doi:10.2533/chimia.2024.288 Chimia 78 (2024) 288–296

Operando Spectroscopy to Understand Dynamic Structural Changes of Solid Catalysts

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Abstract: Solid materials like heterogeneous catalysts are highly dynamic and continuously tend to change when exposed to the reaction environment. To understand the catalyst system under true reaction conditions, *operando* spectroscopy is the key to unravel small changes, which can ultimately lead to a significant difference in catalytic activity and selectivity. This was also the topic of the 7th International Congress on *Operando* Spectroscopy in Switzerland in 2023. In this article, we discuss various examples to introduce and demonstrate the importance of this area, including examples from emission control for clean air (*e.g.* CO oxidation), oxidation catalysis in the chemical industry (*e.g.* oxidation of isobutene), future power-to-X processes (electrocatalysis, CO_2 hydrogenation to methanol), and non-oxidative conversion of methane. All of these processes are equally relevant to the chemical industry. Complementary *operando* techniques such as X-ray absorption spectroscopy (XAS), X-ray diffraction (XRD), diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), and Raman spectroscopy were utilized to derive the ultimate structure of the catalyst. The variety of conditions requires distinctly different *operando* cells that can reach a temperature range of 400–1000 °C and pressures up to 40 bar. The best compromise for both the spectroscopy and the catalytic reaction is needed. As an outlook, we highlight emerging methods such as modulation-excitation spectroscopy (MES) or quick-extended X-ray absorption fine structure (QEXAFS) and X-ray photon in/out techniques, which can provide better sensitivity or extend X-ray based *operando* studies.

Keywords: Cell design · Dynamic structure · *Operando* spectroscopy · Solid catalyst · Synchrotron methods

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1. Introduction

Understanding the catalyst structure during operation (frequently referred to as '*in situ*' or '*operando*') is one of the most challenging tasks in catalysis research, but has become possible with the development of modern spectroscopic tools.[1,2] The term '*operando*' was introduced a while ago[3-5] and refers to investigating the catalyst structure under the true reaction parameters (same temperature, pressure, reaction rates, selectivities, spatiotemporal profile, *etc.*) while simultaneously measuring activity and selectivity, as defined by Banares *et al.*[4,6] Studies that are not able to meet these criteria should be referred to as '*in situ*' investigations. This led to the first International Congress on *Operando* Spectroscopy in Lunteren, Netherlands in 2003. 20 years later, the 7th International Congress on *Operando* Spectroscopy congress was held in Grindelwald in Switzerland (7th – 11th of May, 2023), organized by Davide Ferri and Maarten Nachtegaal (Paul Scherrer Institute, Villigen, Switzerland). Swiss groups are and have been very ac-

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tive in this field of research.[7-9] Since the early times, *operando* spectroscopy has revolutionized the in-depth understanding of solid catalysts, which benefited both academia as well as many industrial processes.[10] One of the early catalytic systems studied with *in situ* and *operando* spectroscopy was the CO/CO_2-hydrogenation to methanol.[11] With *in situ/operando* spectroscopy and microscopy, the structural dynamics in the Cu/ZnO system for methanol synthesis were demonstrated.[12] Early research speculated that oxygen vacancies on the ZnO surface can lead to a stronger interaction of the copper particles with the ZnO surface during the reaction, which in turn leads to a morphological change.[13] Moreover, Nakamura *et al.* showed that Zn atoms from the ZnO support can migrate to the Cu surface and form a Cu-Zn surface alloy, which accelerates the CO_2 hydrogenation reaction.[14] The structure is not yet fully understood, but it is still believed that the interfacial Zn species play a major role during the reaction. The nature of these Zn species is not metallic but instead positively charged under industrial methanol synthesis conditions.[15-17] Another prominent example is the Au-catalyzed hydrochlorination of acetylene where *operando* spectroscopy shed light on the state of the Au species during the reaction.[18] It was shown that a single site redox pair of Au^I/Au^{III} supported on carbon is a crucial factor during the reaction, and a highly oxidizing Cl_2 stream is responsible for maintaining the redox pair. This process, which was up to that point carried out at an industrial scale with hazardous $HgCl_2$/C catalysts[19] to produce over 40 million tons of vinyl chloride annually, has now been commercially replaced with the Au/C catalyst; thanks in part due to these *operando* studies.[20] Another example would be the selective catalytic reduction (SCR) of NO_x by NH_3 over Cu/zeolite catalysts, which is one of the most crucial reactions concerning the reduction of emissions of harmful gases to the environment.[21] Recently, it was shown that the reaction occurs over isolated Cu^{II} sites, which are located inside the zeolite structure.[22-24] Further work by Fahami *et al.* revealed that these isolated Cu sites interconvert between Cu^{II} and Cu^I during the reaction. They generate complexes with ammonia such as $Cu(NH_3)^{2+}$ and further form dimeric *bis*(μ-*oxo*)Cu species in oxidizing gas mixtures.[25] Becher *et al.* further investigated Cu-SSZ-13 catalysts by *operando* X-ray spectrotomography at micrometer spatial resolution, which revealed the local structural changes of the Cu catalysts in 3D under operating conditions.[26] A final introductory example of the benefit of *operando* spectroscopy would be methane dehydroaromatization (DHA), a highly valuable process for converting methane to high-density products such as olefins or aromatic compounds over Mo catalysts.[27] Recent *operando* investigations showed that isolated Mo sites inside the zeolite were essential during the reaction.[28] The isolated MoO_x species agglomerate during the reaction, resulting in molybdenum carbide formation, which reversibly converts back to the isolated site in the presence of oxygen. A more recent study showed that under non-oxidative conditions, methyl radicals form over the isolated Mo centers, which further transform to ethane and finally to ethylene after a dehydrogenation step.[29] This variety of selected studies demonstrates the potential of *in situ/operando* spectroscopy in unraveling the active site of complex systems. Therefore, the continuous development of more sophisticated techniques is inevitable. Further examples can be found in this special issue of *CHIMIA*. In a recent review, we discussed the implementation of synchrotron-based *in situ/operando* X-ray techniques to elucidate the dynamic structural changes of single-atom catalysts under operating conditions.[30] In the present article, we briefly outline the challenge of *operando* spectroscopy, in particular, finding the best compromise between running a catalytic reaction and performing spectroscopy at the same time, and then introduce various examples from our own research. Strategies to design appropriate cells to cope with the different reaction conditions, for example, in liquid–solid, gas–solid, photochemical, or electrochemical systems, or even at mixed interfaces are also highlighted in this review as well as in others from our group in the past.[31]

