Advances in in situ/operando techniques for catalysis research: enhancing insights and discoveries

Linfeng Chen[1], Xinzhi Ding[2,3], Zheren Wang[4], Shutao Xu[2], Qike Jiang[5], Chaochao Dun[1]* and Jeffrey J. Urban[1]*

Abstract

Catalysis research has witnessed remarkable progress with the advent of in situ and operando techniques. These methods enable the study of catalysts under actual operating conditions, providing unprecedented insights into catalytic mechanisms and dynamic catalyst behavior. This review discusses key in situ techniques and their applications in catalysis research. Advances in in situ electron microscopy allow direct visualization of catalysts at the atomic scale under reaction conditions. In situ spectroscopy techniques like X-ray absorption spectroscopy and nuclear magnetic resonance spectroscopy can track chemical states and reveal transient intermediates. Synchrotron-based techniques offer enhanced capabilities for in situ studies. The integration of in situ methods with machine learning and computational modeling provides a powerful approach to accelerate catalyst optimization. However, challenges remain regarding radiation damage, instrumentation limitations, and data interpretation. Overall, continued development of multi-modal in situ techniques is pivotal for addressing emerging challenges and opportunities in catalysis research and technology.

Keywords Catalysis, In situ/operando techniques, Machine learning

1 Introduction

Catalysis, the process of increasing the rate of a chemical reaction by adding a substance known as a catalyst, has been an intriguing area of research in contemporary science. This field plays a paramount role in various

*Correspondence:
Chaochao Dun
cdun@lbl.gov
Jeffrey J. Urban
jjurban@lbl.gov
[1] The Molecular Foundry, Lawrence Berkeley National Laboratory Berkeley, Berkeley, CA 94720, USA
[2] Dalian Institute of Chemical Physics, National Engineering Research Center of Lower-Carbon Catalysis Technology, Chinese Academy of Sciences, Dalian 116023, People's Republic of China
[3] University of Chinese Academy of Sciences, Beijing 100049, People's Republic of China
[4] Science and Technology Division, Corning Incorporated, Corning, NY 14831, USA
[5] Instrumentation and Service Center for Physical Sciences, Westlake University, Hangzhou 310024, Zhejiang, China

industrial and biological processes, underpinning the development of energy-efficient, cost-effective, and sustainable technologies [1–3]. The realm of catalysis research encompasses heterogeneous, homogeneous, and enzymatic catalysis: Heterogeneous catalysis [4], occurring at the interface of different phases, is integral to numerous industrial operations, including petroleum refining and automotive exhaust treatment. Homogeneous catalysis [5], wherein the catalyst and the reactants are in the same phase, holds an immense potential in the synthesis of pharmaceuticals and fine chemicals. Enzymatic catalysis [6], executed by biological catalysts or enzymes, significantly contributes to understanding and harnessing biological processes. The significance of catalysis is profound. From an economic perspective, catalysis is vital for many sectors, including energy, chemicals, pharmaceuticals, and automotive. From an environmental standpoint, catalysis aids in carbon capture [7], thus mitigating climate change. In essence, catalysis research

is not only pivotal to scientific and technological progress but also a catalyst for sustainability and environmental preservation. Despite the strides made, further research is needed to overcome existing limitations and unlock new opportunities, given the rapidly changing global landscape.

The last decades have witnessed transformative advances in catalysis research, largely enabled by new experimental techniques and theoretical approaches [8]. A key trend is the application of in situ techniques in catalysis research that has led to significant strides in our understanding and control of catalytic processes [9–16]. Here, "in situ" by definition refers to the process of gathering spectra of a catalyst as it is being treated or under conditions pertinent to its catalytic function [17]. These in situ characterizations involve the observation and analysis of a functioning catalyst under genuine reaction conditions, alongside simultaneous measurements of its catalytic activity and selectivity, named "operando" [18]. This allows for a more accurate understanding of the behavior of the catalyst under real reaction conditions, rather than relying on measurements made on isolated catalysts outside of the reaction environment.

The importance of detailed information on structure, bonding, and reactivity changes, as obtained through in situ techniques, is paramount in modern catalyst design [19–21]. This information significantly impacts the understanding of catalyst active sites, stability, and longevity. Identifying the exact locations and mechanisms of catalytic reactions at the molecular level enables researchers to design catalysts that are more efficient and selective. Moreover, this information reveals structural changes in catalysts during reactions, essential for designing catalysts that maintain their structure and functionality under operational conditions. Furthermore, detailed bonding information provides deep insights into the mechanistic pathways of catalytic reactions, crucial for designing catalysts that more effectively facilitate desired reactions. Understanding bonding information helps in adjusting the electronic properties of the catalyst, vital for reaction specificity and rates. Reactivity information, such as how a catalyst interacts with different reactants and intermediates, enables researchers to design catalysts with higher selectivity, thereby reducing unwanted by-products. This comprehensive information on structure, bonding, and reactivity also fosters the design of multifunctional catalysts capable of performing multiple reactions simultaneously or in sequence efficiently.

Another significant development is the use of machine learning (ML) algorithms in catalyst discovery and optimization, accelerating the process and reducing the cost [22–24]. The integration of ML algorithms in catalyst discovery and optimization marks a significant advancement, accelerating the process and reducing costs. These advancements in ML and data analytics have enhanced the efficacy of in situ techniques by enabling efficient interpretation of the vast data they generate. The combination of in situ techniques with computational modeling forms a robust platform, correlating experimental findings with theoretical predictions, thereby deepening our understanding of catalytic mechanisms. This synergy not only leads to more accurate simulations and predictions but also significantly improves the precision and effectiveness of catalyst design.

This review, therefore, warrants continued attention and investment of catalysis research. A discussion on the current limitations in catalyst design would highlight the challenges in understanding catalyst behavior under real-world conditions. These include difficulties in observing dynamic behaviors and transient species in catalytic processes, which are crucial for optimizing catalyst performance. The article's focus on various in situ techniques, underscores their importance in addressing these challenges. By providing insights into the structural, bonding, and reactivity changes during catalysis, these techniques offer a more realistic view of catalyst function, leading to more intelligent and efficient catalyst design. The structure includes the discussion of key techniques like new development in situ electron microscopy, in situ synchrotron radiation, etc. in catalysis research. Some advancements in ML and data analytics that further propels in situ techniques, enabling the efficient interpretation of the vast amount of data these methods generate, was also include. This review is believed to bridge the gap between traditional methods and the advanced in situ techniques detailed in the article, underlining their significance in overcoming existing limitations in catalyst research.

2 Historical Overview of in situ Techniques in Catalysis Research

2.1 Limitations of traditional ex situ techniques

A thorough understanding of the development of in situ techniques necessitates an examination of the limitations of traditional ex situ techniques that these methods sought to address. Ex situ techniques, in which catalysts are studied outside their operational environment, have been the backbone of catalysis research for many decades. However, these techniques inherently present several critical limitations:

I. *Loss of Dynamic Information*: One of the most significant limitations is the loss of dynamic information. When a catalyst is removed from its reaction environment for analysis, changes in temperature, pressure, and chemical composition can induce modifications to the catalyst's structure and chemi-

cal state. Consequently, the properties observed ex situ may not accurately reflect those under actual reaction conditions.

II. *Transient Species*: Ex situ methods are generally not suited for the detection of transient species, such as intermediates and unstable compounds, which can quickly decompose upon removal from the reaction environment. These species often play crucial roles in reaction mechanisms and, hence, their observation is fundamental to a comprehensive understanding of catalytic processes.

III. *Limited Temporal Resolution*: Ex situ techniques generally have limited temporal resolution due to the time required to transfer the catalyst from the reactor to the analytical instrument. This makes it difficult to study fast or time-dependent processes.

IV. *Others like incomplete representation*: Ex situ studies typically provide an averaged view over the entire catalyst sample. This can mask spatial heterogeneities, such as variations in the catalyst's activity and selectivity across different sites.

The advent and continued development of in situ techniques have significantly mitigated these limitations. By enabling the study of catalysts under actual operating conditions, in situ and operando methods have opened a new window into the dynamic behavior of catalysts and reaction mechanisms, revolutionizing our understanding and control of catalytic processes that could not be obtained otherwise. Despite the strides made, challenges still remain, including the need for more sensitive and versatile techniques capable of probing catalysts under a wider range of conditions. As such, the evolution of in situ techniques remains an active and essential area of research in catalysis.

2.2 Brief history and development of in situ/operando techniques

In situ techniques under working conditions uncover new structures, compositions and chemistry of catalytic surfaces that differ from measurements in vacuum, which are crucial for guiding catalyst design, providing detailed structural, bonding, and reactivity information. For instance, in situ Transmission Electron Microscopy (TEM) allows direct observation of catalyst structural changes at the atomic level, revealing the dynamics of active site formation, essential for optimization. Synchrotron radiation spectroscopy, like X-ray Absorption Spectroscopy, detects chemical state and electronic structure changes in catalysts, identifying key intermediates and transition states for a deeper understanding of reaction mechanisms. Solid-state Nuclear Magnetic Resonance (NMR) can track reaction processes and captures

intermediates, studying interactions among catalysts, reactants, intermediates, and products, crucial for elucidating reaction mechanisms. Overall, in situ techniques provide multi-dimensional dynamic information under actual reaction conditions, offering valuable data for theoretical calculations and guiding the design and optimization of more efficient catalysts. Therefore, the study of catalysts in their operative state using in situ/operando techniques has been a cornerstone of catalysis research, playing an instrumental role in our understanding and control of catalytic processes [25, 26].

The history of in situ techniques dates back to the early twentieth century, with the development of basic microscopy and spectroscopy. Early practitioners quickly recognized the potential these techniques held for the direct observation of catalysts under working conditions. However, technical limitations, including the lack of suitable instrumentation and difficulties in handling catalysts under reaction conditions, initially hindered progress. The advent of electron microscopy by Max Knoll and Ernst Ruska in the 1930s marked a significant step forward [27]. Early electron microscopes enabled the visualization of catalysts at unprecedentedly high resolutions. However, these studies were generally ex situ due to the vacuum conditions required by electron microscopes, which were incompatible with the gas environment of many catalytic reactions. The development of environmental electron microscopy by Boyes and Gai in the 1970s [28], including the Environmental Scanning Electron Microscope (ESEM) and the Environmental Transmission Electron Microscope (ETEM), represented a crucial milestone. These technologies allowed for the study of catalysts under gaseous environments, providing insights into the morphology and structure of catalysts under actual reaction conditions. They further developed the in situ TEM with atomic resolution for direct probing of gas–solid reactions at high temperature (2000 °C) [29], which opened up opportunities for in situ studies of single-atom dynamics in an aberration-corrected environment. Recent developments in correlative microscopies [30], such as in-situ scanning-tunneling X-ray microscopy [31], have also offered exciting insights by providing detailed chemical information about surface elemental composition and oxidation states, complementing high-resolution electrochemical data.

Meanwhile, advances in spectroscopy, such as Fourier transform infrared spectroscopy (FTIR) [32] and X-ray absorption spectroscopy (XAS) [33, 34], offered new possibilities for in situ studies. Among which, FTIR spectroscopy has been particularly valuable for studying surface reactions, as it enables the direct observation of adsorbed species on catalyst surfaces [35]. Instead of passing the infrared light straight through

Chen *et al. Surface Science and Technology*   (2024) 2:9

Page 4 of 23

the sample in FTIR [36, 37], in diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) is a special version of FTIR, in which the infrared light is diffused and scattered by the sample, and then the reflected light is collected and analyzed [38–40]. XAS, on the other hand, provides information about the oxidation state and coordination environment of catalysts under working conditions. Typically, the X-ray Absorption Near Edge Structure (XANES) region of the spectrum is harnessed to ascertain the electronic state of the atom under examination. It primarily investigates notable characteristics in the 'near-edge' portion of a spectrum, roughly 30 eV beyond the *K*-shell absorption edge [41]. Conversely, the Extended X-ray Absorption Fine Structure (EXAFS) region is generally employed to discern the local geometric structure and coordination environment around the atom in short range order [42]. A major breakthrough came with the advent of synchrotron radiation sources in the late twentieth century. Since then, synchrotron radiation has progressed through four generations of facilities over 50 years, with each generation offering major increases in brightness, flux, and coherence [43]. Key innovations included but not limited to, storage rings, insertion devices, and low emittance/high energy lattices, which greatly enhanced the capabilities of X-ray-based in situ techniques. These high-brilliance light sources enabled more sensitive and detailed studies, transforming our understanding of catalytic processes.

