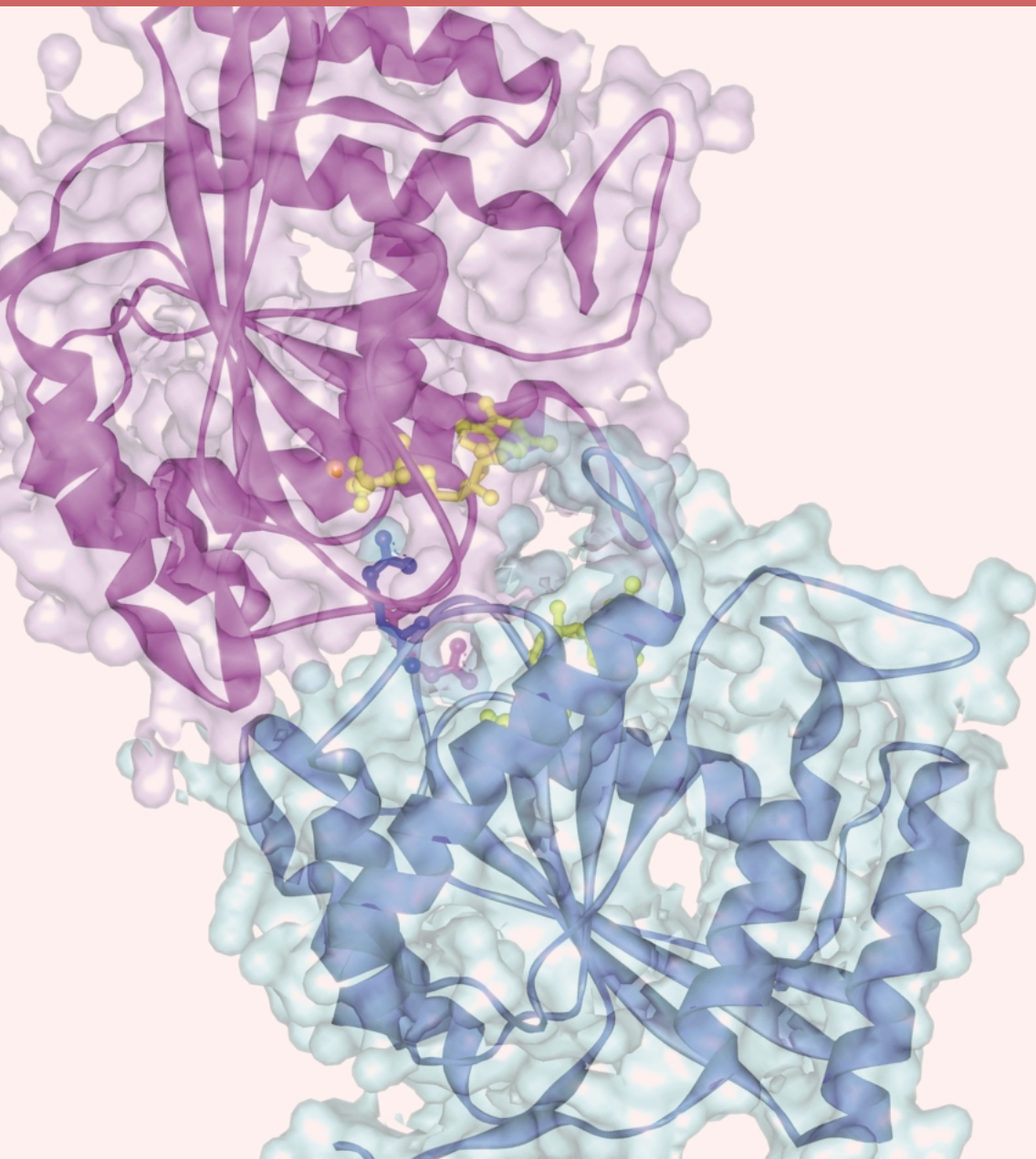


Highlights



2-1 Time-Resolved Energy-Dispersive XAFS Studies on the Structural Change of Metal Species in Zeolites during Catalyst Preparation Processes

The Y-type zeolite is a crystalline porous material composed of supercages of diameter 1.3 nm and channels of 0.7 nm and is expected as a promising support for homogeneous small clusters and highly dispersed metal particles at high loading. It is of great importance to study the structural changes of dispersed metal ions in zeolites and on oxide surfaces during the catalyst preparation process in order to understand the surface chemistry of supported metal ions and to develop efficient metal catalysts. The time-resolved information on the dynamic structural change of metal sites will provide a clue to find the preferable preparation conditions as well as to control the surface behavior of dispersed metal ions.

