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Abstract
There is economic incentive to operate the ethylbenzene dehydrogenation reaction at low steam/ethylbenzene ratios. To develop catalysts capable of performing under these conditions, it is necessary to understand the mechanism whereby the concomitant activity loss occurs. A potentially important mechanism is the reduction of the iron oxide. Thermogravimetric analysis in conjunction with X-ray diffraction is used to characterize the reduction properties resulting from potassium addition to iron oxide. The impacts of potassium addition on the temperature required to initiate reduction with hydrogen and on the apparent activation energy of reduction are determined. Reducibility of the potassium/iron oxide system in the presence of other dehydrogenation catalyst promoters is also presented.

Keywords
catalysts, dehydrogenation, hydrogen, potassium, reduction, thermogravimetric analysis, iron oxide, temperature measurement, thermogravimetry

Disciplines
Chemical Engineering

Comments
Reducibility of Potassium-Promoted Iron Oxide under Hydrogen Conditions

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There is economic incentive to operate the ethylbenzene dehydrogenation reaction at low steam/ethylbenzene ratios. To develop catalysts capable of performing under these conditions, it is necessary to understand the mechanism whereby the concomitant activity loss occurs. A potentially important mechanism is the reduction of the iron oxide. Thermogravimetric analysis in conjunction with X-ray diffraction is used to characterize the reduction properties resulting from potassium addition to iron oxide. The impacts of potassium addition on the temperature required to initiate reduction with hydrogen and on the apparent activation energy of reduction are determined. Reducibility of the potassium/iron oxide system in the presence of other dehydrogenation catalyst promoters is also presented.

Introduction

Commercially, styrene is primarily produced by the dehydrogenation of ethylbenzene using potassium-promoted iron oxide catalysts, which have additional metal oxide promoters. The reaction system is operated at two-stage adiabatic reactor inlet temperatures of 620–650 °C in the presence of excess steam.1,2 Deactivation of the dehydrogenation catalyst can occur at two time scales. Long-term deactivation, which creates the need to change out the catalyst in commercial reactors on about 2-year cycles, has been attributed to the loss of potassium from the catalyst and catalyst sintering.2–7 The second deactivation is a short-term phenomenon that can result from reducing the steam to ethylbenzene (S/EB) ratio in which the reaction is operating. This short-term deactivation is the focus of the current work.

Shown in Figure 1 are adiabatic pilot-plant performance data provided by Shell Chemical Co. for a standard commercial dehydrogenation catalyst. The pilot plant closely resembles the reactor performance in commercial dehydrogenation reactors. The data were obtained by fixing the inlet temperatures of the two-stage adiabatic pilot plant at 625 °C and the outlet pressure at 0.5 atm. Ethylbenzene and steam were first introduced at a molar S/EB ratio of 12 (12 mol of steam/1 mol of ethylbenzene). The reaction was allowed to stabilize and the ethylbenzene conversion recorded. The molar S/EB ratio was sequentially reduced, allowing the reaction to stabilize. As can be seen in the figure, decreasing the molar S/EB ratio from 12 to 8 causes a linear decrease in the steady-state activity. This decrease in activity can be merely explained by kinetic effects in the dehydrogenation reaction due to increased hydrocarbon and hydrogen partial pressures. However, an inflection point occurs in the activity curve at a molar S/EB ratio of about 7.5. This inflection point is followed by a more significant loss of activity, which cannot be simply explained by the dehydrogenation reaction kinetics. The low conversion ensuing below the inflection point as shown in Figure 1 places a lower limit on the S/EB ratio. The economics of styrene manufacture improve from operating at as low a S/EB ratio as possible, so the development of catalysts with a greater tolerance for operation at low S/EB ratio is desirable.

To guide the development of improved catalysts, it is useful to characterize the mechanism of deactivation at low S/EB ratio. Within the context of this low S/EB ratio deactivation, the primary mechanism that has been proposed is the loss of active sites due to increased carbon on the catalyst surface.8,9 Historically, the addition of potassium to the iron oxide catalyst was found to increase catalyst activity and obviate catalyst regeneration when a sufficiently high S/EB ratio was used. Potassium is well-known as a catalyst for carbon gasification via the water gas shift reaction. Devoldere and Froment10 developed a kinetic model to capture both the mechanism for carbon formation and carbon gasification at the catalyst surface on a typical K-promoted iron oxide dehydrogenation catalyst, which was able to predict the catalyst performance under low S/EB ratio operation.