In the twenty-first century, the integration of in situ techniques with computational methods has further elevated the field. Quantum chemical calculations, for example, can provide theoretical validation for experimental observations, enabling a more comprehensive understanding of catalytic processes [44, 45]. The rise of ML and big data has also reshaped the landscape of in situ techniques [46]. These technologies allow for the efficient interpretation of the vast amounts of data generated by in situ studies, accelerating catalyst discovery and optimization. Today, in situ techniques continue to evolve, driven by advancements in instrumentation, computational methods, and data analysis tools. Emerging methods, such as in situ ambient pressure X-ray photoelectron spectroscopy (XPS) [47, 48], in situ NMR spectroscopy [49], in situ electron paramagnetic resonance (EPR) spectroscopy [50, 51], in situ Mössbauer spectroscopy [52–55], in situ Raman spectroscopy [56, 57], promise to shed new light on catalyst behavior and reaction mechanisms.

In sum, the history and development of in situ techniques demonstrate a journey marked by continuous innovation and discovery. These techniques, while challenging, have provided unprecedented insights into catalytic processes, enabling the design of more efficient and sustainable catalysts, as can be seen in Fig. 1.

3 In Situ/Operando Techniques for Catalysis Research

The universal mechanisms that govern catalytic activity, including adsorption–desorption processes, surface reactions, and the role of active sites, are intricately linked to the analytical capabilities of in situ and operando techniques. These techniques, by enabling the real-time monitoring of catalysts under actual reaction conditions, offer profound insights into the dynamic interplay of molecular factors that influence catalytic properties. For example, the adsorption–desorption processes are pivotal in catalysis, serving as the initial and final steps in many catalytic cycles. These processes are influenced by the surface properties of catalysts, such as surface area, porosity, and chemical composition. In situ techniques like Infrared Spectroscopy provide direct evidence of these processes by monitoring the adsorption of reactants and desorption of products from the catalyst surface, revealing the energetics and kinetics involved. Moreover, surface reactions, the heart of catalytic processes, involve the transformation of adsorbed reactants to products. Techniques like in situ XPS and Ambient Pressure X-ray Photoelectron Spectroscopy (AP-XPS) are instrumental in studying these reactions. They provide information on the chemical states and electronic structures of the surface species, elucidating the mechanistic pathways and the role of surface intermediates.

Moreover, the active sites are the specific locations on the catalyst surface where reactions occur. Their nature and distribution are critical for catalytic activity and selectivity. In situ electron microscopy, especially High-Resolution Transmission Electron Microscopy (HRTEM) and Scanning Tunneling Microscopy (STM), allows for the visualization of these sites at the atomic level. Coupled with spectroscopic techniques like XAS, which offers insights into the local electronic and geometric structure of the active sites, these methods unravel the correlation between the structure of active sites and catalytic performance.

In this section, we will present a comprehensive view of how each in situ technique not only characterizes catalysts but also provides deep insights into the mechanisms at play during catalytic reactions. These techniques allow for the elucidation of structural, electronic, and dynamic changes in catalysts, contributing significantly to the understanding and optimization of catalytic processes.
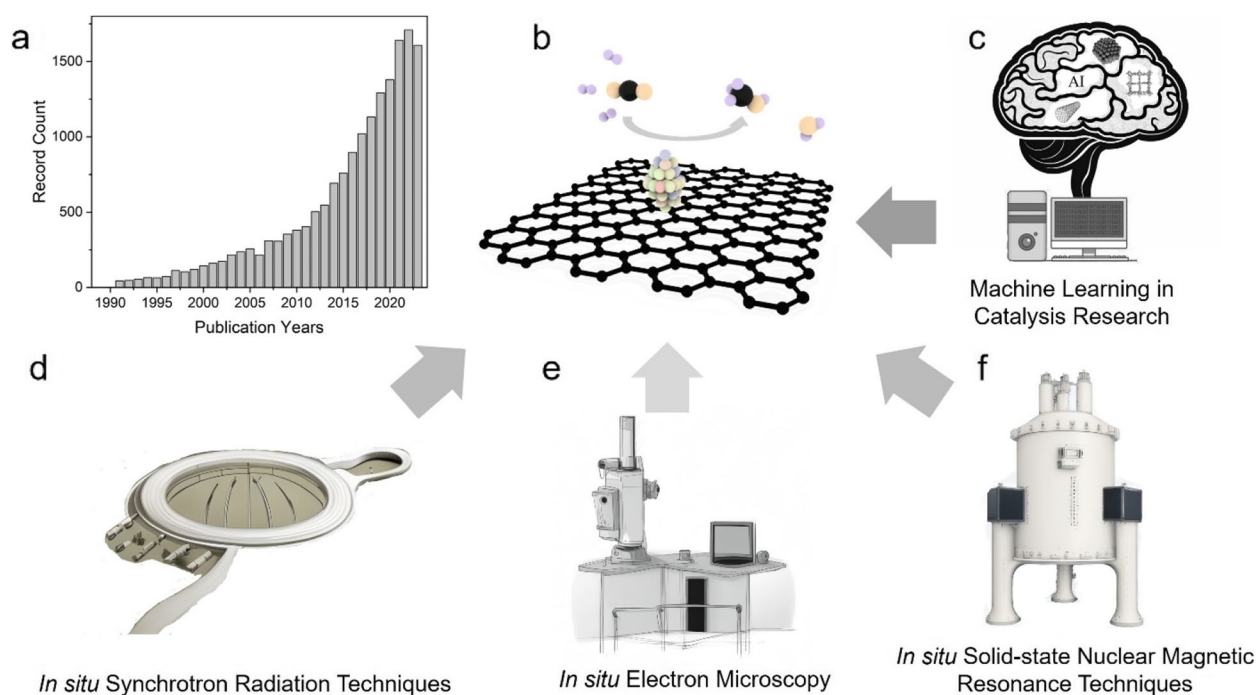
Fig. 1 a The numbers of articles related to In Situ *Techniques for Catalysis Research* published in journals each year (source: web of science, accessed on 1/14/2024). **b**-**f** In Situ *Techniques for Catalysis Research*

3.1 In Situ Electron Microscopy for Catalysis Research

3.1.1 In Situ scanning and transmission electron microscopy (TEM)

In situ scanning [58] and transmission electron [28] microscopy has become vital for catalysis research, offering subatomic spatial resolution and simultaneous spectroscopy at the atomic level. This technology allows the analysis of critical interfaces and surfaces of individual catalysts, a capability complemented by other spectroscopy techniques (See Sect. 3.2). For example, using advanced electron microscopy techniques, including a novel in situ gas cell, Cargnello et. al showed that the Pd@CeO$_2$ structure undergoes significant changes during high temperature calcination in an oxidizing environment, which are highly active catalysts for methane combustion. In situ imaging during heating reveals that the 2–3 nm particles dissociate at 500 °C into atomic "clouds" stabilized by the silica support. At higher temperatures the atoms coalesce into the larger particles and highly dispersed phase. The exceptional catalytic activity is proposed to arise from the highly dispersed Pd-Ce-Si–O phase formed at high temperatures, not the original Pd@CeO$_2$ core–shell structure [59]. So far, a plethora of in situ electron microscopy techniques have been developed over time [10, 11, 60, 61], each with unique advantages prominently featured in various review articles. In this review, we pay special attention to those electron microscopies associated with emerging cutting-edge techniques such as Four-Dimensional Scanning Transmission Electron Microscopy (4D-STEM), along with others that are integrated with in situ synchrotron radiation techniques.

The resolution of in situ TEM images depicting electrochemical processes in a liquid cell has been somewhat restrained up to now [62], partly due to high signal-to-noise ratio, enhanced spatial and temporal resolution, controlled environments or stimuli, and a significant reduction in electron beam effects. Operando 4D-STEM diffraction imaging in liquid brings superior structural knowledge compared to traditional TEM/STEM imaging, due to its enhanced sensitivity and dynamic range [63]. Leveraging a newly developed electron microscope pixel array detector (EMPAD), 4D-STEM can rapidly gather 2D electron diffraction patterns over a grid of probe positions (Fig. 2(a)-(b)). This technology reduces the electron dose significantly while concurrently collecting nanoscale crystallographic data. Such an attribute is vital when studying beam-sensitive materials in a liquid setting for catalysis. For example, Yang et.al, unravels the structural complexity of active Cu sites using correlated electron and X-ray probes based on four-dimensional electrochemical liquid-cell scanning transmission electron, demonstrating the power of advanced operando techniques for elucidating active sites in nanocatalysts [64].
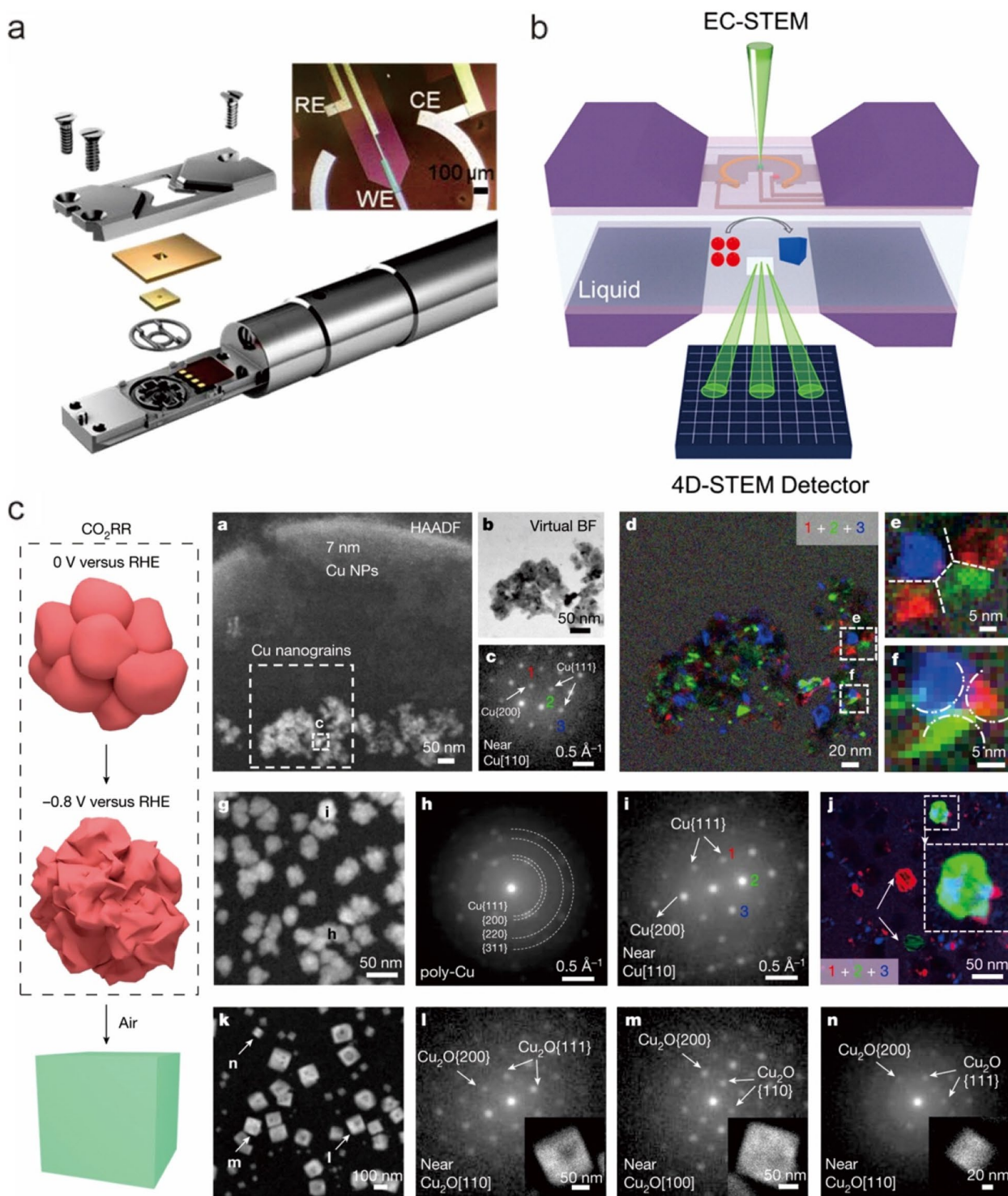
Fig. 2 a Schematic of the layered structure of a Proto-chips Poseidon liquid cell holder. Inset: optical image of the three-electrode microchip loaded with nanoparticle [64]. Reproduced with permission from ref. 64 from Nature publishing group, Copyright 2023. **b** Schematic of Operando EC-STEM with a 4D-STEM detector that enables reliable electrochemistry while monitoring dynamic morphological and structural changes under electrocatalytically relevant conditions. **c** Operando 4D-STEM diffraction imaging of metallic Cu nanograins [65]. Reproduced with permission from ref. 65 from the American Chemical Society, Copyright 2023

