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Site determination of Mo cation located in HY zeolite

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Introduction

Zeolite supported metal catalysts are important materials for chemical industry and fundamental research for their effective catalytic properties. Determination of metal atoms located in a zeolite framework is essential to the understanding of catalysis and design for new catalysts, though it is very difficult unless metal atoms are distributed uniformly, enabling X-ray diffraction analysis. However, if metal atom is located in a crystalline material like zeolite with a homogeneous local structure, EXAFS allows us to analyze the local structure by a careful analysis of higher shell contributions based on a theory including multiple scattering to reproduce EXAFS functions up to higher shells using FEFF8 code [1]. In this study Mo cations were introduced in HY zeolite by the decarbonylation of $Mo(CO)_6$ and the location of Mo cations was analyzed by EXAFS.

Experimental

Sample preparation: HY zeolite, obtained from Toso (HSZ-320HOA), was calcined and evacuated at 723 K was then exposed to the vapor of $Mo(CO)_6$ at room temperature for 15 h corresponding to the saturated adsorption. Decarbonylation of $Mo(CO)_6$/HY was achieved by annealing $Mo(CO)_6$/HY to 573 K under vacuum. These processes were repeated several times to obtain samples with various Mo loadings.

EXAFS measurement and analysis: Mo K-edge EXAFS spectra were measured at BL-10B in a transmission mode. After background subtraction, k^3-weighted EXAFS functions (k range 30-120 nm^{-1}) were Fourier transformed into a R space and curve-fitting analyses were carried out for the first shell using the FEFFIT program [2]. Higher shell contributions were analyzed by the simulation of the EXAFS function using the FEFF8 code [1].

Results and Discussion

Figure 1 shows the Fourier transformed k^3-weighted EXAFS functions for Mo/HY (1-3 CVD cycles). All the spectra show similar feature, indicating that the Mo species are homogeneous irrespective of the CVD cycles. It was found by the curve fitting for the first shell that the nearest neighbour atoms for Mo were oxygen with the bond distance of 0.206 nm and the coordination number is 2. Since the structure of HY zeolite (FAU type) is already known, simulation of higher shell was examined. In FAU-type zeolite all the T-sites are equivalent with respect to the local structure. There are four kinds of O atoms bridging T-sites. Mo is expected to bond with two O atoms among them judging from the first shell analysis. Since it is known that zeolite structure is deformed by the presence of the extra framework cation, the possible position of Mo cation is located 0.2 - 0.26 nm from O atoms and above 0.27 nm from the T-site because of the positive charge. The space satisfying these conditions divided by the three dimensional grid of 0.005 nm resulted in about 40000 points, at all of which Mo cation was placed and FEFF simulation was performed with the nearest neighbour oxygen atoms were deviated to satisfy the Mo-O distance of 0.206 nm. Debye Waller factors for oxygen atoms except the nearest neighbour ones were approximated by the Debye model. Among these calculations the best fitted one corresponding to the S_{III}' site shown in Fig. 2, resulted in the R-factor of 6.86 %. This position is the same as the site for proton in HY, meaning that Mo cation just replace the position of proton in CVD process where H_2 is desorbed. Moreover, analysis for the mild oxidation of Mo/HY was also done and it was found that the increase of Mo oxidation number resulted in the relaxation of the distorted zeolite framework. In summary this study is the first example in which the position of metal cation in zeolite framework was specified by the detailed analysis of EXAFS spectra.

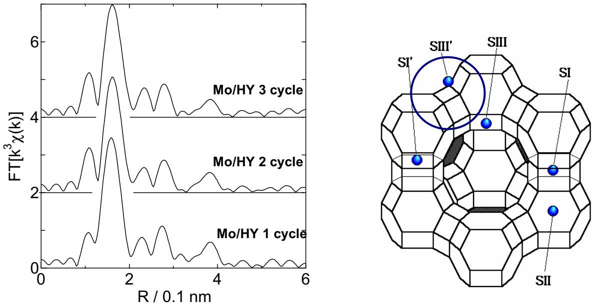

Figure 1. (Left)Fourier transformed EXAFS functions for repeated CVD cycles after decarbonylation. (Right) HY zeolite structure. S_{III}' site is marked with a circle.

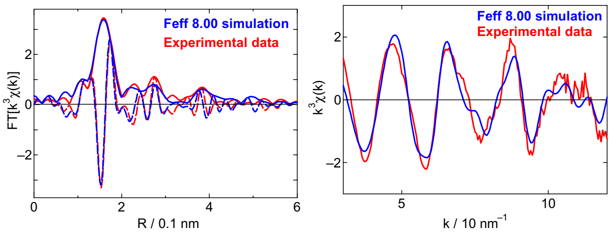

Fig. 2 Simulated and experimental curves for Mo/HY in R space (left) and k space (right).

References

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