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Innovations in catalytic understanding: A journey through advanced characterization

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ABSTRACT

This work provides a comprehensive overview of advanced characterisation techniques to unravel the molecular intricacies of catalytic processes. It begins with an introduction to catalytic processes and emphasises the importance of innovations in characterisation techniques, including SEM, XRD, UV-Vis, FTIR, RAMAN, XPS, NMR, TEM, AFM and the combined application of these techniques for improved catalytic investigation. The review of the development of catalytic processes provides a historical overview of progress and examines paradigm shifts in catalytic mechanisms and catalyst categories. Conventional microscopic and spectroscopic tools are revisited, highlighting the improvements in these techniques that provide insight into catalytic structures through surface analysis. Significant advances, including the application of computational techniques, in the study of catalysts are also discussed, focusing on state-of-the-art techniques that provide unprecedented detail on catalyst properties, mechanisms and processes. Comparative evaluations highlight the advantages and limitations of these techniques. The study concludes by identifying and overcoming challenges, anticipating prospects and emphasising the constant quest for innovation in understanding catalysts. By integrating developments in microscopic and spectroscopic methods, the study provides a comprehensive insight into how these tools improve the precision and depth of catalyst characterisation, driving innovation and future directions in catalysis research.

1. Introduction

Catalysis is a cornerstone of modern chemistry and forms the basis for a variety of industrial processes that are essential for the production of fuels, chemicals and pharmaceuticals. The ability to accelerate chemical reactions and convert them into the desired products with high selectivity is crucial for increasing efficiency, reducing energy consumption and minimising environmental impact. Conventional catalysts, which often consist of transition metals and their compounds, have been extensively studied and optimised. However, the ever-increasing demand for more efficient, sustainable and cost-effective processes is driving the continuous development of catalysis science. This relentless pursuit of improvement requires not only the development of new catalysts but also a deep understanding of catalytic mechanisms at the molecular level.

The handling, processing and detailed study or characterisation of synthesised materials, including nanoparticles, poses major challenges for both industry and researchers in research and development due to their nanoscale dimensions [19]. Catalysts differ from bulk materials in their small size, which gives them unique chemical, optical, electrical and magnetic properties [7]. The shape, size and surface properties of catalysts are generally considered to be their fundamental characteristics, which can be determined using various instrumental methods such as microscopy and spectroscopy [112]. The investigation of the surface of catalysts is crucial for several reasons. The stability of catalysts is closely related to their surface charge, which can be optimised to address stability issues such as coagulation and aggregation [130]. In addition, the surface chemistry of catalysts is linked to their toxicity. Therefore, the surface is often modified to make catalysts safer for delivery in biological systems [136]. Due to their large surface-to-volume ratio, the study of catalyst surfaces is crucial for understanding their

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Nomenclature

Acronyms

ACT	Advanced Characterisation Techniques
AC-TEM	Aberration-Corrected Transmission Electron Microscopy
AET	Atomic Electron Tomography
AFM	Atomic Force Microscopy
AI	Artificial Intelligence
AIMD	Ab Initio Molecular Dynamics
ATR	Attenuated Total Reflectance
BET	Brunauer-Emmett-Teller
BPE	Benzyl Phenyl Ether
CARS	Coherent Anti-Stokes Raman Spectroscopy
CASTEP	Cambridge Sequential Total Energy Package
CCD	Charge-Coupled Device
CMD	Classical Molecular Dynamics
DCE	1,2-dichloroethane
DFT	Density Functional Theory
DNP NMR	Dynamic Nuclear Polarisation Nuclear Magnetic Resonance
DRUV-Vis	Diffuse Reflectance UV-Vis Spectroscopy
EBSD	Electron Backscatter Diffraction
EDS	Energy-Dispersive X-ray Spectroscopy
EPC	Enteromorpha-based char
ETEM	Electron Transmission Electron Microscope
FCC	Face-Centred Cubic
FIB	Focused Ion Beam
FTIR	Fourier Transform Infrared Spectroscopy
FWHM	Full Width at Half Maximum
GL(m)	Gaussian–Lorentzian
HER	Hydrogen Evolution Reaction
HRTEM	High-Resolution Transmission Electron Microscopy
InSb	Indium Antimonide
IR	Infrared Radiation
LUMO	Lowest Unoccupied Molecular Orbital
MAS NMR	Magic-Angle Spinning Nuclear Magnetic Resonance
MCT	Mercury Cadmium Telluride
MDS	Molecular Dynamic Simulation
MeOH	Methanol
MLMD	Machine Learning Molecular Dynamics
MS	Mass Spectrometry
MTH	Methanol to Hydrocarbons
NMR	Nuclear Magnetic Resonance
NPs	Nanoparticles
NPT	Number of particles (N), Pressure (P), and Temperature (T)
NVE	Number of particles (N), Volume (V), and Energy (E)
NVT	Number of particles (N), Volume (V), and Temperature (T)
ODP	Oxidative Dehydrogenation of Propane
OES	Optical Emission Spectroscopy
ONIOM	Our own N-layered Integrated molecular Orbital and Molecular mechanics
ReaxFF	Reaction Molecular Dynamics
S/N	Signal-to-Noise Ratio
SAM	Self-Assembled Monolayer
SCR	Selective catalytic reduction
SCWG	Supercritical Water Gasification
SEIRA	Surface-Enhanced Infrared Absorption
SEM	Scanning Electron Microscopy
SERS	Surface-Enhanced Raman Spectroscopy
SGL(m)	Sum Gaussian–Lorentzian
SHINERS	Shell-Isolated Nanoparticle-Enhanced Raman Spectroscopy
STM	Scanning Tunnelling Microscopy
TEM	Transmission Electron Microscopy
TERS	Tip-Enhanced Raman Spectroscopy
V_2O_5	Vanadium Oxide
VASP	Vienna Ab initio Simulation Package
VCM	Vinyl Chloride Monomer
XAS	X-ray Absorption Spectroscopy
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction
ZPD	Zero-Path-Difference

behaviour and properties [13]. The development and optimization of catalysts are inextricably linked to the ability to characterise their structure, composition, and behaviour under reaction conditions.

Microscopic techniques such as scanning electron microscopy (SEM), transmission electron microscopy (TEM) and atomic force microscopy (AFM) are used to measure size and surface morphology [145,7]. Spectroscopic techniques for the investigation of surfaces include methods such as nuclear magnetic resonance, ultraviolet spectroscopy and mass spectroscopy as well as modern approaches such as Auger electron spectroscopy and ion scattering methods [19]. Conventional characterisation methods such as X-ray diffraction (XRD) and scanning electron microscopy (SEM) have contributed to the understanding of the crystalline structure and morphology of catalysts. However, these techniques are often unable to provide real-time and in-situ information on dynamic catalytic processes. Advanced characterisation techniques provide crucial insights into the molecular intricacies of catalytic processes and reveal the active sites, reaction intermediates and mechanistic pathways. This knowledge is essential for rational catalyst design and enables the customisation of catalytic properties to achieve the desired performance. Modern advances, including various spectroscopic methods and surface analysis techniques, have significantly improved our ability to study catalytic systems at the atomic and molecular level [126].

The emergence of the operando method, coupled with major advances in the chemical modelling of materials and reactions, has transformed the discovery of catalysts [21,22]. This change offers an alternative to the traditional trial-and-error approach, where catalysts were essentially "black boxes" that were characterised before and after their catalytic lifetime, often resulting in data gaps due to differences between material, temperature and pressure and actual working conditions [177]. The operando methodology enables the characterisation of physicochemical properties during operation and thus provides a comprehensive set of tools for sensitive characterisation [20]. The use of different spectroscopic techniques enables specific sensitivities and measurements with different degrees of temporal and spatial resolution. Spatial and temporal constraints are interrelated, so their realisation is crucial for thorough operando mapping of catalysts. Higher spatial resolution must be complemented by improved temporal resolution to be effective. To fully close the "dimensional gap"," it is also necessary to study different parts of the solid and minimise the area studied to identify inhomogeneities and their effects on catalytic performance. The spatially resolved operando technique is now used at the nano-, micro- and macro-scale to study catalyst and molecular phenomena within and between reactors [23].

This comprehensive review explores the conventional and advanced characterisation techniques that have evolved to unravel the molecular intricacies of catalytic processes. The study begins by setting the stage for an advanced understanding of catalysts and highlights the importance of innovation in characterisation techniques. A review of the development of catalytic processes provided a historical overview of progress and emphasised paradigm shifts in catalytic processes. The study concludes by identifying the challenges in catalytic

characterisation while emphasising the constant quest for innovation in catalytic understanding. By addressing the limitations of current techniques and exploring new possibilities, this review highlights the critical role of characterisation in developing the next generation of catalyst technologies.

1.1. Developments in catalysis

Catalysis is a central concept in chemistry and industrial processes. It comprises substances that increase the rate of chemical reactions without being consumed themselves. The development of catalytic processes has had a significant impact on chemical synthesis, energy production and environmental protection. The historical advances in catalysis, the paradigm shifts in catalytic mechanisms and the exploration of new classes of catalysts are discussed, highlighting the need for catalyst characterisation studies.

1.2. Historical overview of catalytic advancements: catalyst development and catalytic processes

The concept of catalysis has evolved considerably since its inception. The term "catalysis" was coined by Jöns Jakob Berzelius in 1835 [179,180]. The history of catalysis is marked by significant milestones that have revolutionised the field. Early discoveries in the 19th century, such as the use of platinum in the oxidation of hydrogen and the development of the contact process to produce sulphuric acid, laid the foundations for industrial catalysis [114]. However, the practical use of catalysts dates to ancient times, involving different processes (Table 1), e.g. in the fermentation of alcohol and the use of enzymes in biological processes. The early 20th century brought significant progress with the development of heterogeneous catalysis (including zeolite catalysts) with groundbreaking innovations such as the Haber-Bosch process by Fritz Haber, which enabled the synthesis of ammonia on a large scale and thus revolutionised agriculture and the production of fertilisers. These advances had a profound impact on the chemical industry and enabled large-scale production processes that are essential to modern society [134]. In the 1920s, Paul Sabatier was awarded the Nobel Prize for his work on hydrogenation with nickel catalysts, underlining the importance of catalysis in organic chemistry [38]. The mid-20th century saw further advances with the Ziegler-Natta catalysts, which enabled the polymerisation of olefins and led to the production of polyethylene and polypropylene, valuable materials in the modern world [115]. In the late 20th and early 21st centuries, the focus was on developing catalysts for more specific, understanding catalyst and catalytic properties through advanced characterisation techniques and efficient reactions, including asymmetric hydrogenation and olefin metathesis, both of which were awarded Nobel Prizes [134,164,48].

In recent decades, the focus has shifted to more sophisticated and specialised catalytic systems. Homogeneous catalysis, in which the catalysts are dissolved in the reaction medium, has gained in importance due to its high selectivity and the ease with which the mechanisms can be studied, However, the difficulties in separation, regeneration and stability problems limit the industrial application, so that heterogeneous catalysts are favoured over homogeneous catalysts [13,14,12]. Enzymatic catalysis, which mimics the precision of nature, has opened new avenues for green chemistry and biotechnology. In addition, the rise of nanocatalysis and single-atom catalysis represents a paradigm shift that promises unprecedented control over catalytic sites and improved efficiency [185]Exploration of novel catalyst classes has been a major focus in catalytic science, with the aim of developing more efficient, selective, and environmentally friendly catalysts.

Table 1
Key Historical Milestones in Catalytic Processes.

Year	Scientist	Discovery/Contribution	Ref.
1835	Jöns Jakob Berzelius	Coined the term "catalysis	Wisniak [179]
1909	Fritz Haber	Haber-Bosch process for ammonia synthesis	Rouwenhorst et al., [134]
1920s	Paul Sabatier	Hydrogenation reactions using nickel catalysts	Che [38]
1960s	Ziegler and Natta	Polymerization catalysts for polyethylene and polypropylene	Mülhaupt [115]
2001	William S. Knowles	Asymmetric hydrogenation	Knowles [90]
2005	Yves Chauvin, Robert H. Grubbs, Richard R. Schrock	Metathesis in organic synthesis	

1.3. Paradigm shifts in catalyst characterisation study

Catalytic mechanisms have undergone a major paradigm shift driven by the need for more efficient and selective catalysts. Originally, catalysis was understood in terms of simple surface interactions. However, modern catalyst science recognises the complexity of these interactions and the need to understand them at the molecular level. The transition from empirical observations to a more theoretical understanding began in the early 1900s with the theory of surface catalysis, which focussed on the interaction of reactants with catalyst surfaces. Following the 1900s, the characterisation of catalysts has undergone a significant paradigm shift over the years, driven by advances in technology and a deeper understanding of catalytic processes (Table 2). These changes have transformed the way scientists study and understand catalysts, enabling more precise design and optimisation of catalytic systems [159,185].

Regardless of the type of catalysis - whether homogeneous, enzymatic or heterogeneous - the basic characteristics remain consistent at the atomic level. This is because, at its core, catalysis involves the interaction between the reactant and the active site, which can be described as the "catalytic trinity" Catalysis takes place at the atomic level, where bonds rearrange to form new molecules. Although the catalytic process takes place at the atomic level, it can still be influenced by constraints that apply over greater distances. In homogeneous catalysis, the interaction takes place directly with the molecules in the reaction medium, so it is crucial to avoid diffusion restrictions. In contrast, heterogeneous and enzymatic catalysis involves larger substances in which gradients play a role. Understanding and controlling these gradients is critical to maximising catalytic performance and minimising diffusion limitations. To understand catalysis and the materials that enable it, it is, therefore, crucial to develop appropriate methods that consider these nodal points [23].

Identification of the chemical phase relevant to the catalytic process is a fundamental concept that applies to all catalyst characterisation techniques. Heterogeneous catalysis requires high surface sensitivity, as the interactions take place at the outermost layer of the catalyst. Therefore, characterisation must focus on the exposed surface, whether external or internal, to accurately represent the active sites. This requirement is a limitation for operando studies that need to characterise the relevant chemical structure and evaluate the corresponding activity. Most spectroscopies are either sensitive to the bulk or sensitive to the near-surface layer. However, many characterisation methods provide signals from both the bulk and the surface, with low selectivity for the outermost layer. In heterogeneous catalysis, the interaction between the bulk and surface domains can be significant. In molecularly dispersed catalysts, the active phase is completely exposed at the surface, so the characterisation refers to the domains exposed to the reactants. For bulk catalysts, the surface-to-volume ratio is determined by the particle size, with nanomaterials exhibiting a dominant surface signal. In contrast, larger particles generate a stronger bulk signal than the outermost active layer. Sintering processes during reactions can dynamically change this ratio by aggregating small, dispersed particles and thus reducing the surface-to-volume ratio [23].

Table 2
Progress in catalyst characterisation study.

Era	Paradigm shift	Main Concept	Ref.
Pre-1900s	Empirical observations	Catalysis observed but not understood mechanistically	Mittasch, Frankenburg [111]
Early 1900s	Surface catalysis theory	Interaction of reactants on catalyst surfaces	Gunter et al., [72]
Mid-1900s	Electronic theory of catalysis	Role of electron transfer in catalytic processes	Foster et al., [61]
Late 1900s	Molecular catalysis	Understanding catalysis at the molecular and atomic levels	Thomas [159]
21st Century	Advanced catalyst characterisation. computational catalysis and nanocatalysis	Use of advanced characterisation techniques, computational models and nanoscale catalysts	Grajciar et al., [185,67,66]

2. Conventional methods of catalyst characterisation and their application - *revisited*

Traditional methods of catalyst characterisation are fundamental to understanding the physical and chemical properties of catalysts, which have a direct impact on their performance in various reactions. These methods, such as spectroscopic (X-ray Diffraction (XRD)), microscopic (Scanning Electron Microscopy (SEM)), and Brunauer-Emmett-Teller (BET) techniques, are essential for understanding the properties and performance of catalysts. They provide insights into the structure, composition and surface properties of catalysts that are crucial for optimising their performance ([39,40,44,65]; X. [157]). The combination of conventional methods with advanced techniques such as mass spectrometry (MS) enables a comprehensive understanding of the properties of catalysts and their effects on reactions, thus facilitating the development and optimisation of more effective catalysts for various industrial applications.

2.1. Improvements in spectroscopy techniques (IR, UV-Vis)

Improvements in IR and UV-Vis spectroscopy have significantly advanced the characterisation of catalysts. Improved resolution and sensitivity in IR spectroscopy enable detailed investigations of catalytic surfaces and reaction intermediates [158,191,192,85]. Fourier transform infrared spectroscopy (FTIR) enables real-time monitoring of reactions and provides insights into reaction mechanisms and active sites on catalysts (Zaera, 2021). For example, FTIR has been used to study the selective reduction of nitric oxide (NO) by ammonia (NH_3) [161] and to identify active sites for hydrogenation over Ru/SBA-15 catalysts [140]. Advanced techniques such as attenuated total reflectance (ATR) have expanded the applicability of IR spectroscopy to study catalysts in different states [11].

Innovative methods such as nanostructure-enhanced IR spectroscopy and surface-enhanced infrared absorption (SEIRA) further improve IR spectroscopy. In nanostructure-enhanced IR spectroscopy, nanostructures are used to amplify IR absorption signals, enabling the detection of molecules at the nanoscale [158]. SEIRA uses metal islands or films to significantly amplify the vibrational signals of molecules and increase the signal intensity by up to 100 times [68]. These methods have been used for sensitive detection in various applications, e.g. for the detection of thiram in apples and malachite green in aquatic products [122,129,41]. UV-Vis spectroscopy has also made significant progress and increased its usefulness in the characterisation of catalysts. Modern UV-Vis spectrometers offer higher resolution and faster data acquisition, enabling the investigation of dynamic processes and volatile species in catalytic reactions. Techniques such as diffuse reflectance UV-Vis spectroscopy (DRUV-Vis) and cavity-enhanced UV-Vis spectroscopy analyse the electronic structure and oxidation states of catalysts [127,59]. UV-Vis spectroscopy has been applied in various investigations, e.g. to characterise MnO-CaLs catalysts for oxidation reactions and ZnO-based heterojunctions for the treatment of dye effluents [3,15,17]. Overall, improvements in IR and UV-Vis spectroscopy techniques have enabled precise real-time and in-situ characterisation of catalysts. These advances enable a deeper understanding of the structural and electronic properties of catalysts, leading to the development of more active, selective and stable catalytic systems.

2.2. Modern applications of X-ray diffraction (XRD)

X-ray diffraction (XRD) continues to be an important technique for material characterisation. Recent advances in materials science necessitate the improvement of XRD techniques to effectively address new challenges [8]. XRD provides detailed information about atomic structures by analysing diffraction patterns and is, therefore, essential for the study of crystalline materials [125,18]. The non-destructive nature and versatility of XRD make it applicable to a wide range of materials, from minerals to synthetic polymers and metals, in various industries such as power generation, aerospace and microelectronics [18]. Modern applications of XRD span several fields, including materials science, pharmaceuticals, nanomaterials and environmental monitoring. In materials science, XRD is used to determine crystal structures, identify phases and quantify crystallite sizes, which is essential for predicting material properties and behaviour [8,1]. In the pharmaceutical industry, XRD ensures the safety and efficacy of drugs by identifying and controlling polymorphic forms of active pharmaceutical ingredients [60,133]. XRD is also crucial in the development of renewable energy technologies, e.g. in the analysis of materials for biofuels, lithium-ion batteries and solar cells to optimise their efficiency (Alamiery, 2024; Gao et al., 2023; Sturman et al., 2022).

2.3. Advanced insights through Scanning Electron Microscopy (SEM)

SEM provides high-resolution images of sample surfaces, revealing intricate surface morphology, texture and microstructures (Mohammed & Abdullah, 2018). In conjunction with energy-dispersive X-ray spectroscopy (EDS), SEM determines elemental composition and distribution, which is essential for material characterisation and failure analysis (Girão et al., 2017; Newbury & Ritchie, 2013). The advanced capabilities of SEM, such as electron backscatter diffraction (EBSD), provide crystallographic information that is crucial for studying the mechanical properties and deformation behaviour of materials (Brodusch et al., 2018; Britton et al., 2016). In-situ SEM experiments allow real-time observations of material behaviour under different conditions, which is invaluable for the development of materials with improved performance (Torres & Ramírez, 2011; Ma et al., 2020). SEM is also used to analyse nanostructures, thin films and biological samples, providing detailed insights into their properties and applications (Buhr et al., 2009). It plays a central role in failure analysis by analysing fracture surfaces and defects at high magnification, providing information for the development of more reliable materials (Silva et al., 2009; Venkataswamy, 2009). Advanced imaging techniques that combine Focused Ion Beam (FIB) with SEM enable precise cross-sections and 3D reconstructions that allow comprehensive analysis of internal structures (Wirth, 2009).

2.4. Deciphering catalytic structures through surface and porosity analysis

Analysing surface area and porosity is fundamental to understanding and improving catalytic performance. Techniques such as Brunauer-Emmett-Teller (BET) surface area analysis measure the specific surface area of catalysts, which is essential for comparing and optimising their performance [16]. Porosity analysis using methods such as mercury intrusion porosimetry and gas adsorption isotherms provides detailed insights into the pore structure that influences reactant diffusion and catalytic efficiency (Dai & Zhang, 2021; Abell et al., 1999; Chilev et al., 2022). The combination of surface area and porosity analysis enables the design of catalysts with tailored properties, such as mesoporous materials for reactions with large molecules. This control is crucial for the development of catalysts for industrial processes such as petrochemical refining and renewable energy production. Regular characterisation of surface area and porosity also helps to monitor structural changes during reactions, which supports the development of strategies to mitigate catalyst deactivation (Gan et al., 2013). Overall, analysing surface area and porosity is essential to decipher the catalytic structures. It helps in developing high performance catalysts and maintaining their effectiveness, thereby promoting efficiency and sustainability in various industrial processes. The combination of these analytical techniques with other characterisation methods enables a comprehensive understanding of catalytic materials and leads to innovations in catalyst development. Table 3 presents the advantages and limitations of some conventional characterisation techniques.

By leveraging the strengths of each technique, researchers can gain a more thorough understanding of material properties and potential areas for improvement in catalyst development.

Table 3
Summary of merits and limitations of conventional characterisation techniques:.

