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An Infrared Study of the Dehydrogenation of Ethylbenzene to Styrene over Iron-Based Catalysts

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The dehydrogenation of ethylbenzene to styrene over unpromoted and potassium-promoted iron catalysts has been studied using kinetic measurements and infrared spectroscopy. Both the rate of styrene production and the activation energy for its formation are dependent on potassium content. The specific rate of styrene production is highest at ~10% potassium loading, while the apparent activation energy of the reaction is lowest at ~30% potassium content. The activity is significantly attenuated for potassium loadings in excess of 30%. Infrared spectra of the unpromoted and potassium-promoted catalyst surfaces after reaction indicate that potassium suppresses the extent of carbonaceous deposits, and that the active sites on both unpromoted and potassium-promoted catalysts are identical. Furthermore, although pure styrene adsorbed on unpromoted Fe_2O_3 is bound to the surface via the aromatic ring, with the vinyl group only slightly perturbed by interaction with the surface, the styrene product of ethylbenzene dehydrogenation binds to the catalyst surface through the vinyl group. © 1994 Academic Press, Inc.

INTRODUCTION

The dehydrogenation of ethylbenzene to styrene occurs over a variety of catalysts and reaction conditions of temperature, diluent, and catalyst promoter. Several catalysts, such as cobalt, copper, iron, and zinc oxides, have been studied, both with and without promoters (1). When promoted with potassium, all catalysts exhibit a significant increase in rate. Reaction rates over dehydrogenation catalysts vary with temperature; typically, the reaction is carried out between 850 and 975 K, under conventional conditions using steam as a diluent. Fe_2O_3 is the commonly used commercial catalyst for ethylbenzene dehydrogenation. The reactivity of Fe_2O_3 is similar to that of cobalt and nickel oxides; however, promotion with potassium (as K_2CO_3) enhances by an order of magnitude the reactivity of iron oxide for styrene formation. Recent studies (2, 3) have indicated that the active phase of the potassium-promoted iron oxide catalyst is potassium ferrite, $KFeO_2$.

For potassium-promoted iron oxide catalysts, steam is ordinarily used as a diluent at commercial reaction conditions (1). There are several potential advantages to using steam in the reaction: (a) heat from the steam is used to maintain the reaction temperature, (b) steam helps to prevent irreversible carbonaceous deposition by reacting with residual surface carbon to form CO and CO_2, and (c) steam has also been shown to be essential in the structural regeneration of the ternary potassium iron oxide, which is thought to be the active site (4).

Little is known regarding the chemical bonding of adsorbed styrene on iron oxide. Clearly, a better understanding of the adsorbed species on both the unpromoted and potassium-promoted catalysts at reaction conditions will be of considerable value in detailing the reaction mechanism and the nature of the "active" catalytic site(s). Infrared spectroscopy (IRS) has been used extensively to study a variety of organic compounds adsorbed on iron catalysts (5–8). Therefore, IRS should provide useful information for developing an understanding of the chemistry of this reaction and could aid in the improvement of catalytic materials for this important industrial process.

The goals of this investigation were threefold: (a) to obtain kinetic data from infrared absorption spectra in order to determine activation energies and conversions, (b) to characterize the surface of iron oxide and potassium-promoted iron oxide catalysts, particularly regarding the identities of the surface species that may be present, including the identification of adsorbed styrene and reaction intermediates, and (c) to determine the effect of potassium promotion on the reaction.

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EXPERIMENTAL

All catalysts used in this study were provided by Dow Chemical U.S.A., and were prepared by thoroughly mixing appropriate amounts of iron oxide (α-Fe_2O_3) powder, potassium dichromate solution ($Kr_2Cr_2O_7$ + 15 wt.% H_2O), and potassium carbonate (K_2CO_3) into a moist paste, and then drying the mixture in an oven at 423 K for ~2 h. The solid mixture was periodically broken up during the drying process, resulting in a coarse powder. After drying, the mixture was calcined at 1048 K for 30 min. The following four catalyst compositions were prepared for detailed study: (a) 90 wt.% Fe_2O_3, 8 wt.% K_2CO_3, 2 wt.% $K_2Cr_2O_7$ (hereafter referred to as 10% K-promoted); (b) 80 wt.% Fe_2O_3, 18 wt.% K_2CO_3, 2 wt.% $K_2Cr_2O_7$ (20% K-promoted); (c) 70 wt.% Fe_2O_3, 28 wt.% K_2CO_3, 2 wt.% $K_2Cr_2O_7$ (30% K-promoted); and (d) 60 wt.% Fe_2O_3, 38 wt.% K_2CO_3, 2 wt.% $K_2Cr_2O_7$ (40% K-promoted). Catalysts containing higher loadings of potassium (50 and 60%) were also made and characterized, but were not used in the kinetic and infrared studies. The 2 wt.% $K_2Cr_2O_7$ was included as a structural stabilizer in all of the catalyst compositions, except for the unpromoted iron oxide, to inhibit sintering. Following calcination, Cr was present primarily as Cr_2O_3, but had no observable effect on the specific activities of any of the catalysts studied.

