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Mini-review

In-situ and *operando* spectroscopies for the characterization of catalysts and of mechanisms of catalytic reactions ☆

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ABSTRACT

For almost as long as catalysts have been part of industrial chemical processes, there has been a parallel effort to understand how catalysis works at a molecular level. Pioneers such as Michel Boudart, to whom this Mini-Review is dedicated, realized that such a goal requires the ability to probe catalytic systems either *in situ* under realistic environments or in *operando* mode as the catalytic processes occur. Much has happened since, and a number of spectroscopies are now available for this purpose. Here we reference the most salient ones, including vibrational spectroscopies such as infrared absorption, Raman, and other non-linear optical arrangements, X-ray absorption, and NMR. We also introduce some surface-sensitive probes used for studies with model catalytic systems. For each of these techniques, we briefly discuss their advantages and disadvantages, and illustrate their use with a couple of recent examples from the literature.

1. Introduction

Heterogeneous catalysts were introduced in the chemical industry approximately a century and a half ago, and have played a pivotal role there ever since [1,2]. The field of catalysis is by its very nature applied, but much effort has also been placed from the very beginning on fundamental studies of catalytic reactions and materials. Although many catalysts have been developed empirically, their design has relied on the so-called "chemical intuition" that comes from basic research: it was early on understood that developing a molecular-level knowledge of how heterogeneous catalysis works would greatly help the tasks of improving catalytic performance and introducing new catalytic processes. Initial catalyst characterization work was carried out *ex situ*, but it soon became clear that both the nature of the catalytic surfaces and the surface reaction steps involved in catalytic reactions depend strongly on, and may be modified by, the presence of the reaction mixtures; it is imperative to study catalytic reactions *in situ*, under environments mimicking those encountered during catalysis, or, better yet, using *operando* methodology, following the time evolution of the catalytic system as the reactions take place [3]. Michel Boudart, to whom this Mini-Review is dedicated, was a pioneer in this area, and contributed to the incorporation of techniques such as Mössbauer [4–7], infrared absorption [8,9], X-ray absorption [10–12], and NMR [13] spectroscopies to the study of catalytic materials and reactions. Much progress has been made since, some of which will be outlined below, but it is thanks to the early efforts from Boudart and his contemporaries that the scientific community gained confidence in the soundness of such approach.

The study of heterogeneous catalysts *in situ* in the presence of gases or liquids requires probes that can penetrate those environments and selectively detect atoms and molecules at the gas–solid or liquid–solid interfaces. This has been a great challenge, but much progress has been made in this area. At one end, optical spectroscopies, because of their reliance on photons, can penetrate the reaction mixture and easily reach solid surfaces under catalytic conditions, but are not in general selective towards signals from species at surfaces. At the other extreme, modern surface-sensitive techniques rely on more interactive particles such as electrons or ions that do not travel well through gases or liquids. It is to the credit of the surface-science community that viable answers to these limitations have been found so that molecular-level characterization studies of catalysts under realistic catalytic conditions have become possible. Next, we briefly introduce some of the most successful approaches implemented to date.

☆ Contribution to the "Michel Boudart Special Issue".
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2. Infrared absorption spectroscopy

From the optical spectroscopies available for the study of catalytic systems, infrared absorption (IR) is by far the most used. IR probes the vibrational modes of molecules and solids, and those are quite specific to molecular details of surfaces and adsorbates [14–16]. IR is also quite flexible and can be implemented in several modes, including transmission, diffuse reflectance (DRIFTS), attenuated total reflection (ATR), and reflection–absorption (RAIRS, or IRAS), to study all kinds of materials such as films, nanoparticles, and powders, both transparent and black. In general, IR is not surface sensitive, but it may be made so in particular instances such as when probing adsorbates on metal substrates, and can in any case often differentiate between free molecules in gas or liquid phases and adsorbates bound to solid surfaces thanks to subtle differences in vibrational frequencies. Because of all these great features, and given its relatively low cost, IR was incorporated to the characterization toolbox in catalysis research long ago, and has been and continues to be used extensively in many laboratories. The advent of Fourier transform IR (FTIR) [17] further helped make this technique ubiquitous in catalysis research laboratories.

IR has been used extensively at all steps of catalyst preparation [18,19] and treatment [20] to follow the properties of their surfaces and the chemistry involved. It has also proven to be an excellent technique, in conjunction with the appropriate choice of probe molecules, to identify and characterize specific surface sites on catalysts. For instance, IR spectra of adsorbed carbon monoxide can be used to assess the availability, oxidation state, and atomic ensemble size of sites in metal nanoparticles [21]. The IR detection of acids such as CO_2 and basis such as pyridine is also quite useful for the titration of basic and both Brønsted and Lewis acidic surface sites [22]. Nevertheless, perhaps the most interesting use of IR in catalysis is to follow the evolution of the intermediates adsorbed on the surface during reaction, to identify their structures as well as to follow the kinetics of the conversion steps [23–26]. Much of that work focuses on simple species such as CO, CO_2, NO_x or H_2O, but the conversion of more complex molecules can be traced this way as well. An example is displayed in Fig. 1, where a transient propionyl ($CH_3CH_2C({=}O){-}Rh$) intermediate was identified in *operando* mode during the hydroformylation of ethylene promoted by a Rh/alumina catalyst using rapid-scan FTIR: the kinetics of the formation and consumption of the propionyl intermediate was followed as a function of reaction time by measuring the intensity of the peak due to its signature C—O stretching mode (ν(C—O)) at 1675 cm^{-1} (which shifts to 1636 cm^{-1} with ^{13}CO) [27]. This case not only points to the usefulness of the specificity of IR signals for the identification of particular adsorbed reaction intermediates, but also illustrates how the signals can be quantified to follow the kinetics of catalytic reactions.

