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Space-Resolved Profiling Relevant in Heterogeneous Catalysis

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Abstract Knowledge of gradients involved in chemical processes, such as heterogeneously catalyzed reactions, on molecular as well as reactor scale is of paramount importance for understanding and optimizing such processes. This review highlights and discusses recent advances in spatially resolved methods for the detection of chemical (structural) and temperature gradients, with particular focus on in situ methods.

Keywords Space-resolution · Spectroscopy · Microscopy · Heterogeneous catalysis

1 Introduction

Today most chemical processes are catalytic and catalysts play a vital role in modern society and the development of future technologies. Profound understanding of reaction mechanisms and structure-activity relationships under working, *operando*, conditions is of central importance for performance optimization of the catalytic system and particularly for a rational catalyst design [1–6]. However, a full comprehension of the catalytic system generally requires knowledge on involved catalytic, chemical, and physical processes and the existing *gradients* on different length-scales. In a continuous heterogeneous catalytic process using a fixed-bed reactor, for example, concentration as well as temperature gradients are often encountered on a large scale, e.g. along axial and radial directions of the

catalyst bed, on a middle scale, e.g. within catalyst pellets and particles, and also on an atomic scale, e.g. variation of surface species on metal surfaces. Recent interests in understanding the gradients and their nature fostered rapid development of in situ and *operando* spectroscopic methods.

In this short review, we highlight and discuss recent progress of space-resolved in situ methods relevant in heterogeneous catalysis. Particular focus is laid on the middle- and large-scale gradient profiling methods and on discussing the current status of methodological selections and advances. Note that this overview is not meant to be exhaustive and some important methods, especially for atomic-scale space-resolved detection, such as in situ scanning tunneling microscopy (STM) [7–10], transmission electron microscopy (TEM) [11–14], and related electron spectroscopy [15] and imaging [16] are not covered. High-throughput screening methods are enclosed when appropriate because of the necessity for efficient profiling of different catalysts where space- and time-resolution is often mandatory. We wish that this review of currently available space-resolved methods stimulates further methodological developments and applications which will help to gain deeper insight into the functioning of heterogeneous catalytic reactions.

1.1 IR

Infrared (IR) spectroscopy is a very popular method to characterize the chemical nature of catalyst materials and adsorbates based on their characteristic vibrations [17, 18]. Typical measurement configurations such as commercially available in situ transmission IRS and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) cells are, however, not suited for space-resolved studies. One of

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the most direct approaches to add space resolution is by means of IR microscopy (IRM). Space resolution in IRM can be achieved by a motorized stage which controls the sample position. Alternatively, recent development of focal plane array (FPA) detectors made highly sensitive measurements with high spatial resolution possible, allowing simultaneous acquisition of spatial and spectral information. In the field relevant to heterogeneous catalysis, IRM was first applied to analyze the elemental distribution of boron in B-ZSM-5 [19], and later widely used for characterizing intracrystalline concentration profiles of different adsorbates within well-defined microporous crystals together with interference microscopy [20, 21]. Also, the orientation of an adsorbed molecule, *p*-xylene, in silicalite I single crystals was studied by polarized IRM [22]. The preparation, i.e. impregnation and drying processes of Ni/ γ -Al₂O₃ catalyst bodies were investigated by IRM combined with UV-Vis spectroscopy, giving insight into the influence of chelating ligands of precursor complexes on the distribution of the active metal sites over the bodies [23]. Recently, the first in situ, space- and time-resolved IRM study of styrene oligomerization within the H-ZSM-5 micropores was demonstrated using a highly brilliant synchrotron IR beam and the non-uniform product distribution within the crystal was rationalized [24].

Furthermore, highly sensitive FPA detectors open various possibilities for in situ monitoring of catalytic processes. A space-resolved study of CO electro-oxidation using attenuated total reflection (ATR)-IR configuration was reported using the FPA detector and evidenced the inhomogeneities of the CO adsorption and reaction rates on the Pt electrode surface [25]. The FPA detector can also be employed in the evaluation of high-throughput screening of catalytic performance. Multiple samples can be analyzed in two ways: (i) chemical analysis by IR microspectroscopy, and (ii) temperature measurements by IR thermography (IRT) of the radiated IR light from samples. The first approach is similar to the above-mentioned ATR-IR configuration with multiple samples located in the light path. This was successfully demonstrated in transmission IR configuration [26] using CO oxidation as the test reaction, monitoring adsorbed CO [27] and gaseous CO₂ concentration [28]. The second approach was first applied in the screening of various metal elements to find the most active one in hydrogen oxidation reaction [29]. Later, drastic hardware development made the detection of down to 10 mK resolution possible, allowing the efficient screening of various reactions with smaller temperature variations [30–33]. Temperature gradients in steam reforming of methane [34, 35] and NO_x storage-reduction [36] over catalyst beds were also reported and the importance of the heat generation and emerging gradient on the reaction mechanism was discussed. It is not related to IR, but it is

