Beamline practice at BL28B2 (DXAFS)

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1 Introduction

The bending magnet beamline, BL28B2, is used for various applications of time-resolved energy dispersive XAFS (DXAFS). In the practical training course, we plan to show how to measure and analysis DXAFS spectra. We will also demonstrate in-situ time-resolved DXAFS measurement of catalyst samples under reaction condition.

2 Plan of practice

9:30 – Introduction of beamline, alignment of optics, major scientific activities at BL28B2.

10:00 – Setup of the DXAFS measurement system.

12:00 – Introduction of preliminary process of DXAFS spectra using software ATHENA.

12:30 – Lunch

13:30 – Introduction of in-situ DXAFS experiment and sample preparation.

14:00 – Setup of in-situ DXAFS equipment system.

15:00 – Measurement of in-situ DXAFS spectra of catalysts during reduction process.

16:00 – Data treatment and preliminary analysis of DXAFS spectra.

17:00 – Close.

3 Outline of DXAFS measurement at BL28B2

3.1 Measurement principle of DXAFS

Figure1 shows schematic of the DXAFS measurement system. White x-rays coming from the bending magnet or undulator light source are diffracted by a bent crystal in the polychromator and focused on the sample. The diffracted x-rays have different energies, depending on the diffraction angle. The x-rays are measured with a position-sensitive detector (PSD) at the position corresponding to their energy. X-ray intensity profiles measured with and without the sample are numerically converted into an absorption spectrum.

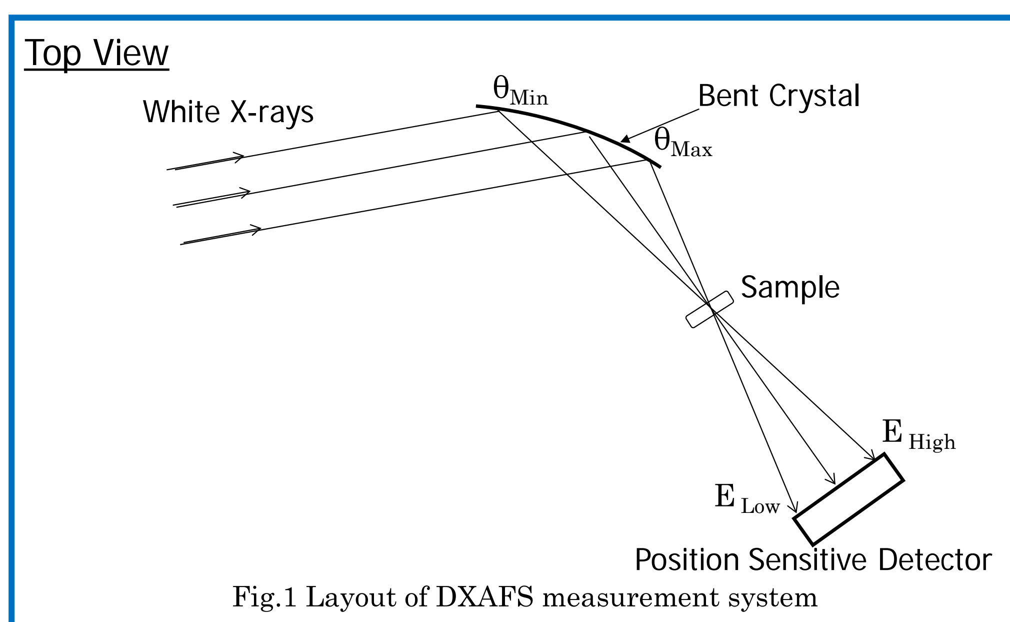

Fig.1 Layout of DXAFS measurement system

3.2 DXAFS station at BL28B2

Figure 2 shows schematic layout of DXAFS spectrometers at BL28B2. The station consists of polychromator, a mirror for cutting a higher harmonics x-rays and position sensitive detector (PSD). There are two types of polychromator; one is for the Laue configuration and another for the Bragg configuration. In the Laue configuration (Fig. 2(b)), the polychromator is a bender with a fixed radius curvature, R=2000mm. The polychromator crystal has Si (111) surface, with dimensions of 90(w) x 20(h) x 0.2(t) mm. In the Bragg configuration, the bender is a four-point bender, which can load an independent bending force on each end of the crystal with dimensions of 200(w) x 40(h) x 1(t) mm. In the energy region from 5 to 12 keV, the crystal is positioned using Bragg geometry (Fig. 2(a)). A Laue configuration is used for the net plane Si (hkk), such as Si (422) or Si (511), in the energy region above 12 keV because the energy resolution decreases due

to the depth of x-ray penetration into the crystal.