However, the role of potassium on the iron oxide catalyst cannot be simply explained as a catalyst for surface carbon gasification.8,9,11–14 The incorporation of potassium into the iron oxide catalyst was found to increase activity beyond that predicted by surface carbon removal.2,8,9,13 A number of studies support potassium ferrite (KFeO2) as the active dehydrogenation catalyst..

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Figure 1. Ethylbenzene steady-state conversion at reaction conditions.
Figure 2. Model for the catalyst under reaction conditions.

site.8,9,12,14 Under reaction conditions, the bulk of the iron oxide in the dehydrogenation catalyst is magnetite (Fe3O4), with iron in the Fe2+/Fe2+ mixed-valence state.9,12,14 However, in situ and ex situ studies strongly support the presence of KFeO2, with only the Fe2+ species, at the active catalyst surface.8,11,14 Therefore, a second possible mechanism for the loss of activity at reduced S/EB ratio is loss of the active site through reduction.

Shown in Figure 2 is a potential sequence for the activation and subsequent deactivation of the K-promoted iron oxide catalyst. Fresh catalysts are typically in the completely oxidized state. Upon introduction of steam and ethylbenzene at reaction conditions, most of the iron oxide is reduced to Fe2O3, with some formation of the KFeO2 active site on the surface.2,15 Lowering the S/EB ratio causes the catalyst to deactivate through two possible mechanisms: (1) carbon deposition on the active sites and/or (2) reduction of the active site. A number of researchers have proposed the two possible deactivation mechanisms.9,16–18 Unfortunately, the manifestation of either mechanism would lead to the same empirical observation of the loss of activity due to active site loss. To guide the development of improved catalysts, understanding whether one of these mechanisms is the dominant deactivation mechanisms is critically important because catalyst synthesis strategies to decrease surface carbon formation would likely be significantly different from strategies to decrease KFeO2 reduction. Therefore, it would be desirable to examine the deactivation mechanism with an approach that would decouple the two potential deactivation mechanisms.

Hirano and Muhler et al.9 conducted experiments in which the active sites were characterized under reaction conditions by stopping the flow of steam and/or ethylbenzene. These studies validated KFeO2 as the active phase of the catalyst and also demonstrated the importance of steam for surface carbon gasification. Hirano’s study was performed at conditions corresponding to the nondeactivated portion of Figure 1, such that the amount of carbon formed on the catalyst cannot easily be correlated to that formed at a lower S/EB ratio. In the work of Muhler et al., the steam flow was stopped, such that carbon covered the surface of the catalyst, which also cannot be extrapolated to low S/EB ratio operating conditions. Therefore, the studies did not address the state of a partially deactivated catalyst when the S/EB ratio was at a moderate level.

Using a K-promoted model iron oxide catalyst under ultrahigh-vacuum conditions, Coulter et al.19 showed from Auger analysis a gradual increase in the C/Fe ratio as the S/EB ratio was decreased. While these data are important, two issues do not allow the data to be used to decouple directly the potential deactivation mechanisms. Most importantly, the complementary information on the degree of iron oxide reduction for decreasing S/EB was not presented, so it is possible that the carbon deposition was preceded by iron oxide reduction. Also, the S/EB ratio that led to carbon buildup on the catalyst surface was significantly lower than the S/EB ratio leading to deactivation that is seen in the actual catalyst operation.

Characterization of the active state of the K-promoted iron oxide catalyst is difficult because it has been conclusively shown that the catalyst changes extensively when removed from reaction conditions,8,5,11,12,14 KFeO2, which has been shown to be present at the catalyst surface during reaction, readily decomposes when cooled from reaction temperatures and exposed to any moisture or carbon dioxide.12,14 In addition, at reduced temperatures potassium in the catalyst rapidly reacts with any ambient carbon dioxide to form potassium carbonate on the catalyst surface.20,21 Adding to the unstable nature of the catalytic surface is the low concentration of active sites. The surface areas of K-promoted iron oxide catalysts are generally in the range of 2–5 m2/g, so even under reaction conditions the population of active sites is quite low.

