

In Situ and *Operando* Spectroscopy: A Powerful Approach Towards Understanding Catalysts

Revealing reaction mechanisms to find the correlation between structure and surface composition

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The improvement of catalytic processes is strongly related to the better performance of catalysts (higher conversion, selectivity, yield and stability). Additionally, the desired catalysts should meet the requirements of being low cost as well as environmentally and user-friendly. All these requirements can only be met by catalyst development and optimisation following new approaches in design and synthesis. This article discusses three major approaches in the design and development of catalysts: (a) high-throughput synthesis; (b) reaction kinetic studies; (c) *in situ* and *operando* spectroscopy for studying catalysts under process conditions. In contrast to approaches based on high-throughput synthesis and reaction kinetic studies, an emerging approach of studying catalysts under process conditions using *in situ* and *operando* spectroscopy and transferring the gained knowledge to design

of new catalysts or the optimisation of existing catalysts is not yet widely employed in the chemical industry. In this article, examples of using *in situ* or *operando* spectroscopy for studying the surface and bulk of catalysts under process conditions are discussed, with an overview of applying *in situ* X-ray absorption spectroscopy (XAS), *in situ* infrared (IR) spectroscopy and *in situ* near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) for monitoring the bulk and surface composition of PdZn/ZnO and Pd₂Ga/Ga₂O₃ methanol steam reforming catalysts.

1. Approaches for Catalyst Development

1.1 Discovery of a 'Lucky Catalyst' via High-Throughput Synthesis

Research and development of more efficient and sustainable catalysts, either the development of novel catalysts or optimisation of existing ones, is a vital part of industrial and academic research. One of the most common approaches for catalyst development is the synthesis of a large number of catalysts, followed by screening of their catalytic activity (known as high-throughput synthesis) (1, 2). A high-throughput synthesis approach is the most common method of catalyst discovery and optimisation and can be strongly boosted by the combinatorial design of experiments and using robotic equipment to synthesise and test catalysts (3–8). One of numerous catalysts prepared using high-throughput synthesis might be very active for a particular reaction (a 'lucky catalyst'). However, employing such an approach

alone without understanding activity-controlling factors often does not lead to a gain in knowledge or deep understanding of factors driving the activity and selectivity of catalysts (for example the nature of active sites and reaction mechanisms).

Understanding the structure-performance relationships of catalysts is a crucial step for the successful development of the next generation of more efficient catalysts and covers different aspects. Some research lines focus on the preparation of catalysts by varying certain parameters (for example preparation methods, elemental composition or loading) and then correlate catalytic properties of the synthesised materials with their structure, reducibility or tendency to adsorb or desorb the educts and products for a particular reaction. Combining knowledge of a catalyst's performance with its structure adds substantially to the understanding of catalytic systems and the potential to transfer knowledge to similar processes or products. Yet this approach provides rather a macroscopic picture of the structure-performance relationships of catalysts, omitting the detailed microscopic insights into the activity-controlling factors driving a particular reaction.

1.2 Reaction Kinetic Studies

Another line of research focuses on microscopic insights and explores the nature of the reaction sites of a catalyst and the mechanisms of reactions (9, 10). The commonly used methodology is based on a detailed study of reaction kinetics (reaction rates and rate laws). It takes its roots back to 1921 when the mechanisms of the catalytic action of platinum in the reactions of carbon monoxide oxidation and hydrogen oxidation were described with the help of kinetics by Irving Langmuir and presented at a Discussion of the Faraday Society held in September 1921 at the Institution of Electrical Engineers in London, UK (11). Langmuir's work was later elaborated by Cyril Hinshelwood. The combined work of Irving Langmuir and Cyril Hinshelwood is known today as the Langmuir-Hinshelwood mechanism and is one of the most common reaction mechanisms describing numerous catalytic reactions (12). According to the Langmuir-Hinshelwood mechanism, a catalytic act is a reaction between two molecules, adsorbed on neighbouring sites (12).

Some years later, in 1938, Dan Eley and Eric Rideal proposed the Eley-Rideal mechanism, in which a catalytic act is a reaction between an adsorbed molecule and a molecule from the gas phase (13).

Later works of Mars and van Krevelen on reducible oxides in 1954 suggested another mechanism that today is called the Mars-van-Krevelen type redox mechanism. According to the Mars-van-Krevelen mechanism, one reactant forms a chemical bond with the catalytic surface; the other reactant reacts directly from the gas phase. A vacancy that is formed when the reaction product desorbs was thought to be filled with an atom from the bulk (14). However, nowadays it is generally accepted that the vacancy created by the reaction is filled with the first reactant again.

The type of mechanism depends on the type of catalyst. The Mars-van-Krevelen type redox mechanism typically applies to reducible metal oxide catalysts, where lattice oxygen is involved in the reaction cycle and generation of vacancies is a crucial reaction step. The Eley-Rideal and Langmuir-Hinshelwood mechanisms typically describe non-reducible oxides and metal nanoparticle catalysts, where a network of elementary reaction steps involves adsorption of reactants on the catalyst surface, a catalytic reaction and desorption of products.

As is demonstrated in the review of Rob Berger *et al.*, in the chemical industry knowledge of the reaction kinetics is of primary importance for: (a) catalyst development; (b) process development; (c) process optimisation; and (d) mechanistic research (12). 29% of the utilisation of kinetic data in industry is dedicated to catalyst development (12). For mechanistic studies and advanced catalyst development, a precise description of the reaction rate is required at the level of elementary steps. This calls for advanced kinetic studies such as fast transient kinetic investigations (employing a temporal analysis of product reactor) (15) and advanced kinetic modelling studies (16–18).

1.3 The *In Situ* and *Operando* Approach

Although studying the kinetics of reactions is a powerful tool for identifying steps of the reaction cycle and for obtaining hints about active sites, it does not allow a complete picture of the reaction mechanism to be obtained. Often several reaction mechanisms can run in parallel; therefore, an exact identification of the reaction mechanism is not feasible. Moreover, for heterogeneous catalytic reactions, the identification of active sites is rather vague especially for solid catalysts because of their complexity. Often solid catalysts are multicomponent and multielement materials. Furthermore, the structures of solid catalysts are usually not well defined; thus, several sites might serve as active

sites and as a result, different reaction pathways might simultaneously run on different reaction sites or in different temperature regimes.

The complementary methodology based on the use of *in situ* and *operando* techniques for studying the catalyst under reaction conditions can overcome some of the limitations of the traditional kinetic methodology and provide a broader insight into the complex network of reaction pathways, thereby strongly contributing to understanding the structure-performance relationships of catalysts, the nature of active sites, reaction mechanisms, the structure of working catalysts and, based on the knowledge gained, the design of new catalysts (19–21).

