

Effect of Carbon Dioxide in Dehydrogenation of Ethylbenzene to Styrene over Zeolite-Supported Iron Oxide Catalyst

Jong-San Chang, Jermim Noh, Sang-Eon Park*, Woo Young Kim, and Chul Wee Lee

Industrial Catalysis Research Laboratory, Korea Research Institute of Chemical Technology (KRICT), Daeduck Danji, P.O. Box 107, Yusong, Taejeon 305-606, Korea

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The dehydrogenation of ethylbenzene with carbon dioxide has been carried out over ZSM-5 zeolite-supported iron oxide catalyst as well as commercial catalyst ($K\text{-Fe}_2\text{O}_3$) and unsupported iron oxide (Fe_3O_4) for comparison. In the dehydrogenation over the ZSM-5 zeolite-supported iron oxide catalyst, ethylbenzene is predominantly converted to styrene by an oxidative pathway in the presence of excess carbon dioxide. Carbon dioxide in this reaction is found to play a role as an oxidant for promoting catalytic activity as well as coke resistance of catalyst. On the other hand, both of commercial catalyst and unsupported Fe_3O_4 exhibit considerable decrease in catalytic activity under the same condition. It is suggested that an active phase for the dehydrogenation with carbon dioxide over ZSM-5 zeolite-supported iron oxide catalyst would be rather a reduced and isolated magnetite (Fe_3O_4)-like phase having oxygen deficiency in the zeolite matrix.

Introduction

The utilization of carbon dioxide, which is a main contributor to the greenhouse effect, has been of global interest from both fundamental and practical viewpoints.¹ In particular, the catalytic conversion of carbon dioxide to useful chemicals has been studied intensively during recent five years.¹⁻³ Most of these studies are concentrated on the utilization of carbon dioxide as a carbon source through catalytic reduction processes. However, in another way, carbon dioxide would be also utilized as an oxygen source or oxidant because it can be considered to be a nontraditional or mild oxidant and oxygen transfer agent.⁴⁻⁶ It has been recently reported that carbon dioxide is utilized as an oxidant for the oxidative conversions of alkanes, alkenes, and alcohols⁶⁻¹⁰ and oxygen generated during CO_2 reduction can participate in both of partial oxidation and dehydrogenation.⁶ In a previous report, we have suggested that carbon dioxide is utilized as an oxidant for the oxidative transformation of hydrocarbons including propane and ethylbenzene (EB) over oxygen-deficient iron oxides on zeolite support.⁹

Catalytic dehydrogenation of EB is of importance in the manufacture of styrene, which is widely used as a starting material of synthetic rubber and polymer. Styrene is now produced commercially by the EB dehydrogenation using potassium-promoted iron oxide catalysts with a large excess of superheated steam.¹¹ This reaction is generally carried out in vapor phase at 600-650 °C under steam. The important roles of steam in the industrial dehydrogenation of EB are classified as follows: providing heat to the endothermic dehydrogenation, diluting EB in order to increase equilibrium conversion, and preventing coke deposition on the catalyst.¹¹ Although steam is widely used in the EB dehydrogenation due to these beneficial roles, the use of steam has a drawback of losing latent heat of condensation during subsequent separation particularly in a mass process.^{11,12} In addition, even a small amount of carbon dioxide formed as a by-product in the EB dehydrogenation is known to inhibit the catalytic activity of commercial catalysts.^{13,14} Considering

these aspects, it is highly desirable to design a new catalytic system based on the use of carbon dioxide instead of steam. It is easily presumable that carbon dioxide can play the same beneficial roles of steam mentioned above. The energy consumption required for the EB dehydrogenation using carbon dioxide is estimated to be much lower than that for the currently operating process using steam.¹² Some selected catalytic systems show promoting effects in the presence of carbon dioxide.¹⁵⁻¹⁷ In particular, we have reported that, in the case of zeolite-supported iron oxide catalysts, carbon dioxide exhibits beneficial effect on improving catalytic activity and preventing coke formation.¹⁷ The aim of the present work is to clarify the effect and the role of carbon dioxide in the EB dehydrogenation over the zeolite-supported iron oxide catalysts.

Experimental

Materials. All chemicals were analytical grade materials and used without further purification. A highly siliceous NaZSM-5 zeolite, Zeocat® PZ-2/980 (CU Chemie Uetikon AG, $\text{SiO}_2/\text{Al}_2\text{O}_3 = 980$; $S_{\text{BET}} = 394 \text{ m}^2/\text{g}$) was used as catalyst support.

