



Characterization and kinetic study of BiMoLa_x oxide catalysts for oxidative dehydrogenation of 1-butene to 1,3-butadiene



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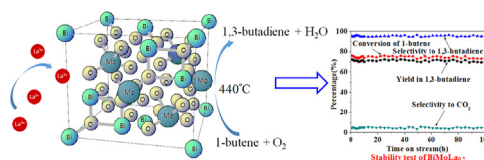
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HIGHLIGHTS

- BiMoLa_x ($x=0-0.4$) oxides are investigated in oxidative dehydrogenation of 1-butene.
- La addition in Bi–Mo oxide catalyst can promote the catalytic activity.
- Yield for 1,3-butadiene could be correlated to the ease of oxygen mobility.
- BiMoLa_{0.2} oxide catalyst exhibits very stable performance.

GRAPHICAL ABSTRACT



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ABSTRACT

BiMoLa_x oxide catalysts with a variation of lanthanum component were prepared by a co-precipitation method, and applied to the oxidative dehydrogenation (ODH) of 1-butene to 1,3-butadiene (BD). The results reveal that the lanthanum content has significant effects on the catalyst performance. BiMoLa_{0.2} exhibits the superior activity and stability during the 100 h test. H₂ temperature-programmed reduction (H₂-TPR), 1-Butene temperature-programmed re-oxidation (TPRO) and temperature-programmed desorption (TPD) characterization show that the oxygen mobility and the adsorption ability of 1-butene of catalysts are two crucial factors determining catalytic performance in ODH reaction. The kinetics analysis finds that the ODH reaction over BiMoLa_{0.2} can occur more easily.

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1. Introduction

1,3-Butadiene (BD) is one of the most important chemical intermediates among C₄ olefines, and it is an essential feedstock for the production of styrene butadiene rubber, poly-butadiene rubber, and acrylonitrile–butadiene–styrene resin (Grasselli, 2002; White, 2007; Yan et al., 2014). The global demand for BD has increased significantly in last decades and the process for the BD production gained much attention. Naphtha steam cracking, the

major process for BD production, has several disadvantages in operation because the steam cracking produces not only BD but also many other petrochemicals like ethylene, propylene, and isobutene. The subsequent separation is required (Kung, 1994; Madeira and Portela, 2002; Rubio et al., 2003). Direct dehydrogenation of n-butene into BD is highly endothermic and requires high reaction temperature (Chaar et al., 1988; Soares et al., 2003; Toledo-Antonio et al., 2002). However, oxidative dehydrogenation (ODH) of n-butene into BD is an exothermic process and costs much less energy than dehydrogenation process. In addition, the ODH of butenes can efficiently produce BD in related high yields (Hong et al., 1984; Liaw et al., 1989). Therefore, it has been recognized as a promising process for the production of BD. The

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key challenge facing this kind of reaction is the design of a suitable catalyst capable of high desired product yield.

Bismuth molybdates have been extensively studied as potential catalysts for the ODH of *n*-butene to BD. However, pure bismuth molybdates exhibits low performance in ODH reaction (Batist et al., 1966, 1968; Burrington et al., 1980; Van Oeffelen et al., 1985). Many promoters have been investigated to improve the properties of Bi–Mo catalysts (Batist et al., 1972; Jung et al., 2008, 2009; Park et al., 2012, 2013). For example, Song et al. have experimentally investigated to enhance the catalytic activity of pure bismuth molybdates by adding oxides such as Co, Fe, and Ni, and the research results have demonstrated that the addition of Co, Fe, and Ni to bismuth molybdates can improve obviously the oxygen mobility and catalyst performance (Jung et al., 2008, 2009; Park et al., 2012, 2013). From current investigations, it is generally believed that oxygen mobility of Bi–Mo-based catalysts influences the ODH of butenes, because the reaction follows the Mars–van Krevelen mechanism (Grasselli, 1997; Porteau, 2001; Sleight, 1977), in which surface catalytic sites are reduced by hydrocarbon with participation of the lattice oxygen and followed by re-oxidation with adsorbed O₂ from the gas phase. Although metal component in the catalyst does not directly take part in the reaction, the nature of oxygen involved in the reaction can vary depending on the identity of metal component bonded to the oxygen (Ruckenstein et al., 1976; Schuit, 1974; Ueda et al., 1984). Lanthana, a rare-earth metal oxide and a promising promoter for ODH catalysts, is well known for its capability to store and release oxygen and low-temperature reducibility. Lanthana has been considered as well-established catalysts for ODH of ethane (Yu et al., 1998), propane dehydrogenation (Zhang et al., 2007; Zhou et al., 2002) and iso-butane dehydrogenation (Wan et al., 2011) successfully.

Thus, in this work, a series of bismuth molybdate lanthanum oxide catalysts (BiMoLa_x) with different lanthanum content were prepared by a co-precipitation method, and used in the ODH of 1-butene to BD. BiMoLa_x oxide catalysts were characterized by using N₂ adsorption, elemental analysis, X-ray diffraction (XRD), H₂ temperature-programmed reduction (H₂-TPR), 1-butene temperature-programmed re-oxidation (TPRO) and temperature-programmed desorption (TPD). The relationship between the catalytic activity and lanthanum content in the catalysts will be discussed, oxygen mobility as well. In addition, the stability and kinetics analysis of the prepared catalyst in the ODH reaction are conducted.

