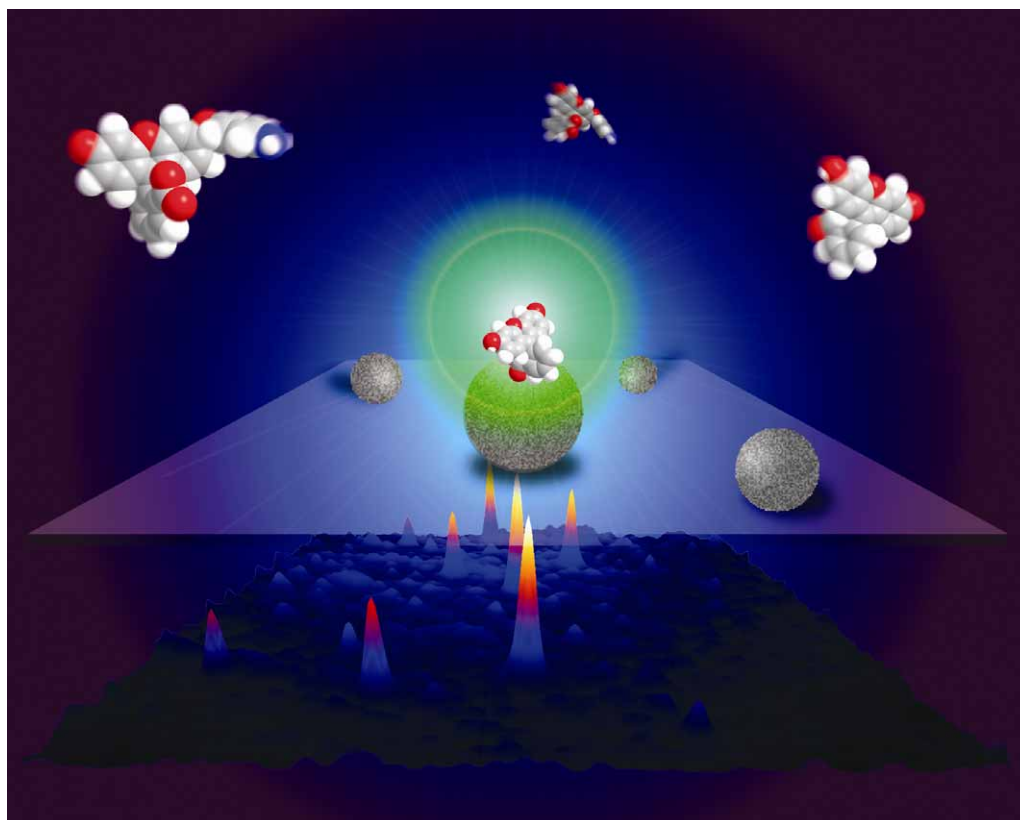# Chem Soc Rev

This article was published as part of the

In-situ characterization of heterogeneous catalysts themed issue

Guest editor Bert M. Weckhuysen

Please take a look at the issue 12 2010 table of contents to access other reviews in this themed issue

Identifying reaction intermediates and catalytic active sites through *in situ* characterization techniques†

Andrew J. Foster and Raul F. Lobo*

This *tutorial review* centers on recent advances and applications of experimental techniques that help characterize surface species and catalyst structures under *in situ* conditions. We start by reviewing recent applications of IR spectroscopy of working catalysis, emphasizing newer approaches such as Sum Frequency Generation and Polarization Modulation-infrared reflection absorption spectroscopy. This is followed by a section on solid-state NMR spectroscopy for the detection of surface species and reaction intermediates. These two techniques provide information mainly about the concentration and identity of the prevalent surface species. The following sections center on methods that provide structural and chemical information about the catalyst surface. The increasingly important role of high-pressure X-ray photoelectron spectroscopy in catalyst characterization is evident from the new and interesting information obtained on supported catalysts as presented in recent reports. X-Ray absorption spectroscopy (XANES and EXAFS) is used increasingly under reaction conditions to great advantage, although is inherently limited to systems where the bulk of the species in the sample are surface species. However, the ability of X-rays to penetrate the sample has been used cleverly by a number of groups to understand how changing reaction conditions change the structure and composition of surface atoms on supported catalyst.

Introduction

The discovery, development and improvement of heterogeneous catalysts are central to the activities of many research groups

Center for Catalytic Science and Technology, Department of Chemical Engineering, University of Delaware, Newark, DE 19716, USA. E-mail: lobo@udel.edu
† Part of the themed issue covering recent advances in the *in-situ* characterization of heterogeneous catalysts.

throughout the world. These activities motivate scientists, and because of their potential impact on society at large are often used as justification for pursuing general research in heterogeneous catalysis. These issues can be approached from a number of directions including high-throughput experimentation where faster and more accurate screening methods are used to identify the 'right' material to carry out a reaction quickly and with high selectivity. Alternatively, the discovery, development and improvement of heterogeneous catalysts can

Andrew J. Foster

Andrew Foster graduated from the University of Washington in 2008 with a BS in Chemical Engineering. He is currently working towards his PhD in chemical engineering at the University of Delaware under the supervision of Dr Raul Lobo. His research focus is on the development of novel catalysts for the conversion of lignocellulosic biomass to sustainable fuels.

Raul F. Lobo

Raul F. Lobo is professor of Chemical Engineering at the University of Delaware. His research interests span the development of novel porous materials for catalysis and separations, the chemistry of zeolites at high temperatures, the development of novel photocatalysts for environmental applications and the scientific aspects of catalyst synthesis. He has published over ninety refereed reports and he is co-inventor in three US patents. He obtained his undergraduate degree in Chemical Engineering at the University of Costa Rica and later moved to California to pursue graduate studies in Chemical Engineering at Caltech. He worked for one year at Los Alamos National Laboratory, New Mexico as a postdoctoral fellow and started his academic career at the Center for Catalytic Science and Technology, Department of Chemical Engineering, University of Delaware in 1995.

This journal is © The Royal Society of Chemistry 2010

Chem. Soc. Rev., 2010, **39**, 4783–4793 | 4783

be approached using a detailed molecular point of view, whereby the catalytic reaction is conceived as a series of elementary reaction steps occurring on an active site. This second approach benefits from insights from *in situ* characterization techniques that examine surface species and surface structure and composition under actual—or near actual—reaction conditions. This short review focuses on new developments in this area and summarizes recent applications of *in situ* catalyst characterization techniques that have impact in the development of catalytic reaction mechanisms and by extension, on the discovery, development and improvement of heterogeneous catalysts.

Given that a catalytic reaction can be described as a series of elementary reaction steps, a reliable reaction pathway that can be used to develop testable hypotheses as to the effect of catalyst modifications on rates and selectivity first needs to be established. The second key ingredient is a molecular-level description of the active catalytic site(s) including the identity of the atoms that form the site, their distribution in three-dimensional space and how geometric and electronic factors in the active site affect reaction rates. *In situ* characterization techniques aim to clarify these two issues, keeping in mind that practical catalysts are complex and dynamic. The development and application of spectroscopic techniques to heterogeneous catalysts during reactions has received increasing attention from the scientific community in recent years.[1–3]

This review centers on recent advances and applications of experimental techniques that help characterize surface species and catalyst structure under *in situ* conditions, especially as applied to supported catalysts. We start by looking into recent applications of IR spectroscopy of catalysis emphasizing newer approaches such as Sum Frequency Generation and Polarization Modulation-infrared reflection absorption spectroscopy. This is followed by a section on recent advances in solid-state NMR spectroscopy for the detection of surface species and reaction intermediates. The following sections center on methods that provide structural and chemical information about the catalyst surface. In particular we describe recent applications of X-ray photoelectron spectroscopy and X-ray absorption spectroscopy (XANES and EXAFS). To maintain brevity, we have omitted environmental Transmission Electron Microscopy, a technique with great promise for elucidating the surface structure of working catalysts under simulated reaction conditions.[4]

Infrared spectroscopy

Infrared spectroscopic techniques are widely used to elucidate the composition of adsorbed species on solid surfaces. The dipole restriction on IR absorption makes some vibrations invisible to IR spectroscopy techniques, but it is possible to study many vibrational modes common in heterogeneous catalysis such as C–O, C–H, N–O, and N–H.[5] Binding to different sites on a solid surface can cause frequency shifts in bond vibrations, and this can give information about the sites themselves.[5] Gas phase subtraction is necessary under *in situ* reaction conditions, as many surface species have IR bands in the same regions as their gas-phase analogs.[6] The degree of gas-phase subtraction needed can be limited by reducing the

pathlength of the IR beam, but the accuracy of this subtraction still limits the extent to which signal intensities can be quantified.[7] Recent examples illustrate the application of classical IR techniques to gain information about reaction mechanisms are discussed below.

