Chapter 11
In Situ and *Operando* Techniques in Catalyst Characterisation and Design

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Abstract This chapter intends to present the classical and modern techniques that are used for in situ characterisation of catalytic materials. Determination of the structure of the catalyst presents three main problems: (1) heterogeneous catalysis phenomena are limited to the outer surface of the material where the molecules adsorb and react, and for this reason, there are only a few methods able to assess catalyst surface structure and composition; (2) the catalyst surface under reaction conditions and upon the influence of the reacting agents is different from that occurring under ambient conditions, which limits the application of the analytical methods to those which operate at normal or elevated pressures and high temperatures, (3) catalytic materials are complex and heterogeneous, so many analytical methods, including surface imaging, should be employed in order to understand the structure–activity relationships. The remedy for the problems is the application of in situ analyses that rely on several complementary spectroscopic methods and utilise surface sensitive probe molecules. Different kinds of probe molecules are described: from universal probes to specific ones that enable the determination of acidic and basic activity. The IR, Raman and UV-Vis methods are presented here and described using examples from the literature. New trends in in situ experimentation involve time-resolved techniques for studying fast reactions, fluorescence methods and coupled techniques for surface in situ imaging.

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11.1 Introduction

Understanding the structure of catalyst surfaces and the surface intermediates appearing during catalytic reactions is one of the key steps in determining the reaction mechanism. Modern catalyst design for any technological process consolidates three scales: microscale, mesoscale and macroscale. The simultaneous development of the technology allows scientists to look deeper into catalyst structure and the elementary activity on the catalyst surface. The golden age of the development of surface techniques started in the 1950 s [1], when new techniques that allowed the detection limit to be decreased to the molecular level were developed. The possibility of preparing ultrafine electronic materials allowed the development of techniques for which ultra-high vacuum conditions are necessary. Nowadays, the wide variety of techniques for catalyst characterisation allows a choice of complimentary techniques for obtaining information about the measured system. Over the years, the palette of available techniques has been increasing gradually. The techniques used for catalyst characterisation described in this chapter are summarised in Table 11.1.

The classical approach to catalyst characterisation was based on the determination of catalyst activity and selectivity for a given process, while the determination of catalyst structure via spectroscopic and microscopic methods was performed in the next stage. Process parameters such as composition of catalysts and reacting mixture, reaction temperature and pressure, activity, selectivity, and chemical and mechanical resistivity of catalytic material used to be determined under external perturbation, for example by increasing reactor temperature while keeping the other variables constant. Indeed, such a methodological approach provided a lot of information about catalytic systems that could be used for catalyst optimisation and design.

Table 11.1 Selected techniques used in catalyst characterisation

Technique	Information provided	Limitations
Atomic force microscopy (AFM)	Catalyst surface structure	– Resolution – Single-crystal model catalyst
X-ray absorption spectroscopy	Catalyst local surface structure, local geometry	– Semi-quantitative – Complex spectra – Limited beam time – Possible probe damage
Fourier transform infrared spectroscopy (FTIR)	Surface intermediates, acidity/basicity of catalysts	– Possible overlapping of support vibrations with active site vibrations – Indirect determination of active sites
Raman spectroscopy (Raman)	Surface intermediates, catalyst structure	– Fluorescence may affect analysis – Possible probe damages
Ultraviolet–visible spectroscopy (UV-Vis)	Catalyst electronic structure	Broad spectrum, complex band assignment

In the past, a majority of techniques relied on the use of the UHV conditions or reaction "freezing" to obtain structural information on the catalyst surface or active sites. However, that approach is far from the working conditions of the catalysts, which for a vast majority of processes entail elevated temperature and pressure. The necessity of observing catalyst structure under real working conditions was the crucial point in the development of the in situ experiments. According to Haw [2], an ideal in situ investigation should look at catalyst structure and morphology, and the reaction intermediates under real working conditions. However, in the literature, the term in situ is also used for the spectroscopic measurements of catalysts or metal oxide surface upon contact with the adsorbate or reacting species [3]. The definition proposed by Daydov [3] does not exclude a whole palette of measurements under HV/UHV, utilising quantitative experiments with probe molecules such as ammonia, pyridine or CO for the determination of surface acidity. Thus, taking into account that there are two different ideas of in situ analysis, the question arises as to whether the application of the UHV technique really reflects the structure of the surface of a working catalytic material. Another question is presented by Daydov's attitude to combining HV/UHV with in situ examinations in order to collect as much information about the catalytic system as possible.

On the other hand, when considering the analytical methods for catalyst characterisation, we have to take into account that the phenomenon of catalysis is limited to the very surface (external surface) of a catalytic material, on which reactants adsorb, form intermediates and then convert to products. Amongst the analytical methods which are able to focus on this surface are the microscopic methods (AFM and, to an extent, SEM), in situ spectroscopic methods (Raman, FTIR and UV/VIS) and ion (LEIS) and light scattering (SAXS). Ambient XPS (rarely available yet in laboratories) and Raman spectroscopy can aid surface studies with only limited confidence, since the signal emanating from a sample, depending on penetration depth, provides information on the external surface (a few monolayers in XPS, a few microns in Raman) to only a limited extent. This important drawback of a majority of the so-called surface methods can be overcome by in situ and *operando* analysis utilising surface probe molecules.

Since in situ characterisation methods provide information on catalyst structure under real reaction conditions, rather than yielding data on overall activity, the development of a methodology able to monitor both parameters at the same time was highly desirable for further assessment of structure–activity relationships. This led to the development of the methodology of *operando* spectroscopic measurements. This term was originally proposed by *Prof. Miguel Bañares* during a discussion with *Eric Gaigneaux*, *Gerhard Mestl* and Bert Weckhuysen at the 220th ACS National Meeting in Washington, in 2002. The term *operando* refers to the Latin word describing working or operating conditions [4, 5]. Since in situ and *operando* methodologies have been established as conventional methods, the number of scientific papers on their use and development for catalyst studies has been growing. According to the Web of Science (Fig. 11.1) both in situ and *operando* techniques have become unwritten standards for studies dealing with the preparation and characterisation of catalysts for various heterogeneous reactions.

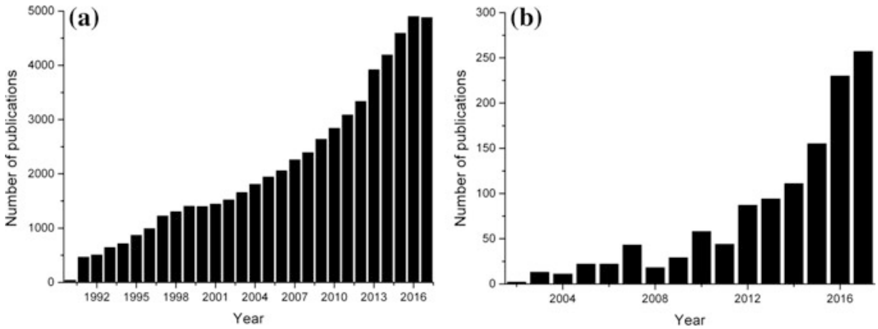


Fig. 11.1 Number of annual publications with **a** "in situ spectroscopy" and **b** "*operando* spectroscopy" in the subject, according to Web of Science

Despite the real progress that has been noted in in situ and *operando* experimental approaches, there are still several problems associated with them, including reaction temperature/pressure influence, catalyst form, catalyst activity and selectivity determination, and in situ cell construction [6]. In fact, it is the appropriate construction of an in situ cell that defines the quality of the acquired spectra. The construction of reaction cells is most often optimised for a specific spectroscopic method and available analytical device. The in situ cell can be "home-made" or chosen from commercially available solutions. Detailed examples of in situ cells for selected spectroscopies can be found in the following exemplary references: IR [6, 7], Raman [4, 6], UV-Vis [4, 6], XAS/XES [4, 8], and SAXS, AP XPS [9].

