Chemistry

10B/2003G287

XAFS analysis of MoO_3/MgO catalysts-effects of loading

Kenta SHIMURA, Saburo HOSOKAWA, Seiichiro IMAMURA, Hiroyoshi KANAI*
Department of Chemistry, Kyoto Institute of Technology, Kyoto 606-8585, Japan

Introduction

A hard-to-epoxidize olefin, allyl acetate, was successfully epoxidized with t-butyl hydroperoxide over MoO_3/MgO catalysts[1]. The selectivity was dependent upon loading of MoO_3 and pore size of MgO. XAFS analysis was carried out to elucidate the structure of MoO_3 supported on MgO. We reported the relationship between the selectivity of epoxide and the pre-edge height of Mo K edge[2]. Here we'll show the effects of MoO_3 loading on the pre-edge of Mo K edge.

Experimental

A known amount of $(NH_4)_6Mo_7O_{24}4H_2O$ was dissolved in deionized water and MgO(Nacalai Tesque Co., particle size 25 μm) was added to the solution. After stirring for 30 min, the solution was evaporated to dryness. The solid portion was dried at 353K overnight, followed by calcination at 823K for 3 h in air. X-ray absorption spectra(Mo K-edge) were obtained at the Beam Line 10B station by a transmission mode.

Results and discussion

The XANES spectra of 2-30 wt% MoO_3/MgO, MoO_3 and $MgMoO_4$ are shown in Fig. 1. The intense pre-edge peaks are assigned to tetrahedral structure. The XANES spectra of 2-30 wt% MoO_3/MgO are almost overlapped with that of $MgMoO_4$ which is a typical tetrahedral compound. To get more precise differences the second derivatives of XANES spectra are shown in Fig. 2. Small but decisive differences were observed. The spectrum of 7 wt% MoO_3/MgO is almost identical to that of $MgMoO_4$. The positions of minimum points in the spectra of 2 and 5 wt% MoO_3/MgO are the same, but their depths are narrower than that of $MgMoO_4$. In the spectra of MoO_3/MgO with 10 wt% and above loadings the positions and depths of their minimum points are different from those of $MgMoO_4$. The epoxide yield of allyl acetate is highest at 7 wt% loading[1]. The results of the second derivative of the XANES spectrum and maximum epoxide yield at 7 wt% loading suggest that the catalytic active species of MoO_3/MgO for epoxidation of allyl acetate with t-butyl hydroperoxide is tetrahedral MoO_4^{2-} species supported on large pore-sized MgO[2]. In fact $MgMoO_4$ itself has no catalytic activity. The slight deviation from regular tetrahedral structure deteriorates selectivity in the formation of the epoxide. The XPS analysis showed that 7 wt% loading is just equivalent to the monolayer amount dispersed on the surface of MgO[1].

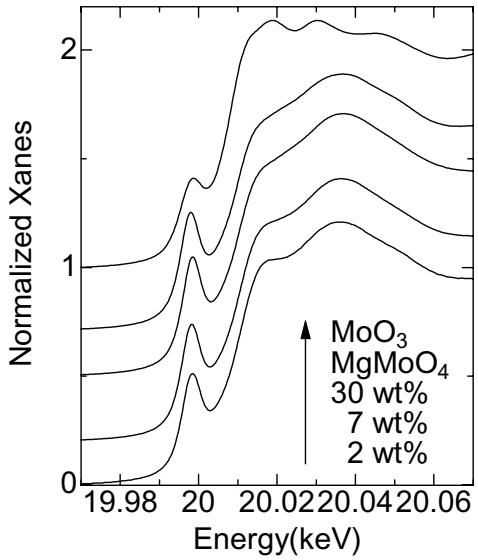

Fig. 1 Normalized XANES spectra of 2-30 wt% MoO_3/MgO and standard molybdenum oxides.

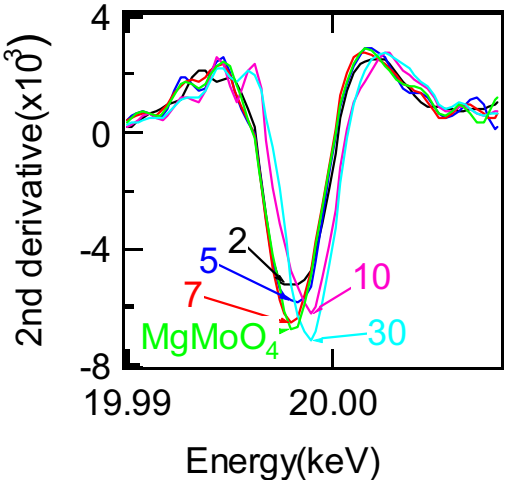

Fig. 2 The second derivatives of XANES spectra of MoO_3/MgO with various loading and $MgMoO_4$.

References

[1] K. Shimura, H. Kanai, K. Utani, K. Matsuyama, S. Imamura, Appl. Catal. A, 283(2005) 117.
[2] K. Shimura, T. Nishiguchi, H. Kanai, S. Imamura, Photon Factory Activity Report 2003 #21 Part B, 35.

* kanai@kit.ac.jp