The mechanism of gas-phase NO_x reduction over Ag–zeolite Y and BaNa–zeolite Y catalysts has been characterized with infrared spectroscopy by Yeom *et al.*[8,9] By monitoring the changes in concentration of nitrogenous species over time using IR the authors were able to identify all of the relevant species under reaction conditions, and monitor how their concentrations changed with time in batch experiments. For the reduction of NO_2 with NH_3, the presence of NO was found to be necessary for the completion of the reaction. NO enables the formation of NH_4NO_2, which degrades quickly into N_2 and H_2O. The observation of the many relevant species during reaction led to a complete mechanistic picture of the reaction, and this level of understanding is necessary to develop fundamentally accurate kinetic models. Interestingly, they do not report a chemisorbed structure for any of the reaction intermediates. All intermediates shown in their reaction scheme are physisorbed species from the gas phase or surface-bound ions. The mechanism by which Ba^{2+} and Na^+ cations facilitate the catalytic reaction still remains to be determined.

Surface species can also be identified with IR during heterogeneously catalyzed reactions in the liquid phase. Ebbesen *et al.*[10] studied the mechanism of nitrite ion hydrogenation over Pt–Al_2O_3 in aqueous solution using attenuated total reflection infrared spectroscopy (ATR-IR). After subtraction of the infrared absorption of water, peaks for several surface-bound nitrogen species could clearly be observed in the IR spectra. By monitoring the intensity of each of these peaks, transient changes in the concentration of several species could be observed in response to sudden changes in reaction conditions. Continuous hydrogenation experiments revealed that a partially hydrogenated unknown species labeled as "HNO" was the most abundant nitrogen-containing surface species. This led to the conclusion that further hydrogenation of this intermediate is the rate-determining step in this reaction.

Infrared spectroscopic techniques are useful not only for identifying the adsorbed species, but also learning new information about where they are bound. Shimizu *et al.* used IR spectroscopy to study the mechanism of isopropanol dehydrogenation over Ag–Al_2O_3.[11] *In situ* IR measurements were used to show that the reaction proceeds *via* an isopropoxide intermediate, and that the rate-determining step is the abstraction of hydrogen to convert bound isopropoxide to acetone. Infrared spectra of isopropanol adsorption on both the bare support and the supported catalyst revealed that during reaction isopropanol adsorbs first to the support and the reaction proceeds *via* hydrogen abstraction by the Ag particles near metal–support boundaries. This mechanism involves multiple active catalytic sites that are not dispersed over the catalyst surface with perfect uniformity, indicating that a simple Langmuir–Hinshelwood kinetic model may not be realistic for this system. This study also reveals a process in which different elementary steps of the reaction occur at

different catalytic sites. Since these sites are segregated, geometric information about the catalyst surface needs to be incorporated to develop effective kinetic models of this system.

Combining infrared spectroscopy with the analysis of isotopic transients is a powerful tool in elucidating the mechanisms involved in surface reactions. By operating under steady-state reaction conditions and quickly switching to feed of isotopically labeled reactants, the rates at which surface species are interchanged can be observed spectroscopically. For instance, Li et al.[12] observed CO oxidation over Au–FePO$_4$. Using isotopic labeling, it was found that oxidation proceeds through two separate pathways with comparable rates. The FePO$_4$ support can be reduced and act as a source of oxygen for the reaction or the reaction can also take place using oxygen directly adsorbed onto the gold particles from the gas phase. These two pathways will have different kinetic behavior, and it would be difficult to capture the temperature and pressure dependence of both mechanisms in a simple Langmuir–Hinshelwood-type kinetic expression. Without the use of isotopic exchange, these two pathways would be nearly impossible to distinguish.

The abundance of a surface species is not always indicative that it is an important reaction intermediate. Tibiletti et al.[13] used diffuse-reflectance IR and isotopic exchange to study the water–gas shift reaction on Pt–ZrO$_2$. The IR experiments showed an abundance of formate species on the Pt surface under reaction conditions. This had been observed before, and past authors[14,15] had concluded that the formates must be intermediates in the most active reaction pathway. However, the use of a steady-state isotopic transient approach showed that after a quick exchange of ^{12}CO for ^{13}CO, the production of ^{13}CO$_2$ reaches a steady-state value long before the surface formates are repopulated as ^{13}C formates, suggesting that the formates are merely a "spectator species" in the reaction.

These examples demonstrate the flexibility of classical infrared techniques for the study of reaction mechanisms. However, due to the limits of gas-phase subtraction the need for techniques which give quantitatively accurate information at higher gas pressures still exists. Two such techniques are sum frequency generation and polarization-modulation infrared reflection-absorption spectroscopy. Both of these techniques lend themselves well to the study of catalytic materials under realistic reaction conditions.

Sum frequency generation

Sum frequency generation (SFG) is a nonlinear optical phenomenon where two incident photons are absorbed, and a photon with a frequency equal to the sum of the frequencies of the incident photons is emitted.[16] Due to the selection rules governing SFG, it does not occur within any medium with inversion symmetry (such as bulk solids, liquids and gases), but can occur near interfaces between two phases.[16] By using a monochromatic visible laser and a tunable IR source, SFG can probe the vibrational levels of species adsorbed on a catalyst surface, yielding information complementary to other IR techniques.[16] No gas phase subtraction or background spectra are needed due to the inherent surface sensitivity of the technique. This makes SFG spectroscopy useful in studying

heterogeneous catalysis because it is not limited by the presence of gas at high pressures, as with other vibrational spectroscopy techniques that require vacuum conditions.[16]

One drawback of the technique is that the strength of the SFG signal decreases dramatically as the dimensions of the particles studied fall below the coherence length of the laser.[17] Multifaceted nanoparticles will also emit SFG photons diffusely, making it difficult to capture a strong SFG signal at a single detector.[16] However, some of these limitations can be overcome by modifying the technique. Reflective substrate materials with well-defined geometry and total internal reflection can be used to enhance the SFG signal.[17] Sum frequency signals also have a limited spectral range and are typically only measurable in the IR energy range from 1600–4000 cm^{-1}, which allows for the identification of some vibrations such as C–O, N–O, and C–H but makes it difficult to study the infrared "fingerprint region" (<1500 cm^{-1}) for bound organic species.[16]

Quantification of SFG spectral data remains difficult as different surface species have different sensitivity to the technique.[18] The sensitivity of many surface species is coverage-dependent and affected by both IR and Raman moments, and the relationship between these factors and the SFG sensitivity has not been accurately predicted by DFT calculations. Backus and Bonn[19] have shown that during CO adsorption on a stepped Pt(533) surface the SFG signal for the C–O stretch may not monotonically increase as coverage is increased. This suggests that a straightforward quantitative relationship between SFG signal and coverage may be impossible to develop for some coverage regimes. This remains as a challenge which must be overcome to make SFG a reliable technique for quantitative in situ measurement of surface coverage. Currently, any quantitative use of SFG signals must first be calibrated using other techniques such as XPS or TPD.

SFG can be used to evaluate mechanistic differences between metal single crystals and supported model catalysts under ambient pressure conditions. Baumer et al.[20] used SFG as part of a study on the decomposition and partial oxidation of methanol on a model Pd–Al$_2$O$_3$ catalyst surface. Comparison of SFG spectra between a Pd single crystal and the supported model catalyst under a reactive atmosphere helped to reveal that methanol C–O bond scission only occurs on the supported catalyst. This suggests the importance of under-coordinated edge sites or metal–support synergy in the catalytic decomposition of methanol.

Similarly, Höbel et al.[21] have studied Pd nanoparticles supported on a thin film of niobia over a copper–gold substrate. The reflectivity of the copper–gold substrate used enhanced the SFG signal and made it possible to observe vibrational spectra of CO on the supported Pd nanoparticles under gas pressures up to 100 mbar. At high CO pressures, the intensity ratio between the bridge-bound CO and linear-bound CO remained the same as observed under UHV conditions.