11.2 Methods for Real-Time Catalyst Investigation

11.2.1 Determination of Active Centres Using Probe Molecules

The acidic properties of a catalyst's surface play an important role in catalytic processes. Many important technological processes, including catalytic cracking [10], isomerization [11] and transesterification [12] rely on solid acid catalysts that allow the use of fixed or fluidised-bed catalytic reactors [13]. The correct understanding of the nature, quantity and strength of the acid/base properties of the catalysts used for technological processes has been the main topic of a vast array of scientific papers over the decades [3, 14–18]. The term "active centre" was originally proposed by Taylor, who suggested that only a small percentage of a catalyst's surface is able to adsorb and promote the catalytic reaction.

Nowadays, active sites are classified into several categories, the boundary of which is redox and acidic/basic sites. The first category distinguishes the sites varying in oxidation states of the metal and the sites composed of the charge transfer metal complexes. The latter follows the definition of Brønsted (protonic) and Lewis (non-protonic) acids and bases. Real industrial catalysts may contain the whole palette of active sites. Furthermore, the two categories overlap if we consider, for example, metal cations which can be regarded as both redox and Lewis non-protonic acidic sites.

The characterisation of active sites is performed at the molecular level. In order to determine the acidic properties of the catalysts, several characterisation methods have been developed. These include titration methods, sorption, adsorption and temperature-programmed desorption of probe molecules, and spectroscopic techniques [11, 19]. Amongst the listed methods, the spectroscopic techniques are most commonly used, due to their versatility and availability.

The selection principles for a probe molecule used in spectroscopic methods to determine desired acidic properties was proposed by Knözinger [13]. The selected probe molecule used in spectroscopic studies must conform to several criteria that cover the following aspects [13, 14]:

- The spectra response of the interaction between probe molecule with active sites must allow for the distinction between Brønsted and Lewis sites.
- Extinction factors are sufficiently high and known to allow for the determination of quality and strength of measured centres.
- The acidic strength of the probe molecule should be selected to achieve the optimum response in acid–base interaction
- The selected probe molecule should be specific to differentiate between the sites of different strengths.
- The size of the probe molecule should be selected for the material under scrutiny, so that it can diffuse through the pores to cover the maximum number of the active sites.
- The measurement conditions (temperature) during surface probing should be selected to avoid reactions other than those with active centres.

In fact, selecting an ideal probe molecule is often a difficult task, because it is impossible in practice to meet all of the above-mentioned criteria completely.

The probe molecules that are commonly used to determine catalyst surface acidity can be divided into two groups, with weak and strong bases. The group of strong bases includes pyridine, ammonia, piperidine, trimethylamine and *n*-butyloamine [13, 20, 21]. The interaction of these probe molecules provides information about both Lewis and Brønsted acid centres. Amongst the group of the strong bases, ammonia and pyridine are the most frequently used [13, 22, 23]. The group of weak bases, which includes benzene and substituted benzenes, CO, N_2, O_2 and H_2, is also used to determine both Lewis and Brønsted acidity [14]. The principle that lies behind the determination of the acidity by weak base probes is the formation of weak hydrogen bonds with the hydroxyl group present on the catalyst surface [14].

An example of the application of the in situ FTIR method to studies of catalyst active sites is a recent study by Ochońska et al. [22], devoted to preparation and characterisation of Cu-exchanged Y, USY and ZSM-5 zeolites used as catalysts for

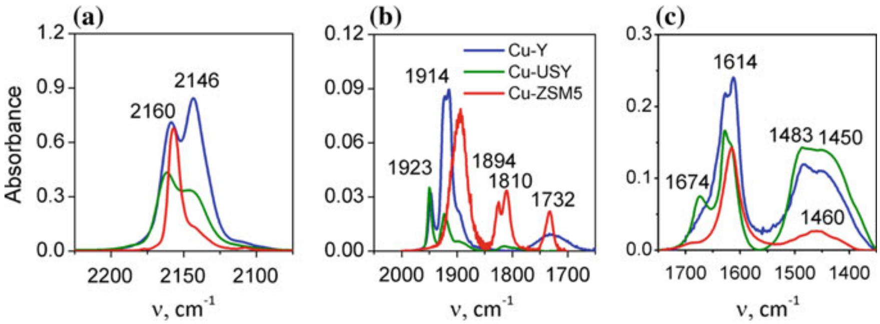


Fig. 11.2 FTIR spectra of zeolites with adsorbed probe molecules; **a** CO, **b** NO, **c** NH_3 Reprinted with permission from [22], copyright (2018) Elsevier

selective catalytic removal of NO_x from stationary sources. In this study, the nature of the active sites was studied using CO, NO and NH_3 probe molecules. The CO sorption at room temperature is able to distinguish two types of Cu^+ Lewis sites of different strengths, which give vibrations with CO at 2160 and 2146 cm^{-1}. In turn, the use of ammonia as a probe molecule is universal and captures both Lewis and Brønsted active sites at the same time [21, 22, 24]. In this case, the characteristic bands around 1620 cm^{-1} correspond to Lewis acidity, while those near 1450 cm^{-1}—relate to Brønsted. The results provide additional information on the existence of non-equivalent Cu active sites, as can be inferred from the appearance of two maxima (Fig. 11.2c): the band around 1614 cm^{-1} attributed to NH_3 bonded to Cu^+, and the band at 1674 cm^{-1}, attributed to NH_3 coordinated to Cu^{2+}.

The characterisation of basic active centres seems far more complicated than that of acidic ones, since probe molecules should contain the acidic part. The most frequently used probe molecules used to study basic active sites on catalyst surfaces are carbon monoxide [25–29]. The adsorption of carbon monoxide is used to characterise metals and metal oxides. CO is also used to assess cationic sites, which are in turn acidic in nature. Comprehensive reviews on carbon monoxide interaction with catalyst surface active sites can be found in the references [14, 23].

The adsorption of carbon monoxide over various catalytic systems results in the formation of carbonyls. The interaction of carbon monoxide with the basic oxygen sites (373 °C) of metal oxide catalysts at decreased temperature leads to the formation of carbonite species [23], which has been studied by many research groups [24–26]. At room temperature, CO can interact exclusively with Cu^+ surface species (Fig. 11.2a), while lowered temperature (liquid nitrogen temperature) also allows for the detection of Cu^{2+} species [14, 24, 30, 31]. In the work by Kryca et al. [24], both room temperature and low-temperature adsorption of CO was used to differentiate between Cu^+ and Cu^{2+} species in the ZSM-5 catalysts (Fig. 11.3b, c). Room temperature adsorption of carbon monoxide gives rise to the formation of Cu^+–CO (2157 cm^{-1}) and $Cu^+(CO)_2$ (2157 cm^{-1}) species [30]. On the other hand, low-temperature CO adsorption results in the interaction with Cu^{2+} species causing the appearance of several bands at 2150, 2170, 2177 and 2191 cm^{-1} (Fig. 11.3C).

