

***In situ* observation of reduction reactions of iron oxides by XAFS [1].**

T. Takayama¹, M. Kimura¹, Y. Uemura², Y. Niwa², M. Nomura²

¹ Advanced Technology Research Laboratories, Nippon Steel Corp., 20-1 Shintomi, Futtu, Chiba 293-8511, Japan.

² Photon Factory, IMSS, KEK, 1-1 Oho, Tsukuba, Ibaraki, 305-0801, Japan

[Background] Pig iron is produced by the reduction of sinter composed of iron oxides and calcium ferrites using a blast furnace. The reduction mechanism has been investigated mainly by use of quenched specimens because of experimental difficulties of direct observation *in situ* measurement technique of XAFS[1] to observe the reduction reaction of iron oxides and related oxides.

[Experiment] We have developed an *in situ* observation technique by the combination of QXAFS [2] and the *in situ* reaction cell [3] with a time resolution of a few seconds. The specimen can be heated up $T= 1173$ K by a rod heater, while switching the two types of gas: O_2/He and H_2/He .

[Results] The main oxide phase of sinter: Fe_2O_3 and a typical calcium ferrite: $CaFe_2O_4$ were used as specimens. The specimens were heated at $T= 1023$ K and 1173 K. XAFS spectra around Fe K-edge were measured with an interval of 20 s after switching the gas from O_2/He to H_2/He (= 20/80 ccm).

The change of XANES spectra showed a clear isosbestic point, suggesting two types of iron states : Fe(0) and Fe(III) are involved in the reaction. The fraction x $\left(x = \frac{Fe(0)}{Fe(0) + Fe(III)} \right)$ was

determined by curve fitting of XAFS spectra (Fig. 1). The change of $\ln(1-x)$ showed an

exponential dependence on time, and it is observed that the reaction rate of Fe_2O_3 is faster than that of $CaFe_2O_4$. It should be noted that an incubation time was observed in the reduction process of $CaFe_2O_4$.

[Summary] An *in situ* observation technique has successfully shown the fundamental information on the reduction of sinter. The difference was observed for the reduction processes among iron oxides.

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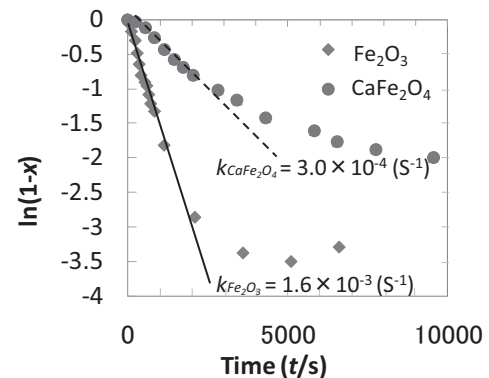


Fig.1: Relationship between the fraction x and the reduction time.

Understanding the Nature of the Kinetic Process in a VO₂ Metal-Insulator Transition

Qinghua Liu, Tao Yao, Zhihu Sun, Ziyu Wu, Yi Xie, and Shiqiang Wei*

National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, Anhui 230029, People's Republic of China

Due to its intriguing thermochromic phenomena, originated from the occurrence of a fully reversible metal–insulator transition (MIT) that induce large changes in the electrical conductivity and in the near-IR optical properties, the vanadium oxide (VO₂) may become a reliable and effective energy-saving material in the future of our daily lives. As one of the prototype materials of correlation effects in condensed matter, the VO₂ MIT mechanism has been for long time a hot topic in condensed matter physics since the discovery of VO₂ MIT in 1950s. To contribute to the debate about the origin of the VO₂ structural phase transition, it is fundamental to monitor *in situ* both atomic and electronic structural changes during its MIT process triggered by temperature.

In this work, based on the temperature-dependent *in situ* x-ray absorption fine structure measurement and density-functional theory calculations, we have revealed that the monoclinic-to-tetragonal phase transition of VO₂ near the critical temperature is characterized by a sharp decrease of the twisting angle δ of the nearest V–V coordination. The VO₂ metallization occurs in the intermediate monocliniclike structure with a large twist of V–V pairs when the δ angle is smaller than 1.4 degree. The correlation between structural kinetics and electronic structure points out that the structural rearrangement is a key factor to narrow the insulating band gap. These results establish a clear correlation between the dynamics of the lattice structure and electronic properties and clarify a possible structural pathway and the mechanism of similar phase transitions in correlated materials.

