Analysis of the external surface of Y zeolites with XPS depth profiling

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Introduction

Proton-exchanged Y-type (HY) zeolites with low Al/Si ratios are extensively used as catalysts in fluid catalytic cracking (FCC) and hydrocracking of petroleum feedstocks. When a HY zeolite is used in heavy oil cracking, particularly when used as a hydrocracking catalyst, diffusional limitation of large molecules in micropores of HY zeolites is a serious and unavoidable problem; namely, the catalytically active sites of HY zeolites are limited to the external surface of the particles, including the mesopore surface.

X-ray photoelectron spectroscopy (XPS) is extensively used for the surface characterization of catalysts because of its capability to analyze the chemical composition, chemical states and depth profiling. In conventional XPS analyses employing characteristic x-ray source such as Mg Kα or Al Kα, however, the surface sensitivity is restricted by the large information depth, which is estimated as about 60 $\AA$ in case of Al or Si in the zeolite. In this study, we measured the Al/Si ratios with depth profiling using the synchrotron radiation, comparing with the conventional methods.

Experimental

HY zeolites were obtained from Na Y zeolite (NaY) by ion exchange using an aqueous solution of $(NH_4)_2SO_4$ and calcining in dry air. This ion-exchange cycle was repeated three times. Al/Si ratio of the zeolite framework was estimated from the unit cell constants, which were determined by X-ray diffractometry. Bulk Al/Si ratio was measured using the ICP analysis.

The XPS measurements were performed at BL13C station using a chamber with a hemispherical electron analyzer. The entrance and exit slit width of the beamline was set at 20 μm. XPS measurements were carried out at the pass energy of 29 eV with the energy range of 260–890 eV. The XPS spectra excited by a conventional Mg Kα was also analyzed. Al/Si ratio was determined from the areas of Al 2p and Si 2p peaks corrected by the photoionization cross sections[1]. The IMFP value of each energy was calculated using a modified Bethe equation and the parameters for SiO_2[2].

Results and Discussion

Table 1 shows the Al/Si ratios in the framework and and bulk of the zeolites. Figure 1 shows the Al/Si ratios calculated from the XPS spectra as a functions of IMFP.

After first ion exchange (HY(IE1)), the Al/Si ratio in the framework and bulk did not change as shown in Table 1. The Al/Si ratio measured by the Mg Kα XPS also did not change in Fig. 1, however, the ratio significantly decreased in the shallower area. This is likely that, in the first ion exchange, the dealumination occured only in the zeolite external surface shallower than a few decades of angstroms. After the second and third ion exchange(HY(IE2),HY(IE3)), the Al/Si ratio decreased in the framework, however, the ratios of the zeolite bulk did not change. The ratios in the surface measured by SR-XPS also did not show significant change. In these cycles, the aluminum in the framework was decreased, which remained in the inner area such as mesopore or micropore.

By the depth profile analysis using SR-XPS, the difference of Al/Si ratios in the frameworks, the bulk, and the surface of the zeolites was revealed, and also the changes of the Al/Si ratio by the dealumination treatments. This analysis is useful for the elucidation of mechanisim of the catalytic activity of the zeolites.

Table 1: Al/Si ratios of the framework and the bulk

	framework(XRD)	bulk(ICP)
NaY	0.36	0.35
HY(IE1)	0.36	0.35
HY(IE2)	0.24	0.31
HY(IE3)	0.20	0.31

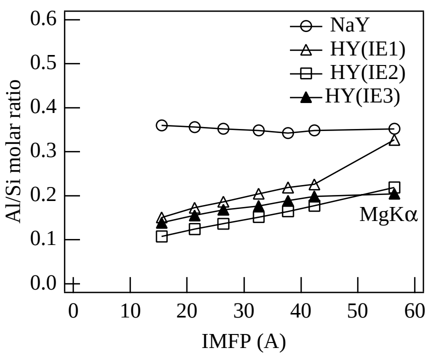

Figure 1: Al/Si ratio as a function of IMFP.

References

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