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Effect of pH in the preparation of γ-Bi_2MoO_6 for oxidative dehydrogenation of *n*-butene to 1,3-butadiene: Correlation between catalytic performance and oxygen mobility of γ-Bi_2MoO_6

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Abstract

γ-Bi_2MoO_6 catalysts were prepared by a co-precipitation method with a variation of pH value (pH 1–7), and they were applied to the oxidative dehydrogenation of *n*-butene to 1,3-butadiene in a continuous flow fixed-bed reactor. Temperature-programmed reoxidation (TPRO) measurements were carried out to determine the oxygen mobility to make up lattice oxygen of γ-Bi_2MoO_6 consumed in the reaction. It was observed that the catalytic performance of γ-Bi_2MoO_6 was closely related to the oxygen mobility of γ-Bi_2MoO_6. The yield for 1,3-butadiene was monotonically increased with decreasing TPRO peak temperature and with increasing TPRO peak area. Among the catalysts tested, the γ-Bi_2MoO_6 catalyst prepared at pH 3 showed the best catalytic performance due to its facile oxygen mobility.

Keywords: γ-Bi_2MoO_6; Effect of pH; *n*-Butene; 1,3-Butadiene; Oxidative dehydrogenation; Oxygen mobility; Temperature-programmed reoxidation (TPRO)

1. Introduction

Selective oxidation of olefins has been considered to be an important subject, because this process can be used in petrochemical industries for the large-scale synthesis of various chemical intermediates [1–3]. In particular, oxidative dehydrogenation of *n*-butene has attracted much attention as a promising process that can produce 1,3-butadiene in a single unit [4]. A number of catalysts have been investigated for the oxidative dehydrogenation of *n*-butene, including ferrite-type catalyst [5], vanadium-containing catalyst [6], manganese oxide molecular sieve [7], Cu–Mo catalyst [8], and bismuth molybdate catalysts [9–12]. Among these catalysts, bismuth molybdates have been widely investigated as efficient catalysts for this reaction [9–15]. Typically, three types of bismuth molybdate catalysts (α-$Bi_2Mo_3O_{12}$, β-$Bi_2Mo_2O_9$, and γ-Bi_2MoO_6) have been considered for the oxidative dehydrogenation of *n*-butene [9,13–15].

It was reported that the oxidative dehydrogenation of *n*-butene to 1,3-butadiene follows Mars–van Krevelen mechanism [16]. That is, lattice oxygen in the bismuth molybdate catalyst directly reacts with *n*-butene, and oxygen in the gas phase makes up oxygen vacancy in the catalyst [9,16]. This means that oxygen mobility of bismuth molybdate catalyst plays an important role on the catalytic performance in the oxidative dehydrogenation of *n*-butene [12,17–19]. In other words, a bismuth molybdate catalyst with facile oxygen mobility may show an excellent catalytic performance in this reaction [9,18–21]. This was well supported by previous works [12,17,18] reporting that γ-Bi_2MoO_6 exhibited the

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best catalytic performance in the oxidative dehydrogenation of *n*-butene due to the highest oxygen mobility among three types of bismuth molybdate catalysts.

Co-precipitation method has been generally used in the preparation of γ-Bi_2MoO_6 catalyst [9,12,22]. It was reported that pH value should be maintained constant during the co-precipitation step in the preparation of γ-Bi_2MoO_6 catalyst, although the reported pH values were somewhat different case by case [9,23,24]. This implies that precise control of pH value during the co-precipitation step is very important for the successful preparation of γ-Bi_2MoO_6 catalyst. However, any systematic investigations to see the effect of pH value in the preparation of γ-Bi_2MoO_6 on the catalytic performance and oxygen mobility have not been attempted yet.

In this work, a series of γ-Bi_2MoO_6 catalysts were prepared by a co-precipitation method with a variation of pH value (pH 1–7), and they were applied to the oxidative dehydrogenation of *n*-butene to 1,3-butadiene. Temperature-programmed reoxidation (TPRO) measurements were carried out to determine the oxygen mobility to make up lattice oxygen of γ-Bi_2MoO_6 consumed in the reaction. A correlation between catalytic performance and oxygen mobility of γ-Bi_2MoO_6 catalysts was established.