New Development of 1W1B-XAFS Station in Beijing Synchrotron Radiation Facility

Zhang Jing* XieYanin ZhengLirong HuTiandou

Beijing Synchrotron Radiation Facility, Institute of High Energy Physics, Chinese Academy of Science, Beijing 100049

1W1B-XAFS station in Beijing synchrotron radiation facility is a general purpose instrument. The light source of 1W1B-XAFS beamline is wiggler magnet with 1.1 mrad horizontal acceptance and 0.12 mrad perpendicular acceptance, The energy range from 5 to 25KeV, The resolution at 10KeV is 2-3eV, The photon flux at 10KeV is about 2×10^{11} photons.s⁻¹ under the electron energy of 2.5 GeV and stored current of 100 mA. The beam size at sample position is 0.7mm(H)*0.4mm(V). Currently, the detection methods and sample environments are developed. 19 elements germanium array detectors system has been set-up and used for fluorescent XAFS of trace elements, It greatly extends the applications of XAFS in life and environment science. On the other hand, multifunctional in situ sample instruments has been improved, including liquid helium temperature in situ XAFS cell, liquid nitrogen temperature XAFS cell, liquid sample cell, high pressure XAFS Instrument, which has supported XAFS measurements on the various conditions such as the low temperature, water solvent, organic solvent and also high pressure up to 40Gpa. Thanks to its versatility, it is useful to a broad scientific community.

Time-resolved XAS beamline at SLRI

P. Chirawatkul¹, Y. Poo-arporn¹, S. Klinkhieo¹, J. Hormes² and P. Songsiriritthigul^{1,3*}

¹ *Synchrotron Light Research Institute, Nakhon Ratchasima, 30000, Thailand*

² *Canadian Light Source, University of Saskatchewan, 101 Perimeter Road, Saskatoon, SK S7N 0X4 Canada*

³ *School of physics, Suranaree University of Technology, Nakhon Ratchasima, 30000, Thailand*

**Corresponding author. E-mail: prayoon@slri.or.th*

Abstract

This report presents the optical layout and the commissioning results of the energy dispersive X-ray absorption spectroscopy beamline at the Synchrotron Light Research Institute in Thailand. The beamline employs a bent Si(111) crystal as an energy dispersive monochromator (EDM). The beamline utilizes radiation from a bending magnet of 1.2 GeV storage ring. The EDM covers X-rays with photon energy from 3 to 8 keV. A linear image NMOS sensor consisting of 1024-element photodiode allows detection in transmission mode with a detector readout time of less than 100 ms, and thus time-resolved may be carried out at this beamline.

Keywords: synchrotron light, XAS beamline, energy dispersive

XANES Database in the CK, NK, and OK Regions of Standard Organic Compounds and Metal Compounds for Chemical Analysis

Yasuji Muramatsu^{1*}, Yusuke Nakayasu¹, Taiji Amano¹, Yuki Kubota¹, Kenta Shimomura¹,
Keishi Kamamoto¹, Satoshi Ueda¹, Kentaro Kuramoto², and Eric M. Gullikson³

¹Graduate School of Engineering, University of Hyogo

²Graduate School of Material Science, University of Hyogo

³Center for X-Ray Optics, Lawrence Berkeley National Laboratory

XANES database in the CK, NK, and OK regions of standard compounds is necessary for the chemical analysis by using XANES of light-element materials including carbon (C), nitrogen (N), and oxygen (O). From the chemical analyses of graphitic carbons [1-3], diamond-related materials [4,5], C/N compounds [6], rubber [7], and other carbon materials [8], we have measured many XANES spectra of various organic compounds such as aromatic hydrocarbons [9, 10], aromatic compounds with oxygenated functional groups [1], aliphatic compounds with oxygenated functional groups [8], and aromatic compounds with nitrogenated functional groups [11] as standard compounds. We have also measured XANES of various metal carbides, nitrides, and oxides as standard compounds for chemical analysis of C, N, O in metal materials. These spectra were measured in the beamline BL-6.3.2 at the Advanced Light Source (ALS) with the energy resolution (E/dE) of 3000 – 5000.

In this study, we accumulate the XANES spectra in the CK, NK, and OK regions of the standard compounds to utilize the XANES database for chemical analysis.