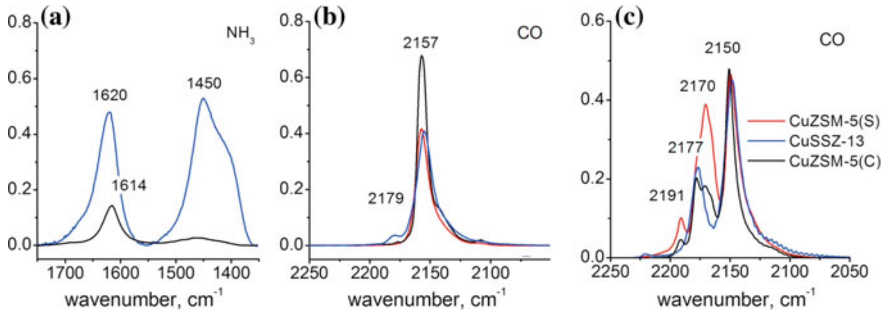


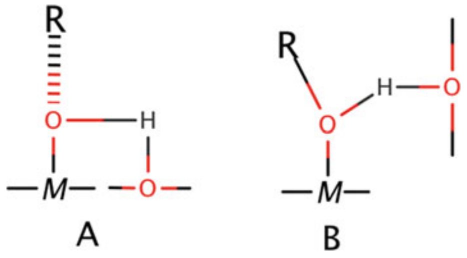
Fig. 11.3 Sorption of probe molecules over zeolite catalysts; **a** NH_3, **b** CO at room temperature, **c** CO at 100 °C Reprinted with permission from [24], copyright (2018) Elsevier

Alternatively, a similar effect to that observed for CO probe molecules can be achieved by NO, which has similar properties [22, 32]. However, the adsorption of NO molecules over copper-exchanged ZSM-5 catalysts at room temperature provides a complex spectroscopic pattern (Fig. 11.2b). The bands shifted to the higher wavenumber (1850–2000 cm^{-1}) can be assigned to Cu^{2+}–NO, whereas those below 1850 cm^{-1} can be assigned to both Cu^{+}–NO and Cu^{2+}–$(NO)_2$.

Amongst the probe molecules, alcohols play a special role in the studies of the nature and number of active sites at a catalyst's surface [33–35]. The literature provides the number of reports of probing catalyst surfaces using alcohols of various acidities, including $(CF_3)_3COH$ (p*K*a = 5.4) $(CF_3)_2CHOH$ (p*K*a = 9.3), CF_3CH_2OH (p*K*a = 12.3) and CH_3OH (p*K*a = 15.1) [23], ethanol, 2-propanol and tetr-butyl [33]. The adsorption of the alcohols proceeds irreversibly with the formation of two species at the catalyst surface (Fig. 11.4). The dissociative chemisorption of alcohols on weak Lewis acid sites results in the formation of alkoxy species (Fig. 11.4a), whereas undissociated species are chemisorbed on strong Lewis acid sites, resulting in the formation of structure B, as shown in Fig. 11.4b [23].

The chemisorption of alcohols over metal oxide catalysts results in the formation of two characteristic regions in the IR spectrum. In the range 3000–2800 cm^{-1}, characteristic –CH vibrations are shifted to higher wavenumber for species B (Fig. 11.4b), whereas dissociative adsorption with the characteristic adsorbed

Fig. 11.4 Chemisorbed species after chemisorption of alcohols over metal oxide catalysts



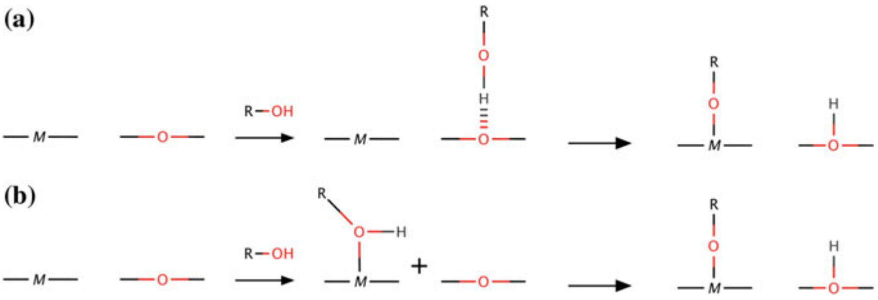


Fig. 11.5 Mechanisms of adsorption of alcohols over metal oxide catalysts

species A is represented by lower –CH frequencies. In the second region, the bending modes of –OH vibrations are coupled with the δ–CH_2 and δ–CH modes. A number of studies have been devoted to the adsorption of halogeno-alcohols over selected metal oxide supports such as alumina or titania, proving dissociative adsorption [34, 36]. The adsorption of acidic alcohols proceeds over active centres with predominant basic properties (Fig. 11.5a), whereas less acidic alcohols including methanol adsorb at acidic Lewis active centres (Fig. 11.5b).

A detailed description of the use of methanol as a probe molecule to study the nature and number of the active sites can be found in the work of Badlani and Wachs [37]. In this work, complimentary studies of methanol adsorption over a series of several dozens of different metal oxides were carried out. The authors found that, for most of the considered metal oxides, the number of active sites for methanol dissociative adsorption is approximately 3 µmol/m^2. Additionally, it was also concluded that the methanol chemisorption at a catalyst surface, and further oxidation on redox active centres, results in the formation of formaldehyde and formic acid. The reaction of methanol over acidic centres results in the formation of dimethyl ether, whereas complete oxidation proceeds at centres of basic character.

11.2.2 in Situ FTIR Spectroscopy

Infrared spectroscopy analysing the vibrational patterns of solid and probe molecule-active site complexes is commonly used as a technique for catalyst characterisation. The development of technology facilitated the modification of infrared spectrometers, allowing measurements not only of the catalysts but also the reaction intermediates at the catalyst surface. The development of sensitive and fast detectors and, more importantly, of interferometers, made IR a common technique for the rapid analysis of low amounts of intermediates appearing during catalytic reactions on solid surfaces. Amongst various available IR techniques, the transmission, diffuse reflectance (DRIFT) [38–44], attenuated total reflectance (ATR) [45–50] and photoacoustic (PAS) [51–55] ones are those most utilised for catalyst studies. However, while transmission experiments are the most frequently used for the determination of the active sites using probe molecules, the question arises as to whether they are pure in situ experiments according to the definition proposed by Haw [56], because UHV or HV are recommended for obtaining reproducible FTIR spectra of adsorbed probe molecules? Since the use of probe molecules in transmission mode to determine acidic properties is the most utilised method, this question remains unanswered.

However, both transmission and DRIFT modes are also used to monitor the surface-active species appearing at a catalyst's surface during the catalytic reaction. Transmission experimentation in FTIR is a direct method of measurement, as it does not create as many secondary optical effects as reflectance-based methods. However, if the simplicity of the catalyst preparation is considered, DRIFT appears to be the method of choice for its ability to analyse the studied material directly, in its original form. In the transmission mode, there is a limited selection of options as KBr wafers, as the dispersal of solids practically prevents their interaction with gaseous agents. The thin, self-supporting or Si wafers on which catalysts are deposited are the method for transmission measurements. What is more, if we consider the structure and mechanical stability of self-supported wafers, it has to be taken into account that the pressure which secures the integrity of the pellets may also change the material structure and properties [7]. To monitor a catalyst's surface in transmission-absorption special in situ cells were developed. Some details of these can be found in several references [6, 7, 57, 58].

