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Effect of $Cs_xH_{3-x}PW_{12}O_{40}$ addition on the catalytic performance of $ZnFe_2O_4$ in the oxidative dehydrogenation of n-butene to 1,3-butadiene

Howon Lee*, Ji Chul Jung*, Heesoo Kim*, Young-Min Chung, Tae Jin Kim**,**
Seong Jun Lee, Seung-Hoon Oh**, Yong Seung Kim**, and In Kyu Song*,†**

*School of Chemical and Biological Engineering, Institute of Chemical Processes,
Seoul National University, Shinlim-dong, Gwanak-gu, Seoul 151-744, Korea
**SK Energy Corporation, Yuseong-gu, Daejeon 305-712, Korea
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Abstract−Oxidative dehydrogenation of n-butene to 1,3-butadiene over $ZnFe_2O_4$ catalyst mixed with $Cs_xH_{3-x}PW_{12}O_{40}$ heteropolyacid (HPA) was performed in a continuous flow fixed-bed reactor. The effect of $Cs_xH_{3-x}PW_{12}O_{40}$ addition on the catalytic performance of $ZnFe_2O_4$ was investigated. $Cs_xH_{3-x}PW_{12}O_{40}$ itself showed very low catalytic performance in the oxidative dehydrogenation of n-butene. However, addition of small amount of $Cs_xH_{3-x}PW_{12}O_{40}$ into $ZnFe_2O_4$ enhanced the catalytic performance of $ZnFe_2O_4$ catalyst. The catalytic performance of $ZnFe_2O_4$-$Cs_xH_{3-x}PW_{12}O_{40}$ mixed catalysts was closely related to the surface acidity of $Cs_xH_{3-x}PW_{12}O_{40}$. Among the catalysts tested, $ZnFe_2O_4$-$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ mixed catalyst showed the best catalytic performance. Strong acid strength and large surface acidity of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was responsible for high catalytic performance of $ZnFe_2O_4$-$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ mixed catalyst. Thus, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ could be utilized as an efficient promoter and diluent in formulating $ZnFe_2O_4$ catalyst for the oxidative dehydrogenation of n-butene.

Key words: Zinc Ferrite, n-Butene, 1,3-Butadiene, Oxidative Dehydrogenation, Cesium-exchanged Heteropolyacid

INTRODUCTION

Oxidative dehydrogenation of n-butene has attracted much attention as a promising process for producing 1,3-butadiene [1-4]. A number of catalysts have been employed for the oxidative dehydrogenation of n-butene, including ferrite-type catalysts [5-8], Cu-Mo catalysts [9], vanadium-containing catalysts [10], and Bi-Mo-based catalysts [11-13]. Among these, $ZnFe_2O_4$ catalyst has been recognized as the most efficient for the oxidative dehydrogenation of n-butene [14,15].

The major factors determining the catalytic performance in the oxidative dehydrogenation of n-butene are different depending on the catalyst system [16-19]. Although fundamental reaction mechanisms have not been clearly elucidated, it has been generally accepted that the reaction mechanism by way of π-allyl intermediate is the most feasible reaction pathway for the production of 1,3-butadiene from n-butene [18,19]. A typical reaction scheme for the oxidative dehydrogenation of n-butene by way of π-allyl intermediate is shown in Fig. 1 [18]. The reaction includes parallel reaction pathways: (1) selective oxidation (oxidative dehydrogenation of n-butene by way of π-allyl intermediate) and (2) combustion. n-Butene is independently adsorbed on the catalyst for parallel reaction. This implies that there are two chemically different active sites on the catalyst surface, and their relative density and reactivity determine the product selectivity. It has been reported that $ZnFe_2O_4$ has high density of selective oxidation sites and low density of combustion sites [15,18], leading to a high catalytic performance of $ZnFe_2O_4$ in the oxidative dehydrogenation of n-butene.

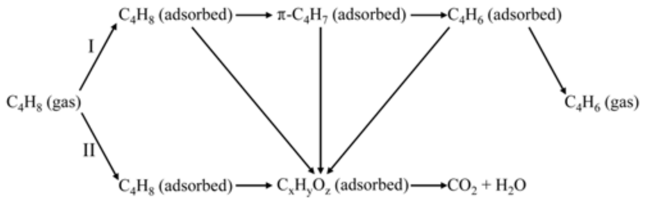

Fig. 1. Typical reaction scheme for the oxidative dehydrogenation of n-butene: I=oxidative dehydrogenation of n-butene, II= combustion [18].

