

Prevention of Catalyst Deactivation in the Oxidative Dehydrogenation of *n*-Butene to 1,3-Butadiene over Zn-Ferrite Catalysts

Young-Min Chung · Yong-Tak Kwon ·
Tae Jin Kim · Seung Jun Lee · Seung-Hoon Oh

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Abstract An efficient method to enhance the catalytic properties of Zn-ferrite catalyst in the oxidative dehydrogenation of *n*-butene to 1,3-butadiene is proposed. The incorporation of phosphorous compound in Zn-ferrite is very effective to improve the catalytic activity as well as to maintain extremely long useful lives at high oxygen to *n*-butene ratio. It is found that the amount of phosphorous is critical and the presence of appropriate amount of phosphorous in catalyst may contribute the catalyst stabilization by which unfavorable reduction of Fe³⁺ sites to Fe²⁺ is effectively suppressed. This suggests that the oxygen mobility is maintained as high as the redox mechanism keeps constantly working. On the other hand, the effort to increase the population of mobile oxygen species by the introduction of external oxygen donor phase is found to be rather ineffective regardless of the external donor oxides used.

Keywords Oxidative dehydrogenation · Ferrite · *n*-Butene · 1,3-Butadiene · Deactivation

1 Introduction

1,3-butadiene is one of the important monomers in the production of a wide range of polymers and demand for which is increasing in recent petrochemical markets. Although 1,3-butadiene production is mainly dependent on the extraction of 1,3-butadiene from crude C4 stream,

additional establishment of naphtha cracking unit is not a good solution to meet the rising demand for 1,3-butadiene because other basic fractions as well as 1,3-butadiene are excessively produced. In this context, the oxidative dehydrogenation of *n*-butene, a reaction for forming 1,3-butadiene and water by reacting *n*-butene with oxygen, becomes more and more interesting because the process is an effective method for on-purpose 1,3-butadiene production [1].¹

With the promising aspect of the reaction, a number of catalysts have been investigated and ferrite or bismuth molybdate type catalyst is known to be favorable to promote the reaction. Recently, Song and colleagues also reported that catalytic performance could be improved by pH control [2–4], divalent metal substitution [5], or calcination condition [6]. It is worth noting, however, that most of the researches have focused on the enhancement of catalytic activity, while only a few reports concerning the long-term stability of catalyst can be found in the literature [7–9]. From the industrial viewpoint, not only the catalytic activity itself but also life span of the catalyst is one of the most important criteria in the selection of catalysts. Therefore, further study for the catalyst deactivation is prerequisite.

To discuss the catalyst deactivation, one should consider the mechanism of the reaction. It is generally known [10, 11] that selective partial oxidation including the oxidative dehydrogenation of *n*-butene proceeds by Mars-van Krevelen Redox mechanism where catalyst undergoes an oxidation-reduction cycle during reaction. In the case of ferrite catalysts, it is proposed that the irreversible deactivation

Y.-M. Chung (✉) · Y.-T. Kwon · T. J. Kim ·
S. J. Lee · S.-H. Oh
SK Energy, 140-1, Wonchon-dong, Yuseong-gu,
Daejeon 305-712, South Korea
e-mail: ymchung@skenergy.com

¹ Recently, Mitsubishi Chemical announced that butadiene production technology from butene has been developed, Mitsubishi Chemical News Release, December 5, 2008.

may be caused by the increase of Fe^{2+} sites at the expense of Fe^{3+} sites in the course of reaction [8]. The unfavorable phase change of catalyst results in the segregation of metal phase and consequently the catalyst gradually loses its catalytic activity. Therefore, effective suppression of the reduction of Fe^{3+} sites to Fe^{2+} during reaction is of importance because the stabilization of catalyst makes it possible to maintain the oxygen mobility as high as the redox mechanism keeps working. Unfortunately, it is difficult to find any efficient method to prevent the catalyst deactivation, though there have been a number of reports on the deactivation of ferrite catalyst.

In this regard, we attempt here to develop an industrially viable catalyst for the oxidative dehydrogenation of *n*-butene to 1,3-butadiene focusing on the prevention of catalyst deactivation. For this purpose, we have chosen Zn-ferrite catalyst because the catalyst itself is very active in the oxidative dehydrogenation but is known to have very short useful lives [9]. It is found that Zn-ferrite catalyst with appropriate treatment shows enhanced catalytic activity and furthermore had extremely long useful life compared to that prepared by conventional method.