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*Corresponding author: murama@eng.u-hyogo.ac.jp

Total-Electron-Yield (TEY) Soft X-Ray Absorption Spectroscopy of the sp^2/sp^3 -Carbon Mixtures; Relationship between the TEY Efficiency and Electrical Conductivity

Tomoyo Yoshinaga¹, Hiroya Tanaka¹, Yasuji Muramatsu^{1*}, and Eric M. Gullikson²

¹Graduate School of Engineering, University of Hyogo

²Center for X-Ray Optics, Lawrence Berkeley National Laboratory

Soft X-ray absorption spectroscopy (XAS) using a total-electron-yield (TEY) method has been a powerful tool for chemical/electronic-state analysis of functional materials. However, some difficulties often arise in TEY-XAS for quantitative analysis, because the TEY signal intensity may depend on the electrical property of the samples and the TEY ratios between sample compositions have not been clearly elucidated [1]. To apply the TEY-XAS for the quantitative analysis of sp^2 - and sp^3 -hybridized carbons, we have investigated the TEY efficiency between sp^2 -C (carbon black, carbon nanotube) and sp^3 -C (diamond) [2]. Thus, it can be found that TEY efficiency of sp^2 -C is higher than that of sp^3 -C.

To further confirm the TEY efficiency of sp^2/sp^3 -C and to reveal the relationship between the TEY efficiency and electrical properties of the compositions, we have measured the TEY-XAS of the sp^2/sp^3 -C powder mixtures (sp^2 -C: graphite, carbon black, carbon nanotube; sp^3 -C: diamond, polyethylene). TEY-XAS measurements were performed in a beamline BL-6.3.2 at the Advanced Light Source (ALS). Additionally, electrical resistivity and conductivity of the mixture samples were measured to compare the TEY efficiency. Thus, it is experimentally found that the logarithm of electrical conductivity of the sp^2/sp^3 -C mixture samples is qualitatively proportional to the TEY intensity. This suggests that TEY clearly depends on the electrical conductivity of sample compositions, and that we should consider the electrical properties of them for quantitative analysis by the TEY-XAS measurements.

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*Corresponding author: murama@eng.u-hyogo.ac.jp

CONTINUOUS OBSERVATION BY DISPERSIVE XAFS TECHNIQUE FOR CATALYTIC REACTION

D. Matsumura¹, Y. Okajima², Y. Nishihata¹, J. Mizuki¹

¹ Japan Atomic Energy Agency, 1-1-1 Koto, Sayo-cho, Sayo-gun, Hyogo 679-5148, Japan

² SPring-8 service Co., Ltd., 1-1-1 Koto, Sayo-cho, Sayo-gun, Hyogo 679-5148, Japan

Dispersive XAFS technique adopting the curved crystal enables us to observe XAFS spectra without mechanical movement at all. We have utilized the advantage of dispersive XAFS technique which is fast and stable observation, and applied to the structure and shape changes of Pd metal fine particles as automotive catalyst [1, 2]. Continuous observation with high relative precision and high frame rate creates many absorption spectra having a slight shift each other. Consistent and fast analysis of XAFS data is very important to obtain full information from many data sets.

Fig. 1 shows the variations of the XAFS parameters during a CO/NO successive flow for the Pd metal particles on the aluminum oxide with a frame rate of 0.2 Hz. From this figure, we determined the changes of structure, shape, and oxidation state for the Pd metal particles during the catalytic reaction. A precise determination of the states of metal particles is realized because the relative precisions of the interatomic distance and the edge shift are only 0.002 Å and 0.05 eV, respectively. We will present some examples of high relative precision and high frame rate with continuous observation.

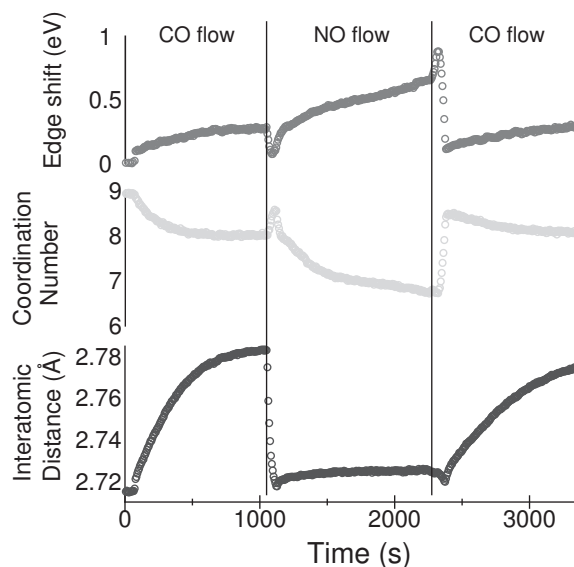


Fig. 1 Variations of XAFS parameters of Pd/Al₂O₃ at 400 °C during CO/NO catalytic reaction.