Transmission experiments are commonly used not only to determine the active sites at a catalyst's surface using probe molecules under HV/UHV conditions, but also in transient-state measurements and examinations of surface intermediates using operando methodology [57, 59–62]. However, the vibrational patterns of surface intermediates are complex and often need additional analysis by complimentary methods to be properly resolved. In the study by Rasmussen et al. [57], the surface properties during NH_3-SCR over $V_2O_5/WO_3/TiO_2$/sepiolite catalyst were characterised by *operando* IR/MS. IR measurements of the catalyst surface under $NO + O_2$ dynamic conditions revealed several bands, including those from adsorbed NH_4^+ appearing at 1435–1450 cm^{-1}, those from ammonia coordinated at the Lewis acid site at 1610–1620 cm^{-1} and those of molecular water adsorbed at the catalyst surface, at 1620 cm^{-1} (Fig. 11.6). The assignment of both NH_3 and OH bands from vibrating adsorbates may be problematic, since both bands overlap. To solve this problem, the chemometric methods are more and more frequently engaged, as Multivariate Curve Resolution Alternating Least Squares (MCR-ALS) methods, for example, can be used to separate the overlapping bands [57].

Since the preparation procedures in classical transmission-absorption mode require fastidious preparation of self-supporting diluted pellets, the DRIFT method has become one of most utilised in situ method for the characterisation of catalysts. The variety of applications of DRIFT analysis in catalyst characterisation, from surface analysis to determination of surface intermediates, is a result of the simplicity of the method. Indeed, catalyst preparation is reduced to minimum, although the impact of particle size and reflectivity of the sample on the spectra cannot be

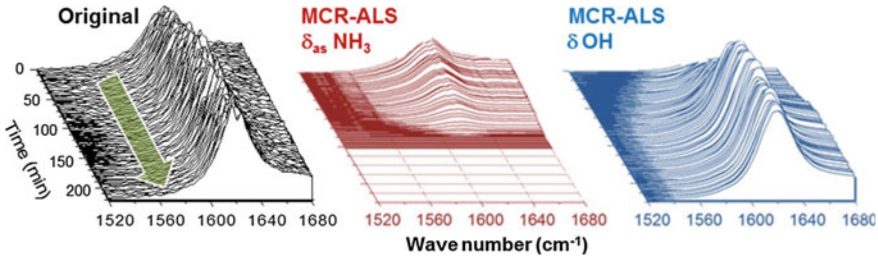


Fig. 11.6 *Operando* FTIR spectra during SCR of NO at 250 °C with pre-adsorbed ammonia. As obtained (left) and components after deconvolution by MCR-ALS: adsorbed ammonia on acid sites (middle) and hydroxyl bending mode (right) Reprinted with permission from [57], copyright (2018) Elsevier

marginalised [63]. Since the first heated DRIFT cell was presented by Hamadeh et al. [64] the several in situ DRIFT cells have been proposed [4, 7]. The currently commercially available high temperature in situ cells are able to achieve temperatures up to 910 °C under vacuum, which increases the applicability of DRIFT analysis for catalyst characterisation.

In the literature, numerous reports describe the application of in situ and *operando* DRIFT spectroscopy to characterise catalyst structure–activity relationships [7, 65–70]. The *operando* studies are not limited only to measuring the gas phase by the detection of effluent gases using gas spectrometers or mass spectrometers, but more detailed catalyst characterisation studies using combined DRIFT/XAS [71, 72] and DRIFT/XANES/MS [73] can be also found.

The possible application of in situ DRFIT spectroscopy for the determination of surface intermediates during the catalytic combustion of methane was presented in work by Jodłowski et al., shown here as an example [66]. DRIFT analysis of the catalyst's surface indicated the different active site occupation under oxygen-rich and oxygen-less conditions. It showed methoxy groups of characteristic bands at 2999 and 2907 cm^{-1}, attributed to –OCH_3, and formate $HCOO^-$ species, respectively. TPSR experiments also show (cf. Figure 11.7) that methane is able to react with the catalyst surface under oxygen-less conditions, indicating the Mars–van-Kreveln mechanism which is involved in its oxidation. This resulted in more intense bands in the 1650–1200 cm^{-1} range for oxygen-free conditions, which were attributed to carbonates and formates. The combination of static and pulse together with oxygen-rich and oxygen-free conditions brought about the recognition of stable surface intermediates, which allowed the methane catalytic combustion mechanism over supported oxide catalyst to be derived (Fig. 11.8).

The *operando* mode of DRIFT experiments seems to be a powerful tool for determining the relations with the structure of active centres and the observed catalytic activity. The detection of the effluent gases is carried out with connected gas analysers, from which Gas chromatographs (GC) or quadrupole mass spectrometers (QMSs) are the most commonly used. GC or QMS allows precise determination and quantitative analysis of the effluent gas composition. In a study

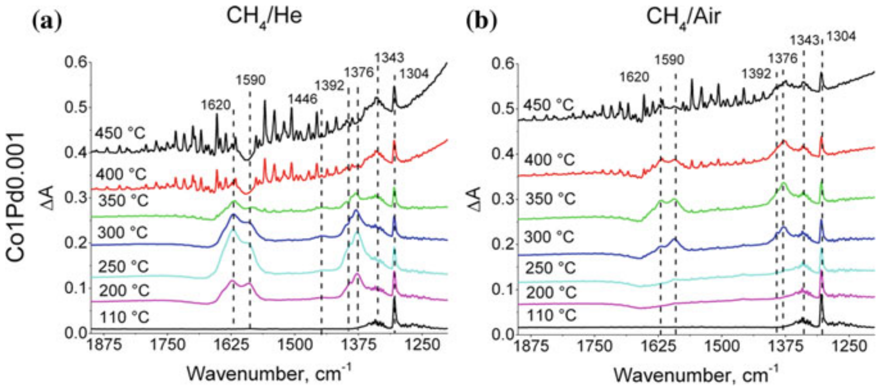


Fig. 11.7 In situ DRIFT experiments of catalytic combustion of methane. Column oxygen-free conditions (left), column oxygen-rich conditions (right) Reprinted with permission from [66], copyright (2018) Elsevier

