

Ethyl Benzene Dehydrogenation in the Presence of Carbon Dioxide Over Fe₂O₃-Cr₂O₃ Catalyst

AHMED AOUISSI*, ZEID ABDULLAH AL-OTHMAN and HOCEINE BAYAHIA
Chemistry Department, College of Science, King Saud University, Riyadh, Saudi Arabia
E-mail: aouissed@yahoo.fr

Fe₂O₃-Cr₂O₃ was prepared by co-precipitation method, characterized by means of FTIR and X-ray diffraction (XRD) and tested in the dehydrogenation of ethyl benzene in the presence of carbon dioxide. It was found that the main oxide phases forming the catalysts were Fe₂O₃ and Cr₂O₃. The effect of the contact time (W/F) and the reaction temperature on the catalytic activity were investigated. It was noted that the conversion and the yield of products increased with an increase in W/F from 4.06-12.20 g h/mol. Further increase of W/F did not influence the activity. As for the effect of the reaction temperature, it was found that at higher temperatures, a decrease in the activity with time on stream occurred, owing to coke deposit. The selectivity of the reaction products remained constant for temperatures below to 700 °C. Further increase in the temperature decreased the selectivity of styrene in favour of that of toluene and benzene.

Key Words: Mixed oxides, Ethyl benzene, Dehydrogenation, Styrene, Carbon dioxide.

INTRODUCTION

Styrene is one of the most important monomers that have been extensively used for the manufacture of synthetic polymers. It is commercially produced by the dehydrogenation of ethyl benzene on the promoted iron oxide catalysts in the presence of a large quantity of steam at temperatures ranging between 600-700 °C. It has been pointed out that the industrial process wastes a large amount of latent heat of steam condensation at a liquid-gas separator. The heat consumption during this process is a substantial part of the total costs of the styrene production. Taking in account the world's demand for styrene, alternative methods for its production are still searched and tested. The process with direct use of oxygen for oxidative dehydrogenation has not been realized yet because of a significant loss of styrene selectivity by the production of carbon oxides and oxygenates caused by burning of hydrocarbons with oxygen¹. An another oxidant *viz.*, SO₂ was tested but its use is not attractive owing to the formation of toxic by products². In recent years, much attention has been paid to utilization of CO₂ because it is an abundant, cheap carbon resource and a non-toxic reaction medium³⁻⁶. Moreover, the process of converting "waste" CO₂ into a versatile chemical product is regarded as a highly green chemical process⁷.

Recently, the utilization of carbon dioxide has been extensively utilized by several authors⁸⁻¹² for the last two decades in the dehydrogenation of ethyl benzene to styrene as oxidant as well as diluent instead of steam. Moreover Mamedov and Corberan¹³ reported that one of the main roles of CO₂ in the catalytic dehydrogenation process is the removal of the deposited coke that contributes to the catalyst deactivation.

Since the industrial process for the dehydrogenation of ethyl benzene in the presence of super heated steam uses supported iron oxide promoted by potassium and chromium catalyst, we report in this work the catalytic properties of a Fe₂O₃-Cr₂O₃ bulk mixed oxide for the reaction in the presence of CO₂. The catalyst was prepared by co-precipitation method and characterized by FTIR and X-ray powder diffraction. The effect of the contact time and the reaction temperature on the activity of the catalyst during the dehydrogenation was investigated.

EXPERIMENTAL

Preparation and characterization of catalysts: The metal salt catalyst precursors were prepared by co-precipitation method according to the Herman-Klier co-precipitation method¹⁴. A desired volumes of 1 M Cr(NO₃)₃·9H₂O and 1 M Fe(NO₃)₃·6H₂O aqueous solutions were mix together in a flask. The volumes were selected to obtain Fe/Cr molar ratio equal to 1/1 in the final binary oxides. The mixture under stirring at 85 °C was co-precipitated by 1 M NaOH. At the end of the co-precipitation (pH 6.5), the heating was stopped, while the stirring was extended for an extra 1 h. Then the resulting precipitate was filtrated, washed twice with distilled water and then dried overnight at 120 °C. The precursor salt was calcined at 750 °C in stainless steel reactor with air flow of 6 l/h. The sample was heated first to 120 °C for 0.5 h then the temperature was increased to 750 °C for 3.5 h.