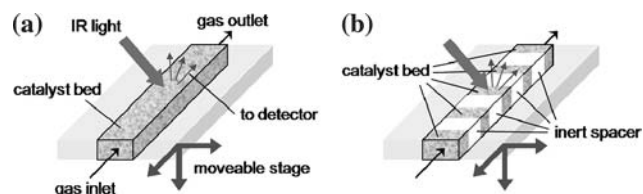


Fig. 1 Schematic sampling configuration of (a) space-resolved DRIFTS and (b) its application for multiple screening

worthwhile to mention the possibility of highly sensitive temperature detection for catalyst screening or other purposes by thermistors allowing 100 μ K resolution [37].

For chemical gradient profiling on a reactor scale, we have recently designed a DRIFTS cell suited for space- and time-resolved studies. Figure 1a shows the schematic sampling configuration. Unlike common DRIFTS cells, the incident IR light hits the sample perpendicular to the axial direction of the catalyst bed. Spatial resolution is added by connecting the cell to a movable *x*–*y*–*z* stage, allowing the sampling along the bed by translating the entire cell. The same configuration can be used for other spectroscopic techniques such as space- and time-resolved Raman spectroscopy. Also, the configuration allows efficient multiple sampling when chemical gradients are negligible, e.g. CO adsorption study [38]. As shown in Fig. 1b, catalyst beds with different compositions can be placed in series separated by an inert spacer, e.g. quartz wool, and the chemical information can be obtained efficiently under identical conditions.

1.2 Raman

Raman spectroscopy is an important technique for chemical analysis and is widely applied in in situ studies of heterogeneous catalytic reactions because of its inherent rich chemical information about molecular structures and surface processes [39–41]. In addition, recent hardware developments, e.g. a submicron laser focus with a motorized sample stage, have facilitated space-resolved Raman studies with some efforts to build appropriate, e.g. heatable and pressurizable in situ cells. The spatial resolution is determined by instrumental parameters and also the excitation laser frequencies, and ca. 0.5 μ m spatial resolution is currently achieved.

Various important aspects of catalyst preparation, such as active sites and phase distribution, have been studied using Raman microscopy and microspectroscopy, e.g. the condition-dependent spreading of MoO₃ active sites on Al₂O₃ surface [42, 43], the structural heterogeneity of MoVW mixed oxide and the identification of the different crystalline phases [44], the elucidations of physicochemical processes and the influence of different complexing agents

on the gradients of active phases within catalyst bodies during the preparations of Mo/ γ -Al₂O₃ [45, 46] and CoMo/ γ -Al₂O₃ [47–49] hydrotreating catalysts.

On a reactor scale, a few studies have been reported so far, e.g. the investigation of the amount of coke formed during propane dehydrogenation along a catalyst bed of Cr/Al₂O₃ [50] and the monitoring of dynamic bulk processes of barium components during NO_x storage-reduction along a Pt–Ba/CeO₂ catalyst bed [51]. On-chip Raman spectroscopy, i.e. Raman microspectroscopy on microreactors, offers very unique and powerful opportunities in optimization and understanding of continuous catalytic processes and provides important information about mass transfer, fluid phases, and catalytic activities along fluid channels and catalyst beds [52, 53]. Recently, we have reported a profiling study of the cyclohexene hydrogenation reaction in supercritical CO₂ using a Pd/Al₂O₃ catalyst under high pressure (>10 MPa), giving crucial insight about the phase of CO₂ in the reaction mixture, fluid diffusivity, and catalytic activity (Fig. 2) [53].

