



Dehydrogenation of Ethylbenzene in the Presence of CO₂ Over Iron-Chrome Binary Oxide Catalytic System

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A series of iron-chrome binary oxide with different ratios were prepared by co-precipitation method and calcination at 750 °C. The oxides were characterized by means of FTIR, X-ray powder diffraction (XRD) and tested in the dehydrogenation of ethylbenzene in presence of carbon dioxide. The results showed that the main oxide phases forming the binary oxides catalysts were α -Fe₂O₃ and Cr₂O₃. Exceptionally, the binary oxides with equal Fe and Cr molar ratio showed modified structural characteristics as compared with the corresponding pure oxides, α -Fe₂O₃ and Cr₂O₃. The catalytic tests for dehydrogenation of ethylbenzene with CO₂ showed that catalysts with high and low Fe content enhanced the formation of cracking products, whereas those with equal Fe/Cr ratios increased the styrene formation.

Key Words: Mixed oxides, Ethylbenzene, Styrene, Carbon dioxide, Iron oxide.

INTRODUCTION

Styrene is one of the most important chemicals in the petrochemical industry. Its production from ethylbenzene by dehydrogenation reaction is one of the most important catalytic processes. The reaction is achieved by using promoted iron oxide catalysts at 600-700 °C, just below the temperature where thermal cracking becomes significant. Due to its highly endothermic and volume-increasing character, a large amount of superheated steam is used to supply heat and to lower the partial pressure of the reactant. However, much of the latent heat of steam is lost in the gas-liquid separator¹. In addition, the process is thermodynamically limited and poorly selective². Furthermore, due to the reversible character of the process, the styrene yield cannot exceed 50 %³. Consequently, research to improve this industrial process is continuously in progress in order to develop new routes. As an alternative way, oxidative dehydrogenation of ethylbenzene using O₂ as an oxidant agent has been proposed in order to circumvent some of the cited difficulties⁴. In fact, the oxidative dehydrogenation of ethylbenzene is free from thermodynamic limitations and can be operated at lower temperatures, due to the exothermic character of the reaction. However, in the oxidative dehydrogenation process the usage of O₂ (strong oxidant) produces undesired by-products (oxygenates) along with styrene resulting in low selectivity of styrene⁵. Another oxidant *viz.*, SO₂ was tested but its use is not attractive owing to the formation of toxic by-products⁶. Recently, the use of carbon dioxide as a

mild oxidant for the dehydrogenation of ethylbenzene has received much attention⁷⁻¹². The reason of this attention is due to the abundance, low cost, the non-toxicity and the non-flammability of the carbon dioxide, compared to oxygen. In addition, its utilization as gas co-feeder in the ethylbenzene dehydrogenation reaction offer several advantages such as enhancement in product selectivity, alleviation of thermodynamic equilibrium limitations, avoidance of total oxidation and prevention of hot spots on the catalyst surface. Hence, alternative oxidative dehydrogenation of ethylbenzene with CO₂ oxidant has been emerging as a potential process¹³⁻¹⁵. Besides, the dehydrogenation of ethylbenzene to styrene in the presence of CO₂ instead of steam is believed to be an energy-saving and environmentally friendly process. In fact, Mimura and Saito¹⁶ reported that the simple replacement of water steam with CO₂ in a styrene installation should diminish the energy consumption. However, the poor reactivity of CO₂ molecule (thermodynamically stable) is a serious drawback. In order to obtain more efficient catalysts, several catalysts have been tested in dehydrogenation of ethylbenzene in presence of CO₂¹⁷⁻¹⁹, it has been reported that the effect of CO₂ on the dehydrogenation of ethylbenzene depend on the nature of the catalyst used. Therefore, the current challenge is to tailor a catalyst capable of favouring hydrogen abstraction from hydrocarbons over the oxygen insertion in the olefins formed²⁰. Catalysts based on iron oxide, supported on aluminum oxide, are reported to be the efficient in the dehydrogenation reaction^{2,21,22}. It is well known that adding Cr₂O₃ to the iron

oxide catalysts enhances their activity and discourages sintering^{23,24}. In order to obtain more detailed information on the dehydrogenation of ethylbenzene in the presence of CO₂ over the iron-based catalyst, the effects of iron content in the binary α -Fe₂O₃ - Cr₂O₃ mixed oxides, the temperature and the change in the activity of the catalyst during the dehydrogenation were investigated in the present study.

