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Effect of Potassium Promoter on Iron Oxide Catalysts for Dehydrogenation of Ethylbenzene to Styrene

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The catalytic activity and the sintering property of iron oxide catalysts with and without potassium additives have been studied. The potassium oxide acts as a promoter and is effective under given conditions in increasing the activity of the catalyst from four to ten times. The effects of the promoter can be classified thus: (1) Structural promoter: The increase in the apparent bulk density and the shrinkage of the catalyst tablet upon calcination during the preparation of the catalyst are prevented by potassium additives. The differences in the specific surface area and in the pore volume of the catalyst between with and without potassium promoter are slight. These effects on iron oxide appear to be caused largely by the formation of $K_2Fe_{22}O_{34}$. (2) Synergetic promoter: The potassium promoter changes the apparent energy of activation of the dehydrogenation reaction from 28 to 43 kcal/mol. The increase in the catalytic activity is due to the increase in the pre-exponential factor. The increase in the factor can be explained in terms of the higher concentration of the active center produced by the interaction of the potassium promoter with iron oxide. (3) Selectivity promoter: The formation of benzene by a side reaction is retarded by potassium additives.

Alkali metal oxide, especially potassium oxide, is extensively used as a promoter in many catalytic reactions, such as water gas shift, ammonia synthesis, and the dehydrogenation of organic compounds. It is well known that the potassium oxide reduces the amount of carbon deposit on the catalyst surface and causes the deposited carbon to be removed by steaming. In examining an iron oxide catalyst used for the dehydrogenation of butene to butadiene, Kearby[1] has described the characteristics of the potassium promoter. Lee and Holmes[2] studied the relations between the catalytic activity and electronic properties of alkali and alkaline earths promoting iron oxide for the dehydrogenation of ethylbenzene to styrene. However, the effect of alkali on an iron oxide catalyst for the dehydrogenation of organic compounds has not been clarified completely. The present paper describes some results of our study of the promoter action of potassium oxide on the iron oxide catalyst used for the dehydrogenation of ethylbenzene to styrene. The results of our experiments show that potassium acts as both a structural and a synergetic promoter. In addition, the formation of benzene is retarded by potassium oxide additives.

Experimental

Materials. The ethylbenzene was of a reagent grade and was obtained from the Wako Pure Chemicals Company; its purity, tested by gas chromatography, was superior to 99.5%, the remaining part being benzene and toluene. The ferric nitrate and potassium carbonate were reagent-grade chemicals and were used without further purification.

Catalyst Preparation. *Catalyst A*: Ferric hydroxide, prepared by the addition of an aqueous solution of ammonia to a solution of ferric nitrate, was decomposed to ferric oxide at 500°C in air. The ferric oxide powder and a suitable amount of potassium carbonate was mixed by hand grinding in an agate mortar, and then compressed into tablets under a pressure of 100 kg/cm^2. The tablet was calcined at 930°C in an electric furnace for two hours in the presence of air, and then crushed into granules.

Catalyst B: The compressed tablet of the ferric oxide powder without potassium additives was calcined in an electric furnace for two hours at 900°C in air. The calcined tablet was then crushed into granules and impregnated with a suitable amount of an aqueous potassium carbonate solution.

For both Catalyst A and Catalyst B, the fraction passing through a 1.5-mm sieve but not a 1.0-mm sieve was chosen for the activity and apparent-bulk-density mesurements.

Activity Measurements. The catalytic activity was measured with a differential reactor, with the conversion of ethylbenzene being kept below 5%. The distributions of the by-products, benzene and toluene, were measured with an integral reactor.

Preheated ethylbenzene and a 9/1 mol ratio of steam were fed into a stainless-steel reactor (10 mm i.d.) at 1 atm, and the reactor effluent was analyzed by gas chromatography. A thermocouple junction for measuring the reaction temperature was located at a center

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1) K. K. Kearby, *Ind. Eng. Chem.*, **42**, 295 (1950).

2) E. H. Lee and L. H. Holmes, Jr., *J. Phys. Chem.*, **67**, 945 (1963).

of the catalyst bed in a stainless steel tube (1.6 mm o.d.) inserted through the bottom of the reactor.

Apparent Bulk Density. A weighed amount of the catalyst granules was placed in an ordinary glass cylinder and then the cylinder was shaken till the granules showed a constant volume.

Shrinkage of the Tablet of the Catalyst. The shrinkage of the tablet (0.5 cm long by 1.00 cm diameter before calcination) by calcination in the process of catalyst preparation was measured by an ordinary micrometer after the tablet had been cooled to room temperature. The maximum variation between samples heated in this way was less than 2%.

X-Ray Diffraction. X-Ray powder diffraction diagrams were recorded by a X-ray diffractometer (Geigerflex). As a X-ray radiation source, vanadium-filtered chrome radiation was used.

