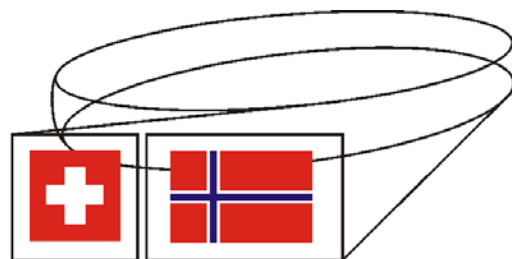
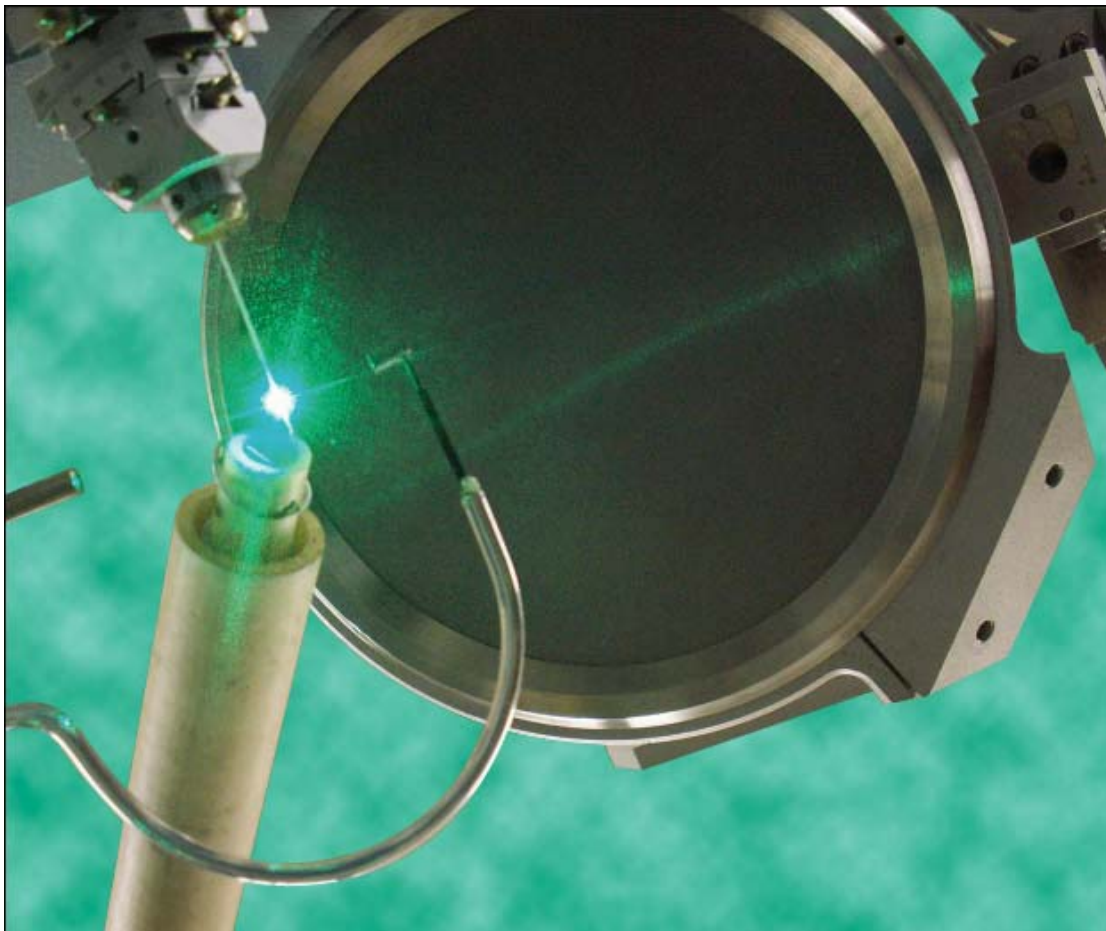


SNBL workshop on simultaneous
Raman-X-ray diffraction/absorption
studies for the in situ investigation of
solid state transformations, and reactions
at non ambient conditions.

June 18-19-2008 ESRF Auditorium



Swiss - Norwegian Beam Lines
at ESRF

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Day 1 - June 18 2008

9:00 Registration ESRF Hall central building

9:50 Welcome (10 min)

David Nicholson, *SNX Foundation & Department of Chemistry, Norwegian University of Science and Technology*

10:00 Introduction to Raman Scattering (25 min)

Jens Kreisel, *Laboratoire Matériaux et Génie Physique, Grenoble Institute of Technology, MINATEC*

10:25 Experimental opportunities, examples and equipment available for combined in-situ studies at SNBL (35 min)

Wouter van Beek, *SNBL at ESRF*

11:00 Coffee (30 min)

11:30 Raman-assisted X-ray crystallography for the analysis of biomolecules (25 min)

Dominique Bourgeois, *Institut de Biologie Structurale, CNRS/CEA/UJF & ESRF*

11:55 Simultaneous μ Raman spectroscopy and X-ray μ Diffraction at ID13 ESRF (25 min)

Richard Davies, *ESRF*

12:20 New imaging techniques in Raman spectroscopy - Defining new standards for high speed image data acquisition (25 min)

KPJ Williams, *Renishaw plc, Spectroscopy Products Division*

12:45 lunch (75 min)

14:00 In situ simultaneous Raman high resolution X-ray powder diffraction study of transformations occurring in materials at non ambient conditions (25 min)

Marco Milanesio, *Università del Piemonte Orientale "Amedeo Avogadro"*

14:25 Structure and Dynamics of water in confined pores - dehydration effects in natural zeolites (25 min)

Dewi Lewis, *University College London, Chemistry*

14:50 In situ and ex situ Raman studies on LiBH_4 and related compounds (25 min)

Hans Hagemann, *Département de chimie physique, Université de Genève*

15:15 Coffee (30 min)

- 15:45 The effect of high-pressure on functional ABO₃ perovskite-type oxides (25min)**
Jens Kreisel, *Laboratoire Matériaux et Génie Physique, Grenoble Institute of Technology, MINATEC*
- 16:10 Combined X-ray diffraction and Raman spectroscopy studies of phase transitions in crystalline amino acids at low temperatures and high pressures. Selected examples (25min)**
E.V. Boldyreva, *Institute of Solid State Chemistry and Mechanochemistry SB RAS, Novosibirsk REC-008 “Molecular Design and Ecologically Safe Technologies”, Novosibirsk State University*
- 16:35 Posters Presentations**
- 16:40 Combined X-ray absorption and X-ray powder diffraction study on silver cluster formation in zeolites; effect of pore geometry and addition of copper (5min)**
Karina Mathisen, *Department of Chemistry, Norwegian University of Science and Technology*
- 16:45 The influence of calcination conditions on phase formation in MoVTaNbO_x catalysts: A simultaneous in-situ-XRD/Raman study (5min)**
M. Scheider, *Leibniz-Institut für Katalyse, Berlin*
- 16:50 Computer modelling of the optics of a dispersive Raman spectrometer (5 min)**
M Sánchez del Río, E Haro-Poniatowski, M Picquart, *ESRF*
- 16:55 The combination of EXAFS, UV-Vis and Raman spectroscopy for investigations of Homogeneous reactions (5 min)**
Matthias Bauer, *Universität Stuttgart Institut für Physikalische Chemie*
- 17:00 Combined in-situ XRD and Raman investigations on the desorption reaction of Li-based Reactive Hydride Composites (5 min)**
U. Bösenberg, *Institute of Materials Research GKSS Research Centre Geesthacht*
- 17:05 Searching for additional functions of fish hemoglobins: evidence of multiple quaternary structures and exogeneous coordination states**
A. Vergara, *Dept. Chemistry, University of Naples “Federico II”, Complesso Universitario Monte S. Angelo*
- 17:10 Posters + Visit to the beamlines**