Why is it so important to study catalysts under process conditions? Solid catalysts are very dynamic under working conditions when high temperatures and pressures are applied. Freshly prepared catalysts often undergo structural changes under activation and pretreatment conditions and further under reaction conditions. Thus, simply speaking, catalysts ‘adjust’ to the reaction environment (22). Monitoring such environment-induced changes of catalysts and understanding why they happen should be taken into account during the design of catalysts.

The traditional approach to gain insights into environment-induced changes was and is still in many cases to study catalysts *ex situ* (meaning outside, off site, out of place). However, this does not allow a clear picture of working catalysts to be obtained (Figure 1). The famous saying of Gabor Somorjai highlights this, stating that knowing the

‘before-reaction part’ or ‘after-reaction part’ “is like studying a life with access only to the prenatal and postmortem states” (23). Moreover, exposing the catalyst to ambient conditions might again change the catalyst’s structural and electronic properties and lead to data misinterpretation (Figure 1).

A more informative way is to monitor the catalyst directly under reaction conditions, *in situ* (meaning on site, in position, undisturbed) (23). Watching the catalyst under reaction conditions by physical-chemical methods and simultaneously recording catalytic data using a mass spectrometer or a gas chromatograph allows the catalytic properties to be correlated directly with electronic and structural changes in the catalyst. This approach is called ‘*operando*’ (24–26). An *in situ* approach is not only used for studying catalysts under working conditions, but can also be applied to the preparation of catalysts. For instance, application of tomographic energy dispersive diffraction imaging during the calcination of $[\text{Ni}(\text{en})(\text{H}_2\text{O})_4]\text{Cl}_2/\gamma\text{-Al}_2\text{O}_3$ and $[\text{Ni}(\text{en})_3](\text{NO}_3)_2/\gamma\text{-Al}_2\text{O}_3$ hydrogenation catalyst bodies was used to study the changes in the structural composition of the catalysts at the macroscopic level (27).

An *operando* or *in situ* approach allows one to study the “birth, life and death” of catalysts, a concept that was recently introduced by Bert Weckhuysen (22). According to his concept, “birth” refers to the stage when a catalyst is prepared, as it is essential to understand how catalytic solids are formed; “life” describes how a catalyst functions

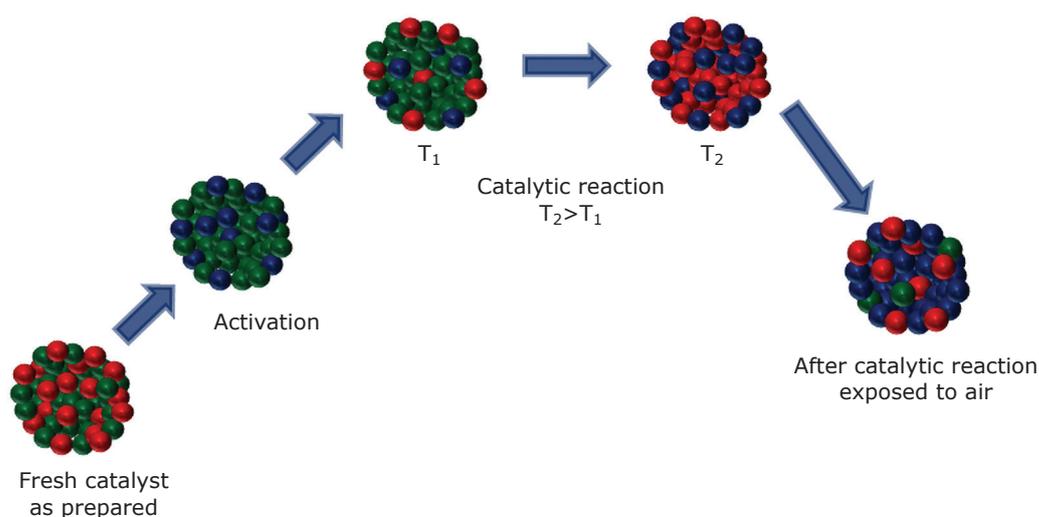


Fig. 1. Catalyst evolution during its lifetime: calcination, activation, during catalytic reaction and post catalytic reaction after being exposed to air

and performs in a catalytic reaction; “death” explains how a catalyst undergoes deactivation.

Generally, *operando* investigation of catalysts can include spectroscopic techniques (for example Raman spectroscopy, infrared (IR) spectroscopy, X-ray photoelectron spectroscopy (XPS), XAS, ultraviolet-visible (UV-Vis) spectroscopy and electron paramagnetic resonance (EPR) spectroscopy), but also microscopy (for example environmental transmission electron microscopy or environmental scanning electron microscopy, X-ray diffraction (XRD) and X-ray total scattering). A number of research groups have demonstrated the strength of combining several *in situ* techniques for the investigation of a range of catalytic systems under reaction conditions to identify dynamic changes to the catalysts under varying conditions (Figure 2) (28–35). Therefore, many efforts and the attention of the *operando* community are directed towards developing an integrated or combined approach, simultaneously applying several techniques (for example IR, Raman, XRD and XAS), for studying catalysts under reaction conditions.

Such an approach is successfully employed in the BM01B beamlines at the European Synchrotron Research Facility (ESRF), where *in situ* XRD, XAS and Raman spectroscopy are combined (36). Other synchrotron facilities have also been taking

steps in this direction. Table I summarises the most commonly used hard X-ray synchrotron beamlines from the European synchrotron facilities where opportunities for *operando* and *in situ* studies of catalysts are provided. Using an integrated approach requires special reaction cells that allow *in situ* experiments to be carried out either simultaneously or sequentially in the same cell. Therefore, many efforts are directed toward the development of cells that can be used for combined measurements, in particular focusing on the cell design to obtain good agreement between the catalytic activity and selectivity of a catalyst measured in a conventional reactor and in a spectroscopic cell (37–39).

2. The Need to Understand the Surface of Catalysts Under Process Conditions

The increased interest in the *in situ* and *operando* approach for studying catalysis is demonstrated by the increased number of research papers where *in situ* and *operando* techniques are employed (40). A lot of money is currently invested into the building and improvement of synchrotron facilities to provide dedicated beamlines for *in situ* and *operando* studies and the topic regularly appears on the agenda at catalysis conferences. Moreover, a dedicated conference on *operando*