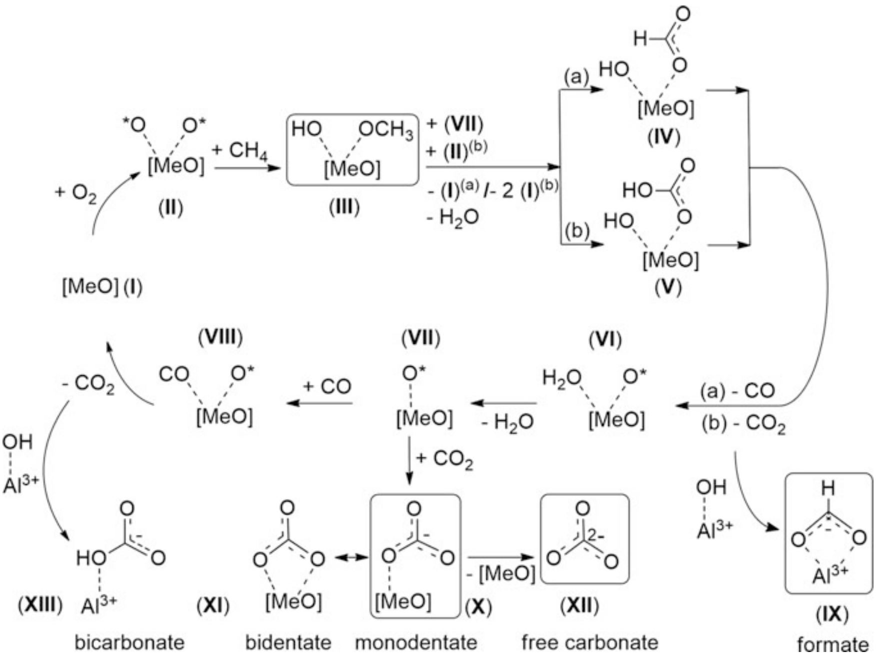


Fig. 11.8 Reaction mechanism determined by in situ DRIFT experiments Reprinted with permission from [66], copyright (2018) Elsevier

by Jodłowski et al. [74], *operando* DRIFT/MS was used to prove that neither formaldehyde nor formic acid were present in the gaseous phase, as previously postulated in the literature.

11.2.2.1 Enhanced in Situ FTIR Techniques

The description of in situ FTIR spectroscopy as a tool for the characterisation of catalysts would be incomplete without consideration of time-resolved techniques, including step-scan and rapid-scan methods. Since the lifetime of the reacting species at the catalyst surface in the form of transition state or intermediate species varies 10^{-12}–10^{-13} s, the development of rapid-scan techniques was highly desired. The rapid-scan method was developed in the 1970 s. Its application during catalyst characterisation allows the collection of spectra in a time of 10^{-3} s in modern FTIR spectrometers. The step-scan method decreases the acquisition time to 10^{-9} s. The significant shortening of the spectra recording using both rapid-scan and step-scan methods made possible experimental spectroscopic studies including transient absorption experiments, pulsed sorption–desorption studies and kinetic studies [75–82]. Nevertheless, the use of the rapid and step-scan techniques is very demanding, requiring highly stable and reproducible conditions during the experiment. Additional factors such as pressure changes or temperature fluctuations may also affect the experimental results [75]. The correct set-up of time-resolved techniques, their complexity and sensitivity to even millisecond condition fluctuations mean that the literature does not contain a great many reports on this matter [75–78, 83–85].

Monitoring fast reactions can be achieved with FTIR analysis by using time or phase-resolved techniques. In a study by Iwamoto and Hoshino [76], the isotopic exchange of ^{14}NO and ^{15}NO species over CoZSM-5 catalysts was measured by the application of rapid-scan FTIR spectroscopy. For the first time in the literature, it was shown that ^{15}NO molecules are rapidly exchanged by ^{14}NO from the gaseous phase until equilibrium in gaseous NO was achieved. Achieving the equilibrium state for the ^{15}NO–^{14}NO exchange was more rapid for mononitrosyl than dinitrosyl adsorbates, and lasted 0.3 s.

In another study, by Thibault-Starzyk et al. [83], the deNO$_x$ process by CO over Ag/Al$_2$O$_3$ catalysts using the step-scan FTIR spectroscopy was investigated. The pulse heating of the reactants was performed by using a femtosecond laser with a 10 Hz repetition rate. The authors concluded that the rate-limiting step in the CO deNO$_x$ reaction is the flipping of cyanide groups from Ag nanoparticles to the alumina support. The lifetime of the rate-limiting step was estimated to be as short as 2 μs. This was evidenced by the gradual decrease in the 2130 cm^{-1} band attributed to AgCN, and the increase of the 2265 cm^{-1} band, attributed to isocyanate species adsorbed on alumina.

Rapid recent development of synchrotron radiation has opened new opportunities to perform *operando* XANES/DRIFT analysis of heterogeneous catalysts. In work by Brieger et al. [72], the structure and surface properties of the EuroPt-1 catalyst (6.3 wt% Pt/SiO$_2$) during CO sorption studies were measured using *operando* XANES/DRIFT. Since XANES is not able to differentiate between the adsorbed CO species over the EuroPt-1 catalyst, the use of DRIFT analysis was demanded. Indeed, the characteristic bands at 2070, 1850 and 1720 cm^{-1} assigned to atop, bridge-bonded and triple-bonded CO species.

11.2.2.2 2D Correlation Spectroscopy

Two-dimensional correlation spectroscopy (2D COS) was originally developed to analyse NMR spectra and untangle the information derived from many overlapping signals [86]. The possibility of analysing the spectra as a function of the two variables represented a breakthrough in spectral analysis. Although the application of 2D COS to the analysis of NMR spectra is still dominant, there is an increasing interest in connecting it with other spectroscopic techniques, including FTIR or Raman. The first application of 2D COS to vibrational spectroscopy was proposed by Noda in 1988 [87]. Since then, 2D COS has attracted a wide group of researchers from various fields such as catalysis and surface science. For the studies of catalysis, the application of 2D COS to spectroscopic studies may provide several advantages [86]:

- simplification of complex spectra by adding a second dimension;
- increase in spectral resolution of derived spectra and separation of overlapping peaks;
- determination of the sequential order during analysis of the individual bands at the asynchronous spectra;
- heterospectral correlation by the correlation of results obtained using different spectroscopies (such as FTIR and Raman spectroscopy);
- correlation between different methods, such as mass spectrometry, gas chromatography, etc.

The use of 2D COS in in situ techniques has been reported in references [88–92]. In work by Chlebda et al. [69], 2D COS was used to improve in situ characterisation and band assignment of surface intermediates appearing on a series of metal oxide catalysts during methane catalytic combustion. During the reaction, oxidative and non-oxidative conditions were applied. Exemplary results of in situ 2D FTIR COS for mixed Co/Pd/γ-Al_2O_3 catalysts under non-oxidative conditions are presented in Fig. 11.8. Synchronous spectrum analysis has revealed two groups of cross-peaks at synchronous spectra (Fig. 11.9a), with positive and negative increase of bands at increasing reaction temperature occurring for cross-peaks. Analysis of the corresponding asynchronous spectrum (Fig. 11.9b) allowed the sequence of the band changes during the experiment to be determined as follows: $1590 \rightarrow 1390 \rightarrow 1380 \rightarrow 1620 \rightarrow 1304 \rightarrow 1520 \rightarrow 1505 \rightarrow 1540 \rightarrow 1420 \rightarrow 1560 \rightarrow 1460 \rightarrow 1350 \rightarrow 1330 \rightarrow 1340$. Further analysis of both synchronous and asynchronous spectra achieved by the application of 2D COS to the in situ FTIR spectroscopies allows the reaction mechanism to be determined, based on in situ 2D COS DRIFT experiments.