Techniques	Merits	Limitations
X-ray diffraction (XRD)	• High precision in determining crystallographic structure • Identifies phase composition, crystal structure, and crystallite size • Useful for multi-component catalysts	• Limited in detecting amorphous materials • Provides bulk properties, not surface-specific information
IR Spectroscopy	• Provides detailed molecular information and functional group analysis. • Enables real-time monitoring of reactions with FTIR. • Enhanced surface sensitivity with techniques like ATR and SEIRA	• Water interference affects accuracy. • Less effective for quantitative analysis. • equires precise sample preparation.
UV-Vis Spectroscopy	• Effective for studying electronic structures and oxidation states. • Fast, non-destructive analysis. • Broad applicability with techniques like DRUV-Vis.	• Limited to UV–visible range. • Lower sensitivity compared to IR spectroscopy. • Interference from colored samples
Nitrogen adsorption (BET)	• Quantifies specific surface area, pore volume, and pore size • Essential for evaluating textural properties • Critical for comparing catalyst performance	• Does not provide chemical composition or nature of active sites • Complex interpretation of adsorption isotherms
Scanning electron microscopy (SEM)	• Provides detailed images of surface morphology and microstructure • High magnification to observe size, shape, and distribution of particles • Coupled with EDS, offers elemental analysis	• Primarily offers surface-level information • Requires conductive samples or coating, potentially altering surface characteristics • May not accurately represent bulk properties
Thermal analysis (TGA, DSC)	• Insights into thermal stability, phase transitions, and kinetic properties • Suitable for polymers, composites, and materials with temperature-dependent characteristics	• Sensitive to experimental conditions • May not capture the full complexity of real-world thermal environments
Combined use (XRD, BET, SEM, TGA-DSC)	• Comprehensive understanding of catalyst properties • Each technique offers unique, valuable insights	• Individual limitations still apply, but techniques complement each other for a holistic view

3. Pushing Boundaries with advanced spectroscopic techniques

This section explores cutting-edge techniques that push the boundaries of catalysis research. By engaging with advanced methods, we gain deeper insights into catalyst properties, reaction mechanisms and surface interactions. These innovations advance the understanding of catalytic processes and enable breakthroughs in material performance and industrial applications.

3.1. Precision with fourier transform infrared spectroscopy (FTIR)

The method for determining the emission or absorption infrared spectrum of a gas, liquid or solid is called Fourier transform infrared spectroscopy (FTIR) [37,69]. Unlike dispersive spectrometers, which measure power across a limited range of frequencies simultaneously, FTIR spectrometers excel in acquiring high-resolution data across a broad spectral range (from 4000 to 400 cm^{-1}) simultaneously. Spectroscopic techniques like UV-Vis and FTIR aim to quantify the absorption of light by materials at each frequency [69]. In the simplest method, called "dispersive spectroscopy"," a monochromatic laser beam is directed at a sample, the quantity of absorbed light is quantified and then the amount of light is recalculated for each frequency [69]. In the FTIR technique, an array or beam is focused that directs multiple frequencies of light onto the sample simultaneously instead of monochromatic light emission (with only one frequency). The array would then quantify the proportion of the beam that is absorbed by the sample. The wave is then modified to include a different combination of frequencies, thereby providing an additional data point. A computer quickly collects the data and runs this cycle frequently. For example, an interferogram, the wave shown in Fig. 1, is generated using a broadband light source that covers the entire frequency range to be calculated. The light beam enters a Michelson interferometer, which consists of a unique arrangement of mirrors, one of which is movable with the help of a motor (more on this in the following section). The interferometer alternately obstructs, modulates, blocks and transmits each light frequency in the beam as the mirror moves. This process assigns specific positions to different frequencies as they interact with the interferometer [37,69].

In order to extract the results (light intensity for each frequency) from the raw data (light intensity for each mirror position), computational post-processing using Fourier transforms is required, as shown in Fig. 1 [37,69]. The Fourier transform translates a spatial range (in this case, the distance of the mirror in cm) into the corresponding frequency range (expressed in cm^{-1}). Currently, FTIR spectrometers are affordable and widely used in analytical laboratories. FTIR offers at least three notable advantages compared to dispersive devices:

(i) The Fellgett or multiplex advantage results from the simultaneous acquisition of all wavelengths, eliminating the need for sequential acquisition as required with scanning monochromators. This leads to a reduction in the scan time for a certain resolution level or to an increase in the signal-to-noise ratio within a certain scan time.

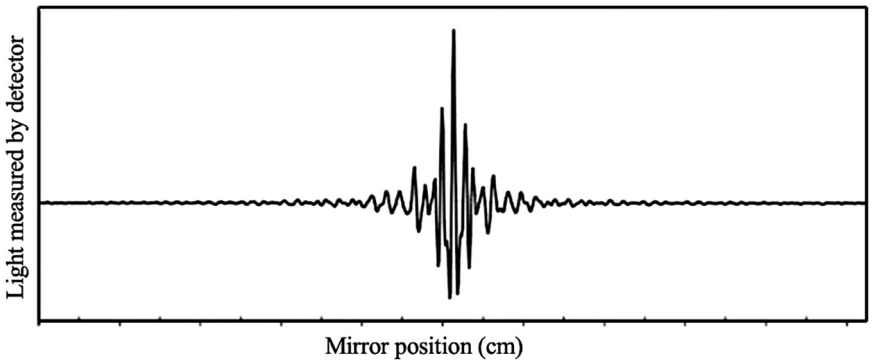

Fig. 1. Visualisation of a typical FTIR interferogram. The ZPD position is the location of the central peak. i.e. at the point of zero path difference or zero retardation. This is the point at which the highest intensity of light flows through the interferometer and reaches the detector.
(a) Reproduced and adapted from ref. (b) Fadlelmoula et al., [56], with permission from MDPI, copyright 2022.

(ii) Jacquinot advantage, also known as throughput, is increased in the FTIR configuration due to the elimination of slits in monochromators. The amount of light that can pass through these openings is limited. The diameter of the collimated beam from the source is the only factor that determines the throughput of FTIR devices.
(iii) The Connes advantage, also known as the ability, to achieve improved wavelength precision, comes from recording the distance (in the moving mirror of the interferometer) rather than the frequency. By utilising the interference pattern generated by a HeNe laser, a high degree of precision can be achieved.

Despite these advantages, there are very few cases in the literature where the characterisation of catalysts has been studied by applying FT-IR spectroscopy, especially in recent years. Monitoring the growth of solid materials during catalytic processes is an interesting application of this technology. For example, Sullivan and colleagues utilised it to monitor fluctuations in a vanadium oxide (V_2O_5) catalyst during the conversion of NO + NH^3 mixtures [150]. They concentrated on the metal-oxygen stretching region in the infrared emission spectra of V_2O_5 to assess proportions of V^{5+} (peaks at 600, 820, and 1020 cm^{-1}, as shown in Fig. 2) versus V^{4+} (appearing at 910 cm^{-1}) at the sample's surface. Their results indicate that the combination of NO and NH_3 does not lead to a significant decrease in the amount of V_2O_5 powder, even

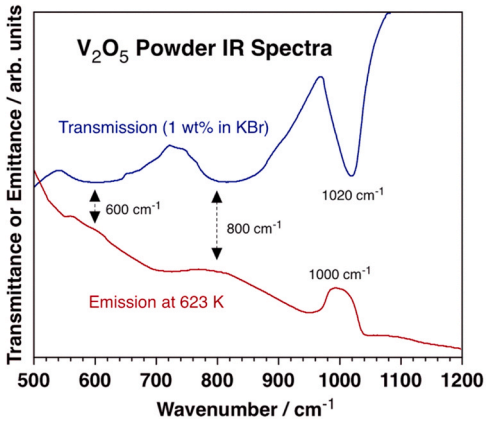

Fig. 2. Comparison of the infrared spectra of a V_2O_5 powder recorded in emission (bottom, red) and transmission mode (top, blue trace) [150]; the emission signals point upwards, while the transmission signals point downwards. The similarity of the signal-to-noise levels between the two spectra is a remarkable observation. The peaks at 600, 800 and 1000–1020 cm^{-1} in both traces indicate the V^{5+} oxide state of the metal.
(a) Reproduced and adapted from ref. (b) Sullivan et al., [150], with permission from Elsevier, copyright 1998.

when an excessive amount of NO is present. Alternatively, attention has been focused on the behaviour of the adsorbates themselves in different studies. The study investigated the adsorption of CO on catalysts based on Rh, Pd, and Pt. The investigation identified many bond types, such as triple-bonded carbonyls (1800 cm^{-1}), bridging carbonyls (1860 cm^{-1}), and geminal dicarbonyls (with bands at 1970 and 2040 cm^{-1}) [54]. Identification of these peaks was relatively easy when analysing metal foil samples, but their intensity decreased more than tenfold when analysing supported catalysts. The authors also identified atop (1996–2063 cm^{-1}), as well as gem-dicarbonyl dimers (1970–2022 and 2063–2092 cm^{-1}) and bridging (1720–1870 cm^{-1}) carbonyl forms of CO adsorbed on Rh/Al_2O_3, Ir, and Pt [50]. As another example, IR emission spectroscopy was used to study the dehydroxylation process of alumina gels [2] and Ni, Mg, and Co hydrotalcite catalysts. Signals associated with the stretching of the O-H bond were detected above 3000 cm^{-1} [110].

As this is a technique where the light absorption is evaluated as an intensity drop from the 100 % intensity of the initial IR beam, the main disadvantage of FTIR instruments is their limited sensitivity. One result of detecting these high intensities is that the signal-to-noise ratio (S/N) of the spectrum is high. This drawback is exacerbated by the fact that FTIR works with white light, which contains numerous frequencies that are not absorbed but still contribute to signal noise. In addition, FTIR generally cannot utilise the sophisticated electronic filtering methods that are sometimes used in dispersive measurements. Although acquisition typically takes only a fraction of a second, advanced instruments can cover approximately four orders of magnitude of light absorption in a single scan. They provide a high signal-to-noise ratio capable of detecting absorption bands as low as 10^{-4} absorption units, with weaker signals detectable through signal averaging.

In addition, there are other alternatives to increase the sensitivity or time resolution of infrared absorption spectroscopy by improving the signal-to-noise ratio. Firstly, high-band, low-band, or bandpass filters can be employed to exclude other frequencies from the infrared source if only the absorption in a particular region of the radiation is of importance for a particular experiment. Remarkably, this is rarely done. Intense sources, including tunable infrared lasers or synchrotron radiation field, can also be used instead of standard glow-bar infrared lamps [153,76]. Tunable lasers only cover a limited frequency range, as they only cover a small part of the high-energy mid-infrared region (and only a relatively small range of wavenumbers can be used to modify their frequencies). Mercury cadmium telluride (MCT) detectors are employed in modern FTIR instruments for their high sensitivity and coverage of the mid-IR frequency range. However, sophisticated detectors can also be used for more specialised applications. Indium antimonide (InSb) detectors, for example, have a sharp cut-off for detecting low frequencies at around 1800 cm^{-1} but a signal sensitivity that is about an order of magnitude above this value. Investing effort in fine-tuning the

signal-to-noise ratio (S/N) of the chosen infrared setup is crucial. This optimization enhances temporal resolution in kinetic studies and enables the detection of adsorbed species with surface concentrations or low cross-sections. Table 4 lists the most used infrared bands in catalytic studies.

3.2. Depth of analysis with X-ray photoelectron spectroscopy (XPS)

XPS is a useful technique for the qualitative and quantitative characterisation of the chemical nature of material surfaces. It can also provide information on the structure, homogeneity and morphology of a sample in relation to its depth. The understanding of novel interfaces (such as electrodes in semiconductors) [131,188], electronically active materials [156,87], catalytic and surface processes [34,49], and solid synthesis pathways [78] can be supported by such methods.

3.2.1. Background of a spectrum

Before assigning certain transitions to an XPS peak, the spectrum's background must be properly subtracted. This background typically originates from photoelectrons with initial kinetic energies higher than the measured kinetic energy. This is due to the fact that inelastic scattering occurred before the energy analyser detected the photoelectrons. An energy analyzer that is differentially pumped or has its input connected to the aperture receives a signal that is greater than the background because the kinetic energy of the photoelectrons is not lost during the transfer from their source atoms. The number of electrons that are not lost is represented by the area above the background. There are several methods for subtracting the background. The variation in background subtraction is the source of uncertainty.

3.2.2. Satellite peak

Some transition metal elements often exhibit satellite peaks in their photoemission. These electrons are generated by the shake-off excitation or shake-up of subshell electrons to valence electrons. They typically exhibit higher binding energies than the primary peak, as the excitation of valence electrons requires a certain amount of kinetic energy. Consequently, their kinetic energies upon leaving the sample are lower than those of photoelectrons that haven't undergone such excitations. Therefore, they are commonly observed on the higher energy side of the primary XPS peak. Factors such as the oxidation state, coordination environment, and subshell of the original electrons contribute to the energy required for the shake-up or shake-off process. For example, the satellite peaks of Co $2p^{3/2}$ in Co^{2+} with octahedral coordination (CoO) appear at 786.8 eV, whereas Co $2p^{1/2}$ in Co^{2+} with tetrahedral coordination (Co_3O_4) exhibits a faint satellite peak at 789.5 eV [34,87].

3.2.3. Deconvolution of a spectrum

Deconvolution of XPS peaks from elements in a catalyst is crucial for a thorough understanding of their chemical environment, especially when quantifying the ratio of atoms in different chemical states.

Table 4
Some Infrared (IR) absorption bands of key functional groups in catalytic studies.

Functional group	Absorption band (s) cm^{-1}
Alkynyl C═C stretch	≈3300
C–O–C stretch	1250–1050
NO_x stretch	1600
Aldehyde C=0	1740–1715
Aromatic C═C bending	1700–1500
N–H stretch	3500–3350
Nitrile CN stretch	2260–2220
Aromatic C–H bending	860–680
Alkynyl CC stretch	2260–2100
Alkenyl C═C stretch	1680–1620
Alkenyl C—H stretch	3100–3010
Alkyl C–H stretch	2950–2850

Accurate peak fitting is essential for analysing XPS data, allowing the identification of chemical states and their respective binding energies through hypotheses or insights from complementary techniques. Spectrum deconvolution is a challenge. It is not just a mathematical approximation. To ensure consistency with models derived from other characterisations, XPS peak fitting must be based on a sound physical framework. There are numerous reports of pitfalls in XPS fitting, including introducing unconstrained peaks without a clear chemical or physical basis, inappropriate background subtraction, and varying full width at half maximum (FWHM) for peaks from different chemical states. Literature reports indicate the development of graphical tools to identify poor peak-fitting [80]. The intrinsic width of each chemical state's XPS peak is typically determined by the instrumental resolution and core-hole lifetime, resulting in uniform peak widths. For accurate analysis, the FWHM of fitted peaks for each chemical state of the same element should be uniform, ensuring consistent measurements across transitions (e.g., Pd $3d^{5/2}$) obtained with the same XPS instrument. The peak fitting process involves first defining a quantification region and subtracting the background. The definition of the energy interval between a background and a peak is called the quantification region. The background region can be generated using the Tougaard, Shirley, and linear approaches either individually or in combination. The spectrum of an insulating material is usually determined by a linear background, which is characterized by a relatively uniform background. For the spectra of transition metal elements, a Shirely background is generated instead. After defining the energy window and subtracting the background, the next step involves developing a fitting formula. In this formula, the peaks are fitted into a series of line shapes and the positions and offset ranges of the peaks are specified, as well as constraints such as spin-orbital separation and the area ratio between two fitted peaks. There are a variety of line shapes that can be used to represent the peak of a chemical state.

In spectral line shapes, theoretical curves (fitted spectra) are typically generated using combinations of Gaussian and Lorentzian line shapes. Synthetic components like sum Gaussian–Lorentzian SGL(m) or Gaussian–Lorentzian GL(m) are commonly used for symmetric peaks (e.g., s- or p-subshells), where m determines the mix of Gaussian (m=0) to Lorentzian (m=100). Asymmetric peaks (e.g., d or f subshells) of transition metals require Lorentzian shapes convolved with Gaussian, such as LA(a,b,n), for generating synthetic line profiles [160]. The Gaussian component, representing analyzer effects and thermal broadening, dominates spectral broadening at core levels, with Lorentzian (core-hole lifetime) contributing less. A 30 % Lorentzian and 70 % Gaussian mix is often used in spectral analysis, maintaining consistency across G/L ratios. For simulating asymmetric XPS peak shapes, the pseudo-Voigt function can be adjusted using a sigmoidal step function [142]. The theoretical curve for peak matching can be generated using this function with an asymmetric shape. The first experimental value of the binding energy is an important parameter in the formulation. The initial trial value can be determined by comparing the chemical state of a sample with a state reported in the literature. An extensive literature review is essential to determine an appropriate initial binding energy for a chemical state and to establish correlations between peak areas or binding energies of different states. For example, if a sample contains both metal (A) and metal oxide (B), then $B = A + \Delta E$, can be used to calculate the binding energy in the metal oxide, where ΔE is the difference in binding energies between the metal and the metal oxide. Constraints on peak areas can be set for different chemical states based on atomic ratios determined by complementary techniques. For example, if surface XRD confirms Co_3O_4 formation, the atomic ratio of Co^{3+} and Co^{2+}in Co $2p_{3/2}$ can be fixed at 1:2. Spin–orbital splitting in p, d, and f orbitals leads to consistent peak separations across different chemical environments, maintaining constant area ratios for split peaks. The energy distance of a particular subshell remains constant regardless of the change in the chemical environment. Spin–orbital splitting is, therefore, consistent in most cases across a wide range of chemical

states. Furthermore, the area ratio of the two split peaks remains constant in all chemical and coordinate environments.

3.2.4. Quantification of XPS spectra

With advancements in XPS instrumentation over the past few decades, the precision of atomic concentration measurements has improved significantly, achieving an accuracy of 1 %–5 %. The high accuracy of XPS quantification relies on precise characterization. XPS operates on the principle that the number of electrons detected by the detector correlates directly with the number of atoms in a specific chemical state. Quantification involves calculating the area under the XPS peak of interest to determine the number of electrons collected. Isolated peaks resulting from singular transitions can be straightforwardly quantified. However, in most cases, peaks from different chemical states are not clearly resolved due to overlapping transitions of atoms in distinct oxidation states. Additionally, transitions from atoms of distinct elements may also overlap. Consequently, a deconvolution of the measured spectrum is necessary to obtain a basic understanding of the coordination and chemical environment of atoms. Detailed guidance on deconvoluting overlapping peaks is provided in Section 3.2.3. Eqs. (1) and (2) can be used to determine the surface composition of element M or A, or the overall atomic ratio of element M to A, respectively:

$$r_{M/A} = \frac{I_M/C_M}{I_A/C_A} \tag{1}$$

$$f_M = \frac{I_M/C_M}{\sum_{I_i} C_i} \tag{2}$$

For a fundamental understanding of catalysis, it is sometimes necessary to determine the atomic ratio of element M to element A in the uppermost layer. This requires computing the area of the XPS peak corresponding solely to the topmost layer of atoms M. However, this computation can be challenging because subsurface atomic layers influence the peak area. If the atoms of element M are uniformly distributed throughout the atomic layers or if their distribution is not depth-dependent, the peak area of the topmost layer of element M can be determined using Eq. (3).

$$I_{M_i} = \frac{I_1 I_M}{I_1 + I_1 e^{d/\lambda} + I_1 e^{3d/\lambda} + \ldots + I_1 e^{(\pi-1)d/\lambda}} \tag{3}$$

Additionally, Eq. (4) simplifies the computation of the atomic ratio of M to A in the topmost layer, denoted as r_{M1}/A_1.

$$r_{M_1/A_1} = \frac{I_{M_1}/C_M}{I_{A_1}/C_A} \tag{4}$$

To determine the relative sensitivity factors, one can refer to a textbook or relevant references. Using these factors, atomic ratios or compositions can be calculated with the given equations. These equations are particularly useful for samples where elements are uniformly distributed throughout both deep and surface layers. However, in practical applications, catalysis often leads to variations in composition with depth. When element M is not uniformly distributed in the surface region, calculating the atomic ratio or composition of the uppermost layers becomes more complex. This is because (Eq. 5):

$$r_{M_1/A_1} = \frac{I_{M_1}/C_M}{I_{A_1}/C_A} \tag{5}$$

3.3. Unveiling molecular secrets with Nuclear Magnetic Resonance (NMR) spectroscopy

Nuclear magnetic resonance (NMR) spectroscopy is not only widely used in various fields of chemistry and biochemistry but also serves as a versatile and informative tool for studying catalysts. Characterising solid samples requires a technique referred to as magic-angle spinning NMR (MAS NMR, also known as SS NMR or solid-state NMR), which involves rapidly rotating the samples. Unfortunately, this technique often yields spectra with lower resolution compared to those obtained in the liquid phase, and it presents challenges for designing catalytic reactors for *operando* or *in-situ* studies. Nonetheless, MAS NMR is widely utilised for characterising catalytic systems, including the investigation of acidity sites in oxides [199,81].

Recently, there have been intriguing reports of operando MAS NMR studies on catalytic conversions of organic reactants. One example, shown in Fig. 3a, involves the hydrogenolysis of benzyl phenyl ether (BPE) catalysed by Ni/γ-Al_2O_3 [169]. The time-dependent NMR data in the top section of Fig. 3 clearly distinguishes the original BPE from the three main products: phenyl isopropyl ether, toluene, and phenol. This data can also be transformed into the kinetic plot shown in the Fig. 3b. Based on the intermolecular transfer of hydrogen atoms, the kinetic data was used to propose a conversion mechanism. According to this mechanism, phenol and toluene are the primary products, while 2-propanol and phenol undergo a subsequent coupling step to produce phenyl isopropyl ether (Fig. 3c).

The primary disadvantage of NMR is its limited sensitivity, which requires a significant number of nuclear spins for accurate detection. This limitation is a significant obstacle when searching for intermediates on the surface or other minority species, but it becomes less of a problem when investigating the major catalytic sites in high surface area catalysts. Many approaches have been tested over the years to address this problem, including the more recent development of dynamic nuclear polarisation (DNP NMR). By transferring the massive electron polarisation of a selected polarising agent via microwave irradiation near or at the transition of the electron paramagnetic resonance, DNP NMR enhances the tiny magnetic moments of the nuclei (such as ^{1}H, ^{13}C and ^{15}N). This method has proven to be very promising in the discovery of important surface species [121,91]. However, DNP NMR experiments must be performed at temperatures below those required for most catalytic processes and require the use of extremely specialised chemicals in the system. While efforts have been made in the field of homogeneous catalysis, there are currently no established applications of *operando* or in-situ modes or DNP NMR to study reactions initiated by heterogeneous catalysts [30]. Regardless of the various obstacles, DNP NMR may soon be included in the toolbox for operando or in-situ characterisation of heterogeneous catalytic processes.

