

脱原油資源を目指した接触酸化脱水素反応による 汎用工業原料の合成研究

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Synthesis of Versatile Chemicals through Oxidative Dehydrogenation on Solid Catalysts of Non-Petroleum Resource

by

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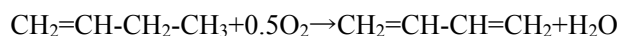
To prepare 1,3-butadiene, one of versatile chemicals, from 1-butene, one of the main components in liquefied petroleum gas (LPG), the oxidative dehydrogenation of 1-butene on α -Bi₂Mo₃O₁₂ doped with cerium was examined. Regardless to the doped amount of cerium, the conversion of 1-butene was constant while the selectivity to 1,3-butadiene decreased with the doped amount of cerium, while the selectivities to 2-butenes, CO and CO₂ increased. It is concluded that the introduction of cerium into α -Bi₂Mo₃O₁₂ resulted in the enhancement of the greater acidic nature of the catalyst while the mild acidic nature of the catalyst seems to be suitable for the effective synthesis of 1,3-butadiene from 1-butene via the oxidative dehydrogenation.

Key words: 1-Butene, 1,3-Butadiene, α -Bi₂Mo₃O₁₂, Cerium doping, Oxidative dehydrogenation

1. Introduction

1,3-Butadiene is one of the most versatile chemicals since it is a crucial chemical ingredient for butadiene rubber that is indispensable to produce various kinds of tires. Generally, 1,3-butadiene is produced from naphtha-cracking while this process has serious disadvantage such as energy consumption and unselective production of various by-products.¹⁾ Furthermore naphtha is obtained from petroleum that will disappear in the future. In the present study, as a raw material for the preparation of 1,3-butadiene, 1-

butene was selected and the oxidative dehydrogenation of 1-butene to 1,3-butadiene was examined on Bi-Mo binary oxide catalyst doped with cerium.



Since 1-butene is one of the main components in liquefied petroleum gas (LPG), which is now mainly used as energy but not precursor of chemicals. If 1,3-butadiene can be prepared from 1-butene, consumption of petroleum can be suppressed. Furthermore the oxidative dehydrogenation of 1-butene to 1,3-butadiene is exothermic reaction and the use of a lower reaction temperature is possible. Therefore, the present study contributes to the reduction of energy and petroleum resource. For the present catalytic conversion, binary oxide catalyst, α -Bi₂Mo₃O₁₂, has been known as an active catalyst.²⁾ Since it has been

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pointed out that the redox nature of Mo-species in α - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ contributes to the great activity,²⁾ doping with cerium that possess greater redox nature than Mo-species³⁾ was examined in the present study.

2. Experimental

α - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ and that doped with cerium were prepared by a co-precipitation method.²⁾ A certain amount of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (Wako Pure Chemical Industries, Ltd.) was dissolved in distilled water previously acidified with concentrated nitric acid (Wako). The solution was then added dropwise into an aqueous solution containing a certain amount of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (Kanto Kagaku Co., Inc.) under vigorous stirring. During the co-precipitation step, the pH of the mixed solution was precisely controlled using ammonia solution to be at pH = 1.5. In case of the preparation of the catalyst doped with cerium, aqueous solution of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Wako) that concentration was adjusted by the valence balance to molybdenum was added into the mixed solution. 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 at 343 K for 3 days and then calcined at 748 K for 5 h. The structural properties of the catalysts, described as α - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ and xmol% CeO_2 - α - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$, were analyzed via X-ray diffraction (XRD; RINT 2500X, Rigaku Co.) and N_2 adsorption-desorption measurement (BELSORP-18SP, Bel Japan Inc.). The acidic properties of the catalysts were characterized via temperature-programmed desorption of NH_3 (TPD; BELCAT-A, Bel Japan Inc.). Details on characterization have been described in our previous paper.⁴⁾ The activity test was performed using fixed-bed continuous flow reactor operated at atmospheric pressure. The catalyst (0.5 g) was fixed with quartz wool and pretreated with 25 mL/min of O_2 gas flow at 723 K for 1 h. After the pretreatment, an activity test was started by flowing 30 mL/min of He, 1- C_4H_8 and O_2 to the reactor. Unless otherwise stated, the reactant gas consisted of $P(1\text{-C}_4\text{H}_8) = 14.4$ kPa, and $P(\text{O}_2) = 8.2$ or 12.3 kPa diluted with He was employed in the present study. Under these conditions, no homogeneous gas phase reaction was observed. The reaction was monitored using an online gas chromatograph (Shimadzu GC-8APT) equipped with a TCD together with a capillary gas chromatograph (Shimadzu GC-2025) equipped with an FID. For the online gas chromatograph, a molecular