20:00 Dinner, La Bastille

Day 2 - June 19 Catalysis Session

- 9:45 Structure-performance relationships in supported vanadia catalysts under working conditions based on complementary operando Raman-GC and in situ xanes spectroscopies (45 min)**
Miguel A. Bañares, *Institute for Catalysis, CSIC; Catalytic Spectroscopy Laboratory*
- 10:30 Combination of X-ray Absorption with Raman Spectroscopies : at the micrometer scale I (25min)**
Delphine Vantelon, *Soleil*
- 10:55 Coffee (30 min)**
- 11:25 Combination of X-ray Absorption with Raman Spectroscopies : at the macrometer scale II (25 min)**
Valerie Briois, *Soleil*
- 11:50 Coupled X-ray scattering and Raman spectroscopy investigations on the synthesis of Mo-based oxides at the μ -spot Beamline at BESSY (25 min)**
Jorg Radnik, *Leibniz-Institut für Katalyse e.V. an der Universität Rostock*
- 12:15 Lunch (90 min)**
- 13:45 High-throughput structure/function screening of materials with multiple spectroscopic techniques (25 min)**
Moniek Tromp, *University of Southampton, School of Chemistry & Diamond*
- 14:10 Combining results from XAS, Raman, STEM and TEOM to obtain reliable information about propane dehydrogenation catalysts (25 min)**
Magnus Ronning, *Department of Chemical Engineering , Norwegian University of Science and Technology*
- 14:35 Sensitivity enhancement and dynamic behavior analysis by Modulation Excitation Spectroscopy: The principle and applications in heterogeneous catalysis (25min)**
Atsushi Urakawa, *ETH Zurich, Institute for Chemical and Bioengineering*
- 15:00 Coffee (30 min)**
- 15:30 Interplay between structural and electronic behavior in iron bearing silicate perovskites at conditions of Earth lower mantle: Inside from combined X-ray diffraction, Mossbauer and Raman spectroscopy, NFS, and XANES studies (25 min)**
Leonid Dubrovinsky, *Bavarian Research institute of Experimental Geochemistry and Geophysics, Bayreuth*
- 15:55 3D mapping of reciprocal space and inelastic X-ray scattering (15 min)**
Dmitry Chernyshov, *SNBL at ESRF*
- 16:10 Discussion**
- 17:00 Visit to the beamlines**

Experimental opportunities, examples and equipment available for combined in-situ studies at SNBL

Wouter van Beek

*SNBL at ESRF,
Dipartimento di Scienze e Tecnologie Avanzate, Università del Piemonte Orientale
email:wouter@esrf.fr*

The purpose of this workshop is two-fold: On the one hand we intend to inform our Swiss and Norwegian user community about recent developments at SNBL. This concerns in particular the integration of a Raman spectrometer and subsequent in-situ equipment.

On the other hand an increasing number of groups is developing various combinations of Raman scattering and x-ray based techniques. However few beamlines are permanently equipped with Raman spectrometers. Similar efforts are also undertaken at homelabs. Therefore we believe the time is right to meet, exchange ideas and progress further.

SNBL has two independent end-stations working in parallel. The A-branch line caters for single crystal and powder diffraction studies whereas the B-branch line provides High-Resolution powder diffraction and XAFS. In periods where the spectrometer is not used for combined x-ray studies it can also operate in stand alone mode for ex- and in-situ Raman experiments.

I will explain the beamline setup and how we have integrated the Raman spectrometer into the existing equipment. Combining techniques only makes sense when the samples are exposed to some external stimuli. We are now capable of creating a wide range of experimental conditions:

- High, low temperature
- Specific gas atmospheres and mixtures
- Hydrothermal and
- High Pressure

Based on a few case studies I will try to give an overview on how these experimental conditions are created. I will also comment on the sometimes unexpected, added value of the combined approach.

Raman-assisted X-ray crystallography for the analysis of biomolecules

Dominique Bourgeois^{1,2}, Eve de Rosny¹ and Philippe Carpentier¹

¹ *Institut de Biologie Structurale, UMR 5075, CNRS/CEA/UJF, 41 rue Jules Horowitz, 38027 Grenoble Cedex 1, France*

and

² *ESRF, 6 rue Jules Horowitz, BP 220, 38043 Grenoble Cedex, France*

We will describe Raman microspectrophotometry applied to crystals of biomolecules [1]. Raman spectra collected *in crystallo* bring structural information highly complementary to X-ray diffraction, relate the crystalline state to the solution state, and allows the identification of ligand-bound or intermediate states of macromolecules [2]. Non-resonant Raman spectroscopy is particularly suitable to the study of macromolecular crystals, and therefore applies to a wide range of non-colored crystalline proteins. Practical issues related to the investigation of crystals by Raman microspectrophotometry, notably at the ESRF/IBS Cryobench laboratory (<http://www.esrf.eu/UsersAndScience/Experiments/MX/Cryobench/>) will be reviewed.

[1] P. Carpentier et al. “Advances in spectroscopic methods for biological crystals, part II: Raman spectroscopy” *J. Appl. Cryst.* (2007), **40**, 1113-1122

[2] G. Katona G et al. “Raman assisted crystallography reveals end-on peroxide intermediates in a non-heme iron enzyme” *Science* (2007) **316**(5823): 449-453

Simultaneous μ Raman spectroscopy and X-ray μ Diffraction at ID13

Richard J. Davies, Manfred Burghammer, Christian Riekell

European Synchrotron Radiation Facility, Grenoble, France

Raman spectroscopy and X-ray scattering are complementary techniques which greatly benefit from combinatorial use. Whilst one provides information relating to molecular bond energies and orientations, the other provides information on crystallographic structure and morphology. Thus, not only do they provide differing information, but this relates to quite different length scales within a materials' hierarchical structure.

Although many applications benefit from combining X-ray and Raman techniques, the majority do not require their in situ combination. Most materials appear homogeneous when studied using macroscopic beams, eliminating the need for accurate sample placement. For dynamic studies, duplicating experimental conditions during sequential experiments is usually feasible when the results are inherently averaged. By contrast, the use of microfocus techniques necessitates an in-situ approach to data collection. Over micron length scales most materials appear highly heterogeneous which makes precise sample alignment critical. Meanwhile, under dynamic experimental conditions, microprobes can be highly sensitive to local variations. In such cases, only an in situ data collection strategy can ensure meaningful results. Not only does this need to provide the capability for simultaneous measurement, but it also requires a common sampling position.

The ESRF-ID13 beamline has developed a globally unique setup of combined μ Raman/ μ Diffraction including μ SAXS. Its in situ μ Raman setup offers on-axis laser beam delivery with X-ray and laser beams sharing a common focal position on the sample and similar spot sizes. The system has been recently upgraded to allow routine offline use with the addition of a stand-alone microscope. This provides the added possibility of characterizing samples either before or after X-ray experiments in order to locate regions of interest or monitor radiation damage.

New imaging techniques in Raman spectroscopy - Defining new standards for high speed image data acquisition

KPJ Williams, M Belleil

*Renishaw plc, Spectroscopy Products Division, Old Town, Wotton under Edge,
Gloucestershire, GL12 7DW, UK*

Raman spectroscopy continues to provide analytical solutions in a variety of applications offering chemical specificity on a micrometer scale.

The ability to create chemical and compositional images by acquiring Raman spectra from an array of positions and then processing them to reveal the parameters of interest is a powerful technique. Traditionally, these spatially-related data have been collected by raster scanning the sample beneath the incident laser spot, typically in micrometer intervals. New approaches to Raman imaging have been developed that enhance the capabilities of modern Raman instruments.

A new method of acquiring confocal Raman images has been developed – ‘Streamline’. Spectra are collected in parallel, rather than in series using the traditional methods. Shorter total acquisition times result, with high quality individual spectra recorded in the order of fifty milliseconds. The method also benefits from ‘on the fly’ data analysis resulting in real time image creation. This innovative approach allows the technique to succeed where others have failed: producing uncompromised data and images for small or large areas at speeds much greater than possible with competing methods. A range of materials examples will be shown to illustrate the benefits of this method. For example large area samples can provide Raman chemical images in minutes, which offers real advantages for surveying and identifying the real areas of interest.

The presentation will also highlight some of the recent developments we have made in providing custom solution for users with very specific and demanding Raman requirements.

In situ Simultaneous Raman High-Resolution X-ray Powder Diffraction Study of Transformations Occurring in Materials at Non-Ambient Conditions

Marco Milanese

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Materials containing light atoms, disordered moieties and/or amorphous or liquid-like phases or showing surface- or defect-related phenomena constitute a problem for their characterization using X-ray powder diffraction (XRPD), and in many cases Raman spectroscopy can provide useful complementary information. The novel experimental set-up for simultaneous *in situ* Raman/High-resolution XRPD experiments developed at SNBL was employed to study four solid-state transformations: *i*) the kinetics of the fluorene:TCNQ solid-state synthesis, *ii*) the photoinduced 2+2 cyclization of (E)-furylidenoxindole; *iii*) the thermal swelling and degradation of stearate-hydrotalcite nanocomposites; *iv*) the decarboxilation process of layered zirconium aminophosphonates. The reported experiments demonstrated that, even though the simultaneous Raman/XRPD experiment is more challenging than the separated ones, high resolution XRPD and Raman data can be collected at *in situ* conditions. The complementarities between Raman and XRPD was fully exploited by an accurate choice of the Green or Red Laser for the Raman experiment.

