

Applications of *operando* hard X-ray spectroscopy in the energy-related and environmental catalysis

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Introduction

Heterogeneous catalysis is ubiquitous, with at least 90% of all chemical processes requiring catalysts [1]. Most importantly, heterogeneous catalysis enables the supply of our industrialized society with energy directly, through synthesis, upgrading, and conversion of fuels to energy, as well as indirectly, through environmental remediation by cleaning exhausts resulting from fuel to energy conversion processes. In order to meet the ever increasing demands for clean and energy-efficient technologies including process chains from renewable resources, heterogeneous catalysts are the key and have to be constantly improved [2–5]. The knowledge-based development requires in-depth understanding of catalyst structure and functionality. Catalysts are highly dynamic systems changing in response to the external conditions, hence, to understand a working catalyst, the structural information needs to be obtained under reaction conditions, with reactors similar to those used in industrial catalysis.

Synchrotron-based hard X-ray techniques are ideal for studying heterogeneous catalysts due to the penetrating power of X-rays which allows the use of *in situ* cells with varying gas, temperature, pressure, and gas flow patterns mimicking even industrial conditions [6]. Catalysts and processes vary greatly depending on the application, leaving no single technique that can be universally applied. Instead, in order to understand the behavior of the specific catalyst in its environment the approach needs to be tailored to the corresponding open questions as well as the catalyst composition and process parameters. In this contribution we concentrate on the fields of energy-related and environmental catalysis and demonstrate the toolbox of hard X-ray spectroscopic tools used by our group to bring forward this field of research.

QEXAFS for studies on the storage of fluctuating renewable energy

One of the main challenges in adopting the renewable energy sources such as wind and solar energy is their fluctuating nature, which requires balancing supply and demand [2,3,7]. Such balancing is possibly via storing renewable energy in form of chemicals (power-to-X concepts). Among them, methanation of CO₂ (power-to-gas) offers a very attractive storage route because it provides possibility to convert CO₂ from the atmosphere or industrial exhausts with hydrogen from solar or wind energy [7]. The produced methane can then be fed directly into the existing natural gas grid. In order to develop catalysts capable of utilizing renewable power sources for methanation of CO₂ their stability and active site evolution due to fluctuating supply of energy to the process plant need to be investigated. Also mechanistically such dynamic reaction conditions are highly interesting. As the hydrogen required for the methanation is supplied via electrolysis of water, one interesting aspect is the variation of hydrogen partial pressure with the most extreme case of a total drop out of hydrogen pressure. To understand the influence of such short-term hydrogen dropouts on Ni/Al₂O₃ catalysts during CO₂ methanation *operando* X-ray absorption spectroscopic (XAS) studies were performed to gather information on the oxidation state and the

atomic structure of Ni active sites during methanation conditions including short periods of hydrogen dropout [8]. The timescale of the dropouts (30–300 s) required the use of quick-scanning EXAFS (QEXAFS) to obtain data in the sub-second regime.

