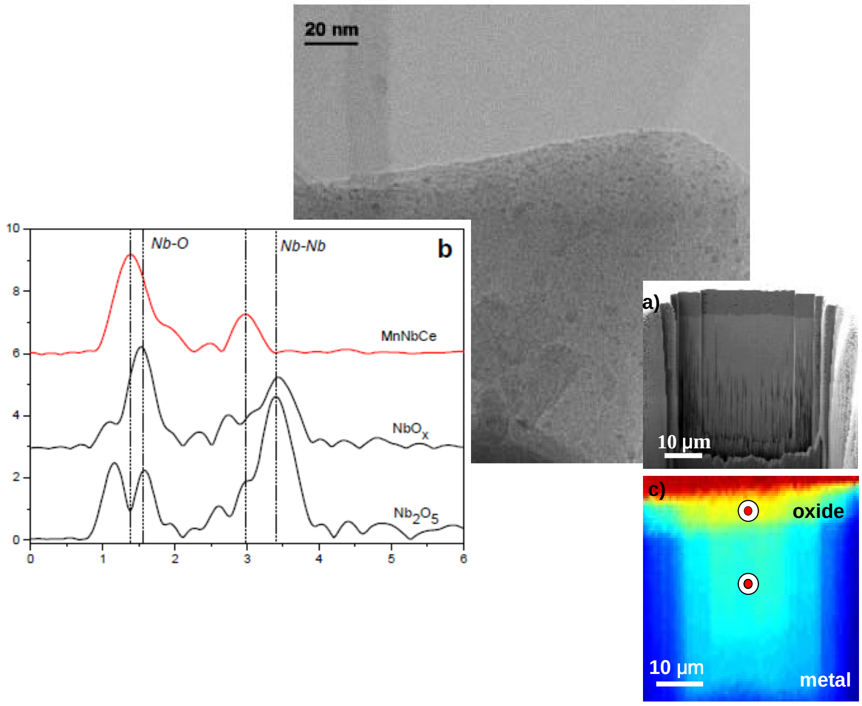

SLS Symposium

X-ray spectroscopies of energy materials

Tuesday, March 2, 2010

10:00 to 12:15, WBGB/019

Program

10:00 Automotive Catalysts studied by XAS
M. Casapu, M. Mehring, S. Brandenberger, O. Kröcher, M. Nachtegaal, M. Harfouche, C. Borca, D. Grolimund

10:30 Combined imaging, diffraction and spectroscopy approach: application to a fuel cladding of the Gösgen nuclear power plant
A. Froideval, S. Abolhassani, D. Grolimund, C. Borca, D. Popov, G. Kuri1, C. Degueldre, J. Bertsch

11:00 Coffee

11:15 Copper-zeolites for the conversion of methane to chemicals
E.M.C. Alayon, M. Nachtegaal and J.A. van Bokhoven

11:45

Hard-X-ray photon-in-photon-out spectroscopy of copper compounds (abstract available later)

E. Kleimenov, M. Nachtegaal, M. Janousch et al

Automotive Catalysts studied by XAS

M. Casapu[1], M. Mehring[1], S. Brandenberger[1], O. Kröcher[1]*

M. Nachtegaal[2], M. Harfouche[2], C. Borca[2], D. Grolimund[2]

[1]General Energy Research Department (ENE), Paul Scherrer Institut, CH-5232 Villigen PSI Switzerland

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

maria.casapu@psi.ch

Automotive catalysts, designed to clean the engine exhaust, were implemented in production for the first time in seventies in the US and Japan and since 1986 in Europe [1]. The earliest automotive after-treatment system (Pt-Pd/Al_2O_3) was used to reduce the residual uncombusted hydrocarbons (HC) and the partial combusted carbon (CO). Starting with 1981, new limits were introduced for the emissions of nitrogen oxides (NO_x) and afterwards for particulate matter (PM). Different catalysts were proposed and intensively investigated by the research community over the last years. However, due to ever-tightening emission legislations only several could be successfully applied under the demanding real exhaust conditions. For that reason additional investigation are currently carried on either for understanding and improving the catalytic activity or for finding new materials.

In this context, XAS is a very valuable tool since it can provide useful information on the catalyst structure and catalytic behavior under various operating conditions. The results presented in this contribution illustrate by means of several examples in the field of DeNOx catalysis how this technique helped in elucidating the mechanism and progress of catalytic reactions, of thermal ageing processes and also in finding the catalytic active sites. Thus, by means of XAS measurements performed at Mn and Nb K-edges it was demonstrated the strong interaction between the manganese and niobium species and the formation of $MnNb_2O_6$ in the MnO_x-NbO_x-CeO_2 low-temperature NH_3-SCR catalyst [2] (Fig. 1). The *ex situ* and *in situ* XAS measurements at the Fe, Cr, Ni, Cu and Zn K-edges helped in identifying the SCR catalytic active sites for a Euro5 Diesel soot sample. XAS was also used to determine the oxidation state and the reactivity of the iron sites in a fresh and hydrothermally aged Fe-ZSM-5 catalyst as a function of temperature and ageing time.