2 Experimental

2.1 Chemicals

Zinc chloride (reagent grade, >98%), iron (III) chloride hexahydrate (97%), bismuth phosphate (99.99%), antimony (III) oxide (reagent grade, 99%), and *n*-pentane (99%) were supplied from Aldrich. Sodium hydroxide was obtained from DC Chemical. All chemicals were used without further purification. Antimony(IV) oxide was prepared by calcination of Sb_2O_3 in air at 500 °C for 20 h. C4-raffinate-3 mixture was sampled from SK energy Ulsan complex.

2.2 Catalyst Preparation

Zn-ferrite catalyst was prepared by coprecipitation of zinc chloride and iron (III) chloride hexahydrate with the atomic ratio of Fe to Zn being 2. 84.9 g of zinc chloride and 336 g of iron (III) chloride hexahydrate was dissolved in 500 ml of distilled water. The metal precursor solution was then coprecipitated with NaOH by slow addition of the metal precursor solution to 3,000 ml of 3 M NaOH solution at 25 °C under vigorous stirring. The solution was stirred for 1 h and aged overnight at room temperature. After filtration, the precipitate was thoroughly washed with distilled water to remove the residual sodium. The filtered Zn-ferrite cakes were dried in a vacuum oven at 120 °C for 12 h and ground for 15 min with mechanical mortar grinder (Retsch

RM-100). The resulting fine powder was shaped into cylindrical pellets using appropriate binding agents. After drying, the extrudates were calcined at 650 °C for 3 h to yield Zn-ferrite catalyst. The extrudates were hard and durable.

The modification of Zn-ferrite with phosphoric acid was carried out as follows: dried Zn-ferrite powder was thoroughly mixed with phosphoric acid to give a damp powder with a moisture content of approximately 30 wt%. Phosphoric acid was present in the final composition in amounts of 1–3.3 wt% based on the total dry weight of the composition. The damp powder was then formed into cylindrical pellets by extrusion. After sequential drying and calcination, phosphoric acid treated Zn-ferrite catalyst was ready to use.

Physical mixtures of two oxides were prepared by two methods, simple grinding and solvent dispersion, respectively. For the former, same amount of calcined Zn-ferrite and one of oxygen donor metal oxides were thoroughly ground for 30 min. For the latter, two kinds of powders were dispersed in *n*-pentane solution for 30 min under stirring followed by filtering and drying in a vacuum oven at 120 °C for 12 h. Prior to use, all of the extrudate catalysts were screened to 16–20 meshed granules by sequential pelletizing, crushing, and size screening. There was no additional calcination.

Zn-ferrite compositions were identified by their characteristic X-ray diffraction patterns (MAC Science, M03XHF) using Cu $K\alpha$ radiation. BET analysis was carried out to measure the surface properties of various Zn-ferrites (Micromeritics, ASAP 2020). Temperature-programmed reduction (TPR) was performed using Micromeritics Autochem II equipped with a thermal conductivity detector. 100 mg of sample was pre-treated at 500 °C for 1 h under He (20 cc/min). After pretreatment, the sample was reduced with a 5% H_2/Ar mixture (40 cc/min). The temperature was raised to 750 °C at a constant heating rate of 10 °C/min and maintained for 30 min.

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 at atmospheric pressure. C4-raffinate-3 mixture was used as a reactant in the reaction and the composition is presented in Table 1. A reactor containing 10 cc of catalyst was raised to 400 °C under nitrogen and then steam made from steam generator was continuously supplied to the reactor. After the steam pretreatment for 3 h, the C4-raffinate-3 mixture was introduced into the reactor in the form of mixed gas together with nitrogen and steam. The reaction was started with changing nitrogen to air. The liquid hourly space velocity (LHSV) of a reaction was 1.5 h^{-1}

Table 1 Feedstock compositions

Composition	Mol %
<i>n</i> -Butane	26.02
Methylcyclopropane	0.07
<i>trans</i> -2-Butene	44.50
1-Butene	6.71
Isobutylene	0.01
<i>cis</i> -2-Butene	22.17
Cyclobutane	0.52
<i>i</i> -Butane	n.d.
<i>i</i> -Pentane	n.d.
Sum	100.00

based on the amount of *n*-butenes in the C4 mixture. The inlet temperature of the reactor was maintained at 400 °C. The ratio of *n*-butene: oxygen: steam was 1:0.75:20. When a reaction was started, the catalyst bed temperature was gradually increased as high as 500 °C. Reaction products were periodically sampled and analyzed with Agilent Refinery Gas Analyzer.