XAFS (X-ray Absorption Fine Structure) is a powerful tool to elucidate the local structure of non-crystalline materials, such as supported metal catalysts. However, the conventional XAFS technique usually takes ca. ten minutes to acquire a spectrum, which does not allow one to provide dynamic structural information. The energy-dispersive XAFS (DXAFS) technique, which measures a whole spectrum simultaneously by using a bent crystal polychromator and a position sensitive detector, is able to record a spectrum in a second or a sub second.

We have investigated the decarbonylation processes of $\text{Mo}(\text{CO})_6/\text{Y}$ zeolites by means of DXAFS at BL-9C of KEK-PF [1-3]. $\text{Mo}(\text{CO})_6$ is often used to prepare highly dispersed Mo species in zeolites because $\text{Mo}(\text{CO})_6$ is readily decarbonylated to produce Mo species in the channels of zeolites. Figure 1 (a) shows the Fourier transformed k^3 -weighted EXAFS signals of $\text{Mo}(\text{CO})_6/\text{NaY}$ during the temperature-programmed decarbonylation. Phase shift correction is not carried out in these spectra. At first, Mo-C and Mo-(C)-O peaks were observed at 0.15 and 0.27 nm (phase shift uncorrected), respectively, as shown in Fig. 1 (a). The intensity of these peaks began to decrease at 320 K, and decreased until 400 K. Above 400 K, Mo-C and Mo-(C)-O peaks shifted to 0.14 and 0.25 nm, respectively, and the intensity of these peaks increased. At 530 K, Mo-C and Mo-(C)-O peaks disappeared and two peaks at 0.15 and 0.27 nm appeared together with an artificial peak at

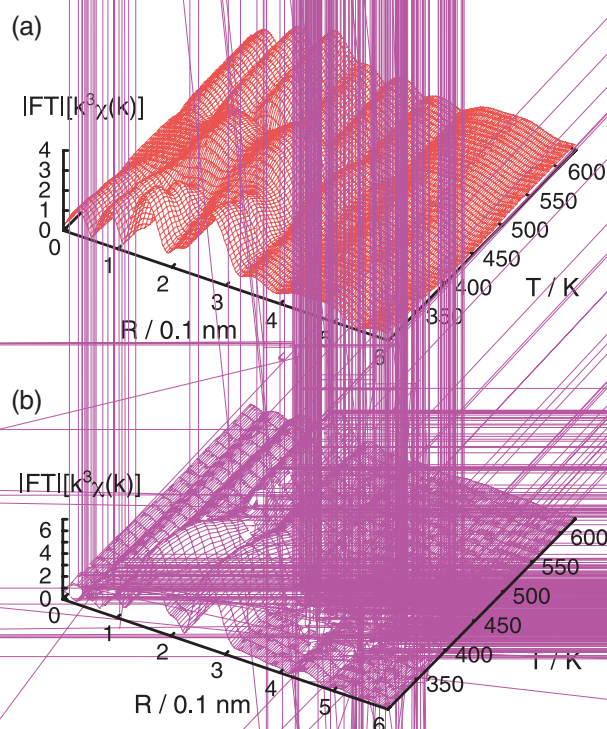


Figure 1 Fourier transformed k^3 -weighted EXAFS signals of $\text{Mo}(\text{CO})_6/\text{NaY}$ (a) and $\text{Mo}(\text{CO})_6/\text{HY}$ (b) during the temperature-programmed decarbonylation.

