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Catalytic Performance of $Co_9Fe_3Bi_1Mo_{12}O_{51}$ Catalysts in the Oxidative Dehydrogenation of n-Butene to 1,3-Butadiene: Effect of pH in the Preparation of $Co_9Fe_3Bi_1Mo_{12}O_{51}$ Catalysts by a Co-precipitation Method

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Abstract $Co_9Fe_3Bi_1Mo_{12}O_{51}$ catalysts were prepared by a co-precipitation method at different pH (pH = 1–7), and were applied to the oxidative dehydrogenation of n-butene to 1,3-butadiene in a continuous flow fixed-bed reactor. Conversion of n-butene and yield for 1,3-butadiene over $Co_9Fe_3Bi_1Mo_{12}O_{51}$ catalysts showed volcano-shaped curves with respect to co-precipitation pH value. O_2-TPD (temperature-programmed desorption) measurements revealed that the catalytic performance of $Co_9Fe_3Bi_1Mo_{12}O_{51}$ was closely related to the oxygen mobility of the catalyst. Yield for 1,3-butadiene was increased with increasing oxygen mobility of the catalyst. Among the catalysts tested, $Co_9Fe_3Bi_1Mo_{12}O_{51}$ catalyst prepared at pH 3 showed the best catalytic performance due to its highest oxygen mobility. The pH value during the co-precipitation step strongly affected the oxygen mobility of $Co_9Fe_3Bi_1Mo_{12}O_{51}$ catalysts, and in turn, the oxygen mobility played a key role in determining the catalytic performance of $Co_9Fe_3Bi_1Mo_{12}O_{51}$ catalysts in the oxidative dehydrogenation of n-butene.

Keywords Multicomponent bismuth molybdate · Effect of pH · Co-precipitation method · Oxidative dehydrogenation of n-butene · 1,3-Butadiene

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1 Introduction

Multicomponent bismuth molybdate catalysts have been widely used for selective oxidation of hydrocarbons in petrochemical industries [1–3]. In particular, oxidative dehydrogenation of n-butene over multicomponent bismuth molybdate catalysts has attracted much attention as a promising process for producing 1,3-butadiene [3–6]. Nonetheless, only limited information on the catalytic property and catalytic performance of multicomponent bismuth molybdates is available in the literature, due to the difficulty in understanding their complicated compositions and structures [1, 7].

Co-precipitation method has been generally employed for the preparation of multicomponent bismuth molybdate catalysts [2, 8]. It has been reported that the catalytic property and catalytic performance of multicomponent bismuth molybdates strongly depend on the preparation conditions such as co-precipitation pH and co-precipitation temperature [8, 9]. In particular, pH value during the co-precipitation step is known to be an important factor for successful design of multicomponent bismuth molybdate catalysts [8, 10], indicating that co-precipitation pH value can serve as a crucial factor determining the catalytic performance of multicomponent bismuth molybdate catalysts. However, much progress has not been made on the effect of pH in the preparation of multicomponent bismuth molybdates on the catalytic performance in the oxidative dehydrogenation of n-butene.

Fundamental structure of multicomponent bismuth molybdate catalysts is composed of four elements including divalent metal (M^{II}), trivalent metal (M^{III}), bismuth, and molybdenum [7, 11]. Although a number of multicomponent bismuth molybdate catalysts can be formed depending on the constituent metal components and their

compositions [12–15], $Co_9Fe_3Bi_1Mo_{12}O_{51}$ has been found to be an efficient catalyst for the oxidative dehydrogenation of n-butene [16, 17]. In this work, therefore, $Co_9Fe_3Bi_1Mo_{12}O_{51}$ was chosen as a model catalyst to see the effect of pH in the preparation of multicomponent bismuth molybdate on the catalytic performance in the oxidative dehydrogenation of n-butene.

It is well known that the oxidative dehydrogenation of n-butene to 1,3-butadiene over multicomponent bismuth molybdate catalysts follows the Mars-van Krevelen mechanism [18–20]. According to this mechanism, oxygen in the catalyst directly reacts with n-butene, and in turn, oxygen in the gas phase makes up oxygen vacancy in the catalyst [21–24]. This indicates that oxygen mobility of the catalyst plays an important role in determining the catalytic performance in the oxidative dehydrogenation of n-butene. Therefore, it is expected that a catalyst with high oxygen mobility will show an excellent catalytic performance in the oxidative dehydrogenation of n-butene.