3 Results and Discussion

3.1 Catalyst Deactivation

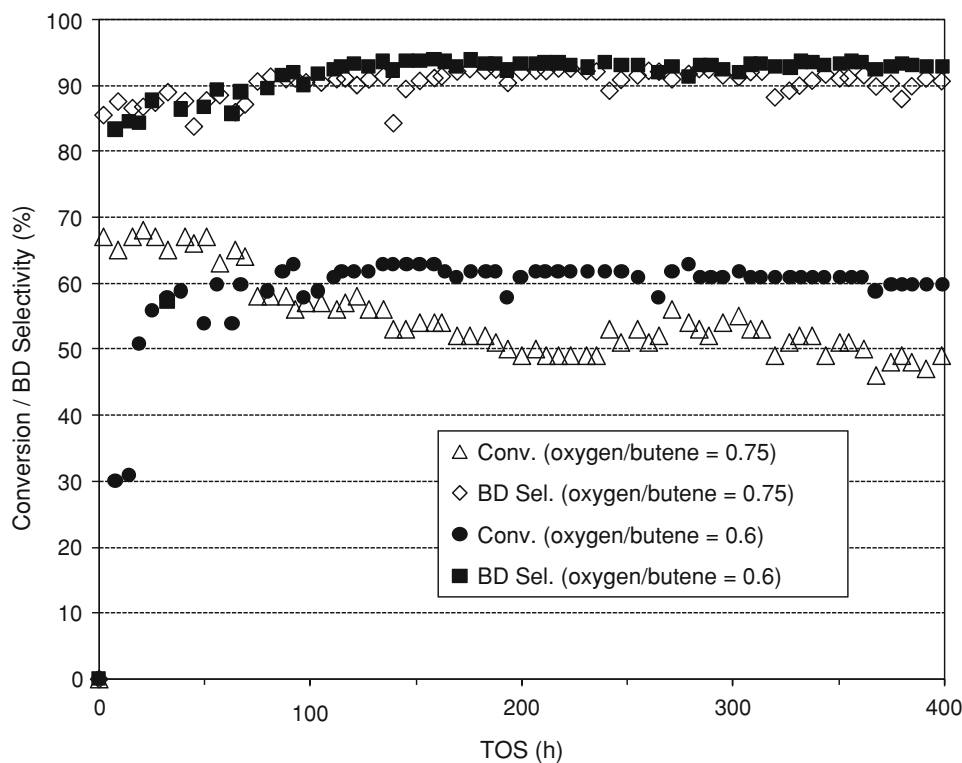
The reaction performance of the oxidative dehydrogenation of *n*-butene to 1,3-butadiene is dependent upon various

reaction parameters such as oxygen to *n*-butene ratio, steam to *n*-butene ratio, inlet temperature, space velocity, and inlet pressure. Among them, the oxygen to *n*-butene ratio is the most important variable because the 1,3-butadiene yield is greatly affected by the oxygen level used [1]. As the oxygen to *n*-butene ratio increases, higher *n*-butene conversion is expected at the expense of 1,3-butadiene selectivity. As shown in Fig. 1, similar result was observed in our experiments where the oxygen to *n*-butene ratio was changed from 0.6 to 0.75.

It is worth noting, however, that the oxygen to *n*-butene ratio significantly impacts on the catalyst life as well as the 1,3-butadiene yield. Fast catalyst deactivation was observed in the case of the oxygen to *n*-butene ratio of 0.75 and the *n*-butene conversion was dropped to about 46% level after 400 h. On the other hand, decreasing the oxygen to *n*-butene ratio to 0.6 was effective to delay the catalyst deactivation. Only 5% reduction of the *n*-butene conversion was observed after 2600 hours (not shown here). The possibility of catalyst deactivation by carbon deposition seems to be low because the carbonaceous residue can be removed from the catalyst surface by reaction with steam [12], which shows the autoregenerative nature of the catalyst [1].

