9A/2000P018

Sulfur K-edge XAFS Study of Supported Ruthenium Cluster Catalysts

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Sulfur K-edge is the direct electronic and structural probe of catalytic fixation for SO_2. However, only limited studies of S K-edge were reported for heterogeneous catalysts because S K-edge is in soft X-ray region, and it is difficult to measure the edge for heterogeneous catalysts in the presence of reaction gas. Instead of S K-edge measurements in vacuum chamber, conventional fluorescence detection setup was used for supported ruthenium cluster catalysts by purging all the beam path from the XY slit in front of I_0 ion chamber to sample room with He. The I ion chamber was purged with N_2 (Figure 1). The sample catalysts were prepared by reacting $[Ru_6C(CO)_{16}]^{2-}$ cluster crystal with TiO_2 powder. Ru content was 1.5wt%. The SO_2 fixation reactions were performed in the presence of H_2 at 443 – 503 K in gas flow system at ambient gas pressure.

The supported cluster catalysts, denoted as $[Ru_6C]/TiO_2$, exhibited remarkable contrast of reactivity; the conversion of SO_2 was 85 and 0% at the reaction temperatures 503 and 443 K, respectively. Figure 2 shows the S K-edge XANES spectra after the SO_2 fixation reactions for the $[Ru_6C]/TiO_2$ catalysts. Two strong peaks were observed at 2474.1 and 2479.0 eV in the case of reaction at 503K (Figure 2a) near the edge. The two peaks were also observed in the case of reaction at 443K, but two peaks at 2472.6 and 2482.7 eV were rather stronger (Figure 2b).

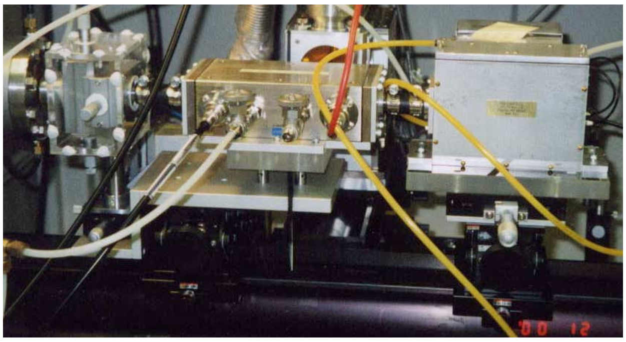

Figure 1. The detection system of S K-edge XAFS measurements utilizing He purge.

Compared to S K-edge spectrum for RuS_x, the peaks at 2472.6 and 2482.7 eV are ascribed to S^{2-} species. Taken the edge jump of Figure 2a and b (0.13 and 0.011, respectively) into account, the intensity ratio of the peak of 2472.6 eV was 17 : 4.9 for Figure 2a and b. Ionic Ru sites reacted with sulfur, e.g. RuS_2, may be more reactive for the reaction $SO_2 + 2H_2 \rightarrow S + 2H_2O$. The assignment of the peaks at 2474.1 and 2479.0 eV are under investigation.

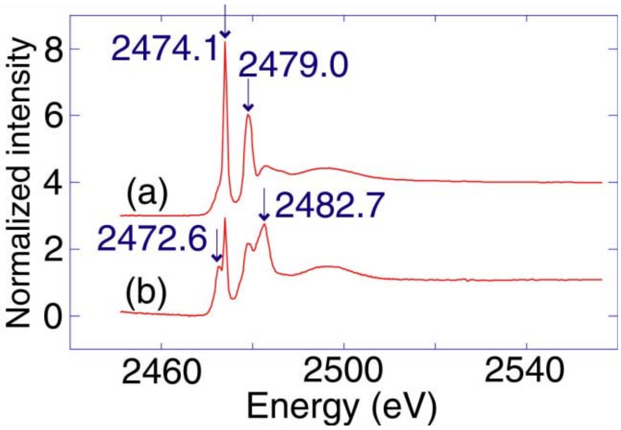

Figure 2. S K-edge XAFS spectra of $[Ru_6C]/TiO_2$ catalyst after the SO_2 fixation in H_2 at 503 (a) and 443K (b).

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