The study of the mechanistic details of catalytic reactions involving a liquid phase are more challenging [28], but can also be addressed with IR as long as setups are implemented to minimize the path of the IR beam through the solvent [29–31]. One interesting problem where *in situ* IR has provided some insights into the reaction mechanism is that of the bestowing of enantioselectivity to metal hydrogenation catalysts via the addition of small amounts of so-called chiral modifiers to the reaction mixture [32,33]. The best example is the so-called Orito reaction, by which the hydrogenation of alpha-keto esters can be promoted enantioselectively with Pt-based heterogeneous catalysts by adding cinchona alkaloids to the solution. *In situ* IR studies have shown that the adsorption mode of those modifiers is critical to the effectiveness of the chiral modification, and that the adsorption geometry changes with surface coverage, which is related to the concentration in the liquid phase. We have shown that the optimum configuration of the adsorbed cinchona on the surface is with its aromatic ring oriented parallel to the surface, and that this arrangements is seen at low concentrations but flips to a tilted geometry as more modifier is added to the solution, to the detriment of the enantioselectivity of the catalytic process (Fig. 2) [34,35]. The details of this chemistry are still being debated [36–38], but what has become clear is that IR is one of the few spectroscopies that can be used to shine light on this problem.

One word of caution needs to be added here, a general concern that applies to studies of catalysis with all spectroscopies, and that is the fact that many surface species present on catalytic surfaces during catalytic conversions are spectators that do not participate in the chemical reactions. To identify the relevant intermediates it is useful to correlate the time dependence of the coverages of the adsorbed species

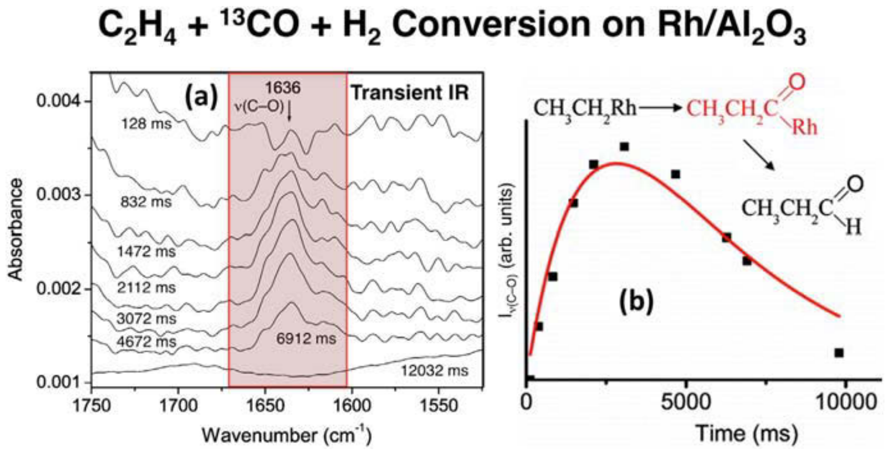

Fig. 1. Example of the use of IR in *operando* mode to follow the formation and consumption of surface intermediates during catalysis [27]. (a) IR spectra acquired at different times after the start of an ethylene hydroformylation reaction promoted by a Rh/alumina catalyst, highlighting the peak at 1636 cm^{-1} due to the C–O stretching (ν(C–O)) frequency of a propionyl surface intermediate (shown in red on the right). (b) Plot of the peak signal intensity of that feature as a function of time to show its transient nature and to calculate the kinetic parameters of the reaction. Adapted. from Ref. [27] with permission, Copyright 2011 American Chemical Society. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

