

Application of a CdTe Solid-State Detector to Polarization-Dependent Total-Reflection Fluorescence XAFS Measurements

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A CdTe solid-state detector was applied to the measurement of polarization-dependent total-reflection fluorescence XAFS spectra. The data revealed that the detector has good sensitivity, and this, together with its compact size, make it appropriate for *in-situ* measurements and removal of X-ray Bragg diffraction. The detector efficiently recorded the high-energy *K*-edge XAFS spectra for molybdenum oxides supported on TiO₂ (110).

Keywords: polarization-dependent total-reflection fluorescence XAFS; CdTe detectors; molybdenum oxide; titanium oxide (110).

1. Introduction

X-ray absorption fine-structure (XAFS) spectroscopy is one of the most useful techniques for the characterization of supported metal catalysts in that it can provide information on bond lengths and coordination number around particular metal sites (Teo, 1986; Koningsberger & Prins, 1988). Since the catalytic properties of supported metals and metal oxides are strongly affected by the morphology of the particle and the interaction with the support, it is indispensable to clarify the active-site structure. However, conventional XAFS spectroscopy using a powder sample has the disadvantage of averaging XAFS information over all directions.

Applying polarized synchrotron radiation to a model catalyst with active sites on a flat surface, it has been possible to separate the information in directions parallel and perpendicular to the surface and to obtain the anisotropic structure of active sites by analyzing polarization-dependent XAFS spectra. The total-reflection fluorescence technique has also been applied as a surface-sensitive technique for heavy elements (Heald, Keller & Stern, 1984). Under these considerations we have applied polarization-dependent total-reflection fluorescence XAFS (PTRF-XAFS) and successfully determined the three-dimensional active-site structure of catalysts supported on flat substrates such as α -Al₂O₃ and quartz (Shirai, Asakura & Iwasawa, 1992; Shirai, Inoue, Asakura & Iwasawa, 1994; Shirai & Iwasawa, 1996).

We have employed a CdTe solid-state detector for the PTRF-XAFS measurements. CdTe is a II–VI semiconductor material having a band gap of 1.47 eV, which can be used as a detector at room temperature (Schlesinger, James, Siffert & Franks, 1993; Siffert, 1983; Zanio, 1978). Moreover, it

has a high X-ray stopping power due to the high atomic numbers of the elements (Cd = 48, Te = 52), which is enough for developing a high-sensitivity PTRF-EXAFS system. In this paper we report the application of the CdTe detector to a PTRF-XAFS study on molybdenum oxides supported on TiO₂ (110).

2. Experimental

CDTE-XBE (Toyo Medic Co. Ltd., Japan) (Fig. 1), a CdTe solid-state detector, was used to monitor the X-ray

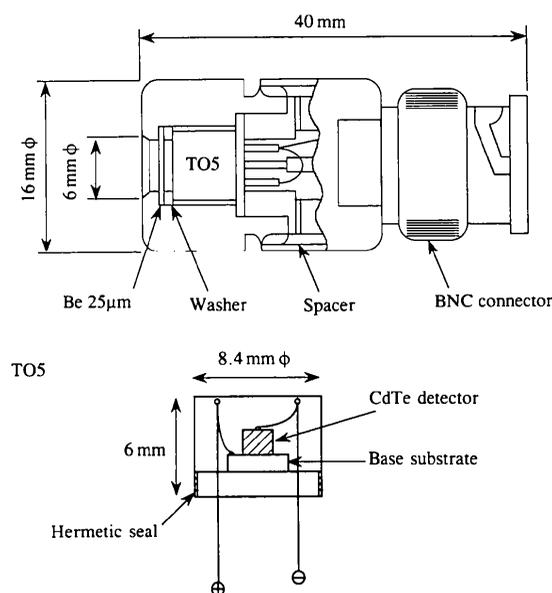


Figure 1
Layout of a CDTE-XBE (CdTe solid-state detector) system.

fluorescence signal from the sample. In this study we employed a CdTe single-crystal ($4 \times 4 \times 2 \text{ mm}^3$) detector for achieving high efficiency. The energy resolution of the detector is 4.5 keV at 54.8 keV. The PTRF-XAFS measurements were carried out at room temperature. We placed the detector as close as possible to the window of the *in-situ* cell where no Bragg diffraction having sharp directionality was observed.

Measurements were performed at BL14A of the Photon Factory at the National Laboratory for High-Energy Physics (KEK-PF). A four-circle goniometer was used to set the particular orientation of the sample against the polarization direction of the incident X-ray and to achieve the total reflection condition. The incident X-ray was monitored by an ion chamber filled with Ar. The PTRF-XAFS spectra at the Mo *K* edge for molybdenum oxide on TiO_2 (110) were obtained with the electric field vector parallel to the [001] direction of TiO_2 (110).

The TiO_2 (110) single crystal ($20 \times 40 \times 1 \text{ mm}^3$) (Earth Jewelry Co. Ltd, Japan) was annealed for 5 h at 823 K in air. Molybdenum oxide was supported on the TiO_2 (110) surface by an impregnation method using an aqueous solution of heptaammonium molybdate, followed by calcination at 773 K. The sample was mounted in a small *in-situ* cell, illustrated in Fig. 2. Details of the sample preparation will be described in a separate paper.