Many researchers agree that the initial abstraction of α-hydrogen from n-butene to form π-allyl intermediate is the rate-determining step in the oxidative dehydrogenation of n-butene [20,21]. This indicates that acid property of the catalyst plays an important role in determining the catalytic performance in the oxidative dehydrogenation of n-butene. Our previous works [5,6] revealed that the catalytic performance of $ZnFe_2O_4$ in the oxidative dehydrogenation of n-butene strongly depended on the surface acidity of the catalyst. Therefore, it is expected that the catalytic performance of $ZnFe_2O_4$ catalyst would be enhanced, if acid property of $ZnFe_2O_4$ is promoted by the addition of another component.

A suitable diluent is required to formulate $ZnFe_2O_4$ catalyst for industrial application. However, not much progress has been made on the investigation of diluent for formulating $ZnFe_2O_4$ catalyst. Therefore, developing an efficient diluent for formulating $ZnFe_2O_4$ catalyst would be of great interest. Furthermore, it would be much better if a diluent can also serve as an efficient promoter for $ZnFe_2O_4$ catalyst in the oxidative dehydrogenation of n-butene.

Heteropolyacids (HPAs) are early transition metal-oxygen anion clusters that have been widely investigated as homogeneous and

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†To whom correspondence should be addressed.
E-mail: inksong@snu.ac.kr

heterogeneous catalysts for acid-base and oxidation reactions [22-25]. HPAs retain stronger acid strength than the conventional solid acid catalysts such as acidic oxides and zeolites [25,26]. One of the great advantages of HPA catalysts is that their acid property can be controlled by changing the identity of constituent metal components [24,27-29]. Their excellent chemical stability also makes HPAs good candidates for catalytic applications that may require harsh environments [30]. Acid sites of HPAs are uniform and easy to control compared to those of other solid acid catalysts [25]. Most HPAs are highly soluble in polar solvents such as water and alcohols, and have low surface area (<10 m^2/g). However, cesium-exchanged HPAs are insoluble and have high surface area by forming a porous tertiary structure [25,26]. Among various cesium-exchanged HPAs, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ is known to have the largest surface acidity [25].

In this work, cesium-exchanged HPAs ($Cs_xH_{3-x}PW_{12}O_{40}$) were prepared with a variation of cesium content (x=2.0, 2.5, and 3.0) for use as an additive for $ZnFe_2O_4$ catalyst, with an aim of taking advantage of high surface area and large surface acidity of $Cs_xH_{3-x}PW_{12}O_{40}$. $ZnFe_2O_4$ catalyst was independently prepared by a co-precipitation method for use as an active catalyst component. $ZnFe_2O_4$ catalyst mixed with $Cs_xH_{3-x}PW_{12}O_{40}$ was then applied to the oxidative dehydrogenation of n-butene to investigate the effect of $Cs_xH_{3-x}PW_{12}O_{40}$ addition on the catalytic performance of $ZnFe_2O_4$. $ZnFe_2O_4$ catalyst was characterized by XRD, BET, TPD, and ICP-AES measurements.

EXPERIMENTAL

1. Catalyst Preparation

$ZnFe_2O_4$ catalyst was prepared by a co-precipitation method. 1.4 g of zinc chloride ($ZnCl_2$, Sigma-Aldrich) and 5.6 g of iron chloride ($FeCl_3\cdot 6H_2O$, Sigma-Aldrich) were successively dissolved in 100 ml of distilled water. The mixed metal precursor solution and an aqueous sodium hydroxide solution (3 N) were then added dropwise into distilled water for co-precipitation under vigorous stirring. During the co-precipitation step, pH of the mixed solution was maintained at 9 by using an aqueous sodium hydroxide solution. After the resulting solution was stirred vigorously at room temperature for 12 h, it was aged overnight at room temperature. The precipitate was filtered to obtain a solid product. The solid product was dried at 175 °C for 16 h, and finally, it was calcined at 650 °C for 6 h to yield the $ZnFe_2O_4$ catalyst.

