



Effect of oxygen capacity and oxygen mobility of supported $\text{Mg}_3(\text{VO}_4)_2$ catalysts on the performance in the oxidative dehydrogenation of n-butane

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ABSTRACT

Vanadium-magnesium oxide ($\text{Mg}_3(\text{VO}_4)_2$) catalysts supported on Al_2O_3 , ZrO_2 , MgO , and CeO_2 were prepared by a wet impregnation method, and they were applied to the oxidative dehydrogenation of n-butane. Effect of oxygen capacity and oxygen mobility of supported $\text{Mg}_3(\text{VO}_4)_2$ catalysts on the catalytic performance in the oxidative dehydrogenation of n-butane was investigated. Experimental results revealed that large oxygen capacity of the catalyst was favorable for obtaining high catalytic activity at the initial stage of reaction, while facile oxygen mobility of the catalyst led to stable catalytic activity during the catalytic reaction in the oxidative dehydrogenation of n-butane.

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1. Introduction

Oxidative dehydrogenation of light paraffins has been recognized as an alternative route for the production of light olefins, because it is an exothermic reaction and the presence of O_2 inhibits carbon deposition [1–3]. Furthermore, catalytic processes for the production of light olefins by oxidative dehydrogenation of corresponding paraffins are attractive because of versatile availability of light paraffin feedstocks. In particular, oxidative dehydrogenation of n-butane has attracted much attention as a promising process for producing C_4 olefins such as n-butene and 1,3-butadiene [4–8]. Increasing demand for n-butene and 1,3-butadiene makes this process more economical, because cheap and abundant n-butane is employed as a starting material for producing n-butene and 1,3-butadiene [9].

Mars–van Krevelen mechanism has been considered as a major reaction pathway controlling the oxidative dehydrogenation of n-butane [10–14]. According to this mechanism, lattice oxygen in the catalyst directly reacts with n-butane, and in turn, gaseous oxygen makes up oxygen vacancy in the catalyst. When considering this mechanism, it can be inferred that the amount of oxygen in the catalyst involved in the reaction (oxygen capacity) may serve as a crucial factor determining the catalytic performance in the

reaction, while the intrinsic mobility of oxygen in the catalyst involved in the reaction (oxygen mobility) may affect the working-regeneration cycles of the catalyst during the reaction [13–15]. However, any systematic investigations to see the effect of oxygen capacity and oxygen mobility on the catalytic performance in the oxidative dehydrogenation of n-butane have not been attempted yet. Therefore, this work was focused on the elucidation of role of lattice oxygen in the oxidative dehydrogenation of n-butane.

Vanadium-magnesium oxide (V-Mg-O) catalysts have been extensively studied as efficient catalysts for the oxidative dehydrogenation of light paraffins and ethyl benzene [16–23]. It is known that there are three stable magnesium vanadate phases; orthovanadate ($\text{Mg}_3(\text{VO}_4)_2$), pyrovanadate ($\text{Mg}_2\text{V}_2\text{O}_7$), and metavanadate (MgV_2O_6). Among these magnesium vanadate phases, $\text{Mg}_3(\text{VO}_4)_2$ phase has been recognized as the most active phase for the oxidative dehydrogenation of n-butane [15,16,22–24]. In this work, therefore, several supported $\text{Mg}_3(\text{VO}_4)_2$ catalysts ($\text{Mg}_3(\text{VO}_4)_2/\text{Al}_2\text{O}_3$, $\text{Mg}_3(\text{VO}_4)_2/\text{ZrO}_2$, $\text{Mg}_3(\text{VO}_4)_2/\text{MgO}$, and $\text{Mg}_3(\text{VO}_4)_2/\text{CeO}_2$) were chosen as model catalysts to investigate the effect of oxygen capacity and oxygen mobility of the catalyst on the catalytic performance in the oxidative dehydrogenation of n-butane.