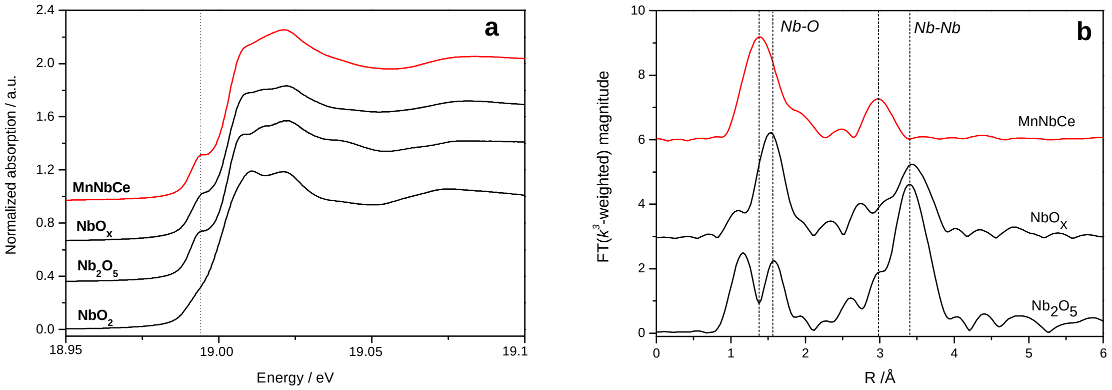

Figure 1. XANES Nb K-edge (a) and magnitude of FT EXAFS (k^3-weighted) spectra (b) of MnNbCe, NbO_x, Nb_2O_5 and NbO_2.

References

[1] M. Shelef, and R.W. McCabe, Catal. Today 62 (2000) 35-50.

[2] M. Casapu, O. Kröcher, M. Mehring, M. Nachtegaal, C. Borca, M. Harfouche, D. Grolimund, J. Phys. Chem. C (2010) , accepted.

Combined imaging, diffraction and spectroscopy approach: application to a fuel cladding of the Gösgen nuclear power plant

A. Froideval[1], S. Abolhassani[1], D. Grolimund[2], C. Borca[2], D. Popov[3], G. Kuri[1], C. Degueldre[1], J. Bertsch[1]

[1]Laboratory for Nuclear Materials, Paul Scherrer Institute, 5232 Villigen PSI, Switzerland
[2]Swiss Light Source, Paul Scherrer Institute, 5232 Villigen PSI, Switzerland
[3]Laboratory for Waste Management, Paul Scherrer Institute, 5232 Villigen PSI, Switzerland
annick.froideval@psi.ch

Zirconium-based alloys are extensively used as materials for fuel claddings, pressure tubes in CANDU reactors and to a certain extent for other structural components such as fuel channels in various types of operating nuclear reactors. It has been demonstrated by several studies that the variation of the chemical composition of the alloys, such as the addition of niobium, can considerably improve the corrosion resistance and the service life of the cladding materials [1]. In this study, a combination of synchrotron-based microprobe techniques such as X-ray absorption spectroscopy (XAS), X-ray fluorescence (XRF) and X-ray diffraction (XRD) has been applied to two Zr-2.5%Nb zirconium alloys -a material irradiated in the Swiss Pressurized Water Reactor (PWR) of Gösgen (neutron fluence of 8.3×10^{21} n/cm^2 (E > 0.821 MeV)) and a non-irradiated material used as reference [2]. Based on this combined analytical approach conducted at the microXAS beamline, spatially resolved micro-scale information on the zirconium coordination environment and on the crystalline phases formed at the metal / oxide interface of both materials have been obtained. Such results deliver insight into the characterization of the microstructure of Zr-Nb alloys used in the above mentioned applications, and contribute to the understanding of the causes of their better performance under reactor conditions.

