

Unlocking the Mysteries of Technical Catalyst Deactivation: A View from Space

Shweta Sharma,^[a] Florian Maurer,^[a] Patrick Lott,^[a] and Thomas L. Sheppard^{*[a, b]}

Modern analytical techniques enable researchers to study heterogeneous catalytic systems at extended length scales and with local probing methods which were previously impractical. Such spatially-resolved analyses are ideal for exploring the complex dynamics governing catalytic activity, and more specifically, deactivation. Here we highlight significant experimental concepts and milestones in the spatially-resolved analysis of technical catalysts, where it is now possible to study catalyst behavior even up to industrially relevant scale. At such extended length scales and in contrast to many model systems, spatial heterogeneities in solid catalyst bodies may play a

crucial role in controlling catalytic properties and may be closely linked to catalyst deactivation. Spatially-resolved studies can therefore provide a unique source of information about such local phenomena. Researchers can gain a deeper insight into the operational life of a catalyst by understanding deactivation patterns, which are one of many factors influencing the dynamics of catalytic reactions. In turn, this information promotes the design of more robust and sustainable catalytic systems. We therefore outline the current state of spatially-resolved characterization, together with its role in deconvoluting the complexity of technical catalysts and their deactivation.

1. Introduction

Catalyst activity is a frequently prioritized metric in academic research on heterogeneous catalysis. In chemical industry however, selectivity and stability often dictate the selection of optimal catalysts.^[1] In the latter case, catalyst lifetimes of months or even years may be needed to maximize productivity, profit, and sustainability. Stability is unique to each catalytic process, depending on fluctuating variables such as temperature, feed composition, or the presence of contaminants.^[2] A low stability implies a loss in activity over time, also known as deactivation. Such phenomena may be observed as gradual deviation in conversion or selectivity from optimal values. This may occur due to changes in active sites or their accessibility, changes in support structure, or numerous other reasons.^[3] In fact the mechanisms involved in deactivation are rather diverse, making it challenging to assess the unified causes and impacts across various catalytic systems and process conditions.^[4] On the other hand, comprehending this stability is crucial to develop strategies to mitigate deactivation and extend the catalyst lifespan.

Fundamental knowledge of catalysis, particularly in academia, is often derived from characterizing model catalytic systems. This leads to a well-known “materials gap” in relating observations from model to technical scale, largely due to differences in catalyst form, heterogeneity/uniformity, and process conditions.^[5] Catalyst stability or deactivation can in turn be heavily influenced by the scale of the study. Connecting between the model and technical scales is a current challenge in catalysis research, requiring careful application of appropriate characterization tools. As highlighted by Rose et al., further pitfalls which may occur between model and technical scale include ignorance of mass and heat transfer limitations, and the role of transient behavior in catalytic performance for example.^[6]

In terms of catalyst deactivation, a recent review by Pérez-Ramírez et al. classified common observations according to type and application field.^[7] In a sense, this highlighted the broad and occasionally inconsistent reporting of deactivation phenomena across subdisciplines of catalysis. A notable statement in the review was that technical scale is rarely addressed. On this point, our observation is that research efforts are often distinctly separated into those of chemistry groups working on model scale or fundamental studies, and those of chemical/process engineering groups dealing with scale-up and technical implementation. However, a comprehensive understanding of catalysis requires combined knowledge from all the above fields. This poses a significant challenge for individual or compartmentalized research efforts which are unfortunately rather common in academia.

This concept article considers emerging characterization tools and experimental approaches specifically with a scale-bridging nature, which may be used to address technical catalyst systems and deactivation processes. Bridging length scales in this manner may be the optimal approach to address current knowledge gaps in catalyst behavior. The specific focus

[a] S. Sharma, Dr. F. Maurer, Dr. P. Lott, Dr. T. L. Sheppard
 Institute for Chemical Technology and Polymer Chemistry (ITCP)
 Karlsruhe Institute of Technology (KIT)
 Engesserstraße 20, 76131 Karlsruhe (Germany)

[b] Dr. T. L. Sheppard
 Institute of Chemical Technology
 Universität Leipzig
 Linnéstraße 3, 04103 Leipzig (Germany)
 E-mail: thomas.sheppard@kit.edu

© 2024 The Authors. ChemCatChem published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

of the concept article is therefore on spatially-resolved characterization techniques that can illuminate the dynamic landscape of catalyst deactivation. A secondary emphasis is on the value of collaboration and cross-pollination of research strategies between chemistry, chemical engineering, and industry, in order to address modern challenges in catalysis.

2. Catalyst Characterization in the 21st Century: from 'still life' to 'livestreaming'

The field of catalyst characterization has undergone pronounced transformation in the past two decades. This has partly been driven by establishment of *in situ/operando* methodology, as a powerful advance over traditional *ex situ* or *post mortem* studies.^[8] Although such monitoring of catalyst structure-activity relations has proven highly successful in understanding catalytic phenomena, it is still challenging to bridge the model and technical scales. A second major advance is the development of spatially-resolved characterization methods. These can identify local heterogeneities in both the solid phase (e.g. structural characterization) and the gas-phase (e.g. activity measurements).^[9,10] Such local spatially-resolved information are highly useful to gain insights into the distribution and behavior of chemical species within a system, including the presence of local heterogeneities or physical or chemical gradients. By

combining spatially-resolved techniques together with *in situ/operando* methods, new possibilities are therefore unlocked to study structural and chemical gradients within solid catalyst bodies and chemical reactors.^[11,12] This section highlights notable examples where this approach was successfully applied to technical catalyst systems.

2.1. Gas-Phase Profiling: Probing Local Chemical Composition

Reaction products in a flow system are typically sampled at the reactor outlet under steady-state conditions. Gas-phase profiling, on the other hand, involves sampling from individual regions along the axial reactor coordinate. This imparts spatial information on local gas-phase composition and therefore extent of reaction. This is equally applicable to elementary processes, as well as more complex multi-step processes. Modern setups can perform spatial profiling measurements up to the cm scale while resolving spatial features typically at around 100 μm axial resolution. Notably, spatial profiling can be performed either with physical probing (e.g. gas sampling) or via spectroscopic probing (e.g. infrared (IR) and Raman spectroscopy, or fluorescence). Examples of such setups are briefly outlined below.

The spatially-resolved capillary-inlet mass spectrometer (SpaciMS) technique was developed in the late 1990s by Partridge et al. and was first applied to examine automotive



Shweta Sharma received her M.Sc. in Chemistry in 2019 from NIT, Jalandhar (India). During her master's, she explored applications of ionic liquids as surfactants and catalysts for lignin depolymerization. Then, she worked at CSIR-NCL, Pune (India) on catalytic synthesis of aromatic dicarbamates and CO₂ hydrogenation. Since 2021, she is a Ph.D. student in the X-ray Microscopy group of Dr. Sheppard with Prof. Grunwaldt at Institute for Chemical Technology and Polymer Chemistry at Karlsruhe Institute of Technology (Germany). Her research focuses on 3D spatial characterization of technical catalysts for emissions control with X-ray microscopy and tomography.



