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Nonoxidative Dehydrogenation of Ethylbenzene over TiO_2–ZrO_2 Catalysts

I. Effect of Composition on Surface Properties and Catalytic Activities

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The acid–base solid, TiO_2–ZrO_2, was examined as a potential catalyst for nonoxidative dehydrogenation of ethylbenzene. The acidic and basic properties and surface area of these catalysts were measured. A good correlation was found between the activity for this reaction and the surface acid–base properties of the catalysts. The high catalytic activity occurred as the two components, TiO_2 and ZrO_2, are presented at compatible amount. The selectivity of styrene increased monotonically with the increase in TiO_2 content. The activity was poisoned not only by K_2O but also by H_3BO_3, indicating that the active sites consist of both acidic and basic sites. A concerted two-center mechanism was proposed.

INTRODUCTION

The catalytic dehydrogenation of ethylbenzene is of industrial importance in the manufacture of styrene. Iron oxide promoted with alkali was used as the catalyst in most of the industrial processes for this reaction (*1–3*). A report has been published on the possibility of carrying out this process on the TiO_2–ZrO_2 system (*4*). However, no study has been made on the mechanism of this reaction and the correlation between the acid–base property and catalytic action of TiO_2–ZrO_2. The acidic and basic properties of TiO_2 (*5*), ZrO_2 (*6*), and mixed oxide catalysts such as TiO_2–SiO_2 (*5–8*), TiO_2–MgO (*9*), TiO_2–V_2O_5 (*10*), TiO_2–MoO_3 (*10*), TiO_2–Al_2O_3 (*11*), TiO_2–ZnO (*12*), TiO_2–SnO_2 (*13*), TiO_2–NiO (*14*), ZrO_2–SiO_2 (*8*), and TiO_2–ZrO_2 (*15*) etc., have been extensively investigated. The acidity of binary oxide is generated by an excess of a negative or positive charge in the structure according to Tanabe's hypothesis (*16*). The study on the selectivity of isomerization of either 1-methylcyclohexene oxide (*15*) or cyclohexene oxide (*17*) over TiO_2–ZrO_2 illustrated the acid–base bifunctional mechanism. This bifunctional mechanism was also found in the selective oxidation or oxidative dehydrogenation reaction over Al_2O_3 (*18*), SnO_2–P_2O_5 (*19, 20*), Fe_2O_3-based mixed oxides (*21–23*), and Na-$SiO_2 \cdot Al_2O_3$ (*24, 25*) catalysts.

In this work, the acid–base properties of a series of TiO_2–ZrO_2 catalysts with different molar ratio of TiO_2 to ZrO_2 were measured and the catalytic activity as well as the selectivity of the dehydrogenation of ethylbenzene were examined. The activity and selectivity of this reaction were correlated well with the surface acid–base properties of the catalyst. This result strongly suggested that the catalytic activity of these catalysts was acid–base bifunctional. Thus, a concerted two-center mechanism, where zirconium ions act like a Lewis acid, and titanium ions as a base, was proposed.

EXPERIMENTAL

Preparation of catalysts. TiO_2–ZrO_2 catalysts with a different molar ratio of TiO_2 to ZrO_2 were prepared by coprecipitation of a

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mixed solution of titanium tetrachloride and zirconium tetrachloride in anhydrous alcohol with aqueous ammonia (28%). The precipitate was aged over water bath for 2 hr and washed with deionized water until no chloride ions were detected with Ag^+ in the filtrate, and dried at 110°C, then calcined at 550°C in air for 2 hr.

TiO_2–ZrO_2–K_2O, which contained 0.1 ~ 2.0 wt% K_2O, was prepared from TiO_2–ZrO_2 (1/1) calcined at 550°C by doping with potassium hydroxide. The doping method was carried out by mixing TiO_2–ZrO_2 with an aqueous solution of KOH to form a paste. The paste was dried at room temperature for 48 hr with occasional remixing, then calcined at 550°C. Another sample, TiO_2–ZrO_2–B_2O_3 with 0.1 ~ 2.0 wt% of B_2O_3, was prepared from TiO_2–ZrO_2 by adding orthoboric acid (H_3BO_3) in a similar way.

