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An Advanced Characterization Toolbox for Selective Olefin Oxidation Catalysts

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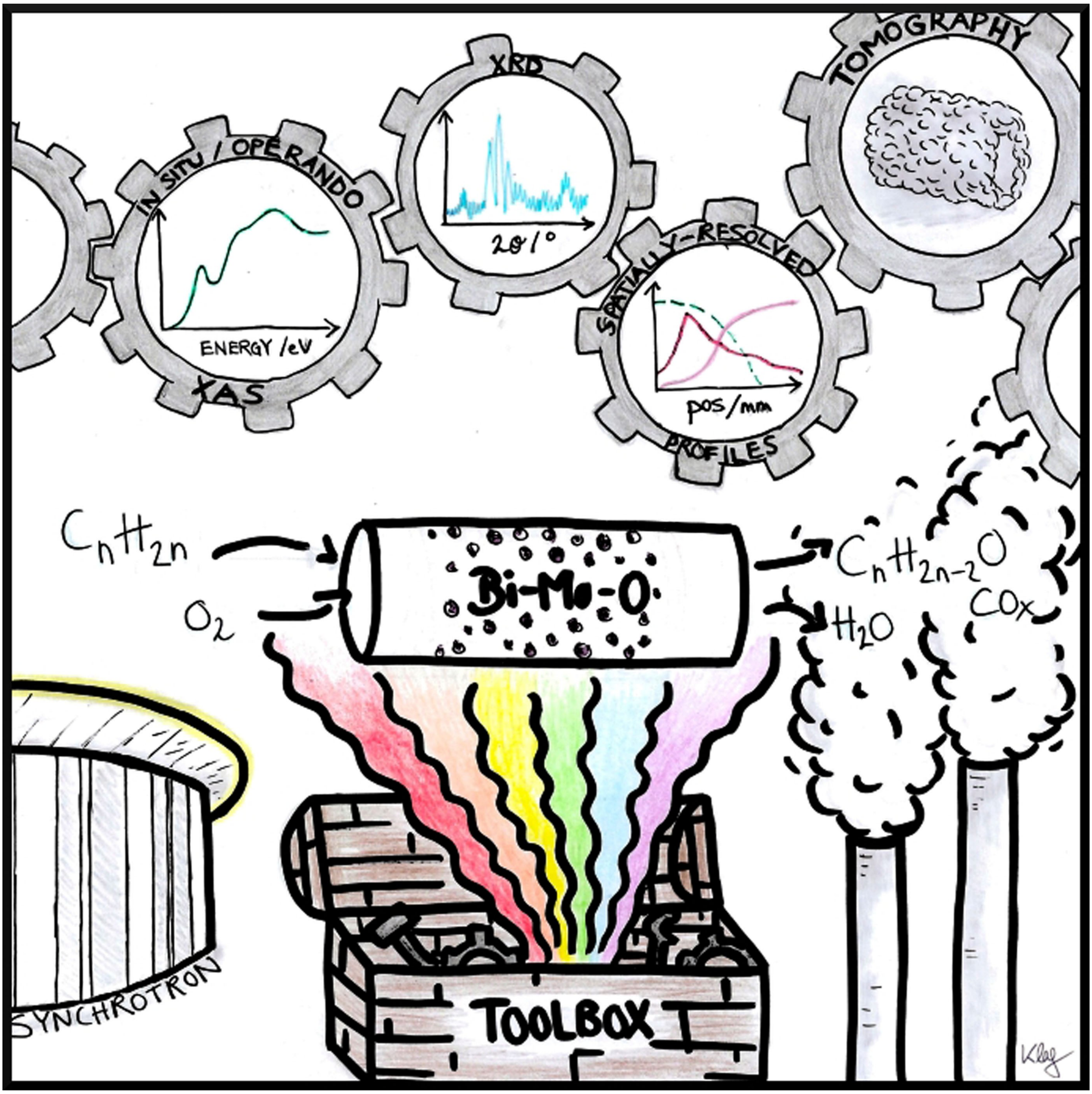

The selective oxidation of propylene and isobutene form a central cornerstone in chemical industry, typically catalysed by bismuth molybdate based multicomponent systems. Over the past decades, a detailed knowledge has been gained on the mechanism by theoretical and experimental studies including *in situ* and *operando* characterization techniques, using simplified model catalysts. These have provided excellent insight, but in industrially applied selective oxidation typically multicomponent catalysts are used, leading to higher activity and selectivity. New concepts and characterization methods allow now studies of the more complex multicomponent catalysts covering the various length and time scales and potentially providing new insights into the dynamics and cooperation during catalysis. Starting with an overview of past concepts and milestones, we report on latest developments and future trends in the field of selective oxidation of lower olefins. Thereby we focus both on conventional spectroscopic and advanced characterisation methods and discuss the importance of integral and spatially-resolved approaches. We conclude that fundamental understanding of such complex oxidation reactions requires combined and interdisciplinary research, now possible with the new characterization tools, data analysis schemes and reactor modelling approaches. This allows bridging the various complexity scales.

