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Study of the Oxidative Dehydrogenation of Ethylbenzene

II. Catalytic Activity and Acid and Base Properties of Na–$SiO_2 \cdot Al_2O_3$

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The oxidative dehydrogenation of ethylbenzene on a series of $SiO_2 \cdot Al_2O_3$ catalysts has been carried out by continuous flow reaction. The addition of sodium has resulted in an increase of activity and a maximum yield of styrene was observed at the value of 17 μmol of Na exchanged/g-cat. The same increase in activity was observed in the pulse reaction. The pulse reaction shows that ethylbenzene is adsorbed reversibly on the catalyst and that active oxygen species is also reversibly adsorbed. Such changes in oxidation activity have been explained by the cooperative effect of the acid and base sites of the catalyst. The acid–base titration shows that the addition of one Na ion increases the number of new acid ($1.5 > H_0 > -5.6$) and base ($17.2 < pK_a < 26.5$) sites tremendously. The acid sites of H_0 between 1.5 and −5.6 are proven to be the active sites to adsorb ethylbenzene reversibly, whose oxidation, on the other hand, occurs on the base sites of pK_a between 17.2 and 26.5. The pulse and flow reactions indicate that these acid–base sites are still effective even after carbonaceous materials have deposited.

INTRODUCTION

In our previous study (*1*, *2*), SnO_2–P_2O_5 catalysts showed the highest activity and the highest selectivity in the oxidative dehydrogenation of ethylbenzene to styrene. In the pulse reaction of ethylbenzene on the SnO_2 catalyst, the nonselective oxidation proceeded, while on the solid-phosphoric acid catalyst, styrene was not formed but instead the unrecovery of ethylbenzene was observed. The addition of phosphorus to SnO_2 suppressed the total oxidation reaction and enhanced the formation of styrene. These results suggest the cooperative effect of the acid–base properties of the catalysts; the role of the basic component, SnO_2, is to activate oxygen and the role of the acidic component, P_2O_5, is to adsorb ethylbenzene in a suitable activated form. Such an activation of aromatic compounds on the acid site has also been shown by quantum mechanical calculations (*3*).

It is important, therefore, to treat the acidity and basicity of the catalysts together with the reaction mechanism of the partial oxidation reactions. The investigation of the detailed role of acid and base sites in the oxidative dehydrogenation of ethylbenzene will then show not only the reaction mechanism of the present reaction but also the general role of acid and base sites in other partial oxidation reactions. Some results in the studies of the oxidation reactions suggest the participation of acid sites (*4*, *5*) and of base sites (*6*) in the partial oxidation reactions. The selectivity of the oxidation reactions is also said to be affected by the acid and base properties of the catalysts (*7–11*). Correlations between the oxidation activity and the amount of acid and/or base sites has been reported in many reactions by Ai (*10*). However, the details of the role of the acid and base sites in a molecular aspect is still not clear.

A silica–alumina catalyst is a typical solid acid catalyst and shows an activity only in the oxidative dehydrogenation of ethylbenzene and not of olefinic compounds (*12*). Therefore, this catalyst meets the purpose

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of this study to investigate the role of the acid and base sites on the oxidation reaction in a molecular aspect.

In the present work, the nature of the active site in the reaction of ethylbenzene on a silica–alumina catalyst is investigated. For this purpose, $SiO_2 \cdot Al_2O_3$ is treated with sodium acetate to control the acid and base properties of the catalyst. Then the effects of sodium on the catalytic activity and on the acid–base properties are studied on such sodium-exchanged silica–alumina catalysts. The roles of the acid and base sites in the oxidation reaction are discussed and the ranges of the acid and base strengths effective for the oxidative dehydrogenation are determined.

EXPERIMENTAL

Catalysts

Sodium-exchanged silica–alumina catalysts (Na–SiAl) were prepared by the ion exchange of the $SiO_2 \cdot Al_2O_3$ (Nikki Chemical Co. N632(H), Al_2O_3, 25%; referred to as the original-SiAl or 0.0Na–SiAl) with sodium acetate. The original-SiAl was precalcined at 773 K for 3 h in air, and was then dipped into an aqueous solution of NaOAc for 3 days at room temperature. The content of NaOAc in the aqueous solution was varied in each case. The resultant $SiO_2 \cdot Al_2O_3$ was washed thoroughly with water, dried at 393 K for 1 day, and calcined at 773 K for 3 h in air. The Na content was determined by atomic absorption spectroscopy. The surface area was determined by the conventional BET methods. The Na content written at the head of the name of the catalyst in micromoles per gram of catalyst corresponds to the increment of Na content due to the ion exchange to the amount of Na on the original-SiAl. For example, 17Na–SiAl contains 17 μmol of Na in addition to the 24 μmol of Na/g-cat on the original-SiAl. The Na content and the BET surface area of the catalysts are shown in Table 1.