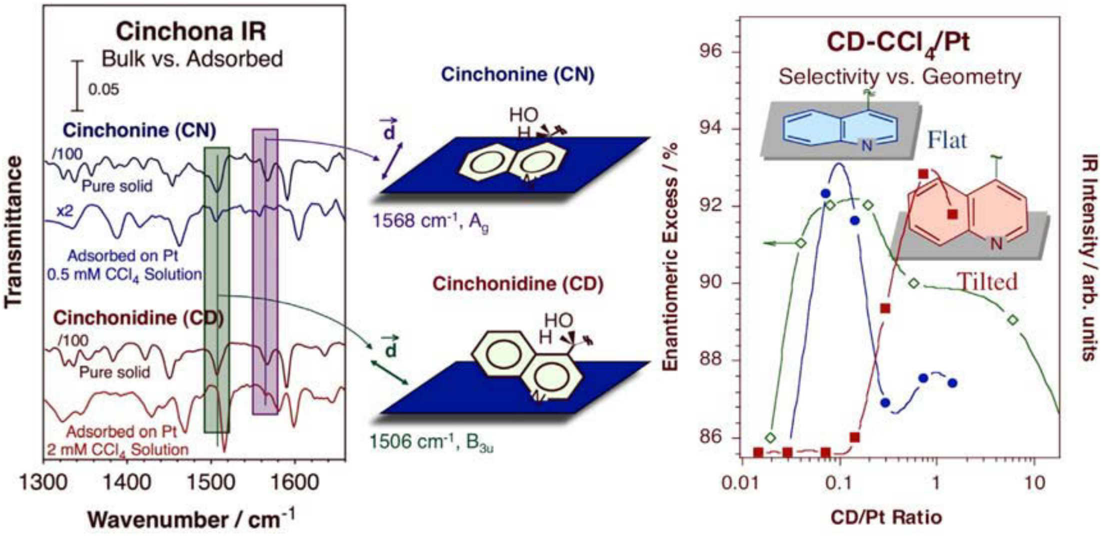

Fig. 2. *In situ* IR characterization of the adsorption geometry of chiral modifiers from solution onto platinum surfaces, and correlation with their catalytic modification efficiency. Left: Low and high coverage spectra for cinchonine (CN, top) and cinchonidine (CD, bottom) [39]. Center: Orientation of the aromatic ring of the adsorbed molecules relative to the surface plane, estimated from the relative intensities of the different peaks in the IR spectra [39]. Right: correlation between ring orientation and the enantioselectivity excess obtained during the hydrogenation of ethyl pyruvate [34]. Optimum performance is seen at the intermediate CD concentrations that favor adsorption with the aromatic ring flat on the surface. Reproduced from Refs. [35] (left and center) and [40] (right) with permission, Copyright 2017 Elsevier B.V. and 2014, Springer Science Business Media New York, respectively.

with the kinetics of the catalytic process. Time-resolved techniques such as modulation excitation (combined with phase sensitive detection) [31,41] and steady-state isotope transient kinetic analysis (SSITKA) [42] can help with this endeavor.

3. Raman and other non-linear optical spectroscopies

An alternative way to obtain vibrational information about solid catalysts and about molecular species adsorbed on catalysts is by using Raman spectroscopy, where inelastically scattered photons are analyzed to measure energy losses due to the excitation of vibrational modes. In many ways, Raman is complementary to IR. For instance, because it follows different selection rules, it is sensitive to a different set of vibrations than IR. Typically, Raman is good at detecting low-frequency modes such as those associated with vibrations within surface oxides clusters [43]. The signals are often weak, but because most catalysts have high surface areas, this is not a significant issue, and in some instances can be circumvented by using resonant or surface-enhanced Raman (SERS) [44,45] or shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS) [46]. High levels of light fluorescence and scattering often interfere with the detection of vibrational peaks in Raman, but this problem can be minimized by using UV instead of visible light as the excitation source [47]. Raman spectroscopy has been used for the imaging of heterogeneous catalysts [14], and has proven particularly adept to probing catalysts *in situ* or with *operando* methodology [48]. Fig. 3 provides an example of the latter, for the case of amorphous cobalt sulfide (CoS_x) electrocatalysts used to promote the hydrogen evolution reaction (HER) [49]. Analysis of the Raman data led, in conjunction with additional XAS results, to the proposal of a model where, under reaction conditions, the metal sulfide forms small clusters in which the cobalt is in an octahedral CoS_2-like state surrounded by a first shell of sulfur atoms exposed to the electrolyte.

Another non-linear optical spectroscopy useful to extract vibrational information out of solid samples is sum frequency generation (SFG), where the energy of the photons from an IR laser is up-converted using a second visible-light laser to generate an outgoing beam with a frequency equal to the sum of the two input frequencies. The non-linear character of this technique confers it surface sensitivity, a plus when compared to IR. On the other hand, the setup is complex and expensive, requiring both visible and tunable IR lasers. In fact, the need for the latter often restricts the frequency range that can be probed. Many catalytic studies with SFG have been carried out with model systems, typically single crystals or foils of metals placed and prepared in controlled (i.e., ultra-high vacuum) environments [50,51], but some examples of the use of SFG to probe more realistic catalysts *in situ* or using *operando* methodology do exist, mainly in investigations of flat electrodes in electrocatalysis. An example is provided in Fig. 4, where *in situ* SFG spectra helped understand the performance of Pt electrodes during the room-temperature electrochemical reduction of CO_2 (CO_2RR) in ionic liquids, 1-butyl-3-methylimidazolium tetrafluoroborate [BMIM][BF_4] in this particular case [52]. Complementary *operando* IR spectroscopy data, exemplified by the spectra shown in the top-right corner of Fig. 4, afforded the identification of an imidazolium carboxylic acid species on the surface at negative potentials (peaks at $\nu_{C=O}$ = 1633 and 1670 cm^{-1}) that can be further converted to formic acid during anodic potential sweeps, whereas the peak that appears around 2150 cm^{-1} in the SFG data at high (−1.05 V) cathodic potentials pointed to the formation of carbon monoxide under those conditions (Fig. 4, top-left). Contrasting studies with other ionic liquids led to the suggestion that it is steric effects that affect the rate of carbon dioxide reduction in these systems.

A third non-linear optical technique available for studies in catalysis is second harmonic generation (SHG). This is a relative of SFG, but its operation is simpler, as it requires only one visible-light laser beam: two photons of the same frequency interact with nonlinear materials and are combined to generate a new photon with twice the energy. The information extracted is not directly connected to specific molecular properties such as vibrational frequencies, but can be correlated with the electronic properties of the surface. SHG has been used mostly in studies with model planar surfaces, but a few examples of *in situ* applications to catalysis do exist [53].