1. Introduction

Selective oxidation reactions play a key role in chemical industry for the functionalization of hydrocarbons.[1] Industrially-relevant products include acrolein and methacrolein, both mainly used as intermediates for the production of *e.g.* plastics.[2] Typical synthesis routes over multi-element mixed metal oxides involve selective oxidation of propylene or isobutene, respectively. Here, bismuth molybdate based catalysts have been established as the dominant catalyst system over the past decades.[3–5] Using typically the *trial and error* approach, historical industrial catalyst development has primarily aimed for higher yields of the desired products. In this context, significant progress in terms of improving selective oxidation process efficiency has been made since the early 1950's, with increasing yields up to 90% in propylene oxidation.[2] At the same time, this rapid development of several generations of bismuth molybdate based catalysts with increasing structural and compositional complexity has resulted in knowledge gaps regarding the fundamental understanding of the catalyst working principles. Although selective propylene oxidation to acrolein in particular is considered as a mature, industrially established technology, further optimization is still being pursued to improve catalyst performance. Since neither selective propylene nor isobutene oxidation runs at a maximum yield of 100%, decreasing the number of undesired by-products, *e.g.* CO_2, is one of the major challenges currently being addressed in industry. Thus, this fine tuning of the existing processes includes an optimization towards more efficient and environmental-friendlier catalysts..[6–7]

Standard catalyst systems for selective propylene and isobutene oxidation can be described with the general formula Mo–Bi-M^{II}-M^{III}-M^{I}-X–Y-O (*e.g.* M^{II} = Co, Ni; M^{III} = Fe, Cr; M^{I} = Na, K; X=Sb, Te; Y=P, B).[8] Hence, modern bismuth molybdate based catalysts are typically complemented with several additional elements for improved catalytic performance. Grasselli postulated seven fundamental principles of selective heterogeneous oxidation catalysis as guidelines for the knowledge-based design of new, improved catalysts.[9] These refer to the role of lattice oxygen, metal-oxygen bond strength, host structure, redox properties, multifunctionality of active sites, site isolation, and phase cooperation. It is certain that none of these concepts alone is sufficient for outstanding catalytic performance, but rather their interaction and cooperation is essential. However, the complex phase compositions of such multicomponent mixed metal oxides and the corresponding dynamic, synergistic phase interplay impede definitive conclusions about the role of individual catalyst phases during catalytic reaction. Thus, structure-activity relationships are still under discussion in literature.[5] As the processes during catalytic reaction are highly dynamic, it is crucial to understand these dynamics on different time and length scales.[10–11] Consequently, different interdisciplinary strategies including experimental and theoretical approaches are required for a holistic understanding.[5,12] This article focuses on present and past concepts and accompanying future challenges in the field of the selective oxidation of lower olefins, highlighting recent developments regarding multimodal and multiscale *in situ* and *operando* characterization techniques.

2. Starting point: bismuth molybdates – the active site in lower olefin oxidation?

In previous years, the focus of fundamental research was mainly laid on studying simplified single or binary metal oxide systems, such as 2-component bismuth molybdates.[13–15] Even though literature agreed on their role as the active component in selective oxidation, partly contrary results concerning the

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performance of individual bismuth molybdate phases were reported. While several studies agreed on γ-Bi_2MoO_6 (aurivillius structure)[16] being the most active bismuth molybdate in propylene oxidation, other studies claimed α-$Bi_2Mo_3O_{12}$[17] or β-$Bi_2Mo_2O_9$[13] (both scheelite structure) to be more active. As the discussed bismuth molybdates differed in parameters such as synthesis method, morphology, reaction conditions or surface area, these results generally emphasize the necessity of consistent material properties and reaction parameters (*e.g.* T, p, feed composition) when determining structure-activity relationships. In other words, catalyst performance is now recognised as being highly sensitive towards *e.g.* synthesis conditions, as relevant catalyst properties like crystallite size, surface area or phase composition are dependent on temperature and gas phase conditions. This underlines the importance of considering the dynamics at play during catalyst synthesis as well as during catalytic reaction.[7,18] Over the last decades, the trend in bismuth molybdate synthesis has moved from conventional synthesis methods (*e.g.* co-precipitation including spray drying, solid-state synthesis, sol-gel synthesis) to novel approaches including spray pyrolysis and hydrothermal synthesis, mainly aiming for an increased number of active sites, certain morphologies and higher surface area. Moreover, direct access to phase pure bismuth molybdates without further treatment (*e.g.* calcination) was extensively studied and achieved by flame spray pyrolysis.[19–20] A comparative study of hydrothermally and flame spray derived bismuth molybdates differing in their $Bi_2O_3 \cdot xMoO_3$ composition ($x = 1$–3) revealed a strong influence of the applied synthesis method on catalytic performance, especially for the aurivillius-type bismuth molybdates (Figure 1).[21] Here, γ-Bi_2MoO_6 prepared *via* flame-spray pyrolysis showed a better performance in propylene oxidation than hydrothermally prepared γ-Bi_2MoO_6, which was primarily attributed to synergistic effects in the flame-made system, as additional (amorphous) α-$Bi_2Mo_3O_{12}$ and β-$Bi_2Mo_2O_9$ were detected after reaction by X-ray absorption spectroscopy (XAS), X-ray diffraction (XRD) and Raman spectroscopy. Hence, the controversial discussions concerning the role of individual phases emphasize not only the need of consistent material properties and reaction parameters but also the necessity of deconvoluting phase interactions, ideally by complementary *in situ/operando* techniques. This implies catalyst characterization under non-ambient temperature, pressure and gas conditions (in situ), preferentially including simultaneous and realistic catalytic performance measurements (denoted "*operando*").[22–25]