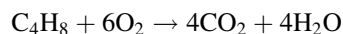
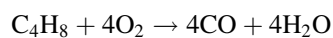
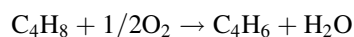
To discuss the catalyst deactivation, therefore, it seems better to start from the mechanistic aspect of the reaction. In the Mars-van Krevelen Redox mechanism, it is of importance that the balance between the rate of oxidation and that of catalyst regeneration step. The regeneration

Fig. 1 Deactivation profiles at various oxygen to butene ratios



involves reoxidation of anion vacancy sites by diffusion of lattice oxygen from the bulk to the surface [10] and the mobility of oxygen through the lattice is crucial to complete the redox cycle. External oxide phase may activate molecular oxygen and convert to spillover oxygen which compensates the lattice oxygen [13]. When the rate of oxidation is higher than that of the catalyst regeneration step, the population of the lattice oxygen gradually decreases and consequently the Fe^{3+} sites becomes unstable and finally reduced to Fe^{2+} in the course of reaction. The reduction of Fe sites may lead to the formation of anion vacancies in layers on and just below the catalyst surface [8]. It was reported that the anion vacancy concentration is very critical in the case of Mg-ferrite. Above 0.6 atomic percent, the ferrite decomposes to a spinel solid solution of Fe_3O_4 in MgFe_2O_4 and excess Mg^{2+} cations are precipitated as a separate MgO phase [14]. The unfavorable phase change of catalyst may also occur in the Zn-ferrite case and results in the segregation of ZnO or formation of defect sites in spinel structure. This may decrease the oxygen mobility and thus cause the decrease in the available lattice oxygen which can participate in the reaction. Through the sequential steps, the catalyst gradually loses its catalytic activity.

Effluent gas analysis revealed that essentially all of the oxygen in the feed was consumed and there was no detectable oxygen at the oxygen to *n*-butene ratio of 0.75, though larger amount of oxygen was supplied to the reactor. On the other hand, about 0.5% oxygen was detected in the effluent gas at the oxygen to *n*-butene ratio of 0.6. The phenomena may be ascribed to the different oxygen consumption for combustion at different oxygen to *n*-butene ratios. Compared to the oxidative dehydrogenation which needs 0.5 mol of oxygen, a combustion reaction to CO_2 consumes 6 mol of oxygen (12 times).



Although larger amount of oxygen was supplied at higher oxygen to *n*-butene ratio, the oxygen consumed for combustion was also significantly increased. Therefore, the reaction consumed essentially all of the oxygen in the feed and oxygen level in the effluent was nearly zero at the oxygen to *n*-butene ratio of 0.75 [1]. This suggests that, as the combustion becomes dominant at high oxygen to *n*-butene ratio, the amount of molecular oxygen converted to spillover oxygen decreases, which results in the lattice oxygen being deficient [8].

In the XRD analysis represented in Fig. 2, only characteristic peaks of spinel ferrite structure were observed in the fresh catalyst and this indicates that they have pure

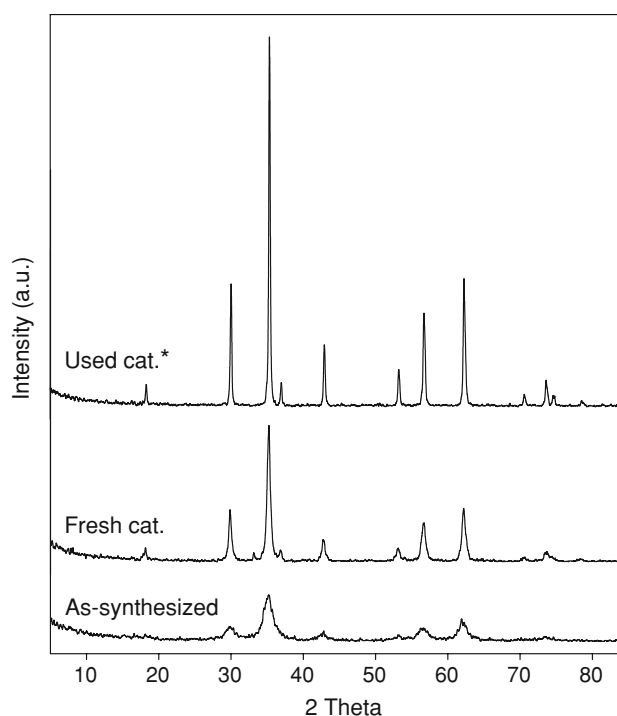


Fig. 2 Crystallinity change of Zn-ferrite during oxidative dehydrogenation of *n*-butene. * Reaction time 400 h