2. The Challenge of *Operando* Spectroscopy and Design of Appropriate Cells

In *operando* spectroscopy, the simultaneous structure determination and measurement of the catalytic performance are essential. Fig. 1, shows various spectroscopic techniques that can be adopted when light of different wavelengths interacts with the

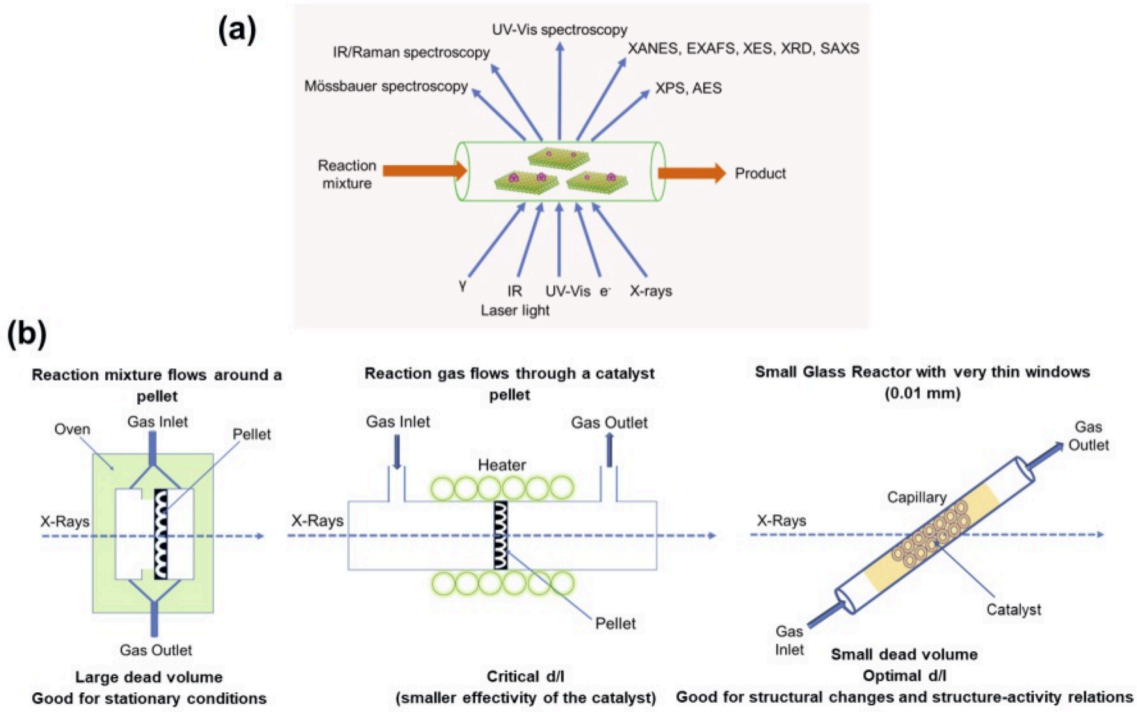

Fig. 1. (a) Interaction of light with the catalyst under operating conditions, which can be exploited *via* various spectroscopic techniques, and (b) several *operando* cells designed in the earlier studies by our group. Adapted with permission from ref. [32].

catalyst as well as some of the early designs of *operando* cells that have been developed by our group.[32] In order to find the best compromise for tracking the catalyst by *operando* spectroscopy with conditions as close as possible to working conditions and spectroscopy data with the highest quality, we propose to follow the well-known 10 commandments[33,34] for a catalytic experiment as shown in Fig. 2. Why are these commandments important? Let us consider the internal and external mass transport in solid catalysts, which if not appropriated for can ultimately lead to mis-interpretation of data obtainable from *operando* studies.[32] In order to obtain the best compromise between optimal design for spectroscopic characterization and catalytic results, film diffusion (τ_{film}), pore diffusion (τ_{pore}) and the connected effectiveness factor (Thiele modulus) play an important role and need to be considered.[32] In addition, the shape of the catalyst, measurement geometry, reaction interfaces, and window materials for cells also need to be considered. To meet these criteria, some of the best beamlines to combine for *operando* studies are SuperXAS at PSI,[35] CATACT at KIT light source,[36] ROCK/SAMBA at SOLEIL,[37] and NSLS at Brookhaven National Laboratory,[38] where multiple spectroscopic techniques (XAS, DRIFTS, XRD, Raman spectroscopy *etc.*) can be implemented or combined.