Linda Klag received both her B.Sc. and M.Sc. in Chemistry from Technical University of Berlin (Germany) in 2017 and 2019. During her studies, she worked on solid state kinetics and structure-activity relationships of model catalysts for selective propylene oxidation in the group of Prof. Thorsten Ressler. Since 2019, she is a Ph.D. student in the group of Prof. Jan-Dierk Grunwaldt at Institute for Chemical Technology and Polymer Chemistry at Karlsruhe Institute of Technology (Germany). Her current research focuses on investigating mixed metal oxide catalysts used for lower olefin oxidation by (synchrotron-based) in situ/operando and spatially-resolved techniques.

Thomas Sheppard is currently a senior scientist at Karlsruhe Institute of Technology (KIT, Germany), leading a junior research group "X-ray Microscopy in Catalysis" supported by independent third party funding. He received his PhD in Chemistry in 2014 from Queen's University Belfast, followed by postdoctoral research with Prof. Jan-Dierk Grunwaldt at KIT from 2014–2017. Since 2018, his independent junior research group currently focuses on advanced catalyst characterisation with synchrotron radiation, mainly X-ray microscopy. His research interests include unconventional catalyst characterization tools, in situ/operando studies, and studying structure-activity relations. He is a visiting scholar at Deutsches Elektronen-Synchrotron DESY since 2020.

Jan-Dierk Grunwaldt obtained his PhD at ETH Zürich, worked as project leader at Haldor Topsoe/DK and was full professor in chemical engineering at DTU in Denmark, before he started in 2010 as full professor in chemical technology and catalysis at KIT. His group works on heterogeneous catalysis and operando spectroscopy with focus on chemical energy storage, sustainable chemistry, power-to-X processes, selective oxidation, emission control and in situ characterization of heterogeneous catalysts using especially synchrotron radiation sources. He is presently speaker of the initiatives "TrackAct" (CRC1441, www.trackact.kit.edu) and "DynaKat" (SPP2080, www.spp2080.org). He is adj. professor at DTU and was visiting professor in Padua/Italy in 2022.

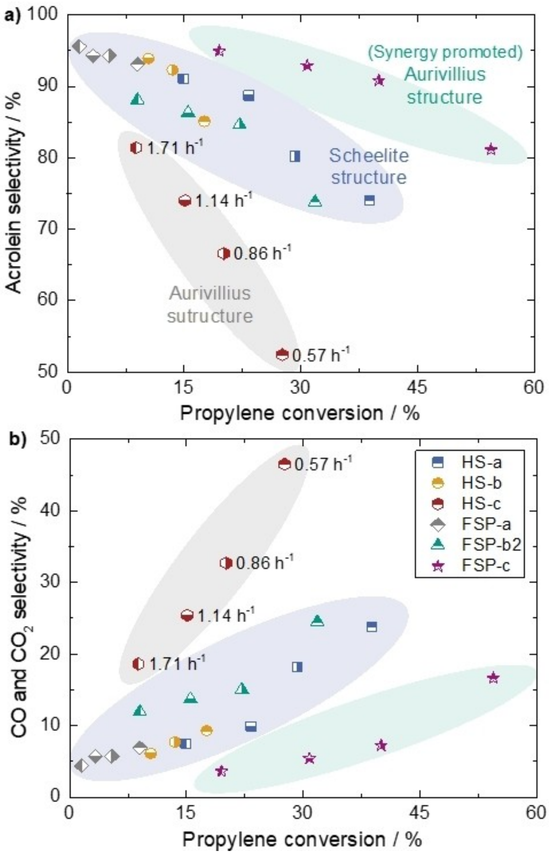

Figure 1. Catalytic performance of bismuth molybdates during selective propylene oxidation. Tested in a lab-reactor at 380 °C catalyst bed temperature at WHSVs 0.57–1.71 h^{-1}. Reprinted with permission from reference [21]. Copyright © 2018 American Chemical Society.

