Contents lists available at SciVerse ScienceDirect



Applied Catalysis A: General

CATALYSIS

journal homepage: www.elsevier.com/locate/apcata

Effects of iron content on bismuth molybdate for the oxidative dehydrogenation of *n*-butenes to 1,3-butadiene

Jung-Hyun Park^a, Hyeryeung Noh^b, Ji Won Park^b, Kyoungho Row^b, Kwang Deog Jung^c, Chae-Ho Shin^{a,*}

^a Department of Chemical Engineering, Chungbuk National University, Chungbuk 361-763, Republic of Korea

^b Process Solution Team, Kumho Petrochemical R&BD Center, Daejeon 305-348, Republic of Korea

^c Clean Energy Center, Korea Institute of Science and Technology, Seoul 136-791, Republic of Korea

ARTICLE INFO

Article history: Received 8 November 2011 Received in revised form 31 March 2012 Accepted 19 April 2012 Available online 26 April 2012

Keywords: Bismuth molybdenum iron oxide Oxidative dehydrogenation *n*-Butenes 1.3-butadiene Oxygen mobility

1. Introduction

1,3-Butadiene (BD) is an important raw material for the manufacture of such as styrene butadiene rubber, poly-butadiene rubber, and acrylonitrile-butadiene-styrene resin and demand for it is increasing. It is mainly produced by extracting C4 raffinates from naphtha cracking, though the limited supply of C4 raffinates has encouraged the use of alternative intermediates such as butenes and ethanol for BD production. The oxidative dehydrogenation (ODH) of butenes can efficiently produce BD in high yields [1,2]. Tested transition metal oxide catalysts for the ODH of 1-butene include manganese oxide molecular sieves [3], K-doped VO_x/Al₂O₃ [4], zinc ferrites [5–9], and multicomponent oxides based on bismuth molybdate [10-19]. Bismuth molybdates can be classified into three phases – α -Bi₂Mo₃O₁₂, β -Bi₂Mo₂O₉, and γ -Bi₂MoO₆ – according to Bi/Mo molar ratio and its structural effects have been investigated for the ODH of butenes [10-15], the ammoxidation of propylene [20] and the selective oxidation of propane to acrolein [21]. Matsuura et al. [15] have compared the catalytic activities of bismuth molybdate catalysts with different molar ratios of Bi/Mo. The catalytic activity of γ - and α -type bismuth molybdate has been less than β -type or mixed phases of γ - and α -type, though the structural effects of bismuth molybdate on its catalytic activity are

ABSTRACT

BiMoFe_x oxide catalysts (x = 0-1.00) were prepared by co-precipitation and their catalytic activities in the oxidative dehydrogenation of *n*-butenes were tested. X-ray diffraction (XRD) and Raman spectroscopy showed that the main solid phases were composed of Bi₃Mo₂FeO₁₂ as oxygen acceptor and Fe₂(MoO₄)₃ as oxygen donor and the mixing of these phases enhanced catalytic activity. XRD patterns showed that Fe₂(MoO₄)₃ was reduced to FeMoO₄ during the reaction. The peak temperature of programmed reduction of 1-butene and successive oxidation (TPRO) was dependent on Fe contents in BiMoFe_x oxide catalysts and was minimized at x = 0.65, which showed the greatest oxygen mobility. The peak position in the low temperature region of TPRO profiles could be correlated with butene conversion and BD yield.

© 2012 Elsevier B.V. All rights reserved.

not fully elucidated. However, it is generally accepted that oxygen mobility of bismuth molybdate catalysts affects the ODH of butenes, likely related to the Mars-van Krevelen mechanism [11–13,17]. Ruckenstein et al. [22] reported that oxygen diffusivity and catalytic activity could be varied with phase, increasing in the order: $\gamma > \beta > \alpha$. Jung et al. [18] also reported that γ -Bi₂MoO₆ showed good catalytic activity in the ODH of butenes due to facile oxygen mobility. Multicomponent oxides based on bismuth molybdate for ODH reaction have been extensively studied to enhance catalytic activity by adding oxides such as P, Co, Fe, and Ni, etc. [7,20,23–28].

This work reports the comparison of catalytic activities for the ODH of 1-butene to BD over $BiMoFe_x$ oxide catalysts with different iron contents (x = 0-1.00) prepared by co-precipitation. The Bi/Mo molar ratio was set at 1.0 and the various concentrations of iron were tested to maximize the conversion and selectivity to BD in the ODH of 1-butene. $BiMoFe_x$ oxide catalysts with different Fe contents were characterized by using N₂ sorption, X-ray diffraction (XRD), temperature-programmed reduction (TPR)-successive oxidation (TPRO), 1-butene temperature-programmed desorption (TPD), Raman spectroscopy, and elemental analysis.

2. Experimental

2.1. Preparation of bismuth molybdenum iron catalysts

BiMoFe_x oxide catalysts (x=0-1.00) were prepared by conventional co-precipitation. The desired amount of bismuth

^{*} Corresponding author. Tel.: +82 43 261 2376; fax: +82 43 269 2370. *E-mail address:* chshin@chungbuk.ac.kr (C.-H. Shin).