Ethylbenzene and styrene were obtained from commercial vendors and were purified by conventional vacuum distillation prior to use. Water, used in the reaction as the steam diluent, was deionized and then vacuum distilled to remove dissolved CO_2.

BET surface area measurements, using N_2 adsorbate at 77 K, were performed using a Micromeritics ASAP-2000 instrument. X-ray photoelectron (XPS) spectra were obtained on a PHI-555 instrument using a cylindrical mirror analyzer and an Al$K\alpha$ monochromatic source. Samples for X-ray powder diffraction (XRD) studies were mounted on a SCINTAG PAD 5 diffractometer (Cu$K\alpha$ radiation). Standard conditions for all data collections were $2\theta = 5$–80° and a .03 chopper increment. Identifications of bulk phases were made by comparison to Joint Committee on Powder Diffraction Standards (JCPDS) patterns.

The reaction/infrared cell used in these experiments has been described in detail elsewhere (9). The cell was connected to a standard Pyrex glass vacuum manifold and gas handling system which was used to introduce reactants. The cell was resistively heated by an external furnace. The 50–70-mg catalyst samples were pressed into self-supporting wafers and mounted into a quartz sample holder, which was then suspended by a copper wire from a windlass, permitting samples to be transported *in situ* between the heated and spectral regions of the cell. Samples were first suspended in the cell in the heated region, and the temperature of the furnace was then increased to the desired reaction temperature. Ethylbenzene and water vapor were allowed to expand into the cell, which had been previously evacuated, to a pressure of $<5 \times 10^{-5}$ Torr. An ethylbenzene : water molar ratio of 1 : 3 was typically used, with a total pressure of 24 Torr. Following the desired period of reaction, the catalyst sample was then lowered into the spectral region of the cell for IR data collection.

Infrared spectra were obtained using a Perkin–Elmer model 1760 Fourier-Transform spectrometer, equipped with a liquid-nitrogen cooled broad-band mercury–cadmium–telluride (MCT) detector having a spectral range of ~800–4000 cm^{-1}. This detector was used when the sample transmittance was extremely low. A conventional TGS detector was used for collecting gas-phase spectra and for those surface spectra in which spectral information below 800 cm^{-1} was desired. Gas-phase spectra of reactants and products were obtained by averaging 50 spectra and then subtracting the background. For surface species, 50 spectra of the calcined catalyst sample were taken prior to reaction. These were then averaged and subtracted from the accumulated spectrum of the sample after reaction. The resulting spectrum then exhibited only those bands arising from the adsorbates and from any changes in the surface structure during reaction.

RESULTS AND DISCUSSION

Characterization of Catalysts

BET–N_2 surface areas of the unused catalysts are reported in Table 1. The surface area of the unpromoted Fe_2O_3 increases slightly with the addition of 10 wt.% potassium, but then decreases with further increase in potassium content. As will be shown below, the variation of surface area with potassium content parallels variations in the observed ethylbenzene dehydrogenation reaction rate. Increasing the potassium content above 10% leads to increased sintering of the catalysts during use.

X-ray powder diffraction (XRD) data and X-ray photoelectron spectra (XPS) were obtained for each of the unused catalysts. The XRD data indicate that hematite (α-

TABLE 1

Surface Areas of Model Catalysts

Catalyst	Surface Area (m^2/g)
Unpromoted Fe_2O_3	3.0
10% K-promoted Fe_2O_3	3.5
20% K-promoted Fe_2O_3	2.9
30% K-promoted Fe_2O_3	1.6
40% K-promoted Fe_2O_3	1.0

Fe_2O_3) is the major phase in the 10% K-promoted catalyst, with a very minor K_2CO_3 phase also present. In the 20- and 30%-K promoted catalysts, hematite is also the major phase, with minor $KFeO_2$ and K_2CO_3 phases as well. As the potassium content is increased to 40%, $KFeO_2$ becomes a major phase. However, the crystallinity of the samples decreases significantly at these high potassium contents, as reflected by an overall decrease in intensity of the XRD peaks.

The surface concentrations of iron, potassium, and oxygen, as a function of bulk potassium content, were obtained from the XPS spectra. Quantitative determinations were made using areas of the O 1*s*, Fe 2*p*'s, and K $2p_{3/2}$ peaks, after corrections for differing sensitivity factors. Surface enrichment in potassium was observed in all of the catalysts, as shown in Fig. 1, where the atomic% of surface oxygen species and the K/Fe surface ratio are depicted as a function of potassium content. (For reference purposes, the overall bulk K/Fe atomic ratio, based on initial catalyst composition, is indicated by the dotted curve.) The K/Fe surface ratio increases monotonically with increasing potassium content up to ~30 wt.% K content, above which the slope of the line increases abruptly. This change in slope occurs just prior to the marked decrease in crystallinity of the catalysts observed by XRD and the corresponding increase of the $KFeO_2$ component into a major bulk phase. Despite the development of the $KFeO_2$ bulk phase, however, a substantial fraction of the excess potassium promoter, presumably as K_2CO_3 and/or K_2O, still segregates to the catalyst surface, as shown by the continuing increase in surface K/Fe ratio with increasing potassium content.