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XAFS measurements from Mg to Zn *K*-edges at Beamline 8 of Siam Photon Laboratory

W. Klysubun^{1,*}, P. Sombunchoo¹, W. Deenan¹, N. Wongprachanukul¹, S. Limpijumnong², S. Rujirawat², and P. Songsiriritthigul^{1,2}

¹*Synchrotron Light Research Institute (Public Organization), Nakhon Ratchasima 30000, Thailand*

²*School of Physics, Suranaree University of Technology, Nakhon Ratchasima 30000, Thailand*

The beamline 8 (BL8) of Siam Photon Laboratory is routinely utilized for x-ray absorption fine structure (XAFS) experiments in various research areas, for examples, material science, biochemistry, environmental science, and archeology. The number of users has been steeply increased since 2006. A noted distinction of BL8 from other x-ray absorption beamlines is its ability to perform *K*-edge absorption for an element as light as magnesium (photon energy =1303 eV) up to zinc (9659 eV). Depending on the range of photon energy needed, there are four types of crystals available for the double crystal monochromator: KTP(011), InSb(111), Si(111), and Ge(220). Due to its small size and practical design of the monochromator, changing crystal and fine tuning can be quickly done within 1 to 2 hours. Near-edge and extended absorption fine structure spectra can be collected in either transmission or fluorescence modes. Elemental sensitivity is about 50 ppm. Instrumental specifications, functional control, and data acquisition of BL8 and its XAFS station will be described. An example of recent measurements on the mixed phases of tetrahedral and octahedral structures in MgZnO alloys will be present. It is found that XAFS results on the MgZnO alloys provide elemental specific information that was not seen by traditional x-ray powder diffraction.

* Corresponding author (wantana@slri.or.th)

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Time-resolved *in situ* XAFS studies on formation and oxidation of Pd-Zn nanoparticles on ZnO

Yohei Uemura¹⁾, Yasuhiro Inada²⁾, Yasuhiro Niwa¹⁾, Masao Kimura³⁾, Kyoko Bando⁴⁾, Akira Yagishita¹⁾, Yasuhiro Iwasawa⁵⁾, Masaharu Nomura¹⁾

1) KEK-PF, 2) Ritsumeikan University, 3) Nippon Steel Corporation, 4) AIST, 5) Univ.

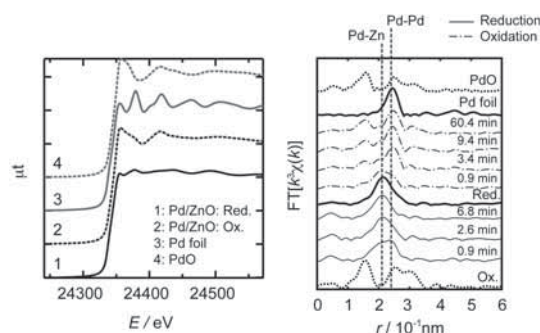
Electro-Commun.

Email: yuemura@post.kek.jp

Bimetallic nanoparticles are widely used as catalysts. Despite their potentials, the relationship between their catalytic activities and their chemical properties remains ambiguous, because there is not enough knowledge about their structures and electronic states under reaction conditions. Moreover, the recent study on Rh-Pd bimetallic nanoparticles revealed that the structures of bimetallic nanoparticles changed dynamically under reaction conditions.* We have studied formation and oxidation mechanism of PdZn nanoparticles supported on ZnO and γ -Al₂O₃ with time-resolved *in situ* XAFS (Quick XAFS and Dispersive XAFS) measurements. PdZn nanoparticles are active for the oxidative dehydrogenation of methanol. Our results pointed out that both formation and oxidation of PdZn nanoparticles proceed through a two-step reaction scheme.

Most of experiments were conducted in Photon Factory Advanced Ring (PF-AR), KEK, Tsukuba Japan. QXAFS experiments were conducted at NW10A and DXAFS experiments were conducted at NW2A. QXAFS experiments of Zn K edge were conducted at BL-9C, PF.