Dr. Florian Maurer is currently working as a postdoctoral researcher at the Institute of Technical Chemistry and Polymer Chemistry (ITCP) at the Karlsruhe Institute of Technology (KIT). At KIT, he received his Bachelor's degree in Chemistry in 2014 and his Master's degree in Chemistry in 2016. In 2021, he received his doctorate under Prof. Jan-Dierk Grunwaldt and has since been coordinator of the CRC1441 Collaborative Research Center "TrackAct" (www.trackact.kit.edu). His research focuses on *in situ* and *operando* spectroscopy of noble metal-based catalysts using hard X-rays with the aim of identifying and tracking the active sites in heterogeneous catalysts.



Dr. Patrick Lott is head of the "Pollution Control" group at the Institute for Chemical Technology and Polymer Chemistry and Chief Technology Officer at the Exhaust Gas Center Karlsruhe at the Karlsruhe Institute of Technology (KIT), Germany. After studying Chemistry and after a research stay at the University of Houston (UH), USA, he received his doctorate in Chemistry in 2019 at KIT under Prof. Olaf Deutschmann. His research aims at developing, understanding, and improving chemical reactors and processes for reducing local and global pollutants by means of *in situ* techniques that provide insights into chemical reactors with spatial and temporal resolution.



PD Dr. Thomas Sheppard obtained his PhD in Chemistry (2014) from Queen's University Belfast UK and completed habilitation in technical chemistry at Karlsruhe Institute of Technology (2023), under the mentorship of Prof. Jan-Dierk Grunwaldt. He is currently interim professor of heterogeneous catalysis at Leipzig University (2023–), visiting researcher at the German Electron-Synchrotron DESY (2020–), and an independent research group leader at Karlsruhe Institute of Technology (2018–). His research interests include a delicate balance of chemistry (catalysis), chemical reaction engineering, and X-ray physics, with a strong focus on catalyst characterisation, structure-activity relationships, and scale-bridging analyses.

catalyst systems. This method involved the use of a thin fused silica capillary to achieve quantitative and high-temporal-response measurements of honeycomb type catalysts. A sketch of the instrument is illustrated in Figure 1.^[13,14] This technique has since found various applications among several groups. In the realm of catalyst deactivation, Partridge et al. used SpaciMS to study the effect of sulfur poisoning in technical scale NO_x storage reduction catalysts depicting that sulfur accumulation led to diminished NO_x storage capacity along the catalyst, and a progressive displacement of the NO_x storage zone downstream.^[15] Goguet et al. more recently investigated CO oxidation within a commercially aged Pd/Al₂O₃ monolith catalyst using SpaciMS, discovering that deactivation significantly affected the diffusion parameters, with molecular and Knudsen diffusion being dominant in the substrate and wash-coat respectively.^[16] Deutschmann et al. studied total and partial oxidation reactions on Pt/Pd/Al₂O₃ and Rh-based catalytic monoliths, establishing correlations between catalytic activity, surface area, and aging effects.^[17–19] Schmidt and Horn et al. developed a distinct capillary technique for minimally perturbing the concentration, flow, and temperature fields in foam monolith catalysts during spatial profiling. This involved use of a capped-end capillary with a side sampling orifice, which was used to investigate both methane partial oxidation, and oxidative dehydrogenation of ethane to ethylene.^[20–22] The design introduced by Horn et al. facilitated measurements up to 1300 °C and pressures up to 45 bar, with later enhancements enabling capillary rotation for improved spatial resolution.^[23]

While early spatial profiling focused mainly on monolithic or honeycomb catalysts, the method was further developed to examine gas-phase product distribution within packed or powder catalyst beds in a minimally invasive manner, particularly by Goguet et al. who introduced the Spaci-FB (fixed bed) approach. The design featured a manual linear transfer mechanism with a closed-end sampling capillary with 3 pairs of sampling holes. Validation tests run for CO oxidation over 1 wt% Pd/Al₂O₃ demonstrated sensitivity to temperature and feed variations.^[24] Following design enhancements including automation, improved heating, and simultaneous temperature/

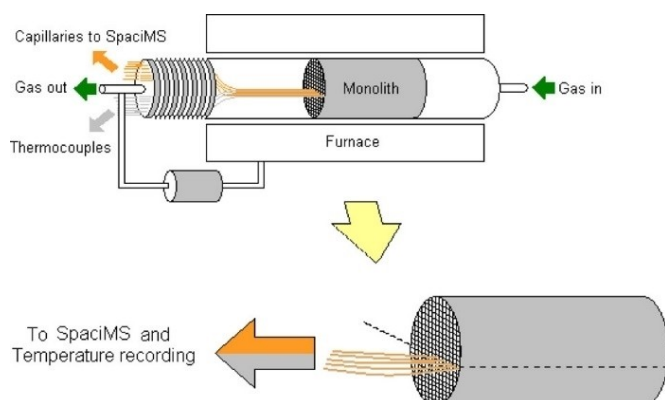


Figure 1. Sketch of SpaciMS instrument. Reproduced from reference [14] with permission from the Royal Society of Chemistry.

concentration measurements, additional catalytic tests showed improved resolution during profiling with Spaci-FB.^[25]

In terms of following the deactivation behavior of heterogeneous catalysts, spatially-resolved capillary setups offer improved accuracy over simple outlet measurements, while allowing a broad range of detectable gas-phase species with appropriate analytics (e.g. IR, MS). However, the time resolution of gas sampling makes it challenging to monitor deactivation mechanisms on the order of minutes or faster.^[14] In particular, with designs involving multiple sampling capillaries, care has to be taken regarding the invasiveness of the method.^[26] Nevertheless, by enabling local measurement of gas-phase chemistry within catalytic reactors, the spatial profiling approach provides unique characterization potential which is particularly suited for technical scale systems, as demonstrated for structured honeycombs and packed bed reactors. Typical outcomes of spatially-resolved gas-phase measurements include local kinetic behavior, local chemical potential as a function of axial position, as well as valuable information on reaction intermediates and selectivity, particularly for multistep or sequential reaction processes. However, it is equally vital to explore solid-phase transformations (discussed below) to gain insights into structural modifications and compositional dynamics, which are critical for a deep understanding of catalytic processes. This dual perspective ensures a more effective approach to catalysis research.

2.2. Solid Phase Profiling: Probing Local Structural Composition

With the awareness that the solid catalyst can be highly influenced by temperature, pressure, concentration, and flow rates for example, there has been a recent focus on developing *in situ/operando* reactors appropriate for technical scale measurements.^[27] Such systems generally allow various probes such as spectroscopy and diffraction methods to analyze the solid catalyst within the reactor. Beyond laboratory methods including IR or Raman spectroscopy, modern approaches include X-ray analytics at synchrotron radiation sources, all of which are discussed below. Synchrotron X-ray spectroscopy or diffraction are typically used to measure samples on mm scale, with resolution mainly depending on the focus size of the X-ray beam, but typically on the order of tens or hundreds of μm.

