



Effects of catalyst crystal structure on the oxidation of propene to acrolein



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ABSTRACT

Bismuth molybdate is known to be active for the oxidation of propene to acrolein and its activity can be altered by substitution of other elements (e.g. Fe, V, W) into the scheelite phase of α - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$. This work has further revealed that the apparent activation energy for acrolein formation correlates with the band gap of the catalyst measured at reaction temperature. It is, therefore, of interest to establish to how the crystal structure of the catalyst affects the activation energy. We report here an investigation of propene oxidation conducted over Bi, Mo, V oxides having the aurivillius structure with the composition $\text{Bi}_4\text{V}_{2-x}\text{Mo}_x\text{O}_{11+x/2}$ ($x=0-1$) and compare them with oxides having the scheelite structure with the composition $\text{Bi}_{2-x/3}\text{Mo}_x\text{V}_{1-x}\text{O}_{12}$ ($x=0-1$). The aurivillius-phase catalysts again show a correlation between the apparent activation energy and the band gap of the oxide, and the only difference being that for a given band gap, the apparent activation energy for the aurivillius-phase catalysts is 1.5 kcal/mol higher than that for the scheelite-phase catalysts. This difference is attributed to the lower heat of propene adsorption on the aurivillius-phase catalysts. A further finding is that for catalysts with band gaps greater than ~ 2.1 eV, the acrolein selectivity is $\sim 75\%$ for the conditions used and independent of the propene conversion. When the band gap falls below ~ 2.1 eV, the intrinsic selectivity to acrolein decreases rapidly and then decreases further with increasing propene conversion. This pattern shows that when the activity of oxygen atoms at the catalyst surface becomes very high, two processes become more rapid – the oxidation of the intermediate from which acrolein is formed and the sequential combustion of acrolein to CO_2 .

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1. Introduction

The oxidation of propene to acrolein has been widely studied because of the importance of acrolein as a monomer for acrylic polymers [1,2]. The principle catalysts used to promote this reaction are bismuth molybdates in which a part of the molybdenum is substituted by one or more other metals in order to enhance the catalyst activity and selectivity [3–10]. A number of groups have investigated the mechanism of propene oxidation on α - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ with the aim of understanding the elementary processes leading to acrolein and the influence of added elements on these processes [11–16]. These efforts have led to the following findings. On a fully oxidized catalyst, propene oxidation occurs via a Mars van Krevelen mechanism in which propene adsorbs reversibly and then reacts with an oxygen atom of the catalyst. This rate-limiting step leads to cleavage of one of the C–H bonds of the methyl group of

the adsorbed propene and results in the formation of an adsorbed OH group and a loosely adsorbed allyl radical that is rapidly stabilized as an adsorbed vinylalkoxide. Loss of an H atom from the later species leads to the formation of acrolein. Consistent with this mechanism and with the observed kinetics, the rate of acrolein formation is first order in the partial pressure of propene and zero order in the partial pressure of oxygen.

Several investigations have shown that the apparent activation energy for propene oxidation to acrolein can be reduced by the replacement of Mo by Fe or V for catalysts maintaining a scheelite structure over fully oxidized catalyst [3,17–20]. We have reported in previous sections that the activation barrier for the rate-limiting step is well described by the band-gap of such catalysts, the activation energy decreasing with the band gap [21]. What is not known, though, is how the correlation might be affected by the crystal structure of the catalyst. Therefore, the present study was undertaken in order to extend the exploration of the relationship between catalyst composition/structure and catalyst activity/selectivity to a different crystal structure.