The PSD used is CCD (spatial resolution, 9.9 micrometer; minimum readout time, 6 msec) coupled with a fluorescent screen and a lens system (Fig. 3). The fluorescent materials and their thickness were optimized for measurement in the x-ray range.

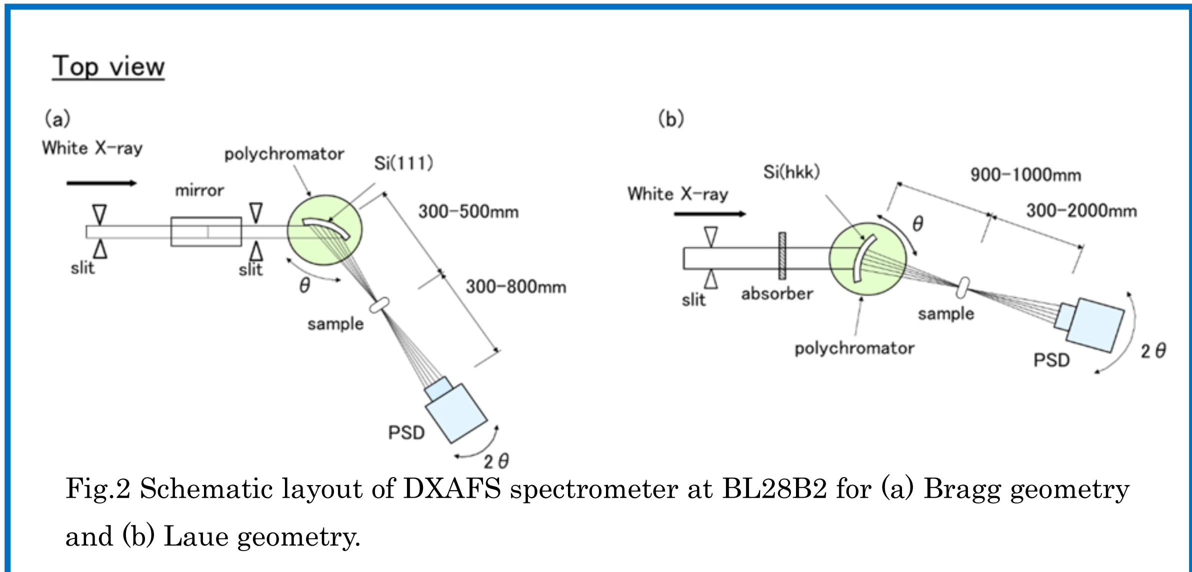

Fig.2 Schematic layout of DXAFS spectrometer at BL28B2 for (a) Bragg geometry and (b) Laue geometry.

