

Short communication

Unusual catalytic behavior of β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ in the oxidative dehydrogenation of *n*-butene to 1,3-butadiene

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Abstract

A β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ catalyst was prepared by a co-precipitation method and applied to the oxidative dehydrogenation of *n*-butene to 1,3-butadiene. It was found that the β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ catalyst retained lower oxygen mobility than γ - Bi_2MoO_6 . It was also revealed that the β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ was thermally unstable and decomposed into α - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ and γ - Bi_2MoO_6 at a reaction temperature of 420 °C. However, the β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ showed a higher catalytic performance than the α - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ and γ - Bi_2MoO_6 catalysts in the oxidative dehydrogenation of *n*-butene, in spite of its thermal instability and low oxygen mobility. Moreover, the β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ showed a stable catalytic performance with time on stream without catalyst deactivation. The high and stable catalytic performance of β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ can be attributed to the synergy effect of α - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ and γ - Bi_2MoO_6 formed via the decomposition of β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ during the catalytic reaction, to the high intrinsic catalytic activity of β - $\text{Bi}_2\text{Mo}_2\text{O}_9$, and to the well-crystallized parts of β - $\text{Bi}_2\text{Mo}_2\text{O}_9$.

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1. Introduction

Bismuth molybdates are widely employed as efficient catalysts for the oxidative dehydrogenation of *n*-butene to 1,3-butadiene [1–5]. Three types of bismuth molybdate catalysts, α - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$, β - $\text{Bi}_2\text{Mo}_2\text{O}_9$, and γ - Bi_2MoO_6 , have been typically investigated for this reaction [6–8]. However, it has been reported that β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ was thermally unstable and decomposed into α - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ and γ - Bi_2MoO_6 in the temperature range of 400–550 °C [9–11]. Therefore, major studies on the oxidative dehydrogenation of *n*-butene over bismuth molybdate catalysts have been focused on α - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ and γ - Bi_2MoO_6 catalysts.

In spite of many studies on the use of bismuth molybdate catalysts for the oxidative dehydrogenation of *n*-butene, the origin of the differences in the catalytic performance of bismuth molyb-

dates is still debatable [1–5,12]. However, many researchers agree that oxygen mobility is one of the crucial factors determining the catalytic performance of bismuth molybdates in the oxidative dehydrogenation of *n*-butene [12–16], because the reaction follows the Mars–van Krevelen mechanism [12,17]. Therefore, it is likely that a bismuth molybdate catalyst with higher oxygen mobility would show a better catalytic performance in this oxidative dehydrogenation reaction [13–16,18].

Interestingly, it has been reported that β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ exhibited the best catalytic performance in the oxidative dehydrogenation of *n*-butene among the three types of bismuth molybdate catalysts [6,12], although the β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ catalyst is known to be thermally unstable within a certain temperature range [9–11]. Therefore, a more detailed investigation on the thermal stability and catalytic performance of β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ in the oxidative dehydrogenation of *n*-butene would be desirable.

In this work, a β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ catalyst was prepared by a co-precipitation method for use in the oxidative dehydrogenation of *n*-butene. Temperature-programmed reoxidation (TPRO) measurement was carried out to investigate the oxygen mobility of

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β - $\text{Bi}_2\text{Mo}_2\text{O}_9$. The thermal stability of β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ was examined by means of XRD analyses before and after the TPRO measurement, and before and after the catalytic reaction. The unusual catalytic behavior of β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ in the oxidative dehydrogenation *n*-butene was reported and discussed.

2. Experimental

A β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ was prepared by a co-precipitation method. A known amount of bismuth nitrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ from Sigma–Aldrich) was dissolved in distilled water that had been acidified with nitric acid. The solution was then added dropwise into an aqueous solution containing a known amount of an ammonium molybdate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ from Sigma–Aldrich) under vigorous stirring. During the co-precipitation step, the pH value of the mixed solution was precisely controlled at 5.0 using known amounts of an ammonia solution. After stirring the resulting solution 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 it was then calcined at 475 °C for 5 h in a stream of air to yield the β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ catalyst.

Temperature-programmed reoxidation (TPRO) measurement was carried out to investigate the oxygen mobility of the β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ catalyst. Prior to the TPRO measurement, the β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ catalyst was partially reduced by carrying out the oxidative dehydrogenation of *n*-butene at 420 °C for 3 h in the absence of an oxygen feed in order for the catalyst to consume lattice oxygen for the reaction. After placing the reduced catalyst in a conventional TPRO apparatus, a mixed stream of oxygen (10%) and helium (90%) was introduced to the catalyst sample. The furnace temperature was increased 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 (TCD).