Yeganeh et al.[17] developed a method to enhance the net SFG signal from high surface area materials composed of small particles. By supporting catalyst particles on a single crystal sapphire prism and using total internal reflection within the prism, the effects of destructive interference on the SFG signal were reduced (Fig. 1). Using total internal reflection
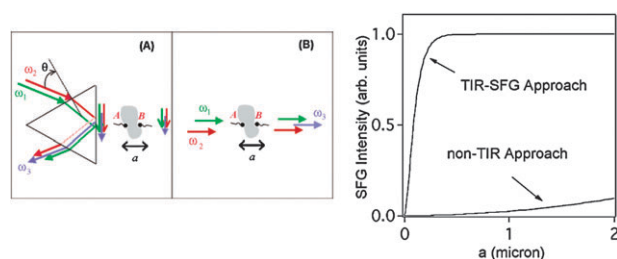
Fig. 1 An illustrated comparison of SFG spectroscopy using the (A) TIR approach and the (B) non-TIR approach. The graph on the right shows the signal strength advantage of using TIR geometry for SFG measurements on small particles. Reproduced with permission from ref. 17.

SFG (TIR-SFG), methanol adsorption on porous powdered silica was measurable: this was not possible using conventional SFG techniques. This modification to SFG measurements expands the potential application of SFG beyond flat model catalysts, to the point where it can possibly be applied to a more realistic powdered catalyst.

Waldrup and Williams[23] have also used TIR-SFG for studying adsorbates on a powdered, supported catalyst. The signal enhancement was demonstrated by studying CO adsorption on a supported Pt–Al_2O_3. The results were in good agreement with IR studies on CO binding in other Pt–Al_2O_3 systems. Bratlie et al.[22] have applied TIR-SFG to the hydrogenation of pyridine on Pt nanocubes supported on a sapphire-reflecting prism. Using different combinations of s- and p-polarized laser pulses, it is possible to determine the orientation of surface adsorbates. The SFG spectra revealed that the hydrogenation reaction proceeds via a pyridinium cation bound to the surface through the nitrogen atom (Fig. 2). This example demonstrates that SFG can be a useful tool for identifying the presence and conformation of surface intermediates at ambient pressures on catalytic nanoparticles. This further demonstrates that TIR-SFG is a viable technique to study adsorbate vibrational properties on real catalysts under in situ conditions.

A recent study has reported the measurement of SFG spectra in the 1290–1410 cm^{-1} energy region, within the IR "fingerprint" region. Bozzini et al.[24] used SFG to observe the formation of surface species during electrocatalytic oxidation of ethanol over Pt–WC. SFG peaks appearing at 1330 cm^{-1}
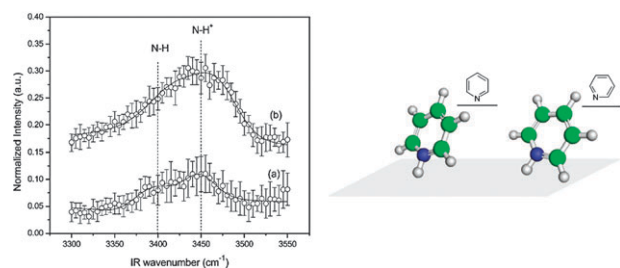

Fig. 2 SFG vibrational spectrum of adsorbed pyridine on Pt nanoparticles (left). The appearance of the N–H$^+$ peak suggested that pyridine binds to the nanoparticle surfaces primarily as upright pyridinium cations, as shown on the right. Reproduced with permission from ref. 22.

and 1345 cm^{-1} allowed the O=C=O asymmetric vibration of a bound acetate species and the combined O–H, C–H, and CH_2 wagging modes of surface ethanol.

The application of SFG to the study of catalysis has not been extensive in the last few years, but it has demonstrated its value for the in situ study of bound surface species. Improvements in the resolution and the sensitivity of the technique are needed to match the detail of spectra collected in other methods. The technique is difficult to apply in practice, and a small number of research groups have used the technique to study catalysis. However, the application of SFG to real, powdered catalysts under high pressures could make it a powerful tool for the elucidation of reaction mechanisms under industrially relevant conditions.

PM-IRAS

Polarization modulation infrared reflection absorption spectroscopy (PM-IRAS) is performed by taking two infrared reflection-absorption measurements: one with s-polarized light (parallel to surface) and one with p-polarized light (parallel to surface normal).[25] The gas phase contribution to the spectrum recorded with either polarization will be the same, but surface species are much more sensitive to p-polarized light than s-polarized light. By taking the difference between the two spectra, the gas phase IR absorbance can be removed, leaving behind the contribution of the surface species. This technique makes it possible to get vibrational spectra of bound species, even under high gas pressures. PM-IRAS has a shorter acquisition time than SFG and makes it possible to study a wider frequency range.[25] Gas phase spectra are also acquired in the process, allowing for side-by-side comparison to surface spectra. Also, the intensities of the IR signals have simpler coverage dependence than SFG, which makes quantitative interpretation of PM-IRAS less difficult.[19] PM-IRAS requires a planar reflective surface, and this hinders the application of the technique to real, powdered catalysts.[26] Multifaceted surfaces scramble polarized fields, and this leads to the disappearance of the difference between the s- and p-polarized spectra. Consequently, most published PM-IRAS studies have been over single crystal surfaces. However, if samples are prepared carefully, it is possible to observe surface species on more complex materials using PM-IRAS and a few groups have begun to apply the technique to supported model catalysts.

PM-IRAS on model catalysts can be used to connect information from single crystal studies to more realistic materials. Ozensoy et al.[27] used PM-IRAS to study the adsorption and dissociation of CO on a Pd–SiO_2–Mo(112) model catalyst. The IR peak corresponding to CO bound to the primarily (111)-faced Pd nanoparticles disappeared at around 600 K, similar to observations on a Pd(111) single crystal. However, Auger electron spectroscopy measurements revealed the presence of surface carbon on the Pd nanoparticles, and this was not observed in single crystal studies. The PM-IRAS data allowed the authors to conclude that CO dissociation can occur on the defect sites of the Pd nanoparticles. Although this work is not a major extension from experiments over a single crystal, it is one of the first efforts to

take spectroscopic measurements on a metal surface with defects and undercoordinated sites. This is a step towards studies of surface species present on nanoparticulate metal catalysts containing many of these sites.

PM-IRAS on model catalysts has been valuable in identifying changes occurring between vacuum and ambient pressures. Gao et al.[28] used PM-IRAS to study the effects of alloying in a Pd–Au–TiO$_2$ model catalyst for CO oxidation. Under vacuum, it was found that alloying Au into the Pd particles dramatically reduced the activity of the catalyst. However, the Pd–Au alloy particles were much more active than the purely Pd catalyst under higher pressure conditions. This increase in activity is assigned to the preferential segregation of Pd to the surface of the catalyst. PM-IRAS allowed for the identification of different bound states of CO. In temperature-programmed spectroscopic measurements, it was shown that the peak assigned to CO bound atop Au disappeared at relatively low temperatures, suggesting that Au aided in CO desorption. This is an example of the dramatic changes in catalytic activity that can take place when crossing the "pressure gap", emphasizing the need for spectroscopic techniques capable of probing surface species at high gas pressures.

Surface-specific spectroscopic techniques can also be used to monitor the coverage of reactive species. Diemant et al.[29] have applied PM-IRAS to CO adsorbates on Au nanoparticles on a TiO$_2$ film supported over a Ru(0001) substrate. By using PM-IRAS to monitor surface coverage at near-ambient pressures (50 mbar) and using coverage-pressure behavior to calculate binding strength, it was shown that at low coverage CO binds more strongly to gold nanoparticles as their size is decreased. As CO coverage is increased, the CO binding energy approaches similar values for all particle sizes.

PM-IRAS has also been applied to a powdered, supported catalyst. Oosterbeek[26] used the technique to study CO vibrations at ambient pressures on Co Fischer–Tropsch catalyst surfaces. By spin-coating a powdered, supported Co/SiO$_2$ catalyst on a reflecting gold substrate, infrared surface reflection was enhanced enough to allow PM-IRAS measurements of CO adsorption on the Co metallic sites. The study also showed that on a clean Co surface, CO adsorption was observed on atop sites, while on a defect-covered surface, CO was observed to form geminal dicarbonyl species. On the powdered catalyst,

the C–O stretch peak observed was in the same region as the geminal species found on the defected crystal surface. In the presence of syngas the geminal species disappeared from the spectra, and this was attributed to Fischer–Tropsch chain growth occurring on defect sites, with the terrace sites acting as a source of CO "monomers." The evidence provided by PM-IRAS has shown the mechanistic importance of the different surface sites on a supported Co catalyst.