Commercially available $H_3PW_{12}O_{40}$ which was purchased from Sigma-Aldrich was thermally treated at 300 °C for 2 h for precise quantification, prior to the preparation of cesium-exchanged HPAs. A set of cesium-exchanged HPAs ($Cs_xH_{3-x}PW_{12}O_{40}$) were prepared by an ion-exchange method with a variation of cesium content (x=2.0, 2.5, and 3.0) for use as an additive for $ZnFe_2O_4$ catalyst. Known amount of cesium nitrate ($CsNO_3$, Sigma-Aldrich) was dissolved in distilled water. The solution was added dropwise into an aqueous solution containing $H_3PW_{12}O_{40}$ with constant stirring. The resulting solution was then slowly heated at 60 °C for 12 h to obtain a solid. The solid product was dried overnight at 70 °C, and finally, it was calcined at 300 °C for 2 h to yield the $Cs_xH_{3-x}PW_{12}O_{40}$ (x=2.0, 2.5, and 3.0).

Mechanical mixtures of $ZnFe_2O_4$ and $Cs_xH_{3-x}PW_{12}O_{40}$ were prepared for use as a catalyst by mixing two powders with physical shaking. Composition of the mixed catalysts was expressed as follows. All the mixed catalysts used in this work were prepared on the basis of identical amount of $ZnFe_2O_4$ catalyst.

$$R_m = \frac{\text{weight of } Cs_xH_{3-x}PW_{12}O_{40}}{\text{weight of } ZnFe_2O_4 + \text{weight of } Cs_xH_{3-x}PW_{12}O_{40}} \qquad (1)$$

2. Characterization

Formation of $ZnFe_2O_4$ catalyst was confirmed by XRD (MAC Science, M18XHF-SRA) measurement. Atomic ratio of constituent metal components of $ZnFe_2O_4$ was determined by ICP-AES (Shimadz, ICP-1000IV) analysis. Surface area of $ZnFe_2O_4$ and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ catalysts was measured with a BET apparatus (Micromeritics, ASAP 2010). Acid properties of $ZnFe_2O_4$, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, and $ZnFe_2O_4$-$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ mixed catalyst were measured by NH_3-TPD experiments. Each catalyst (0.3 g for $ZnFe_2O_4$, 0.03 g for $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, and 0.33 g for $ZnFe_2O_4$-$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ mixed catalyst) was charged into a tubular quartz reactor of the conventional TPD apparatus. The catalyst was pretreated at 200 °C for 1 h under a flow of helium (20 ml/min) to remove any physisorbed organic molecules. 20 ml of NH_3 was then pulsed into the reactor every minute at room temperature under a flow of helium (5 ml/min), until the acid sites were saturated with NH_3. The physisorbed NH_3 was removed by evacuating the catalyst sample at 50 °C for 1 h. Furnace temperature was increased from room temperature to 600 °C at a heating rate of 5 °C/min under a flow of helium (10 ml/min). The desorbed NH_3 was detected with a GC-MSD (Agilent, MSD-6890N GC).

3. Oxidative Dehydrogenation of n-Butene

Oxidative dehydrogenation of n-butene to 1,3-butadiene over $ZnFe_2O_4$, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, and $ZnFe_2O_4$-$Cs_xH_{3-x}PW_{12}O_{40}$ mixed catalysts was carried out in a continuous flow fixed-bed reactor in the presence of air and steam. Prior to the catalytic reaction, the catalyst was pretreated at either 470 °C or 430 °C for 1 h with an air stream. 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. Feed composition was fixed at n-butene : oxygen : steam=1 : 0.75 : 15. Water was sufficiently vaporized by passing through a pre-heating zone and was continuously fed into the reactor together with n-butene and air. GHSV (gas hourly space velocity) was modulated on the basis of feed rate of n-butene and total volume of mixed catalyst. The catalytic reaction was performed at 420 °C. Reaction products were periodically sampled and analyzed with gas chromatographs. A Varian CP-3380 gas chromatograph equipped with a 50 m GS-alumina column and a flame ionization detector was employed for analyzing hydrocarbons; and a Younglin ACME 6000 gas chromatograph equipped with a 1.8 m Porapak Q column and a thermal conductivity detector was used for analysis of CO and CO_2. 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.

$$\text{Conversion of n-butene} = \frac{\text{moles of n-butene reacted}}{\text{moles of n-butene supplied}} \qquad (2)$$

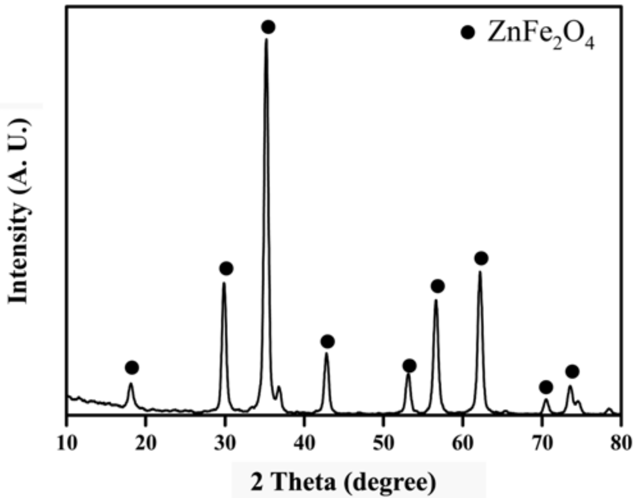

Fig. 2. XRD pattern of $ZnFe_2O_4$ catalyst.

