Effect of Cs$_{x}$H$_{3-x}$PW$_{12}$O$_{40}$ addition on the catalytic performance of ZnFe$_2$O$_4$ in the oxidative dehydrogenation of n-butene to 1,3-butadiene


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(Received 20 December 2008 • accepted 21 January 2009)

Abstract—Oxidative dehydrogenation of n-butene to 1,3-butadiene over ZnFe$_2$O$_4$ catalyst mixed with Cs$_{x}$H$_{3-x}$PW$_{12}$O$_{40}$ heteropolyacid (HPA) was performed in a continuous flow fixed-bed reactor. The effect of Cs$_{x}$H$_{3-x}$PW$_{12}$O$_{40}$ addition on the catalytic performance of ZnFe$_2$O$_4$ was investigated. Cs$_{x}$H$_{3-x}$PW$_{12}$O$_{40}$ itself showed very low catalytic performance in the oxidative dehydrogenation of n-butene. However, addition of small amount of Cs$_{x}$H$_{3-x}$PW$_{12}$O$_{40}$ into ZnFe$_2$O$_4$ enhanced the catalytic performance of ZnFe$_2$O$_4$ catalyst. The catalytic performance of ZnFe$_2$O$_4$-Cs$_{x}$H$_{3-x}$PW$_{12}$O$_{40}$ mixed catalysts was closely related to the surface acidity of Cs$_{x}$H$_{3-x}$PW$_{12}$O$_{40}$. Among the catalysts tested, ZnFe$_2$O$_4$-Cs$_{2}$H$_{5}$PW$_{12}$O$_{40}$ mixed catalyst showed the best catalytic performance. Strong acid strength and large surface acidity of Cs$_{2.5}$H$_{5}$PW$_{12}$O$_{40}$ was responsible for high catalytic performance of ZnFe$_2$O$_4$-Cs$_{2.5}$H$_{5}$PW$_{12}$O$_{40}$ mixed catalyst. Thus, Cs$_{2.5}$H$_{5}$PW$_{12}$O$_{40}$ could be utilized as an efficient promoter and diluent in formulating ZnFe$_2$O$_4$ 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$_2$O$_4$ 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$_2$O$_4$ has high density of selective oxidation sites and low density of combustion sites [15,18], leading to a high catalytic performance of ZnFe$_2$O$_4$ in the oxidative dehydrogenation of n-butene.

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$_2$O$_4$ 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$_2$O$_4$ catalyst would be enhanced, if acid property of ZnFe$_2$O$_4$ is promoted by the addition of another component.

A suitable diluent is required to formulate ZnFe$_2$O$_4$ catalyst for industrial application. However, not much progress has been made on the investigation of diluent for formulating ZnFe$_2$O$_4$ catalyst. Therefore, developing an efficient diluent for formulating ZnFe$_2$O$_4$ catalyst would be of great interest. Furthermore, it would be much better if a diluent can also serve as an efficient promoter for ZnFe$_2$O$_4$ 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
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 m²/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, Cs₂.₅H₀.₅PW₁₂O₄₀ is known to have the largest surface acidity [25].

In this work, cesium-exchanged HPAs (CsₓH₃₋ₓPW₁₂O₄₀) were prepared with a variation of cesium content (x=2.0, 2.5, and 3.0) for use as an additive for ZnFe₂O₄ catalyst, with an aim of taking advantage of high surface area and large surface acidity of CsₓH₃₋ₓPW₁₂O₄₀. ZnFe₂O₄ catalyst was independently prepared by a co-precipitation method for use as an active catalyst component. ZnFe₂O₄ catalyst mixed with CsₓH₃₋ₓPW₁₂O₄₀ was then applied to the oxidative dehydrogenation of n-butene to investigate the effect of CsₓH₃₋ₓPW₁₂O₄₀ addition on the catalytic performance of ZnFe₂O₄. ZnFe₂O₄ catalyst was characterized by XRD, BET, TPD, and ICP-AES measurements.