⁰⁹²⁶⁻⁸⁶⁰X/\$ - see front matter © 2012 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.apcata.2012.04.028

nitrate $(Bi(NO_3)_3 \cdot 5H_2O)$, Junsei Chemical, 98%) was dissolved in de-ionized water acidified with 10% nitric acid and added dropwise into ammonium molybdate solution $((NH_4)_6Mo_7O_{24}\cdot 4H_2O)$, Sigma–Aldrich, 99%) under vigorously stirring at 60 °C. Ferric nitrate (Fe(NO_3)_3 \cdot 9H_2O), Samchun, 98%) in de-ionized water was then added. The mixture was adjusted to pH 5 by aqueous 35 wt% NH₄OH and aged at room temperature for 4 h. Excess water was then removed at 60 °C using a rotary evaporator. The resulting powder was dried at 100 °C overnight and calcined at 550 °C for 2 h in an air flow. The catalysts were labeled BiMoFe_x (x = 0–1.0). For the comparison of catalytic activities of BiMoFe_x oxide catalysts, bismuth molybdate with different molar ratios of Mo/Bi = 3/2, 2/2, and 1/2 were prepared by co-precipitation method.

2.2. Characterization

Elemental analysis was carried out with a Jarrell-Ash Polyscan 61E inductively coupled plasma spectrometer with a PerkinElmer 5000 atomic emission spectrophotometer (ICP-AES). Powder XRD patterns were collected on a Siemens D5005 diffractometer with Cu K α radiation (30 kV and 50 mA). Raman spectra were recorded on a Bruker Optic GMBH FRA 106/S with an Nd:YAG laser (300 mW, 500 scan). Raman spectra of pure Bi₃Mo₂FeO₁₂ and Fe₂(MoO₄)₃ synthesized by co-precipitation were recorded for reference. BET surface areas and total pore volumes were determined from N₂ adsorption isotherms (Micromeritics ASAP 2020) at -196 °C. The relationship between catalytic activity and Fe content was assessed through the temperature-programmed reduction of 1-butene and subsequent oxidation (TPRO) recorded on fixed-bed, flow-type apparatus attached to a Balzers QMS200 quadruple mass spectrometer. For the temperature programmed reduction by 1-butene, 0.3 g catalyst was pretreated at 420 °C for 3 h in flowing 1-butene (20 cm³ min⁻¹), held for 1 h at that temperature and then cooled to room temperature in flowing He (20 cm³ min⁻¹). Subsequent temperature programmed oxidation was performed in flowing 5% O_2/N_2 (20 cm³ min⁻¹) from room temperature to 500 °C at 10°C min⁻¹. 1-Butene TPD was carried out on the same apparatus. 1-Butene was adsorbed at 50°C and purged under flowing He $(50 \text{ cm}^3 \text{ min}^{-1})$ for 0.5 h before TPD from 50 to 800 °C at $10 \circ C \min^{-1}$. Mass signals of $m/z = 18 (\circ H_2 O), 44 (\circ CO_2), 54 (\circ C_4 H_6),$ and 56 (${}^{\bullet}C_{4}H_{8}$) were detected.

In order to elucidate the concept of oxygen acceptor and donor in BiMoFe_x oxide catalysts, $Bi_3Mo_2FeO_{12}$ and $Fe_2(MoO_4)_3$ which were the main component in BiMoFe_x oxide catalysts were independently prepared and the mechanical mixture of $Bi_3Mo_2FeO_{12}$ and $Fe_2(MoO_4)_3$ was also prepared by using ultrasonic waves in hexane as solvent. The composition of the mixture of $Bi_3Mo_2FeO_{12}$ and $Fe_2(MoO_4)_3$ was 9:1 in wt%. After that, the hexane was removed by using a rotary evaporator and dried at 100 °C for 12 h. The catalysts were used without heat treatment. Pulse O_2 adsorption experiments of $Bi_3Mo_2FeO_{12}$, $Fe_2(MoO_4)_3$ and the mixture of Bi₃Mo₂FeO₁₂ and Fe₂(MoO₄)₃ (9:1 in wt%) were performed at 420 °C. Each 0.1 g catalyst was placed in the U-shape quartz reactor (I.D. 12 mm) with densely packed quartz wool. All catalysts were pretreated at 420 °C for 1 h under flowing 5% H₂/Ar (50 cm³ min⁻¹) and subsequently purged for 0.5 h under flowing He (50 cm³ min⁻¹). After that, pulse O₂ adsorption experiments were carried out by contacting fixed amounts of reactant gases with He as the carrier gas. The amount of O₂ in each pulse, which was introduced using a volumetric sample loop of 2 cm³ (71 µmol) and the pulse was repeated seven times with 10 min interval. The mass signal of m/z = 32 (•O₂) was detected.