In this work, $Co_9Fe_3Bi_1Mo_{12}O_{51}$ catalysts were prepared by a co-precipitation method with a variation of pH value (pH = 1–7), and were applied to the oxidative dehydrogenation of n-butene to 1,3-butadiene. O_2-TPD (temperature-programmed desorption) experiments were carried out to determine the oxygen mobility of $Co_9Fe_3Bi_1Mo_{12}O_{51}$ catalysts. A correlation between oxygen mobility and catalytic performance of $Co_9Fe_3Bi_1Mo_{12}O_{51}$ catalysts was then established.

2 Experimental

2.1 Preparation of $Co_9Fe_3Bi_1Mo_{12}O_{51}$ Catalysts

$Co_9Fe_3Bi_1Mo_{12}O_{51}$ catalysts were prepared by a co-precipitation method with a variation of pH value (pH = 1–7) during the co-precipitation step. 7.9 g of cobalt nitrate ($Co(NO_3)_2{\cdot}6H_2O$, Sigma-Aldrich) and 3.7 g of ferric nitrate ($Fe(NO_3)_3{\cdot}9H_2O$, Sigma-Aldrich) were successively dissolved in distilled water (Solution A). 1.5 g of bismuth nitrate ($Bi(NO_3)_3{\cdot}5H_2O$, Sigma-Aldrich) was separately dissolved in distilled water that had been acidified with concentrated nitric acid (Solution B). Solution B was then added into Solution A to obtain a mixed solution. The mixed nitrate solution was added dropwise into an aqueous solution containing 6.4 g of ammonium molybdate ($(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, Sigma-Aldrich) under vigorous stirring. During the co-precipitation step, pH value of the mixed solution was precisely controlled from 1 to 7 using ammonia solution. After stirring the resulting solution vigorously at room temperature for 1 h, it was evaporated to obtain a solid product. The solid product was dried overnight at 175 °C, and it was then calcined at 475 °C for 5 h in an air stream to yield the $Co_9Fe_3Bi_1Mo_{12}O_{51}$ catalyst.

2.2 Characterization

Formation of $Co_9Fe_3Bi_1Mo_{12}O_{51}$ catalysts was confirmed by XRD (MAC Science, M18XHF-SRA) measurements. Atomic ratios of the prepared catalysts were determined by ICP-AES (Shimadz, ICP-1000IV) analyses. Surface areas of the catalysts were measured using a BET apparatus (Micromeritics, ASAP 2010).

O_2-TPD experiments were conducted in order to determine the oxygen mobility of $Co_9Fe_3Bi_1Mo_{12}O_{51}$ catalysts. Each catalyst (0.3 g) was charged into a quartz reactor of the TPD apparatus, and then it was pretreated at 420 °C for 1 h with a stream of helium (20 ml/min). After cooling the catalyst sample to room temperature, it was purged with a stream of helium (20 ml/min) for 1 h. Unlike the conventional TPD measurements, no oxygen was pre-adsorbed onto the catalyst sample for direct measurement of lattice oxygen evolved from the catalyst. In other words, O_2-TPD experiments conducted in this work are thermal desorption measurements of lattice oxygen evolved from the catalyst. Furnace temperature was increased from room temperature to 900 °C at a rate of 10 °C/min under a flow of helium (10 ml/min). The desorbed lattice oxygen was detected using a GC-MSD (Agilent, MSD-6890 N GC).