**EXPERIMENTAL**

1. **Catalyst Preparation**

   ZnFe₂O₄ catalyst was prepared by a co-precipitation method. 1.4 g of zinc chloride (ZnCl₂, Sigma-Aldrich) and 5.6 g of iron chloride (FeCl₃·6H₂O, 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 ZnFe₂O₄ catalyst.

   Commercially available H₃PW₁₂O₄₀ 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 (CsₓH₃₋ₓPW₁₂O₄₀) 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 ZnFe₂O₄ catalyst. Known amount of cesium nitrate (CsNO₃, Sigma-Aldrich) was dissolved in distilled water. The solution was added dropwise into an aqueous solution containing H₃PW₁₂O₄₀ 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 CsₓH₃₋ₓPW₁₂O₄₀ (x=2.0, 2.5, and 3.0).

   Mechanical mixtures of ZnFe₂O₄ and CsₓH₃₋ₓPW₁₂O₄₀ 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 ZnFe₂O₄ catalyst.

   \[ R_s = \frac{\text{weight of CsₓH₃₋ₓPW₁₂O₄₀}}{\text{weight of ZnFe₂O₄} + \text{weight of CsₓH₃₋ₓPW₁₂O₄₀}} \]  (1)

   **2. Characterization**

   Formation of ZnFe₂O₄ catalyst was confirmed by XRD (MAC Science, M18XHF-SRA) measurement. Atomic ratio of constituent metal components of ZnFe₂O₄ was determined by ICP-AES (Shimadzu, ICP-1000IV) analysis. Surface area of ZnFe₂O₄ and CsₓH₃₋ₓPW₁₂O₄₀ catalysts was measured with a BET apparatus (Micromeritics, ASAP 2010). Acid properties of ZnFe₂O₄, CsₓH₃₋ₓPW₁₂O₄₀, and ZnFe₂O₄-CsₓH₃₋ₓPW₁₂O₄₀ mixed catalyst were measured by NH₃-TPD experiments. Each catalyst (0.3 g for ZnFe₂O₄, 0.03 g for CsₓH₃₋ₓPW₁₂O₄₀, and 0.33 g for ZnFe₂O₄-CsₓH₃₋ₓPW₁₂O₄₀ 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 NH₃ 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 NH₃. The physisorbed NH₃ 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 NH₃ 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 ZnFe₂O₄, CsₓH₃₋ₓPW₁₂O₄₀, and ZnFe₂O₄-CsₓH₃₋ₓPW₁₂O₄₀ 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. C₄ raffinate-3 containing 57.9 wt% n-butene (data 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). C₄ 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 Youllgin 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 CO₂. 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.

\[ \text{Conversion of n-butene} = \frac{\text{moles of n-butene reacted}}{\text{moles of n-butene supplied}} \]  (2)
RESULTS AND DISCUSSION

1. Formation of ZnFe₂O₄ Catalyst

Fig. 2 shows the XRD pattern of ZnFe₂O₄ catalyst. Spinel phase of ZnFe₂O₄ could be identified by its characteristic diffraction peaks using JCPS, indicating the successful formation of ZnFe₂O₄ catalyst. Atomic ratio of Fe/Zn and BET surface area of ZnFe₂O₄ 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 ZnFe₂O₄ catalyst was successfully prepared. BET surface area of ZnFe₂O₄ catalyst was ca. 30 m²/g.