Specific Surface Area and Total Pore Volume. The specific surface area was obtained by applying the B. E. T. method to the adsorption isotherm of nitrogen at −196°C. The total pore volume was obtained from the amount of nitrogen adsorbed at the relative pressure of 0.98 in the adsorption of nitrogen at −196°C.

Results and Discussion

Sintering of the Iron Oxide during Catalyst Preparation. The apparent bulk density of the granules of Catalyst A with various concentrations of potassium additives is shown in Fig. 1. The concentration of potassium additives is indicated as a weight percentage of the potassium oxide. The apparent bulk densities of these catalysts before calcination ranged from 1.40 to 1.45 g/cc; after calcination, in the course of preparing a catalyst at 930°C for two hours, the value increased to 1.85 g/cc without potassium additives. The increase in the apparent bulk density upon calcination diminishes progressively with an increase in the concentration of potassium oxide. When the concentration of potassium reaches above about 3%, the apparent bulk density of the catalyst after calcination becomes lower than that of the uncalcined catalyst. Figure 2 shows the effect of the concentration of potassium oxide on the shirnkage or swelling of the Catalyst A tablet in the course of the catalyst preparation. The shrinkage and swelling of the tablet are indicated as changes in the diameter (1.00 cm before calcination). The shrinkage of the tablet without potassium additives is about 7%, whereas a swelling of the tablet is observed when the concentration of potassium oxide reaches above 3%. As is shown in Fig. 3, the

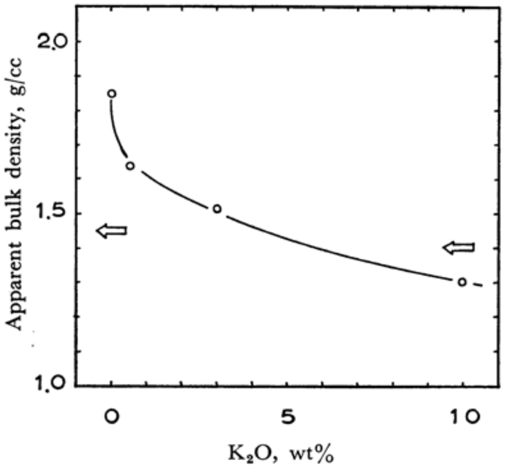


Fig. 1. Apparent bulk density of the iron oxide catalyst with various content of potassium oxide. The arrows indicate the apparent bulk density of catalyst before calcination.

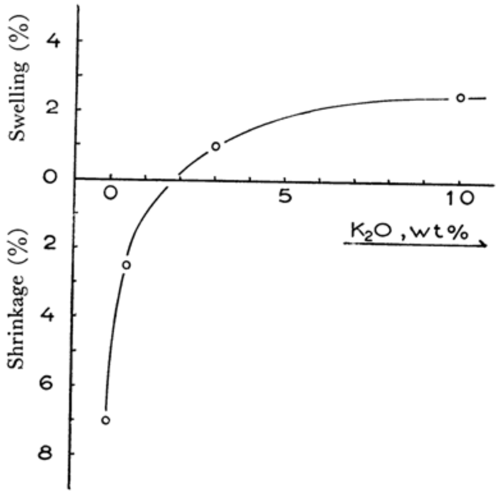


Fig. 2. Shrinkage or swelling of the Catalyst A by calcination in the process of catalyst preparation.

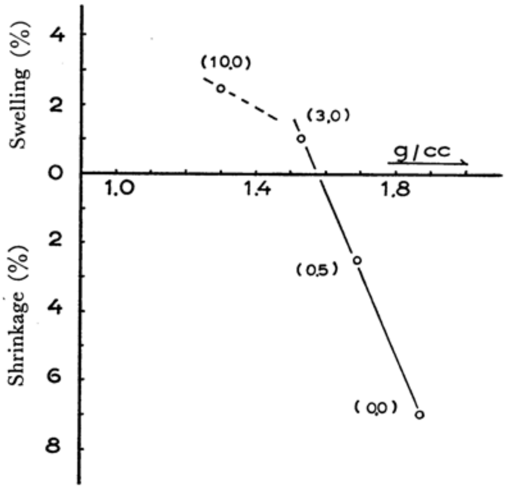


Fig. 3. Relation between apparent bulk density and shrinkage or swelling of the Catalyst A. The numerals in parentheses are the weight percent of potassium oxide.