Ethylbenzene adsorption measurement. The amount of adsorption of ethylbenzene over the catalysts with various compositions was measured by a Perkin-Elmer TGS-2 apparatus. The vapor of ethylbenzene, which was carried by nitrogen gas, passed continuously through the catalyst sample at 150°C. The weight gain of the sample was considered as the amount of adsorption.

Acidity measurement. The acid strength and acid amounts of catalysts were measured by titrating the powder suspended in benzene with 0.1 N *n*-butylamine benzene solution, using dicinnamalacetone ($pK_a = -3.0$) and methyl red ($pK_a = +4.8$) as indicators. The acidic properties of the catalysts were also measured by *n*-butylamine adsorption. The catalyst was first put in a desiccator with saturated *n*-butylamine vapor at room temperature for 48 hr. Then the same TG apparatus in flow system as mentioned above was used to measure the weight loss of the adsorbed sample at programmed temperature ($40°C \xrightarrow{40°C/min} 500°C$).

Basicity measurement. The basicities of the catalysts were measured by the same adsorption method as described by *n*-butylamine adsorption. Acetic acid was chosen as the adsorbate.

Surface area and X-ray analysis. The specific surface area of catalysts was determined by applying the BET method. A quantasorb apparatus was used. X-Ray diffraction patterns were measured over the range of $2\theta = 4$–$60°$ for the powdered samples which had been calcined for 2 hr in air at 550°C.

Reaction equipment and experimental procedure. Conversion and selectivity data were obtained in a continuous-flow fixed bed microreactor. A schematic diagram of the system is shown in Fig. 1. Two separated streams of nitrogen at designed flow rates were metered through an ethylbenzene saturator and a water saturator at room temperature. Another dilution nitrogen stream was used to control the partial pressure of ethylbenzene in feed. The reactor is a quartz glass tube with an inside diameter of 1.3 cm. It was heated by an electrical heater and the temperature at the center of the catalyst bed was controlled by a Eurotherm 101 temperature controller. The reactor was packed from top to bottom with layers of inert ceramic, catalyst particles (0.5 g, 12 ~ 20 mesh) and inert ceramic. The bed was first heated up to 580°C with a nitrogen stream at a flow rate of 50 ml/min to remove contamination. Then, the reaction was studied under the following conditions: temperature, 580 ~ 600°C (580°C, if not specified); total pressure, 760 mm Hg (absolute); EB partial pressure, 2 mm Hg; H_2O/EB mole ratio, 10; NTP space velocity, 3,000 ~ 12,000 hr^{-1} (12,000 hr^{-1}, if not specified). During each run, samples of the feed and product were taken at intervals and analyzed to check the EB partial pressure of the feed and to determine the composition of the product until steady values were reached.

Both feed and product were analyzed by a Schimadzu GC-7A gas chromatograph equipped with a flame ionization detector (FID) and a Schimadzu C-R1A data processor. The column chosen for analysis was a

