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Preparation of $ZnFe_2O_4$ Catalysts by a Co-precipitation Method Using Aqueous Buffer Solution and Their Catalytic Activity for Oxidative Dehydrogenation of *n*-Butene to 1,3-Butadiene

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Abstract Zinc ferrite ($ZnFe_2O_4$) catalysts were prepared by a co-precipitation method using aqueous buffer solution with different pH ($pH = 6-12$), and applied to the oxidative dehydrogenation of *n*-butene to 1,3-butadiene. Conversion of *n*-butene and yield for 1,3-butadiene showed volcano-shaped curves with respect to pH value employed during the co-precipitation step. NH_3-TPD experiments were conducted to correlate the acid property with the catalytic performance of zinc ferrite catalysts. It was revealed that the catalytic performance of zinc ferrite catalysts in the oxidative dehydrogenation of *n*-butene was closely related to the surface acidity of the catalysts. Conversion of *n*-butene and yield for 1,3-butadiene increased with increasing surface acidity of the catalysts. Among the catalysts tested, the zinc ferrite catalyst prepared at $pH = 8$ showed the best catalytic performance in the oxidative dehydrogenation of *n*-butene, which was attributed to its largest surface acidity.

Keywords Zinc ferrite · *n*-Butene ·
Oxidative dehydrogenation · Buffer solution ·
Surface acidity

1 Introduction

Selective oxidation of hydrocarbons has been considered to be an important subject for the production of various chemical intermediates in the petrochemical industries [1, 2]. In particular, oxidative dehydrogenation of *n*-butene has attracted much attention as a promising process for producing 1,3-butadiene, an important raw material for manufacturing various chemical products [1, 3–5]. A number of catalysts have been employed for the oxidative dehydrogenation of *n*-butene, including bismuth molybdate catalyst [5, 6], vanadium-containing catalyst [7], Cu-Mo catalyst [8], and ferrite-type catalyst [9–11]. Among these catalysts, zinc ferrite has been widely investigated as an efficient catalyst for this reaction [12, 13].

It is well known that the oxidative dehydrogenation of *n*-butene over zinc ferrite catalyst is affected by various catalytic properties. However, many researchers agree that acid property of the catalyst is one of the crucial factors determining the catalytic performance in the oxidative dehydrogenation of *n*-butene [14–17], because the reaction follows the reaction mechanism by way of π-allyl intermediate [11, 14, 18, 19]. It is generally accepted that the initial hydrogen abstraction step from *n*-butene to form π-allyl intermediate is the rate-determining step in the oxidative dehydrogenation of *n*-butene. It has also been reported that acid property of the catalyst plays a key role in abstracting an α-hydrogen atom from *n*-butene for the formation of π-allyl intermediate in this reaction [14, 20, 21]. Furthermore, it has been proposed that the catalytic activity in the oxidative dehydrogenation of olefins is generally governed by an activation of olefin over the acidic sites on the catalyst surface [14, 15, 22].

Co-precipitation method has been generally used in the preparation of zinc ferrite catalyst. In our previous work [19], it was revealed that the catalytic performance of zinc ferrite in the oxidative dehydrogenation of *n*-butene strongly depended on the pH value employed during the co-precipitation step. This indicates that the precise control

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of pH value during the co-precipitation step is very important in the preparation of zinc ferrite catalyst for oxidative dehydrogenation of *n*-butene. In the conventional co-precipitation method, the metal precursor solution (acidic solution) and sodium hydroxide solution (basic solution) are simultaneously added into distilled water for the preparation of zinc ferrite catalyst [23, 24]. The pH value during co-precipitation step has also been adjusted by controlling the injection rate of two solutions [19, 25]. However, controlling the pH value during the co-precipitation step in a conventional method is difficult and less reproducible, because the pH value is highly sensitive to the acid and base strength of precursor solutions. Therefore, it is expected that the pH value can be easily and precisely controlled, if aqueous buffer solution instead of distilled water is used as a co-precipitation medium. The reproducibility of catalyst preparation would be much improved, if aqueous buffer solution is used for the preparation of zinc ferrite catalyst.