3. Towards multicomponent systems: the need of (advanced) complementary *operando* characterization techniques

In accordance with the concept of phase cooperation,[4,9,26] interactions between two or more phases directly influence catalytic performance and can explain contrary trends discussed in literature when comparing single, binary and multicomponent metal oxides. This further emphasizes the need of both, conventional and advanced spectroscopic methods, for unravelling the structural complexity and composition of mixed metal oxide phases in detail. Consequently, this also requires more studies with focus on multicomponent systems that provide a composite of selective, active, inert and promotor phases. Moro-Oka *et al.* highlighted the outstanding catalytic performance of $Mo_{12}Bi_1Co_8Fe_3O_x$ in propylene oxidation, being superior to 2-, 3- and even 4-component systems with different metal cations (*e.g.* $Mo_{12}Bi_1Co_8Cr_3O_x$).[4] In accordance with the first particle model proposed by Wolfs *et al.*,[26] Moro-Oka *et al.* assigned different roles to the phases detected, namely α-$Bi_2Mo_3O_{12}$ serving as selective phase on the particle surface, while β-$CoMoO_4$ and $FeMoO_4$/$Fe_2Mo_3O_{12}$ act as promoting phases located in the core. This conclusion was also drawn by Udalova *et al.* during isobutene oxidation.[27] However, in the past, the number of studies in literature focusing on multicomponent bismuth molybdate based catalysts during propylene or isobutene oxidation was very limited and mainly included *ex situ* results. This is reflected by hesitation to tackle the more complex multicomponent systems and can be traced back to the lack of appropriate characterisation tools to address this complexity. However, the characterisation landscape has changed rapidly in the last 20 years with the introduction of synchrotron-based techniques with better resolution, spatially-resolved studies and *operando* methodology to probe structure-activity relations, which find ideal application in such complex challenges.[28–29] In particular, the use of multimodal techniques has become possible at synchrotron radiation sources.[30] Recently, Stehle *et al.* investigated selective propylene oxidation over 4-component Bi–Mo-Co–Fe-oxide catalysts using complementary *operando* XAS, synchrotron-based XRD and Raman spectroscopy.[31] They revealed strong structural changes under different gas atmospheres in terms of short- and long-range order of the catalysts. A high catalytic performance was attributed to the presence of scheelite α-$Bi_2Mo_3O_{12}$ and its synergistic interplay with ternary β-$Co_{0.7}Fe_{0.3}MoO_4$ and $Bi_3(FeO_4)(MoO_4)_2$, thus complementing the earlier-stated particle model that referred to the *ex situ* phase composition of $Mo_{12}Bi_1Co_8Fe_3O_x$. Monitoring the incorporation of Fe^{2+} and Fe^{3+} in β-$CoMoO_4$ and α-$Bi_2Mo_3O_{12}$, respectively, together with the corresponding formation of MoO_3 during reaction was essential to correlate the phase composition with catalyst activity and selectivity (Figure 2). Notably, the low instrumental line broadening and high intensity and monochromaticity of X-rays produced at synchrotron radiation sources results in much higher quality X-ray powder patterns compared to laboratory X-ray sources (Figure 2a**, b**). The high intensity with shorter recording time further makes *in situ* and *operando* studies more accessible. Based on the results, an unselective role was attributed to MoO_3, if present in high quantity and not further incorporated in other phases during reaction as highlighted in Figure 2d. Similar phase transformations were observed by *operando* Raman spectroscopy in a Bi–Mo-Co-Fe–O catalyst during selective propylene ammoxidation, underlining the importance of unravelling the dynamics of the Fe^{3+}/Fe^{2+} redox couple and its correlation with catalytic performance.[32] Thus, this *operando* approach is crucial for monitoring the dynamics of the catalyst's working state, *e.g.* phase (trans-) formations during catalyst activation and phase interactions. In fact, the number of studies investigating (mixed) metal oxides by complementary *in situ/operando* techniques has steadily risen in recent years.[21,31,33–35] To underline this, a schematic illustration of a typical *operando* microreactor setup for complementary XRD, XAS and/or Raman spectroscopy experiments is shown in Figure 3. At its core, a quartz glass capillary serves as fixed-bed reactor with optimal heat and mass transfer properties.[25] Due to the high demand for such studies, laboratory based XRD and XAS studies have strongly come into focus.[36–37] These offer the great advantage of easy accessibility and thus give a new opportunity for in house XAS studies, *e.g.* catalyst screenings. However, due to low photon flux, time-

