



	<b>Experiment title:</b> Investigating the Electrochemical Reduction of Nitrate to Ammonia on Single- Atom Catalysts via Operando X-ray Absorption Spectroscopy	<b>Experiment number:</b> MA5254
<b>Beamline:</b> BM23	<b>Date of experiment:</b> from: 08.04.2022 to: 11.04.2022	<b>Date of report:</b> 09.09.2022
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## Report:

## Overview

The main objective of the project was to utilize *in situ* X-ray absorption spectroscopy (XAS) in order to provide a fundamental understanding of the complex changes occurring in the geometric and local electronic structures for electrocatalysts active for the nitrate reduction reaction (NO<sub>3</sub>RR). The electrocatalyst material of primary interest consisted of MoO<sub>x</sub> nanoparticles supported on an iron and nitrogen-doped carbon support (MoO<sub>x</sub>@FeNC), which represents a promising catalyst for the electro-reduction of NO<sub>3</sub><sup>-</sup> to NH<sub>3</sub>. During this measurement time we investigated the roles the Fe and Mo active sites by closely monitoring the electronic state and local geometric structure under NO<sub>3</sub>RR operating conditions (i.e. as a function of the applied electrochemical potential and the electrolyte pH). Our state-of-the-art molybdenum dendrite catalyst supported on Ni form (Mo@NiF) was measured in a similar manner in order to identify the changes in the Mo oxidation state and local structure that occur during NO<sub>3</sub>RR. In addition, a series of synthetic Fe-S clusters, which mimic the Fe-S cubane active centers in complex enzymatic systems (e.g. in nitrogenases that reduce N<sub>2</sub> to NH<sub>3</sub>), were also measured *ex situ* in order to reveal changes in the formal oxidation state and coordination environment of Fe that occur as the ligand environment is varied.

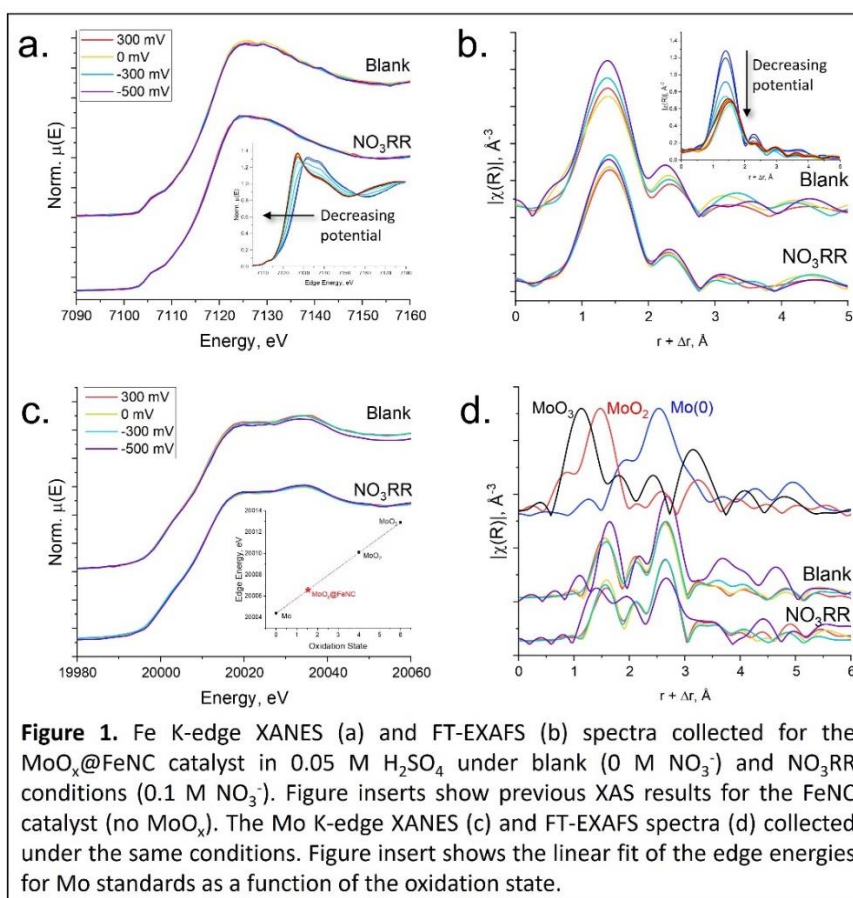
## Quality of the measurement/data

*In situ* XAS spectra were obtained in fluorescence mode at the Fe K-edge for our MoO<sub>x</sub>@FeNC material under NO<sub>3</sub>RR conditions ( $k$ -range ca.  $>8 \text{ \AA}^{-1}$ ). Similarly, *in situ* measurements at the Mo K-edge for our MoO<sub>x</sub>@FeNC and Mo@NiF catalysts yielded  $k$ -ranges of  $10 \text{ \AA}^{-1}$  and  $12.5 \text{ \AA}^{-1}$ , respectively. In all cases, clear changes in the XAS spectra related to the activity of the electrochemical reaction under investigation can be observed, indicating that our spectro-electrochemical flow cell worked as intended and that our materials were well-suited for *in situ* XAS analysis. Some difficulty measuring at high overpotentials was encountered due to the simultaneous production of H<sub>2</sub> bubbles at the working electrode, which causes changes in the beam attenuation and therefore fluctuations in the measured signal. In addition to *in situ* measurements, several molecular Fe-S catalyst complexes were measured *ex situ* at the Fe K-edge. High quality XAS spectra ( $k$ -range ca.  $>12 \text{ \AA}^{-1}$ ) were obtained in transmission mode for the Fe-S clusters, which allowed for a detailed XANES and EXAFS analysis.