In this work, a series of zinc ferrite ($ZnFe_2O_4$) catalysts were prepared by a co-precipitation method using aqueous buffer solution (pH = 6–12) as a co-precipitation medium, and applied to the oxidative dehydrogenation of *n*-butene to 1,3-butadiene. The formation of zinc ferrite catalysts was confirmed by XRD and ICP-AES measurements. The acid properties of zinc ferrite catalysts were measured by NH_3-TPD experiments. A correlation between catalytic performance and acid property of zinc ferrite catalysts was then established.

2 Experimental

2.1 Preparation of Aqueous Buffer Solution

Seven aqueous buffer solutions in the pH range of 6–12 with an interval of 1 were prepared for use as a co-precipitation medium. Three categories of aqueous buffer solutions with different pH were prepared, as listed in Table 1. For the preparation of aqueous buffer solutions with pH 6 and 7, a sodium tetraborate ($Na_2B_4O_7 \cdot 10H_2O$, Sigma-Aldrich) solution and a 37 wt.% hydrochloric acid solution (Sigma-Aldrich) were used. After dissolving 57.2 g of sodium tetraborate in 1,000 mL of distilled water at 50 °C under vigorous stirring, the solution was cooled at room temperature. Hydrochloric acid solution was then added dropwise into the sodium tetraborate solution until the pH of the mixed solution became 6 and 7. The commercially available aqueous buffer solutions with pH 8, 9, and 10 were purchased from Samchun Chem. For the preparation of aqueous buffer solutions with pH 11 and 12, a sodium hydrogen carbonate ($NaHCO_3$, Sigma-Aldrich) solution and a 5 N sodium hydroxide solution (Sigma-Aldrich) were used. A total of 42.0 g of sodium hydrogen carbonate was dissolved in 1,000 mL of distilled water at room temperature under vigorous stirring. Sodium hydroxide solution was then added dropwise into the sodium hydrogen carbonate solution until the pH of the mixed solution became 11 and 12.

Table 1 Preparation of aqueous buffer solutions with different pH

pH	Buffer solution	Buffer system
6	Sodium tetraborate ($Na_2B_4O_7 \cdot 10H_2O$)	$Na_2B_4O_7 \cdot 10H_2O$ + 37% HCl
7		$Na_2B_4O_7 \cdot 10H_2O$ + 37% HCl
8	Commercial	Commercial (pH = 8)
9		Commercial (pH = 9)
10		Commercial (pH = 10)
11	Sodium hydrogen carbonate ($NaHCO_3$)	$NaHCO_3$ + 5 N NaOH
12		$NaHCO_3$ + 5 N NaOH

2.2 Preparation of Zinc Ferrite ($ZnFe_2O_4$) Catalysts

A series of zinc ferrite ($ZnFe_2O_4$) catalysts were prepared by a co-precipitation method with a variation of pH value during the co-precipitation step. A total of 1.4 g of zinc chloride ($ZnCl_2$, Sigma-Aldrich) and 5.6 g of iron chloride ($FeCl_3$ $6H_2O$, Sigma-Aldrich) were successively dissolved in 100 mL of distilled water. The metal precursor solution was then added dropwise into an aqueous buffer solution for co-precipitation under vigorous stirring. In order to prepare the zinc ferrite catalysts at different pH, the aqueous buffer solution with corresponding pH value was used as a co-precipitation medium. During the co-precipitation step, the initial pH value of the mixed solution was maintained constant by the use of aqueous buffer solution. The resulting solution was stirred vigorously at room temperature for 12 h for complete co-precipitation, and then it was aged overnight at room temperature. The precipitate was filtered and washed with distilled water to obtain a solid product. The solid product was dried overnight at 175 °C, and finally, it was calcined at 650 °C for 6 h in a stream of air to yield the zinc ferrite ($ZnFe_2O_4$) catalyst.

2.3 Characterization

The formation of zinc ferrite ($ZnFe_2O_4$) catalysts was confirmed by XRD (MAC Science, M18XHF-SRA) measurements. The Fe/Zn atomic ratios of the prepared catalysts were determined by ICP-AES (Shimadz, ICP-1000IV) analyses. The surface areas of zinc ferrite catalysts were measured using a BET apparatus (Micromeritics, ASAP 2000).