TABLE 1

Sodium Content and BET Surface Area of Na–SiAl

Catalyst	Na content[a] (μmol/g-cat)	BET surface area (m^2/g-cat)
0.0Na–SiAl[b]	0.0	320
1.7Na–SiAl[a]	1.7	317
8.5Na–SiAl	8.5	317
17Na–SiAl	17.0	317
43Na–SiAl	43.0	318
85Na–SiAl	85.0	320

[a] Amount of Na increased by ion exchange. 1.7Na-SiAl contains 1.7 μmol of Na/g-cat as well as 24 μmol of Na/g-cat in the original-SiAl catalyst.

[b] 0.0Na–SiAl represents the original-SiAl which contained 24 μmol of Na/g-cat.

Procedure

The catalytic activity was measured by using a conventional continuous flow reactor at atmospheric pressure. The catalyst particles were dispersed in fused alumina particles to prevent a local increase of the temperature and were packed in a reactor made of Pyrex glass. The reactor was installed in a fluidized sand bath which was heated electrically, in order to heat the catalyst bed uniformly. The liquid products were collected by traps cooled with ice and dry ice, and analyzed by gas chromatography with a 1.5-m PEG column and a 1-m DOP column at 383 K. The gaseous products were analyzed instead by gas chromatography with a 80-cm Porapak Q column and a 1.5-m MS-13X column at room temperature. Conversion of ethylbenzene was calculated on the basis of ethylbenzene fed. In each of the following figures, the reaction conditions, such as catalyst weight (W), feed rate (F), reaction temperature (T), and partial pressure of ethylbenzene (P_{EB}), oxygen (P_{O_2}), steam (P_{H_2O}), and nitrogen (P_{N_2}) are indicated.

Acid–Base Properties

Acid and base distributions of the catalysts precalcined at 773 K for 2 h in air were determined by titrating with *n*-butylamine

(*13, 14*) and benzoic acid (*13, 15*) using the following indicators; Neutral red (H_0 = 6.8), 4-benzeneazodiphenylamine (1.5), benzalacetophenone (−5.6), Antraquinone (−8.2), and 2,4-dinitrotoluene (−12.7) for acidities, and 4-chloroaniline (pK_a = 26.5), 4-chloro-2-nitroaniline (17.2), and phenolphthalein (9.3) for basicities.

Pulse Reaction

The pulse reaction of the oxidative dehydrogenation of ethylbenzene was carried out with a conventional pulse reaction apparatus. Helium was used as a carrier gas after being purified by the passage through a silica gel trap at 77 K. The effluents were analyzed by gas chromatography with the same columns as in the case of the flow reaction. Catalyst, 0.2 g, was packed in a Pyrex glass tubing with an inside diameter of 4 mm, and was calcined at 768 K for 2 h in a flow of oxygen, then at 718 K for 1 h in a flow of carrier gas in the case of the fresh catalyst, immediately before the pulse reaction. In the case of the catalyst used in the flow reaction (used catalyst), which contained coke, the calcination was performed only in a flow of carrier gas at 718 K for 1 h. The pulse reaction experiments were carried out at 718 K with a helium flow rate of 0.74 cm^3/s in the following sequence: (I) 1 mm^3 of ethylbenzene only was injected (EB pulse), (II) 2 cm^3 of oxygen was injected and after 10 min, 1 mm^3 of ethylbenzene was injected ($O_2 \rightarrow$ EB pulse), (III) 2 cm^3 of oxygen and 1 mm^3 of ethylbenzene were injected simultaneously (EB + O_2). In order to remove the coke deposited on the catalyst the catalyst was reoxidized after these pulse reactions. The reoxidation was performed in a flow of air at 718 K for 1 h and in a flow of oxygen at 768 K for 2 h in the case of the fresh catalyst, and the reoxidation in the flow of oxygen was prolonged for an additional 4 h at 768 K in the case of the used catalyst which had been used in the continuous flow experiment before the pulse reaction. Pulse reactions I, II, and III were carried out again on the reoxidized catalyst. Besides the standard pulse experiment mentioned above, other pulse reactions were carried out. The procedures of the experiment are described with their corresponding results.