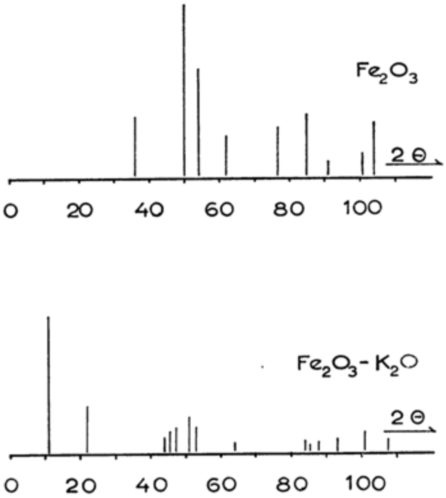
relation of the shrinkage or swelling to the apparent bulk density is linear except when the concentration of potassium oxide is above 3%. The Table 1 illustrates the specific surface area and the total pore volume of the catalyst with and without a potassium promoter.

Table 1. Surface area and pore volume of the catalyst

	Surface area m^2/g	Pore volume cc/g
Fe_2O_3 uncalcined	28	0.33
Fe_2O_3 calcined	2.5	0.20
Fe_2O_3-K_2O (3 wt%) uncalcined	29	0.33
Fe_2O_3-K_2O (3 wt%) calcined	3.0	0.18

The difference between the specific surface area and the pore volume of the catalyst with and without a potassium promoter is slight. The effect of a potassium promoter in preventing the sintering of the catalyst appears to be caused largely by the formation of $K_2Fe_{22}O_{34}$. The specific gravity of $K_2Fe_{22}O_{34}$ is 4.24,[3,4] whereas that of ferric oxide is 5.13,[5] and it has been reported that $K_2Fe_{22}O_{34}$ is obtained by the calcination of a mixture of ferric oxide and potassium carbonate.[6] X-Ray diffraction diagrams of the iron oxide catalyst with and without potassium additives are shown in Fig. 4. The diagram of iron oxide with potassium additives is essentially the same as that of $K_2Fe_{22}O_{34}$ reported by other workers.[4,7,8] The weight percentage of K_2O in $K_2Fe_{22}O_{34}$ is 5.06; this value is near to the composition where the deviation from the linear relation was observed, as is shown in Fig. 3. The composition of the Catalyst A may be $K_2Fe_{22}O_{34}\cdot nFe_2O_3$ when the content of K_2O is lower than 5.06 wt%; above this concentration the composition may be $K_2Fe_{22}O_{34}\cdot mK_2O$.

Activity Measurements of Catalyst A. To test the stability of the catalyst, the variation of the conversion with the time was tested. After a rapid initial fall of the conversion with the time during the first two hours after ethylbenzene was fed in, the catalyst came to a steady state and the conversion remained constant. The samples used for analyzing the reaction products were withdrawn two hours after the start of feeding. Figure 4 shows the temperature dependence of the rate of the dehydrogenation of ethylbenzene using a differential reactor. The reaction rates per unit volume of the catalyst, r, were determined from the $r=(F/V)\cdot X$ relation, where F represents the feed rate of ethylbenzene into the reactor in g-mol per sec, where V represents the volume of the catalyst in ml, and where X represents the fraction of ethylbenzene converted to styrene. The styrene made from the gas-phase reaction in the empty reaction vessel was subtracted from the total conversion. As is shown in Fig. 5, the potassium



K_2O, 10 wt%

Fig. 4. X-Ray powder diffraction diagrams of iron oxide catalyst with and without potassium promoter. (Radiation: Cr$K\alpha$)

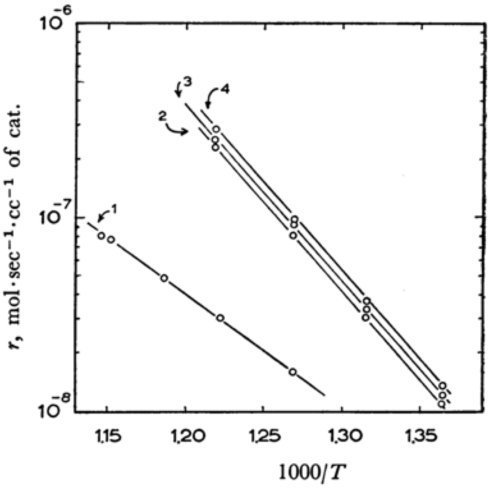


Fig. 5. The effect of temperature on the rate of ethylbenzene dehydrogenation on Catalyst A.
1, Fe_2O_3; 2, Fe_2O_3-K_2O(0.5 wt%);
3, Fe_2O_3-K_2O(3.0 wt%);
4, Fe_2O_3-K_2O(10.0 wt%)

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[3] V. Cirilli and C. Brisi, *Gazz. Chim. Ital.*, **81**, 50 (1951).

[4] Y. Otsubo and K. Yamaguchi, *Nippon Kagaku Zassi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **82**, 676 (1961).

[5] N. A. Lange, "Handbook of Chemistry," Tenth Ed., McGraw-Hill Book Co., New York (1961), p. 251.

[6] V. Adelsköld, *Arkiv. Kemi. Min. Geol.*, **12A**, 1 (1938).

[7] S. Hilpert and A. Linder, *Z. Phys. Chem.*, **22B**, 395 (1933).