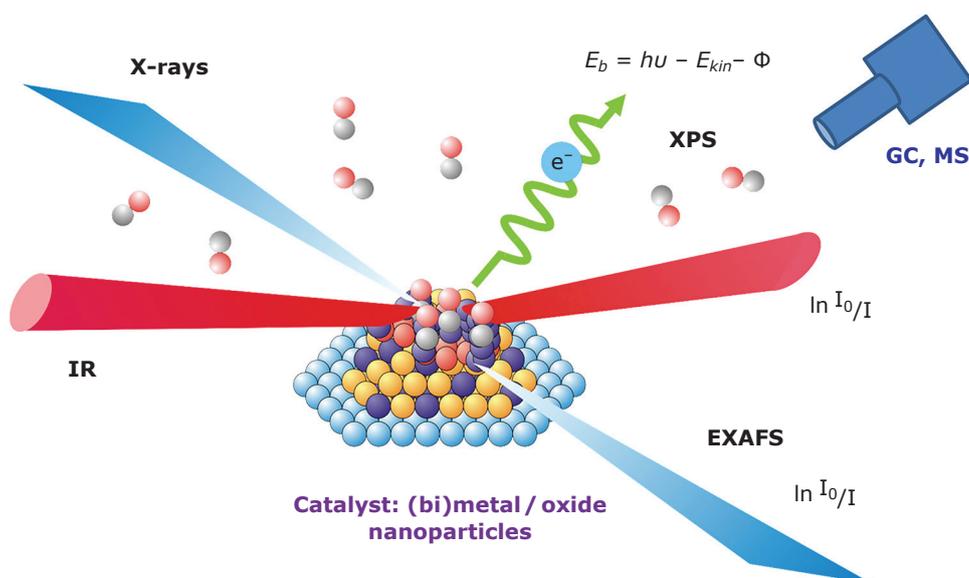


Fig. 2. Combined *in situ* and *operando* spectroscopy approach for studying catalyst under process conditions. Adapted with permission from (32)

Table I Hard X-ray Synchrotron Beamlines from the European Synchrotron Facilities that Provide Opportunities for *Operando* and *In Situ* Studies of Catalysts

Beamline	Energy range, keV	Techniques	Facility name	Location
P07 The High Energy Materials Science	30–200	XRD, PDF, SAXS, 3D-XRD, tomography	PETRA III	DESY, Germany
P22 Hard X-ray Photoelectron Spectroscopy	2.4–30	Ambient pressure HAXPES	PETRA III	DESY, Germany
P64 Advanced X-ray Absorption Spectroscopy	4–44	EXAFS, Q-EXAFS, RXES	PETRA III	DESY, Germany
P65 EXAFS Beamline	4–44	EXAFS, XANES	PETRA III	DESY, Germany
ID22 High Resolution Powder Diffraction	6–80	XRD, PDF, anomalous diffraction, anomalous scattering	European Synchrotron Radiation Facility	Grenoble, France
ID22 Energy Dispersive X-ray Absorption Spectroscopy	5–27	XAS, EXAFS, FTIR, MicroXANES	European Synchrotron Radiation Facility	Grenoble, France
ID26 High Brilliance X-ray Spectroscopy	2.4–27	XAS, XES, IXS, REXS, XMCD, RIXS	European Synchrotron Radiation Facility	Grenoble, France
BM23 XAS Beamline	5–75	EXAFS, XRD, XRF, XMLD, MicroXANES, XANES, XAFS	European Synchrotron Radiation Facility	Grenoble, France
BM26A Dubble Dutch-Belgian XAFS Beamline	5–50	XAS, XRD	European Synchrotron Radiation Facility	Grenoble, France
BM31 The Swiss-Norwegian Beamline	4.9–70	XAS, HRXRD, Raman	European Synchrotron Radiation Facility	Grenoble, France
SAMBA	6–35	XAS, Raman, UV-Vis, XRD, differential scanning calorimetry	SOLEIL	Paris, France
LUCIA	0.6–8	XAS, Raman	SOLEIL	Paris, France
ROCK	4.5–40	XAS, Raman, UV-Vis, XRD, differential scanning calorimetry, Q-EXAFS	SOLEIL	Paris, France
I11	6–25	HRXRD	Diamond Light Source	Oxfordshire, UK
B18	2.05–35	XAS, XRF, XRD	Diamond Light Source	Oxfordshire, UK
I15-1	40, 65, 76	XRD, PDF	Diamond Light Source	Oxfordshire, UK
X10DA SuperXAS	4.5–35	XAS (QEXAFS), HRXES, PXEX, pump-sequential-probes XAS	Swiss Light Source	Paul Scherrer Institute, Switzerland
PHOENIX X07MA/B	0.8–8/04–2.0	High quality EXAFS for low-Z elements	Swiss Light Source	Paul Scherrer Institute, Switzerland

Continued

Beamline	Energy range, keV	Techniques	Facility name	Location
Balder	2.4–40	XAS, XES	MAX IV 3 GeV storage ring	MAX IV, Sweden
DanMAX	15–35	XRD, imaging, absorption, phase and diffraction contrast tomography	MAX IV 3 GeV storage ring	MAX IV, Sweden
CAT	3.1–60	XAS, (XRD, XES, IR – under construction/ planned)	ANKA	Karlsruhe Institute of Technology, Germany
ANKA XAS	2.4–27	XAS	ANKA	Karlsruhe Institute of Technology, Germany
BL04 MSPD	8–50	HRXRD	ALBA	Barcelona Synchrotron Park, Spain
BL22 CLÆSS	2.4–63.2	XAS, XES	ALBA	Barcelona Synchrotron Park, Spain

spectroscopy was launched in 2003 in Lunteren, The Netherlands, and successfully takes place every three years.

Despite numerous studies on catalysts using *in situ* and *operando* investigations including those using combined techniques, very limited knowledge exists in the literature about the surface composition of catalysts under reaction conditions, as most of the techniques characterise the bulk of the catalysts. The changes in surface composition, however, are the most relevant for explaining catalytic events that take place at catalyst surfaces (41). Importantly to note, the average bulk structure of materials does not represent the surface composition as was demonstrated in a recent study by Karim *et al.* on the size-dependent redox behaviour of iron, where it was shown that during oxidation iron grows in layers, forming Fe(0)/FeO/Fe₃O₄/Fe₂O₃ core-shell structures (42).

Dynamic surface variations under reaction conditions for catalysts are often not taken into account (for example, surface segregation processes). Assumptions are mainly made on the basis of the average bulk structure that leads to misleading conclusions on the active phase, active sites, role of promoters or deactivation mechanisms, thus hindering further optimisation and development of catalysts. As an example, despite intensive studies of high temperature water gas shift (HTWGS) iron-based catalysts, the nature of active sites and the HTWGS reaction mechanism (redox vs. associative) are still subject to ongoing

debate. Open questions and contradictory results concern the interaction of chromium oxide with iron oxide (the formation of a Cr-enriched shell around the iron oxide phase, magnetite, vs. strong interaction of Cr³⁺ with magnetite) as a way of stabilising iron oxide against sintering (28, 29, 43).

To study catalysts, often *operando* IR spectroscopy is combined with bulk techniques such as XAS, Raman and XRD. *Operando* IR spectroscopy is a crucial technique for studying surface adsorbed species, particularly important for revealing reaction intermediates (39, 44); however, it does not provide insights into the redox properties of the catalyst surface. One of the most important factors that governs the catalytic activity, selectivity and stability of catalysts in particular for redox reactions is the redox properties (the oxidation state and interplay between oxidation states during the reaction) of the surface.