2.3. Oxidative dehydrogenation (ODH) of 1-butene

The ODH of 1-butene was performed at atmospheric pressure in a conventional continuous-flow microreactor. Prior to the reaction, the catalyst was routinely activated under flowing N₂ (50 cm³ min⁻¹) at 500 °C for 2 h. The reaction temperature was fixed at 420 °C and 1-butene, air and water reagents with a 1:5.75:5 molar ratios were used at a constant flow rate of 100 cm³ min⁻¹. The water feed was continuously vaporized in a pre-heating zone at 180°C. The reaction products were analyzed by on-line gas chromatography (Varian 3800) on an Al₂O₃/KCl column of 50 m length and 0.32 mm diameter with a flame ionization detector (FID) to analyze hydrocarbons and a Porapak Q packed column of 2 m length and 1/8 in. diameter with a thermal conductivity detector (TCD) to analyze CO and CO₂. The reaction products consisted of dehydrogenation products (BD), isomerization products (trans and cis-2-butene) and combustion products (CO and CO₂). Cracking products (CH₄, C₂H₄, C₂H₆, C₃H₆ and C₃H₈) were almost negligible. The isomerization products of 1-butene to cis- and trans-2-butene were considered as reactants. The conversion of butenes was calculated as the molar ratio of the butenes reacted to the 1-butene fed. The selectivity and yield in BD were calculated on the basis of mass balance and the yield was obtained by multiplying the conversion and the selectivity of BD.

3. Results and discussion

3.1. Characterization of the BiMoFe_x oxide catalysts

Table 1 lists BET surface area, total pore volume, elemental analyse and solid phases of the fresh and used BiMoFe_x oxides. BET surface area and total pore volume of samples calcined at 550 °C increased with increasing Fe content in the range $1.4-3.8 \text{ m}^2 \text{ g}^{-1}$. Elemental analysis showed that the samples maintained atomic ratios of each element similar to their nominal compositions.

XRD patterns of samples were recorded before and after the ODH of 1-butene at 420 °C for 14 h (Fig. 1). The XRD patterns of bismuth molybdate with different molar ratios of Bi/Mo before and after ODH reaction are also shown in Table SI 1 and Fig. SI 1.

Table 1

Atomic ratio, BET surface area, total pore volume and XRD phases of BiMoFe_x oxide catalysts with different Fe contents.

| Catalyst | Atomic ratio ^a | | | $S_{\text{BET}}(\text{m}^2 \text{g}^{-1})$ Pore volume | Pore volume | XRD phases calcined ^b | After reaction ^c | |
|------------------------|---------------------------|------|------|--|------------------|---|--|--|
| | Bi | Мо | Fe | | $(cm^{3}g^{-1})$ | | | |
| BiMoFe _{0.20} | 1.0 | 0.98 | 0.21 | 2.6 | 0.008 | β -Bi ₂ Mo ₂ O ₉ > Bi ₃ Mo ₂ FeO ₁₂ > α -Bi ₂ Mo ₃ O ₁₂ | β -Bi ₂ Mo ₂ O ₉ > Bi ₃ Mo ₂ FeO ₁₂ > α -Bi ₂ Mo ₃ O ₁₂ | |
| BiMoFe _{0.35} | 1.0 | 0.97 | 0.34 | 2.8 | 0.009 | β -Bi ₂ Mo ₂ O ₉ > Bi ₃ Mo ₂ FeO ₁₂ > α -Bi ₂ Mo ₃ O ₁₂ | β -Bi ₂ Mo ₂ O ₉ > Bi ₃ Mo ₂ FeO ₁₂ > α -Bi ₂ Mo ₃ O ₁₂ > FeMoO ₄ | |
| BiMoFe _{0.50} | 1.0 | 0.96 | 0.50 | 3.1 | 0.012 | $Bi_3Mo_2FeO_{12} > Fe_2(MoO_4)_3$ | Bi ₃ Mo ₂ FeO ₁₂ > FeMoO ₄ | |
| BiMoFe _{0.65} | 1.0 | 0.97 | 0.65 | 3.6 | 0.014 | $Bi_3Mo_2FeO_{12} > Fe_2(MoO_4)_3$ | Bi ₃ Mo ₂ FeO ₁₂ > FeMoO ₄ | |
| BiMoFe _{0.75} | 1.0 | 0.95 | 0.74 | 3.8 | 0.023 | $Bi_3Mo_2FeO_{12} > Fe_2(MoO_4)_3$ | Bi ₃ Mo ₂ FeO ₁₂ > FeMoO ₄ | |
| BiMoFe _{0.85} | 1.0 | 0.98 | 0.87 | 3.5 | 0.027 | $Bi_3Mo_2FeO_{12} > Fe_2(MoO_4)_3$ | $Bi_3Mo_2FeO_{12} > FeMoO_4$ | |
| BiMoFe _{1.00} | 1.0 | 1.04 | 1.07 | 3.4 | 0.030 | $Bi_3Mo_2FeO_{12} > Fe_2(MoO_4)_3$ | $Bi_3Mo_2FeO_{12} > FeMoO_4$ | |

^a Determined by ICP-AES.