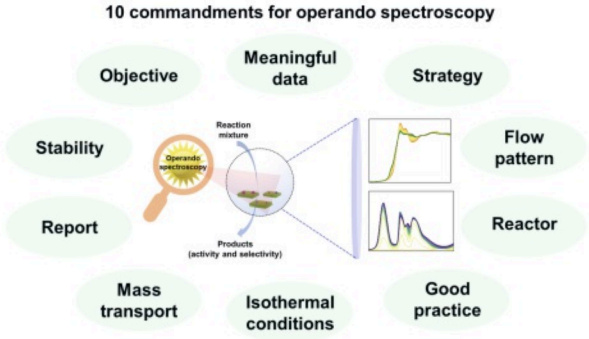

Fig. 2. 10 commandments for *operando* spectroscopy covering a wide range of reaction conditions.

Over the past two decades, our group has been continuously developing new tools for *operando* research covering a wide variety of reaction conditions.[30,31,39] Several different spectroscopic techniques have therefore been employed and some of the main information we have received with it is summarized in Fig. 3. In the following sections, we will explore some recent examples of these *operando* studies in more detail.

2.1 *Selective Oxidation of Isobutene Using Operando Synchrotron-based X-ray Absorption Spectroscopy, Raman Spectroscopy and X-ray Diffraction*

A nice and recent example for the challenges in *operando* spectroscopy is the oxidation of isobutene to methacrolein, which is an important intermediate in the production of polymethyl methacrylate (PMMA), commonly known as acrylic glass.[40] This reaction is catalyzed by a Bi-Mo multicomponent catalyst and the role of each component is strongly debated.[41] For example, why do 4-component Bi-Mo-Co-Fe-O systems perform better than the 2-component Bi-Mo-O systems? Even among the 2-component Bi-Mo-O systems, various phases, for example, α-$Bi_2Mo_3O_{12}$, β-$Bi_2Mo_2O_9$, and γ-Bi_2MoO_6 show different selectivity, requiring in-depth investigation. To answer those questions, we have synthesized the Bi-Mo-Co-Fe-O catalysts for *operando* investigations by flame spray pyrolysis (FSP), enabling a uniform nanocrystalline metal oxide with high surface area.[42] Three catalysts with different metal ratios were synthesized. While *operando* Raman spectroscopy provided insights into the different bulk phases of the catalysts which evolved during the reaction, *operando* XRD in combination with Rietveld refinement revealed the crystallinity and the quantitative composition of the metal oxide phases. The *operando* XAS measurements were carried out at Mo K-, Bi L_3-, Co K-, and Fe K-edges independently and simultaneously in a quartz micro-reactor. Synchrotron-based XRD techniques did not only provide information on the structural transformations of the crystalline phases in the catalysts but also showed the presence of several additional phases that could not be detected with laboratory-based XRD.

The findings from the *operando* studies are summarized in Fig. 4. The catalysts containing less than 50% Mo (FSP-Fe and FSP-Co) showed the formation of single metal oxides (Fe_3O_4, Co_3O_4, Bi_2O_3), which resulted in high conversion and formation of undesired (overoxidation) products, such as CO and CO_2. On the other hand, the catalysts containing 50% Mo (FSP-U) resulted in better selectivity *via* transformations into Mo structures such as α-$Bi_2Mo_3O_{12}$ and $Fe_2Mo_3O_{12}$. Additionally, the presence of β-$CoMoO_4$/β-$Co_{0.7}Fe_{0.3}MoO_4$, α-$Bi_2Mo_3O_{12}$ and $Bi_3FeMo_2O_{12}$ phases in the catalyst, FSP-U resulted in the best catalytic performance. XAS investigations proved that Fe^{III} is converted to Fe^{II} during the reaction. We further explored temperature and activity correlations by spatial reactor profile measurements, which will be combined with *operando* techniques in the future.[43]

We have recently discussed how various 1D, 2D and 3D advanced characterization techniques can be used to derive structural information on such Mo-based catalysts as shown in Fig. 5 in our concept article.[44] These results will further open up new possibilities for designing the next generation of catalysts for such an industrially relevant reaction.

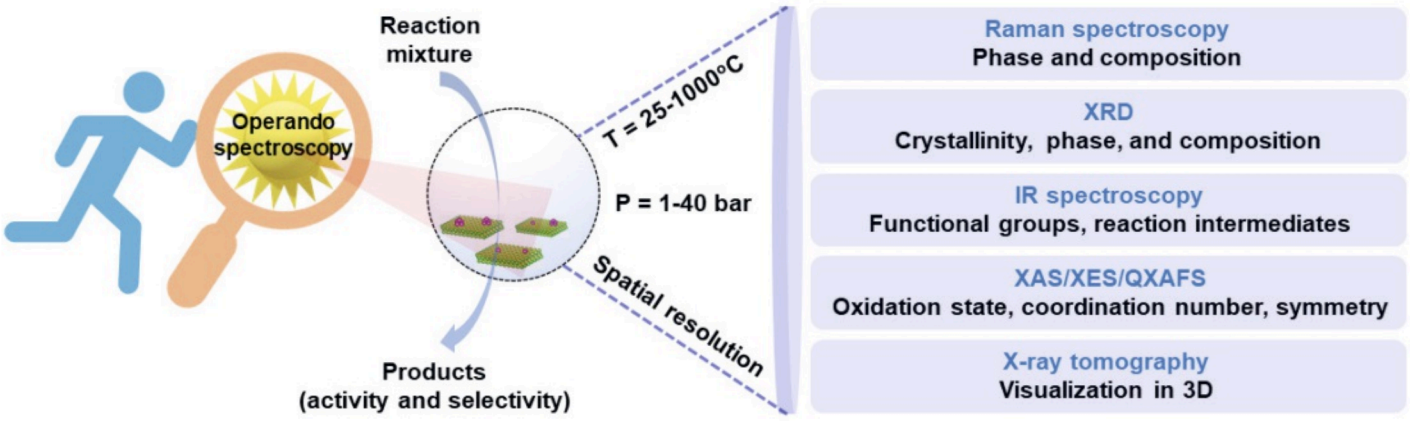

Fig. 3. Schematics of *operando* spectroscopy and the information derived from a few *operando* techniques are highlighted in this review.

