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

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In dehydrogenation of ethylbenzene with carbon dioxide over zeolite-supported iron oxide catalyst, ethylbenzene was predominantly converted into styrene by an oxidative manner. Carbon dioxide in this reaction played a role as an oxidant to greatly improve catalytic activity as well as coke resistance of catalyst.

Various reactions have been tried to transform carbon dioxide into valuable products by catalytic methods.[1] Most of them are concentrated on the utilization of carbon dioxide as a carbon source through catalytic reduction processes. However, carbon dioxide can play a role as an oxygen source or oxidant since it has been considered as a nontraditional, unusual or mild oxidant in several oxidative conversions.[2-5] Commercially, styrene is produced mainly by dehydrogenation of ethylbenzene (EB) using iron oxide-based catalysts with superheated steam. In this case, small amount of carbon dioxide formed as a by-product was known to inhibit the catalytic activity of commercial catalyst.[6,7] Recently, there has been some reports which carbon dioxide showd positive effects to promote catalytic activities on the reaction over several catalysts.[5,8,9] This study is a trial to figure out the role of carbon dioxide in dehydrogenation of ethylbenzene over ZSM-5 zeolite-supported iron oxide catalyst.

Zeolite-supported iron oxide (FeNaZ) catalyst was prepared by precipitation of aqueous suspension of $FeSO_4$ onto zeolite support in slightly alkaline solution at 60 °C under N_2 atmosphere to avoid oxidative condition. Highly siliceous NaZSM-5 zeolite (Uetikon PZ-2/980, Si/Al = 1900) was used for supporting catalyst. This catalyst was dried in vacuo at 80 °C and calcined under N_2 flow at 400 °C for 3 h. Loading of iron oxide was 5.0 wt.% as Fe_3O_4. Bulk Fe_3O_4 oxide which was prepared by above method in the absence of zeolite support and commercial catalyst (bulk K-Fe_2O_3, Nissan Girdler G-64 JX) were compared their catalytic activities with FeNaZ. Dehydrogenation of ethylbenzene into styrene was carried out in a conventional flow-type quartz reactor (10 mm i.d., 300 mm length) operated at 600 °C and under atmospheric pressure. Ethylbenzene was supplied to the reactor by flowing carbon dioxide or nitrogen through ethylbenzene saturator kept at 25 °C.

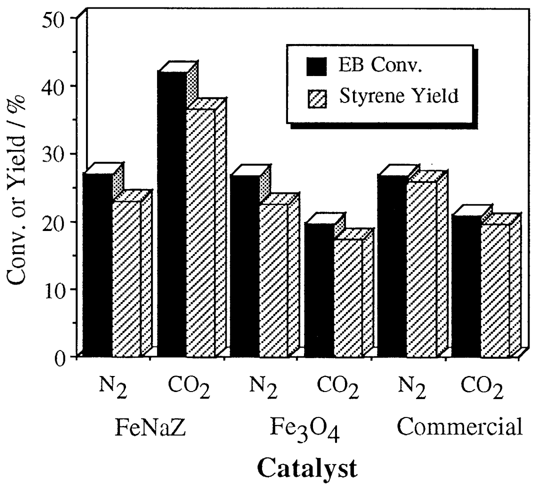

Figure 1. Effect of CO_2 oxidant on ethylbenzene dehydrogenation over FeNaZ catalyst: Temp. = 600 °C, W/F = 300 g.h/mol, CO_2 (or N_2)/EB = 80 (mol. ratio).

Dehydrogenation activity of ethylbenzene was measured after treating catalysts with nitrogen flow at 600 °C for 1 h prior to reaction. Dehydrogenation of ethylbenzene with carbon dioxide over FeNaZ catalyst produced styrene, water and carbon monoxide with small amount of hydrogen, which was only less than 25 % of carbon monoxide produced. Moreover, small amount of oxygenated by-product such as benzaldehyde was formed with benzene and toluene. This result showed that dehydrogenation over zeolite-supported iron oxide catalyst was predominantly enhanced by oxidative pathway. The formation of water as well as carbon monoxide in this reaction implied that CO_2 molecule could be dissociated into CO and surface oxygen which could abstract hydrogen from ethylbenzene and form water. In addition, water would be also produced partially via reverse water-gas shift reaction. It was known that the alleviation of the equilibrium limitation in the dehydrogenation of ethylbenzene was achieved by effective removal of produced hydrogen through coupling reaction with the reverse water-gas shift reaction.[9] Catalytic behaviors of FeNaZ, bulk Fe_3O_4, and commercial K-promoted Fe_2O_3 catalysts were shown to have great differences in the presence or the absence of carbon dioxide (Figure 1). When the reaction was conducted under an inert nitrogen stream, these catalysts showed similar dehydrogenation activities. However, catalytic activities between FeNaZ and latter two catalysts were quite different when carbon dioxide was used instead of nitrogen as a carrier gas. Latter bulk catalysts exhibited considerable decrease of catalytic activity in the presence of carbon dioxide. On the other hand, the use of carbon dioxide over FeNaZ catalyst induced large enhancement of the activity. In the presence of CO_2, styrene yield on FeNaZ catalyst was more than 2.5 times comparing with those on bulk catalysts. This explains that carbon dioxide played a role as an oxidant in dehydrogenation of ethylbenzene on FeNaZ catalyst, whereas on the two catalysts carbon dioxide were considered to decompose active phase or inhibit the dehydrogenation on their active sites.[6]