[8] E. W. Gorter, *Philips Res. Rep.*, **9**, 259 (1954).

oxide acts as a promoter and is, under given conditions, effective in increasing the activity of the catalyst from four to ten times. The activity of the catalyst is not so sensitive to the potassium oxide concentration in the range from 0.5 to 10.0 wt%, although the rate of dehydrogenation increased slightly with an increase in the concentration of potassium oxide. The apparent energies of activation were obtained from the slopes of the straight lines shown in Fig. 5; they were found to be 28 kcal/mol without potassium additives and 43 kcal/mol with them. Within the limits of experimental error the energy of activation was the same for all the iron oxide catalysts with potassium promoters. The interaction of the potassium promoters with iron oxide is assumed to give an active center which is less reactive than iron oxide without the promoter. The high activity of the potassium-promoted catalyst is caused by a high pre-exponential factor, which compensates for the high activation energy. The increase in the pre-exponential factor can tentatively be explained in terms of the higher concentration of the active center, as the difference between the specific surface area of the catalyst with and without a potassium promoter is slight. It was concluded that the promotion of the iron oxide catalyst by potassium is not only structural but also synergetic in nature. This conclusion was rendered certain by the discovery of the change in the activation energy, since the structural promotion should not alter the temperature coefficient. This conclusion is also supported by the results of the experiments using Catalyst B.

Table 2 shows the distribution of the two by-products, benzene and toluene, together with that of the main product, styrene. These results were measured with an integral reactor.

TABLE 2. DISTRIBUTION OF PRODUCTS
(Reaction temp., 600°C)

Catalyst	Benzene (mol%)	Toluene (mol%)	Styrene (mol%)
Fe_2O_3	2.4	0.55	12.5
Fe_2O_3-K_2O (0.5 wt%)	1.5	2.2	63.9
Fe_2O_3-K_2O (3.0 wt%)	1.1	2.6	65.5
Fe_2O_3-K_2O (10.0 wt%)	1.2	4.3	68.0

As is shown in Table 2, the addition of potassium decreased the catalytic activity of the benzene formation, in spite of the fact that the potassium increased the catalytic activity of the dehydrogenation reaction. Generally, alkylation and dealkylation are catalyzed by an acid. The acidity on iron oxides, if any, must be neutralized by the addition of potassium compounds. Therefore, it is natural to think that the decrease in the activity of benzene formation is mainly due to the neutralization of the acidity of the catalyst by a potassium promoter, rather than to a retardation by the styrene formed.

The formation of toluene increases with an increase in the concentration of potassium oxide. This increase in the activity of toluene formation is partly due to the increased yield of styrene, as the toluene is mainly produced from styrene.

Activity Measurement of Catalyst B. Figure 6 shows the temperature dependence of the rate of the dehydrogenation on Catalyst B. The procedure and the experimental conditions were the same as those of the experiments using Catalyst A. The potassium carbonate-impregnated catalyst showed a drastic change in catalytic performance, displaying sharp increases in the rate of the formation of styrene. The activity of these catalysts was insensitive to the potassium oxide content in the range from 0.5 to 3.0 wt%. The apparent energies of activation were found to be 28 kcal/mol without potassium additives and 46 kcal/mol with them. The high activity of the catalyst with a potassium promoter is caused by a high pre-exponential factor, which compensates for the high activation energy. The increase in the pre-exponential factor is due to the increase in the concentration of the active center which is newly-produced by the interaction of the potassium promoter with iron oxide.

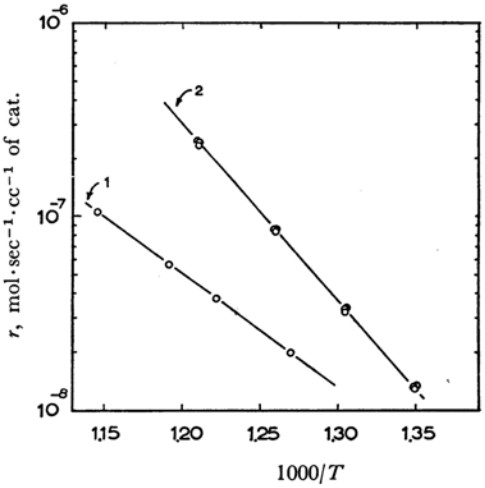

Fig. 6. The effect of temperature on the rate of ethylbenzene dehydrogenation on Catalyst B.
1, Fe_2O_3; 2, Fe_2O_3-K_2O (0.5—3.0 wt%)

As may be seen from the method of preparing Catalyst B, potassium carbonate was impregnated to the calcined iron oxide, and the calcination process was carried out in the absence of potassium carbonate; accordingly, in the case of Catalyst B the effect of the potassium promoter is to enhance the intrinsic activity of the iron oxide catalyst.