One widely used standard for spatially-resolved characterization of solid catalysts is the quartz capillary micro-reactor (CMR), as demonstrated in the early 1990s by Clausen et al. and since adopted by numerous other groups.^[28] Commonly the plug-flow geometry of such reactors mimic realistic conditions for small powder samples, while still allowing complementary characterization techniques.^[29–31] For example, Grunwaldt et al. investigated different emission control reactions such as selective catalytic reduction of NO_x by NH₃ over Cu-based catalysts; CO and hydrocarbon oxidation over Pt/CeO₂; and CO oxidation over Pt/Al₂O₃, by combining X-ray absorption spectroscopy (XAS), infrared thermography, and online mass spectrometry (MS).^[32–34] For the latter reaction, this approach uncovered

axial gradients, i.e. due to oscillatory deactivation and re-activation phenomena or related to changes in the oxidation state and size of the Pt nanoparticles, which can occur on a (sub-) second time scale. As a further example, Weckhuysen et al. combined *operando* XAS and X-ray diffraction (XRD) to reveal the formation of cobalt carbide and its effect on catalyst deactivation during Fischer–Tropsch synthesis over Co/TiO₂.^[35] The next logical progression in this field involved correlating spatial catalytic activity measurements as described previously, with spatially- and time-resolved structural studies. For this purpose, Morgan et al. pioneered the simultaneous spatial profiling of temperature, concentration, and XAS spectra in catalytic fixed beds.^[36] They investigated structural and chemical effects in the promotion of CO oxidation by hydrogen, using a so-called SPACI-FB-XAFS setup.

In order to detect local changes leading to catalyst deactivation, it is mandatory to exclude temperature or pressure gradients. Here, capillary setups often run into issues with heating, potentially resulting in non-uniform conditions that influence structural and chemical gradients.^[37] To address this, and to expand from powder catalyst beds towards larger packed beds, Horn et al. demonstrated a synchrotron compact profile reactor (CPR) optimized for XAS. The integrated design of the CPR, as shown in Figure 2, offers precise and uniform sample heating, as compared to CMR, together with capillary-based spatial profiling. This allows to study local catalyst structure as well as local activity for larger scale technical packed bed reactors, as currently demonstrated for XAS or XRD measurements.^[38,39] The reactor was used to investigate induced structural gradients caused by oxygen depletion during simulated deactivation of a 30 wt% MoO₃/γ-Al₂O₃ catalyst for oxidative dehydrogenation of ethane to ethylene.

The measurement concept of spatial profiling in the gas-phase, combined with spectroscopic or diffraction probing of the solid phase, illustrates a promising approach for combined spatially-resolved structure–activity profiling, mainly in terms of deactivation. However, catalyst deactivation occurs on multiple length scales, from atomic or nanoscale changes to macroscopic alterations. Thus, understanding deactivation phenomena at each level becomes crucial in bridging the knowledge and scale gap between model and technical catalyst systems.

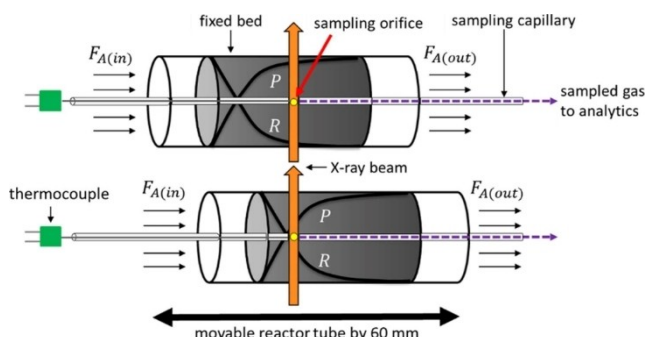


Figure 2. Working principle of the spatial profile measurement technique. F_A denotes the molar flow rate of a chemical species in the reaction mixture. Reproduced from reference [39], under the terms and conditions of the Creative Commons license (CC BY 4.0).

2.3. Chemical Imaging: Resolving Structure–Activity Relationships in 2D and 3D

Chemical imaging here refers to spatially-resolved methods which generate localized 2D microscopic or 3D tomographic information collected over a specific field of view, in this case a solid catalyst body or reactor. By analyzing catalysts under working conditions, local chemical information can further be related to catalyst structure. The chemical imaging approach at both macro- and micro- scales has gained importance over the last decade.^[40] In further detail, this section is divided into infrared (IR) imaging, optical or visible-wavelength imaging (i.e. Raman spectroscopy), and X-ray imaging, each of which provides specialized insights into the chemical composition or the solid structure of catalyst bodies. In this way, deactivation phenomena can be identified and linked across multiple length and complexity scales from sub-nm regime up to mm scale or above.

2.3.1. Infrared Imaging

IR spectroscopy or imaging, based on the coupling of an IR spectrometer and an optical microscope, provides detailed information about molecular structures and chemical bonds, including dynamic changes in surface structure or adsorbates under operating conditions.^[41] Modern applications of IR imaging extend beyond crystal model systems to technical catalysts based on zeolites. For example, Weckhuysen et al. evaluated acidity variations in single fluid catalytic cracking (FCC) catalyst particles with IR microscopy, revealing inconsistencies in acid site distribution resulting from industrial deactivation protocols.^[42] IR imaging has also been used for mapping 1D spatial distributions of reactants and products in a flow microreactor as demonstrated by Somorjai et al. for the synthesis of dihydrofuran over Au nanoparticles.^[43] The same study illustrated the synergy between IR imaging and X-ray microspectroscopy. Kim et al. developed an *operando* IR thermography system for high-throughput screening of catalytic reactivity in ozone-assisted oxidation under realistic operating conditions, providing two-dimensional temperature distribution in the catalyst bed, which is sensitive in detecting undesirable “hot-spot” formation, as illustrated in Figure 3.^[44] IR imaging therefore has demonstrated versatile applications in the study of local surface structure and structural heterogeneities, even extended to technical catalyst bodies.

Although IR imaging is a powerful technique to understand dynamics in catalytic reactions, achieving higher spatial resolution, improving spectral analysis methods, and enhancing instrument sensitivity are crucial for advancing the field of IR imaging. Providing more accurate insights into gas–solid interactions at the catalyst surface and on the active sites can contribute to understanding reaction mechanisms, and therefore optimization of catalyst design and performance.

