Synthesis of crystalline orthorhombic Mo-V-Cu oxide for selective oxidation of acrolein to acrylic acid

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Abstract: Cu could be successfully introduced into the heptagonal channels of the orthorhombic Mo_3VO_x complex oxide. In the acrolein (ACR) selective oxidation, the introduction of Cu caused a negative effect on the ACR conversion (ACR conversion at 250 °C: Mo_3VO_x, 76 %; MoVCuO, 40 %). On the other hand, the selectivity to acrylic acid (AA) increased by the introduction of Cu from 92 % to 98 % at every studied reaction temperature. AA selectivity over MoVCuO remained unchanged in spite of the increase of ACR conversion.

Keywords: Acrolein oxidation, Crystalline Mo_3VO_x, Cu Promoter.

1. Introduction

Acrylic acid (AA) is one of the most important chemicals and has been widely used for producing super absorber, polymer, adhesive, etc. Currently, AA is produced by the two steps propylene based oxidation in which acrolein (ACR) produced by the first step propylene oxidation over Mo-Bi based mixed metal oxide is oxidized into AA by the second step oxidation over Mo-V based mixed metal oxide. In the selective oxidation of acrolein, various promoters are added into Mo-V based mixed metal oxide in order to tune the catalytic activity. These promoters are indeed effective for improving the catalytic activity. However, the detailed catalytic roles of the promoters are difficult to investigate due to the amorphous nature of the catalysts. This situation hinders the further development of the catalysts. We have reported that the crystalline orthorhombic Mo_3VO_x oxide (MoVO) showed outstanding catalytic activity for the selective oxidation of ACR and the heptagonal channel in the MoVO structure is responsible for catalyzing ACR oxidation. Here, we successfully introduced Cu into MoVO without altering its crystalline structure. The detailed characterizations and reaction tests successfully clarify the role of Cu as the promoter of MoVO for ACR oxidation.

2. Experimental

MoVO was synthesized by the reported procedure[1]. Orthorhombic Mo-V-Cu oxide (MoVCuO) was synthesized by hydrothermal condition at 175 ºC for 20 h using the precursor solution prepared by methyl ammonium heptamolybdate $(CH_3NH_3)_6Mo_7O_{24}$ (10 mmol), vanadyl sulfate $VOSO_4\cdot nH_2O$ (2.5 mmol) and copper sulfate $CuSO_4\cdot 5H_2O$ (0.625 mmol). The elemental composition measured by ICP was Mo/V = 1/0.38 in MoVO and Mo/V/Cu = 1/0.37/0.07 in MoVCuO, respectively. ACR oxidation was carried out under the following reaction conditions. Reaction temperature, 190 °C~250 °C; gas composition, $ACR/O_2/H_2O/He/N_2$ = 0.8/4.0/9.7/19.8/12.0mL/min; catalyst amount: 0.13 g ~ 0.25 g.

3. Results and discussion

XRD patterns of MoVO and MoVCuO are shown in Figure 1. MoVO showed the XRD peaks at 2θ = 6.7°, 7.9°, 9.0° and 22.2°, which were attributed to the diffraction of (020), (120), (210) and (001) planes of MoVO, respectively. MoVCuO showed almost the same XRD pattern with MoVO. However, XRD peak intensity derived from (210) plane was clearly increased by the introduction of Cu, indicating that Cu was introduced inside the MoVO structure. Then, N_2 adsorption was carried out for MoVO and MoVCuO.

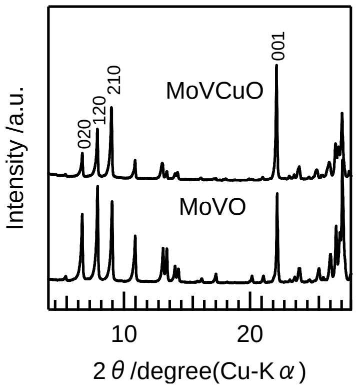

Figure 1. XRD pattern of MoVO and MoVCuO.

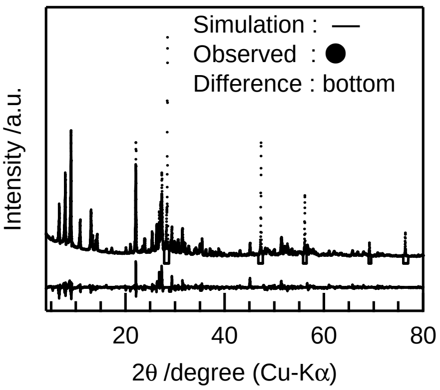

Figure 2. Results of Rietveld refinement of MoVCuO.