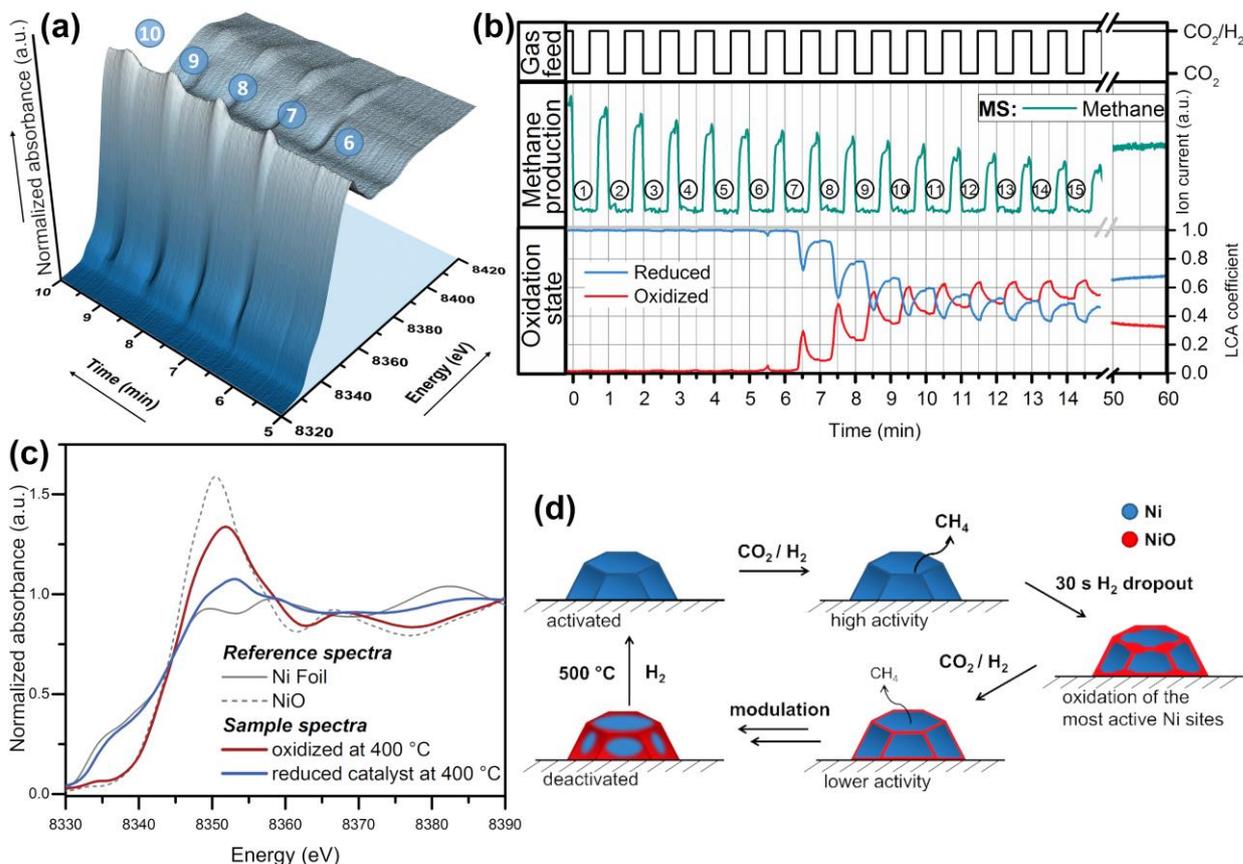


Figure 1. (a) XANES region of the QEXAFS spectra and (b) extracted oxidation states obtained via LCA alongside catalytic activity data (right) measured during CO₂ methanation with periodic 30 s H₂ dropouts. Conditions: H₂/CO₂ = 4; 75% He, 400 °C. (c) The corresponding XANES spectra of the Ni/Al₂O₃ catalyst after reduction (50% H₂) and oxidation (5% O₂) and reference Ni compounds used for the LCA. (d) A schematic representation of the structural changes of supported Ni particles during methanation with continuous short H₂ dropouts. Adapted from [8], used under CC BY 4.0, Copyright © 2017.

Selected results are summarized in Figure 1 [8]. To simulate repeated short H₂ dropouts the feed was switched every 30 s between 5% CO₂/He and methanation conditions (H₂/CO₂ = 4) at 400 °C (at which the highest activity and selectivity were observed). At first, a stable high methane signal and fully reduced Ni nanoparticles (NPs) were observed by mass spectroscopy (MS) and QEXAFS, respectively. Short H₂ cut-offs lead to loss of CH₄ production, which was not completely recovered during the following methanation period. Methane production decreased further with consecutive H₂ dropouts, however, only after 5.5 min changes in the Ni site structure could be observed by QEXAFS. At first, slight oxidation of 6% of Ni during the 6th H₂-free period (according to linear combination analysis (LCA) of XANES after approx. 5.5 min), and then fast and significant oxidation of Ni during the following H₂ dropouts were observed, indicated by the increasing intensity of the white line (Fig. 1 a, c). The oxidation of Ni in the absence of H₂ was caused by traces (approx. 1000 ppm) of oxygen present in the technical CO₂, which is typically used for methanation. Further catalyst operation with H₂ in the gas mixture could only partially reduce Ni sites and regain CH₄ production rate, confirming a correlation between the oxidized

fraction of Ni and poisoning of methane formation. The QEXAFS results obtained during this study demonstrated that it is possible to titrate the most active Ni-sites (low coordinated Ni surface atoms) and also that local effects can occur in catalytic reactions (further examples, see e.g. [9]). Finally, it was uncovered that the methanation temperature of 400 °C was too low to fully reduce Ni NPs and reactivate the catalyst *in situ*. Reactivation at 500 °C in hydrogen was required to regain full catalytic activity after H₂ dropouts. Note that with Fe-Ni catalysts this behavior can be strongly altered [10].