2. Experimental section

2.1. Preparation of BiMoLa_x catalysts

Bi–Mo-based with different lanthanum content oxide catalysts ($x=0-0.4$) were prepared by conventional co-precipitation method. The desired amount of lanthanum nitrate solution (La(NO₃)₃, Aladdin, AR) was dissolved in deionized water at 70 °C and added dropwise into ammonium molybdate solution ((NH₄)₆Mo₇O₂₄·4H₂O, Sino-pharm Chemical Reagent Co., Ltd., 99%) under vigorously stirring at 70 °C. Afterwards, bismuth nitrate solution (Bi(NO₃)₃·5H₂O, Sino-pharm Chemical Reagent Co., Ltd., AR) acidified with 10% nitric acid was added dropwise into the above-mentioned mixture. The mixture was adjusted to pH 5 by aqueous 27 wt% NH₄OH and aged at room temperature for 4 h and then stirred to viscous solid at the water bath to remove the excess water. The resulting viscous solid was dried at 80 °C overnight and calcined at 550 °C for 2 h in an air atmosphere and then pressed, crushed and sieved to 40–60 meshes before reaction test. The catalysts were designated by BiMoLa_x ($x=0-0.4$), where x is the molar ratio of lanthanum in the catalyst.

2.2. Catalysts characterization

Element composition of the prepared catalysts was determined by inductively coupled plasma and atomic emission spectroscopy (ICP-AES, Thermo iCAP6300) analyses. The BET surface area and pore volume of the catalysts were determined from multipoint BET isotherms using N₂ adsorption (Micromeritics ASAP 2020). X-ray powder diffraction (XRD) patterns of BiMoLa_x oxide was recorded on XRD 6000 equipped with Cu K α radiation at 40 kV and 30 mA. Data were collected in the 2θ range of 10–60° with a scan rate of 1° min⁻¹.

For H₂-TPR measurement, 50 mg catalysts samples were charged in a U-shape quartz tubular reactor and were heated linearly at a rate of 10 °C min⁻¹ under a flowing H₂–Ar mixture (10.0% H₂ by volume) of 30 cm³ min⁻¹. The consumption of hydrogen was detected by an on-line GC.

The relationship between oxygen mobility and lanthanum content was assessed through 1-butene temperature-programmed re-oxidation (TPRO) on fixed-bed reactor attached to a Hiden QIC-20 quadruple mass spectrometer. For the temperature programmed reduction by 1-butene, 0.2 g catalyst was pretreated at 440 °C for 2 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 (30 cm³ min⁻¹). Subsequent temperature programmed oxidation was performed in flowing 2% O₂/He (30 cm³ min⁻¹) from room temperature to 500 °C at 10 °C min⁻¹. 1-Butene-temperature-programmed desorption (TPD) was carried out on the same apparatus. 1-Butene was adsorbed at 50 °C and purged under flowing He (30 cm³ min⁻¹) for 0.5 h before the desorption temperature from 50 to 800 °C at the rate of 10 °C min⁻¹. The mass signals of $m/z=54$ (C₄H₆) was monitored.

2.3. Catalytic measurement

Catalytic testing was performed in a tubular fixed-bed reactor (inside diameter = 8 mm) with 1.5 g catalyst under atmospheric pressure. The total flow rate is 112.5 cm³/min with a gaseous hourly space velocity (GHSV) of 300 ml·(g cat)⁻¹·h⁻¹ (on the basis of 1-butene), and the volume ratio of the feed gases was 1/0.8/10 of 1-butene/oxygen/steam. Prior to the reaction, the catalyst was routinely activated with flowing air stream (50 cm³ min⁻¹) at 440 °C for 2 h. The water feed was continuously vaporized by passing through a pre-heating zone at 120 °C and fed into the reactor together with 1-butene and air. The reactants and products were analyzed by on-line gas chromatography detectors with two columns. A KB–Al₂O₃/Na₂SO₄ column of 30 m length and 0.32 mm diameter with a flame ionization detector (FID) were used to analyze hydrocarbons. A TDX-01 column of 0.5 m length and 3 mm diameter with a thermal conductivity detector (TCD) was used for the separation of CO and CO₂.

3. Results and discussion

3.1. Structure and composition characterization of BiMoLa_x oxide catalysts

BET surface area, total pore volume and elemental analysis of the BiMoLa_x oxides catalyst are listed in Table 1. BET surface areas of the prepared catalysts are very low (1.2–3.7 m²/g), as reported in the previous works (Grasselli, 1997; Park et al., 2012, 2013; Sleight, 1977). There is no clear relationship between the BET surface areas and lanthanum content, and the total pore volume does not change significantly with the increasing of lanthanum content. Elemental analysis of metal components in the catalysts

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