Catalyst Preparation. Zeolite-supported iron oxide (FeNaZ) catalysts were prepared by deposition of aqueous suspension of iron(II) sulfate onto the NaZSM-5 zeolite support ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 980$) at 60 °C and $\text{pH} = 11$ under N_2 atmosphere to avoid oxidative condition. Dissolved oxygen gas in distilled water was removed by bubbling nitrogen gas through water solution for few hours. In typical preparation, 0.2 g of iron(II) sulfate was dissolved in 100 mL of distilled water. Suspension of the NaZSM-5 zeolite powder in 100 mL of distilled water was poured into the aqueous iron solution after removing dissolved oxygen. The pH of the solution was fixed at 11 by dropwise addition of aqueous ammonia solution, which resulted in deposition of $\text{Fe}(\text{OH})_2$ on the support. Solid product obtained from the deposition of iron component onto zeolite support was filtered and washed thoroughly with 2 L of distilled water. The filtrate

was dried in vacuo at 80 °C and calcined under N₂ flow at 400 °C for 3 h. The content of iron oxide in the catalyst was determined by inductively coupled plasma (ICP) emission. Loading of iron oxide on the prepared catalysts was in the range of 1.5-20 wt.%. The catalysts are designated as FeNaZ with a preceding number to denote wt.% of iron oxide (based on Fe₃O₄). Bulk Fe₃O₄ oxide was prepared by the above method in the absence of the zeolite support. K-Fe₂O₃ catalyst (Nissan Girdler G-64 X) was used as a commercial catalyst.

X-ray Powder Diffraction and Surface Area Measurements. X-ray diffraction (XRD) patterns of the samples were recorded using a Rigaku 2155D6 diffractometer (Ni-filtered Cu-K α , 40 kV, 50 mA). The samples were mounted on sample boards and the measurement was carried out immediately after preparation. The specific surface areas of the catalyst samples were measured by nitrogen adsorption at -196 °C using a sorption analyzer (Micromeritics, model ASAP-2400).

Catalytic Measurement. EB dehydrogenation into styrene was carried out in a conventional fixed bed reactor made of a quartz tube (10 mm i.d., 300 mm length) at 600 °C and atmospheric pressure. 200 mg of catalyst powder was placed on fritted quartz disk in the reactor. Before introducing EB into the reactor, the catalyst was pretreated as follows: it was heated under a nitrogen stream from room temperature to 600 °C with a heating rate of 10 °C/min, and then the catalyst was maintained at this temperature for 1 h. To examine the effect of pretreatment conditions, the activities of the FeNaZ catalysts were compared after different pretreatments, *i.e.*, at 600 °C with 5% H₂ diluted in nitrogen for 60 min, with carbon dioxide for 10 min or with air for 10 min. After these treatments the reaction was carried out at 600 °C for 1-5 h. EB was supplied to the reactor by passing carrier gas with 30 mL/min of a flowrate through the EB saturator kept at 25 °C. The effluent from the reactor was condensed in two traps containing ice water and NaCl salt. Separation of reaction products was carried out with a FID gas chromatograph (Chrompack, model 9001) equipped with a capillary column (Hewlett-Packard, HP-1) and analysis of gaseous products with a TCD gas chromatograph (Chrompack, model 9001) using a stainless steel column packed with a carbon molecular sieve.

Results and Discussion

Dehydrogenation of Ethylbenzene into Styrene.

Figure 1 describes the results of the dehydrogenation reaction over various iron-based catalysts depending on the presence or the absence of carbon dioxide. When the reaction is conducted under a nitrogen stream, styrene and hydrogen are produced as main products over the iron-based catalysts. The ZSM-5-supported and unsupported iron oxide catalysts exhibit similar dehydrogenation activity. In addition to styrene and hydrogen, by-products such as benzene, toluene, methane, and ethylene are formed by cracking and hydrocracking reactions of ethylbenzene. For styrene formation, the commercial catalyst gives high selectivity above 95%, whereas the zeolite-supported iron oxide catalyst does rather low selectivity.