The formation of β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ catalyst was confirmed by XRD (MAC Science, M18XHF-SRA) and Raman spectroscopy (Horiaba Jobin Yvon, T64000) measurements. The Bi/Mo atomic ratio of β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ was determined by ICP-AES (Shimadzu, ICP-1000IV) analysis. The surface area of the catalyst was determined using an ASAP 2010 instrument (Micromeritics). The catalyst stability of β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ was investigated by conducting XRD analyses before and after the TPRO measurement, and before and after the catalytic reaction.

The 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. The feed composition was fixed at *n*-butene:O₂:steam = 1:0.75:15. Water was sufficiently vaporized by passing through a pre-heating zone and continuously fed into the reactor together with *n*-butene and air. A C₄ 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 source of *n*-butene, and air was used as an oxygen source (nitrogen in the air served as a carrier gas). Prior to the catalytic reaction, the β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ catalyst was pretreated at 470 °C for 1 h with a stream of air. The catalytic reaction was carried out at 420 °C. GHSV (gas hourly space velocity) was fixed at 300 h⁻¹

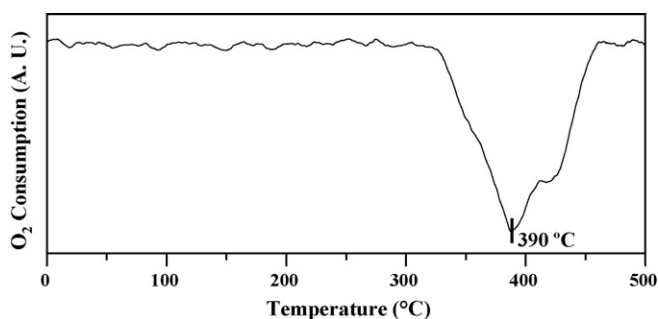


Fig. 1. TPRO profile of partially reduced β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ catalyst.

on the basis of *n*-butene. The reaction products were periodically sampled and analyzed with a gas chromatography. The conversion of *n*-butene and the selectivity for 1,3-butadiene were calculated on the basis of carbon balance as follows. The yield for 1,3-butadiene was calculated by multiplying the 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

The formation of β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ catalyst was verified by XRD, Raman spectroscopy, and ICP-AES measurements. The characteristic XRD pattern and Raman spectrum of the prepared β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ were well consistent with those reported in previous works [6,9,10,13], although these are not shown here. BET surface area of β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ was very low (2.9 m²/g). Bi/Mo atomic ratio of β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ was determined to be 0.98, in good agreement with the theoretical value of 1.0. These results strongly support that a β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ catalyst was successfully prepared.

Fig. 1 shows the TPRO profile of partially reduced β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ catalyst. The experimental result showed that the TPRO peak in the β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ catalyst appeared at 390 °C. A previous study [19] performing TPRO measurements for α - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ and γ - $\text{Bi}_2\text{Mo}_6\text{O}_{12}$ catalysts under the same conditions revealed that the TPRO peaks in the α - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ and γ - $\text{Bi}_2\text{Mo}_6\text{O}_{12}$ catalysts appeared at 390 and 285 °C, respectively. These results indicate that the oxygen mobility of bismuth molybdate catalysts decreases in the order of γ - $\text{Bi}_2\text{Mo}_6\text{O}_{12}$ > α - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ \approx β - $\text{Bi}_2\text{Mo}_2\text{O}_9$. In other words, β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ retains lower oxygen mobility than γ - $\text{Bi}_2\text{Mo}_6\text{O}_{12}$ and similar oxygen mobility to α - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$. Therefore, one may expect that β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ would show a lower catalytic performance than γ - $\text{Bi}_2\text{Mo}_6\text{O}_{12}$ and would exhibit a similar catalytic performance to α - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$, if oxygen mobility is a major factor affecting the catalytic performance of bismuth molybdate catalysts.

In order to investigate the thermal stability of β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ catalyst, XRD analyses were carried out before and after the

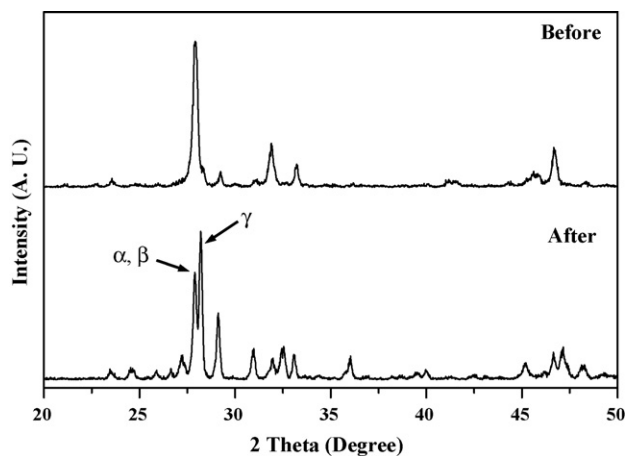


Fig. 2. XRD patterns of β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ catalyst obtained before and after the TPRO measurement.