The 2D COS spectroscopy can also be successfully applied for in situ μRaman structural studies of cobalt catalysts deposited on metallic supports [70]. The methodology presented in work by Chlebda et al. [70] shows that the use of in situ DRIFT, μRaman and DR-UV-Vis methods in parallel with the application of 2D COS provides complimentary information on the catalysts. The 2D COS in situ

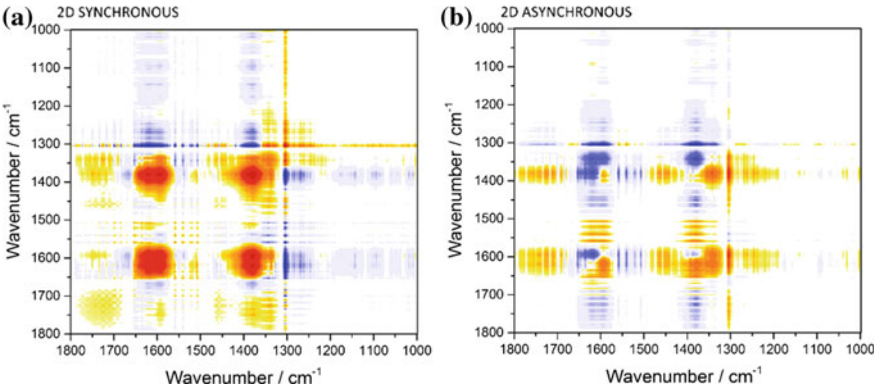


Fig. 11.9 Synchronous (A) and asynchronous (B) 2D infrared correlation spectra Co/Pd/γ-Al_2O_3 catalyst in methane oxidative conditions 1.6% CH_4/20% O_2/He 25 cm^3•min^{-1} Reprinted with permission from [66], copyright (2018) Elsevier

Raman and in situ DR-UV-Vis experiments show that the surface of the cobalt catalyst deposited at the metallic support oxidised during catalytic combustion on *n*-nonane. Analysis of 2D correlation μRaman spectra reveals that the band at 520 cm^{-1}, attributed to the cobalt spinel oxide, broadens with increased temperature. Additionally, analysis of the asynchronous DRIFT spectra reveals bands that were not easily observable in standard and synchronous spectra.

A series of investigations devoted to 2D COS FTIR spectroscopy transmission-absorption mode is reported in the references [88–90]. The in situ FTIR studies were performed to characterise xylene isomerisation over hierarchical zeolites. The complexity of the spectra for individual products of isomerisation and by-products makes overall analysis and further insights into mechanistic studies challenging. Analysis of 2D correlation spectra has also confirmed that the high selectivity towards the *p*-xylene was also influenced by the microporous character of the selected zeolites.

11.2.3 in Situ Raman Spectroscopy

Raman spectroscopy is based on an outstanding effect that occurs upon light scattering in contact with matter. It happens that a part of the scattered light undergoes inelastic effects as opposed to Rayleigh phenomena, which are dominant. Depending on the distribution of bosons, representing the vibrating molecules in ground and excited vibrational states, two effects occur. Notwithstanding the further mechanism, the low-temperature effect called Stokes effect, leads to a change in the occupancy of the states towards the excited vibrational state, as the majority of the molecules are originally located on the ground state (as described by the Bose–Einstein distribution function). The anti-Stokes effect is opposite, shifting the distribution of the bosons from the excited to the ground state. It is obvious that the described effects are analogical to the excitation and de-excitation induced by IR radiation but occur for entirely different molecular structures. Stokes effects are more intense under conditions of catalytic reaction, although they vanish in the prevailing Rayleigh scattered light. For this reason, Raman spectroscopy was losing favour for many years, until new instrumentation was developed around 30 years ago, giving it new applications in the fields of catalysis.

Unlike IR spectroscopy, Raman does not require any optical arrangements to collect light from the surface of the solids, or any special optical windows except glass. The majority of set-ups use microscopes which are able to transfer laser incident light and collect back-scattered light. The choice of incident laser light wavelength depends on the catalytic system studied. The in situ Raman experiments also require proper choice of the in situ cells. There are two temperature cells available commercially that are designed to comply with Raman microscopes for the purpose of catalyst surface investigation. The Linkam cell, although designed to reach a temperature of 1000 °C, is equipped with a ceramic cup that glows at high temperature, disturbing the weak Raman signal. The Harrick is made entirely of steel, but allows a temperature no higher than 550 °C. Both are equipped with heating and gas supplying systems.

In fact, both IR and Raman spectroscopy are perfect choices for the in situ molecular characterisation of catalysts, as their selection rules depend on the molecular structure of the studied material, and they can provide real-time information on its changes. Additionally, Raman is entirely complementary to the IR method. This is not only because of the opposite selection rules, but also because of the specific absorption of typical materials used in heterogeneous catalysis. IR is especially suitable for the analysis of the adsorbed probe molecules as they absorb light above 1000 cm^{-1}, and while the typical support oxides such as Al_2O_3 or SiO_2 do not give any signals, Raman spectroscopy compensates for this. In Raman spectroscopy, the majority of the support oxides do not scatter light above 100 cm^{-1}, which gives perfect circumstances for the analysis of the majority of the metal oxides used in catalysis and which give Raman signals, typically in the range 200–1200 cm^{-1}. An important advantage of Raman spectroscopy over IR is that water, a ubiquitous molecule in a great many reactions, is practically invisible in Raman. However, we have to take into account that the structure of a working catalyst exposed to high temperatures is different from that which occurs under ambient conditions in which water molecules are incorporated to the structure of the metal oxides both of the catalyst and the support materials. This is another important reason why in situ methods are the only adequate approach for assessing catalyst structure under working conditions.

Amongst the catalytic systems most intensely studied by Raman spectroscopy are bulk metal oxides and supported metal oxides. There are also examples of the application of Raman spectroscopy to zeolite and metallic catalysts. The bulk metal oxides can be studied in terms of the existence of different crystalline phases, their transformation, and the extent of their crystallisation. If aided with a microscope, Raman spectroscopy also provides information on the special distribution of bulk metal oxides.

As regards supported metal oxides, Raman spectroscopy is able to provide useful data on the molecular structure of the metal oxide on the support, its specific location and surface coverage and surface acidity. If used in an in situ mode upon a catalytic reaction, the technique is able to trace the changes in the structure of the metal oxide catalyst, and in particular the engagement of the metal-oxygen bonds in the reaction mechanism [93, 94]. For this class of catalysts, great efforts were made to understand the vanadium and chromium group of elements, due to their widespread application in many chemical industrial processes, examples of which can be found in numerous works by Bañares and Wachs. Raman is especially suitable for the study of those systems because the double bond between the metal and oxygen that is formed on the surface of a metal oxide support gives a strong signal in the Raman spectrum, around 1000 cm^{-1} (see Fig. 11.10 showing the Raman spectrum of an Mo-ZSM-5 catalyst).

Raman can also be utilised for the chemisorption studies, following the methods used for IR studies described in Sect. 11.2.2. The information obtained is complementary to that obtained using IR.

An example of this is the in situ Raman study of Mo-ZSM-5 catalysts (Si/Al = 40), initially calcined at 500 °C. A characteristic feature of the spectrum is the Raman band at 1000 cm^{-1}, arising from dioxo v_s(Mo(=O)$_2$) species on the octahedral framework. There is also a band characteristic of bridging Mo–O–Mo bands at 835 (v_{as}) and 501 (v_s) cm^{-1} [95]. A very weak and broad Raman band at around 900 cm^{-1} can be assigned to the bridging Mo–O–Al support bond, with a corresponding weak band at around 360 cm^{-1} for the δ(O–Mo–O) mode, which interferes with ZSM-5 support vibrations. These bands vanish upon adsorption of methanol at 100 °C, which then desorbs at temperatures above 200 °C and restores the original vibrational pattern of the Mo-ZSM-5 catalyst.