Reaction Kinetics

Kinetic data for the unpromoted and K-promoted catalysts were obtained by measuring changes in intensity of a characteristic absorption band of styrene (909.6 cm^{-1}, vide infra) in the infrared spectrum of the reactant/product gases. The volume of the reaction/infrared assembly was determined; the integrated area of the IR band at 909.6 cm^{-1} was measured as a function of gaseous styrene concentration over the range of interest, and the corresponding extinction coefficient was then calculated. Rates for a particular catalyst at a chosen temperature were computed from the areas of the 909.6-cm^{-1} band, measured as a function of reaction time, and then converted to styrene concentrations. Under batch-reaction conditions at 853 K, the steady-state concentration of ethylbenzene approached its equilibrium value of 7×10^{-5} *M* within ~1–1.5 h, corresponding to ~78% conversion with all of the catalysts studied. After ~1 min of reaction over equal weights of each catalyst, conversions were ~4% for the unpromoted Fe_2O_3, ~21% for the 10% K-promoted catalyst, ~16% for the 20% K-promoted catalyst, ~11% for the 30% K-promoted catalyst, and ~4% for the 40% K-promoted catalysts. It should also be noted that the same general trends observed in this study using a batch reactor have also been observed in previous work (10, 11) using flow reactors at relatively high space velocities and at higher total pressures (up to ~1 atm).

Figure 2 shows typical data obtained for the 10% K-promoted catalyst. Arrhenius plots of styrene production over the unpromoted and all of the K-promoted catalysts are shown in Fig. 3. Table 2 summarizes the apparent

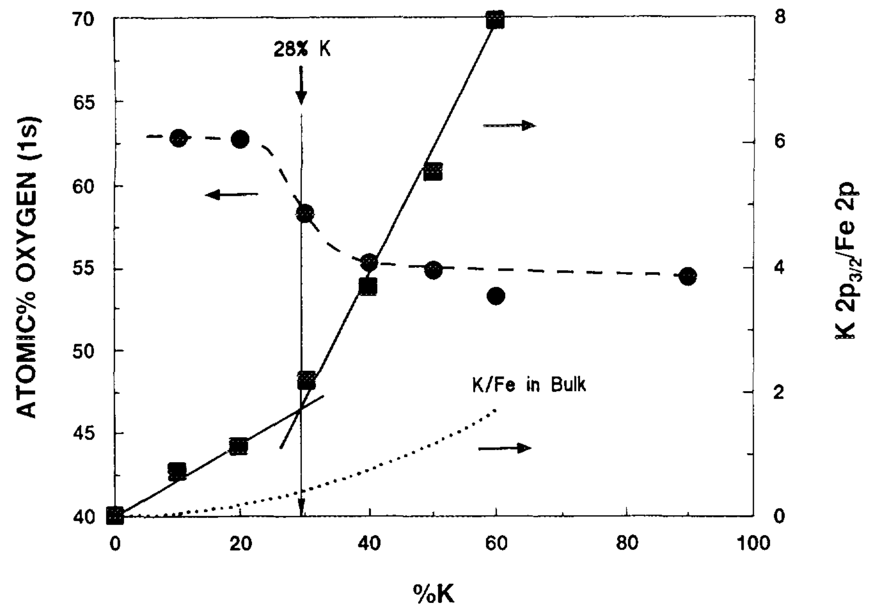

FIG. 1. Surface concentration of oxygen and surface K : Fe ratio for various bulk potassium contents, determined by XPS. Dotted curve is bulk K/Fe ratio, based on initial catalyst composition.

activation energies determined from Fig. 3 for the various catalysts, as well as the measured rates of reaction at 853 K. The relatively low activity measured for the unpromoted catalyst compares favorably with values reported previously for unpromoted iron oxide catalysts (10). A potassium loading of ~10 wt.% causes a decrease in activation energy and an accompanying increase in the specific rates (i.e., per g of catalyst) of styrene production at all temperatures in the range studied. However, potassium loadings in excess of 10% result in specific rates that are lower than that of the optimum 10% level. This observed attenuation of reaction rate at high potassium loadings is consistent with previous reports (1, 10, 11) and has been attributed to the poisoning effects of excess potassium, perhaps caused by the formation of deactivating potassium hydroxide at active sites (3, 4).