2.3 Oxidative Dehydrogenation of n-Butene

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. Each catalyst (0.5 g) was pretreated at 470 °C for 1 h with an air stream (16 ml/min). Water was sufficiently vaporized by passing through a pre-heating zone and continuously fed into the reactor 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 57.9 wt% n-butene [1-butene (7.5 wt%) + trans-2-butene (33.9 wt%) + cis-2-butene (16.5 wt%)] was used as a n-butene source, and air was used as an oxygen source (nitrogen in air served as a carrier gas). C_4 raffinate-3 was composed of 57.9 wt% n-butene, 41.6 wt% n-butane, 0.3 wt% cyclobutane, 0.1 wt% methyl cyclopropane, and 0.1 wt% residue. The catalytic reaction was carried out at 420 °C. GHSV (gas hourly space velocity) was fixed at 475 h^{-1} on the basis of n-butene. Reaction products were periodically sampled and analyzed with gas chromatographs. Conversion of n-butene and selectivity for 1,3-butadiene were calculated on the basis of carbon balance as follows. Yield for 1,3-butadiene was calculated by multiplying conversion of n-butene and selectivity for 1,3-butadiene.

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

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

3 Results and Discussion

3.1 Formation and Characterization of $Co_9Fe_3Bi_1Mo_{12}O_{51}$ Catalysts

Successful formation of $Co_9Fe_3Bi_1Mo_{12}O_{51}$ catalysts was well confirmed by XRD measurements. Fig. 1 shows the XRD patterns of $Co_9Fe_3Bi_1Mo_{12}O_{51}$ catalysts prepared at different pH. Each phase was identified by its characteristic diffraction peaks using JCPDS. It was found that all the $Co_9Fe_3Bi_1Mo_{12}O_{51}$ catalysts were composed of four major mixed phases of β-$CoMoO_4$, α-$CoMoO_4$, $Fe_2(MoO_4)_3$, and γ-Bi_2MoO_6. This result was in good agreement with a previous report [8], indicating successful formation of $Co_9Fe_3Bi_1Mo_{12}O_{51}$ catalysts.

It is known that bismuth molybdates are located on the surface of the catalyst and serve as active phases in the multicomponent bismuth molybdate catalyst system [8, 10]. On the other hand, divalent and trivalent metal molybdates are concentrated in the bulk of the catalyst. It has also been reported that divalent and trivalent metal molybdates in the bulk of the catalyst facilitate the migration of active oxygen species to the bismuth molybdates on the catalyst surface, leading to an enhanced oxygen mobility of multicomponent bismuth molybdate catalysts compared to the pure bismuth molybdate catalysts [1].

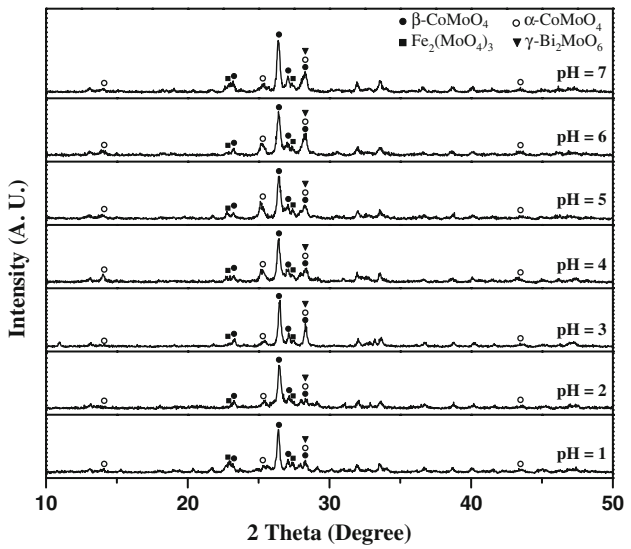

Fig. 1 XRD patterns of $Co_9Fe_3Bi_1Mo_{12}O_{51}$ catalysts prepared at different pH

It should be noted in Fig. 1 that relative XRD peak intensities of metal molybdate phases in the $Co_9Fe_3Bi_1Mo_{12}O_{51}$ catalysts were different depending on the pH value. This indicates that $Co_9Fe_3Bi_1Mo_{12}O_{51}$ catalysts prepared at different pH might have different abilities for transferring active oxygen species to the bismuth molybdates on the catalyst surface, leading to different oxygen mobility of $Co_9Fe_3Bi_1Mo_{12}O_{51}$ catalysts. Therefore, it is expected that the catalytic performance of $Co_9Fe_3Bi_1Mo_{12}O_{51}$ would be different depending on the co-precipitation pH value. This implies that pH value during the co-precipitation step can be a crucial factor determining the catalytic performance of $Co_9Fe_3Bi_1Mo_{12}O_{51}$ catalysts in the oxidative dehydrogenation of n-butene.