ME-XAS for hydrotreating catalysts

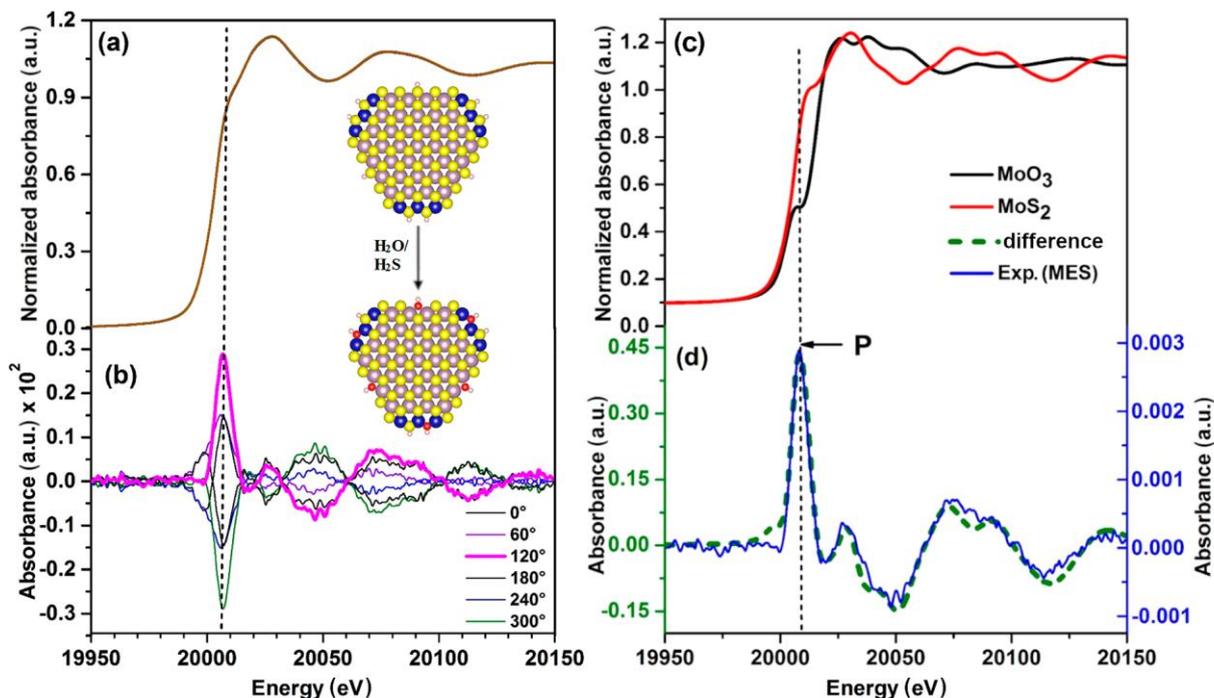


Figure 2. (a) 36 normalized time-resolved Mo K edge XANES spectra covering 10 s each during 3% H₂O/H₂ (0–180 s) vs 1000 ppm of H₂S/H₂ (180–360 s) cycling. (b) The corresponding demodulated spectra at selected values of phase angle ($\Delta\phi$). (c) MoS₂ and MoO₃ XANES spectra and (d) their difference spectrum compared to the maximum amplitude signal obtained after demodulation. Inset in the left figure: schematic representation of deactivation of a Ni-MoS₂ particle (purple Mo, blue Ni, yellow S, red O, and pink H). Adapted and reprinted with permission from [11]. Copyright © 2019 American Chemical Society.