The dual complication of ex situ instability of the active site combined with the low concentration of active sites makes direct quantitative measurement of the active catalyst surface quite difficult. This measurement difficulty creates a dilemma for designing experiments that can decouple the reduction and/or carbon deposition mechanisms occurring during deactivation at low S/EB ratios. While in situ X-ray diffraction (XRD) may seem to be a promising technique to characterize reduction in this system, the low concentration of KFeO2 even under reaction conditions limits the utility of XRD. In the current work, reduction results are measured using thermogravimetric analysis (TGA), which was found to give more sensitive reduction information than XRD.

Because of the number of competing effects that could be occurring upon a decrease of the S/EB ratio, it is necessary to quantify the individual potential effects of the competing deactivation mechanisms. To this end, the work presented here focuses on the reduction behavior of K-promoted iron oxide in the presence of hydrogen only. In addition, the effects of several metal promoters on the reduction behavior of K-promoted iron oxide are presented.

Experimental Section

The materials used in the experiments were iron oxide (α-Fe2O3), potassium carbonate (K2CO3), chromium oxide (Cr2O3), and vanadium pentoxide (V2O5), which were provided by Shell Chemical Co. Iron oxide, which has been promoted, is expressed as the weight percent of the promoter cation per total sample weight. For example, the iron oxide samples with single promoters were as follows: (a) 82 wt % Fe2O3, 18 wt % K2CO3 (K-Fe2O3); (b) 93 wt % Fe2O3, 7 wt % Cr2O3 (Fe2O3 w/Cr); (c) 91 wt % Fe2O3, 9 wt % V2O5 (Fe2O3 w/V). Experiments were also performed with dual-promoted iron oxide in which either Cr/K or V/K was simultaneously mixed with the iron oxide, yielding the following: (d) 75 wt % Fe2O3, 18 wt % K2CO3, 7 wt % Cr2O3 (K-Fe2O3 w/Cr); (e) 73 wt % Fe2O3, 18 wt % K2CO3, 9 wt % V2O5 (K-Fe2O3 w/V).

The samples were prepared by mixing Fe2O3 with the desired promoter precursor in a mortar. This mixing was followed by calcination of the promoter/Fe2O3
mixtures for 3.5 h at 800 °C using flowing air in a tube furnace. Following calcination, the powders were ground in a mortar to decrease the aggregate particle size.

Potassium ferrite (KFeO₂) was synthesized as follows: mix and grind in a mortar K₂CO₃ and Fe₂O₃ (47 wt% Fe₂O₃, 53 wt% K₂CO₃) followed by calcination at 800 °C using flowing air in a tube furnace. The calcined sample was olive green, which corresponds to the KFeO₂ phase. XRD was used to confirm the synthesis of KFeO₂, and the results were in good agreement with those reported previously. KFeO₂ was stored in a desiccator because the phase was found to decompose after 4 h of exposure to ambient air. It has been suggested that this decomposition is due to the reaction of the potassium with carbon dioxide and moisture to form the carbonates K₂CO₃·3/2H₂O and KHCO₃ or with moisture to form predominantly KOH. The synthesized KFeO₂, which was desiccated, was subsequently promoted with either V or Cr as follows: (g) 93 wt% KFeO₂, 7 wt% Cr₂O₃ (KFeO₂ w/Cr); (h) 91 wt% KFeO₂, 9 wt% V₂O₅ (KFeO₂ w/V). The promoted KFeO₂ was prepared by mixing the synthesized KFeO₂ with either the V or Cr precursor by grinding in a mortar followed by calcination at 800 °C using flowing air in a tube furnace. Following calcination, the samples were ground prior to characterization.