 $^{\rm b}\,$ Calcined at 550 $^\circ C$ for 2 h in air flow.

 $^{\rm c}$ XRD patterns were obtained after 14 h on stream in ODH of 1-butene at 420 $^{\circ}{\rm C}$ for BiMoFe_x oxide catalysts.



Fig. 1. Powder XRD patterns of BiMoFe_x oxide catalysts with different Fe contents before (A) and after 14 h reaction at 420 °C (B); (a) mixture of β -Bi₂Mo₂O₉ and γ -Bi₂MoO₆, (b) x in BiMoFe_x oxide = 0.2, (c) 0.35, (d) 0.5, (e) 0.65, (f) 0.75, (g) 0.85, and (h) 1.00.

The solid phases of α -Bi₂Mo₃O₁₂ and γ -Bi₂MoO₆ catalyst were not changed after ODH of 1-butene at 420 °C for 6 h. However, β -Bi₂Mo₂O₉ catalyst, which was stable after calcination at 350 °C, was partly decomposed to β -Bi₂Mo₂O₉ and γ -Bi₂MoO₆ by the calcination at 550 °C. In addition, the peak intensity of γ -Bi₂MoO₆ phase increased after ODH of 1-butene, while that of β -Bi₂Mo₂O₉ phase decreased. This means the addition of H₂O in reactants is favorable to decompose β -Bi₂Mo₂O₉ to α - and γ -phase.

The solid phases of the fresh BiMoFe_x oxides were consisted of β -Bi₂Mo₂O₉, Bi₃Mo₂FeO₁₂, α -Bi₂Mo₃O₁₂, and Fe₂(MoO₄)₃. Bismuth molybdate can be formed in three phases: α -Bi₂Mo₃O₁₂, β -Bi₂Mo₂O₉ and γ -Bi₂MoO₆ [10–15]. At x<0.35, fresh samples showed mainly β -Bi₂Mo₂O₉ and minor phases of Bi₃Mo₂FeO₁₂ and α -Bi₂Mo₃O₁₂, β -Bi₂Mo₂O₉ with Bi/Mo = 1/1 is thermally unstable at 420 °C and was decomposed to a mixture of α - and γ -phases [15]. However, the β -Bi₂Mo₂O₉ in BiMoFe_{0.35} oxide was conserved after 14 h ODH of 1-butene and a new solid phase of FeMoO₄ was observed by the partial decomposition of Bi₃Mo₂FeO₁₂. BiMoFe_x oxide with x > 0.5 showed crystalline phases of Bi₃Mo₂FeO₁₂ and Fe₂(MoO₄)₃. Fe₂(MoO₄)₃ could be partially transformed to FeMoO₄ after 14 h ODH of 1-butene, changing the oxidation state of Fe from +3 to +2. The formation FeMoO₄ was maximized at x = 0.65. After 14 h reaction, α -Bi₂Mo₃O₁₂ in BiMoFe_x decreased with increasing Fe content and was not observed in BiMoFe_{0.65} oxide. Stoichiometrically, BiMoFe_{0.65} oxide should comprise equal parts of Bi₃Mo₂FeO₁₂ and FeMoO₄. However, XRD patterns showed mainly Bi₃Mo₂FeO₁₂ with a minor FeMoO₄ phase after 14 h reaction.

Raman spectroscopy was used to investigate the compositions and structures of catalysts (Fig. 2). Pure $Bi_3Mo_2FeO_{12}$ and $Fe_2(MOO_4)_3$, verified by XRD and elemental analysis, were used as references. Optical signals representing the vibrational modes of MOO_4 have been reported at 700–900 cm⁻¹ and its bending at 300–400 cm⁻¹. BiO bands have been recorded at 400–600 cm⁻¹ [15,29–31]. Hoefs et al. [30] suggested that the bands at 720 and 680 cm⁻¹ were due to the dioxo bridge connected to the molybdenum atom, which shows lattice oxygen. Pure bismuth iron molybdate, $Bi_3Mo_2FeO_{12}$ which could be noted as $Bi_3FeO_4(MOO_4)_2$ showed bands at 875, 783, 715, 323, 283, 133 cm⁻¹, in good agreement with reported data [31]. Fe₂(MOO₄)₃ showed a main peak at 783 cm⁻¹ and MoO₃ and MoO₄ modes at 283 cm⁻¹ and 355 cm⁻¹, respectively [33]. MoO₃ contains six oxygen atoms in an octahedral structure; with five of the oxygen atoms shared in distorted MoO₆ structures and the remainder as unshared Mo=O. BiMoFe_{0.2} oxide catalyst showed low-intensity absorption bands at 240–450 cm⁻¹ and 900 cm⁻¹ ascribed to the α phase [30]. The band at 958 cm⁻¹ was attributed to the β phase; that at 816 cm⁻¹ to the γ phase [15]. Raman spectra of BiMoFe_x oxide catalysts with *x* > 0.65 were almost consistent with that of pure Bi₃Mo₂FeO₁₂ [26], supporting the XRD pattern.

