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Influence of the catalyst composition in the oxidative dehydrogenation of 1-butene over BiV_xMo_{1-x} oxide catalysts

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ABSTRACT

BiV_xMo_{1-x} oxide catalysts with varying compositions were investigated in the oxidative dehydrogenation (ODH) of 1-butene to 1,3-butadiene (BD). Notably, incorporation of vanadium in the Bi-Mo oxide significantly enhanced the catalytic performance in the ODH of 1-butene. Among the tested catalysts, the $BiV_{0.6}Mo_{0.4}$ oxide catalyst exhibited superior oxygen mobility in temperature-programmed re-oxidation experiments, revealed the facile desorption of adsorbed BD species in the temperature-programmed desorption of 1-butene, and displayed the highest performance (72.2% conversion of 1-butene and 64.0% yield in BD) in the ODH of 1-butene. Moreover, the performance of the tested catalysts decreased in the following order $BiV_{0.6}Mo_{0.4} > BiV_{0.4}Mo_{0.6} > BiV_{0.8}Mo_{0.2} > BiV_{0.2}Mo_{0.8} > BiMo > BiV$. In addition, the $BiV_{0.6}Mo_{0.4}$ oxide catalyst displayed stable performance over 85 h and its excellent catalytic ability makes it economically viable.

1. Introduction

1,3-Butadiene (BD) constitutes an important raw material for the production of compounds such as styrene butadiene rubber (SBR), poly-butadiene rubber (BR), and acrylonitrile-butadiene-styrene resin (ABS) [1]. Over 98% of the global BD supply is produced by extracting C4 raffinates from naphtha cracking. However, the generated BD supply from this process does not satisfy the demands of the petrochemical market. Therefore, alternative methods are required for the efficient production of BD. Of the available alternatives, the oxidative dehydrogenation (ODH) of *n*-butenes has received significant attention, because this reaction can produce BD in a high yield [2,3]. Various metal oxide catalysts such as manganese oxide molecular sieves [4], K-doped VO_x/Al_2O_3 [5], ferrite catalysts [6,7], and pure bismuth-molybdate catalysts or bismuth-molybdate based multicomponent oxide catalysts [8–17] have been tested in the ODH of *n*-butenes. Among these catalysts, bismuth-molybdate-based catalysts have been studied intensively. In particular, multicomponent oxide catalysts composed of various transition metals and non-metals have been widely investigated in an attempt to improve the low catalytic performance of pure bismuth-molybdate catalysts [8–17]. In previous works, we compared the catalytic performance of multicomponent Bi-Fe-Me(x)-Mo oxide catalysts prepared by the addition of different transition metals. Notably, $BiFe_{0.65}Ni_{0.05}Mo$ oxide exhibited the best catalytic performance in the ODH of 1-butene [11]. Jung et al. [13] reported that $Co_9Fe_3Bi_1Mo_{12}O_{51}$ showed the highest oxygen mobility and the best catalytic performance in the ODH of *n*-butenes.

Vanadium oxide is an effective catalyst or promoter of selective oxidation to yield acrolein from propylene and from *n*-butenes to butadiene [18–21]. Rossi et al. [22] reported the catalytic performance of a scheelite-structured catalyst containing vanadium in the ODH of 1-butene. Notably, the cationic vacancy of the catalysts facilitated allylic oxidation and lattice oxygen diffusion. Ueda et al. [23] reported that in the oxidation of propylene, the catalytic performance of $Bi_{1-x/3}V_{1-x}Mo_xO_4$ with a scheelite-like structure increased upon substitution of V^{5+} ions with Mo^{6+} ions, without any concomitant changes in the selectivity toward acrolein.

The ODH of *n*-butenes occurs via three major elementary steps according to the Mars-van Krevelen (MvK) mechanism [24]. First, the alkene is adsorbed on the catalyst surface and is activated by the abstraction of the α hydrogen to the double bond to produce an allylic intermediate. Next, the catalyst oxygen is inserted into the activated allylic intermediate and the intermediate reacts via the lattice oxygen to form the desired products. Finally, the reduced catalyst is oxidized by a supply of gaseous oxygen. The oxygen mobility of the catalyst is critical to the catalytic activity in ODH reactions, and many researchers have measured this property using various analytical tools such as temperature programmed re-oxidation [9–11,25], temperature-programmed desorption of O_2 [26,27], and $^{18}O/^{16}O$ isotopic exchange measurements [28],

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etc. In previous works, we performed temperature programmed re-oxidation measurements to determine the oxygen mobility of certain catalysts and found that catalysts with high oxygen mobility exhibited superior performance in the ODH of 1-butene [9–11].