Another developing trend in the efficient use of resources is the increasing use of biomass waste for production of transportation fuels [12]. The shift from the oxygen poor (> 0.3 wt.%) crude oil to bio-oil, containing 20–50 wt.% of oxygen, significantly influences stability and chemical composition of the active sites of sulfide-based hydrotreating catalysts (used, primarily, to decrease sulfur content in the fuels). Typical hydrotreating catalysts are Co- and Ni-doped MoS₂ sulfides with active sites located at edges and corners of rather large MoS₂ platelets (Figure 2) [11]. Conventional XAS, being a bulk technique, is not able to reveal changes in the structure of Mo sites due to increased chemical potential of the feedstock as the number of active corner/edge Mo sites is far less than the total Mo content (Figure 2a). To reveal the transformation of the reactive surface sites of MoS₂ with respect to the substitution of sulfur by oxygen *in situ* QEXAFS coupled with modulation excitation spectroscopy (MES) was employed. MES experiments were

carried out by periodically cycling between H₂O and H₂S containing hydrogen at 400 °C. Mo K edge XANES and EXAFS data extracted by the demodulation of the ME spectra (Figure 2b) showed that for approximately 1% of the Mo atoms, sulfur atoms were reversibly replaced by oxygen when exposed to H₂O (Figure 2c, d) fitting to structural models from surface science and given in Figure 2a. As a result, applying MES enabled not only identification of minute spectral changes but also their precise quantification as well as resolving the kinetic information. For instance, in the case of the Ni-MoS₂ catalyst, MES-XAS measurements at the Ni K edge revealed fast oxidation of Ni-sites while oxidation of Mo sites was slower proving the positive effect of Ni-doping on the catalyst stability [11].

Bridging the time gap between synchrotron radiation studies and industrial plant operation

An important topic in industrial catalysis is the long-term stability of heterogeneous catalysts during the whole life cycle in real plant operation. Using *operando* XAS and XRD at CAT-ACT beamline at the KIT synchrotron radiation source [13] we monitored the structural changes of a commercial Co-Ni-Re/ γ -Al₂O₃ catalyst of the Fischer-Tropsch process (hydrogenation of CO to liquid hydrocarbon fuels) for the first-time over >300 hours on stream while actually producing liquid fuels under industrially relevant conditions (30 bar and 250 °C) [14]. Hence, catalyst performance and product distribution (including gaseous and liquid products, see some of the synthetic fuel collected in inset in Figure 3c) could be correlated with the catalyst structure on a timescale much longer than available for typical X-ray absorption studies (Fig. 3). During the experiment, three regimes of catalyst activity and selectivity were identified based mainly on the analysis of formed products: (1) a fast deactivation during the first 8 h on stream without any visible change of the active sites, attributed to fouling of the catalyst pores by formed wax; (2) moderate deactivation between 8 h to 60 h on stream attributed to the formation of CoAl₂O₄ (identified by a new peak at 7717 eV in the derivative XANES spectra); (3) formation of carbonaceous species during longer exposure to the conditions of the Fischer-Tropsch synthesis. The possibility to run such long tests for the first time provided direct evidence for the origin of slower deactivation routes (2) and (3) and highlights the need for synchrotron beamlines dedicated for catalysis research.