RESULTS

Flow Reaction

Figure 1 shows the respective changes in the conversion of ethylbenzene and in the rates of formation of styrene (r_{ST}) and carbon oxides (r_{CO_X}) with time on stream. The rate of styrene formation increased gradually and reached the stationary state. A similar tendency was observed in the rate of CO and CO_2 formation. However, it is noteworthy that, in Fig. 1a, the conversion of ethylbenzene remained constant. The formations of coke on the catalyst, a slight amount of benzene, and high-boiling products were also observed. High-boiling products which may be the oligomer of the styrene formed may have caused about 4% of incomplete recovery in the 38.4 μmol/g · s of ethylbenzene fed at the stationary state. The coke formed on the catalyst was removed by the reoxidation of the used catalyst by air under the conditions shown in Fig. 1b. The reoxidized catalyst

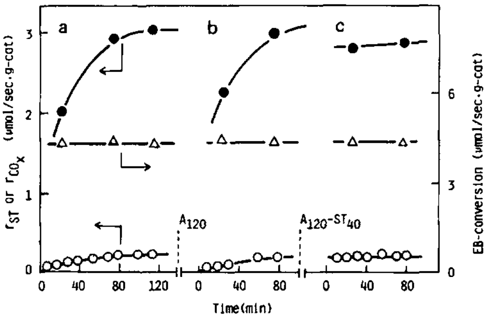

FIG. 1. Time course of the reaction of ethylbenzene on original-SiAl catalyst. T = 723 K, W = 0.300 g, F = 290 mmol/h, P_{EB} = 0.143 atm, P_{O_2} = 0.050 atm, P_{H_2O} = 0.322 atm, and P_{N_2} = 0.485 atm. F_{EB} = 38.4 μmol/g-cat · s. Δ, EB conversion; ●, r_{ST}; ○, r_{CO_X}. A_{120}, reoxidation of catalyst with air at 723 K for 120 min, A_{120}–ST_{40}, styrene treatment of the catalyst in the absence of oxygen for 40 min after the reoxidation.

showed the same results as were obtained in the case of the fresh catalyst. The hydrogen treatment at 723 K for 1.5 h after the reoxidation showed no effect on the time course. In Fig. 1c, the effect of the treatment of the catalyst by styrene is also shown. After the styrene treatment, r_{ST} remained constant with time.

Effect of Na on the Flow Reaction

The catalytic behavior of Na-treated catalysts was studied. On each catalyst, the time course was the same as that on the original-SiAl catalyst shown in Fig. 1. The catalytic activity was varied with Na content and the order of the activity of each catalyst did not change with the reaction time.

Figure 2 shows the effect of Na content on the rates of formation of styrene, CO + CO_2, and benzene at 90 min after the initiation of the reaction at 718 K. The rate of styrene formation which increased with Na content, achieved a maximum at 17 μmol of Na/g-cat and then decreased gradually. It is important that not only the poisoning effect but also the promoting effect of the addition of Na was observed in the oxidation reaction. The rates of the formations of benzene and CO + CO_2, respectively, depended on Na content in a similar way to that of styrene but to a lesser extent. The same tendencies were observed at 768 K.

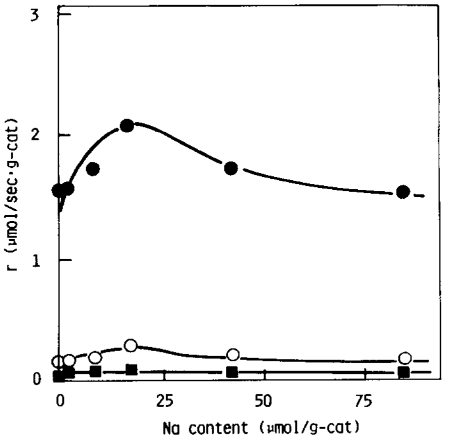

FIG. 2. Effect of Na on the reaction rates at 723 K. ■, r_B; for the other symbols, see Fig. 1. T = 723 K, W = 0.400 g, F = 255 mmol/h, P_{O_2} = 0.066 atm, P_{EB} = 0.060 atm, P_{H_2O} = 0.369 atm, and P_{N_2} = 0.505 atm.

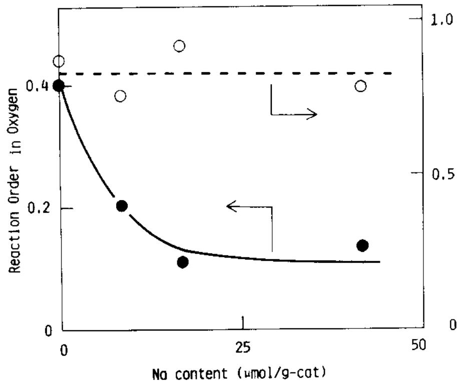

FIG. 3. Effect of Na on the reaction order. W = 0.200 g, T = 723 K, P_{H_2O} = 0.490 atm, and P_{N_2} = balance. The reaction order with respect to O_2 (●) was measured at constant P_{EB} (= 0.061 atm), and the reaction order with respect to ethylbenzene (○) was measured at constant P_{O_2} (= 0.061 atm).