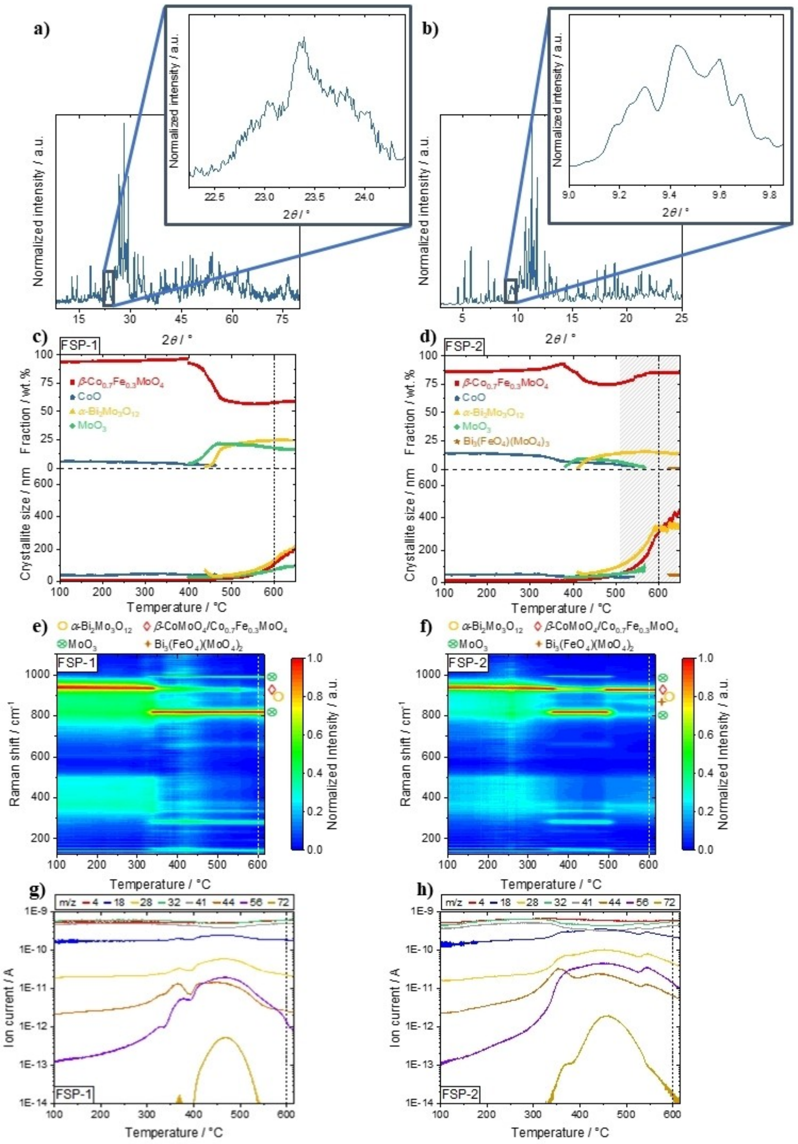

Figure 2. Comparison of S/N ratio for XRD patterns recorded *via* laboratory source (a, Cu K_α ratio, ~2,5 h acquisition time) and synchrotron source (b, $\lambda = 0.62779$ Å at BM01, ESRF, 30 s acquisition time). Structural evolution of Bi–Mo-Co-Fe–O catalysts during temperature-programmed propylene oxidation (100–600 °C, $He/O_2/C_3H_6/H_2O = 72/12/8/8$ vol %) derived from XRD (c, d), Raman spectroscopy (e, f) and simultaneously acquired mass spectrometric data (g, h). Adapted from reference [31], under the terms and conditions of the Creative Commons CC BY licence.

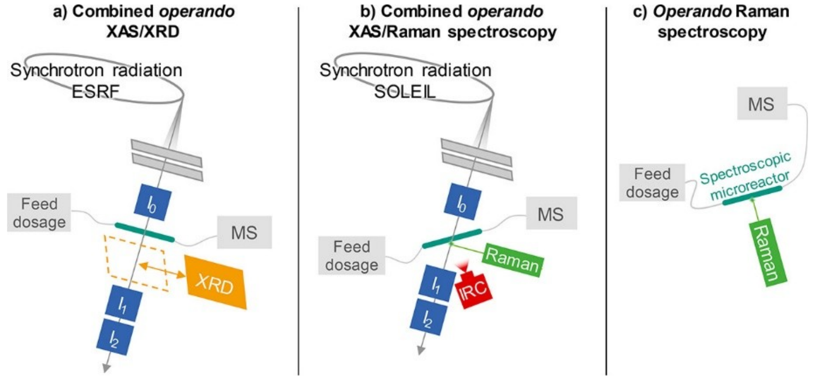

Figure 3. Schematic illustration of combined operando XAS/XRD (a, *e.g.* at BM31, ESRF), XAS/Raman spectroscopy (b, *e.g.* at ROCK, SOLEIL) and Raman spectroscopy (c, *e.g.* at KIT) setups. Reprinted with permission from reference [21]. Copyright © 2018 American Chemical Society.

resolved *in situ/operando* studies including spatially-resolved approaches are currently hardly feasible with such setups.

