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Effect of pH in the preparation of $Ni_9Fe_3Bi_1Mo_{12}O_{51}$ for oxidative dehydrogenation of *n*-butene to 1,3-butadiene: Correlation between catalytic performance and oxygen mobility of $Ni_9Fe_3Bi_1Mo_{12}O_{51}$

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Abstract

A series of $Ni_9Fe_3Bi_1Mo_{12}O_{51}$ catalysts were prepared by a co-precipitation method with a variation of pH value (pH 3–9), and were applied to the oxidative dehydrogenation of *n*-butene to 1,3-butadiene in a continuous flow fixed-bed reactor. O_2-temperature-programmed desorption (TPD) and X-ray photoelectron spectroscopy (XPS) measurements were carried out to determine the oxygen mobility of $Ni_9Fe_3Bi_1Mo_{12}O_{51}$ catalysts. It was revealed that the catalytic performance of $Ni_9Fe_3Bi_1Mo_{12}O_{51}$ was closely related to the oxygen mobility of the catalysts. The yield for 1,3-butadiene was monotonically increased with increasing oxygen mobility of $Ni_9Fe_3Bi_1Mo_{12}O_{51}$ catalysts. Among the catalysts tested, the $Ni_9Fe_3Bi_1Mo_{12}O_{51}$ catalyst prepared at pH 8 showed the best catalytic performance due to its facile oxygen mobility. Thus, oxygen mobility played a key role in determining the catalytic performance of $Ni_9Fe_3Bi_1Mo_{12}O_{51}$ catalysts in the oxidative dehydrogenation of *n*-butene.

Keywords: Multicomponent bismuth molybdate; Effect of pH; C_4 raffinate-3; 1,3-Butadiene; Oxidative dehydrogenation

1. Introduction

Selective oxidation of olefins such as oxidation of propylene to acrolein, ammoxidation of propylene to acrylonitrile, and oxidative dehydrogenation of *n*-butene to 1,3-butadiene has been widely investigated in petrochemical industries due to its significance in producing large-scale chemical intermediates [1–4]. In particular, the oxidative dehydrogenation of *n*-butene has been recognized as a promising process for producing 1,3-butadiene which is an important raw material for manufacturing a large number of chemical products such as acrylonitrile–butadiene–styrene (ABS), polybutadiene rubber (BR), and styrene–butadiene rubber (SBR) [5–7]. 1,3-Butadiene that is currently provided in the market is mostly produced through a naphtha cracking process. However, the oxidative dehydrogenation of *n*-butene has many advantages over the naphtha cracking process, because this process can be operated as a single unit and is independent of the naphtha cracking unit in producing 1,3-butadiene. Furthermore, no additional major naphtha cracking products such as ethylene and propylene are produced in the oxidative dehydrogenation of *n*-butene [4,8].

A large number of metal oxides have been investigated as catalysts in the oxidative dehydrogenation of *n*-butene, including vanadium-containing catalyst [9], ferrite-type catalyst [10], manganese oxide molecular sieve catalyst [11], and bismuth molybdate catalyst [12–14]. Among these

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catalysts, bismuth molybdates have been widely investigated as efficient catalysts for this reaction [12–14]. Although three types of pure bismuth molybdate catalysts (α-$Bi_2Mo_3O_{12}$, β-$Bi_2Mo_2O_9$, and γ-Bi_2MoO_6) have been studied as efficient catalysts [15–17], multicomponent bismuth molybdate catalysts have also been widely employed due to their high catalytic activity [18–21].

Co-precipitation method has been generally used in the preparation of pure bismuth molybdate and multicomponent bismuth molybdate catalysts [4,18]. It has been reported that pH value in the co-precipitation step is an important factor for the successful formation of active phases in the preparation of bismuth molybdate catalysts [16,22]. This implies that pH value in the preparation of multicomponent bismuth molybdate catalysts by a co-precipitation method can serve as a crucial factor determining the catalytic performance of multicomponent bismuth molybdate catalysts. Nonetheless, 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, due to the difficulty in understanding the complex structure and oxygen mobility of the catalysts.