3.4. Exploring vibrational signatures through RAMAN spectroscopy

Raman spectroscopy, which measures energy losses due to the activation of vibrational modes by analyzing inelastically scattered photons, is an alternative method for obtaining vibrational information about solid catalysts and molecular species adsorbed on catalysts. Raman and FTIR spectroscopy are complementary in many ways, as they are sensitive to different sets of vibrations due to distinct selection rules. Raman spectroscopy is particularly effective in identifying low-frequency modes, such as those caused by vibrations within surface oxide clusters [168]. Due to the typically large surface areas of most catalysts, the signals are often weak. However, this challenge can sometimes be overcome by using shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS) (Zhang et al., 196) or resonant Raman, surface-enhanced Raman (SERS) [51,89]. A high level of light fluorescence and scattering often interferes with the detection of vibrational peaks in Raman spectroscopy. The use of UV light as an excitation source instead of visible light can help to alleviate this problem [94]. Raman spectroscopy has been used to image heterogeneous catalysts and has proven highly effective for probing catalysts in-situ or using *operando* techniques [21,22]. An example of the latter is shown in Fig. 4, where an amorphous cobalt sulfide (CoSx) electrocatalysts are used to stimulate the hydrogen evolution reaction (HER) [94]. The Raman data analysis, together with additional XAS results, led to the proposal of a model in which the metal sulphide forms small clusters under reaction conditions,

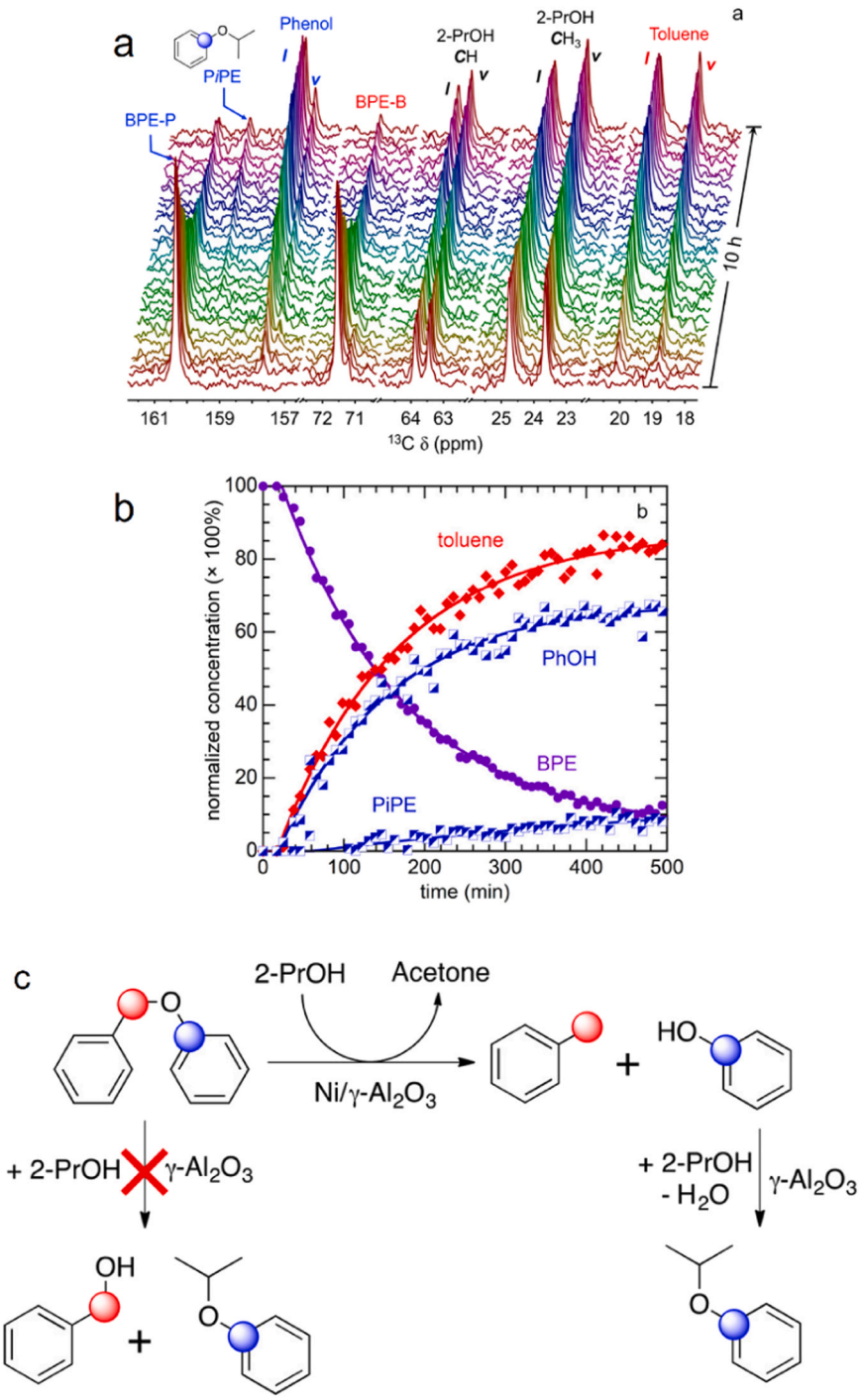

Fig. 3. a. Time-resolved ^{13}C MAS NMR spectra were obtained during the hydrogenolysis of benzyl phenyl ether (BPE) in 2-propanol using a Ni/alumina catalyst. (b) The top section displays the unprocessed data with assigned peaks. Kinetic profiles for phenol (PhOH), toluene, phenyl isopropyl ether (PiPE), and BPE derived from these data. (3c) illustrates the proposed mechanism.
(a) Reproduced & adapted from ref. (b) Walter et al., [169], with permission from American Chemical Society (ACS), copyright 2018.

with cobalt in an octahedral CoS_2-like state surrounded by a first shell of sulphur atoms exposed to the electrolyte.

In heterogeneous catalysis, Raman spectroscopy is very effective due to its sensitivity to collective vibrational modes involving different atoms. Raman spectroscopy is superior to FT-IR spectroscopy in many aspects:

- Water interference is minimal because of the minor scattering effect of water molecules.
- Catalysts can often be tested directly in the reactor using a transparent glass without pretreatment.
- Raman spectroscopy is particularly suitable for the detection of functional groups with high symmetry and low polarity, such as C-C, S-S, and C═C.
- Raman spectroscopy excels in detecting signals in the low-wavenumber region.

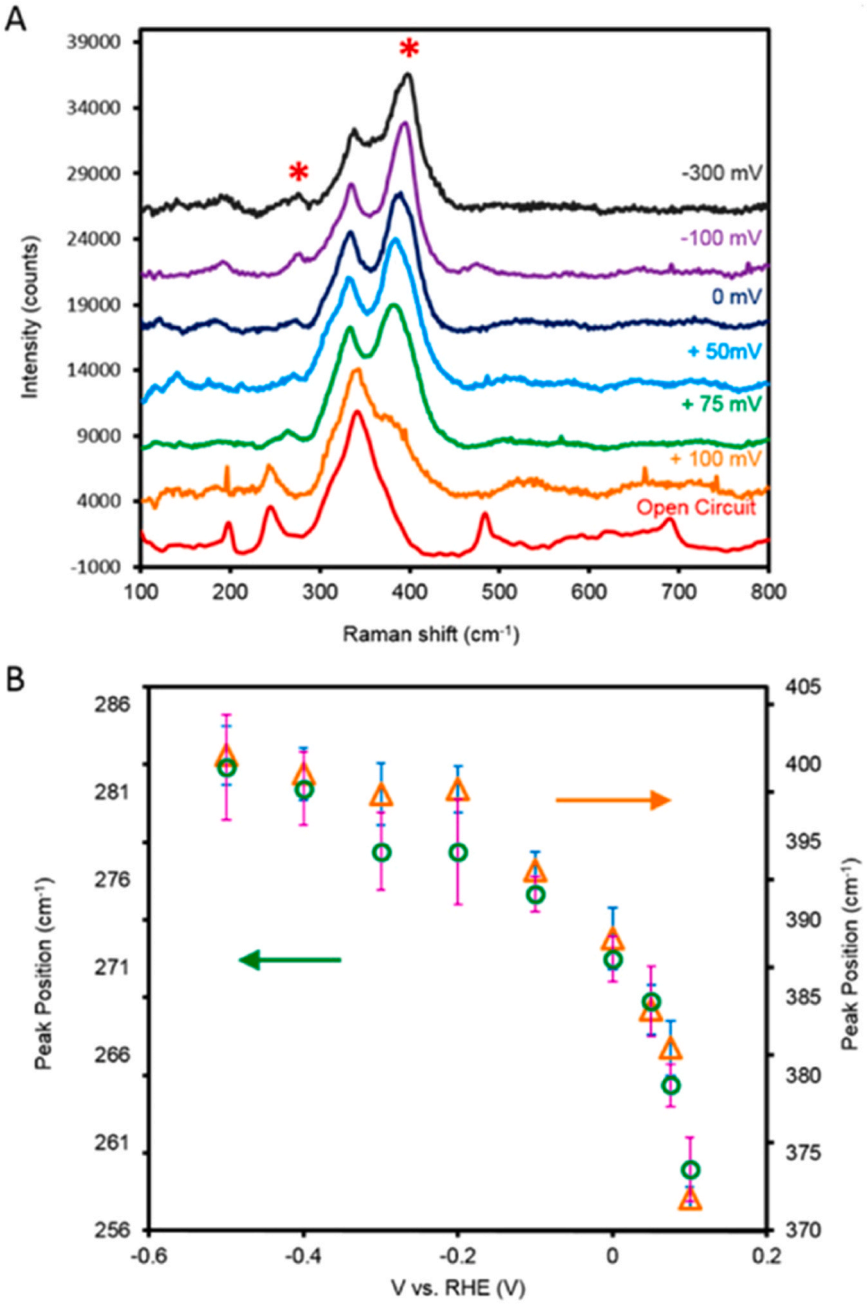

Fig. 4. a. An illustration of the application of Raman spectroscopy in *operando* mode to elucidate the specifics of catalytic sites in the investigation of hydrogen production via electrochemical methods using amorphous cobalt sulfide. Two novel peaks, marked by asterisks, were assigned to the formation of CoS_2-like clusters on the electrode surface. Fig. 4b shows a blue shift with increasing negative potentials, indicating that the Co-S bond is becoming stronger. The proposed atomic model, derived from these findings, is illustrated in the inset.
(a) Reproduced & adapted from ref. (b) Kornienko et al., [94], with permission from American Chemical Society (ACS), copyright 2015.

3.5. Comparative evaluation of advanced spectroscopic techniques

In order to understand the relationships between properties and structures in catalytic materials, it is essential to know the existence and arrangement of isolated single atoms. Detecting changes in individual atoms in-situ poses a challenge due to the need for high-resolution instruments. In recent decades, characterization techniques have been developed that achieve atomic-level resolution and generate signals at different ensemble levels for all reactive species. This methodology minimizes the likelihood of inaccurate information and accurately represents the active atomic species. Table 5 displays extensively reported characterization techniques for examining the properties of catalytic materials, including FTIR, XPS NMR, and Raman spectroscopy. The table outlines their principles, strengths, limitations, and analytical costs.

3.6. Merits and limitations of some advanced techniques

Advanced spectroscopic techniques such as FTIR NMR, XPS, and Raman spectroscopy are pivotal in catalysis research. These methods provide deep insights into the structural, electronic, and chemical properties of catalysts, improving the understanding of catalytic mechanisms and material behaviour. Each technique, however, has its unique merits and limitations. In addition, in-situ, synchrotron radiation

Table 5
Comparative evaluation of advanced spectroscopic techniques [117,173,191,192,4].

Aspects	FTIR	XPS	NMR	RAMAN
Common uses	Functional group identification, impurity detection, and polymer characterization	XPS allows for the determination of the chemical state of surfaces and excels in quantitative analysis for all elements except for two. It is effective in identifying differences in chemical states among materials and can distinguish oxidation states of molecules	Provides detailed, non-destructive analysis of chemical and biological samples. It is a powerful tool for determining molecular structure, composition, dynamics and interactions across many scientific disciplines.	Identifying minerals, analysing crystalline structures, and studying biological samples
Polarizability	Is independent of the sample's polarizability	XPS spectroscopy is highly sensitive to surface chemistry and electronic structure. However, it does not require the sample to be polarized for the emission and detection of photoelectrons	NMR spectroscopy detects signals from atoms based on their nuclear spin properties in a magnetic field, unlike other spectroscopic methods that rely on sample polarization	Raman intensity is dependent on the sample's polarizability
Information depth	Provides near-surface information due to limited penetration depth	Valence state determination Time-resolved operando information In-situ/ Ex-situ	Time-resolved operando information Sample polarization Chemical shift (structural assignments of surface species) In-situ/ Ex-situ	The data can be sourced from multiple layers within the sample
Analytical use	Frequently utilized in pharmaceutical and chemical analyses	Commonly used for studying surfaces and interfaces in diverse fields such as materials science, chemistry, physics, and biology.	Used in academic research, industry, and various scientific disciplines such as pharmaceutical, material, environmental, food science and agriculture science, etc.	Utilized in materials science, geology, and biological research
Imaging applications	Restricted to imaging applications	XPS can be operated in a mapping mode to analyze elemental distributions across the surface of a sample.	NMR spectroscopy does not offer conventional imaging of catalytic surfaces like microscopy, but its capability to investigate molecular interactions, dynamics, and reaction mechanisms enhances catalytic studies, fostering the advancement of efficient and sustainable processes.	Used for chemical mapping in Raman imaging
Instrumentation	Utilizes an infrared light source (e.g., FT-IR, dispersive IR)	It relies on a high-energy X-ray source for excitation, an electron analyzer to measure emitted photoelectron energies, and a vacuum system to maintain ultra-high vacuum conditions	It depends on a strong magnet for generating a homogeneous magnetic field	Depends on a laser light source and Raman spectrometer
Spatial resolution	Generally, has lower spatial resolution	The spatial resolution of XPS is considered low compared to microscopy techniques capable of achieving resolutions down to the nanometer scale	Has a lower spatial resolution	Has the potential to attain a higher spatial resolution
Analytical cost	Medium	Medium-High	Medium	Medium - High
Drawback	Susceptible to water interference; necessitates meticulous sample preparation	Poor lateral resolution	Faces challenges in analyzing higher molecular weight molecules due to the complexity and difficulties in interpreting their spectra	Weaker signals; limited applicability to specific molecules due to fluorescence interference
Benefit	Offers insights into functional groups and supports quantitative analysis	Chemical bonding, no sample damage	Provides detailed insights into the atomic-scale structure, host-guest interactions, and dynamic behaviours of materials. It plays a crucial role in characterizing zeolite catalysts, which are widely used in industrial catalytic processes	Provides complementary information to FT-IR; particularly effective for samples exhibiting strong fluorescence
Sensitivity	Moderate sensitivity	XPS is sensitive to surface areas investigated in 3 nm below the surface because the inelastic mean free path is short	The sensitivity of NMR machines depends on the magnetic moment of the specific element. However, if the magnetic moment is too low, obtaining NMR spectra with sufficient peak intensity for accurate analysis can be challenging	Typically, lower sensitivity, yet capable of enhancement through surface-enhanced Raman spectroscopy (SERS)
Water interference	Prone to interference from water absorption bands in the spectra	It is susceptible to interference from water absorption bands in the spectra	It is susceptible to water interference, but techniques such as solvent suppression methods, gradient pulses, and selective excitation are employed to mitigate this interference, thereby improving spectral quality and resolution	Shows reduced susceptibility to water interference
Sample preparation	Typically requires samples in liquid, solid, or gas form	Generally, requires samples in solid form	Typically requires samples prepared in liquid, solid, or gaseous forms to facilitate analysis across various states of matter	Samples can be solids, liquids, or gases; typically requiring minimal sample preparation
Information obtained	Bond types, Functional groups, and molecular structure	Elemental and chemical		Similar to FT- IR spectroscopy, yet offers complementary information in certain cases
Vibrational modes	Excites molecular vibrations that involve dipole moments	It does not excite molecular vibrations involving dipole moments. It analyzes the binding energies of photoelectrons emitted from atoms' core levels to determine elemental composition and chemical states on the surface	It does not excite molecular vibrations involving dipole moments but detects and analyzes radiofrequency signals emitted by nuclei in a magnetic field, revealing details about their chemical environment and molecular structure.	Excites molecular vibrations regardless of dipole moments

(*continued on next page*)

Table 5 (*continued*)

Aspects	FTIR	XPS	NMR	RAMAN
Interaction	Absorption of infrared radiation by molecules	It uses X-rays to eject core-level electrons from atoms in a sample, analyzing their kinetic energy to determine elemental composition and chemical environment.	It interacts by applying radiofrequency (RF) pulses to nuclei in a strong magnetic field. It detects RF signals emitted by nuclei as they relax back to their equilibrium states after excitation, revealing details about molecular structure and chemical environment	Scattering of laser light due to molecular vibrations

[a]Cost per sample/ analytical hour based on client consultation
Very high = >669 USD
High = 333–669 USD
Medium = 133–333 USD
Low = <1

techniques have revolutionised catalysis research by providing unprecedented sensitivity and detail enabled by innovations such as high-energy lattices, storage rings, insertion devices and low emittance. Table 6 presents a concise summary of the advantages and obstacles of each technique in the context of catalysis research.

4. Visualizing catalyst in action

When visualising catalysts in action, advanced imaging techniques are used to observe catalysts interaction of catalysts at the molecular level. This provides real-time insights into their structure, dynamics and performance, which are crucial for optimising catalyst design and improving reaction efficiency in chemical processes.

4.1. Nanoscale Insights from Transmission Electron Microscopy (TEM)

In recent years, in-situ TEM has emerged as an effective technique that enables imaging in real space with sub-Angstrom spatial resolution, micro-electron volt energy resolution and millisecond time scales, facilitating the dynamic tracking of nanomaterial evolution [103,149,190]. Advanced techniques in in-situ TEM, including liquid cell TEM, environmental TEM (ETEM) and gas holder TEM, allow direct injection of gases and liquids and the introduction of various stimuli such as heating, biassing, force application, illumination and controlled atmosphere [175,182]. Precise control of electron beam parameters in the TEM, including accelerating voltage, beam current density and scanning position, enables the fabrication of novel nanostructures [187,195]. This state-of-the-art in-situ TEM instrument enables direct imaging of processes such as nanocrystal nucleation and growth, as well as dynamic variations in simulated environments, with intuitive real-time data for future utilisation. Using advanced microelectromechanical systems, ultrathin SiNx or carbon membranes are integrated into microelectrode systems to observe samples in-situ under conditions such as heating, pressure and liquid environments. These in-situ TEM analyses are crucial to directly observe how materials react under different operating conditions in liquid-solid, gaseous, solid– and electrical systems. The structure-activity features of materials at the atomic level can be elucidated by characterising structural evolution in different environments, which can lead to advances in material development and optimisation of material characteristics. With its ability to collect atomic-scale information with microsecond temporal resolution, in-situ electron microscopy promises to improve our knowledge of the properties and behaviour of nanocrystals [198].

4.1.1. Growth of nanocrystal study using TEM

Nanocrystals are mainly synthesised in the liquid phase. The nucleation phase, which follows the initial formation of nanocrystals, is of crucial importance as it determines the size, morphology and surface structure of the resulting products and thus determines their characteristics [181]. To effectively control nanocrystals, it is important to understand the driving forces, mass transfer channels and facet development that occur during their growth at the atomic level. With a liquid cell transmission electron microscope (TEM), Zheng et al. [200] studied the growth of platinum nanocrystals and discovered that the growth rate of different facets of platinum varied based on the size of the nanocrystal [102]. All low-index facets grew at similar rates until the (100) facets stopped growing, whereupon the continued growth of the remaining facets led to the formation of nanotubes, as shown in Fig. 5a. Similar phenomena with growth-regulated nanocrystals have been observed in other monometallic and alloyed nanocrystals [101,200,24]. These observations provide insights into the shape control of nanocrystals by facet-based growth rates. Crystal symmetry also plays a crucial role. Noble metal nanocrystals typically maintain their shape within the O_h-point group, indicating the development of face-centred cubic (FCC) cores in most cases [138]. With in-situ liquid cell TEM, Sun et al. [151] observed tetrahedral gold nanoparticles with a Td point group emerging from rhombic nuclei with an Oh point group and proposed a mechanism for symmetry-breaking [151]. They identified tris-tetrahedral intermediates during the transformation of rhombic dodecahedral Au nuclei into tetrahedral nanoparticles (Fig. 5b). This symmetry breaking from the O_h to the T_d point group could be partly due to the lower surface energy of the tetrahedral framework. Ostwald ripening, a size-controlled process, is another well-known phenomenon in which smaller nanocrystals dissolve to facilitate the growth of larger nanocrystals [58]. This thermodynamically driven process favours energetically larger particles over smaller, more soluble particles. By manipulating thermodynamic parameters, the size and solubility of nanocrystals can be controlled. Using liquid cell TEM, Khelfa et al. [88] found that smaller (38.1 nm) and larger (>57.2 nm) Au nanoparticles shrank and disappeared at 85 °C (Fig. 5c) [88]. The increased solubility of gold at higher temperatures, in combination with a higher concentration of hydroxyl radicals, probably drives the Ostwald ripening process.