A secondary rate-altering effect may be due to the facile migration of potassium over and into the catalyst, as well as potassium sublimation from the catalyst during reaction. This phenomenon has been observed on iron-based catalysts for Fischer–Tropsch synthesis (12, 13) and for dehydrogenation reactions (1, 14). Connell and Dumesic (15) have studied the mobility of potassium on iron overlayers and have found that potassium migration is enhanced by the presence of hydrogen and water. Both of the latter components are present in both Fischer–Tropsch and in ethylbenzene dehydrogenation reactions. The loss or redistribution of potassium can, understandably, cause variations in reaction rate. For example, the loss of potassium can, under certain circumstances, increase the reaction rate by opening microchannels in the catalyst, effectively increasing the surface area of iron oxide (1). The possible occurrence of such potassium migration and/or loss by sublimation was not separately investigated for the present catalysts, however.

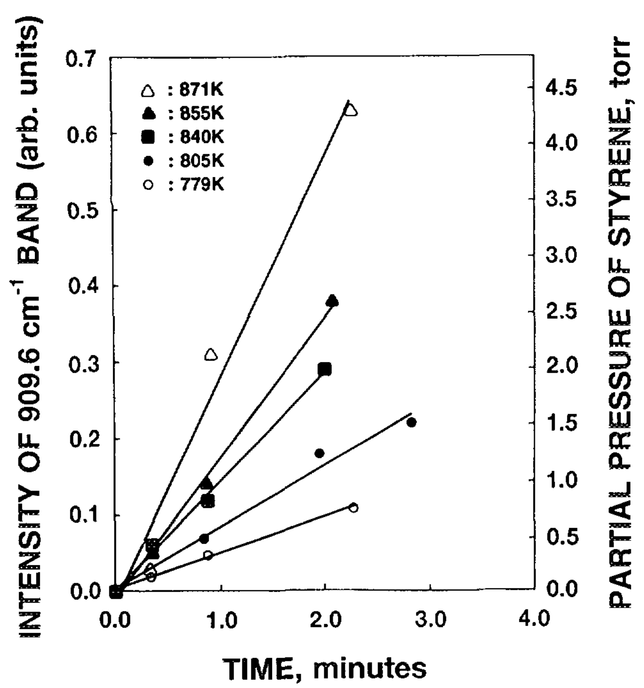

FIG. 2. Styrene production over a 10% K-Promoted Fe_2O_3 catalyst. (H_2O : EB = 3; P_T = 24 Torr.)

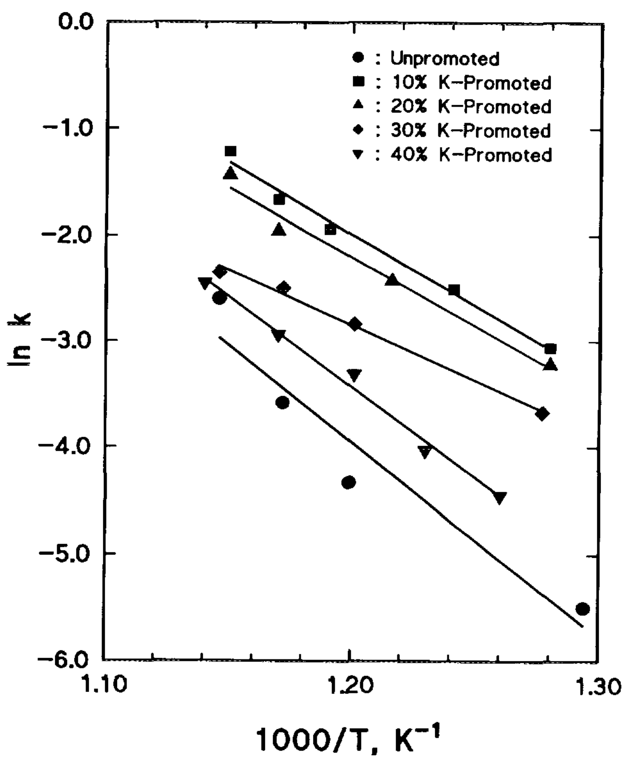

FIG. 3. Arrhenius plots of unpromoted and K-promoted catalysts. (H_2O : EB = 3; P_T = 24 Torr.)

Figures 4a and 4c show the effect of potassium loading on the specific rates of styrene production and on the apparent activation energy of reaction, respectively. It is noteworthy that, although the optimum *specific* rate occurs at 10 wt.% potassium loading, the lowest activation energy is observed for the 30 wt.% potassium catalyst. This observation would seem contrary to the hypothesis

TABLE 2

Kinetic Data for Ethylbenzene Dehydrogenation to Styrene

	Rate of styrene formation[a]		E_a for styrene formation	
Catalyst	This study	Ref. (14)	This study	Ref. (14)
Unpromoted Fe_2O_3	4–5	3.2	37 ± 1	34
10% K-promoted Fe_2O_3	25–30		26 ± 1	
20% K-promoted Fe_2O_3	18–23	33.8	25 ± 1	30
30% K-promoted Fe_2O_3	15–18	24.7	21 ± 1	30
40% K-promoted Fe_2O_3	4–5		34 ± 1	

[a] mol/g/min × 10^5 at 853 K; ethylbenzene : water = 1 : 3.