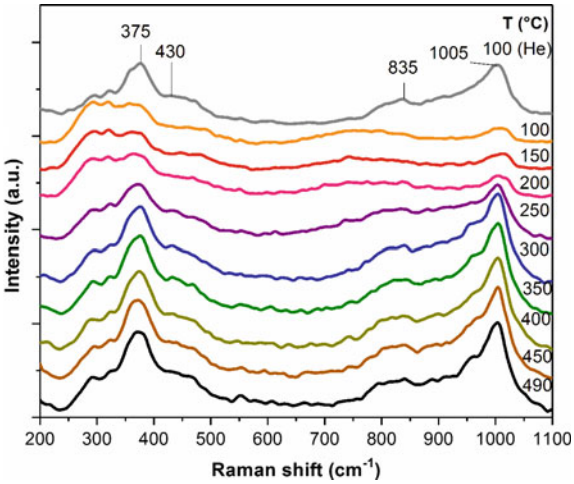


Fig. 11.10 In situ Raman spectra of an Mo-ZSM-5 (Si/Al = 40) catalyst upon interaction with methanol pre-adsorbed at 100 °C and then exposed to increasing temperature

11.2.4 In Situ UV-Vis Spectroscopy

Electron transition molecular spectroscopy is one of the oldest techniques used to investigate catalyst materials, but its role is limited due to complexity of the absorption signals. The instrumentation used for in situ catalyst investigations relies mainly on the diffuse reflectance and fibre optic spectroscopy, and on microscopy in a similar manner to IR. The same concerns the choice and arrangements of the temperature cells.

A broad presentation of examples of the use of UV-Vis in situ techniques can be found in the review [96]. The most important domains of the application of this technique for solving catalytic problems are the determination of the coordination of transition metal ions to surface oxygens and quantitative determination of the oxidation states of transition metal ions. An interesting application of UV-Vis analysis is for the determination of the degree of "polymerisation" or clusterisation of surface metal oxides, as for example in Bañares et al. [97]. For this purpose, edge energy is derived from the UV-Vis spectra of single supported metal oxides [98].

An example of the use of the in situ UV-Vis DRS technique to analyse a dehydrated Mo-ZSM-5 catalyst under oxidative conditions is shown in Fig. 11.11, as difference spectra possessing a single O (2*p*) to Mo (*d*) orbital centred at 242–245 nm. The absence of any *d-d* transitions at ~400 nm from crystalline MoO_3 indicates that this phase is not present. The corresponding E_g values for the molybdena species at ~245 nm drop in the range 4.3 to 4.4 eV, which indicates

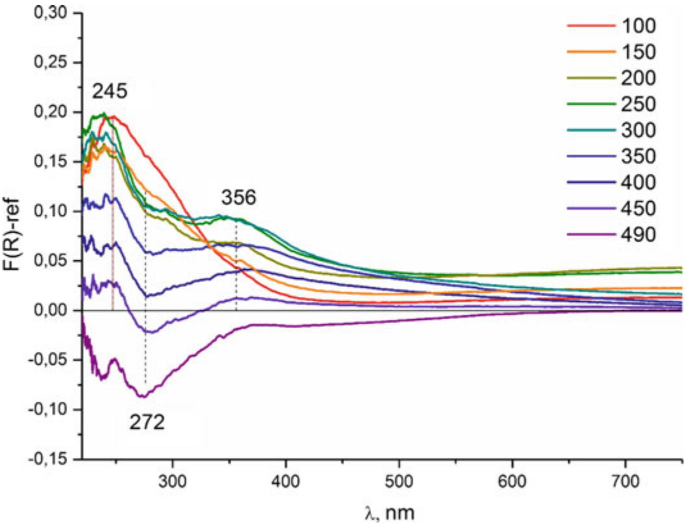


Fig. 11.11 In situ UV-Vis spectra of an Mo-ZSM-5 (Si/Al = 40) catalyst upon interaction with methanol pre-adsorbed at 100 °C and then exposed to increasing temperature

the presence of $O_2Mo(=O)_2$ species coordinated to SiO_2, exhibiting two charge transfer transitions at ~237 and 274 nm corresponding to an E_g value of 4.1 eV. Precise analysis of the E_g values for molybdenum-supported catalysts can be found in Lee and Wachs [99].

11.3 New Trends in in Situ Investigation of Catalysts

The new methods that have been developed are a logical response to the urgent need for a new strategy of active catalyst design and process control. The strategy is based on managing the three scales of catalytic reactor functioning from macroscale, where structured reactors are designed and modelled, through mesoscale, where catalysts are formed on the surface of structured carriers, up to microscale, where catalytic active centres are designed. On the real-time mesoscale, a few methods should be considered for catalytic material heterogeneity, the majority of which are based on UV-Vis and Raman, MRI and UV-Vis, and tomography and Raman-conjugated systems and are thoroughly described by Weckhuysen in terms of real-time imaging of catalysts [65]. At microscale, the majority of the methods able to reach atomic scale are based on fluorescence effects.

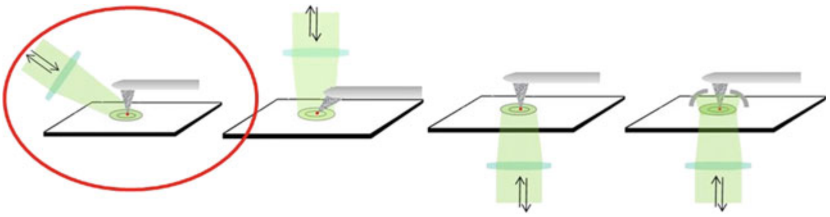
11.3.1 Conjugated AFM/Raman Spectroscopy

Amongst the conjugated techniques, AFM coupled with Raman microscopy gives the opportunity of simultaneous analysis of both structure and texture of the catalyst surface, yielding chemical information at high spatial resolution (down to nanometre scale). The method can be utilised for catalyst surface mapping generally in two boundary modes, with (near-field) or without (far-field) the tip-enhanced Raman effect (TERS), as shown by Łojewska et al. [100]. The principles of AFM-Raman and its applications in catalytic systems can be found in recent review papers [101–106].

The differences in spatial resolution between Raman and AFM are the main problem encountered with far-field mode mapping. The spatial resolution of a Raman microscope is related to the diffraction limit of the laser in the optical parts of the microscope, which for a laser wavelength from a visible range reaches a minimum of around 200 nm, while AFM can go down to atomic scale.

Amongst the vast array of near-field effects [96] is the surface or, more precisely, tip-enhanced effect [101–103]. In theory, Raman enhancement can reach up to 106× but in practice only a 103× increase has been reported to date [107]. There are several optical arrangements in which the interfaced AFM/Raman analyses can be performed, as shown in Table 11.2.