Equally important as the catalyst structure on an atomic level is the elemental and phase distribution in three-dimensional space (3D). Tomographic techniques allow such a 3D visualization and additionally provide the possibility of unravelling individual catalyst phases present, whose features typically overlap during integral characterization by XRD, XAS or Raman spectroscopy for example. The emerging chemical imaging techniques (i.e. hard X-ray tomography) have already been proven to be a valuable tool for unravelling structural changes of Bi–Mo-Co–Fe-oxides[38–39] and other multi-component catalyst systems under *in situ* or *operando* conditions.[40–41] Sprenger *et al.* observed by 3D X-ray nanotomography studies on spent Bi–Mo-Co-Fe–O particles a heterogeneous metal oxide phase distribution[38] and elemental distribution with a strong bismuth aggregation[39] within the whole catalyst volume (Figure 4). This bismuth segregation from the catalyst surface was in good agreement with XPS, XAS and TEM-EDX results and further indicates that the previously proposed core-shell like particle model with a bismuth molybdate rich surface cannot generally be applied to describe such complex catalyst systems.

Moreover, the entirety of these results could hint to a replacement of pure α-$Bi_2Mo_3O_{12}$ as the active central phase during lower olefin oxidation. This generally emphasizes to consider all the spatial dimensions within a particle and further within a catalyst pellet[42] when investigating structure-activity relationships in mixed metal oxide catalysts. This challenge can be further addressed through spatially-resolved characterisation.

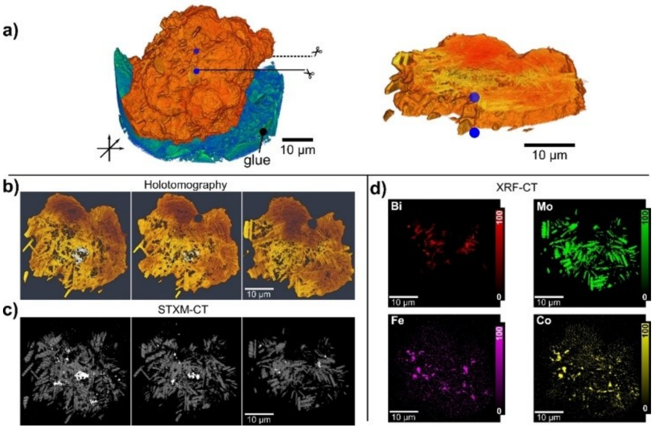

Figure 4. Holotomography visualisation of a Bi–Mo-Co-Fe–O particle (a) and identical orthogonal slices (b) after catalytic testing during selective propylene oxidation. Scanning transmission X-ray tomography (STXM-CT, c) and scanning X-ray fluorescence nanotomography (XRF-CT, d) showing approximate distribution of each metal component. Self-absorption effects were not accounted for in this study. Reprinted from reference [38], under the terms and conditions of the Creative Commons CC BY-NC-ND 4.0 licence. Copyright © 2021 The Authors.

4. Towards *in situ/operando* spatially-resolved techniques: monitoring catalyst dynamics along the reactor

The challenge in understanding the working principles of mixed metal oxide catalysts is not only related to the dynamic chemical processes on the nano- and mesoscale, but also includes changes on the micro- and macroscale. These are strongly linked, as for example structural transformations on the atomic level directly change the catalyst's chemical properties, and therefore its performance. Here, it is crucial to consider that these changes are not limited to a certain position in the catalyst bed, but may affect the whole reactor by the formation of gas concentration, temperature and structural gradients.[43–44] Particularly for industrial scale, such gradients can presently only be predicted from simulations but are equally important to be determined experimentally. A significant advance to monitor such gradients along the catalyst bed was the implementation of *in situ* and *operando* spatially-resolved techniques applied to bench- and lab-scale testing units, as highlighted by Morgan *et al.*,[45] Urakawa *et al.*[46] and Grunwaldt *et al.*[25] While most of the presented techniques referred to the investigation of structured catalysts, Touitou *et al.* developed a technique for simultaneously measuring temperature and concentration[47–48] as well as simultaneous structure (XAS) profiles[49] along packed powder catalyst beds. Gänzler *et al.* determined the structure and activity by a combination of thermography and QEXAFS (quick-scanning extended X-ray absorption fine structure).[50] In contrast to the traditional black box approach (in- and outlet measurements), spatial profiling considers spatial heterogeneities occurring during catalytic reaction inside the reactor which are otherwise challenging to observe experimentally.[51–53] This knowledge can be used for kinetic modelling studies,[54–57] considering various reaction conditions and leading to improved accuracy and validation of models. Furthermore, this allows to draw conclusions on reaction networks, thus enabling to optimize process parameters and reactor design. Recently, Ganzer and Freund presented a detailed reaction network derived from spatially-resolved experiments during selective propylene oxidation over bismuth molybdate catalysts under industrially relevant process conditions (Figure 5).[58] Stehle *et al.* investigated selective propylene oxidation over Bi–Mo-Co-Fe–O catalysts by spatially-resolved experiments under realistic conditions (i.e. high conversion), providing activity and temperature profiles (Figure 6).[59] However, these are the only studies presenting (in situ*)* spatially-resolved insights in lower olefin oxidation until now and much more work in this direction needs to be conducted.

