

# Trends and Advances in *Operando* Methodology

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## Abstract

After the introduction of the term, *operando*, the catalysis community has taken significant steps forward to understand chemistry and physics taking place within catalyst body and catalytic reactor on different length and time scales with great motivation to firmly establish catalyst structure vs. catalytic performance relationships. Herein recent advances, current trends and possible future directions in *operando* methodology are briefly summarized.

## Introduction

Nearly 15 years has passed since the Latin word, *operando*, was coined by Miguel A. Bañares, Eric M. Gaigneaux, Gerhard Mestl, and Bert M. Weckhuysen to distinguish the experimental conditions from *in situ* and the first papers mentioning *operando* appeared in 2002 [1-4]. As described in detail by Bañares [5] and Weckhuysen [6], this historical action was motivated by the necessity to highlight the importance of studying catalyst materials under working conditions (i.e. showing practically relevant catalytic activity) by analytical and visualization techniques. The definition of catalysts' working condition naturally requires verification of catalytic activity and selectivity. Hence, the condition of *in situ* study of catalyst materials and/or catalytically active species together with simultaneous evaluation of catalytic performance is generally defined as *operando* methodology. The term has now widespread to various research fields such as gas sensors [7,8] and battery [9-11] when

spectroscopic measurements and spectro-imaging are performed under technologically relevant conditions to elucidate structure-performance relationships.

The birth of *operando* methodology in catalysis was urged by the increasing number of examples showing large temperature, pressure and materials *gaps* where catalytically active species and sites could be uniquely formed under specific reaction conditions, typically a combination of high-pressure, high-temperature, and specific nano-structured catalyst materials deposited over inorganic materials which are shaped in a pellet form (Figure 1). Nowadays, it is widely recognized that the structure of catalyst surface is dynamic and often undergoes reconstruction when reactants interact with the outer surface. A notable example is the atmospheric-pressure STM study of CO oxidation by Hendriksen and Frenken [12]. When the partial pressure of O<sub>2</sub> to CO was sufficiently high, the Pt surface was reconstructed, forming PtO<sub>2</sub>-like islands which were remarkably more active in CO oxidation than the clean Pt surface [13,14]. When O<sub>2</sub> concentration became low, the Pt surface reconstructed back to flat Pt surface, showing the dynamic nature of the catalytic surface.[12,15] Similar insights were also gained for Pd surface and the widely observed oscillatory behavior of CO oxidation activity could be elegantly explained by formation and disappearance of the highly active nano-oxide phase of Pd.[16] These studies show that well-defined materials under *operando* conditions can yield precise and important physical and chemical insights on the atomic scale.

Obtaining the key information on catalyst materials and reaction conditions directly linked to the reactivity of catalysts on the laboratory or industrial scale requires, however, further efforts in simulating and understanding the complexity of the catalyst material, diffusional characteristics, and hydrodynamics on different length scales, i.e. those of atom, catalyst particle, pellet and reactor [17,18]. When catalyst pellets are packed in a reactor and a fluid of reactant(s) passes through it, there are always concentration gradients of reactants,

products and possible intermediates in the fluid and over catalyst surface along the axial and possibly radial direction of the reactor. On a smaller scale, within the catalyst pellet, reactions take place and concentration gradients of reactants, intermediates and products arise. On the same scale, elemental and concentrational heterogeneities of catalytically active materials within the pellet may be present deliberately or accidentally. On the smallest scale, catalytic activity is induced and influenced by various physical and chemical phenomena such as atomic/molecular adsorption, surface reaction, desorption, surface reconstruction, active site formation, and/or surface poisoning, which also create concentrational heterogeneities because actual catalyst surfaces are never flat like perfect single crystals but complexly shaped mountains and valleys composed of various chemical elements. It is important to realize that the above gradients on the scales of reactor and catalyst pellet can directly influence the atomic scale surface chemistry because they impact on the concentrations of chemical species in the fluid phase, which can be even time-dependent [19]. Moreover, temperature may vary on each length scales and understanding these gradients can be of direct relevance for full comprehension of heterogeneous catalytic processes [20].

Furthermore, even when technology allows studying physicochemical processes on the different length and desired time scales, there is another issue of studying catalytically active sites and species *selectively* under *operando* conditions without the information buried in the overwhelming signals of spectator chemical species, solvent and catalyst support materials. This is inherent to any measurement techniques and becomes serious under *operando* conditions, where surface chemical species are present at high concentrations and selection of detection methods is limited by the typical operational conditions of high temperature and pressure.