In the first two experiments the surface-bulk complementarities of the Raman and XRPD probes were exploited. Raman allowed to detect the reaction speed at the surface in the first step of the reactions, when no reaction is detected by XRPD. The mechanism of the reaction for the formation of the Fluorene/TCNQ complex was fully characterized and a kinetic analyses carried out, with the determination of the activation energy and the reaction order for the reaction at the surface and in the bulk. Concerning the photoinduced 2+2 cyclization of (E)-furylidenoxindole, the complex polymorph space of the product phase (one stable and two metastable crystalline phase and one amorphous phase) was fully understood and the structure of one metastable phase was also solved.

In the last two experiments the sensitivity of Raman to the structure and conformation of organic moieties (not easily detectable by XRPD alone, especially when disorder is present) was exploited. Concerning stearate-hydrotalcite experiment, a detailed description of the structural changes occurring at 365 K to both organic and inorganic moieties in the ST-HT sample was obtained. The XRPD data gave clear information on the swelling of the inorganic lamellar component of the hybrid nanocomposite. Raman spectra indicated that, up to 365 K, the all-*trans* conformation is prevalent for the organic chains, whereas above this temperature the occurrence of folded chains due to *gauche* conformations became significant. Finally the decarboxilation of layered zirconium aminophosphonates was studied. When heated this compound shows a phase transformation with a remarkable reduction of its interlayer distance (detected by XRPD), due to the loss of HF and to a change in the zirconium environment (detected by the Raman probe).

Structure and Dynamics of water in confined pores - dehydration effects in natural zeolites

Dewi W Lewis¹, Mark A Green, Dervishe Salih, A Rabdel Ruiz-Salvador, W van Beek, A Lobo, M Rodriquez Albelo

¹University College London, Chemistry

The nature of water within the nanopores of zeolites is far from being liquid. However, the fluidity of this water is critical in not only forming these materials (naturally and synthetically) but also as the transport medium for ion exchange. Our work in simulating (computationally) the formation and properties of these materials requires careful parameterisation and as part of this work we have undertaken parallel experimental work to validate some of our methods and results. Here we will discuss the specific case of the zeolite Goosecreekite and its dehydration. The availability of a combination of X-ray diffraction and Raman spectroscopy at the SNBL allowed us to probe the dynamics and structure of this material during dehydration, revealing metastable phases with changes in water dynamics, which we have subsequently been able to simulate.

In situ and ex situ Raman studies on LiBH₄ and related compounds

Hans Hagemann

Département de Chimie Physique, Université de Genève

We have obtained in situ temperature dependent Raman and synchrotron X-ray diffraction data for LiBH₄ between 300 and 393K. We have obtained separately further temperature dependent Raman data between 7 and 450 K as well as synchrotron powder diffraction data at low temperatures.

The in situ experiment reveals directly from the X-ray data that at the phase transition, both phases coexist, while this does not appear so clearly in the Raman data. The first order nature is seen in a heating and cooling run for the Raman spectra alone and reveals clearly a hysteresis loop.

The temperature dependent Raman data show significant spectral shifts in the lattice mode region. Using the available thermal expansion data obtained at SNBL, we can model the quasi-harmonic contribution (related to the lattice expansion) to the Raman band shift for two well defined lattice modes. It appears that above ca 80 K, a further anharmonic contribution must be considered.

It is also interesting to note that above ca 80K, the splitting of the E –symmetry deformation band of the BH₄⁻ ions starts to decrease significantly from ca 47 cm⁻¹ at 10 K to 20 cm⁻¹ at the phase transition.

Preliminary results on other systems will be presented.

The effect of high-pressure on functional ABO_3 perovskite-type oxides

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The understanding of ABO_3 perovskite is one of the most challenging topics at the interface between solid state chemistry and solid state physics. In particular, the understanding of phase transitions induced by external parameters like temperature, pressure, strain, magneto-electric fields etc. remains of great interest. Compared to temperature, the external parameter high pressure is of particular interest since it acts only on interatomic distances and can be much easier simulated by potentially insightful ab-initio calculations.

In our presentation we will first recall the perovskite structure and the relation between different structural distortions and physical properties. We will then discuss the historic and famous rules of Samara [1] which have guided for years the interpretation of the effect of high-pressure on perovskites. In the second part of the talk we will present observations by high-pressure Raman scattering and synchrotron scattering experiments on perovskite-type and nano-structured relaxor ferroelectrics [2-7]. We will namely show and discuss that their local *and* average structure is fundamentally modified under high-pressure, what is in sharp contrast to the effect of temperature, which is known to lead generally to only small evolutions in the average structure of relaxors. We will finally discuss recent findings [8-13] which challenge Samara's longstanding rules for some specific perovskites and which have led to new fundamental insight into the structural physics of perovskite-type oxides. All along the presentation a main emphasis will be put on the importance of using Raman and synchrotron scattering in a complementary way.

- [1] G. A. Samara, T. Sakudo, K. Yoshimitsu, *Phys. Rev. Lett.* **35**, 1767–1769 (1975).
- [2] J. Kreisel, A. M. Glazer, P. Bouvier, G. Lucazeau, *Phys. Rev. B* **63**, 174106 (2001).
- [3] J. Kreisel, P. Bouvier, B. Dkhil *et al.* *Phys. Rev. B* **68**, 014113 (2003).
- [4] J. Kreisel, B. Dkhil, P. Bouvier, J. M. Kiat, *Phys. Rev. B* **65**, 172101 (2002).
- [5] B. Chaabane, J. Kreisel, B. Dkhil, *et al.* *Phys. Rev. Lett.* **90**, 257601 (2003).
- [6] P. E. Janolin, B. Dkhil, P. Bouvier, J. Kreisel, *et al.* *Phys. Rev. B* **73**, 094128 (2006).
- [7] M. Ahart, R. E. Cohen *et al.* *Phys. Rev. B* **71**, 144102 (2005).
- [8] P. Bouvier, J. Kreisel, *J. Phys.: Condens. Matter* **14**, 3981 (2002).
- [9] T. Tohei, A. Kuwabara, T. Yamamoto, *et al.* *Phys. Rev. Lett.* **94**, 035502 (2005).
- [10] R. J. Angel, J. Zhao, N. L. Ross, *Phys. Rev. Lett.* **95**, 025503 (2005).
- [11] I. A. Kornev, L. Bellaiche, P. Bouvier, *et al.* *Phys. Rev. Lett.* **95**, 196804 (2005).
- [12] Z. Wu, R. E. Cohen, *Phys. Rev. Lett.* **95**, 037601 (2005).
- [13] P. Hermet, P. Ghosez, *Phys. Rev. B* **74**, 180101 (2006).

Combined X-ray diffraction and Raman spectroscopy studies of phase transitions in crystalline amino acids at low temperatures and high pressures. Selected examples

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REC-008 "Molecular Design and Ecologically Safe Technologies", Novosibirsk State University*

Crystalline amino acids are interesting as molecular materials (ferroelectrics, piezoelectrics, non-linear optical materials), drugs, and also as biomimetics, which can be used to study the structure and dynamics of molecular fragments of biopolymers [1]. The structure-forming units in the crystals of amino acids – head to tail chains of amino acids linked by hydrogen bonds – are similar to those in peptides [2]. The motions of molecular fragments of the amino acids – either as residues in the peptides, or as zwitter-ions in the crystals – is important for dynamic transitions in these systems (conformational changes related to biological functions in biopolymers; phase transitions in crystalline amino acids). The motions of different groups have different temperature and pressure dependence, what is important for biological functions of biopolymers [3], and manifest themselves differently when spectroscopic or diffraction techniques are used. Diffraction techniques give direct information on the average positions of atoms (first of all – and pressure. Spectroscopic techniques have an obvious advantage, as far as the estimates of the energies of intermolecular interactions and the studies of dynamics of molecular fragments are concerned. In the present contribution the advantage of complementing diffraction and Raman spectroscopy studies will be illustrated at several selected examples: low-temperature [4-6] and high-pressure [7] phase transitions in L- and DL-cysteine, low-temperature [8,9] and high-pressure [10,11] phase transitions in β -glycine, a high-pressure transition in γ -glycine [12-14], a high-pressure phase transition in β -alanine [15], low-temperature [16,17] and high-pressure [18,19] phase transitions in L-serine.

The work was supported by Interdisciplinary Projects of SB RAS #49 and #110, and a grant BRHE NO-008-XI-BG6108. Powder diffraction experiments at high hydrostatic pressures were carried out at SNBL ESRF (Grenoble, France) and were supported by grants from SNBL. The assistance of the staff of the Swiss-Norwegian Beamlines is gratefully acknowledged.