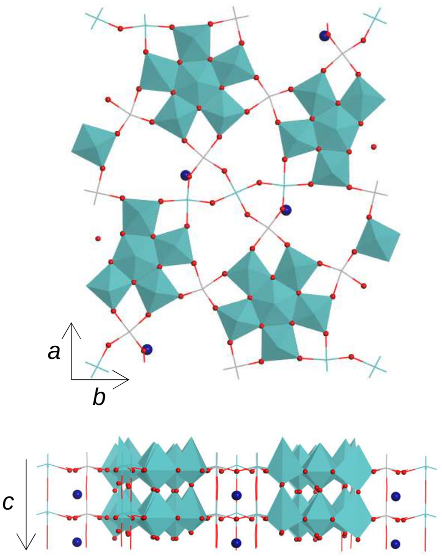

Figure 3. Structural model of MoVCuO. Ball in the structural model represents Cu.

MoVO showed micropore adsorption derived from the empty heptagonal channel in the crystal structure. On the other hand, no such the adsorption could be observed in MoVCuO, indicating that Cu is located at the heptagonal channel site. Based on the above results and the other characterization results such as XRD simulation and geometry optimization calculation, we conclude that Cu is placed between the two layers of *a*-*b* planes at the heptagonal channel. Rietveld refinement carried out using the obtained structural model was well converged (Figure 2), supporting the validity of our proposed structural model of MoVCuO. Results of the ACR selective oxidation using MoVO and MoVCuO as the catalyst are shown in Figure 3. In this reaction, AA was formed as the main product and acetic acid, CO, CO_2 was formed as byproducts. The ACR conversion was decreased by the introduction of Cu in the MoVO structure and the ACR conversion at 250 °C was 76 % for MoVO and 40 % for MoVCuO. However, AA selectivity was clearly increased by the introduction of Cu and the AA selectivity above 98 % was achieved, while the AA selectivity over MoVO was 92 %. AA selectivity over MoVCuO remained unchanged regardless of the increase of ACR conversion and AA selectivity over MoVCuO was clearly higher than that of MoVO even at the same ACR conversion level. We have reported that the heptagonal channel works as a catalysis field for the ACR conversion[1]. The location of Cu may stabilize the heptagonal channel which may decrease the reactivity for ACR conversion. However, such the stabilization prevents the over oxidation of ACR and the sequential oxidation of AA which enhanced the AA selectivity.

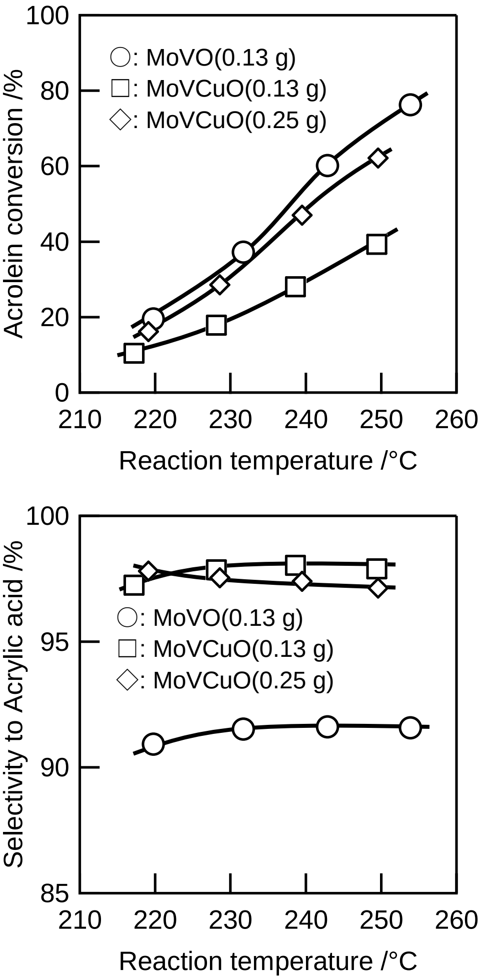

Figure 4. Acrolein oxidation over MoVO (○, 0.13 g) and MoVCuO (□, 0.13 g), MoVCuO (◊, 0.25 g).

4. Conclusions

Cu could be successfully introduced into the Orth-MoVO structure. AA selectivity was increased by the introduction of Cu.

References

1. T. Konya, T. Katou, T. Murayama, S. Ishikawa, M. Sadakane, D. Buttrey, W. Ueda, Catal. Sci. Technol. 3 (2013) 380.