The acid properties of zinc ferrite ($ZnFe_2O_4$) catalysts were measured by NH_3-TPD experiments. Each catalyst (0.3 g) 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. Twenty milli liter 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 100 °C for 1 h. The 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 using a GC-MSD (Agilent, MSD-6890N GC).

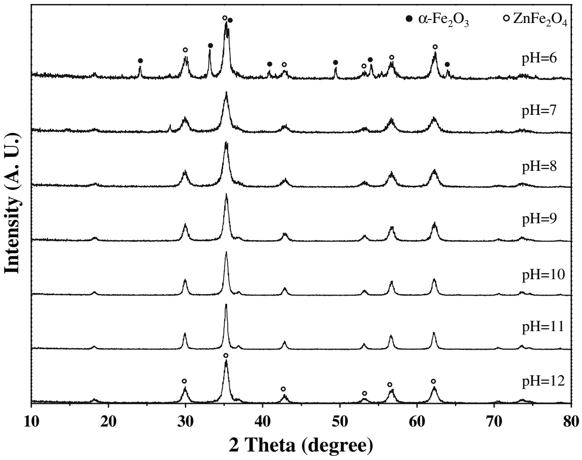

Fig. 1 XRD patterns of zinc ferrite catalysts prepared at different pH (pH = 6–12)

2.4 Oxidative Dehydrogenation of *n*-Butene

The oxidative dehydrogenation of *n*-butene to 1,3-butadiene was carried out in a continuous flow fixed-bed reactor in the presence of air and steam. Each catalyst (0.33 g) was pretreated at 470 °C for 1 h with an air stream (16 mL/min). Water was sufficiently vaporized by passing through a pre-heating zone and continuously fed into the reactor together with *n*-butene and air. 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). The feed composition was fixed at *n*-butene:oxygen:steam = 1:0.75:15. The catalytic reaction was carried out at 420 °C. The GHSV (gas hourly space velocity) was fixed at 475 h^{-1} on the basis of *n*-butene. Reaction products were periodically sampled and analyzed with gas chromatographs. 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 and selectivity.

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

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

3 Results and Discussion

3.1 Formation of Zinc Ferrite ($ZnFe_2O_4$) Catalysts

The formation of zinc ferrite ($ZnFe_2O_4$) catalysts was well confirmed by XRD and ICP-AES measurements. Figure 1 shows the XRD patterns of zinc ferrite catalysts prepared at different pH (pH = 6–12). Each phase was identified by its characteristic diffraction peaks using JCPDS. Zinc ferrite catalyst prepared at pH = 6 retained a mixed phase of α-Fe_2O_3 and $ZnFe_2O_4$, while a pure zinc ferrite ($ZnFe_2O_4$) phase was formed in the catalysts prepared at pH = 7–12, in good agreement with the previous result [19].

The Fe/Zn atomic ratios of the catalysts prepared at different pH are summarized in Table 2. The Fe/Zn atomic ratio of the catalyst prepared at pH = 6 was much higher than the theoretical value of 2.0, due to the presence of α-Fe_2O_3 phase. On the other hand, the Fe/Zn atomic ratios of the catalysts prepared at pH = 7–12 were in the range of 1.93–2.11, in good agreement with the theoretical value. This result is well consistent with the XRD result (Fig. 1). The above results indicate that zinc ferrite catalysts were successfully formed by a co-precipitation method in the pH range of 7–12, when aqueous buffer solution was used as a co-precipitation medium. An advantage of the use of aqueous buffer solution instead of distilled water as a co-precipitation medium in the preparation of zinc ferrite

Table 2 Atomic ratios and BET surface areas of zinc ferrite catalysts prepared at different pH

pH	Atomic ratio of Fe/Zn	BET surface area (m^2/g)
6	3.24	25.0
7	2.11	17.3
8	2.05	47.3
9	1.93	48.5
10	1.94	35.7
11	1.99	24.0
12	2.00	63.4

catalyst is that the pH value of the co-precipitation medium can be easily and precisely controlled during the co-precipitation step, resulting in improved reproducibility of catalyst preparation.

The BET surface areas of zinc ferrite catalysts prepared by a co-precipitation method at different pH are also summarized in Table 2. It was found that the BET surface areas of the catalysts showed no consistent trend with respect to pH value.