EXPERIMENTAL

Preparation and characterization of catalysts: The metal salt catalyst precursors were prepared according to the Herman-Klier co-precipitation method²⁵. The procedure consists of addition by drops of a molar solution of Na₂CO₃ into an aqueous mixture solution of 1 M Cr(NO₃)₃·9H₂O and 1 M Fe(NO₃)₃·6H₂O having 1 M concentration each. The volumes in the mixture solution were selected to obtain the desired Fe/Cr molar ratio in the final binary oxides. The mixture was stirred and maintained at 85 °C. The evolution of the co-precipitation was followed with a pH-meter. 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 and washed twice with distilled water and then dried overnight at 120 °C. The precursor salt was calcined at 750 °C in stain 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. The final products are referred to as Cr-Fe-x, where x represents the iron molar ratio in Cr-Fe. Cr-Fe-x oxides with x values of 0, 10, 30, 50, 70, 90 and 100 were prepared.

Characterization of catalysts: The powder X-ray diffraction (XRD) patterns were obtained on a Siemens D5000 diffractometer with CuK α (λ = 1.5418 Å) 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.

Catalyst tests: The dehydrogenation of ethylbenzene in the presence of CO₂ was carried out in flow fixed bed reactor at a contact time of 13.8 g h/mol under atmospheric pressure. Prior to dehydrogenation of ethylbenzene, 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(ethylbenzene) (11.7/1 molar ratio) at a flow rate of 50 mL min⁻¹ was passed through the catalyst at 700 °C. The flow of CO₂ gas was controlled by mass flow controller. Ethylbenzene was fed to the reaction system with syringe pump. The reaction products were analyzed with a gas phase chromatograph (Agilent 6890 N) 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

X-ray powder diffraction: The XRD patterns of samples with different compositions calcined at 750 °C are shown in Fig. 1. It can be seen from the figure that Fe₂O₃ and Cr₂O₃-alone products showed the typical patterns of the corresponding oxides, α -Fe₂O₃ with hematite structure and Cr₂O₃, matching the JCPDS No. 84-0307 and JCPDS No. 01-1294 respectively. As for the rest of the series of catalysts, the results showed

that they contain as main component α -Fe₂O₃ and Cr₂O₃ oxide. Nevertheless, other phases could be present as traces. In fact, it has been reported for several oxides, the coexistence of various phases besides the main phase^{26,27}. Table-1 presents the *d*-spacings that correspond to the most significant peaks in the patterns of the three composites and the two pure oxides. The results indicated that the mixed oxides have slightly different values than the pure oxides depending on the Cr/Fe ratio. In the cases of low concentration of one component, Cr-Fe-10 and Cr-Fe-90, the deviation from the corresponding one-metal oxides, α -Fe₂O₃ and Cr₂O₃ respectively, is very small or negligible. The peaks lie in between those of α -Fe₂O₃ and Cr₂O₃ and have relative intensities different from those of both oxides. As for, the XRD pattern of Cr-Fe-50, the peak with inter-planar *d* = 3.616 increased in intense. These changes in the diffraction patterns suggest the formation of a solid solution of Cr-Fe mixed oxide. The possible formation of this solid solution might be due to the similarity in the radii of both metal ions; Cr³⁺ = 61 pm and Fe³⁺ = 64 pm for six coordination²⁸.