Over the past years, significant progresses were made to tackle the above challenging aspects of *operando* methodology and catalysis research in general. Recent trends and

advances made in the field from my personal view are briefly highlighted in Figure 2 and summarized below.

### **Multi-probe approach**

Using a single characterization technique often fails to give a sufficiently precise picture of catalytic processes and materials because it is limited in probing area (space-resolution), speed (time-resolution), transition (type of excitation/relaxation), element, electronic structure and/or geometrical structure (long/short-range ordering). Therefore, combined use of complementary techniques is desired to gain holistic views on catalytic processes (Figure 2a) [21]. Powerful combination to gain molecular, electronic and structural information is vibrational (IR/Raman) spectroscopy combined with X-ray spectroscopy/diffraction [22]. Newton has pioneered the combination of diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS) and X-ray absorption spectroscopy (XAS), the former providing information about chemical bonds of surface species and the latter providing geometrical and electronic structures of active metals [23]. The advent of low-noise, high-resolution 2D detectors has enabled X-ray diffraction (XRD) to be combined with other techniques like XAS using the same capillary reactor cell [21,22,24,25]. Another combination gaining popularity recently using X-ray is XAS/X-ray emission spectroscopy (XES), which can yield a detailed picture of electronic states (unoccupied and occupied orbitals). Also, local coordination (e.g. adsorbate or ligand) environment can be studied by the latter technique more precisely. An elegant use of the combination was recently demonstrated by Jacob and Grunwaldt to elucidate the chemistry around active Fe center located in a zeolite structure for selective catalytic reduction (SCR) of NO by NH<sub>3</sub> [26]. Possibilities for the combination of *operando* probes are infinite and it is important to choose the most appropriate techniques to investigate the key information under question.

## Space-resolved spectroscopy/diffraction, imaging and tomography

Seeing the reality by eyes (with the help of light) is often worth more than a number of catalytic experiments. This approach is very rapidly evolving and has been recently demonstrated by several research groups under *operando* conditions. Generally, three different modes are used to add space-resolution to a technique on reactor, pellet and atomic scale with/without the help of post-mathematical reconstruction of images.

The first one (Figure 2b) makes use of a focused light and one gains a space-resolution by moving a pellet/reactor. Confocal Raman spectroscopy operates in this mode and has been applied to study water transport within proton-conducting polymer electrolyte under *operando* condition [27]. Along entire catalyst beds, *operando* space- and time-resolved DRIFTS-Raman [19], XAFS [28] and XRD [29] were used to study catalyst materials in deNO<sub>x</sub> chemistry and methanol-to-olefin (MTO) process. The second mode (Figure 2c) is to obtain the full picture in one shot using a 2D detector with a great advantage in the time-resolution [30]. Such a fast 2D detector was used also for single-molecule counting based on total internal reflection fluorescence microscopy (TIRFM) to prove that a cycloaddition reaction took place over the surface of Cu nanoparticles and not in the solution by possible leached Cu species [31].

The third mode (Figure 2d) for chemical/structural imaging or tomography, slice by slice, is widely used in magnetic resonance imaging (MRI) well known for medical applications. MRI is also actively employed in heterogeneous catalysis research by Koptug to gain unique insights into mass transport and heat transfer on the pellet and reactor scales [32]. Similar slicing approach using computed tomography (CT) of XRD, XAS, and X-ray fluorescence (XRF) have been pioneered by Beale, Jacques, Di Michiel, and Weckhuysen among others using mainly synchrotron facilities [33,34] and even in the lab [35]. Inside the complex membrane reactors for oxidative coupling of methane (OCM) reaction could be seen

through [36] and in another study even a catalyst particle in liquid phase chemistry could be studied [37]. Impressive time-resolution ( $>1$  Hz) was demonstrated in battery research under *operando* thermal runaway using CT-tomography and radiography combined with thermal imaging [38].

### **Multivariate analysis**

Analysis of *operando* spectroscopic data often suffers from three issues. One is related to the detection *selectivity* towards what we would like to hunt as described above. Another challenge is the interpretation of spectra, which is often hindered by overlapping signals of coexisting multiple components in the bulk and/or on the surface of catalyst solids. Under *operando* conditions, the situation is significantly more challenging compared to that under well-defined UHV conditions. Even worse, appropriate reference spectra are often unavailable because catalytically active species and phases may be only present stably or transiently under *operando* conditions.