Figure 3 shows the effect of Na content on the apparent reaction order with respect to ethylbenzene and oxygen. The reaction order was measured under the differential reaction conditions, i.e., the degree of conversion was about 10%. The reaction orders with respect to ethylbenzene are on the same order of magnitude as that with respect to oxygen. This implies that the activations of both ethylbenzene and oxygen have almost an identical rate on original-SiAl. The effect of Na content on the reaction order with respect to ethylbenzene is not clear, but that with respect to oxygen decreased as the Na content increased, thereby showing that Na treatment enhances the activation of oxygen.

Acidity and Basicity of Na–$SiO_2 \cdot Al_2O_3$ Catalysts

Figure 4 shows the dependence of the amount of acid of a specified acid strength on Na content. The original-SiAl has only strong acid ($H_0 < -8.2$) and weak acid ($H_0 > 1.5$) sites, but no medium-strength sites ($1.5 > H_0 > -8.2$). The strongest acid sites

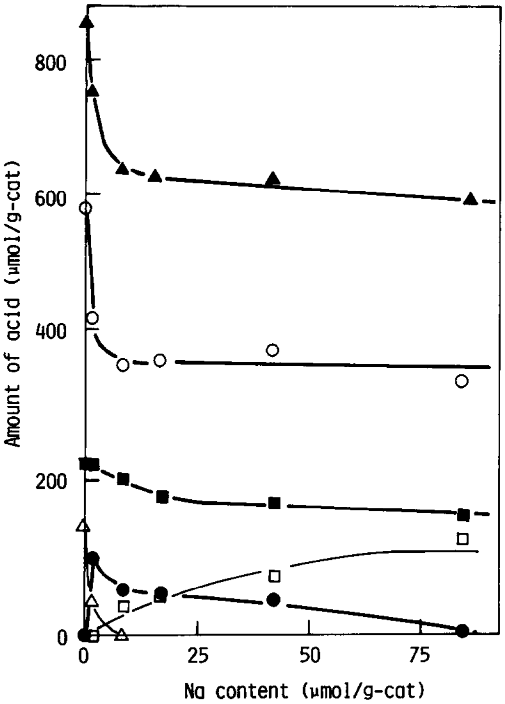

FIG. 4. Effect of Na on the acid amount at different H_0 ranges: ○, ~6.8–1.5; ●, ~1.5–−5.6; □, ~−5.6–−8.2; ■, ~−8.2–−12.7; △, ~−12.7; ▲, total amount.

($H_0 < -12.7$) decreased abruptly and then disappeared, while the strong acid sites ($-12.7 < H_0 < -8.2$) decreased gradually with Na content. The weak acid sites ($H_0 >$ 1.5) decreased abruptly below the Na content of 8.5 μmol/g-cat and remained almost constant above it. The medium–high acid sites ($-5.6 > H_0 > -8.2$) increased gradually, while the medium–low acid sites ($1.5 > H_0 > -5.6$) at first increased and then decreased with the increase of Na content. These results show that the sodium ion not only neutralizes the exchanged acid sites but also donates electrons to more than ten acid sites to reduce the acid strength. The weak acid sites may be weakened to such an extent that a portion of them cannot be detected by the present method, and this results in a decrease in the total acidity.

The basicities at various base strengths of Na–SiAl catalysts are shown in Fig. 5. As the difficulty in determining the total amount of basic sites of $SiO_2 \cdot Al_2O_3$ with bromothymol blue has been reported (16), phenolphthalein ($pK_a = 9.3$) was used instead. The basic sites of pK_a between 9.3 and 26.5 were observed. The amount of weaker sites ($9.3 < pK_a < 17.2$) did not change greatly by the Na treatment, while the more basic sites ($17.2 < pK_a < 26.5$) increased from 210 to 280 μmol/g-cat as the Na content increased to 17 μmol/g-cat. Namely, the ion exchange with Na affected not only the distribution of the acid sites but also that of the basic sites. However, the change in the base sites was not as great as that in the acid sites. The effect of one Na ion to increase the number of acid and base sites numerously indicates that the base sites are generated adjacent to the acid sites affected by the Na treatment.