0.089 nm caused by the low frequency component after background subtraction. According to the curve fitting analysis of the DXAFS spectra, three CO molecules desorb from the initial $\text{Mo}(\text{CO})_6$ species in NaY and change to molybdenum monomer subcarbonyl species $\text{Mo}(\text{CO})_3(\text{O}_L)_3$ coordinated by three CO ligands and three oxygen atoms of the zeolite framework at 320 K. The $\text{Mo}(\text{CO})_3(\text{O}_L)_3$ was stable between 440-490 K. In the second step of the decarbonylation, two $\text{Mo}(\text{CO})_3(\text{O}_L)_3$ species merged with each other and formed dimeric molybdenum species $\text{Mo}_2(\text{C})\text{O}_x$ at 500-550 K, as shown in Fig. 2(a).

On the other hand, the XANES analysis and curve fitting analysis suggests that the decarbonylation of $\text{Mo}(\text{CO})_6/\text{HY}$ also proceeds through subcarbonyl species. Figure 1 (b) shows Fourier transformed k^3 -weighted EXAFS signals of $\text{Mo}(\text{CO})_6/\text{HY}$ during the temperature-programmed decarbonylation. Mo-C and Mo-(C)-O contributions were observed from 400-500 K by DXAFS analysis. The intermediate species could be similar to $\text{Mo}(\text{CO})_3(\text{O}_L)_3/\text{NaY}$ because the Mo-C and Mo-(C)-O distances of the intermediate were observed at 0.192 and 0.309 nm, which are similar to those of $\text{Mo}(\text{CO})_3(\text{O}_L)_3/\text{NaY}$ and because the XANES spectra

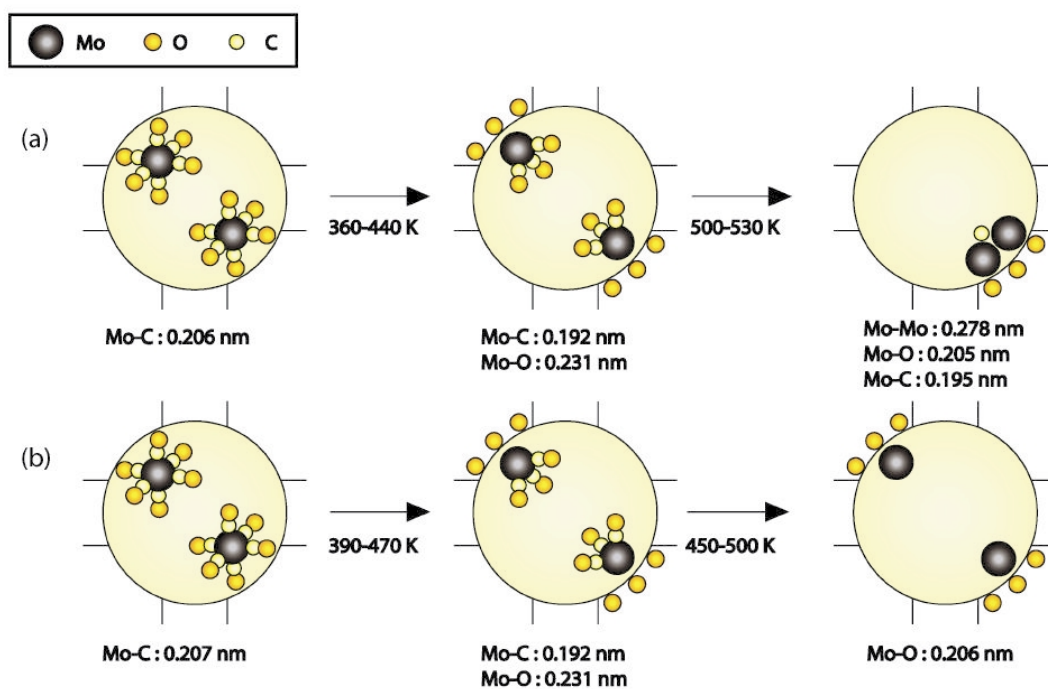


Figure 2 The structural transformation during the temperature-programmed decarbonylation of $\text{Mo(CO)}_6/\text{NaY}$ (a) and $\text{Mo(CO)}_6/\text{HY}$ (b).

