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HERFD-XANES and XES as complementary *operando* tools for monitoring the structure of Cu-based zeolite catalysts during NO_x-removal by ammonia SCR

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Abstract. In this article, we demonstrate the potential of hard X-ray techniques to characterize catalysts under working conditions. *Operando* high energy resolution fluorescence detected (HERFD) XANES and valence to core (vtc) X-ray emission spectroscopy (XES) have been used in a spatially-resolved manner to study Cu-zeolite catalysts during the standard-SCR reaction and related model conditions. The results show a gradient in Cu oxidation state and coordination along the catalyst bed as the reactants are consumed. Vtc-XES gives complementary information on the direct adsorption of ammonia at the Cu sites. The structural information on the catalyst shows the suitability of X-ray techniques to understand catalytic reactions and to facilitate catalyst optimization.

1. Introduction

Over the past years, X-ray absorption spectroscopy (XAS) has been successfully applied to elucidate the structure of metal sites in a variety of solid compounds and liquid phase complexes. The application of high energy resolution fluorescence detected - X-ray Absorption Near Edge Structure (HERFD-XANES) spectroscopy offers the possibility to unravel additional spectral features and thus more information on the sample compared to conventional XAS [1,2]. This high resolution is achieved by measuring the fluorescence signal of the K β -line (3p \rightarrow 1s). The 3p orbitals interact more with the valence 3d and 4p orbitals and therefore show a stronger influence on the environment than the less pronounced mixing of 2p and 3d orbitals, which results in the K α -line [3]. By selecting a K β -line as a single fluorescence channel, a higher energy resolution is achieved as the core-hole life-time during the X-ray absorption process can be circumvented [4].

An additional technique to characterize metal sites is X-ray emission spectroscopy (XES), where electrons from an occupied higher orbital are transferred to an empty lower orbital. Information on occupied states is therefore gained by XES, whereas XANES is a long established complementary technique that provides information on the electron transfer to unoccupied states [5]. Particularly the transfer of electrons from valence orbitals provides new insights into the interaction between metal



and its ligands. The weak transitions from the valence level to the 1s orbital are the $K\beta_{2,5}$ -line and its satellite feature $K\beta''$. They are strongly sensitive to the coordination number and geometry. As the ligand 2s orbitals interact with the metal valence orbitals, their energy affects the position of the $K\beta''$ -line and offers the possibility to distinguish between different ligands with close atomic numbers like oxygen or nitrogen atoms [6], which is otherwise not possible using conventional EXAFS.

So far, these techniques have been applied to study mainly model compounds. Particularly for catalytic reactions, the structure of the catalyst is of interest not only *ex situ* but especially *in situ* or *operando*, i.e. while measuring the catalytic performance. The interaction of reactants with the catalyst can give more insights into the reaction pathways. For the removal of nitrogen oxides from exhaust gas, the selective catalytic reduction (SCR) with ammonia is commonly used. Giordanino et al. [7] recorded HERFD-XANES and XES *in situ* while dosing ammonia over the catalyst Cu-SSZ-13. The interaction with ammonia led to the reduction of Cu^{2+} to linearly coordinated Cu^+ . The adsorption of ammonia on the Cu-sites was additionally supported by the XES data, where a shift of the $K\beta''$ -line proves nitrogen atoms (from ammonia) coordinated to Cu. These findings show the valuable application of these spectroscopic methods under *in situ* conditions, giving hints to understand reaction mechanisms.

The logical consequence is the combination of *operando* conditions with the spectroscopic tools. Ideally, the catalyst should be studied during operation. As this is usually not possible for commercial processes, a setup and reaction conditions which reflect as close as possible the real process are used. For studying heterogeneous catalysts, the microreactor setup based on quartz capillaries has shown a good comparability with real fixed bed reactors [8]. The microreactor can be heated to relevant reaction temperatures and various gas mixtures can be dosed and monitored by conventional gas analyzers (e.g. MS, IR etc.). Depending on the X-ray beam size, XAS and XES spectra of the catalyst can be recorded in a spatially-resolved manner, allowing observation of gradients along the catalyst bed, which can give essential information to understand the reaction mechanism [9]. This is particularly important at high temperatures where the reaction occurs mainly at the inlet of the catalyst bed, as demonstrated for the SCR process by Luo et al. [10].