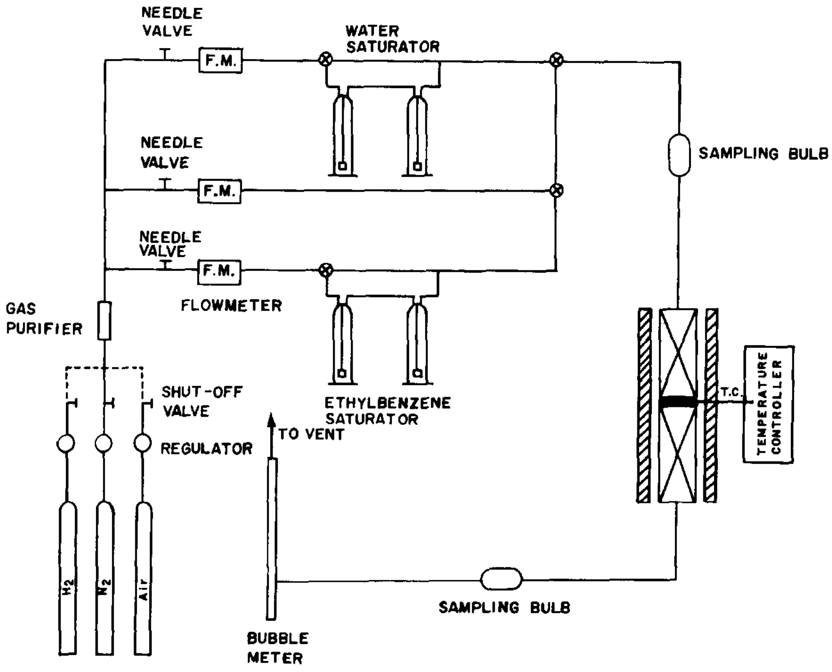
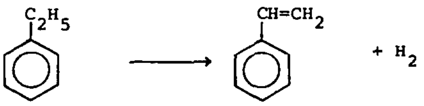


FIG. 1. The flow diagram of reaction system.

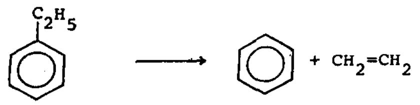
8-ft × 1/8-in.-o.d. stainless-steel column packed with 5% SP 1200/1.75% Bentone 34 on 100/120 Supelcoport. The GC was operated under the following conditions: oven temperature, 110°C; flow rate, 40 ml/min N_2; injection volume, 0.5 ml.

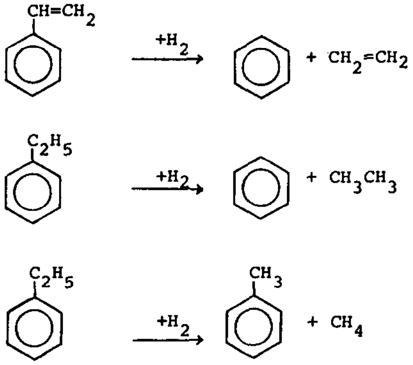
RESULTS AND DISCUSSION

The nonoxidative dehydrogenation of ethylbenzene (EB) over TiO_2–ZrO_2 catalysts gives styrene (ST) as the major product and small amount of benzene and toluene as by-products. The main reaction can be expressed as:



The by-products, benzene and toluene, could be visualized to be produced according to the reactions as follows.





In the presence of steam, trace amount of CO and CO_2 might be produced by the steam reforming and the water–gas-shift reactions. In this study, catalyst performances will be expressed according to the following formulas:

Ethylbenzene conversion, $C(\%)$

$$= \frac{\text{EB inlet} - \text{EB outlet}}{\text{EB inlet}} \times 100$$

Product selectivity, S_i (%, mole)

$$= \frac{\text{Product } (i)}{\text{EB inlet} - \text{EB outlet}} \times 100$$

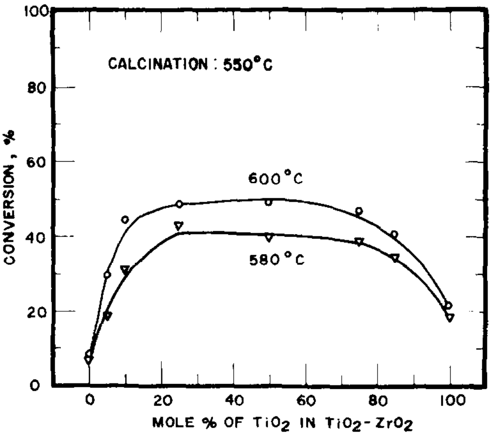


FIG. 2. Activity of ethylbenzene dehydrogenation over TiO_2–ZrO_2 at various compositions; (○), reaction temperature 600°C; (▽), reaction temperature 580°C.