Like SFG, PM-IRAS is not limited to the vapor phase. Meier et al.[30] have applied PM-IRAS to study the liquid-phase reaction of benzyl alcohol over a sputtered Pd film (Fig. 3). PM-IRAS allowed the authors to clearly distinguish some vibrations of surface-bound species. Although strong absorption from the cyclohexane solvent limited the useful range of the PM-IRAS spectrum, accurate liquid-phase IR subtraction showed aromatic vibrational features ($\sim$1590 cm^{-1}) which would be difficult to detect with SFG.

Nuclear magnetic resonance

Nuclear magnetic resonance (NMR) spectroscopy can be applied under in situ conditions to study the mechanisms of catalytic reactions. ^{1}H and ^{13}C are the most common nuclei studied by NMR, but it can be applied to any nucleus with nonzero spin. NMR has the advantage of being a quantitative technique able to detect minute changes in the chemical state of the nuclei being studied. When magic-angle spinning is used to sharpen NMR peaks (MAS-NMR), spectra with excellent resolution can be obtained allowing the identification and quantification of adsorbed intermediates.[31]

NMR has an inherently low sensitivity and measurements often take much longer than the lifetime of intermediates, so the detection of intermediates present in low concentrations can be especially difficult.[31,32] This is an issue when studying supported metal catalysts; materials that have a relatively limited area where reactive species are present. As a result, the majority of in situ MAS-NMR studies of catalysts have been performed on zeolites and other porous materials containing enough adsorbed reactant to generate a measurable NMR signal.[31–34] NMR techniques are also not surface-specific, and adsorbed chemical species may be difficult to resolve from their fluid-phase analogs. The dependence of spin
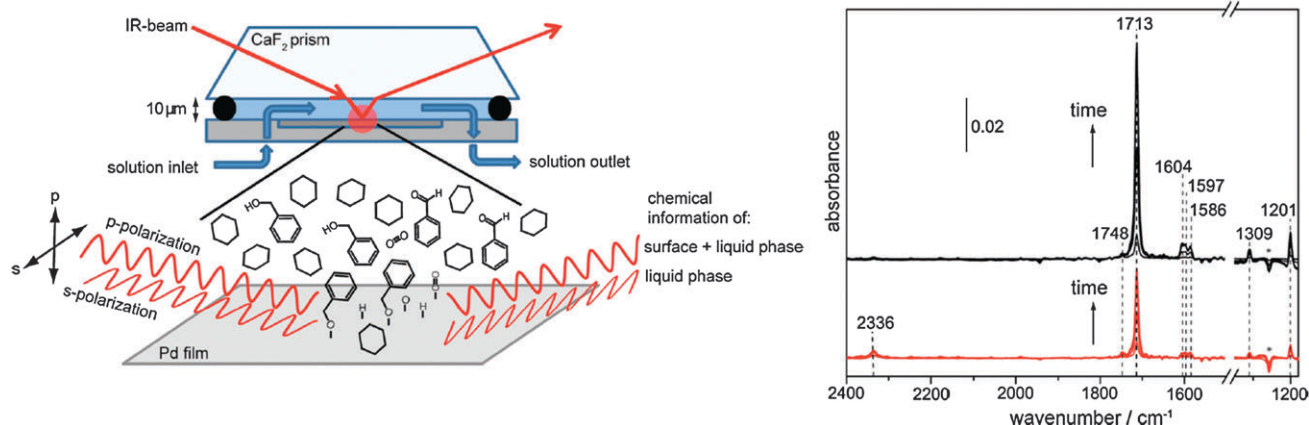

Fig. 3 An illustration of the combined ATR-PM-IRAS used to record liquid-phase surface spectra. Reproduced with permission from ref. 30.

alignment on temperature leads to an NMR signal reduction at higher temperatures.[31] This limitation is important for the study of many catalysts which typically operate at high temperatures in an industrial setting. Often, the effect of elevated temperatures needs to be offset using stronger external magnetic fields, longer data acquisition times, and isotopic enrichment of reactants.[31,33] At present, *in situ* MAS-NMR cells are limited to operating temperatures of below 500 °C.[35]

MAS-NMR experiments can be performed on catalyst samples in glass ampoules to simulate batch reaction conditions.[36] These ampoules are loaded with reactive gases, sealed, and observed using commercially available MAS-NMR equipment.[36] Batch experiments require the reaction to occur significantly slower than the time to heat the catalyst sample to reaction temperature and record NMR spectra.[31] MAS-NMR measurements under continuous flow conditions are considerably more demanding than the batch experiments described above.[35] Continuous flow cells have the advantage of being able to record steady-state MAS-NMR spectra, but have not been widely used due to the difficulty of their construction.[35] Achieving a gas-tight seal between the rotating sample chamber and the gas inlet/exhaust is necessary for taking measurements at elevated pressures.[33] To date, rotation speeds up to 3 kHz are possible while maintaining a seal between the rotating sample and the remainder of the equipment at gas pressures above 10 MPa.[38] There have been several successful *in situ* NMR studies on heterogeneously catalyzed reactions using batch cells and some using flow cells and a selected set of examples is discussed in this section.

In situ ^{1}H and ^{13}C batch MAS-NMR techniques have been used by various groups to study the mechanism of alkane aromatization over Zn-exchanged zeolites. Arzumanov et al.[39] used ^{13}C NMR to study the mechanism of ethane aromatization over Zn/H-Beta, and found that zinc–methyl and zinc–ethyl species formed by dissociative adsorption. This suggested that hydrogen abstraction by Zn–O sites was a necessary step in the aromatization reaction. In a similar study,[40] ^{13}C NMR was used to show that the formation of zinc–propyl species was followed by further hydrogen extraction to form propene over Zn/H-ZSM-5. In these cases, reaction intermediates and the sites to which the intermediates were bound could be identified by NMR. The sensitivity of magnetic precession frequency to chemical environment makes it possible to detect minute chemical changes, unnoticeable through other spectroscopic techniques. This level of detail makes it possible to observe the interaction between reactants and catalytic sites.

In situ batch NMR experiments can be highly effective at identifying reactive intermediates for reactions which occur slower than the NMR scan time. Roy et al.[37] used *in situ* ^{1}H and ^{13}C NMR measurements to characterize the room-temperature reaction of anthranilimide and acetone to quinazolinone over sulfonic acid-grafted silica. The NMR spectra collected over the course of the reaction revealed that a Schiff base is an important intermediate. They show it is formed early in the reaction and disappears as the reaction reaches completion. Evidence from the aromatic proton region of the spectra (6.5–8 ppm) made it possible to propose two possible mechanisms for the reaction (Scheme 1). Because this reaction
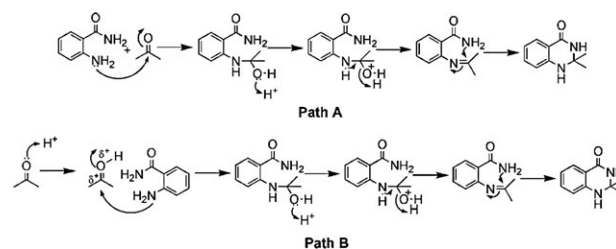
Scheme 1 Possible mechanisms for quinazolinone formation from anthranilimide as determined by Roy *et al.* Reproduced with permission from ref. 37.

occurred relatively slowly, spectra recorded at different points during the reaction were able to clearly resolve the progressive shift from the reactants to intermediate species and products.

Huang et al.[42] used ^{13}C MAS-NMR to study the mechanism of ethylbenzene disproportionation on zeolites X, Y, and ZSM-5. It was found that in the case of large-pore zeolites X and Y that ethylbenzene disproportionation occurred *via* a bimolecular pathway, forming a diphenyl species inside the zeolites. Protonation of one of the phenyl groups allowed for the cleavage of the diphenyl bond, and disproportionation to diethyl benzene and benzene. NMR during the same reaction over medium-pore zeolite ZSM-5 revealed a different dominant reaction mechanism. A ^{13}C signal occurring at 73 ppm indicated the formation of ethoxy groups bound within the zeolite, most likely a result of direct protonation of ethyl benzene by the zeolite acid sites. These bound ethoxy groups are able to react with ethyl benzene to form diethyl benzenes. This example shows how *in situ* NMR techniques were able to distinguish two different reaction mechanisms occurring on acid zeolites, dependent on the accessibility of transition states constrained within the zeolite pores.