Operando electron microscopy in Fig. 2(c) shows the dynamic formation of polycrystalline Cu nanograins from NPs under bias, with X-ray spectroscopy confirms the transition to metallic Cu. The findings reveal that metallic Cu nanograins support a high density of under-coordinated active sites selective for C–C coupling and multi-carbon production. It was also confirmed that 7 nm Cu NPs are initially Cu@Cu$_2$O core–shell but evolve into metallic Cu nanograins under CO$_2$ reduction potentials while larger NPs maintain a partial Cu@Cu$_2$O core–shell structure. These smaller NPs form a higher density of nanograin boundaries, proposed to contain undercoordinated Cu active sites selective for C$_{2+}$ formation: A quantitative structure–activity correlation shows 7 nm NPs with 100% nanograins have 6 times higher C$_{2+}$ selectivity than 18 nm NPs with 32% nanograins.

3.1.2 In situ high-speed scanning tunneling microscopy (STM)

In situ high-speed STM enables real-time atomic imaging [31], with lateral resolution ∼100 pm and vertical resolution ∼1–3 pm at room temperature [66]. STM can observe individual/single atoms and their arrangement on a catalyst surface, providing unprecedented insights into catalytic mechanisms. A schematic cross section of the 'Reactor-STM' was given in Fig. 3(a). One typical example of the application is the exploration of CO$_2$ reduction reaction catalyzed by CoPc using in situ electrochemical STM by Wan et.al [31], in which a monolayer of CoPc was assembled on an Au(111) surface, and CO$_2$-saturated electrolyte revealed CoPc-CO$_2$ complexes. In situ electrochemical STM demonstrated reversible transformations between CoPc- CO$_2$ and CoPc, controlled by the potential during CO$_2$ reduction. Another example is that, Patera et.al demonstrated the catalytic role played by single metal adatoms during the technologically relevant process of graphene growth on Ni using in situ STM [67]. The research identifies that at high temperatures, carbon diffuses onto the nickel surface, fostering the growth of graphene islands with zigzag and Klein terminated structures. By monitoring the layer formation at the atomic scale and with a time resolution down to milliseconds through STM, the researchers observed mobile nickel adatoms at the kink sites of the graphene edges, functioning as single-atom catalysts (Fig. 3(b)). Density functional theory calculations showed that these adatoms bind strongly to the kinks, lower the energy barrier for carbon attachment, and facilitate the addition of carbon dimers, thus promoting graphene growth. This research offers atomic-level insights into the growth mechanism of graphene, highlighting the potential of dynamic high-speed STM imaging for understanding surface processes at the atomic scale.

Furthermore, high or ambient pressure pairs with ambient temperature, facilitating weakly interacting species to densely cover surfaces at room temperature in equilibrium with high gas pressure. This aids in overcoming activation barriers and triggering atomic structure reconstructions, often forming new structures for surface catalysts, which is highlighted by the use of high-pressure STM [66]. For example, Salmeron et.al used STM to observe the formation of clusters at step edges of Cu(111) under CO pressure at room temperature in the pressure range 0.1 to 100 Torr [69]. At 0.1 Torr CO, clusters appeared, while terraces stayed flat. At 0.2 Torr CO, nanoclusters covered the terraces, increasing in density with CO pressure (Fig. 3(c)). STM identified two cluster types: 0.5 nm triangular clusters (3 Cu atoms) and 1.5 nm hexagonal clusters (19 Cu atoms). High resolution STM images showed bright maxima (CO molecules) at cluster perimeters. From 0.2 to few Torr CO, clusters demonstrated mobility through splitting, diffusing, and coalescing. Clusters persisted after CO evacuation, losing atomic resolution but showing enhanced reactivity by dissociating water. DFT confirmed STM findings, showing CO binding stabilizes 19-atom clusters, with enhanced tunneling contrast from CO on corner atoms.

In sum, STM and TEM are key for understanding catalysis at molecular and atomic levels in catalytic science. In situ STM excels in examining surface properties of single crystals, revealing detailed electronic and geometric aspects of catalysis. In contrast, in situ TEM is ideal for observing nanoparticle catalysts in real-time, shedding light on their structural changes and chemical reactions during the catalytic process [70]. These techniques offer complementary insights: TEM explores how nanoparticle size affects catalysis, particularly at low-coordinated edge and corner sites, while STM investigates the influence of atomic-scale structures on catalytic activity [71]. Additionally, they help study the critical interactions within bimetallic nanoparticles, especially at metal-oxide interfaces, crucial for forming active catalytic sites [72–74].

Research in this field, supported by studies like those of Tsung et al. [70] and Somorjai et al. [71], highlights STM and TEM's roles in revealing the intricate structural and chemical dynamics essential for catalysis. Together, they form a comprehensive set of tools for catalysis research, enhancing our understanding of catalytic mechanisms and aiding in the development of more efficient, robust catalysts.

3.2 In Situ Synchrotron Radiation Techniques for Catalysis Research

Synchrotron radiation light sources, with their broad spectrum, high brightness and coherence, have surpassed conventional means in several applications and made
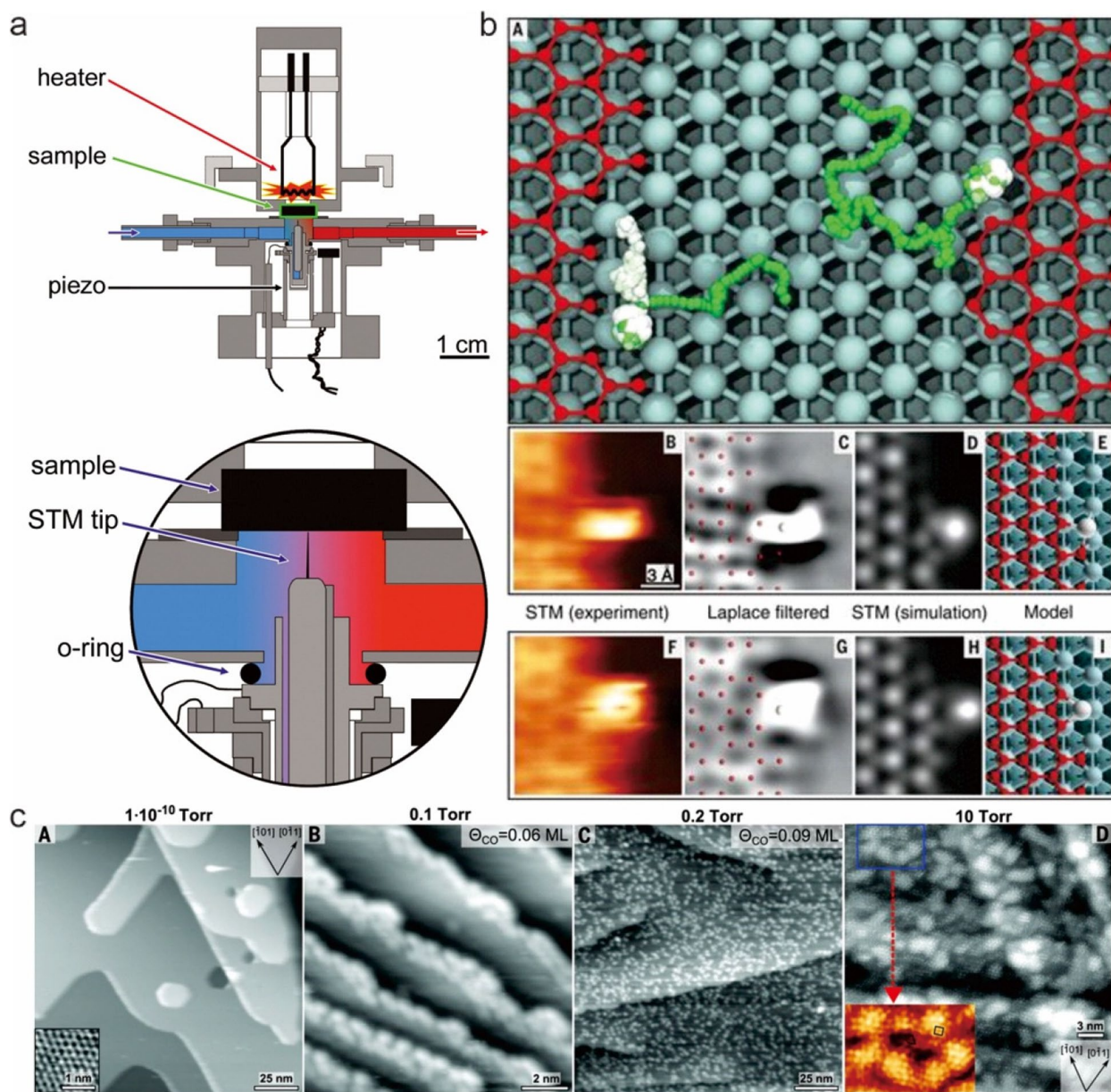
Fig. 3 a Schematic cross section of the 'Reactor-STM'. The apparatus possesses the ability to render images of a material's surface while it serves as an active catalyst under gas flow conditions, accommodating pressures of up to 5 bar and temperatures reaching 500 K. Excluding the sample surface, only the STM tip comes into contact with the circulating gas mixture, which can be both heated and pressurized [68]. Reproduced with permission from ref. 68 from Elsevier, Copyright 2005. **b** Real-time imaging of adatom-promoted graphene growth on nickel [67]. Reproduced with permission from ref. 67 from Science, Copyright 2016. **c** STM images of Cu(111) showing clusters filling the terraces as a function of ambient CO pressure [69]. Reproduced with permission from ref. 69 from Science, Copyright 2016

substantial contributions to the field of catalysis research, including crystal and electronic structure analysis, surface composition checks, and detection of chemisorbed species and reactive intermediates [75].

