SLS Symposium on

Chemistry and Physics

Tuesday, December 4, 2012

10:00 to 12:15, WBGB/019

10:00 Interface Fermi states of LaAlO3/SrTiO3 and related heterostructures
C. Cancellieri, M.L. Reinle-Schmitt, M. Kobayashi, V. N. Strocov, T. Schmitt, S. Gariglio, J.-M. Triscone, P.R. Willmott

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 Stampanoni

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

C. Cancellieri[1], M.L. Reinle-Schmitt[1], M. Kobayashi[1], V. N. Strocov[1], T. Schmitt[1], S. Gariglio[2], J.-M. Triscone[2], P.R. Willmott[1]

[1] *Swiss Light Source, Paul Scherrer Institute, 5232 Villigen, Switzerland*

[2]*DPMC, University of Geneva, 24 Quai Ernest-Ansermet, 1211 Geneva4, Switzerland*

claudia.cancellieri@psi.ch

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 *3d* 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.
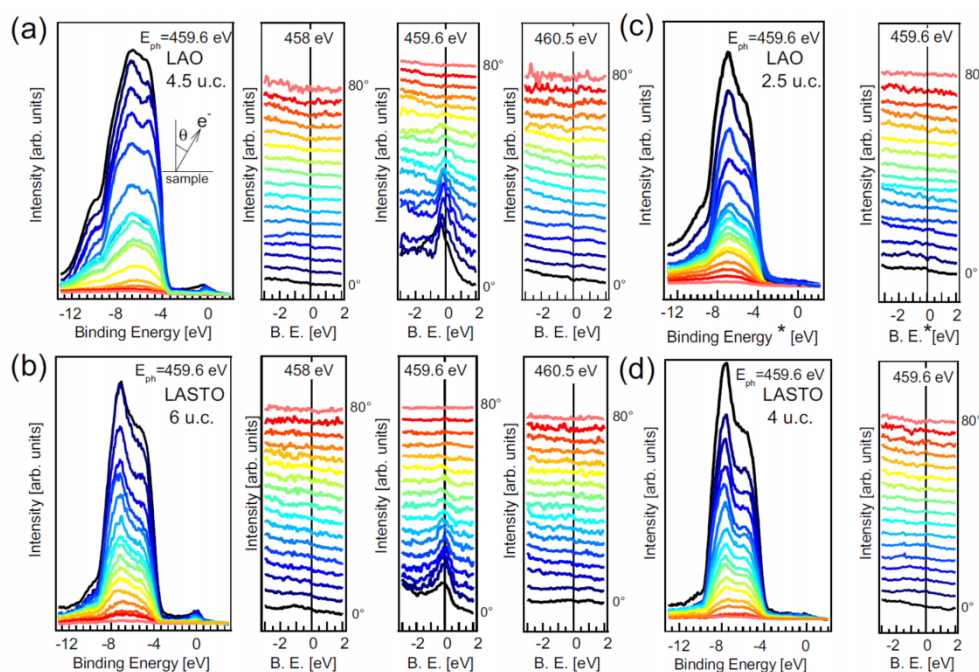
Fig.1 (a) (Color) Photoemission spectra at different photon energies for conducting (a) 4.5 u.c. LAO/STO and (b) 6 u.c. LASTO/STO and for insulating (c) 2.5 u.c. LAO/STO and (d) 4 u.c. LASTO/STO. The color map corresponds to different emission angles θ, indicated on the right of each panel, from 0° (normal emission, black lines) to 80◦ (grazing emission, pink lines) in 5° steps.

References:
[1] S. Thiel *et al.,* Science **313**, 1942 (2006).
[2] M. L. Reinle-Schmitt *et al.*, Nat. Comm. **3**, 932 (2012).

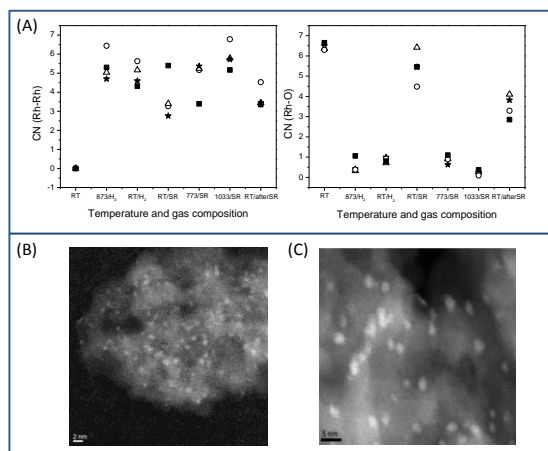# Structure of a functioning catalyst for methane steam reforming

Renata Bessa Duarte[a,b], José M. Corrêa Bueno[b], Maarten Nachtegaal[c], Olga Safonova[c], and Jeroen van Bokhoven[a,c]

[a] _Institute for Chemical and Bioengineering, Swiss Federal Institute for Technology, Wolfgang-Pauli-Strasse 10, 8093 Zürich, Switzerland,_ [b] _Universidade Federal de São Carlos, Rod. Washington Luis Km 235, 13565-905 São Carlos-SP, Brazil,_ [c] _Paul Scherrer Institute (PSI), 5232 Villigen, Switzerland_

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.[1] The most common support for methane reforming catalysts is γ-Al_2O_3. 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 CeO_2 it can be promoted with Sm_2O_3.[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. Giving this, Rh catalysts supported on mixed oxides of Sm_2O_3-CeO_2-Al_2O_3 were investigated _in situ_ by X-ray absorption spectroscopy (XAS) in combination with on-line mass-spectrometry.