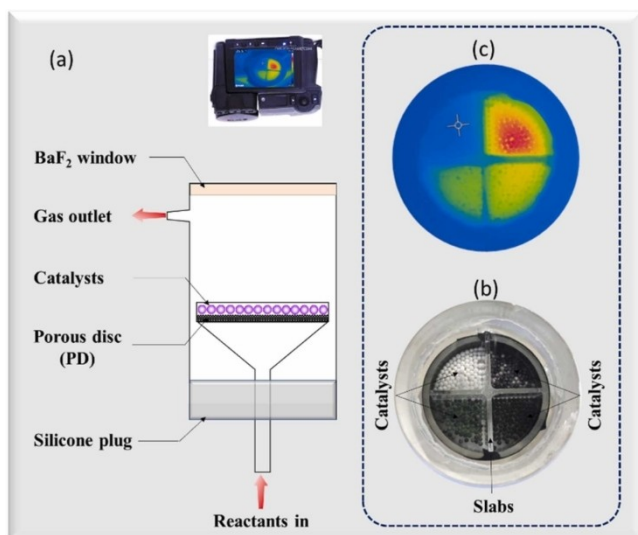


Figure 3. a) Schematic diagram of the IR thermography system, b) upper view of the IR cell containing 4 catalysts under reactions, and c) IR thermography of catalysts in (b). Reprinted with permission from reference [44], © 2022 Elsevier B. V.

2.3.2. Optical Imaging

Optical imaging includes a diverse set of techniques such as Raman spectroscopy, UV-vis, and optical fluorescence imaging, allowing for an accurate understanding of catalytic mechanisms. These methods can for example be combined with confocal microscopy, offering non-invasive high-resolution visualization of both surface and interior sample structure and therefore deactivation phenomena like leaching or volatilization. In this context, Wachs and Briand et al. employed Raman imaging to determine the distribution of crystalline MoO₃ in spent bulk Fe–Mo based methanol oxidation catalyst pellets.^[45] This led to development of a novel regeneration method, tackling the issue related to Mo–OCH₃ volatilization and methanol transport limitations in catalyst pellets. Additionally, Weckhuysen et al. mapped large zeolite ZSM-5 crystals with confocal Raman spectroscopy to identify structural and chemical changes induced during a steam treatment,^[46] while Bonino et al. focused on deactivation of acidic zeolites due to leaching of aluminum atoms from the framework.^[47]

Since *in situ* or *operando* measurements often hold greater scientific relevance over *post mortem* studies on catalyst materials, there are numerous examples of optical imaging to study catalysis and/or deactivation while obtaining real-time information. Moulijn et al. applied time-resolved Raman imaging to measure coke profiles in industrial spent hydroprocessing catalyst pellets.^[48] Roefflaers et al. applied a combination of Raman microscopy, SEM and confocal fluorescence microscopy (CFM) to investigate dealuminated mordenite (MOR) zeolite particles, uncovering intra- and interparticle heterogeneities in Brønsted acid site distribution, as depicted in Figure 4.^[49] Although Raman spectroscopy is a useful technique to characterize carbon species under reaction conditions, inherent fluorescence from some samples, e.g. as in the case of zeolite-

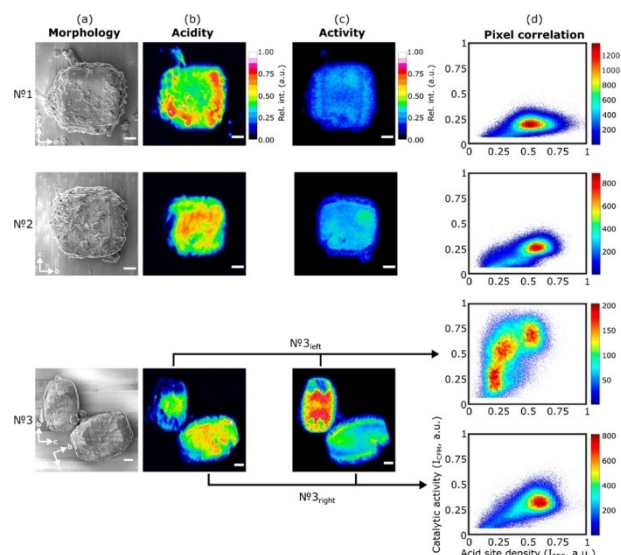


Figure 4. a) SEM images of Meso-MOR crystals (scale bar = 2 μm). b) Raman images (1006 cm⁻¹) of the pyridinium ion adsorbed in the crystals after evacuation at 150 °C (scale bar = 2 μm). c) CFM image of the furfuryl alcohol oligomers formed and accumulated within the dealuminated mordenite crystals after 20 min of reaction (scale bar = 2 μm). d) Correlation plot of the intensity of CFM versus Raman microscopy pixel per pixel. The heat map indicates the corresponding amount of correlations per bin. Reprinted with permission from reference [49]. Copyright © 2020 American Chemical Society.

based catalysts, may hinder data interpretation and thus impede drawing unambiguous conclusions. In this context, Beale et al. utilized *operando* Kerr-gated Raman spectroscopy, that can differentiate between the Raman signal and fluorescence based on the temporal differences between the two processes. This approach provided insights into the formation and evolution of active and deactivating hydrocarbon species, respectively, during the methanol-to-olefins (MTO) reaction on zeolite catalysts.^[50]

A later review explored novel tools to directly observe the 3D distribution of contaminant species within catalyst pore networks, mainly in industrially relevant systems.^[51] Utilizing UV-vis micro-spectroscopy and confocal fluorescence microscopy, Weckhuysen et al. explored the Brønsted acidity, spatial reactivity, and deactivation of zeolite Y- or ZSM-5-based FCC catalyst particles and examined the interaction and location of thiophene-like poisons in such catalysts.^[52] The group also investigated the influence of an external silicalite-1 shell on the acidity and coke formation process of H-ZSM-5 crystals using the same combination of techniques under *in situ* conditions.^[53] Optical imaging therefore provides a useful counterpart to IR imaging particularly in terms of coking and other poisoning or fouling mechanisms, which has been shown for such deactivation studies on technical catalyst systems.

Despite promising results in the field of optical imaging of technical catalysts, there are certain challenges in UV-Vis and Raman applications, including limited spatial resolution, possible interference from fluorescence effects, and poor signal-to-noise ratio due to the weak Raman scattering signal. Modern developments in this field to address these issues may include:

(i) use of super-resolution imaging, which although mainly known in life sciences is finding increasing applications for inorganic materials research, including catalysis;^[54] (ii) fluorescence suppression in Raman spectroscopy for example by utilizing UV wavelengths, or time-resolved measurements;^[55] (iii) integrating optical imaging with complementary techniques such as gas phase analysis, or high-resolution electron microscopy.^[56] These complementary imaging strategies may enhance the depth of insights into the structure and behavior of technical catalysts.