1. E. V. Boldyreva. In: Models, Mysteries, and Magic of Molecules, Eds. J.C.A. Boeyens & J.F. Ogilvie, 2008, Dordrecht: Springer, P. 167.
2. C. G. Suresh, M. Vijayan, *ibid.*, 1983, 22(2), 129.
3. D. Ringe, G. A. Petsko, *Biophysical Chem.*, 2003, 105, 667.
4. I.E. Paukov, Yu.A. Kovalevskaya, V.A. Drebuschak, T.N. Drebuschak, E.V. Boldyreva, *J. Phys. Chem. B*, 2007, 111, 9186.
5. B. A. Kolesov, V. S. Minkov, E. V. Boldyreva, T.N. Drebuschak, *J. Phys. Chem. B*, submitted.
6. V. S. Minkov, N. A. Tumanov, B. A. Kolesov, E. V. Boldyreva, S. N. Bizyaev, *J. Phys. Chem. B*, submitted.
7. V. S. Minkov, A. N. Krylov, E. V. Boldyreva, S. V. Goryainov, A. V. Vtyurin, *J. Phys. Chem. B.*, accepted.
8. V. A. Drebuschak, E. V. Boldyreva, Yu. A. Kovalevskaya, I. E. Paukov, T. N. Drebuschak, *J. Therm. Analys. Calorim.*, 2005, 79, 65.
9. B. N. Kolesov, E. V. Boldyreva, G. B. Chernobai, in preparation.
10. S. V. Goryainov, E. N. Kolesnik, E. V. Boldyreva, *Physica B Condensed Matter*, 2005, 357, 340.
11. N. A. Tumanov, E. V. Boldyreva, H. Ahsbahs, *Powder Diffraction*, 2008, accepted.
12. E. V. Boldyreva, S. N. Ivashevskaya, H. Sowa, H. Ahsbahs, H.-P. Weber, *Dokl. Akad. Nauk, Phys. Chem.*, 2004, 396, 358.
13. E. V. Boldyreva, S. N. Ivashevskaya, H. Sowa, H. Ahsbahs, H.-P. Weber, *Z. Krist.*, 2005, 220, 50.
14. S. V. Goryainov, E. V. Boldyreva, E. N. Kolesnik, *Chem. Phys. Letters*, 2006, 419, 496.
15. E. V. Boldyreva, S. V. Goryainov, Y. V. Seryotkin, H. Ahsbahs, V. P. Dmitriev, *Proceed. NSU, Ser. Physics* 2007, 2, 30.
16. H. N. Bordallo, B. A. Kolesov, E. V. Boldyreva, F. Juranyi, *J. Amer. Chem. Soc.*, 2007, 129, 10984.
17. B. A. Kolesov, E. V. Boldyreva, *J. Phys. Chem. B*, 2007, 111, 14387.
18. E. N. Kolesnik, S. V. Goryainov, E. V. Boldyreva *Doklady Phys. Chem.*, 2005, 404, 169 (Engl.).
19. E. V. Boldyreva, H. Sowa, Y. V. Seryotkin, T. N. Drebuschak, H. Ahsbahs, V. V. Chernyshev, V. P. Dmitriev, *Chem. Phys. Letters*, 2006, 429, 474.

Combined X-ray absorption and X-ray powder diffraction study on silver cluster formation in zeolites; effect of pore geometry and addition of copper

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Adding hydrogen to the selective catalytic reduction (SCR) hydrocarbons (HC) deNO_x process over silver systems leads to enhanced activity. This has been ascribed to the formation of silver nano clusters. Subsequent treatment in NO disperses the metal clusters through oxidation to silver(I). The reversibility of the valence states with the formation of clusters in both systems is significant part of the overall mechanism for reducing NO_x. The silver environments in the two microporous systems Ag:ZSM-5 and Ag:Y have been studied by *in situ* X-ray Absorption spectroscopy (XAS) at the Ag K-edge. Samples were heated stepwise in hydrogen while collecting Extended X-ray Absorption Fine Structure (EXAFS), powder diffraction (XRD) to determine the cluster size as a function of temperature. The EXAFS yields information about the local environment of silver such as bond distances and number of neighbours. Silver(I) is reduced to form clusters of metallic silver by hydrogen, but the degree of reduction depends highly on the parent zeolite and the addition of copper to the system.

The influence of calcination conditions on phase formation in MoVTenbOx catalysts: A simultaneous in-situ-XRD/Raman study

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Motivation and Objectives

Mixed MoVNbTe oxides are versatile catalysts for the selective oxidation of lower alkanes and olefins. Their catalytic performance depends sensitively on the presence of target phases such as $[\text{Mo}(\text{V},\text{Nb})]_5\text{O}_{14}$, M1 and M2, while MoO_3 and MoO_2 are detrimental and have to be suppressed. Tailoring the calcination process to the preferential and reproducible formation of the target phases is highly desirable but difficult to realize since their crystallization is governed, apart from the synthesis of the precursor, by the calcination conditions, the influence of which is not sufficiently known so far.

Therefore, we have performed a systematic in-situ-XRD/Raman study to elucidate the influence of gas atmosphere, heating rate, final temperature and reactor geometry on the formation of different phases within the MoVNbTe oxide system. Special benefits derive from the simultaneous coupling of both techniques due to their different sensitivity, which is realized in a simple laboratory setup. Thus, Raman spectroscopy can detect nanocrystalline XRD-silent MoO_3 while XRD visualizes the formation of reduced phases more sensitively than Raman.

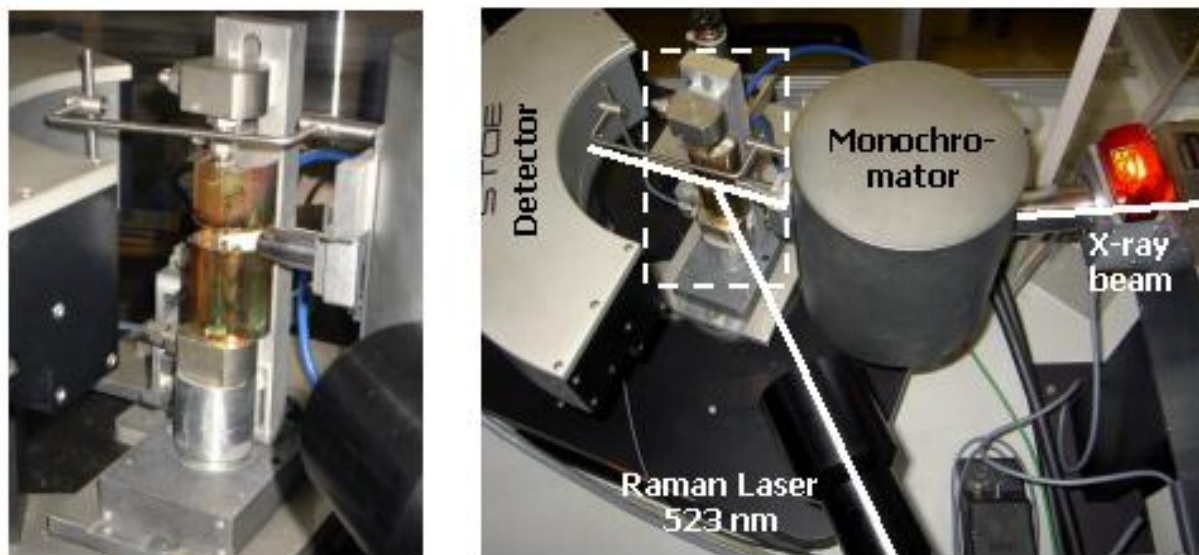


Fig. 1. Setup for simultaneous in-situ XRD/Raman-spectroscopy

Results

Two MoVNbTe oxide precursors of similar composition but different preparation history (hydrothermal synthesis vs co-precipitation + spray drying) were analyzed in a capillary fixed-bed reactor (Fig. 1) between 20 and 460 °C in flowing air or nitrogen using heating rates of 1, 5 and 10 K/min as well as isothermal hold intervals at different temperatures. For comparison, selected calcination runs were also performed in shallow bed geometry to test the influence of the reactor geometry.

Generally, calcination in air flow favours the formation of undesired MoO₃ in nanocrystalline XRD-silent form at all heating rates and already at temperatures as low as 320 °C (Fig. 2). Pronounced MoO₃ formation was also observed at low heating rate (1 K/min) in N₂ flow and in runs with several isothermal holds between 300 and 400 °C, which were necessary for recording the XRD patterns. In contrast, heating with 10 K/min in N₂ leads to crystalline MoO₂ when performed in the capillary reactor, while the target phases [Mo(V,Nb)]₅O₁₄, M1 and M2 are preferentially formed when the sample is calcined in a shallow bed. In this case, NH₃ which is liberated upon decomposition of the precursor can quickly leave the sample while in the capillary reactor, it is passed by the carrier gas through the whole catalyst bed. This causes deeper reduction. This result illustrates the crucial influence of the reactor cell when monitoring the calcination of such sensitive materials like MoVNbTe oxides. Further limitations of the capillary reactor relate to the low signal-to-noise ratio connected with measurements in transmission mode due to the thickness of the capillary. To overcome these problems, a simultaneous in-situ-XRD/Raman setup with shallow bed geometry for XRD measurements in reflection mode is currently under construction.

