Kinetics of the dehydrogenation of ethylbenzene to styrene over unpromoted and K-promoted model iron oxide catalysts

K. Coulter, D.W. Goodman

Department of Chemistry, Texas A&M University, College Station, TX 77843, USA

and

R.G. Moore

Dow Chemical USA, Hydrocarbons Research, Freeport, TX 77541, USA

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The dehydrogenation of ethylbenzene to styrene over unpromoted and potassium-promoted model iron oxide catalysts has been studied using ultrahigh vacuum techniques in conjunction with elevated pressure reaction kinetics. Model iron oxide catalysts were prepared by oxidizing a polycrystalline Fe sample that was subsequently dosed with metallic potassium. At 875 K the unpromoted catalyst exhibited a turnover frequency of 5×10^{-4} molecules/site s and an activation energy of 39 kcal/mol, both in excellent agreement with the results found for an analogous iron oxide powder catalyst. Potassium promotion increased the turnover frequency to 1.0×10^{-3} molecules/site s and lowered the activation energy to 36 kcal/mol for the dehydrogenation reaction. Similarities between the activation energies on the unpromoted and promoted catalysts indicate that the active site is the same on both catalysts. Creation of the active site was dependent upon the formation of an Fe^{3+} metastable species, consistent with the formation of a $KFeO_2$ phase, upon the addition of potassium.

Keywords: ethylbenzene; styrene; iron oxide; potassium promotion

1. Introduction

The catalytic dehydrogenation of ethylbenzene to styrene is a major industrial process that produces eight billion pounds of product per year within North America [1]. Several catalysts including oxides of aluminum, cobalt, zinc and manganese [2] have been utilized for this large volume process with the industrial catalyst of choice being potassium-promoted iron oxide operated in steam. The K-promoted iron oxide catalyst exhibits an order of magnitude higher activity compared to all other types of catalysts. Several studies have been carried out on the iron oxide catalyst to determine the kinetics of the dehydrogenation reaction [3,4], the role of potassium [5–7] and the catalyst deactivation process [8,9].

The one aspect of the ethylbenzene dehydrogenation reaction that has received the most attention is the identification of the active site on the K-promoted iron oxide surface. Several models have been proposed, all pointing to the importance of Fe^{3+} ions in the dehydrogenation process. Recently Muhler et al. [10,11], found evidence for a $KFeO_2$ active phase that was formed in a series of slow, solid-state chemical transformations from an initially unstable concentration of defective Fe^{3+} ions to a stable magnetite structure. The catalyst activity and selectivity were found to be dependent on the surface concentration of Fe^{3+} ions and K^+ ions with an optimum ratio of one Fe^{3+} ion to one K^+ ion. Recently, Addiego et al. [12] found that the rate of styrene production maximized at $\sim$ 10% potassium loadings while the activation energy was minimized at $\sim$ 30% potassium loadings. These authors also found that potassium suppressed the extent of carbonaceous deposits on the surface. Furthermore, their results were consistent with the active sites being the same for the promoted and unpromoted catalysts.

The studies mentioned above were carried out on powder, bulk oxide catalysts. These materials are not generally amendable to typical surface science investigations due to their insulating properties. In this investigation a model iron oxide catalyst, compatible with the use of surface science techniques, is employed for kinetic studies of the ethylbenzene dehydrogenation to styrene reaction. The use of the model for surface analysis permits a comprehensive surface science study to address the nature of the active site on the promoted and unpromoted catalyst, to identify reaction intermediates and to establish surface chemical transformations during the course of the reaction. The kinetic results of the ethylbenzene to styrene reaction carried out at pressures of $\sim$ 15 Torr over the model catalysts are presented and compared to the results obtained for the corresponding technical or "real-world" catalyst. Preliminary findings with respect to the implied active site are also presented.

2. Experimental

The experiments were carried out in a combination ultrahigh vacuum (UHV)/reactor apparatus equipped with Auger electron spectroscopy (AES), temperature programmed desorption (TPD) and gas and metal dosing capabilities. A double differentially pumped sliding seal allows the catalyst to be rapidly transferred from the reactor (1000 Torr) to the UHV ($\sim 1.0 \times 10^{-10}$ Torr) surface analysis chamber. The reaction products were analyzed with gas chromatography (GC) utilizing a flame ionization detector. A detailed description of the combined UHV/reactor apparatus can be found elsewhere [13].