The problem of detection selectivity may be elegantly solved by exerting a perturbation of an external parameter (temperature, concentration, light flux, etc.) to a catalytic system such that the reaction rates and concentrations of species/phase of interest vary. Such step/pulse-response experiments are widely used. Among them, steady-state isotopic transient kinetic analysis (SSITKA) is an experimental technique to follow the kinetics of catalytic reactions by varying reactant concentration in the form of isotopomers without disturbing the chemistry [40]. Another approach to add selectivity with drastic improvement in detection sensitivity is modulation excitation spectroscopy (MES) [41]. MES uses periodic change of an external parameter (e.g. varying reactant concentration, ideally from that of steady-state one for *operando* studies). Spectra are continuously measured over a number of stimulus-relaxation cycles and averaged into one cycle (first S/N improvement)

and then the one-cycle data are further processed by phase-sensitive detection (PSD) to filter out static signal (e.g. due to solvent and catalyst support) and noise (second S/N improvement) and to kinetically differentiate evolving signals in the so-called phase domain [41]. MES can be combined with any techniques such as IR [42] and XAFS [43]. Recently, the theory of MES for diffraction has been developed and the technique is called modulation enhanced diffraction (MED) [44]. By MED one can study active sublattices [45] and element-specificity can be achieved by applying X-ray energy MED [46].

SSITKA and MES can extract valuable information, but both often suffer from signal overlaps and occasional unavailability of spectral references for interpretation. Recently, an increasing number of applications of multivariate spectral analysis suited for blind source separation has been witnessed. In such analysis, one measures spectra over a period of time with/without external perturbation and directly post-process the spectroscopic data by the mathematical engine to separate them into kinetically pure components and respective concentration profiles (Figure 2e). *Blind* means there is no reference required for the spectral separation process. Band-target entropy minimization (BTEM) actively applied in homogeneous catalysis [47] was also employed to identify surface species measured by DRIFTS during the reaction of CO and NO over Pd [48]. Non-negative matrix factorization (NNMF) was used to separate overlapping UV-Vis spectra to identify deactivating species during MTO process over H-SSZ-13 [49]. Multivariate curve resolution (MCR) became very popular across different disciplines for blind source separation and it has been successfully used for XAS [50,51] and IR spectroscopy [52] with kinetic analysis of heterogeneous catalytic reactions with a strong emphasis to simplify the spectral analysis by the conversion of numerous spectra to a few to some component spectra and respective concentration profiles.

## **Outlook**

Categorizing specific areas of *in situ* into *operando* has promoted the awareness of researchers about the importance of *operando* methodology in catalysis research to study catalysts under technologically relevant conditions and to look at important spots within catalytic reactors and catalyst materials. The intentional use of the term, *operando*, urged by the awareness of the “gaps” has obviously driven the great technological advances in demanding and sophisticated space- and time-resolved measurements on different length scales. There are clear next steps in the three main streams of *operando* methodology described here by employing more complementary probes measured simultaneously, enhancing further the space/time resolution, and improving the blind source spectral separation methods. Yet, the challenges of *operando* community still remain as indicated by the generally poor penetration of *operando* methodology in industry or by scarce collaboration between academic and industry researchers using *operando* methodology from the author’s view. The point is less scientific but more opportunities for dialogs between researchers in academia and industry are crucial to enhance the relevance of research work to know exactly what kind of aspects are more relevant in industrial processes and to know conditional constraints in commercial processes. Along the same line, the relevance is best ascertained when *operando* studies are performed in a reactor where catalytic performance makes practical sense. For this, chemical engineering aspects like hydrodynamics, mass transport, and reaction kinetics are ideally taken into account in *operando* spectroscopic reactor design. These aspects are actually best clarified by also *operando* methodologies using spectroscopic and visual inspection to see through *operando* reactor mimicking industrial processes or envisioned future catalytic processes.

### **Acknowledgements**

MINECO is acknowledged for support through Severo Ochoa Excellence Accreditation 2014–2018 (SEV-2013-0319) and CTQ2012-34153.