The most common one is the synchrotron radiation X-ray diffraction (SRXRD) technique, which is used to identify crystalline materials and analyze their structure

[76]. By bombarding a sample with X-rays and observing the diffraction pattern, researchers can determine the arrangement of atoms within the crystal structure. For example, Wei et.al reported the synthesis and characterization of Co-doped TiO_2 nanorods with single Co sites substituted in the brookite TiO_2 (210) surface, and their oxygen evolution reaction (OER) catalysis [34]: $Co-TiO_2$

nanorods were synthesized with uniform size/shape and Co substitutional doped as single sites in the TiO_2 matrix, mainly on the (210) facet. The Co-TiO_2 shows high OER activity, with low overpotentials of 332 and 396 mV at 10 and 100 mA/cm^2, respectively. They further used in situ XRD and EXAFS to confirm it is the brookite TiO_2 structure and isolated Co sites that are maintained during OER without changes. XAS shows Co is initially present as Co^{2+} but converts to higher oxidation state after electrocatalysis, indicating stronger Co–O hybridization. This combined synthesis, spectroscopy, and DFT approach establishes the detailed OER mechanism over the single-site Co electrocatalyst, providing a methodology to further optimize such catalytic centers. Xia et.al presents a novel method for fabricating Ru icosahedral nanocages using a face-centered cubic (*fcc*) structure [77]. The process involves conformally coating Pd icosahedral seeds with Ru shells and selectively removing Pd cores, with bromide ions playing a crucial role in Ru deposition. In situ XRD confirms the stability of the *fcc* structure and icosahedral shape up to 300 °C. These nanocages demonstrate enhanced catalytic activity in 4-nitrophenol reduction and hydrazine decomposition, linked to twin boundaries. Predictions from density functional theory propose that the nanocage's unique structure and high surface area bolster catalytic performance, particularly beneficial for ammonia synthesis.

Scanning transmission X-ray microscopy (STXM) is an advanced microscopy approach that utilizes X-rays to produce high-resolution images of a specimen. This technique offers the unique ability to obtain detailed information about the chemical state of a material at the nano-level, providing spatially resolved insights on the electronic and chemical structure of the catalyst material. Technically, STXM operates through a process known as a raster scan, where an X-ray probe is directed to move systematically across the specimen. It captures the intensity of transmitted X-rays at each probe position. By introducing an additional rotation of the sample, STXM can be further utilized for tomography, providing three-dimensional imaging of the specimen. The resolution achievable in STXM is contingent on several factors, primarily the size of the X-ray spot. This, in turn, depends on the coherence of the X-ray source, the accuracy of the experimental setup, and the performance of the focusing

lenses used. These aspects collectively contribute to the resolution limitations of STXM, drawing a parallel with the resolution constraints observed in transmission X-ray nano-computed tomography [78]. Related studies on in situ STXM including the comparation between STXM-XAS and STEM-EELS (scanning transmission electron microscopy–electron energy loss spectroscopy) was summarized by Weckhuysen et.al [79], which will not be included here.

Given the multifaceted nature of catalytic reactions, the development of synchrotron-radiation-based multi-techniques is vital for accurately capturing the dynamism of catalytic processes. It can include but not limited to,

3.2.1 X-ray Absorption Spectroscopy (XAS)

XAS, including XANES and EXAFS, is a popular technique for characterizing catalysts at the atomic level. Figure 4(a)-(b)shows a schematics of a typical X-ray absorption spectrum and processes occurring during X-ray absorption. XANES can reveal the oxidation state and local symmetry of a given atom, while EXAFS provides information about the atom's local structure [80]. XAS can be used to provide information about the local structure and chemical state of a catalyst and can be used to monitor changes in the oxidation state of the catalyst during reaction. This information can provide insight into the reaction mechanisms and the behavior of the catalyst during reaction [81, 82]. Specifically, NEXAFS segment of the spectrum spans the excitation close to the threshold for electron ionization, also referred to as the 'edge'. This area incorporates excitations to unfilled orbitals, such as antibonding orbitals, Rydberg states, or unoccupied sections of a solid-state density of states plot. Consequently, the NEXAFS area (around the absorption edge) can yield insights about the chemical environment, including the formal oxidation state, symmetry, or local charge distribution. Meanwhile, EXAFS region of the spectrum arises from photoelectrons fully expelled from the atom, but potentially subject to backscattering from the electron clouds of nearby atoms, leading to oscillations relative to X-ray energy. This data delivers details about the local environment, specifically the count and nature of coordinating atoms, along with the distances to these neighboring atoms. In situ/Operando XAS holds a significant advantage over traditional XAS in that

(See figure on next page.)
Fig. 4 a, **b** Schematics of a typical X-ray absorption spectrum and processes occurring during X-ray absorption [82]. Reproduced with permission from ref. 82 from the Royal Society of Chemistry, Copyright 2020. **c** Illustration of operando X-ray absorption spectroscopy (XAS) in transmission and fluorescence mode [83]. Reproduced with permission from ref. 83 from the Wiley, Copyright 2021. **d**, **e** [34] and **f-j** [33], two examples of in situ Hard X-ray absorption spectroscopy and in situ Soft X-ray absorption spectroscopy. Reproduced with permission from ref. 33 and ref. 34 from Nature publishing group, Copyright 2018 and 2019
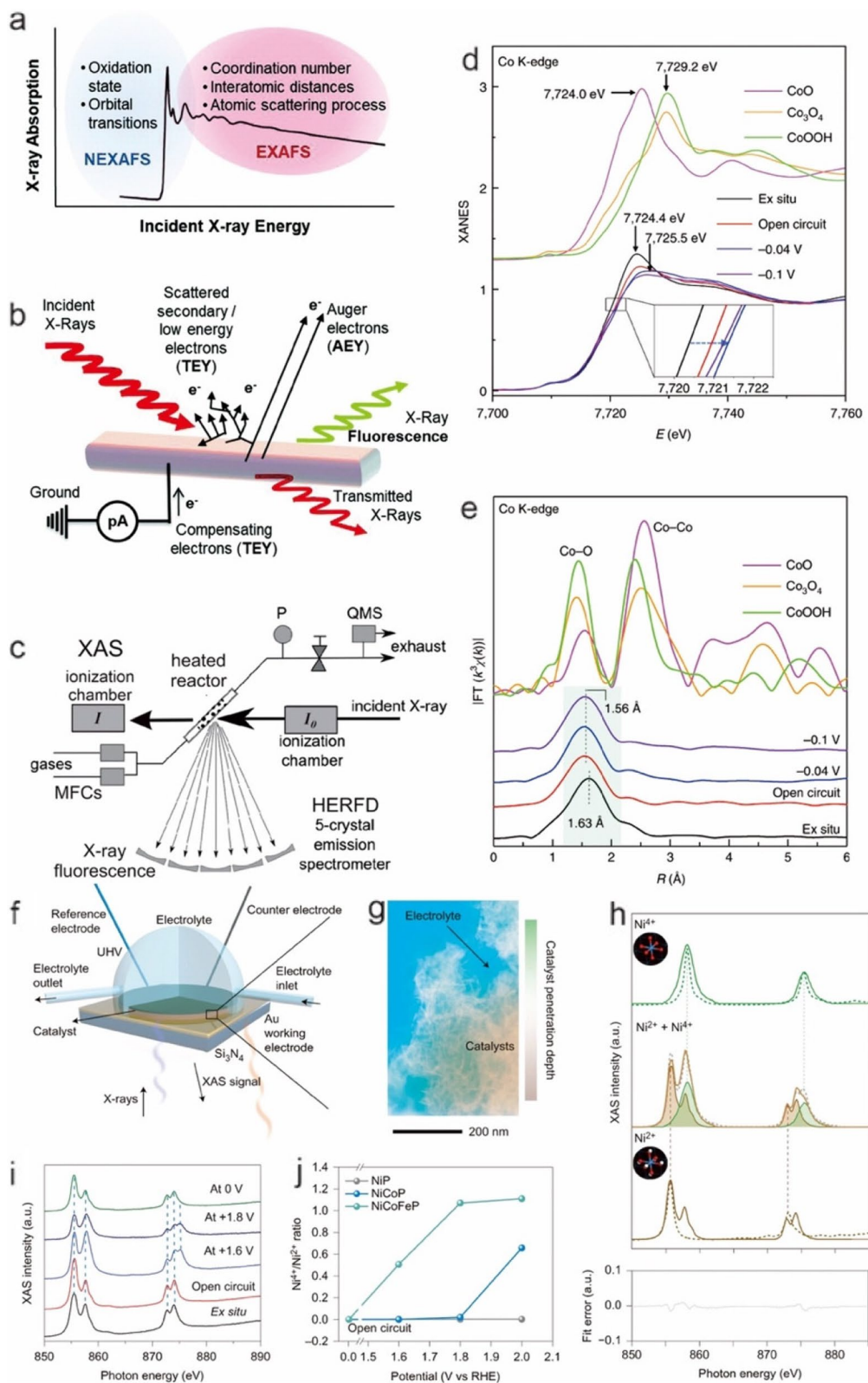
Fig. 4 (See legend on previous page.)

Chen *et al. Surface Science and Technology*   (2024) 2:9

Page 11 of 23

it allows for the real-time study of chemical reactions under realistic operating conditions, with illustration of operando XAS given in Fig. 4(c).

Hard X-ray absorption spectrSoscopy (h-XAS) has been seen in in situ and operando studies, primarily due to its relatively uncomplicated setup that operates effectively in an ambient environment. Wei et.al utilized in situ h-XAS to uncover the dynamic active structure of single-atom cobalt catalysts during the electrocatalytic hydrogen evolution reaction (HER) [34]. They discovered that original Co_1-N_4 sites, part of a single-atom cobalt catalyst they prepared, adsorbed hydroxyl groups from the electrolyte under open-circuit conditions, forming high-valence HO-Co_1-N_2 sites. These sites facilitated water dissociation, accelerating the typically slow Volmer step and contributing to the catalyst's high activity. This study reveals how susceptible single-atom catalyst structures can be under operational conditions, providing valuable insights for designing single-atom catalysts by manipulating the coordination environment (Fig. 4(d)-(e)). Another study by Chen et.al, who examined the electronic and structural shifts in a cobalt-nitrogen/carbon (Co-N_x/C) catalyst, derived from pyrolyzed vitamin B12, during the oxygen reduction reaction (ORR) [84]. They found the detection of a single oxygen atom attached to the Co atom, with a bond length of ~1.84 Å, when the catalyst was under 0.4–1.0 V biases. Operando XANES analysis revealed partial oxidation of the Co metal from +2 to a state between +2 and +3 under catalytic conditions, signifying electron transfer during catalysis, Theoretical computations also showed that the adsorbed oxygen atom formed an antibonding orbital with the Co d-orbitals, thereby weakening the oxygen bond and promoting activation and reduction of the oxygen molecule. These results demonstrated the catalyst preferentially adsorbs oxygen molecules and goes through a four-electron reduction pathway to produce water via intermediate states.

Performing in situ Soft X-ray absorption spectroscopy (s-XAS), on the other hand, is more challenging, particularly when dealing with liquid phase conditions. Despite these challenges, s-XAS has unique advantages over h-XAS as it can examine systems containing elements like carbon, nitrogen, and oxygen [82]. Also, it's sensitive to surface-level interactions—crucial for studying catalysts where reactions occur on surfaces. These experimental challenges can be overcome using photon-in–photon-out techniques in the *s*-XAS range with an information depth of a few hundred nanometers. Sargent et.al uses density functional theory (DFT) calculations and in situ s-XAS to study multi-metal oxides for electrocatalytic activity [33] (Fig. 4 (f)-(j)). They

demonstrated that doping Ni-based oxides with Co, Fe, and P can optimize the electronic structure and lower the energy required to generate Ni^{4+} sites essential for O_2 evolution. The NiCoFeP oxyhydroxide catalysts synthesized exhibited enhanced Ni^{4+} generation at low overpotential, outperforming IrO_2 in water oxidation with exceptional stability. Furthermore, the research achieved a 1.99 V cell voltage and 64% electricity-to-fuel efficiency for CO_2 reduction to CO with water oxidation in a membrane-free electrolyze using NiCoFeP. The study showcases a promising approach in designing functional electronic structures in multi-metal oxides through theory-guided strategies using in situ synchrotron radiation techniques.