2.3.3. X-ray Imaging

Hard X-ray microscopy and computed tomography (CT) provide a powerful toolbox for exploring relatively large samples such as technical catalysts. This is enabled by the high penetration depth of X-ray radiation in comparison to the above-mentioned methods, as highlighted in a recent review paper by our group.^[57] X-ray tomography in particular can provide a comprehensive spatially-resolved view of interior composition and structure within entire catalyst samples up to technical scale, without causing significant structural damage.^[57] Large-scale research infrastructures such as synchrotron radiation sources are especially useful for such studies, as they offer high intensity X-rays with tunable energy and therefore broad experimental flexibility. This allows the measurement of samples with a wide range of sizes e.g. μm - to cm -scale, and with variable spatial resolution, e.g., nm - to μm -scale, along with the application of various chemical contrast modes e.g. XAS, XRD or X-ray fluorescence (XRF).^[58,59]

In the context of catalyst deactivation, which often involves minute changes in local structure or composition, high resolution imaging with high sensitivity is particularly beneficial. Phase contrast imaging methods including ptychographic X-ray computed tomography (PXCT) or holographic X-ray computed tomography (HXCT) are therefore highly relevant in the study of complex solid samples, such as in heterogeneous catalysis research. Both PXCT and HXCT provide exceptional spatial resolution and quantitative information on local electron density.^[60,61] This is particularly useful for deactivation methods involving light elements such as carbon and sulfur, which can be challenging to resolve with absorption contrast imaging. Electron density information has been applied to detect and localize coking, as demonstrated in studies on artificially coked $\text{Ni}/\text{Al}_2\text{O}_3$ catalysts using PXCT by our group, and similarly for an industrial FCC catalyst particle by Meirer et al. using holotomography.^[62,63] This illustrates that electron density data from PXCT or HXCT offers a level of chemical sensitivity, complementing the high spatial resolution of the measurements.

Beyond high resolution studies, tomography offers the possibility to combine multiscale and multimodal imaging by employing different X-ray contrast modes. For example, Beale et al. combined XRF-CT, XAS-CT and XRD-CT to explore the degradation of a single FCC catalyst particle, detecting Ni and V species as contaminants with egg-shell distribution of Ni.^[64]

Similarly, Bare et al. correlated metal poisons and zeolite degradation in spent FCC catalyst particles through X-ray nanotomography, XRF, and XRD mapping.^[65] Meirer et al. expanded this method using XRF-CT to map a broad range of deposited metal impurities (Fe, Ni, V, Ca) as well as catalyst constituents (La, Ti) with submicron voxel size (resolution of ca. $1.4 \mu\text{m}$) and high chemical sensitivity, as clearly indicated in Figure 5.^[66] While FCC particles have been thoroughly studied in early explorations of hard X-ray imaging, these methods have started to expand towards other technical systems including Ziegler-Natta polymerization catalysts, and vanadium phosphate catalyst for butane oxidation to maleic anhydride.^[67,68]

The potent capabilities of hard X-ray tomography for both structural and chemical characterization have furthermore been combined with *in situ* or *operando* measurements. This effectively enables visualization of structure-activity relationships in 3D space, showing a dynamic portrait of catalysts in action. Wragg et al. employed *operando* XRD-CT revealing the radial and axial gradients in coke deposition within a zeolite/ Al_2O_3 -based catalyst extrudate during methanol-to-hydrocarbon conversion. The study demonstrated that a significant portion of extrudate remained completely untouched, indicating incomplete catalyst utilization.^[69] Beale et al. combined μ -XRD-CT with atomic pair distribution function CT (μ -PDF-CT) to reveal the spatial distribution and evolution of Co-containing phases in a

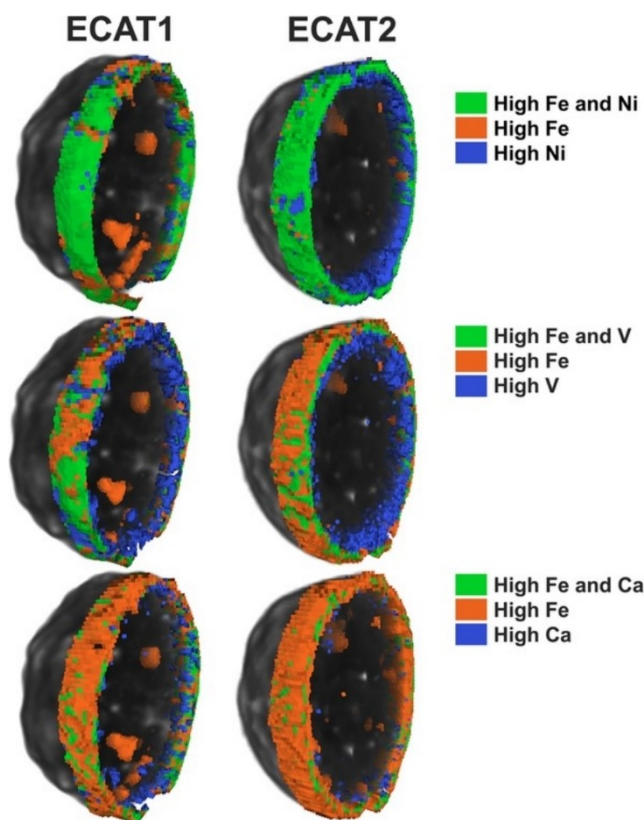


Figure 5. 3D volumes representing regions of high concentration, indicating correlation between specific metal pairs. Reproduced from reference [66], under the terms and conditions of the Creative Commons CC BY-NC 4.0 license.

Co/ γ -Al₂O₃ catalyst pellet during reduction and under Fischer–Tropsch synthesis (FTS) conditions, implying the dependence of catalyst deactivation on the original synthesis parameters. The findings illustrated the challenges in generating a structured FTS-active Co/ γ -Al₂O₃ pellet, emphasizing the potential value of *in situ* chemical imaging in optimizing the design of industrial catalysts.^[70] The same group later used 5D tomographic diffraction imaging to explore the spatial and temporal physicochemical changes in Ni–Pd/CeO₂–ZrO₂/Al₂O₃ catalysts for methane reforming under different chemical environments. The experiments revealed the formation of an unstable Ni–Pd metallic alloy, the deposition of graphitic carbon, and the impact of the interaction between the catalyst components.^[71] As these methods gain increasing attention from the catalysis community, numerous other applications are expected in future.

While the golden rule of tomography means compromising between two out of three optimal parameters – measurement time, sample size, and spatial resolution–future advances in synchrotron radiation, particularly the transition to 4th generation sources with higher brilliance, promises to overcome these limitations.^[57] Moreover, the further development of sample environments for *in situ/operando* measurements will play a central role in further understanding deactivation phenomena at technical scale. An additional aspect to consider with the acquisition of larger and more complex datasets is the role of machine learning methods to aid in image processing and interpretation. This will become increasingly relevant as data volumes become too numerous or complex to evaluate manually in all situations. In the context of chemical imaging, early applications of machine learning have been demonstrated for evaluating XRD–CT datasets by Jacques et al.,^[72] while efforts in XAS interpretation by machine learning particularly in the context of *operando* measurements have been advanced by

Timoshenko et al. and Frenkel et al.,^[73] although this has not yet been extended to tomography. In conclusion, the profound capabilities of X-ray imaging open new frontiers for gaining insights into structural and chemical dynamics of technical scale catalysts. Ideally, these insights can facilitate targeted improvements in catalytic systems by providing a unique source of localized structural data at high resolution, even on larger technical systems.