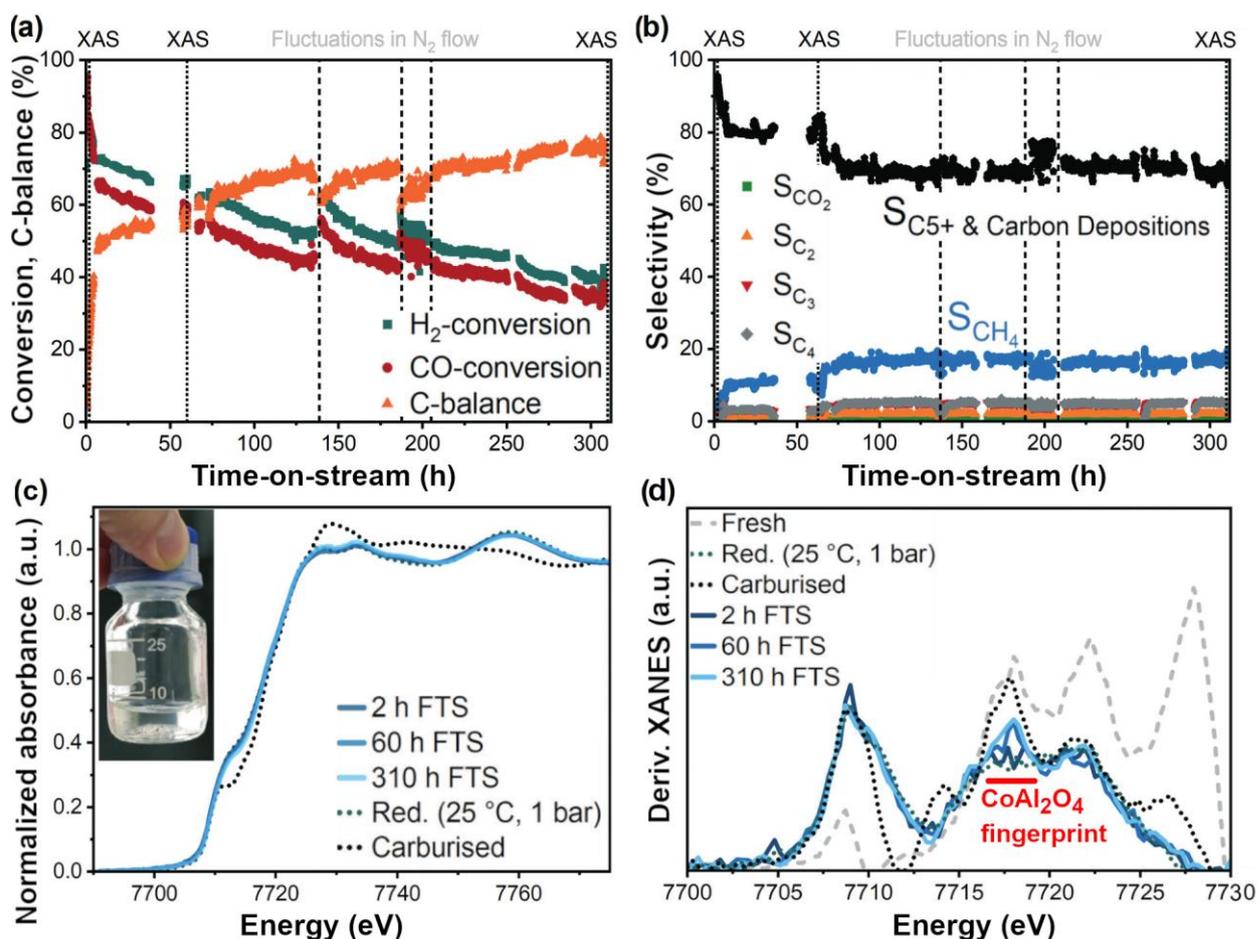


Figure 3. (a) Conversion of the reactants and carbon balance for the gaseous products, (b) selectivities (S), and the corresponding (c) Co K edge XANES and (d) derivative XANES spectra obtained during the long term XAS study of the commercial Co-Ni-Re/ γ -Al₂O₃ catalyst. Inset in (c) shows synthetic fuel produced during the spectroscopic study. Adapted and reprinted from [14], used under CC BY 3.0 license, Copyright © 2020.

Total oxidation catalysts

HERFD-XAS reveals nature of adsorbed species during CO oxidation over Pt/CeO₂

Carbon-based fuels, in future especially also derived from renewable resources, will continue to play an important part in energy storage and transportation markets due to the high energy density [2,3]. Despite the emissions can be reduced by using an optimal synthetic fuel blend, efficient emission control systems will be needed [5]. The majority of aftertreatment systems include total oxidation catalysts based on ceria-supported Pt and other noble metals that are scarce. Significant efforts are thus devoted to reduce the amount of noble metals needed, particularly by improved understanding, increased stability and regeneration during operation. In this regard, monitoring the catalysts under dynamic conditions with high time and spatial resolution is particularly important. Apart from *operando* EXAFS, investigating variations of the XANES region is in this case important, as exemplified here for the Pt/CeO₂ system.