Table 1. Atomic ratio of Fe/Zn and BET surface area of $ZnFe_2O_4$ catalyst

Catalyst	Atomic ratio of Fe/Zn	BET surface area (m^2/g)
$ZnFe_2O_4$	2.04	30.1

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

RESULTS AND DISCUSSION

1. Formation of $ZnFe_2O_4$ Catalyst

Fig. 2 shows the XRD pattern of $ZnFe_2O_4$ catalyst. Spinel phase of $ZnFe_2O_4$ could be identified by its characteristic diffraction peaks using JCPDS, indicating the successful formation of $ZnFe_2O_4$ catalyst. Atomic ratio of Fe/Zn and surface area of $ZnFe_2O_4$ catalyst are listed in Table 1. Atomic ratio of Fe/Zn was found to be 2.04, in good agreement with the theoretical value of 2.0. Together with the XRD result (Fig. 2), this result also supports that $ZnFe_2O_4$ catalyst was successfully prepared. BET surface area of $ZnFe_2O_4$ catalyst was ca. 30 m^2/g.

2. Effect of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ Addition

The effect of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ addition on the catalytic performance of $ZnFe_2O_4$ in the oxidative dehydrogenation of n-butene was investigated. For this purpose, a catalytic reaction was carried out over $ZnFe_2O_4$-$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ mixed catalyst. The catalytic reaction was also done over $ZnFe_2O_4$ catalyst mixed with inert quartz for reference (volume of quartz was identical to that of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$). Fig. 3 shows the steady-state catalytic performance of $ZnFe_2O_4$-quartz mixed catalyst and $ZnFe_2O_4$-$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ mixed catalyst in the oxidative dehydrogenation of n-butene at 420 °C after a 6 h-reaction (R_m=0.3, GHSV=340 h^{-1}). In the catalytic reaction, CO_2 was mainly produced as a by-product and CO formation was negligible. Conversion of n-butene and yield for 1,3-butadiene over $ZnFe_2O_4$-$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ mixed catalyst were higher than those over $ZnFe_2O_4$-quartz mixed catalyst. This result indicates that $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ favorably served as an additive for $ZnFe_2O_4$ catalyst in the oxidative dehydrogenation of n-butene.

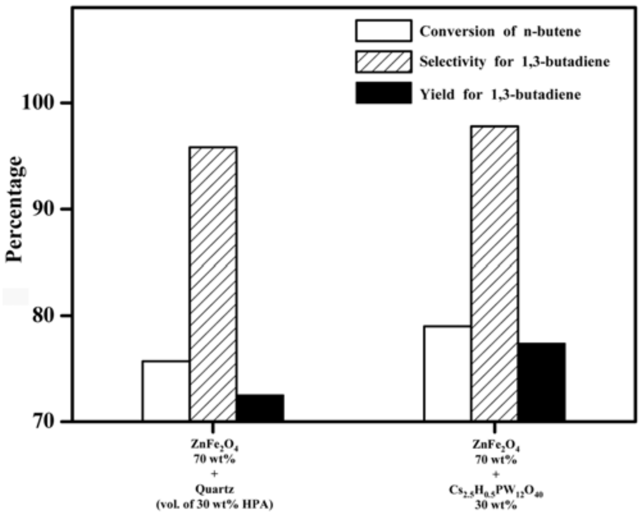

Fig. 3. Steady-state catalytic performance of $ZnFe_2O_4$-quartz mixed catalyst and $ZnFe_2O_4$-$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ mixed catalyst in the oxidative dehydrogenation of n-butene at 420 °C after a 6 h-reaction (R_m=0.3, GHSV=340 h^{-1}): pretreatment temperature=430 °C.