Here, we show the potential of spatially-resolved HERFD-XANES and XES to study the SCR-mechanism on Cu-SSZ-13 under operating conditions.

2. Experimental section

The zeolite SSZ-13 was prepared in a similar manner as described by Deka [11] and Zones [12]. It was ion-exchanged with $\text{Cu}(\text{OAc})_2$ to 1.2 wt.% Cu-SSZ-13 [13]. HERFD-XANES and XES were measured in fluorescence mode with a beam size of 0.2 x 1 mm at the ID26 beamline at ESRF (European Synchrotron Radiation Facility). The HERFD-XANES was recorded by scanning the incident beam energy with the monochromator (Si(111) double crystal monochromator), while the energy of the fluorescence detector was kept fixed at the maximum of the $K\beta_{1,3}$ -emission line (8903.6 eV). In turn, for the XES measurements, the incident beam energy was kept fixed with the monochromator above the K edge at 9100 eV and the fluorescence detector scanned the photons emitted from the sample. A sieved fraction of the catalyst sample (100 - 200 μm , 8 - 10 mm bed length) was loaded into a 1 mm quartz capillary (20 μm wall thickness), which served as a plug-flow reactor, and mounted above a hot air gas blower (FMB Oxford). Gases were dosed with individual mass flow controllers to obtain a gas mixture of 0-1000 ppm NO, 0-1000 ppm NH_3 , 10% O_2 and ~1.5% H_2O in He and analysed by an FTIR spectrometer (MKS 2030). Further experimental details are given elsewhere [13].

3. Results and discussion

In a first step, the local structure is typically analysed by a comparison of its spectrum with reference spectra of well-characterised materials, an approach that is used in a similar manner for catalysts under reaction conditions. For Cu-SSZ-13, there are several XAS and XRD studies combined with computational modelling that suggest Cu in positions close to six or eight membered rings in the

zeolite pores [14,15]. Under reaction conditions though, reactive gases are expected to adsorb at the Cu sites and therefore change coordination number, geometry and oxidation state of these sites. This makes it necessary to additionally study the influence of each gas separately and in combination with other gases.

Three reference spectra are given in Figure 1, showing the effect on the Cu sites of oxygen, ammonia and their combination. As discussed in more detail earlier [13], Cu is fully oxidized under oxygen flow, but becomes reduced in the presence of ammonia, as the decreased pre-edge feature (specific for Cu^{2+} , $3d^9$) confirms. The intense feature in the rising edge at 8982.7 eV is related to Cu^+ in linear coordination [7] and is even more pronounced without oxygen. These observations under model gas compositions already show, that the catalytic centres are affected by the single reactants and change their oxidation state and local structure, confirming the *in situ* results by Giordanino et al. [7]. Under reaction conditions, where gases adsorb, react and desorb from the active centres, the reaction progresses along the catalyst bed, resulting in concentration gradients and thus catalytic sites in different states. As essential information on the reaction kinetics can be derived by monitoring the gas concentrations along the reactor [16], also monitoring the catalyst structural dynamics at different positions is equally relevant for understanding the reaction mechanism. The HERFD-XANES spectra obtained at three positions (beginning, middle and end) of the catalyst bed under SCR reaction conditions are depicted in Figure 1, showing clear differences and demonstrating the importance of spatially-resolved compared to integral studies. The decrease in intensity of the feature in the rising edge indicates less linearly coordinated Cu^+ , which is in line with the ammonia consumption along the reactor. The intensity of the pre-edge feature suggests a mixture of Cu^+ and Cu^{2+} , with almost no variation under these conditions. By increasing the temperature and thus the reaction rate, a stronger gradient is observed for both features [17].