Here, the catalytic performance of BiV_xMo_{1-x} oxide catalysts with different V/Mo molar ratios ($x = 0–1.00$; Bi to V/Mo molar ratio was set at 1.0), prepared by co-precipitation, were evaluated in the ODH of 1-butene to BD. BiV_xMo_{1-x} oxide catalysts were characterized using X-ray diffraction (XRD), N_2 sorption, Raman spectroscopy, Inductively coupled plasma atomic emission spectroscopy (ICP-AES), 1-butene temperature-programmed desorption (1-butene TPD) and temperature-programmed re-oxidation (TPRO).

2. Experimental

2.1. Catalyst preparation

A series of BiV_xMo_{1-x} oxide catalysts ($x = 0.0–1.0$) was prepared by co-precipitation. Bismuth nitrate ($Bi(NO_3)_3·5H_2O$, Junsei, 98%), ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24}·4H_2O$, Junsei, 99%), and ammonium metavanadate (NH_4VO_3, Sigma–Aldrich, 99%) were used as received without further purification. Mixed metal oxide samples were prepared according to the following procedure: bismuth nitrate was dissolved in deionized water acidified with 10% nitric acid. Ammonium metavanadate and ammonium heptamolybdate were dissolved in deionized water at 70 °C, respectively. To prepare the mixed metal solution, the vanadium- and bismuth-containing solutions were added to the molybdenum-containing solution with vigorous stirring at 70 °C and the pH of the mixed metal solution was adjusted to 8 using NH_4OH (Samchun, 28–30 vol%). The resulting solution was vigorously stirred at 70 °C for 1 h and was then filtered and washed several times with deionized water. The solid product was dried at 100 °C for 12 h and calcined at 550 °C for 2 h under a flow of air.

2.2. Characterization

The crystalline structures of the BiV_xMo_{1-x} oxide catalysts were recorded on an X-ray diffractometer (Bruker D5005) using CuKα radiation (30 kV and 50 mA) with a scan rate of 1.2° min^{-1}. The XRD phases of the BiV_xMo_{1-x} oxide catalysts were identified by their characteristic diffraction peaks using JCPDS files. The surface areas and pore volumes of the catalysts were determined by N_2 adsorption at −196 °C using a Micromeritics ASAP 2020. Prior to the measurement, 0.5 g of the sample was degassed at 250 °C for 4 h. The surface area was determined using the Brunauer–Emmett–Teller (BET) equation in the range of $P/P_o = 0.05–0.20$ and the total pore volume was measured at $P/P_o = 0.99$.

Elemental analysis was carried out using inductively coupled plasma atomic emission spectroscopy (ICP-AES, Jarrell-Ash Polyscan 61E) in combination with a Perkin-Elmer 5000 atomic absorption spectrophotometer. Scanning electron microscopy (SEM) images of the catalysts were acquired on a Hitachi S-2500C scanning electron microscope at an acceleration voltage of 5 kV. Raman spectra were recorded on a Bruker Optic GMBH FRA 106/S with an Nd:YAG laser (300 mW, 500 scans).

Temperature-programmed re-oxidation (TPRO) was performed in a U-shaped quartz reactor, and 0.15 g of the catalyst was used for each measurement in order to elucidate the oxygen mobility. Prior to the analysis, the catalysts were pretreated at 420 °C for 1 h with a mixture of 50% H_2 in Ar (100 cm^3 min^{-1}) and were then cooled to room temperature (RT) under the same atmosphere. In this step, the catalysts would be reduced by the H_2-Ar flow. To confirm the degree of oxygen consumption by the oxidation reaction occurring on the reduced sites of the catalysts, a flow of 5% O_2 in N_2 (20 cm^3 min^{-1}) was utilized in the reactor and the catalyst was subsequently heated to 600 °C from RT at a heating rate of 10 °C min^{-1}. The mass signal of $m/z = 32$ ($^•O_2$) in the outlet gas was measured by mass spectroscopy (MS, Pfeiffer vacuum QMS 200).