In this work, four supported $\text{Mg}_3(\text{VO}_4)_2$ catalysts were prepared by a wet impregnation method with a variation of metal oxide support (Al_2O_3 , ZrO_2 , MgO , and CeO_2), and they were applied to the oxidative dehydrogenation of n-butane. Formation of supported $\text{Mg}_3(\text{VO}_4)_2$ catalysts was confirmed by XRD, XPS and ICP-AES analyses. Oxidative dehydrogenation of n-butane over supported

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$\text{Mg}_3(\text{VO}_4)_2$ catalysts was also carried out in the absence of oxygen feed, with an aim of measuring the oxygen capacity of the catalyst. Temperature-programmed reoxidation (TPRO) experiments were carried out to determine the oxygen capacity and oxygen mobility of the catalyst. Effect of oxygen capacity and oxygen mobility of supported $\text{Mg}_3(\text{VO}_4)_2$ catalysts on the catalytic performance in this reaction was then discussed.

2. Experimental

2.1. Preparation of supported $\text{Mg}_3(\text{VO}_4)_2$ catalysts

Al_2O_3 , ZrO_2 , MgO , and CeO_2 supports were prepared by a gel-oxalate co-precipitation method according to the procedures reported in the literatures [25,26]. 36.8 g of aluminum chloride ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, Sigma–Aldrich), 9.5 g of zirconium chloride (ZrCl_4 , Sigma–Aldrich), 11.8 g of magnesium chloride (MgCl_2 , Sigma–Aldrich), and 12.6 g of cerium nitrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, Sigma–Aldrich) were separately dissolved in 500 ml of ethanol. 100 ml of ethanol solution containing excess amount of oxalic acid was then added dropwise into ethanol solution containing each metal precursor for co-precipitation under vigorous stirring. After the resulting solution was stirred vigorously at room temperature for 3 h, it was aged overnight at room temperature. The precipitate was then separated by centrifuge, and it was dried at 80°C overnight. The dried product was finally calcined at 550°C for 3 h to yield the corresponding metal oxide support (Al_2O_3 , ZrO_2 , MgO , and CeO_2).

$\text{Mg}_3(\text{VO}_4)_2/\text{MgO}$ catalyst was prepared by a wet impregnation method using an aqueous oxalic acid solution containing vanadium precursor (NH_4VO_3 , Sigma–Aldrich). After heating the impregnated sample at 70°C , the resulting solid was calcined at 550°C for 3 h in the presence of air to yield the $\text{Mg}_3(\text{VO}_4)_2/\text{MgO}$ catalyst. Vanadium content in the $\text{Mg}_3(\text{VO}_4)_2/\text{MgO}$ was fixed at 9.0 wt%.

For the preparation of $\text{Mg}_3(\text{VO}_4)_2/\text{Al}_2\text{O}_3$, $\text{Mg}_3(\text{VO}_4)_2/\text{ZrO}_2$, and $\text{Mg}_3(\text{VO}_4)_2/\text{CeO}_2$ catalysts, magnesium was first impregnated on each metal oxide support using an aqueous solution of magnesium precursor ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Sigma–Aldrich). After heating the impregnated sample at 70°C , the resulting solid was calcined at 550°C for 3 h in the presence of air to yield the MgO/MeOx support ($\text{MeOx} = \text{Al}_2\text{O}_3$, ZrO_2 , and CeO_2). Vanadium was then impregnated on the prepared MgO/MeOx support using an aqueous oxalic acid solution containing vanadium precursor (NH_4VO_3 , Sigma–Aldrich). The impregnated sample was heated at 70°C , and finally, it was calcined at 550°C for 3 h in the presence of air to yield the $\text{Mg}_3(\text{VO}_4)_2/\text{Al}_2\text{O}_3$, $\text{Mg}_3(\text{VO}_4)_2/\text{ZrO}_2$, and $\text{Mg}_3(\text{VO}_4)_2/\text{CeO}_2$ catalysts. Vanadium and magnesium contents in the $\text{Mg}_3(\text{VO}_4)_2/\text{Al}_2\text{O}_3$, $\text{Mg}_3(\text{VO}_4)_2/\text{ZrO}_2$, and $\text{Mg}_3(\text{VO}_4)_2/\text{CeO}_2$ catalysts were fixed at 9.0 wt% and 6.4 wt%, respectively.