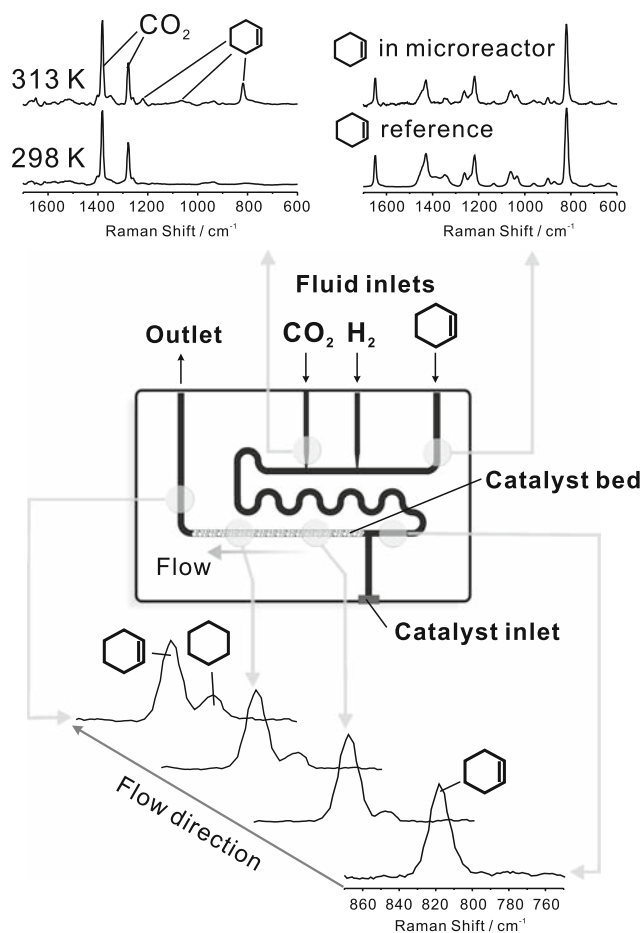


Fig. 2 Overview of on-chip Raman profiling during the cyclohexene hydrogenation over Pd/Al₂O₃ at 10 MPa, 313 K [53]. Reproduced by permission of The Royal Society of Chemistry (RSC)

Moreover, atomic scale chemical gradients are accessible by surface-enhanced Raman scattering (SERS) driven tip-enhanced Raman spectroscopy [54, 55]. The tip of the atomic force microscope (AFM) or scanning tunneling microscope (STM), made of materials which exhibit a strong SERS [56–58] effect such as Au and Ag, is utilized to monitor surface morphology while the local chemical structure and environment near the tip head is sensitively probed by Raman spectroscopy.

Temperature measurements and profiling by Raman scattering is also a powerful application. Temperature of substances (gas, liquid, solid) can be measured by the intensity of Stokes [59, 60] or anti-Stokes [61, 62], Stokes/anti-Stokes ratio [63, 64], rotational Raman scattering [59, 65, 66], Raman shifts [67], or even Rayleigh scattering [59, 68]. Most of the methods require a good calibration procedure, still Raman based thermometry has a great potential for combined thermo-spectroscopy, i.e. simultaneous measurements of temperature and chemical compositions on a scale ranging from μ m to m.

Another important aspect encountered during space-resolved study by Raman spectroscopy is the local sensitivity of Raman spectroscopy in the depth direction. The effective penetration depth into SiC, for example, changes from 50 to 100 nm using a 244 nm excitation laser to 2 mm when a 500 nm excitation laser is employed [69].

1.3 Synchrotron X-ray

The recent development of synchrotron light sources and related optics and detectors has promoted enormous advances in spectroscopy using the extremely brilliant light, especially under in situ conditions with excellent time- and space-resolutions. In heterogeneous catalysis related fields, X-ray based microscopy and spectroscopy is most widely applied compared to the methods based on other available wavelengths at synchrotron.

One of the most popular methods is X-ray absorption fine structure spectroscopy (XAFS). It can be further divided into two categories, (i) X-ray absorption near-edge structure (XANES) alternatively called as near-edge X-ray absorption fine structure (NEXAFS); and (ii) extended X-ray absorption fine structure (EXAFS). The former method, XANES, probes local state of charge, coordination, and magnetic moment of a specific element in molecules and extended structures such as solids, while the latter method, EXAFS, provides information about its surrounding neighbors. Imaging and tomography using XAFS have been described and discussed in great deal [70, 71] and largely categorized into two forms: (i) micro focus optics and scanning sample by movable stage; and (ii) full-field imaging by charge-coupled device (CCD) detector. By the first method, the variations of the oxidation states of

the active metals along a Pt–Rh/Al₂O₃ fixed-bed during the partial oxidation of methane [72] and a Rh/Al₂O₃ fixed-bed during CO oxidation [73] have been elucidated. Moreover, time-resolved 2D mapping of the oxidation state during the same reaction by Rh/Al₂O₃ as shown in Fig. 3 has recently been demonstrated by the second method, which clearly showed its superiority in space- and time-resolved investigations [74, 75]. In addition, the latter detection mode can be applied in high-throughput screening of catalyst states [76], similar to the screening by IR microspectroscopy using FPA detectors discussed above. Furthermore, the 3D mapping of chemical states of a CuO/ZnO catalyst was also reported by the sample rotation and mathematical reconstruction [77].