during the decarbonylation of $\text{Mo(CO)}_6/\text{HY}$ can be fitted better by including the XANES of $\text{Mo(CO)}_3(\text{O})_3/\text{NaY}$ as a reference spectrum. However, the $\text{Mo(CO)}_3(\text{O})_3$ species was easily oxidized by zeolite protons and changed to oxomolybdenum species MoO_x immediately in the case of HY, as shown in Fig. 2(b). The oxomolybdenum species after the decarbonylation of $\text{Mo(CO)}_6/\text{HY}$ at 623 K could be fitted without Mo-Mo contribution, indicating a monomer structure in contrast to the dimer structure in NaY. During the transformation of $\text{Mo(CO)}_3(\text{O})_3$ to MoO_x , oxidation of the molybdenum species occurs by the zeolite OH group and the chemistry of the molybdenum oxidation in HY zeolite resembles that found for many transition metal carbonyl complexes on hydroxylated supports. On the other hand, in the case of NaY zeolite, the $\text{Mo(CO)}_3(\text{O})_3$ species was not oxidized because NaY zeolite does not have H^+ cations, which compose OH groups in zeolite, but Na^+ cations.

It has been demonstrated that DXAFS is a powerful technique to characterize the dynamic behavior of metal sites dispersed in zeolites on the second timescale.

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2-2 Molecular Self-Assembly Studied by XAFS

Self-assembly of amphiphile molecules is one of current key subjects in various research fields such as nano-scale technology, biotechnology and molecular science. The ordering process of self-assembled monolayers (SAMs) of alkanethiolate, particularly on the (111) surface of gold, has been extensively studied as the simplest prototypical SAM system to understand the self-assembly mechanism [1,2]. It is widely known that the Au-thiolate interface structure on the Au(111) surface is similar to the hexagonal molecular lattice in the (001) plane of single-crystal bulk alkane, leading to facile formation of strain-free well-ordered monolayers. In case of Cu(100), however, there is an obvious difference in structure between the four-fold-symmetry surface and the molecular packing in the bulk alkane, which will cause significant lattice mismatch between the Cu-thiolate interface and the alkyl-chain layer. The goal of this study is to elucidate how the alkanethiolate molecules reconcile the lattice mismatch to form a self-assembled monolayer. This will be quite important to understand the self-assembly mechanism because this kind of situation is rather general for actual molecular self-assembling systems.

STM observations for a hexanethiolate monolayer adsorbed on Cu(100) revealed that the two-dimensionally (2D) ordering process needs a much longer period (more than 10 hours) compared to that on Au(111). This enables us to trace the self-assembling process by using the surface XAFS technique. S-K and C-K XAFS spectra

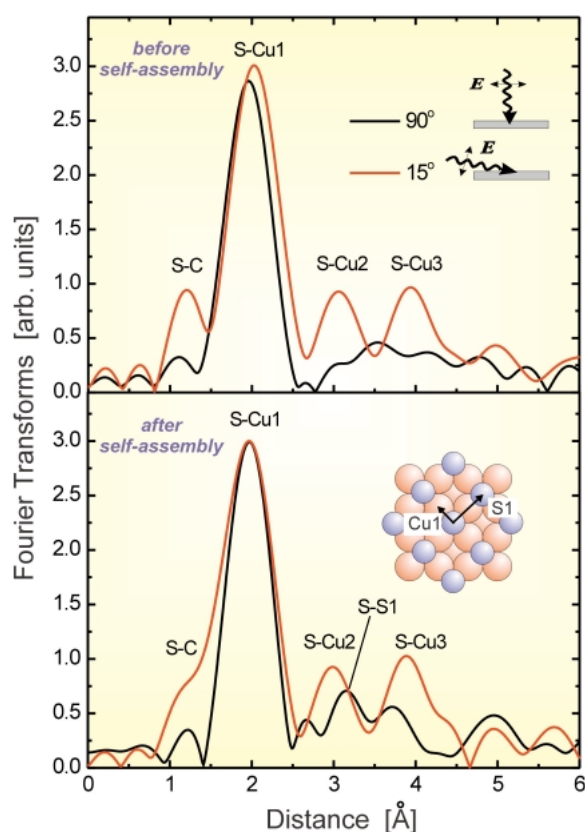


Figure 3
Fourier transforms of S-K EXAFS oscillation for a hexanethiolate monolayer on Cu(100) before (top) and after (bottom) self-assembly.