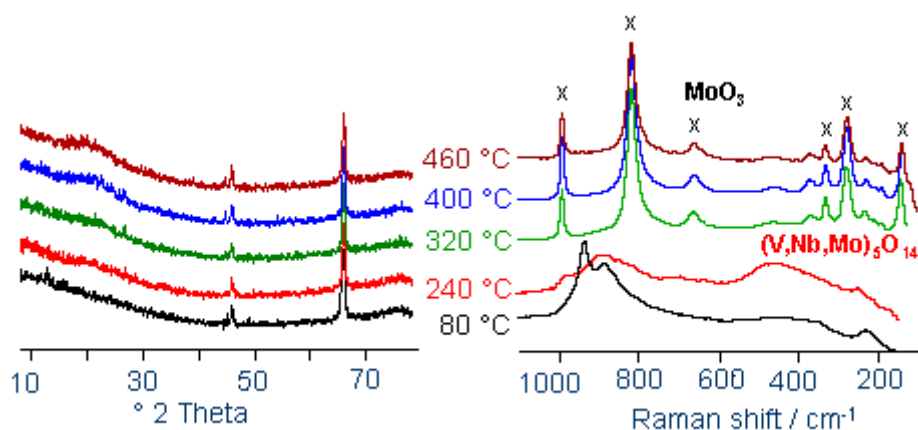


Fig.2. Simultaneous XRD/Raman-measurement during heating in air flow with 1 K/min.

Conclusions

Comprehensive investigations of the influence of calcination conditions (temperature, heating rate, gas atmosphere, reactor geometry) on the formation of different phases in the MoVNbTe oxide system were performed. The target phases [Mo(V,Nb)]₅O₁₄, M1 and M2 are preferentially formed at moderate heating rates in inert gas and shallow bed geometry. Calcination in air favours MoO₃ crystallization already at rather low T while fast heating in a capillary tube reactor leads to deep reduction and MoO₂ formation. Special benefits derive from the simultaneous coupling of XRD and Raman due to their different sensitivity for various phases.

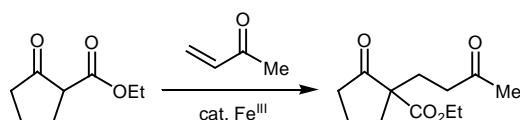
The combination of EXAFS, UV-Vis and Raman spectroscopy for investigations of Homogeneous reactions

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Although XAFS spectroscopy can presently be almost considered as standard method for structural characterization in solution, its use for the investigation of homogeneous metal catalyzed reactions is limited. Its property of averaging over all present species makes the identification of different compounds in catalytic solutions difficult. Especially such of small concentrations can not be detected due to this effect, although they might present the catalytically active species. Nevertheless, the structural information provided by XAFS spectroscopy is needed to achieve a detailed picture of catalytic systems. Thus a combination of XAFS UV-Vis and Raman spectroscopy can be used to obtain complementary information about the compounds present in the reaction mixture.

As an example of this combination, the Iron(III) catalyzed Michael addition reaction was studied and the results will be presented. In this reaction, a β -dicarbonyl compound (DC) is added to a α,β -unsaturated ketone catalyzed by Iron(III) salts. The overall reaction is shown below:



With Fe^{III}(ClO₄)₃ instead of Fe^{III}Cl₃ as catalyst an increased reaction rate is found. With XAFS spectroscopy, this fact was found to be due to the formation of complex [Fe^{III}Cl₄]⁻[Fe^{III}(DC)₂(H₂O)₂]⁺. Both parts of the complex could be identified with UV-Vis and Raman spectroscopy and prove the results of the EXAFS investigation.

The results of this study stimulated the construction of a cell for *in-operando* investigations of reactions under real conditions. Here, the simultaneous recording of XAFS and UV-Vis spectra offers two advantages: additional information on the structure of the present compounds can be obtained and the chemical stability of the solution during longer EXAFS scans can be monitored by UV-Vis spectroscopy. For this purpose, a energy dispersive UV-Vis spectrometer with an acquisition time of milliseconds is used. The ecological important hydroxylation reaction of diketones with molecular oxygen catalyzed by Cerium(III) serves as a model reaction to demonstrate the potential of the setup.

Combined in-situ XRD and Raman investigations on the desorption reaction of Li-based Reactive Hydride Composites

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Hydrogen is one of the favoured future energy carriers due to its high energy content. However, reliable and safe storage is a critical issue for mobile applications. The chemical storage in metal hydrides has to fulfil high requirements on weight capacity, thermodynamic and kinetic properties to be applicable e.g. with a fuel cell in a car. At present, none of the single light metal hydrides fulfil all the requirements at once. By the development of the reactive hydride composites this drawback was overcome. They show a reduced reaction enthalpy at high gravimetric capacities due to an exothermic reaction during the endothermic desorption. In the present work, the focus is laid on the system $2 \text{LiBH}_4 + \text{MgH}_2 \leftrightarrow 2 \text{LiH} + \text{MgB}_2 + 4\text{H}_2$. So far, the desorption kinetics of the reaction are poor and take place in reasonable times only at elevated temperatures of approximately 400°C in a two step mechanism. To facilitate the formation of MgB_2 a hydrogen back pressure of 5 bar is applied. This is in contrast to the calculated equilibrium temperature at 1 bar H_2 of 170°C for these composites. To specifically improve the desorption reactions it is wise to identify intermediate and rate limiting steps. To reveal these, in-situ studies offer the best opportunities. By in-situ XRD a large range of the reaction can be covered and the initial and final products be identified. LiBH_4 has a low melting point of 270°C and therefore the tracking of the desorption reaction at the high temperatures e.g. 400°C by XRD is not possible. Also possible amorphous intermediates as they have been observed for pure LiBH_4 by Orimo et al. or Bowman et al. cannot be detected. However, the BH_4^- -tetrahedron and other Boron compounds have defined stretching and bending modes and therefore they should show Raman scattering also at these elevated temperatures. For that reason, we combined in-situ XRD and Raman scattering at BM01B at the ESRF to follow the decomposition reaction of $\text{LiBH}_4/\text{MgH}_2$ -composites in detail.

Two-in-one: XRD and Raman diagnostics combined

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Introduction

Changing demands in industry make tailor-made zeolites necessary especially in view of their wide use and high potential as catalysts and adsorbents. For this, detailed knowledge of the crystallization processes and also the catalytic mechanisms is absolutely essential. We designed a unique combined XRD-Raman system with high flexibility allowing closure of the diagnostic gap between molecular short range interaction and long range structure.

As examples, two research topics which will greatly profit by the two-in-one approach.

Experimental

To meet scientific demands, the machine (Diffram) is designed with a unique flexibility in diffractometer and Raman parts. For zeolite and guest-host analysis the Raman setup allows the choice of different excitations in the ultraviolet and the visible electromagnetic spectrum. This avoids well known fluorescence problems and opens the possibility to exploit resonance Raman effects. A triple spectrometer which can be operated in additive or subtractive mode makes optimization of intensity versus resolution feasible. The XRD diffractometer combines the three most common measurement configurations: Transmission, Bragg-Brentano and micro-diffraction geometry. This is achieved using focusing optics and variable source-sample-detector distances.

Results

The all-silica molecular sieve Silicalite-1 is chosen as a model for zeolite formation studies. Silicalite-1 is crystallized by heating a clear solution of tetraethylorthosilicate and aqueous tetrapropylammonium hydroxide as template. The latter directs silica condensations towards specific precursor silicate polyanions, of which the largest one has a connectivity approaching the MFI framework topology. These units locally enrich and condense in a self-assembly process which eventually results in a zeolite. Raman spectroscopy is very sensitive to follow the formation of these molecular silicate-species, and specifically the template-silicate interaction. X-rays contribute to the study from the moment of particle formation, manifesting in the low angle region till onset of crystallization detectable in Bragg scattering.