XPS is one of the most powerful spectroscopic tools for obtaining chemical information about the surfaces of solid materials. It is based on the photoelectric effect theory (the ejection of electrons from the surface in response to incident photons). This technique is also known as electron spectroscopy for chemical analysis (ESCA). The ESCA term was introduced in 1967 (45) by the Swedish physicist Kai Siegbahn, who in 1954 recorded the first high energy resolution XPS spectrum of cleaved NaCl (46), to highlight the importance of obtaining chemical information like oxidation states for materials investigated

with XPS. In 1981 Siegbahn was awarded the Nobel Prize in Physics as acknowledgment "for his contribution to the development of high-resolution electron spectroscopy".

Traditionally, XPS is known to be an ultra-high vacuum (UHV) technique that can only operate at pressures below 10^{-9} mbar because of the strong scattering of photoelectrons by gas molecules. However, the first 'non-UHV' XPS experiments were performed in the Kai Siegbahn research group (47, 48). In 1973 Kai Siegbahn together with his son Hans Siegbahn published a study in which the first spectrum of a liquid (formamide) was presented (47). In 1979 Wyn Roberts published a study entitled "A 'High-Pressure' Electron Spectrometer for Surface Studies", where he described the development of the first photoelectron spectrometer capable of studying solid surfaces in the presence of gas up to 1.3 mbar (49). A new type of photoemission spectrometer, based on several differential pumping stages with electrostatic lenses between the sample surface and the photoelectron detection, was developed by the groups from the Advanced Light Source, Berkeley, California, USA, and the Fritz Haber Institute of the Max Planck Society, Berlin, Germany (50). A schematic representation of the differential pumping system of the NAP-XPS setup from the Innovative Station for *In Situ* Spectroscopy (ISS) beamline, BESSY II, is given in Figure 3. This setup enables operation at pressures close to ambient (up to 20 mbar).

Although these pressures are still far away from pressures used in industrial fixed-bed flow reactors,

NAP-XPS experiments can model the reaction environment and allow the dynamic variations of a catalyst surface and its catalytic properties to be studied (52–56). Today, NAP-XPS is the most powerful technique for studying the surface of redox catalytic materials under process conditions (57), particularly when employing synchrotron radiation as a light source. Using the tuneability of synchrotron radiation, different information depths can be studied by NAP-XPS ranging from ~ 0.5 nm to 3 nm, which is not achievable with routinely available lab-based XPS. Table II summarises the most commonly used soft X-ray synchrotron beamlines, where opportunities for *operando* and *in situ* NAP-XPS, ambient pressure XPS (AP-XPS) and XAS studies of catalysts are provided.

To gain improved understanding of redox-based catalytic systems, one can combine *in situ* NAP-XPS or near edge X-ray absorption fine structure (NEXAFS) for surface-specific chemical information with *in situ* Raman, XRD or XAS studies which provide information on local coordination environment, structure and oxidation state of the bulk of a material.

3. *In Situ* and *Operando* Studies Providing Information on Surface and Bulk Properties of Working Catalysts

There are only a few *operando* studies reported in the literature in which XAS, XRD or Raman and NAP-XPS were performed on the same catalytic system, giving valuable insights into bulk *versus*

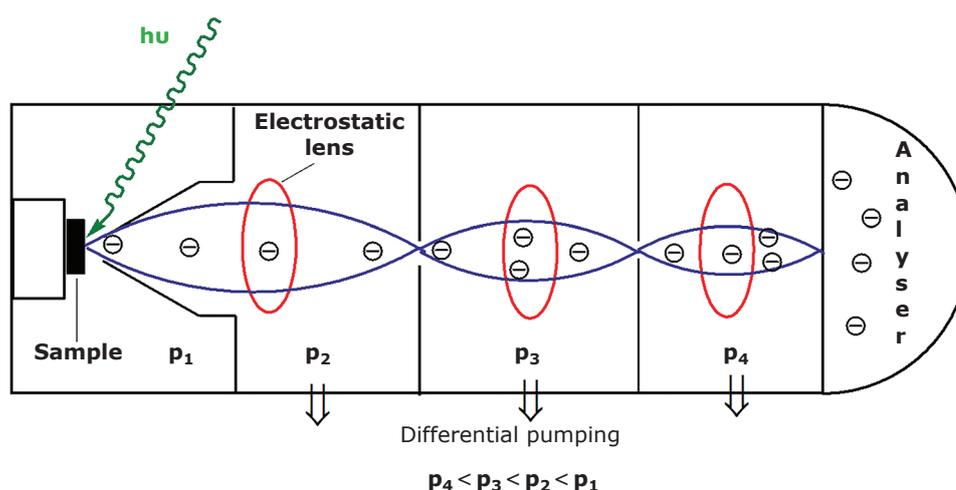


Fig. 3. Schematic representation of the differential pumping from the ISS beamline for the NAP-XPS setup (51)

Table II Soft X-Ray Synchrotron Beamlines (Worldwide) that Provide Opportunities for Operando and In Situ Studies of Catalysts (NAP-XPS/AP-XPS and XAS)

Beamline	Energy range, keV	Techniques	Facility name	Location
TEMPO	0.05–1.5	NAP-XPS	SOLEIL	Paris, France
23-ID-2 <i>in situ</i> and operando Soft X-ray Spectroscopy	0.25–2	AP-XPS, XAS	National Synchrotron Light Source	Brookhaven National Laboratory, US
9.3.2 Ambient-Pressure Soft X-Ray Photoelectron Spectroscopy (S-APXPS)	0.2–0.9	AP-XPS, XAS	Advanced Light Source	Lawrence Berkeley National Laboratory, US
B07	0.05–2.8	NAP-XPS, NEXAFS	Diamond Light Source	Oxfordshire, UK
HIPPIE	0.3–2000	AP-XPS	MAX IV 3 GeV storage ring	MAX IV, Sweden
SPECIES	0.027–1.5	AP-XPS, NEXAFS, XAS	MAX IV 1.5 GeV storage ring	MAX IV, Sweden
ISIS	0.08–2.0	NAP-HE-XPS	BESSY II	Helmholtz-Zentrum Berlin, Germany
EMIL	0.08–10	PES, PEEM, HAXPES, XES, XRF, XRD, ambient-pressure-HAXPES	BESSY II	Helmholtz-Zentrum Berlin, Germany
BL24 CIRCE	0.1–2	NAP-XPS	ALBA	Barcelona Synchrotron Park, Spain
Mobile station operates between PHOENIX X07MA and SIM X11MA beamlines	0.005–8	APPES	Swiss Light Source	Paul Scherrer Institute, Switzerland

surface properties. As examples, recent studies by Israel Wachs' group demonstrate the importance of employing a surface sensitive technique like NAP-XPS for studying HTWGS and shed light on iron-based HTWGS catalysts in combination with *in situ* XAS and Raman (28, 29). Looking at data from the respective techniques in isolation could lead to wrong conclusions. Examples from our own work at the Institute of Materials Chemistry, TU Wien, Austria, comprise preferential CO oxidation (PROX) on Co_3O_4 and $\text{CeO}_2\text{-Co}_3\text{O}_4$ catalysts studied by operando NAP-XPS and XAS (30). During PROX both the bulk and surface of Co_3O_4 were fully oxidised up to 523 K, while in CO the surface reduction of Co_3O_4 occurred from 373 K. Preferential oxidation of CO to CO_2 in an excess of H_2 was suggested to follow predominantly the Mars-van-Krevelen mechanism. Promotion of Co_3O_4 with 10 wt% CeO_2

increased the reduction temperatures in CO and H_2 and enhanced the PROX activity. Since CeO_2 is a less active material, this can only be explained by higher activity of the Co-O-Ce ensembles and creation of oxygen vacancies as detected by NAP-XPS in Ce 3d spectra.