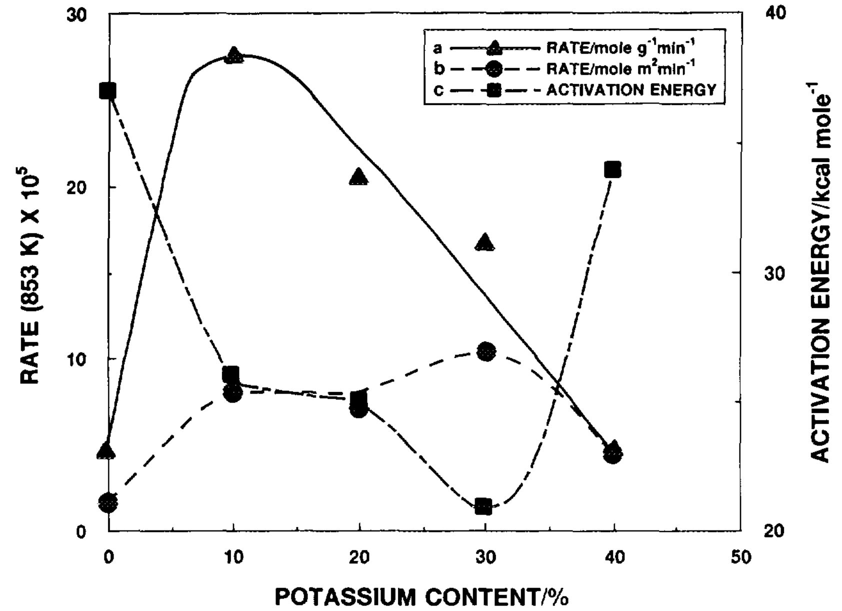

FIG. 4. Effect of potassium loading on activation energy and rate of styrene production at 853 K over Fe_2O_3 catalysts. ($H_2O:EB = 3$; $P_T = 24$ Torr.)

that a deactivating species forms at the active sites with increasing potassium content. However, when corrected for differing catalyst surface areas (Fig. 4b), the rates mirror the effect of potassium on the activation energy, i.e., a decrease in E_a is accompanied by a corresponding increase in rate. This implies that the decrease in the activities of the catalysts at potassium loadings in excess of 10% are due to a blockage of potential active sites by the excess potassium.

Styrene Adsorption on Unpromoted Fe_2O_3

Figure 5 shows the infrared spectra of gas-phase styrene (a), and of styrene absorbed onto a calcined sample of unpromoted Fe_2O_3 (b). For gas-phase styrene, the skeletal C–C stretching modes of the aromatic ring occur at ~1600–1610, 1590, 1500, 1450, 1200, 1070, and 1020 cm^{-1} (16, 17). The four bands occurring between 2000 and 1700 cm^{-1} are characteristic of the absorption pattern produced by monosubstituted aromatics (16, 17), and arise from combination bands that are independent of the nature of the substituents. The two aromatic out-of-plane bending modes occurring at 775 and 700 cm^{-1} are characteristic of mono-substituted rings. The out-of-plane skeletal mode at 700 cm^{-1} is present for all mono-substituted benzenes and is not sensitive to the nature of the substitutent. The position of the C–H out-of-plane bend at 775 cm^{-1}, however, *is* sensitive to the nature of the substituent. This band occurs at 775 cm^{-1} for styrene, 740 cm^{-1} for ethylbenzene, and 725 cm^{-1} for toluene. The other aromatic mode that is present in styrene, but not in benzene, toluene, or ethylbenzene, and which is characteristic of styrene, is the band at 1200 cm^{-1}. The vinyl group of styrene has several characteristic bands: (a) the C=C stretching mode observed in Fig. 5a at 1645 cm^{-1}; (b) the C–H out-of-plane bending modes of the vinyl group, $=CH_2$ and –CH=C–, at 910 and 990 cm^{-1}, respectively; (c) the overtone of the 910 cm^{-1} band at ~1820 cm^{-1}; and (d) the C–H in-plane bending modes of the vinyl group, $=CH_2$ and –CH=C–, at 1395 and 1300 cm^{-1}, respectively (17).