Sample surface areas were measured using a Micromeritics ASAP 2000 Branauer-Emmett-Teller (BET) apparatus, with krypton as the adsorbing gas. The XRD characterization was performed using a Siemens D 500 X-ray diffractometer with a Cu Kα radiation source. Surface morphology was evaluated using a Hitachi S-2460N variable-pressure scanning electron microscope (SEM). For the TGA experiments, a Perkin-Elmer TGA 7 was used. The sample containing 0.8 vol % H₂ in N₂ was combined with an ultrahigh-purity N₂ purge gas. In the TGA reaction chamber, the inlet H₂ partial pressure (pH₂) was 0.003 atm with a total gas flow rate of 70 mL/min. The heating rate was 5 °C/min with a temperature range of 50–900 °C and sample weights of 15–25 mg.

The TGA conditions were established to provide reproducible weight loss results. Experiments using heating rates of 10, 5, and 3 °C/min were performed. The heating rates of 5 and 3 °C/min were found to yield similar TGA curves with reproducible and well-resolved weight loss features, while the 10 °C heating rate led to unresolved weight loss events. Sample weights from 15 to 60 mg were evaluated. The maximum sample size that gave reproducible TGA results was 25 mg. This limit is consistent with other work that has reported the need to keep the sample size small so that thermal transport limitations within the sample are kept to a minimum. Finally, the low H₂ partial pressure was used to minimize over-reduction of the surface Fe because the transition from hematite to magnetite was the desired reaction to be studied.

Results and Discussion

Experimental Results. Replicate iron oxide samples were first evaluated under the standard TGA conditions to obtain a baseline for the reduction behavior. Shown in Figure 3 are a typical thermogravimetric (TG) curve and the concomitant derivative TG (DTG) curve for iron oxide. Three distinct weight loss regions can be seen from the curves. An initial weight change in the temperature range from 50 to 120 °C can be attributed to loss of physisorbed water, decreased air buoyancy, increased convection, and heat effects on the balance mechanisms. An empty pan baseline subtraction did not remove these disturbances completely from the curves. The second weight loss period was initiated at about 300 °C and reached a maximum rate at about 450 °C. This second weight loss event was completed by 550 °C, as demonstrated by the zero value on the DTG curve. The final weight loss period began at about 550 °C and continued until the experiment was terminated at 900 °C.

To determine the cause of the second and third weight loss periods, successive TGA experiments were stopped at 100 °C temperature increments starting at 500 °C. These samples were then each analyzed using XRD. The sample removed after reduction up to 500 °C was found to consist of hematite. The XRD analysis of the 600 °C sample also revealed only the presence of hematite phase. In contrast, the 700 °C sample was determined by XRD to consist of hematite (α-Fe₂O₃), maghemite (γ-Fe₂O₃), and magnetite (Fe₃O₄). Finally, the sample above 800 °C was found to contain these three phases as well as wustite (FeO).
and wustite phases has been previously reported for hematite reduction studies.27-30

The results from the 500 and 600 °C samples indicate that no reduction, as observable by XRD, has occurred despite the existence of a weight loss period between 300 and 550 °C. As noted previously, this weight loss period concludes with a DTG value of zero at 550 °C, indicating that the physical cause of the weight loss has reached a conclusion and the subsequent weight loss initiating at 550 °C can be assigned to a different mechanism. Weight loss in the temperature range of 300–550 °C for hematite under TGA conditions has been previously ascribed to the loss of surface hydroxyls and not reduction.12 The current combined TGA and XRD results are consistent with this assignment.

XRD of the 700 °C sample clearly shows reduction because the magnetite phase is present. In addition, the maghemite phase is present. Previous studies with hematite have shown that maghemite forms as an intermediate phase upon reduction to magnetite,29–31 so the presence of maghemite in the 700 °C sample further supports the initiation of reduction. Studies by Lecznar have shown that the transformation of hematite to maghemite occurs in the 550–750 °C temperature range.30 The final weight loss period appears to begin at about 550 °C, but no reduction phases were present at 600 °C. A TGA experiment was performed in which the temperature ramp was stopped at 600 °C and subsequently held at 600 °C for 100 min. The XRD analysis of this sample did show the presence of the maghemite phase. Therefore, the final weight loss period commencing at about 550 °C is associated with the onset of reduction. The XRD analysis of this sample did show the presence of the maghemite phase.