2. Effect of Cs₂.₅H₀.₅PW₁₂O₄₀ Addition

The effect of Cs₂.₅H₀.₅PW₁₂O₄₀ addition on the catalytic performance of ZnFe₂O₄ in the oxidative dehydrogenation of n-butene was investigated. For this purpose, a catalytic reaction was carried out over ZnFe₂O₄-Cs₂.₅H₀.₅PW₁₂O₄₀ mixed catalyst. The catalytic reaction was also done over ZnFe₂O₄ catalyst mixed with inert quartz for reference (volume of quartz was identical to that of Cs₂.₅H₀.₅PW₁₂O₄₀). Fig. 3 shows the steady-state catalytic performance of ZnFe₂O₄-Cs₂.₅H₀.₅PW₁₂O₄₀ mixed catalysts in the oxidative dehydrogenation of n-butene at 420 °C after a 6 h-reaction (Rm=0.3, GHSV=340 h⁻¹); pretreatment temperature=430 °C.

3. Effect of Pretreatment Temperature

The effect of pretreatment temperature of ZnFe₂O₄-Cs₂.₅H₀.₅PW₁₂O₄₀ mixed catalysts on the catalytic performance in the oxidative dehydrogenation of n-butene was investigated. Fig. 4 shows the steady-state catalytic performance of ZnFe₂O₄-Cs₂.₅H₀.₅PW₁₂O₄₀ mixed catalysts in the oxidative dehydrogenation of n-butene at 420 °C after a 6 h-reaction (Rm=0.3 and GHSV=340 h⁻¹ for Rm=0.3 and GHSV=430 h⁻¹ for Rm=0.1). The mixed catalysts were pretreated at either 430 °C or 470 °C.

Selectivity for 1,3-butadiene = moles of 1,3-butadiene formed moles of n-butene reacted

Fig. 2. XRD pattern of ZnFe₂O₄ catalyst.

Table 1. Atomic ratio of Fe/Zn and BET surface area of ZnFe₂O₄ catalyst

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Atomic ratio of Fe/Zn</th>
<th>BET surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnFe₂O₄</td>
<td>2.04</td>
<td>30.1</td>
</tr>
</tbody>
</table>

Fig. 3. Steady-state catalytic performance of ZnFe₂O₄-quartz mixed catalyst and ZnFe₂O₄-Cs₂.₅H₀.₅PW₁₂O₄₀ mixed catalyst in the oxidative dehydrogenation of n-butene at 420 °C after a 6 h-reaction (Rm=0.3, GHSV=340 h⁻¹); pretreatment temperature=430 °C.

Fig. 4. Steady-state catalytic performance of ZnFe₂O₄-Cs₂.₅H₀.₅PW₁₂O₄₀ mixed catalysts in the oxidative dehydrogenation of n-butene at 420 °C after a 6 h-reaction (GHSV=340 h⁻¹ for Rm=0.3 and GHSV=430 h⁻¹ for Rm=0.1). The mixed catalysts were pretreated at either 430 °C or 470 °C.
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\(_2\)O\(_4\)-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\(_2\)O\(_4\)-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\(_2\)O\(_4\), Cs\(_{2.5}\)H\(_{0.5}\)PW\(_{12}\)O\(_{40}\), and ZnFe\(_2\)O\(_4\)-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\(_2\)O\(_4\) catalyst showed a NH\(_3\)-TPD profile with peak maximum at 185 °C. On the other hand, ZnFe\(_2\)O\(_4\)-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\(_2\)O\(_4\) 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\(_2\)O\(_4\).

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 \( \pi \)-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 \( \pi \)-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 \( \pi \)-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\(_2\)O\(_4\) catalyst are required to adsorb and activate n-butene (a base molecule) [18,20, 21]. This implies that the catalytic performance of ZnFe\(_2\)O\(_4\) 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\(_2\)O\(_4\) catalyst. This was well evidenced by the catalytic performance of ZnFe\(_2\)O\(_4\)-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...
Fe₃O₄-CsₓHₓ₋ₓPW₁₂O₄₀ mixed catalysts in the oxidative dehydrogenation of n-butenes was also investigated. Fig. 6 shows the steady-state catalytic performance of ZnFe₂O₄-CsₓHₓ₋ₓPW₁₂O₄₀ mixed catalysts in the oxidative dehydrogenation of n-butenes at 420 °C after a 6-h reaction (R = 0.1, GHSV = 430 h⁻¹). Conversion of n-butenes and yield for 1,3-butadiene increased in the order of ZnFe₂O₄-CsₓHₓ₋ₓPW₁₂O₄₀<ZnFe₂O₄-CsₓHₓ₋ₓPW₁₂O₄₀<ZnFe₂O₄CsₓHₓ₋ₓPW₁₂O₄₀. Among the catalysts tested, ZnFe₂O₄-CsₓHₓ₋ₓPW₁₂O₄₀ mixed catalyst showed the best catalytic performance. Yield for 1,3-butadiene over ZnFe₂O₄-CsₓHₓ₋ₓPW₁₂O₄₀ mixed catalyst was found to be 79.1%.