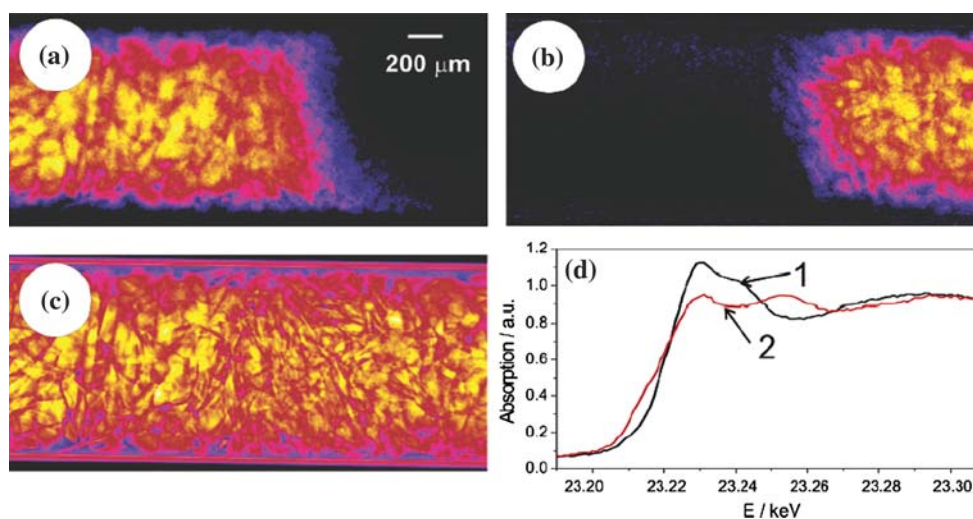
The information on material structure and its variations can be accessed by diffraction methods. Two diffraction methods have been reported, namely X-ray diffraction (XRD) [78–81] and energy-dispersive X-ray diffraction tomography (EXDT) or alternatively called tomographic energy dispersive diffraction imaging (TEDDI) [82–86], where the former uses monochromatic X-ray while the latter makes use of polychromatic X-ray radiation. Despite the fact that diffraction itself does not give element-specific information, a recent study demonstrated its capability to monitor spatial distribution of specific chemical phases by recording diffraction and fluorescence signals simultaneously, and the distribution and composition of metal oxide species in CoMo/γ–Al₂O₃ catalyst have been elucidated [87].

A powerful method for investigating elemental composition and distribution is X-ray fluorescence spectroscopy (XRF) [88] and imaging (2D [79–81, 89] and 3D [90]). Excellent spatial resolutions of 0.5–1 μm range for hard X-rays (>3 keV) and ca. 50 nm for soft X-rays (<1 keV) can be achieved [70]. Although XRF imaging and microspectroscopy have not been widely used in heterogeneous

catalysis so far, we can foresee their wider and more frequent applications due to quick scanning capability, element specificity, high sensitivity (sub-ppm level), good spatial resolution, and possibilities of in situ measurements. By its combination with other techniques such as XRD and XAFS, elemental, chemical, and structural information can be obtained, which can be of great help in identifying various processes occurring under reaction conditions [79–81, 91].

Photoelectron microscopy (PEM) is another type of space-resolved method used in the imaging of solid surfaces [92]. Two methods are well-known within this category, namely (i) photoelectron emission microscopy (PEEM); and (ii) scanning photoelectron microscopy (SPEM or SPM). The methodological principles, applications, and possible combinations of PEM with other techniques have been described in detail [92, 93]. The two microscopic methods are equivalent in their physical working principle; however the different optical and detection methods give distinct characteristics such as micro-spot spectroscopy (e.g. μ-XPS) in SPEM and very fast surface state imaging by PEEM. Taking both advantages, dynamic reaction fronts in NO + O₂ reaction on Rh have been studied, clearly showing the chemical waves and the dynamic changes in surface elemental compositions [94]. Complex electrode processes on solid electrolytes have also been investigated in situ by SPEM/XPS combined with PEEM [95]. PEEM typically applies UV light, and when an X-ray source is used for excitation it is called, for clarity, X-ray photoelectron emission microscopy (XPEEM). In the 1990s the great potentials of PEEM have been demonstrated, for example, by monitoring the reaction fronts and their propagation mechanisms during CO oxidation on Pt [96–98] and during reactions of NO with H₂ and NH₃ on Pt [99], and the deactivation process during ethylbenzene dehydrogenation over iron oxide catalysts

Fig. 3 Gradients in the oxidation state of Rh along the Rh/Al₂O₃ catalyst bed during partial oxidation of methane. Oxidized Rh (1 in d) and reduced Rh (2 in d) are highlighted in (a) and (b), respectively. The homogeneous distribution of a signal due to the catalyst support is shown in (c). Reprinted with permission from [74]. Copyright (2006) American Chemical Society



[100]. Synchrotron X-ray based XPEEM has improved the spatial resolution drastically (ca. 20 nm) and also allowed combination with other special techniques such as X-ray magnetic circular dichroism (XMCD) and X-ray magnetic linear dichroism (XMLD), uncovering distribution of antiferromagnetic and ferromagnetic domains of Co films grown on LaFeO₃ [101]. Orbital mapping between sp² and sp³ states of thin carbon films has also been demonstrated combined with micro-XANES [102].