Atomic ratios of constituent metal components are listed in Table 1. Atomic ratio of a metal component was calculated as the ratio of the amount of each metal component (Co, Fe, and Mo) with respect to that of Bi. Atomic ratios determined by ICP-AES analyses are in good agreement with the theoretical values. This result also supports that $Co_9Fe_3Bi_1Mo_{12}O_{51}$ catalysts were successfully prepared in this work. BET surface areas of $Co_9Fe_3Bi_1Mo_{12}O_{51}$ catalysts are also summarized in Table 1. BET surface areas of the catalysts were found to be very low (6.8–15.1 m^2/g), as reported in the previous works [17–19]. BET surface areas of $Co_9Fe_3Bi_1Mo_{12}O_{51}$ catalysts showed no consistent trend with a variation of pH value.

3.2 Catalytic Performance in the Oxidative Dehydrogenation of n-Butene

Fig. 2 shows the catalytic performance of $Co_9Fe_3Bi_1Mo_{12}O_{51}$ catalysts in the oxidative dehydrogenation of n-butene to 1,3-butadiene at 420 °C after a 6 h-catalytic reaction, plotted as a function of pH value. It is known that CO and CO_2 are produced as by-products in this reaction [8]. In our catalytic reaction system, however, CO_2 was

Table 1 Atomic ratios and BET surface areas of $Co_9Fe_3Bi_1Mo_{12}O_{51}$ catalysts prepared at different pH

pH	Atomic ratio				BET surface area (m^2/g)
	Co	Fe	Bi	Mo	
1	8.8	2.9	1.0	12.1	6.8
2	9.0	3.0	1.0	11.9	11.2
3	8.9	2.9	1.0	11.5	7.0
4	8.8	2.9	1.0	11.8	9.2
5	8.9	3.0	1.0	11.7	9.0
6	8.7	3.1	1.0	12.0	15.1
7	9.1	3.0	1.0	11.6	11.3

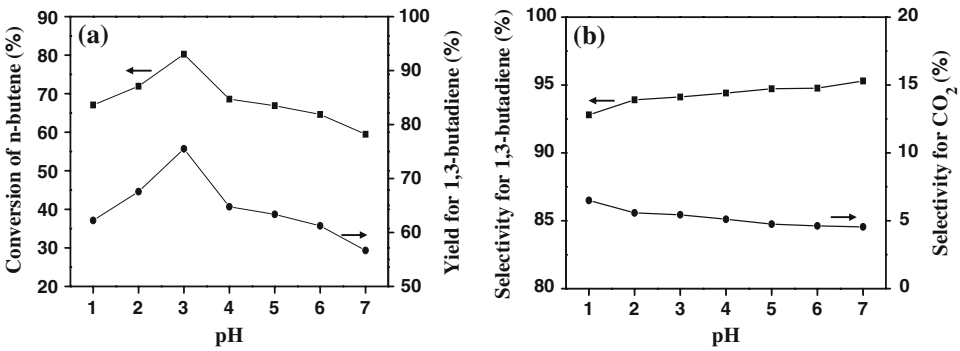

Fig. 2 Catalytic performance of $Co_9Fe_3Bi_1Mo_{12}O_{51}$ catalysts in the oxidative dehydrogenation of n-butene to 1,3-butadiene at 420 °C after a 6 h-catalytic reaction, plotted as a function of pH value

mainly produced as a by-product and CO formation was negligible. Selectivity for 1,3-butadiene slightly increased while selectivity for CO_2 slightly decreased with increasing pH value. What is noticeable is that conversion of n-butene and yield for 1,3-butadiene showed volcano-shaped curves with respect to pH value. Among the catalysts tested, $Co_9Fe_3Bi_1Mo_{12}O_{51}$ catalyst prepared at pH 3 showed the best catalytic performance in terms of conversion of n-butene and yield for 1,3-butadiene.