Characterization of catalysts: Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku diffractometer Ultima IV using monochromatized Cu-K α ($\lambda = 1.5418 \text{ \AA}$) radiation. Fourier transform-infrared spectra of the samples were recorded with Shimadzu FTIR Spetrometer 8400S at ambient conditions *via* grinding the sample with KBr and then pressed.

Reaction and analysis: The dehydrogenation of ethyl benzene in the presence of CO₂ was carried out in flow fixed bed reactor loaded with a fresh sample of catalyst under atmospheric pressure. Prior to dehydrogenation of ethyl benzene, a sample of a mixed oxides catalyst was pretreated at 700 °C for 1 h with 50 mL min⁻¹ CO₂ gas. Then, the reactant mixture n(CO₂)/n(C₆H₅C₂H₅) (11.7/1.0 molar ratio) at a flow rate of 50 mL min⁻¹ was passed through the catalyst at 660 °C. The flow of CO₂ gas was controlled by mass flow controller. Ethyl benzene was fed to the reaction system with syringe pump. The reaction products were analyzed with a gas phase chromatograph (Agilent 6890N) equipped with a flame ionization detector, a thermal conductivity detector and a capillary column (HP-PLOT Q length 30 m ID 0.53 mm).

RESULTS AND DISCUSSION

The infrared spectrum of the sample in the range from $4000\text{-}400\text{ cm}^{-1}$ is shown in Fig. 1. The IR band at 3464 cm^{-1} corresponds to the stretching vibrations of adsorbed H_2O molecules. The IR band at 1626 cm^{-1} is normally attributed to O-H bending vibrations¹⁵. The bands in the region between 800 and 400 cm^{-1} could be assigned to M-O lattice vibration¹⁶⁻²¹. The band at 945 and 897 cm^{-1} are assigned to Cr-O-Cr vibrations and Fe-O-H bending vibrations²², respectively.

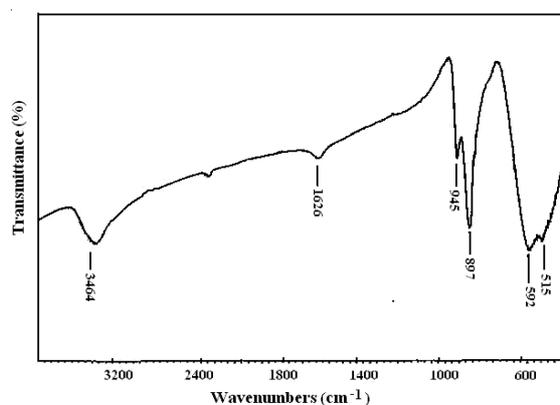


Fig. 1. FTIR spectra of the prepared $\text{Fe}_2\text{O}_3\text{-Cr}_2\text{O}_3$

Phase identification was performed by comparing the experimental X-ray diffraction pattern results (Fig. 2) with the reported XRD data in ICDD (international centre for diffraction data) and JCPDS (joint committee on powder diffraction standards). The main oxide phases identified were Fe_2O_3 (JCPDS card file. 84-0307) and Cr_2O_3 (JCPDS No. 01-1294). Nevertheless, other phases were could be present as traces. In fact, it has been reported for several oxides, the coexistence of various phases besides the main phase²³⁻²⁵.