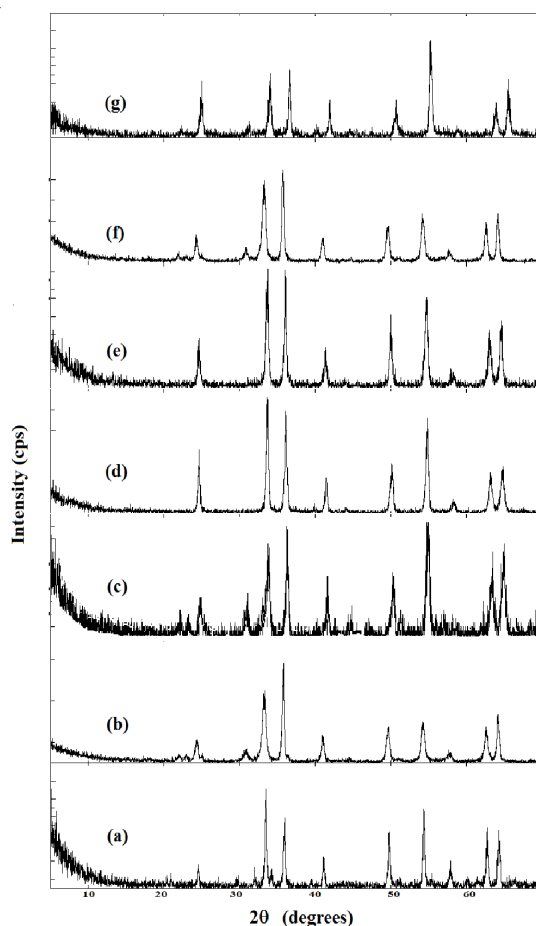


Fig. 1. The XRD patterns of the binary oxides obtained by co-precipitation method and calcination at 750 °C : (a) Fe-Cr-100 (b) Fe-Cr-90, (c) Fe-Cr-70, (d) Fe-Cr-50, (e) Fe-Cr-30, (f) Fe-Cr-10, Fe-Cr-0

FT-IR analysis: Additionally, the mixed oxides were characterized by FT-IR spectroscopy. The infrared spectra of the samples in the range from 4000-400 cm⁻¹ are shown in Fig. 2. The IR band at 3464 cm⁻¹ corresponds to the stretching vibrations of adsorbed H₂O molecules. The IR band at 1626 band 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 (Cr-O/Fe-O) lattice vibration²⁹⁻³². The band at 945 and 897 cm^{-1} are assigned to Cr-O-Cr vibrations and Fe-O-H bending vibrations²², respectively. Compared with the Cr- and Fe-alone oxides, all mixed oxides showed the same features in their FT-IR spectra. However, the spectrum of Fe-Cr-50 (Fig 2d) shows new features, that distinguish it from those of α - α - Fe_2O_3 and Cr_2O_3 alone oxides. This result corroborates that obtained by XRD suggesting the formation of a solid solution of Cr-Fe mixed oxide.

TABLE-1
d-SPACINGS CORRESPONDING TO THE MOST SIGNIFICANT PEAKS IN THE XRD PATTERNS OF THE Fe-Cr-x BINARY OXIDES SERIES (THE 100 % INTENSITY IS IN BOLD)

Composition	d-Spacings						
0/100	2.676	2.671	2.493	-	1.687	-	1.480
10/90	2.684	-	2.506	-	1.687	-	1.450
30/70	2.653	2.641	2.474	-	1.678	-	1.437
50/50	2.659	-	2.485	-	1.673	-	1.437
70/30	2.656	-	2.489	2.486	1.679	-	1.444
90/10	2.690	-	2.513	-	1.692	-	1.451
100/0	2.629	-	2.451	-	1.662	1.660	1.422