Using carbon dioxide as a carrier gas, these catalysts

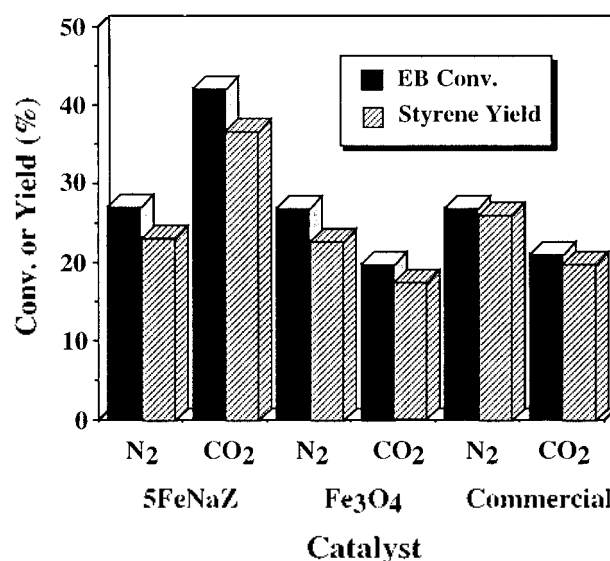


Figure 1. Effect of carrier gas in dehydrogenation of ethylbenzene to styrene depending on catalysts: temp.= 600 °C, W/F = 300 g.h/mol, CO₂ (or N₂)/EB = 80 (molar ratio).

show quite different activities. When the reaction is carried out under a carbon dioxide stream instead of nitrogen, both of the commercial catalyst and bulk Fe₃O₄ oxide show considerable decrease of catalytic activity without any effects in the styrene selectivity. The activity decrease of the commercial catalyst is consistent with a previous observation^{13,14} that carbon dioxide depresses the dehydrogenation activity of a K- α -Fe₂O₃ catalyst. On the other hand, the use of carbon dioxide as a carrier gas promotes greatly the catalytic activity of 5FeNaZ catalyst. Comparing with using nitrogen carrier gas, the dehydrogenation of EB with carbon dioxide over the 5FeNaZ catalyst produces styrene, water and carbon monoxide together with the small amount of hydrogen, which is less than 25% of the amount of carbon monoxide produced. Moreover, it is found that small amount of benzaldehyde as an oxygenated by-product in the EB dehydrogenation with carbon dioxide is formed along with benzene and toluene, and benzaldehyde contains about 2% among the by-products. However, there is no formation of benzaldehyde over the commercial catalyst and bulk Fe₃O₄ oxide even in the presence of carbon dioxide. These results indicate that the EB dehydrogenation over the zeolite-supported iron oxide catalyst is predominantly enhanced by oxidative pathway in the presence of a large excess of carbon dioxide. The formation of water as well as carbon monoxide implies that on the zeolite-supported iron oxide catalyst CO₂ molecule dissociates CO and surface oxygen which can abstract hydrogen from EB, and then results in the generation of water. The enhancement of the dehydrogenation activity in the presence of carbon dioxide is certainly ascribed to the promotion of this oxidative process by carbon dioxide.

Figure 2 represents EB conversion and selectivity to styrene as a function of iron oxide loading over the FeNaZ catalysts. EB conversion increases with an increase in the loading of iron oxide up to 5 wt.%, and above this level the conversion decreases. Therefore, among the zeolite-supported iron oxide catalysts, the 5FeNaZ catalyst exhibits highest

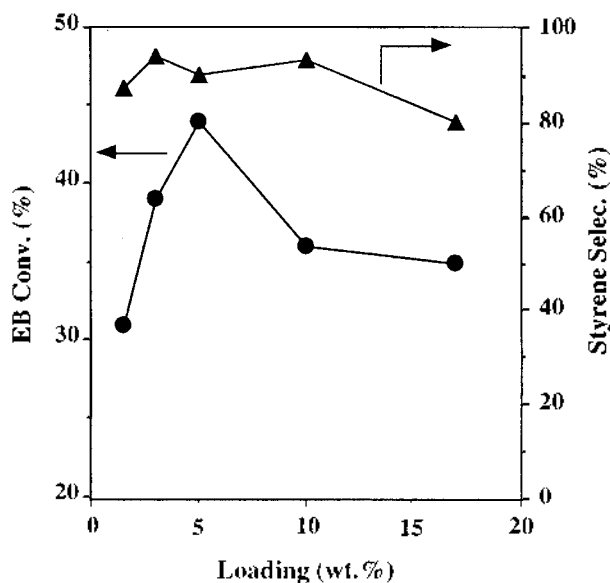


Figure 2. Effect of iron oxide loading of FeNaZ catalysts in dehydrogenation of ethylbenzene: See Figure 1 for reaction conditions.

catalytic activity.