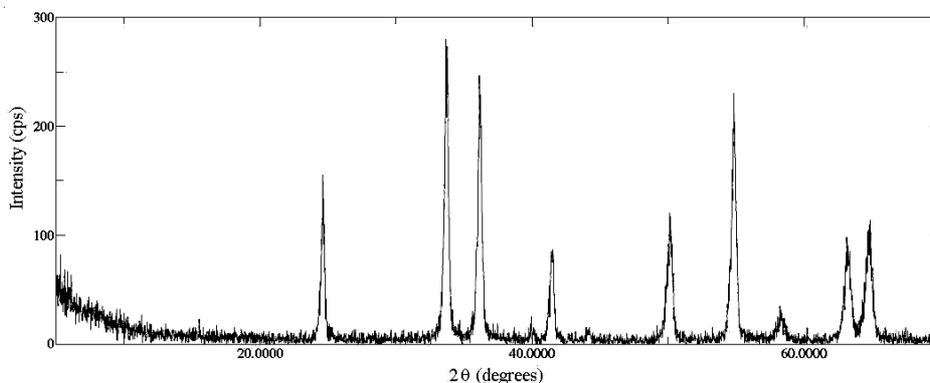


Fig. 2. XRD patterns of the prepared $\text{Fe}_2\text{O}_3\text{-Cr}_2\text{O}_3$

Catalytic activity

Change in the activity with time on stream for various contact time: The dependence of ethyl benzene conversion with time on stream for various contact time (W/F) is presented in Fig. 3. The data were obtained by varying the weight of the catalyst keeping the flow rates of ethyl benzene as well as CO₂ constant at 11.7 molar ratio of CO₂ to ethyl benzene. It can be seen that for short contact time the conversion remains stable with time on stream, whereas for longer contact time a decrease of the conversion was observed. The deactivation was due to the carbon deposit which is proportional to the conversion. As for the selectivity of the ethyl benzene products, it can be seen from the Fig. 4 that the styrene selectivity decreases slightly for almost W/F. This result is in agreement with that of Nakagawa *et al.*²⁶ where it was mentioned that the acidic sites are the active sites for the dehydrogenation of ethane in the presence of CO₂, so CO₂ may promote rapid desorption of products from the surface of the catalyst and then suppress coke formation.

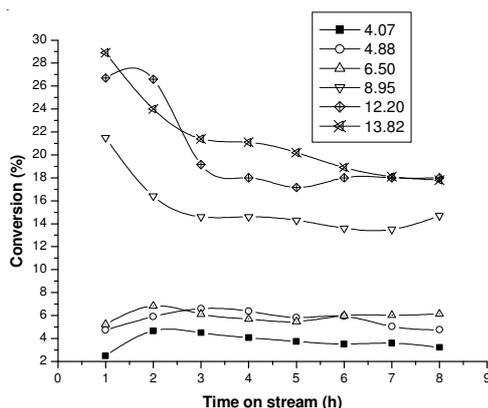


Fig. 3. Variation of the conversion with time on stream for various W/F over Fe₂O₃-Cr₂O₃ catalyst

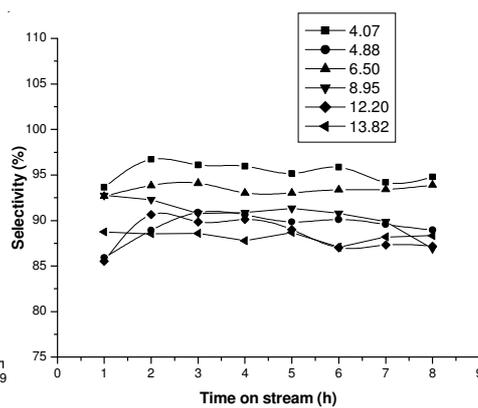


Fig. 4. Variation of the selectivity of styrene with time on stream for various W/F Fe₂O₃-Cr₂O₃ catalyst

Dependence of the activity on the contact time: The effect of W/F on the activity of ethyl benzene is shown in Fig. 5. It can be seen that the conversion and the yields increased sharply when W/F was increased from 4-11 g h/mol. Further increase of contact time did not influence the ethyl benzene conversion considerably. Fig. 6 showed that the W/F has no influence on the selectivities in this range of W/F. The selectivity of styrene (89 %) and that of cracking products (11 %) remains constant. This result is in agreement with that of Ohishi *et al.*²⁷ where it was reported that W/F has no significant effect on the selectivity of styrene.