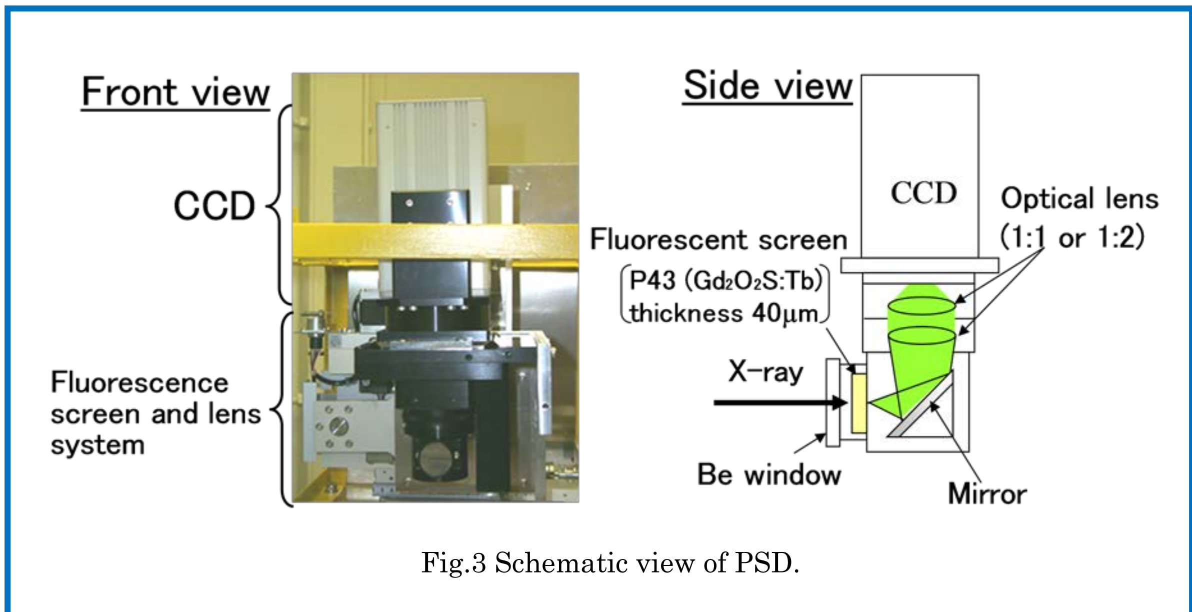

Fig.3 Schematic view of PSD.

4 Alignment of DXAFS spectrometer

- Set the polychromator for the Laue configuration.
- Roughly adjust the diffraction angle of the polychromator crystal to cover the energy range for the DXAFS measurement.
- Adjust the position of the 2 θ arm and PSD on the diffracted x-ray beam.
- Finely adjust the diffraction angle of the polychromator crystal by measuring the transmission image of the standard sample to set the absorption edge on the adequate position in the PSD image.
- Adjust the rotation angle around axis normal to the polychromator crystal surface to remove unwanted diffractions (glitches) observed in the PSD image.
- Adjust the tilt angle of the PSD for the vertical line of the PSD to be parallel to the absorption line.
- Find the focal point of the diffracted x-ray beam by slit scan in the horizontal direction, and set sample on the focal point.
- Adjust the PSD position to detect the DXAFS image.

5 DXAFS measurement of the standard sample

- Figure 4 shows the setup of the DXAFS measurement system in the Laue configuration.
- Set the standard sample at the focal point.
- Measure the I0 and I1 images by the PSD.
  - The I0 images are measured by removing the sample form the x-ray beam using a stepping motor stage.
- Set the measurement time of the PSD.
  - Select exposure time of the CCD not to saturate the CCD pixels.
  - Set the number of measurement images to achieve data quality enough for the XANES or EXAFS analysis, which decide the time resolution of the measurements.
- Measure the dark images.
  - The dark images are measured by closing the beam shutter.
  - The dark images are subtracted from the I0 and I1 images as the dark noise of the PSD.
  - The exposure time and number of the dark images are set to the same as those of I0 and I1.
- Calculate absorption spectrum
  - After subtracting the dark images, I0 and I1 images are summed each other.

   - The 2-dimensional I0 and I1 data are summed in the vertical direction to get 1-dimensional I0 and I1 data.
   - The absorption spectra are calculated by dividing I1 by I0 and calculating logarithm.
- Calibrate the x-ray energy
   - The horizontal axis of the PSD in the absorption spectra is converted to the x-ray energy by comparison with the conventional XAFS spectra of the same standard sample.

6 Preliminary process of XAFS spectra using software ATHENA

- The row data of DXAFS spectra are processed to the ATHENA-readable data format.
- ATHENA processes the measured XAFS spectra, such as background removal and Fourier transforms.
   - ATHENA is one of most popular free software for processing XAFS data. http://cars9.uchicago.edu/~ravel/software/
   - Model fitting of XAFS data is done by another software ARTEMIS including interfaces to ATOMS and FEFF.

7 Measurement of in-situ DXAFS spectra

7.1 Sample preparation

- The sample for the in-situ DXAFS measurement is packed into the cylindrical sample holder by hand with very weak pressing force.（Fig.5）.