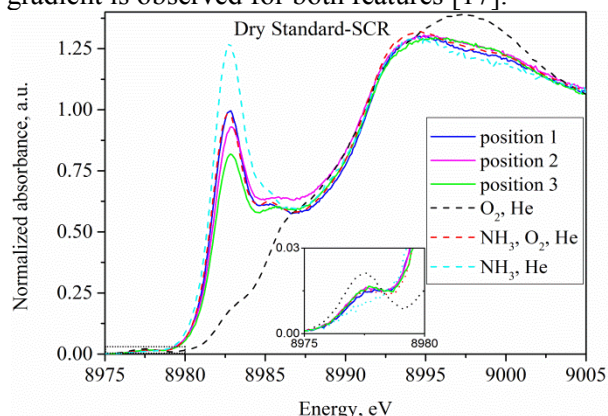


Figure 1. Spatially-resolved HERFD-XANES spectra of Cu-SSZ-13 under model gas feeds and at three positions along the catalyst bed under Dry Standard-SCR reaction conditions (1000 ppm NO, 1000 ppm NH_3 , 10% O_2 , He; GHSV = 200,000 h^{-1}) at 200 °C.

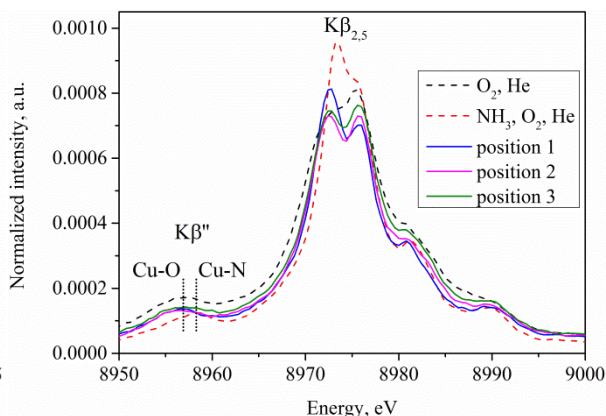


Figure 2. Spatially-resolved X-ray Emission Spectra of Cu-SSZ-13 at three positions along the catalyst bed under Standard-SCR reaction conditions (1000 ppm NO, 1000 ppm NH_3 , 10% O_2 , 1.5% H_2O , He; GHSV = 200,000 h^{-1}) at 400 °C and reference spectra in O_2 , He and NH_3 , O_2 , He recorded at 200 °C.

A similar effect is visible in the XES results (Figure 2), where the *operando* spectra vary along the catalyst bed. Especially the $\text{K}\beta_{2,5}$ -line shows a decrease of the feature at 8972.6 eV and increase of the feature at 8975.8 eV from the inlet towards the outlet of the catalyst bed. As an additional benefit for catalytic reactions, typically information on the ligand nature can be derived from $\text{K}\beta''$ region. Also for Cu-SSZ-13 coordination of N or O atoms is clearly resolved at 200°C when adding NH_3 to the O_2 -He stream. However, at 400°C due to a higher reaction rate but also due to a different interaction with H_2O and NH_3 molecules the variation of the $\text{K}\beta''$ feature is less pronounced. Only at position 3 of the catalyst bed a slight broadening was observed which could be caused by the interaction with the

zeolite framework, as indicated by similar spatially resolved EXAFS studies (not shown). However, DFT simulated XES/XANES spectra and additional measurements at high temperatures under model conditions are necessary to obtain a better understanding of this phenomenon, as not only the ligands but also the coordination geometry have an influence on the spectrum. This is currently carried out by our team and a more comprehensive analysis will be reported in our next paper.

4. Conclusion

The application of HERFD-XANES and XES to study a catalyst in a spatially-resolved manner under reaction conditions has been demonstrated. Significant structural gradients along the catalyst bed could be observed with both methods, showing less adsorbed ammonia on the Cu-sites towards the end of the reactor. This experiment has illustrated the possibility of describing coordination sphere of metal sites of working catalysts and, thus, the suitability of XAS and XES to give insights into reaction mechanisms. As these methods are not limited to a specific reaction, they could be applied also to other catalytic reactions as understanding a catalyst is the best way for its further optimisation.

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