Many parameters have been proposed for the enhancement of catalysis in the ODH of 1-butene to favor BD production. They can be classified into five groups related to lattice oxygen ions, cations,



Fig. 2. Raman spectra of BiMoFe_x oxide catalysts with different Fe contents calcined at $550 \circ C$ for 2 h; (a) pure Bi₃Mo₂FeO₁₂, (b) x in BiMoFe_x oxide = 0.2, (c) 0.5, (d) 0.65, (e) 0.75, (f) 0.85, (g) 1.00 and (h) pure Fe₂(MoO₄)₃.



Fig. 3. (A) TPRO profiles of partially reduced BiMoFe_x oxide catalysts and (B) correlation between catalytic performance and oxygen mobility of BiMoFe_x oxide catalysts; (a) *x* in BiMoFe_x oxide = 0.2, (b) 0.5, (c) 0.65, (d) 0.85, and (e) 1.00.

electron mobility, cation-oxygen bonds and crystallographic structures [32]. The most widely applied parameter is oxygen mobility, which can be verified by TPRO and TPD analyses. In order to examine the role of lattice oxygen in the ODH of *n*-butenes to BD, TPRO analysis of BiMoFe_x oxide catalysts was performed (Fig. 3). Prior to TPRO analysis, catalysts were reduced under flowing 1-butene at 420 °C for 3 h. It is generally accepted that peak position in low temperature region of TPRO profile, that is related with the oxygen mobility, could be correlated with the catalytic activities for the ODH reaction of *n*-butenes [10,18]. Two main peaks were observed for each catalyst, implying the BiMoFe_x oxide had diverse oxygen vacancy sites. The first peak is observed in the 130-230 °C and the other one is in the 320-450 °C. The first peak of TPRO profiles could be contributed to the oxidation of bismuth species partially reduced and the second peak is assigned to the oxidation process of molybdenum and iron partially reduced [34]. Fig. 3(B) shows a correlation



Fig. 4. MS signals of 1-butene TPD of BiMoFe_{0.65} oxide catalyst. m/z = 18 (•H₂O), 44 (•CO₂), 54 (•C₄H₆) and 56 (•C₄H₈) were recorded during 1-butene TPD analysis.

between the oxygen mobility and catalytic performance of BiMoFe_x oxide catalysts in the ODH of *n*-butenes to BD. The catalytic activity of the BiMoFe_x oxide catalysts with different Fe content was related to the oxygen mobility. Yield in BD increased with decreasing peak temperature. This result means that the catalytic activity could be increased with increasing oxygen mobility of the catalyst. The oxygen mobility showed a linear plot with respect to BD yield and the peak temperature of TPRO profiles was minimized at x = 0.65, indicating that BiMoFe_{0.65} oxide catalyst had the highest oxygen mobility.

The adsorption of 1-butene on the catalysts was assessed by TPD (Figs. 4 and 5). Fig. 4 shows 1-butene TPD profiles from the most active catalyst, BiMoFe_{0.65} oxide. The m/z = 56 (•C₄H₈) mass signal progressively decreased with increasing desorption temperature. The mass signal m/z = 54 (•C₄H₆), possibly produced by the dehydrogenation of 1-butene, showed maxima at 70–140 and



Fig. 5. MS signals of m/z = 54 (•C₄H₆) recorded during 1-butene TPD of BiMoFe_x oxide catalyst with different Fe contents; (a) Bi₃Mo₂FeO₁₂, (b) Fe₂(MoO₄)₃, (c) *x* in BiMoFe_x oxide = 0.2, (d) 0.5, (e) 0.65, (f) 0.75, (g) 0.85, and (h) 1.00.



Fig. 6. Pulse O₂ adsorption profiles at 420 °C for (A) partially reduced catalysts of (a) $Fe_2(MoO_4)_3$, (b) $Bi_3Mo_2FeO_{12}$, and (c) $Bi_3Mo_2FeO_{12}/Fe_2(MoO_4)_3 = 9/1$ which was mechanically mixed in weight, and (B) the quantity of total O₂ adsorbed. Pulse O₂ adsorption experiments were repeated seven times with 10 min interval at 420 °C and O₂ consumption was calculated by integrating each pulse signal of O₂.

400–550 °C, respectively, due to weakly or strongly adsorbed 1butene with lattice oxygen of the catalyst.

1-Butene TPD profiles from the samples with different Fe contents show two desorption peaks (Fig. 5). The low temperature peak (α position) was related to oxygen donor sites; that at higher temperature (β position) was related to the active sites for dehydrogenation. The temperatures of both α and β positions were lowest at x = 0.65 in BiMoFe_x oxide catalysts. Desorbed BD was also maximized at x = 0.65. Pure solid phase Fe₂(MoO₄)₃ did not show β position, suggesting that the α position was related to oxygen donor sites. For the better understanding the role of oxygen acceptor and donor of BiMoFe_x oxide catalysts we performed the experiments of pulse O₂ adsorption.