The integration of high-resolution XAS with state-of-the-art electron microscopy is also pivotal for advancements in catalysis. For example, Wu et.al presents a new propane dehydrogenation (PDH) catalyst comprised of sub-nanometric Pt clusters located inside the pores of a germanosilicate zeolite (Pt@Ge-UTL) [85]. The zeolite was acid-treated for stabilization, enriched with Germanium (Ge) atoms that provide anchoring for the Pt. Cutting-edge electron microscopy like Cs-corrected HAADF-STEM and integrated differential phase contrast STEM (iDPC-STEM) were used to directly visualize the Pt clusters attached near Ge-enriched units within the zeolite channels. Additionally, in situ XAFS, 19F MAS NMR, and synchrotron PDF analysis were employed to understand the local atomic structure, revealing Pt4 clusters linked through Pt-O-Ge to Ge2-d4r sites. The catalytic sites of the novel Pt4-Ge2-d4r@UTL structure promote PDH with superior activity, selectivity, and stability by decreasing the barrier for C-H bond cleavage. At the same time, Velasco-Velez et.al provided insights into the Cu electrode's electronic structure and morphological shifts during CO_2 electrochemical reduction using in situ techniques including in situ scanning electron microscopy (SEM) under reaction conditions in the presence of aqueous electrolyte using a continuous flow cell and in situ s-XAS [14]. Utilizing two distinct in situ electrochemical cells, they captured changes in both surface and bulk electronic structures. The researchers revealed that under CO_2 reduction conditions, both surface and deep layers of the electrode reduce to metallic copper, contrary to the previously thought active Cu^+ and Cu^{2+} oxides. This transformative process, documented through in situ microscopy, creates a rougher copper surface, facilitating enhanced catalytic activity and selectivity. This study underscores metallic copper as the pivotal active sites, guiding the design of effective CO_2 reduction electrocatalysts.

3.2.2 Synchrotron radiation ambient pressure photoelectron spectroscopy (APPES)

APPES, especially, APXPS and ambient pressure X-ray absorption spectroscopy (APXAS) (Fig. 5(a)), provides information about the electronic structure of a catalyst, including its elemental composition, chemical state, and electronic state of the elements present [58, 89]. For APXPS, it can provide valuable information about catalysts' surfaces, as the information depth is usually only a few nanometers (5 ~ 10 nm). For example, Liu *et.al* investigated the interaction of oxygen gas with Cu (100) and Cu (111) single crystal surfaces using APXPS [90]. The study finds that under low pressure, Cu (100) adsorbs oxygen more readily through dissociative chemisorption compared to Cu (111). However, at higher oxygen pressures, an oxide layer forms more readily on the Cu (111) surface. The presence of a specific reconstruction on Cu (100) seems to slow down oxidation, indicating the process is orientation-dependent and may proceed via different mechanisms. Moreover, the study suggests that an operating ion gauge can facilitate sample oxidation, which requires control. The results demonstrate that the surface reconstruction on Cu (100) might alter subsurface oxygen abundance, thus impacting the oxidation rate.

Salmeron *et.al* studied the synthesis of CoPd alloy nanoparticles of varying compositions and their ensuing characterizations using advanced techniques like in situ APXPS and scanning transmission electron microscopy coupled with electron energy loss spectroscopy (STEM-EELS) [87] (Fig. 5(b)-(c)). The alloy composition of $Co_{0.24}Pd_{0.76}$ was found to achieve complete CO conversion to CO_2 at the lowest temperature. APXPS revealed that Co segregates to the nanoparticle surface as an oxide after pretreatment, and exposure to CO or O_2 influences the surface segregation of Pd and Co. This segregation was less evident with higher Co content, with the surface fully covered by CoO_x at $Co_{0.52}Pd_{0.48}$. The coexistence of Pd and CoO_x on the nanoparticle surface was seen to enhance CO oxidation, with the synergy being maximized when CoO_x partially covers the surface, likely at the $Co_{0.24}Pd_{0.76}$ composition.

The combination of APXAS and APXPS provides complementary information about a material. While APXPS gives detailed information about the surface chemistry and electronic structure, APXAS provides insight into the bulk properties and deeper layers of the material. For example, Serov et.al presents a novel platinum group metal-free (PGM-free) electrocatalyst, nickel-molybdenum supported on carbon black (NiMo/KB), for the
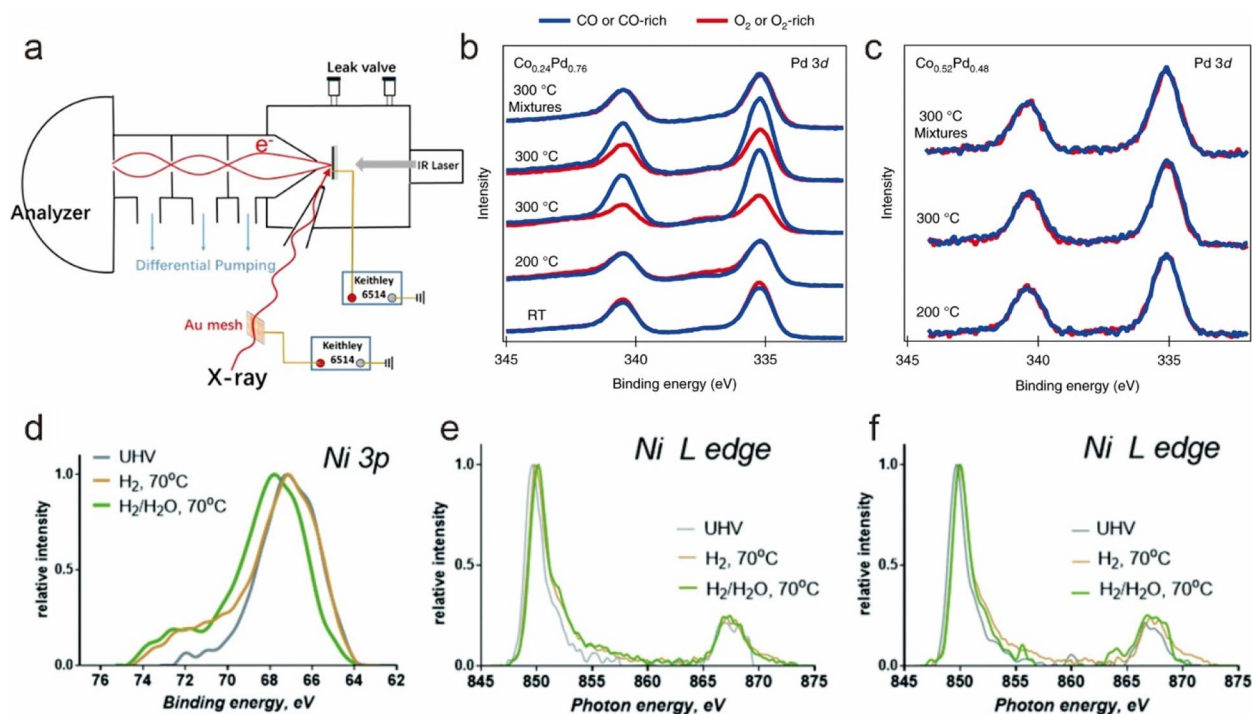

Fig. 5 a Schematic diagram of ambient pressure electron yield mode X-ray absorption spectroscopy at the APPES [86]. Reproduced with permission from ref. 86 from Taylor & Francis Group, Copyright 2022. **b**, **c** AP-XPS measurements on Pd and CoPd nanoparticles under reaction conditions [87]. Reproduced with permission from ref. 87 from Nature publishing group, Copyright 2019. **d-f** In situ APXPS and APXAS confirm Ni as the active site for HOR [88]. Reproduced with permission from ref. 88 from the Royal Society of Chemistry, Copyright 2017

hydrogen oxidation reaction (HOR) in alkaline exchange membrane fuel cells [88]. The NiMo/KB catalyst exhibits high HOR activity, with a mass activity of 4.5 A/g, surpassing prior PGM-free catalysts. This is attributed to the molybdenum lowering the nickel-hydrogen binding energy, thereby enhancing HOR kinetics. The catalyst, used as an anode in AEMFC tests, achieves a peak power density of 120 mW/cm2 at 0.5 V, a record for PGM-free anodes. Performance is further improved by reducing anode humidity from 100 to 70%, mitigating anode flooding. In situ APXPS and APXAS confirm Ni as the active site for HOR (Fig. 5(d)-(f)), while Mo alters Ni's electronic properties to boost HOR activity, without adsorbing hydrogen. The catalyst demonstrates good stability over 115 h of voltage hold testing at 0.7 V. The NiMo/KB catalyst, therefore, offers promising potential for advancing PGM-free AEMFC performance, providing valuable insights into material design for future improvements.

Despite the fact that APXPS and APXAS can provide evolution of elemental and chemical information during in situ environments, ambient-pressure mapping of resonant Auger electron spectroscopy (AP-mRAS) can be more powerful in that XAS data can be collected in AEY mode with kinetic energy resolved, i.e., compared to XAS, mRAS provides an additional dimension along the kinetic energy of the emitted Auger electrons at each resonant energy (Fig. 6(a)). Thus, mRAS

can reveal the valence and unoccupied states at the absorption threshold, enhancing the sensitivity to the electronic states near the absorption edge. Also, the details of a secondary decay process at different photon energy, including the non-resonant or normal Auger and resonant Auger process, can be extracted from mRAS. For example, recently, Liu et.al used in situ AP-XPS and AP-mRAS to investigate Rhodium's oxidation under different temperatures and oxygen pressure, revealing sequential formation of various Rh-O species [92]. The experiments identified unique features of different Rh-O species, supplemented with AP-mRAS fingerprint spectra. Figure 6(b) showcases the utility of AP-mRAS in characterizing Rh-O species on a Rh (110) surface, which presents AP-mRAS spectra for three distinct species: chemisorbed oxygen atoms (2×1)-O, O-Rh-O tri-layer surface oxide, and Rh_2O_3 bulk oxide. Each species exhibits unique fingerprint peaks, helping distinguish them. This data is supplemented by O K-edge XAS spectra, which reveal distinct absorption features for each species. This systematic use of AP-mRAS and XAS provides insights into the electronic structure evolution during Rh (110) oxidation, showcasing AP-mRAS's potential to work in tandem with XPS and XAS to characterize metal-oxide species under reaction conditions.
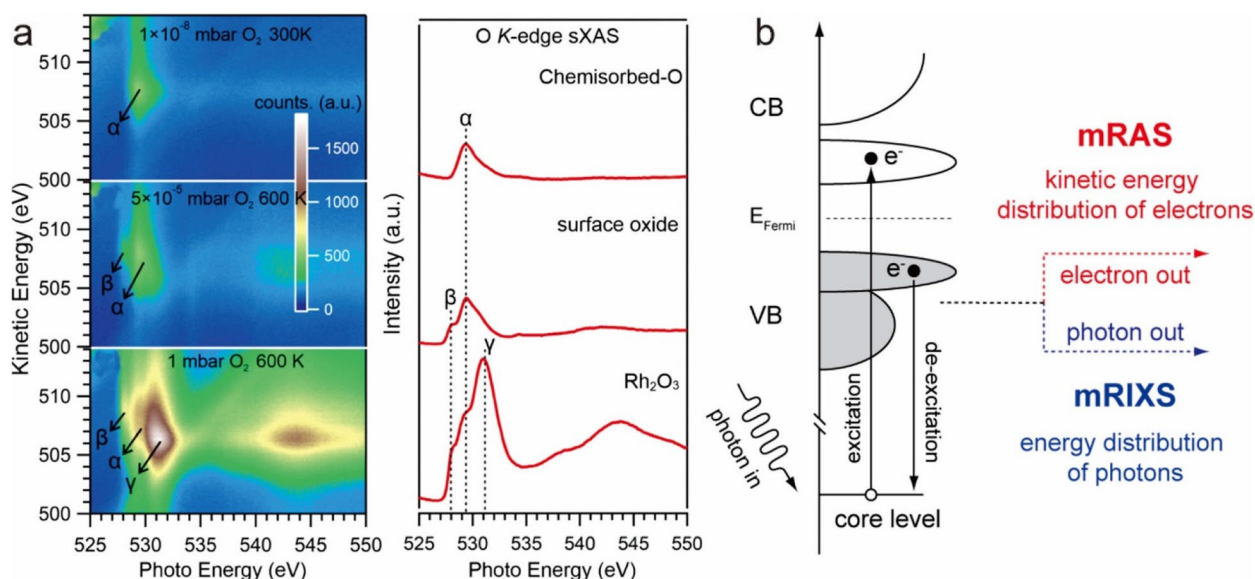

Fig. 6 **a** Schematic diagram of the fundamental process of mRAS and mapping of resonant inelastic X-ray scattering (mRIXS) (mRIXS) [91]. The mRAS and mRIXS processes begin with core level electron excitation, followed by two parallel de-excitation channels. These provide energy-resolved maps along incident photon energy and emitted photon/electron axis, aiding in spectrum overlap resolution. mRAS, with its limited probe depth, is surface-sensitive, while mRIXS, with deeper photon penetration is bulk-sensitive. Reproduced with permission from ref. 91 from the Wiley, Copyright 2023. **b** AP-mRAS spectra of Rh (110) collected near the O K-edge under varying conditions; O K-edge XAS in AEY under identical experimental conditions, integrated from all kinetic energy ranges in AP-mRAS spectra [92]. Reproduced with permission from ref. 92 from the American Chemical Society, Copyright 2023

3.2.3 Infrared (IR) spectroscopy

IR spectroscopy, with scanning probe microscopy, allows precise analysis of heterogeneous materials at the nanoscale. Synchrotron infrared nano-spectroscopy enhances this by utilizing low-noise, broadband synchrotron infrared radiation, offering broadband spatio-spectral analysis for catalysis research (Fig. 7(a)) [93].