## Results

The *in situ* XAS spectra for the  $\text{MoO}_x\text{@FeNC}$  catalyst in acidic media are depicted in Figure 1. Compared here are the Fe K-edge and Mo K-edge spectra for the catalyst under blank conditions ( $0.05 \text{ M H}_2\text{SO}_4$ ) and  $\text{NO}_3\text{RR}$  conditions ( $0.05 \text{ M H}_2\text{SO}_4 + 0.1 \text{ M NaNO}_3$ ). All polarization measurements were conducted by stepping the electrode potential cathodically from the OCP (e.g.  $300 \text{ mV}$ ) to ca.  $-500 \text{ mV}$  vs.  $\text{Ag/AgCl}$ , where the  $\text{NO}_3\text{RR}$  is known to take place. From Figure 1a, we observe that no reduction of the Fe center occurs as the potential is reduced from OCP to  $\text{NO}_3\text{RR}$  conditions. This is in contrast to our previous results for the bare FeNC material (i.e. without  $\text{MoO}_x$  nanoparticles), which showed strong changes in the absorption edge related to the reduction of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  (see Figure 1a insert for comparison). The FT-EXAFS show that the amplitude of the first coordination shell, which can be attributed to the 4 nearest neighboring nitrogen atoms of the porphyrin site, generally increases as the potential is decreased. This likely indicates an increase of the coordination number, which may be related to adsorption of oxo species (e.g. from water) or sulfate (e.g. from the electrolyte) to the surface under blank conditions or the adsorption of nitrate under  $\text{NO}_3\text{RR}$  conditions. This result is also in contrast to our previous results obtained on the pure FeNC material, where we observed a strong decrease in amplitude as the potential was decreased under both blank and  $\text{NO}_3\text{RR}$  conditions (see Figure 1b insert for comparison to FeNC).

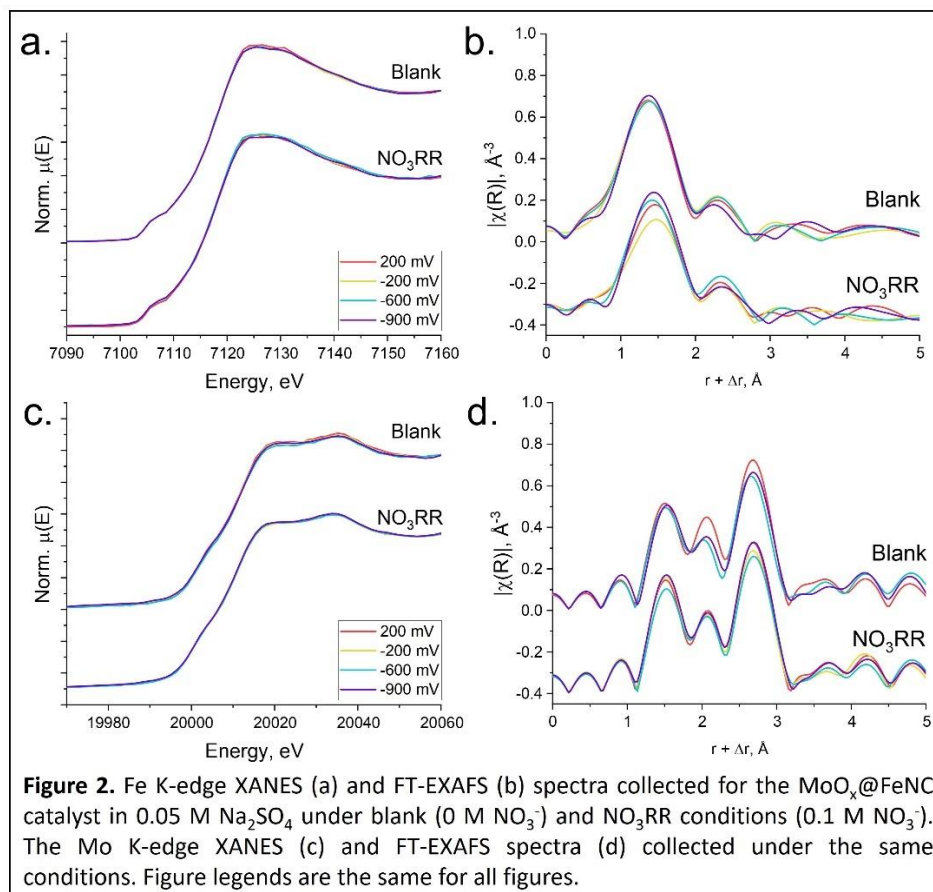
Figure 1c-d show the *in situ* Mo K-edge spectra for  $\text{MoO}_x\text{@FeNC}$  in acidic media. Similar to the Fe K-edge, we observe no major shifts in the edge position, indicating that Mo does not experience a strong reduction upon polarization. Using a series of Mo standards, it was determined that Mo resides in an average oxidation state of 1.4, suggesting that the  $\text{MoO}_x$  nanoparticles likely contain a metallic Mo core and an oxide surface. This is further supported by comparing the FT-EXAFS of  $\text{MoO}_x\text{@FeNC}$  to the measured Mo standards in Figure 1d. Overall, the FT-EXAFS show little change during the first few potential steps (i.e. from  $300$  to  $-300 \text{ mV}$ ). At  $-500 \text{ mV}$ , however, the FT-EXAFS spectra show dramatic changes that suggest a restructuring of the catalyst under  $\text{NO}_3\text{RR}$  conditions. Although further fitting of the Mo K-edge FT-EXAFS spectra is needed, the lack of any major changes in the Fe K-edge data suggests that  $\text{MoO}_x$  has a significant influence on the  $\text{NO}_3\text{RR}$  mechanism in acidic media. Specifically, the presence of  $\text{MoO}_x$  seems to inhibit the reduction of Fe under  $\text{NO}_3\text{RR}$  conditions and may be the preferred active site at the potentials examined.