Sieve 5A (MS 5A, 0.2 m \times Φ 3 mm) for O_2 , CH_4 and CO and a Hayesep R (2.0 m \times Φ 3 mm) for CO_2 , C_2 , C_3 , and C_4 products were used as the columns. Since this column system was insufficient for the separation of C_4 products, the capillary gas chromatograph was used, in which the column was a Rt-Alumina BOND/ Na_2SO_4 (30 m \times 0.53 mm \times 10 μm) (Restek Co.). The carbon balance between the reactant and the products was within $\pm 5\%$. The product selectivity and 1- C_4H_8 conversion were calculated on a carbon basis.

3. Results and Discussion

Figure 1 shows the effects of the partial pressure of O_2 for the oxidative dehydrogenation of 1- C_4H_8 on α - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$. It was evident that the increase of the partial pressure of O_2 from 8.2 to 12.3 kPa resulted in the decrease of the selectivity to 1,3- C_4H_6 while both of the selectivities to CO and CO_2 increased. This behavior is sometimes observed in the oxidative dehydrogenation of various alkanes, indicating that the deep oxidation to CO and CO_2 proceeds.

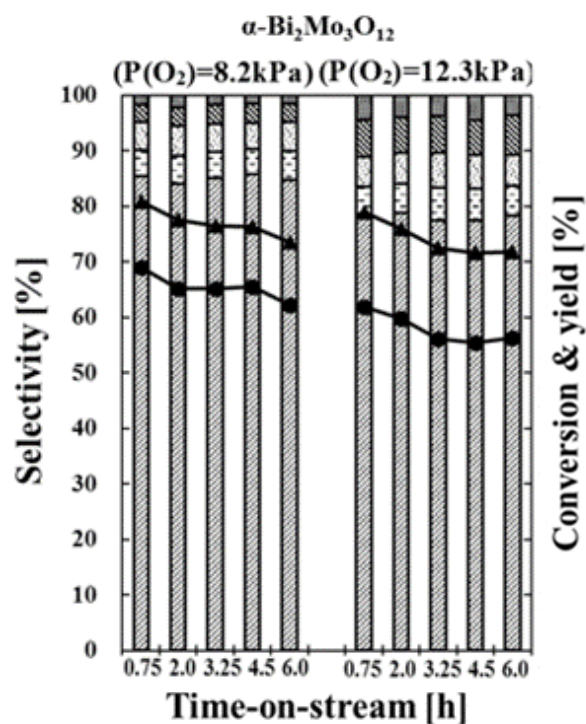


Fig. 1 The effect of partial pressure of oxygen on the oxidative dehydrogenation of 1-butene on α - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$. Symbols: \blacktriangle and \blacksquare were 1- C_4H_8 conversion and 1,3- C_4H_6 yield, respectively. Bars: ▨ , ▬ , ▮ , ▩ , and ▧ were selectivities to 1,3- C_4H_6 , cis-2- C_4H_8 , trans-2- C_4H_8 , CO_2 and CO , respectively.

As shown in Fig. 1, α - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ showed the great activity expected from the previous paper.²⁾ In the present system, abstract of lattice oxygen around Mo-species and incorporation of oxygen into vacancy of lattice oxygen in the catalyst, that is, reduction and oxidation (redox) would be important. If an element with stronger redox nature is incorporated into the catalyst, the redox nature of the catalyst would be enhanced, followed by the improvement of the activity. Therefore the activity on 1 mol% CeO_2 - α - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ was investigated at $P(\text{O}_2) = 8.2$ and 12.3 kPa (Fig. 2).