Fig. 7 shows the dependence of the yields on the conversion. It can be seen that the yield of each product namely styrene, toluene and benzene is directly proportional to the conversion. This result indicates that the formation of the products is

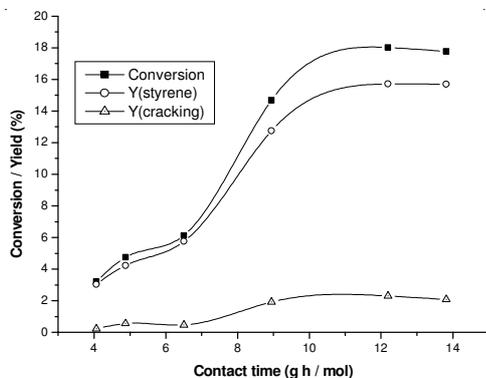


Fig. 5. Evolution of the conversion of ethylbenzene and the yield of the products with W/F $\text{Fe}_2\text{O}_3\text{-Cr}_2\text{O}_3$ catalyst

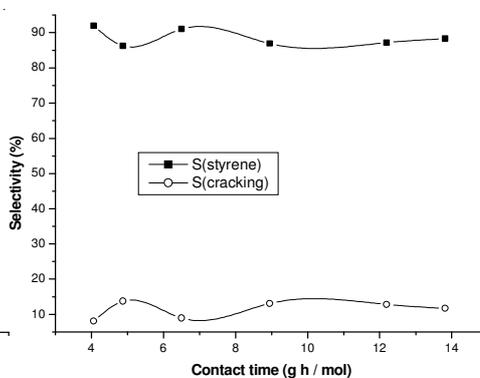


Fig. 6. Evolution of the selectivity to styrene and cracking products with W/F over $\text{Fe}_2\text{O}_3\text{-Cr}_2\text{O}_3$ catalyst

achieved by parallel reactions. It is likely that a part of benzene forms directly from ethyl benzene by thermal cracking, whereas toluene mainly forms *via* catalytic C-C bond fission from ethyl benzene or styrene over the catalyst.

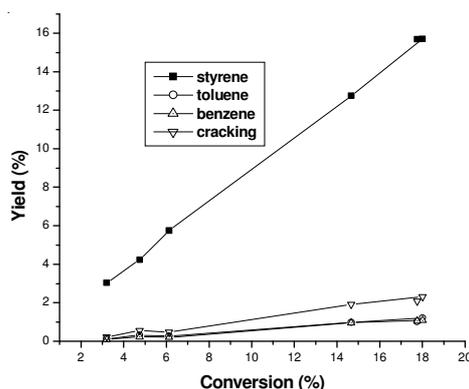


Fig. 7. The dependence of the product yields on the conversion ethyl benzene over $\text{Fe}_2\text{O}_3\text{-Cr}_2\text{O}_3$ catalyst

Effect of reaction temperature

Change in the activity with time on stream: The effect of reaction temperature was investigated at the temperatures ranging from 620-770 °C. The change of the conversion and the selectivity of the products at each reaction temperature with time on stream are shown in Fig. 8. It can be seen that the deactivation of the catalyst occurred for higher temperatures. The deactivation is due to the formation of coke at higher temperatures which inhibited the active sites of the catalyst. As for the change of the selectivity with time on stream for various reaction temperatures (Figs. 9 and 10), it was noted that higher temperatures decreased the selectivity of styrene in favour of the selectivity of the cracking products with time on stream.

