Acrylic acid, the simplest unsaturated mono-carboxylic acid, is an important intermediate which is widely used in polymer industry, for instance absorbent materials, coatings, and additives in textile production. Efficient catalysts for acrylic acid production are highly desired with the increase of acrylic acid consumption in the past decades. Molybdenum-vanadium-based complex oxides (Mo-V-O) with a variety of promoters have been reported as the best catalysts for selective oxidation of acrolein to acrylic acid. In the industrial Mo-V-based catalysts, W and Cu are widely employed; however, the effects of these metals are poorly understood because of the complexity of structure and composition of these catalysts. One of the possible approaches to overcome this problem is to make a catalytically highly active material with simpler components and structure. Recently, a series of crystalline Mo-V-O named as orthorhombic, trigonal, tetragonal, and amorphous phase were successfully synthesized by Ueda et al. The application of these crystalline Mo-V-Os to the selective oxidation of acrolein to acrylic acid gained remarkable results. Additionally, these crystalline Mo-V-Os can supply suitable models to investigate the structure-activity relationships and to identify the effects of additional metals such as W and Cu.

This thesis mainly focuses on the synthesis of highly efficient crystalline Mo-V(-W-Cu)-O catalysts for the selective oxidation of acrolein to acrylic acid. A series of crystalline Mo-V-W-O, Mo-V-Cu-O, and Mo-V-W-Cu-O catalysts were successfully synthesized by a hydrothermal method. Selective oxidation of acrolein to acrylic acid was performed in gas phase over these catalysts. Effects of W and Cu on acrolein oxidation were also revealed.

In chapter 2, W was successfully introduced into Mo-V-O with keeping the orthorhombic, trigonal, and amorphous structures. Synthesized crystalline Mo-V-W-O with orthorhombic and trigonal structures, both of which possess heptagonal channels, showed catalytic activity for the gas phase acrolein selective oxidation to acrylic acid superior to amorphous Mo-V-W-O and to tetragonal Mo-V-O. The results strongly suggest that the crystalline Mo-V-Os with orthorhombic and trigonal structures are real active phase of industrial acrolein oxidation catalysts.

In chapter 3, a series of crystalline Mo-V-W-O complex oxides with the orthorhombic or trigonal structure were synthesized by a hydrothermal method, and were characterized by inductively coupled plasma atomic emission spectroscopy, TEM, STEM-EDX, X-ray diffraction, Rietveld analysis, and a N₂ adsorption method. It was found for the first time that W can be successfully incorporated into the trigonal Mo-V-O structure by using (CH₃CH₂NH₃)₂Mo₇O₁₉. The alkylammonium cation acted as a structural stabilizer that was requisite for the formation of a trigonal structure when additional metal ions were present. For the orthorhombic Mo-V-W-O structure, introduction of W into the orthorhombic structure caused a rod segregation effect by which nanoscale crystals formed and the external surface area greatly increased. Additionally, these Mo-V-W-O materials were applied as catalysts to the gas phase selective oxidation of acrolein to acrylic acid. The best catalyst was assigned to orthorhombic
Mo-V-O-W7.5%, which possessed an ordered arrangement of heptagonal and hexagonal channels and a large external surface area.

In chapter 4, a series of crystalline Mo-V-Cu-O complex oxides with an orthorhombic structure were synthesized for the first time by a hydrothermal method using \((\text{CH}_3\text{NH}_3)_6\text{Mo}_7\text{O}_{24}\). Cu ions were determined to be in the heptagonal channels by scanning transmission electron microscopy (STEM), X-ray diffraction (XRD), Rietveld refinement, and N\(_2\)-adsorption methods. Addition of Cu into the orthorhombic structure can enhance acrylic acid selectivity to more than 99% in the gas phase acrolein selective oxidation to acrylic acid. Active site of Mo-V-Cu-O complex oxides for the reaction was proposed to be located in the 7-membered ring.

In chapter 5, a series of crystalline Mo-V-W-Cu-O complex oxides with an orthorhombic structure were synthesized. These crystalline Mo-V-W-Cu-O complex oxides are efficient catalysts for selective oxidation of acrolein to acrylic acid. Compared to Mo-V-O catalysts, both catalytic activity and selectivity to acrylic acid were enhanced. As the best catalyst, Orth-MoVW7.5%Cu7.5%O achieved more than 90% acrolein conversion and 99% selectivity to acrylic acid at 230 °C.

In chapter 6, a variety of crystalline Mo-V-M-O (M= Mn, Fe, Co, Ni, Zn) complex oxides with an orthorhombic structure were synthesized by a hydrothermal method using \((\text{CH}_3\text{NH}_3)_6\text{Mo}_7\text{O}_{24}\) as Mo precursor. Transition metals were determined to be in the heptagonal channels. These materials are good catalysts for the acrolein oxidation to acrylic acid, and they are expected to expand the application domain of crystalline Mo-V-based complex oxides.

In chapter 7, general conclusions were drawn. Highly efficient crystalline Mo-V-W-Cu-O catalyst for acrolein oxidation to acrylic acid was successfully synthesized by a hydrothermal method. Addition of W and Cu into orthorhombic structure exhibits highly positive effect on the catalytic activity and selectivity to acrylic acid, respectively. Many years have passed since the discovery of active Mo and V-based oxide catalyst for the selective oxidation of acrolein to acrylic acid. The present work proposes that crystalline Mo-V-O with orthorhombic or trigonal structure is the real active phase for this reaction, and crystalline structure as well as the external surface area is important factor to impact catalytic activity.