10:00 Interface Fermi states of LaAlO3/SrTiO3 and related heterostructures

10:30 Structure of a functioning catalyst for methane steam reforming
Renata Bessa Duarte, José M. Corrêa Bueno, Maarten Nachtegaal, Olga Safonova, and Jeroen van Bokhoven

11:00 Coffee

11:15 The cold stage: A new sample environment for TOMCAT
Annabelle Medebach, Bernd R. Pinzer, Cedric Dubois, Hans Joerg Limbach, Martin Schneebeli and Marco Stamparani

11:45 High Repetition Rate Laser Pump / X-Ray Probe Studies on Biological Systems, Metal Oxide Nanoparticles and Metal Complexes
J. Rittmann, Ch. Milne, M. Reinhardt, M.H. Rittmann-Frank, F. Santomauro, M.Silatani, R. Abela, and M. Chergui
Interface Fermi states of LaAlO$_3$/SrTiO$_3$ and related heterostructures

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At the interface between complex oxides, unexpected electronic properties different from those of the constituent bulk materials can arise. A particularly interesting example is the appearance of 2-dimensional conductivity at the interface of the band insulators LaAlO$_3$ (LAO) and SrTiO$_3$ (STO) above a critical LAO thickness of 4 unit cells (u.c.) [1]. A very recent related heterostructure is the diluted system of (LaAlO$_3$)$_x$(SrTiO$_3$)$_{1-x}$/SrTiO$_3$ (LASTO:x/STO) which also shows interfacial conductivity above a certain critical LASTO thickness which scales inversely to the LAO content [2].

The interfaces of LAO/STO and LASTO:0.5/STO heterostructures have been investigated by soft x-ray photoelectron spectroscopy for different layer thicknesses across the insulator-to-metal interface transition. The valence band and Fermi edge were probed using resonant photoemission across the Ti L$_{2,3}$ absorption edge. The presence of a Fermi-edge signal originating from the partially filled Ti 3$d$ orbitals is only found in the conducting samples. No Fermi-edge signal could be detected for insulating samples below the critical thickness. Furthermore, the angular dependence of the Fermi intensity allows the spatial localization perpendicular to the interface of the conducting electron density.

References:


Structure of a functioning catalyst for methane steam reforming

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Conversion of methane into higher value products is an important process to reduce our dependence on petroleum. Rh is one of the most active metals for methane steam reforming which produces hydrogen.\textsuperscript{[1]} The most common support for methane reforming catalysts is \(\gamma\)-\(\text{Al}_2\text{O}_3\). \(\text{CeO}_2\) attracts attention mainly due to its oxygen-storage properties and chemical interaction with noble metals. To further enhance the temperature stability of supported \(\text{CeO}_2\) it can be promoted with \(\text{Sm}_2\text{O}_3\).\textsuperscript{[2]} To understand the influence of cerium and samarium oxides on the structure of rhodium nanoparticles and its relation to catalytic performance during methane steam reforming (SR) it is important to determine the structure under reaction conditions. Given this, Rh catalysts supported on mixed oxides of \(\text{Sm}_2\text{O}_3\)-\(\text{CeO}_2\)-\(\text{Al}_2\text{O}_3\) were investigated \textit{in situ} by X-ray absorption spectroscopy (XAS) in combination with on-line mass-spectrometry. The values of \(\text{CH}_4\) conversion obtained for the catalysts during methane steam reforming were higher for the samples supported on alumina promoted by \(\text{CeO}_2\) and \(\text{Sm}_2\text{O}_3\). All catalysts showed deactivation with time on stream; however \(\text{Rh/Al}_2\text{O}_3\) showed the strongest decrease in activity. The effect of the addition of \(\text{Sm}_2\text{O}_3\) and \(\text{CeO}_2\) on \(\text{Rh/Al}_2\text{O}_3\) catalysts was revealed by changes on the structure and electronic properties of Rh particles, as seen in Fig. A. In the unpromoted catalyst the nanosized Rh\(^0\) particles redispersed under reaction conditions. A greater metal-support interaction in the presence of promoters was observed. The STEM images for the Rh/\(\text{Al}_2\text{O}_3\) catalyst after reduction at 873 K (Fig. B) and after MSR at 1033 K (Fig. C) clearly show that sintering of the metallic particles took place during reaction. This process was more pronounced for Rh/\(\text{Al}_2\text{O}_3\).\textsuperscript{[3]}

References


The cold stage: A new sample environment for TOMCAT

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Over the past years the need for special thermal boundary conditions during a scan at the TOMCAT beamline has been increasing. After commissioning a laser furnace in 2011 for high temperature scans we are now commissioning a new dedicated setup for the temperature range between $-45^\circ\text{C}$ and $+20^\circ\text{C}$. This temperature range has been chosen as many materials, for example snow and ice cream, show interesting structural changes in this range. This research complements the material science research done in our group at high temperatures by investigating ternary systems that are highly variable.

In order to study samples at temperatures below room temperature at the TOMCAT Beamline so far a CryoJet has been used. The CryoJet can only cool a very small area. This can lead to highly fluctuating temperatures and undesired high temperature gradients inside the sample. To overcome these problems a new sample environment has been taken into operation. The cold stage provides temporally and spatially stable thermal boundary conditions for the samples throughout the measurement including movement into and out of the beam. Additionally, the temperature boundaries during the sample transfer are also controlled. We present the cold stage and its characterization.

The cold stage has been used for first experiments on frozen sucrose in water solution. Using propagation based phase contrast imaging (PCI) we can differentiate the similarly absorbing sugar solution from the ice crystals without the addition of contrast agents. We show the results of a first time lapse study at constant temperature.

(a) Temperature stability at the sample over 10 hours with scans every 30 minutes

(b) Ice crystals in sucrose solution grown at $-30^\circ\text{C}$
High Repetition Rate Laser Pump / X-Ray Probe Studies on Biological Systems, Metal Oxide Nanoparticles and Metal Complexes

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The talk will provide an overview of our recent time-resolved studies on various systems in solution using our recently implemented high repetition rate laser pump / x-ray probe setup [1].

We will present the first picosecond X-ray absorption studies of a protein, myoglobin, in physiological solutions (pH7, room temperature and pressure) where we probed the photo-induced ligand detachment and recombination in solution. By recording the Fe K-edge absorption spectra, we are able to specifically monitor the dynamics at the active site, i.e. the Fe atom in the porphyrin.

We performed studies on bare and dye coated metal oxide nanoparticles (NPs), such as TiO₂ and ZnO NP as used in dye sensitized solar cells, in order to follow the charge carrier dynamics. The ruthenium dye sensitizer coated TiO₂ NPs were probed at the Ti K-edge and the Ru L-edges. We were able to monitor the relaxation dynamics of NPs excited via direct band gap excitation and electron injection via the dye, allowing us to obtain a detailed picture of the electron injection induced electronic and structure changes in the conduction band of the NP.

Finally, in studies on metal complexes such as Fe(CN)₆ and Cu-diimine complexes, we aim at exploring the role of solvent effects on the relaxation processes of these complexes. The static and transient x-ray absorption spectra allow an unambiguous assignment of electronic and geometric structure in both, the ground and the excited state (cf. fig 1) and provide information about chemical processes such as photoaquation in the case of Fe(CN)₆.

Figure 1 left: Transient X-Ray absorption (excited state – ground state) signal at the Fe K edge (blue). The transient can be explained by a solvation of CN in the excited state and replacement with an H₂O molecule (black, calculated). Right: Structure of the ground state (a) and the excited state (b) of the complex.