TPRO measurement. Fig. 2 shows the XRD patterns of β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ catalyst obtained before and after the TPRO measurement. It was clearly observed that β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ was decomposed into α - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ and γ - Bi_2MoO_6 during the TPRO measurement. This indicates that β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ is thermally unstable at temperatures below 500°C . In a previous work [19], however, it was reported that both α - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ and γ - Bi_2MoO_6 catalysts showed no difference in XRD patterns before and after the TPRO measurements, indicating that the α - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ and γ - Bi_2MoO_6 catalysts are thermally stable.

The thermal instability of β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ catalyst was also verified by conducting XRD measurements before and after the catalytic reaction. Fig. 3 shows the XRD patterns of β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ catalyst obtained before and after the catalytic reaction (80 h-reaction at 420°C). Once again, it was observed that the β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ was decomposed into α - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ and γ - Bi_2MoO_6 during the catalytic reaction. This indicates that β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ is thermally unstable during a catalytic reaction performed at 420°C . Therefore, one may expect that β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ will not show a stable catalytic performance in the oxidative dehydrogenation of *n*-butene. However, it should be noted that

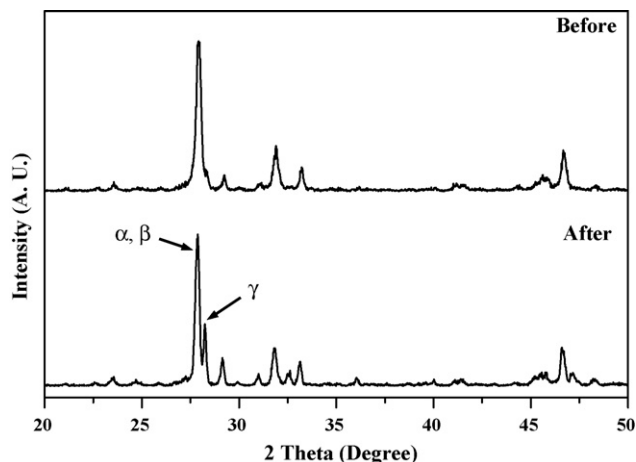


Fig. 3. XRD patterns of β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ catalyst obtained before and after the catalytic reaction (80 h-reaction at 420°C).

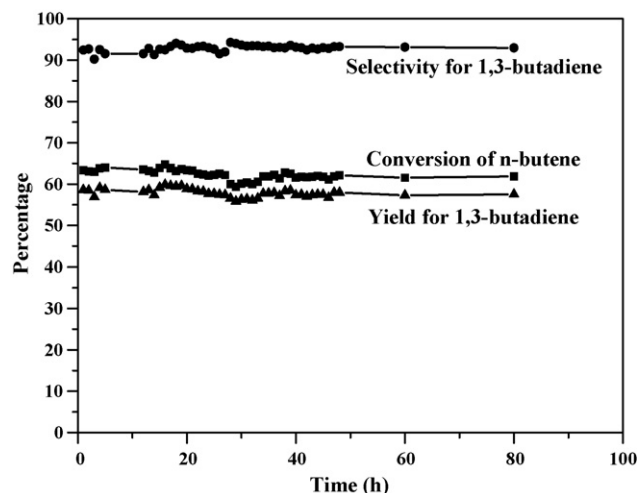


Fig. 4. Catalytic performance of β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ in the oxidative dehydrogenation of *n*-butene at 420°C with time on stream.

β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ was gradually decomposed into α - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ and γ - Bi_2MoO_6 with time on stream not instantaneously [9]. According to a previous report [9], β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ began to decompose into α - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ and γ - Bi_2MoO_6 after 12 h under normal treatment conditions with an air stream at 420°C . The above results indicate that β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ retains its own structure for a certain initial time period of the catalytic reaction at 420°C .