The non-destructive character of X-ray spectroscopy and microscopy and the contained information concerning elemental analysis, oxidation state, and structure are the major advantages which render these techniques powerful for in situ investigations of catalytic reactions. Clearly, the developments of X-ray spectroscopy is greatly promoted by the development of synchrotron light sources and high space- and time-resolutions can be achieved. Further continuous improvements of the methods for measurements under realistic conditions, i.e. high pressure and temperature, can be expected.

1.4 NMR/MRI

Liquid- and solid-state nuclear magnetic resonance (NMR) has been widely applied in numerous fields and used frequently in both homogeneous and heterogeneous catalysis because of its high sensitivity, detailed structural parameters extracted from various correlation methods, and rich information about the state and chemical environment of nuclei. Magnetic resonance imaging (MRI) or alternatively called nuclear magnetic resonance tomography (NMRT), routinely employed in medical fields, has found its powerful application also in the field of heterogeneous catalysis [103–106]. Spatial resolution of 30 μm can be achieved [107].

MRI has been used to study mainly chemical and physical phenomena such as sorption, mass transfer, and flow patterns and their dynamics on the middle scale, i.e. within catalyst body, and on the large scale, i.e. in reactor and flow channels. It has yielded a great amount of crucial information about catalyst, e.g. active site distributions, and for reactor design, e.g. mass transfer limitations. Structural heterogeneity of catalyst supports such as alumina and silica as well as the mass transports in the pores have been studied by time-resolved imaging or pulsed gradient spin echo (PGSE) NMR to obtain diffusion constants [108–114]. MRI showed its practical importance in deriving design parameter for reactor performance optimization, e.g. fluid flow behavior and gas/liquid distribution within structured catalyst beds such as packed beds and monoliths [115–119]. Direct spatial variation of catalytic conversion within a fixed-bed reactor and coke distribution within catalyst pellets have been also investigated [120–122]. Furthermore, physicochemical processes during

catalyst preparation and resulting distribution of catalytically active metals have been studied, giving rational reasoning for the distribution processes and patterns as shown in Fig. 4 [123–126].

NMR can also be used to profile temperature. Recently, space-resolved NMR thermometry was applied to monitor the temperature gradients along a fixed-bed reactor consisting of Pd/γ-Al₂O₃ beads during propylene hydrogenation [127]. Special applications using NMR tomography such as solid and gas imaging have been excellently described [107].