Adsorption of styrene onto the Fe_2O_3 surface at 298 K (spectrum b) has only a minimal effect on the positions and relative intensities of the gas-phase vibrational structure

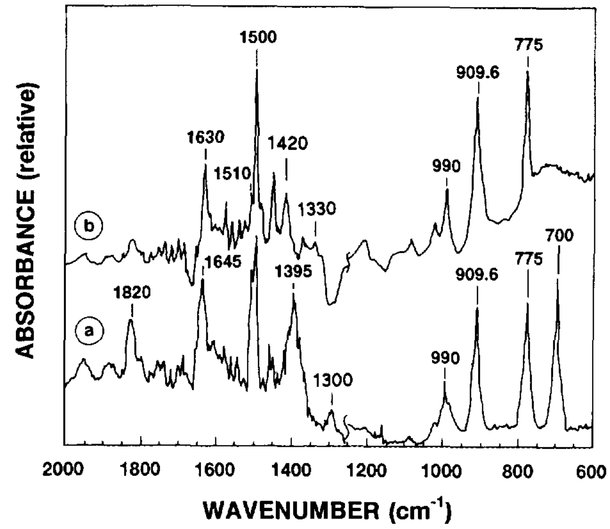

FIG. 5. Infrared spectra of (a) gas-phase styrene (2 Torr) and (b) styrene adsorbed onto unpromoted Fe_2O_3 at 298 K.

corresponding to the vinyl group. The C=C stretching band frequency decreases from 1645 to ~1630 cm^{-1}, and the in-plane C–H bends of $=CH_2$ and $-CH=C-$ increase from 1395 and 1300 cm^{-1} to 1420 and 1330 cm^{-1}, respectively. The bending modes at 910 and 990 cm^{-1} are unaffected by the adsorption. Thus, the vinyl group of styrene is only moderately perturbed by adsorption onto the unpromoted Fe_2O_3 surface.

In the case of adsorbed styrene (Fig. 5b), however, the out-of-plane skeletal mode at 700 cm^{-1} is completely absent from the vibrations arising from the aromatic ring, suggesting that the ring is constrained in its movement due to surface interactions. The skeletal C–C stretching bands between 1600 and 1000 cm^{-1}, and the C–H out-of-plane bend at 775 cm^{-1} are largely unaffected by the adsorption, exhibiting only slight shifts to lower frequencies in the bands at ~1510 and 1600 cm^{-1}. This indicates that the styrene is very weakly adsorbed through the aromatic ring, presumably via a π-type bonding interaction. The fact that only one of the aromatic spectral bands is eliminated by adsorption indicates that the aromatic ring is not bonded parallel to the surface, but is skewed, possibly due to steric and/or bonding constraints of the vinyl group. The absorption bands for a mono-substituted benzene molecule in the 2000–1700 cm^{-1} region are also not perturbed. This would again indicate that no strong bonding interaction between the styrene and the Fe_2O_3 surface occurs at 298 K.

Reaction of Ethylbenzene over Unpromoted Fe_2O_3

Over unpromoted Fe_2O_3, the dehydrogenation reaction, which follows a Langmuir–Hinshelwood-type mechanism (10), is zero-order with respect to ethylbenzene and is essentially complete within ~45 min of reaction at 850–900 K. Figure 6 shows the gas-phase spectra of the reaction gases before reaction (a), after 15 min of reaction (b), and after 1 h of reaction (c) at 873 K. All of the spectra were collected after quenching the sample to 298 K. C–H stretches in the aromatic ring occur between 3000 and 3100 cm^{-1}, while the bands between 2850 and 3000 cm^{-1} are due to C–H stretches from the CH_3 group in ethylbenzene (17). The broad band due to O–H stretches of the steam is observed at 3200–3600 cm^{-1}.

After 1 h of reaction at 873 K, the features associated with ethylbenzene and steam are significantly attenuated. Concomitant with the decrease in ethylbenzene is the appearance of the P and R branches of the C=O stretch of CO_2, centered at ~2345 cm^{-1}. Presumably, the CO_2, which appears within the first 15 min of reaction, results from the reaction of water with surface carbon. In addition, weak bands due to the P and R branches of CO at ~2143 cm^{-1} also appear and intensify after 1 h of reaction. The intensities of the CO_2 and CO gas-phase bands do not increase significantly after ~1 h of reaction.

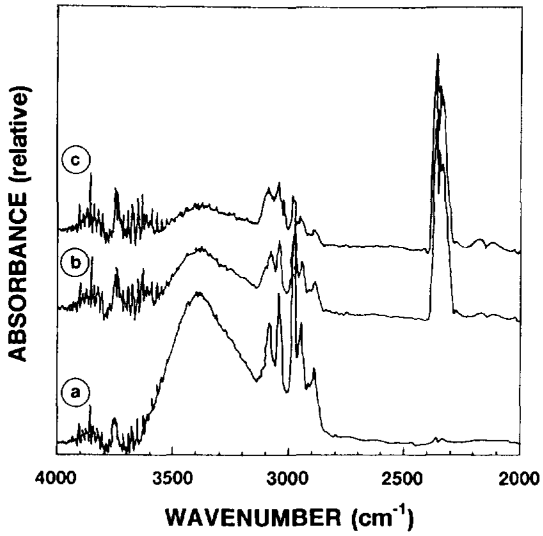

FIG. 6. Infrared spectra of (a) gas-phase reactants prior to reaction over unpromoted Fe_2O_3, (b) gas-phase reactor gases following 15 min of reaction at 873 K, and (c) gas-phase reactor gases following 1 h of reaction at 873 K. (H_2O : EB = 3; P_T = 24 Torr.)