4.1.2. Imagining lattice strain and strain control using TEM

Bimetallic alloys often exhibit lattice strain, which plays a decisive role in several applications, including electrocatalysis, energy storage and data storage. For example, one study showed that a nanocrystal made from a platinum-based alloy with a slight compression seft, attributed to the segregation of Pt at the surface, increased catalytic activity. This improvement was attributed to the weak adsorption of O_2-species on the strained Pt surface caused by a lowered d-band centre of the Pt. It is widely recognized that metal nanocrystals with an FCC crystal framework often exhibit multiple twinned frameworks, including icosahedra or decahedra, particularly in very few particles. Research has shown that the surface free energy of nanocrystals is correlated with strain energy and twinning energy. At the near surface of magnetic icosahedral FePt nanocrystals, a relaxation was observed. High-resolution transmission electron microscopy (HRTEM) with sub-angstrom resolution was utilized to quantitatively analyse the periodic shell framework and surface reconstruction of icosahedral FePt nanocrystals. The lattice spacings of FePt (111) planes were found to decrease exponentially from the surface to the body with atomic shell numbers, revealing lattice strain near the surface of the nanoparticles (Fig. 6a)

Table 6
Summary of strengths and challenges of each advanced spectroscopic technique associated with their use in catalysis research [166,176,39,40,45].

Technique	Mertits	Limitations	Contribution to Catalytic Mechanisms
FTIR	Offers superior structural insights, heightened sensitivity, and an extensive dynamic range, with rapid acquisition of 2D electron diffraction patterns. Very suitable for metals supported on electronically non-metallic powders and powders that are electronically non-metallic. Enables probing of gas-phase products, reactants, and intermediates. Easily deployable and readily available for purchase. Compatible with in-situ and operando measurements for specific systems and with step-scan infrared spectroscopy	Challenges include studying beam-sensitive materials and the necessity for specialized detectors. Their limited sensitivity is the main limitation of FTIR spectroscopy. In this method, a non-zero background is created to quantify the light absorption by reducing the intensity of the infrared beam from its original intensity of 100 %. It is not sensitive to surface phenomena	Directly investigates differences in catalytic activity between sites on metal nanoparticles, crucial for understanding mechanisms in heterogeneous catalysis
XPS	With a detection limit of around 0.1 at %, it can detect every element except hydrogen and helium. Its adaptability makes it perfect for analysing conductive and insulating materials, including metals, composites, glasses, polymers, semiconductors and strongly adsorbed liquids or gases on surfaces.	Identification of chemical composition Artefacts such as preferential etching of elements, alteration of oxidation states, doping with ions and mixing of atoms during ion beam sputtering can make it difficult to determine the thickness and depth profiles of thin films thicker than 10 nm. (ii) Analyzing insulating specimens is complicated by surface charging, which causes asymmetry, broadening, peak shifts, and potentially leading to complex or inaccurate analysis results.	It serves as a valuable tool for surface characterization of catalysts, offering elemental analysis of the solid catalyst surface. Moreover, it facilitates the study of catalyst dispersion on the support material
NMR	Investigates structural changes, captures reaction intermediates and studies host–guest interactions while monitoring catalytic reaction processes.	High-pressure in-situ NMR under flow conditions has not yet been achieved, and it suffers from low temporal and spatial resolutions. The low sensitivity of NMR is its major limitation, as it requires a considerable number of nuclear spins to achieve reliable detection. Although this is less of a problem when studying major catalyst sites in large surface area catalysts, it makes it difficult to study intermediates on the surface or other minor species.	Molecular reaction pathways are uncovered, which is very helpful for research into heterogeneous catalysis and the detection of transient intermediates.
RAMAN	Provides precise chemical information without necessitating extensive sample preparation for measurement	A weak signal can result in long acquisition times. It also involves sophisticated data analysis.	It provides crucial insights into reaction mechanisms by revealing specific details about the catalysts' bulk and surface structures, including defects, as well as identifying adsorbates and reaction intermediates

[170]. Energy-filtered TEM, together with theoretical calculations, revealed that forming a Pt-enriched shell in alloy nanocrystals was energetically favourable. These strained FePt nanoparticles, featuring Pt-enriched shells and site-specific vacancies, demonstrated resistance to oxidation and stability under electron beam irradiation [171,174].

Niu et al., [118] used liquid cell transmission electron microscopy to follow the dynamic evolution of strain in a gas-solid phase reaction. They observed the formation of gas bubbles and their movement within the nanoparticles during the transformation of Pb@FeOOH with core shells into Pb@Fe_3O_4 [118]. The shell lattice around the bubbles exhibited a tensile strain of about 1.5 %, which was due to the gas pressure inside the bubbles (Fig. 6b). This bubble expansion changed the strain distribution around the core and bubble, showing positive strain around the bubble and negative strain around the core. This indicates that tensile strain significantly affects the morphology of the nanoparticles and can slow down oxidation processes.

Historically, conventional TEM only provided two-dimensional projections. Understanding the three-dimensional strained structure and its correlation with properties is essential for three-dimensional nanocrystals but remains a challenge. Atomic electron tomography (AET) is invaluable for imaging three-dimensional atomic structures. Yang et al. used deep learning-assisted AET to create a comprehensive three-dimensional map of the strain tensor of two Pt nanoclusters during coalescence [99]. They found that the migration of atoms at the interface determines the coalescence, surface reconstruction and tensile strain. These three-dimensional atomic data could facilitate the correlation of the strain structures of the nanocrystals with the reaction activity of oxygen reduction at the level of the individual atoms.

4.1.3. *Visualising oxidation reaction using TEM*

Research on nanoparticle catalysts under oxidising reaction conditions is extensive, particularly for metals including Pd and Pt, which are used in oxidation processes ([109,135,53]; D. [193]; X. [194]). In a study using the electron transmission electron microscope (E-TEM), the surface oxidation of large truncated Pd octahedrons (20 nm edge length) and spherical Pd nanoparticles (7 nm diameter) was studied (Fig. 7a–h) (D. [193]). It was found that oxidation in Pd octahedra started at the step edges of the (111) surface and formed up to two monolayers of

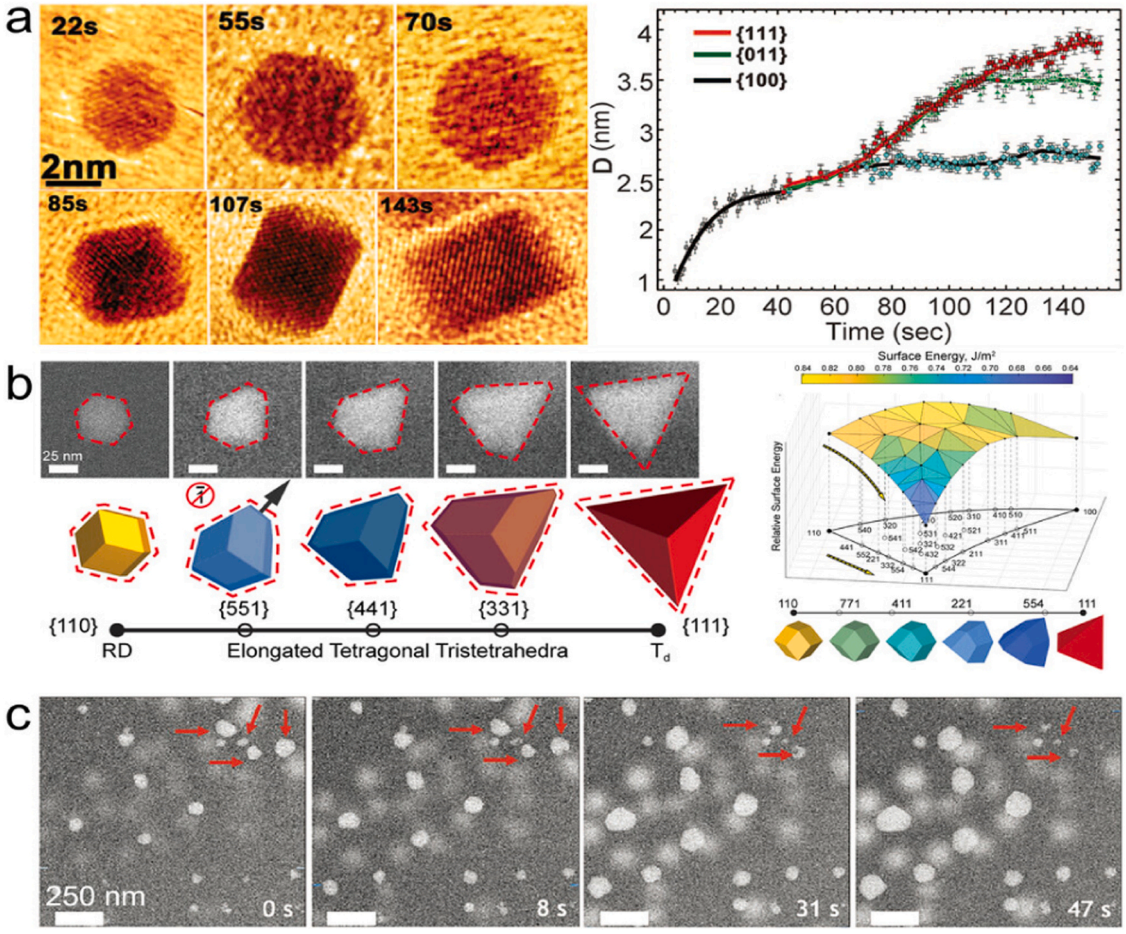

Fig. 5. a) Real-time TEM tracks Pt nanoparticle facet growth and measures distances from the crystal center over time. b) In-situ TEM reveals tetrahedral nanoparticle formation from rhombic dodecahedron seeds with crystallographic analysis. (c) In-situ STEM images showing the formation and dissolution of Au nanoparticles during the Ostwald ripening process. Reproduced with permission. Reproduced and adapted with permission from refs. Liao et al., [102], [151] & [88], with permissions from American Association for the Advancement of Science (AAAS), American Chemical Society (ACS), & John Wiley & Sons, Inc., copyright 2014, 2021 & 2021 respectively.

tetragonal PdO, with subsequent lateral growth (Fig. 7a–d). In contrast, the neighbouring (100) and (1−1−1) surfaces were unaltered and vertical growth occurred at a much slower rate. For spherical Pd nanoparticles, oxidation begins at the vertices between two (111) facets, and PdO propagates towards one of the (111) facets (Fig. 7e–h). This indicates that oxidation likely starts at low coordination sites, including step edges or vertices, before progressing to facet oxidation. A remarkable comparison can be made with the oxidation of $PtRh_2$ under NAP-CO oxidation environment and the oxidation of Pd nanocrystals in E-TEM. Initially, the variation in the chemical nature of the surface begins with molecular O_2, while in the next phase, it begins with O– radicals generated by the electron beam. This illustrates the significant difference between the two scenarios and emphasises the need to understand the interplay between the electron beam, the environment and the sample, as well as to control the beam flow during catalysis studies [28].

4.2. Topographical analysis through Atomic Force Microscopy (AFM)

In chemical research, AFM is often employed to characterise catalyst powders, especially nanoparticles. The functionality of catalysts is often affected by the particle size and the surface properties of the powder. Increasing the surface area of catalysts exposed to reactants can increase their efficiency. Hence, the aim is to produce smaller nanoparticles with an improved surface area using the same quantity of material. However, measuring the size and surface characteristics of these nanoparticles is a challenge. Compared to other commonly used instruments, including SEM, TEM, light scattering and various macroscopic techniques, AFM offers advantages, including the ability to work under environmental conditions, unlike SEM and TEM, which need high vacuum environments. In addition, AFM does not require coating for insulating and semiconducting samples. In contrast to light scattering and macroscopic methods, AFM can measure very small particles individually. In particular, the different variants of AFM allow researchers to observe different variations in the catalyst properties concurrently [152].

Researchers obtained better control over the synthesis of HKUST-1, which allowed them to significantly influence crystallinity and defect concentrations by adjusting certain synthesis parameters. Mandemaker et al. [105] emphasised the importance of nanospectroscopy techniques such as AFM-IR in investigating these irregularities. Using the high spatial resolution of AFM-IR, they observed the desorption of the self-assembled monolayer (SAM) in HKUST-1 synthesised at increasing temperatures (Fig. 8a). The absence of the strong band at 1700–1800 cm^{-1} associated with the stretching vibration of the SAM carboxylates C═O in the blue labelled regions (Fig. 8b) indicates the desorption process. This suppression of nucleation was also observed using in-situ liquid phase AFM at 50 °C. In addition, they found that a defect-rich, non-crystalline Cu_3BTC_2 layer, referred to as a "carpet"," surrounds the larger crystals, a contentious issue in the field.

Another recent study utilised microspectroscopy to examine the topology-defect relationship in thin films of SURZIF-8(Zn). Weckhuysen et al., [178] used a combination of AFM, Raman spectroscopy, PCA and DFT to identify the intergrowths of SURZIFs (Fig. 8c). They quantified

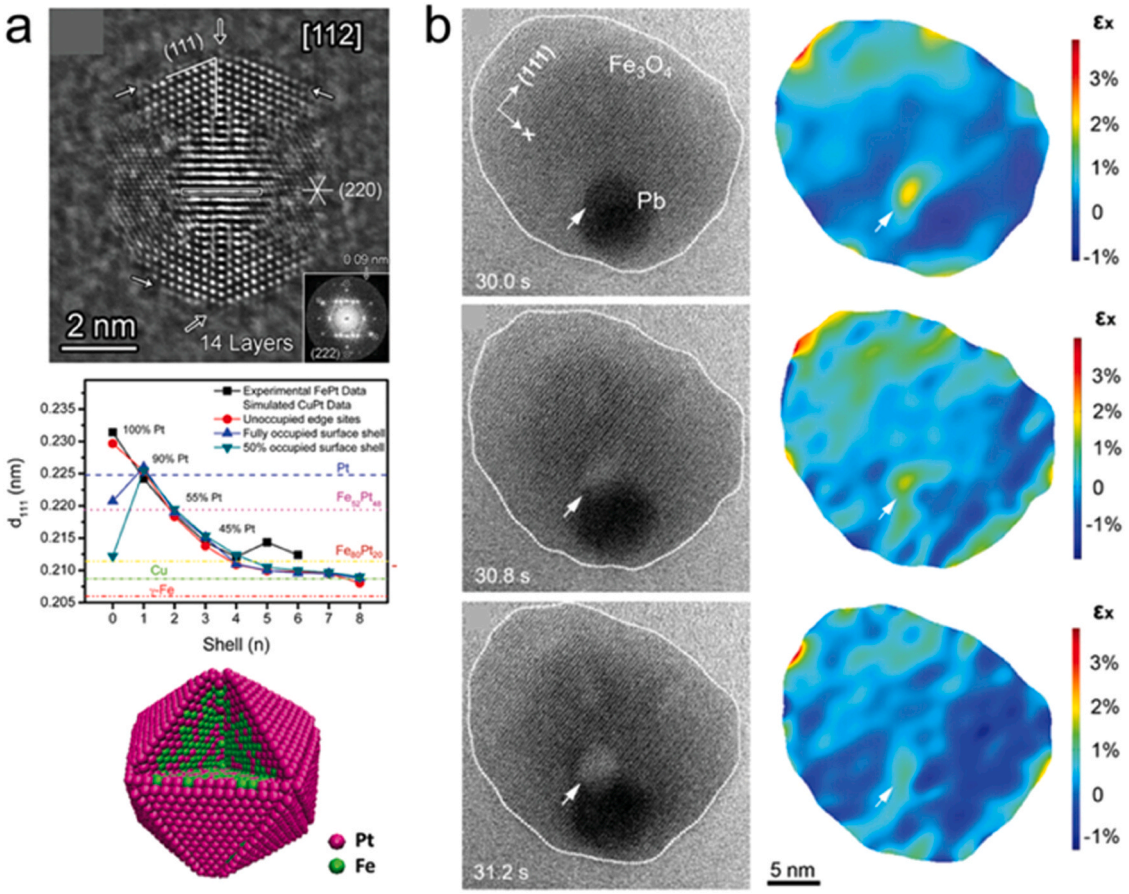

Fig. 6. a) layer relaxation on the surface of magnetic FePt icosahedral nanoparticles, b) In-situ TEM images and strain field calculations based on (111) Bragg reflection of the Fe_3O_4 shell analyse bubble propagation.
(a) Reproduced and adapted with permission from ref. (b) Wang et al., [174] and [118] with permission from American Chemical Society (ACS) and the National Academy of Science, copyright 2009 and 2015 respectively.

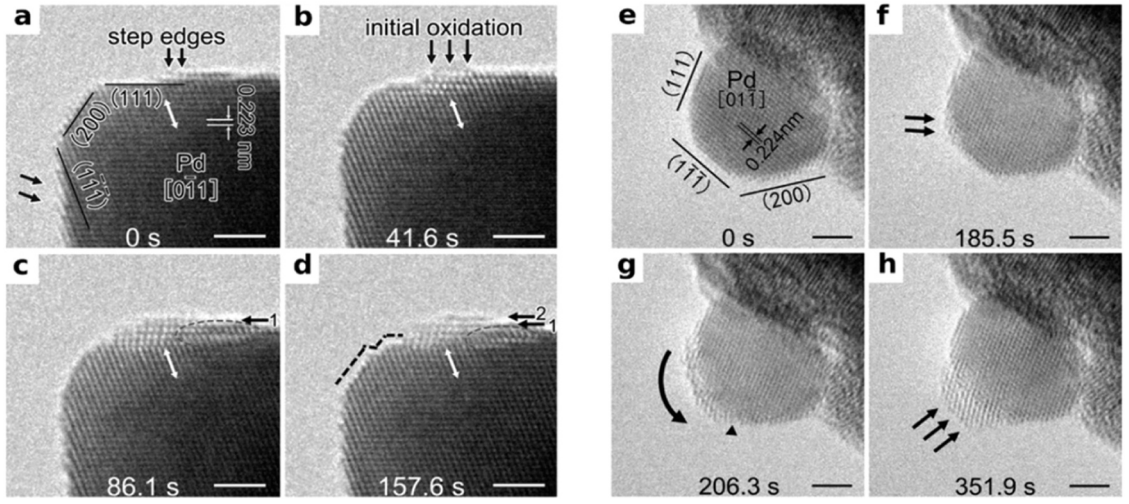

Fig. 7. In-situ, electron transmission microscopy (E-TEM) images illustrate Pd nanoparticles (NPs) shaped as truncated octahedrons in (a)–(d) and as spheres in (e)–(h) during initial oxidation. The proposed oxidation process of the nanoparticles is also depicted. An ex-situ atomic force microscopy (AFM) image is included as an insert. (D.
(a) Images (a)–(h) are reproduced and adapted from ref. (b) [193]), with permission from Royal Society of Chemistry (RSC), copyright 2017.

the defect richness using different spectral regions, including a sharp band at 284 cm^{-1}, a high ratio of 675/686 cm^{-1}, a low intensity of the 1180 cm^{-1} bands (indicating Zn^{2+} with a single linker), a low ratio of the 1135/1144 cm^{-1} band, and a low ratio of the 1458/1498 cm^{-1} band, all indicating defect-poor material. These spectral fingerprints revealed phase barriers in thin twenty-cycle films, while fifty-cycle films were more chemically uniform (Fig. 8d) [178]. AFM can determine the morphology of films both in direct substrate growth and in combined

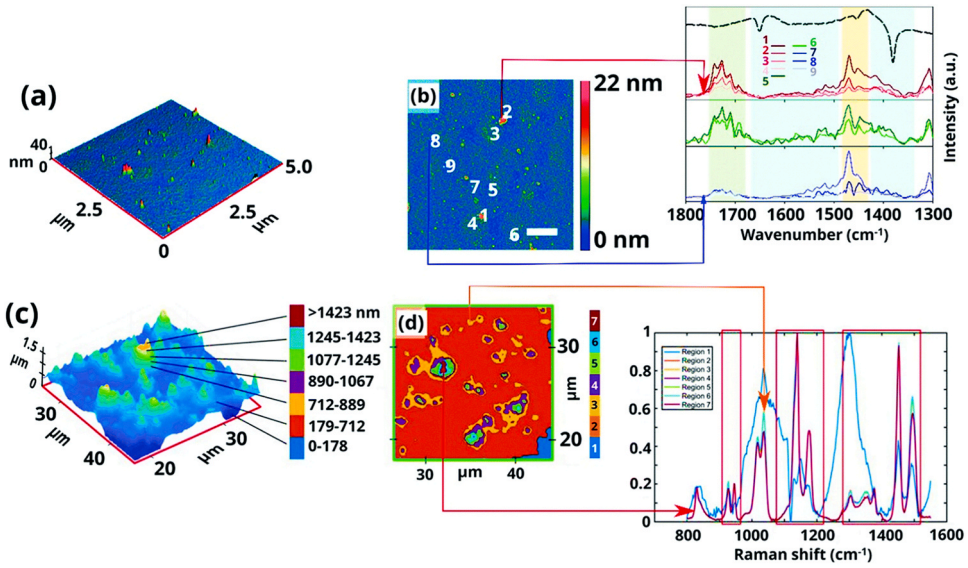

Fig. 8. (a) 3D representation and (b) atomic force microscopy micrograph with corresponding infrared spectra (right), labeled by numbers and sorted by morphological features (red = grain, green = circle/patch, blue = in-between patches). The blue areas show the removal of the self-assembled monolayer (C═O stretch). Scale bar in (b) is 1 μm.
(a) Reproduced and adapted from refs. (b) Mandemaker et al., [105], with permission from American Chemical Society (ACS), copyright 2018.

nucleation and growth processes. For example, Öztürk et al. [124] investigated the effects of factors, including reagent ratios and temperature, on the crystallisation of ZIF-8 and ZIF-67 on Au substrates. The quality of the film, including density and packing, can be carefully curbed by modifying the number of deposition steps. Mandemaker et al. [106] demonstrated that changing the morphology of Cu-BTC nanostructures has a direct impact on their catalytic capabilities. They adjusted the aspect ratio and crystalline phase of these nanowebs through spin-coating, which affected the deposition rate and consequently changed the amount of Cu^{+} and Brønsted sites on the surface. This study underlines the need to use nanoscale instruments in addition to vibrational spectroscopy to characterise the films thoroughly.

(c) 3D representation of an AFM micrograph displaying height segmentation, which is used in (d) to define regions for averaging Raman spectra, providing chemical information through spectroscopic fingerprints linked to topographical features. The Raman colour code corresponds to the colour map of each region on the left. Reproduced and adapted from ref. Weckhuysen et al., [178] with permission from John Wiley & Sons, Inc., copyright 2019.