ZnFe_2O_4 composition. However, it was difficult to find any evidence of deactivation such as characteristic peaks of ZnO in the used catalyst. It seems that the phase change is occurred within only a few atomic layers of the catalyst surface and the amount of ZnO is too small to detect. One may assume that the catalyst deactivation may be ascribed to the high crystallinity of the used catalyst. If crystallinity of a catalyst is too high, the mobility of oxygen through the lattice is severely suppressed and thus the catalyst is too resistant to reduction. This implicates that redox mechanism is not working in the highly ordered system and results in low catalytic activity. As we reported previously [15], however, not all the catalysts with high XRD intensity mean low catalytic activity. Although the crystallinity of catalyst grew up during reaction, the deactivation was not severe in the case of oxygen to *n*-butene ratio of 0.6. This suggests that the oxygen mobility through lattice was not significantly suppressed in the course of reaction.

The comparison of reduction behavior of fresh Zn-ferrite with that of used one was also carried out. As shown in Fig. 3, two large reduction peaks for Zn-ferrite [16] were observed from the TPR profiles of both fresh and used catalyst. This suggests that Zn-ferrite structure was maintained after reaction.

On the basis of the reaction mechanism described above, it is clear that the crucial factor for the prevention of catalyst deactivation is maintaining the sufficient lattice oxygen partial pressure to insure surface coverage by

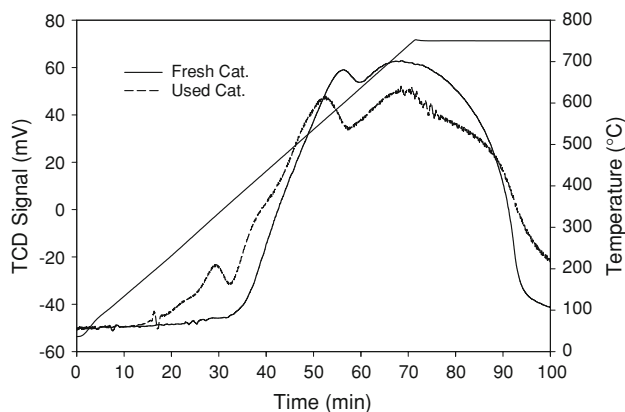


Fig. 3 Comparison of TPR profiles of fresh Zn-ferrite with that of used one

oxygen and/or diffusion of oxygen into the lattice. In this regard, we carried out two methods such as treatment of phosphoric acid and introduction of external oxygen donor phase to solve the deactivation problem. The postulated