Pulse Reaction

Figure 6 shows examples of the results of the pulse reaction on the fresh catalyst and the used catalyst, respectively. Figure 6a shows the results on the fresh original-SiAl catalyst. When only ethylbenzene was injected (pulse I) and when it was injected 10 min later than the oxygen pulse (pulse II), benzene and ethylene were formed but not styrene. On the other hand, when ethylbenzene and oxygen were injected simultaneously (pulse III), a considerable amount of styrene and benzene was formed. No hy-

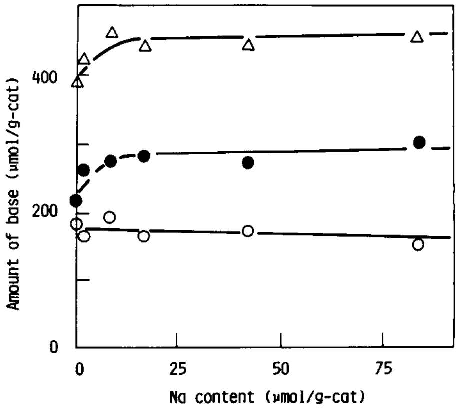

FIG. 5. Effect of Na on the base amount at different pK_a ranges: ○, ~9.3–17.2; ●, ~17.2–26.5; △, total amount.

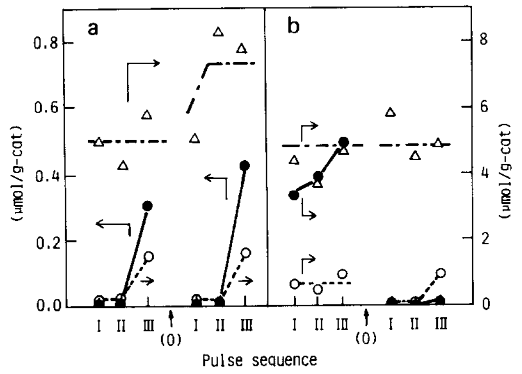

FIG. 6. Pulse reaction on the fresh original-SiAl catalyst (a) and on the used original-SiAl catalyst (b). I, ethylbenzene pulse; II, oxygen pulse → ethylbenzene pulse; III, oxygen pulse + ethylbenzene pulse. (O), Reoxidation of the catalyst at 718 K for 1 h with air and then at 768 K for 2 h with O_2 for the fresh one and for the used one, 4 h more with O_2 at 768 K. ●, amount of styrene formed; ○, amount of benzene formed; △, amount of ethylbenzene unrecovered.

drogen could be detected, indicating that styrene was formed through oxidative dehydrogenation. The recovery of ethylbenzene was not complete in all pulses I, II, and III, that is, the total amount of effluents was less than the amount of ethylbenzene injected. As shown in Fig. 6a, the amount of unrecovered ethylbenzene was essentially identical in all pulses I, II, and III.

In the case of the used catalyst, as shown in Fig. 6b, styrene was formed not only in pulse III but also in pulses I and II, and the amount of styrene formed was larger than that on the fresh catalyst. The amount of styrene formed increased slightly as follows: pulse I < II < III. However, the amount of unrecovered ethylbenzene was identical to that on the fresh catalyst. The results obtained after the reoxidation of the catalyst were the same as those on the fresh catalyst shown in Fig. 6a. This is similar to the effect of reoxidation on the continuous flow reactions.

The results on the sodium-ion-exchanged catalysts were similar to those on the fresh original-SiAl catalyst shown in Fig. 6a, but the amount of the products varied with the Na content. Figure 7 shows the effect of Na

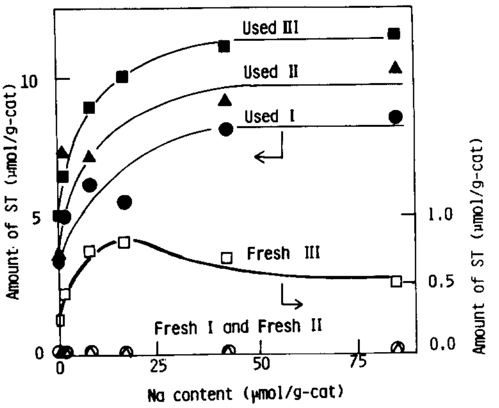

FIG. 7. Effect of Na on the amount of styrene formed in the pulse reaction. ○, I; △, II; □, III. Open symbols are for the fresh catalysts; solid symbols are for the used catalysts.

content on the amount of styrene formed. On the fresh catalyst, styrene was formed only in the presence of oxygen (pulse III). The amount of styrene formed increased with the Na content below 8.5 μmol of