Fig. 1 a) shows *in situ* Pd K edge XANES of PdZn/ZnO at 400 °C. In Fig. 1a), Pd atoms in the reduced PdZn/ZnO is quite different from metallic Pd, which should be PdZn nanoparticles. On the other hand, the XANES of the oxidized PdZn/ZnO resembles that of PdO. Fig. 1 b) shows the Fourier transforms of *in situ* EXAFS of PdZn/ZnO. The Pd-Zn peak appeared at the end of the reduction, which means the formation of PdZn nanoparticles from PdO nanoparticles on ZnO



under the reductive condition. According to the detailed analyses, PdO nanoparticles are reduced to Pd nanoparticles, then PdZn nanoparticles are formed from these Pd nanoparticles on ZnO. On the other hand, the PdZn interaction quickly disappeared and the PdPd interaction appeared to form Pd nanoparticles in turn when oxidized. The Pd-O interaction was observed in 60 min, but its intensity was much smaller than that of the initial state of the reduction process. Pd nanoparticles emerged under oxidation conditions and they were very stable to not be oxidized even under 400 °C oxidative conditions. More details based on chemical kinetic analyses are going to be discussed.

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Determination of electronic and geometric structure of Molybdenum in molybdenum-based catalysts using L-edge X-ray Absorption Spectroscopy

C. Kongmark^a, W. Klysubun^a, F. Meneau^b, S. Gillot^c, C. Lancelot^c, S. Cristol^c

^a*Synchrotron Light Research Institute, 111 University Avenue, Muang,
P.O. box 93, 30000 Nakhon Ratchasima, Thailand*

^b*Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin
BP 48, 91192 Gif-sur-Yvette Cedex, France*

^c*Unité de Catalyse et de Chimie du Solide, UMR 8181, Université Lille I, ENSCL,
BP 90108, 59652 Villeneuve d'Ascq Cedex, France*

ABSTRACT

Mesostructured or mesoporous oxides have been the focus of intensive research for their successful applications in chemical, fuel and environmental processes as a catalyst support. Controlling the porosity of these materials is very desirable; it is interesting to note that the chemical/physical properties and structural texture are strongly related to the preparation procedure. The use of high surface area mesoporous oxide supports may give rise to well-dispersed and stable nanoparticles of catalyst in the pore surface and thus can improve the catalyst performance

In this research, molybdenum-based catalyst, which is well known to be active and selective in several types of reactions such as partial oxidation of hydrocarbons, partial oxidation alcohol as well as hydrodesulfurization [1], was prepared by impregnation method on mesoporous TiO₂-SBA15 composite support [2]. A well dispersed polymolybdate species in all solid and a homogenously deposit of anatase nanocrystals in the silica (SBA15) mesopores were confirmed by TEM and Raman spectroscopy. The catalyst supports, with molybdenum oxide loading between 5 and 40 wt%, was tested in thiophene hydrodesulfurization. The relationship between the catalytic performance and the structure of catalyst were studied by X-ray absorption spectroscopy (Mo L-edge). The experiment was carried out on the Beamline 8 at the Synchrotron Light Research Institute in Thailand. It was found that the loading concentration of catalyst may influence on the state of the oxo-molybdate phase and their catalytic activity as well.

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Weak Interaction Effect Study of Blue Copper Protein with XAS

Takahide Yamaguchi^a, Yuko Nihei^a, Sayaka Asamura^a, Junko Yano^c and Vittal Yachandra^c and Takamitsu Kohzuma^{a,b}

^a Graduate School of Science and Engineering, Ibaraki University, Mito, Ibaraki, 310-8512, Japan (email: 11nm023s@mcs.ibaraki.ac.jp)

^b Ibaraki Frontier Research Center, Ibaraki University, Tokai, Ibaraki, 319-1106, Japan

^c Lawrence Berkeley National Laboratory, Berkley, CA, 94720, USA

Non-covalent weak interactions play important roles for stabilization of protein structure and expression of function. In particular, non-covalent weak interactions near active site (second coordination sphere) of metalloprotein have great effect to tune the active site properties [1,2]. Pseudoazurin from *Achromobacter cycloclastes* is well characterized Type 1 copper protein, which has two His(His40, His81), Cys(Cys78) and Met(Met81) ligands with copper ion and exhibits significantly intense absorption band due to CysS⁻ → Cu(II) charge transfer (CT) transition around at 600 nm [3]. CT band is very sensitive and good probe to detect the precise electronic structure of active site. Spectroscopic and electrochemical studies of Met16X and Thr36X variants of pseudoazurin from *Achromobacter cycloclastes* have been performed to elucidate the effect of non-covalent weak interaction [4].