In our previous work investigating the effect of co-precipitation pH on the catalytic performance of $Ni_9Fe_3Bi_1Mo_{12}O_{51}$ catalysts [10], it was revealed that $Ni_9Fe_3Bi_1$ $Mo_{12}O_{51}$ catalyst prepared at pH 8 showed the best catalytic performance in the oxidative dehydrogenation of n-butene. The above results indicate that optimal pH values in the preparation of multicomponent bismuth molybdate catalysts were different depending on the constituent metal components.

3.3 Oxygen Mobility of $Co_9Fe_3Bi_1Mo_{12}O_{51}$ Catalysts

Oxygen mobility of various metal oxide catalysts has been measured using various experimental techniques such as $^{18}O/^{16}O$ isotope exchange [25, 26], TPRO (temperature-programmed reoxidation) [27], TPR (temperature-programmed reduction) [26], O_2-TPD (temperature-programmed desorption) [26, 28], and XPS (X-ray photoelectron spectroscopy) measurements [29]. Among these experimental tools, O_2-TPD measurements were employed to determine the oxygen mobility of $Co_9Fe_3Bi_1Mo_{12}O_{51}$ catalysts in this work.

Figure 3 shows the typical O_2-TPD profile of Co_9Fe_3 $Bi_1Mo_{12}O_{51}$ catalyst prepared at pH 3. The catalyst showed three oxygen desorption peaks at temperatures above 500 °C in the absence of oxygen pre-adsorption. In the conventional O_2-TPD experiments over metal oxide catalysts, it is known that oxygen species adsorbed on the catalyst surface are desorbed in low temperature region (<500 °C), while lattice oxygen species are evolved from the catalyst in high temperature region (>500 °C) [28, 29]. A conventional O_2-TPD experiment over $Co_9Fe_3Bi_1Mo_{12}O_{51}$ catalyst was also carried out in order to confirm the oxygen adsorption behavior

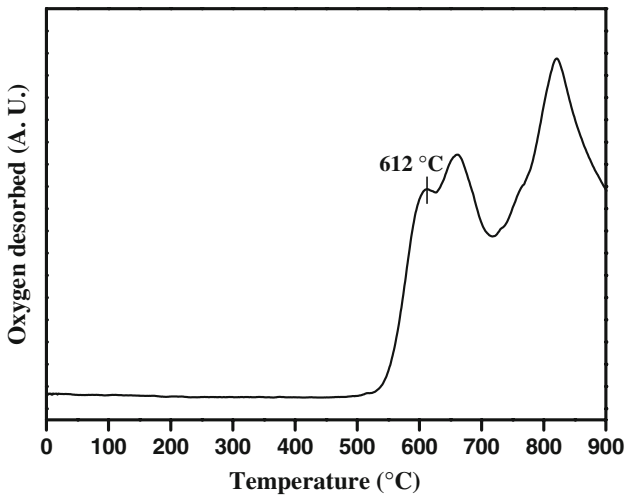

Fig. 3 Typical O_2-TPD profile of $Co_9Fe_3Bi_1Mo_{12}O_{51}$ catalyst prepared at pH 3

of $Co_9Fe_3Bi_1Mo_{12}O_{51}$ catalyst. Prior to the measurement, a mixed stream of oxygen (25%) and helium (75%) was introduced to the catalyst sample for 1 h for oxygen pre-adsorption. In this case, however, O_2-TPD profile was almost identical to that shown in Fig. 3. This result strongly suggests that the three peaks observed in Fig. 3 were attributed to lattice oxygen evolved from $Co_9Fe_3Bi_1Mo_{12}O_{51}$ catalyst. In our O_2-TPD experiments, all the $Co_9Fe_3Bi_1Mo_{12}O_{51}$ catalysts prepared at different pH showed oxygen desorption peaks at temperatures above 500 °C.

It is believed that lattice oxygen species evolved at lower temperature may be mainly responsible for the oxidative dehydrogenation of n-butene, because this oxygen species can be easily evolved from the catalyst, and therefore, can easily react with n-butene. In our previous work measuring the oxygen mobility of $Ni_9Fe_3Bi_1Mo_{12}O_{51}$ catalysts prepared at different pH [10], it was also revealed that the lower O_2-TPD peak temperature well reflected the oxygen mobility of the catalysts. In this work, therefore, the lower (the first) O_2-TPD peak temperature was used as an index for the oxygen mobility of $Co_9Fe_3Bi_1Mo_{12}O_{51}$ catalysts. The lower desorption peak temperature corresponds to the higher oxygen mobility of the catalyst.