Product yield, Y_i (%, mole)

$$= \frac{\text{Product } (i)}{\text{EB inlet}} \times 100 = C \times S_i.$$

The relation between ethylbenzene conversion and the composition of TiO_2–ZrO_2 is shown in Fig. 2, where we refer to the ethylbenzene conversion as the activity index and all the catalysts were calcined at 550°C for 2 hr. By itself, TiO_2 or ZrO_2 is impractical as a catalyst for dehydrogenation of ethylbenzene. For example, the conversion for this reaction over ZrO_2 alone is below 10%. However, the binary oxide, TiO_2-ZrO_2, is very effective, and the activity increased as the percentage content of TiO_2 and ZrO_2 were becoming more comparable. It was of interest that if neither the content of TiO_2 nor ZrO_2 was less than 25%, the catalysts showed the approximately same activity as shown in Fig. 2.

ZrO_2 has basic and weak acidic character and exhibits very small concentration of acid sites (*26*, *27*). TiO_2 shows acidic sites when evacuated at low temperatures (400°C). These acidic sites would be eliminated when evacuated at higher temperatures. At high temperature electron-donating sites were generated (*5*), and such basic sites were attributed to the formation of Ti^{3+} by the reduction of Ti^{4+} during the evacuation (*28*). In the study of isomerization of butene, the high temperature evacuated TiO_2 had a basic character as ZrO_2 (*13*). In this study, the amounts of both acidic and basic sites of TiO_2–ZrO_2 with different composition were measured by the adsorption of basic and acidic molecules in the vapor phase. The results are shown in Figs. 3 and 4, respectively. The results show that both acidity and basicity increased by mixing TiO_2 and ZrO_2 up to

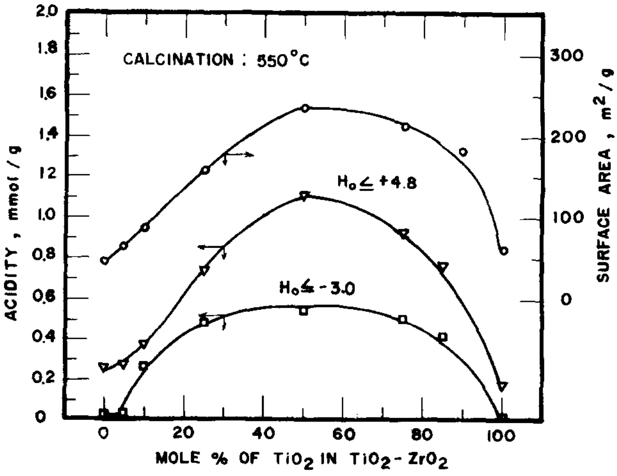


FIG. 3. Surface area and acidity of TiO_2–ZrO_2 at various compositions; (○), surface area; (▽), acid strength $H_0 \leq +4.8$; (□), acid strength $H_0 \leq -3.0$.

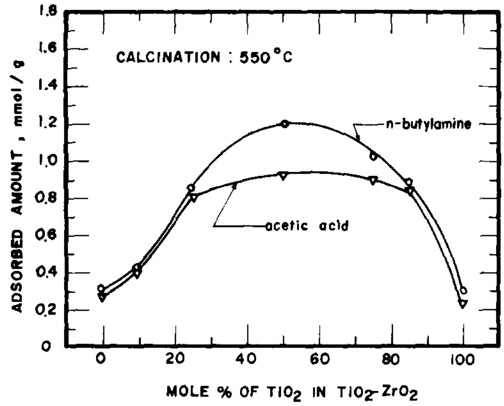


FIG. 4. Amounts of *n*-butylamine and acetic acid adsorbed over TiO_2–ZrO_2; calcined at 550°C.