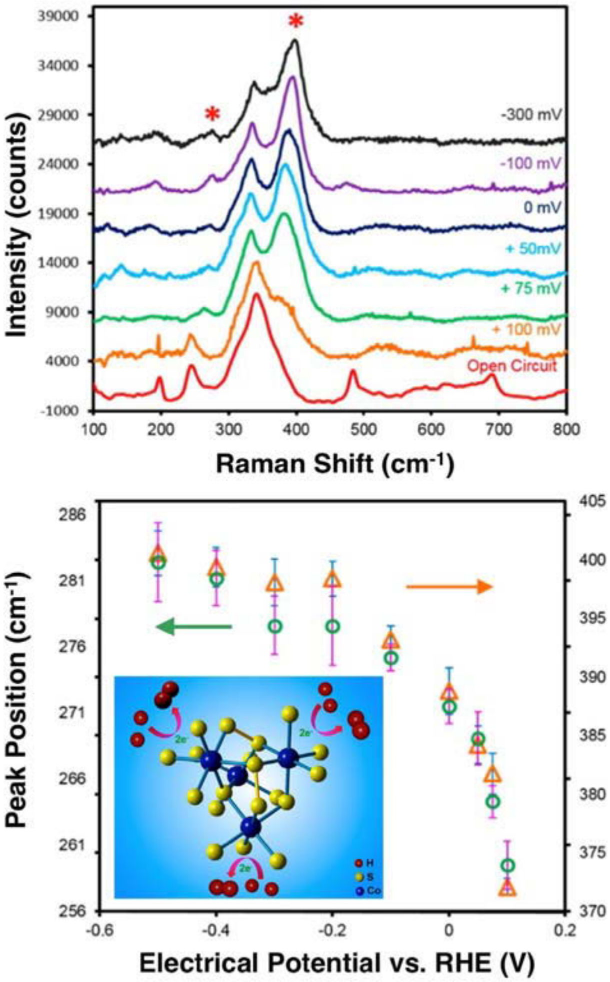

Fig. 3. Example of the use of Raman spectroscopy in *operando* mode to elucidate the details of catalytic sites. Amorphous cobalt sulfide was tested for the promotion of the electrochemical production of hydrogen [49]. The two new peaks indicated by asterisks were attributed to the formation of CoS_2-like clusters on the surface of the electrodes (top). These peaks blueshift with increasing negative potentials (bottom), indicating Co–S bond strengthening. The inset shows the atomic model proposed on the basis of these results. Reproduced from Ref. [49] with permission, Copyright 2015 American Chemical Society.

4. X-ray absorption spectroscopies

By using higher-energy photons, the electronic properties of the solid materials used in catalysis and those of the molecules that adsorb on their surfaces during reaction can be probed as well. The use of spectroscopies based on X rays in particular has become quite common in the catalysis community: although the wavelength of X rays is difficult to tune and scan with regular X-ray sources, this can be routinely done at synchrotron facilities [54,55]. X-ray-based spectroscopies are even less surface sensitive than the other optical techniques discussed above, but this is not as serious of an issue when characterizing active phases finely dispersed in the form of small nanoparticles on high-surface-area supports. Another concern is that X-ray radiation can damage samples: these techniques are the most useful for the characterization of stable solids, and are less commonly employed for the study of adsorbates. On the other hand, X-ray absorption spectroscopy (XAS) can be easily implemented for catalytic studies *in situ* or using *operando* methodology [56]. XAS data acquired around the energy required for a particular electronic excitation, what is referred to as X-ray absorption near-edge spectra (XANES, sometimes also known as NEXAFS), can be used to identify particular elements, quantify their contribution to the composition of the solid, and determine some details associated with their oxidation state. For instance, the *operando* XANES data shown in Fig. 5 was used to explain the 500-fold oxygen evolution reaction (OER) activity enhancement achieved in the electrocatalytic splitting of water using mixed (Ni,Fe)oxyhydroxides in terms of an optimum octahedral site for the Fe^{3+} cations with unusually short Fe—O bond distances [57].

Analysis of the extended fine structure seen at photon energies above the electronic excitation edges (the so-called extended X-ray absorption fine structure, or EXAFS) can provide information about the local geometry around the element being probed in the form of bond distances and coordination numbers. For instance, in the case reported in Fig. 6, *in situ* EXAFS measurements on Pd (left panels) and Pt (right panels) catalysts dispersed on silica supports highlighted their difference in catalytic performance during the hydrogenation of ethylene. The behavior in both cases is complex, but it is worth highlighting the unique dynamic hydrogen intercalation seen in Pd/SiO_2, which was shown to depend on the competitive adsorption of hydrogen and ethylene on the surface of the metal: under H_2-rich gas compositions (Q_{H2} > 50%), the coordination number decreases and the Pd—Pd bond distance increases, a sign of the reversible formation of a metal hydride phase. Also notable in the case of the Pt/SiO_2 catalyst is the decrease in coordination number seen upon exposure to