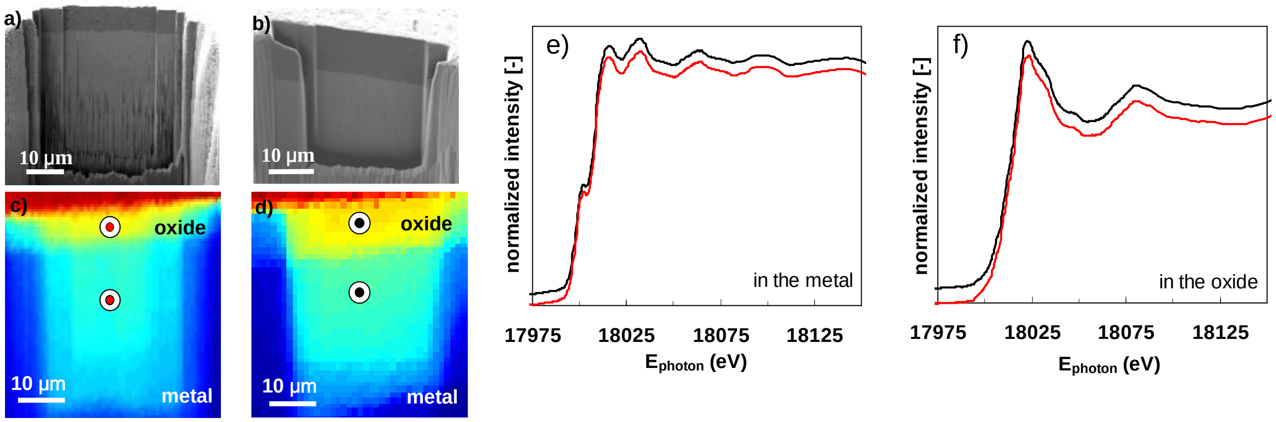

Figure: Electron and X-ray microscopic results for the neutron irradiated (left column, red circles) and the non-irradiated autoclaved reference (right column, black circles) Zr-2.5%Nb materials: (a, b) SEM images of the sample windows manufactured by FIB, and (c, d) corresponding high resolution 2D-XRF images recorded at the Zr K-edge. The circles correspond to the positions within the metal and oxide parts of the interface at which absorption spectra (e, f) have been measured at the Zr K-edge. The spectra recorded on the irradiated material are represented in red. (Acquisition parameters: beam size (horz. × vert. = approx. 1 µm × 1 µm), transmission mode, room temperature).

References:

[1] H. Anada, K. Takeda, S. Hagi, T. Murata, A. Oe, T. Miyashita, Proceeding of the ANS International Topical Meeting on LWR Fuel Performance, IAEA, Park City, (445-456), 2000

[2] A. Froideval, S. Abolhassani, D. Gavillet, D. Grolimund, C. Borca, J. Krbanjevic, C. Degueldre, J. Nucl. Mater. 385 (2009) 346-350

Abstract

Copper-zeolites for the conversion of methane to chemicals

E.M.C. Alayon[1,2]***, M. Nachtegaal***[1]***, and J.A. van Bokhoven***[1,2]
[1] *Paul Scherrer Institute, CH 5232 Villigen, Switzerland*
[2] *ETH Zurich, Wolfgang Paulistrasse 10, CH 8093 Zurich, Switzerland*

evalyn.alayon@psi.ch

Providing a reaction route for the conversion of methane to chemicals at mild conditions is a highly economical and environmentally attractive alternative to the energy-intensive steam-reforming process. Activating the very strong C-H bond without total oxidation requires an active and selective catalyst at low temperature. Copper-zeolites have been shown to convert methane to methanol at low temperatures [1]; however, the catalytic process is hindered by the strong sorption of methanol on the catalyst surface. Conversion of methanol to chemicals, such as dimethyl ether and dimethyl carbonate, has also been shown to occur on similar copper-zeolites [2,3]. A route of converting methane directly to chemicals is thus envisioned to be possible by performing these successive reactions on the same catalyst.

The viability of the process largely depends on the nature of the active site. X-ray absorption spectroscopy is sensitive to the local electronic and geometric structure and provides information on the changes occurring to the catalyst during the reaction. The HERFD XAS technique allowed us to distinguish the subtle features in the XANES in relation to the electronic transitions brought about by the bonding of copper to ligands under different gas environments.

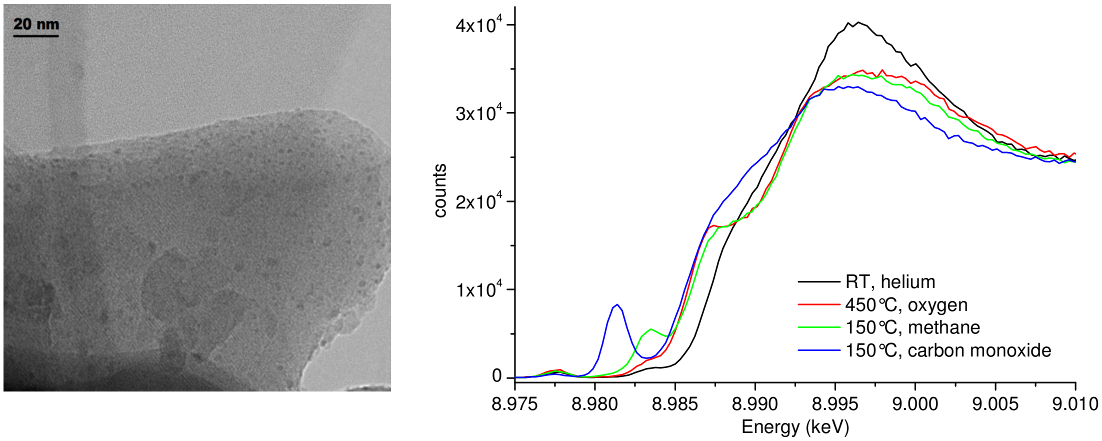

Figure1. TEM micrograph of copper-exchanged on mordenite (left) and its HERFD XANES spectra taken under different gas environments (right)

References:

[1] M.H. Groothaert, P.J. Smeets, B.F. Sels, P.A. Jacobs, R. A. Schoonheydt, J. Am. Chem. Soc. 127 (2005)1394.
[2] S.T. King, J. Catal. 161 (1996) 530.
[3] Y. Zhang, I.J. Drake, D.N. Briggs, A.T. Bell, J. Catal. 244 (2006) 219.