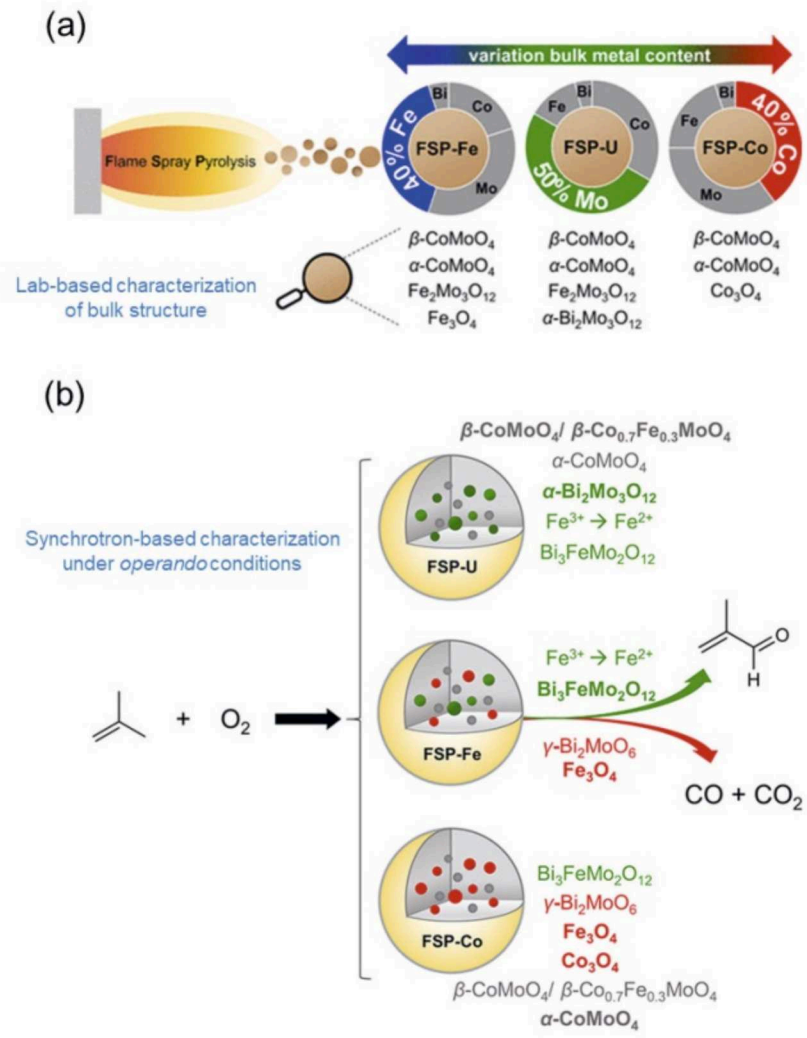

Fig. 4. (a) Description of catalyst components synthesized by FSP and the corresponding metal oxide phases characterized by laboratory-based techniques (XRD and Raman) and (b) schematic representation of the isobutene oxidation with various catalyst compositions identified by synchrotron-based techniques under operating conditions. Green represents metal oxide phases favoring the selective reaction pathway to methacrolein (MAC); red represents metal oxide phases favoring the unselective reaction pathways (formation of CO and CO_2), and gray represents primary phases detected in all three catalyst systems. Catalyst compositions are FSP-Co (5% Bi, 35% Mo, 40% Co, 20% Fe), FSP-Fe (5% Bi, 35% Mo, 20% Co, 40% Fe), and FSP-U (4.2% Bi, 50% Mo, 33.3% Co, 12.5% Fe). Adapted with permission from ref. [42].

2.2 *Investigation of CO_2 Hydrogenation to Methanol via in situ DRIFTS and Operando XAS*

Hydrogenation of CO_2 to methanol is one of the most promising routes to mitigate the CO_2 in the atmosphere and to tackle global warming.[45] As discussed in the introduction, Cu/ZnO is one of the most investigated catalysts for the CO_2 hydrogenation to methanol,[17,46,47] where Zn tends to migrate to the Cu surface during the reaction. Our first question is: How is Zn influenced by Cu? Many studies have addressed this question. Recently, we have synthesized an inverse ZnO/Cu/MgO catalyst and conducted *in situ* XAS and XRD studies.[48] The results showed that the ZnO fraction in direct contact with Cu is reduced first and afterwards, a Cu-Zn surface alloy formed above 300 °C. Above 400 °C, we observed bulk alloy formation. Finally, we found that the reduced Zn-species at the interface played a pivotal role during the methanol synthesis.

A further question was if the migration of Zn could be potentially controlled by adding another component, which would suppress formate decomposition to CO decreasing the H_2 dissociation energy, would this boost the methanol production rate?[49] Zirconia is one of the supports, which is known to enhance the methanol production rate. Therefore, we have synthesized a series of Cu-Zn-Zr catalysts (Cu-ZnZr, Zr-CuZn, Zn-CuZr, and CuZnZr) applying double-nozzle flame spray pyrolysis (DFSP) and tested them for CO_2 hydrogenation to methanol.[50] The various catalysts synthesized for this study, their catalytic activity, and the proposed reaction pathways are shown in Fig. 6.

