions of important societal topics, such as the energy change, but also their practical realization. As a consequence, the *CatLab* project was founded. Within this project hosted at one of the German centers for catalysis, Berlin, new technologies are being explored for a more efficient hydrogen conversion and release. Recently, the digitalization of science has become an important aspect in Robert's scientific endeavor, which focuses not only on machine automation but also on the development of data storage routines for effective data mining and machine learning to derive important descriptors for heterogeneous catalysis.<sup>166</sup> Also in this regard, he has been ahead of his time and enforced the electronic storage and management of the scientific data generated in his Department since 1997. The workflows today include a strict

adherence to a catalysis handbook and close interaction with theory.<sup>166</sup>

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

### Notes

The authors declare no competing financial interest.

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