equal components. These results agrees with those of Tanabe's (*15*). Figures 2 and 4 indicates clearly that the catalytic activity of TiO_2–ZrO_2 in the dehydrogenation of ethylbenzene could be correlated well with the acid–base properties (especially the basicity) of the catalysts. The relationship between the surface area and composition of TiO_2–ZrO_2 is also shown in Fig. 3. As well as the acidity and the basicity, the surface area and the amount of EB adsorption (as shown in Fig. 5) increased by mixing TiO_2 and ZrO_2, and attained a maximum at equal components of TiO_2 and ZrO_2. Since titanium and zirconium belong to the same group (IVB), they are expected to have similar physical and chemical properties. When their oxides are coprecipitated together, the mutual chemical interaction (*14*) might be profound. From the XRD spectra of TiO_2–ZrO_2 (calcined at 550°C) with various compositions, as shown in Fig. 6, we found that TiO_2–ZrO_2 became amorphous if neither the content of TiO_2 nor ZrO_2 was less than 25%. The crystallization of these binary oxides was inhibited with each other. The significant changes of surface area, acidity, basicity, and catalytic activity could be explained by this mutual interaction.

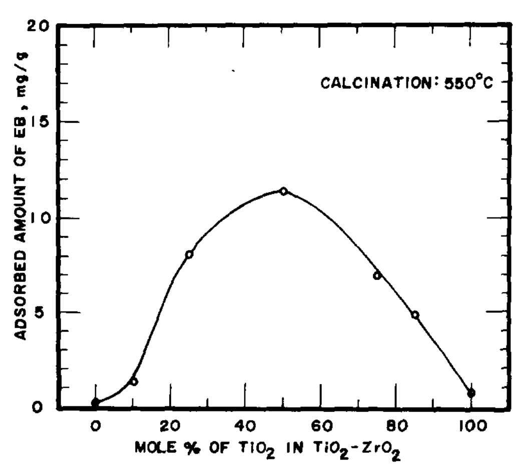


FIG. 5. Amounts of ethylbenzene adsorbed over TiO_2–ZrO_2 at various compositions; adsorption temperature 150°C.

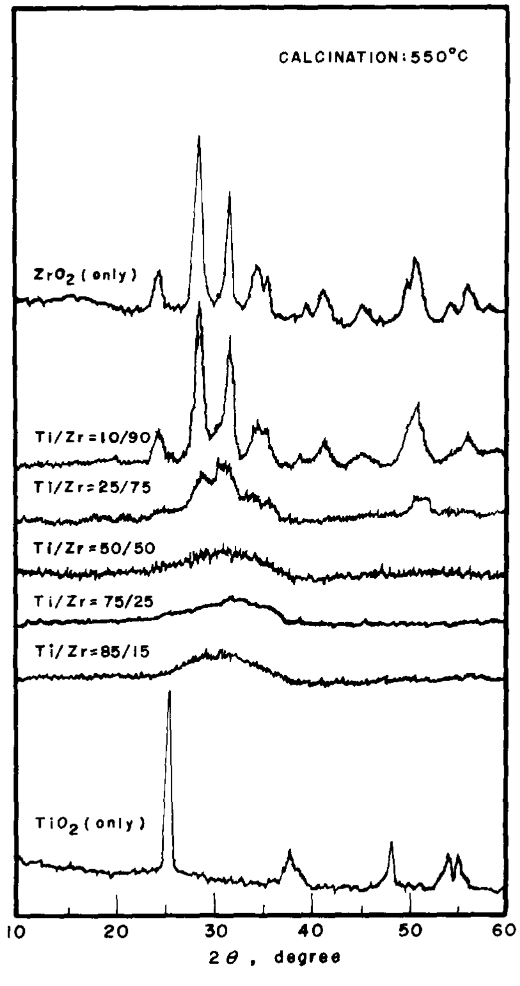


FIG. 6. X-Ray diffraction pattern of TiO_2–ZrO_2 at various compositions; calcination temperature 550°C.