A recent example for guest-host (active site) studies, is analysis of a Ru-complex in a Y zeolite. Preliminary results show a change in the active trimer-structure with the inclusion into the zeolite and also modifications during the ad- and desorption of NO_x. The sensitivity of the Raman spectrum towards changes in metal-coordination helps understanding the local processes during ad- and desorption

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Searching for additional functions of fish hemoglobins: evidence of multiple quaternary structures and exogeneous coordination states

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All fish hemoglobins (Hb) show a high auto-oxidation rate, and some fish Hbs are endowed with Root effect (drastic drop of cooperativity at acidic pH). Differently from temperate fish Hbs, at physiological pH Antarctic fish Hbs (AFHbs) in the ferric state show both an aquomet form and two distinct hemichromes within a R / T intermediate quaternary structure (1). Interestingly, AFHbs exhibit a peroxidase activity higher than that observed for mammalian and temperate fish Hbs, thus suggesting that a partial hemichrome state in tetrameric Hbs does not protect them from peroxidation as previously proposed (2). At acidic pH, a combined EPR / x-ray crystallography approach has revealed, only for Root-effect AFHbs, significant amount of pentacoordinated (5C) high-spin Fe(III) species.(3) Furthermore, along the oxidation pathway, a combined x-ray crystallography / Resonance Raman spectroscopy of AFHbs has revealed a hybrid valence state [$\alpha(\text{O}_2)/\beta(\text{Fe}^{3+}$, pentacoordinate)].(4) This valence hybrid states prompted us to test a FeSOD activity, that is as low as human Hb. A combined x-ray crystallography / FT-IR study has revealed at least two coordination states of the carbomonoxy form of AFHbs, one corresponding to a His assisted CO binding (band III at 1951 cm^{-1}), and another to a not-His assisted CO binding (band IV at 1968 cm^{-1}). The band IV, typical of both temperate fish (carp and trout) Hbs and AFHbs, assigned to the second CO coordination state, justifies the high auto-oxidation rate of fish Hbs. Furthermore, this novel CO coordination in AFHb occurs within a R-T intermediate quaternary structure. These findings provide an alternative structural explanation of the Root effect, in terms of a three state model .(5)

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1. Vergara, A., Franzese, M., Merlino, A., Vitagliano, L., di Prisco, G., Verde, C., Lee, H. C., Peisach, J., and Mazzearella, L. (2007) *Biophys. J.* **93**, 2822-2829
2. Feng, L., Zhou, S., Gu, L., Gell, D., Mackay, J., Weiss, M., Gow, A., and Shi, Y. (2005) *Nature* **435**, 697-701
3. Vergara, A., Franzese, M., Merlino, A., Bonomi, G., Verde, C., di Prisco, G., Lee, H., Peisach, J., and Mazzearella, L. . submitted.
4. Vitagliano, L., Vergara, A., Bonomi, G., Merlino, A., Smulevich, G., Howes, B., di Prisco, G., Verde, C., and Mazzearella, L., *J. Am. Chem. Soc.* **in press**.
5. Edelstein, S. J. (1996) *J. Mol. Biol.* **256**, 737-744

Structure-Performance Relationships in supported vanadia catalysts under working conditions based on complementary operando Raman-GC and in situ XANES spectroscopies

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Catalysts with large surfaces are much more complex than the model single crystals. To single out the active site under real working conditions of the catalyst is an enormous task. It requires a combination of techniques and the development or adaptation of techniques, which allow measurements under catalytic conditions (high temperatures and high pressures). This is the field of *in situ* spectroscopy. We have recently developed a new methodology that combines the determination of catalyst activity/selectivity and its molecular structure in a single experiment (1,2). We have named this methodology “*operando*” (Latin for “working”).

We will present Raman studies to assess structure-activity relationships on supported oxides (namely V, Cr, Mo) during alkane and ammonia activation (ammonoxidation). In addition, a combination of in situ Raman, XANES, and EPR spectroscopies is used to study the nature of the interaction between V and Ce in the ceria-supported vanadia catalysts for ethane oxidative dehydrogenation. Vanadium oxide species disperse on ceria up to 9 V atoms/nm² of support. Surface V⁵⁺ species closely interacts with ceria support promoting a reduction of surface Ce⁴⁺ to Ce³⁺. Upon heating or during reaction surface vanadia reacts with ceria support forming a CeVO₄ phase. The active site appears to be V⁵⁺-O-Ce³⁺ for both systems. The redox cycle for oxidative dehydrogenation appears to be associated with Ce, rather than with V sites (3).

Acknowledgements

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References

1. “*Operando* Raman study of alumina-supported Sb-V-O catalyst during propane ammonoxidation to acrylonitrile with on line activity measurement”, M. O. Guerrero-Pérez and M. A. Bañares, **Chem. Commun.** 12, 1292 (2002).
2. “*Operando* Methodology: combination of *in situ* spectroscopy and simultaneous activity measurements under catalytic reaction conditions”, Miguel A. Bañares, **Catal. Today** 100, 71 (2005) (SPECIAL ISSUE NUMBER 100)
3. “Nature of the Vanadia-Ceria Interface in V⁵⁺/CeO₂ Catalysts and its Relevance for the Solid-State Reaction Towards CeVO₄ and Catalytic Properties” M.V. Martínez-Huerta, J. M. Coronado, M. Fernández-García, A. Iglesias-Juez, G. Deo, J.L.G. Fierro, M.A. Bañares, **J. Catal.** **225** (2004) 240-248

Combination of X-ray Absorption with Raman Spectroscopies : at the macro- and micrometer scale

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The use of complementary techniques in Materials Science is a well-established prerequisite for accessing to a deeper structural description of a given material. This approach which offers a simultaneous access to different kinds of information for the same material has great advantages with respect to separate experiments to rid oneself of errors due to differences in sample environment, thermal history, ageing, temperature, sample preparation. Even more important is the possibility to resolve ambiguities in the understanding of processing by allowing accurate determination of the order of occurrence of the chemical and physical events with a high time framing rate. Additionally, the results from one technique can be used as external constraints on the analysis of the other data.

In the past years, we have successfully developed a new experimental approach for studying materials processing based on the simultaneous combination of X-ray Absorption Spectroscopy (XAS) with techniques routinely applied in materials science, such UV-Vis or Raman spectroscopies [1]. Dealing with the combination with Raman spectroscopy, the powerful of such approach has been first probed at the macro-scale with experiments at LURE. Indeed, the flexibility for the focal length of the Raman optics connected by optical fibers to the Raman spectrometer (here the RXN1 model from Kaiser Optical Systems, Inc) makes appreciably easy the design of sample environment to study systems under constraints. Therefore, a lot of systems were investigated by combined XAS and Raman spectroscopies. Among them we can mention, the study of ionic conduction into K(CF₃SO₃)-doped polyelectrolytes at the potassium K-edge (3.6 keV), of the oxydation of ethanol by Ce(IV) at the Ce L₃ edge (5.7 keV), of the thermally induced spin transition in the Fe(NCS)₂(o-phen)₂ complex at the iron K-edge (7.1 keV), of Cisplatin based drug release at the Pt L₃ edge (11.5 keV) of the sol-gel transition of zirconia based systems (18 keV), of the rehydration process of Mo-based heterogeneous catalysts (20 keV) and the study of hydrolysis-condensation of SnCl₄.5H₂O in ethanolic medium at the tin K-edge (29.2 keV). Some examples of studies belonging to this list will be presented [1-2] with the main purpose to emphasize how complementary are the information obtained by both techniques. It is noteworthy that such combination is today routinely proposed on the SAMBA beamline at SOLEIL.

Recently, we have successfully undertaken to combine micro X-ray absorption (μ -XAS) and micro-Raman (μ -Raman) on the LUCIA beamline at SLS. Both techniques allow to give a detailed insight of spatially ill-structured materials at the micrometer scale. The original set-up developed on LUCIA will be presented, and its applications for the study of minerals [3] and of the alteration of samples belonging to cultural heritage will be discussed.

[1] Briois, V., Belin, S., Villain, F., Bouamrane, F., Lucas, H., Lescouëzec, R., Julve, M., Verdagner, M., Tokumoto, M.S., Santilli, C.V., Pulcinelli, S.H., Carrier, X., Krafft, J.M., Jubin, C., Che, M. (2005). *Physica Scripta*, **T115**, 38

[2] Briois, V., Lützenkirchen-Hecht, D., Villain, F., Fonda, E., Belin, S., Grisebock, B., Frahm R. (2005). *J. Phys. Chem. A*, **109**, 320.

[3] Briois, V., Vantelon, D., Villain, F., Couzinet, B., Flank, A. M., Lagarde, P. (2007) *J. Synch. Radiation*. **14**, 403.