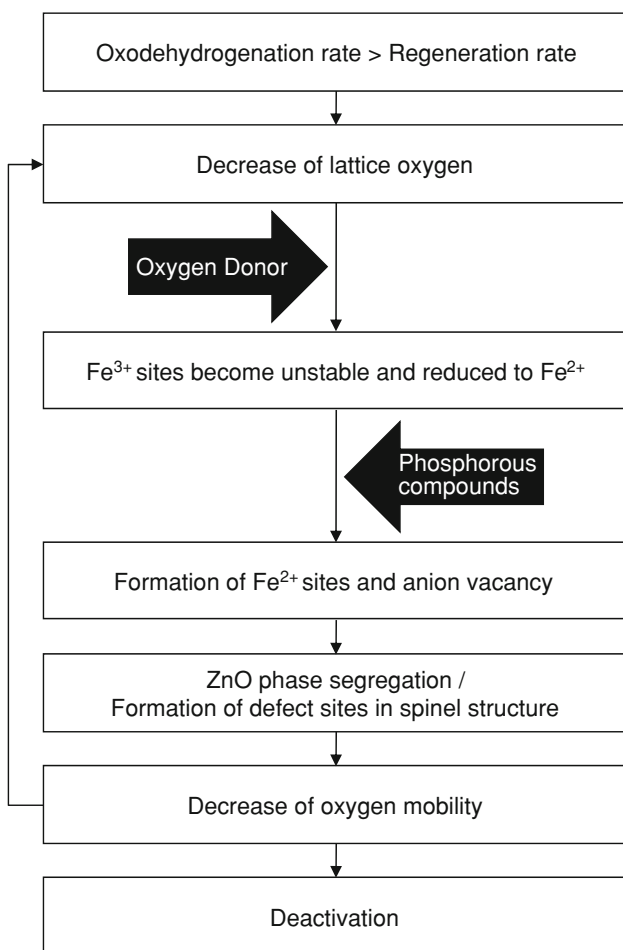


Fig. 4 Postulated deactivation of Zn-ferrite catalyst and its prevention

deactivation of Zn-ferrite catalyst and its prevention is presented in Fig. 4.

3.2 Effect of Phosphoric Acid

In selective oxidation, there have been a lot of studies on the enhancement of catalyst life, mechanical strength, or improvement of catalytic activity and selectivity by the addition of other element in catalyst [17]. Concerning the ferrite catalysts, it was reported that the addition of phosphorous compound was effective to increase catalyst life by stabilizing Mg-ferrite catalyst [18]. To investigate the effect of phosphorous compounds on the catalytic activity, we prepared phosphoric acid treated Zn-ferrite catalysts with various phosphorous contents. Surface properties of the resulting Zn-ferrites are presented in Table 2. Compared to untreated catalyst (ZF-2), it is difficult to find any apparent changes in surface properties by the incorporation of phosphoric compound except for the decrease of average pore diameter. In the XRD analysis, it was observed that there was little change in the crystallinity after phosphoric acid treatment. This indicates that pure ZnFe_2O_4 composition was retained after modification.

The catalytic performances of the phosphorous acid treated Zn-ferrite catalysts are very interesting. As summarized in Table 3, the presence of phosphorous in Zn-ferrite greatly affects on the catalytic performance. In the case of ZF-3 with 1 wt% of H_3PO_4 , catalyst deactivation was appreciably retarded and only 5% reduction in conversion was observed after 465 h of reaction. When phosphoric acid content was slightly increased to 1, 5 wt% (ZF-4), striking change was showed up. As represented in Fig. 5, *n*-butene conversion was increased from 65% (50 h) to 78% (450 h) in the course of the reaction accompanied with the improvement of 1,3-butadiene selectivity. We assumed that the remarkable improvement in the catalytic performance may be attributed to the catalyst stabilization [18]. Probably, the unfavorable reduction of Fe^{3+} sites to Fe^{2+} was effectively suppressed by virtue of the phosphorous incorporated in Zn-ferrite catalyst. It should be noted, however, addition of larger amount of phosphoric acid in catalyst was found to be detrimental. Severe reduction in *n*-butene conversion as well as 1,3-butadiene selectivity was observed in the case of ZF-5 (3.3 wt% of H_3PO_4). This result clearly shows that the amount of phosphorous is critical and the presence of appropriate amount of phosphorous in Zn-ferrite catalyst makes it possible to prevent catalyst deactivation and furthermore to enhance the catalytic performance.

3.3 Effect of External Oxygen Donor

As an alternative method to solve the catalyst deactivation, we also attempted to increase the population of mobile

Table 2 Surface properties of various Zn-ferrites

Catalyst	Treatment	Surface area (m ² g ⁻¹)	Pore vol. (ml g ⁻¹)	Avg. pore dia. (nm)
ZF-1	Untreated (As-synthesized)	102.4	0.21	80.9
ZF-2	Untreated (Calcined)	28.3	0.12	201
ZF-3	1 wt% H ₃ PO ₄	27.9	0.15	220
ZF-4	1.5 wt% H ₃ PO ₄	27.27	0.12	176.4
ZF-5	3.3 wt% H ₃ PO ₄	28.1	0.1	187.4