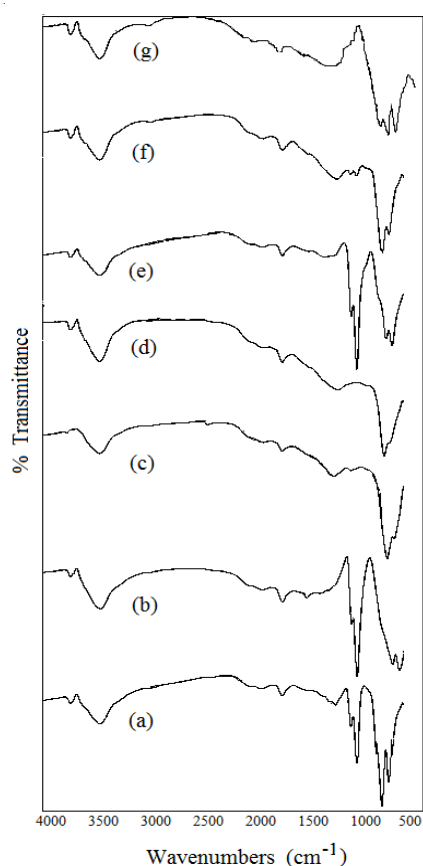
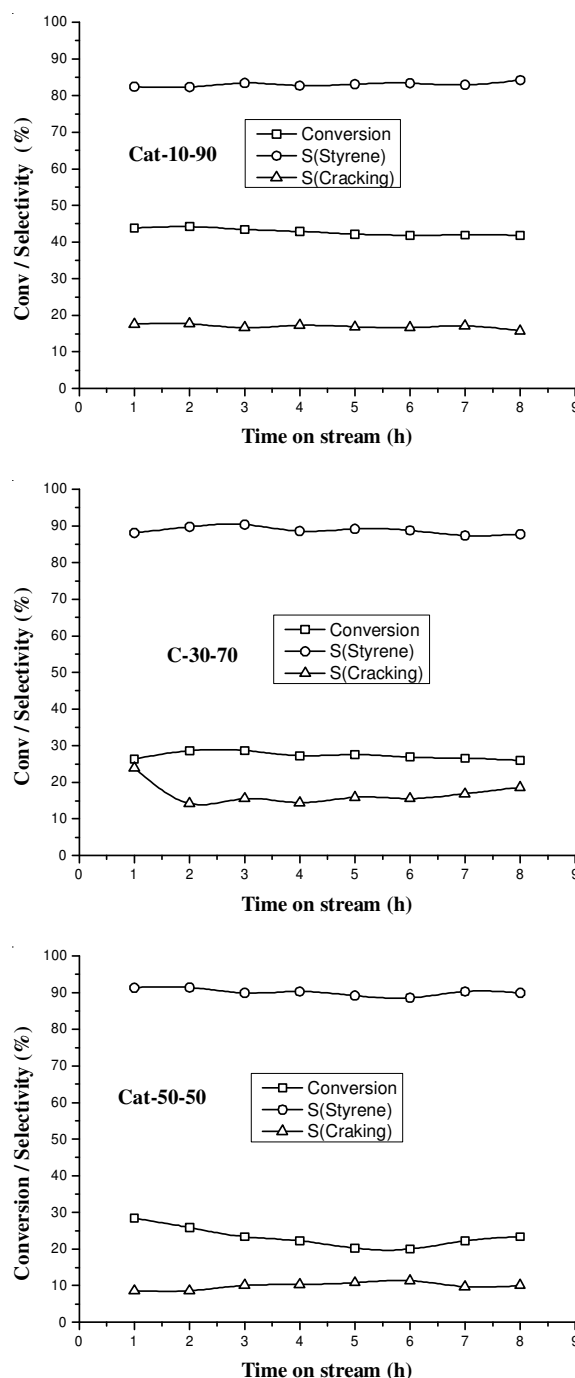


Fig. 2. Infrared spectra of the binary oxides obtained by co-precipitation method and calcination at 750 oC : (a) Fe -Cr-100 (b) Fe -Cr-90, (c) Fe -Cr-70, (d) Fe -Cr-50, (e) Fe -Cr-30, (f) Fe -Cr-10, (g) Fe -Cr-0

Catalytic activity

Effect of time on stream on the dehydrogenation of ethylbenzene: The variation of the ethylbenzene conversion and styrene selectivity with time on stream was shown in Fig. 3. It can be seen from the curves that the catalyst Fe-Cr-10, with the low content in iron oxide was the most stable in term

of activity compared to the series of the Fe-Cr catalysts. Whereas, the catalyst Fe-Cr-90, that has the high content in iron oxide was the less stable of the series. The decrease in the ethylbenzene conversion with time on stream, which is distinct for the rest of catalysts, might be due to the coke formation resulting in cracking reactions. In fact, the results showed that this catalyst preferentially forms cracking products (CP) instead styrene. It can be seen from the figure that the selectivity of the cracking products increased with time on stream in detriment of that of styrene. The increasing of coke deposition on the catalyst during the cracking reaction occurrence decreased gradually the activity of the catalyst. It is observed that the stability of the conversion and the selectivities with time on stream decreased slightly when the iron content increased in the catalyst composition.