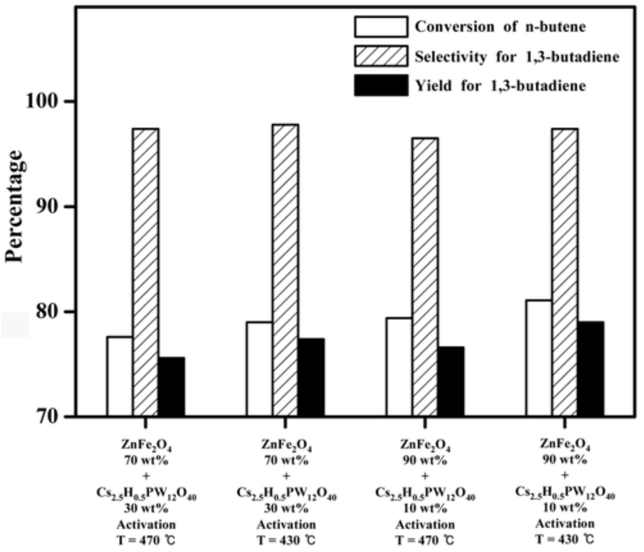

Fig. 4. Steady-state catalytic performance of $ZnFe_2O_4$-$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ mixed catalysts in the oxidative dehydrogenation of n-butene at 420 °C after a 6 h-reaction (GHSV=340 h^{-1} for R_m=0.3 and GHSV=430 h^{-1} for R_m=0.1). The mixed catalysts were pretreated at either 430 °C or 470 °C.

3. Effect of Pretreatment Temperature

The effect of pretreatment temperature of $ZnFe_2O_4$-$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ mixed catalysts on the catalytic performance in the oxidative dehydrogenation of n-butene was investigated. Fig. 4 shows the steady-state catalytic performance of $ZnFe_2O_4$-$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ mixed catalysts in the oxidative dehydrogenation of n-butene at 420 °C after a 6 h-reaction. GHSV was fixed at 340 h^{-1} for R_m=0.3 and 430 h^{-1} for R_m=0.1. Conversion of n-butene and yield for 1,3-butadiene obtained after the treatment of 430 °C were higher than those obtained after the treatment of 470 °C. At the same pretreatment temperature, on the other hand, the catalyst with R_m=0.1 showed a better performance than that with R_m=0.3. This result indicates that the addition of excess amount of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ is not always favorable for the oxidative dehydrogenation of n-butene due to the enhanced inert nature of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ component.

The high catalytic performance of $ZnFe_2O_4$-$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ mixed catalyst after the treatment at 430 °C can be explained by the thermal behavior of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$. It is well known that HPAs have excellent thermal stability at temperature below 450 °C [24,25]. However, HPAs are thermally unstable and start to decompose at 450-500 °C. Therefore, it is believed that the suppressed catalytic performance of $ZnFe_2O_4$-$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ after the treatment at 470 °C was attributed to the thermal instability of HPA component.

4. Effect of Cesium Content and Surface Acidity

Fig. 5 shows the NH_3-TPD profiles of $ZnFe_2O_4$, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, and $ZnFe_2O_4$-$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ mixed catalyst. $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ showed a broad NH_3-TPD profile with peak maximum at 390 °C. $ZnFe_2O_4$ catalyst showed a NH_3-TPD profile with peak maximum at 185 °C. On the other hand, $ZnFe_2O_4$-$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ mixed catalyst showed a major TPD peak at 185 °C and a shoulder at around 390 °C. The above results clearly showed that $ZnFe_2O_4$ and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ retained significantly different acid strength. It was found that $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ retained stronger acid strength than $ZnFe_2O_4$.