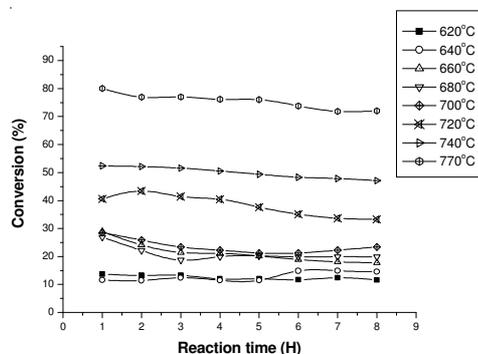


Fig. 9. Variation of the conversion with time on stream for various reaction temperature over $\text{Fe}_2\text{O}_3\text{-Cr}_2\text{O}_3$ catalyst

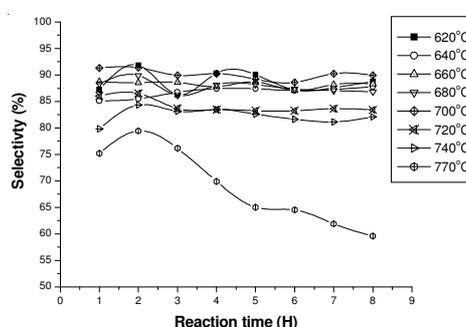


Fig. 10. Variation of the styrene selectivity with time on stream for various reaction temperature over $\text{Fe}_2\text{O}_3\text{-Cr}_2\text{O}_3$ catalyst

Effect of reaction temperature: The influence of the conversion and the yield of the reaction products with the reaction temperature are shown in the Fig. 11. It was found that the conversion and the cracking yield increased with increasing the temperature in all the range of the temperature, whereas for the styrene yield, no significant change was observed for the temperatures above 740 °C. Fig. 12 presents the effect of variation of reaction temperature on the selectivity. It was found that the selectivity of styrene and cracking products are almost constant for the temperatures below 740 °C. For further temperatures, the selectivity of styrene decreased in favour of that of toluene and benzene. It was reported²⁷ that benzene forms directly from ethyl benzene by thermal cracking, whereas toluene mainly forms *via* catalytic C-C bond fission from ethyl benzene over the catalyst. Since toluene formation was significantly enhanced above 740 °C it is concluded that catalytic cracking of ethyl benzene was more accelerate than thermal cracking at high temperatures over $\text{Fe}_2\text{O}_3\text{-Cr}_2\text{O}_3$ catalysts.

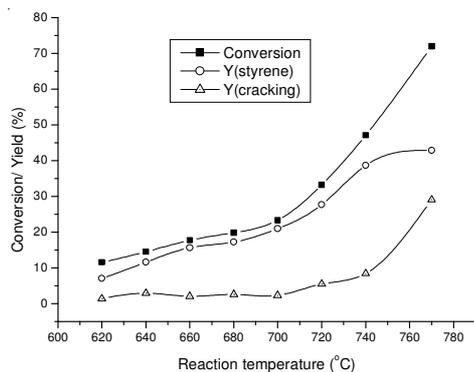


Fig. 11. Variation of the conversion with time on stream for various reaction temperatures

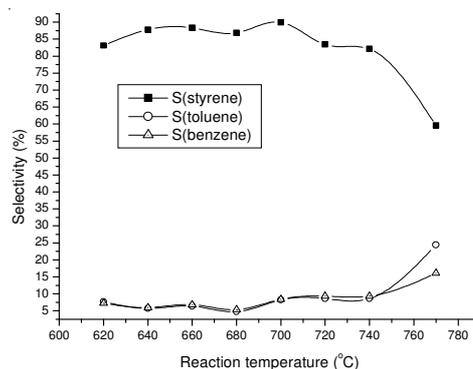


Fig. 12. Variation of the selectivity of styrene and cracking products with time on stream for various reaction temperature

Conclusion

The increase of W/F increased the conversion of dehydrogenation of ethylbenzene in the presence of CO₂ over Fe₂O₃-Cr₂O₃, but did not have a significant change in the activity for higher W/F. The increase of W/F decreased the selectivity of styrene in favour of the selectivity of cracking products, probably owing to the inhibition of the active sites by carbon deposited. The directly proportionality of the yield of styrene, toluene and benzene, to the conversion suggests that the formation of these products occurs by parallel reactions. The decrease in styrene selectivity with the increase of the reaction temperature was due to cracking of ethyl benzene into benzene and toluene. Enhancement of toluene formation compared with that of benzene was above 740 °C suggests that catalytic cracking of ethyl benzene was more accelerated than thermal cracking at high temperatures over Fe₂O₃-Cr₂O₃ catalyst.