The *operando* XAS study carried out in a tailor-made stainless steel high pressure cell[51] revealed that during the reaction highly dispersed Zn species are induced due to the strong interaction of Zn-Zr, which leads to a decrease in formate decomposition to CO and of the H_2 dissociation energy. Therefore, the methanol production was significantly enhanced. The *in situ* and

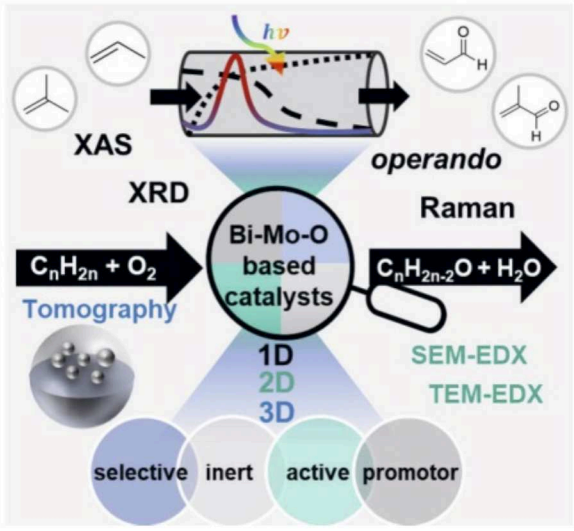

Fig. 5. Toolbox of advanced characterization techniques for deriving structural information of Bi-Mo-O-based catalysts for selective oxidation of olefins under *operando* conditions. Reproduced with permission from ref. [46].

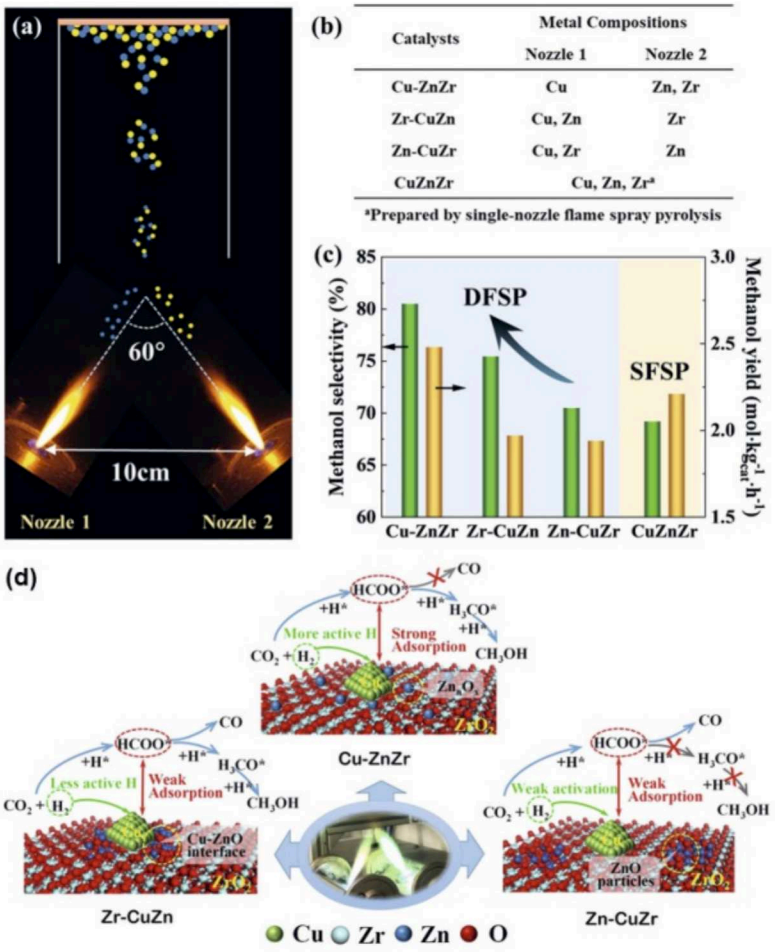

Fig. 6. (a) Schematic representation of the DFSP method, (b) Composition of the catalysts synthesized by DFSP method, (c) Methanol yield and selectivity obtained from CO_2 hydrogenation, and (d) Proposed mechanistic pathway towards CO_2 hydrogenation. DFSP and SFSP stand for double and single flame spray pyrolysis respectively. Adapted with permission from ref. [50].

operando DRIFTS studies were carried out at a temperature of 230 °C and a pressure of 3.0 MPa using a dedicated reaction cell (PIKE Diffus IR_{TM}). We observed that the Zn species, which formed during the reaction, promoted the selective conversion of CO_2 to methoxy species and subsequently to methanol *via* the strong formate adsorption. These results reveal that the nature of the Zn species is truly essential during methanol synthesis and can be modified with the introduction of other components such as Zr. With the help of *operando* spectroscopy we further found that the introduction of single-site Zr species in a Cu catalyst supported over amorphous SiO_2 promotes reverse water-gas shift + CO-hydro pathway, thus improving methanol production.[52]

In another recent high pressure *operando* study by our group, using a similar *operando* cell, we have conducted *operando* XRD and XAS investigations on Fischer-Tropsch synthesis at 30 bar and 250 °C, thereby bridging the gap between industrially relevant catalysts and fundamental science at synchrotron radiation facilities.[51] This turns out to be very important also in the field of renewable aviation fuels (see *e.g.* project CARE-O-SENE, https://care-o-sene.com). Pioneering research has been conducted here by the University of Cape Town and SASOL using especially *in situ* and *operando* magnetometry.[53,54]

