

## Experimental comparison between the conversion electron yield and X-ray fluorescence in catalyst analysis

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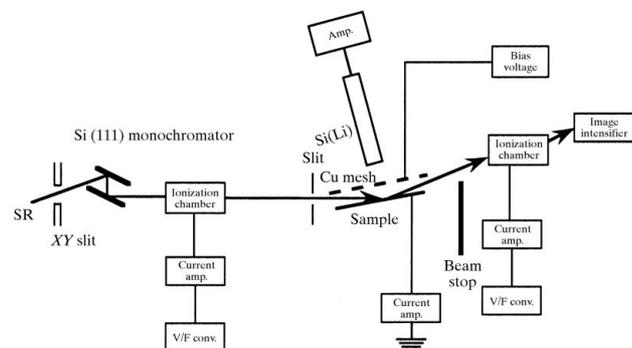
To evaluate the application of the conversion-electron-yield (CEY) method in catalyst analysis, the intensities of the CEY and X-ray fluorescence (XRF) as a function of glancing angle were measured simultaneously. The probing depth of the CEY method is shallower than that of the XRF method. The CEY method also shows potential application for the analysis of even a powder specimen of a low-concentration zeolite catalyst.

**Keywords:** CEY; XRF; XANES; zeolites.

### 1. Introduction

Since most catalytic reactions are typically carried out in a gas environment, characterization of the catalyst by an *in situ* analytical technique is particularly needed. Although X-ray absorption near-edge structure (XANES) spectroscopy has been recognized as a powerful technique for *in situ* measurements in transmission methods (Kuper & Macromol, 1994) and X-ray fluorescence (XRF) methods (Herron *et al.*, 1992), these methods probe the bulk properties of solids rather than their surface properties. X-ray total reflection combined with fluorescence detection is better suited for studying thin films, since the X-ray penetration is typically only 50 Å or less (Shiral *et al.*, 1995). However, almost all studies of the active metal sites of solid catalysts have been carried out on powder samples. XRF from a very thin film or a specimen with a dilute absorbing species is commonly assumed to be proportional to the absorption coefficient. The absorption spectra measured by XRF, however, are distorted when the fluorescence signal is obtained from a thick specimen containing concentrated absorbers (Iida & Noma, 1993).

The conversion-electron-yield (CEY) method is an *in situ* technique. It is carried out in a gas environment and measures the



**Figure 1**  
The schematic experimental set-up for the measurement of CEY and XRF at atmospheric pressure.

electrons resulting from ionization events initiated by high-energy electrons emitted from the specimen. This technique has only recently been used in catalyst studies (Moggridge *et al.*, 1992). The present paper compares the application of the CEY and XRF methods in catalyst research. To compare the probing depths of the two methods, the intensities of the CEY signal and the XRF as functions of the glancing angle were measured simultaneously for 1300 and 200 Å Au films on Si wafers at 13 keV photon energy and atmospheric pressure. The CEY method of detecting XANES was also used for a concentrated specimen. In addition, we tried to extend the use of the CEY method to the determination of the surface chemical state of low-concentration Ni adsorbed on a zeolite.

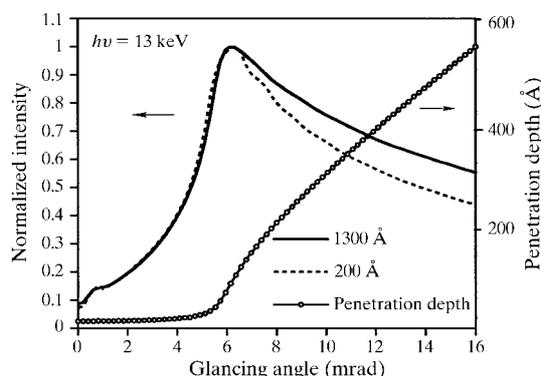
### 2. Experimental

Experiments were performed on beamline 4A at the Photon Factory, National Laboratory for High Energy Physics (KEK), Tsukuba, Japan. The apparatus for measuring the glancing-angle dependence of the CEY and the XRF is shown in Fig. 1. Beamline 4A is equipped with an Si(111) crystal monochromator. A biased (+50 V) copper grid was placed 2 mm from the specimen surface to enhance the detection efficiency of ion–electron pairs. The specimen current was measured with a current amplifier. The X-ray fluorescence was detected by a solid Si(Li) detector positioned perpendicular to the specimen surface.