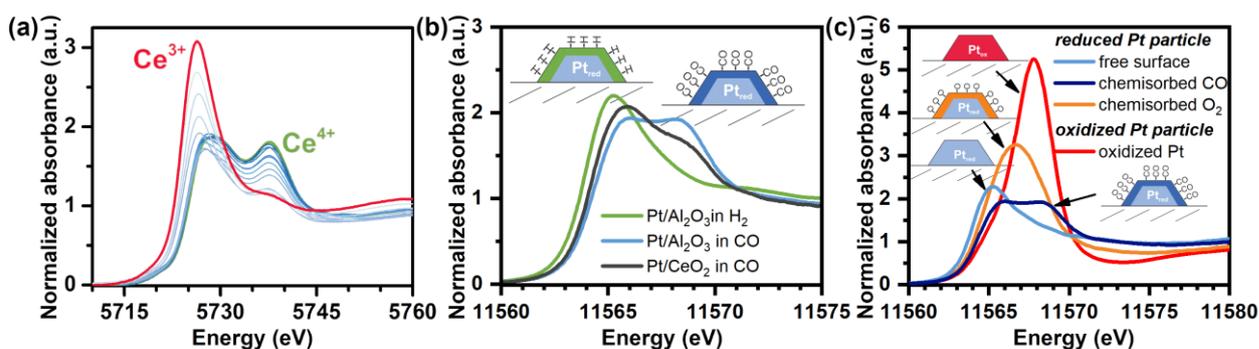


Figure 4. (a) Ce L₃ XANES spectra recorded during temperature programmed reduction of Pt/CeO₂-Al₂O₃ in 2 % CO/He (25 to 530 °C at 5 °C/min ramp rate). (b) Variation of Pt L₃ HERFD-XANES spectra due to CO adsorption. (c) Reference Pt L₃ HERFD-XANES spectra of reduced Pt NPs with free, CO covered and oxygen covered surface, as well as oxidized Pt NPs. Adapted and reprinted with permission from [15] and [9]. Copyright © 2019 American Chemical Society.

In order to be able to use XANES for structural identification, the spectra need to display well resolved features, which can be unequivocally assigned to structural information. This is generally not a problem for absorption edges lying at relatively low energies, e.g. Ce L₃ edge (Figure 4a), however it is impossible to obtain comparable energy resolution by conventional XAS at higher energies, e.g. Pt L₃ edge, due to core hole lifetime broadening. In order to reveal the structure of Pt sites including the adsorbed species we used advanced photon-in/photon-out technique high energy resolution fluorescence detected (HERFD) XANES spectroscopy (allowing to circumvent the core hole lifetime broadening). The resulting Pt L₃ HERFD-XAS spectra are thus rich in features. Employing HERFD XAS enables clear distinction between different types of reduced Pt sites, with or without adsorbed CO (Figure 4b), otherwise impossible by conventional XANES. These results allowed establishing a library of reference HERFD-XANES spectra of catalytically active Pt species (Figure 4c) that could be used to resolve kinetics of CO adsorption and oxidation on Pt/Al₂O₃ and Pt/CeO₂-Al₂O₃ catalysts, even in spatiotemporal manner in catalytic reactors (details, cf. ref. [9]).

Selective catalytic reduction of NO_x

HERFD-XANES and vtc-XES reveal the structure of Cu sites in zeolite catalysts

Lean-burn engines (e.g. diesel and lean-burn gasoline) attract lots of attention thanks to their lower fuel consumption and CO₂ emissions. On the downside, they require sophisticated emission control systems with dedicated NO_x removal catalysts. Zeolites doped with transition metals such as Fe or Cu are commonly used in road vehicles for removal of NO_x via selective catalytic reduction with ammonia (NH₃-SCR) due to their high activity and reasonable stability [5]. In order to improve their stability under hydrothermal conditions and their resistance to catalyst poisons understanding of the active site structure under reaction conditions is required. One limiting factor is the similarity of spectral features of reactants, intermediates, and products which may enter the coordination sphere of the transition metals. Conventional EXAFS is not capable of distinguishing between nearest neighbors with similar Z-numbers such as N and O and, thus, can provide only limited information on the adsorbed species [16].

To overcome this limitation we used a combination of valence-to-core X-ray emission spectroscopy (vtc-XES) with HERFD-XANES to probe Cu sites in a 1.2 wt.% Cu-SSZ-13 zeolite under SCR and related gas mixtures at 200 °C [16]. Appearance of nitrogen resulting from adsorption of ammonia in the first coordination shell of Cu was observed by a shift of the $K\beta''$ emission line in the vtc-XES spectra (Figure 5) and is supported by theoretical calculations. At the same time, HERFD XANES spectra allowed quantitative evaluation of oxidation state of Cu sites using the well-resolved $1s \rightarrow 3d$ pre-edge feature of Cu(II) at 8978 eV. The qualitative indication of NO binding to Cu sites resulted in the change of the absorption edge shape whereas NH_3 binding to Cu sites induced a prominent edge feature at 8983 eV. Vtc-XES spectral features located above the $K\beta_{2,5}$ line (at 8982 and 8990 eV) were used as a fingerprint for Cu sites of different nuclearity, as supported by conventional EXAFS analysis and electron paramagnetic resonance [17]. Thus, a combination of *in situ* and *operando* techniques combined with theoretical calculations allowed detailed insights in the structure and performance of zeolite catalysts for NO_x removal.