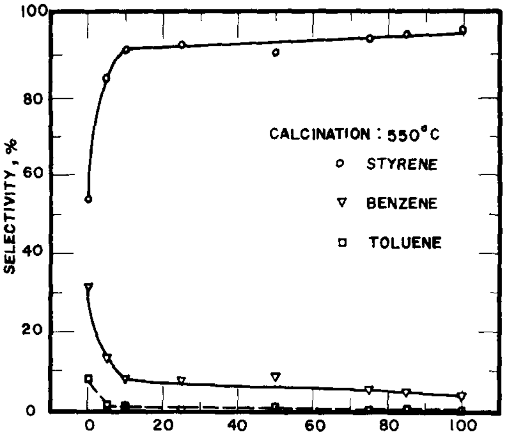


FIG. 7. Selectivity of styrene, benzene, and toluene at various compositions [reaction temperature, 600°C; conversion, 50 ± 1%; except pure ZrO_2 (40% at 620°C)].

Figure 7 gives the relation between the selectivity of styrene and the composition of TiO_2–ZrO_2 at 50% conversion level. Pure ZrO_2 had a low selectivity of styrene (below 55%), while pure TiO_2 possessed a considerably high selectivity (above 96%). As for binary oxides, TiO_2–ZrO_2, those that are ZrO_2 rich showed a sharp increase of selectivity with the increase of TiO_2 content up to 10 mol%. The selectivity of styrene increased slightly with a further increase of TiO_2 content. The selectivities of the undesired products of benzene and toluene are also shown in Fig. 7. The yield of toluene is negligibly small for the reaction over TiO_2-rich catalysts. It is of interest to note that for the reactions over TiO_2–ZrO_2 catalysts, the yield of benzene is always larger than that of toluene. This result is in contrast with commercial iron catalysts, which give larger yields of toluene than benzene (*2*).

The fact that the selectivity of styrene increases with the TiO_2 content indicates that TiO_2 has a special property favoring the formation of styrene. Since Ti^{3+} could be created by the reduction of the surface (*13*), it can be thought that the increase of TiO_2 content in TiO_2–ZrO_2 results in the increase of the amount of Ti^{3+} which accelerates the formation of styrene.

In order to demonstrate the role of acidic sites played in the dehydrogenation of ethylbenzene, K_2O was introduced by incipient wetness impregnation of TiO_2–ZrO_2. The dehydrogenation reaction was carried out over TiO_2–ZrO_2 (1/1) which doped with various quantities of K_2O (0.1 ~ 2.0 wt%). Figure 8 shows that increasing the K_2O content of the catalysts reduces both the total conversion of ethylbenzene and the

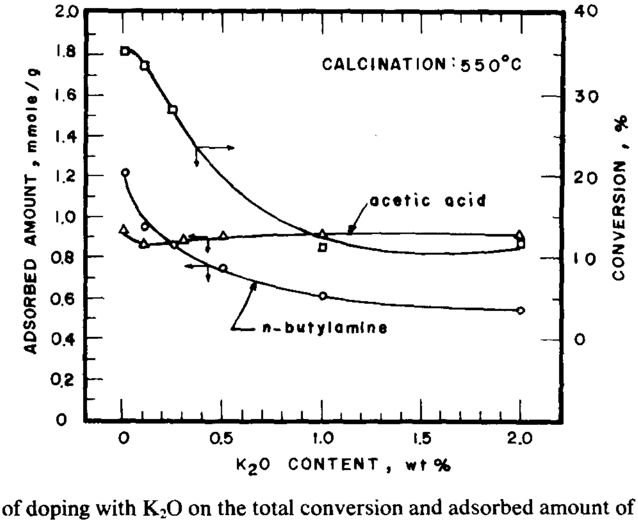


FIG. 8. Effect of doping with K_2O on the total conversion and adsorbed amount of *n*-butylamine and acetic acid over TiO_2–ZrO_2 (1/1).