O_2-pulse experiments were performed using the same apparatus as that used for TPRO in order to measure the quantity of oxygen consumed during catalyst re-oxidation. Prior to the analysis, 0.15 g samples were reacted at 420 °C for 1 h under the specified reaction conditions and were flushed for 1 h with a 30 cm^3 min^{-1} Ar flow. To measure the oxygen consumption of the reduced catalyst sites, 71.0 μmol of O_2 with an Ar carrier (2 cm^3 sample loop) was introduced into the catalyst bed every 5 min and pulse experiments were repeated 8 times. The mass signal of $m/z = 32$ ($^•O_2$) in the outlet gas was measured using the same MS analyzer as that in the TPRO experiments.

In order to elucidate the adsorption–desorption behavior of 1-butene, temperature-programmed desorption of 1-butene (1-butene TPD) was carried out using a similar apparatus to that in the TPRO measurements. Prior to the analysis, the catalysts were pretreated at 200 °C for 1 h with Ar (30 cm^3 min^{-1}) and then cooled to RT. The catalyst was then treated at RT for 0.5 h with $1–C_4H_8$ (20 cm^3 min^{-1}). Following the adsorption of 1-butene at RT, the sample was purged under a flow of Ar (30 cm^3 min^{-1}) for 0.5 h. TPD was performed from 50 to 800 °C at a heating rate of 10 °C min^{-1}. The mass signals of $m/z = 18$ ($^•H_2O$), 44 ($^•CO_2$), and 54 ($^•C_4H_6$) were detected using the same MS analyzer as that used in the TPRO experiments.

2.3. Catalytic testing

The ODH of 1-butene was carried out at ambient pressure with 0.5 g of the catalyst in a continuous flow fixed-bed reactor. Prior to the reaction, all catalysts were pretreated at 500 °C for 2 h with a flow of N_2 (50 cm^3 min^{-1}) and were cooled to 420 °C under the same atmosphere. The feed composition was fixed at $1–C_4H_8$/air/steam = 1/3.75/5 with a total flow rate of 78 cm^3 min^{-1}. Steam was sufficiently vaporized by passage through an evaporator. The products were analyzed by an on-line gas chromatograph (Varian 3800) with an Al_2O_3/KCl column (FID detector) for hydrocarbons and a Porapak Q packed column (TCD detector) for CO and CO_2. The production of CO was negligible under the reaction conditions. Cracking products such as CH_4, C_2H_6, and C_3H_8 were minor or negligible. The conversion, selectivity and yield in BD were calculated following previously reported procedures [29].

3. Results and discussion

3.1. Characterization of catalysts

Fig. 1 shows the XRD patterns of the BiV_xMo_{1-x} oxide catalysts prepared with different V/Mo molar ratios. Generally, BiMo oxide is composed of three phases, α-$Bi_2Mo_3O_{12}$, β-$Bi_2Mo_2O_9$, and γ-$Bi_2Mo_1O_6$. β-$Bi_2Mo_2O_9$ partially decomposed to α-$Bi_2Mo_3O_{12}$ and γ-$Bi_2Mo_1O_6$ due to the calcination temperature [9,30]. BiMo oxide with Bi/Mo = 1.0 calcined at 550 °C contained two mixed phases, namely, γ-$Bi_2Mo_1O_6$, and β-$Bi_2Mo_2O_9$. The BiV oxide catalyst showed the typical $BiVO_4$ phase. The BiV_xMo_{1-x} oxide catalysts exhibited different phases according to their composition. Catalysts with high vanadium contents ($BiV_{0.8}Mo_{0.2}$, $BiV_{0.6}Mo_{0.4}$, and $BiV_{0.4}Mo_{0.6}$), displayed $Bi_{0.93}Mo_{0.21}V_{0.79}O_4$ and $Bi_{0.93}Mo_{0.37}V_{0.63}O_4$ with a minor phase of γ-$Bi_2Mo_1O_6$, respectively, while the catalyst with a low vanadium content ($BiV_{0.2}Mo_{0.8}$) crystallized primarily in the γ-$Bi_2Mo_1O_6$ phase (Table 1). The