The catalytic activity of heterogeneous catalysts is closely related to the coordination number of surface atoms. Surface defects and edge regions tend to exhibit higher catalytic activity due to low-coordinated surface atoms. Directly probing the catalytic activity of different sites on metal nanoparticles is crucial for understanding heterogeneous catalysis mechanisms. However, conventional infrared and Raman spectroscopies are diffraction-limited in spatial resolution and cannot achieve this goal. High-spatial-resolution synchrotron-radiation-based infrared nano-spectroscopy (SINS), can map site-dependent differences in reactivity on single particles, infrared nano-spectroscopy line scans were conducted following exposure of the sample to various reaction conditions, can directly probe the catalytic activity differences between sites on metal nanoparticles. A SINS schematic was given in Fig. 7(b). For example, Gross et.al employed SINS with a spatial resolution of 25 nm to analyze the catalytic activity of different regions on single Pt nanoparticles in the oxidation and reduction of hydroxyl-functionalized N-heterocyclic carbenes [94]. They chemically anchored these NHCs to the Pt nanoparticle surfaces and then SINS line-scanning was used to monitor the infrared absorption changes of NHCs at the edge and center of Pt nanoparticles under various oxidizing and reducing conditions (Fig. 7(c)-(d)). Findings revealed that the edge-anchored NHCs displayed higher catalytic activity compared to the center under both mild oxidation and reduction conditions, affirming the superior activity of low-coordinated surface atoms at the nanoparticle edge. The same methodology, when applied to nitro functionalized NHCs on Au nanoparticles, confirmed similar results. Therefore, this high-resolution infrared spectroscopy technique can directly probe the catalytic activity differences between sites on metal nanoparticles, providing important insights into heterogeneous catalysis and guiding the design and optimization of catalysts.

In sum, despite the unparalleled contributions of synchrotron radiation techniques to catalysis research, certain constraints warrant attention. Primarily, the intense X-ray radiation can induce structural alterations in catalyst samples, engendering potential discrepancies between observed and innate catalyst properties, an effect known as 'radiation damage' [75]. Additionally, the necessity of sophisticated instrumentation and high operational expertise limits the widespread utilization of these techniques. The interpretation of the large and complex datasets generated often necessitates advanced computational methodologies and substantial domain expertise. Finally, the experimental conditions achievable at synchrotron facilities may not comprehensively emulate industrial process conditions, creating potential limitations in the direct translation of research findings. Therefore, while synchrotron radiation techniques are indispensable, their application necessitates careful consideration of these inherent limitations.

3.3 In situ solid-state Nuclear Magnetic Resonance (NMR) Techniques for Catalysis Research

In situ solid-state NMR has become a powerful tool to explore the mechanism of catalytic reactions. This technique can track the catalytic reaction process in situ, capture the species of reaction intermediates, study the structural changes of catalysts, reactants, intermediates and products and their host–guest interactions with catalysts, explore the reaction process close to the real reaction conditions from the molecular level, and reveal the reaction mechanism. At present, there are two main types of in-situ solid-state NMR technology: batch-like [95] and continuous-flow [96]. Batch like (Fig. 8(**a**)), that is, the catalyst is pretreated with the sample outside the probe and adsorbed a certain amount of reactants, then loaded into the NMR rotor, and then transferred to the probe, heated to the specified reaction temperature by the probe, and at the same time the spectrum obtains a series of reactants in the process of NMR spectra. The operation process of this method is relatively simple and easy to implement, which can realize the reaction under high temperature and high-pressure conditions and is widely used in catalytic reactions. However, since the vast majority of reactions are carried out under continuous flow conditions, which is very different from this static method, changes in reaction flow velocity may lead to different reaction results, the continuous flow NMR technology (Fig. 8(b)) can realize the exploration of the reaction mechanism under real flow conditions.

Among them, especially for heterogeneous catalysis, the continuous-flow NMR technology reproduces the real catalytic reaction process to the greatest extent, thereby revealing the reaction mechanism in the actual reaction process. Using this technology, many research teams have made outstanding results in catalytic reaction mechanism, reaction intermediate species capture, and reaction kinetics. Hunger et al. [100–102] used continuous-flow NMR technique to investigate the MTO mechanism, in which surface methoxy species had been considered as a very important intermediate for the formation of the first C–C bond. Xu et al. [103] conducted in-depth research on the formation of the initial C–C
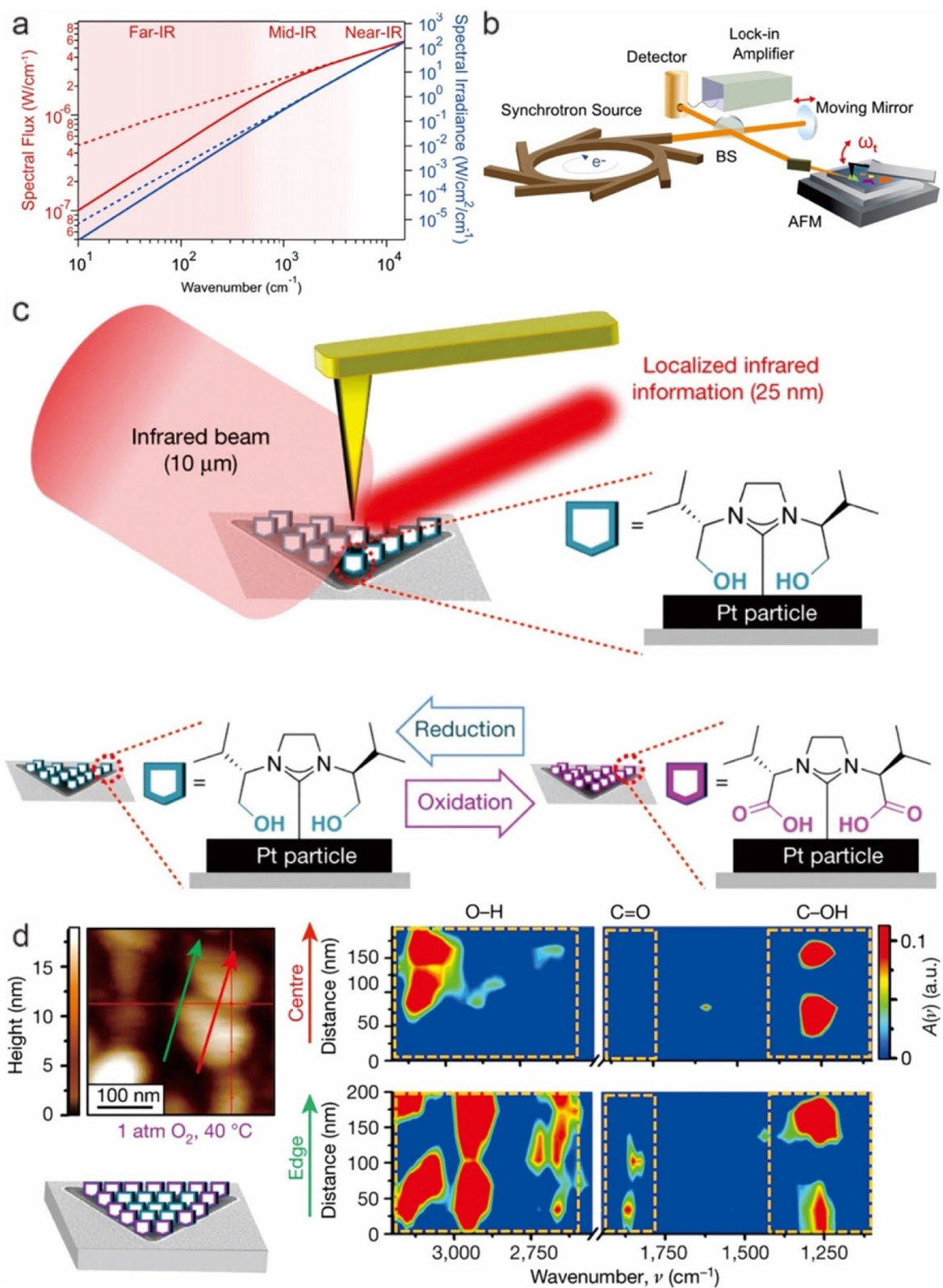
Fig. 7 **a** Calculated spectral flux (red) and spectral irradiance (blue) for bend magnet radiation at the Advanced Light Source Division, Lawrence Berkeley National Laboratory [93]. Reproduced with permission from ref. 93 from Elsevier, Copyright 2020. **b** SINS schematic. **c, d** Infrared nanospectroscopy line-scan measurements on the centre and edge of Pt particles [94]. Reproduced with permission from ref. 94 from Nature publishing group, Copyright 2017
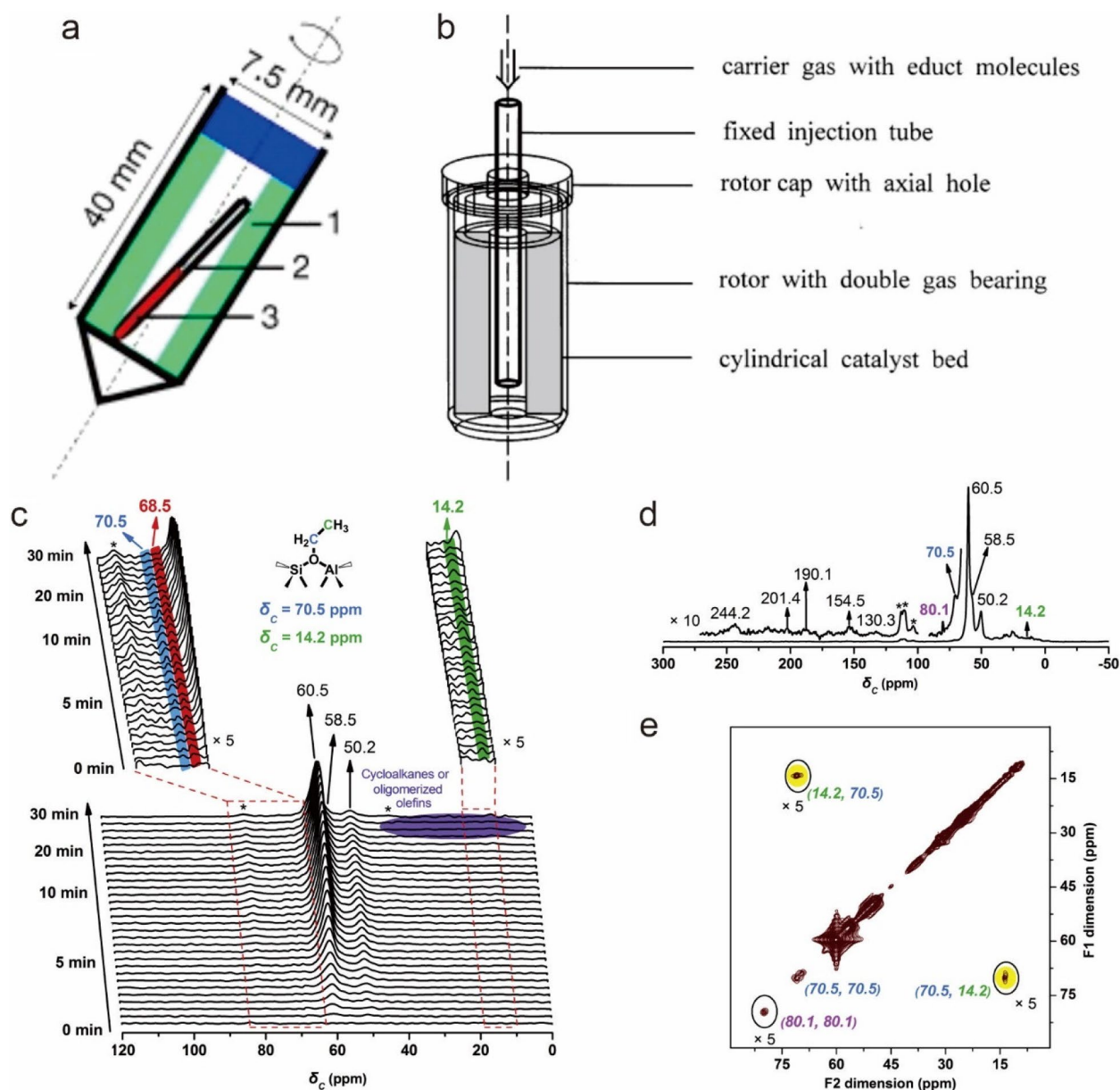
Fig. 8 **a** Schematic illustration of the setup for the in situ adsorption experiment inside the solid-state NMR rotor: 1) nano-porous material compacted on the walls of the rotor by prior spinning; 2) thin-walled glass capillary tube; 3) liquid to be adsorbed on the nanoporous material [97]. Reproduced with permission from ref. 97 from the Wiley, Copyright 2007. **b** Schematic drawing of the 7 mm double bearing MAS rotor modified for in situ MAS NMR investigations under continuous-flow conditions [98]. Reproduced with permission from ref. 98 from Elsevier, Copyright 1997. **c** In situ solid-state 13C MAS NMR spectra of HSSZ-13 with continuous-flow (CF) 13C-methanol conversion at 220 ℃. The spectra were recorded every 30 s from 0 to 10 min and then every 120 s from 10 to 30 min. **d** The 13C CP/MAS NMR spectrum of HSSZ-13 after in situ 13C-methanol conversion at 220 ℃ for 30 min. **e** 2D 13C–13C CORD spin diffusion MAS NMR spectrum of the sample in (**d**) with a mixing time of 50 ms [99]. Reproduced with permission from ref. 99 from Cell Press, Copyright 2021