For the commercial catalyst, it is assumed that the existence of carbon dioxide as a carrier gas depresses the activity due to the decomposition of an active KFeO_2 phase by the interaction between carbon dioxide and catalyst.^{18,19} Although the reason for small catalytic activity of bulk Fe_3O_4 oxide in the presence of carbon dioxide is not fully understood until now, it is reasonable that carbon dioxide molecules inhibit the adsorption of EB on the surface of Fe_3O_4 oxide or preoccupies the active sites of the Fe_3O_4 oxide. In this case, it will be difficult to activate both of EB and carbon dioxide efficiently. Therefore, it may be concluded that highly dispersed iron oxide catalysts are more preferable for the EB dehydrogenation in the presence of excess carbon dioxide.

In respect of the styrene selectivity, the zeolite-supported iron oxide catalysts are a little less selective than the commercial catalyst regardless of carrier gas. Decrease in the selectivity over the zeolite-supported catalysts would be accounted for by cracking or hydrocracking of EB due to the weak acidity of zeolite support. In addition, non-selective decomposition with carbon dioxide would be partly attributed to decrease in the styrene selectivity.

Active Phase. Figure 3 represents detectable phase by XRD and surface areas of supported and unsupported iron oxide catalysts. The XRD patterns of the zeolite-supported catalysts show no strong crystalline phases of iron oxides up to 10 wt.% of iron oxide loading. The catalyst surface area did not decrease even at loading of 5 wt.% iron oxide. This result indicates that iron oxide phases are highly dispersed in the ZSM-5 zeolite support below critical dispersion capacity which denotes the border line to start the appearance of crystalline oxide phase.²⁰ Highly dispersed iron oxide catalyst used in this study were characterized by XPS of previous work.²¹ According to XPS result, the Fe 2p spectra of the ZSM-5 zeolite-supported iron oxide catalysts showed intrinsic pattern of Fe_3O_4 oxide without satellite structure at

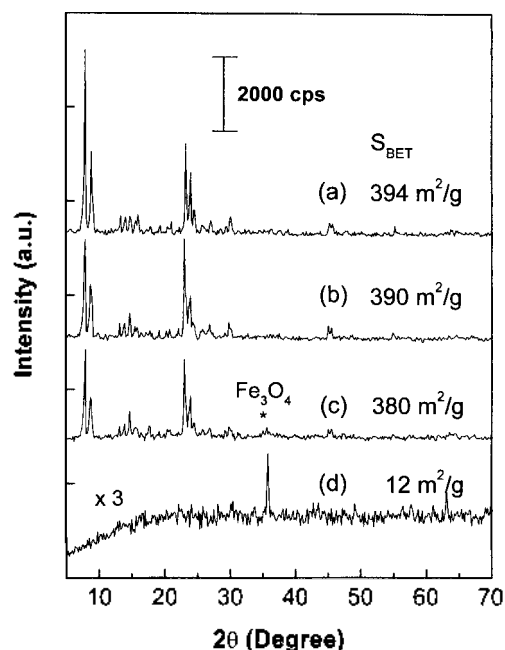


Figure 3. Powder X-ray diffraction patterns of FeNaZ catalysts and bulk Fe_3O_4 oxide: (a) 5FeNaZ, (b) 10FeNaZ, (c) 17FeNaZ, and (d) Fe_3O_4 .

719.1 eV. In addition, the O 1s binding energies of the zeolite-supported iron oxides were observed at 530.3 eV, making it for discriminating from O 1s of the zeolite lattice at 532.4 eV. The supported iron oxide catalysts showed high surface Fe/Si ratios, indicating high dispersion of iron oxide and surface enrichment of iron on the zeolite surface. Therefore, the iron oxide in the supported catalysts was identified to be mainly a metastable Fe_3O_4 -like phase.²¹

Major phase in the commercial catalyst (K-promoted Fe_2O_3) was confirmed to be KFeO_2 by XRD although it had poor crystallinity. Several reports have pointed out that generally KFeO_2 or $\text{K}_2\text{Fe}_2\text{O}_4$ oxide is an active phase for the dehydrogenation of EB in the presence of steam.^{13,12,18,19} Unsupported commercial catalyst and bulk Fe_3O_4 oxide have low surface areas compared to the supported iron oxide catalysts.