Table 11.2 Optical arrangements of AFM/Raman-conjugated systems and their applicability to different materials

Configuration	Angled	Aligned	Inverted	Inverted
				
Raman detection	+	+ +	+ +	+ + +
TERS	+ +	+ + +	+ +	+ +
TERS mapping	+ +	+ + +	+ +	+ +
Application	Solids, opaque, rough	Solids, opaque, rough	Solids, transparent, flat	Solids, transparent, flat
In situ	Only temperature control	Temperature and gas phase control	Temperature and liquid phase	Temperature and liquid phase

For non-transparent samples such as catalyst materials, several different solutions with an aligned [108] and angled [107] optical configuration have been developed to obtain coupled AFM/Raman maps in reflection mode of solid materials, the advantages and disadvantages of which are discussed in the literature [104]. The general observation of coupled AFM/Raman system users is that the maps with molecular resolution utilising the TERS effect are difficult to obtain and can be recorded using the aligned configuration [107].

An example of studying the heterogeneity of a cobalt palladium-doped catalyst supported on alumina is given in Fig. 11.12 [109]. There, the system was adapted to describe the catalyst surface at mesoscale, upon catalyst formation. It was demonstrated that, on the catalyst surface, PdO grains of micrometre size were formed, which was further used to optimise the preparation method.

Another important and equally interesting direction in which the AFM/Raman technique is developing is the in situ investigation of catalyst surface changes with simultaneous information on the texture and structure. First attempts at this kind of analysis were made by Harvey [110] and show rhodamine oxidation on Ag nanoparticles by in situ TERS analysis.

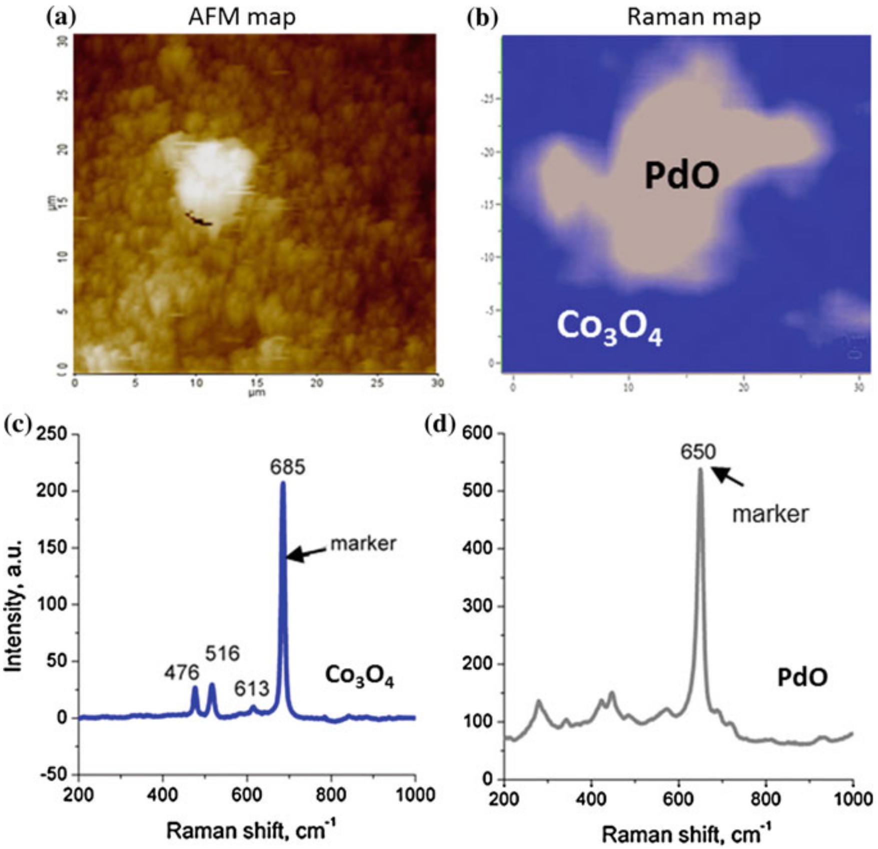


Fig. 11.12 Heterogeneity of pre-calcined Kanthal steel (Al sample) deposited with cobalt oxide and doped with palladium, imaged by interfaced AFM/Raman microscopy. **a** AFM topography map 30 × 30 µm; **b** Raman coupled map of the same size and the same area as in (**a**), obtained using two marker bands of Co_3O_4 (685 cm^{-1}) and PdO (654 cm^{-1}); **c** exemplary Raman spectrum of Co_3O_4; **d** exemplary Raman spectrum of PdO Reprinted with permission from [109], copyright (2018) Elsevier

11.4 Summary

A golden rule of catalytic material engineering is that, to be able to design it, we have to understand it. There are different scales at which a catalyst is approached, designed and manufactured. At microscopic level, the focus of this chapter, fundamental relationships between catalyst structure and activity are surveyed with the aid of advanced methods for catalyst surface characterisation. Since reactions occur exclusively on the very surface of the material in heterogeneous catalysis, there are in fact only a few methods able to analyse surface structure. However, any bulk analytical method becomes a surface method when combined with probing with surface sensitive molecules, providing information on real-time changes in the structure of the catalyst surface. The in situ approach fills the so-called *material* and *process* gaps in catalyst investigation when model simplified materials where studied under conditions far removed from those inside industrial rectors.

In this chapter, the main spectroscopic techniques used for the in situ characterisation of catalyst materials are described. These include FTIR, Raman and UV-Vis spectroscopies. Notwithstanding the spectroscopic method under scrutiny, the strategy for choosing probe molecules is the same. Depending on the type of active centre, different chemical agents can be used for both qualitative and quantitative analysis. Alcohols, however, can be used as universal probes, as they are able to convert to various products upon interaction with different active centres, in brief: on acidic centres—to eters, on basic—to carbonates, on redox—to aldehydes or carboxylic acids. For analysis of Brønsted and Lewis acidic sites, molecules that are their basic pairs are used, and vice versa. Amongst the molecules with basic properties, pyridine and ammonia are used most frequently, and amongst the acidic molecules, carbon monoxide is most prevalent. Special devices are designed for the titration of active sites on a catalyst surface, for the determination of their number that is necessary for the derivation of turnover-frequency values (TOF). Despite the fact that determination of TOF is not always obvious, especially if there are many different kinds of active sites and if they are not fully accessible for a given probe molecule, TOF is unquestionably the most universal gauge for measuring and comparing catalyst activity.

Different spectroscopic methods that are utilised for in situ catalyst characterisation are able to focus on different aspects of a catalyst surface during a chemical process, and in this sense they are regarded as complementary. While IR can focus on the structure of the probe molecule-active site complexes, Raman spots the changes in the structure of metal oxides (the most commonly used catalytic materials) upon these interactions, and UV-Vis captures the shifts in electronic states that accompany the changes. For studies of reaction mechanisms, in situ methods are used for tracking the above-mentioned changes during the catalytic process. Additionally, *operando* techniques allow simultaneous analyses of reaction products, giving insight into changes not only in the surface structure, but also in catalyst activity. The spectroscopic in situ and *operando* methods are discussed in terms of the used instrumentation, sampling and specific realms of their application, and discussed using examples from the literature.

Finally, new trends in the development of in situ methods are presented, with particular reference to:

- Time-resolved techniques for tracing fast reactions demonstrated for IR spectroscopy.
- Coupled techniques, such as UV-Vis/Raman, used for imaging catalyst surfaces at mesoscale and microscale, including in in situ mode. The AFM/Raman technique is discussed in more detail.
- Fluorescence techniques at nanoscale, distinguishing changes on the catalyst surface.

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