2.3.4. Regarding Complementary High-Resolution Imaging Methods

It should be noted that other complementary methods exist for high-resolution imaging of catalyst materials (Figure 6), notably including atomic scale methods such as transmission electron microscopy (TEM) and atom probe tomography (APT), which have been extensively reviewed elsewhere.^[74,75] These methods, while providing optimal spatial resolution, are however highly limited in the applicable field of view. In the context of this perspective article, which addresses technical scale catalyst systems, the above methods are inevitably performed on model samples (this includes minute sub-volumes extracted from technical samples) or under model conditions. In summary, there is a risk of providing unrepresentative results due to the discrepancy between the visible field of view (e.g. 10–100 nm scale) and the parent sample size (e.g. mm–cm scale). This is a widely acknowledged limitation in literature which is particularly relevant with increasing sample complexity, such as in composite catalyst materials. In contrast, the approaches discussed in section 2.3 operate at universally lower spatial resolution, but are applicable to extended sample volumes, therefore bridging the length scale between model systems and technical applications.

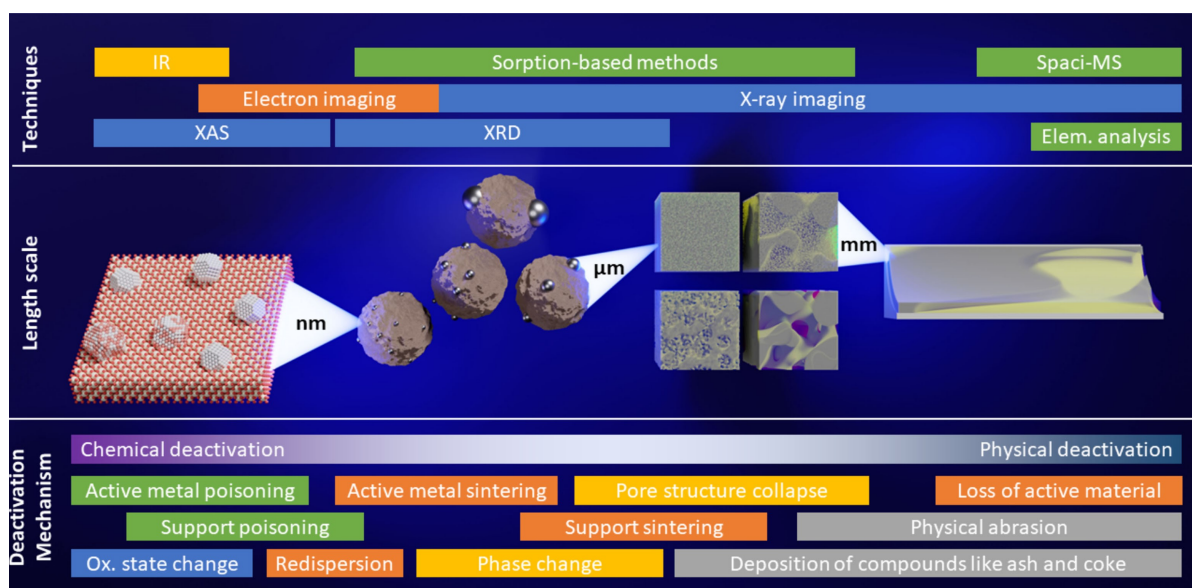


Figure 6. Illustration of deactivation mechanisms related to changes in oxidation state (highlighted blue), poisoning (green), migration (orange), macro-structure (yellow) of the catalyst or other phenomena, and selected potential spatial characterization techniques (based on using X-rays (blue), electrons (orange), IR (yellow) or other methods (green) across multiple length scales.

3. Summary and Outlook

Technical catalytic systems have inherent structural complexity which increases with length scale, extending beyond that of analogous model systems. Understanding the deactivation mechanisms of such technical catalysts is crucial for eventually proposing methods to enhance their efficiency and longevity. Traditional characterization methods often fall short in providing detailed insights into the spatially-resolved changes occurring within technical catalysts during operation. Such dynamic changes may include formation of chemical gradients within the catalyst particle or pellet, as well as spatial variations in temperature, gas species concentration, or other structural gradients along the catalyst bed within the reactor. Recent advances in spatially-resolved methods include simultaneous application of complementary *operando* spectroscopy or microscopy techniques along the reactor, presenting novel pathways for unraveling structure-activity relationships on a larger scale. Scale-bridging techniques are key to success and a careful choice of the respective method, possibly even a combination of complementary methods, is often essential to properly address catalyst deactivation. This is especially relevant on technical scale, where a multitude of deactivation mechanisms may occur sequentially or simultaneously. Figure 6 illustrates the intricate landscape of deactivation mechanisms in heterogeneous catalysis occurring over multiple length scales, along with an overview of selected spatial characterization methods. Such methods include local observation of the gas-phase in solid-gas catalyzed processes, along with local probing of solid structure. These methodologies not only aid in identifying localized deactivation patterns but may also contribute to strategies for optimizing catalyst performance in various industrial applications. By resolving spatial heterogeneities within technical catalysts, these can in principle be further related to kinetic modelling, flow simulations, transport phenomena, or numerous other outlets, therefore providing valuable information for optimization of catalyst design. This concept briefly outlines several such spatially-resolved characterization tools which we believe still have untapped potential for the study of technical catalysts, and particularly their deactivation or regeneration.

Acknowledgements

We gratefully acknowledge current and former colleagues and cooperation partners, particularly those at Karlsruhe Institute of Technology (Prof. Dr. Jan-Dierk Grunwaldt, Prof. Dr. Olaf Deutschmann, Dr. Sebastian Weber, Dr. Reihaneh Pashminehazar, Dr. Johannes Becher, Srashtasrita Das, Leonardo Almeida de Campos). We thank the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) for financial support via CRC 1441 "TrackAct" (Project ID 426888090). S. S. thanks YounGeCats for the opportunity to showcase parts of this research at the annual meeting of the German Catalysis Society in Weimar (2023). Open Access funding enabled and organized by Projekt DEAL.

Conflict of Interests

The authors declare no conflict of interest.

