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Effect of pH in the preparation of $ZnFe_2O_4$ for oxidative dehydrogenation of *n*-butene to 1,3-butadiene: Correlation between catalytic performance and surface acidity of $ZnFe_2O_4$

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Abstract

A series of zinc ferrite ($ZnFe_2O_4$) catalysts were prepared by a co-precipitation method with a variation of pH value (pH 3–12), and applied to the oxidative dehydrogenation of *n*-butene to 1,3-butadiene. It was found that a zinc ferrite phase was formed at pH 6–12. Conversion of *n*-butene, selectivity for 1,3-butadiene, and yield for 1,3-butadiene were very high at low pH value (pH 6–10), but were drastically decreased with increasing pH value (pH 11–12). 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 was closely related to the surface acidity of the catalysts. Conversion of *n*-butene was increased with increasing surface acidity of the catalysts. Among the catalysts tested, the zinc ferrite catalyst prepared at pH 9 with the largest surface acidity showed the best catalytic performance in the oxidative dehydrogenation of *n*-butene.

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1. Introduction

Selective oxidation of olefins has been considered to be an important subject for the production of a number of chemical intermediates in the petrochemical industries [1–4]. In particular, oxidative dehydrogenation of *n*-butene has attracted much attention as a promising process for producing 1,3-butadiene [5–7], which is an important raw material for manufacturing a large number of chemical products. Various metal ferrite catalysts such as magnesium ferrite [8–11], zinc ferrite [9,10,12], cobalt ferrite [10,13], and copper ferrite [13] have been employed in the oxidative dehydrogenation of *n*-butene. Among these catalysts, zinc ferrite has been widely investigated as an efficient catalyst for this reaction [14–18].

The oxidative dehydrogenation of *n*-butene is strongly affected by various catalytic properties. It is known that the major factors determining the catalytic performance in the oxidative dehydrogenation of *n*-butene are different depending on the catalyst system. A number of investigations on the reaction mechanism for oxidative dehydrogenation of *n*-butene over ferrite-type catalysts have been made in order to elucidate the catalytic active sites [11,19,20]. It has been generally accepted that the reaction mechanism by way of π-allyl intermediate is the most feasible reaction pathway for the formation of 1,3-butadiene from *n*-butene [9,10,16,21].

According to the reaction mechanism [16,22], the oxidative dehydrogenation of *n*-butene over ferrite-type catalyst

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consists of five sequential elementary steps; (i) chemisorption of *n*-butene, (ii) abstraction of α-hydrogen from *n*-butene to form π-allyl intermediate, (iii) abstraction of one more hydrogen atom from π-allyl intermediate to form 1,3-butadiene, (iv) dissociation of oxygen in the gas phase to make up oxygen vacancy in the catalyst, and (v) reoxidation of multivalent cations. Many researchers agree that the abstraction of α-hydrogen from *n*-butene is the rate-determining step in the oxidative dehydrogenation of *n*-butene [10,21,22]. It has also been reported that acid property of the catalyst plays a key role in abstracting an α-hydrogen atom from *n*-butene to form π-allyl intermediate [10,23–25]. Therefore, it is believed that acid property of ferrite-type catalyst would be an important factor determining the catalytic performance in the oxidative dehydrogenation of *n*-butene.

Co-precipitation method has been generally used in the preparation of zinc ferrite catalyst. It has been reported that pH value during the co-precipitation step is an important factor for the successful formation of active phase in the preparation of zinc ferrite catalyst [17,26–29]. This implies that pH value in the preparation of zinc ferrite catalyst by a co-precipitation method can serve as a crucial factor determining the catalytic performance of zinc ferrite catalyst in the oxidative dehydrogenation of *n*-butene. Nonetheless, no systematic investigation on the effect of pH value in the preparation of zinc ferrite catalyst on the catalytic performance in the oxidative dehydrogenation of *n*-butene has been reported yet.

In this work, a series of zinc ferrite ($ZnFe_2O_4$) catalysts were prepared by a co-precipitation method with a variation of pH value (pH 3–12) for use in the oxidative dehydrogenation of *n*-butene to 1,3-butadiene. 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 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. Known amounts of zinc chloride ($ZnCl_2$ from Sigma–Aldrich) and iron chloride ($FeCl_3 \cdot 6H_2O$ from Sigma–Aldrich) were dissolved in distilled water. The metal precursor solution and an aqueous sodium hydroxide solution (3N) were then added dropwise into distilled water for co-precipitation under vigorous stirring. During the co-precipitation step, pH value of the mixed solution was precisely controlled using aqueous sodium hydroxide solution. The pH value was varied from 3 to 12 with an interval of 1 in the preparation of zinc ferrite ($ZnFe_2O_4$) catalysts. After the resulting solution was stirred vigorously at room temperature for 12 h, it was aged overnight at room temperature. The precipitate was filtered and washed 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 zinc ferrite ($ZnFe_2O_4$) catalyst.

2.2. Characterization

The formation of zinc ferrite ($ZnFe_2O_4$) catalysts was confirmed by XRD (MAC Science, M18XHF-SRA) measurements. The atomic ratios of constituent metal components were determined by ICP-AES (Shimadz, ICP-1000IV) analyses. The surface areas of zinc ferrite catalysts were measured using a BET apparatus (Micromeritics, ASAP 2010). The acid properties of zinc ferrite catalysts were measured by NH_3-TPD experiments. Each catalyst (0.1 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 millilitres 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. 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).

2.3. 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. 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. Prior to the catalytic reaction, each catalyst was pretreated at 470 °C for 1 h with an air stream. 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.

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

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

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