3. Results and discussion

3.1. CdTe detector

Using synchrotron radiation from BL14A at KEK-PF to excite the $K\alpha$ fluorescence lines from molybdenum and titanium of the sample, we compared the measurement of a benchmark with three different-sized (1–4 mm^2) CdTe detectors. The detectors exhibited an energy resolution of *ca* 4 keV FWHM for the Mo $K\alpha$ line. The $4 \times 4 \times 2 \text{ mm}^3$ CdTe single crystal was found to have good efficiency in Mo *K*-edge XAFS measurements. However, in the photon energy region below 10 keV, the pulse height of the X-ray fluorescence signal was at the same level as the noise. Thus, the application of a CdTe detector is limited to fluorescent X-ray measurement at energies higher than 10 keV.

3.2. Mo *K*-edge XAFS

We used a specially devised small cell for the Mo sample applicable to *in-situ* measurements, as shown in Fig. 2. Since the total counting rate is 10^3 – $2 \times 10^4 \text{ counts s}^{-1}$ due to the small size of the incident X-ray, it is desirable to place the detector as close to the window of the cell as possible. Large detectors such as a solid-state detector or a conventional scintillation counter could not be placed close to the sample surface because of the geometrical hindrance of the *in-situ* cell. The small and light CdTe detector is an ideal solution in this sense. We set the CdTe detector close to the window of the cell (within 1 mm) using a simple adjustment device. Since the Bragg diffraction has a sharp

directionality, the adjustment device made it easy to find the non-Bragg parts of reciprocal space for the CdTe detector.

Fig. 3(b) shows the PTRF-XANES spectra at the Mo *K* edge in the 19 950–20 100 eV energy region recorded by the CdTe detector. The measuring time for each point was only 5 s. For comparison, the spectrum was also measured

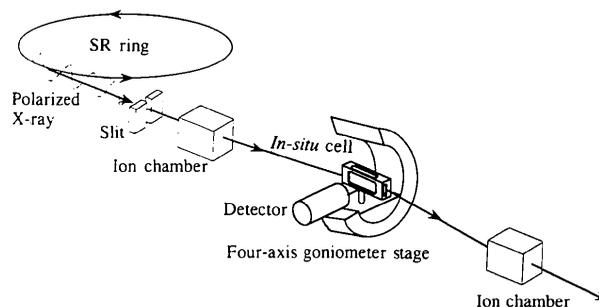


Figure 2 Schematic diagram for a PTRF-XAFS measurement system with an *in-situ* cell.

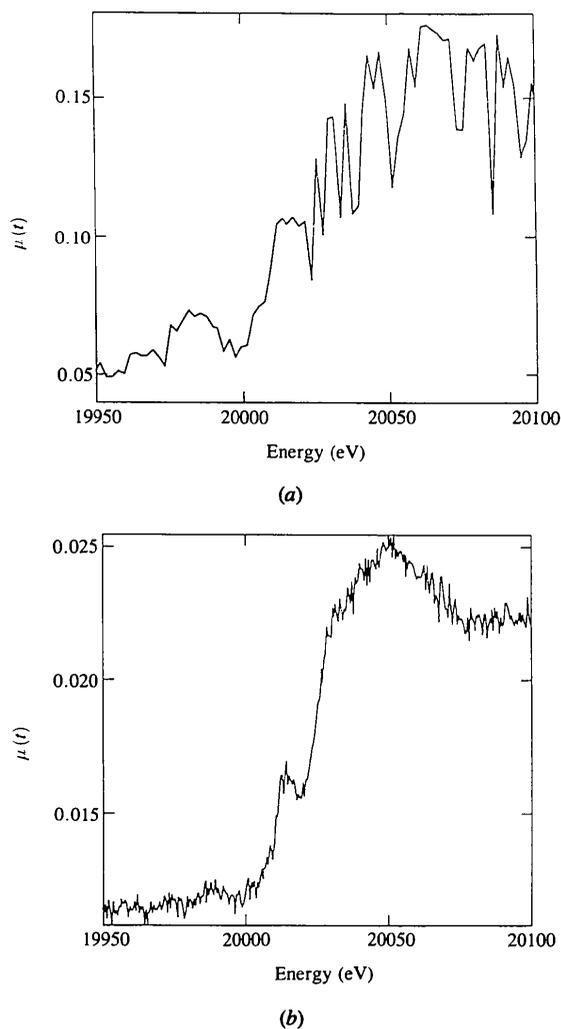


Figure 3 Mo *K*-edge PTRF-XANES spectra for molybdenum oxide on TiO_2 (110) recorded by (a) a NaI scintillation counter, and (b) a CdTe detector.

by an NaI scintillation counter ($45\phi \times 120$ mm), as shown in Fig. 3(a). Since the size of the scintillation counter was large, it was difficult to place it to within even 30 mm of the window of the cell. Thus, the signal-to-noise ratio of the spectrum was very low with the scintillation counter. It is clear that the quality of the spectra is much improved by employing the CdTe detector. The $1s \rightarrow 5p/4d$ transition peak in the *K*-edge region can be seen distinctly in the case of the CdTe detector. The XANES spectrum indicates a Td structure around the Mo atom (Evans & Mosselmans, 1991).

4. Conclusions

The CdTe detector showed good efficiency and high cost-performance in the measurement of *in-situ* PTRF-XAFS spectra. The small detector made it easy to avoid Bragg diffraction from the substrate by setting it at an appropriate position and direction. The price of the detector including a preamplifier and a main amplifier was not high (\$5000). The compact body and cheap price of the CdTe detector are a great advantage when constructing a multi-element detection system. However, the CdTe detector has a fatal disadvantage: owing to the high noise peak height in the low-energy region it is difficult to use the CdTe detector for elements with X-ray absorption edges lower than 10 keV.

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