



# Selective oxidation and oxidative dehydrogenation of hydrocarbons on bismuth vanadium molybdenum oxide



Zheng Zhai, Xuan Wang, Rachel Licht, Alexis T. Bell\*

Department of Chemical and Biomolecular Engineering, The University of California Berkeley, Berkeley, CA 94720-1462, USA

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## ABSTRACT

A systematic investigation of the oxidative dehydrogenation of propane to propene and 1- and 2-butene to 1,3-butadiene, and the selective oxidation of isobutene to methacrolein was carried out over  $\text{Bi}_{1-x/3}\text{V}_{1-x}\text{Mo}_x\text{O}_4$  ( $x = 0-1$ ) with the aim of defining the effects of catalyst and reactant composition on the reaction kinetics. This work has revealed that the reaction kinetics can differ significantly depending on the state of catalyst oxidation, which in turn depends on the catalyst composition and the reaction conditions. Under conditions where the catalyst is fully oxidized, the kinetics for the oxidation of propene to acrolein and isobutene to methacrolein, and the oxidative dehydrogenation of propane to propene, 1-butene and trans-2-butene to butadiene are very similar—first order in the partial pressure of the alkane or alkene and zero order in the partial pressure of oxygen. These observations, together with XANES and UV–Vis data, suggest that all these reactions proceed via a Mars van Krevelen mechanism involving oxygen atoms in the catalysts and that the rate-limiting step involves cleavage of the weakest C–H bond in the reactant. Consistent with these findings, the apparent activation energy and pre-exponential factor for both oxidative dehydrogenation and selective oxidation correlate with the dissociation energy of the weakest C–H bond in the reactant. As the reaction temperature is lowered, catalyst reoxidation can become rate-limiting, the transition to this regime depending on ease of catalyst reduction and effectiveness of the reacting hydrocarbons as a reducing agent. A third regime is observed for isobutene oxidation at lower temperatures, in which the catalyst is more severely reduced and oxidation now proceeds via reaction of molecular oxygen, rather than catalyst lattice oxygen, with the reactant.

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## 1. Introduction

The oxidation of propene to acrolein and isobutene to methacrolein and the oxidative dehydrogenation of *n*-butene to 1,3-butadiene are used to produce commodity chemicals and monomers for a variety of polymers. Most of the catalysts used to promote these reactions are based on bismuth molybdate to which other metals are added to enhance activity and product selectivity [1–22]. For this reason, there is considerable interest in understanding the influence of catalyst composition on catalyst activity and selectivity reaction process, and the effects of reactant composition on rate of product formation and the distribution of products formed. Surprisingly, though, there have been relatively few in depth investigations conducted on this subject.

Of the several systems of interest, the one that has been investigated most extensively is the oxidation of propene to acrolein over bismuth molybdate. This reaction has been shown to proceed via a Mars van Krevelen mechanism [23]. The rate-limiting step

has been shown to involve the abstraction of an H atom from the methyl group of propene to form an allyl intermediate, which is then stabilized on the catalyst surface as a vinyl alkoxide. Acrolein is then produced by the abstraction of a second H atom from the alkoxide species [24,25]. Much less is known, though, about the reactions of other hydrocarbons over bismuth molybdate-based catalysts. Studies of the oxidative dehydrogenation of *n*-butenes to butadiene over bismuth molybdate have been carried out, and mechanism for this reaction is thought to resemble that for the oxidation of propene [26–30]. On the other hand, several different mechanisms have been proposed for the oxidation of isobutene to methacrolein, including a Langmuir–Hinshelwood mechanism and a redox model [31–33].

It is notable that previous studies of reaction mechanism and kinetics have tended to be reactant specific, and very few have involved a systematic investigation of the effects of catalyst and reactant composition. A notable exception has been the case of propene oxidation to acrolein over  $\text{Bi}_{1-x/3}\text{V}_{1-x}\text{Mo}_x\text{O}_4$  ( $x = 0-1$ ) [34] prepared with a scheelite structure. Ueda et al. [12] and Sleight et al. [35,36] have reported that  $\text{Bi}_{1-x/3}\text{V}_{1-x}\text{Mo}_x\text{O}_4$  is more active for the oxidation of propene than either bismuth molybdate

\* Corresponding author.

E-mail address: [bell@cchem.berkeley.edu](mailto:bell@cchem.berkeley.edu) (A.T. Bell).

( $x = 1$ ) or bismuth vanadate ( $x = 0$ ). Our previous work proposed a generalized model for the kinetics of propene oxidation over  $\text{Bi}_{1-x/3}\text{V}_{1-x}\text{Mo}_x\text{O}_4$ , and explained the exact roles of Bi, Mo, and V in affecting the activity and selectivity of  $\text{Bi}_{1-x/3}\text{V}_{1-x}\text{Mo}_x\text{O}_4$  [37–39]. By contrast, very little is known about the oxidation and oxidative dehydrogenation of butene isomers over vanadium-substituted bismuth molybdate. Therefore, many questions are still open. For example, will both reactions follow a mechanism similar to that propene oxidation for all catalyst compositions, and how does the composition and structure of the reactant affect reactant reactivity? Another question not fully understood is whether the reaction kinetics are the same independent of reaction conditions and if different for different reaction conditions, what are the mechanistic implications?