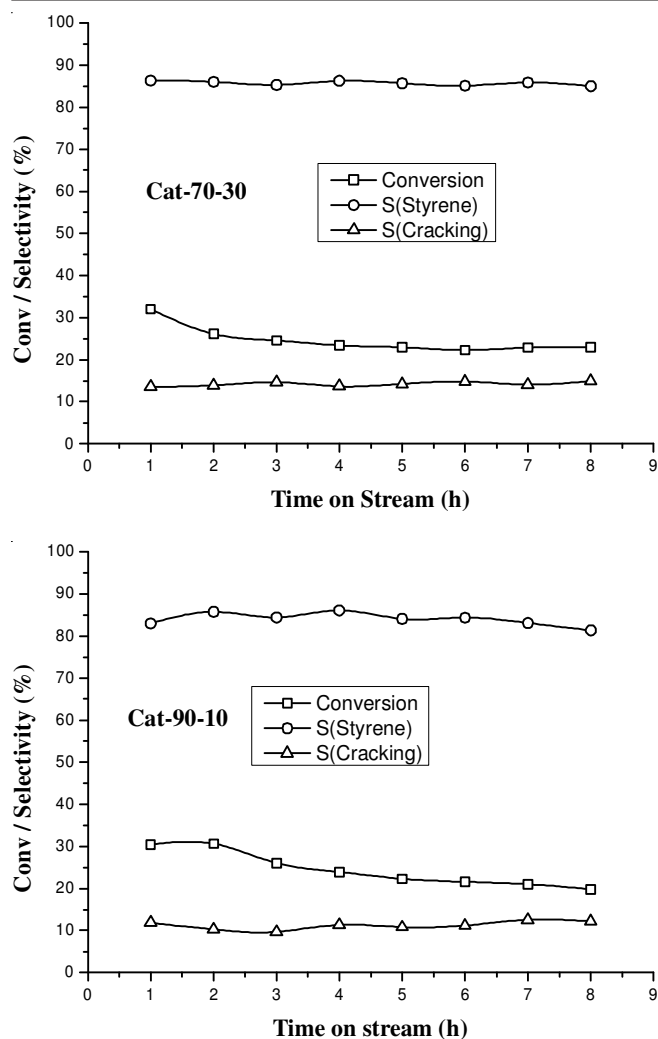


Fig. 3. Variation of the conversion selectivity products at 700 °C with time on stream for the series of catalysts : Fe-Cr-10; Fe-Cr-30; Fe-Cr-50; Fe-Cr-70; Fe-Cr-90 W/F = 13.8 g catalyst h/mol, CO₂/EB = 11.7 (molar ratio)

Effect of Fe/Cr ratio on the dehydrogenation of ethylbenzene: The catalytic performances of the binary oxides (ethylbenzene conversion and products selectivity) at the steady state are shown in Fig. 4. It can be seen from this figure that the highest conversion of ethylbenzene (41.9 %) was obtained over Fe-Cr-10 that have the less content in iron oxide. This result is in agreement with those reported in the literature³³, which indicated that the increase of Cr₂O₃ content enhances the activity. As for the selectivity, it was found that the highest value (89.94 %) was observed over the Fe-Cr-50 binary oxide. The Fe-Cr-90 catalyst was found the less active with a conversion of (19.8 %) and the less selective in styrene (81.4 %). It is well known that combining both metals in one oxide matrix has an effect on the nature of the reaction products. The profiles of the products from reactions over the mixed oxides were dependent on the Cr/Fe ratio. While Fe-Cr-90 significantly enhanced the formation of cracking products, Cr-Fe-50 showed a significant potential for complete oxidation, forming more styrene to the detriment of the cracking products. Therefore, the enhanced formation of cracking products over Cr-Fe-90 indicates the dominance of the role of Lewis acid sites on its surface. On the other hand, the formation of styrene reflects

the oxidation-reduction ability of the catalyst surface. Hence, the enhancement of styrene formation over the Cr-Fe-50 catalyst indicates stronger oxidation-reduction potential of its surface to the detriment of its acidic behaviour. Indeed, further work is needed for a better understanding of the reactions and to elucidate appropriate mechanisms, which is the subject of an ongoing study. Meanwhile, it can be concluded, based on the current results, that Cr-Fe mixed oxide catalysts with, generally, low Fe or low Cr content are suitable for cracking reactions, while catalysts with equal Cr and Fe contents are more suitable for styrene formation. These results are in agreement with those reported by Khaleel *et al.*³⁴. In fact, in their investigation for the methanol conversion over a series of binary oxides prepared by sol-gel method, it has been found that a mixture of DME and CO₂ was mainly formed on a pure Cr₂O₃ while dimethyl ether was mainly formed over α -Fe₂O₃. It is well known that dimethyl ether formation from methanol dehydration reaction occurs on Lewis acid sites. As for the Cr-Fe mixed oxide catalyst with equal Cr and Fe contents, it was found that is the most efficient for methanol oxidation reaction.