2. Experimental

A series of γ-Bi_2MoO_6 were prepared by a co-precipitation method with a variation of pH value during the co-precipitation step. Known amount of bismuth nitrate ($Bi(NO_3)_3 \cdot 5H_2O$ from Aldrich) was dissolved in distilled water acidified with nitric acid. The solution was then added dropwise into the aqueous solution containing known amount of ammonium molybdate ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ from Sigma) under vigorous stirring. During the co-precipitation step, pH value of the mixed solution was precisely controlled using ammonia solution. The pH value was varied from 1 to 7 with an interval of 1 in order to prepare seven γ-Bi_2MoO_6 catalysts. After the resulting solution was stirred vigorously at room temperature for 1 h, the precipitate was filtered to obtain a solid product. The solid product was dried overnight at 110 °C, and then it was calcined at 475 °C for 5 h to yield γ-Bi_2MoO_6 catalyst.

The prepared γ-Bi_2MoO_6 catalysts were characterized by XRD (MAC Science, M18XHF-SRA), Raman spectroscopy (Horiaba Jobin Yvon, T64000), BET (Micromeritics, ASAP 2010), and ICP-AES (Shimadz, ICP-1000IV) analyses. In order to measure the oxygen mobility to make up lattice oxygen of γ-Bi_2MoO_6 catalysts, temperature-programmed reoxidation (TPRO) experiments were carried out. Prior to the TPRO measurement, each catalyst was partially reduced by carrying out the oxidative dehydrogenation of *n*-butene at 420 °C for 3 h in the absence of oxygen feed. After the reduced catalyst was placed in a conventional TPRO apparatus, a mixed stream of oxygen (10%) and helium (90%) was introduced to the catalyst sample. Furnace temperature was then raised from room temperature to 500 °C at a heating rate of 5 °C/min. The amount of oxygen consumed was detected using a thermal conductivity detector.

Oxidative dehydrogenation of *n*-butene to 1,3-butadiene was carried out in a continuous flow fixed-bed reactor in the presence of air and steam. Water was sufficiently vaporized by passing a pre-heating zone and fed into the reactor continuously together with *n*-butene and air. Feed composition was fixed at *n*-butene:O_2:steam = 1:0.75:15. C_4 raffinate-3 containing 72.5 wt% *n*-butene (1-butene(14.2 wt%) + trans-2-butene(38.3 wt%) + cis-2-butene(20.0 wt%)) was used as a *n*-butene source, and air was used as an oxygen source (nitrogen in air served as a carrier gas). Each catalyst was pretreated at 470 °C for 1 h with an air stream, and then catalytic reaction was carried out at 420 °C. GHSV (gas hourly space velocity) was fixed at 300 h^{-1} on the basis of *n*-butene. Reaction products were periodically sampled and analyzed with gas chromatography. Conversion of *n*-butene and selectivity for 1,3-butadiene were calculated on the basis of carbon balance as followings. Yield for 1,3-butadiene was calculated by multiplying conversion and selectivity.

$$\text{Conversion of } n\text{-butene} = \frac{\text{moles of } n\text{-butene reacted}}{\text{moles of } n\text{-butene supplied}}$$

$$\text{Selectivity for 1,3-butadiene} = \frac{\text{moles of 1,3-butadiene formed}}{\text{moles of } n\text{-butene reacted}}$$

3. Results and discussion

Formation of γ-Bi_2MoO_6 catalysts was well confirmed by XRD, Raman spectroscopy, and ICP-AES measurements. Fig. 1 shows the XRD patterns and Raman spectra of γ-Bi_2MoO_6 catalysts prepared at different pH. XRD patterns and Raman spectra were well consistent with those reported in previous works [9,12,25,26], indicating successful formation of γ-Bi_2MoO_6 catalysts. Bi/Mo atomic ratios of γ-Bi_2MoO_6 catalysts determined by ICP-AES measurements were in the range of 1.94–1.97, in good agreement with theoretical value of 2.0. The above results demonstrate that γ-Bi_2MoO_6 catalysts were successfully prepared within the wide range of pH values. BET surface areas of γ-Bi_2MoO_6 catalysts were found to be very low, and they were in the range of 2.1–4.5 m^2/g with no great difference.

Fig. 2 shows the catalytic performance of γ-Bi_2MoO_6 in the oxidative dehydrogenation of *n*-butene to 1,3-butadiene at 420 °C after 12-h catalytic reaction, plotted as a function of pH value. In this reaction, CO and CO_2 were mainly produced as by-products. Selectivity for 1,3-butadiene over γ-Bi_2MoO_6 catalysts was almost constant (ca. 90%). What is noticeable is that conversion of *n*-butene and yield for 1,3-butadiene showed volcano curves with respect to pH value. As shown in Fig. 2, the γ-Bi_2MoO_6 catalyst prepared at pH 3 showed the best catalytic performance in this reaction.

In order to correlate catalytic performance with oxygen mobility to make up lattice oxygen of γ-Bi_2MoO_6 catalysts,