Here, we would like report tuning of blue copper site and protein stabilization induced by weak interaction accompanied by the unique pH dependency of Met16His/Thr36Lys PAz. X-ray absorption spectroscopic measurement (XAS) was performed to obtain the geometric features and electronic structure. The pre-edge intensity of various variants have good correlation with active site geometry, for the mixture of two conformers.

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XAS Studies on Electronic Structure of Metal Sites in a Blue Copper Protein, Plastocyanin from Fern *Dryopteris crassirhizoma*

Hiromi Togashi¹, Junko Yano², Vittal K. Yachandra², Takamistu Kohzuma¹

1, Inst. Appl. Beam Sci., Ibaraki Univ.

2, Lawrence Berkeley National Laboratory.

Non-covalent weak interactions play important roles in biological systems. In particular, such interactions in the second coordination shell of metal ions in proteins may modulate the structure and reactivity of the active site in functionally significant ways. Recently, π - π interactions between metal ion coordinated histidine imidazoles and aromatic amino acids have been recognized as potentially important contributors to the properties of metal ion site of a blue copper protein, pseudoazurin¹.

Plastocyanin is also well known to be a member of blue copper protein, which functions as electron carrier in photosynthesis. The reduced form of higher plant plastocyanin is deactivated at acidic pH by the dissociation of the solvent-exposed histidine ligand from the copper center². Plastocyanin isolated from a fern, *Dryopteris crassirhizoma* (DPc) maintains the electron transfer activity even under acidic pH conditions in contrast to the higher plant plastocyanin. Fern plastocyanin commonly has a Phe12 instead of Leu in the structurally identical position of higher plant plastocyanin, and Phe12 takes π - π interaction between coordinated His90. The π - π interaction in the second sphere has been considered as a factor for preventing the protonation of His90, which coordinated to Cu center.

X-ray absorption spectroscopy (XAS) is used to probe a electronic structure of metal site of protein molecules. XAS was measured to obtain the effect of non-covalent weak interaction in the second sphere on the electronic structure of the copper center in plastocyanin. XAS was performed at Stanford Synchrotron Light Source. Plastocyanin from *Ulva pertusa* (UPc) was measured for the comparison to DPc. Cu(I) K-edge of plastocyanins were measured at low pH condition and showed a band at 8982 eV. The Cu(I) K-edge of UPc indicated the coordination number of copper was decreased to be three-coordination. Cu(I) K-edge of DPc demonstrated the four-coordinated copper site. Cu(II) K-edge EXAFS data of plastocyanins were analysed based on the crystal structures. In the EXAFS of UPc, the distances between copper and coordinated atoms were evaluated to almost identical values of the crystal structural data.

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Status of the Toyota Beamline at the SPring-8

Yusaku Nishimura, Takamasa Nonaka, Tohru Araki, Yujiro Hayashi,
Yasutaka Nagai, Kazuhiko Dohmae*, Yoshiki Seno, and Yoshiharu Hirose

Toyota Central R&D Laboratories, Inc.
41-1, Yokomichi, Nagakute, Aichi 480-1192, JAPAN

*Corresponding author: kdohmae@mosk.tytlabs.co.jp

We have designed and constructed an industrial research beamline BL33XU (the Toyota Beamline) at the SPring-8 in collaboration with JASRI and RIKEN. The beamline is aimed at studies in a wide variety of materials for our sustainable vehicle technologies (*e.g.*, automotive exhaust catalysts, secondary batteries, and fuel cells). Our recent interest is focused on developing apparatuses and programs for *in situ* measurement and analysis.

Some features of the Toyota Beamline are a tapered undulator and a compact monochromator, enabling XAFS measurement with time resolutions of several tens of milliseconds (super quick XAFS). Figure 1 demonstrates the performance of our super quick XAFS system. XANES spectra for Cu foil were measured with various time resolutions in an angular range of 0.2°. Well-defined spectra are obtained with the highest time resolution of 10 ms/spectrum. This super quick XAFS measurement system can be a very useful tool to observe dynamic phenomena in the process of chemical reactions.

Other feature is a high-speed gas reaction analysis system in our experimental hutch. The system consists of (i) three independent gas-supply lines, (ii) a high-speed gas switching and mixing apparatus, and (iii) a mass spectrometer at a sampling rate of 50 ms. They are embedded in the wall of the experimental facility building. This gas reaction analysis system enables us to conduct *operando* XAFS measurements under various atmospheric conditions. For instance, in the case of exhaust catalysts, the chemical state and the molecular structure of catalytically active sites can be clarified from XAFS analysis, and the catalytic activity can be evaluated from the gas analyzer. This *operando* system can make a real-time visualization of catalytic working state.