To examine the effect of oxidation state of iron towards the dehydrogenation, the activity of the supported iron oxide catalyst was compared after different pretreatment. As presented in Figure 4, the 5FeNaZ catalyst pretreated with nitrogen shows rather high activity compared to that pretreated with carbon dioxide, air or 5% H_2 in N_2 stream. This result explains that partial reduction during the heat treatment under nitrogen flow reaches a certain optimum oxidation state of the iron oxide. Since the reaction occurs in the presence of hydrogen, EB and carbon dioxide, it is possible for the iron oxide phase on the catalyst to undergo both partial oxidation by carbon dioxide as well as partial reduction by hydrogen and EB. Therefore, this population would be controlled properly in the gaseous mixture of EB, hydrogen and excess carbon dioxide during the reaction.

Oxygen Deficiency. Tamaura and co-workers have extensively studied on the decomposition of CO_2 over oxygen-deficient magnetite and the role of its oxygen deficiency on this reaction.^{22,23} Oxygen deficiency of unsupported iron oxide has been characterized by chemical analysis and

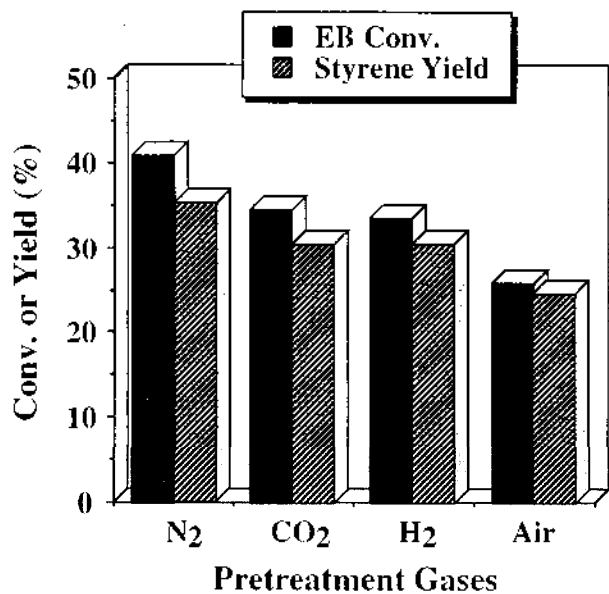


Figure 4. Effect of pretreatment conditions of 5FeNaZ catalyst in dehydrogenation of ethylbenzene: See Figure 1 for reaction conditions except for pretreatments. The pretreatments consist of heating at 600 °C with 20 mL of several carrier gases, *i.e.*, N₂ for 60 min, CO₂ for 10 min, and 5% H₂ for 60 min, respectively. Letters in parenthesis denote carrier gas for pretreatment.

thermogravimetric analysis, assuming that the weight loss is due to the removal of the oxygen ions from iron oxide.^{22,23} However, for the dispersed iron oxides it is very difficult to measure exactly the oxygen deficiencies due to low content of iron and mix-up of lattice oxygens between iron oxide and zeolite support. Oxygen deficiencies of the supported iron oxide catalysts were examined indirectly by measuring CO produced from the CO₂ dissociation *via* CO₂ pulse reaction after slightly reducing the catalysts with 5% H₂ at 500 °C for 1 h. Oxygen deficiencies of the iron oxide-based catalysts produced by reductive treatments provide significant activity for the CO₂ dissociation even at 400 °C as shown in Table 1. In all cases, the amount of CO formed during the CO₂ pulse experiments decreased greatly at initial stage and gradually at later stages with an increase of the pulse numbers. Highly dispersed iron oxides in zeolite matrix give the higher specific activities as compared to unsupported Fe₃O₄. It is considered that oxygen deficiency of iron oxide in the supported catalyst is one of the most important factors on promoting the catalytic activity in the presence of CO₂. Oxygen-deficient sites of the supported iron oxide catalyst seem to produce CO efficiently from the

Table 1. Dissociation of carbon dioxide over zeolite-supported and unsupported iron oxide catalysts at 400 °C*

Catalyst	Amount of CO formed (μmol/g-cat.) ^a	Specific Conversion ^b
Fe ₃ O ₄	11.8	2.7
1.5FeNaZ	4.6	70.9
5FeNaZ	6.2	28.7

*measured after reduction at 500 °C for 1 h with 5% H₂. ^aOne pulse contained 30.2 μmol of CO₂. ^bunit: mol of CO mol of metal oxide.