Fig. 4 shows the catalytic performance of β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ in the oxidative dehydrogenation of *n*-butene at 420°C with time on stream. What is surprising is that β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ catalyst showed a stable catalytic performance during 80 h-catalytic reaction without catalyst deactivation. This catalytic behavior of β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ is very unusual when judged from the fact that β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ was thermally unstable and decomposed at a reaction temperature of 420°C after a certain period of time. Another noticeable point is that the β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ showed a higher catalytic performance than the α - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ and γ - Bi_2MoO_6 catalysts, contrary to our expectation. As shown in Fig. 4, the yield for 1,3-butadiene over β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ catalyst was ca. 59%. In a previous study [19], however, the yields for 1,3-butadiene over α - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ and γ - Bi_2MoO_6 catalysts at the same reaction conditions were found to be ca. 10% and 46%, respectively. In other words, the yield for 1,3-butadiene over the bismuth molybdate catalysts was decreased in the order of β - $\text{Bi}_2\text{Mo}_2\text{O}_9 > \gamma$ - $\text{Bi}_2\text{MoO}_6 > \alpha$ - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$. This trend is not consistent with the trend for the oxygen mobility of bismuth molybdate catalysts (γ - $\text{Bi}_2\text{MoO}_6 > \alpha$ - $\text{Bi}_2\text{Mo}_3\text{O}_{12} \approx \beta$ - $\text{Bi}_2\text{Mo}_2\text{O}_9$). This suggests that the oxygen mobility cannot be the sole determining factor for the catalytic performance of bismuth molybdate catalysts in this reaction. We thus conclude from the experimental observations that β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ showed the best catalytic performance in the oxidative dehydrogenation of *n*-butene, even though it was thermally unstable and retained low oxygen mobility.

Such an unusual catalytic behavior of β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ is difficult to explain. The high catalytic performance of β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ at the initial stage is believed to be due to the high intrinsic

catalytic activity of β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ with its own original structure. Considering that β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ is thermally decomposed after a certain period of time, however, the unusual stable catalytic performance of β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ may be partly explained by the synergy effect of α - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ and γ - Bi_2MoO_6 formed via the decomposition of β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ during the catalytic reaction. It was previously reported that a mixed phase of α - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ and γ - Bi_2MoO_6 catalysts enhanced the catalytic performance in the several catalytic reactions due to the synergy effect between two components [11,12,20–22]. In our previous work [23], it was also observed that a mixture of α - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ and γ - Bi_2MoO_6 showed a better catalytic performance than the pure individual catalysts in the oxidative dehydrogenation of *n*-butene. Although β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ was decomposed into α - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ and γ - Bi_2MoO_6 during the catalytic reaction, it is likely that α - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ and γ - Bi_2MoO_6 formed via the decomposition of β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ during the reaction showed a synergy effect in this reaction. Another possible reason for the high and stable catalytic performance of β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ would be due to the invariant and well-crystallized parts of β - $\text{Bi}_2\text{Mo}_2\text{O}_9$. It is believed that the high and stable catalytic performance of β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ is due to the synergy effect of α - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ and γ - Bi_2MoO_6 formed via the decomposition of β - $\text{Bi}_2\text{Mo}_2\text{O}_9$, to the high intrinsic catalytic activity of β - $\text{Bi}_2\text{Mo}_2\text{O}_9$, and to the well-crystallized parts of β - $\text{Bi}_2\text{Mo}_2\text{O}_9$.

4. Conclusions

A β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ catalyst was prepared by a co-precipitation method for use in the oxidative dehydrogenation of *n*-butene. TPRO measurement revealed that the β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ retained low oxygen mobility. It was also found that the β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ was thermally unstable and decomposed into α - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ and γ - Bi_2MoO_6 at a reaction temperature of 420 °C. However, the β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ showed a stable catalytic performance without catalyst deactivation. Furthermore, the β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ showed a higher catalytic performance than the α - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ and γ - Bi_2MoO_6 catalysts in the oxidative dehydrogenation of *n*-butene, in spite of its thermal instability and low oxygen mobility. Although such an unusual catalytic behavior of β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ is not clearly understood, it is likely that α - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ and γ - Bi_2MoO_6 formed via the decomposition of β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ during the reaction showed a synergy effect in this reaction. It is also believed that the invariant and well-crystallized parts of

β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ were partly responsible for the unusual catalytic behavior of β - $\text{Bi}_2\text{Mo}_2\text{O}_9$. It can be concluded that the high and stable catalytic performance of β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ is due to the synergy effect of α - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ and γ - Bi_2MoO_6 formed via the decomposition of β - $\text{Bi}_2\text{Mo}_2\text{O}_9$, to the high intrinsic catalytic activity of β - $\text{Bi}_2\text{Mo}_2\text{O}_9$, and to the well-crystallized parts of β - $\text{Bi}_2\text{Mo}_2\text{O}_9$.

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