As mentioned above, *in situ* or *operando* XAFS measurement is crucial for investigating dynamic phenomena (*e.g.*, clarifying mechanism of bond formation in a material process and variation of the oxidation number of active species in exhaust catalysts and in electrochemical energy devices). Recently, we have been developing a program of EXAFS fitting analysis based on IFEFFIT for an enormous amount of XAFS spectra. The program makes it possible for us to find the change in coordination states as well as that in oxidation numbers of the interested atoms. Some examples will also be shown in our poster.

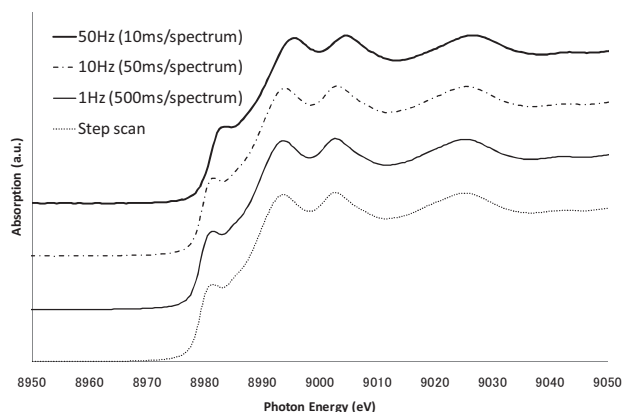


Figure.
Super quick XAFS spectra for
Cu foil obtained with various
temporal resolutions.

Dynamic Investigation of Photoinduced Phase Transition by picosecond time-resolved XAFS

Shunsuke Nozawa^a, Tokushi Sato^a, Ayana Tomita^b, Manabu Hoshino^b,
Hiroko Tokoro^c, Shin-ichi Ohkoshi^c, Shin-ichi Adachi^a, Shin-ya Koshihara^b

^aHigh Energy Accelerator Research Organization, Tsukuba, Japan.

^bTokyo Institute of Technology, Meguro-ku, Japan.

^cThe University of Tokyo, Bunkyo-ku, Japan.

E-mail: noz@post.kek.jp

Prussian blue analogs have recently attracted great interest due to their various characteristics in the photoinduced phase transition (PIPT) as a photo-induced magnetization as well as photo-induced structural change.[1,2] The investigation of the dynamics of PIPT allows us to obtain information how the photo-excitation in the single site expands into a macroscopic phase transition. Picosecond time-resolved XAFS experiments were performed on the NW14A at the Photon Factory Advanced Ring (PF-AR).[3,4] The time-resolved XAFS spectra were collected by the pump-probe technique with a femtosecond laser system. In EXAFS and XANES regions, transient features attributed to the PIPT were obtained at 100 ps resolution. The detailed results will be presented.

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Observation of the $^3\text{MLCT}$ state of $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$ by picosecond Time-resolved Ru K -edge XAFS

Tokushi Sato^a, Shunsuke Nozawa^a, Ayana Tomita^a, Manabu Hoshino^{b,c},
Shin-ya Koshihara^{b,c}, Shin-ichi Adachi^{a,d}

^a*Photon Factory (PF), High Energy Accelerator Research Organization, Ibaraki, Japan.*

^b*Department of Chemistry and Materials Science Tokyo Institute of Technology, Tokyo, Japan.*

^c*CREST, Japan Science and Technology Agency (JST).*

^d*PRESTO, Japan Science and Technology Agency (JST).*

E-mail: tokushi.sato@kek.jp

Ruthenium(II)-*tris*-2,2'-bipyridine ($[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$) has been extensively studied as an efficient photocatalyst for the conversion of solar energy.^[1-3] However, it is difficult to measure the structure of the $^3\text{MLCT}$ state with atomic resolution using conventional optical techniques. Thus, we conducted a study of the transient $^3\text{MLCT}$ state of $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$ using time-resolved X-ray absorption fine structure (TR-XAFS) to investigate the structure of the $^3\text{MLCT}$ state at KEK PF-AR undulator beamline NW14A.^[4,5]

The TR-XAFS study revealed that the Ru-N distances decrease in the $^3\text{MLCT}$ state compared with the ground state. The Debye-Waller factor increases in the $^3\text{MLCT}$ state, suggesting that the electron localized on a single bpy ligand causes structural distortion of the $^3\text{MLCT}$ state *versus* the ground state.