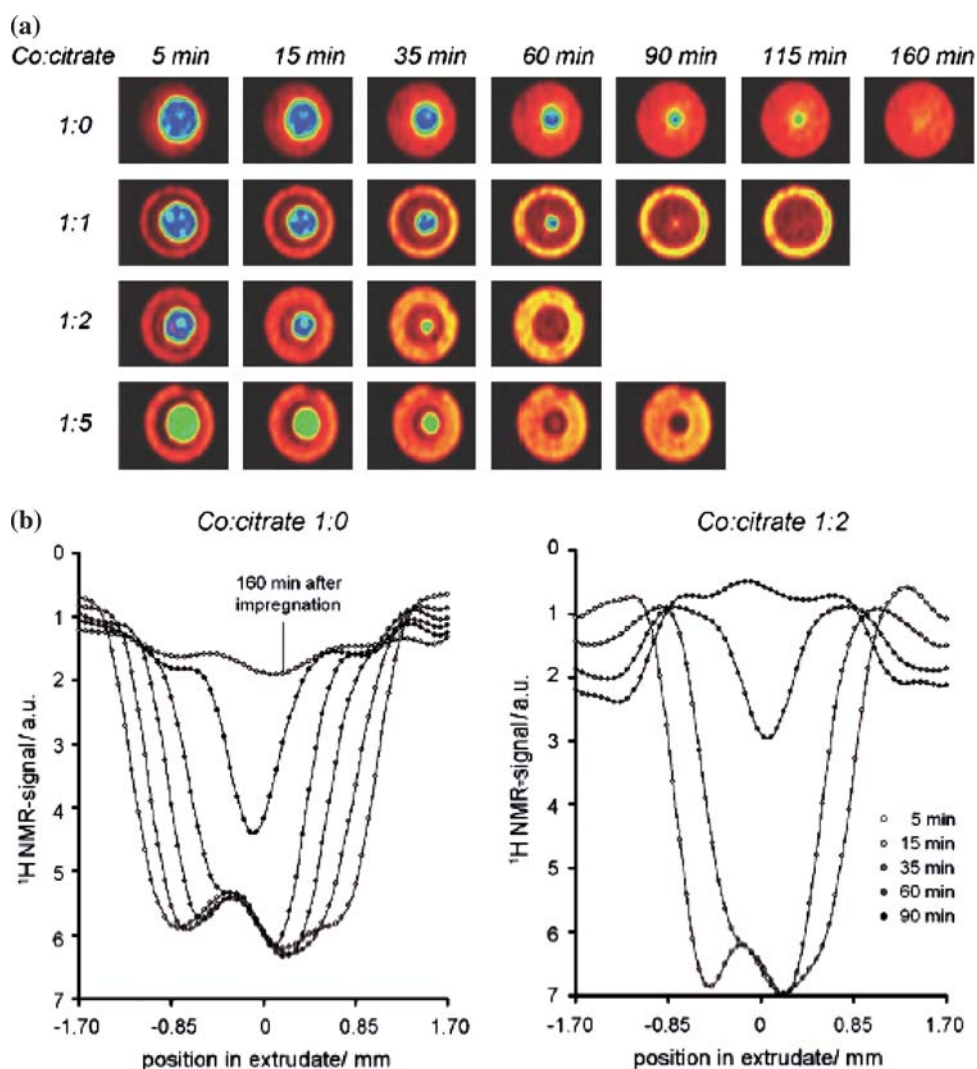
1.5 Fluorescence

Space- and time-resolved fluorescence microscopy is becoming a routine tool for single-molecule detection in biological systems due to its high sensitivity [128–130]. The same technique has been applied in heterogeneous catalysis giving precise chemical information on micro- and nanometer scale. For example, diffusion behavior and kinetics of fluorescent dyes [131], concentration-dependent guest molecule distribution [132] within zeolite L crystal, and also inhomogeneous distribution of guest molecules in zeolite X crystals [133] have been reported. Other studies on ZSM-5 crystals have answered several key questions on diffusivity of substrates, activity of different facets, and micro and mesoporous structures within the crystal [134–137]. The evaluation of the catalytic activity at different crystal faces of layered double hydroxide catalysts has been demonstrated by single turnover counting [138].

1.6 UV-Vis-NIR

UV-Vis-NIR spectroscopy is widely applied in heterogeneous catalysis to study synthesis of solid catalysts, metal-support interactions, and the modification of solid catalysts during calcination and poisoning [2]. However, the addition of space dimension into UV-Vis-NIR spectroscopy was reported only recently. By means of space-resolved UV-Vis microspectroscopy the distributions of metal sites during the impregnation processes in the preparations of Ni/γ-Al₂O₃, Cr/γ-Al₂O₃, and Co/γ-Al₂O₃ have been identified [47, 139]. It was combined with Raman microspectroscopy in a time-resolved manner. The combined studies revealed time-dependent gradients of precursor concentration profiles in a catalyst body during catalyst preparations of CoMo/γ-Al₂O₃ hydrodesulphurization catalyst [48, 49, 140], providing detailed insight into the impregnation and drying processes. UV-Vis-NIR was also combined with IR microscopy to investigate the effect of Ni precursor on the distribution of catalytic active sites during impregnation and drying processes of Ni/γ-Al₂O₃ catalyst preparation [23]. At a reactor scale, multiple UV-Vis probes were used to monitor chemical processes at

Fig. 4 Example of impregnation process monitoring by MRI. The spatial distribution processes and the final states largely differ depending on the composition of the precursor solution. J. A. Bergwerff, A. A. Lysova, L. Espinosa-Alonso, I. V. Koptug and B. M. Weckhuysen: “monitoring transport phenomena of paramagnetic metal-ion complexes. Inside catalyst bodies with magnetic resonance imaging”, *Chem.-Eur. J.* 14 (2008) 2363. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission



different positions of a chromium oxide catalyst bed during propane dehydrogenation [141]. Moreover, UV-Vis detectors can be used to record spectra of space-resolved optical microscopy [142].

UV-Vis-NIR spectroscopy yields valuable information on the state of metals, although the identification and assignments of signals are often difficult due to lack of comparable information and broad bands. The recent mobile sensitive detectors and fiber optics probes facilitate combination of the UV-Vis-NIR spectroscopy with other complementary techniques such as Raman spectroscopy. The addition of space-resolution is also rather facile with the flexible configuration. The space-resolved CCD detection may give another opportunity in this field.

1.7 MS

Mass spectrometry (MS) is one of the most versatile detection methods in gas analysis to evaluate chemical

conversion and selectivity from the compositions. It is not a popular method for profiling due to a specialized detector configuration, still the direct detection of gas compositions along catalyst beds under reaction conditions with an excellent time-resolution has been attempted. Generally, the space-resolved detection can be achieved by simply placing the gas probe at a desired position of the catalyst bed. Some studies utilized the leak rate of the sampling orifice for temperature measurements at the same time [143, 144]. The spatially resolved MS assisted to understand the reaction mechanisms at different locations of the catalyst bed, e.g. in NO_x storage-reduction by Pt/K/Al₂O₃ monolith catalyst [145] and catalytic partial oxidation of methane over Rh, Pt, and Ce based catalysts [146–150]. The latter studies employed a capillary of a small diameter (0.6 mm) containing an orifice and thermocouple, which was inserted into the hole drilled through a foam monolith as shown in Fig. 5. Gas profiling at a very high temperature (>1500 K) [146] and also under relatively high pressure