bond of methanol conversion on ZSM-5 zeolite by *in-situ* solid ^{13}C MAS NMR technology, and proposed the reaction mechanism of the activation of methanol/dimethyl ether by surface methoxy/trimethyloxonium ion to generate initial C–C bond. Recently, they used in situ solid-state NMR technology to directly capture the highly reactive ethylene precursor, that is, the surface ethoxy species, for the first time under a true MTH reaction (Fig. 8 (c)-(e)) [99]. These findings and in situ captured activated C1 reactants linked C1 species and initially generated ethylene, where C1-mediated activation of methanol/DME to form the first C–C bond. In addition,

the ab initio molecular dynamics (AIMD) technique was used to simulate the reaction path formed by methanol/DME and methoxy/trimethyloxonium ions to form C–C bonds, and the reaction process was visually reproduced. Based on the experimental evidence of NMR and theoretical calculation results, the zeolite catalyst and active C1 intermediates contribute together to the first C–C bond formation in a synergistic manner. This continuous-flow NMR technology not only helps solve many important problems in the formation of initial C–C bonds from methanol to olefins, but also becomes a powerful tool in the reaction of ethanol to low carbon olefins (ETO), revealing the formation mechanism of important olefin products in the ETO reaction catalyzed by molecular sieve at the molecular level [104, 105].

The developments of in situ MAS NMR combined with other techniques will give more insights into the reaction mechanism. For example, Hunger et. al [106] used improved continuous-flow NMR technology coupled with UV–Vis spectroscopy to capture carbenium ions formed during the conversion of methanol on ZSM-5 catalysts, providing indirect evidence for the identification of hydrocarbon pool species such as polymethylbenzene in the hydrocarbon pool mechanism. Xu et al. [107] reported a design of laser-hyperpolarized xenon premixed with a reactant outside the probe head then entered the high-field coil region with an MAS NMR rotor to investigate the catalytic kinetics in nanocages by in situ continuous-flow MAS NMR. The adsorption and reaction processes at the earliest stage can be monitored by ^{129}Xe NMR spectroscopy with much higher sensitivity and shorter acquisition time (~10 s per spectrum) under real working conditions.

In summary, this section highlights the fundamental principles of catalysis, such as the critical roles of adsorption–desorption dynamics, surface reactions, and active sites in influencing catalytic outcomes. It emphasizes the significance of in situ TEM and STM for investigating molecular-scale factors that dictate catalytic behavior. It also reveals how in situ synchrotron radiation techniques have revolutionized catalysis research by offering unprecedented sensitivity and detail, thanks to key innovations such as storage rings, insertion devices, and low emittance/high energy lattices. A concise overview of each technique's strengths and the challenges associated with their use in catalysis research is provided in Table 1.

Nevertheless, to probe the molecular-scale factors influencing catalytic properties, a combination of in situ and operando techniques is paramount. On one hand, electron microscopy provides spatial resolution down to the atomic level, revealing the structural dynamics of catalysts under reaction conditions. Spectroscopic methods like XAS, including both XANES and EXAFS, offer insights into the electronic structure and coordination environment of the catalytic sites, crucial for understanding the activation and transformation of reactants. On the other hand, synchrotron-based techniques enhance the capabilities of these spectroscopic methods by providing higher intensity and resolution, enabling the study of fast and transient phenomena in catalysis. The integration of insights from both techniques enriches our understanding of catalysis, bridging nanoparticle and single crystal research to offer a holistic view of the factors governing catalytic efficiency and selectivity. For example, high-resolution IR spectroscopy, when combined with scanning probe microscopy, provides detailed insights into the coordination number of surface atoms and their catalytic activity. Synchrotron infrared nanospectroscopy (SINS) enhances this capability by offering broadband spatio-spectral analysis, crucial for mapping site-dependent reactivity differences on single particles under various reaction conditions. This approach is essential for understanding and optimizing heterogeneous catalysts at the nanoscale. Moreover, the integration of these techniques with computational modeling and machine learning further enhances the understanding of catalytic mechanisms, facilitating the design and optimization of new catalysts with improved performance, which will be discussed in Sect. 4.

4 The Integration of in situ Techniques with Machine Learning

Machine Learning (ML) for catalysis research combines computational modeling and experimental data to understand and predict the behaviors of catalysts, ultimately aiding the design of more efficient systems [23]. Supervised learning allows automatic comparison of experimental spectra to standard spectral databases, and it can also map spectra to catalysts' structural/chemical descriptors like coordination numbers and oxidation states, enabling swift, real-time structural elucidation [108]. Unsupervised learning, such as principal component analysis, can help discern contributions from various chemical species present in the catalysts.

ML is known for its low cost compared to physics-based simulations, enabling the accelerating simulations of large and complex systems. ML Interatomic Potentials (MLIP) and ML Force Fields (MLFF) [109] have arisen and are employed to expedite physics-based simulations, thus, scale modeling large and complex systems. For instance, Li et al. have built a neural network potential to rapidly explore the global structure and reaction space in acetylene hydrogenation for the Pd–Ag-C-H system for the first time, enabling to understand the surface state of the PdAg catalyst [110]. Additionally, in situ-formed iron carbides on Fe-based catalysts have been studied in

Table 1 Strengths and challenges of each in situ technique associated with their use in catalysis research

In Situ Technique	Key Capabilities	Limitations	Contribution to Catalytic Mechanisms
Scanning and Transmission Electron Microscopy (STEM/TEM)	Subatomic spatial resolution, simultaneous spectroscopy at the atomic level, analysis of critical interfaces and surfaces	Limited resolution in some cases due to high signal-to-noise ratio, controlled environments or stimuli required	Provides real-time visualization of catalysts at work, revealing structural changes and active sites during catalytic reactions
Four-Dimensional Scanning Transmission Electron Microscopy (4D-STEM)	Superior structural knowledge, enhanced sensitivity and dynamic range, rapid gathering of 2D electron diffraction patterns	Challenges in studying beam-sensitive materials, requires specialized detectors	Offers detailed crystallographic information, crucial for understanding the structural evolution of catalysts under reaction conditions
High-Speed Scanning Tunneling Microscopy (STM)	Real-time atomic imaging with excellent resolution, observation of individual atoms and their arrangement	Requires controlled conditions for high or ambient pressure and temperature, limited to surface-level interactions	Enables direct observation of surface reactions and dynamic processes, such as adsorption and diffusion of reactants
Synchrotron Radiation Techniques	Broad spectrum, high brightness, coherence, contributions to structure and electronic analysis	Complexity of setups, reliance on large-scale facilities	Essential for identifying chemical states, electronic structures, and bonding environments of catalysts under operational conditions
X-ray Absorption Spectroscopy (XAS)	Characterization at the atomic level, monitoring changes in oxidation states during reaction	Requires synchrotron radiation sources, challenges in real-time chemical reaction studies	Provides insights into the electronic structure and local environment of catalytic sites, crucial for understanding activation and reaction pathways
Infrared (IR) Spectroscopy	Allows precise analysis of heterogeneous materials at the nanoscale, especially with synchrotron infrared nano-spectroscopy for enhanced resolution	Conventional IR spectroscopy is diffraction-limited in spatial resolution	Directly probes catalytic activity differences between sites on metal nanoparticles, crucial for understanding heterogeneous catalysis mechanisms
Solid-state Nuclear Magnetic Resonance (NMR)	Tracks catalytic reaction processes, captures species of reaction intermediates, studies structural changes, and host–guest interactions	High-pressure in situ NMR under in situ flow conditions has not been achieved, and the temporal and spatial resolutions are low	Reveals reaction mechanisms at the molecular level, especially useful for studying heterogeneous catalysis and capturing transient intermediates

a similar manner [110]. The same team also developed ML-based grand canonical global optimization, which incorporates MLIP, stochastic surface walking (SSW) global optimization, and grand canonical Monte Carlo (GCMC). Specifically, MLIP accelerates by four orders of magnitude compared to DFT calculations. Coupled with a high-throughput search using the optimization, the in situ structure of the Mo-Doped Pt-Ni catalyst during electrochemical oxygen reduction has been well studied [111].

Another typical example is that Han et al. developed a ML approach integrated with first-principles data to identify high-performing ternary PtFeCu electrocatalysts for the oxygen reduction reaction (ORR) (Fig. 9) [112]. They used Density Functional Theory (DFT) calculations to create an accurate database for PtFeCu nanoparticle models, which was analyzed using ML to develop neural network potentials (NNPs). The NNPs mapped the ternary phase diagram and identified promising structures. Four compositions—PtFe, $PtFe_{high}Cu_{low}$, $PtFe_{low}Cu_{high}$, and pure Pt—were selected for validation. The nanoparticles, synthesized at a 2 g scale, matched computational models in size, composition, and structure. Experiments showed $PtFe_{high}Cu_{low}$ exhibited the best ORR performance—thrice higher specific and mass activities than Pt/C, aligning with computational predictions. Cu was found to modulate strain and prevent Fe surface segregation, with optimal strain achieved when Cu replaced Fe in subshells. $PtFe_{high}Cu_{low}$ maintained high activity post-accelerated stress testing, surpassing the 2020 US DOE targets for mass activity and stability. This work illustrates a promising strategy of merging ML, physics-based simulations, and experiments to systematically design and validate high-performance electrocatalysts, going beyond traditional Pt or Pt alloys.