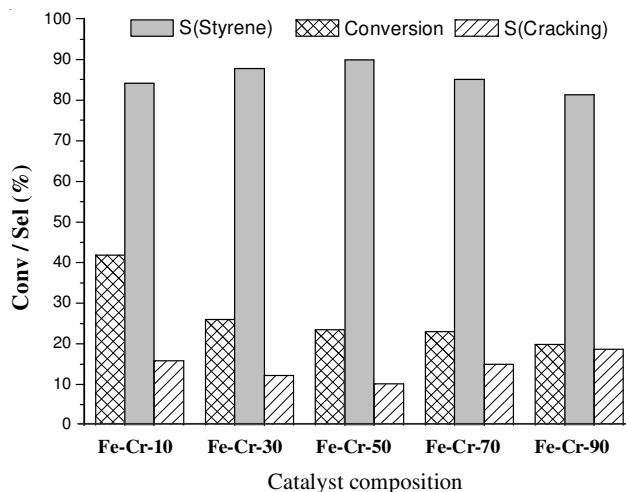


Fig. 4. Conversion and styrene selectivity values at 700 °C at the steady state for the series of catalysts : Fe -Cr-10; Fe -Cr-30; Fe -Cr-50; Fe -Cr-70 ; Fe -Cr-90

Activation energy for the formation of styrene was examined in the temperature range: The temperature range 620 to 770 °C over Fe-Cr-50 catalyst that have given the highest selectivity in styrene (Fig. 5). The activation energy determined from the slope of Arrhenius plots is 97.4 kJ/mol. This activation energy value is close to those obtained by Miyakoshi *et al.*³⁵ for Fe-K oxides and 20 % Mn-Fe-K, prepared by sol-gel method, 93.7 kJ/mol and 91.6 kJ/mol respectively. In the opinion of the author, the activation energy is essentially unchanged with the Mn-substitution in Fe-K oxide. It is concluded that this result indicates that the nature of active sites for styrene formation is essentially unchanged, but the number of sites increased, due to the Mn-substitution with Fe-K oxide.

Conclusion

Iron-chromium binary mixed oxides with different Fe/Cr ratios were prepared by co-precipitation method. The product

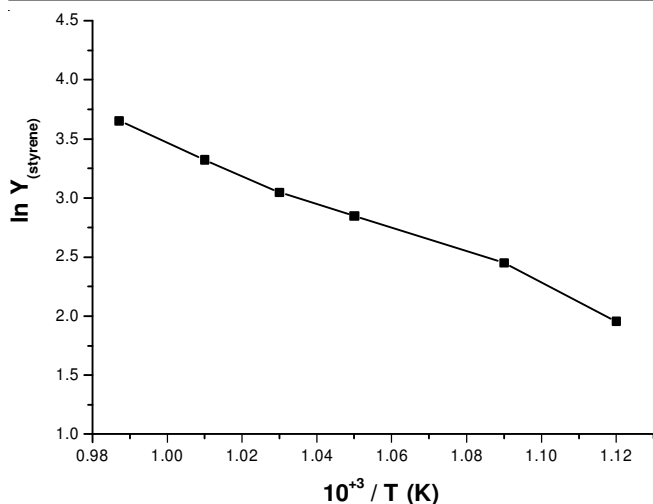


Fig. 5. Arrhenius plots of styrene formation over Fe-Cr-10 catalyst

with low Fe content showed the typical XRD pattern of Cr_2O_3 while that with high Fe content showed an XRD pattern that represents $\alpha\text{-Fe}_2\text{O}_3$. The mixed oxides with equal Fe and Cr molar ratio showed significantly modified textural characteristics as compared with the corresponding pure oxides, $\alpha\text{-Fe}_2\text{O}_3$ and Cr_2O_3 . The nature of the products formed over the mixed oxides, were dependent on the Fe/Cr ratio. Oxides with high and low Fe content enhanced the formation of cracking products, while those with equal Fe/Cr ratios significantly enhanced the styrene formation. The enhanced formation of cracking products over Fe-Cr with low and high Fe content indicates the dominance of the role of Lewis acid sites, whereas, the formation of styrene over the Cr-Fe-50 indicates the dominance of oxidation role of the Fe/Cr binary oxide.

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