Still, the potential of this approach is high, especially considering the high exothermicity of selective oxidation reactions and the resulting gradients along the reactor. One of the main challenges addresses the optimization of such heat and mass transfer processes, for example towards the compensation of heat-generation effects (*e.g.* hot-spots) that lead to undesirable by-products. Therefore, reactor concepts including dual/multiple catalyst bed zones have been established, but

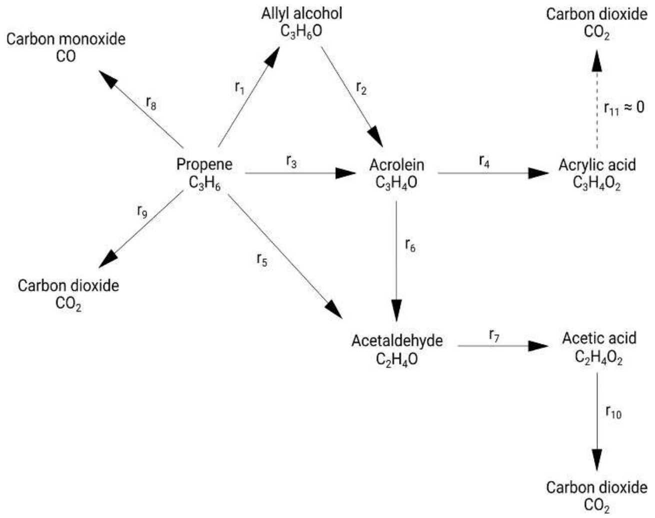

Figure 5. Proposed reaction network for propylene oxidation over a Bi–Mo–O catalyst. Reprinted with permission from reference [58]. Copyright © 2019 American Chemical Society.

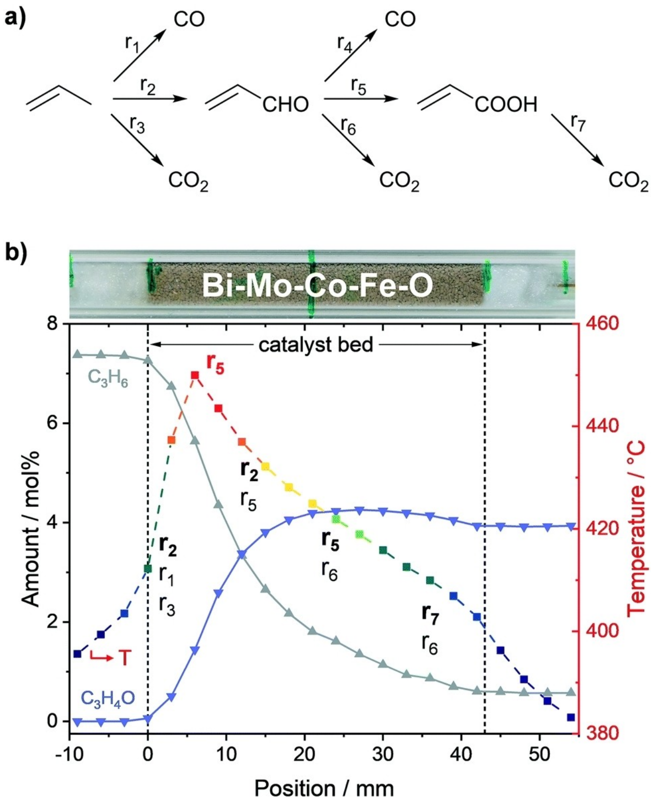

Figure 6. Proposed reaction network (a), temperature and gas phase concentration gradients along a Bi–Mo-Co-Fe–O catalyst bed (b) during selective propylene oxidation. Reproduced from reference [59] under the terms and conditions of the Creative Commons CC BY 3.0 licence. Copyright © 2021 The Royal Society of Chemistry.

mainly applied on an industrial level so far.[60–61] Typically, a series of several catalysts that differ in activity is layered and leads to an improved overall catalyst performance and lifetime by flattening the temperature profile along the reactor. As such temperature and resulting reactant/product concentration gradients can directly affect the catalyst structure and stability, investigating the dynamics in such multi-zone catalyst beds seems very promising for systematic study using *operando* spatially-resolved techniques in future.