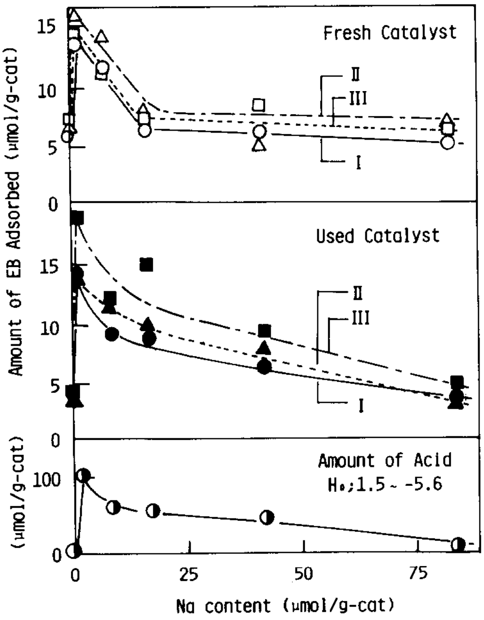

FIG. 8. Effect of Na on the amount of ethylbenzene adsorbed and on the acid amount of $1.5 > H_0 > -5.6$ (◑). ○, Ethylbenzene adsorbed in pulse reaction I; △, II; □, III. Open symbols are for the fresh catalysts; solid symbols are for the used catalysts.

Na/g-cat, reached the maximum at ~8.5–17 μmol of Na/g-cat, and then decreased gradually. Such a dependence of the activity on Na content agrees well with that observed in the flow technique shown in Fig. 2. On the other hand, on the used catalyst, styrene was formed both in the presence and in the absence of oxygen, and the amount of styrene formed in all pulses I, II, and III increased with Na content. But it should be noted that the difference in the amount of styrene formed between pulses III and II is almost equivalent to that formed on the fresh catalyst.

Figure 8 shows the effect of Na content on the amount of unrecovered ethylbenzene. It should be noted that, on each catalyst, the amount of unrecovered ethylbenzene remained constant throughout the pulse experiments I, II, and III, both on the fresh and used catalysts. The amount of unrecovered ethylbenzene increased steeply with Na content below 1.7 μmol/g-cat, reached the maximum at 1.7 μmol/g-cat, and then decreased gradually. It is also worth noting that the tendency of the unrecovered ethylbenzene is in good agreement with the tendency of the acidity of H_0 between 1.5 and -5.6 as shown in Fig. 8. The physical meaning of unrecovered ethylbenzene will be discussed later.

DISCUSSION

In order to discuss the detailed role of the acid and base sites on the oxidation activity, catalysts with varied acidity and basicity are required. The acid and base properties of catalysts were controlled by treating the original-SiAl in NaOAc solution with various concentrations.

The results of the flow reaction, shown in Fig. 2, show that the activity is influenced by the Na content of the catalysts. The same dependence on the Na content was observed in the case of the pulse technique (Fig. 7). Such tendencies show that the addition of an adequate amount of sodium does not suppress but promotes the oxidation reaction; however, an excess amount of sodium shows a poisoning effect. The tendency to have maximum activity suggests the cooperative effect of the acid and base properties of the catalysts which decrease and increase with increasing Na content, respectively.

As shown in Figs. 4 and 5, changes in the acid and base properties with the amount of Na were observed and such changes can be interpreted as follows. The addition of one sodium ion weakens the acid strength of around ten acid sites, showing that the sodium ion effects not only the neutralization of acid sites but also the weakening of the acid strength by its inductive effect (*17*, *18*). At the same time, the addition of sodium generated strong base sites and such an effect is also understood by considering the electron-donating properties of the sodium ion (*18*). The result that one sodium ion weakens acid sites and enhances base sites suggests that the acid and base sites should be situated in immediate neighborhoods. Therefore, before the Na ion exchange is carried out (original-SiAl), the strong acid sites exist alone and/or with weak base sites. After the Na ion exchange, however, the strong base sites are generated and the adjacent strong acid sites are weakened. Thus the Na ion can control the acid–base properties of the catalyst without changing the BET surface area.

As shown in Fig. 1a, the constant value of ethylbenzene conversion shows that the active site to react with ethylbenzene does not change during the flow reaction. The time course of the regenerated catalyst (shown in Fig. 1b) in the flow reaction and the effect of the reoxidation of the catalyst in the pulse reaction (shown in Fig. 6b) also support this. From the results of the styrene pretreatment (shown in Fig. 1c), the apparent increase of the rate of styrene formation with time can be explained by the subsequent reaction of the styrene produced and will be discussed later.

In the pulse reaction on the used catalyst, the amount of styrene formed was largest when ethylbenzene and oxygen were pulsed at the same time, as shown in Fig. 6b. The difference in styrene yield between pulses III and II, which corresponds to the amount of ethylbenzene oxidatively dehydrogenated by oxygen species from gaseous oxygen, is nearly equal to the styrene yield in pulse III on the fresh catalyst. Thus the active site on the fresh catalyst should still be effective even after the coke had deposited during the flow reaction. The agreement of the dependence of r_{ST} on Na content in the flow reaction (Fig. 2) with that in the pulse reaction (Fig. 7) shows that the same site is active under each reaction condition. This agreement of the results of the flow reaction with pulse III but not with I nor II, also shows that the active oxygen is not the lattice oxygen (pulse I) nor the stable adsorbed oxygen (pulse II) but the unstable adsorbed oxygen species (pulse III).