The oxide phase chosen for study is the aurivillius structure [22]. This phase has the general stoichiometry of $\text{Bi}_2\text{A}_{n-1}\text{B}_n\text{O}_{3n+3}$

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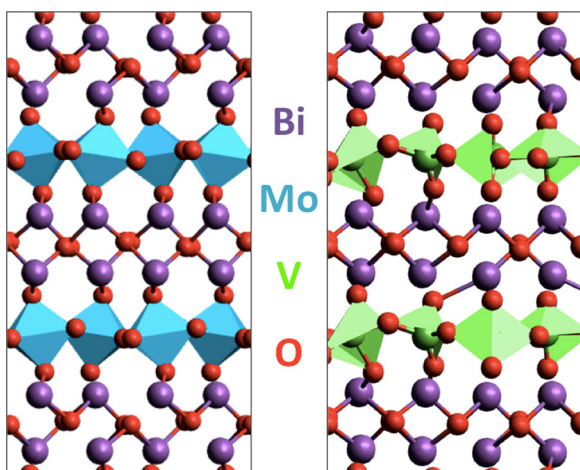


Fig. 1. Aurivillius crystal structures of Bi_2MoO_6 (left) and distorted oxygen deficient $\text{Bi}_4\text{V}_2\text{O}_{11}$ (right). Crystallographic data from [23] and [24].

and consists of n perovskite-like layers ($\text{A}_{n-1}\text{B}_n\text{O}_{3n+1}$ sandwiched between bismuth–oxygen sheets $(\text{Bi}_2\text{O}_2)^{2+}$ [22]. The simplest crystal structure has $n=1$ and corresponds to Bi_2MoO_6 (the gamma phase of the bismuth molybdate) or Bi_2WO_6 . $\text{Bi}_4\text{V}_2\text{O}_{11}$ is related to the first member of the family of aurivillius compounds, but is oxygen-deficient and can be expressed as $(\text{Bi}_2\text{O}_2)(\text{VO}_{3.5}\square_{0.5})$ [23]. Fig. 1 shows the structures of Bi_2MoO_6 and $\text{Bi}_4\text{V}_2\text{O}_{11}$ plotted using the crystal structure refinement data in references [23] and [24] respectively. Bi_2MoO_6 is characterized by fluorite-like layers of $(\text{Bi}_2\text{O}_2)^{2+}$ alternating with perovskite-like layers of $(\text{MoO}_4)^{2-}$. The structural similarity between Bi_2MoO_6 and the distorted oxygen-deficient $\text{Bi}_4\text{V}_2\text{O}_{11}$ is apparent from Fig. 1, where the later structure consists of $(\text{Bi}_4\text{O}_4)^{4+}$ layers that alternate between layers of joined 4- and 5-coordinate vanadia species with overall $(\text{V}_2\text{O}_7)^{4-}$ composition. The work presented here reveals the similarities and differences between the mechanism and kinetics of propene oxidation to acrolein over oxides having an aurivillius structure with the stoichiometry $\text{Bi}_4\text{V}_{2-x}\text{Mo}_x\text{O}_{11+x/2}$ ($x=0-1$) and oxides having a scheelite structure with the stoichiometry $\text{Bi}_{2-x/3}\text{Mo}_x\text{V}_{1-x}\text{O}_4$ ($x=0-1$).

2. Methods

2.1. Catalyst preparation

Molybdenum-substituted bismuth vanadate catalysts ($\text{Bi}_4\text{V}_{2-x}\text{Mo}_x\text{O}_{11+x/2}$) were prepared by the complexation method, as described in more detail elsewhere [17]. Bismuth (III) nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$) (99.98% Sigma-Aldrich), ammonium metavanadate (NH_4VO_3) (99% Sigma-Aldrich) and ammonium molybdate tetrahydrate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 5\text{H}_2\text{O}$) (99.98% Sigma-Aldrich) are used as precursors. These metal precursors were mixed to achieve atomic ratios of $\text{Bi}:\text{V}:\text{Mo}=4:(2-x):x$ in order to produce materials with the stoichiometry $\text{Bi}_4\text{V}_{2-x}\text{Mo}_x\text{O}_{11+x/2}$. The metal precursors were added 50 mL of water together with citric acid (1:1 molar ratio with metal precursors). The resulting solution was heated at 353 K for about 24 h in air to form a gel. The gel was then dried at 393 K and calcined in flowing air at 1023 K for 12 h. The material was then slowly cooled in air at 30 K/h to 573 K and then at 60 K/h to room temperature.