The co-feeding of carbon dioxide had also an influence on the catalyst stability. As shown in Figure 2, the activity of FeNaZ catalyst under a N_2 stream decreased monotonically with the reaction time and the reaction was abruptly stopped due to

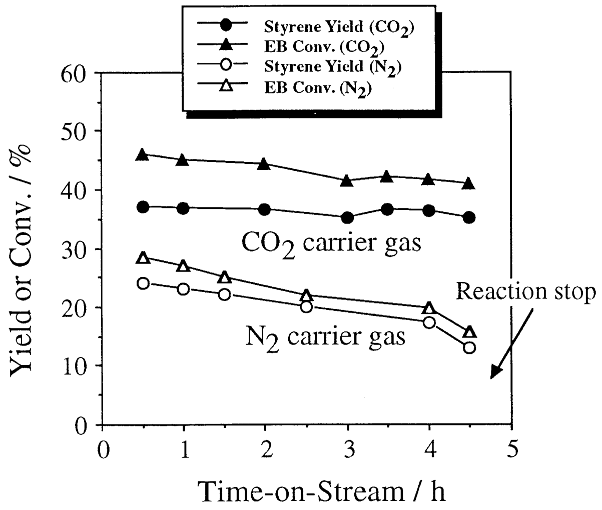

Figure 2. Change in activity with time-on-stream on ethylbenzene dehydrogenation over FeNaZ catalyst depending on carrier gas. See Figure 1 for the reaction conditions.

the plugging of coke after 5 h of the reaction time. This catalyst deactivation under a N_2 stream seemed to be mainly caused by coke deposition from the growth of polyaromatics on catalyst surface. However, the catalytic activity under a CO_2 stream was maintained without significant decay of activity. This means that carbon dioxide contributed to the enhancement of the coke resistance of FeNaZ catalyst and consequently it gave a prolonged catalyst lifetime. Accordingly, it is demonstrated that carbon dioxide could play a role as an oxidant in the dehydrogenation of ethylbenzene by producing CO and supplying surface oxygen simultaneously, which could prevent the deposition of coke over supported iron oxide catalyst and could enhance the dehydrogenation activity by abstracting hydrogen from ethylbenzene like oxidative manner.

Even with the same iron oxide loading and support, catalyst prepared by impregnation under fully oxidizing condition exhibited much lower activity than the FeNaZ catalyst. In addition, the catalyst pretreated with nitrogen at 600 °C showed high activity compared to the case of pretreatment with air or H_2 at 600 °C. These results suggest that the catalyst need to get optimum population of oxidation states of Fe, which is probably between +2 and +3, in order to show high and stable activity in the dehydrogenation of ethylbenzene with carbon dioxide. This population could be controlled properly under carbon dioxide stream. Therefore, an active phase of iron oxide in the catalyst would be considered to be rather reduced iron oxide like Fe_3O_4 dispersed on zeolite support.[10] BET analysis showed that iron oxide of ZSM-5 zeolite-supported catalysts was highly dispersed in the zeolite matrix.[10] XPS results of the Fe 2p and O 1s spectra provided that highly dispersed iron oxide on the supported catalysts was found to be mainly metastable Fe_3O_4-like phase,[10] showing characteristic of Fe_3O_4 oxide with an apparent lack of satellite structure at 719.1 eV, different from Fe_2O_3 oxide. In addition, oxygen deficiency of iron oxide in FeNaZ catalyst also affected on the catalytic activity.[10] Oxygen deficient sites of supported iron oxide would stimulate the CO_2 dissociation into CO. The dissociated oxygen on the catalyst surface would abstract hydrogen of ethylbenzene or convert hydrogen molecule produced into water. Dispersion of the oxygen deficient sites or oxygen defects seemed to be major factor for the CO_2 dissociation and thereby the oxidative dehydrogenation of ethylbenzene.

Therefore, it can be concluded that carbon dioxide contributes to remarkable enhancement of the dehydrogenation activity as well as the coke resistance in the reaction, and that active phase of iron oxide in the catalyst is considered to be rather reduced iron oxide like Fe_3O_4 dispersed in zeolite matrix.

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