Table 3 Catalytic performance of phosphoric acid treated Zn-ferrite

Catalyst	H ₃ PO ₄ (wt%)	TOS (h)	Conv. (%)	BD Sel. (%)	BD Yield (%)
ZF-2	–	50	67	89	60
ZF-3	1	450	62	90	56
ZF-4	1.5	450	78	91.7	71.5
ZF-5	3.3	40	20	65	13

oxygen species by the introduction of external oxygen donor phase. It was proposed [19, 20] that the spillover oxygen created and migrated from oxygen donor may increase the replenish rate of lattice oxygen. Furthermore, creation of new catalytic sites or regeneration of the deactivated sites is also expected. Sb₂O₄ and BiPO₄ are believed to have the ability to activate the molecular oxygen into mobile oxygen species. In this context, we prepared two types catalysts in the form of a mechanical

mixture, e.g., ZnFe₂O₄–BiPO₄ and ZnFe₂O₄–Sb₂O₄ to investigate the cooperation between two metal oxides.

We anticipated that the addition of BiPO₄ may be very advantageous to enhance the catalytic activity by virtue of the characteristic features of BiPO₄: (1) stabilization of catalyst by phosphorous and (2) sufficient supply of lattice oxygen from BiPO₄ by oxygen spillover. Contrary to our expectation, however, any positive effect was not observed in the ZnFe₂O₄–BiPO₄ system. As presented in Table 4 and Fig. 6, the introduction of BiPO₄ was unsuccessful in prevention of catalyst deactivation or in enhancing the catalytic activity regardless of preparation methods. In the case of ZnFe₂O₄–Sb₂O₄, *n*-butene conversion was significantly dropped to about 16%. The result suggests that it is difficult to realize the cooperation between Zn-ferrite and external donor phase by physical mixing. However, the potential of external donor phase should not be overlooked and further study on the addition of external donor phase in catalyst shaping step is in due course.

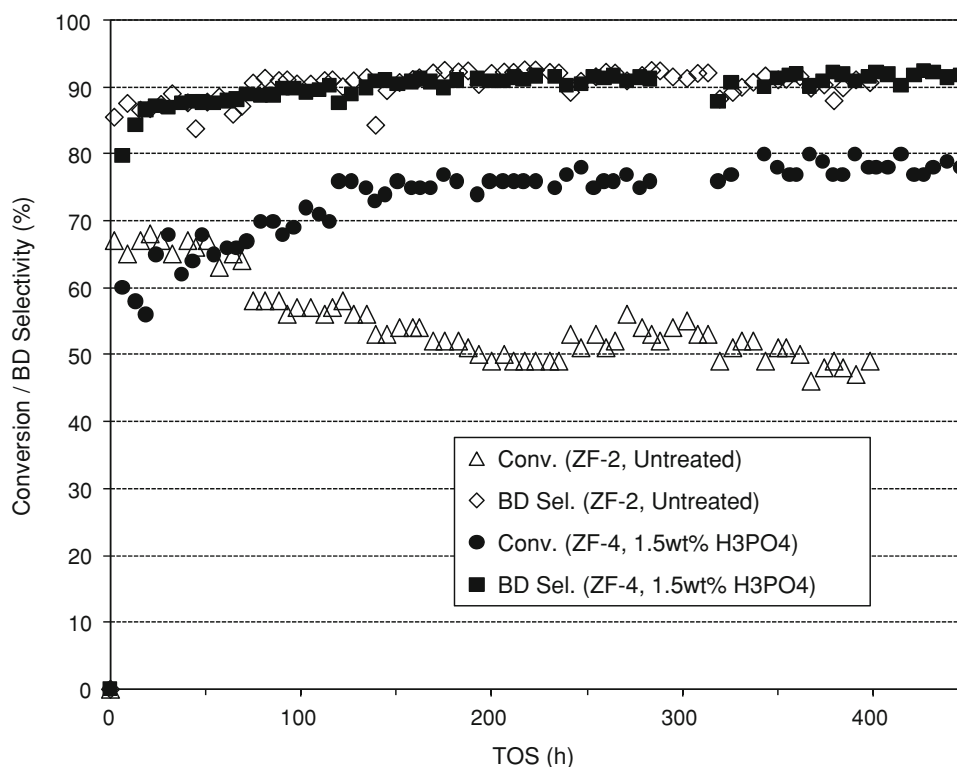
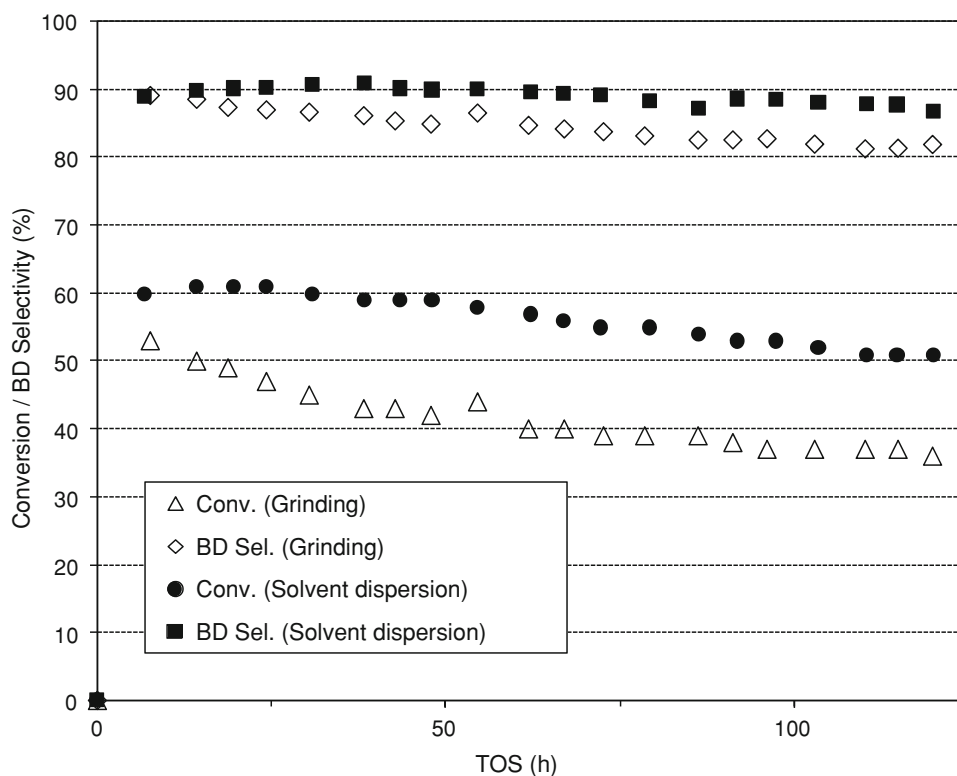
Fig. 5 Effect of phosphoric acid on the prevention of catalyst deactivation