2.3. *Operando Electrochemical Oxygen Evolution Reaction (OER) – Overcoming the Influence of Bubble Formation*

Production of green hydrogen *via* water splitting is one of the prominent ways to replace fossil based resources and to meet the future energy demand.[55] During water electrolysis, the oxygen evolution reaction (OER) occurs at the anode whereas the hydrogen evolution reaction (HER) takes place at the cathode. It requires four electrons and high over potentials for the OER process. OER is best catalyzed by Ir- and Ru- based oxide catalysts. Abbott *et al.* with the help of *operando* XAS showed correlation between particle size, morphology, and the surface hydroxo layer of the IrO_x based catalysts during OER.[56] According to the report, IrO_2 synthesized at 350 °C, and consisting of 1.7±0.4 nm particles with a specific surface area of 150 m^2g^{-1}, shows the highest OER activity. Reier *et al.* found that crystalline IrO_2 obtained at high temperature is detrimental, whereas amorphous Ir oxy-hydroxides present at low temperature are highly active and efficient catalysts for the OER.[57] Pfeifer *et al.* with the help of *in situ* XPS found that the surface of metallic Ir converts to a mixed valent species containing both O^{II-} and O^{I-}, which is of high relevance during OER.[58] Following these pioneering works, our group has investigated the OER mechanism in-depth with the help of *operando* XAS and probed the high stability of IrO_2 as well as the Ir-Ir interaction during OER at high potentials.[59] As an alternative to *in situ* XPS,[58] modulation excitation spectroscopy (MES) in combination with XAS was implemented to achieve surface sensitivity and to understand the dynamic structural changes during the reaction. The XAS experiments were performed with the electrochemical flow cell setup at the SuperXAS beamline of the Swiss Light Source.[60] We found that oxygen vacancies in the IrO_2 are crucial in its stability and thus play an important role in the mechanism of the OER when changing from low to high overpotentials, as shown in Fig. 7. Relevant points to consider in the future are mass transport processes and improved electrocatalysts.

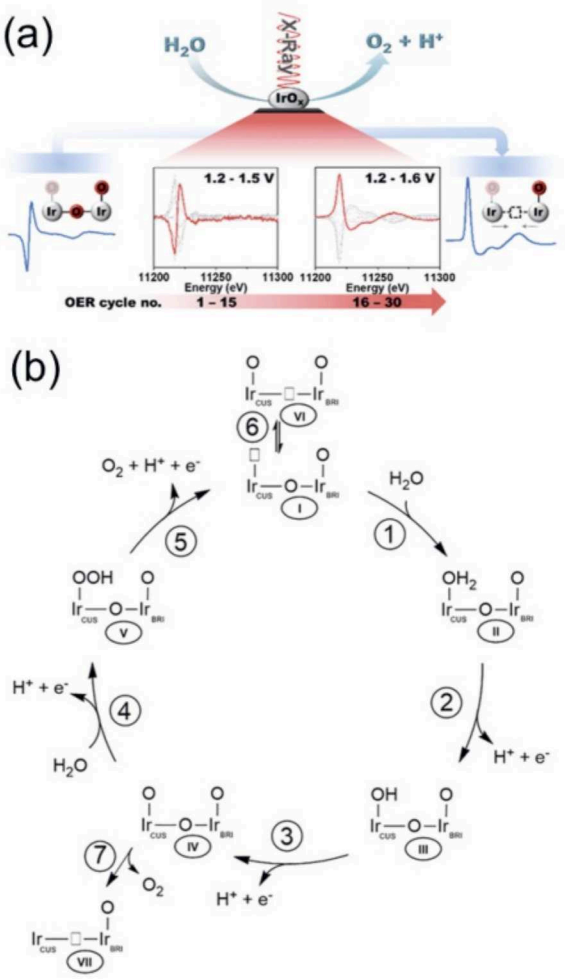

Fig. 7. (a) Summary of the *operando* XAS results during OER over an IrO_x catalyst, and (b) proposed adsorbate evolution mechanism (AEM) during OER in acidic medium. Adapted with permission from ref. [59].