3.2 Catalytic Performance of Zinc Ferrite ($ZnFe_2O_4$) Catalysts

Figure 2 shows the catalytic performance of zinc ferrite catalysts in the oxidative dehydrogenation of *n*-butene at 420 °C after a 6 h-reaction, plotted as a function of pH value. The conversion of *n*-butene showed a volcano-shaped curve with respect to pH value. On the other hand, the selectivity for 1,3-butadiene was high (ca. 90%) at pH = 6–10, but was slightly decreased at pH = 11–12. The yield for 1,3-butadiene also exhibited a volcano-shaped curve with respect to pH value, and showed the same trend as the conversion of *n*-butene with respect to pH value. Among the catalysts tested, the zinc ferrite catalyst prepared at pH = 8 showed the best catalytic performance. The yield for 1,3-butadiene over zinc ferrite catalyst prepared at pH = 8 was found to be 78.9%.

It is interesting to note that the catalyst prepared at pH = 6 exhibited a relatively high catalytic performance, although α-Fe_2O_3 phase that was less active in the oxidative dehydrogenation of *n*-butene was detected in the catalyst. However, this catalytic behavior can be explained by the synergetic effect of α-Fe_2O_3 and $ZnFe_2O_4$. It was previously reported that the phase cooperation caused by the close contact between α-Fe_2O_3 and $ZnFe_2O_4$, which facilitated oxygen transfer from α-Fe_2O_3 to $ZnFe_2O_4$, led to the enhanced catalytic performance in the oxidative dehydrogenation of *n*-butene [26].

3.3 Correlation Between Catalytic Performance and Surface Acidity

In order to elucidate different catalytic performance of zinc ferrite catalysts (Fig. 2), an attempt has been made to correlate the catalytic performance with the BET surface area (Table 2) of zinc ferrite catalysts. However, the catalytic performance was not directly correlated with the BET surface area of zinc ferrite catalysts.

NH_3-TPD experiments were conducted in order to investigate the effect of acid properties on the catalytic performance of zinc ferrite catalysts. Figure 3 shows the NH_3-TPD profiles of selected zinc ferrite catalysts. All the catalysts showed a broad NH_3-TPD peak. It is noticeable that no great difference in acid strength (peak temperature) was observed with a variation of pH value. This means that the acid strength could not be correlated with the catalytic performance of zinc ferrite catalysts. However, the zinc ferrite catalysts showed a significant difference in total acidity (peak area) with respect to pH value. Therefore, our attempts have been made to correlate the catalytic performance with the acidity (acid amount) of the catalysts. Unfortunately, it was found that the total acidity was not directly correlated with the catalytic performance of zinc