Keywords: Deactivation · Characterization · Heterogeneous Catalysis · Spatially-resolved · Technical Catalyst

- [1] I. Melián-Cabrera, *Ind. Eng. Chem. Res.* **2021**, *60*, 18545–18559.
- [2] S. L. Scott, *ACS Catal.* **2018**, *8*, 8597–8599.
- [3] F. Gramigni, U. Iacobone, N. D. Nasello, T. Sella, N. Usberti, I. Nova, *Ind. Eng. Chem. Res.* **2021**, *60*, 6403–6420.
- [4] S. Mitchell, N.-L. Michels, J. Pe'rez-Ramirez, *Chem. Soc. Rev.* **2013**, *42*, 6094; *rez, Chem. Soc. Rev.* **2013**, *42*, 6094.
- [5] A. Beck, M. Zabitskiy, M. A. Newton, O. Safonova, M. G. Willinger, J. A. Bokhoven, *Nat. Catal.* **2021**, *4*, 488–497.
- [6] U. I. Kramm, R. Marschall, M. Rose, *ChemCatChem* **2019**, *11*, 2563–2574.
- [7] A. J. Martín, S. Mitchell, C. Mondelli, S. Jaydev, J. Pérez-Ramírez, *Nat. Catal.* **2022**, *5*, 854–866.
- [8] B. M. Weckhuysen, *Phys. Chem. Chem. Phys.* **2003**, *5*, 4351–4360.
- [9] J.-D. Grunwaldt, B. S. Clausen, *Top. Catal.* **2002**, *18*, 37–43.
- [10] A. M. Beale, S. D. M. Jacques, B. M. Weckhuysen, *Chem. Soc. Rev.* **2010**, *39*, 4656–4672.
- [11] M. Geske, O. Korup, R. Horn, *Catal. Sci. Technol.* **2013**, *3*, 169.
- [12] D. Livio, C. Diehm, A. Donazzi, A. Beretta, O. Deutschmann, *Appl. Catal. A* **2013**, *467*, 530–541.
- [13] J.-S. Choi, W. P. Partridge, C. S. Daw, *Appl. Catal. A* **2005**, *293*, 24–40.
- [14] J. Sá, D. Luis Abreu Fernandes, F. Aiouache, A. Goguet, C. Hardacre, D. Lundie, W. Naeem, W. P. Partridge, C. Stere, *Analyst* **2010**, *135*, 2260–2272.
- [15] J.-S. Choi, W. P. Partridge, C. S. Daw, *Appl. Catal. B* **2007**, *77*, 145–156.
- [16] Y. Wang, C. Stere, G. McCullough, M. Li, A. Goguet, *Catal. Sci. Technol.* **2023**, *13*, 1802.
- [17] K. A. Karinshak, P. Lott, M. P. Harold, O. Deutschmann, *ChemCatChem* **2020**, *12*, 3712–3720.
- [18] M. Hettel, C. Diehm, B. Torkashvand, O. Deutschmann, *Catal. Today* **2013**, *216*, 2–10.
- [19] D. Chan, S. Tischer, J. Heck, C. Diehm, O. Deutschmann, *Appl. Catal. A* **2014**, *156–157*, 153–165.
- [20] R. Horn, K. Williams, N. Degenstein, L. Schmidt, *J. Catal.* **2006**, *242*, 92–102.
- [21] R. Horn, N. J. Degenstein, K. A. Williams, L. D. Schmidt, *Catal. Lett.* **2006**, *110*, 169–178.
- [22] B. C. Michael, D. N. Nare, L. D. Schmidt, *Chem. Eng. Sci.* **2010**, *65*, 3893–3902.
- [23] R. Horn, O. Korup, M. Geske, U. Zavyalova, I. Oprea, R. Schlögl, *Rev. Sci. Instrum.* **2010**, *81*, 64102.
- [24] J. Touitou, K. Morgan, R. Burch, C. Hardacre, A. Goguet, *Catal. Sci. Technol.* **2012**, *2*, 1811–1813.
- [25] J. Touitou, R. Burch, C. Hardacre, C. McManus, K. Morgan, J. Sá, A. Goguet, *Analyst* **2013**, *138*, 2858–2862.
- [26] T. Hlavatý, P. Kočí, M. Isoz, D. Deka, W. Partridge, *Chem. Eng. Sci.* **2023**, *282*, 119272.
- [27] M. A. Bañares, M. Daturi, *Catal. Today* **2023**, *423*, 114255.
- [28] B. S. Clausen, G. Steffensen, J. Villadsen, R. Feidenhans'l, H. Topsøe, *J. Catal.* **1991**, *132*, 524–535.
- [29] J.-D. Grunwaldt, S. Hannemann, C. G. Schroer, A. Baiker, *J. Phys. Chem. B* **2006**, *110*, 8674–8680.
- [30] F. Maurer, J. Jelic, J. Wang, A. Gänzler, P. Dolcet, C. Wöll, Y. Wang, F. Studt, M. Casapu, J.-D. Grunwaldt, *Nat. Catal.* **2020**, *3*, 824–833.
- [31] J. Becher, S. Weber, D. Ferreira Sanchez, D. E. Doronkin, J. Garrevoet, G. Falkenberg, D. M. Meira, S. Pascarelli, J.-D. Grunwaldt, T. L. Sheppard, *Catalysts* **2021**, *11*, 459.
- [32] A. M. Gänzler, M. Casapu, A. Boubnov, O. Müller, S. Conrad, H. Lichtenberg, R. Frahm, J.-D. Grunwaldt, *J. Catal.* **2015**, *328*, 216–224.
- [33] F. Maurer, A. Gänzler, P. Lott, B. Betz, M. Votsmeier, S. Lorient, P. Vernoux, V. Murzin, B. Bornmann, R. Frahm, O. Deutschmann, M. Casapu, J.-D. Grunwaldt, *Ind. Eng. Chem. Res.* **2021**, *60*, 6662–6675.
- [34] D. E. Doronkin, M. Casapu, T. Günter, O. Müller, R. Frahm, J.-D. Grunwaldt, *J. Phys. Chem. C* **2014**, *118*, 10204–10212.
- [35] I. K. Van Ravenhorst, A. S. Hoffman, C. Vogt, A. Boubnov, N. Patra, R. Oord, C. Akatay, F. Meirer, S. R. Bare, B. M. Weckhuysen, *ACS Catal.* **2021**, *11*, 2956–2967.