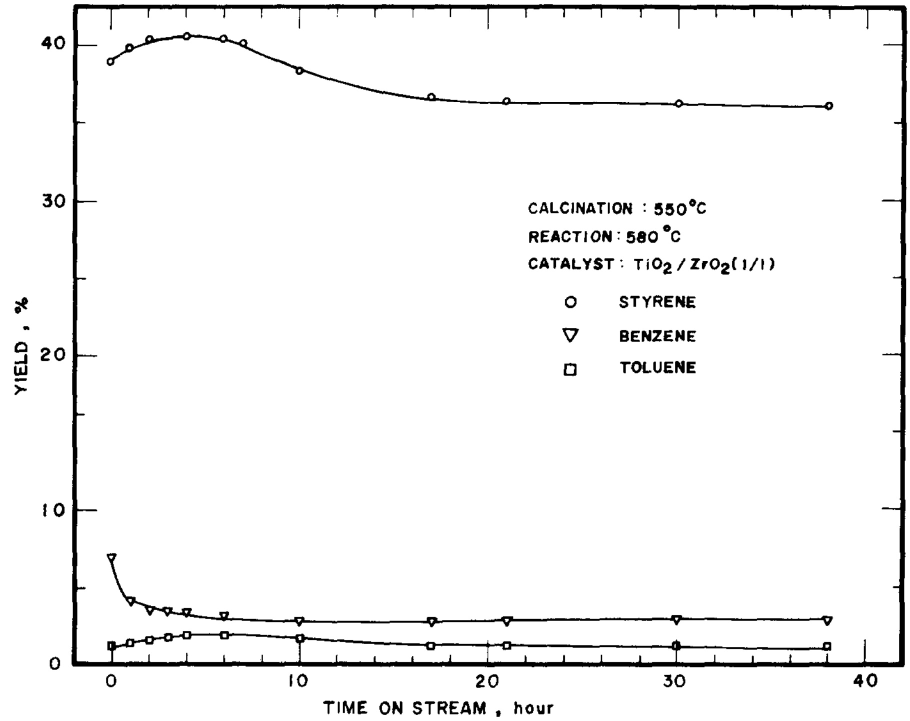


FIG. 9. Product distribution for ethylbenzene dehydrogenation reaction as a function of time on stream.

adsorbed amount of *n*-butylamine. Based on these results and the results of good correlation of the amount of EB adsorption with acidity (Figs. 4 and 5), we concluded that the acidity of TiO_2–ZrO_2 plays an important role in the nonoxidative dehydrogenation reaction.

Figure 9 gives the changes of the product distribution for the reaction over TiO_2–ZrO_2 (1/1) at 580°C along with time on stream. In the beginning of the reaction, the yield of benzene is in a significant amount (7%) only second to that of styrene (37%). After an overnight run, the yield of benzene reduces to 2.8% and that of styrene was 36.1%. This sharp reduction of benzene yield and the slightly increasing of styrene yield at an early stage of the reaction reveal that the dealkylation of ethylbenzene and hydrocracking of styrene both of which are catalyzed by strong acid sites diminished due to the coke formation on strong acid sites. This phenomena combined with the effect of K_2O doping indicate that both the modest and weak acid sites dominate the yield of styrene.

TiO_2–ZrO_2 doped with 0.1 ~ 2.0 wt% H_3BO_3 were also used to test the influence of basicity. The activity of ethylbenzene conversion over this catalyst decreased slightly upon the addition of H_3BO_3 as shown in Fig. 10. This slight reduction of activity may be due to mild poisoning of basic site.

