

Effects of extra-framework Al species for the preparation of Mo/USY catalysts

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Introduction

Ultrastable Y-type zeolites (USY) with Mo sulfide are promising catalysts for the hydrocracking of the heavy oil because of the proper acidity and mesopores which efficiently accommodate the large size molecules. Mesopores in Y-type zeolite are formed generally by steaming over 800 K, which simultaneously causes dealumination from the zeolitic framework and resulting formation of the extra-framework Al species (EFAL). EFAL affects not only the physical properties of the prepared catalysts but also Mo dispersion on the zeolite, both of which are important factors for the performances of hydrocracking catalysts. In the present study, we prepared Mo/USY with different amounts of EFAL. The effects of EFAL on the mesoporosity and Mo dispersion were investigated by using Mo K-edge EXAFS.

Experimental

Tosoh 330HUA was chosen as the starting USY zeolite (USY-A) containing 67 % of EFAL in total Al. USY-B was prepared by treating USY-A in a 0.1 mol/l HCl solution for 1 h at 298 K. USY-C was obtained from USY-B by repeating HCl treatment. Mo/USY catalysts (MoO₃ = 6.7 wt%) were prepared by the impregnation method with an aqueous solution of ammonium heptamolybdate ((NH₄)₆Mo₇O₂₄). After the impregnation, the catalysts were dried at 393 K and calcined at 823 K. Mo K-edge EXAFS was measured at the BL-10B of the Photon Factory at the High Energy Accelerator Research Organization (Tsukuba, Japan).

Results and Discussion

By the loading of Mo, the mesopore volume decreased. The order of mesopore decrease was Mo/USY-A > Mo/USY-B > Mo/USY-C. It is corresponded to the order of the amount of EFAL.

Figure 1 shows the Fourier transformed EXAFS spectra of reference materials and Mo/USY catalysts. The spectrum of Na₂MoO₄·2H₂O (Fig. 1(a)) gave an intense peak at 0.178 nm that is assigned to tetrahedrally coordinated Mo-O scattering. In contrast, the spectrum of MoO₃ (Fig. 1(b)) gave a broad peak between 0.17 nm - 0.20 nm that is assigned to octahedrally coordinated Mo-O scattering and another peak at about 0.36 nm that is assigned to Mo-Mo scattering in the second nearest shell.

The spectra of three catalysts (Fig. 1(c)-(e)) gave peaks between 0.172 nm and 0.180 nm. Considering the relatively low and broad peaks, these peaks are likely

assigned to Mo-O scattering of mixed MoO₄ tetrahedra and MoO₆ octahedra. Among the three USY zeolites, the Mo-O peak shifted from 0.180 nm of USY-A (c) to 0.172 nm of USY-C (e). The short Mo-O distance observed for USY-C is likely ascribed to dominant presence of octahedral Mo-O bonding, whereas the long Mo-O distance observed for USY-A is likely due to dominant presence of tetrahedral Mo-O bonding.

Mo on SiO₂ favored octahedrally coordinated MoO₃-like structure, whereas Mo on Al₂O₃ favored tetrahedral coordination at low Mo loading [1]. That is, the relative ratio of octahedral Mo-O bonding increases with increasing amount of EFAL in the USY zeolites. Note that the surface of USY zeolite with high Si/Al ratios has similar chemical properties as those of SiO₂.

Heptamolybdate anions (Mo₇O₂₄⁶⁻) cannot penetrate into the micropores during the impregnation and are deposited on the mesopore surface. The deposited Mo oxide species migrate into the micropores during the calcination over 573 K [2]. In the case of USY-C, Mo oxide could migrate into the micropores during the calcination, whereas the migration of Mo was restricted by the relatively strong interaction between Mo oxide and EFAL in the case of USY-A. It caused the decrease of mesopores by the plugging of mesopores.

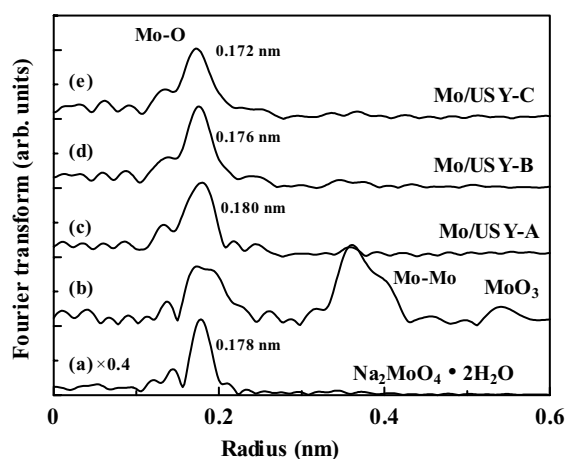


Fig. 1 Fourier transforms of the Mo K-edge spectra.

References

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