Meanwhile, An et al. developed a deep reinforcement learning (DRL) framework in conjunction with density functional theory (DFT) to map catalytic reaction networks [113]. The method reimagines the chemical reaction path as a Markov decision process guided by DFT-calculated energetics, with an AI agent building the reaction network from reactants to products. This process reveals latent reaction mechanisms without the need for predefined sequences. Applied to the Haber–Bosch process for ammonia synthesis on Fe (111) surface, the DRL agent identified a lower barrier path than previous mechanisms, primarily via the order of H desorption and N_2 adsorption steps. This path, which was confirmed as more kinetically favorable by DFT calculations, demonstrates the potential of integrating DRL with DFT to uncover optimal reaction networks without the need for prior expert knowledge. In essence,

this work highlights DRL as a promising strategy for studying intricate catalytic reaction mechanisms, potentially offering more efficient solutions to complex catalysis problems.

In catalysis research, the integration of in situ techniques with ML is a new trend in catalysis research [22, 46]. In situ characterization provides real-time, microscopic information about catalyst behavior, which ML processes into predictive models for more efficient catalyst design. Techniques such as X-ray absorption spectroscopy and environmental electron microscopy offer initial data, which ML algorithms use to predict catalytic behavior and leverage the model's generalization ability to guide novel catalyst design. This amalgamation is believed to deepen our understanding of catalytic mechanisms and advances catalysis research. For example, Timoshenko et.al explores the use of fast X-ray absorption spectroscopy and ML to study the structural and chemical changes in $Co_xFe_{3-x}O_4$ oxide electrocatalysts during the oxygen evolution reaction [46]. Unsupervised learning (principal component analysis) of XANES spectra tracked the changes in Co oxidation state during activation and reaction, indicating the possible involvement of Fe. A neural network analysis of EXAFS spectra uncovered the local structure evolution and phase segregation: in the Co-rich phase, Co (II) oxides irreversibly transformed into spinel-type oxides, which further oxidized to form layered CoOOH active phases. In contrast, Fe and Co in the Fe-rich phase remained largely unchanged. The synergy between Co and Fe improved the oxygen evolution activity of $Co_xFe_{3-x}O_4$, with the Co-rich phase being more active while the Fe-rich phase acted as a support. This combined approach provides insights into complex oxide electrocatalysts, informing better design.

Furthermore, ML enables the processing of large-scale in situ characterization data and accelerating simulations of large and complex systems. Specifically, neural networks have been used to independently map XANES [114] or EXAFS [115] spectra onto structural parameters, such as coordination numbers and bond length distributions. For example, spatially- and time-resolved data from XAS studies, which are important to understand catalysts under working conditions [108]. Liu et al. utilized machine learning approaches to analyze X-ray absorption near-edge structure spectra, unveiling precise speciation details of the Cu_xPd_y cluster types and providing structural information for each type during the propane oxidation reaction [116]. Additionally, ML can seamlessly integrate insights from physics-based simulations, such as DFT calculations, into the XAS experimental data to understand latent mechanisms [108].
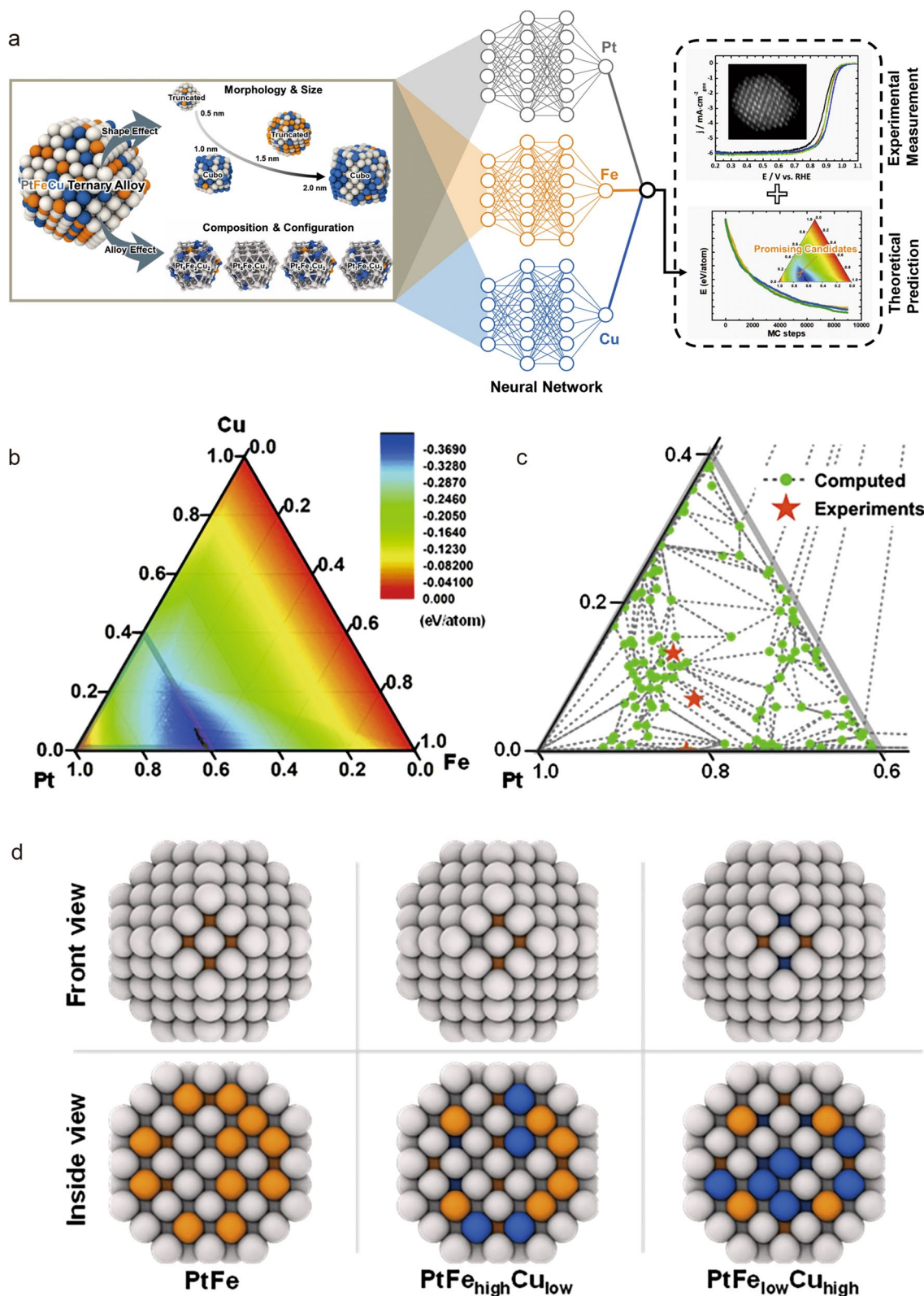
Fig. 9 a Schematic diagram of ternary alloy configuration search and theoretical predictions and experimental validation. **b** Ternary diagram and (**c**) the convex hull points of PtFeCu ternary nanoparticles (2.0 nm) in the range of 0.6 < Pt < 1. The orange stars are synthesized compositions. **d** Structural information of representative compositions of PtFe and PtFeCu nanoparticles [112]. Reproduced with permission from ref. 112 from Cell Press, Copyright 2021

Chen *et al. Surface Science and Technology*   (2024) 2:9

Page 21 of 23

5 Conclusions and Future Perspective

The catalysis sector stands at a crucial crossroads, with the increasing demand for sustainable and efficient catalyst systems taking center stage. Catalyst design currently faces significant limitations in deeply elucidating dynamic catalyst behaviors under actual reaction conditions. Conventional ex situ characterization techniques cannot capture transient intermediates or transition states that emerge during reactions, nor can they accurately reflect morphological and compositional changes on catalyst surfaces. They also struggle to precisely delineate the evolution of chemical states and coordination environments of active sites, which are pivotal to elucidating catalytic mechanisms. Additionally, thermodynamic and kinetic parameters obtained under model laboratory conditions often deviate considerably from real-world situations, hampering predictive modeling and catalyst optimization efforts. Advanced in situ techniques such as in situ electron microscopy, synchrotron spectroscopy, and solid-state NMR can directly monitor structural and performance changes of catalysts under working environments in real-time, overcoming deficiencies of traditional methods. By enabling insights into functioning catalysts previously inaccessible, these in situ techniques promise to drive major advances in catalytic science and technology by elucidating mechanistic pathways and guiding rational catalyst design. Continual development of novel in situ approaches is therefore critical for progress in the catalysis field. Among the various methodologies being explored to drive advancements in this field, the role of in situ methods cannot be understated. Their continual evolution has redefined the approach to understanding catalysis, laying the foundation for the next era of catalytic innovations. A key trend is the application of multi-scale and multi-modal techniques. This direction signifies a future where in situ catalysis will encompass a broader, more comprehensive range of techniques.

To add to this, the multi-scale approaches are particularly noteworthy for their ability to elucidate both the micro-level molecular mechanisms and the macro-level process dynamics. These techniques involve sophisticated analytical tools like high-resolution electron microscopy and synchrotron radiation-based spectroscopies, which provide unprecedented insights into the atomic and molecular landscapes of catalytic systems. Additionally, computational modeling plays a crucial role in complementing experimental observations, offering predictive insights into reaction pathways and catalyst behaviors. On the other hand, multi-modal techniques focus on exploring different modes, from electronic intricacies to the more tangible morphological changes. The integration of various spectroscopic and microscopic methods allows for the simultaneous observation of electronic, structural, and chemical transformations during catalytic reactions. This convergence of multiple observational modes yields a more robust and nuanced understanding of catalyst functionality. From this viewpoint, the integration of multi-scale and multi-modal techniques promises a holistic perspective on catalytic processes. By bridging gaps between different scales and modes of observation, researchers can gain a more thorough understanding of catalyst behavior and function. This comprehensive approach holds the potential to unearth previously overlooked or misunderstood facets of catalysis, paving the way for groundbreaking discoveries.

Meanwhile, the advancement of operando techniques is also crucial in catalysis research due to their capacity for real-time, in situ analysis of catalytic reactions under actual working conditions. These techniques are essential for understanding the dynamic behavior of active sites and how varying reaction conditions—such as temperature, pressure, and atmosphere—affect the structure and mechanism of catalysis. This insight is invaluable for designing and optimizing catalysts that are robust and efficient across various operational environments. Moreover, data from *operando* studies enhance theoretical models, driving innovation in sustainable catalysis.

In conclusion, the ongoing advancements in characterization techniques and operando methods are set to revolutionize our understanding of catalytic processes profoundly. As the realm of catalysis research expands and the demand for sustainable solutions grows, the emphasis on advanced in situ methods becomes increasingly paramount. By embracing interdisciplinary approaches and leveraging technological innovations, the field is poised to make significant strides. The evolution towards multi-scale and multi-modal chemical dynamics signifies a promising trajectory. This integrated methodology will not only deepen our understanding of catalysis but also spur innovations that are efficient, sustainable, and tailored to specific applications. Embracing this approach is crucial for developing catalysts that address key global challenges in energy and environmental sustainability, setting the stage for a greener and more efficient future.

Authors' contributions
Chaochao Dun (CD) conceptualized the review content and drafted the original manuscript. Linfeng Chen (LC) and Xinzhi Ding (XD) aided CD in drafted the original manuscript and creating figures. Zheren Wang (ZW), Shutao Xu (SX), and Qike Jiang (QJ) aided CD to revise the manuscript. CD and Jeffrey J. Urban (JJU) provided overall supervision. All authors read and approved the final manuscript.

Chen *et al. Surface Science and Technology*   (2024) 2:9

Page 22 of 23

Declarations

Competing interests

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