The values of CH_4 conversion obtained for the catalysts during methane steam reforming were higher for the samples supported on alumina promoted by CeO_2 and Sm_2O_3. All catalysts showed deactivation with time on stream; however Rh/Al_2O_3 showed the strongest decrease in activity. The effect of the addition of Sm_2O_3 and CeO_2 on Rh/Al_2O_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 re-dispersed under reaction conditions. A greater metal-support interaction in the presence of promoters was observed. The STEM images for the Rh/Al_2O_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/Al_2O_3.[3]

References

[1] G. Jones, J. G. Jakobsen, S. S. Shim, J. Kleis, M. P. Andersson, J. Rossmeisl, F. Abild-Pedersen, T. Bligaard, S. Helveg, B. Hinnemann, J. R. Rostrup-Nielsen, I. Chorkendorff, J. Sehested, J. K. Nørskov. _Journal of Catalysis_ **259** (2008) 147–160

[2] Y. She, Q. Zheng, L. Li, Y. Zhan, C. Chen, Y. Zheng, X. Lin, _Int. J. Hydrogen energy_ **34** (2009) 8929-8936

[3] R.B. Duarte, M. Nachtegaal, J.M.C. Bueno, J.A. Van Bokhoven, accepted manuscript, Journal of Catalysis, 2012

The cold stage: A new sample environment for TOMCAT

Annabelle Medebach[1], Bernd R. Pinzer[1], Cédric Dubois[2], Hans Joerg Limbach[2], Martin Schneebeli[3] and Marco Stampanoni[1,4]

[1]*Paul Scherrer Institut, Swiss Light Source, 5232 Villigen PSI*
[2]*Nestlé Research Center, Department of Food Science & Technology, 1000 Lausanne 26*
[3]*WSL Institute for Snow and Avalanche Research SLF, Snow and Permafrost, 7260 Davos Dorf*
[4]*Institute of Biomedical Engineering, ETH Zurich, 8092 Zürich, Switzerland*

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°C and $+20$°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.
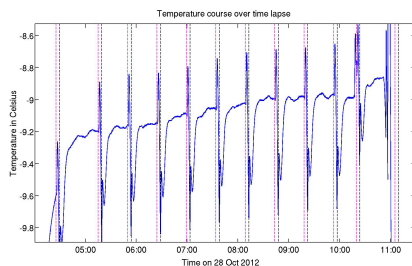
(a) Temperature stability at the sample over 10 hours with scans every 30 minutes
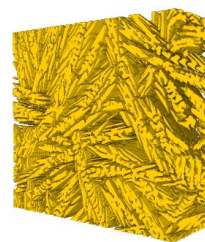
(b) Ice crystals in sucrose solution grown at -30°C

High Repetition Rate Laser Pump / X-Ray Probe Studies on Biological Systems, Metal Oxide Nanoparticles and Metal Complexes

J. Rittmann[1,3], Ch. Milne[2], M. Reinhardt[3], M.H. Rittmann-Frank[1,3], F. Santomauro[1,3], M.Silatani[1,3], R. Abela[2], and M. Chergui[3]

1 Swiss Light Source, Paul Scherrer Institut, CH 5232 Villigen, Switzerland
2 SwissFEL, Paul Scherrer Institut, CH 5232 Villigen, Switzerland
3 École Polytechnique Fédérale de Lausanne, Laboratoire de Spectroscopie Ultrarapide, Facultè des Sciences de Base, CH-1015 Lausanne, Switzerland
jochen.rittmann@psi.ch

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 TiO_2 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 $Fe(CN)_6$.
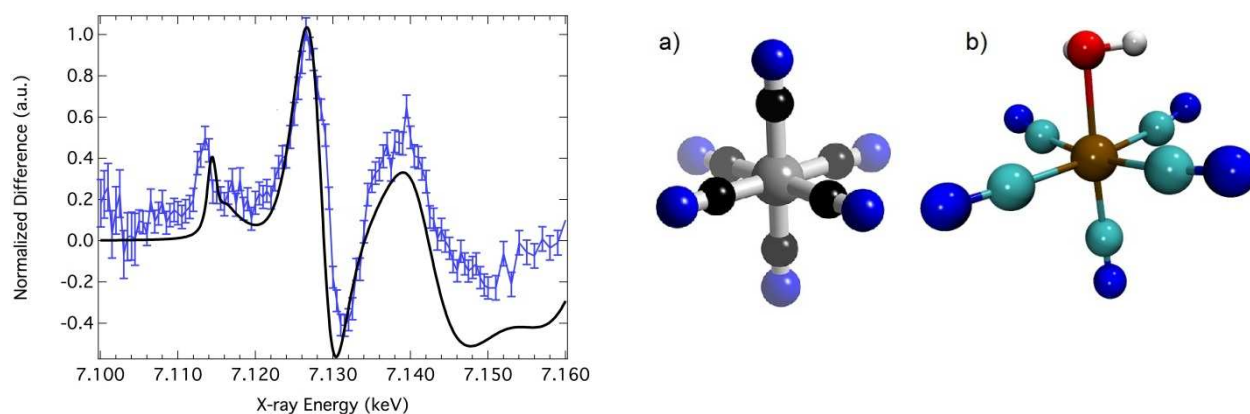

Figure 1 left: Transient X-Ray absorption (excited state – ground state) signal at the Fe K edge (blue). The transient can be explained by a solvation of CN in the excited state and replacement with an H2O molecule (black, calculated). Right: Structure of the ground state (a) and the excited state (b)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

[1] Lima, F. A. et al *Rev Sci Instrum* **2011**, *82*