Marthala et al.[43] used a combination of ^{1}H, ^{13}C, ^{15}N, and [29]Si to study the mechanism of the Beckmann rearrangement of cyclohexanone oxime over zeolites and mesoporous silica. Using isotopically labeled cyclohexanone oxime, the reaction was found to proceed first to an O-protonated caprolactam. The adsorbed intermediate could then go through a ring-opening step to form aminocapric acid either directly or after a proton transfer from the oxygen to the amine group in the caprolactam. The use of *in situ* NMR made it possible to identify all of these intermediates during reaction and help elucidate the likely intermediates in the reaction. ^{29}Si NMR on the catalysts during reaction showed that Si(OSi)$_3$OH groups were most abundant on the most active silica-based catalyst tested, suggesting that these are the source of the acidic proton for the initial protonation step.

Continuous flow MAS-NMR studies have been less common than batch studies, but they have also recently been performed to characterize the reaction of methanol over zeolite catalysts. Jiang et al.[44] studied intermediates during the methanol-to-olefin (MTO) reaction over SAPO-34 using a combined ^{13}C NMR/UV-VIS cell. At temperatures below 250 °C dimethyl ether was the only product formed. Only two peaks were observed in the NMR spectra under these conditions at 61 ppm and 50 ppm, corresponding to dimethyl ether and methanol, respectively. At higher temperatures, new

NMR peaks begin to form in the alkane region (ranging from 10–40 ppm) and the aromatic/alkene region of the spectra (from 120–140 ppm), suggesting the formation of polyalkylated aromatics within the cages of the zeolite structure. The intensity of these aromatic peaks correlated strongly with the rate at which light olefins were produced from the reaction, suggesting that they play an important role in the desired reaction chemistry.

X-Ray photoelectron spectroscopy

X-Ray photoelectron spectroscopy (XPS) is a widely used technique for elemental characterization of catalysts under UHV conditions.[45] As opposed to IR, XPS provides information about the composition of the catalytic surface, and little about the reactive species present on the surface.[45] This technique is inherently surface-sensitive as ejected electrons can only escape from a few nanometres below the gas–solid interface.[46] The need to accurately determine the energy of ejected photo-electrons makes XPS difficult to apply under high gas pressures, due to electron scattering by the gas phase.[47] However, the application of smaller aperture sizes and differentially pumped vacuum chambers has made it possible to record XP spectra at pressures up to 1 mbar.[47] The technique is still not able to perform measurements at atmospheric pressure, but has successfully bridged the "pressure gap" by several orders of magnitude in recent years. This technique is relatively new, and only two instruments capable of taking high pressure XPS (HP-XPS) measurements are currently available to the scientific community.

HP-XPS identification of the surface elemental composition of catalysts under *in situ* conditions has the potential to reveal a great deal about the active surfaces for catalytic reactions. Reactants in the gas phase above a catalyst can cause reversible migrations of metal atoms within catalytic particles, and often this restructuring cannot be observed by XPS measurements on the catalyst "post-mortem" under vacuum conditions.[25] These changes in surface composition will influence the kinetics of adsorption, surface reaction, and desorption processes on the catalyst.

HP-XPS has been used by Caballero *et al.*[41] to observe the metal–support interaction in a nickel–ceria catalyst. Under a hydrogen atmosphere at 300 °C, the nickel nanoparticles change from an oxidized state to metallic state. However, as temperature is increased to 500 °C, the nickel particles become buried under the ceria support. This phenomenon could not be observed by conventional *ex situ* XPS, as evacuating the gas above the catalyst leads to ceria migration away from the nickel particles (Fig. 4).

A related surface restructuring has been observed by Tao *et al.*[48] using HP-XPS on bimetallic nanoparticles. Rh–Pd and Pt–Pd (50 wt% Pd in both cases) core–shell nanoparticles were observed to undergo significant changes in surface composition when conditions inside the HP-XPS cell were changed from oxidizing to reducing. In bimetallic particles composed of equal parts Rh and Pd, oxidizing conditions cause Rh to preferentially segregate to the particle surface, while reducing conditions drives the Pd to the surface. This information is vital to understanding the activity of the catalyst under
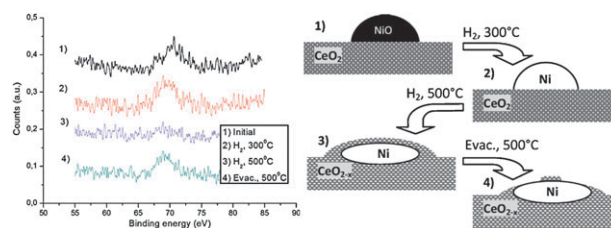

Fig. 4 HP-XPS spectra of the Ni–CeO$_2$ catalyst under changing reaction conditions. The spectra show the catalyst (1) in its initial state, (2) reduced to metallic Ni under 300 °C of hydrogen, (3) Ni burial at 500 °C, and (4) return of Ni to the surface after evacuation. Reproduced with permission from ref. 41.

different operating conditions, and the restructuring could potentially be used to develop gas-responsive dynamic catalysts. Indirectly, a thorough understanding of surface composition under reaction conditions is useful for the identification of plausible surface species and reactive intermediates.

Piccinin *et al.*[49] have shown that Ag–Cu catalyst particles for ethylene epoxidation undergo surface structural changes dependent on reactant pressures and temperature. Under vacuum, Cu seems to preferentially segregate to the surface of the Ag particles, and this effect is enhanced by placing the samples in oxygen or a mixture of ethylene and oxygen. HP-XPS experiments performed at BESSY showed that the surface copper formed an oxide layer on the outer surface of the particles, which is very different from the Cu–Ag surface alloy previously assumed to be the active catalytic surface. This is a demonstration of how HP-XPS can be used as a tool to study the dynamic changes that catalysts undergo with changes in reactant pressures. This type of information is valuable for the construction of accurate molecular models of surface chemistry.

Changing gas composition can also drive the migration of catalytic species in mixed oxide catalysts. M1 is a potential catalyst for selective oxidation reactions on hydrocarbons. Sanfiz *et al.*[50] have shown that the M1 phase (a MoVTeNb mixed oxide) undergoes changes in surface composition in response to the gas atmosphere. *In situ* XPS measurements showed that the most active catalyst sample for this reaction had the highest surface concentration of Te under reaction conditions, and the lowest concentration of Mo of samples tested. This suggests that surface Te species play a valuable role in this catalytic reaction. The authors further showed that at elevated temperature in the presence of water, the volatile Mo and Te species tended to migrate, leading to significant changes in the surface composition throughout the experiment.

By tuning the incident X-ray energy, a depth profile can be generated to study the catalyst composition as a function of distance from the catalyst surface.[46] Vass *et al.*[51] have reviewed the use of HP-XPS depth profiling to study the role that carbon deposition from gas phase reactants can play in catalytic activity. It was found that the deposited carbon behaves in a number of different ways, depending on the catalyst used and the reaction conditions. In the case of hydrocarbons reacting over Pd, deposited carbon was found to dissolve into the bulk to form a PdC phase. This new phase

has a different electronic and geometric structure than metallic Pd, and was found to be less active but more selective for partial hydrogenation of 1-pentyne. The carbide phase was found to decompose back to metallic Pd in the absence of 1-pentyne, suggesting that the formation of this catalytic phase could not have been observed under *ex situ* conditions.

Slight shifts in the position of XPS peaks can be used to determine some information about the chemical environment of the elements in a catalyst.[45] Herranz *et al.*[52] have used the technique to study CO oxidation over Au nanoparticles supported by TiO_2. Through HP-XPS measurements, the authors concluded that the majority of gold remains in the metallic state under reaction conditions. The higher catalytic activity of Au–TiO_2 than Au–SiO_2 was attributed to charge transfer between the particles and the reducible TiO_2 support, and this effect was observed as Au peak broadening in the HP-XPS measurement. It should be noted that in a related study,[53,54] *ex situ* XPS measurements were used to show that cationic Au is the catalytic species responsible for CO oxidation over an Au–CeO_2 catalyst, even when these species are present only in small amounts. It is also possible that this is the case over the Au–TiO_2 catalyst. Just as the abundance of a surface species does not necessarily imply its mechanistic importance, the abundance of a particular element on the catalytic surface does not necessarily mean it is the most active catalytic phase.

The examples discussed above show that HP-XPS is useful for understanding the relationship between surface composition and catalytic activity. This technique is still limited to gas pressures near 1 mbar, but this limit can be increased by decreasing aperture sizes and improving differentially pumped vacuum chambers.[56] In addition, the signal-to-noise ratio for these measurements is very low relative to XPS measurements carried out under UHV.[56] This restricts the precision of surface composition measurements under *in situ* conditions.

