Final Report Long Term Project CH2234

The implementation of a simultaneous Raman-X-ray diffraction/absorption approach for the in situ investigation of solid state transformations and transitions at non ambient conditions.

Scientific results and benefits for LTP members and ESRF user community

X-ray diffraction, X-ray absorption spectroscopy and Raman scattering are commonly used for studying structural, electronic and vibrational behaviour of materials. All three techniques have their strong points and limitations but by combining them into one experimental set-up it is possible to exploit their complementarities. The biggest advantage of such a multi-technique approach lies in the observation of dynamic processes. This is where (quasi-) simultaneous data acquisition with different techniques ensures a perfect correlation between these measurements. As a result one obtains information about the materials structure which goes beyond the sum obtained by individual experimental methods. The success of the multiple technique approach depends strongly on the rigorous optimization of all related experimental details. We believe to have successfully contributed to a new tool in the ESRF infrastructure, unique in the world, easy to use and extremely versatile. The complementarities of the various techniques with Raman spectroscopy was fully exploited and the analysis and interpretation strategies of simultaneous data tested and used to obtain impacting results in many areas of science as demonstrated by detailed publications. The development and optimization of the setup allowed to LTP members to achieve a deep expertise in the experimental details and the possibility to test and use it in several fields, thanks to the continuity of access to beamtime. The setup was also quickly made available to a large part of ESRF user community, including Structural Biologist, Materials Scientists, Chemists and Physicists. A workshop series about combining optical spectroscopic techniques with synchrotron radiation was initiated by LTP members. The aim was two-fold: 1) exchange practical know-how about the different upcoming installations around the world and 2) to educate scientists not familiar yet with Raman and help them with designing experiments and interpreting data. By doing so we did not only simply install a spectrometer but we also created and keep on building the necessary user community to make proper use of this kind of instrumentation.

Finally, we would also like to point out that the Raman installation has attracted the attention of scientist outside the traditional synchrotron user community. A part of the people involved in the Raman LTP have started to collaborate with these 'new' people and so far this has already resulted in one paper on a: Combined Modulation Enhanced Diffraction and Spectroscopic Study. Modulation allows to significantly enhance the selectivity and sensitivity of all combined techniques. In our opinion this ground breaking work would not have been possible without our interdisciplinary approach and it could turn out to be one of the most important outcomes of this LTP.

Publications

All 22 publications coming from the newly implemented equipment on the Beamline are listed below. This list only contains accepted publications. In the original proposal it was stated "*At the end of the LTP the developed Raman-XRD and the Raman-XAS in situ experimental setup on BM1A and BM1B will be available to all ESRF users*". However the equipment was made available to all ESRF users well before, during the end of year II of the LTP, as demonstrated by publications from several groups outside LTP consortium in 2010. Lots of data is also still being processed and prepared for publication.

2011

22. Urakawa A,van Beek W, Monrabal-Capilla M, Galán- Mascarós J R, Palin L, and Milanesio M, *A Combined, Modulation Enhanced X-ray Powder Diffraction and Raman Spectroscopic Study of Structural Transitions in the Spin Crossover Material [Fe(Htrz)$_2$(trz)](BF$_4$).* J Phys Chem C, 2011 in press

21. Hersleth, H P, Andersson K K *How different oxidation states of crystalline myoglobin are influenced by X-rays*, Bioch & Bioph Acta (BBA) 2011 in press

20. van Beek W, Safonova O V, Wiker G, Emerich H. SNBL *A dedicated beamline for combined in-situ X-ray diffraction, X-ray absorption and Raman scattering experiments.* Phase Transitions, 2011 in press

19. Bøyesen K.L., Meneau F., Mathisen K., *A Combined in situ XAS/Raman and WAXS Study on Nanoparticulate V2O5 in Zeolites ZSM-5 and Y.* Phase Transitions, 2011 in press

2010

18. De Smit, E., Cinquini, F., Beale, A.M., Safonova, O., van Beek, W., Sautet, Ph., Weckhuysen, B. M. *Stability and Reactivity of* $\epsilon-\chi-\theta$ *Iron Carbide Catalyst Phases in Fischer-Tropsch Synthesis: Controlling* μ_C J. Am. Chem. Soc., 2010, 132 (42) 14928-14941

17. Kongmark, C., Martis, V., Pirovano, C., Löfberg, A., van Beek, W., Sankar, G., Rubbens, A., Cristol, S. et al. *Synthesis of γ-Bi_2MoO_6 catalyst studied by combined high-resolution powder diffraction, XANES and Raman spectroscopy* Catalysis Today, 2010, 157, 257-262