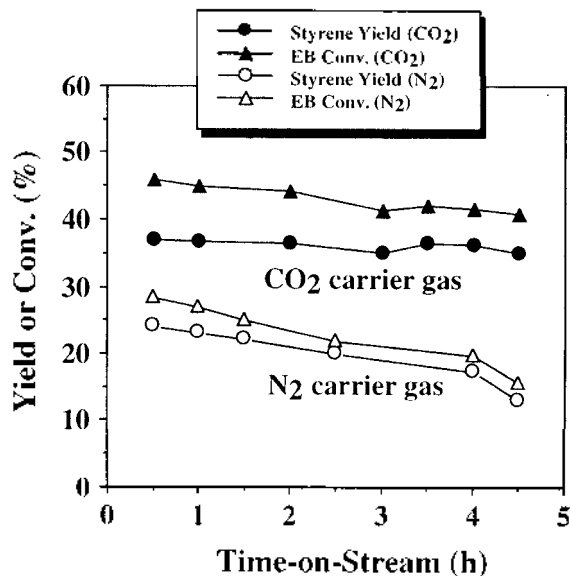


Figure 5. Change in catalytic activity with reaction time on dehydrogenation of ethylbenzene over 5FeNaZ catalyst depending on carrier gas. See Figure 1 for reaction conditions.

CO₂ dissociation, and the adsorbed oxygen on the catalyst surface can also play a role on hydrogen abstraction from EB. Dispersion of the oxygen-deficient sites or oxygen defects in the supported iron oxide catalysts seems to be more efficient for the CO₂ dissociation and thereby the oxidative dehydrogenation of EB.

The Role of Carbon Dioxide. In addition to the enhancement of the catalytic activity, the use of carbon dioxide as a carrier gas has also a great influence on the catalyst stability. As shown in Figure 5, the activity of the 5FeNaZ catalyst under a N₂ stream decreases monotonically with the reaction time, while the formation of hydrogen increases remarkably with the reaction time due to acceleration of coke formation. It is known that reversible short-term deactivation is caused by deposition of carbonaceous material from product condensation.¹¹ The deactivation of catalyst in this reaction seems to be mainly caused by the coke deposition from growth of polyaromatics on the catalyst surface, which was reduced rapidly compared to CO₂ atmosphere. However, the catalytic activity under a CO₂ stream maintains without significant decay of the activity. This means that carbon dioxide leads to enhancing the coke resistance to the supported iron oxide catalyst and consequently extending catalyst lifetime during the reaction. Suzuki and co-worker showed that iron loaded on activated carbon has high activity in the CO₂ gasification of various carbon materials.²⁴ According to our previous result, the surface enrichment of adsorbed CO₂ species on supported Ni catalyst could contribute to enhancement of the coke resistance and lifetime of the catalyst during the CO₂ reforming of methane.²⁵ In other words, the oxidation step of surface carbon with carbon dioxide or surface oxygen produced from the dissociative adsorption of CO₂ over supported Ni catalyst contributed to maintaining high catalyst stability through the effective removal of surface coke species. In this respect, it can be also concluded that carbon dioxide in the EB dehydrogenation plays a role of

oxidant for promoting the oxidation of surface coke over the supported iron oxide catalyst.

Conclusions

Dispersed iron oxide catalyst on NaZSM-5 zeolite support has been prepared by suspension-deposition method in nitrogen atmosphere. The catalytic activity has been compared with those of bulk Fe_3O_4 oxide and a commercial catalyst towards dehydrogenation of ethylbenzene with carbon dioxide or nitrogen. The dehydrogenation of ethylbenzene with carbon dioxide over the NaZSM-5 zeolite-supported iron oxide catalyst proceeds predominantly via an oxidative pathway to produce styrene. Using carbon dioxide as an oxidant and carrier, the remarkable enhancements have been achieved with our FeNaZ catalysts in not only the dehydrogenation activity but also the coke resistance. However, the catalytic activities of the commercial catalyst and bulk Fe_3O_4 oxide decreased in the presence of carbon dioxide. From these results, it may be concluded that the active site for the oxidative dehydrogenation with carbon dioxide is a reduced and isolated magnetite-like phase with oxygen deficiency in zeolite matrix, rather than bulk Fe_3O_4 .

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