4.3. Unrevealing catalyst dynamics

Advanced characterisation techniques, particularly time-resolved spectroscopy, have greatly improved our ability to observe these processes in real-time. For example, time-resolved in-situ UV/vis-DR spectroscopy has been used to study the reduction and oxidation kinetics of various catalysts and to gain insight into the transient behaviour of catalytic species [75]. Raman scattering cross sections are generally smaller than IR absorption coefficients, which makes the Raman technique inherently less sensitive. However, this limitation has been greatly improved with the emergence of high-throughput single-stage spectrometers equipped with notch filters and charge-coupled device (CCD) cameras. These advances facilitate time-resolved examination of catalytic reactions and the acquisition of kinetic data due to the improved sensitivity and stability of these spectrometers. In addition, the sensitivity of Raman spectroscopy can be further enhanced by resonance effects, as is the case with high-resolution microscopy and spectroscopy techniques, including resonance Raman spectroscopy, coherent anti-Stokes Raman spectroscopy (CARS), surface-enhanced Raman spectroscopy (SERS) and tip-enhanced Raman spectroscopy (TERS). These innovations have resulted in the development of advanced Raman microscopy techniques that can achieve spatial resolution down to the level of a single molecule. Despite the potential of these improved Raman approaches, their improved sensitivity has been relatively under-explored in the field of catalysis [75]. It is important to note that the terms "scattering" and "spectroscopy" are used interchangeably in CARS, SERS and TERS.

4.3.1. Time-resolved in-situ UV/vis-DR spectroscopy

The temporal dimension is crucial in the study of catalytic reactions for two main reasons. Firstly, data acquisition must occur on the same time scale as the chemical phenomena to capture the essential components of the process. Secondly, the reconstruction of the time sequence of these phenomena is necessary to understand the reaction mechanism accurately. Rivallan et al. [132] presented a method using rapid pressure jumps and microsecond-scale infrared spectroscopy to observe adsorbed CO as a probe molecule to improve the ability to discriminate between spectator species. This approach was employed to examine the accessibility and evolution of Pt nanoparticles on ZSM-5, revealing several sintering processes both in the mesopores and on the outer surface of the zeolite. In addition, time-resolved optical emission spectroscopy (OES) provided insights into the species present in a spark as early as about 100 nanoseconds after discharge. This technique facilitated the identification of the primary stages of material degradation and the calculation of the quenching rate of the generated metal vapour using the emission spectra of the spark [92].

Time-resolved in-situ UV/vis-DR spectroscopy was used to analyse and determine the kinetics of CrO_3 reduction by CO [27]. For heterogeneous catalytic gas-phase reactions using the same solid catalyst, it is possible to perform steady-state, time- and spatial-resolved in-situ UV/vis measurements together with catalytic tests and isotope tracking under identical reaction conditions. The kinetic parameters for the reoxidation of reduced VOx species by O_2 and N_2O and the reduction of oxidised VOx species by C_3H_8 were evaluated by quantitative analysis of the temporal variations of the Kubelka–Munk function at 700 nm. This was performed after switching between oxidising (O_2/Ne = 20/80) and

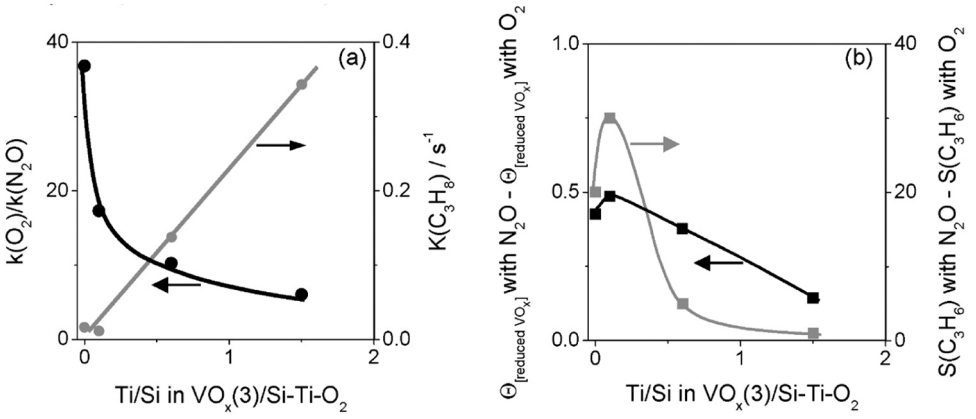

Fig. 9. (a) Kinetic parameters for reduction (by C3H8) and reoxidation (by O_2 and N_2O) of VOx over VOx (3 wt%)/(Ti–Si)O_2 materials. (b) Differences in reduced VOx species coverage and propene selectivity in the ODP reaction with N_2O and O_2 over VOx (3 wt%)/(Ti–Si)O_2 materials. Reaction conditions: T = 500 °C, C_3H_8:O_2: Ne = 40:20:40, C_3H_8:N_2O:Ne = 40:40:20.
(a) Reproduced and adapted from ref. (b) Kondratenko [93] with permission from Elsevier, copyright 2010.

reducing (C3H8/Ne = 40/60) feeds and back to oxidising (O_2/Ne = 20/80 or N_2O/Ne = 40/80) feeds. These conditions as a function of the titanium-silicon ratio in the silicon oxide (VOx/(Ti–Si)O_2) are summarised in Fig. 9a. It was observed that increasing the titanium content in these samples led to an increase in the constant of catalyst reduction by C_3H_8. It is crucial to note that the pure supports without VOx species showed no activity for C_3H_8 oxidation, suggesting that titanium doping in SiO_2 improved the reduction rate of VOx species by C_3H_8. The study confirmed a Mars–van Krevelen redox cycle with lattice O_2 and reduced V^{3+} or V^{4+} centres, as TOF values of C_3H_8 transformation increased similarly in steady-state oxidative dehydrogenation of propane (ODP) catalyst tests with carbon dioxide and nitrogen dioxide. In addition, titanium affected the ratio between the reoxidation constant of the reduced VOx species by oxygen and the reoxidation constant by nitrogen dioxide. This ratio declined with increasing titanium content (Fig. 9b, indicating that the difference in oxidising ability between oxygen and nitrogen dioxide for the reoxidation of reduced VOx species decreases with a higher titanium dioxide (Ti) content in the system [123].

4.3.2. Ultraviolet resonance Raman (UVRR) spectroscopy

Fluorescence is known to interfere with Raman spectroscopy of zeolites or similar framework structures, and this issue can also arise in hydrocarbon environments [100,32]. The use of UV excitation significantly reduces fluorescence and increases Raman sensitivity. UV radiation also improves the Raman signal, which is attributed to increased scattering. Beato et al. [26] showed the utility of UV Raman spectroscopy for the study of zeolites in the conversion of methanol-to-hydrocarbons (MTH). Fig. 10 shows the operando UV Raman spectra of ZSM-5 (ZSM-22) during MTH at 350 °C (450 °C) obtained with an excitation of 244 nm. A fluidised bed technique was used to hinder any UV laser-induced reactions. The decomposition of methanol was observed without particle motion at the same laser power, which led to the formation of a broad band around 1560 cm^{-1} attributed to carbon species from the laser-induced polycondensation and dehydration of methanol. Methanol pulses led to the appearance of hydrocarbon-related Raman bands, first at 1602 cm^{-1} and then mainly at 1376 cm^{-1}, while the intensity of the ZSM-5 scaffold vibrations was significantly reduced (Fig. 10). This focuses on ZSM-5 pretreated in air at 550 °C to eliminate all pre-adsorbed molecules. This behaviour indicates that the hydrocarbon molecules have started to accumulate in the zeolite pores. In particular, the bands at 1602 cm^{-1} and 1360 cm−1 corresponded to olefins and aromatic compounds, respectively. The study also showed that these species are not strongly bound to the zeolite surface, as shown by the flow of He at reaction temperature. Similar behaviour was observed for ZSM-22, with differences due to its 1D structure [26].

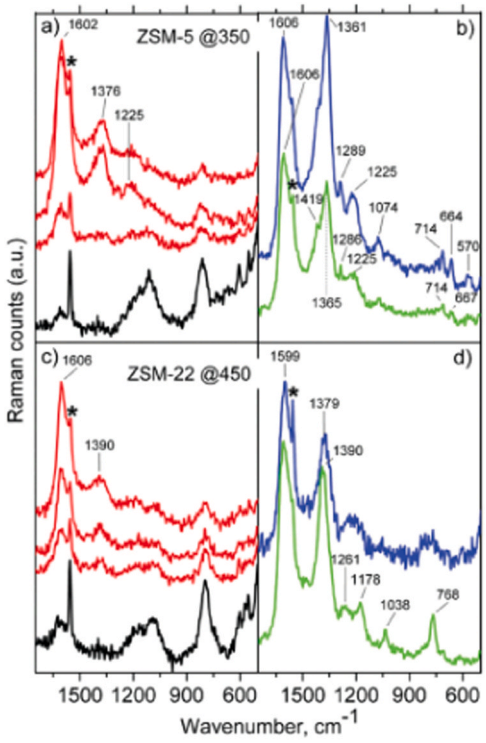

Fig. 10. Operando 244 nm Raman spectra of ZSM-5 and ZSM-22 during MeOH conversion to hydrocarbons (MTH) at 350 °C and 450 °C, respectively. Shown after (a and c) activation in air at 550 °C (black) and three MeOH pulses (red), and after (b and d) a long MeOH pulse (blue) and flushing with He (green).
(a) Reproduced and adapted from ref. (b) Beato et al., [26] with permission from Elsevier, Copyright 2013.

5. Computational frontiers in catalysis

The rapid development of computer technology has revolutionized the study of solid materials, introducing new methodologies and directions. As computational methodologies continue to advance, the field

of catalysis stands to benefit significantly from these innovative tools and techniques [42]. Over the past few decades, computational chemistry has greatly impacted design strategies for developing active, selective, and stable catalysts, earning its place alongside traditional laboratory techniques such as infrared spectroscopy (IR), nuclear magnetic resonance (NMR), and X-ray diffraction (XRD) [137,167]. Computational methods have proven to be invaluable for investigating catalytic processes, particularly in the valorization of biomass [116]. By integrating computational approaches such as density functional theory, micro-kinetic modeling, high-throughput data analysis, and machine learning with experimental characterization and theoretical foundations, researchers can effectively explore catalytic principles and guide catalyst design through mechanistic insights [147]. For instance, Dolz et al., (52) employed a multi-faceted computational approach to study the heterogeneous catalysis of the reverse water gas shift reaction, emphasizing the importance of thermodynamics, kinetics, and surface dynamics in understanding catalytic performance. Similarly, Siahrostami and Murray [143] demonstrated that computational material design has been crucial in driving materials discovery for catalysis, especially in sustainable energy applications.

The unparalleled capability of computational methods to explore atomic-level details of catalytic systems holds immense promise for the bottom-up design of novel heterogeneous catalysts, which are vital to the chemical and energy industries [116,42]. Advanced data storage and processing techniques facilitate the simultaneous analysis of extensive catalytic information, enabling the creation of predictive models that capture the multidimensional aspects of catalyst design in a machine-readable format [139]. By simulating the behaviour of catalysts at the molecular level, computational modeling can elucidate reaction pathways, identify active sites, and optimise catalyst structures for enhanced activity and selectivity [67,66]. In addition to its predictive role in catalyst design, computational methods significantly reduce time and cost, inspire experimental efforts, and generate testable hypotheses [55]. Unlike traditional experimental approaches, which involve synthesising and testing candidate catalysts, computational simulations only require electricity and computers, making them more economical and sustainable [108]. By elucidating reaction mechanisms, predicting catalyst properties, and navigating the vast chemical space, computational simulations offer a strategic pathway towards optimising catalytic activity and advancing the frontier of catalyst research. The success of computational modeling in catalysis relies on its predictive accuracy, the development of key parameter-based screening, and close collaboration with experimentalists to enhance the understanding of active sites and reaction conditions [148].

5.1. *Unleashing the power of Density Functional Theory (DFT) in catalytic study*

Density Functional Theory (DFT) has become a cornerstone in catalysis research, offering predictive insights into the atomic-level behaviour of catalysts. Renowned for its balance between accuracy and computational cost, DFT is the preferred method for computational studies [148]. Its ability to explore complex chemical environments under realistic conditions enhances its value in studying catalysts [167]. DFT is extensively used for analysing homogeneous reactions, heterogeneous catalysis, and electrochemical reactions [98]. By providing a theoretical framework to understand the electronic structure and reactivity of materials, DFT has transformed catalyst design and optimization [120]. It allows researchers to examine the interactions between catalytic species and surfaces, including adsorption and desorption processes and the impact of surface defects. Whether dealing with oxide catalysts, zeolite catalysts, or the various stages of a chemical reaction, DFT offers valuable information that informs the entire catalytic process, from adsorption to reaction dynamics, aging, and poisoning [71]. DFT's core strength lies in solving quantum mechanical equations to predict electron-nucleus interactions within materials, leading to precise forecasts of catalytic activity and selectivity. This capability enables better management of existing reactions, deeper insights into specific elements of the catalytic process, and the development of practical methods for rational catalyst design [9].

Using DFT calculations, Deng et al. [47] demonstrated that silver particles (Ag^{+}, $Ag^{2\delta+}$, $Ag^{3\delta+}$, and $Ag^{4\delta+}$) on the γ-Al_2O_3 surface align with experimental data, highlighting their role as catalytic centers. This indicates that both individual silver atoms and small neutral or positively charged silver clusters on γ-Al_2O_3 are essential for selective catalytic reduction (SCR) [47]. Additionally, DFT is particularly adept at identifying trends across different catalysts. Recent studies have shown that DFT can predict reaction barrier differences between catalysts with an error margin of only ±5 kJ/mol, despite intrinsic errors of 50 kJ/mol in individual reaction steps [128]. Xu et al. [183] used DFT calculations to explore the catalytic mechanisms of $RuCl_3$, $AuCl_3$, and $BaCl_2$ for the 1, 2-dichloroethane (DCE)-acetylene exchange reaction. They found that the initial formation of the acetylene-DCE complex with low adsorption energy and its subsequent reaction to vinyl chloride monomer (VCM) could be the rate-determining step. Their prediction that $BaCl_2$ would outperform $RuCl_3$ and $AuCl_3$ in catalytic activity was confirmed experimentally. This study identified critical steps such as adsorption and chloride transfer, providing valuable insights for designing catalysts to improve VCM production efficiency. Elsewhere, Shen and Xiao [141] employed DFT calculations to investigate an inverse CeOx/Ag (111) catalyst for the electrochemical reduction of CO_2. They found that Ag atoms donate electrons to partially reduce Ce^{4+} to Ce^{3+} in CeOx clusters, forming active Ce^{3+} sites at the interface. These sites enhance CO_2 adsorption and reduction, demonstrating how metal oxides on metal electrodes create favourable conditions for CO_2 activation and subsequent reduction processes, leveraging their conductivity and electron-rich environments [141]. These studies underscore the power of DFT in providing detailed mechanistic insights and guiding the design of more efficient catalysts through the understanding of atomic and electronic interactions.

In addition to its predictive capabilities, the DFT calculation method aids in the discovery of new, high-performance catalysts by enabling researchers to investigate surface structures, reaction mechanisms, and design catalysts for environmental applications [104]. For instance, Tosoni et al. [163] utilized DFT to study the electronic structure of metals and metal oxides, providing insights into the properties of new catalysts and supporting simulations of catalysis and adsorption in biomass thermal conversion. DFT revealed that carboxyl, hydroxyl, pyridine, and pyrrole groups in *Enteromorpha*-based char (EPC) enhance guaiacol adsorption and conversion to phenol by lowering reaction energy barriers, thus offering molecular insights for designing efficient biochar catalysts [184]. Furthermore, DFT calculations can analyse the intrinsic mechanisms and specific pathways of persulfate-based advanced oxidation processes (P-AOPs) at a microscopic level, which is challenging to achieve experimentally [83]. Recent advancements in DFT, as investigated by Singha and Ray [146], have enabled the design of innovative photocatalysts by analysing the electronic properties and mechanisms, with a focus on TiO_2 and ZnO as base materials. Their results highlighted the impact of adding CuO, an active material for CO_2 photoreduction, to these bases, revealing modifications in band structures and electronic states. The separation efficiency (D) values indicated decreased recombination rates: 8.11 (CuO/TiO_2) > 7.22 (CuO/ZnO) > 6.103 (TiO2) > 3.302 (ZnO). This demonstrates how DFT can guide the development of effective photocatalysts by providing detailed insights into their electronic properties and mechanisms [146].

At the same time, DFT verifies the correctness of experimental results and gives full play to its practical value, which is of great significance for the synthesis and improvement of catalysts [71]. Montejo-Valencia et al. [113] employed DFT calculations with long-range corrections and ONIOM to investigate the mechanism of converting CO_2 and CH_4 to acetic acid using MFI zeolite with various metal cations (Be, Co, Cu, Mg, Mn, Zn). Their study revealed that CH_4 dissociation presents the highest

reaction barrier, influenced by the lowest unoccupied molecular orbital (LUMO) energy and the electronegativity of the metal cations. They also found significant charge transfer and low energy barriers for CO_2 insertion and acetic acid desorption, which were facilitated by water coadsorption, especially in Cu-MFI. These findings underscore the importance of DFT in understanding and optimizing catalytic processes. Also, DFT calculations provide unparalleled opportunities for exploring electrocatalytic mechanisms and identifying potential catalysts by examining the configuration-properties relationship at the atomic level. These calculations provide detailed insights into the electronic structures of nanomaterials and interface characterization, enhancing the understanding of electroanalysis mechanisms. The current mainstream DFT tools used in catalysis include VASP, CP2K, Gaussian, and CASTEP [71]. Despite the significant advancements enabled by DFT, challenges remain, particularly in accurately modeling complex systems and accounting for dispersion forces. Additionally, selecting an appropriate exchange-correlation function, which accounts for electron-electron interactions, is a major challenge in DFT [139].

5.2. Molecular dynamic simulations: a computational window into catalysis

Molecular dynamics (MD) simulations, known for their ability to calculate the motion and equilibrium of molecules or atoms, have gained global recognition for providing insights into the behavioural properties of substances in gas, liquid, and solid states at molecular or atomic scales [144]. These simulations offer atomic-level data on the locations and velocities of reactants, solvents, and catalysts, enabling predictive modeling, feature extraction, and experimental design. They also provide valuable insights into thermodynamic and kinetic characteristics by solving Newtonian dynamic equations numerically [10]. MD simulations open a computational window into the dynamic interactions between reactants, catalysts, and their environments, offering insights that are often challenging to obtain experimentally [77]. By modeling the motion of individual atoms and molecules over time, MD simulations can reveal the formation and breaking of chemical bonds, the rearrangement of molecular structures, and the influence of environmental factors on the catalytic process [5]. This information is crucial for understanding the driving forces behind reactions, differentiating between proposed mechanistic models, and guiding the design of more effective catalysts [79]. Recent advancements in computational power and sophisticated force fields have enabled the dynamic simulation of increasingly complex catalytic systems, including those involving heterogeneous catalysts, enzyme-catalysed reactions, and multistep reaction networks [42].

In MD simulations, interaction energies based on potential function forms, force field conditions, and thermodynamic ensembles, with common ensembles including microcanonical NVE - Number of particles (N), Volume (V), and Energy (E) and canonical NVT - Number of particles (N), Volume (V), and Temperature (T) [154]. One of the merits of molecular dynamics simulations is their capability to surmount energy barriers and predict the time-base behaviour of molecular systems, providing valuable insights that complement and inform the design of new experiments [197]. They also allow investigation of the underlying mechanisms of catalytic supercritical water gasification (SCWG) of biomass at an atomic level [189]. MD simulations can be categorised based on their focus and techniques, including Classical Molecular Dynamics (CMD), Ab Initio Molecular Dynamics (AIMD), Reaction Molecular Dynamics (ReaxFF), and Machine Learning Molecular Dynamics (MLMD) [172]. AIMD and ReaxFF are particularly prevalent in mechanistic studies of various catalytic interactions. The ReaxFF simulations can model the cleavage and formation of chemical bonds to identify elementary pathways [189], while AIMD follows the dynamics of nuclei over time by integrating Newtonian equations of motion with potential energy derived from first principles, solving the quantum-mechanical many-body problem for electrons [165].

For instance, MD simulations using the ReaxFF method have shown that microwave-assisted catalytic pyrolysis of waste plastics with Fe catalysts significantly enhances hydrogen generation. These simulations revealed that microwaves improve Fe cluster adsorption capacity, lower the dissociation energy of C-H bonds, and promote C-C bond cleavage at lower temperatures, resulting in increased H_2 production, reduced reaction temperatures, and decreased formation of small gaseous hydrocarbons and tar [186]. Kumar and Sahu [96] studied aluminium catalysts' efficiency in water splitting at temperatures above 327 °C. Their simulations showed that hydrogen yield decreases with increasing diameter of aluminium nanotubes and that the nanotubes' inner surfaces experience severe erosion during the process, offering insights into optimizing aluminium catalysts for large-scale hydrogen production from water and other solvents. In another study, Jin et al. [82] synthesized a novel Cu@4 A zeolite nano-catalyst that significantly improved the catalytic pyrolysis performance of oil shale. MD simulations revealed the catalyst's impact on hydrocarbon configurations within nanopores, showing a 68.3 % decline in the first density peak of C_3H_6 at 300 °C and provided insights into the catalytic mechanism, highlighting the role of acidic sites in decomposing kerogen and facilitating subsequent reactions. As shown in Table 7, The work of Castro-Marcano and van Duin [36] demonstrated that ReaxFF reactive molecular dynamic simulation could be a useful approach for examining the complex chemistry associated with hydrocarbon cracking. Some previous research on the applications and insights from MD simulations in catalysis are summarized in Table 7.

One limitation of MD simulations is that the trajectory length achievable within a reasonable timeframe is significantly shorter by several orders of magnitude than the timescales of most chemical and physical processes, which typically occur in nanoseconds or longer [197]. Additionally, MD simulations demand precise force field parameters, substantial computational resources, and apt modeling assumptions to yield accurate and meaningful results [25].

6. Identifying and navigating challenges and anticipating future perspectives

Advanced characterisation techniques (ACT) for catalysis comprise high-resolution imaging, spectroscopy, and computational modelling to understand the structure, composition, and behaviour of catalysts at atomic sizes [63]. These techniques face challenges such as high sensitivity to detect minute changes (Yao et al., 2014), the complexity of interpreting large datasets [60] and integrating experimental and theoretical approaches [155]. Addressing these challenges requires multidisciplinary collaboration and the development of novel methodologies. Future perspectives include leveraging machine learning to analyse data, anticipate catalytic performance, and develop enhanced efficiency and selectivity catalysts. Moreover, Kalz et al. [86] highlighted the importance of in-situ and operando characterization techniques in understanding catalytic processes under realistic reaction conditions.