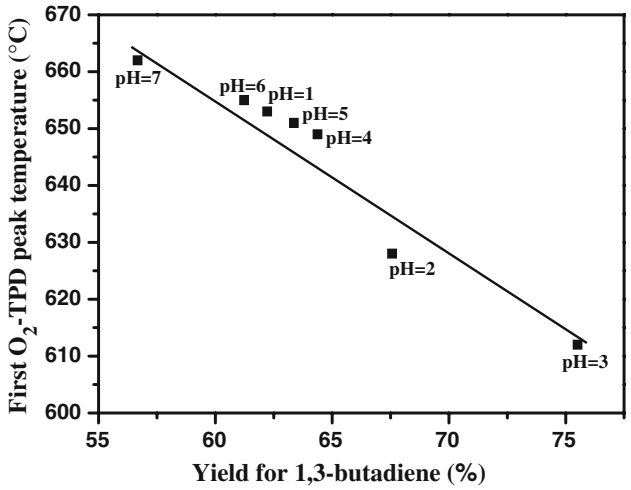

Fig. 4 A comprehensive correlation between oxygen mobility and catalytic performance of $Co_9Fe_3Bi_1Mo_{12}O_{51}$ catalysts in the oxidative dehydrogenation of n-butene to 1,3-butadiene. Catalytic performance data were taken from Fig. 2

3.4 Correlation Between Oxygen Mobility and Catalytic Performance of $Co_9Fe_3Bi_1Mo_{12}O_{51}$

Fig. 4 shows a comprehensive correlation between oxygen mobility and catalytic performance of $Co_9Fe_3Bi_1Mo_{12}O_{51}$ catalysts in the oxidative dehydrogenation of n-butene to 1,3-butadiene. As expected, the catalytic performance of $Co_9Fe_3Bi_1Mo_{12}O_{51}$ catalysts was closely related to the oxygen mobility of the catalysts. It was revealed that the first (the lower) O_2-TPD peak temperature was directly correlated with the catalytic performance. Yield for 1,3-butadiene was increased with decreasing O_2-TPD peak temperature, that is, with increasing oxygen mobility of the catalyst. This results indicates that oxygen mobility of $Co_9Fe_3Bi_1Mo_{12}O_{51}$ catalyst is a crucial factor determining the catalytic performance in the oxidative dehydrogenation of n-butene to 1,3-butadiene. Among the catalysts tested, $Co_9Fe_3Bi_1Mo_{12}O_{51}$ catalyst prepared at pH 3, which retained the highest oxygen mobility, showed the best catalytic performance.

4 Conclusions

$Co_9Fe_3Bi_1Mo_{12}O_{51}$ catalysts were prepared by a co-precipitation method with a variation of pH value (pH = 1–7) for use in the oxidative dehydrogenation of n-butene to 1,3-butadiene. Successful formation of $Co_9Fe_3Bi_1Mo_{12}O_{51}$ catalysts was well confirmed by XRD and ICP-AES analyses. Conversion of n-butene and yield for 1,3-butadiene over $Co_9Fe_3Bi_1Mo_{12}O_{51}$ catalysts showed volcano-shaped curves with respect to co-precipitation pH value. The catalytic performance of $Co_9Fe_3Bi_1Mo_{12}O_{51}$ was closely related to the oxygen mobility of the catalyst. Yield for 1,3-butadiene was increased with increasing oxygen mobility of the catalyst. Among the catalysts tested, $Co_9Fe_3Bi_1Mo_{12}O_{51}$ catalyst prepared at pH 3 showed the best catalytic performance. The highest catalytic performance of $Co_9Fe_3Bi_1Mo_{12}O_{51}$ prepared at pH 3 was due to its highest oxygen mobility. Thus, pH value during the co-precipitation step served as an important factor determining the catalytic performance of $Co_9Fe_3Bi_1Mo_{12}O_{51}$ catalysts in the oxidative dehydrogenation of n-butene.

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