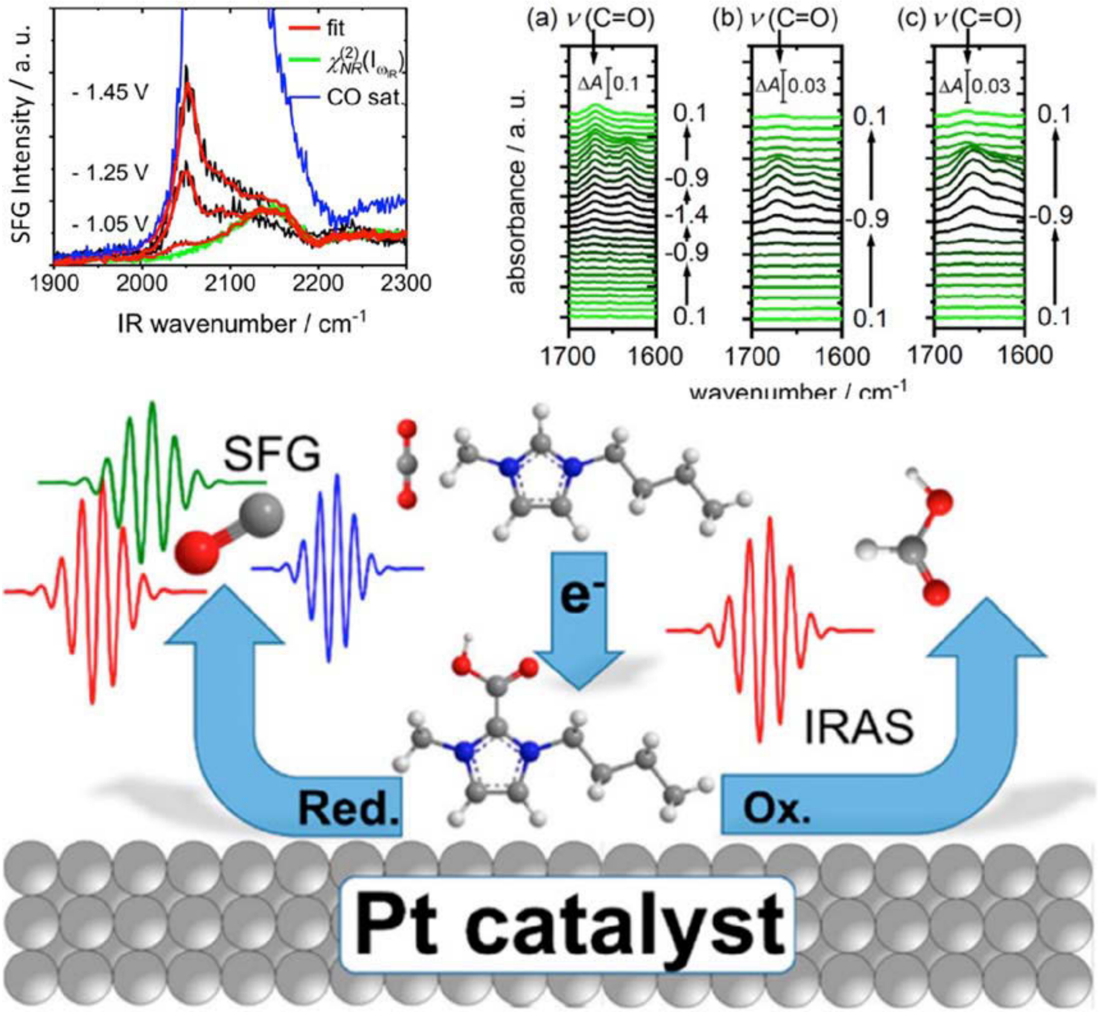

Fig. 4. *In situ* SFG and *operando* IR study of the surface species that form on Pt electrodes during the room-temperature electrocatalytic reduction of CO_2 in ionic liquids [52]. The potentiodynamic IR absorption spectra in the carbonyl stretching region (top-right) show the reversible formation of an imidazolium carboxylic acid species on the surface at negative potentials (potentials indicated on the right of each panel), especially in the presence of H_2O (middle panel) or D_2O (right). Moreover, under reducing condition, the *in situ* SFG traces point to the formation of CO (top-left). The conclusions from these studies, namely, the formation of CO and HCHO under reducing and oxidizing conditions, respectively, are summarized in the bottom half of the figure. Reproduced from Ref. [52] with permission, Copyright 2019 American Chemical Society.

ethylene-rich gas mixtures (Q_{H2} < 45%), which was interpreted as the result from the appearance of new Pt—C surface species [58]. This type of *in situ* and *operando* experiments can be used to follow the changes in the solid catalysts as a function of their surrounding environments as well as the progress of catalytic reactions.

5. NMR

Nuclear magnetic resonance (NMR) spectroscopy is a very versatile and informative technique used extensively in many fields of chemistry and biochemistry, and has been incorporated into the study of catalysts as well. In order to characterize solid samples, those need to be rotated at high speeds in a modality known as magic-angle spinning NMR (MAS-NMR, sometimes referred to as solid-state NMR –SS-NMR–); this, unfortunately, results in spectra with lower resolution than those obtained in liquid phase, and imposes some restrictions on the design of catalytic reactors for *in situ* or *operando* studies. Nevertheless, MAS-NMR characterization of catalytic systems is widespread, to probe the acidity of sites in oxides, for instance [59,60]. Some interesting *operando* MAS-NMR studies of catalytic conversions of organic reactants have also been reported in recent years, including the example in Fig. 7, which refers to the promotion of the hydrogenolysis of benzyl phenyl ether (BPE) catalyzed by Ni/γ-Al_2O_3 [61]. The time-dependent NMR data shown on the top clearly differentiated the different species present in the solution (which include the original BPE as well as the main products, namely, toluene, phenol, and phenyl isopropyl ether), and could be converted into the kinetic plot shown on the bottom-left of the figure. The kinetic data were in turn used to propose a mechanism for the conversion based on the intermolecular transferring of hydrogen atoms in which toluene and phenol are primary products whereas phenyl isopropyl ether is made via a subsequent coupling step between phenol and 2-propanol (Fig. 7, bottom-right).

