Introduction of Sb into trigonal Mo_3VO_x oxide and its crystal transformation to orthorhombic Mo_3VO_x by heat treatment

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Abstract: Sb was introduced into trigonal Mo_3VO_x (Tri-MoVO) by an ion exchange under acidic condition and the obtained solid was heat-treated. Without the introduction of Sb, Tri-MoVO was collapsed by the heat-treatment at 550 °C for 2 h under N_2 flow, resulting in the formation of MoO_3, $(V_{0.07}Mo_{0.93})_5O_{14}$ and $(V_{0.97}Mo_{0.95})O_5$. On the other hand, Tri-MoVO containing Sb was transformed to orthorhombic Mo_3VO_x (Orth-MoVO) by the above heat-treatment. Since no such the phase transformation was observed in the physical mixture of Tri-MoVO and Sb_2O_3, Sb inside the crystal structure of Tri-MoVO was found to work for inducing this crystal transformation.

Keywords: Crystalline Mo_3VO_x, crystal phase transformation, heat-treatment

1. Introduction

Mo-V-Te-Nb oxide (MoVTeNbO) is well known as an extremely active catalyst for the selective oxidation of light alkanes[1]. MoVTeNbO is formed by an appropriate heat-treatment of an amorphous solid comprised of the constituent elements. Much effort has been devoted for clarifying this crystal formation process of MoVTeNbO under the heat-treatment since the clear understanding of the transformation process may allow the rational crystal design of MoVTeNbO. However, no clear conclusion has been obtained up to the date, because the amorphous nature of the MoVTeNbO precursor cannot provide clear characterization results during this crystal transformation process. Crystalline Mo_3VO_x (MoVO) has several crystal phases, including orthorhombic phase (Orth-MoVO) and trigonal phase (Tri-MoVO). Among the crystal phases of MoVO, Orth-MoVO has identical crystal framework with MoVTeNbO. Here, we firstly found that the crystal structure of Tri-MoVO was transformed into the Orth-MoVO structure by the heat-treatment under the heat-treatment condition to form MoVTeNbO when Sb was introduced into Tri-MoVO structure. This crystal phase transformation process may provide critical information about the crystal structure formation process of MoVTeNbO.

2. Experimental

Tri-MoVO was prepared by the reported procedure[2]. Sb was introduced into Tri-MoVO by ion exchange method under acidic solution. First, the desired amount of Sb_2O_3 was completely dissolved in 40 mL of diluted HCl solution (1.2M) at 60 °C. Then, 0.5 g of Tri-MoVO was dispersed in the Sb containing solution, followed by the stirring for 24 h at 60 °C and by the filtration. Thus obtained solids were abbreviated as *x*Sb, where *x* indicates 100×Sb/Mo ratio measured by ICP. Heat-treatment of *x*Sb was conducted at 550 °C for 2 h under 50 mL min^{-1} of N_2 flow.

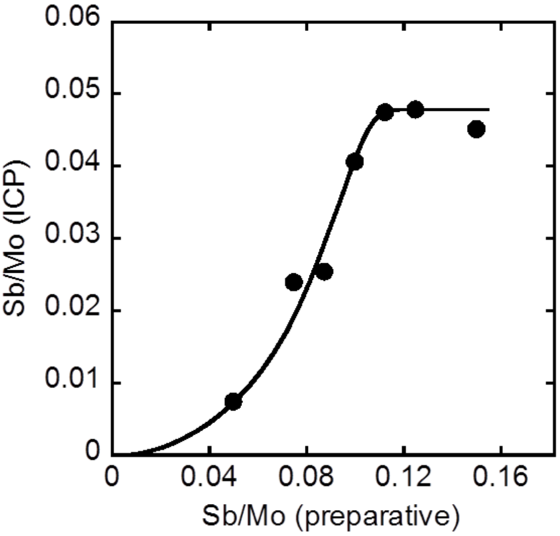

Figure 1. Relationship between preparative Sb/Mo ratio and Sb/Mo ratio in the solid.

3. Results and discussion

Figure 1 shows the relationship between the preparative Sb/Mo ratio and the Sb/Mo ratio of the obtained solid measured by ICP. The amount of Sb in the