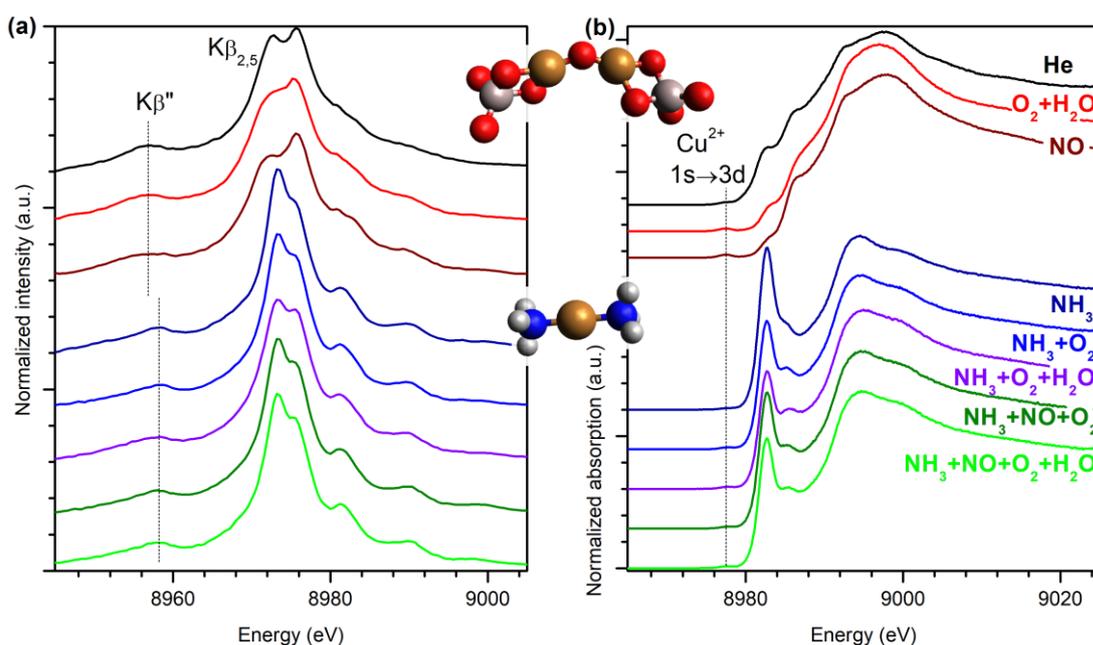


Figure 5. Selected (a) vtc-XES and (b) HERFD-XANES spectra of a Cu-SSZ-13 catalyst measured under SCR and related conditions. Overlaid are the dominating structural motifs of Cu sites in NH_3 -containing and NH_3 -free gas feeds (gold color is Cu, red is O, blue is N, white is H). Further details in ref. [16].

XES as an efficient tool to probe V sites in mixed oxide catalysts

Industrially relevant catalysts are often based on complex mixed oxide systems. A prominent example are V-based catalysts, widely used in exhaust gas aftertreatment as well as in various industrial partial oxidation processes. The typical V catalyst applied in NH_3 -SCR contains VO_x species supported on tungsta-doped titania (2% V_2O_5 -9% WO_3/TiO_2 , denoted as VWT [18]). Due to the redox activity of V species understanding their structure under reaction conditions is of vital importance for the catalyst development. V K edge XANES region is very sensitive to the oxidation state and coordination environment. However, it is very difficult to obtain high quality *in situ* or *operando* conventional XAS data on these catalysts. Transmission XAS is further prohibited by the low X-ray energy at the V K edge (5465 eV), which is absorbed by tungsten,

while conventional fluorescence measurements are difficult due to the overlapping V $K\alpha_{1,2}$ with $K\beta_{1,3}$ lines of Ti. Apart from this, gas-tight *in situ* cells with low absorbing X-ray windows at these low energies are a challenge [18].