2.2. Catalyst characterization

X-ray diffraction patterns were obtained with a Bruker-AXS D8 Discover GADDS diffractometer using $\text{Cu K}\alpha$ radiation. Data were collected in the range of $10^\circ < 2\theta < 80^\circ$ every 0.02° .

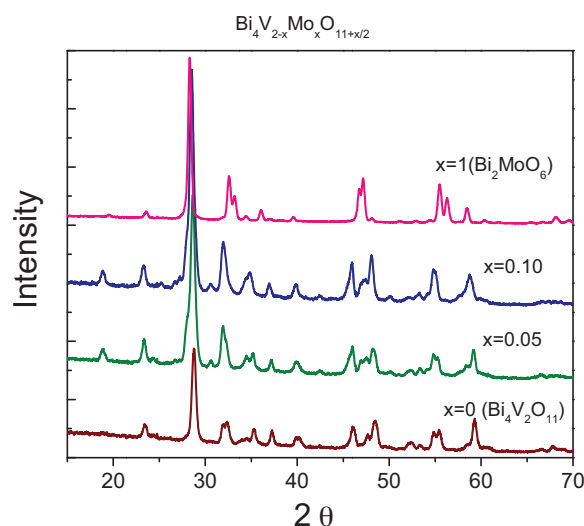


Fig. 2. XRD patterns of $\text{Bi}_4\text{V}_{2-x}\text{Mo}_x\text{O}_{11+x/2}$ catalysts.

Diffuse reflectance UV–vis–NIR spectra were acquired using a Fischer Scientific EVO 300 spectrometer equipped with a Praying Mantis reflectance chamber and an in situ high-pressure cell (Harrick Scientific, Inc), fitted with quartz windows. Spectra were referenced to the diffuse reflectance spectrum of a Teflon reference tile. The procedure used to extract band-gap energies from absorption edge data is given in the Supporting Information.

2.3. Catalyst activity and selectivity

Measurements of reaction rates and product distributions were performed using a packed bed quartz tube reactor (10 mm in diameter) loaded with 100–800 mg of catalyst. The catalyst was preheated to the reaction temperature in air over night prior to starting a reaction. The operating temperature is between 623 and 713 K and assures that no bulk phase changes occurred in the catalyst. All experiments were carried out at atmospheric pressure with 3.3–16.7% propene (99.9%, Praxair) and 3.3–16.7% oxygen (supplied from 20% oxygen in helium, Praxair), balanced as needed with additional helium (99.995%, Praxair). Organic products were analyzed using a gas chromatograph (GC) equipped with a 30 m HP-PLOT Q column and a flame ionization detector (FID). An Alltech Hayesep DB packed column and a thermal conductivity detector (TCD) were used to analyze for oxygen, CO and CO_2 . Data were collected at steady-state. Conversion was calculated on the basis of products formed and product selectivity was defined as the moles of propene converted to the product over the sum of the moles of olefins converted to all products, based on a carbon balance. All selectivities reported in this study are intrinsic selectivity, extrapolated when the conversion is very low ($< 1\%$).

3. Results

3.1. Catalyst characterization

Powder X-ray diffraction patterns of $\text{Bi}_4\text{V}_{2-x}\text{Mo}_x\text{O}_{11+x/2}$ for $x=0$, 0.05, 0.1, and 1.0 are shown in Fig. 2. Comparison of these patterns with those in the literature shows that each material is a pure phase [25,26]. $\text{Bi}_4\text{V}_2\text{O}_{11}$ is stable in the α -phase polymorph for temperatures of below 723 K, and therefore the diffraction pattern for this material is assigned to α - $\text{Bi}_4\text{V}_2\text{O}_{11}$. For $\text{Bi}_4\text{V}_{2-x}\text{Mo}_x\text{O}_{11+x/2}$, where $x=0.5$ and 0.1, the material is taken to be in the β -phase based on previous studies showing this phase to be stable for $0.05 < x < 0.225$ [24,27].

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