

Mo₃VO_x with High Dimensional Structures as True Active Phase for Catalytic Acrolein Oxidation and Ethane Oxidation

Toru Murayama, Kosuke Nakatani, Takeshi Konya, and Wataru Ueda*
Catalysis Research Center, Hokkaido University, N21-W10, Kita-ku, Sapporo 001-0021, Japan
*ueda@cat.hokudai.ac.jp

Introduction

Mo-V-based oxides are known as one of the most important oxidation catalysts. Amongst many Mo-V-based oxides with various structural states, new crystalline solids of Mo₃VO_x we have successfully synthesized for the first time are quite unique in terms of crystal structure[1] and are found to be extremely active for the selective acrolein oxidation to acrylic acid and the oxidation of ethane to ethylene. In order to elucidate the origin of the high activity for the reactions, we here compare four catalysts with the same chemical composition Mo₃VO_x but different crystal structures, orthorhombic, trigonal, tetragonal, and amorphous. The former two materials have the same structure units of pentagonal ring, 6-membered ring, and 7-membered ring in particular arrangements in *a-b* plane structure(Figure 1)[2]. The third one does not have the 7-membered ring and the fourth has a disordered arrangement of these structural units.

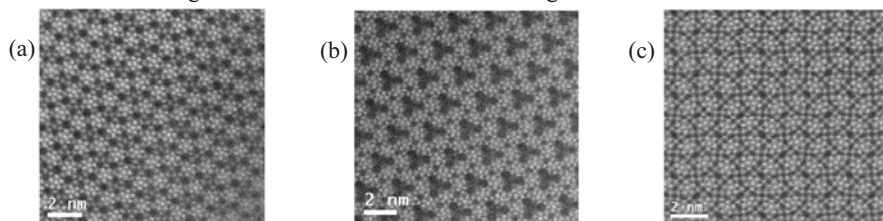


Figure 1. HAADF-STEM images of (a) orthorhombic, (b) trigonal, and (c) tetragonal Mo₃VO_x

Experimental

Crystalline and amorphous Mo₃VO_x were synthesized hydrothermally at 175 °C for 20 h. Tetragonal Mo₃VO_x was prepared by calcination of orthorhombic Mo₃VO_x in air at 613 K. Catalytic oxidations in gas phase were carried out in a conventional fixed bed reactor.

Results/Discussion

The catalytic activities for acrolein oxidation and ethane oxidation over the four structural types of Mo₃VO_x catalysts were shown in Figure 2 and 3, respectively. The selectivities to the major products, acrylic acid and ethylene, are as high as about 95 % and 80 %, respectively, and are

almost independent of the structure types. On the other hand, the conversions strongly depended on the catalyst structures as seen in the figures. Briefly, the tetragonal catalyst was inactive for both the reactions. The amorphous catalyst showed activities to some extent but obviously much less than the orthorhombic. The trigonal catalyst showed slightly different catalytic behaviour depending on the reaction. The catalyst was fairly active for the acrolein oxidation like the orthorhombic but was comparable to the amorphous in the ethane oxidation.

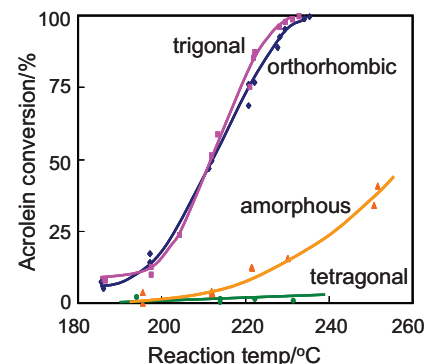


Figure 2 Catalytic acrolein oxidation

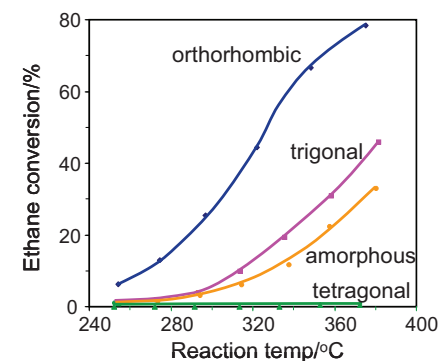


Figure 3 Catalytic ethane oxidation

These considerable differences in the catalytic oxidation activity cannot be simply explained by outer surface area because all the catalysts have rod-shaped morphology in a similar crystal size. The structural unit arrangement in the *a-b* plane of the catalysts should be dominant in the genesis of the oxidation activity. By simple analogical comparison among the catalysts, the 7-membered ring site could be responsible for the acrolein oxidation activity, since the orthorhombic and the trigonal catalysts have almost the same numbers of the 7-membered units and apparently more numbers than the amorphous has because of less ordering of the units. This consideration cannot be simply extended to the ethane oxidation. Since it was found that the activity order for the ethane oxidation clearly coincided with the sequence of the microporosity ascribable to the empty 7-membered ring. A part of the 7-membered rings was occupied by metal octahedra in the trigonal catalysts as ascertained by HAADF-STEM analysis, which is the reason why the activity was lower than the orthorhombic in the ethane oxidation and would suggest that the empty 7-membered ring can accept ethane molecule to active oxidatively and efficiently.

References.

1. M. Sadakane, K. Yamagata, K. Kodato, K. Endo, K. Toriumi, Y. Ozawa, T. Ozeki, T. Nagai, Y. Matsui, N. Sakaguchi, W. D. Pyrz, D. J. Buttrey, D. A. Bolm, T. Vogt, W. Ueda, *Angew. Chem. Int. Ed.*, **48**, 3782(2009)
2. W. Pyrz, D. Blom, M. Sadakane, K. Kodato, W. Ueda, T. Vogt, D. Buttrey, *Proc. Natl. Acad. Sci. USA*, **107**, 6152(2010)