In another recent work, we utilised NAP-XPS to study the surface composition of Cu-promoted Ni/ZrO₂ catalysts in methane atmosphere at mbar pressures and relevant reaction temperatures. An important result from this work was that the surface composition changed from a Cu-enriched state after reduction to a Ni-enriched surface in methane at $T > \sim 700$ K which was the active state (58). The surface segregation of Ni⁰ was driven by the strong interaction between Ni and carbon and was corroborated by density functional theory (DFT) calculations (59).

4. Operando FTIR, XAS and NAP-XPS Investigation of Methanol Steam Reforming on Pd-Based Intermetallic Compounds: Surface vs. Bulk

An exemplary study will be discussed here in more detail to illustrate the insights into catalyst structure and composition under reaction conditions and the reaction mechanism gained from the *operando* approach using surface sensitive methods. In the discussed work we aimed at obtaining a detailed understanding of the fundamental processes occurring at the surface and in the bulk of ZnO and Ga₂O₃ supported Pd nanoparticles applied as methanol steam reforming (MSR) catalysts (60–69). In addition, the work should contribute to the improvement and development of active, selective and stable catalysts for the production of clean (CO-free) hydrogen, which can be used for example in proton exchange membrane fuel cells.

Our goal was to understand the selectivity of the desired MSR reaction (Equation (i)) producing CO₂ and H₂ and the unwanted methanol decomposition (MDC) (Equation (ii)) yielding CO and H₂, by combining information on surface and bulk composition, structure and electronic properties under reaction conditions obtained by *operando* XAS, XRD and NAP-XPS with mechanistic understanding obtained by Fourier transform infrared (FTIR) spectroscopy.



4.1 Active and Selective Phase Under Reaction Conditions: Operando XAS and NAP-XPS

By *in situ* quick-extended X-ray absorption fine structure (QEXAFS) spectroscopy we followed in real time how the Pd/ZnO nanoparticles dynamically adapt to the surrounding atmosphere (62), which presented the first direct proof for the formation of PdZn alloy in methanol/water starting from Pd/ZnO without prior high temperature reduction. PdZn alloying occurred *via* spillover and reduction of the ZnO by H₂ generated in the reaction and was accompanied by a simultaneous change in reactivity, from an unselective state characteristic of metallic Pd to a highly selective state due to the formation of a PdZn intermetallic compound (IMC). The XAS near-edge region is shown in **Figure 4** and resembles the progressive transition from the structural and electronic properties characteristic of Pd to those of the tetragonal Pd:Zn IMC with a 1:1 stoichiometry occurring with time on stream in methanol/water. By combining time resolved *in situ* QEXAFS with FTIR spectroscopy we could clarify the processes occurring when switching

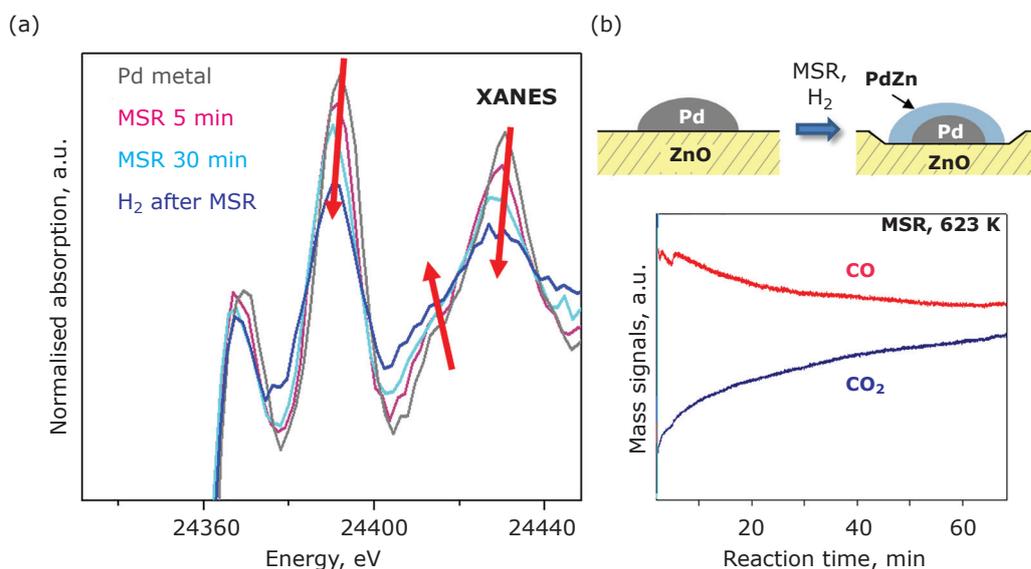


Fig. 4. (a) Pd K edge XANES spectra obtained upon exposure of a 7.5 wt% Pd/ZnO catalyst to MSR conditions at 623 K without pre-reduction ($p_{\text{CH}_3\text{OH}} = p_{\text{H}_2\text{O}} = 20$ mbar). The arrows illustrate the changes due to *in situ* formation of PdZn; (b) corresponding mass spectrometry traces of the products CO and CO₂ which are representative for the selectivity to MDC and MSR, respectively. Adapted with permission from (62)

between reducing (methanol, H₂) and oxidising (alloy formation and decomposition with ZnO island formation on the Pd nanoparticle surface) atmospheres (62). The studies on powder catalysts were complemented by surface science work on single crystal-based UHV grown model systems (PdZn surface alloys), which were in excellent agreement with the PdZn/ZnO powder catalysts and DFT calculations (67).

For the related system Pd/Ga₂O₃ the combination of techniques of different surface sensitivity, namely *in situ* XRD, synchrotron-based *in situ* XPS, FTIR and XAS, were used to identify the formation of the MSR-selective intermetallic Pd₂Ga phase under relevant reaction conditions as well as upon reduction at medium temperature around 573–673 K (63, 65). One of the major advantages of XAS in catalysis is its suitability for *in situ* studies, due to the high penetrating power of the hard X-rays used. Fitting the extended fine structure function identified Pd₂Ga as the active phase present under MSR conditions (65). Interestingly, different intermetallic phases exhibited a different reactivity (63) with Pd₂Ga showing the best catalytic performance.

