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Polarization-dependent EXAFS Studies on the Structures of Mo Oxides on Various Oxide Single Crystals

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Introduction

Mo is a key element for many catalytic reactions such as selective oxidation and ammoxidation of hydrocarbons, oxidative dehydrogenation of alcohols and hydrodesulfurization of crude oil. The previous structural investigations were carried out by Raman, conventional EXAFS, and so on. However, Raman spectroscopy is more sensitive to crystalline material like MoO_3 and thus the isolated species and amorphous species are not well characterized. Conventional EXAFS gives the one-dimensional information and thus it is not so sensitive to the symmetry and distorted structure. We carried out the polarization dependent total reflection fluorescence EXAFS on the Mo supported on various oxide single crystals to obtain 3 dimensional information about the Mo species on the support surface.

Experimental

Single crystals (Al_2O_3, MgO) purchased from the Earth Jewelry Co. were washed well with deionized water and calcined at 873 K. The single crystals were impregnated with $(NH_4)_6Mo_7O_{24}$ aqueous solutions. Then the samples were calcined again at 873 K. The samples were mounted on a 4-axis goniometer at BL14A in Photon Factory (KEK-PF) to obtain a total reflection conditions and to adjust the polarization directions. The EXAFS measurements were carried out using synchrotron radiation emitted from the storage ring. The X-ray was monochromatized with a Si (311) double crystal. Fluorescence signal was detected by a small scintillation counter. In this paper we define s- and p-polarizations as follows. S-polarization is the electric vector parallel to the surface and thus gives the information parallel to the surface while p-polarization is electric vector perpendicular to the surface giving the structure in the corresponding direction. The EXAFS oscillation was calculated using FEFF6 program based on several model structures.

Results

Fig. 1 shows the XAFS spectra of Mo on MgO(001) crystal. No polarization dependence was found and FEFF simulation indicated that the tetrahedral MoO_4^{2-} species was stabilized on the surface. Fig.2 shows the Mo species on Al_2O_3(0001) surface. The EXAFS oscillation for both directions are different from each other, suggesting the anistropic structure as shown in Fig. 3 where square pyramidal Mo structure is present on the Al_2O_3 surface. In our previous work[1] , Mo octahedral dimer was found on TiO_2(110) surface. Such structure dependence on support can be explained by the acidity and basicity of the support oxides.

[1] W.-J. Chun, K. Asakura and Y. Iwasawa, *J.Phys.Chem.*, **102,**9006-9014(1998).

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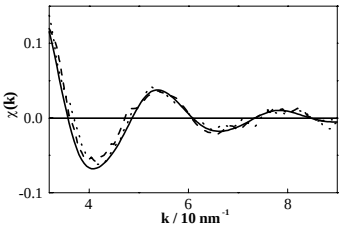

Fig.1 XAFS of Mo on MgO(001)(dot and broken lines are s- and p-polarizations, respectively.) and simulated one (solid line).

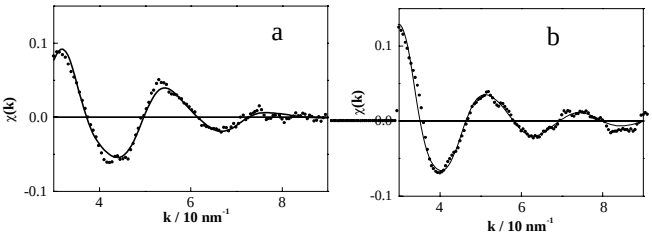

Fig.2 XAFS of Mo on Al_2O_3(0001) a) :s-pol b) p-pol. Dotted is observed and solid line is simulated one.

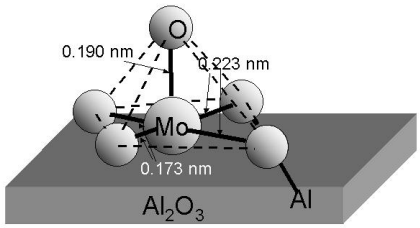

Fig.3 Proposed model structure for Mo on Al_2O_3 (0001) surface.