Fig. 6 shows pulse O_2 adsorption profiles at $420 \circ C$ for partially reduced catalysts of $Fe_2(MOO_4)_3$, $Bi_3Mo_2FeO_{12}$, and $Bi_3Mo_2FeO_{12}/Fe_2(MOO_4)_3 = 9/1$ which was mechanically

mixed in weight. The amount of consumed O₂ on the mixture of $Bi_3Mo_2Fe_1O_{12} + Fe_2(MoO_4)_3$ oxide was much larger than that of the only $Bi_3Mo_2FeO_{12}$ and $Fe_2(MoO_4)_3$ catalyst. The sequence of O₂ consumption is Bi₃Mo₂FeO₁₂+ $Fe_2(MoO_4)_3 > Bi_3Mo_2FeO_{12} > Fe_2(MoO_4)_3$. This means that the adsorption capability of mixed Bi₃Mo₂FeO₁₂ + Fe₂(MoO₄)₃ catalyst is higher than that of pure $Bi_3Mo_2FeO_{12}$ and $Fe_2(MoO_4)_3$ catalyst, meaning that the addition of Fe₂(MoO₄)₃ phase in pure Bi₃Mo₂FeO₁₂ phase could promote the O₂ adsorption. Weng and Delmon [32] reported that the synergy of multicomponent oxide catalysts containing several oxide phases is attributed to the remote association of the donor and acceptor of oxygen or electrons in allylic oxidation and ODH. In such a mechanism, a donor phase dissociates oxygen to form a surface mobile species that can move to the acceptor phase, which is potentially the active phase. Stable Bi₃Mo₂FeO₁₂ has been shown to be an active phase (Table 2). Therefore, the less active redox couple of Fe₂(MoO₄)₃/FeMoO₄

could be a donor of oxygen. Chang et al. [33] reported that the presence of $Fe_2(MoO_4)_3$ phase in multicomponent BiMoFeCoP oxide promoted the mobility of surface oxygen or electrons formed by the transformation of Fe^{3+} to Fe^{2+} . Thus, in our system, it can be deduced that the phase of Bi₃Mo₂FeO₁₂ and Fe₂(MoO₄)₃ could be acceptor and donor of oxygen, respectively.

3.2. ODH of 1-butene

Based on bismuth molybdate catalyst with Bi/Mo=1/1, catalytic activities over BiMoFe_x oxide catalysts (x = 0 - 1.00) which were butene conversion, selectivities to BD and CO₂ and yield in BD are summarized in Table 2 and Fig. 7. For comparison, the catalytic performance of α -Bi₂Mo₃O₁₂, β -Bi₂Mo₂O₉, and γ -Bi₂MoO₆ catalyst was also tested and the results were shown in Table 2 and SI 2. Although initial conversion of butenes on γ -Bi₂MoO₆ catalyst was superior to the other bismuth molybdates catalysts, the rapid deactivation was observed. Among the bismuth molybdates catalysts used, the catalytic activity of bismuth molybdate with Bi/Mo = 1/1 was stable and showed the best catalytic activity after 6h on stream in the ODH reaction. The main products were BD and CO₂, with negligible by-products of C1-C3 compounds formed by C-C bond cleavage of 1-butene. Pure solid phase Bi₃Mo₂FeO₁₂ catalyst was stable during the reaction and showed the highest initial yields of BD and CO₂. BD yields of the BiMoFe_x oxide catalysts were much higher than that of pure bismuth molybdates and iron molybdates indicating that Bi₃Mo₂FeO₁₂ was an active phase in the ODH of 1-butene. After 14 h reaction, BiMoFe_{0.65} oxide catalyst consisting of Bi3Mo2FeO12 and FeMoO4 showed the highest butene conversion and BD yield. Conversion on BiMoFe_x oxides with x < 0.65 did not increase greatly with time on stream. BD yield on BiMoFe_x with x > 0.65 decreased, indicating that isolated Fe lowered BD selectivity. The low conversion and selectivity of $Fe_2(MoO_4)_3$ indicate that the redox couple of $Fe_2(MoO_4)_3$ /FeMoO₄ was not directly related to the catalytic reaction. Overall these results showed that enhanced catalysis by BiMoFe_x oxide in the ODH of 1-buene was due to the coexistence of Bi₃Mo₂FeO₁₂ and $Fe_2(MoO_4)_3$. Water is widely used in the dehydrogenation processes and it is added to help in the removal of the heat released in the dehydrogenation reaction [35]. When water was not fed in reactant stream, the conversion of *n*-butenes and the selectivity to CO_2 were higher than that of while the water-cofeeding [11]. However, the heat of reaction by the formation of CO_2 is \sim 20 times higher comparing to that for the formation of BD. The higher heat of reaction may cause hot spot during the ODH reaction. Therefore, it is necessary that the water is supplied for the suppression of CO₂ formation and safe operation in the ODH reaction.