were measured at BL-11B and BL-7A, respectively, for the hexanethiolate monolayer [3]. Figure 3 shows Fourier transforms of S-K EXAFS oscillations for the hexanethiolate monolayer measured before (top) and after self-assembly (bottom). Quantitative analyses for S-Cu shells indicated that the sulfur atom of the thiolate is located at the four-fold hollow site of the unreconstructed Cu(100) surface irrespective of self-assembly. Although no drastic change was observed after self-assembly, it is appreciable that a new peak appears at around 3.2 Å in the normal incidence curve, which is associated with the contribution from the nearest-neighbor (NN) sulfur atoms. Curve-fitting analysis for this peak reveals that the NN sulfur atoms are located at a distance of $c(2 \times 2)$ lattice (S1 in the Inset). The absence of the 3.2 Å peak before self-assembly implies poor ordering at the Cu-S interface, though C-K NEXAFS shows standing-up alignment of the alkyl chains even just after adsorption. Thus, surface thiolates rapidly form a *well-aligned* but *2D-disordered* monolayer while randomly occupying the hollow sites. This rapid process is followed by slow evolution of the 2D-ordered structure via surface diffusion. Combination of the EXAFS results and force field calculations revealed that a large lattice mismatch between the S/Cu layer and the alkyl-chain layer (31% max) is effectively reduced (7% max) by tilting half of the S-C bonds that bridges

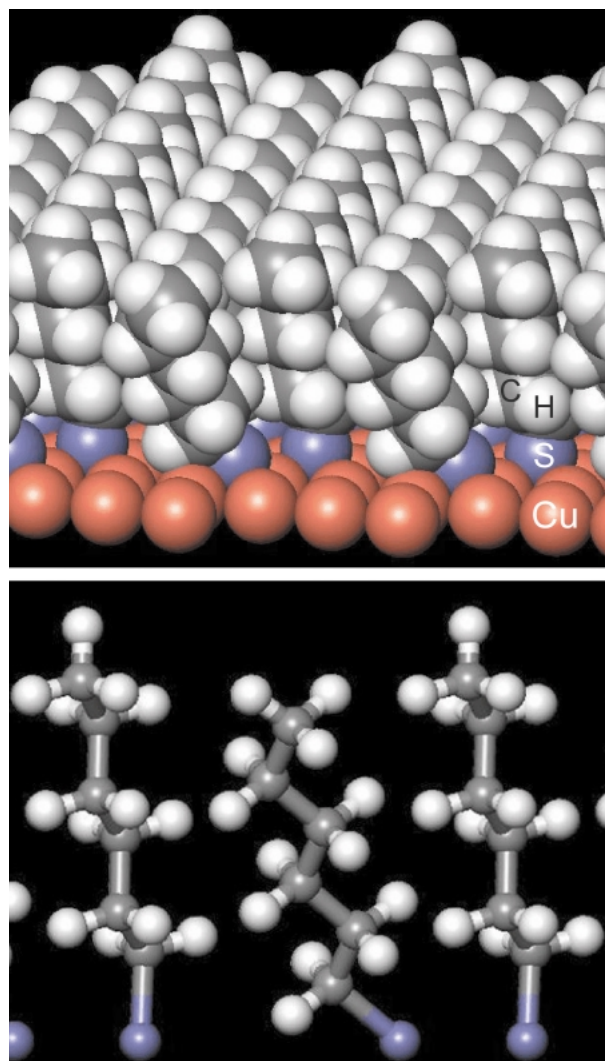


Figure 4
Structure model of hexanethiolate self-assembled monolayer on Cu(100) determined by combination of the XAFS results and the molecular force-field calculation. (top) bird's-eye view. (bottom) side view.

the two layers as shown in Fig. 4. The S-C bond tilting was detected as a decrease in polarization dependence of the S-C contribution in the S-K XAFS spectra after self-assembly. The present XAFS study provides clear evidence for the self-assembly mechanism, in which the lattice mismatch is effectively accommodated by the internal degree of freedom of the molecule at the interface.

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