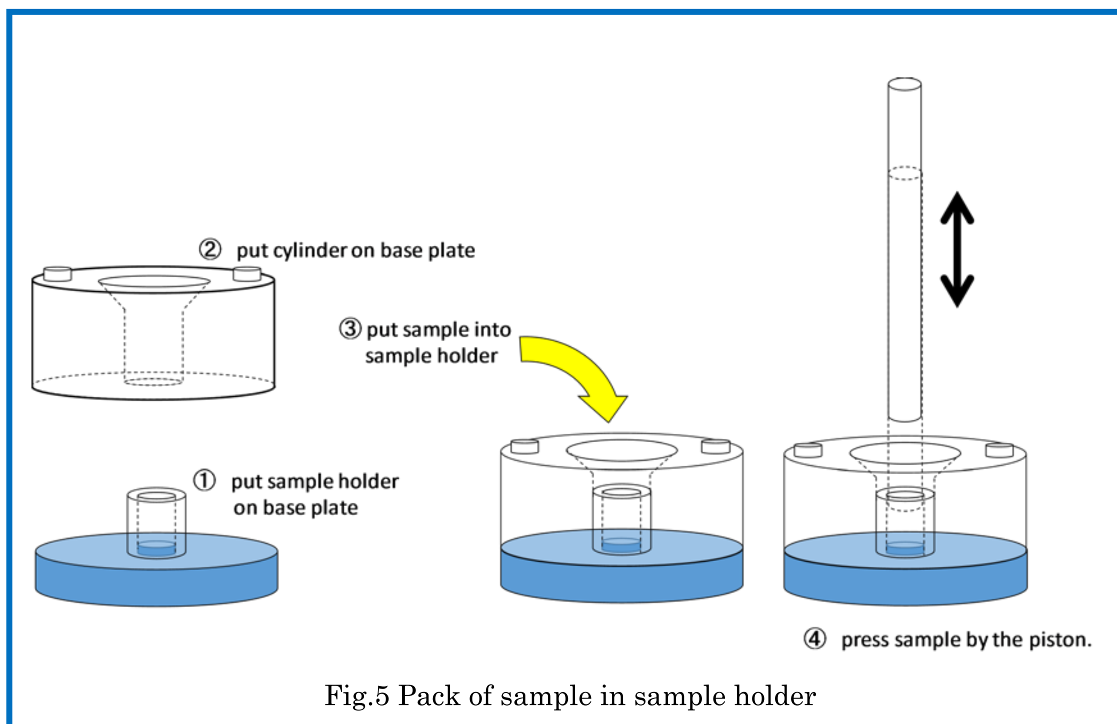

Fig.5 Pack of sample in sample holder

7.2 Setup of in-situ DXAFS equipment

- Experimental condition in this in-situ measurement.
  - Sample: Pd/USY catalyst.
  - Measurement energy: around Pd K– edge (24.3keV)
  - Sample temperature: room temperature.
  - Reaction gases: H_2 and He and their mixture.
- Set the sample cell including the sample.
- Connect q-mass outlet of the sample cell to monitor the concentration of each outlet gases (Figs. 6 and 7).