The spectra of the adsorbed reactor gases on the unpromoted Fe_2O_3 catalyst following increasing times of reaction at 873 K are shown in Fig. 7. Two points should be noted when considering these spectra: (a) the surface morphology of the iron oxide catalyst is known to be altered during the reaction from essentially unreduced Fe_2O_3 before reaction to a mixture of both Fe_2O_3 and Fe_3O_4 after reaction (1, 2), and (b) considerable hydrocarbon deposition onto the surface occurs during reaction (1, 4). The spectral features of the surface reach a steady-

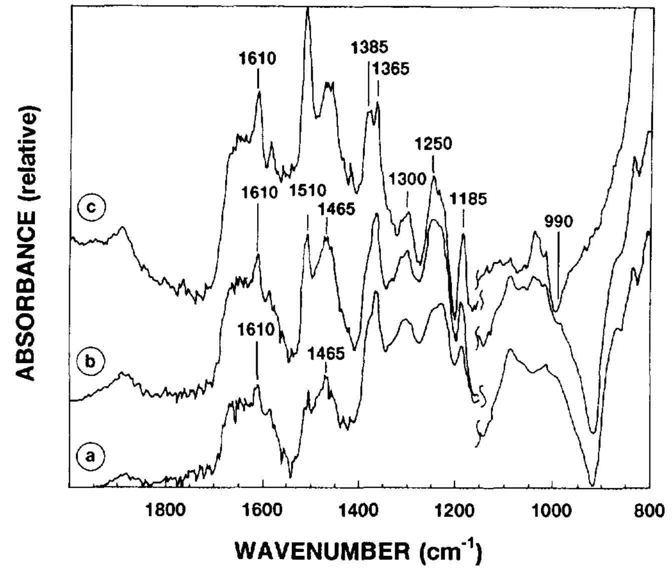

FIG. 7. Infrared spectra of adsorbed gases on unpromoted Fe_2O_3 following reaction at 873 K for (a) 2 h, (b) 5 h, and (c) 10 h. (H_2O : EB = 3; P_T = 24 Torr.)

state condition after ~1.5 h of reaction. Longer reaction times did not alter the apparent composition of the surface, but did lead to higher coverages of adsorbed species, as indicated by an overall increase in band intensities. It should be noted, however, that the concentration of gas-phase styrene did not increase significantly after ~1 h of reaction time, which is consistent with the reaction having reached equilibrium.

In spectrum (a) of Fig. 7, a multiplet of features is observed between 1550 and 1700 cm^{-1}. These are interpreted as two bands, one at ~1645 cm^{-1}, corresponding to the C═C stretch of the vinyl group in styrene. This band is obscured by a second set of features between 1600 and 1630 cm^{-1}, corresponding to the C–C stretches of surface aromatic species, including styrene. After longer periods of reaction time, the band intensities at 1385, 1510, and 1610 cm^{-1} increase. These bands are all due to aromatic stretching modes found in all of the product species present in the reaction. However, the band at 1385 cm^{-1} is very weak in the styrene spectrum, but is a fairly strong mode in the spectra of both ethylbenzene and toluene (17). The bands at 1365 and 1465 cm^{-1} are believed to correspond to hydrocarbon decomposition fragments (18), presumably as oligomers of reactant and/or product species. The band in the vicinity of 1590 cm^{-1} has been ascribed to the C═C stretching vibration of polycyclic aromatic compounds (i.e., coke) on the surface (18, 19).

Bands indicative of unperturbed styrene, at 910 and 990 cm^{-1}, are not observed on the catalyst after reaction; however, styrene can be recovered from the catalyst following reaction by evacuation and trapping. Thus, adsorption of styrene onto a fresh Fe_2O_3 catalyst leads to a different styrene surface conformation from that found for adsorbed styrene produced from reaction. Styrene formed by the dehydrogenation of ethylbenzene may be adsorbed at the vinyl group. Subsequent to its formation, the styrene remains attached to the surface through the vinyl group, presumably because of kinetic considerations, rather than converting to the more stable aromatically bonded complex. Interpretation of the spectrum is complicated by the presence of low concentrations of benzene, toluene, and/or hydrocarbon fragments, which exhibit bands between 1200 and 1600 cm^{-1}. The presence of the bands at 1300, 1420, and 1630–1640 cm^{-1}, corresponding to vinyl C–H bending and C–C stretching modes, suggest that styrene is a major surface species. The band at 1185 cm^{-1} may correspond to a ring bending mode, δ(CH), of adsorbed styrene. As mentioned previously, gas-phase styrene exhibits a band at 1200 cm^{-1}, whereas benzene, toluene, and ethylbenzene do not.