The Au specimens studied were 200 and 1300 Å Au films evaporated onto Si wafers. To prepare the zeolite specimens, samples in powder form were placed on an Al plate and several drops of ethanol were applied to the powder. The specimens were dried and mounted on the specimen holder. Zeolite Ni/H-ZSM-5 (0.1 wt% loading) was prepared using a commercially available reagent with a zeolite of silica-to-alumina ratio of 44:1. Ni was introduced by the ion-exchange method.

### 3. Results and discussion

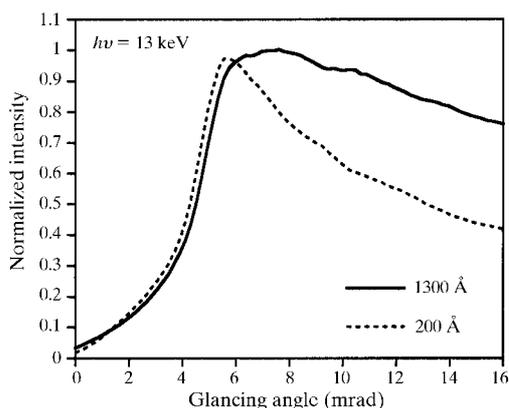
The glancing-angle dependence of the CEY for 1300 Å (solid line) and 200 Å (dashed line) Au films on Si wafers is shown in Fig. 2. The profiles have been normalized to the maxima in the curves. If the X-rays penetrate deeper than 200 Å, all of the electrons from the 1300 Å film would be excited from Au atoms. However, for the 200 Å Au film, some electrons would be excited from the Si



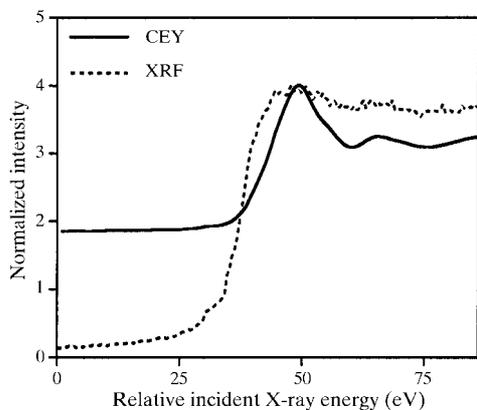
**Figure 2**  
A comparison of the experimental glancing-angle dependence of the CEY signal for the 1300 (solid line) and 200 Å (dashed line) Au films, and the calculated glancing-angle dependence of the X-ray penetration depth (open circles).

substrate. The number and depth of excited electrons are proportional to the element absorption coefficient and the effective absorption length. Thus, the numbers and depths of electrons excited from 1300 and 200 Å Au films would be different if the X-rays penetrated more than 200 Å. However, the two specimens show almost identical curves. We therefore deduce that all of the detected electrons originated from Au layer atoms at less than 200 Å depth. The glancing-angle dependence of the XRF of Au  $L\alpha$  from the 1300 (solid line) and 200 Å (dashed line) Au films on Si wafers is plotted in Fig. 3. These profiles were also normalized to the maxima in the curves. The intensity of Au  $L\alpha$  XRF from the 200 Å film was only 54% of that from the 1300 Å film at a glancing angle of 16 mrad, confirming that the probing depth of the XRF method at 16 mrad is deeper than 200 Å.

There is a slight discrepancy between the signals for the 200 and 1300 Å Au film specimens at deeper X-ray penetration depths in Fig. 2, where the signal intensity for the 1300 Å Au film is slightly stronger than that for the 200 Å Au film. The difference can be interpreted as follows. When the incident X-rays penetrate into regions beyond 200 Å, the XRF from these regions are Au  $L\alpha$  and  $L\beta_2$  for the 1300 Å Au film, and Si  $K\alpha$  for the 200 Å Au film. The energies of Au  $L\alpha$  and  $L\beta_2$  are 9.711 and 11.58 keV, respectively, and the energy of Si  $K\alpha$  is 1.739 keV. For elemental Au, the average  $M$ -shell binding energy [ $E_m = (E_{m1} + E_{m2} + E_{m3} + E_{m4} + E_{m5})/5$ ] is 2.763 keV. Thus, the Si  $K\alpha$  fluorescent X-rays do not have sufficient energy to excite Au  $M$ -shell photoelectrons. On the



**Figure 3**  
A comparison of the experimental glancing-angle dependence of the XRF signal for the 1300 (solid line) and 200 Å (dashed line) Au films.