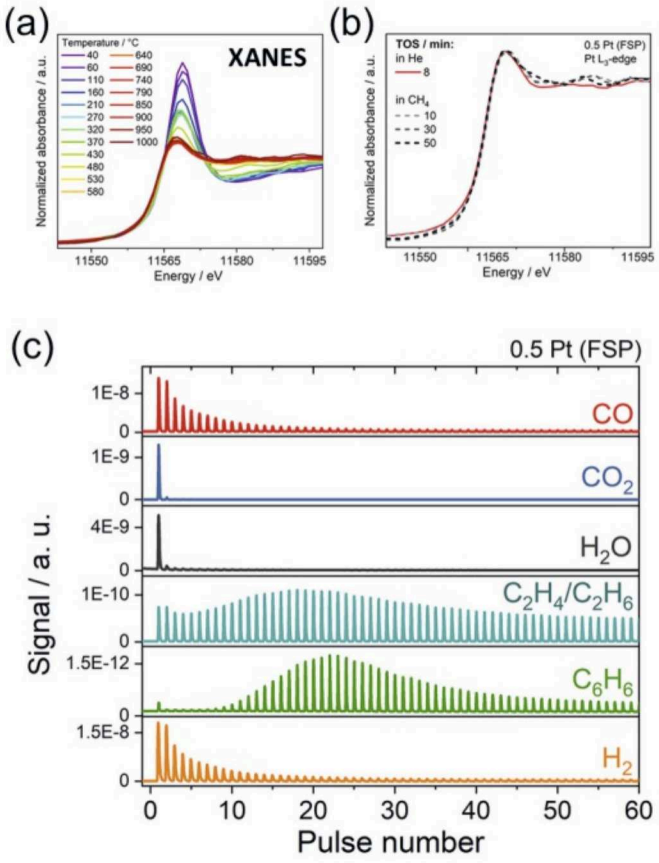

Fig. 8. (a) Normalized XANES spectra at the Pt L_3-edge of the Pt/CeO_2 (FSP) catalyst at various temperatures under He atmosphere, (b) *operando* XANES spectra at 975 °C in 90% CH_4/He atmosphere and (c) pulse reaction products at 975 °C. Adapted with permission from ref. [64].

2.4. *Operando* XAS Investigation for the Non-oxidative Coupling of Methane – The Challenge of High Temperature

Direct conversion of methane to olefins and aromatics is one of the holy grails in comparison to the traditional multi-step processes of syngas conversion *via* Fischer-Tropsch (FT) synthesis or the methanol to olefin (MTO) process.[61,62] However, direct conversion of methane occurs at a much higher temperature (typically above 600 °C) than in MTO or FT synthesis processes, which makes it challenging to investigate the catalyst under operating conditions. In this regard, we have built a cell that can reach up to 1,000 °C, which makes it ideal for these kind of studies.[63] We have synthesized two sets of Pt/CeO_2 catalysts *via* FSP and incipient wetness impregnation (IWI).[64] The *operando* XAS experiments were carried out at 975 °C. The catalyst prepared *via* the FSP method showed atomically dispersed Pt, whereas the IWI method mainly resulted in Pt clusters on the CeO_2 support. Pulsed reactions with methane showed three stages of the reaction: (a) reduction of CeO_2 during activation; (b) induction phase; and (c) stable catalytic cycle. The *operando* X-ray absorption near edge structure (XANES) spectra at the Pt L_3-edge collected at various temperatures under He and CH_4/He flow at 975 °C with the products obtained are shown in Fig. 8.

Operando XAS, in combination with theoretical simulations of the extended X-ray absorption fine structure (EXAFS) and XANES spectra confirmed an increase in Pt-Ce interactions under reaction conditions (at 975 °C under CH_4 flow). The gas phase reaction intermediates were analyzed by synchrotron-based ultraviolet photoionization mass spectrometry (SVUV-PIMS), which showed the formation of methyl radicals. This indicates that the strong Pt-Ce interaction probably leads to the activation of CH_4 *via* formation of methyl radicals suppressing the coke formation and ultimately enhancing the catalytic activity. These results revealed the structural evolution of the Pt/CeO_2 catalyst under industrially relevant conditions, which will help in further understanding the complex reaction pathways at such high temperatures.

2.5. *Operando* High-energy-resolution Fluorescence Detected (HERFD) XAS Investigation During CO Oxidation Over Pt Single-atom Catalyst (SACs)

Single-atom catalysts, an emerging field in heterogeneous catalysis, attract the interest of many researchers because they show the promise to achieve maximum theoretical efficiencies with minimum metal loadings.[65,66] Since the term SAC was coined, investigations on many reactions, which were believed to be catalyzed by nano-particles or clusters showed that SACs can be a viable alternative.[67-70] It is also worth mentioning here that when it comes to single-atom catalysts, complementary spectroscopic techniques such as Fourier transform infrared (FTIR)[71,72] are mandatory as X-ray based techniques have certain limitations.[73] We have recently shown that diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) can be a complementary spectroscopic method to X-ray based techniques for elucidating the local structural changes under operating conditions.[74] Jones *et al.* showed that Pt single atoms trapped inside CeO_2 supports at 800 °C in air are highly stable and active for the CO oxidation reaction.[75] With the help of *operando* XAS, our group has shown in the past that Pt nano-particles on CeO_2 are highly dynamic in nature when operated as emission control catalysts.[76] Following this, we have synthesized a single-site Pt/CeO_2 catalyst under hydrothermal conditions at 800 °C and tested it for CO (as well as C_3H_6 and