Since the catalytic properties of a material are mainly determined by its composition and the structure and properties of the surface and near-surface region, we have further characterised the Pd₂Ga/Ga₂O₃ catalyst by applying synchrotron radiation-based NAP-XPS as a surface sensitive

technique. Upon reduction in H₂ or in the H₂ produced from methanol a species attributed to zerovalent Ga evolved in the Ga 3d binding energy range shifted by 2.2 eV relative to Ga³⁺, whereas the Pd 3d signal was shifted by ca. 0.5 eV to higher values upon IMC formation because of the charge transfer from Ga to Pd (Figure 5). The composition of the surface was in very good agreement with the Pd:Ga stoichiometry 2:1 (Figure 5). Depth profiling by varying the incident photon energy and thereby the kinetic energy of emitted photoelectrons reveals equal relative amounts of Ga⁰ and Pd with a ratio of about 2:1 and therefore uniform distribution in the experimentally accessible depth range (63).

4.2 Stability and Origin of Unwanted CO Formation: *Operando* FTIR

Special attention was paid to the stability of the PdZn and Pd₂Ga surfaces. Importantly, *in situ* FTIR spectroscopic results reveal for the very first time the limited stability of the intermetallic surfaces (PdZn and Pd₂Ga) under MSR reaction conditions (61, 63). Besides intermetallic PdZn and Pd₂Ga the presence of domains of metallic Pd catalysing the unwanted methanol decomposition to CO and H₂ was detected in both catalysts (Figure 6). Metallic Pd and Pd present within the IMC can be distinguished by CO adsorption. While linear, bridge and hollow bonded CO are characteristic for adsorption

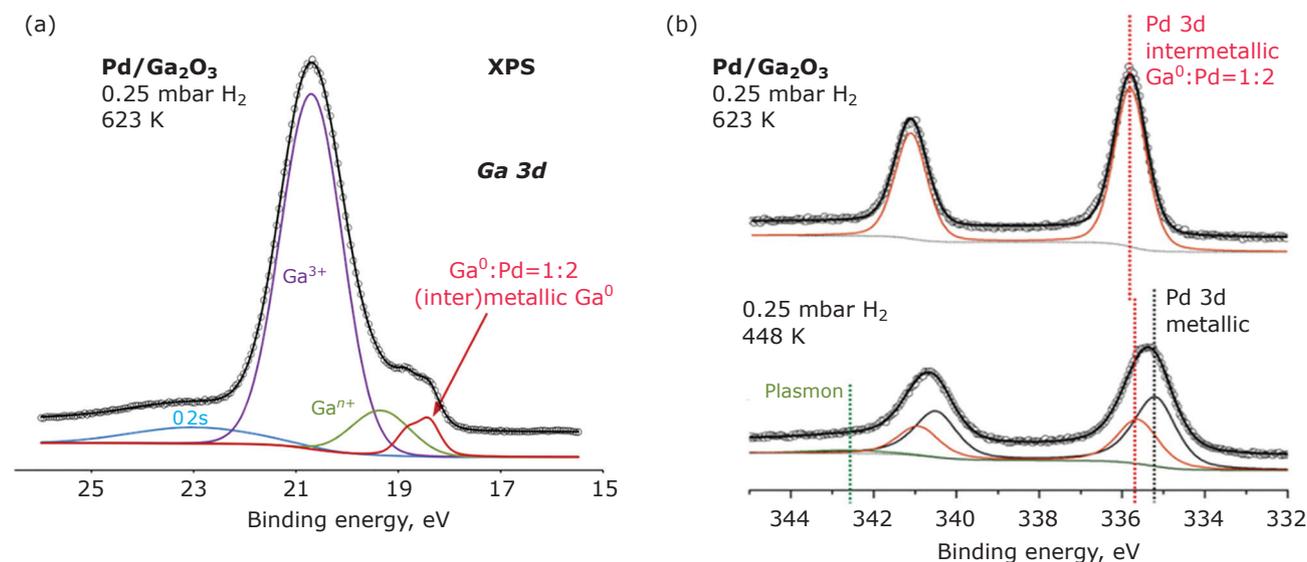


Fig. 5. (a) Synchrotron-based XPS spectra of the Ga 3d region during reduction of Pd/Ga₂O₃ in 0.25 mbar H₂ at 623 K; (b) synchrotron-based XPS spectra of the Pd 3d region recorded *in situ* during reduction of Pd/Ga₂O₃ in 0.25 mbar H₂ at 448 K (metallic and intermetallic Pd are present) and at 623 K (corresponds to complete IMC formation). Adapted with permission from (63)

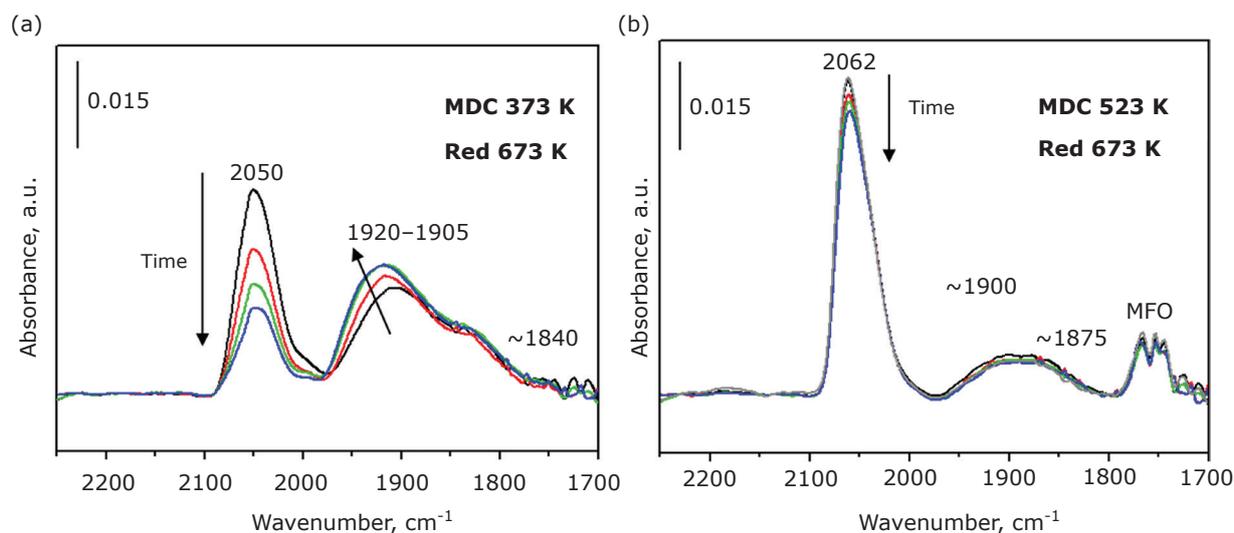


Fig. 6. Time-resolved *in situ* FTIR spectra obtained in flowing methanol over Pd₂Ga/Ga₂O₃ at: (a) 373 K; and (b) 523 K reaction temperatures after reduction at 673 K. The CO stretch vibration range is displayed for spectra recorded every 5 min in 1 vol% methanol in He. Besides on-top CO adsorbed on intermetallic Pd₂Ga, bridge and hollow bonded CO on metallic Pd is present indicating partial instability of Pd₂Ga in the methanol feed, which is more pronounced at lower reaction temperatures. Adapted with permission from (61)

on metallic Pd with vibrational bands at around 2090 cm⁻¹, 1990 cm⁻¹ and 1940 cm⁻¹, CO adsorbs on only on-top sites on Pd in PdZn and Pd₂Ga (61–63, 67). In addition, a shift of the on-top band to ~2070 cm⁻¹, because of the charge transfer, is observed for PdZn (62, 67).