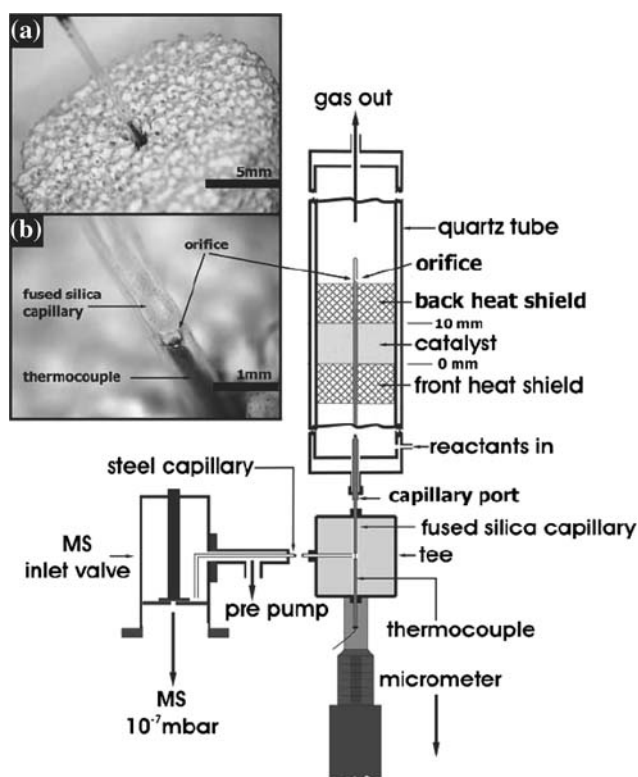


Fig. 5 An example of the axial gas and temperature sampling system along a catalyst bed. With kind permission from Springer Science+Business Media: R. Horn, N. J. Degenstein, K. A. Williams and L. D. Schmidt, *Catal. Lett.*, “Spatial and temporal profiles in millisecond partial oxidation processes”, 110 (2006) 169, Fig. 1

have been achieved, and pressure dependent changes of spatial composition profiles in the range of 0.1–1.1 MPa could be studied [150]. As in the other techniques, this movable probe design can be applied in high-throughput sampling. A recent study showed an efficient screening of reaction selectivity by space-resolved MS and also suggested its possible combinations with other techniques to enhance quantitative and chemical information [151].

1.8 Other Techniques

Besides the techniques discussed above, there are a number of other techniques which can be applied to probe spatial gradients at different scales with unique characteristics in their operating conditions such as pressure and temperature. In particular, recent progress in atomic resolution microscopy and microspectroscopy studied under more practically relevant conditions is remarkable as witnessed by, for example, 2D/3D imaging by electron microscopy [13, 14, 16], electron microspectroscopy [15], scanning force microscopy (SFM) [152–154], STM [7–10], and ballistic electron emission microscopy and spectroscopy

(BEEM/BEES) [155, 156]. In this section, some of the spatially resolved techniques which are not commonly used in heterogeneous catalysis are briefly described.

Electron spin/paramagnetic resonance (ESR/EPR), a popular analytical method in various branches in chemistry and physics, has become an important method for in situ investigation of heterogeneous catalytic reactions [157]. Like MRI, it can be used for imaging, thus called ESRI/EPRI (‘I’ stands for imaging), which is now a well-liked analytical method in biology [158]. The sensitivity is an issue, still its attainable high spatial resolution (10 μm) [159] as well as good time-resolution compared to MRI offers a large potential for its future application in heterogeneous catalysis to monitor active site distributions and also mass transfer behavior in a reactor using an ESR active probe molecule.

Ellipsometry for surface imaging (EMSI) and reflection anisotropy microscopy (RAM) allow monitoring chemical variations of surfaces by the complex refractive index as well as the effective thickness of a surface layer and by the contrast of different reflection anisotropy, respectively. Due to the nature of its optical detection, measurements at high pressure and temperatures are possible, however surface flatness is a prerequisite. The spatiotemporal self-organization of surface species during CO oxidation on Pt was clarified by a combined EMSI-RAM study [160]. Surface plasmon microscopy, with a fixed angle of incident light and monitoring local variations of the state of the electrode, was used to study local chemical gradients at solid–liquid interfaces, e.g. the surface reduction of $\text{S}_2\text{O}_8^{2-}$ on Ag thin film electrode [161, 162].