X-Ray absorption spectroscopy

X-Ray absorption spectroscopy (XAS) is a technique that can be used to extract quantitative chemical and structural information about a catalyst sample.[57] XAS lends itself well to *in situ* studies, as incident X-rays are not strongly absorbed by gases, even at very high pressures.[58] Because XAS experiments require scanning through a range of X-ray energies, these techniques can only be performed with a synchrotron radiation source. The use of *in situ* XAS cells allows for the development of detailed correlations between catalyst activity and catalyst structure.[57] One of the short-comings of XAS techniques is that they are not strictly surface-sensitive.[59] As a result of XAS experiments operating by transmitting an X-ray beam through pressed catalyst wafers, the chemical information obtained by XAS reflects the entire bulk catalyst and not only the catalytic surface.[59] Many catalysts, however, are formed of small particles and the contribution of surface atoms to the measured spectrum can be significant.[57]

Extended X-ray absorption fine structure (EXAFS) is a widely used XAS technique used to study the structure of operating catalysts. By fitting the absorption fluctuations at incident X-ray energies slightly above the absorption edge, the coordination between metal atoms and other atoms within the catalyst can be quantified.[57] This coordination information can be extended to determine the extent of bimetallic bonding within the catalyst, and estimate the average particle size. Due to the nature of the data fitting, the data obtained from EXAFS reflect only the average properties of the catalyst.[60] Supporting techniques such as TEM are needed to capture the full distribution of particle sizes and structures in a sample. At higher temperatures, the thermal motion of atoms within catalyst particles becomes difficult to account for in EXAFS models.[60] This leads to higher uncertainty in the calculated coordination and an apparent contraction in calculated bond lengths from the data.[60]

EXAFS can be used to study the degree of metal–oxygen coordination during oxidation reactions. Alayon *et al.*[61] have used EXAFS to show that supported Pt particles form a Pt-oxide overlayer above 225 °C under oxygen, which is highly active for CO oxidation. At low temperatures under O_2 and CO, EXAFS results showed that the structure of the Pt catalyst was virtually the same as under vacuum. On heating in the presence of CO and O_2, a sudden Pt–Pt coordination number decrease was observed, along with a concurrent increase in Pt–O coordination. The temperature of the change occurred at the ignition temperature for the oxidation reaction, leading to the conclusion that the oxide overlayer was responsible for catalytic activity. The change in average Pt–O coordination was observed to increase as particle size was decreased, suggesting that the oxide phase formed only near the surface of the material, and did not penetrate all the way into the bulk. When cooled below 195 °C, the Pt-oxide layer was reduced back to metallic Pt. This example demonstrates the value of EXAFS in identifying the true catalytically active phase under *in situ* conditions.

Quick EXAFS (QEXAFS) is a modification of conventional EXAFS involving rapid scanning through monochromated X-ray energies.[55] The rapid scanning allows for *in situ* observations of transient structural changes occurring in catalysts with subsecond resolution. The rate of XAS measurements is currently limited by the speed at which the incident X-ray energy can be adjusted and the sensitivity of the X-ray detectors, but improvements in both of these components could improve this resolution down to milliseconds.[55] One interesting example is the QEXAFS study by Grunwaldt *et al.*[55] on the extinction and ignition of methane partial oxidation over Pt– and Pt/Rh–Al_2O_3 (Fig. 5). They demonstrated that reduction of Pt and Rh occurred within seconds upon reaction ignition, and returned slowly to an oxidized state on extinction. The time at which ignition occurred varied with axial position along the reaction chamber, which was observable even with the small reactor setup used. This indicates that catalytic restructuring in response to gas-phase conditions can possibly lead to multiple catalytic regimes with different catalytic behavior.

The oxidation/reduction behavior of Rh particles supported on silica was studied using QEXAFS coupled with temperature-programmed reaction (TPR) in the work of Miyazawa *et al.*[62] QEXAFS spectra taken during TPR showed that the addition of a CeO_2 promoter to the Rh–SiO_2 decrease the temperature at which Rh is oxidized and reduced.
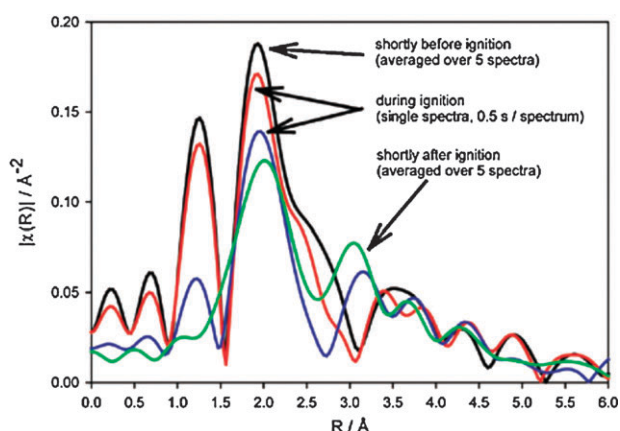
Fig. 5 QEXAFS measurements on a PtRh–Al₂O₃ catalyst during CH₄ partial oxidation show changes in the coordination environment of Pt during ignition. It was observed that ignition led to a decrease in Pt–O bonding (∼1.2 Å) and higher metal–metal coordination. Reproduced with permission from ref. 55.

Analysis of the spectra suggested the formation of a Ce–O–Rh bidentate structure, and it was hypothesized that these sites serve as the source of active oxygen for oxidation reactions. The speed of QEXAFS measurements allowed a wide range of temperatures to be studied, and the point at which the bidentate structure formed could be identified.

Energy dispersive EXAFS (DXAFS) is another XAS technique capable of recording time-resolved absorption spectra.[64] DXAFS takes a spectrum using a single pulse of high-intensity polychromated X-rays.[65] This technique is more demanding than QEXAFS both in terms of necessary equipment and sample preparation. The energy range of a single DXAFS spectrum is not as broad as is possible with QEXAFS, limiting

the flexibility of this technique for the study of multiple edges simultaneously.[65] However, this is currently the only XAS technique that can resolve structural changes in catalysts at timescales as short as milliseconds.[55] As an example, Uenishi *et al.*[64] studied the response timescale of changing gas conditions above a LaFePdO₃ automotive catalyst using DXAFS. Oxidation and reduction of the Pd species in the catalyst under working conditions were found to occur within 1–2 s of changes in gas phase composition. These changes in the catalyst occur faster than typical gas composition fluctuations in automobile exhaust, and the catalyst activity will change dynamically during use.

The dynamic behavior of CeO₂–ZrO₂ mixed oxides and supported Pt particle sintering have also been studied using DXAFS. Nagai *et al.*[63] found that the rate of sintering of Pt supported on Ce–Zr–Y mixed oxides could be correlated to the degree of Ce reduction in the support. Ce⁴⁺ is thought to bind strongly to Pt, limiting its mobility. As Ce⁴⁺ is reduced to Ce³⁺, the Pt atoms are able to migrate on the surface more easily, and particle sintering occurs more rapidly. In addition, it was found that a higher extent of Ce–O–Zr bonding led to a high oxygen release capacity for oxidation reactions (Fig. 6).

Near-edge X-ray absorption spectroscopy (XANES or NEXAFS) studies the X-ray absorption behavior of a sample with incident photon energies ranging from slightly below the core-level electron transition energy to about 50 eV above the absorption edge.[57] XANES can be used to estimate the oxidation state of an element in a solid sample and provide information about local coordination geometry in some cases.[66] XANES may have future applications in quantitatively determining the electronic density of states for the d-electrons relevant in metal catalysts, but the theoretical understanding of whiteline intensities needed for this calculation is not developed enough to do so accurately.[57]
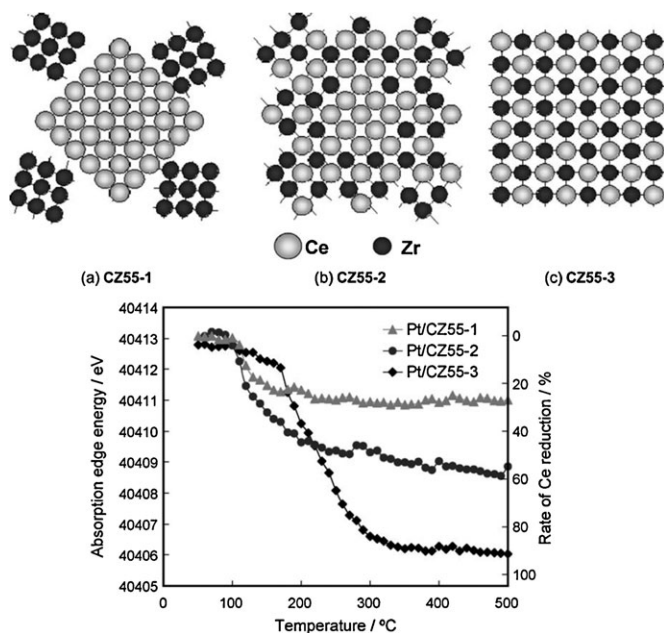

Fig. 6 DXAFS was used by Nagai *et al.* to study the oxygen storage and release capacity of Pt–CeO₂/ZrO₂. DXAFS measurements showed that Ce–O–Zr bonding facilitated oxygen release from the material. Reproduced with permission from ref. 63.