Coupled X-ray scattering and Raman spectroscopy investigations on the synthesis of Mo-based oxides at the μ -spot Beamline at BESSY

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Mo or V containing mixed oxides belong to a new class of heterogeneous catalysts with a high potential for the partial oxidation of alkanes [1]. During the synthesis of catalyst precursors the preparation method, the nature of used components as well as the reaction conditions are an important factor. However, the influence of these parameters is not fully understood and systematically investigated. For such investigations combining X-ray scattering with Raman spectroscopy seems to be promising: From the scattering experiments information about the precipitate could be derived, such as state of agglomeration of particles, crystallite size, and phases formed during the precipitation. The Raman spectroscopic measurements provide additionally structural information on the precipitate and the anions in solution. Such an experimental setup combining X-ray scattering and Raman spectroscopy was recently established at the μ -spot beamline at BESSY [2]. The influence of different synthesis parameters on the structure and crystallinity of the catalyst precursors has been elucidated. Therefore, this might affect the structure and performance of the final catalysts.

The synthesis of the Mo-oxide precursors has been carried out in an Erlenmeyer flask. Afterwards the suspension was pumped within a closed circuit of flexible tubes through two capillary glass tubes, one used for the Raman measurements, the second one for the scattering experiments and back to the flask. The experimental setup is described in detail elsewhere [2].

Several measurements were included to investigate the precipitation of metal molybdates by mixing solutions of ammonium heptamolybdates (AHM) and metal nitrates of nickel, iron and bismuth. After mixing, Bragg reflexes appear indicating the formation of a crystalline precipitate. Simultaneously, a Raman band at 957 cm^{-1} could be observed, typical for $[\text{Mo}_8\text{O}_{26}]^{4-}$. After addition of H_3PO_4 at room temperature this band loses intensity and a new one at 979 cm^{-1} appears which could be correlated to $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ showing the formation of a Keggin structure. At the same time, the intensity of the Bragg reflexes decreases. After heating to 50°C , the Bragg reflexes disappeared. This indicates a loss of crystallinity of the precipitate. The increasing intensity at lower scattering vectors below 10 nm^{-1} indicates changes in the formation of particles. Raman spectra show, that the Keggin structure is predominant at these conditions.

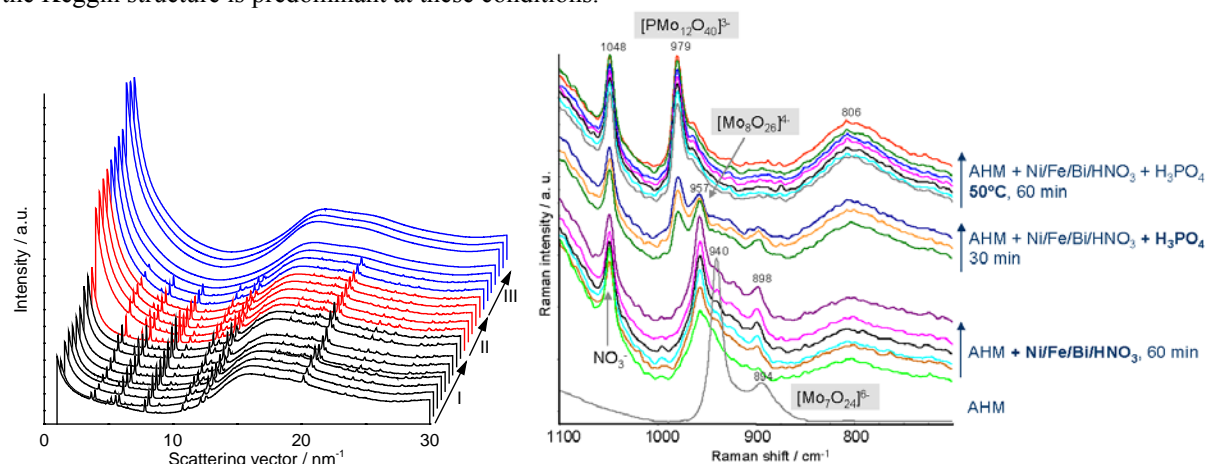


Fig. 1: X-ray scattering curves (left) after mixing the nitrates with AHM (I, black), addition of H_3PO_4 (II, red) and increasing the temperature to 50°C (III, blue) and Raman spectra (right) obtained simultaneously.

References

[1] F. Schüth, *Chem. Ing. Tech.* 2005, 77, 1399-1416.

[2] J. Radnik, U. Bentrup, U. Armbruster, M. Schneider, A. Martin, A. Brückner, J. Leiterer, F. Emmerling, „New experimental setup for online-monitoring of mixed oxide catalyst synthesis at the μ -spot beamline at BESSY“, Poster, ESRF Workshop “Time resolved and in-situ study of heterogeneous catalysts and catalytic process using X-rays: current possibilities and future prospects”, 5-7 February 2008

High-throughput structure/function screening of materials with multiple spectroscopic techniques

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Combinatorial or high throughput (HTP) synthesis is increasingly applied to generate libraries of inorganic materials. In addition to parallel synthesis techniques obtaining large amounts of new materials in the quest for new, interesting, ones, combinatorial or HTP screening is growing rapidly in its application to optimize the composition of materials to obtain specific physical or chemical properties and (fundamentally) understand their origin.

X-ray diffraction methods (XRD) are now well-established for HTP characterisation of crystalline bulk phases. In comparison, HTP X-ray absorption fine structure (XAFS) spectroscopy is a virtually unexplored technique. XAFS is readily applied *in situ* and with high time-resolution, providing opportunities for a wide range of HTP applications. With suitable ancillary techniques, both the structure and the function of a wide range of systems can thus be dynamically monitored under process conditions.

At Southampton, we have developed an environmental chamber¹, allowing *in situ* studies on arrays of samples while X-ray absorption fine structure spectroscopy, Raman spectroscopy, X-ray diffraction and/or mass spectrometry can be applied simultaneously to characterize the system under process conditions in a time-resolved manner. The chamber accommodates a diverse range of samples from surface science to materials chemistry to heterogeneous catalysis. Data acquisition and data logging software is developed to handle large quantities of diverse but related information. New data logging, processing and analysis procedures and programs are developed which will allow fast structure-function relationships characterization.

In this exemplar study we apply the multi-technique HTP screening approach to understand and optimise/fine-tune the properties of mixed metal oxides (e.g. BiMoVO_x Bi₂V_{1-x}Me_xO_{5.5- δ} materials) suitable as inorganic pigments as well as low temperature oxidation catalysts.^{1,2} The chemical and physical properties of these oxides are strongly dependent on their structure and the location and distribution of cations in their structure. The structure and cation distribution in itself is strongly dependent on the pre-treatment procedure, with the temperature being the most important factor. Arrays of these multiple cation oxides (generated efficiently using robotic methodologies) are studied and analysed for metal ion distributions. HTP methodologies are required in order to delineate local structural features rapidly.

1. M. Tromp, et al., AIP, CP882 (858), 2007.
2. S. Russu, et al., AIP, CP882 (535), 2007.

Combining results from XAS, Raman, STEM and TEOM to obtain reliable information about propane dehydrogenation catalysts

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Dehydrogenation of propane (DHP) has been studied over a series of Cr-SBA-15 and Cr-Al₂O₃ catalysts, prepared by incipient wetness impregnation, to gain a better understanding of the nature and distribution of Cr species and their catalytic function. To this end, the catalysts were characterized by N₂-physisorption, X-ray diffraction (XRD), UV-Raman spectroscopy, scanning transmission electron microscopy – energy dispersive X-ray spectroscopy (STEM – EDXS) and X-ray absorption spectroscopy (XANES and EXAFS). All these characterization techniques support that ≤ 1 wt.% Cr, SBA-15 contains a highly uniform distribution of chromium as isolated Cr(VI) species in tetrahedral (T_d) coordination whilst on γ -Al₂O₃ a fraction of oligomers (including dimers) is present along with isolated species. At ≥ 5 wt.% Cr, SBA-15 is dominated with crystalline α -Cr₂O₃ particles besides a fraction of isolated Cr(VI) species in T_d coordination. In contrast, Cr on γ -Al₂O₃ contains mainly oligomers with different degrees of nucleation and a fraction of isolated species but no Cr₂O₃ particles. Among Cr-SBA-15 catalysts, those containing exclusively isolated Cr species (i.e., ≤ 1 wt.% Cr) exhibit higher activity and selectivity per mole of Cr than the catalyst dominated with crystalline α -Cr₂O₃ particles (≥ 5 wt.% Cr). The intrinsic activity of these isolated Cr species is higher than those observed on γ -Al₂O₃ (≤ 1 wt.% Cr). Among Cr-Al₂O₃ catalysts dominated by oligomeric species show the highest activity indicating the important role of the species in the reaction. In situ XAS studies evidence that active Cr sites are apparently generated on site during the reaction and that Cr is typically in (III) oxidation state. Based on ex situ and in situ characterization results and catalytic data, it appears that the activity of Cr species is different in x Cr-SBA-15 and x Cr-Al₂O₃. For x Cr-SBA-15, isolated Cr(III) sites with coordination number greater than four are more active, selective and stable than Cr sites on the surface of crystalline Cr₂O₃. In contrast, for x Cr-Al₂O₃, oligomeric Cr species are more active and selective than the isolated Cr sites.

