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### Spin state and satellite structures in Co and Fe based absorber materials and catalyst

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We use resonant photoelectron spectroscopy at the Fe2p and the Co2p absorption edges to report on spectroscopic investigation of Co-oxides and Fe-oxides prepared by sol-gel, ALD, and as nanoparticles (NP) [1].  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> is commonly used as photocathode for water splitting for the hydrogen production [2]. On the other hand  $\epsilon$ -Fe<sub>2</sub>O<sub>3</sub> is of interest because of its magnetic properties [3]. Co-oxide as prepared as Co-Pi is a catalyst for the OER reaction [6, 7].

For both well-defined oxidic systems we analyze the electronic structure and determine the partial density of states for the valence and conduction bands. From these data we can derive a band scheme and compare it with recent band structure calculations [4] of the corresponding bulk phases.

The resPES data at the Fe2p and Co2p absorption edge spectra are analyzed to give evidence about the involved spin states in both phases. We find that for the  $\epsilon$ -Fe<sub>2</sub>O<sub>3</sub> the majority is due to Fe3d<sup>5</sup> HS state. Contributions of the corresponding LS state are small and are found to be higher for the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> phase. In  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> prepared by ALD we identify in addition a LS 3d<sup>6</sup>L state [5]. In Co-Pi we find a transition from Co<sup>2+</sup> to Co<sup>3+</sup> species depending on the catalysts film thickness. In addition we identify a Co3d<sup>7</sup>L CT state right at the Fermi energy. We attribute such an electronic constellation being favorable for a multiple charge transfer reaction.

[1] P. Brázda, D. Nižňanský, J.-L. Rehspringer, and J. P. Vejpravová, *J Sol-Gel Sci Technol*, 51(1), **8** (2009).

[2] K. Sivula, F. Le Formal and M. Grätzel, *ChemSusChem* 2011, **4**, 432.

[3] Gich M, Frontera C, Roig A, Taboada E, Molins E, Rechenberg HR, Ardisson JD, MacedoWAA, Ritter C, Hardy V, Sort J, Skumryev V, Nogues J (2006) *Chem Mater* 18:3889.

[4] Timo Jakob, private communication.

[5] K. Kukli, M. Chandra Dimri, A. Tamm, M. Kemell, T. Käämbre, M. Vehkamäki, M. Puttaswamy, R. Stern, I. Kuusik, A. Kikas, M. Tallarida, D. Schmeißer, M. Ritala, and M. Leskelä, *ECS JSST 2 N45-N54* (2013).

[6] M.Richter, D.Schmeißer, *ECS Transactions* **50** (2013) 113.

[7] M.Richter, D.Schmeißer, *Applied Physics Letters* **102** (2013) 253904.

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### Spectroscopic insights into nitrogenase structure

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The fundamental processes behind the making and breaking of chemical bonds are essential to nearly every facet of human lives. Inert dinitrogen from the atmosphere must be converted into a bioavailable form for incorporation into amino acids or/and DNA. The process of reducing dinitrogen to ammonia is also essential for producing fertilizers that feed the world's growing population. [1]

In nature, the conversion of dinitrogen (N<sub>2</sub>) into ammonia (NH<sub>3</sub>) is realized by the enzyme known as Mo-nitrogenase. Nitrogenase is a large protein containing an active multimetallic site (so called FeMoco) consisting of 1 molybdenum atom, 7 iron atoms, 9 sulphur atoms and a carbide in the middle (Figure 1). The central carbon was recently revealed by X-ray emission spectroscopy, X-ray crystallography and ESEEM. [2,3]

While the atomic composition of FeMoco is now complete, the left questions towards understanding the mechanism of dinitrogen reduction remain in the lacking of electronic structure like oxidation states and total charge of the cluster.

Recently, we have utilized high energy resolution fluorescence detected X-ray absorption spectroscopy (HERFD XAS) to evaluate the oxidation state of the Mo atom in this cluster. Based on this determination [4,5] and the proposed main oxidation state assignments we took similar approach to investigate Fe oxidation states in FeMoco. Although HERFD XAS allow spectra to be obtained at resolutions below the core hole lifetime broadening of the Fe 1s electron, the presence of 7 iron atoms and the lack magnetic information in such spectra, limits the information that can be deduced from such spectra. To overcome these limitations, we have applied X-ray Magnetic Circular Dichroism spectroscopy on series of Fe-Mo-S model complexes of FeMoco, allowing quantitative assessment of the obtained data.

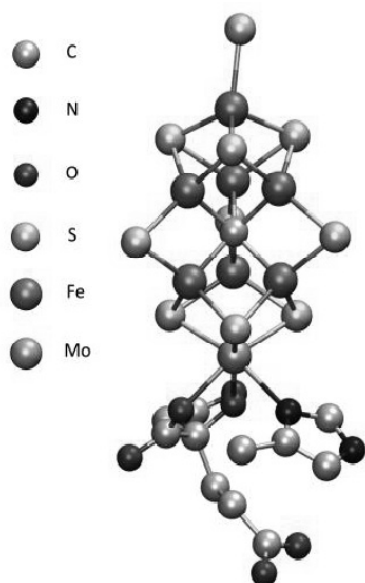


Figure 1. FeMoco cluster of nitrogenase [4].

Fe HERFD XAS and XMCD data on series of Fe-S and Mo-Fe-S model complexes and FeMo cofactor will

be presented. Based on both experimental data and theoretical calculations possible scenarios will be presented, as well as future directions towards understanding the structure and mechanism of nitrogenase.

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- [4] B. E. Smith, *Science* **297** (2002) 1654.
  - [1] K. M. Lancaster, M. Roemelt, P. Eppenhuber, Y. L. Hu, M. W. Ribbe, F. Neese, U. Bergmann, O. Einsle, S. DeBeer, *Science* **334** (2011) 974.
  - [2] T. Spatzal, M. Aksoyoglu, L. Zhang, S. L. Andrade, E. Schleicher, S. Weber, D. C. Rees, O. Einsle, *Science* **334** (2011) 940.
  - [3] R. Bjornsson, F. A. Lima, T. Weyhermüller, P. Glatzel, T. Spatzal, O. Einsle, E. Bill, F. Neese, S. DeBeer, *Chem. Science* (2014) doi: 10.1039/C4SC00337C.
  - [4] F. A. Lima, R. Bjornsson, T. Weyhermüller, P. Chandrasekaran, P. Glatzel, F. Neese, S. DeBeer, *Phys. Chem. Chem. Phys.* **15** (2013) 20911.