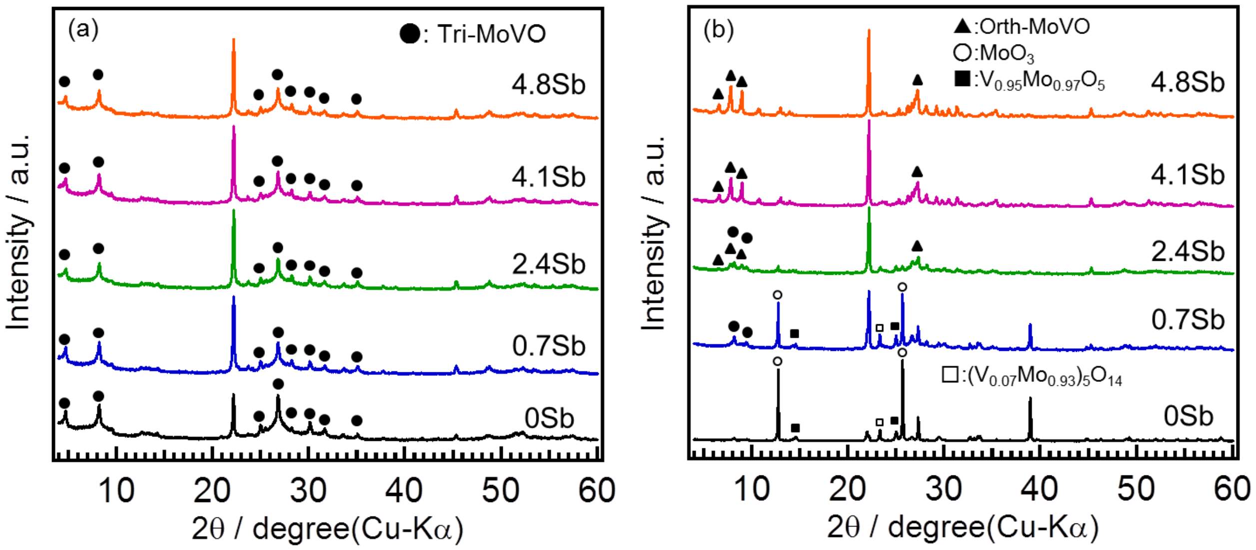

Figure 2. XRD patterns of *x*Sb before (a) and after (b) the heat-treatment.

solid was increased with the increase of the preparative Sb/Mo ratio. However, no further increase in Sb/Mo ratio in the solid was observed when preparative Sb/Mo ratio reached 0.05. This value corresponds one Sb atom against the one unit cell of Tri-MoVO. Figure 2 shows the XRD patterns of *x*Sb before and after the heat-treatment. Before the heat-treatment (Figure 2 (a)), *x*Sb showed the XRD peaks at 2θ = 4.7°, 9.0° and 22.2° attributable to the diffraction of (100), (110) and (001) planes of Tri-MoVO structure, respectively. Almost the same XRD pattern was observed in *x*Sb and no peaks related to Sb were observed. After the heat-treatment of *x*Sb (Figure 2(b)), XRD pattern of 0Sb (Tri-MoVO) showed the formation of MoO_3, $(V_{0.07}Mo_{0.93})_5O_{14}$ and $V_{0.97}Mo_{0.95}O_5$. However, the intensities of XRD peaks derived from MoO_3, $(V_{0.07}Mo_{0.93})_5O_{14}$ and $V_{0.97}Mo_{0.95}O_5$ decreased in the Sb containing Tri-MoVO and new XRD peaks at 2θ = 6.7°, 7.9° and 9.0° derived from the diffraction of (010), (120) and (210) plane of Orth-MoVO structure appeared after the heat-treatment. Further increase of *x* increased the peak intensities of Orth-MoVO structure and almost no peaks related to MoO_3, $(V_{0.07}Mo_{0.93})_5O_{14}$ and $V_{0.97}Mo_{0.95}O_5$ were observed. No crystal transformation was observed by the heat-treatment of the physical mixture of Sb_2O_3 and Tri-MoVO. Based on the above results, Sb in the Tri-MoVO was found to induce the crystal phase transformation from Tri-MoVO structure to Orth-MoVO structure by the appropriate heat-treatment (Figure 3). Details about the location site of Sb in Tri-MoVO and Orth-MoVO structure and the observed crystal transformation mechanism will be discussed.

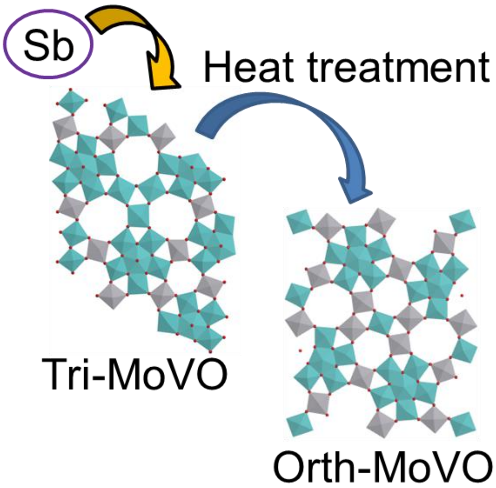

Figure 3. Structure transformation from Tri-MoVO and Orth-MoVO.

4. Conclusions

Tri-MoVO was collapsed to MoO_3, $(V_{0.07}Mo_{0.93})_5O_{14}$ and $V_{0.95}Mo_{0.97}O_5$ by the heat-treatment at 550 °C under N_2 flow. However, Tri-MoVO containing Sb was transformed to Orth-MoVO structure by the same heat-treatment. (Figure 3)

References

1. R. K. Grasselli, Catal. Today 99 (2005) 23.
2. M. Sadakane, N. Watanabe, T. Katou, Y. Nodasaka, W. Ueda, Angew. Chem. Int. Ed. 46 (2007) 1493.