XANES was recently used by Saib et al.[67] to study the oxidative deactivation of a Co–SiO$_2$ catalyst for the Fischer–Tropsch reaction. When exposed to water vapor at elevated temperatures, XANES showed that the outer shell of Co nanoparticles was oxidized to a state resembling a Co$_3$O$_4$ structure. This structure could be reduced back to its original metallic state, but required temperatures in excess of 400 °C under a flow of pure H$_2$. The degree of particle oxidation was found to vary with Co particle size, consistent with the formation of a thin outer layer of the oxide. This example demonstrates the utility of XANES for monitoring the chemical state of metal catalysts to identify conditions which cause otherwise unexpected structural changes.

Kumar et al.[68] used XANES to determine the nature of the active Pd species for methane combustion in an automotive three-way catalyst. In situ measurements during methane combustion showed that Pd-based catalysts are more active for combustion when they form an oxide layer. The Pd was found to be reduced back to the metallic state on cooling below 650 °C, which corresponded to a sharp decrease in methane conversion. Similarly, Li et al.[12] also used XANES to characterize the oxidation state of Au during CO oxidation.

One further use of XAS is the study of reactant adsorption on metallic particles. Bus et al.[69] used XANES to observe structural changes in supported Pt and Au particles during ethene absorption. Electron donation from the C–C π bond in ethene affects the density of empty states in the d-orbital of platinum, and this can be seen in near-edge absorption spectra. Ethene was found to bind to atop or bridge sites on Au, and bridge or hollow sites on Pt by comparing the XANES difference spectra to a theoretical model. The EXAFS region of X-ray absorption spectra also showed features which could be fit well by inclusion of Pt/Au–C coordination. However, any XANES signal arising related to Pt/Au–C coordination would be difficult to separate from the contribution of Pt/Au–O at the metal–support boundary. The Pt–Pt bond length calculated by EXAFS is nearly unaffected by ethene adsorption, so the information from XANES difference spectra were crucial in determining the binding sites.

XANES is also effective for taking measurements during liquid-phase reactions with the assistance of specially designed reaction cells. The selective oxidation of cinnamyl alcohol over a Pd/Al$_2$O$_3$ catalyst has been studied by XANES, and it was shown that the formation of a surface Pd-oxide layer is necessary for maintaining high catalytic activity.[70] When reduced under H$_2$, the Pd was found to return for a metallic state which was no longer active for the oxidation reaction. The promoting effect of Bi on benzyl alcohol oxidation over Pt/Al$_2$O$_3$ has also been studied in situ using XANES. In this case, the formation of Pt-oxides was found to be detrimental to catalytic activity. Because Bi is more easily oxidized, the addition of Bi to the catalyst prevented the over-oxidation of the Pt species, and aided the catalyst in maintaining catalytic activity for longer.[71]

These selected examples demonstrate the extent to which catalyst structures can be characterized using XAS techniques. X-rays are only weakly absorbed by most fluid phases, making XAS a very useful technique for in situ measurements of catalyst structure.

Concluding remarks

We have reviewed recent and important contributions to the in situ characterization of reaction mechanisms and catalytically active sites in heterogeneous catalysts. In all cases these studies bring new light into the identity and concentration of surface species that are part of the reaction mechanism, or provide information that is useful to construct a model of the active site for the catalyst.

IR spectroscopy remains the most frequently employed technique for the characterization of surface species and, perhaps as a consequence, is the most helpful to investigate heterogeneous catalysts under in situ conditions. It is relatively inexpensive and uses instruments that can be purchased directly from manufacturers. Much progress is evidenced by the recent applications of SFG and PM-IRAS to determine the structure of surface species at high pressures or in the liquid phase. The application of both SFG and PM-IRAS remains difficult and is only conducted by a small number of research groups. Modularization and standardization of the different optical elements that are needed to apply these two techniques seems an important objective to make them more available to the wider catalysis community. Certain problems (such as liquid/solid heterogeneous catalysis) are best investigated using SFG or PM-IRAS (see Fig. 3) and thus the potential is real to have widespread impact on the science and technology of catalysis. NMR spectroscopy has unique advantages but the experimental constraints intrinsic to the use of magic angle spinning make in situ NMR of working catalyst slow and not very popular. It is hard to envision that groups without specialized equipment and know-how can apply this technique effectively for catalyst characterization.

X-Ray based characterization techniques have provided novel and useful information about the structure of working catalysts for many reaction systems. We believe there is great potential for the further use of HP-XPS and XAS to investigate working catalysts as each become more widely available and more user friendly to new investigators. In particular, accessibility to HP-XPS instruments is very limited (we know of only two) and efforts should be made to make similar or improved versions of existing HP-XPS instrumentation available at catalysis user facilities.

Acknowledgements

Notes and references

1 G. A. Somorjai, H. Frei and J. Y. Park, *J. Am. Chem. Soc.*, 2009, **131**, 16589–16605.

2 A. F. Lee, V. Prabhakaran and K. Wilson, *Chem. Commun.*, 2010, **46**, 3827–3842.

3 G. Rupprechter and C. Weilach, *Nano Today*, 2007, **2**, 20–29.

4 P. L. Gai, E. D. Boyes, S. Helveg, P. L. Hansen, S. Giorgio and C. R. Henry, *MRS Bull.*, 2007, **32**, 1044–1050.

5 M. Diem, *Introduction to Modern Vibrational Spectroscopy*, 1993.

6 J. D. Grunwaldt, R. Wandeler and A. Baiker, *Catal. Rev.*, 2003, **45**, 1.

7 J. D. Grunwaldt and A. Baiker, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3526.

8 Y. H. Yeom, J. Henao, M. J. Li, W. M. H. Satchler and E. Weitz, *J. Catal.*, 2005, **231**, 181.

9 Y. H. Yeom, M. J. Li, A. Savara, W. M. H. Satchler and E. Weitz, *Catal. Today*, 2008, **136**, 55.

10 S. D. Ebbesen, B. L. Mojet and L. Lefferts, *J. Phys. Chem. C*, 2009, **113**, 2503.

11 K. I. Shimizu, K. Sugino, K. Sawabe and A. Satsuma, *Chem. Eng. J.*, 2009, **15**, 2341.

12 M. J. Li, Z. Wu, Z. Ma, V. Schwartz, D. R. Mullins, S. Dai and S. H. Overbury, *J. Catal.*, 2009, **266**, 98.

13 D. Tibiletti, F. C. Meunier, A. Goguet, D. Reid, R. Burch, M. Boaro, M. Vicario and A. Trovarelli, *J. Catal.*, 2006, **244**, 183.

14 E. Chenu, G. Jacobs, A. Crawford, R. Keogh, P. Patterson, D. Sparks and B. Davis, *Appl. Catal., B*, 2005, **59**, 45.

15 G. Jacobs, P. Patterson, L. Williams, D. Sparks and B. Davis, *Catal. Lett.*, 2004, **96**, 97.

16 G. Rupprechter, *MRS Bull.*, 2007, **32**, 1031–1037.

17 M. S. Yeganeh, S. M. Dougal and B. G. Silbernagel, *Langmuir*, 2006, **22**, 637–641.

18 M. Morkel, H. Unterhalt, T. Kluner, G. Rupprechter and H. J. Freund, *Surf. Sci.*, 2005, **586**, 146–156.

19 E. Backus and M. Bonn, *Chem. Phys. Lett.*, 2005, **412**, 152.

20 M. Baumer, J. Libuda, K. M. Neyman, N. Rosch, G. Rupprechter and H. J. Freund, *Phys. Chem. Chem. Phys.*, 2007, **9**, 3541.