6.1. Identifying obstacles in advanced characterisation

ACT for catalysis, such as high-resolution transmission electron microscopy (HRTEM), X-ray photoelectron spectroscopy (XPS), and in-situ/operando methods, are crucial for understanding catalytic processes at atomic and molecular sizes. However, these techniques face several significant obstacles. One of the primary challenges is achieving the necessary spatial and temporal resolution to observe catalytic interactions. Catalytic reactions often occur at the diminutive scale and over very short timeframes, requiring instruments capable of resolving such minute details. For example, while HRTEM can provide imperceptible resolution, it often struggles with the dynamic nature of catalytic processes, which necessitate rapid data acquisition and real-time analysis [97].

Table 7
Applications and insights from molecular dynamics simulations in catalysis.

Application Area	Catalytic System	Simulation Details	Key Findings	Benefits	Challenges	Ref.
Hydrogen production via thermochemical water splitting	Aluminium nanotubes	Simulation type: ReaxFF molecular dynamics simulation	Aluminum catalyst makes it possible to split water at temperatures higher than $T > 327$ °C	Reaction mechanism between aluminum nanotubes and water at various temperatures was established	High temperatures required for efficient H_2 production	Kumar, Sahu [96]
Hydrocarbon configurations	Cu@4 A zeolite nano-catalyst	Simulation type: Molecular Dynamics, energy minimization, NPT, NVT	The first density peak of C_3H_6 declined by 68.3 % after catalyzed by Cu@4 A at a temperature of 300 °C. The interaction energy of hydrocarbon would decrease when the system temperature increases.	the catalytic mechanism was elucidated,	high heating temperature and low oil recovery	Jin et al., [82]
Hydrocarbon Cracking	Amorphous silica, hydrated amorphous silica, and amorphous aluminosilicate nanoparticles	Temperature: 1477–1677 °C, Pressure: 4–7 MPa Simulation type: ReaxFF force field	Hydrocarbon cracking produces hydrogen and a range of hydrocarbons; CAC bond scission followed by radical reaction is key	Insight into complex reaction networks and mechanisms	High computational demand at high temperatures and pressures	Castro-Marcano, van Duin [36]
Catalytic Oxidation	Pd-based nanoparticles (with/ without oxygen coating)	Temperature: 127–727 °C, Simulation type: ReaxFF Molecular Dynamics	CH_4 dissociation is easier on oxygen-coated Pd at low temperatures	Insights into reaction mechanisms; temperature and oxygen coverage impact on CH_4 dissociation rates	High computational cost, requires accurate force fields	Mao et al., [107]
Hydrogen Production	Mg nanoparticles	Temperature: >1727 °C, Simulation type: ReaxFF molecular dynamics simulation	Water splits at room temperature forming Mg–H bonds; H_2 generation starts at T > 927 °C	Insight into slow-kinetics of Mg-water reaction for Hydrogen production	High temperatures required for efficient H_2 production	Kumar et al., [95]
Electrocatalysis	Pt(111) and Fe–N–C catalysts	Simulation type: AIMD simulations, simulated annealing	Enthalpy of solvation for adsorbed intermediates determined	Improved energetics and structure–activity–stability predictions	Complex electrochemical interface modeling	Chun et al., [43]
Electric Field Catalysis	Liquids under strong electric fields	Simulation type: Ab Initio Molecular Dynamics	Modification of activation barriers and reaction pathways	Enhanced understanding of field-induced catalysis	High computational cost for accurate simulations	Cassone et al., [35]

Another major hindrance is the complexity of sample environments required for in-situ and operando processes. These techniques intend to monitor catalysts under realistic reaction conditions, including high pressures, temperatures, and reactive gas environments [84]. Maintaining the balance and accuracy of the instruments under these conditions is technically demanding. Operando XPS requires sophisticated setups to ensure that the sample environment imitates industrial catalytic conditions without compromising the integrity of the measurements (Zaera, 2021). The correlating of the observed catalytic properties with their performance can be challenging. This issue is compounded by the fact that catalysts often undergo dynamic changes during reactions, making it stressful to determine clear relationships [162]. The non-uniform and complex structure of the catalyst adds another layer of difficulty. Catalysts are often composed of multiple components with varying structures and phases, and their Characterization requires techniques that differentiate between different components and interactions. This is particularly challenging for complex nanostructured catalysts, where different regions may exhibit distinct properties (Zaera, 2012).

Furthermore, the lack of standardization in characterization protocols and data reporting can hinder the comparison and reproducibility of results across different studies. Variations in experimental conditions, sample preparation, and instrument calibration can lead to inconsistencies in results [29]. Ensuring reproducibility involves standardizing methodologies and developing robust protocols for sample handling and data acquisition (Wachs, 2013). Lastly, interpreting characterization data poses another significant challenge. ACT often generates large amounts of complex data, requiring sophisticated analysis methods for extraction. Datye & Votsmeier [46] stressed the importance of data interpretation, stating that the challenge is to extract the relevant information from the vast amount of data generated and relate it to the catalytic performance.

Identifying and navigating the challenges in advanced characterization is essential for the progress of catalysis research. Researchers face these primary obstacles, which require an advanced and systematic approach. By overcoming these hurdles, they can gain a deeper understanding of catalytic processes, ultimately leading to the design of more efficient and sustainable catalytic systems.

6.2. *Addressing challenges in advanced characterization*

A multifaceted approach is necessary to address the challenges in ACT for catalysis, involving several aspects of the approach. Firstly, developing novel instrumentation and methodologies is crucial and unique in its ability to improve spatial and temporal resolution. This advancement enables observing catalytic processes at the atomic scale and in real-time, a previously unattainable feat. Notably, advances in electron microscopies, such as aberration-corrected TEM (AC-TEM) and environmental TEM (ETEM), have already shown promise in providing unprecedented insights into catalytic systems [6,64]. Secondly, the design of innovative sample environments that can effectively replicate realistic reaction conditions while preserving the integrity of the measurements [198]. Standardization of characterization protocols and data reporting is also vital to this process, ensuring reproducibility and facilitating comparisons across different studies [31]. Thirdly, integrating experimental characterization with computational modelling. This approach is critical to deciphering the complexity of catalytic systems and establishing structure-performance relationships. Computational methods, such as density functional theory (DFT) and molecular dynamics simulations (MDS), can offer valuable insights into atomic relationships and aid in the interpretation of experimental data [31]. Moreover, machine learning techniques can be utilized to analyse large datasets and identify patterns that may not be discernible through convectional analysis methods [70].

Finally, the significance of fostering multidisciplinary collaboration cannot be overstated in tackling the challenges in advanced

characterization. Catalysis research benefits from the expertise of scientists from various fields. Collaborative efforts can lead to the development of innovative solutions and accelerate progress. With continued advancements in these solutions, researchers can effectively overcome the obstacles. These efforts will lead to a deeper understanding of advanced characterization, ultimately enabling more efficient and sustainable catalytic systems design.

6.3. Identifying promising avenues for further research and innovation

Exploring promising avenues for further research and innovation of ACT of catalysts is crucial for developing more efficient catalytic processes. Catalysts are vital in various industrial applications, including chemical synthesis (Xiong et al., 2017), energy production [73], and environmental remediation [57]. A deep understanding of catalyst structural, chemical, and electronic properties is essential to optimizing performance and designing novel catalytic materials.

One of the most thrilling avenues for further research is applying in-situ and operando characterization techniques. These methods can transform our understanding of catalysts by enabling real-time monitoring under realistic reaction conditions. This offers invaluable insights into the dynamic changes that occur during catalytic processes. For instance, in-situ, X-ray absorption spectroscopy (XAS) has been used to study the oxidation state and local coordination environment of metal nanoparticle catalysts during CO oxidation reactions [62]. Similarly, in-situ TEM has allowed the direct observation of catalyst nanoparticle sintering and restructuring under various gas environments [74]. Further research could focus on developing advanced in-situ and operando techniques with improved spatial and temporal resolution and integrating multiple complementary approaches to gain a more comprehensive understanding of catalyst performance and function. Moreover, another promising avenue for research is the application of advanced spectroscopic and microscopic techniques for characterizing catalyst surfaces and interfaces. The surface properties of catalysts, such as composition, morphology, and electronic structure, are pivotal in determining their catalytic performance (Wen et al., 2022). Techniques such as scanning tunnelling microscopy (STM), atomic force microscopy (AFM), and X-ray photoelectron spectroscopy (XPS) have been widely used to study catalyst surfaces at the atomic and molecular levels. Future research could focus on developing advanced surface-sensitive techniques with improved resolution and sensitivity and applying these methods to more complex and realistic catalyst systems, underscoring the importance of your work in this field.

In addition to experimental characterization techniques, the role of computational methods in catalyst research cannot be ignored. The DFT calculations and MDS have emerged as powerful tools for investigating the electronic structure, reaction mechanisms, and kinetics of catalytic processes at the atomic and molecular levels [119,33]. Further research could focus on developing more accurate and efficient computational methods and integrating computational and experimental techniques to gain a more comprehensive understanding of catalyst behaviour. Identifying promising avenues for further research and innovation of ACT is essential for developing more efficient and sustainable catalytic processes. By combining these techniques and approaches, researchers can gain a deeper understanding of the complex dynamics and mechanisms of catalysts under realistic reaction conditions, leading to the design of novel catalytic materials with improved performance and sustainability.

7. Conclusion

In summary, the journey through the advanced techniques used to characterise catalysts has highlighted the transformative impact of these innovations on our understanding of catalytic processes. From early empirical observations to the sophisticated, multidisciplinary approaches of today, catalyst characterisation has evolved to provide detailed insights into the structure, composition and behaviour of catalysts. These advances have not only deepened our fundamental understanding of catalysis but have also led to significant advances in the development and application of catalysts, resulting in more efficient, selective and sustainable catalytic processes. As the field of catalysis continues to evolve, the ongoing development and integration of advanced characterisation techniques will be critical to meeting future challenges and driving further innovation. The integration of advanced microscopy, spectroscopy, computational modelling and in-situ techniques represents the pinnacle of catalyst characterisation and provides comprehensive tools to tackle complex catalytic challenges. The ability to study catalytic systems at an unprecedented level of detail, coupled with the power of computational modelling and data-driven approaches, promises to open up new possibilities and take the field to new frontiers. In addition, the integration of machine learning and artificial intelligence (AI) into catalyst characterisation is an exciting new development. Machine learning algorithms can analyse large data sets generated by advanced characterisation techniques, identifying patterns and correlations that may not be immediately apparent to human researchers. This approach can accelerate the discovery and optimisation of new catalysts by providing data-driven insights and guiding experimental efforts.

CRediT authorship contribution statement

Yusuf Makarfi Isa: Writing – review & editing, Resources. **Sherif Ishola Mustapha:** Writing – original draft, Investigation, Formal analysis, Data curation. **Darlington Ashiegbu:** Writing – original draft, Investigation, Formal analysis, Data curation. **Emeka Michael Enemuo:** Writing – original draft, Investigation, Formal analysis, Data curation. **Stephen Okiemute Akpasi:** Writing – original draft, Investigation, Formal analysis, Data curation. **Ifeanyi Michael Smarte Anekwe:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

[1] 2021, How Calc. Cryst. Size X-Ray Diffr. (XRD) Using Scherrer Method10.17509/ijost.v6ix.
[2] A. Blat, T. Stepanenko, K. Bulat, A. Wajda, J. Dybas, T. Mohaissen, F.C. Alcicek, E. Szczesny-Malysiak, K. Malek, A. Fedorowicz, Spectroscopic signature of red blood cells in a D-galactose-induced accelerated aging model, Int. J. Mol. Sci. 22 (5) (2021) 2660.2021, , 2660..
[3] M. Aceto, E. Calà, F. Gulino, F. Gullo, M. Labate, A. Agostino, M. Picollo, The Use of UV-Visible Diffuse Reflectance Spectrophotometry for a Fast, Preliminary Authentication of Gemstones, Molecules 27 (15) (2022), https://doi.org/10.3390/molecules27154716.
[4] K. Adarsh, N. Chandrasekaran, V. Chakrapani, In-situ spectroscopic techniques as critical evaluation tools for electrochemical carbon dioxide reduction: a mini review, Front. Chem. *8* (2020) 137.
[5] S.A. Adcock, J.A. McCammon, Molecular Dynamics: Survey of Methods for Simulating the Activity of Proteins, Chem. Rev. *106* (5) (2006) 1589–1615, https://doi.org/10.1021/cr040426m.
[6] Advanced electron microscopy techniques toward the understanding of metal nanoparticles and clusters. Metal Nanoparticles and Clusters: Advances in Synth., Prop. Appl. , 2017, , 219–287, 10.1007/978-3-319-68053-8_7/FIGURES/49..
[7] B. Akbari, M.P. Tavandashti, M. Zandrahimi, Particle size characterization of nanoparticles–a practical approach, Iran. J. Mater. Sci. Eng. *8* (2) (2011) 48–56.
[8] A. Ali, Y.W. Chiang, R.M. Santos, X-Ray Diffraction Techniques for Mineral Characterization: A Review for Engineers of the Fundamentals, Applications, and Research Directions, Minerals 12 (2) (2022), https://doi.org/10.3390/min12020205.
[9] O. Alioui, M. Badawi, A. Erto, M.A. Amin, V. Tirth, B.-H. Jeon, S. Islam, M. Balsamo, M. Virginie, B. Ernst, Y. Benguerba, Contribution of DFT to the optimization of Ni-based catalysts for dry reforming of methane: a review, Catal. Rev. *65* (4) (2023) 1468–1520, https://doi.org/10.1080/01614940.2021.2020518.

[10] Alrhia, L. (2022). *Molecular Dynamics and Catalysis* (2476-2296). (Journal of Fluid Mechanics, Issue.

[11] J.M. Andanson, A. Baiker, Exploring catalytic solid/liquid interfaces by in situ attenuated total reflection infrared spectroscopy, Chem. Soc. Rev. 39 (12) (2010) 4571–4584, https://doi.org/10.1039/b919544k.

[12] I.M.S. Anekwe, Y.M. Isa, Catalytic conversion of low alcohol to hydrocarbons: challenges, prospects, and future work considerations, Int. J. Energy Res. *2023* (2023) 1648449, https://doi.org/10.1155/2023/1648449.

[13] Anekwe, I.M.S., Isa, Y.M., & Oboirien, B. (2023). Bioethanol as a Potential Eco-friendlier Feedstock for Catalytic Production of Fuels and Petrochemicals. *Journal of Chemical Technology & Biotechnology*.

[14] I.M.S. Anekwe, N. Nyembe, L.C. Nqakala, M. Madikizela, Y.M. Isa, Sustainable fuels: Lower alcohols perspective, Environ. Prog. Sustain. Energy (2023) e14175.

[15] M. Arian, H. Mollabagher, S. Taheri, A. Zamanian, S.A.H.S. Mousavi, Preparation and characterization of nano MnO-CaLs as a green catalyst for oxidation of styrene, Turk. J. Chem. 45 (6) (2021) 1882–1894, https://doi.org/10.3906/kim-2101-26.

[16] D.C. Ashiegbu, N. Moloto, H. Potgieter, Improved photocatalytic activity of ZnO-[10%]BiOI and ZnO-[10%]WO3 heterostructure in the destruction of 2-chlorobiphenyl, Environ. Sci.: Adv. 2 (2) (2022) 325–338, https://doi.org/10.1039/d2va00222a.

[17] D.C. Ashiegbu, H.J. Potgieter, ZnO-based heterojunction catalysts for the photocatalytic degradation of methyl orange dye, Heliyon 9 (10) (2023), https://doi.org/10.1016/j.heliyon.2023.e20674.

[18] W.N.A.W. Azahar, R. Johari, H.M.R.A. Rahman, M.M. Rahim, S. Shahar, X-Ray Diffraction Analysis of Bitumen Containing Untreated and Treated Waste Cooking Oil, Int. J. Recent Technol. Eng., 8(3S3), 435-438 (2019), https://doi.org/10.35940/ijrte.c1020.1183s319.

[19] D.R. Baer, M.H. Engelhard, G.E. Johnson, J. Laskin, J. Lai, K. Mueller, P. Munusamy, S. Thevuthasan, H. Wang, N. Washton, Surface characterization of nanomaterials and nanoparticles: Important needs and challenging opportunities, J. Vac. Sci. Technol. A *31* (5) (2013).

[20] M.A. Bañares, In situ to operando spectroscopy: From proof of concept to industrial application, Top. Catal. *52* (2009) 1301–1302.

[21] Bañares, M.A. (2011a). Operando spectroscopy: the knowledge bridge to assessing structure–performance relationships in catalyst nanoparticles. In: Wiley Online Library.

[22] Bañares, M.A. (2011b). Operando spectroscopy: the knowledge bridge to assessing structure–performance relationships in catalyst nanoparticles. In: Wiley Online Library.

[23] M.A. Bañares, M. Daturi, Understanding catalysts by time-/space-resolved operando methodologies, Catal. Today *423* (2023) 114255, https://doi.org/10.1016/j.cattod.2023.114255.

[24] D.J. Banner, E. Firlar, P. Rehak, A.H. Phakatkar, T. Foroozan, J.K. Osborn, L. V. Sorokina, S. Narayanan, T. Tahseen, Y. Baggia, In Situ Liquid-Cell TEM Observation of Multiphase Classical and Nonclassical Nucleation of Calcium Oxalate, Adv. Funct. Mater. *31* (18) (2021) 2007736.

[25] S. Barbhuiya, B.B. Das, Molecular dynamics simulation in concrete research: a systematic review of techniques, models and future directions, J. Build. Eng. *76* (2023) 107267, https://doi.org/10.1016/j.jobe.2023.107267.

[26] P. Beato, E. Schachtl, K. Barbera, F. Bonino, S. Bordiga, Operando Raman spectroscopy applying novel fluidized bed micro-reactor technology, Catal. Today *205* (2013) 128–133, https://doi.org/10.1016/j.cattod.2012.09.030.

[27] A. Bensalem, B.M. Weckhuysen, R.A. Schoonheydt, In situ diffuse reflectance spectroscopy of supported chromium oxide catalysts: kinetics of the reduction process with carbon monoxide [Article], J. Phys. Chem. B *101* (15) (1997) 2824–2829, https://doi.org/10.1021/jp962488p.

[28] A. Bergmann, B. Roldan Cuenya, Operando insights into nanoparticle transformations during catalysis, ACS Catal. *9* (11) (2019) 10020–10043, https://doi.org/10.1021/acscatal.9b01831.

[29] T. Bligaard, R.M. Bullock, C.T. Campbell, J.G. Chen, B.C. Gates, R.J. Gorte, C. W. Jones, W.D. Jones, J.R. Kitchin, S.L. Scott, Toward benchmarking in catalysis science: best practices, challenges, and opportunities, ACS Catal. *6* (4) (2016) 2590–2602, https://doi.org/10.1021/ACSCATAL.6B00183/ASSET/IMAGES/LARGE/CS-2016-00183B_0008.JPEG.

[30] P.A. Boeg, J.Ø. Duus, J.H. Ardenkjær-Larsen, M. Karlsson, S. Mossin, Real-time detection of intermediates in rhodium-catalyzed hydrogenation of alkynes and alkenes by dissolution dnp, J. Phys. Chem. C. *123* (15) (2019) 9949–9956.

[31] J.Q. Bond, E.E. Stangland, V.J. Cybulskis, Best practices in the characterization of bulk catalyst properties, J. Catal. *433* (2024) 115487, https://doi.org/10.1016/J.JCAT.2024.115487.

[32] S. Bordiga, C. Lamberti, F. Bonino, A. Travert, F. Thibault-Starzyk, Probing zeolites by vibrational spectroscopies [Review], Chem. Soc. Rev. *44* (20) (2015) 7262–7341, https://doi.org/10.1039/c5cs00396b.

[33] P. Brault, E.C. Neyts, Molecular dynamics simulations of supported metal nanocatalyst formation by plasma sputtering, Catal. Today *256* (2015) 3–12, https://doi.org/10.1016/J.CATTOD.2015.02.004.

[34] V. Bukhtiyarov, A. Boronin, O. Baschenko, ARXPS-based analysis of different oxygen states adsorbed at silver foil, Surf. Rev. Lett. *1* (04) (1994) 577–579.

[35] G. Cassone, J. Sponer, F. Saija, Ab initio molecular dynamics studies of the electric-field-induced catalytic effects on liquids, Top. Catal. *65* (1) (2022) 40–58, https://doi.org/10.1007/s11244-021-01487-0.

[36] F. Castro-Marcano, A.C.T. van Duin, Comparison of thermal and catalytic cracking of 1-heptene from ReaxFF reactive molecular dynamics simulations, Combust. Flame *160* (4) (2013) 766–775, https://doi.org/10.1016/j.combustflame.2012.12.007.

[37] J. Chai, K. Zhang, Y. Xue, W. Liu, T. Chen, Y. Lu, G. Zhao, Review of MEMS based Fourier transform spectrometers, Micromachines *11* (2) (2020) 214.

[38] M. Che, Nobel Prize in chemistry 1912 to sabatier: organic chemistry or catalysis? Catal. Today *218-219* (2013) 162–171, https://doi.org/10.1016/j.cattod.2013.07.006.

[39] L. Chen, X. Ding, Z. Wang, S. Xu, Q. Jiang, C. Dun, J.J. Urban, Advances in in situ/operando techniques for catalysis research: enhancing insights and discoveries, Surf. Sci. Technol. *2* (1) (2024) 9.

[40] L. Chen, X. Ding, Z. Wang, S. Xu, Q. Jiang, C. Dun, J.J. Urban, Advances in in situ/operando techniques for catalysis research: enhancing insights and discoveries, Surf. Sci. Technol. 2 (1) (2024), https://doi.org/10.1007/s44251-024-00038-5.

[41] Z. Chen, Y. Sun, J. Shi, W. Zhang, X. Zhang, X. Huang, X. Zou, Z. Li, R. Wei, Facile synthesis of Au@Ag core–shell nanorod with bimetallic synergistic effect for SERS detection of thiabendazole in fruit juice, Food Chem. 370 (2022), https://doi.org/10.1016/j.foodchem.2021.131276.