REFERENCES

1. F. Cavani and F. Trifiro, *Appl. Catal. A.*, **133**, 219 (1995).
2. C.R. Adams and T.J. Jennings, *J. Catal.*, **17**, 157 (1970).
3. J.H. Clark, *Green Chem.*, **1**, 1 (1999).
4. P.T. Anastas, *Green Chem.*, **5**, 29 (2003).
5. T.C. Williamson, M. Kirchoff and P.T. Anastas, *Green Chem.*, **2**, 85 (2000).
6. P.T. Anastas and R.L. Lankey, *Green Chem.*, **2**, 289 (2000).
7. J.C. Choi, T. Sakakura and T. Sako, *J. Am. Chem. Soc.*, **121**, 3793 (1999).
8. M. Sugino, H. Shimada, T. Turuda, H. Miura, N. Ikenaga and T. Suzuki, *Appl. Catal. A.*, **121**, 125 (1995).
9. N. Mimura, I. Takahara, M. Saito, T. Hattori, K. Ohkuma and M. Ando, *Catal. Today*, **45**, 61 (1998).
10. T. Badstube, H. Papp, P. Kustrowski and R. Dziembaj, *Catal. Lett.*, **55**, 169 (1998).
11. M.S. Park, V.P. Vislovskiy, J.-S. Changa, Y.-G. Shul, J.S. Yoo and S.-E. Park, *Catal. Today*, **87**, 205 (2003).
12. J.-N. Park, J. Noh, J.-S. Chang and S.-E. Park, *Catal. Lett.*, **65**, 75 (2000).
13. E.A. Mamedov and V.C. Corberan, *Appl. Catal. A*, **127**, 1 (1995).
14. R.G. Herman, K. Klier, G.W. Simmons, B.P. Finn and J.B. Bulko, *J. Catal.*, **56**, 407 (1979).
15. A. Zecchina, S. Coluccia, E. Guglielminotti and G. Ghiotti, *J. Phys. Chem.*, **75**, 2774 (1971).
16. G. Arzamendi, V.A. de la Pena O'Shea, M.C. Alvarez-Galvan, J.L.G. Fierro, P.L. Arias and L.M. Gandia, *J. Catal.*, **261**, 50 (2009).
17. C.-Y. Chen, C.-K. Lin, M.-H. Tsai, C.-Y. Tsay, P.-Y. Lee and G.-S. Chen, *Ceramics Int.*, **34**, 1661 (2008).
18. L. Verdonck, S. Hoste, F.F. Roelandt and G.P. Van der Kelen, *J. Mol. Struct.*, **79**, 273 (1982).
19. P. Cambier, *Clay Miner.*, **21**, 191 (1986).
20. X. Xua., J. Wang, C. Yang, H. Wu and F. Yang, *J. Alloys Compounds*, **468**, 414 (2009).
21. Y. Hong, T.T. Pan, Y.P. Han, H.Z. Li, J. Ding and S.J. Han, *J. Magn. Magn. Mater.*, **310**, 37 (2007).
22. Z.-M. Yao, Z.-H. Li and Y. Zhang, *J. Colloid Interface Sci.*, **266**, 382 (2003).
23. M.M. Rashad, *Mater. Sci. Eng. B*, **127**, 123 (2006).
24. L. Biernacki and S.J. Pokrzywnicki, *Thermal Anal. Calorimetry*, **55**, 227 (1999).
25. T. Kohler, T. Armbruster and E. Libowitzky, *J. Solid State Chem.*, **133**, 486 (1997).
26. K. Nakagawa, C. Kajita, K. Okumura, N. Ikenaga, M. Nishitani, T. Anpo, T. Kobayashi and T. Suzuki, *J. Catal.*, **203**, 87 (2001).
27. Y. Ohishi, T. Kawabata, T. Shishido, K. Takaki, Q. Zhang, Y. Wang and K. Takehira, *J. Mol. Catal. A: Chem.*, **230**, 49 (2005).