*In situ* XAS measurements of the  $\text{MoO}_x\text{@FeNC}$  catalyst were also performed in neutral media ( $0.05 \text{ M Na}_2\text{SO}_4$ ). Shown in Figure 2 are the XANES and FT-EXAFS spectra at the Fe K-edge (Figure 2a-b) and Mo K-edge (Figure 2c-d). Similar to the case in acidic media, we observe no shifts in the absorption edge position at either K-edge, indicating that neither Fe nor Mo experience a significant change in electronic state under electrocatalytic conditions. Interestingly, the FT-EXAFS spectra also suggests that there is no significant change in the local structure. These results tend to suggest that

the NO<sub>3</sub>RR may proceed through a separate mechanism in neutral media in which there is no specific adsorption of NO<sub>3</sub><sup>-</sup> at the potentials we examined (e.g. outer sphere reaction mechanism).

Analysis of the *in situ* data for our state-of-the-art Mo@NiF catalysts is still in progress. The *in situ* XANES spectra recorded in neutral media (Na<sub>2</sub>SO<sub>4</sub>) suggest that the Mo sites initially exist in a Mo<sup>3+</sup> state, which is then reduced to Mo<sup>2+</sup> under NO<sub>3</sub>RR conditions. Furthermore, strong structural changes are observed in the FT-EXAFS spectra. A large increase in the first coordination shell and the appearance of strong features at r values >3 suggest that the structure becomes more ordered as the potential is decreased into the NO<sub>3</sub>RR regime, which may be essential to high catalytic activity and selectivity that we have observed with this material.



Finally, we systematically investigated the room temperature XAS spectra of the synthetic iron-sulfur cubanes, K<sub>n</sub>[Fe<sub>4</sub>S<sub>4</sub>(DmpS)<sub>4</sub>] (where n=0-4) (Figure 3a). This was part of a larger spectroscopic study involving a large array of magnetic and electronic techniques techniques (SQUID, Mössbauer, EPR, UV-Vis). From the XANES spectra shown in Figure 3b, we can identify systematic changes in the absorption edge energy as well as the line shape that are caused by changes in oxidation state and the coordination sphere from distorted tetrahedral to tetrahedral, respectively. While these changes are well documented by our previous single-crystal X-ray diffraction analyses (Proc. Natl. Acad. Sci. 119, 1–14 (2022)), they are also supported by our analysis of the EXAFS region of the spectrum in Figure 3c. We expect that this analysis and our corresponding documentation of the XAS Fingerprint of these cubanes will enable biochemists to identify the oxidation state of biological Fe<sub>4</sub>S<sub>4</sub> cofactors using synchrotron techniques with higher certainty and ease, since, in contrast to the usually performed Mössbauer spectroscopy, no isotopic enrichment of the protein by <sup>57</sup>Fe is necessary to measure the spectrum. We are currently planning future studies to investigate the so-called "ligand XAS spectra" of our Fe<sub>4</sub>S<sub>4</sub> complexes, since XANES Fingerprints measured at the S K-edge have been used to gauge the contributions of super- and double-exchange to valence delocalization in these systems in the past (J. Am. Chem. Soc. 126, 8320–8328 (2004)). We hope that this will also enable us to understand even better their fundamental electronic structure and reveal which oxidation states are dominated by super- and which by double-exchange.

