

XAFS analysis of MoO₃/MgO as catalysts for the selective epoxidation of refractory olefins

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INTRODUCTION

A chlorohydrin process has been the most effective method to produce epoxides, but this method is not desirable from the environmental point of view because of the use of harmful chlorine. One promising process is epoxidation with hydroperoxide (ROOH) as an oxidizing agent. Olefins having electron-withdrawing groups are hard to be epoxidized. We have found that allyl acetate as one of them was selectively epoxidized over MoO₃/MgO. The selectivity depends largely on the particle size of MgO. The local structures and electronic properties of molybdenum oxides have been analyzed from XANES spectra of Mo K edges.

EXPERIMENTAL

A known amount of (NH₄)₆Mo₇O₂₄·4H₂O was dissolved in deionized water and MgO(Nacalai Tesque Co., particle size 25 μm) or MgO(Reference catalysts, Catalysis Society of Japan, particle size 10-200 nm) 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

We have found that the epoxidation of allyl acetate was successfully achieved over MoO₃/MgO. The selectivity is largely dependent on the kinds of MgO. We used five MgOs. Their particle sizes and pore radii are different. The larger the particle size is, the higher the epoxide selectivity is. The yields of epoxide are parallel to the particle size as follows:

$$53\% (25 \mu\text{m}) > 26\% (200 \text{ nm}) > 24\% (100 \text{ nm}) > 6.4\% (50 \text{ nm}) > 1.2\% (10 \text{ nm})$$

where the figures in parentheses are particle sizes of MgO.

The normalized XANES spectra of 7 wt% MoO₃/MgO are shown in Fig. 1. The pre-edge peaks assigned to 1s-4d transition are attributed to the tetrahedral structure of MoO₄²⁻. The differences in the peak heights are small but are decisively observed. The epoxide yield increases with the pre-edge peak height. The peak of 7 wt% MoO₃/MgO(25 μm) and MgMoO₄ overlap each other.

Another difference appears in the peak of 20017 eV. Contrary to the pre-edge peak the peak height becomes smaller with the increase in the particle size of MgO. These differences in the XANES spectra are well correlated with the epoxide selectivity. These absorption peaks reflect the structural and electronic properties of molybdenum oxides on MgO. Haller observed the change of edge-position of V with the change of the pore size of MCM-41.[1] This reflects the reactivity in methanol oxidation. He interpreted it due to the change of oxidation potential of V with the change of the pore size.

The pore size of MgO increases with the increase in particle size of MgO. Since there are no shifts of Mo K-edge position, the oxidation states of MoO₃/MgO should be the same. The structure of all MoO₃/MgO is essentially tetrahedral. Only minute difference in the electronic state or a small distortion might be caused by the pore size. We are now investigating the effects of pore(particle) size of MgO in terms of structural and electronic properties of molybdenum oxide.

[1] G. L. Haller, J. Catal., 216(2003) 12.

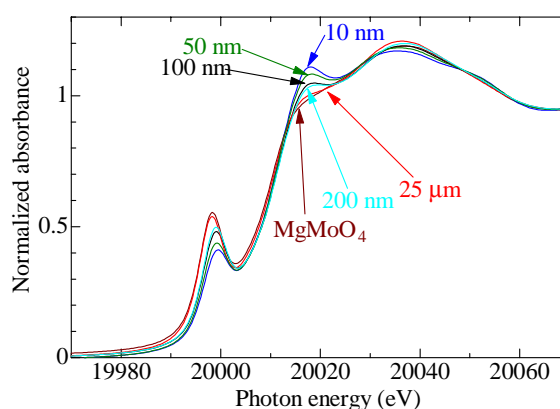


Fig. 1 Normalized XANES spectra of MoO₃-MgO. The numbers are particle sizes.

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