The main drawback of NMR is that its sensitivity is quite low, requiring large numbers of nuclear spins for proper detection. This is not as much of a problem when probing major catalytic sites in high-surface-area catalysts, but it is limiting when searching for surface intermediates or other minority species. Several approaches have been explored over the years to overcome this shortcoming, including the

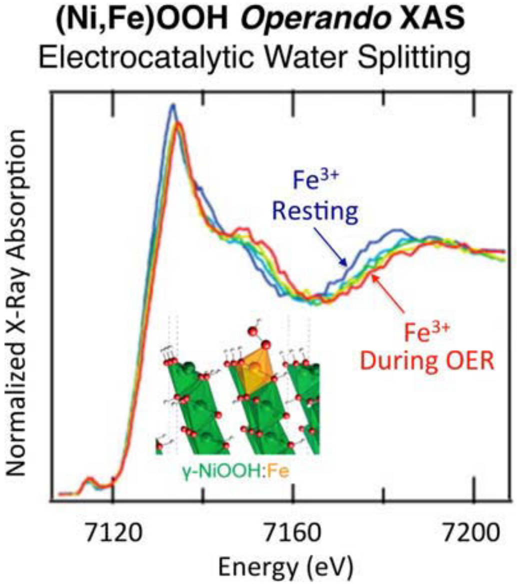

Fig. 5. *Operando* Fe K-Edge XANES spectra of (Ni, Fe)oxyhydroxide catalysts acquired during the electrocatalytic splitting of water. The changes seen upon exposure to the reaction conditions are indicative of the adoption by the Fe^{3+} ions of a unique and highly reactive coordination. Reproduced from Ref. [57] with permission, Copyright 2015 American Chemical Society.

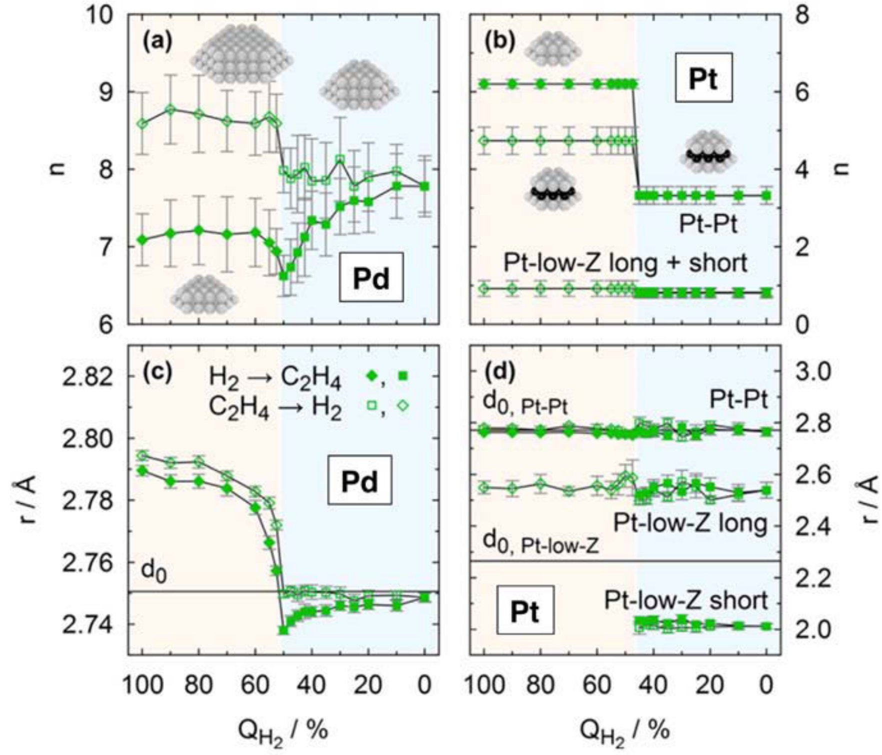

Fig. 6. Values of coordination numbers (n, top row – a, b) and bond distances (r, bottom – c, d) extracted from EXAFS data recorded *in situ* during the catalytic hydrogenation of ethylene with Pd/SiO_2 (left column – a, c) and Pt/SiO_2 (right – b, d) catalysts, plotted as a function of gas composition [58]. Dynamic changes in the metal nanoparticles were observed with variations in the H_2 content of the H_2 + C_2H_4 mixtures, including an expansion of the Pd crystal lattice with increasing H_2 content and the formation of carbonaceous deposits on the Pt nanoparticles in ethylene-rich mixtures. Reproduced from Ref. [58] with permission, Copyright 2015 American Chemical Society.

recent advancement of dynamic nuclear polarization (DNP-NMR), where the small magnetic moments of the nuclei under study (^{1}H, ^{13}C, ^{15}N) are enhanced via the transfer of the large electron polarization of a chosen polarizing agent using microwave irradiation near or at the electron paramagnetic resonance transition. The technique has shown great promise for the detection of key surface species [62,63], but the experiments require the addition of very specific chemicals to the system, and are run at low temperatures, lower than those needed for