2.2. Characterization

Formation of $\text{Mg}_3(\text{VO}_4)_2/\text{Al}_2\text{O}_3$, $\text{Mg}_3(\text{VO}_4)_2/\text{ZrO}_2$, $\text{Mg}_3(\text{VO}_4)_2/\text{MgO}$ and $\text{Mg}_3(\text{VO}_4)_2/\text{CeO}_2$ catalysts was confirmed by XRD (MAC Science, M18XHF-SRA) and XPS (Thermo VG, Sigma Probe) analyses. XPS analyses were conducted to measure the binding energies of V ions of magnesium vanadate phase in the supported $\text{Mg}_3(\text{VO}_4)_2$ catalysts using C 1s peak (284.5 eV) as a reference. Mg:V atomic ratios and V contents in the catalysts were determined by ICP-AES (Shimadzu, ICP-1000IV) analyses. Surface areas of the catalysts were measured using a BET apparatus (Micromeritics, ASAP 2010).

In order to determine the oxygen capacity and oxygen mobility of the catalysts, temperature-programmed reoxidation (TPRO) experiments were carried out. For the TPRO experiment, each catalyst was reduced by carrying out the oxidative

dehydrogenation of n-butane at 500°C for 1 h in the absence of oxygen feed in order for the catalyst to consume lattice oxygen. 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 raised from room temperature to 900°C at a heating rate of $5^\circ\text{C}/\text{min}$. The amount of oxygen consumed was measured using a thermal conductivity detector.

2.3. Oxidative dehydrogenation of n-butane

Oxidative dehydrogenation of n-butane was carried out in a continuous flow fixed-bed reactor in the presence of oxygen. Feed composition was fixed at n-butane:oxygen:nitrogen = 4:8:88. Catalytic reaction was carried out at 500°C . Gas hourly space velocity (GHSV) was fixed at 2000 h^{-1} on the basis of n-butane. Reaction products were periodically sampled and analyzed with gas chromatographs. Conversion of n-butane, selectivity for total dehydrogenated products (TDP, n-butene and 1,3-butadiene), and selectivity for 1,3-butadiene were calculated on the basis of carbon balance as follows. Yield for TDP was calculated by multiplying conversion of n-butane and selectivity for TDP.

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

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

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

3. Results and discussion

3.1. Formation of supported $\text{Mg}_3(\text{VO}_4)_2$ catalysts

Successful formation of $\text{Mg}_3(\text{VO}_4)_2/\text{Al}_2\text{O}_3$, $\text{Mg}_3(\text{VO}_4)_2/\text{ZrO}_2$, $\text{Mg}_3(\text{VO}_4)_2/\text{MgO}$, and $\text{Mg}_3(\text{VO}_4)_2/\text{CeO}_2$ catalysts was confirmed

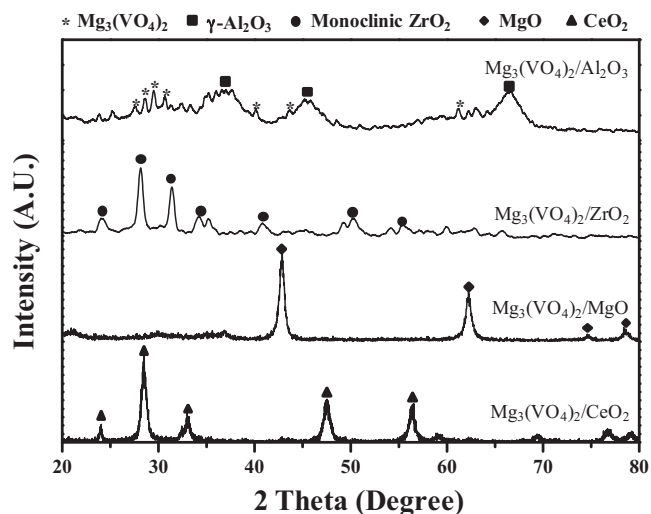


Fig. 1. XRD patterns of $\text{Mg}_3(\text{VO}_4)_2/\text{Al}_2\text{O}_3$, $\text{Mg}_3(\text{VO}_4)_2/\text{ZrO}_2$, $\text{Mg}_3(\text{VO}_4)_2/\text{MgO}$, and $\text{Mg}_3(\text{VO}_4)_2/\text{CeO}_2$ catalysts.

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