[42] B.W.J. Chen, L. Xu, M. Mavrikakis, Computational methods in heterogeneous catalysis, Chem. Rev. *121* (2) (2021) 1007–1048, https://doi.org/10.1021/acs.chemrev.0c01060.

[43] H.-J. Chun, A. Morankar, Z. Zeng, J. Greeley, Solvation enthalpy determination for aqueous-phase reaction adsorbates using ab initio molecular dynamics-based structure sampling, J. Phys. Chem. C. *128* (4) (2024) 1621–1632, https://doi.org/10.1021/acs.jpcc.3c06870.

[44] M.B. Cutad, M.J. Al-Marri, A. Kumar, Recent developments on CO2 hydrogenation performance over structured zeolites: a review on properties, synthesis, and characterization, Catalysts 14 (5) (2024) 328, https://doi.org/10.3390/catal14050328.

[45] G.E. Cutsail III, S. DeBeer, Challenges and opportunities for applications of advanced X-ray spectroscopy in catalysis research, ACS Catal. *12* (10) (2022) 5864–5886.

[46] A.K. Datye, M. Votsmeier, Opportunities and challenges in the development of advanced materials for emission control catalysts, Nat. Mater. *20* (8) (2021) 1049–1059, https://doi.org/10.1038/S41563-020-00805-3.

[47] H. Deng, Y. Yu, F. Liu, J. Ma, Y. Zhang, H. He, Nature of Ag Species on Ag/γ-Al2O3: a combined experimental and theoretical study, ACS Catal. *4* (8) (2014) 2776–2784, https://doi.org/10.1021/cs500248a.

[48] E.G. Derouane, Catalysis in the 21st century, lessons from the past, challenges for the future, CATTECH *5* (4) (2001) 214–225, https://doi.org/10.1023/A:1014036813345.

[49] K. Devriendt, H. Poelman, L. Fiermans, G. Creten, G. Froment, Angular resolved XPS applied to V2O5-based catalysts, Surf. Sci. *352* (1996) 750–754.

[50] R. Di Santo, S. Romanò, A. Mazzini, S. Jovanović, G. Nocca, G. Campi, M. Papi, M. De Spirito, F. Di Giacinto, G. Ciasca, Recent advances in the label-free characterization of exosomes for cancer liquid biopsy: from scattering and spectroscopy to nanoindentation and nanodevices, Nanomaterials *11* (6) (2021) 1476.

[51] S.T. Dix, S. Linic, In-operando surface-sensitive probing of electrochemical reactions on nanoparticle electrocatalysts: Spectroscopic characterization of reaction intermediates and elementary steps of oxygen reduction reaction on Pt, J. Catal. *396* (2021) 32–39.

[52] Dolz, D., De Armas, R., Lozano-Reis, P., Morales-García, Á., Viñes, F., Sayós, R., & Illas, F. Understanding the Reverse Water Gas Shift Reaction over Mo2C MXene Catalyst: A Holistic Computational Analysis. ChemCatChem, n/a(n/a), e202400122. https://doi.org/https://doi.org/10.1002/cctc.202400122.

[53] J. Drnec, M. Ruge, F. Reikowski, B. Rahn, F. Carlà, R. Felici, J. Stettner, O. M. Magnussen, D.A. Harrington, Initial stages of Pt (111) electrooxidation: dynamic and structural studies by surface X-ray diffraction, Electrochim. Acta *224* (2017) 220–227.

[54] V. Edmond, F. Dufour, G. Poiroux, K. Shoji, M. Malleter, A. Fouqué, S. Tauzin, R. Rimokh, O. Sergent, A. Penna, Downregulation of ceramide synthase-6 during epithelial-to-mesenchymal transition reduces plasma membrane fluidity and cancer cell motility, Oncogene *34* (8) (2015) 996–1005.

[55] D. Ess, L. Gagliardi, S. Hammes-Schiffer, Introduction: Computational Design of Catalysts from Molecules to Materials, Chem. Rev. *119* (11) (2019) 6507–6508, https://doi.org/10.1021/acs.chemrev.9b00296.

[56] A. Fadlelmoula, D. Pinho, V.H. Carvalho, S.O. Catarino, G. Minas, Fourier transform infrared (FTIR) spectroscopy to analyse human blood over the last 20 years: a review towards lab-on-a-chip devices, Micromachines *13* (2) (2022) 187.

[57] Y. Fang, Y. Guo, Copper-based non-precious metal heterogeneous catalysts for environmental remediation, Chin. J. Catal. *39* (4) (2018) 566–582, https://doi.org/10.1016/S1872-2067(17)62996-6.

[58] J. Feng, Y. Yin, Self-templating approaches to hollow nanostructures, Adv. Mater. *31* (38) (2019) 1802349.

[59] I.M. Fermor-Worth, C. Chimerel, Broadband cavity enhanced UV–VIS absorption spectroscopy for picolitre liquid samples, Analyst 148 (8) (2023) 1797–1804, https://doi.org/10.1039/d3an00143a.

[60] A.P. Ferreira, J.F. Gamble, M.M. Leane, H. Park, D. Olusanmi, M. Tobyn, Enhanced Understanding of Pharmaceutical Materials Through Advanced Characterisation and Analysis, AAPS PharmSciTech *19* (8) (2018) 3462–3480, https://doi.org/10.1208/S12249-018-1198-6/FIGURES/10.

[61] S.L. Foster, S.I.P. Bakovic, R.D. Duda, S. Maheshwari, R.D. Milton, S.D. Minteer, M.J. Janik, J.N. Renner, L.F. Greenlee, Catalysts for nitrogen reduction to ammonia, Nat. Catal. *1* (7) (2018) 490–500, https://doi.org/10.1038/s41929-018-0092-7.

[62] A.I. Frenkel, Q. Wang, N. Marinkovic, J.G. Chen, L. Barrio, R. Si, A.L. Cámara, A. M. Estrella, J.A. Rodriguez, J.C. Hanson, Combining X-ray absorption and X-ray diffraction techniques for in situ studies of chemical transformations in

heterogeneous catalysis: advantages and limitations, J. Phys. Chem. C. *115* (36) (2011) 17884–17890, https://doi.org/10.1021/JP205204E/SUPPL_FILE/JP205204E_SI_001.PDF.
[63] H. Friedrich, P.E. De Jongh, A.J. Verkleij, K.P. De Jong, Electron tomography for heterogeneous catalysts and related nanostructured materials, Chem. Rev. *109* (5) (2009) 1613–1629, https://doi.org/10.1021/CR800434T/ASSET/IMAGES/MEDIUM/CR-2008-00434T_0004.GIF.
[64] P.L. Gai, K. Yoshida, C. Shute, X. Jia, M. Walsh, M. Ward, M.S. Dresselhaus, J. R. Weertman, E.D. Boyes, Probing structures of nanomaterials using advanced electron microscopy methods, including aberration-corrected electron microscopy at the angstrom scale, Microsc. Res. Tech. *74* (7) (2011) 664–670, https://doi.org/10.1002/JEMT.20933.
[65] A. Gil, Classical and new insights into the methodology for characterizing adsorbents and metal catalysts by chemical adsorption, Catal. Today 423 (2023), https://doi.org/10.1016/j.cattod.2023.01.023.
[66] L. Grajciar, C.J. Heard, A.A. Bondarenko, M.V. Polynski, J. Meeprasert, E. A. Pidko, P. Nachtigall, Towards operando computational modeling in heterogeneous catalysis, Chem. Soc. Rev. *47* (22) (2018) 8307–8348, https://doi.org/10.1039/c8cs00398j.
[67] L. Grajciar, C.J. Heard, A.A. Bondarenko, M.V. Polynski, J. Meeprasert, E. A. Pidko, P. Nachtigall, Towards operando computational modeling in heterogeneous catalysis [Review], Chem. Soc. Rev. *47* (22) (2018) 8307–8348, https://doi.org/10.1039/c8cs00398j.
[68] N.G. Greeneltch, M.G. Blaber, G.C. Schatz, R.P. Van Duyne, Plasmon-sampled surface-enhanced raman excitation spectroscopy on silver immobilized nanorod assemblies and optimization for near infrared (λex = 1064 nm) studies, J. Phys. Chem. C. 117 (6) (2013) 2554–2558, https://doi.org/10.1021/jp310846j.
[69] P.R. Griffiths, Fourier transform infrared spectrometry, Science *222* (4621) (1983) 297–302.
[70] Y. Guan, D. Chaffart, G. Liu, Z. Tan, D. Zhang, Y. Wang, J. Li, L. Ricardez-Sandoval, Machine learning in solid heterogeneous catalysis: Recent developments, challenges and perspectives, Chem. Eng. Sci. *248* (2022) 117224, https://doi.org/10.1016/J.CES.2021.117224.
[71] B. Guan, H. Jiang, Y. Wei, Z. Liu, X. Wu, H. Lin, Z. Huang, Density functional theory researches for atomic structure, properties prediction, and rational design of selective catalytic reduction catalysts: current progresses and future perspectives, Mol. Catal. *510* (2021) 111704, https://doi.org/10.1016/j.mcat.2021.111704.
[72] P.L.J. Gunter, J.W. Niemantsverdriet, F.H. Ribeiro, G.A. Somorjai, Surface science approach to modeling supported catalysts, Catal. Rev. *39* (1-2) (1997) 77–168, https://doi.org/10.1080/01614949708006469.
[73] E. Halakoo, A. Khademi, M. Ghasemi, N.M. Yusof, R.J. Gohari, A.F. Ismail, Production of sustainable energy by carbon nanotube/platinum catalyst in microbial fuel cell, Procedia CIRP *26* (2015) 473–476, https://doi.org/10.1016/J.PROCIR.2014.07.034.
[74] P.L. Hansen, J.B. Wagner, S. Helveg, J.R. Rostrup-Nielsen, B.S. Clausen, H. Topsøe, Atom-resolved imaging of dynamic shape changes in supported copper nanocrystals, Science *295* (5562) (2002) 2053–2055, https://doi.org/10.1126/SCIENCE.1069325.
[75] C. Hess, New advances in using Raman spectroscopy for the characterization of catalysts and catalytic reactions, Chem. Soc. Rev. *50* (5) (2021) 3519–3564.
[76] F. Hoffmann, N. Levinos, B. Perry, P. Rabinowitz, High-resolution infrared reflection absorption spectroscopy with a continuously tunable infrared laser: CO on Ru (001), Phys. Rev. B *33* (6) (1986) 4309.
[77] D.V. Ilyin, W.A. Goddard, 3rd, J.J. Oppenheim, T. Cheng, First-principles-based reaction kinetics from reactive molecular dynamics simulations: application to hydrogen peroxide decomposition, Proc. Natl. Acad. Sci. USA *116* (37) (2019) 18202–18208, https://doi.org/10.1073/pnas.1701383115.
[78] M.A. Isaacs, L.J. Durndell, A.C. Hilton, L. Olivi, C.M. Parlett, K. Wilson, A.F. Lee, Tunable Ag@ SiO 2 core–shell nanocomposites for broad spectrum antibacterial applications, RSC Adv. *7* (38) (2017) 23342–23347.
[79] A. Ivančič, J. Košmrlj, M. Gazvoda, Elucidating the reaction mechanism of a palladium-palladium dual catalytic process through kinetic studies of proposed elementary steps, Commun. Chem. *6* (1) (2023) 51, https://doi.org/10.1038/s42004-023-00849-x.
[80] A. Jablonski, C.J. Powell, Relationships between electron inelastic mean free paths, effective attenuation lengths, and mean escape depths, J. Electron Spectrosc. Relat. Phenom. *100* (1-3) (1999) 137–160.
[81] N.R. Jaegers, K.T. Mueller, Y. Wang, J.Z. Hu, Variable temperature and pressure operando MAS NMR for catalysis science and related materials, Acc. Chem. Res. *53* (3) (2020) 611–619.
[82] J. Jin, J. Sun, K. Lv, Q. Hou, X. Guo, K. Liu, Y. Deng, L. Song, Catalytic pyrolysis of oil shale using tailored Cu@zeolite catalyst and molecular dynamic simulation, Energy *278* (2023) 127858, https://doi.org/10.1016/j.energy.2023.127858.
[83] B. Jing, J. Li, C. Nie, J. Zhou, D. Li, Z. Ao, Flow line of density functional theory in heterogeneous persulfate-based advanced oxidation processes for pollutant degradation: a review, Crit. Rev. Environ. Sci. Technol. *53* (4) (2023) 483–503, https://doi.org/10.1080/10643389.2022.2070404.
[84] K. Jungjohann, C.B. Carter, In Situ and Operando, Transm. Electron Microsc. (2016) 17–80, https://doi.org/10.1007/978-3-319-26651-0_2.
[85] K. Kaczmarek, A. Leniart, B. Lapinska, S. Skrzypek, M. Lukomska-Szymanska, Selected spectroscopic techniques for surface analysis of dental materials: A narrative review, Materials 14 (10) (2021), https://doi.org/10.3390/ma14102624.
[86] K.F. Kalz, R. Kraehnert, M. Dvoyashkin, R. Dittmeyer, R. Gläser, U. Krewer, K. Reuter, J.D. Grunwaldt, Future Challenges in Heterogeneous Catalysis: Understanding Catalysts under Dynamic Reaction Conditions, ChemCatChem *9* (1) (2017) 17–29, https://doi.org/10.1002/CCTC.201600996.
[87] Y. Kawabata, J. Taniguchi, I. Miyamoto, XPS studies on damage evaluation of single-crystal diamond chips processed with ion beam etching and reactive ion beam assisted chemical etching, Diam. Relat. Mater. *13* (1) (2004) 93–98.
[88] A. Khelfa, J. Nelayah, H. Amara, G. Wang, C. Ricolleau, D. Alloyeau, Quantitative in situ visualization of thermal effects on the formation of gold nanocrystals in solution, Adv. Mater. *33* (38) (2021) 2102514.
[89] H. Kim, K.M. Kosuda, R.P. Van Duyne, P.C. Stair, Resonance Raman and surface- and tip-enhanced Raman spectroscopy methods to study solid catalysts and heterogeneous catalytic reactions, Chem. Soc. Rev. *39* (12) (2010) 4820–4844.
[90] W.S. Knowles, Asymmetric Hydrogenations (Nobel Lecture 2001), Adv. Synth. Catal. *345* (1-2) (2003) 3–13, https://doi.org/10.1002/adsc.200390028.
[91] T. Kobayashi, M. Pruski, Spatial distribution of silica-bound catalytic organic functional groups can now be revealed by conventional and DNP-enhanced solid-state NMR methods, ACS Catal. *9* (8) (2019) 7238–7249.
[92] A. Kohut, L. Ludvigsson, B.O. Meuller, K. Deppert, M.E. Messing, G. Galbács, Z. Geretovszky, From plasma to nanoparticles: optical and particle emission of a spark discharge generator, Nanotechnology *28* (47) (2017) 475603.
[93] E.V. Kondratenko, Using time-resolved methods to monitor and understand catalytic oxidation reactions, Catal. Today *157* (1) (2010) 16–23, https://doi.org/10.1016/j.cattod.2010.01.031.
[94] N. Kornienko, J. Resasco, N. Becknell, C.-M. Jiang, Y.-S. Liu, K. Nie, X. Sun, J. Guo, S.R. Leone, P. Yang, Operando spectroscopic analysis of an amorphous cobalt sulfide hydrogen evolution electrocatalyst, J. Am. Chem. Soc. *137* (23) (2015) 7448–7455.
[95] R. Kumar, S. Kumar, A.J. Kailath, R.K. Sahu, Mechanistic investigation of hydrogen generation from water and magnesium catalyst reaction: Advanced reactive molecular dynamics simulation, Int. J. Hydrog. Energy *52* (2024) 1440–1445, https://doi.org/10.1016/j.ijhydene.2023.07.247.
[96] S. Kumar, R.K. Sahu, Aluminum nanotubes as an efficient catalyst for hydrogen production via thermochemical water splitting: a reactive molecular dynamics simulation [10.1039/D3CP00890H], Phys. Chem. Chem. Phys. *25* (19) (2023) 13487–13497, https://doi.org/10.1039/D3CP00890H.
[97] N.E. Larm, A. Roy, P. Ishtaweera, L. Adhikari, G.A. Baker, Selective aerobic oxidation of benzyl alcohol under ambient conditions using polyionic nanoclay-supported gold/palladium nanoparticles, Mol. Catal. *546* (2023) 113237, https://doi.org/10.1016/J.MCAT.2023.113237.
[98] Y.-K. Lee, Density functional theory (DFT) calculations and catalysis, Catalysts *11* (4) (2021) 454. ⟨https://www.mdpi.com/2073-4344/11/4/454⟩.
[99] J. Lee, C. Jeong, T. Lee, S. Ryu, Y. Yang, Direct observation of three-dimensional atomic structure of twinned metallic nanoparticles and their catalytic properties, Nano Lett. *22* (2) (2022) 665–672.
[100] I.R. Lewis, H. Edwards, Handbook of Raman spectroscopy: from the research laboratory to the process line, CRC press, 2001.
[101] J. Li, F.L. Deepak, In situ generation of sub-10 nm silver nanowires under electron beam irradiation in a TEM, Chem. Commun. *56* (35) (2020) 4765–4768.
[102] H.-G. Liao, D. Zherebetskyy, H. Xin, C. Czarnik, P. Ercius, H. Elmlund, M. Pan, L.-W. Wang, H. Zheng, Facet development during platinum nanocube growth, Science *345* (6199) (2014) 916–919.
[103] L. Luo, M. Su, P. Yan, L. Zou, D.K. Schreiber, D.R. Baer, Z. Zhu, G. Zhou, Y. Wang, S.M. Bruemmer, Atomic origins of water-vapour-promoted alloy oxidation, Nat. Mater. *17* (6) (2018) 514–518.
[104] Y. Ma, J. Xiong, P. Zhang, Y. Li, S. Zhang, Z. Wang, L. Xu, H. Guo, K. Chen, Y. Wei, Recent progress on density functional theory calculations for catalytic control of air pollution, ACS EST Eng. *4* (1) (2024) 47–65, https://doi.org/10.1021/acsestengg.3c00208.
[105] L.D.B. Mandemaker, M. Filez, G. Delen, H. Tan, X. Zhang, D. Lohse, B. M. Weckhuysen, Time-resolved in situ liquid-phase atomic force microscopy and infrared nanospectroscopy during the formation of metal–organic framework thin films, J. Phys. Chem. Lett. *9* (8) (2018) 1838–1844, https://doi.org/10.1021/acs.jpclett.8b00203.
[106] L.D.B. Mandemaker, M. Rivera-Torrente, G. Delen, J.P. Hofmann, M. Lorenz, A. Belianinov, B.M. Weckhuysen, Nanoweb Surface-Mounted Metal–Organic Framework Films with Tunable Amounts of Acid Sites as Tailored Catalysts, Chem. – A Eur. J. *26* (3) (2020) 691–698, https://doi.org/10.1002/chem.201903761.
[107] Q. Mao, A. van Duin, K. Luo, Investigation of methane oxidation by palladium-based catalyst via ReaxFF Molecular Dynamics simulation, Proc. Combust. Inst. *36* (2016), https://doi.org/10.1016/j.proci.2016.08.037.
[108] Y. Mao, H.-F. Wang, P. Hu, Theory and applications of surface micro-kinetics in the rational design of catalysts using density functional theory calculations, WIREs Comput. Mol. Sci. *7* (6) (2017) e1321, https://doi.org/10.1002/wcms.1321.
[109] L.R. Merte, F. Behafarid, D.J. Miller, D. Friebel, S. Cho, F. Mbuga, D. Sokaras, R. Alonso-Mori, T.-C. Weng, D. Nordlund, Electrochemical oxidation of size-selected Pt nanoparticles studied using in situ high-energy-resolution X-ray absorption spectroscopy, ACS Catal. *2* (11) (2012) 2371–2376.
[110] E. Mitri, G. Birarda, L. Vaccari, S. Kenig, M. Tormen, G. Grenci, SU-8 bonding protocol for the fabrication of microfluidic devices dedicated to FTIR microspectroscopy of live cells, Lab Chip *14* (1) (2014) 210–218.
[111] A. Mittasch, W. Frankenburg, Early Studies of Multicomponent Catalysts, in: W. G. Frankenburg, V.I. Komarewsky, E.K. Rideal (Eds.), Advances in Catalysis, Vol. 2, Academic Press, 1950, pp. 81–104, https://doi.org/10.1016/S0360-0564(08)60375-2.

[112] M.M. Modena, B. Rühle, T.P. Burg, S. Wuttke, Nanoparticle characterization: what to measure? Adv. Mater. *31* (32) (2019) 1901556.

[113] B.D. Montejo-Valencia, Y.J. Pagán-Torres, M.M. Martínez-Iñesta, M.C. Curet-Arana, Density functional theory (DFT) study to unravel the catalytic properties of M-exchanged MFI, (M = Be, Co, Cu, Mg, Mn, Zn) for the conversion of methane and carbon dioxide to acetic acid, ACS Catal. *7* (10) (2017) 6719–6728, https://doi.org/10.1021/acscatal.7b00844.

[114] G.T. Morgan, Achievements of British chemical industry in the lasT TWENTY-FIVE YEARS: Lecture I, J. R. Soc. Arts *87* (4525) (1939) 991–1008. ⟨http://www.jstor.org/stable/41359404⟩.

[115] R. Mülhaupt, Catalytic polymerization and post polymerization catalysis fifty years after the discovery of Ziegler's catalysts, Macromol. Chem. Phys. *204* (2) (2003) 289–327, https://doi.org/10.1002/macp.200290085.

[116] B.M. Murphy, B. Xu, Foundational techniques for catalyst design in the upgrading of biomass-derived multifunctional molecules, Prog. Energy Combust. Sci. *67* (2018) 1–30, https://doi.org/10.1016/j.pecs.2018.01.003.

[117] J.W. Niemantsverdriet, Spectroscopy in catalysis: an introduction, John Wiley & Sons, 2007.

[118] K. Niu, T. Frolov, H.L. Xin, J. Wang, M. Asta, H. Zheng, Bubble nucleation and migration in a lead–iron hydr (oxide) core–shell nanoparticle, Proc. Natl. Acad. Sci. *112* (42) (2015) 12928–12932.