A reoxidation experiment was performed to further validate the assignment of the 300–550 °C weight loss to surface hydroxyls rather than reduction. In this experiment, the TGA reduction experiment was run as usual up to 900 °C. Once the sample reached 900 °C, the gas was switched from the reducing gas to dry air. The sample was held at 900 °C for the reoxidation. The sample increased in weight to a level below that corresponding to the hydroxylated sample (i.e., before 300 °C). XRD of the reoxidized sample gave predominantly the hematite phase with a trace of maghemite. The reoxidation would not be expected to introduce hydroxyl groups, so the fact that the weight gain did not replicate the weight loss supports the previously discussed assignment for the 300–550 °C weight loss event.

To provide a quantitative comparison of the reduction behavior of the different samples included in the current study, a reduction onset temperature was derived from the TGA runs. The reduction onset temperature was determined by taking a horizontal tangent line on the TG curve located at the final dwt/dT = 0 point prior to reduction (e.g., horizontal tangent at 475 °C in Figure 3). A second line was drawn tangent to the TG weight loss curve, with the end point corresponding to the temperature at which maximum weight loss due to reduction is observed (e.g., tangent to the curve passing through 800 °C in Figure 3). The reduction onset temperature is given by the intersection of these two tangent lines. The TG and DTG curves shown in Figure 3 correspond to a single TGA run; multiple TGA runs were performed on replicate samples to determine a mean reduction onset temperature. The mean reduction onset temperatures for the samples in the current study are given in Figure 4.

Shown in Figures 5 and 6 are the TG and DTG curves for the K-Fe2O3 and KFeO2 samples. For comparison, the analogous iron oxide curves are also included in the figures. As can be seen from Figures 5 and 6, the K-Fe2O3 system appears to have three significant weight loss periods. The first weight loss that continues until about 150 °C can be attributed to desorption of adsorbed water. Although attempts were made to minimize exposure of the sample to ambient moisture, the K-Fe2O3 system is highly hygroscopic. K2O in the fresh K-Fe2O3 system is free to adsorb water and/or react with ambient carbon dioxide because XRD indicated none of the KFeO2 phase in the fresh K-Fe2O3 sample. The second weight loss in the K-Fe2O3 system initiates at about 450 °C. This weight loss event can be attributed to the loss of surface hydroxyls.12 XRD results indicated that no

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\text{Figure 4. Mean reduction onset temperature using } p_{H_2} = 0.003 \text{ atm.}
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detectable reduction had occurred during this second weight loss period. A temperature ramp of the K-Fe$_2$O$_3$ system to 600 °C followed by a hold at 600 °C for 60 min resulted in predominantly hematite with some presence of maghemite. It is interesting to note that this 600 °C sample had olive green particles upon removal from the TGA device, which is the characteristic color of the KFeO$_2$ phase. However, the color rapidly changed to red, indicative of hematite. This observation would seem to support the formation of KFeO$_2$ on the particle surface. The third weight loss for the K-Fe$_2$O$_3$ sample can be attributed to iron oxide reduction. A sample removed after 700 °C in the TGA experiment was found from XRD analysis to contain mixed phases of hematite, maghemite and magnetite. The presence of the K promoter with the Fe$_2$O$_3$, which had a mean reduction onset temperature of 625 °C, clearly appears to delay the onset of reduction relative to the unpromoted Fe$_2$O$_3$.

As can be seen from Figures 5 and 6, the KFeO$_2$ sample was found to have only one significant weight loss period, which was initiated above 700 °C. Despite the measured weight loss, XRD of the KFeO$_2$ sample at the end of the TGA experiment still gave KFeO$_2$ as the only phase present in the sample. Therefore, the weight loss, which still can be most likely attributed to reduction, was sufficiently small as to not give a reduction phase that was measurable by XRD. Assuming the weight loss can be attributed to reduction, the mean reduction onset temperature was found to be 727 °C. The enhanced reduction resistance of the KFeO$_2$ phase relative to Fe$_2$O$_3$ is consistent with previously reported temperature-programmed reduction studies for supported KFeO$_2$.20,21