Coked alumina has been reported to be an active catalyst for oxidative dehydrogenation of ethylbenzene. However, nonoxidative dehydrogenation of ethylbenzene was not observed over coked alumina (*18*). The reaction mechanism of oxidative dehydrogenation of ethylbenzene has also been studied over $NaSiO_2 \cdot Al_2O_3$ catalysts (*24, 25*). They proposed the acid–base bifunctional mechanism, and the acid site was attacked by the aromatic ring followed by the abstraction of α-hydrogen of ethylbenzene.

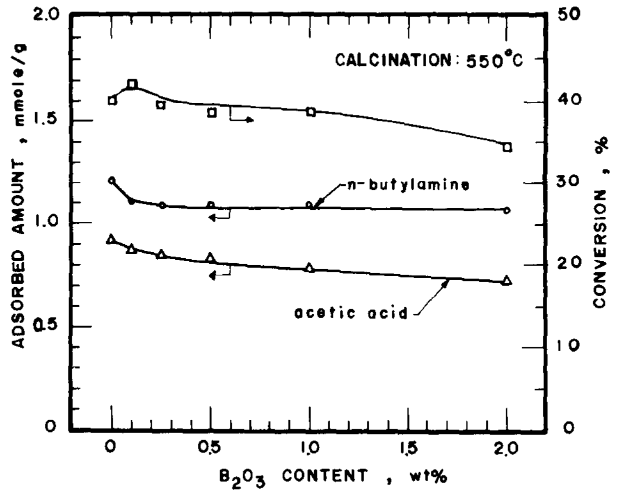


FIG. 10. Effect of doping with B_2O_3 on the total conversion and adsorbed amount of *n*-butylamine and acetic acid.

TiO_2–ZrO_2, which contains adjacent electron-acceptor and electron-donor sites, is known to be an effective acid–base bifunctional catalyst (*15, 17*). In our present work, a concerted mechanism is proposed for the nonoxidative dehydrogenation of ethylbenzene over TiO_2–ZrO_2, in which the α-hydrogen of ethylbenzene attacks the acid site of the catalyst, and simultaneously the β-hydrogen attacks the basic site of the catalyst as shown in Fig. 11. The partial positive charge on the α-carbon of transition state could be stabilized by the aromatic ring. From this figure, it is clear that the nonoxidative dehydrogenation of ethylbenzene is facilitated by TiO_2–ZrO_2, a catalyst on which two active groups, one acidic and one basic, are properly oriented.

In marked contrast to TiO_2–ZrO_2, it was found that the basicity of iron catalyst (e.g., Shell 105) is strong enough to abstract the β-hydrogen. (*1b, 29*). The nonoxidative dehydrogenation of ethylbenzene over iron catalyst can be classified as a typical base-catalyzed model reaction, and the acidic sites of the catalyst are unnecessary for this reaction. This is why the iron catalysts have high selectivity to styrene and give a larger yield of toluene than benzene. However, on TiO_2–ZrO_2 catalysts, the basicity originated from mixing of TiO_2 and ZrO_2 is not strong enough, and thus the presence of adjacent acidic sites is essential to accelerate the dehydrogenation of ethylbenzene.

On the bases of the facts discussed above we are able to conclude that the nonoxidative dehydrogenation activity of TiO_2–ZrO_2 catalysts can be interpreted in connection

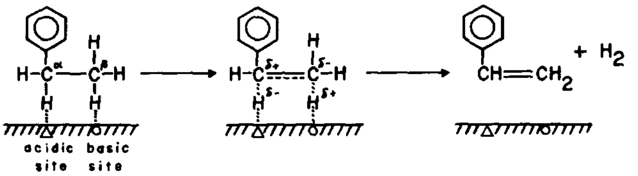


FIG. 11. Acid–base bifunctional mechanism proposed for the nonoxidative dehydrogenation of ethylbenzene.

with their acid–base properties, which are strongly changed by the catalyst composition.

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