The crystal used for these experiments was a polycrystalline iron disk with a diameter of approximately 0.5 cm. The crystal was mounted on platinum legs for resistive heating; platinum was chosen due to its demonstrated inertness under reaction conditions. The temperature was monitored using a tungsten–rhenium thermocouple spot-welded to the back of the sample.

The sample was cleaned first by oxidation in 1×10^{-6} Torr O_2 at 600 K for 30 min. The catalyst was then transferred to the reactor cell and reduced in 10 Torr of H_2 at 700 K for 10 min. Following reduction the sample was transferred to the UHV chamber and heated to 1200 K for 10 min. Auger analysis indicated that all impurities, except oxygen, were reduced to $< 1\%$.

The unpromoted catalyst was prepared according to the procedure of Yates and coworker [14]. The sample was oxidized in 1×10^{-6} Torr O_2 at 600 K for 30 min, producing an Fe_2O_3 substrate as determined by the Fe/O elemental ratio. Subsequently the sample was activated in 15 Torr of a 5 : 1 molar ratio of H_2O to ethylbenzene at 873 K for 2 h. It is noteworthy that without this activation period no detectable styrene product was formed. Preparation of the promoted model catalyst was carried out by dosing metallic K onto a clean, oxidized iron substrate using a SAES GETTERS doser. The flux of potassium was monitored using a mass spectrometer in-line with the metal doser. After dosing the potassium, the catalyst was reoxidized under the same conditions as those used for the unpromoted sample. Subsequently the stoichiometry of the catalyst was determined by AES. Activation of the promoted catalyst using the same conditions as those for the unpromoted catalyst was required to produce detectable styrene product.

Reactions were typically run with a 5 : 1 molar ratio of H_2O to ethylbenzene and a total pressure of 15 Torr. Standard reaction runs were 1 h; reaction temperatures ranged from 850 to 950 K. Aldrich (99.99%) ethylbenzene was used for these studies following purification by triple distillation; high purity deionized water was used as a reactant. Products were analyzed by GC using an AT-1200 Bentone 34 column. Following each reaction the sample was cooled in the reaction mixture and subsequently transferred to the UHV surface analysis chamber. An AES spectrum was acquired following each reaction to monitor any changes in the surface during reaction.

3. Results and discussion

The initial experiments were carried out to validate the use of the model catalyst for the ethylbenzene–styrene reaction. The results of these kinetic studies are shown in Arrhenius form in fig. 1. At 875 K the unpromoted model catalyst exhibited a steady-state turnover frequency of 5.0×10^{-4} molecules/site s. This activity compares very favorably with the reported value of 1.0×10^{-3} molecules/site s [3] for the unpromoted technical catalyst at this temperature. The turnover frequency calculated for the model is a lower limit value since in estimating the rate the assumption was made that every surface iron atom ($\sim 10^{16}$) of the catalyst was active. The close correlation of the rates and activation energies of the model iron

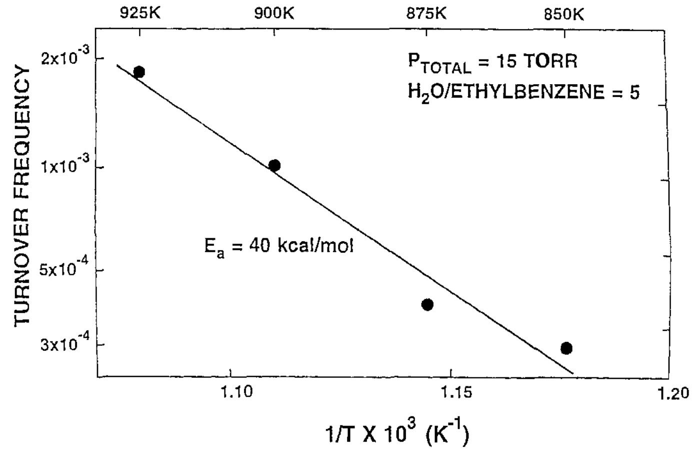

Fig. 1. An Arrhenius plot of the unpromoted iron oxide catalyst. $H_2O/EB = 5$; $P_T = 15$ Torr.

oxide catalysts and the technical catalyst, therefore, validates the use of the model for these studies.