To elucidate the effect of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ addition in the oxidative dehydrogenation of n-butene, the catalytic reaction was performed over pure $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ catalyst. The catalytic performance of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ is summarized in Table 2. Conversion of n-butene over $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was found to be low (27.0%). On the other hand, selectivity for 1,3-butadiene (19.6%) was much lower than that for butene isomers (79.4%). The weight fraction of trans-2-butene in C_4 raffinate-3 was observed to decrease (33.9 wt%→26.0 wt%) after the catalytic reaction, while that of the others was slightly increased (cis-2-butene: 16.5 wt%→17.9 wt%, 1-butene: 7.5 wt%→12.9 wt%). This result indicates that a double-bond isomerization reaction rather than dehydrogenation reaction of n-butene favorably occurred in the catalytic reaction over $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ catalyst. It has been reported that the most likely mechanism for the double-bond isomerization of n-butene also involves the adsorption of n-butene and the subsequent abstraction of hydrogen to form π-allyl intermediate [31,32]. Therefore, it can be inferred that $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ played an important role in adsorbing and activating n-butene to form π-allyl intermediate, although $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ itself did not efficiently catalyze the subsequent reactions to produce 1,3-butadiene from π-allyl intermediate. Surface area and surface acidity of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ catalyst determined by BET and NH_3-TPD measurements were 103.8 m^2/g and 0.105 $\mu mol/m^2$, respectively, in good agreement with the previous results [25]. Therefore, it is believed that strong acid strength (Fig. 5) and large surface acidity of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ catalyst may be responsible for its high capability in adsorbing and activating n-butene. As mentioned earlier, it has been reported that sufficient acid sites of $ZnFe_2O_4$ catalyst are required to adsorb and activate n-butene (a base molecule) [18,20, 21]. This implies that the catalytic performance of $ZnFe_2O_4$ would be improved, if $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ efficient for adsorbing and activating n-butene is used as an additive for $ZnFe_2O_4$ catalyst. This was well evidenced by the catalytic performance of $ZnFe_2O_4$-$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ mixed catalysts (Fig. 3 and Fig. 4).

The effect of cesium content on the catalytic performance of Zn

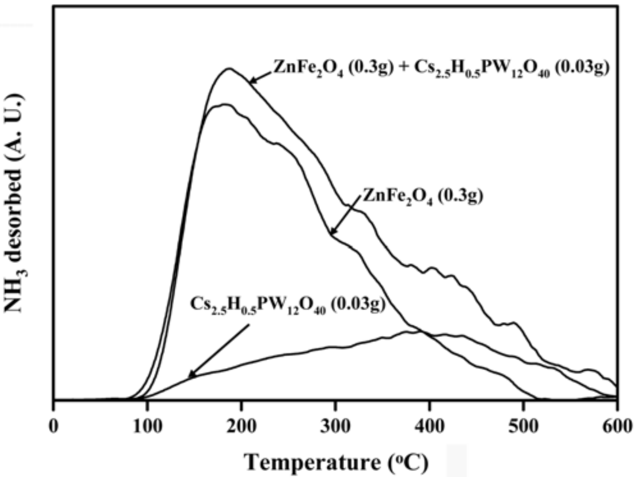

Fig. 5. NH_3-TPD profiles of $ZnFe_2O_4$, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, $ZnFe_2O_4$-$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ mixed catalyst.

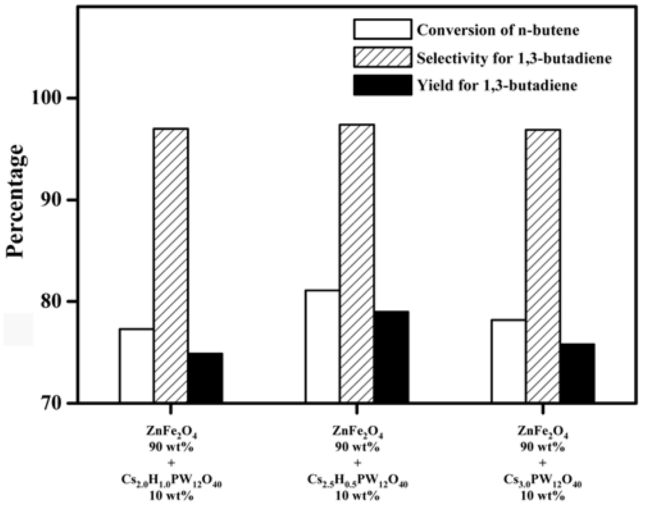

Fig. 6. Steady-state catalytic performance of $ZnFe_2O_4$-$Cs_xH_{3-x}PW_{12}O_{40}$ mixed catalysts in the oxidative dehydrogenation of n-butene at 420 °C after a 6 h-reaction (R_m=0.1, GHSV=430 h^{-1}): pretreatment temperature=430 °C.