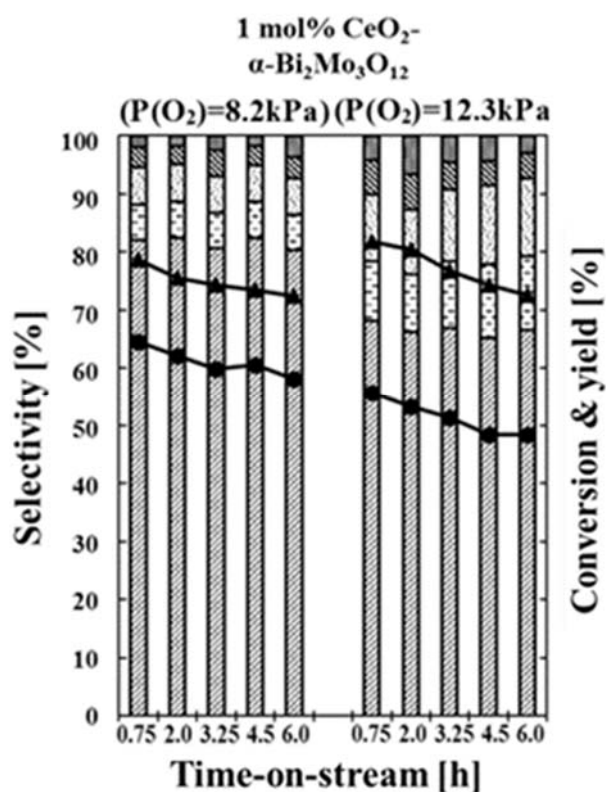


Fig. 2 The effect of partial pressure of oxygen on the oxidative dehydrogenation of 1-butene on 1 mol% CeO_2 - α - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$. Symbols: \blacktriangle and \blacksquare were 1- C_4H_8 conversion and 1,3- C_4H_6 yield, respectively. Bars: diagonal lines , horizontal lines , dots , vertical lines , and cross-hatch were selectivities to 1,3- C_4H_6 , cis-2- C_4H_8 , trans-2- C_4H_8 , CO_2 and CO , respectively.

Regardless to $P(\text{O}_2)$, the conversion of 1- C_4H_8 was essentially identical to that on α - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$, while the decrease of the selectivity to 1,3- C_4H_6 was evident. Therefore, as expected, the doping with 1 mol% CeO_2 into α - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ resulted in the enhancement of the redox nature of the catalyst, followed by the increase of the deep oxidation of 1,3- C_4H_6 to CO and CO_2 . The

same effect of the doping on the oxidative dehydrogenation of 1- C_4H_8 was also observed on 3 mol% CeO_2 - α - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ (Fig. 3).