The set of TG curves for Fe$_2$O$_3$, K-Fe$_2$O$_3$, and KFeO$_2$ demonstrates that K promotion does increase the reduction resistance for iron oxide. This resistance occurs even when KFeO$_2$ is not present in measurable quantities but is most pronounced for preformed KFeO$_2$. The apparent presence of KFeO$_2$ formed in situ during the TGA experiments with K-Fe$_2$O$_3$, as indicated by the
for just the K-Fe₂O₃ system. Therefore, the addition of very similar to the reduction onset temperature found dehydrogenation catalysts. Cr has been described catalyst activity, selectivity, and/or stability. The oxides of Cr and V are promoters that have been used in as a structural promoter for maintaining the activity under reduced S/EB ratio operation. In contrast, V promotion can improve the selectivity of dehydrogenation catalysts while decreasing the stability for low S/EB ratio operation. Therefore, the reducibility of the K-Fe₂O₃ system may be impacted by promotion with either Cr or V.

Shown in Figure 7 are the DTG curves for the K-Fe₂O₃ system promoted with Cr and V as well as for K-Fe₂O₃ without promotion. As can be seen from the figure, these systems display increasingly complex weight loss phenomena. Unlike the K-promoted Fe₂O₃ systems discussed above, the transition to the weight loss period associated with actual iron oxide reduction is not clearly resolved from the preceding weight loss events. Therefore, determination of the onset reduction temperature becomes more problematic because the weight loss periods are no longer distinct. Nonetheless, a combination of the TGA data with XRD results could be used to estimate mean reduction onset temperatures.

The initiation of the weight loss due to reduction is particularly difficult to resolve for the K-Fe₂O₃ w/Cr system. XRD analysis of a sample removed at 600 °C yielded only the presence of hematite and maghemite, whereas a sample removed at 700 °C was found to contain hematite, maghemite, and magnetite. In both samples, no Cr-containing phase was discernible. The estimated mean reduction onset temperature for the K-Fe₂O₃ w/Cr system was found to be 620 °C, which is very similar to the reduction onset temperature found for just the K-Fe₂O₃ system. Therefore, the addition of Cr to the K-Fe₂O₃ system does not appear to impact the mean reduction onset temperature. Separate experiments in which only Cr was added to Fe₂O₃ were also performed. In these tests the Cr addition was similarly found to have no impact on the reduction performance of the iron oxide. XRD of the freshly calcined K-Fe₂O₃ w/Cr and Fe₂O₃ w/Cr gave no indication of mixed Cr/Fe or Cr/K phases, which is consistent with Cr addition having no effect on the resulting reduction behavior.

In contrast, the K-Fe₂O₃ w/V system was found to yield an estimated mean reduction onset temperature of 702 °C, which is above that for the K-Fe₂O₃ system. At calcination conditions similar to those used in the current study, the phase diagram for vanadium and iron oxide shows the potential for the existence of the FeVO₄ phase. This phase was not observed for the K-Fe₂O₃ w/V system but was observed when Fe₂O₃ was only promoted with V. The Fe₂O₃ w/V system was found to give a mean reduction onset temperature of 640 °C. Therefore, the formation of the FeVO₄ phase was found to improve significantly the reduction resistance relative to Fe₂O₃ by itself. The observation of V providing reducing stabilization on K-Fe₂O₃ has been reported previously. In that work, the role of V was speculated to cause decreased chemical reactivity of the Fe³⁺ ions.

TGA experiments were also performed on KFeO₂ that was subsequently promoted by either Cr or V. The TG curves for these systems are shown in Figure 8. As can be seen in the figure, the addition of either promoter decreased the reduction onset temperature relative to the unpromoted KFeO₂. Therefore, the interaction of promoters with the KFeO₂ phase appears to decrease the resistance of the iron oxide to reduction. In particular, Cr, which has been reported as a structural stabilizer in dehydrogenation catalysts, does not enhance the reducibility of potassium/iron oxide systems under the reduction conditions used in the current work. Promotion with V appears to have a more complex interaction with potassium/iron oxide systems. Its addition to KFeO₂ decreases the reducibility, whereas its addition to K-Fe₂O₃ aids the stability. The enhanced stability seen in the V promotion of K-Fe₂O₃ may be attributable to limited formation of an FeVO₄ phase. In contrast, V promotion of KFeO₂ cannot readily lead to formation of the FeVO₄ phase because none of the Fe₂O₃ phase is available.

