

# Location of Mo cations in HY zeolite prepared by decarbonylation of $\text{Mo}(\text{CO})_6$

Fusao Nakagawa, Takafumi Shido, and Yasuhiro Iwasawa\*  
 Graduate School of Science, the University of Tokyo  
 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

## Introduction

To know the cation site in zeolite cages is indispensable to understand catalysis of cations in zeolites. The cation site has mainly studied by XRD and several cation exchange sites have been elucidated [1-3]. The drawback of XRD, however, is that it requires a long-range order, which are not possessed in many systems. On the other hand, EXAFS does not require such a long-range order and the cation site can be elucidated by a careful analysis of higher shell contributions. Recently, a theory including multiple scattering has been developed (FEFF8 [4]) and higher shell contributions can be reproduced by theoretical calculation.

The goal of this study is to determine the Mo cation site in HY zeolite prepared by decarbonylation of  $\text{Mo}(\text{CO})_6$  by higher shell analysis of EXAFS data. We have simulated Mo-K edge EXAFS functions for Mo cations located at several sites and compared them with observed data.

## Experimental

Mo/HY sample was prepared as follows:  $\text{Mo}(\text{CO})_6$  was introduced into HY zeolite which was evacuated at 723 K by CVD at room temperature. Then the sample was evacuated at 573 K to remove CO ligands. The cycle of CVD-thermal decarbonylation was repeated for several times.

Mo K edge EXAFS spectra were measured at BL-10B at room temperature. After background subtraction,  $k^3$  weighted EXAFS functions were Fourier transformed into a R space ( $k$  range = 3.0-12.0  $\text{\AA}^{-1}$ ) and the first shell was analyzed by curve fitting. In addition, higher shell contributions were analyzed by the simulation of the EXAFS function using the FEFF8 code.

## Result and discussions

Figure 1 (a)–(c) show Fourier transformed EXAFS functions of decarbonylated Mo/HY (1-3 cycles). Phase shifts are not corrected in this figure. For decarbonylated sample, Mo-O contribution was observed at 0.16 nm, and higher shell contributions were observed at 0.22, 0.24, and 0.38 nm. The EXAFS functions of decarbonylated Mo/HY sample was very similar up to three cycles, which suggests that the local structure of the Mo species in HY cages are homogeneous. This allows us to determine the cation site by a careful analysis of higher shells. To determine the cation site, we have simulated Mo K edge EXAFS functions of Mo cations at a certain position in the cages. To simulate EXAFS functions, a Mo cation was located in the cages of HY zeolite and moved the adjacent

oxygen atoms so that Mo—O distance satisfied the result of conventional curve fitting for the first shell. A Debye model was used to estimate the Debye Waller factors for the higher shells. Figure 2 shows the position of Mo cation determined by the simulation. The simulation revealed that the Mo is near S3' site. Other site cannot reproduce the observed EXAFS function. This is the first study that determines the cation site by EXAFS.

## References

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\*iwasawa@chem.s.u-tokyo.ac.jp

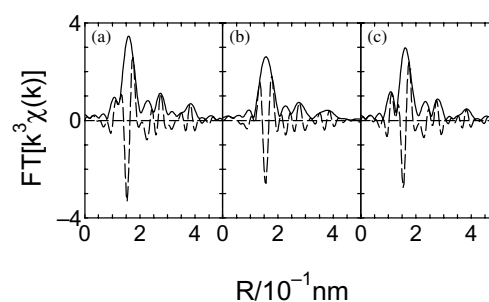


Figure 1. Fourier transformed EXAFS functions for decarbonylated Mo/HY. (a) 1 cycle, (b) 2 cycles, and (c) 3 cycles.

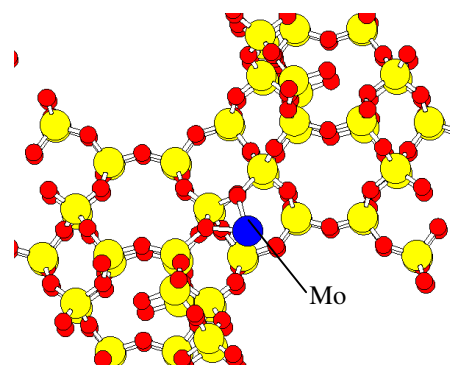


Figure 2. Position of Mo cation determined by EXAFS analysis.