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Upgrade of the ESRF x-ray absorption spectroscopy beamlines:
The general purpose EXAFS beamline BM23

O. Mathon, T. Mairs and S. Pascarelli
ESRF, BP220, F-38043 Grenoble, France

In this poster, we describe the main features of the upgraded general purpose EXAFS beamline of the ESRF, BM23. This new beamline substitutes the former BM29, which has been closed in 2010. BM23 is optimized for standard EXAFS in transmission geometry in a large energy range (4-75 KeV). It also offers fluorescence detection, angle resolved XRD, as well as Quick-EXAFS on the second timescale.

Upgrade of the ESRF x-ray absorption spectroscopy beamlines:
The energy dispersive EXAFS beamline ID24

O. Mathon, T. Mairs and S. Pascarelli
ESRF, BP220, F-38043 Grenoble, France

In this poster, we describe the main features of the upgraded energy dispersive EXAFS beamline of the ESRF, ID24. The new ID24 has been rebuilt to host two independent EDXAS branches, which use beam on a time-shared basis. The new facility provides optimised x-rays for small and large spot activities, improved stability, and 1000-fold increase in time resolution for single shot studies.

Upgrade of the ESRF x-ray absorption spectroscopy beamlines: The scientific case

O. Mathon, T. Mairs and S. Pascarelli
ESRF, BP220, F-38043 Grenoble, France

The ESRF has started an ambitious project spread over 10 years aimed at an upgrade of the accelerator, beamlines and infrastructure. Through this upgrade, we have proposed a refurbishment of the scanning EXAFS beamline BM29 (rebuilt on BM23) and of the Energy Dispersive XAS (EDXAS) beamline ID24. This project (UPBL11), dedicated to time resolved and extreme conditions X-ray Absorption Spectroscopy, is the first of the upgrade projects to become operational: BM23 has been opened to user operation in March 2011 and the upgraded ID24 is planned to be operational for users starting in May 2012.

UPBL11 will provide the user community new opportunities for investigating industrially relevant materials, and matter at extreme conditions of pressure, temperature and magnetic field. Target experiments for the future include kinetic studies of chemical reactions at high pressure and temperature, and investigation of extreme states of matter that can be maintained only over very short periods of time.

High-accuracy measurements of the x-ray mass-attenuation coefficient of copperJ. L. Glover¹, C. T. Chantler¹, Z. Barnea¹, N. A. Rae¹, C. Q. Tran², D. C. Creagh³

¹*School of Physics, University of Melbourne, Parkville, Vic. 3010 Australia;* ²*Department of Physics, La Trobe University, Victoria 3086, Australia;* ³*Division of Science and Design, University of Canberra, Australian Capital Territory 2601, Australia*

The x-ray mass-attenuation coefficient of copper was measured at 108 energies between 5 and 20 keV using synchrotron radiation. The measurements are accurate to between 0.09% and 4.5%, with most measurements being accurate to better than 0.12%. The imaginary component of the form factor of copper was also determined after subtracting the attenuation contribution due to scattering. Measurements were made over an extended range of experimental parameter space, allowing us to correct for several systematic errors present in the data. These results represent the most extensive and accurate dataset of their type for copper in the literature and include the important and widely studied region of the *K*-edge and x-ray absorption fine structure. The results are compared with current theoretical tabulations as well as previous experimental measurements and expose inadequacies in both.

XAFS and XANES analysis: A study in errors

C. T. Chantler, J. L. Glover

School of Physics, University of Melbourne, Parkville, Vic. 3010 Australia

XAFS and XANES analysis are extremely effective and widely used techniques and can be used to obtain a multitude of parameters related to molecular and atomic structure and bonding. We will look at the limitations in the generic data collection approaches used worldwide with a view to how they limit XAFS and XANES analyses. A number of analysis techniques were investigated in both the near-edge and extended energy regions. Using experimental data of high accuracy and accurate theoretical tabulations of mass-attenuation coefficients, various experimental and analysis errors were simulated including harmonics, bandwidth, detector response and energy determination errors. Particular attention was paid to how these errors can affect the conclusions and derived parameters. We found the effectiveness of many XAFS and XANES analyses are limited by experimental and data reduction techniques, particularly relating to determinations of photon energy.