The instability of the intermetallic surface in methanol/water has been suggested as the main factor limiting MSR selectivity and was attributed to the detrimental effect of CO. The degradation of the IMC surface was found to strongly depend on the reaction temperature (61) being more critical at lower reaction temperatures (Figure 6). Thus, we suggest the presence of a dynamic equilibrium between IMC formation by H₂ and decomposition by CO. As a consequence, CO formation in MSR could not be fully avoided. Understanding the origin of unwanted CO is a first step towards the development of strategies to avoid CO formation and is therefore a highly important result.

4.3 Insights into the Reaction Mechanism: *Operando* FTIR

Vibrational spectroscopy was applied to investigate the reaction mechanism of MSR over Pd₂Ga/Ga₂O₃ (64). The mechanistic study explored the interaction of the catalyst with methanol and water by combining temperature-programmed,

steady state and concentration modulation FTIR experiments. A different surface chemistry on low temperature reduced (unselective) Pd/Ga₂O₃ and high temperature reduced (selective) Pd₂Ga/Ga₂O₃ was detected. Formation of intermediate surface formate species was observed at much lower temperatures on Pd₂Ga/Ga₂O₃ (Figure 7) and was attributed to reactive oxygen sites in the Ga₂O₃ surface modified by the high temperature reduction and IMC formation. The presence of H₂O strongly affected the stability of the formates.

A reaction mechanism involving the interconversion of formate species was proposed, as described in more detail elsewhere (64). This work provides important new insights into the reaction mechanism of MSR and emphasises the crucial role of the oxide support. The reaction seems to predominantly proceed on the reduced Ga₂O₃ surface near the IMC nanoparticles or at the interface and is promoted by the intermetallic particles. An additional and necessary effect of IMC formation is the slowdown of the unwanted MDC to CO and H₂ on metallic Pd.

4.4 Reactivity of the Oxide Support

Concerning the reactivity of the oxide support, special attention was paid to the role of oxygen vacancies. This was investigated by applying

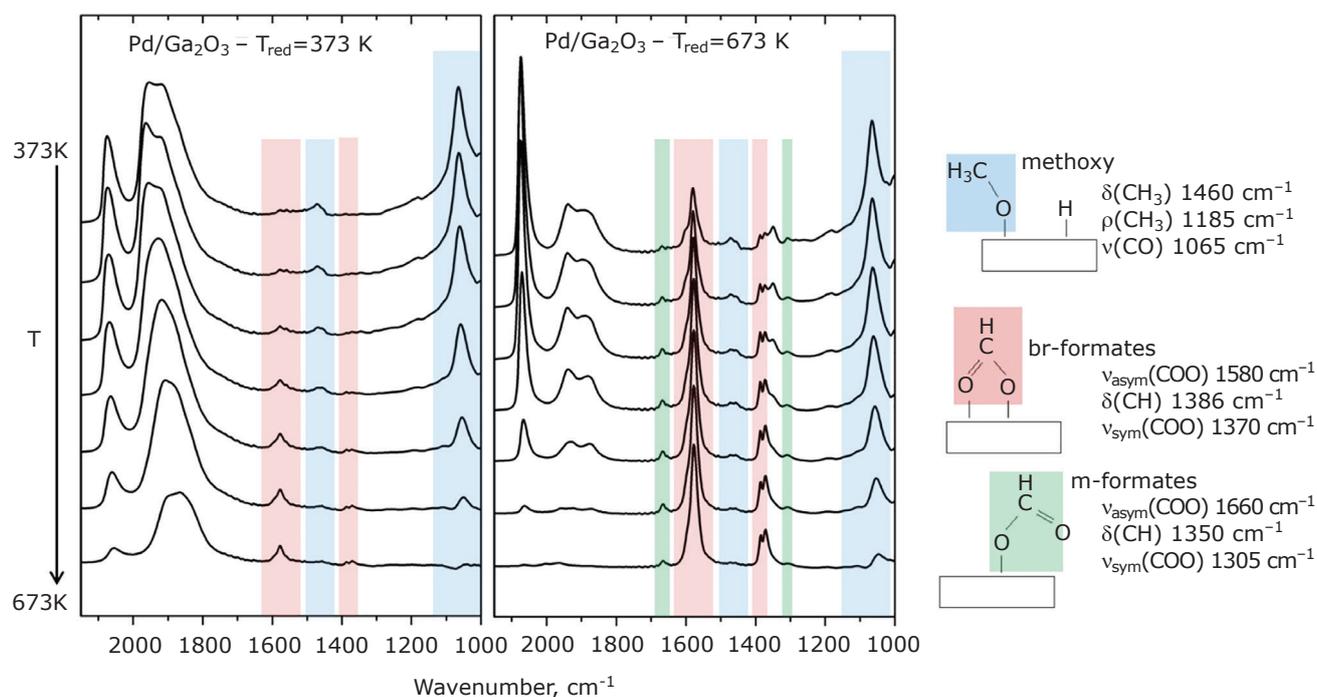


Fig. 7. Temperature-dependent evolution of surface species after adsorption of methanol on: (a) Pd/Ga₂O₃ reduced at 373 K; and (b) Pd₂Ga/Ga₂O₃ reduced at 673 K. FTIR spectra were recorded during heating from 373 K to 673 K in high vacuum. Bands in the spectral range from 2100 cm⁻¹ to 1750 cm⁻¹ originate from adsorbed CO, vibrations in the range between 1700 cm⁻¹ and 1000 cm⁻¹ are assigned to methoxy (CH₃O) and formate (HCOO) species. Adapted with permission from (64)

different reducing pretreatments with subsequent quantification of vacancy sites by titration with O₂. This approach was successfully applied to study the defect chemistry of Ga₂O₃ (68, 69). Strongly related to the work on MSR, the reactivity of Ga₂O₃ for reverse water gas shift (RWGS), a follow-up reaction of the MSR products CO₂ and H₂ and potential source of unwanted CO, was investigated by combining FTIR spectroscopy and temperature-programmed methods. By looking in detail at the interaction of Ga₂O₃ in different defective states in terms of nature and concentration of vacancies with H₂, CO, CO₂, water and their mixtures, the reactivity of Ga₂O₃ for water gas shift (WGS) and RWGS was explored. Ga₂O₃ is catalytically active for these reactions, with the reaction most likely proceeding *via* oxygen vacancies. Ga₂O₃ on its own (without metal promotion) is capable of H₂ activation; formed oxygen vacancies can then be re-oxidised by CO₂ yielding CO in the catalytic RWGS reaction.