The work reported here was undertaken in order to determine catalyst and reactant composition, as well as reaction conditions affect the kinetics for the oxidative dehydrogenation of propane and 1- and 2-butene, and the selective oxidation of propene and isobutene over  $\text{Bi}_{1-x/3}\text{V}_{1-x}\text{Mo}_x\text{O}_4$ . The oxidation state of the catalyst reduction was probed by in situ XANES and UV–Vis spectroscopy. The results of this work demonstrate that  $\text{Bi}_{1-x/3}\text{V}_{1-x}\text{Mo}_x\text{O}_4$  can operate in one of three regimes depending on the reactant and catalyst composition, the reaction temperature, and the partial pressure of the reactants. Under conditions where the catalyst is maintained in its fully oxidized state, all reactions follow a Mars van Krevelen mechanism. Under these conditions, the reaction kinetics are first order in the partial pressure of the reactant and zero order in oxygen, and both the apparent activation energy and the apparent pre-exponential factor increase with the strength of the weakest C–H bond of the reactant involved in the rate-limiting step. When the rate of catalyst reoxidation cannot keep up with the rate of catalyst reduction, the reaction becomes zero order in reactant and fractional order in oxygen partial pressure. In this case, the apparent activation energy and pre-exponential factor become independent of the reactant composition and reflective of the activation energy for catalyst reoxidation. When the catalyst is more severely reduced, reaction kinetics become inverse order in reactant and first order in oxygen partial pressure. Under these conditions, the apparent activation energy is very high and the reaction is thought to proceed via the reaction of adsorbed molecular  $\text{O}_2$  and the reactant.

## 2. Methods

### 2.1. Catalyst preparation

Catalysts were prepared by the complexation procedure [37]. The metal precursors, ammonium molybdate tetrahydrate (99.98%, Sigma–Aldrich), bismuth (III) nitrate pentahydrate (99.98%, Sigma–Aldrich), and ammonium metavanadate (99%, Sigma–Aldrich), at the atomic ratios of Bi:V:Mo =  $(1 - x/3):(1 - x):x$  ( $x = 0\text{--}1.0$ ), were mixed with citric acid (1:1 M ratio with metal precursors) to produce materials with the stoichiometry  $\text{Bi}_{1-x/3}\text{V}_{1-x}\text{Mo}_x\text{O}_4$ . Metal precursors with citric acid were dissolved separately and then mixed together slowly. 2 M  $\text{HNO}_3$  was used in place of water to dissolve bismuth nitrate to prevent precipitation of bismuth hydroxides. The resulting solution was dried at 60 °C for about 24 h in air to form a gel, which was then dried at 120 °C and calcined in flowing air at 600 °C for 6 h. Powdered catalysts were obtained.

### 2.2. Catalyst characterization

X-ray absorption spectroscopy (XAS) measurements were performed at the Advanced Photon Source at Argonne National

Laboratory (ANL) on beam line 10BM. Measurements were performed as described previously [37]. Data were acquired at the Bi  $L_{3}$ -edge, and at the Mo and V K-edges before and after exposure to reactant at 713 K. Additional data were acquired in situ at the Mo K-edge under steady-state reaction conditions. These experiments were carried out in a controlled-atmosphere cell that could be heated up to 743 K in the presence of flowing gas [40].

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.). Spectra were referenced to the diffuse reflectance spectrum of a Teflon reference.

### 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 50–200 mg of catalyst. Prior to reaction, the catalyst was preheated to the reaction temperature in air. All experiments were carried out at atmospheric pressure with 3.3–16.7% propene (99.9%, Praxair), 1-butene (99%, Praxair), trans-2-butene (99%, Praxair), isobutene (99%, Praxair), propane (99%, Praxair), and 3.3–16.7% oxygen (supplied from 20% oxygen in helium, Praxair), balanced as needed with additional helium (99.995%, Praxair). Data were collected at steady state between 573 K and 713 K. Products were analyzed using a gas chromatograph (Agilent 6890A) equipped with a 30 m HP-PLOT Q column and a flame ionization detector (FID), for analyzing hydrocarbons. An Alltech Hayesep DB packed column connected to a thermal conductivity detector (TCD) was used to analyze for oxygen, and carbon mono- and di-oxides. Reactant conversion was calculated on the basis of products formed. Product selectivity was defined as the moles of reactant converted to the product over the sum of the moles of reactant converted to all products, based on a carbon balance. All selectivities reported in this study are intrinsic selectivities, extrapolated to a conversion of <1%.

## 3. Results

### 3.1. Kinetics

#### 3.1.1. Product distribution

The main product of 1-butene and trans-2-butene oxidation over  $\text{Bi}_{1-x/3}\text{V}_{1-x}\text{Mo}_x\text{O}_4$  is 1,3-butadiene, and the principle by-products are trans-, cis-2-butene, and 1-butene. The influence of vanadium content on catalyst activity for 1,3-butadiene formation from 1-butene and trans-2-butene is presented in Fig. 1. In both cases, the activity passes through a maximum at  $x = 0.45$  in a manner similar to that observed for propene oxidation to acrolein production over the same catalysts [37].

The selectivities to products formed from 1-butene and trans-2-butene are presented in Fig. 2. For both 1-butene and trans-2-butene, the product selectivities are similar and in each case the main product is 1,3-butadiene. However, the selectivity to 1,3-butadiene is higher starting from 1-butene than from trans-2-butene. For both isomers of butene, the selectivity to 1,3-butadiene passes through a shallow minimum at  $x = 0.45$  with increasing value of  $x$ . By contrast, the selectivity to isomers of the reactant passes through a maximum at the same value of  $x$ .

The main product of isobutene oxidation is methacrolein, and the principle by-products are CO,  $\text{CO}_2$ , and ethene. As shown in Fig. 3, the activity for methacrolein formation at 703 K increases with the value of  $x$ , and then reaches a maximum for  $\text{Bi}_{0.85}\text{Mo}_{0.45}\text{V}_{0.55}\text{O}_4$  ( $x = 0.45$ ). Product selectivities are also presented in Fig. 3. The selectivity to methacrolein is 55% for  $x = 0$ ,

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