Interference microscopy (IFM), as mentioned in the IR section, is a powerful tool to monitor concentration profiles within crystals with a good time-resolution. The good spatiotemporal resolution was beneficial to study, for example, inhomogeneous distribution, sorption, and diffusion kinetics of guest molecules in nanoporous host materials [20, 21, 163, 164]. Another non-invasive imaging method which allows monitoring diffusional properties is optical coherence tomography (OCT). OCT is a powerful non-invasive method mainly applied in the field of biology for in vivo and in vitro imaging [165, 166].

A spectroscopic method suited for depth profiling is photoacoustic spectroscopy (PAS) [167–169]. Its application in the infrared region in combination with modern FT-IR spectrometers, FT-IR/PAS, has gained considerable attention in catalysis research. The key characteristics of PAS are: the method is non-destructive, applicable to micro- and macrosamples, insensitive to surface morphology, capable of the detection from the ultraviolet to far infrared range, and contact free [167].

An interesting method which can measure very sensitively the composition of gas, liquid, and solid is laser-

induced breakdown spectroscopy (LIBS, alternatively called laser-induced plasma spectroscopy, LIPS) [170]. LIBS is becoming a more versatile tool to investigate spatial distribution of elements, such as metal composition mapping of minerals [171] and catalysts [172, 173]. The method is not matured currently, but its wider application can be foreseen from the rapid development.

2 Concluding Remarks

Proper understanding of gradients in the concentrations of chemical species, their states, and also temperature at molecular to reactor scale is doubtless important to fully rationalize the final outcome of heterogeneous catalytic reactions. There are several aspects and directions, which we believe to be of importance in the near future for space-resolved profiling relevant in heterogeneous catalysis.

One of the most decisive factors for achieving higher spatial resolution is further technical development of the various crucial parts of the measuring systems. In the past years many new detection methods have been developed and also the scope of existing methods has been broadened thanks to the rapid developments of optical components and light sources. Particularly, the good worldwide availability of synchrotron facilities nowadays promotes the drastic developments of synchrotron-based microspectroscopic techniques. The brilliance of the light is necessary not only for achieving high space- and time-resolution but also for in situ measurements especially under high-pressure conditions where the light is largely absorbed by reaction media.

Certainly, methodological development with innovative ideas can significantly contribute to adding and improving spatial resolution. Tip-enhanced Raman spectroscopy is a good example to add atomic resolution into the ordinary Raman spectroscopy with μm spatial resolution. Adaptions of measurement configurations can also be utilized to vary the local sensitivity of a technique as recently shown for IR spectroscopy [174]. For example, depth profiling and mass transfer studies would be possible by applying variable angle ATR configuration for UV-Vis, fluorescence, and IR spectroscopies. Moreover, lateral space-resolution and high time-resolution may be gained in addition to the depth profiling by employing 2D CCD/FPA detectors.

As shown by a number of recent studies, there is a limitation of the information gained by a single technique, and the combination of complementary techniques, such as UV-Vis/Raman and IFS/IRM under in situ conditions with innovative cell designs, is extremely beneficial and can greatly deepen and improve the knowledge about investigated systems. Often it is even crucial to simultaneously monitor the spatial gradients in chemical concentration,

structure, and temperature by complementary techniques in order to firmly correlate their effects on the catalytic performance. Recent hardware developments and availability of mobile spectrometers occasionally coupled with optical fibers, e.g. for IR, Raman, UV-Vis and fluorescence spectroscopies, facilitate such combined investigations at laboratories and synchrotrons.

Important gradients for optimization of heterogeneous catalytic reactions range from the scale of the catalyst body to the reactor. Although there are steady progresses in the methodological developments for elucidating such gradients, it seems that the tools for the investigations are currently limited compared to those available for molecular-level detections and therefore need to be developed further. For instance synchrotron X-ray based tomography can serve as a microspectroscopic method for such purposes, and generally a well-thought multi-purpose cell design, e.g. made of or equipped with optically transparent materials for UV-Vis and Raman spectroscopy along catalyst beds, may greatly help for gaining a deeper understanding and finally for efficient optimization of catalytic processes.

Currently, software and algorithm developments are very important and critical for the evaluation of 2D/3D space-resolved data to construct useful images. Also, data analysis scheme such as 2D correlation [175] and phase-domain analysis in the framework of modulation excitation spectroscopy [176] can significantly enhance the sensitivity and hence improve the time- and space-resolutions. Such correlation analysis may provide more detailed, space-resolved information by choosing appropriate experimental parameters, and can be achieved with no extra experimental effort when more than a single analytical method is already in use.

The recent progress in high-throughput screening in heterogeneous catalysis as well as micro-analytic systems, e.g. lab-on-chip, was made possible by great advances in detection methods in both space- and time-resolved manner [177, 178]. Careful observation of the progress in detection methods in these fields could spur further development of novel and efficient detections of spatial gradients relevant in heterogeneous catalysis and related fields.

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