16. Newton, M. A., van Beek, W. *Combining synchrotron-based X-ray techniques with vibrational spectroscopies for the in situ study of heterogeneous catalysts: a view from a bridge* Chem. Soc. Rev., 2010, 39, 4845-4863

15. Renaudin, G., Filinchuk, Y., Neubauer, J., Goetz-Neunhoeffer, F. *A comparative structural study of wet and dried ettringite* Cement and Concrete Res., 40, 3, 370-375, 2010

14. Røhr, Å., Hersleth, H.-P., Andersson, K. *Tracking Flavin Conformations in Protein Crystal Structures with Raman Spectroscopy and QM/MM Calculations* Angewandte Chemie Int. Ed., 49, 13, 2324–2327, 2010

2009

13. Croce, G., Carniato, F., Milanesio, M., Boccaleri, E., Paul, G., van Beek, W., Marchese, L. *Understanding the physico-chemical properties of polyhedral oligomeric silsesquioxanes: a variable temperature multidisciplinary study* Phys. Chem. Chem. Phys., 11, 10087 - 10094, 2009

12. Del Río, M.S., Boccaleri, E., Milanesio, M., Croce, G., van Beek, W., Tsiantos, C., Chyssikos, G.D., Gionis, V. et al. *A combined synchrotron powder diffraction and vibrational study of the thermal treatment of palygorskite–indigo to produce Maya blue* J. Materials Science, 44, 20, 5524-5536, 2009

11. Grunwaldt, J-D., Van Vegten, N., Baiker, A., van Beek, W. *Insight into the structure of Pd/ZrO2 during the total oxidation of methane using combined in situ XRD, X-ray absorption and Raman spectroscopy* J. Phys. Conf. Ser. 190, 012160-012164, 2009

10. Hagemann, H., Filinchuk, Y., Chernyshov, D., van Beek, W. *Lattice anharmonicity and structural evolution of LiBH4: an insight from Raman and X-ray diffraction experiments* Phase Transitions A, 82, 4, 344 – 355, 2009

9. Hamon, L., Llewellyn, Ph., Devic, Th., Ghoufi, A., Clet, G., Guillerm, V., Pirngruber, G. Maurin G, Serre C, Driver G, van Beek W, Jolimaitre E, Vimont A, Daturi M and Ferey G. *Co-adsorption and Separation of CO_2 - CH_4 Mixtures in the Highly Flexible MIL-53(Cr) MOF* J. Am. Chem. Soc., 131, 47, 17490–17499, 2009

8. Kongmark, Ch., Martis, V., Rubbens, A., Pirovano, C., Löfberg, A., Sankar, G., Bordes-Richard, E., Vannier, R.-N., van Beek, W. *Elucidating the genesis of Bi_2MoO_6 catalyst by combination of synchrotron radiation experiments and Raman scattering* Chem. Commun., 4850 - 4852, 2009

7. Kumar, S., Carniato, F., Arrais, A., Croce, G., Boccaleri, E., Palin, L., van Beek, W., Milanesio, M. *Investigating Surface vs Bulk Kinetics in the Formation of a Molecular Complex via Solid-State Reaction by Simultaneous Raman/X-ray Powder Diffraction* Cryst.Growth. Design, 9, 8, 3396–3404, 2009

6. van Beek, W., Carniato, F., Kumar, S., Croce, G., Boccaleri, E., Milanesio, M. *Studying modifications and reactions in materials by simultaneous Raman and X-ray powder diffraction at non-ambient conditions: methods and applications* Phase Transitions A, 82, 4, 293 – 302, 2009

5. Van Vegten, N., Maciejewski, M., Krumeich, F., Baiker, A. *Structural properties, redox behaviour and methane combustion activity of differently supported flame-made Pd catalysts* Applied Catalysis B: Environmental, 93, 1-2, 38-49, 2009

4. Wragg, D.S., Johnsen, R. E., Balasundaram, M., Norby, P., Fjellvåg, H., Grønvold, A. et al. *SAPO-34 methanol-to-olefin catalysts under working conditions: A combined in situ powder X-ray diffraction, mass spectrometry and Raman study* J. Catalysis, 268, 290-296, 2009

2008

3. Bosak, A., Schmalzl, K., Krisch, M., van Beek, W., Kolobanov, V. *Lattice dynamics of beryllium oxide: Inelastic x-ray scattering and ab initio calculations* Phys. Rev. B 77, 224303-224310, 2008