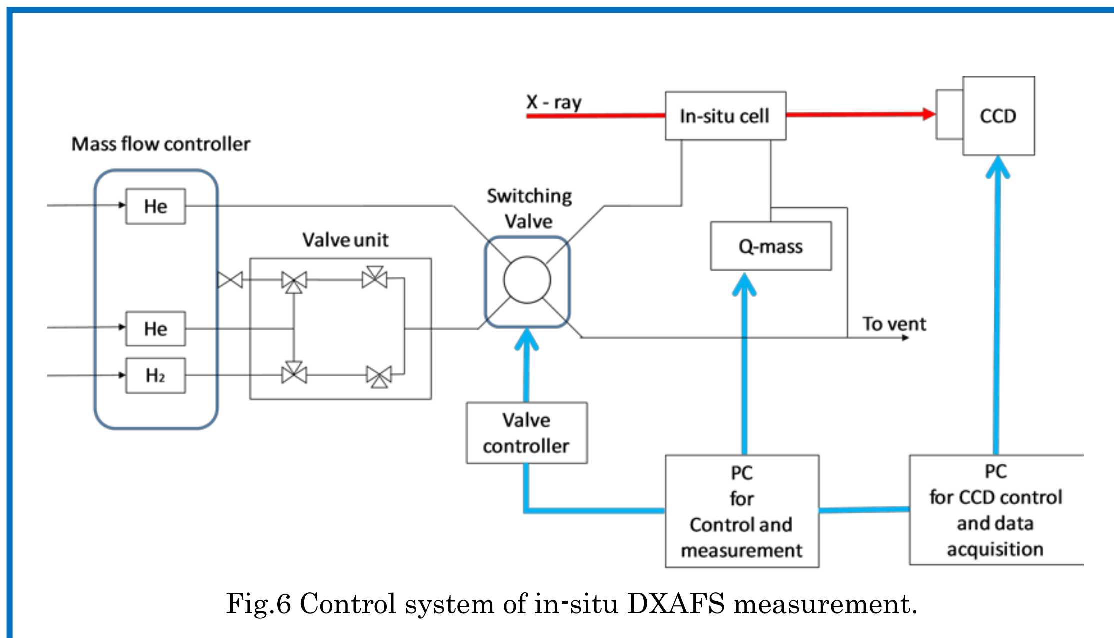

Fig.6 Control system of in-situ DXAFS measurement.

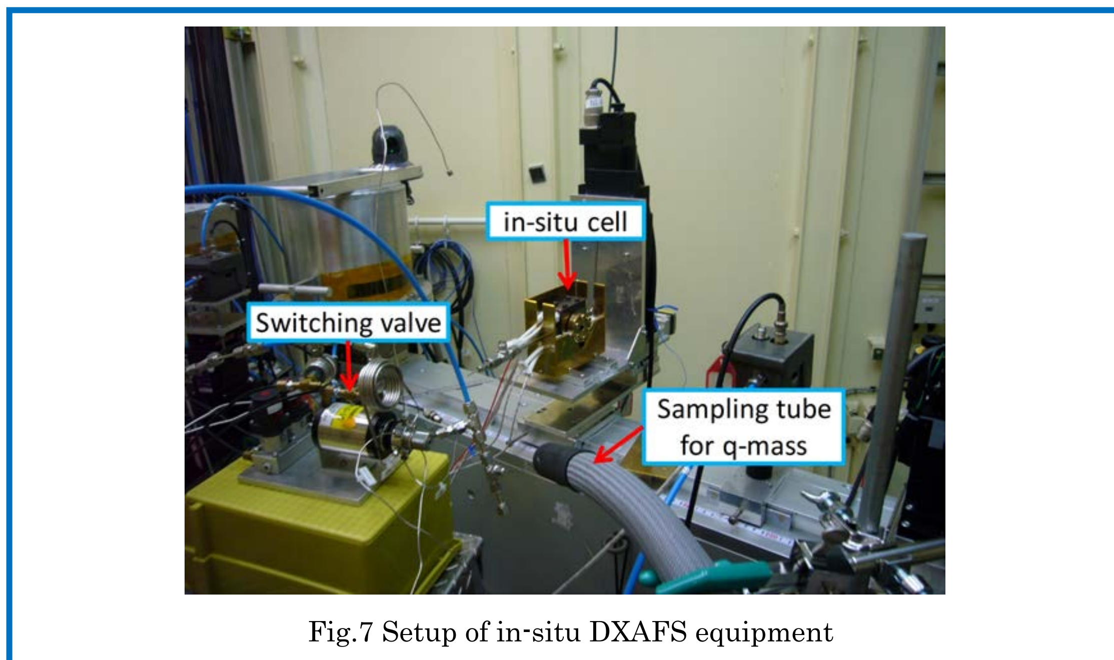

Fig.7 Setup of in-situ DXAFS equipment

7.3 In-situ DXAFS measurement of catalyst during reduction process.

- DXAFS measurement of the catalyst in initial state.
  - Flow 100% - He 90ccm into the sample cell.
  - Measure DXAFS spectra.
- DXAFS measurement of the sample during reduction process.
  - Flow 8% - H_2/He 90ccm (H2: 7 ccm, He: 83 ccm) into the sample cell for 15 - 20 min.

- Continually measure DXAFS spectra every 5 min during gas flow.
- Check changes of Fourier transform–DXAFS spectra during reduction process using ATHENA.
- Switch 8%-H_2/He to 100% - He flow.
- Flow 100% - He for 10 – 15 min until no residual H_2 in the sample cell (checking by Q-mass).
- Measure DXAFS spectra.
- Check the sample color.