Data Analysis. The mechanism of hematite reduction using H₂ or CO as the reducing gas has been studied extensively, but the focus of these studies has generally been the complete reduction to iron metal. While the current work examines the partial reduction of hematite to magnetite, the previous reduction studies still provide useful mechanistic information because hematite reduction to iron metal proceeds through the partially reduced magnetite and wustite phases. These reduction studies have shown that the rate of hematite reduction depends on the partial pressure and flow rate of the reducing gas, temperature, sample composition, and number of surface defect sites. A nucleation and growth mechanism has been found to describe reasonably the phenomenon associated with the reduction of hematite to magnetite. In the mechanism, the reducing gas reacts at the oxide surface, following an induction period, causing the loss of surface oxygen, leading to the nucleation of a magnetite phase. This magnetite phase is porous, allowing growth of the nucleated phase by continuous exposure of the unreduced oxide surface to the reducing gas.

Kinetic studies on the reduction of hematite have demonstrated that the reduction reaction is primarily limited by the gas/metal oxide surface reaction under conditions similar to those used in the current experiments. The rate of this surface reaction has been shown to be proportional to the partial pressure of the reductant gas. In the current study, TGA runs were performed with pH₂ varying from 0.003 to 0.08 atm,
which validated that the rate of reduction was proportional to $p_{H_2}$.

To analyze the reduction results, a kinetic model was developed based on a surface-controlled reduction reaction. Nonisothermal TGA data have been used to determine the apparent activation energy ($E_a$) for solid-state reaction and decomposition. For these types of systems, TGA data can be analyzed using the difference-differential method, integral method, or differential method.$^{26,41-44}$ In the current work, only the differential method was found to give a satisfactory fit of the kinetic data, which is consistent with previous studies.$^{25,42}$

The differential method applied to solid-state reactions requires a reaction order based on the particle geometry corresponding to the movement of the solid-gas interface through the particle.$^{26,43,45,46}$ The primary particle morphology for the iron oxide in the current study, which was found from SEM to be acicular with branching, could best be represented by either cylindrical or spherical particle geometry. Therefore, reaction orders of $n = 1/2$, corresponding to cylindrical morphology, and $2/3$, corresponding to spherical morphology, were both considered in the analysis. In general, calcination of the iron oxide samples, following addition of the promoters, did not induce significant morphological changes in the primary particles. The exceptions where the synthesis of KFeO$_2$, which led to larger, more tabular particles, and the promotion of Fe$_2$O$_3$ with V creating the FeVO$_4$ phase, which generated larger, more spherical particles.

Development of the reduction model using the differential method$^{42}$ is given by

$$\frac{da}{dt} = k(p_{H_2}/p_T)f(\alpha)$$

where $\alpha$ is the fraction of the total solid reacted based on the sample weight at the initiation of reduction, $k$ is the rate constant, $p_{H_2}$ is the hydrogen partial pressure, $p_T$ is the total pressure of 1 atm, $E_a$ is the apparent activation energy, $T$ is the temperature, $T_0$ is the initial temperature at the start of the TGA experiment, $\beta$ is the heating rate, and $A$ is the preexponential factor.

The $p_{H_2}$ term was included in eq 1 because the rate of surface reaction was found to be directly proportional to the hydrogen partial pressure. The differential form of eq 1 can be expressed as

$$\ln(\frac{dR}{dT})/f(R)(p_{H_2}/p_T) = \ln(A/\beta) - \frac{E_a}{RT}$$

with

$$f(\alpha) = (1 - \alpha)^n$$

The function $f(\alpha)$ is defined for reaction orders corresponding to either cylindrical ($n = 1/2$) or spherical ($n = 2/3$) geometry. A plot of $\ln(\frac{dR}{dT})/f(R)(p_{H_2}/p_T)$ versus $1/T$ yields the apparent activation energy.

Shown in Figure 9 are the $E_a$ values determined from the TGA data for each of the samples. Included are the standard error bars resulting from at least three replicate runs for each sample as well as model results for either cylindrical or spherical particle geometry. Good linear fits using eq 4 were obtained for all of the sample runs except for the K-Fe$_2$O$_3$ w/Cr system, which could not be fit well.