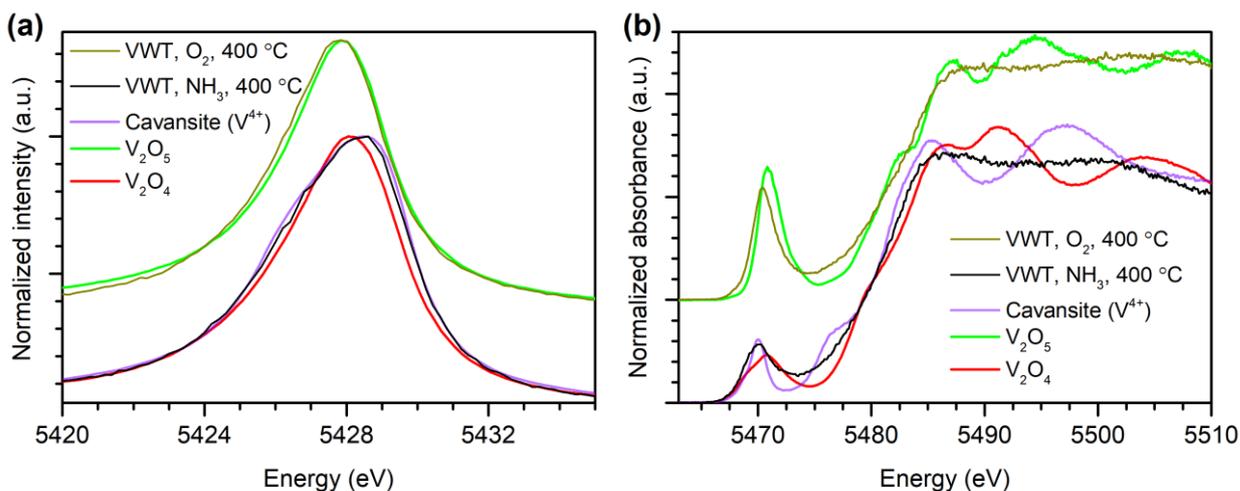


Figure 6. *Operando* (a) $K\beta_{1,3}$ XES and (b) HERFD XANES spectra of the V/ WO_3 / TiO_2 (VWT) catalyst measured in 1000 ppm NH_3 /He and 5% O_2 /He at 400 °C and alongside the spectra of reference compounds. Further details in ref. [18].

To overcome the limitations of conventional XAS we applied photon-in / photon-out hard X-ray techniques by combining a source with high photon flux and a high resolution Johann-type X-ray fluorescence spectrometer capable of resolving V $K\alpha_{1,2}$ and Ti $K\beta_{1,3}$ and probing only the V bands. In this way we were able to successfully monitor the redox response of V species under conditions relevant for NH_3 -SCR. Figure 6 summarizes *in situ* $K\beta_{1,3}$ XES and V K-edge HERFD-XANES spectra under the most reducing (NH_3) and oxidizing (O_2) conditions compared to the spectra of reference V^{4+} and V^{5+} compounds [18]. Although, HERFD resulted in high quality XANES spectra, it is difficult to extract quantitative information on the oxidation state due to the additional variation of the shape of XANES due to local geometric surrounding of the ligands and thus not appropriate reference spectra. Instead, analyzing $K\beta_{1,3}$ XES appeared to be the most unambiguous tool to quantify oxidation states of V species because of its direct dependence on the oxidation and spin states but much lower dependence on the geometry of V. Since $K\beta_{1,3}$ XES is recorded as a part of the HERFD XANES measurement it proved to be also the fastest way to analyze the oxidation state of V in VWT catalysts under reaction conditions.

Conclusions and outlook

Synchrotron studies of heterogeneous catalysts are challenging due to the necessity of *in situ* and *operando* experiments, complexity of the catalytically active systems and various timescales including local effects in catalytic reactors. We have illustrated some of the challenges faced during our everyday work and highlighted approaches how to tackle those challenges using advanced synchrotron based hard X-ray techniques including QEXAFS, XES, and HERFD-XAS as well as beamlines dedicated to catalysis. We expect further improvements in the field of data analysis to be capable of “big data” treatment and especially complementary modelling of XANES and XES data, which appear inevitable when interpreting vtc-XES or RIXS data. MES XAS is one of the emerging approaches to increase sensitivity towards active sites and we expect that machine learning algorithms will play a bigger role in the future.

Acknowledgments

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