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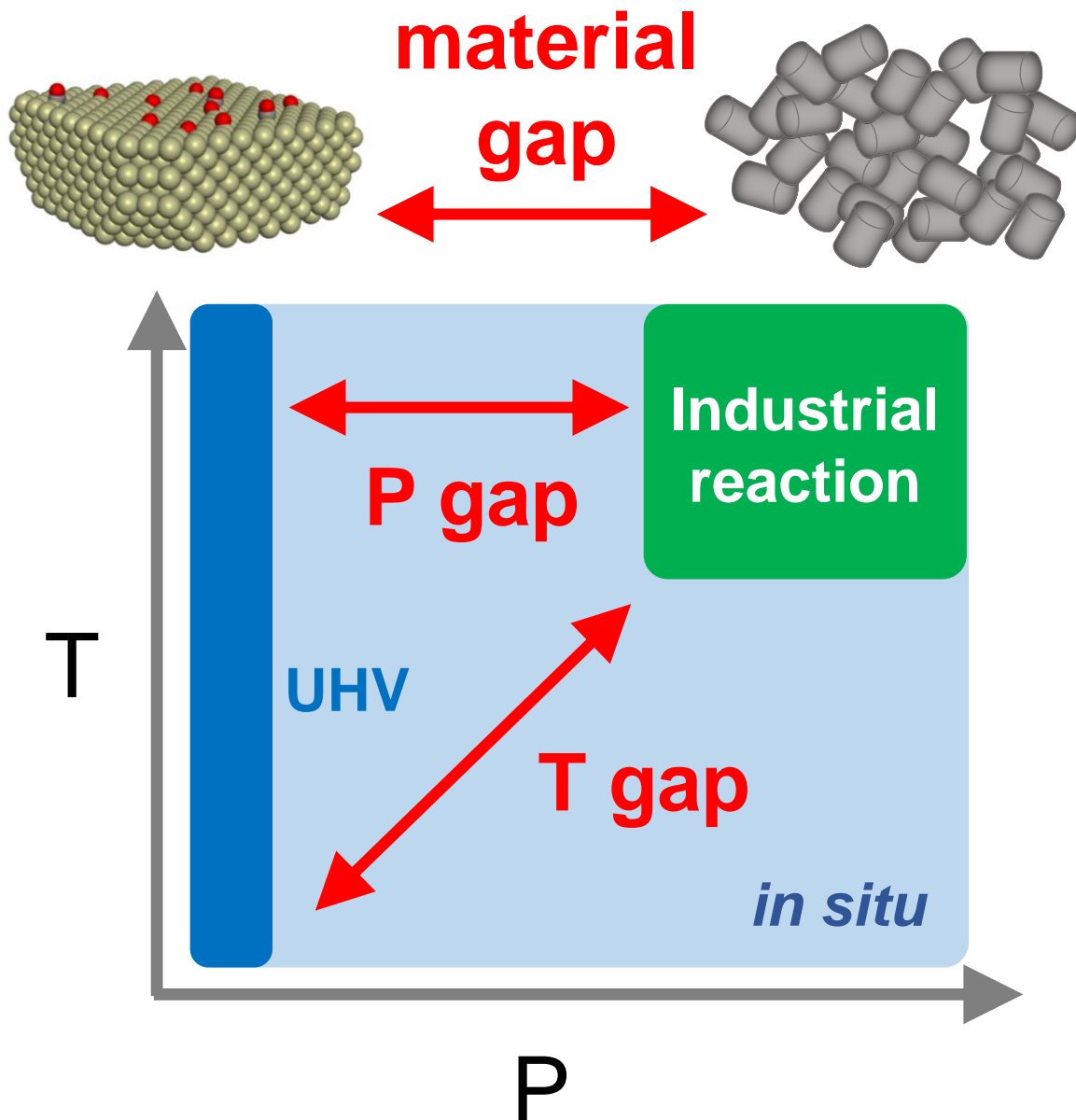
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**Figure 1.** Three major gaps (material gap, temperature gap and pressure gap) often causing problems in *practical relevance* of spectroscopic and diffraction studies of catalyst materials. These gaps have to be filled to address real situation of catalyst material at work under technologically relevant conditions. UHV stands for ultra-high vacuum.



**Figure 2.** Trends in *operando* methodology: (a) multi-probe approach, (b-d) space- and possibly time-resolved approach, where spatial resolution is achieved by (b) moving a sample (reactor/catalyst particle), (c) using 2D detector, (d) first sliced 2D then 3D spectroimaging by sample translation, and (e) multivariate analysis to identify spectroscopically “pure” components and their concentration profiles often without the need of reference sample measurements. For (a-d) the approach can be used for studying a single catalyst particle or pellet.