The apparent activation energy that has been typically reported for Fe$_2$O$_3$ reduction to iron metal is about 15 kcal/mol,$^{36,37}$ In the current work, the average $E_a$ values for Fe$_2$O$_3$ reduction to Fe$_3$O$_4$ were 18 kcal/mol for $n = 1/2$ and 21 kcal/mol for $n = 2/3$. The addition of K significantly increased the $E_a$ values, with the $E_a$ for reduction of the KFeO$_2$ phase more than doubling that of Fe$_2$O$_3$. It is likely that the high apparent activation energy calculated for KFeO$_2$ is due to the model not adequately representing the reduction mechanism for KFeO$_2$. The $E_a$ value determined for K-Fe$_2$O$_3$ was intermediate between that of Fe$_2$O$_3$ and KFeO$_2$. While
only the Fe₂O₃ phase was observed from XRD of the calcined K-Fe₂O₃ system, an olive color was visible on the sample in the TGA experiment when it was near the reduction temperature. Therefore, the reductive stabilization realized by K addition to Fe₂O₃ could be due to the formation of a surface KFeO₂ phase near reduction conditions, or a mixed K/Fe₂O₃ phase could be formed during calcination that cannot be detected by XRD analysis.

Promotion of K-Fe₂O₃ or KFeO₂ with either Cr or V led to decreases in the \( E_a \) values. With the exception of K-Fe₂O₃ w/V, promotion of either system with Cr or V also led to decreased values of the mean reduction onset temperature. Therefore, the presence of either additional promoter appears to retard the effectiveness of K in improving the reduction resistance of Fe₂O₃.

By definition of \( \alpha \) as the fraction of the total solid reacted based on the sample weight at the initiation of reduction, the effect of differences in surface areas between the samples on the apparent activation energy has been removed. Nevertheless, it is interesting to look at the surface areas for the samples used in the study. Shown in Figure 10 are the surface areas of the calcined samples as well as their surface areas after removal from the TGA experiment. Only the K-Fe₂O₃ sample had a higher surface area after calcination than the original Fe₂O₃. In addition, all of the samples experienced significant surface area loss following reduction even when only low levels of reduction were achieved such as with the KFeO₂ phase. Promotion by either Cr or V led to higher surface area retention following the reduction experiment. Therefore, the retention of surface area in the samples during reduction did not correlate with the reduction onset temperature. These results further support the conclusion that Fe₂O₃ is stabilized against reduction as a result of the presence of the KFeO₂ phase.

Conclusions

To aid in the development of ethylbenzene dehydrogenation catalysts with improved performance at low S/EB ratio operation, it is necessary to understand the mechanism of activity loss. Because the competing mechanisms of carbon deposition and active site reduction cannot be discriminated from reaction data alone, there is a need to design experiments that can decouple the two mechanisms. The current work has demonstrated that TGA experiments in conjunction with XRD analysis can provide insight into the reduction characteristics of the potassium-promoted iron oxide system. The TGA experiments were able to provide more sensitive information about reduction properties than could be independently accessed by XRD. However, complementary XRD was needed to analyze the TGA results because multiple weight loss phenomena were observed.

The addition of K to Fe₂O₃ at levels similar to those used in commercial dehydrogenation catalysts was found to increase the reduction resistance of Fe₂O₃. The
improved reduction tolerance was even more evident when preformed KFeO2 was used. While the presence of KFeO2 in the K-Fe2O3 system at reduction conditions could not be validated by XRD because of the instability of the KFeO2 phase, visual observation strongly suggested its presence. Therefore, stabilization of FeO2 to reduction appears to be accomplished by the formation at least at the surface of the KFeO2 phase. The impact of Cr and V addition, which are known dehydrogenation catalyst promoters, was also examined. These promoters appear to have the effect of decreasing the reductive stabilization realized by the formation of the KFeO2 phase. While the current work demonstrates the role of K in stabilizing FeO2 against reduction, further work is needed to extend this reduction work to the more complex reaction environment present under dehydrogenation conditions in which reductants such as hydrogen and the steam oxidant are simultaneously present.

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