Table 2. Catalytic performance of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ in the oxidative dehydrogenation of n-butene at 420 °C after a 6 h-reaction (GHSV=475 h^{-1})

Catalyst	Conversion of n-butene (%)	Selectivity (%)			Yield for 1,3-butadiene (%)
		1,3-Butadiene	CO_2	Others	
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	27.0	19.6	1.0	79.4	5.3

Fe_2O_4-$Cs_xH_{3-x}PW_{12}O_{40}$ mixed catalysts in the oxidative dehydrogenation of n-butene was also investigated. Fig. 6 shows the steady-state catalytic performance of $ZnFe_2O_4$-$Cs_xH_{3-x}PW_{12}O_{40}$ mixed catalysts in the oxidative dehydrogenation of n-butene at 420 °C after a 6 h-reaction (R_m=0.1, GHSV=430 h^{-1}). Conversion of n-butene and yield for 1,3-butadiene increased in the order of $ZnFe_2O_4$-$Cs_{2.0}H_{1.0}PW_{12}O_{40}$<$ZnFe_2O_4$-$Cs_{3.0}PW_{12}O_{40}$<$ZnFe_2O_4$-$Cs_{2.5}H_{0.5}PW_{12}O_{40}$. Among the catalysts tested, $ZnFe_2O_4$-$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ mixed catalyst showed the best catalytic performance. Yield for 1,3-butadiene over $ZnFe_2O_4$-$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ mixed catalyst was found to be 79.1%.

It has been reported that surface area and surface acidity of $Cs_xH_{3-x}PW_{12}O_{40}$ significantly vary at cesium content of 2.0-3.0 [25,26,33]. Surface area of $Cs_xH_{3-x}PW_{12}O_{40}$ drastically increases with increasing cesium content from 2.0 to 3.0, while surface acidity of $Cs_xH_{3-x}PW_{12}O_{40}$ shows a volcano-shaped curve with respect to cesium content [25,26,32]. Among $Cs_xH_{3-x}PW_{12}O_{40}$ catalysts, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ is known to have the largest surface acidity [25,26,32]. Therefore, the highest catalytic performance of $ZnFe_2O_4$-$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ mixed catalyst was attributed to the strong acid strength (Fig. 5) and large surface acidity of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$. Thus, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ could be utilized as an efficient promoter and diluent in formulating $ZnFe_2O_4$ catalyst for the oxidative dehydrogenation of n-butene.

CONCLUSIONS

$Cs_xH_{3-x}PW_{12}O_{40}$ HPAs were prepared with a variation of cesium content (x=2.0, 2.5, and 3.0) for use as an additive for $ZnFe_2O_4$ catalyst, and $ZnFe_2O_4$ was prepared by a co-precipitation method for use as an active catalyst component. $ZnFe_2O_4$-$Cs_xH_{3-x}PW_{12}O_{40}$ mixed catalysts were then applied to the oxidative dehydrogenation of n-butene to 1,3-butadiene. The effect of $Cs_xH_{3-x}PW_{12}O_{40}$ addition on the catalytic performance of $ZnFe_2O_4$ catalyst was investigated. Although $Cs_xH_{3-x}PW_{12}O_{40}$ itself showed very low catalytic performance in the oxidative dehydrogenation of n-butene, it was revealed that the addition of small amount of $Cs_xH_{3-x}PW_{12}O_{40}$ into $ZnFe_2O_4$ enhanced the catalytic performance of $ZnFe_2O_4$ catalyst. The catalytic performance of $ZnFe_2O_4$-$Cs_xH_{3-x}PW_{12}O_{40}$ mixed catalysts was closely related to the surface acidity of $Cs_xH_{3-x}PW_{12}O_{40}$. Among $ZnFe_2O_4$-$Cs_xH_{3-x}PW_{12}O_{40}$ mixed catalysts, $ZnFe_2O_4$-$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ mixed catalyst showed the best catalytic performance due to the strong acid strength and large surface acidity of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$. It is concluded that $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ could be utilized as an efficient promoter and diluent in formulating $ZnFe_2O_4$ catalyst for the oxidative dehydrogenation of n-butene.