| Table 2 | |
|-----------|----|
| Catalytic | no |

| cutary de performance or bimor ex onde cutarysts with amereneres |
|--|
|--|

| Catalyst | Conversion | (%) | Selectivity (wt%) | | | | Yield (wt%) | |
|--|------------|------|-------------------|------|-----------------|------|--------------|------|
| | t = 0 | 14 h | 1,3-BD | | CO ₂ | | 1,3-BD | |
| | | | t = 0 | 14 h | t = 0 | 14 h | <i>t</i> = 0 | 14 h |
| α -Bi ₂ Mo ₃ O ₁₂ ^a | 15.1 | 16.7 | 64.3 | 77.8 | 29.8 | 13.0 | 9.0 | 12.6 |
| β -Bi ₂ Mo ₂ O ₉ ^a | 48.9 | 43.6 | 81.0 | 84.1 | 18.5 | 15.7 | 39.6 | 36.7 |
| γ -Bi ₂ Mo ₁ O ₆ ^a | 47.8 | 10.9 | 75.4 | 38.8 | 10.1 | 52.0 | 36.4 | 3.8 |
| BiMoFe _{0.20} | 40.9 | 40.0 | 90.5 | 91.4 | 9.2 | 7.6 | 37.0 | 36.6 |
| BiMoFe 0.35 | 41.7 | 46.0 | 82.1 | 92.0 | 17.7 | 7.5 | 34.2 | 42.3 |
| BiMoFe 0.50 | 43.7 | 52.4 | 86.9 | 92.7 | 12.3 | 7.3 | 38.0 | 48.6 |
| BiMoFe 0.65 | 50.3 | 68.6 | 85.5 | 91.4 | 14.3 | 8.5 | 43.0 | 62.7 |
| BiMoFe 0.75 | 42.4 | 67.2 | 85.5 | 90.7 | 14.6 | 9.3 | 36.3 | 61.0 |
| BiMoFe 0.85 | 49.3 | 65.1 | 79.7 | 87.6 | 17.3 | 12.3 | 39.3 | 57.0 |
| BiMoFe 1.00 | 49.5 | 57.7 | 72.1 | 79.6 | 19.6 | 18.1 | 35.7 | 45.9 |
| Bi ₃ Mo ₂ FeO ₁₂ | 70.5 | 70.8 | 77.5 | 79.2 | 22.2 | 18.8 | 54.7 | 56.1 |
| $Fe_2(MoO_4)_3$ | 16.4 | 22.9 | 61.4 | 69.5 | 37.1 | 26.4 | 10.0 | 15.9 |
| FeMoO ₄ | 11.8 | 16.4 | 31.8 | 39.9 | 67.1 | 57.6 | 3.8 | 6.5 |

^a Conversion, selectivity, and yield for bismuth molybdate catalysts were obtained after 6 h on stream.



Fig. 7. Catalytic performance of $BiMoFe_x$ oxide catalysts as a function of Fe content in the ODH of 1-butene; (A) conversion of 1-butene and yield in BD and (B) selectivity to BD and CO_2 . The data were chosen after 14 h on stream.

4. Conclusions

BiMoFe_x (x=0-1.00) oxide catalysts were prepared by coprecipitation and used in the ODH of 1-butene to BD. Their main solid components confirmed by XRD and Raman spectroscopy was Bi₃Mo₂FeO₁₂ and Fe₂(MoO₄)₃. Their conversion of 1-butene and selectivity to BD depended on their Fe content due to synergy between the Bi₃Mo₂FeO₁₂ and Fe₂(MoO₄)₃ phases and was maximized at x = 0.65 in BiMoFe_x oxide catalysts. The peak temperature of TPRO profiles was dependent on Fe contents in BiMoFe_x oxide catalysts and was minimized at x = 0.65, which showed the greatest oxygen mobility. The peak position in the low temperature region of TPRO profiles could be correlated with butene conversion and BD yield.

Acknowledgments

The authors acknowledge the financial support of the Korea Energy Management Cooperation (KEMCO). This work is part of the Energy Technology Innovation Project (ETI) under the Energy Resources Technology Development Program.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/ 10.1016/j.apcata.2012.04.028.