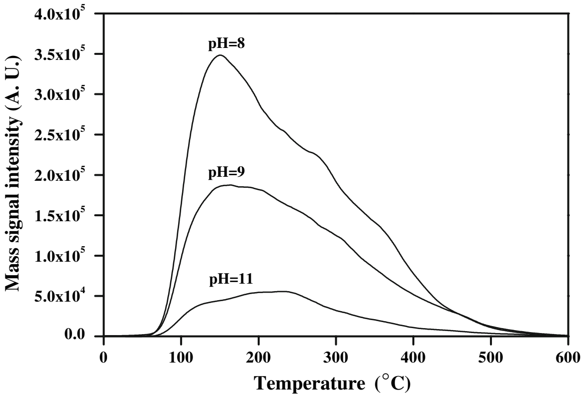

Fig. 3 NH_3-TPD profiles of selected zinc ferrite catalysts

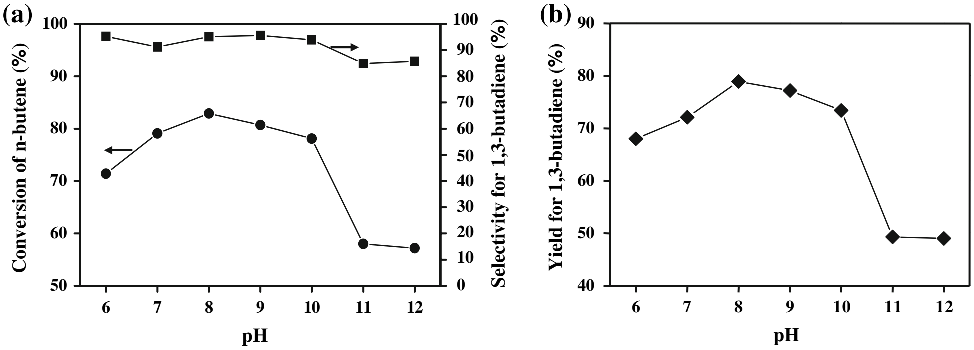

Fig. 2 Catalytic performance of zinc ferrite catalysts in the oxidative dehydrogenation of *n*-butene at 420 °C after a 6 h-reaction, plotted as a function of pH value: (**a**) conversion of *n*-butene and selectivity for 1,3-butadiene, and (**b**) yield for 1,3-butadiene

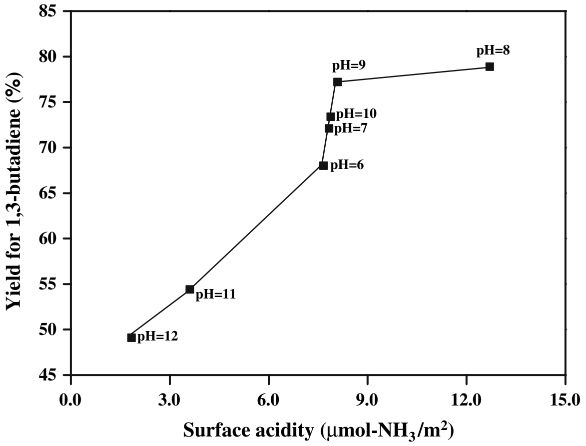

Fig. 4 A correlation between yield for 1,3-butadiene and surface acidity of zinc ferrite catalysts

ferrite catalysts. However, a reliable correlation between catalytic performance and surface acidity of the catalyst could be established. The surface acidity was defined as the amount of adsorbed NH_3 per unit surface area of the catalyst.

Figure 4 shows a comprehensive correlation between yield for 1,3-butadiene and surface acidity of zinc ferrite catalysts. The correlation clearly shows that the yield for 1,3-butadiene increased with increasing surface acidity of the catalyst. This result is well consistent with the previous results reporting that the surface acidity of the catalyst is one of the crucial factors affecting the catalytic performance in the oxidative dehydrogenation of *n*-butene [14, 15, 19, 22]. Among the catalysts tested, the zinc ferrite catalyst prepared at $pH = 8$ with the largest surface acidity showed the best catalytic performance. The conversion of *n*-butene also showed the same trend as the yield for 1,3-butadiene with respect to surface acidity. As described earlier, the acid property of zinc ferrite catalyst plays an important role in abstracting an α-hydrogen atom from *n*-butene to form π-allyl intermediate [11, 14, 18–21]. From the experimental findings, it can be concluded that large surface acidity of zinc ferrite catalyst is favorable for the facile adsorption and activation of *n*-butene (a base molecule). Thus, the surface acidity of zinc ferrite catalyst serves as a crucial factor determining the catalytic performance in the oxidative dehydrogenation of *n*-butene to 1,3-butadiene.

4 Conclusions

A series of zinc ferrite ($ZnFe_2O_4$) catalysts were prepared by a co-precipitation method using aqueous buffer solution with different pH ($pH = 6$–12). XRD and ICP-AES analyses revealed that a pure $ZnFe_2O_4$ phase was successfully formed at $pH = 7$–12, while a mixed phase of α-Fe_2O_3 and $ZnFe_2O_4$ was formed at $pH = 6$. The use of aqueous buffer solution as a co-precipitation medium provided a reproducible method for the preparation of zinc ferrite catalysts by a co-precipitation method. In the oxidative dehydrogenation of *n*-butene to 1,3-butadiene, conversion of *n*-butene and yield for 1,3-butadiene showed volcano-shaped curves with respect to pH value. Among the catalysts tested, the zinc ferrite catalyst prepared at $pH = 8$ showed the best catalytic performance. The surface acidity of zinc ferrite catalysts served as a crucial factor determining the catalytic performance in the oxidative dehydrogenation of *n*-butene. The catalytic performance was increased with increasing surface acidity of zinc ferrite catalysts. The highest catalytic performance of zinc ferrite catalyst prepared at $pH = 8$ was due to its largest surface acidity.

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