It has been reported that surface area and surface acidity of CsₓHₓ₋ₓPW₁₂O₄₀ significantly vary at cesium content of 2.0-3.0 [25,26,32]. Surface area of CsₓHₓ₋ₓPW₁₂O₄₀ drastically increases with increasing cesium content from 2.0 to 3.0, while surface acidity of CsₓHₓ₋ₓPW₁₂O₄₀ shows a volcano-shaped curve with respect to cesium content [25,26,32]. Among CsₓHₓ₋ₓPW₁₂O₄₀ catalysts, Cs₂.₅H₀.₅PW₁₂O₄₀ is known to have the largest surface acidity [25,26,32]. Therefore, the highest catalytic performance of ZnFe₂O₄-CsₓHₓ₋ₓPW₁₂O₄₀ was observed when Cs content (x=2.0, 2.5, and 3.0) for use as an additive for ZnFe₂O₄ catalyst. The catalytic performance of ZnFe₂O₄ catalyst was enhanced by formulating ZnFe₂O₄ catalyst for the oxidative dehydrogenation of n-butene at 420 °C after 6 h reaction (R = 0.1, GHSV = 430 h⁻¹).

**CONCLUSIONS**

CsₓHₓ₋ₓPW₁₂O₄₀ HPAs were prepared with a variation of cesium content (x = 2.0, 2.5, and 3.0) for use as an additive for ZnFe₂O₄ catalyst, and ZnFe₂O₄ was prepared by a co-precipitation method for use as an active catalyst component. ZnFe₂O₄-CsxHₓ₋ₓPW₁₂O₄₀ mixed catalysts were then applied to the oxidative dehydrogenation of n-butenes to 1,3-butadiene. The effect of CsₓHₓ₋ₓPW₁₂O₄₀ addition on the catalytic performance of ZnFe₂O₄ catalyst was investigated. Although CsₓHₓ₋ₓPW₁₂O₄₀ itself showed very low catalytic performance in the oxidative dehydrogenation of n-butenes, it was revealed that the addition of small amount of CsₓHₓ₋ₓPW₁₂O₄₀ into ZnFe₂O₄ enhanced the catalytic performance of ZnFe₂O₄ catalyst. The catalytic performance of ZnFe₂O₄-CsₓHₓ₋ₓPW₁₂O₄₀ mixed catalysts was closely related to the surface acidity of CsₓHₓ₋ₓPW₁₂O₄₀. Among ZnFe₂O₄-CsₓHₓ₋ₓPW₁₂O₄₀ mixed catalysts, ZnFe₂O₄-CsₓHₓ₋ₓPW₁₂O₄₀ mixed catalyst showed the best catalytic performance due to the strong acid strength and large surface acidity of CsₓHₓ₋ₓPW₁₂O₄₀. It is concluded that Cs₂.₅H₀.₅PW₁₂O₄₀ could be utilized as an efficient promoter and diluent in formulating ZnFe₂O₄ catalyst for the oxidative dehydrogenation of n-butenes.

**ACKNOWLEDGMENTS**

The authors wish to acknowledge support from the SK Energy Corporation (POST-BK21 Program).

**REFERENCES**


July, 2009