2007

2. Beukes, J. A. , Mo, F., van Beek, W. *X-ray induced radiation damage in taurine - A combined X-ray diffraction and Raman study* [Phys. Chem. Chem. Phys., 9, 4609-4724, 2007]

1. Boccaleri, E., Milanesio, M., Carniato, F., Croce, G., Viterbo, D., van Beek, W., Emerich, H. *In situ simultaneous Raman/<High-Resolution X-ray Powder Diffraction> study of transformations occurring in materials at non-ambient conditions* [J .Appl.Cryst., 40, 684-693, 2007]

Impact Factors

Several papers in leading journals have been published during the LTP runtime. The Angewandte Chemie Paper by Å. Røhr et al. is also selected for the 2011 ESRF highlights. Based on the 22 papers, for what its worth, the average impact factor of the Raman papers is 4.51 compared to ~3.6 for the beamlines average in the same period.

Chem Soc Rev	1	20,086	20,086	
Angw. Chemie Int Ed	1	10,88	10,88	
JACS	2	8,091	16,182	
Chem Comm	1	5,34	5,34	
Journal of Catalysis	1	5,288	5,288	
Applied Catal B	1	5,252	5,252	
Cryst Growth and Design	1	4,215	4,215	
PCCP	2	4,064	8,128	
Catal Today	1	3,526	3,526	
J Phys Chem C	1	3,396	3,396	
Phys Rev B	1	3,322	3,322	
J Applied Cryst	1	3,2	3,2	
Biochim. et Biophys. Acta (BBA)	1	2,48	2,48	
cement and concrete research	1	1,549	1,549	
Phase Transitions	4	1,201	4,804	
J. Materials Science	1	1,181	1,181	
J Phys Conf Series	1	0,5	0,5	
	22	83,571	99,329	4,514955

Key publication:

It is hard or impossible to select *the* key publication as the report guidelines suggest. All of the papers below can be considered as key publications. These studies have namely brought vital new detail by exploiting at best different aspects of the complementarities between RAMAN, XAS and XRD.

- Paper 4 introduces crystallographic data analysis methods in operando catalysis experiments (locate coke build up) and uses Raman data to provide information on the nature of the coke. This shows that no compromise on data quality needs to be made.
- Paper 6 and 20 describes the experimental setup with its potentialities and limitations
- Paper 7 utilizes the difference in penetration depth of the probes and applies kinetic analysis to bring detailed information on crystal growth and its advancement model.
- Paper 9 manages to make reliable quantitative observations during gas sorption and separation experiments that would have been impossible without the Raman data

- Paper 11 combines the different crystallite size sensitivities of the techniques with oxidation state information to understand the origin of the overall catalytic activity profile measured at the same time with a Mass Spectrometer
- Paper 14 monitors the flavin vibrational modes by Raman spectroscopy altered during X-ray crystal-data collection therefore shining new light on a slowly the altering flavin state indicating that many structures in databases need to be taken with a lot of care.
- Paper 22 for providing information on the local and long range to understand a phase transition hysteresis introducing and exploiting novel methods and strategies (correlation analysis and modulation technique) for a combined analysis of diffraction and spectroscopy data

We have finally selected paper 22 Urakawa, A. et al, J Phys Chem C, 2011 paper as more representative key publications, since most of the innovation introduced during the LTP are exploited. In fact the research described in the paper exploits novel methods and strategies to quantitatively correlate the data from XRPD and Raman probes; it opens up the way to enhance sensitivity and introduces selectivity into all combined techniques. We also believe the modulation technique presented here has a lot of future potential.

Phd's

Besides papers the Raman data from SNBL has also contributed to 5 PhD's.

Van Vegten, N, *Aerosol Synthesis of Supported Metal and Metal Oxide Systems and their Catalytic Applications*, ETH Zurich, Switzerland 2010

Rohr, A K, *Structural and spectroscopic studies of the flavoprotein NrdI, thioredoxin BC3987, and ribonucleotide reductase diiron-protein R2.* University of Oslo, Norway 2010

de Smit, E, *Iron-based Fischer-Tropsch Synthesis: New Insights from in-situ (Micro)Spectroscopy, Diffraction and Theory.* University Utrecht, The Netherlands 2010

Kongmark, C, *Genesis of Bismuth Molybdenum Oxide Catalyst followed by In-situ Techniques and its Use in Catalytic Dense Membrane Reactor.* University Lille I France 2010

Kumar, S, *Synthesis and Characterization of novel compounds for radical detection and photo/electro luminescence: Facile methods to obtain hybrid materials* .University of Piemonte Orientale, Italy 2010