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REFERENCES

1. B. J. Liaw, D. S. Cheng and B. L. Yang, *J. Catal.*, **118**, 312 (1989).
2. F. Hong, B. L. Yang, L. H. Schwartz and H. H. Kung, *J. Phys. Chem.*, **88**, 2525 (1984).
3. J. C. Jung, H. Lee, S. Park, Y.-M. Chung, T. J. Kim, S. J. Lee, S.-H. Oh, Y. S. Kim and I. K. Song, *Korean J. Chem. Eng.*, **25**, 1316 (2008).
4. R. J. Rennard, Jr., R. A. Innes and H. E. Swift, *J. Catal.*, **30**, 128 (1973).
5. H. Lee, J. C. Jung, H. Kim, Y.-M. Chung, T. J. Kim, S. J. Lee, S.-H. Oh, Y. S. Kim and I. K. Song, *Catal. Commun.*, **9**, 1137 (2008).
6. H. Lee, J. C. Jung, H. Kim, Y.-M. Chung, T. J. Kim, S. J. Lee, S.-H. Oh, Y. S. Kim and I. K. Song, *Catal. Lett.*, **122**, 281 (2008).
7. M. A. Gibson and J. W. Hightower, *J. Catal.*, **41**, 431 (1976).
8. W. R. Cares and J. W. Hightower, *J. Catal.*, **23**, 193 (1971).
9. P. N. Tiwari, T. G. Alkhazov, K. U. Adzamov and A. K. Khanmamedova, *J. Catal.*, **120**, 278 (1989).
10. J. A. Toledo-Antonio, N. Nava, M. Matínez and X. Bokhimi, *Appl. Catal. A*, **234**, 137 (2002).
11. J. C. Jung, H. Lee, H. Kim, Y.-M. Chung, T. J. Kim, S. J. Lee, S.-H. Oh, Y. S. Kim and I. K. Song, *Catal. Commun.*, **9**, 447 (2008).
12. J. C. Jung, H. Lee, H. Kim, Y.-M. Chung, T. J. Kim, S. J. Lee, S.-H. Oh, Y. S. Kim and I. K. Song, *J. Mol. Catal. A*, **271**, 261 (2007).
13. J. C. Jung, H. Kim, Y. S. Kim, Y.-M. Chung, T. J. Kim, S. J. Lee, S.-H. Oh and I. K. Song, *Appl. Catal. A*, **317**, 244 (2007).
14. H. Lee, J. C. Jung, H. Kim, Y.-M. Chung, T. J. Kim, S. J. Lee, S.-H. Oh, Y. S. Kim and I. K. Song, *Catal. Lett.*, **124**, 364 (2008).
15. H. H. Kung, B. Kundalkar, M. C. Kung and W. H. Cheng, *J. Phys. Chem.*, **84**, 382 (1980).
16. M. Zhang, R. Lan, J. Liu, X. Chen and W. Zhou, *J. Chem. Soc. Farady Trans.*, **99**, 637 (1992).
17. W. Q. Xu, Y.-G. Yin, G.-Y. Li and S. Chen, *Appl. Catal. A*, **89**, 117 (1992).
18. H. H. Kung and M. C. Kung, *Adv. Catal.*, **33**, 159 (1985).
19. W. Q. Xu, Y.-G. Yin, G.-Y. Li and S. Chen, *Appl. Catal. A*, **89**, 131 (1992).
20. C. F. Cullis and D. J. Hucknall, *A specialist periodical report: catalysis*, Royal Chem. Soc., London (1982).
21. R. K. Grasselli and J. D. Burrington, *Adv. Catal.*, **30**, 133 (1981).
22. K. W. La, H. Kim, J. C. Jung, J. Lee, D. R. Park, S. H. Lee and I. K. Song, *Korean J. Chem. Eng.*, **25**, 710 (2008).
23. H. Kim, J. C. Jung, D. R. Park, J. Lee, K. M. Cho, S. Park, S. H. Lee and I. K. Song, *Korean J. Chem. Eng.*, **25**, 231 (2008).
24. M. Misono, *Catal. Rev. -Sci. Eng.*, **29**, 269 (1987).
25. T. Okuhara, N. Mizuno and M. Misono, *Adv. Catal.*, **41**, 113 (1996).
26. S. Park, S. H. Lee, S. H. Song, D. R. Park, S.-H. Baeck, T. J. Kim, Y.-M. Chung, S.-H. Oh and I. K. Song, *Catal. Comm.*, **10**, 391 (2009).
27. I. V. Kozhevnikov, *Chem. Rev.*, **98**, 171 (1998).
28. D. R. Park, J. H. Song, S. H. Lee, S. H. Song, H. Kim, J. C. Jung and I. K. Song, *Appl. Catal. A*, **349**, 222 (2008).
29. D. R. Park, S. H. Lee, J. Lee, S. H. Song, H. Kim, J. H. Song and I. K. Song, *Catal. Lett.*, **126**, 308 (2008).
30. M. T. Pope, *Heteropoly and isopoly oxometalates*, Springer, New York (1983).
31. R. J. Rennard and W. L. Kehl, *J. Catal.*, **21**, 282 (1971).
32. F. E. Massoth and D. A. Scarpiello, *J. Catal.*, **21**, 294 (1971).
33. T. Okuhara, T. Nishimura and M. Misono, *Chem. Lett.*, 155 (1995).