5. Conclusions and Perspectives

The selective oxidation of propylene and isobutene are highly relevant reactions in chemical industry. Over the past 60 years, usage of mixed metal oxide catalysts based on bismuth molybdates has been established, but there is still room for improvement of the catalytic processes in terms of selectivity and efficiency. On the fundamental research level, *in situ* and *operando* methods have been optimized within the past decades, mainly with focus on simplified systems (*e.g.* 2-component Bi-Mo–O). The next step towards investigating more complex multi-component catalyst systems is promising and possible with respect to the new and improved synchrotron radiation sources including novel infrastructure. These provide higher flux and thus will enable more advanced time-resolved studies and benefits for photon-in photon-out spectroscopy. Although terabytes or even petabytes of data are generated, new insights into phase cooperation and mechanistic studies of catalysts closer to the industrially-relevant systems are now possible. In particular, detailed investigations of 4-component Bi–Mo-Co-Fe–O catalysts differing in catalytic performance (*e.g.* selective vs. unselective systems) are highly interesting for such purposes, as various mixed metal oxide phases (*e.g.* ternary phases) can be identified and directly correlated to catalytic activity or selectivity. Furthermore, a direct comparison of multicomponent catalyst performance during selective propylene and isobutene oxidation may extend the fundamental understanding of their working principles. Based on the challenge in analysing the dynamic behaviour of multi-component systems on several time and length scales, complementary advanced characterization techniques are one essential approach to understand the catalytic processes in their entirety. This includes integral and spatially-resolved insights in the chemical gradients within a catalyst particle and pellet, as well as into temperature, gas concentration and structural gradients along the catalyst bed within a reactor. The spatially-resolved methodology was optimized with respect to *in situ/ operando* investigations under industrially relevant conditions, while latest advances move towards applying complementary *operando* spectroscopy techniques simultaneously along the reactor.[62] This allows to directly monitor the structural response to gas concentration and temperature gradients along the reactor, thus opening new paths to investigate structure-activity relationships on larger scale and to further combine such new insights with reactor modelling for process optimization in future. To this end, studying long-term stability of the catalysts should also receive further attention, as insights into deactivation mechanisms (*e.g.* structural changes during extended time on stream) constitute another essential part of understanding the catalyst working principles. Despite its high importance, the lack of ageing studies is a common problem in the catalysis literature so far and should be addressed more in future.[5,63]

Overall, the developments presented in this article mainly focused on multiscale spectroscopic and imaging techniques. However, it is important to keep in mind that interdisciplinary strategies including the diverse expertise of experimentalists, theoreticians, data analysts and engineers will be required for further knowledge-based optimizations of such complex, dynamic processes. Apart from developing techniques, detectors and *operando* cells, data analysis is one of the current bottlenecks which is strongly in focus and requires a concerted, community-wide effort to resolve. This is also reflected in the latest strategies of implementing experimental handbooks for systematically investigating catalysts in their multidimensionality[64] and further creating unified research data infrastructures (*e.g.* NFDI4CAT,[65] DAPHNE4NFDI[66]) for properly documenting, analysing and linking the resulting large data sets as metadata for further use in data science. Only by fully exploiting the joint knowledge from and within academia and industry on various disciplines, further progress in this important field of selective oxidations can be achieved in future.[67]

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Selective oxidation · bismuth molybdate based mixed metal oxides · *operando* spectroscopy · spatially-resolved characterization · X-ray tomography

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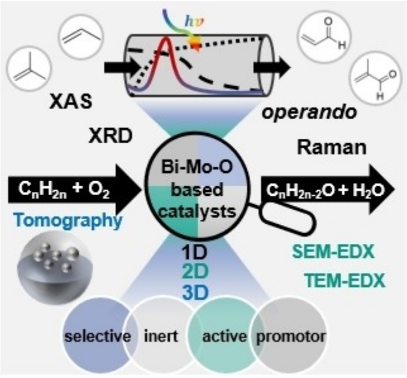
CONCEPT

Advanced Characterization for Olefin Oxidation Catalysts: Selective olefin oxidations over bismuth molybdate based mixed metal oxide catalysts are highly complex and dynamic reactions. A holistic understanding of the catalytic processes includes knowledge about structure-activity relationships on multiple time and length scales, as well as on all spatial dimensions. To tackle these criteria, a toolbox of complementary characterization techniques is presented within the scope of this concept article.



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An Advanced Characterization Toolbox for Selective Olefin Oxidation Catalysts

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