As mentioned under Results, the recovery of ethylbenzene was incomplete in all pulse reactions I, II, and III both on the fresh and used catalysts. Such an incomplete recovery has been observed on the solid-phosphoric acid catalyst (*1*). To clarify the meaning of the incomplete recovery, repeated pulse reactions were carried out. The results are shown in Fig. 9. Two successive pulses of ethylbenzene were injected at various time intervals. The chromatogram obtained consisted of four peaks: two peaks of benzene and two peaks of ethylbenzene. No other products were formed, because no oxygen pulses were injected. The amount of benzene formed was so small that it could be neglected in the calculation of the recovery of ethylbenzene. The second ethylbenzene peak represents the degree of recovery of the second pulse. In Fig. 9, the amount of unrecovered ethylbenzene is plotted against the time interval between the two successive pulses. As the time interval decreased, the amount of unrecovered ethylbenzene decreased and the recovery became complete. These results indicate that the incomplete recovery is due to the reversible adsorption of ethylbenzene. The remaining ethylbenzene from the first pulse will increase the recovery of the second pulse. One of the present authors attributes the incomplete recovery to the strong reversible adsorption of the reactant (*19*). In such a case, the recovery becomes complete by repeating the pulses of the reactant in short intervals. Thus, the results show that the incomplete recovery can be attributed to the strong reversible adsorption of ethylbenzene on the catalyst surface.

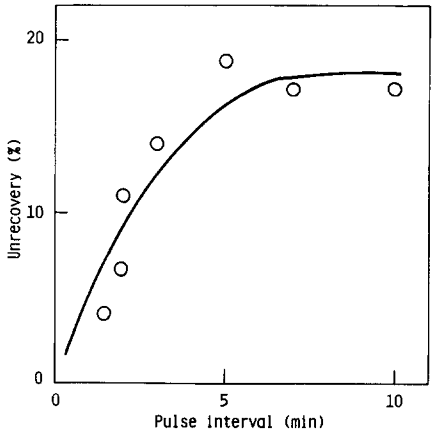

FIG. 9. Effect of the pulse intervals in the repeated ethylbenzene pulse on the percentage unrecovery of ethylbenzene on 1.7Na–SiAl catalyst.

The effect of Na content on the amount of unrecovered ethylbenzene is shown in Fig. 8. It is noteworthy that the amount of adsorbed ethylbenzene on the catalyst was identical in all pulses I, II, and III both on the fresh and used catalysts. The same adsorption site is revealed to be active under every condition. The amount of adsorbed ethylbenzene increased steeply as the Na content increased from 0.0 (original) to 1.7 μmol of Na/g-cat and decreased gradually above 1.7 μmol of Na/g-cat. It is also notable that this tendency for the adsorption of ethylbenzene to vary with Na content is similar to the tendency of the treatment of the acid sites of H_0 between 1.5 and -5.6. Any other relationships between adsorption and acid sites cannot be observed in any other range of acid strength. This leads to the conclusion that the active sites which adsorb ethylbenzene can be represented by acid sites in the range of acid strength 1.5 and −5.6 of H_0, which is weaker than the acid strength required for the dealkylation of alkylbenzene, i.e., $H_0 < -5.6$ (*13, 20, 21*). The strong acid sites ($H_0 < -5.6$) can be active for the dealkylation of alkylbenzene and the polymerization of the styrene formed, then can be covered with coke and become inactive during the stationary state of the flow reaction. However, this is not the case for acid sites weaker than $H_0 = -5.6$. Such a hypothesis is supported by the pulse reaction on the used catalyst which shows that an identical amount of ethylbenzene is adsorbed on it as on the fresh catalyst. From the above discussion, the time course of styrene formation (Fig. 1), in which the apparent rate of styrene formation increased with time and reached a stationary state while the conversion of ethylbenzene remained constant, can be well explained. That is, ethylbenzene is converted to styrene from the beginning of the reaction but the styrene formed is polymerized to coke which deposits gradually on the strong acid site of $H_0 < -5.6$. Thus, the apparent rate of styrene formation is low at the beginning of the reaction. However, since the coke formed deactivates the sites of coke formation with time, the polymerization of styrene is hindered and its formation increases to reach a stationary state. The reoxidation of the catalyst (Fig. 1b) removes the coke, regenerates the fresh state, and repeats the time course. The pretreatment with styrene after the reoxidation (Fig. 1c) deactivates the coking site before the flow reaction, while the active site of the oxidative dehydrogenation of ethylbenzene is still effective, which removes the apparent increase of the rate of styrene formation with time. These interpretations of the time course are completely different from those of Alkhazov and Lisovskii (*22*), which have stated that the coke formed on the catalyst is an active site.