Multicomponent bismuth molybdate catalysts have a general form of $M_a^{II}M_b^{III}Bi_cMo_dO_e$, which includes divalent metal (M^{II}), trivalent metal (M^{III}), bismuth, and molybdenum [21,23]. Although a number of multicomponent bismuth molybdate catalysts can be formed depending on the constituent metal components and their compositions, it is generally accepted that Ni is suitable for M^{II} and Fe is suitable for M^{III} in the multicomponent bismuth molybdate catalyst system [18,23]. In our previous investigation [24], it was also revealed that the metal ratio of M^{II}:M^{III}:Bi:Mo = 9:3:1:12 was favorable for the oxidative dehydrogenation of *n*-butene. In this work, therefore, $Ni_9Fe_3Bi_1Mo_{12}O_{51}$ was chosen as a model catalyst to investigate the effect of pH in the preparation of $Ni_9Fe_3Bi_1Mo_{12}O_{51}$ on the catalytic performance in the oxidative dehydrogenation of *n*-butene.

It is well known that the oxidative dehydrogenation of *n*-butene over multicomponent bismuth molybdates is affected by various catalytic properties [21,25]. However, many researchers agree that oxygen mobility of the catalyst is one of the crucial factors determining the catalytic performance in the oxidative dehydrogenation of *n*-butene [26–28], because the reaction follows the Mars–van Krevelen mechanism [4,28]. Therefore, it is expected that a catalyst with high oxygen mobility will show an excellent catalytic activity in the oxidative dehydrogenation of *n*-butene.

In this work, a series of multicomponent bismuth molybdate catalysts ($Ni_9Fe_3Bi_1Mo_{12}O_{51}$) were prepared by a co-precipitation method with a variation of pH value (pH 3–9), and were applied to the oxidative dehydrogenation of *n*-butene to 1,3-butadiene. O_2-TPD and XPS measurements were carried out to determine the oxygen mobility of $Ni_9Fe_3Bi_1Mo_{12}O_{51}$ catalysts. A correlation between catalytic performance and oxygen mobility of $Ni_9Fe_3Bi_1Mo_{12}O_{51}$ catalysts was then established.

2. Experimental

2.1. Preparation of $Ni_9Fe_3Bi_1Mo_{12}O_{51}$ catalysts

A series of $Ni_9Fe_3Bi_1Mo_{12}O_{51}$ catalysts were prepared by a co-precipitation method with a variation of pH value in the co-precipitation step. 7.9 g of nickel nitrate ($Ni(NO_3)_2 \cdot 6H_2O$, Sigma–Aldrich) and 3.7 g of ferric nitrate ($Fe(NO_3)_3 \cdot 9H_2O$, Sigma–Aldrich) were successively dissolved in 50 ml of distilled water (Solution A). 1.5 g of bismuth nitrate ($Bi(NO_3)_3 \cdot 5H_2O$, Sigma–Aldrich) was separately dissolved in 10 ml of distilled water that had been acidified with 3 ml of concentrated nitric acid (Solution B). The Solution B was then added into Solution A to obtain a mixed nitrate solution. The mixed nitrate solution was added dropwise into an aqueous solution (100 ml) 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, the pH value of the mixed solution was precisely controlled using ammonia solution. The pH value was varied from 3 to 9 with an interval of one in order to prepare seven $Ni_9Fe_3Bi_1Mo_{12}O_{51}$ catalyst samples. 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 $Ni_9Fe_3Bi_1Mo_{12}O_{51}$ catalyst.

2.2. Characterization

Formation of $Ni_9Fe_3Bi_1Mo_{12}O_{51}$ 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). Thermal stability of $Ni_9Fe_3Bi_1Mo_{12}O_{51}$ catalysts was examined by TGA analyses (Pheometric Scientific, TGA-100). XPS analyses (Thermo VG, Sigma probe) were conducted to measure the binding energies of lattice oxygen in the $Ni_9Fe_3Bi_1Mo_{12}O_{51}$ catalysts using C 1s peak (284.5 eV) as a reference.

O_2-TPD experiments were carried out in order to determine the oxygen mobility of $Ni_9Fe_3Bi_1Mo_{12}O_{51}$ 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 preadsorbed onto the catalyst sample for direct measurement of lattice oxygen evolved from the catalyst. Therefore, the O_2-TPD experiments conducted in this work represent the thermal desorption measurements of lattice oxygen