Investigation of local structure of Re active site of Re/HZSM–5 catalysts by Re–K edge EXAFS

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We have found that Re/HZSM–5 catalyst possesses an unique property in olefin selective oxidation and ammoxidation. The catalyst produce acrolein and acrylonitrile quite selectively. The catalytic properties is affected by the type of zeolite, counter cations, and preparation conditions. Only Re/HZSM–5 prepared by CVD shows good catalytic performances. In addition, the reaction is promoted by coexisting ammonia in catalytic conditions. No acrolein nor acrylonitrile was produced in the absence of ammonia. In this study, we measured Re–K edge EXAFS to elucidate the active Re species and origin of ammonia promotion effect.

The Re/HZSM–5 catalyst was prepared by chemical vapor deposition (CVD) of CH_3ReO_3 to HZSM–5 which is evacuated at 673 K before CVD. The sample was heated at 673 K after CVD. The loading of Re was 5 wt%.

The spectra were recorded at 13 K in a transmission mode. A Si(511) double crystal was used as monochromator. K^3 weighted EXAFS functions were Fourier transformed into R–space and curve fitting analysis was done in a R–space using UWXAFS package. The k range for Fourier transformation was 40–140 nm^{-1}. The phase shift and backscattering amplitude were calculated by the FEFF8 code.

Table 1 shows results of curve fitting analysis for the samples after CVD and after heating. The fitting was dome properly indicated by small residual factors. The fitting R–range for the sample after CVD and after heating were 0.1–0.2 and 0.1–0.4 nm, respectively.

After CVD, Re–O and Re–C contributions were observed at 0.170 nm (coordination number (CN) = 3.2) and 0.204 nm (CN = 1.2), respectively. No longer distance contributions were observed. The structural parameters calculated by curve fitting analysis agree with those of CH_3ReO_3, which suggest that the CH_3ReO_3 species retained the structure after CVD.

When the sample was heated at 673 K, Re–Re contributions at 0.27–0.38 nm were observed as shown in Table 1. The structural parameters were somehow similar to those of ReO_2. However, the local structure of the sample after heating was significantly different from that of bulk ReO_2. The biggest difference is in the structural parameters for nearest Re–Re contribution. The distance and coordination number (CN) of the nearest Re–Re contribution after heating were 0.277 nm and 3.2, while those in bulk ReO_2 were 0.261 nm and 2.0. This result indicates that small ReO_x clusters were formed after heating. Small CN (0.6) for second nearest Re–Re contribution in the sample also indicates the formation of small clusters.

EXAFS studies of samples after exposed to NH_3, to $O_2 + C_3H_6$ and after ammoxidation reaction indicate that The ReO_x small clusters were stabilized by ammonia. The ReO_x clusters converted into isolated [ReO_4] species in the absence of NH_3.

As conclusions, small ReO_x cluster is the active species for selective oxidation of ammoxdation of olefin, and they are stabilized by coexisting ammonia in reaction conditions.

Table 1. Structural parameters for Re/HZSM–5 samples delivered by Re K–edge EXAFS.

sample / shell	CN	R / 0.1 nm	σ / 10^{-4} nm	ΔE_0 / eV	Rf / %
after CVD 5 wt%					
Re–O	3.2	1.70	3	7	0.4
Re–O	1.2	2.04	6		
after pretreatment 5 wt%					
Re–O	2.2	2.00	3	12	0.7
Re–O	1.1	2.11	6		
Re–Re	3.3	2.77	7		
Re–Re	0.6	3.71	7		

Polarization Dependence of the Local Structure of Crystal Thin Film of Alkali Halides

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Single crystals grown in a cell composed of a pair of thin quartz plates have been extensively studied mainly in the energy region of intrinsic absorption of valence electrons.[1)] As the thickness of the samples is typically less than of the order of μm, the transmission of the photons in the intrinsic absorption region can be measured. The materials show various interesting properties such as shift in energy of the absorption edge, appearance of new emission bands. The properties have been interpreted due to the strain caused by the confinement of the crystal into very thin region between two quartz plates. However, no direct observation of the deformation of the materials has been done so far.

X-ray absorption is one of the appropriate techniques for the study. As the sample grown in a very thin space between two quartz plates, a strong strain is caused on the surface of the sample, resulting in a deformation of the local lattice. Moreover, the deformation of the lattice in the plane parallel to the quartz plate may be different from that perpendicular to the plate. If it is the case, a dichroism may be observed in the absorption spectra taken for two configurations of sample settings; that are the surface of the quartz plate placed parallel to the polarization of the beam (parallel setting), and perpendicular to it (perpendicular setting). In the experiment of proposal 1999B0070, we succeeded to perform simultaneous measurements of absorption and fluorescence at BL01B1 with a "parallel configuration" of the sample setting.

In order to extend the measurement, we tried to again the absorption measurements both with the parallel and the perpendicular settings for Cs K edge of CsI. As the lifetime broadening of the Cs K-XAFS spectrum is remarkable, the absorption measurements must be performed at low temperature.

The sample cell was fixed on a small goniometer to tilt about 2° from the horizontal surface for the parallel setting. For the perpendicular setting, the sample cell was mounted perpendicularly to the goniometer. The goniometer was then mounted in the cryostat to cool the sample down to about 30 K.

Figure 1 shows the absorption spectrum for both configuration measured at low temperature at about 30 K.

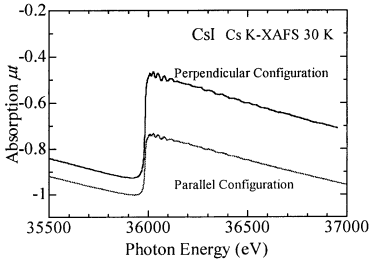

Figure 1. Absorption spectra of Cs K-XAFS measured with parallel and perpendicular configurations at about 30 K.

As is clearly seen in the Figure, the absorption spectra for both configuration was successfully measured. We are now analyzing data with comparing the spectra of the powder sample.

Reference: 1. M. Inaba and S. Hashimoto, Phys. Stat. Sol. (b) **195**, 433 (1996).