- [36] C. C. Stewart, E. K. Gibson, K. Morgan, G. Cibin, A. J. Dent, C. Hardacre, E. V. Kondratenko, V. A. Kondratenko, C. Mcmanus, S. Rogers, C. E. Stere, S. Chansai, Y.-C. Wang, S. J. Haigh, P. P. Wells, A. Goguet, *ACS Catal.* **2018**, *8*, 8255–8262.
- [37] M. A. Newton, S. Checchia, A. J. Knorpp, D. Stoian, W. Van Beek, H. Emerich, A. Longo, J. A. Van Bokhoven, *Catal. Sci. Technol.* **2019**, *9*, 3081.
- [38] B. Wollak, D. E. Doronkin, D. Espinoza, T. L. Sheppard, O. Korup, M. Schmidt, S. Alizadefanloo, F. Rosowski, C. Schroer, J.-D. Grunwaldt, R. Horn, *J. Catal.* **2022**, *408*, 372–387.
- [39] B. Wollak, D. Espinoza, A.-C. Dippel, M. Sturm, F. Vrljic, O. Gutowski, I. G. Nielsen, T. L. Sheppard, O. Korup, R. Horn, *J. Synchrotron Radiat.* **2023**, *30*, 571–581.
- [40] J.-D. Grunwaldt, J. B. Wagner, R. E. Dunin-Borkowski, *ChemCatChem* **2013**, *5*, 62–80.
- [41] E. Stavitski, B. M. Weckhuysen, *Chem. Soc. Rev.* **2010**, *39*, 4615–4625.
- [42] I. L. C. Buurmans, F. Soulimani, J. Ruiz-Martínez, H. E. van der Bij, B. M. Weckhuysen, *Microporous Mesoporous Mater.* **2013**, *166*, 86–92.
- [43] E. Gross, X.-Z. Shu, S. Alayoglu, H. A. Bechtel, M. C. Martin, F. D. Toste, G. A. Somorjai, *J. Am. Chem. Soc.* **2014**, *136*, 3624–3629.
- [44] A. A. Abdelaziz, Y. Teramoto, T. Nozaki, H. Kim, *Appl. Catal. A* **2022**, *644*, 118843.
- [45] H. Tian, I. E. Wachs, L. E. Briand, *J. Phys. Chem. B* **2005**, *109*, 23491–23499.
- [46] Ö. Attila, H. E. King, F. Meirer, B. M. Weckhuysen, *Chem. Eur. J.* **2019**, *25*, 7158–7167.
- [47] M. Signorile, F. Bonino, A. Damin, S. Bordiga, *J. Phys. Chem. C* **2016**, *120*, 18088–18092.
- [48] B. M. Vogelaar, A. D. van Langeveld, S. Eijssbouts, J. A. Moulijn, *Fuel* **2007**, *86*, 1122–1129.
- [49] G. Fleury, M. B. J. Roeffaers, *ACS Catal.* **2020**, *10*, 14801–14809.
- [50] I. Lezcano-Gonzalez, E. Campbell, A. E. J. Hoffman, M. Bocus, I. V. Sazanovich, M. Towrie, M. Agote-Aran, E. K. Gibson, A. Greenaway, K. De Wispelaere, V. Van Speybroeck, A. M. Beale, *Nat. Mater.* **2020**, *19*, 1081–1087.
- [51] E. T. C. Vogt, D. Fu, B. M. Weckhuysen, *Angew. Chem. Int. Ed.* **2023**, *62*, e202300319.
- [52] J. Ruiz-Martínez, I. L. C. Buurmans, W. V. Knowles, D. van der Beek, J. A. Bergwerff, E. T. C. Vogt, B. M. Weckhuysen, *Appl. Catal. A* **2012**, *419–420*, 84–94.
- [53] S. P. Verkleij, G. T. Whiting, S. P. Esclapez, S. Li, M. M. Mertens, M. Janssen, A.-J. Bons, M. Burgers, B. M. Weckhuysen, *ChemCatChem* **2020**, *12*, 5465–5475.
- [54] D. Wöll, C. Flors, *Small Methods* **2017**, *1*, 1700191.
- [55] C. Hess, *Chem. Soc. Rev.* **2021**, *50*, 3519–3564.
- [56] J. Van Loon, A. V. Kubarev, M. B. J. Roeffaers, *ChemNanoMat* **2017**, *4*, 6–14.
- [57] S. Das, R. Pashminehazar, S. Sharma, S. Weber, T. L. Sheppard, *Chem. Ing. Tech.* **2022**, *94*, 1591–1610.
- [58] J.-D. Grunwaldt, C. G. Schroer, *Chem. Soc. Rev.* **2010**, *39*, 4741–4753.
- [59] A. M. Beale, S. D. M. Jacques, B. M. Weckhuysen, *Chem. Soc. Rev.* **2010**, *39*, 4656–4672.
- [60] F. Pfeiffer, *Nat. Photonics* **2017**, *12*, 9–17.
- [61] P. Cloetens, W. Ludwig, J. Baruchel, D. Van Dyck, J. Van Landuyt, J. P. Guigay, M. Schlenker, *Appl. Phys. Lett.* **1999**, *75*, 2912–2914.
- [62] S. Weber, D. Batey, S. Cipiccia, M. Stehle, K. L. Abel, R. Gläser, T. L. Sheppard, *Angew. Chem. Int. Ed.* **2021**, *60*, 21772–21777.
- [63] M. Vesely, R. Valadian, L. Merten Lohse, M. Toepperwien, K. Spiers, J. Garrevoet, E. T. C. Vogt, T. Salditt, B. M. Weckhuysen, F. Meirer, *ChemCatChem* **2021**, *13*, 2494–2507.
- [64] J. Ruiz-Martínez, A. M. Beale, U. Deka, M. G. O'Brien, P. D. Quinn, J. F. W. Mosselmans, B. M. Weckhuysen, *Angew. Chem. Int. Ed.* **2013**, *52*, 5983–5987.
- [65] S. R. Bare, M. E. Charochak, S. D. Kelly, B. Lai, J. Wang, Y. K. Chen-Wiegart, *ChemCatChem* **2014**, *6*, 1427–1437.
- [66] S. Kalirai, U. Boesenberg, G. Falkenberg, F. Meirer, B. M. Weckhuysen, *ChemCatChem* **2015**, *7*, 3674–3682.
- [67] K. W. Bossers, R. Valadian, S. Zanon, R. Smeets, N. Friederichs, J. Garrevoet, F. Meirer, B. M. Weckhuysen, *J. Am. Chem. Soc.* **2020**, *142*, 3691–3695.
- [68] J. Ihli, L. Bloch, S. Boecklein, P. Rzepka, M. Burghammer, J. C. Da Silva, G. Mestl, J. A. Van Bokhoven, *ACS Catal.* **2021**, *11*, 8274–8283.
- [69] D. S. Wragg, G. N. Kalantzopoulos, D. K. Pappas, I. Pinilla-Herrero, D. Rojo-Gama, E. Redekop, M. Di, P. Beato, L. F. Lundegaard, S. Svelle, *J. Catal.* **2021**, *401*, 1–6.
- [70] P. Senecal, S. D. M. Jacques, M. Di Michiel, S. A. J. Kimber, A. Vamvakeros, Y. Odarchenko, I. Lezcano-Gonzalez, J. Paterson, E. Ferguson, A. M. Beale, *ACS Catal.* **2017**, *7*, 2284–2293.
- [71] D. Matras, A. Vamvakeros, S. D. M. Jacques, V. Middelkoop, I. Z. Ismagilov, E. V. Matus, *J. Mater. Chem. A* **2021**, *9*, 11331–11346.
- [72] N. E. Omori, A. D. Bobitan, A. Vamvakeros, A. M. Beale, S. D. M. Jacques, *Phil. Trans. R. Soc. A* **2022**, *381*, 20220350.
- [73] J. Timoshenko, A. I. Frenkel, *ACS Catal.* **2019**, *9*, 10192–10211.
- [74] D. S. Su, B. Zhang, R. Schlögl, *Chem. Rev.* **2015**, *115*, 2818–2882.
- [75] T. Li, A. Devaraj, N. Kruse, *Cell Rep. Phys. Sci.* **2022**, *3*, 101188.

Manuscript received: December 15, 2023
Revised manuscript received: February 19, 2024
Accepted manuscript online: February 19, 2024
Version of record online: March 8, 2024