Fig. 1 yields an activation energy of 39 kcal/mol for the model unpromoted iron oxide. This value is in excellent agreement with the activation energy of 37 kcal/mol found for the corresponding unpromoted industrial catalyst [12]. This agreement in the activation energies suggests a correspondence between the reaction pathways and active sites for the model unpromoted catalyst and the technical, unpromoted catalyst.

Fig. 2 shows the Arrhenius plot obtained following the addition of potassium to the model catalyst. The increase in styrene production with increasing potassium concentration follows the trend observed for the corresponding powder catalyst. Low coverages of potassium not only increase the activity but also lower the apparent activation energy for reaction. For a K/Fe AES ratio of 2.4 the activation energy was reduced from 39 to 28 kcal/mol; with a further increase in the potassium loading to a K/Fe AES ratio of 4.8, the apparent activation energy increased to 36 kcal/mol. This initial decrease followed by an increase in the apparent activation energy with increasing amounts of potassium can be rationalized in the following way. The addition of potassium initially promotes the formation of active sites utilized in the rate-determining step; however, a large surface coverage of potassium inhibits access by the reactants to the active sites, thereby lowering the overall activity.

The relatively small difference between the apparent activation energies of the promoted (28–36 kcal/mol) and the unpromoted (39 kcal/mol) iron oxide samples suggests that the active sites very likely are the same on both catalysts. These results are in agreement with the conclusions of Addiego et al. [12], and emphasize the role of potassium as a promoter in the synthesis and stabilization of active catalytic sites for this reaction on an iron oxide catalyst. The enhancement of the turn-

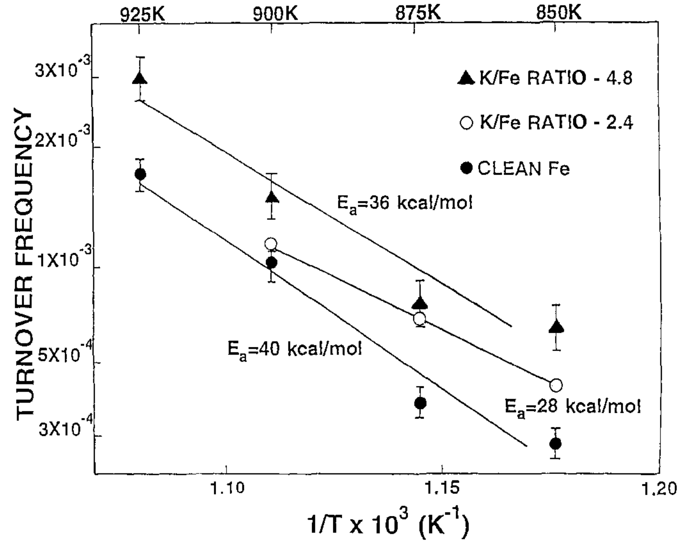

Fig. 2. An Arrhenius plot of the unpromoted and the K-promoted iron oxide catalyst at two K loadings. $H_2O/EB = 5$; $P_T = 15$ Torr.

over frequency following the addition of K relates to the increase in the density of active sites on the catalyst; that is, to an increase in the pre-exponential factor for the reaction.