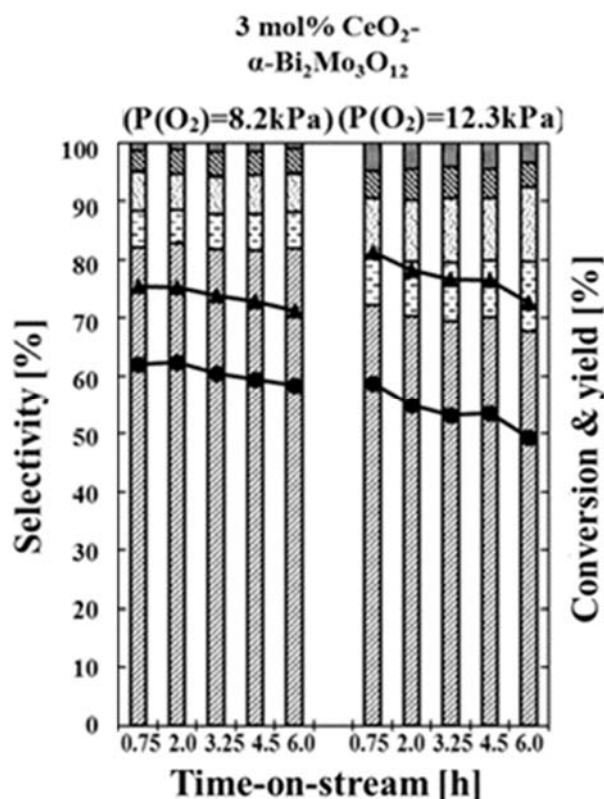


Fig. 3 The effect of partial pressure of oxygen on the oxidative dehydrogenation of 1-butene on 3 mol% CeO_2 - α - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$. Symbols: \blacktriangle and \blacksquare were 1- C_4H_8 conversion and 1,3- C_4H_6 yield, respectively. Bars: diagonal lines , horizontal lines , dots , vertical lines , and cross-hatch were selectivities to 1,3- C_4H_6 , cis-2- C_4H_8 , trans-2- C_4H_8 , CO_2 and CO , respectively.

It is worthwhile to mention that the doping with cerium resulted in the enhancement of the selectivities to isomerized compounds of 1- C_4H_8 , such as cis-2- C_4H_8 and trans-2- C_4H_8 , together with those to CO and CO_2 . Therefore the doping of α - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ with cerium on the oxidative dehydrogenation of 1- C_4H_8 results in the increase of the selectivities to CO , CO_2 , cis-2- C_4H_8 and trans-2- C_4H_8 together with the decrease of the selectivity to 1,3- C_4H_6 while the conversion of 1- C_4H_8 is not sensitive to the doping, due to the enhancement of the redox nature of the catalysts and the structural nature of the catalyst.

It is of interest to note that the conversion of 1- C_4H_8 was almost same on α - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$, 1 mol% CeO_2 - α - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ and 3 mol% CeO_2 - α - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$. In

order to estimate the contribution of the specific surface area, N₂ adsorption-desorption behaviors of those catalysts measurement were measured (Fig. 4).

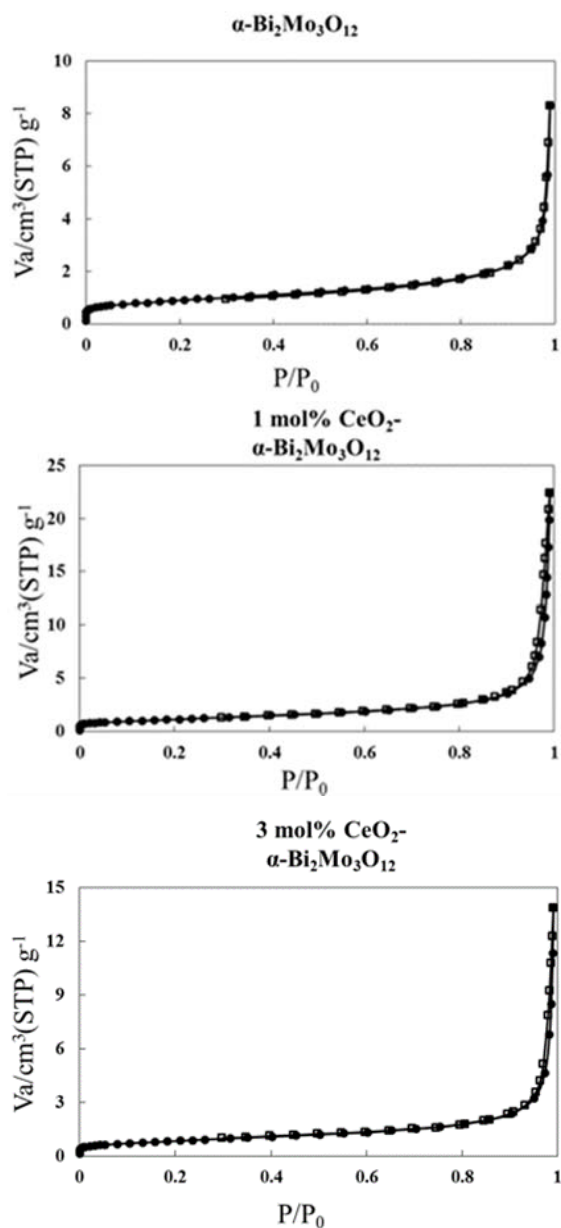


Fig. 4 N₂ adsorption-desorption isotherms of α -Bi₂Mo₃O₁₂, 1 mol% CeO₂- α -Bi₂Mo₃O₁₂, and 3 mol% CeO₂- α -Bi₂Mo₃O₁₂. Symbols: ● and □ were adsorption and desorption, respectively.