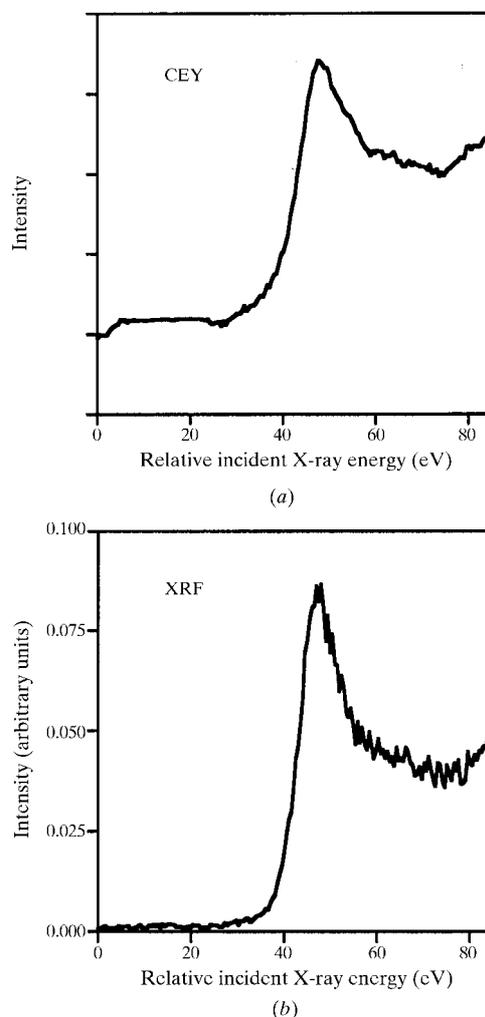


**Figure 4**  
Normalized CEY (solid line) and XRF (dashed line) Ni  $K$ -edge XANES spectra for NiO powders.

other hand, Au  $L\alpha$  and  $L\beta_2$  fluorescence can excite Au  $M$ -shell photoelectrons, and some  $MNN$  Auger electrons from nonradiative processes are emitted. Therefore, more electrons arise from fluorescent excitations for the 1300 Å Au film than for the 200 Å Au film.

The surface-sensitive total-electron-yield (TEY) method is appropriate for studying surface properties when the near-surface region has different properties from the bulk (Kawai *et al.*, 1995). Although the probing depth of the CEY method is deeper than that of the TEY method, owing to selective detection of high-energy electrons in the CEY method (Zheng *et al.*, 1997), it is much more surface sensitive than the XRF technique.

Fig. 4 shows Ni  $K$ -edge XANES spectra for NiO powders. The profiles are normalized to the maxima in the curves. A higher edge-jump ratio (which is defined as the apparent edge jump divided by the apparent background yield) is found for the fluorescence spectrum. However, a very big deformation of the fluorescence spectrum is clearly observed because of a self-absorption effect. On the other hand, the CEY method gives a good measurement of the X-ray absorption cross section, because the escape depths of the electrons are far shorter than the X-ray penetration.



**Figure 5**  
(a) CEY and (b) XRF Ni  $K$ -edge XANES spectra of 0.1 wt% Ni adsorbed on a zeolite. Both spectra were normalized to the incident beam. The vertical scales are arbitrary.

Fig. 5 shows the absorption spectra of a practical catalyst specimen of Ni/H-ZSM-5. The spectra have been normalized to the signal of the incident-beam monitor. The shape of the peaks occurring at the absorption edge is almost identical to that of the CEY spectrum of NiO shown in Fig. 4. Although it is well known that XRF is particularly effective for trace-component analysis by XANES, the results presented here demonstrate that the CEY method is also effective for the chemical-state analysis of very low concentrations (0.1 wt%).

#### 4. Conclusions

To study catalyst reactions on solid surfaces, it is very important to acquire information from the surface region under real-gas conditions. The CEY method does not require a high vacuum. Our experimental results imply that the CEY method is more surface sensitive than XRF, which is advantageous for catalysis analysis. Our experimental results also demonstrate that the CEY method is effective for the detection of low concentrations (0.1 wt%), so it is useful for the study of the near-surface regions of low-concentration zeolites. In addition, XANES spectra measured by the CEY method are far less distorted for high concentrations than those measured by the XRF method. Although transmission methods also show no deformation of the spectra at high concentration, they require the preparation of a specimen of appropriate thickness. In contrast, the CEY method is directly applicable to powders, and practically there is no limitation to the

thickness of the specimen. Thus, the CEY method is more convenient than transmission methods for practical applications.

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