In a previous study [3], water was found to influence the reaction by lowering the surface carbon level as well as maintaining an active Fe^{3+} catalytic phase. The importance of water with respect to the maintenance of a low surface carbon level is clearly demonstrated by the data of fig. 3. This figure plots the AES C/Fe ratio following reaction versus the water-to-ethylbenzene ratio, H_2O/EtB. A H_2O/EtB

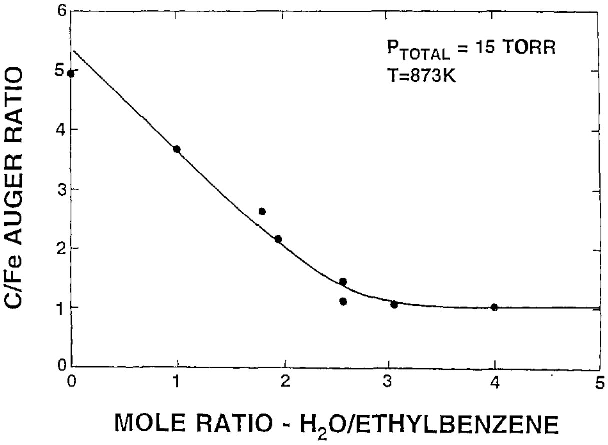

Fig. 3. Carbon levels for increasing amounts of H_2O in the reaction as determined by Auger spectroscopy. $T = 873$ K; $P_T = 15$ Torr.

molar ratio of three is sufficient in these studies to minimize the carbon level while maintaining the activity of the catalyst at its maximum.

The stoichiometry of the catalyst surface was studied during its growth, activation, and deactivation. The surface carbon levels as a function of reaction time for the K-promoted and unpromoted catalysts are shown in fig. 4. For both catalysts, the surface carbon increased gradually to a steady-state level, after which the activity of the catalysts was found to be steady-state. This behavior implies that under the steady-state conditions, the active sites are free of carbon or that under the dynamic reaction conditions, active sites are "covered" and "uncovered" at an equal rate. It is noteworthy that the growth of carbon deposits on the catalyst generally has been assumed to be the major deactivation mechanism [9]; however, these results imply that carbon deposition occurs primarily during the initial "activation" period.

The effect of the potassium promoter on the accumulation of surface carbon is evident in fig. 4. The addition of potassium decreases significantly the overall surface carbon level below that observed for the unpromoted catalyst. This supports the conclusion that one of the promotional effects of K is to maintain a relatively low surface carbon level. Furthermore, it can be argued that an increase in the density of active sites on the catalyst necessarily lowers the density of those sites involved in the formation of inactive carbon or coke. The addition of potassium also decreases the induction period to steady-state activity, in that a steady-state carbon level is achieved more rapidly for the K-promoted catalyst. More significantly, the catalytic activity reaches a steady-state value more quickly for the K-promoted catalyst.

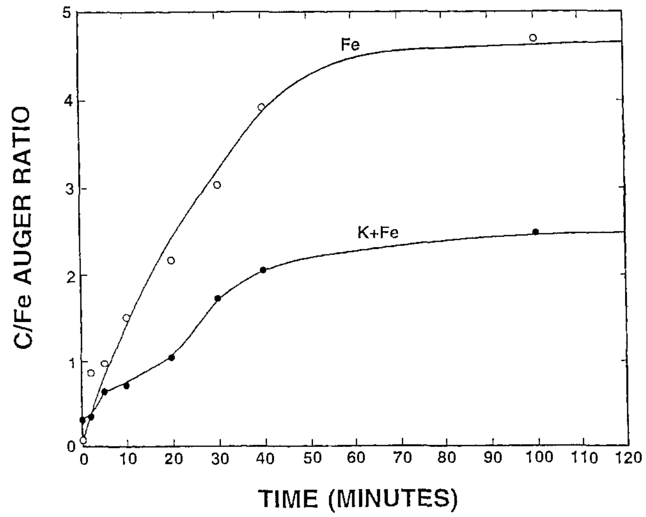

Fig. 4. Carbon buildup with time for the unpromoted and K-promoted catalyst. $T = 873$ K; $H_2O/EB = 5$; $P_T = 15$ Torr.

Changes in the surface coverages of potassium and carbon on the promoted catalyst were monitored during the initial induction period. Fig. 5 shows the initial decrease and subsequent stabilization of the potassium surface coverage. During the first few minutes of reaction, the potassium coverage fell from an initial value of 3.5 K/Fe AES ratio to a steady-state value of 1.5. The surface oxygen coverages, monitored by AES, are also shown in fig. 5. This ratio remained constant throughout the induction period and during subsequent reactions. Based upon the relative Auger intensities of the K, Fe, and O, the stoichiometry of the steady-state catalyst surface is approximately that of $KFeO_2$. The AES ratios of the steady-state catalyst surface were observed to be invariant with respect to stoichiometry. That is, no apparent change in the surface coverage of potassium was evident with reaction time.