Table 4 Catalytic performance of external oxygen donor added Zn-ferrite (Reaction time 120 h)

Catalyst	Oxygen donor	Preparation method	Conv. (%)	BD Sel. (%)	BD Yield (%)
ZF-6	BiPO ₄	Solvent dispersion	50	87	43.5
ZF-7	BiPO ₄	Grinding	36	82	29.5
ZF-8	Sb ₂ O ₄	Solvent dispersion	16	85	13.6

Fig. 6 Effect of BiPO₄ on the prevention of catalyst deactivation

4 Conclusion

An efficient method to prevent the deactivation of Zn-ferrite catalyst in the oxidative dehydrogenation of *n*-butene to 1,3-butadiene is proposed. The catalytic activity of Zn-ferrite is significantly dependent upon the oxygen to *n*-butene ratio and fast deactivation is observed at high oxygen to *n*-butene ratio. It is found that the treatment of Zn-ferrite with phosphoric acid greatly affects on the catalytic performance and the amount of phosphorous in catalyst is of importance. In the case of Zn-ferrite catalyst containing 1.5 wt% phosphorous, *n*-butene conversion is greatly increased in the course of the reaction accompanied with the improvement of 1,3-butadiene selectivity. It is assumed that the incorporation of phosphorous renders the catalyst being more stable, which leads to the effective suppression of the unfavorable reduction of Fe³⁺ sites to Fe²⁺. This suggests that the oxygen mobility is maintained as high as the redox mechanism keeps constantly working.

Therefore, the remarkable improvement in the catalytic property may be ascribed to the catalyst stabilization.

On the other hand, the effort to increase the population of mobile oxygen species by the introduction of external oxygen donor phase is found to be ineffective regardless of external donor oxide such as Sb₂O₄ or BiPO₄. Further study on the use of external donor phase is needed.

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