It is concluded from quantum mechanical calculations that acid sites can coordinate the benzene ring of toluene and withdraw the ring electron, resulting in the activation of α-hydrogen and its interaction with the neighboring base sites (*3*). Such acid sites and neighboring base sites can exist on the Na–SiAl catalysts and the effective acid strength is revealed to be of H_0 between 1.5 and −5.6.

The turnover frequency of the formation of styrene was calculated from the results obtained in the flow reaction, assuming that the active site is the acid site of H_0 between 1.5 and −5.6 as discussed above;

$$\text{Turnover frequency} = \frac{r_{\mathrm{ST}} \text{ in continuous flow reaction}}{\text{Amount of acid of } 1.5 > H_0 > -5.6}.$$

So this turnover frequency represents the activity to produce styrene per one active site to adsorb ethylbenzene. The effect of Na content on the turnover frequency is shown in Fig. 10. The effects at 718 and 768 K resemble each other. It is significant that these tendencies observed in the turnover frequency are in good agreement with the tendency of the amount of base sites of pK_a between 17.2 and 26.5. These results suggest that the rate-determining step of this

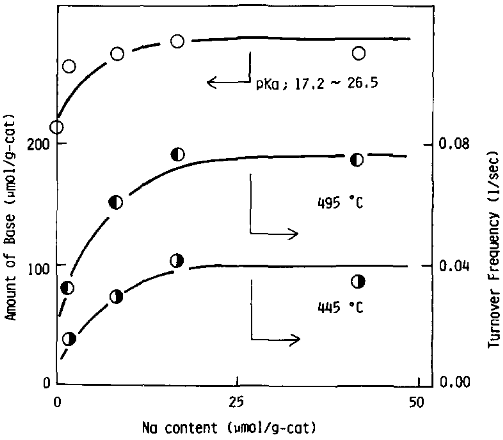

FIG. 10. Correlation between basicity and turnover frequency. Turnover frequency = r_{ST} in continuous flow reaction/amount of acid of $1.5 > H_0 > -5.6$ ◑, at 718 K; ◐, at 768 K; ○, amount of base of 17.2 < pK_a < 26.5.

reaction is the oxidation of the reversibly adsorbed intermediate of ethylbenzene on the base sites of pK_a between 17.2 and 26.5.

Such a tendency for the amount of base sites to vary with Na content is also similar to the tendency in the decrease of the reaction order with oxygen (Fig. 3) indicating that the addition of Na reduces the difficulty in activating oxygen. The formation of styrene was observed only in pulse III, where ethylbenzene and O_2 were pulsed simultaneously on the fresh catalyst. This shows that the active oxygen species in this flow reaction is the adsorbed one with short lifetime on the catalyst. Thus the role of the base site of pK_a 17.2 and 26.5 is concluded to adsorb oxygen into an activated form and to oxidize the adsorbed intermediate of ethylbenzene which is reversibly adsorbed on the acid sites of H_0 between 1.5 and -5.6. These conclusions agree well with the role of acid and base sites assumed in the case of Sn–P catalysts (*1*).

CONCLUSION

The effect of the acid and base properties on the oxidative dehydrogenation of ethylbenzene has been studied in the continuous flow reaction, pulse reaction, and acid–base titrations on a series of Na–$SiO_2 \cdot Al_2O_3$ catalysts. As the amount of Na increases, the activity increases initially, reaches the maximum, and then decreases both in the flow and pulse reactions. Such an effect of Na can be explained by the cooperative effect of the acid and base sites. The addition of Na not only eliminates a part of the acid sites but also generates moderately strong acid sites of $1.5 > H_0 > -8.2$ and increases base sites of $17.2 < \text{p}K_a < 26.5$. Each Na ion added increases such acid and base sites numerously. The reversible adsorption of ethylbenzene occurs on acid sites of $1.5 > H_0 > -5.6$. The turnover frequency, based on the flow reaction and amount of acid sites of $1.5 > H_0 > -5.6$, shows that the step to oxidize the adsorbed ethylbenzene and form styrene is affected by base sites of $17.2 < \text{p}K_a < 26.5$. Such active sites required to form styrene have been shown to be still effective at the stationary state of the continuous flow reaction.

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