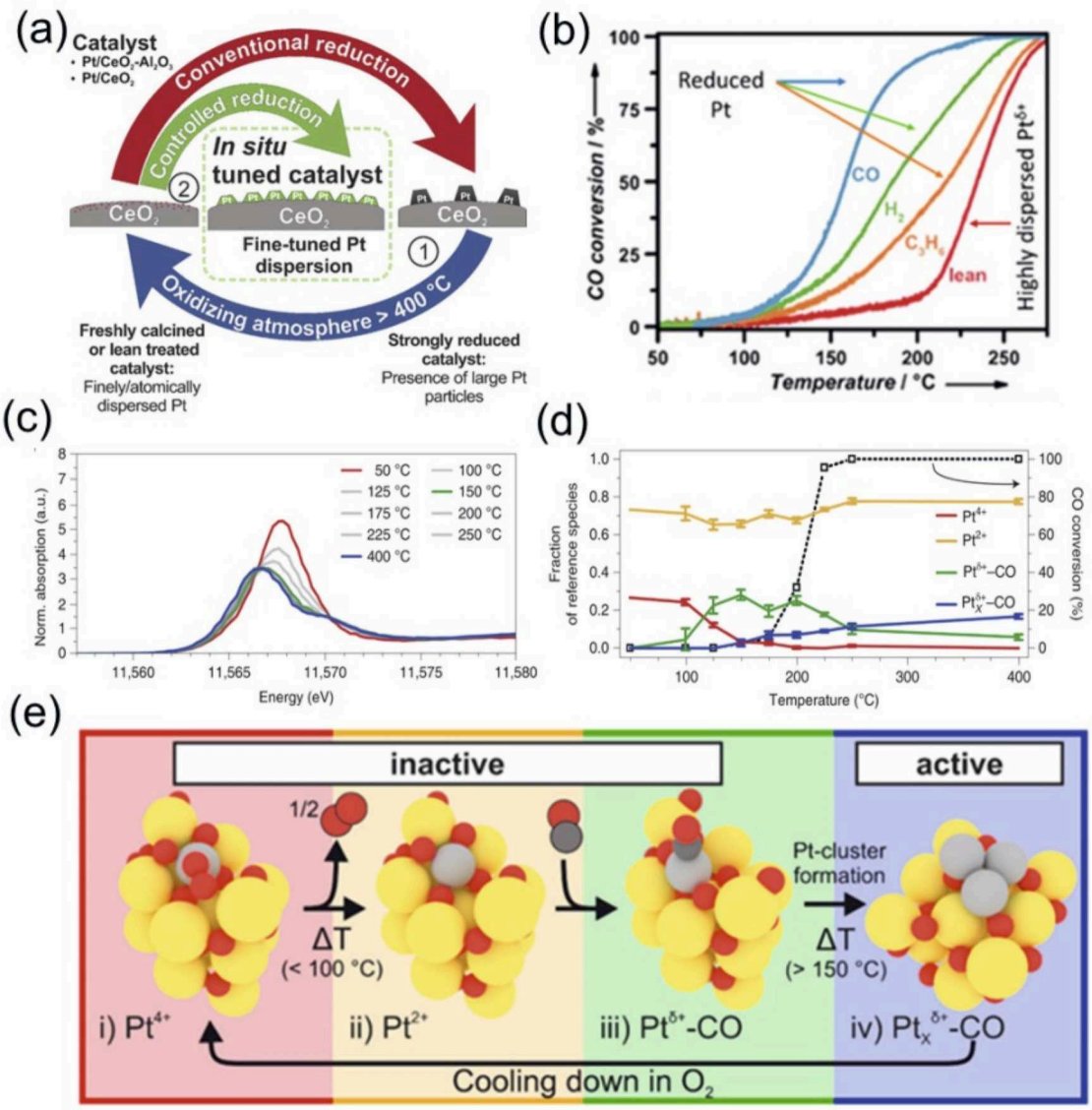

Fig. 9. (a) Schematic representation of the state of the Pt/CeO_2 catalyst under various reaction conditions,[76] (b) CO light-off curve after activation of the Pt/CeO_2 catalyst (single site and clusters) with different reductant, (c) HERFD XANES spectra at Pt L_3-edge at different temperatures under CO oxidation conditions, (d) fraction of Pt species derived from multivariate curve resolution-alternating least-squares (MCR-ALS) with linear combination analysis (LCA), and (e) scheme representing changes in the Pt single sites during CO oxidation shown in our previous work. Adapted with permission from ref. [77].

CH_4) oxidation reaction.[77] The *in situ* IR and *operando* HERFD XAS studies demonstrated that under CO oxidation conditions, Pt single sites migrate from four-fold hollow sites, resulting in Pt clusters of a few atoms, which form the catalytically active centers. Hence, several atom clusters are the active species. The different states of the catalyst under varying reaction environments, the CO light-off curve, and the results of the HERFD XAS studies are summarized in Fig. 9. In Fig. 9 (c), the HERFD XANES spectra at the Pt L_3-edge clearly shows that the white line intensity significantly decreases under the reaction conditions indicating the formation of small Pt clusters, which was not detected in the conventional XAS experiment. This study demonstrates that *operando* spectroscopy (beyond conventional XAS) may be necessary to prove the fate of single-atom catalysts. Recently, with the help of *in situ/operando* XAS and DRIFTS we have shown that noble metals (Pt, Ir, Pd, Rh, and Ru) dispersed on CeO_2 are highly dynamic in their behavior already at room temperature under CO oxidizing conditions.[74] A spatiotemporal investigation[78] during CO and hydrocarbon oxidation over a Pt/CeO_2 catalyst deposited as a layer in a honeycomb structure showed different reaction rates at the first zone of the catalyst and presence of large Pt nanoparticles. In this work, we implemented combination of *operando* infrared thermography and spatially and time-resolved XAS during CO oxidation reaction conducted on a fixed bed microreactor. Using IR thermography, the position and extent of hotspots was identified, which can be further extended with industrially relevant emission control catalysts. This concept has been recently further transferred to the Pd and Rh L_3-edge in vacuum tender X-ray emission spectrometer (TEXS) of beamline ID26 at European Synchrotron Research Facility (ESRF).[39]

3. Conclusion and Outlook

Operando spectroscopy is inevitable to elucidate the true nature of catalysts under operating conditions. In many of the examples discussed above, we have found that the structure of the catalysts is very dynamic and that even a small change in the catalyst structure can make a huge difference when it comes to activity and selectivity. In our first example of isobutene oxidation, synchrotron based techniques (XRD and XAS) provided much more structural information compared to the state-of-the-art laboratory-based methods, which suggests that synchrotron-based techniques will be more routine in the future when it comes to *operando* investigations. In addition, spatially resolved studies become important to understand phase cooperation effects. The

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