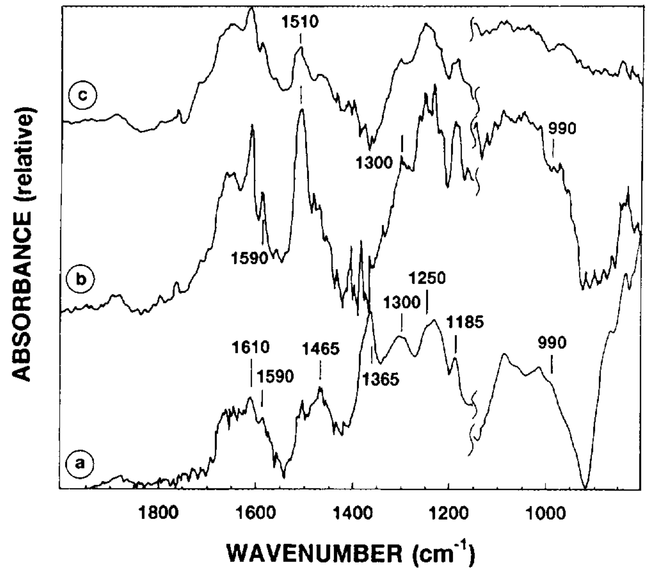

FIG. 8. Infrared spectra of adsorbed gases following reaction at 873 K for (a) 2 h on unpromoted catalyst, (b) 3 h on 10% K-promoted catalyst, and (c) 3 h on 30% K-promoted catalyst. (H_2O : EB = 3; P_T = 24 Torr.)

Reaction of Ethylbenzene over K-Promoted Fe_2O_3

Figures 8b and 8c show the spectra of a 10% K-promoted and a 30% K-promoted catalyst, respectively, after 3 h of reaction at 873 K. The spectrum for the unpromoted catalyst is shown in Fig. 8a for reference. The spectra of the two K-promoted catalysts after 3 h of reaction are similar; however, the 30% K-promoted catalyst exhibits weaker overall band intensities than does the 10% K-promoted catalyst. The marked spectral differences between the two K-promoted catalysts and the unpromoted catalyst indicate that the presence of potassium alters the nature of the surface species that are present during reaction. The most significant effect is in the bands associated with hydrocarbon decomposition fragments at 1365 and 1465 cm^{-1} on the unpromoted Fe_2O_3. These bands are very weak or absent on the K-promoted catalysts. Thus, potassium promotion appears to suppress the formation of the species which generate these features. However, bands in the vicinity of 1590 cm^{-1} that have been ascribed to coke formation on the surface (18, 19) are still present, suggesting that a certain amount of coke is present even on the promoted catalysts. The 1250 cm^{-1} band, observed on all catalysts, has not been identified at this time.

There are several changes in the spectrum associated with the product surface species, i.e., ethylbenzene, styrene, and toluene. The band at ~1645 cm^{-1}, due to the styrene vinyl C═C stretching mode, is more intense than on the unpromoted catalyst. The styrene vinyl C–H stretching mode at 1410 cm^{-1} has shifted slightly from the 1420 cm^{-1} seen on the unpromoted surface. There is also a marked decrease in the intensity of the aromatic stretching mode at 1385 cm^{-1}, which results primarily from the reaction by-products, ethylbenzene, and toluene. The principal differences between the unpromoted and promoted Fe_2O_3 surfaces are a decrease in the amounts of reaction by-products, ethylbenzene, toluene, and other hydrocarbon fragments on the promoted catalysts. The adsorption geometry and nature of the catalytic site seem to be unaffected by the presence of potassium.

CONCLUSIONS

For the ethylbenzene/styrene reaction, a clear correlation exists among the activation energy, rate, and potassium loading of an iron oxide catalyst. Potassium promotes the rate of dehydrogenation of ethylbenzene and lowers the activation energy with increased loading. The specific activity maximizes at ~10 wt.% K, whereas the activation energy is minimized at ~30% K. For potassium loadings in excess of ~10%, the catalytic activity is severely attenuated, and for potassium loadings in excess of ~30%, the activation energy of reaction increases.

Infrared spectral data indicate that the surface species present following reaction are essentially the same on all catalysts. That is, significant frequency shifts of absorption bands due to variations in potassium content were not observed among the catalysts studied. This suggests that the adsorption sites on the unpromoted and the potassium-promoted catalysts are essentially the same. Styrene produced as a product of ethylbenzene dehydrogenation is bound to the surface through the vinyl group, while for styrene adsorbed onto an unreacted Fe_2O_3 catalyst the dominant bond to the surface is via the aromatic ring, with the vinyl group remaining essentially unperturbed.

ACKNOWLEDGMENT

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