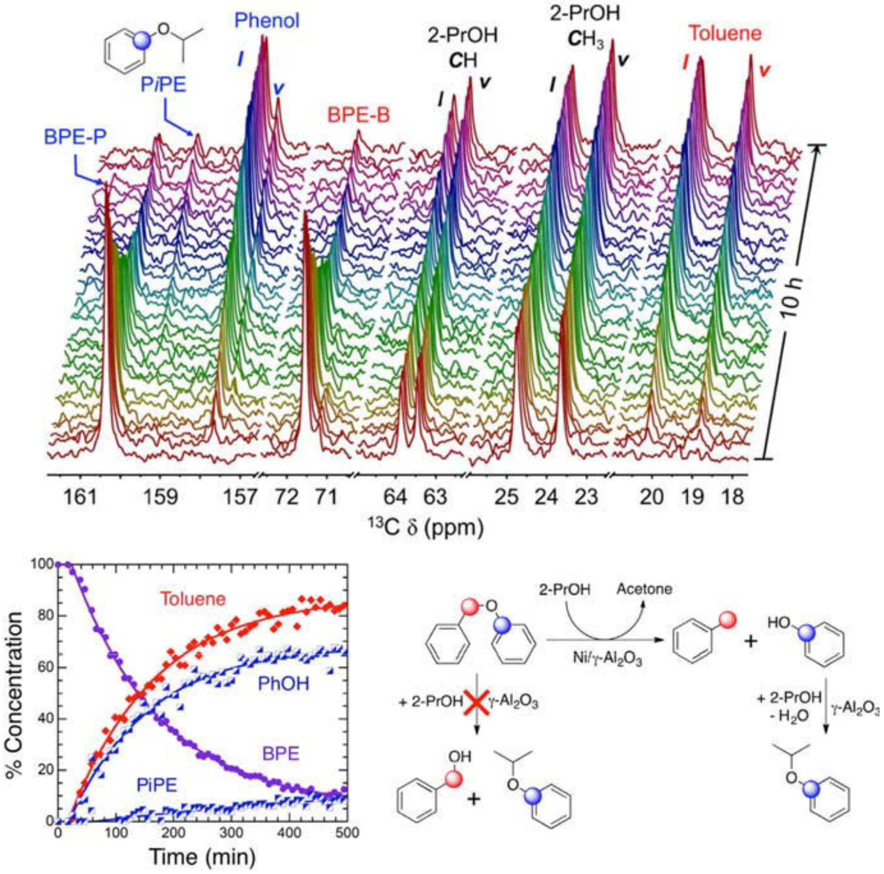

Fig. 7. Time-resolved ^{13}C MAS-NMR spectra recorded during the hydrogenolysis of benzyl phenyl ether (BPE) in 2-propanol promoted by a Ni/alumina catalyst [61]. Top: raw data with peak assignment. Bottom-left: kinetic profiles extracted from those data, for toluene, phenol (PhOH), BPE, and phenyl isopropyl ether (PiPE). Bottom-right: proposed mechanism. Reproduced from Ref. [61] with permission, Copyright 2018 American Chemical Society.

most catalysis. Although we are not aware of any applications where DNP-NMR has been used *in situ* or in *operando* mode for the study of reactions promoted by heterogeneous catalysts, this has been attempted in homogeneous catalysis [64]. The challenges are many, but it may be that DNP-NMR will be incorporated to the *in situ* or *operando* characterization toolbox of heterogeneous catalytic processes in the near future.

6. Studies with model systems

The many advances in spectroscopy discussed so far have afforded a more detailed characterization of catalysts *in situ* or using *operando* methodology than ever before, but the amount of molecular detail on reaction mechanisms that can be acquired this way is still limited. One of the most powerful developments in the field of catalysis in the past few decades has been the incorporation of unique and novel surface-sensitive techniques to studies with model systems under controlled conditions [65]. The original work was carried out with simple solids such as single crystals or polished foils and under vacuum, but both those conditions have been relaxed over the years in an attempt to look at more realistic systems, an approach that has become known as bridging the materials and pressure gaps, respectively [66–69]. As a result, today it is possible to use electron-based spectroscopies such as X-ray photoelectron spectroscopy (XPS) to characterize catalytic surfaces under reactive gases [70,71], and even at the solid/liquid interface [72,73]. In fact, near-ambient-pressure XPS (NAP-XPS) has been extended to the *in situ* study of real catalysts. Fig. 8 provides an example of this where the reducibility of Ni/ceria catalysts was shown to be enhanced by the addition of zirconia, facilitating methane activation during dry reforming [74].

7. Concluding remarks

The brief Mini-Review provided above provides a glimpse of the progress that has been made in terms of developing the tools needed to study catalytic systems *in situ* or using *operando* methodology. The ability to use and combine techniques such as IR, Raman, XAS and NMR can provide a level of detail on catalytic systems well beyond what was possible during the time of Boudart and other pioneers. In fact, other techniques not mentioned above such as electron paramagnetic resonance (EPR) spectroscopy [75–78], X-ray (XRD) [79], neutron diffraction [80], and neutron spectroscopy [81] can provide complementary information about catalytic systems, and microscopies, in particular environmental electron microscopies [82–84] but also scanning probes [85–87], can also be operated *in situ* or using *operando* methodology, provide much structural information on catalytic surfaces, and be combined with spectroscopic tools [88,89] to further characterize those systems. Nevertheless, there is much room for improvement. First, the information that can be extracted *in situ* or using *oper-*