The stoichiometry of the active phase of the promoted catalyst agrees with the results of Muhler et al. [10]. These authors' description of a metastable oxide active phase that acts as a storage medium for Fe^{3+} ions is entirely consistent with the data of this study. That the promoted and unpromoted samples have significant activity is consistent with the active site containing Fe^{3+}. The potassium promotes the formation and stabilization of these Fe^{3+} centers as a $KFeO_2$ phase.

Further work is in progress to detail more specifically the role of the $KFeO_2$ in activating the ethylbenzene as well as its possible role in lowering the binding energy of the product to the catalyst.

4. Conclusions

These studies have demonstrated that iron oxide and K-promoted iron oxide catalysts prepared under ultrahigh vacuum conditions can be utilized to accurately

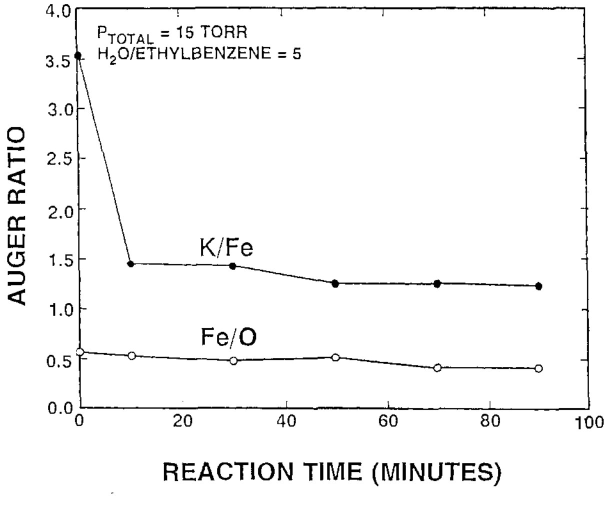

Fig. 5. Potassium and oxygen surface coverages versus reaction time. $T = 873$ K; H_2O/EB = 5; $P_T = 15$ Torr.

model the more realistic ethylbenzene–styrene catalyst. Surface analysis of the active catalytic surface suggests that the active surface sites consist of Fe^{3+}, specifically in the form of $KFeO_2$ for the K-promoted catalyst. The mechanism of the potassium promotion is via the stabilization of Fe^{3+} centers on the catalyst leading to a more active and more carbon-free surface.

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References

[1] Chem. Eng. News 69 25 (1991) 31.
[2] E.H. Lee, Catal. Rev. Sci. Eng. 8 (1973) 285.
[3] T. Hirano, Appl. Catal. 28 (1986) 119.
[4] K.K. Kearby, Catalytic dehydrogenation, in: *Catalysis*, Vol. III (Reinhold, New York, 1955).
[5] A.K. Vijh, J. Chem. Phys. 72 (1975) 5.
[6] T. Hirano, Appl. Catal. 26 (1986) 65.
[7] J. Lundin, K. Engvall, L. Holmlid and P.G. Menon, Catal. Lett. 6 (1990) 85.
[8] J. Matsui, T. Sodesawa and F. Nozaki, Appl. Catal. 51 (1989) 203.
[9] J. Matsui, T. Sodesawa and F. Nozaki, Appl. Catal. 67 (1991) 179.
[10] M. Muhler, R. Schlögl, A. Reller and G. Ertl, Catal. Lett. 2 (1989) 201.
[11] M. Muhler, R. Schlögl, A. Reller and G. Ertl, J. Catal. 126 (1990) 339.
[12] W.P. Addiego, C.A. Estrada, M.P. Rosynek, D.W. Goodman and R.G. Moore, J. Catal. 146 (1994) 407.
[13] J. Szanyi and D.W. Goodman, Rev. Sci. Instr. 64 (1993) 2350.
[14] V.S. Smentkowski and J.T. Yates, Surf. Sci. 232 (1990) 113.