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XAFS study on the preparation process of Mo_6 and Nb_6 cluster

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Introduction

Delineating the relationships between structure and reactivity is a common goal in many areas of science. In catalysis, such determinations are pivotal to understanding how a given catalyst works and, therefore, how the design should be modified for a specific purpose. And then, it is important to provide the information on the inter-atomic distances and, coordination numbers between the particular metal and the surrounding atoms on, structural changes of catalytic metal sites during catalyst preparation, which could not be done several yeas ago.

Extensive effort has been directed at the syntheses of halide clusters. In contrast to carbonyl clusters, halide clusters have not been used as catalysts. Chihara et al. studied reactivity of halide clusters, however, relationship of reactivity and structure is unkown. In catalysis, such relationship is the key to understanding how a given catalyst works and, therefore how one may design or modify a catalyst for a specific purpose. Herein, we report novel issues found as by the time resolved DXAFS characterization of halide clusters, namely, temperature scale and reactivity.

Experimental

The $[(Nb_6Cl_{12})Cl_2(H_2O)_4]4H_2O$ and $(H_3O)_2[(Mo_6Cl_8)Cl_6]6H_2O$ sample were pressed to a disk and placed at a holder of an in-situ DXAFS cell and DXAFS measurements at Nb and Mo K edge were carried out at BL-9C in KEK-PF.

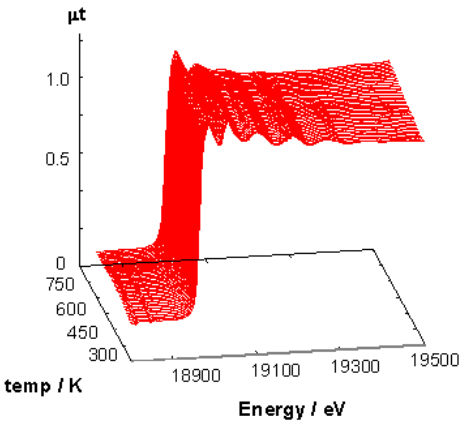

Fig. 1. A series of DXAFS spectra at the Rh K edge of Nb6 cluster from 298 to 800 K. The acquisition time of each spectrum is 500 ms. Cat. weight (wefer) = 13 mg.

Results and Discussion

Halide cluster of Nb and Mo at 523 K gave them catalytic activity for double bond isomerization of the olefin.Fig.1, 2 shows DXAFS spectra and their Fourier transformed functions for Nb_6 cluster at the Nb Kedge from 298 to 800 K. By the curve fitting results of DXAFS, Mo_6 cluster are stable complex at 523 K, on the other hands, by loosing some of the Cl ligands with the Nb_6 clster metal frame work intact.

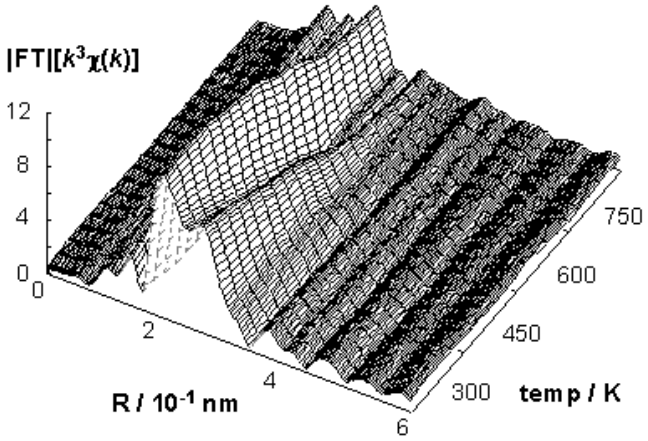

Fig. 2. A series of Fourier transformed k^3-weighted EXAFS functions for Nb6 cluster at the Nb K-edge from the DXAFS spectra in Fig.1.

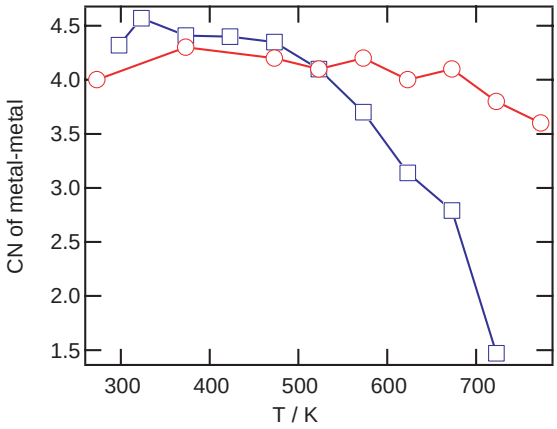

Fig.3 The values of coordination number (C.N.) by the carve fitting of DXAFS spectra; □:Nb-Nb of Nb_6cluster; ○:Mo-Mo of Mo_6Cluster.