Sensitivity enhancement and dynamic behavior analysis by Modulation Excitation Spectroscopy: The principle and applications in heterogeneous catalysis

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Modulation Excitation Spectroscopy (MES) is a powerful technique to investigate the dynamic behavior of chemical and physical systems.^{1,2} When a system is perturbed by a periodic change of a parameter (so-called *stimulation*), e.g. concentration, pH, light flux, and temperature, affecting a chemical or physical state of a system, the response of the state will also be periodic. The periodically alternating response can be selectively detected and the signal to noise ratio can be significantly enhanced by the detection method of the MES, Phase Sensitive Detection (PSD). The MES shows its great unique strength upon combination with broadband spectroscopy, e.g. IR and Raman spectroscopy or the combination of those, allowing kinetic differentiation of species and hence giving insights into transformation mechanisms and pathways.

In this talk, the principle of MES, how we achieve drastic sensitivity enhancement leading to high time-resolution and how we can study kinetics of a system using the phase-domain analysis, is presented, followed by some examples of MES in heterogeneous catalysis at gas-solid and solid-liquid interfaces. Finally, possibilities and expected advantages of MES combined with *in situ* XRD/Raman/XAS are discussed.

[1] D. Baurecht, and U.P. Fringeli, *Rev. Sci. Instrum.* (2001) 72, 3282

[2] A. Urakawa, T. Bürgi, and A. Baiker, *Chem. Eng. Sci.* in press

Interplay between structural and electronic behavior in iron bearing silicate perovskites at conditions of Earth lower mantle: Inside from combined X-ray diffraction, Mossbauer and Raman spectroscopy, NFS, and XANES studies

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A major goal in the geosciences is to understand (and predict) how the Earth works, which requires a detailed knowledge of how the mineral phases which make up the Earth behave under high pressure and high temperature conditions. Much attention has been focused on the silicate perovskite phase, since it makes up nearly half of the Earth's interior, and special attention has been focused on phase transitions due to their significant implications for mantle behaviour. The majority of measurements have been made on *pure* MgSiO₃ perovskite, however, and almost exclusively using X-ray powder diffraction. Although the importance of Fe and Al as minor components of the silicate perovskite phase has been well documented in the past decade in numerous papers including many published in Science and Nature, the few studies using methods sensitive to these elements (e.g., X-ray emission spectroscopy and nuclear forward scattering) were not sufficiently systematic and/or sensitive to recognise any significant changes in the pressure range below 100 GPa. We studied silicate perovskites (Mg_{0.88}Fe_{0.12})SiO₃ and (Mg_{0.9}Fe_{0.1})(Si_{0.975}Al_{0.025})O₃ by means of high resolution X-ray powder diffraction, Mossbauer and Raman spectroscopy, nuclear forward scattering and XAS at pressure up to 120 GPa and temperature above 2500 K. We will discuss effects of changes in iron electronic state on structure of perovskites.

3D mapping of reciprocal space and inelastic X-ray scattering

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Combination of powder diffraction and Raman scattering allows to correlate average crystal structure with zone-center vibrations. With single crystals one could go beyond and measure diffracted intensity and inelastic scattering at any vector in reciprocal space. Inelastic scattering measurements, X-ray or neutron, are very time consuming. Diffraction could be measured fast with an area detector; but diffracted intensities are integrated over energy of the phonon system. Mapping of reciprocal space in diffraction experiment followed by inelastic X-ray scattering allows to locate vectors in reciprocal space with strong diffuse scattering signals and then uncover a vibrational contribution. This combination of methods will be illustrated with diffuse scattering in Mn-based Prussian Blue analogue, dynamic diffraction effects in Si, charge density wave in ZrTe_3 , and Kohn anomalies in Zn.

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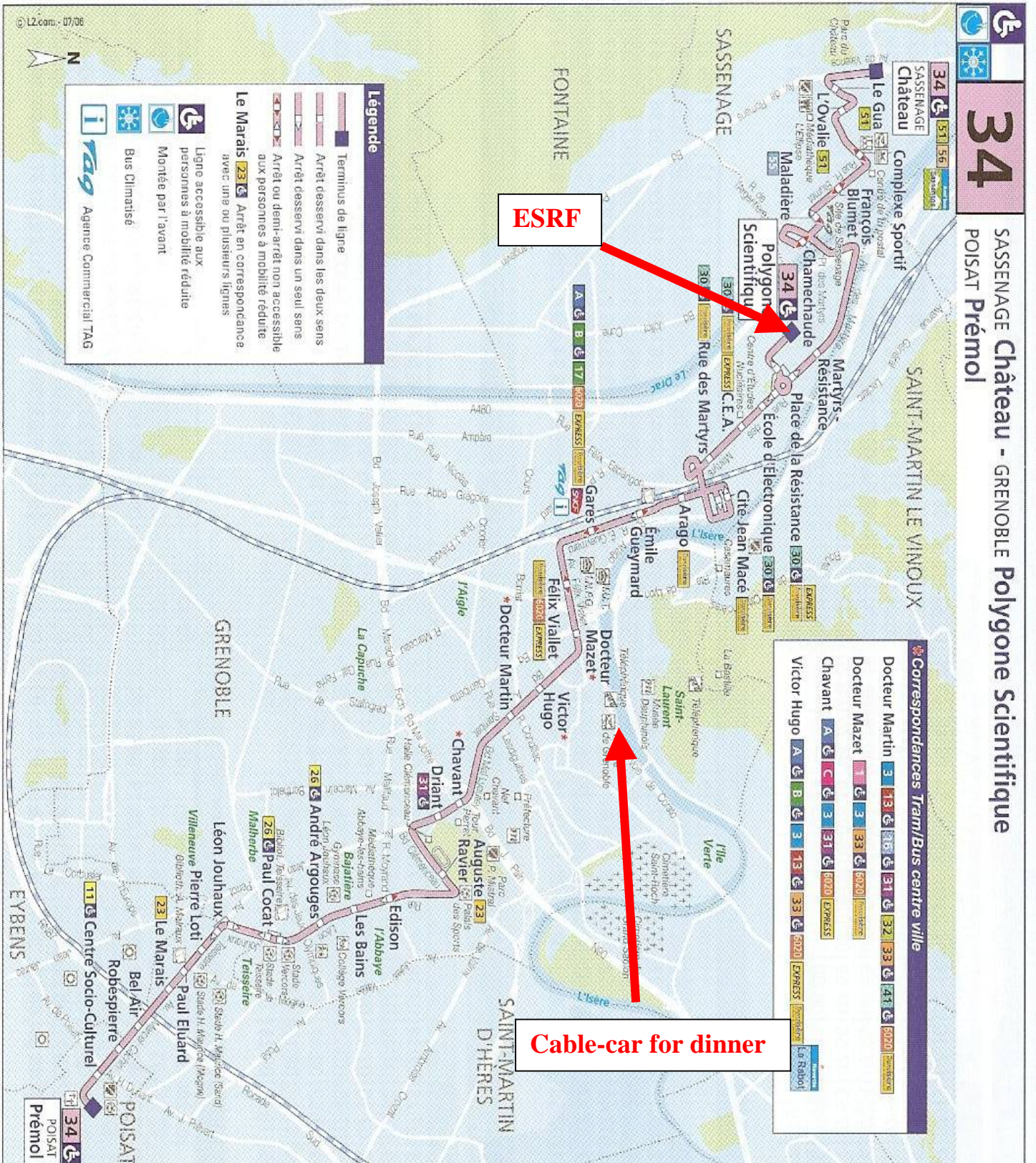
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Practical information




Bus line 34





Lunches and Dinner

If you choose to register for lunch and dinner, you will be handed the following tickets :

Lunch Wednesday 18th June 2008		EUR 15,00
Dinner Wednesday 18th June 2008		EUR 55,00
Lunch Thursday 19th June		EUR 15,00

A receipt will be provided when you register for lunch/es and dinner on Wednesday 18th June 2008, before 10 a.m. Payment: either cash or cheque.

Dinner Wednesday 18th June 2008

Time : 8 p.m.

Meeting time at the Cable-Cars,
at the latest : 7.30 p.m.

If the weather allows it is nice to go earlier and take a small walk or a drink on the terrace and simply enjoy the surroundings.

Name of the Restaurant: Le Teleferique

Please wear your badge when you go to Dinner, otherwise you will be asked to pay for the cable car.

Lunch Wednesday 18th June 2008 and Thursday 19th June 2008

On ESRF site.

Notes