[119] J.K. Nørskov, F. Abild-Pedersen, F. Studt, T. Bligaard, Density functional theory in surface chemistry and catalysis, Proc. Natl. Acad. Sci. USA *108* (3) (2011) 937–943, https://doi.org/10.1073/PNAS.1006652108/ASSET/5E0F9BD1-E0A3-40E9-9BBF-DC911461E379/ASSETS/GRAPHIC/PNAS.1006652108FIG09.JPEG.

[120] Y. Nzuzo, C.O. Oseghale, A. Chike-Ekwughe, M. Maumela, N. Bingwa, Electronic distribution and dynamics as catalytic descriptors in heterogeneous catalysis: a mini review, Catal. Commun. *187* (2024) 106901, https://doi.org/10.1016/j.catcom.2024.106901.

[121] T.C. Ong, W.C. Liao, V. Mougel, D. Gajan, A. Lesage, L. Emsley, C. Copéret, Atomistic description of reaction intermediates for supported metathesis catalysts enabled by DNP SENS, Angew. Chem. Int. Ed. *55* (15) (2016) 4743–4747.

[122] L. Ouyang, L. Yao, T. Zhou, L. Zhu, Accurate SERS detection of malachite green in aquatic products on basis of graphene wrapped flexible sensor, Anal. Chim. Acta 1027 (2018) 83–91, https://doi.org/10.1016/j.aca.2018.04.052.

[123] O. Ovsitser, M. Cherian, A. Brückner, E.V. Kondratenko, Dynamics of redox behavior of nano-sized VOx species over Ti-Si-MCM-41 from time-resolved in situ UV/Vis analysis [Article], J. Catal. *265* (1) (2009) 8–18, https://doi.org/10.1016/j.jcat.2009.04.005.

[124] Z. Öztürk, M. Filez, B.M. Weckhuysen, Decoding nucleation and growth of zeolitic imidazolate framework thin films with atomic force microscopy and vibrational spectroscopy, Chem. – A Eur. J. *23* (45) (2017) 10915–10924, https://doi.org/10.1002/chem.201702130.

[125] N. Pappas, Calculating retained austenite in steel post magnetic processing using X-ray diffraction, B. S. Undergrad. Math. Exch. 4 (1) (2006) 8–14.

[126] R.M. Patil, P.P. Deshpande, M. Aalhate, S. Gananadhamu, P.K. Singh, An Update on sophisticated and advanced analytical tools for surface characterization of nanoparticles, Surf. Interfaces *33* (2022) 102165, https://doi.org/10.1016/j.surfin.2022.102165.

[127] Pinto, D.G. (2019). Cavity-Enhanced Absorption Spectroscopy with a Deep UV-LED [PhD Thesis, Heriot-Watt University]. ⟨https://www.ros.hw.ac.uk/bitstream/handle/10399/4298/PintoDG_0120_eps.pdf?sequence=1&isAllowed=y⟩.

[128] P.N. Plessow, F. Studt, How accurately do approximate density functionals predict trends in acidic zeolite catalysis? J. Phys. Chem. Lett. *11* (11) (2020) 4305–4310, https://doi.org/10.1021/acs.jpclett.0c01240.

[129] H. Pu, Z. Huang, F. Xu, D.W. Sun, Two-dimensional self-assembled Au-Ag core-shell nanorods nanoarray for sensitive detection of thiram in apple using surface-enhanced Raman spectroscopy, Food Chem. 343 (2021), https://doi.org/10.1016/j.foodchem.2020.128548.

[130] M.K. Rasmussen, J.N. Pedersen, R. Marie, Size and surface charge characterization of nanoparticles with a salt gradient, Nat. Commun. *11* (1) (2020) 2337.

[131] O. Renault, E. Martinez, C. Zborowski, J. Mann, R. Inoue, J. Newman, K. Watanabe, Analysis of buried interfaces in multilayer device structures with hard XPS (HAXPES) using a CrKα source, Surf. Interface Anal. *50* (11) (2018) 1158–1162.

[132] M. Rivallan, E. Seguin, S. Thomas, M. Lepage, N. Takagi, H. Hirata, F. Thibault-Starzyk, Platinum sintering on H-ZSM-5 followed by chemometrics of CO adsorption and 2D pressure-jump IR spectroscopy of adsorbed species, Angew. Chem. Int. Ed. *49* (4) (2010) 785–789.

[133] I. Rodríguez, R. Gautam, A.D. Tinoco, Using x-ray diffraction techniques for biomimetic drug development, formulation, and polymorphic characterization, Biomimetics 6 (1) (2021) 1–23, https://doi.org/10.3390/biomimetics6010009.

[134] K.H.R. Rouwenhorst, A.S. Travis, L. Lefferts, 1921–2021: A Century of Renewable Ammonia Synthesis, Sustain. Chem. *3* (2) (2022) 149–171. ⟨https://www.mdpi.com/2673-4079/3/2/11⟩.

[135] M. Ruge, J. Drnec, B. r Rahn, F. Reikowski, D.A. Harrington, F. Carlà, R. Felici, J. Stettner, O.M. Magnussen, Structural reorganization of Pt (111) electrodes by electrochemical oxidation and reduction, J. Am. Chem. Soc. *139* (12) (2017) 4532–4539.

[136] M.J. Rybak-Smith, Effect of surface modification on toxicity of nanoparticles, Encycl. Nanotechnol. *2012* (2012) 645–652.

[137] T.P. Senftle, A.C.T. van Duin, M.J. Janik, Application of Computational Methods to Supported Metal–Oxide Catalysis, in: In.A. Asthagiri, M.J. Janik (Eds.), Computational Catalysis, The Royal Society of Chemistry, 2013, p. 0, https://doi.org/10.1039/9781849734905-00157.

[138] D. Seo, J.C. Park, H. Song, Polyhedral gold nanocrystals with O h symmetry: From octahedra to cubes, J. Am. Chem. Soc. *128* (46) (2006) 14863–14870.

[139] Shambhawi, O. Mohan, T.S. Choksi, A.A. Lapkin, The design and optimization of heterogeneous catalysts using computational methods [10.1039/D3CY01160G], Catal. Sci. Technol. *14* (3) (2024) 515–532, https://doi.org/10.1039/D3CY01160G.

[140] H. Shen, X. Wu, D. Jiang, X. Li, J. Ni, Identification of active sites for hydrogenation over Ru/SBA-15 using in situ Fourier-transform infrared spectroscopy, Chin. J. Catal. 38 (9) (2017) 1597–1602, https://doi.org/10.1016/S1872-2067(17)62835-7.

[141] Y. Shen, Z. Xiao, Reducible inverse CeOx-based catalyst as a potential candidate for electroreduction, Catalysts *9* (1) (2019) 22. ⟨https://www.mdpi.com/2073-4344/9/1/22⟩.

[142] D.A. Shirley, High-resolution X-ray photoemission spectrum of the valence bands of gold, Phys. Rev. B *5* (12) (1972) 4709.

[143] S. Siahrostami, N. Murray, The success of computational material design for sustainable energy catalysis, Can. J. Chem. *102* (5) (2024) 298–309, https://doi.org/10.1139/cjc-2023-0232.

[144] S. Sinehbaghizadeh, A. Saptoro, S. Amjad-Iranagh, P. Naeiji, A.N.T. Tiong, A. H. Mohammadi, A comprehensive review on molecular dynamics simulation studies of phenomena and characteristics associated with clathrate hydrates, Fuel *338* (2023) 127201, https://doi.org/10.1016/j.fuel.2022.127201.

[145] P.K. Singh, A.K. Srivastava, A. Dev, B. Kaundal, S.R. Choudhury, S. Karmakar, 1, 3β-Glucan anchored, paclitaxel loaded chitosan nanocarrier endows enhanced hemocompatibility with efficient anti-glioblastoma stem cells therapy, Carbohydr. Polym. *180* (2018) 365–375.

[146] B. Singha, K. Ray, Density functional theory insights on photocatalytic ability of CuO/TiO2 and CuO/ZnO, Mater. Today.: Proc. *72* (2023) 451–458, https://doi.org/10.1016/j.matpr.2022.08.313.

[147] Z.-Y. Song, Y.-Y. Li, W. Duan, X.-Y. Xiao, Z.-W. Gao, Y.-H. Zhao, B. Liang, S.-H. Chen, P.-H. Li, M. Yang, X.-J. Huang, Decisive role of electronic structure in electroanalysis for sensing materials: insights from density functional theory, TrAC Trends Anal. Chem. *160* (2023) 116977, https://doi.org/10.1016/j.trac.2023.116977.

[148] F. Studt, Grand Challenges in Computational Catalysis [Specialty Grand Challenge], Front. Catal. *1* (2021), https://doi.org/10.3389/fctls.2021.658965.

[149] D.S. Su, B. Zhang, R. Schlögl, Electron microscopy of solid catalysts transforming from a challenge to a toolbox, Chem. Rev. *115* (8) (2015) 2818–2882.

[150] D. Sullivan, M. Harold, W. Conner Jr, Catalyst transformation during NO+ NH3Reaction over vanadium oxide usingin SituFTIR emission spectroscopy, J. Catal. *178* (1) (1998) 108–118.

[151] M. Sun, Z. Cheng, W. Chen, M. Jones, Understanding symmetry breaking at the single-particle level via the growth of tetrahedron-shaped nanocrystals from higher-symmetry precursors, ACS Nano *15* (10) (2021) 15953–15961.

[152] Y. Sun, K. Zeng, Characterization of catalysts by advanced scanning probe microscopy and spectroscopy, ChemCatChem *12* (14) (2020) 3601–3620, https://doi.org/10.1002/cctc.201901877.

[153] L.F. Sutcu, J. Wragg, H. White, Tunable-diode-laser infrared reflection absorption spectroscopy of carbon monoxide on Pt (111), Phys. Rev. B *41* (12) (1990) 8164.

[154] R.E. Swai, A review of molecular dynamics simulations in the designing of effective shale inhibitors: application for drilling with water-based drilling fluids, J. Pet. Explor. Prod. Technol. *10* (8) (2020) 3515–3532, https://doi.org/10.1007/s13202-020-01003-2.

[155] B. Szappanos, K. Kovács, B. Szamecz, F. Honti, M. Costanzo, A. Baryshnikova, G. Gelius-Dietrich, M.J. Lercher, M. Jelasity, C.L. Myers, B.J. Andrews, C. Boone, S.G. Oliver, C. Pál, B. Papp, An integrated approach to characterize genetic interaction networks in yeast metabolism, Nat. Genet. 2011 43:7 *43* (7) (2011) 656–662, https://doi.org/10.1038/ng.846.

[156] E. Talik, M. Kruczek, H. Sakowska, W. Szyrski, XPS studies of chemically etched surfaces of (La, Sr)(Al, Ta) O3 single crystals, J. Alloy. Compd. *361* (1-2) (2003) 282–288.

[157] X. Tan, Z. Huang, Y. Li, G. Wang, Improved spectroscopy techniques for catalyst characterization, J. Catal. 389 (2024) 205–218, https://doi.org/10.1016/j.jcat.2024.03.015.

[158] T. Tanaka, Y. Miyake, K. Shimizu, Advanced IR spectroscopy for catalyst characterization, Chem. Rev. 122 (15) (2022) 10395–10435, https://doi.org/10.1021/acs.chemrev.1c01067.

[159] J.M. Thomas, Turning points in catalysis, Angew. Chem. Int. Ed. Engl. *33* (9) (1994) 913–937, https://doi.org/10.1002/anie.199409131.

[160] H. Tokutaka, N. Ishihara, K. Nishimori, S. Kishida, K. Isomoto, Background removal in x-ray photoelectron spectroscopy, Surf. Interface Anal. *18* (10) (1992) 697–704.

[161] H. Topsoe, Mechanistic aspects of the selective catalytic reduction of NO by ammonia, Appl. Catal. B: Environ. 3 (4) (1994) 305–323, https://doi.org/10.1016/0926-3373(94)80002-7.

[162] H. Topsøe, Developments in operando studies and in situ characterization of heterogeneous catalysts, J. Catal. *216* (1–2) (2003) 155–164, https://doi.org/10.1016/S0021-9517(02)00133-1.

[163] S. Tosoni, H.-Y.T. Chen, G. Pacchioni, A DFT study of Ni clusters deposition on titania and zirconia (101) surfaces, Surf. Sci. *646* (2016) 230–238, https://doi.org/10.1016/j.susc.2015.04.004.

[164] A.S. Travis, Nobel prizes and new technologies, in: A.S. Travis (Ed.), The Synthetic Nitrogen Industry in World War I: Its Emergence and Expansion, Springer International Publishing, 2015, pp. 111–143, https://doi.org/10.1007/978-3-319-19357-1_5.

[165] V. Van Speybroeck, M. Bocus, P. Cnudde, L. Vanduyfhuys, Operando modeling of zeolite-catalyzed reactions using first-principles molecular dynamics simulations, ACS Catal. *13* (17) (2023) 11455–11493, https://doi.org/10.1021/acscatal.3c01945.
[166] A.M. Venezia, X-ray photoelectron spectroscopy (XPS) for catalysts characterization, Catal. Today *77* (4) (2003) 359–370.
[167] K.D. Vogiatzis, M.V. Polynski, J.K. Kirkland, J. Townsend, A. Hashemi, C. Liu, E. A. Pidko, Computational approach to molecular catalysis by 3d transition metals: challenges and opportunities, Chem. Rev. *119* (4) (2019) 2453–2523, https://doi.org/10.1021/acs.chemrev.8b00361.
[168] I.E. Wachs, C.A. Roberts, Monitoring surface metal oxide catalytic active sites with Raman spectroscopy, Chem. Soc. Rev. *39* (12) (2010) 5002–5017.
[169] E.D. Walter, L. Qi, A. Chamas, H.S. Mehta, J.A. Sears, S.L. Scott, D.W. Hoyt, Operando MAS NMR reaction studies at high temperatures and pressures, J. Phys. Chem. C. *122* (15) (2018) 8209–8215.
[170] R. Wang, O. Dmitrieva, M. Farle, G. Dumpich, H. Ye, H. Poppa, R. Kilaas, C. Kisielowski, Layer resolved structural relaxation at the surface of magnetic FePt icosahedral nanoparticles, Phys. Rev. Lett. *100* (1) (2008) 017205.
[171] R. Wang, O. Dmitrieva, M. Farle, G. n Dumpich, M. Acet, S. Mejia-Rosales, E. Perez-Tijerina, M.J. Yacaman, C. Kisielowski, FePt icosahedra with magnetic cores and catalytic shells, J. Phys. Chem. C. *113* (11) (2009) 4395–4400.
[172] Y. Wang, H. Shao, C. Zhang, F. Liu, J. Zhao, S. Zhu, M.K.H. Leung, J. Hu, Molecular dynamics for electrocatalysis: Mechanism explanation and performance prediction, Energy Rev. *2* (3) (2023) 100028, https://doi.org/10.1016/j.enrev.2023.100028.
[173] J. Wang, C. Tung, Y.-F. Chen, C. Kwei, The surface effect on Au 4f X-ray photoelectron spectra, Nucl. Instrum. Methods Phys. Res. Sect. B: Beam Interact. Mater. At. *108* (3) (1996) 331–338.
[174] R. Wang, H. Zhang, M. Farle, C. Kisielowski, Structural stability of icosahedral FePt nanoparticles, Nanoscale *1* (2) (2009) 276–279.
[175] L. Wang, Y. Zhang, Z. Zeng, H. Zhou, J. He, P. Liu, M. Chen, J. Han, D.J. Srolovitz, J. Teng, Tracking the sliding of grain boundaries at the atomic scale, Science *375* (6586) (2022) 1261–1265.
[176] B.M. Weckhuysen, Snapshots of a working catalyst: possibilities and limitations of in situ spectroscopy in the field of heterogeneous catalysis, Chem. Commun. (2) (2002) 97–110.
[177] B.M. Weckhuysen, Preface: recent advances in the in-situ characterization of heterogeneous catalysts, Chem. Soc. Rev. *39* (12) (2010) 4557–4559.
[178] B.M. Weckhuysen, Z. Öztürk, R.P. Brand, J.M. Boereboom, F. Meirer, Vibrational fingerprinting of defects sites in thin films of zeolitic imidazolate frameworks, Chem. – A Eur. J. *25* (34) (2019) 8070–8084, https://doi.org/10.1002/chem.201806414.
[179] J. Wisniak, Jöns Jacob berzelius a guide to the perplexed chemist, Chem. Educ. *5* (6) (2000) 343–350, https://doi.org/10.1007/s00897000430a.
[180] J. Wisniak, The history of catalysis. from the beginning to nobel prizes, Educ. óN. Química *21* (1) (2010) 60–69, https://doi.org/10.1016/S0187-893X(18)30074-0.
[181] K.-J. Wu, C. Edmund, C. Shang, Z. Guo, Nucleation and growth in solution synthesis of nanostructures–from fundamentals to advanced applications, Prog. Mater. Sci. *123* (2022) 100821.
[182] D.-G. Xie, Z.-J. Wang, J. Sun, J. Li, E. Ma, Z.-W. Shan, In situ study of the initiation of hydrogen bubbles at the aluminium metal/oxide interface, Nat. Mater. *14* (9) (2015) 899–903.
[183] H. Xu, B. Man, G. Luo, Catalytic mechanism comparison between 1,2-dichloroethane-acetylene exchange reaction and acetylene hydrochlorination reaction for vinyl chloride production: DFT calculations and experiments, Catalysts *10* (2) (2020) 204. ⟨https://www.mdpi.com/2073-4344/10/2/204⟩.
[184] X. Yang, B. Cao, D. Jiang, S. He, C. Yuan, H. Li, S.R. Naqvi, S. Wang, Catalytic pyrolysis of guaiacol on Enteromorpha-based biochar: a combination of experiments and density functional theory, Fuel Process. Technol. *239* (2023) 107527, https://doi.org/10.1016/j.fuproc.2022.107527.
[185] F. Yang, D. Deng, X. Pan, Q. Fu, X. Bao, Understanding nano effects in catalysis, Natl. Sci. Rev. *2* (2) (2015) 183–201, https://doi.org/10.1093/nsr/nwv024.
[186] L. Yao, F. Zhang, Z. Song, X. Zhao, W. Wang, Y. Mao, J. Sun, ReaxFF MD simulation of microwave catalytic pyrolysis of polypropylene over Fe catalyst for hydrogen, Fuel *340* (2023) 127550, https://doi.org/10.1016/j.fuel.2023.127550.
[187] H. Yoshida, Y. Tomita, K. Soma, S. Takeda, Electron beam induced etching of carbon nanotubes enhanced by secondary electrons in oxygen, Nanotechnology *28* (19) (2017) 195301.
[188] B.T. Young, D.R. Heskett, C.C. Nguyen, M. Nie, J.C. Woicik, B.L. Lucht, Hard X-ray photoelectron spectroscopy (HAXPES) investigation of the silicon solid electrolyte interphase (SEI) in lithium-ion batteries, ACS Appl. Mater. Interfaces *7* (36) (2015) 20004–20011.
[189] M. Yu, C. Chen, Z. Xing, X. Jiang, ReaxFF molecular dynamics simulation of nickel catalysed gasification of cellulose in supercritical water, Int. J. Hydrog. Energy *48* (1) (2023) 123–137, https://doi.org/10.1016/j.ijhydene.2022.09.202.
[190] Y. Yuan, K. Amine, J. Lu, R. Shahbazian-Yassar, Understanding materials challenges for rechargeable ion batteries with in situ transmission electron microscopy, Nat. Commun. *8* (1) (2017) 15806.
[191] F. Zaera, New advances in the use of infrared absorption spectroscopy for the characterization of heterogeneous catalytic reactions, Chem. Soc. Rev. *43* (22) (2014) 7624–7663.
[192] F. Zaera, Probing catalytic reactions at surfaces by infrared spectroscopy, ChemPhysChem 15 (18) (2014) 3116–3136, https://doi.org/10.1002/cphc.201402432.
[193] D. Zhang, C. Jin, H. Tian, Y. Xiong, H. Zhang, P. Qiao, J. Fan, Z. Zhang, Z. Li, J. Li, An In situ TEM study of the surface oxidation of palladium nanocrystals assisted by electron irradiation, Nanoscale *9* (19) (2017) 6327–6333.
[194] X. Zhang, J. Meng, B. Zhu, J. Yu, S. Zou, Z. Zhang, Y. Gao, Y. Wang, In situ TEM studies of the shape evolution of Pd nanocrystals under oxygen and hydrogen environments at atmospheric pressure, Chem. Commun. *53* (99) (2017) 13213–13216.
[195] L. Zhang, B.K. Miller, C. Peter, Atomic level in situ observation of surface amorphization in anatase photocatalyst during light irradiation in water vapor, Microsc. Microanal. *19* (S2) (2013) 1724–1725.
[196] H. Zhang, C. Wang, H.-L. Sun, G. Fu, S. Chen, Y.-J. Zhang, B.-H. Chen, J. R. Anema, Z.-L. Yang, J.-F. Li, In situ dynamic tracking of heterogeneous nanocatalytic processes by shell-isolated nanoparticle-enhanced Raman spectroscopy, Nat. Commun. *8* (1) (2017) 15447.
[197] L. Zhao, J.S. Gao, C.M. Xu, Methods and applications of molecular simulation in catalyst research, Pet. Sci. Technol. *24* (12) (2006) 1395–1415, https://doi.org/10.1080/10916460500295140.
[198] H. Zhao, Y. Zhu, H. Ye, Y. He, H. Li, Y. Sun, F. Yang, R. Wang, Atomic-scale structure dynamics of nanocrystals revealed by in situ and environmental transmission electron microscopy, Adv. Mater. *35* (50) (2023) 2206911, https://doi.org/10.1002/adma.202206911.
[199] A. Zheng, S.-J. HUANG, W. Qiang, H. Zhang, D. Feng, L. Shang-Bin, Progress in development and application of solid-state NMR for solid acid catalysis, Chin. J. Catal. *34* (3) (2013) 436–491.
[200] L. Zheng, L. Zhao, S. Zhao, X. Zhang, K.C. Bustillo, Y. Yao, X. Yi, M. Zhu, W. Li, H. Zheng, A unique pathway of PtNi nanoparticle formation observed with liquid cell transmission electron microscopy, Nanoscale *12* (3) (2020) 1414–1418.