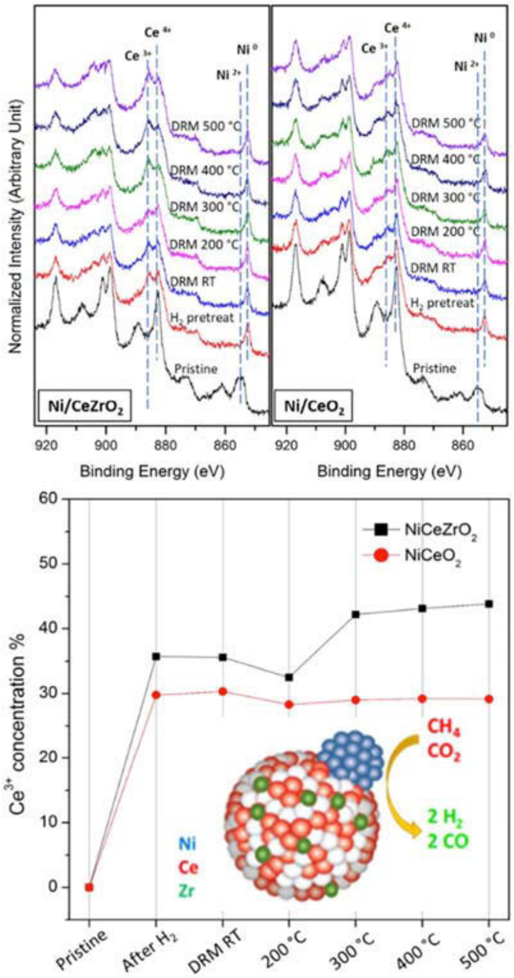

Fig. 8. Ce 3d and Ni 2p NAP-XPS study of the reducibility of ceria-supported nickel catalysts used for dry methane reforming (inset drawing) [74]. Top: raw spectra for Ni/$CeZrO_2$ (left) and Ni/CeO_2 (right) under a H_2 gas as a function of temperature. Bottom: Fraction of reduced Ce^{3+} in these catalysts versus temperature, from quantification of the raw NAP-XPS data. Reproduced from Ref. [74] with permission, Copyright 2020 American Chemical Society.

ando methodology from the available spectroscopies is still limited and many times difficult to assemble into a coherent and complete molecular-level picture of the catalytic process. Luckily, the experimental work is now routinely complemented with quantum mechanics computational calculations, which have become quite powerful and can often address complex systems consisting of up to hundreds of atoms [90] immerse in non-vacuum environments [91]. This symbiosis between theory and experiments is expected to become stronger and to help advance mechanistic studies in catalysis.

A second consideration for future developments is the spatial and temporal resolution of the data acquired during the characterization of catalytic processes. Some of the spectroscopies available for *in situ* and *operando* studies in catalysis have already been implemented with some degree of spatial resolution and can image the progress of reaction within a catalytic reactor. Nevertheless, the resolution of those techniques cannot in general address molecular issues, or even image the individual nanoparticles typically used as active phases in heterogeneous catalysis. Environmental electron microscopy has attained such atomic resolution, but can by and large only map the structure of the solid phase, not that of the adsorbates. Perhaps new ideas will be needed to extract molecular-level information *in situ* during catalysis. In this context, it is encouraging to note that there are already some examples where this has proven possible in model systems; witness, for instance, the work reported using tip-enhanced infrared absorption [92] or Raman spectroscopy [93,94]; more is expected to come. Temporal resolution is also important in catalytic studies, because kinetic information can be closely connected and used to propose reaction mechanisms. The techniques discussed above have in some cases been implemented with time resolution already (see, for instance, the data in Fig. 1), but in general this is still quite difficult to do. Moreover, the time resolution of the data acquisition available in a given study may not match that needed to detect the short-lived surface intermediates that usually form during catalysis.

One consideration when designing characterization experiments with either spatial or temporal resolution is that higher resolution is often obtained at the expense of signal sensitivity, a fact that makes the detection of transient phenomena involving minority species particularly difficult. Encouragingly, many of the spectroscopies described in this article (Raman, SFG) rely on the use of lasers, intense sources that can be pulsed with pico- or even femto-second time resolution. This capability has been exploited to study the progress of electronic excitations in photocatalysis [95,96], for example, or to follow conversion with sub-second time resolution and within individual nanoparticles by using fluorescent probe molecules [97], but has not yet been generally extended to the study of the dynamics of catalytic reactions. It should be noted, however, that in the pursue of high signal intensities to afford better spatial and/or temporal resolution, high photon or electron fluxes may be used that may damage the catalyst and affect the progress of the reactions taking place at the surface. Mass transport limitations can also interfere with kinetic measurements, and can facilitate product readsorption and catalyst poisoning. A balance needs to be found between signal acquisition and catalyst stability. The need for better spatial and temporal resolution in *in situ* and *operando* spectroscopic studies of catalysts offers great opportunities to be taken by researchers in the near future.

Finally, the *in situ* and *operando* study of catalytic reactions at solid–liquid interfaces is still in its infancy, and significantly lags the progress made in the characterization of solid–gas analogs [35,98]. Some examples were introduced above to illustrate the additional difficulties introduced by the presence of a condensed (liquid) phase above the catalytic surfaces, which include the strong absorption and interaction of the probing particles (photons, electrons) used in the characterizing spectroscopy with liquids as well as the modification of the environment around the catalytic centers. The presence of solutions during the promotion of catalytic reactions in many electrocatalysis and photocatalytic systems is unavoidable, and solvents are also common in many organic conversions. There is much room for improvement in the *in situ* and *operando* studies of such systems.

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.

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