21 F. Höbel, A. Bandara, G. Rupprechter and H. J. Freund, *Surf. Sci.*, 2006, **600**, 963.

22 K. M. Bratlie, K. Komvopoulos and G. A. Somorjai, *J. Phys. Chem. C*, 2008, **112**, 11865.

23 S. B. Waldrup and C. T. Williams, *Catal. Commun.*, 2007, **8**, 1373–1376.

24 B. Bozzini, G. De Gaudenzi, B. Busson, C. Humbert, C. Six, A. Gayral and A. Tadjeddine, *J. Power Sources*, 2010, **195**, 4119.

25 G. Rupprechter and C. Weilach, *J. Phys.: Condens. Matter*, 2008, **20**, 1.

26 H. Oosterbeek, *Phys. Chem. Chem. Phys.*, 2007, **9**, 3570–3576.

27 E. Ozensoy, B. K. Min, A. K. Santra and D. W. Goodman, *J. Phys. Chem. B*, 2004, **108**, 4351–4357.

28 F. Gao, Y. Wang and D. W. Goodman, *J. Phys. Chem. C*, 2010, **114**, 4036.

29 T. Diemant, H. Hartmann, J. Bansmann and R. J. Behm, *J. Catal.*, 2007, **252**, 171–177.

30 D. M. Meier, A. Urakawa and A. Baiker, *J. Phys. Chem. C*, 2009, **113**, 21849–21855.

31 M. Hunger and W. Wang, *Adv. Catal.*, 2006, **50**, 150.

32 I. Ivanova, *Colloids Surf., A*, 1999, **158**, 189.

33 J. Haw, *Top. Catal.*, 1999, **8**, 81.

34 F. Deng, Y. Yang and C. Ye, *Mod. Magn. Reson.*, 2006, **1**, 201.

35 M. Hunger, *Prog. Nucl. Magn. Reson. Spectrosc.*, 2008, **53**, 105.

36 X. Han, Z. Yan, W. Zhang and X. Bao, *Curr. Org. Chem.*, 2001, **5**, 1017.

37 A. Roy, K. Jayalakshmi, S. Dasgupta, R. Roy and B. Mukhopadhyay, *Magn. Reson. Chem.*, 2008, **46**, 1119.

38 V. Sundaramurthy, J. P. Cognec, K. Thomas, B. Knott, F. Engelke and C. Fernandez, *C. R. Chim.*, 2006, **9**, 459.

39 S. Arzumanov, A. Gabrienko, D. Freude and A. Stepanov, *Solid State Nucl. Magn. Reson.*, 2009, **35**, 113.

40 I. Ivanova, Y. Kolyagin, V. Ordomsky, E. Asachenko, E. Pasynkova and Y. Pirogov, *J. Mol. Catal. A: Chem.*, 2009, **305**, 47.

41 A. Caballero, J. P. Holgado, V. M. Gonzalez-delaCruz, S. E. Habas, T. Herranz and M. Salmeron, *Chem. Commun.*, 2009, 1097.

42 J. Huang, Y. Jiang, V. R. Marthala and M. Hunger, *J. Am. Chem. Soc.*, 2008, **130**, 12642.

43 V. R. Marthala, S. Rabl, J. Huang, S. Rezai, B. Thomas and M. Hunger, *J. Catal.*, 2008, **257**, 134.

44 Y. Jiang, J. Huang, V. R. Marthala, Y. Ooi, J. Weitkamp and M. Hunger, *Microporous Mesoporous Mater.*, 2007, **105**, 132.

45 H. Bluhm, M. Havecker, A. Knop-Gericke, M. Kiskinova, R. Schlogl and M. Salmeron, *MRS Bull.*, 2007, **32**, 1022.

46 M. Salmeron and R. Schlogl, *Surf. Sci. Rep.*, 2008, **63**, 169.

47 F. Ogletree, H. Bluhm, E. Hebenstreit and M. Salmeron, *Nucl. Instrum. Methods Phys. Res., Sect. A*, 2009, **601**, 151.

48 F. Tao, M. E. Grass, Y. Zhang, D. R. Butcher, J. R. Renzas, Z. Liu, J. Y. Chung, B. S. Mun, M. Salmeron and G. A. Somorjai, *Science*, 2008, **322**, 932.

49 S. Piccinin, S. Zafeiratos, C. Stampfl, T. W. Hansen, M. Havecker, D. Teschner, V. I. Bukhtiyarov, F. Girgsdies, A. Knop-Gericke, R. Schlogl and M. Scheffler, *Phys. Rev. Lett.*, 2010, **104**, 035503.

50 A. C. Sanfiz, T. W. Hansen, D. Teschner, P. Snorch, F. Girgsdies, A. Trunschke, R. Schlogl, M. H. Looi and S. B. A. Hamid, *J. Phys. Chem. C*, 2010, **114**, 1912.

51 E. Vass, M. Havecker, S. Zafeiratos, D. Teschner and A. Knop-Gericke, *J. Phys.: Condens. Matter*, 2008, **20**, 1.

52 T. Herranz, X. Deng, A. Cabot, P. Alivisatos, Z. Liu, G. Soler-Illia and M. Salmeron, *Catal. Today*, 2009, **143**, 158.

53 Q. Fu, H. Saltsburg and M. Flytzani-Stephanopoulos, *Science*, 2003, **301**, 935.

54 W. Deng, J. Jesus, H. Saltsburg and M. Flytzani-Stephanopoulos, *Appl. Catal., A*, 2005, **291**, 126.

55 J. D. Grunwaldt, M. Beier, B. Kimmerle, A. Baiker, M. Nachtegaal, B. Griesebock, D. Lutzenkirchen-Hecht, J. Stotzel and R. Frahm, *Phys. Chem. Chem. Phys.*, 2009, **11**, 8779.

56 A. Knop-Gericke, E. Kleimenov, M. Havecker, R. Blume, D. Teschner, S. Zafeiratos, R. Schlogl, V. Bukhtiyarov, V. Kaichev, I. Prosvirin, A. Nizovskii, H. Bluhm, A. Barinov, P. Dudin and M. Kiskinova, *Adv. Catal.*, 2009, **52**, 213.

57 S. Bare and T. Ressler, *Adv. Catal.*, 2009, **52**, 339.

58 J. D. Grunwaldt, M. Caravati, S. Hannemann and A. Baiker, *Phys. Chem. Chem. Phys.*, 2004, **6**, 3037.

59 M. Newton, *Chem. Soc. Rev.*, 2008, **37**, 2644.

60 J. C. Fierro-Gonzalez, S. Kuba, Y. Hao and B. C. Gates, *J. Phys. Chem. B*, 2006, **110**, 13326–13351.

61 E. Alayon, J. Singh, M. Nachtegaal, M. Harfouche and J. van Bokhoven, *J. Catal.*, 2009, **263**, 228.

62 T. Miyazawa, K. Okumura, K. Kunimori and K. Tomishige, *J. Phys. Chem. C*, 2008, **112**, 2574.

63 Y. Nagai, K. Dohmae, K. Teramura, T. Tanaka, G. Guilera, K. Kato, M. Nomura, H. Shinjoh and S. Matsumoto, *Catal. Today*, 2009, **145**, 279.

64 M. Uenishi, H. Tanaka, M. Taniguchi, I. Tan, Y. Nishihata, J. Mizuki and T. Kobayashi, *Catal. Commun.*, 2008, **9**, 311.

65 J. Evans, A. Puig-Molina and M. Tromp, *MRS Bull.*, 2007, **32**, 1038.

66 J. Evans, A. Puig-Molina and M. Tromp, *MRS Bull.*, 2007, **32**, 1038–1043.

67 A. Saib, A. Borgna, J. van de Loosdrecht, P. van Berge, J. Geus and J. Niemantsverdriet, *J. Catal.*, 2006, **239**, 326.

68 M. Kumar, A. Eyssler, P. Hug, N. van Vegten, A. Baiker, A. Weidenkaff and D. Ferri, *Appl. Catal., B*, 2010, **94**, 77.

69 E. Bus, D. Ramaker and J. van Bokhoven, *J. Am. Chem. Soc.*, 2007, **129**, 8094.

70 A. F. Lee and K. Wilson, *Green Chem.*, 2004, **6**, 37–42.

71 C. Mondelli, J. D. Grunwaldt, D. Ferri and A. Baiker, *Phys. Chem. Chem. Phys.*, 2010, **12**, 5307–5316.