As shown in Fig. 4, regardless to the doped amount of cerium, the surface structure was almost same to each other. The specific surface areas of α -Bi₂Mo₃O₁₂, 1 mol% CeO₂- α -Bi₂Mo₃O₁₂, and 3 mol% CeO₂- α -Bi₂Mo₃O₁₂ estimated from Fig. 4 were 3.2, 4.1, and 3.0 m²/g, respectively, indicating that the

insensitive conversion of 1-C₄H₈ to the doping is reasonable.

Figure 5 showed XRD patterns of α -Bi₂Mo₃O₁₂, and 3 mol% CeO₂- α -Bi₂Mo₃O₁₂ before (fresh catalyst) and after the oxidative dehydrogenation of 1-C₄H₈ at p_H(O₂) = 8.2 and 12.3 kPa.

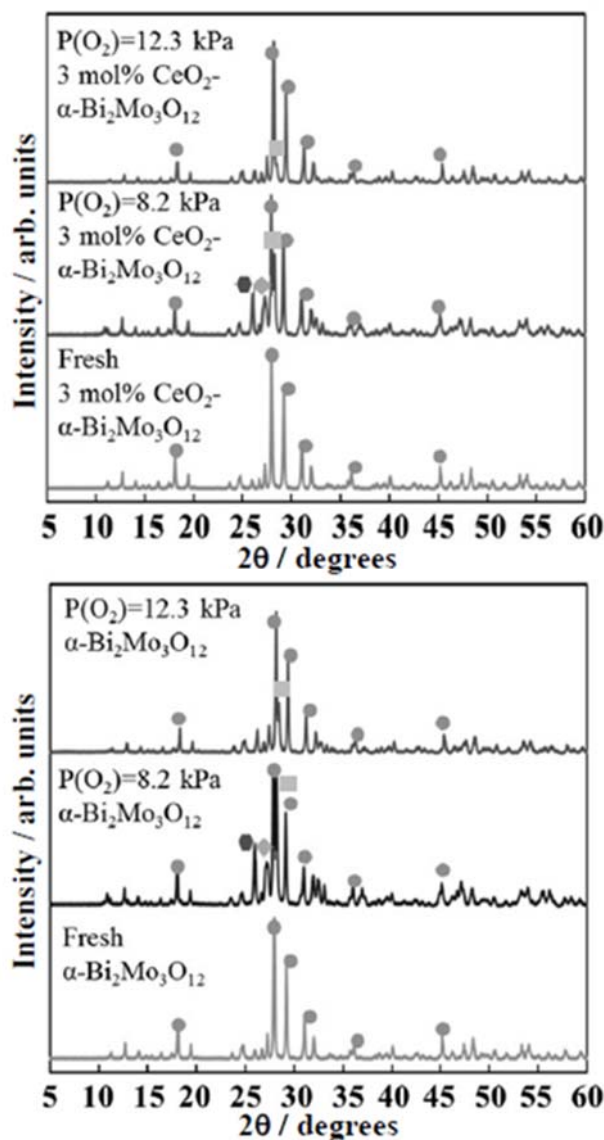


Fig. 5 XRD patterns of α -Bi₂Mo₃O₁₂, and 3 mol% CeO₂- α -Bi₂Mo₃O₁₂ before and after the oxidative dehydrogenation at p_H(O₂) = 8.2 and 12.3 kPa. Symbols: ●, ■, ◆, and ● were α -Bi₂Mo₃O₁₂, γ -Bi₂MoO₆, α -MoO₃, and h-MoO₃, respectively.