The molecular level understanding of the reaction mechanism, the factors controlling selectivity and the correlation of catalyst structure and composition with catalytic properties enable a more scientific approach to catalyst optimisation on a rational

basis. Only the combination of various *operando* methods providing complementary information on the composition of the catalyst surface, the reacting species and the catalytic properties allowed an almost complete picture of the surface chemistry of PdZn/ZnO and Pd₂Ga/Ga₂O₃ MSR catalysts to be obtained.

5. Perspectives: A Combined Approach for the Successful Development of the Next Generation of More Efficient Catalysts

The work described in this paper clearly demonstrates the importance of combining several *operando* techniques in studying catalysts under steady state as well as dynamic conditions for revealing reaction mechanisms and for finding correlations between the structure and surface composition and the activity and selectivity of catalysts. In particular surface-sensitive information is crucial. Moreover, the presented results highlight the great potential of *in situ* NAP-XPS for obtaining redox and structural information on the (near) surface changes of catalytic materials for different information depths.

For the successful development of the next generation of more efficient catalysts, it is essential to combine three approaches (**Figure 8**): (a) high-throughput synthesis in combination with correlating catalytic performance with the electronic and geometric structure of synthesised materials (structure-performance relationship); (b) reaction

kinetic studies; (c) *in situ* and *operando* investigation of catalysts under reaction conditions. Using such a combined approach and interconnecting the obtained information is a powerful research tool that can boost the research and development of more efficient catalysts with the desired catalytic properties.

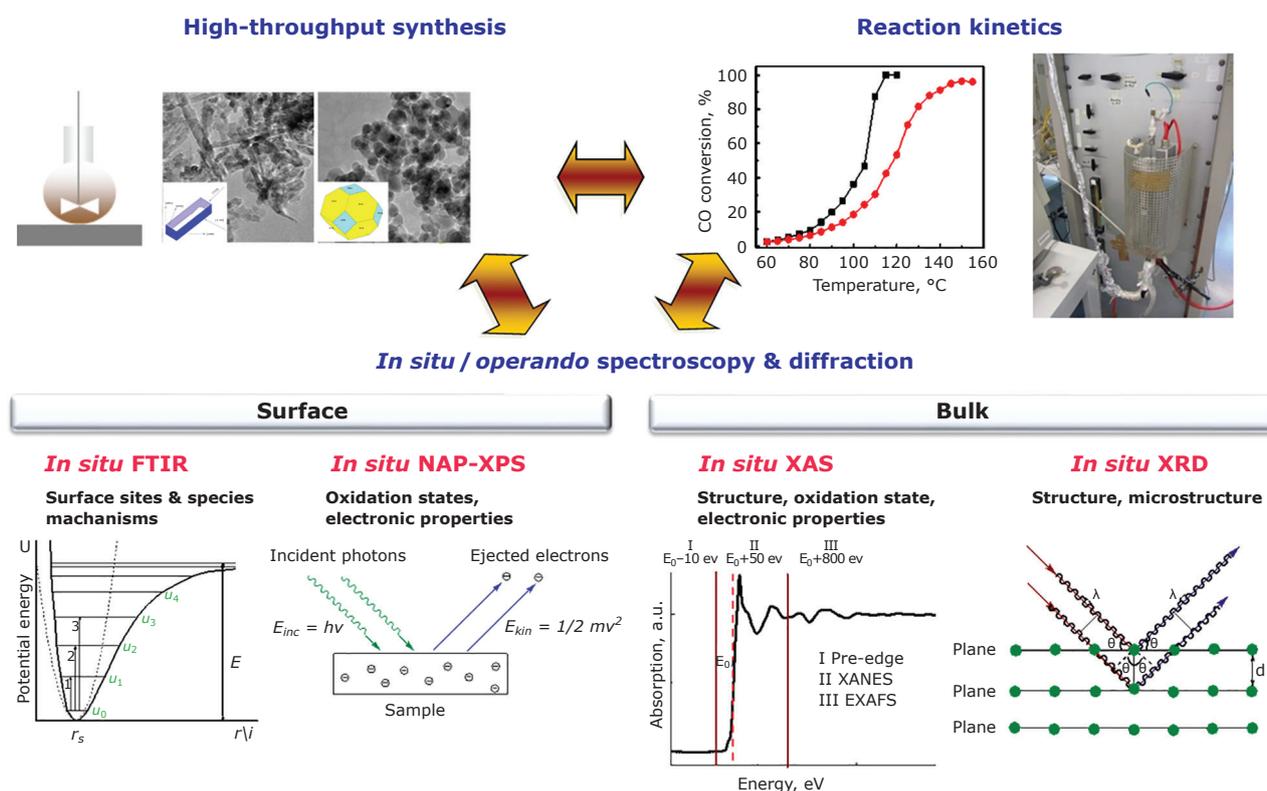


Fig. 8. Combined approach, which includes high-throughput synthesis, reaction kinetic studies and *in situ* and *operando* spectroscopy, for catalyst development

Glossary of Techniques

APPES	ambient pressure photoelectron spectroscopy	HRXRD	high-resolution X-ray diffraction
AP-XPS	ambient pressure X-ray photoelectron spectroscopy	IR	infrared
DFT	density functional theory	IXS	inelastic X-ray scattering
EPR	electron paramagnetic resonance	NAP-HE-XPS	near-ambient pressure high energy X-ray photoelectron spectroscopy
ESCA	electron spectroscopy for chemical analysis	NAP-XPS	near ambient pressure X-ray photoelectron spectroscopy
EXAFS	extended X-ray absorption fine structure	NEXAFS	near edge X-ray absorption fine structure
FTIR	Fourier transform infrared	PDF	Pair distribution function
HAXPES	hard X-ray photoelectron spectroscopy	PEEM	photoemission electron microscopy
		PES	photoelectron spectroscopy

RIXS	resonant inelastic X-ray scattering	XAS	X-ray absorption spectroscopy
RXES	resonant x-ray emission spectroscopy	XMCD	X-ray magnetic circular dichroism
SAXS	small angle X-ray scattering	XMLD	X-ray magnetic linear dichroism
UV-Vis	ultraviolet-visible	XPS	X-ray photoelectron spectroscopy
XANES	X-ray absorption near edge structure	XRD	X-ray diffraction
		XRF	X-ray fluorescence

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