References

- [1] H.H. Kung, Ind. Eng. Chem. Prod. Res. Dev. 25 (1986) 171–178.
- [2] M.M. Bhasin, J.H. McCain, B.V. Vora, T. Imai, P.R. Pujado, Appl. Catal. A 221 (2001) 397-419.
- [3] V.V. Krishnan, S.L. Suib, J. Catal. 184 (1999) 305-315.
- [4] J.M.L. Nieto, P. Concepcion, A. Dejoz, F. Melo, H. Knozinger, M.I. Vazquez, Catal. Today 61 (2000) 361–367.
- [5] J.A. Toledo-Antonio, N. Nava, M. Martinez, X. Bokhimi, Appl. Catal. A: Gen. 234 (2002) 137–144.
- [6] H.W. Lee, J.C. Jung, H.S. Kim, Y.M. Chung, T.J. Kim, S.J. Lee, S.H. Oh, Y.S. Kim, I.K. Song, Catal. Lett. 122 (2008) 281–286.
- [7] J.C. Jung, H.W. Lee, H.S. Kim, Y.M. Chung, T.J. Kim, S.J. Lee, S.H. Oh, Y.S. Kim, I.K. Song, Catal. Lett. 123 (2008) 239–245.
- [8] H.W. Lee, J.C. Jung, H.S. Kim, Y.M. Chung, T.J. Kim, S.J. Lee, S.H. Oh, Y.S. Kim, I.K. Song, Catal. Lett. 124 (2008) 364–368.
- [9] H.W. Lee, J.C. Jung, I.K. Song, Catal. Lett. 133 (2009) 321–327.
 [10] J.C. Jung, H.W. Lee, H.S. Kim, Y.M. Chung, T.J. Kim, S.J. Lee, S.H. Oh, Y.S. Kim, I.K.
- Song, J. Mol. Catal. A: Gen. 271 (2007) 261–265. [11] J.C. Jung, H.S. Kim, Y.S. Kim, Y.M. Chung, T.J. Kim, S.J. Lee, S.H. Oh, I.K. Song, Appl.
- Catal. A: Gen. 317 (2007) 244–249. [12] J.C. Jung, H.W. Lee, H.S. Kim, Y.M. Chung, T.J. Kim, S.J. Lee, S.H. Oh, Y.S. Kim, I.K. Song, Catal. Lett. 124 (2008) 262–267.

- [13] J.C. Jung, H.W. Lee, D.R. Park, J.G. Seo, I.K. Song, Catal. Lett. 131 (2009) 401–405.
- [14] A.P.V. Soarew, L.D. Dimitrov, M.C.R.A. Oliveria, L. Hilaire, M.F. Portela, R.K. Grasselli, Appl. Catal. A 253 (2003) 191–200.
- [15] I. Matsuura, R. Schut, K. Kirakawa, J. Catal. 63 (1980) 152–166.
- [16] J.C. Jung, H.W. Lee, H.S. Kim, D.R. Park, Y.M. Chung, T.J. Kim, S.J. Lee, S.H. Oh, Y.S. Kim, I.K. Song, Catal. Commun. 9 (2008) 2059–2062.
- [17] J.C. Jung, H.W. Lee, H.S. Kim, Y.M. Chung, T.J. Kim, S.J. Lee, S.H. Oh, Y.S. Kim, I.K. Song, Catal. Commun. 9 (2008) 943–949.
- [18] J.C. Jung, H.W. Lee, H.S. Kim, Y.M. Chung, T.J. Kim, S.J. Lee, S.H. Oh, Y.S. Kim, I.K. Song, Catal. Commun. 8 (2007) 625–628.
- [19] J.C. Jung, H.S. Kim, A.S. Choi, Y.M. Chung, T.J. Kim, S.J. Lee, S.H. Oh, I.K. Song, J. Mol. Catal. A 259 (2006) 166–170.
- [20] A. Batist, J.F.H. Bouwens, G.C.A. Shuit, J. Catal. 25 (1973) 1–11.
- [21] J.N. Wu, H.P. Yang, Y.N. Fan, B.L. Xu, Y. Chen, J. Fuel Chem. Technol. 35 (2007) 684–690.

- [22] E. Ruckenstein, R. Krishnan, K.N. Rai, J. Catal. 45 (1976) 270-273.
- [23] C. Daniel, G.W. Keulks, J. Catal. 29 (1973) 475-478.
- [24] T. Notermann, G.W. Keulks, A. Skliarov, Y. Maximov, L.Y. Margolis, O.V. Krylov, J. Catal. 39 (1975) 286–293.
- [25] W.J. Linn, A.W. Sleight, J. Catal. 41 (1976) 134-139.
- [26] P.L. Villa, A. Szabo, F. Trifiro, M. Carbucicchio, J. Catal. 47 (1977) 122-133.
- [27] P. Forzatti, P.L. Villa, N. Ferlazzo, F. Jones, J. Catal. 76 (1982) 188-207.
- [28] T.S.R. Prasada Rao, K.R. Krishnamurthy, J. Catal. 95 (1985) 209-219.
- [29] W.M. Sears, W.J. Keeler, Appl. Spectrosc. 46 (1992) 1898–1903.
- [30] E.V. Hoefs, J.R. Moinner, G.W. Keulks, J. Catal. 57 (1979) 331–337.
- [31] I. Wachs, L. Briand, PCT WO99/52630.
- [32] L.-T. Weng, B. Delmon, Appl. Catal. A 81 (1992) 141–213.
- [33] T.S. Chang, S.G. Lee, C.H. Shin, Y.K. Lee, S.S. Yun, Catal. Lett. 68 (2000) 229-234.
- [34] H. Miura, Y. Morikawa, T. Shirasaki, J. Catal. 39 (1975) 22–28.
- [35] B.L. Yang, D.S. Cheng, S.B. Lee, Appl. Catal. 70 (1991) 161-173.