From both fresh catalysts, signals due to α -Bi₂Mo₃O₁₂ (JCPDS 21-0103) were detected as expected. After the oxidative dehydrogenation at P(O₂) = 8.2 kPa, signals due to γ -Bi₂MoO₆ (JCPDS 21-0102), α -MoO₃ (JCPDS 05-0508), and h-MoO₃

(JCPDS 21-0569) were also detected from both catalysts, while signals due to α -MoO₃ and h-MoO₃ were disappeared after the reaction at P(O₂) = 12.3 kPa. Since the doped amount of cerium was limited, evident difference could not be detected in XRD for α -Bi₂Mo₃O₁₂, and 3 mol% CeO₂- α -Bi₂Mo₃O₁₂ while it may be concluded that the stability of the catalyst structure is influenced by partial pressure of O₂ that directly contributes to redox nature of the present catalyst system.

As shown in Figs. 1-3, the doping of cerium into α -Bi₂Mo₃O₁₂ resulted in the enhancement of isomerization from 1-C₄H₈ to cis-2-C₄H₈ and trans-2-C₄H₈. Since it is generally accepted that a catalytic isomerization favorably proceeds on an acidic catalyst, we examined NH₃-TPD of α -Bi₂Mo₃O₁₂, and 3 mol% CeO₂- α -Bi₂Mo₃O₁₂ (Fig. 6).

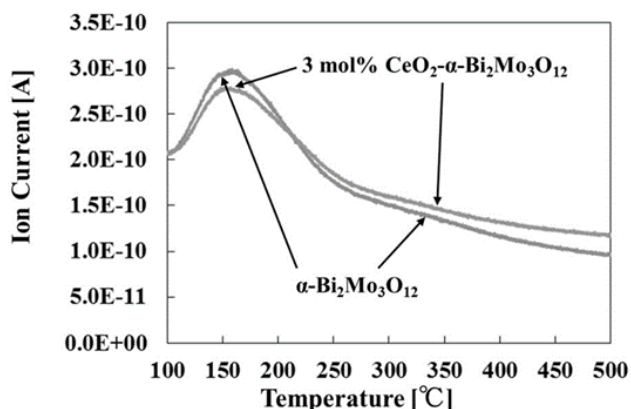


Fig. 6 NH₃-TPD of α -Bi₂Mo₃O₁₂, and 3 mol% CeO₂- α -Bi₂Mo₃O₁₂.

Since evident difference in NH₃-TPD between two catalysts was not detected, acid amount for both catalysts was estimated to as 0.005 mmol/kg from Fig. 6. It should be noted that that a rather broader peak at a temperature greater than 250 °C was detected from 3 mol% CeO₂- α -Bi₂Mo₃O₁₂, indicating that the acid strength of 3 mol% CeO₂- α -Bi₂Mo₃O₁₂ may be greater than that of α -Bi₂Mo₃O₁₂. Therefore the stronger acid strength of CeO₂- α -Bi₂Mo₃O₁₂ contributes to the enhancement of isomerization from 1-C₄H₈ to cis-2-C₄H₈ and trans-2-C₄H₈. Furthermore, the mild acidic nature of the catalyst that was detected at a temperature lower than 250 °C seems to be suitable for the effective synthesis of 1,3-C₄H₆ from 1-C₄H₈ via the oxidative dehydrogenation.

4. Conclusion

The doping of cerium into α -Bi₂Mo₃O₁₂ that was one of the active catalysts for the oxidative dehydrogenation of 1-butene to 1,3-butadiene resulted in the enhancement of the selectivities to CO, CO₂, cis-2-butene and trans-2-butene, while the conversion of 1-butene was insensitive to the doping. However the selectivity to 1,3-butadiene was suppressed by the doping. Based on the results obtained from the catalytic activity test, XRD, N₂ adsorption-desorption experiment and NH₃-TPD, it can be concluded that the improvement of the redox nature of the catalyst by the doping, essentially identical surface area of the catalyst regardless to the doping, and the enhancement of the acidic nature of the catalyst by the doping directly contribute to the catalytic activity.

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