Initiated workshop series

In June 2008 SNBL has organized together with the LTP members a workshop on: *Simultaneous Raman-X-ray Diffraction/Absorption Studies for the In Situ Investigation of Solid-State Transformations and Reactions at Non-Ambient Condition.* The aim was two-fold aim: 1) exchange practical know-how about the different upcoming installations around the world and 2) to educate scientists not familiar yet with Raman and help them with designing experiments and interpreting data. 78 Participants from 14 countries as well as industrial partners were present. Proceedings were published in Phase Transitions April 2009. The Soleil synchrotron has organized a follow up workshop in June 2010 enlarging the scope a little to: *Simultaneous Combination of Spectroscopies with X-ray Absorption, Scattering and* Diffraction. The Swiss Light Source has agreed to organize the next edition in 2012. We hope to have contributed to the continuity of this kind of instrumentation at SNBL and elsewhere in the world.

Several contributions to international congresses were given by LTP members and also specific micro-symposia on combined spectroscopy and X-ray based techniques were organized by the spokeperson M. Milanesio at EPDIC12 congress (Darmstadt, Germany, August 2010) and at XXII IUCR meeting (Madrid, Spain, August 2011). They were also invited to present their experiences at other synchrotrons (Diamond, SLS), interested to develop similar experimental devices.

Technical accomplishments

A Raman spectrometer is permanently installed at SNBL and can be used in both Experimental stations for in-situ measurements. Off-line Raman measurements can also be taken in the sample preparation laboratory. The SNBL has a pool of equipment filled with a wide variety of 'in-situ instruments', which are either custom-designed or adapted to the beamline. Some of these instruments are relatively standard temperature controllers (a hot-air blower, a cryo-stream and a cryostat) together offering a temperature range from 4.5 to 1200 K. However, temperature alone is often not sufficient when performing so-called operando studies. During operando experiments scientists try to reproduce the realistic conditions of a chemical process (e.g. composition of reactive media, pressure, space velocity of reactants etc.) at the beamline while following the structural changes of the working catalyst or other functional materials such as gas sensors or electrochemical devices. All of the mentioned devices have been tested with the Raman setup and a clear understanding on the possibilities and limitations is obtained. On the one hand the success of such multi-technique approach relies onto the rigorous optimisation of many experimental details. On the other hand we would strongly like to advocate that the 'ease of use' aspect for both beamline scientist and visiting user is of prime importance for the overall success of the implementation of any additional technique. At SNBL the Raman spectrometer can be added to almost any experiment in 15 minutes even it was not foreseen. This enhances its overall use and the hence likelihood for accidental discoveries. The off-line capabilities of the Raman instrument also provides a service tool for people that occasionally need a Raman or Photoluminescence Spectrum from their sample and know their way to the beamline. The benefits are hard to quantify in terms of scientific output but it can for instance be said that in case of emergency several ESRF high pressure DAC experimentalists have used this service extensively to calibrate the pressure. Also the inelastic x-ray scattering people use it to provide them with an absolute reference and the system is also used to select diamonds based on their optical quality.

Conclusion

The final paragraph from the original proposal is quoted:

"Expected long-term benefits to the ESRF User Community such as new instrumentation, new techniques, new areas of research with potential user base.

We believe to have showed with this proposal that a wide variety of scientific areas can benefit enormously from the combination of Raman spectroscopy with XRD or XAS methods in a simultaneous experiment, from chemistry to materials science to physics. Since SNBL is a multi-purpose beamline, with state of the art single crystal, powder diffraction and XAS instrumentation, the acquired Raman spectrometer will not be dedicated to one instrument but an integral part of the whole beamline. A large part of the ESRF's scientific community **can therefore** *also benefit from the acquired spectrometer, environmental chambers and moreover indispensable know how at the beamline. Through collaborations one could imagine the use of the Raman instrument on other ESRF* *beamlines too. We believe furthermore that this project enhances the quality of the science performed at the ESRF and serves a groundbreaking role for many spectrometers to be installed on many synchrotrons*."

We believe to have accomplished all long term benefits as foreseen in the proposal and required for a successful LTP: new instrumentation, new techniques and new areas of research with potential user base. ESRF users outside LTP consortium exploited the setup and new users joined the ESRF community. By organization of a workshop we also think to have contributed to the necessary education to actually make efficient use of the new tool. We also believe to have provided the publications necessary to indicate that the setup is now mature and capable of providing excellent data with a potentially (very) high impact.