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Study of the Oxidative Dehydrogenation of Ethylbenzene

III. Mechanism for Styrene Formation

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The reaction mechanism of oxidative dehydrogenation of ethylbenzene has been investigated using the pulse technique, isotope exchange reaction, and ESR measurement. Collecting the effluents of the pulse reaction has shown the reversible adsorption of ethylbenzene. The deuterium exchange reaction has shown that the adsorbed intermediates of ethylbenzene are dissociated at the α position. Neutrally adsorbed molecular oxygen species and O^- species are observed on the prereduced SiAl catalysts by the ESR measurement, showing the ability of the catalysts to activate gaseous oxygen. The reaction of the oxygen species with ethylbenzene has shown the active oxygen species to be O^- species. The O^- species consumed by the reaction are supplied from gaseous oxygen through O_{2ad} species. The reversible adsorption of ethylbenzene and the correlation between the turnover frequency and basicity suggest that the rate of the overall reaction at above 723 K is determined by the reaction of adsorbed ethylbenzene species and O^- in abstracting the β-hydrogen. From the above results, a reaction mechanism is proposed as follows: the acid site of H_0 between 1.5 and -5.6 adsorbs ethylbenzene, reversibly abstracting the α-hydrogen at the basic OH adjacent to the acid site, and the base site of pK_a between 17.2 and 26.5 activates gaseous oxygen to form O^- which abstracts the β-hydrogen.

INTRODUCTION

In the preceding paper (*1*), it has been concluded that the active site of the oxidative dehydrogenation of ethylbenzene exists on the native $SiO_2 \cdot Al_2O_3$ catalyst and that the acid site of H_0 between 1.5 and -5.6 activates ethylbenzene and the base site of pK_a between 17.2 and 26.5 activates oxygen. The reaction mechanism including allylic intermediates has been proposed in detail in the oxidation of olefinic compounds (*2*). Oxidation of ^{13}C-labeled propylene on Bi · Mo (*3*), Bi · Mo–P (*4*), and Cu_2O (*5*) suggested the existence of the symmetric allyl intermediates. The product distribution obtained in the reaction of deuteriopropylene (*6–8*) on Cu_2O, Bi · Mo, and U · Sb also indicated the same propylene intermediate in which the α-hydrogen had been abstracted. The same intermediate was also detected on ZnO (*9*) using spectroscopic methods. Moreover, the rate-determining step has been proven to be in the abstraction of the α-hydrogen (*7, 10, 11*). In the case of ethylbenzene, a similar intermediate has been supposed; however, the details are not clear (*12, 13*).

A number of studies have been devoted to the active oxygen species. An activity of the lattice oxygen was observed on the Mo-containing oxides (*14*), and activities were also found in the oxygen double bonded to the metal (M═O) (*10, 15, 16*) and in the adsorbed oxygen species (i.e., O^-) on the ferrite spinel catalysts (*10, 15, 17*). Adsorbed oxygen species have also been proposed on other oxide catalysts (*3, 17, 18*). In the case of $Na\text{–}SiO_2 \cdot Al_2O_3$ catalysts, the possibility of the participation of the lattice oxygen has been denied by the pulse reaction in the preceding paper (*1*). Many studies have been done on the adsorbed oxygen species with the aid of ESR (*19*) and the activity of the adsorbed oxygen species (i.e., O_2^-, O^-, O_3^-) has also been studied in

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the oxidation of hydrocarbons (*20–22*). The adsorbed oxygen species (i.e., O_2^-) was observed on the insulators, such as $SiO_2 \cdot Al_2O_3$ (*19*), Al_2O_3 (*19*), and zeolites (*19, 23*), only in the case of uv- and γ-irradiated samples. On the other hand, the base catalysts such as MgO were observed to activate oxygen to form O_2^- ion without prior irradiation but only with heat treatment (*24*).

In this study, the reaction mechanism is discussed on the basis of the activation of both reactants, that is, ethylbenzene and oxygen. Details of the activation of ethylbenzene are investigated using the pulse technique and deuterium exchange experiments. Those of oxygen are investigated by ESR spectroscopy. The reactivities of both adsorbed intermediates are also studied. Each step of the reaction is discussed carefully and a reaction mechanism in the molecular aspect is proposed.

EXPERIMENTAL

Catalyst

The preparation of the Na-exchanged $SiO_2 \cdot Al_2O_3$ catalysts (Na–SiAl) and their acid and base properties were described in the preceding paper (*1*). The content of Na was written at the head of the name of the catalyst in micromoles per gram of catalyst, which means that the amount of Na increased compared to that on the original-$SiO_2 \cdot Al_2O_3$ due to the ion exchange. For example, 17Na–SiAl contains 17 μmol of Na in addition to the original-SiAl which contained 24 μmol of Na/g-cat. Pure-SiAl catalyst was prepared by the gradual hydrolysis of a mixture of aluminum alcholate and *ortho*-ethyl silicate, containing 20% Al_2O_3.

Procedure

Pulse experiments. For the collection of the effluents of the pulse reaction, a silica gel trap was installed between the reactor and the gas chromatograph. The effluents were trapped at 77 K and then heated to 423 K to be vaporized and carried to the gas chromatograph. In some cases, both gaseous and liquid effluents were simultaneously analyzed. The effluents were split into two; one for gas analysis and the other for liquid analysis. The chromatographic column used was the same as the one reported previously (*1*). This system, which needed about twice as much carrier gas (100 ml/min) as in the ordinary pulse apparatus (44.5 ml/min), would have an effect on the amount of unrecovered reactants.

ESR measurement. The catalyst was pretreated with a conventional high-vacuum apparatus in the following manner.

(1) The sample in a quartz ESR sample tube with an inside diameter of 3 mm was evacuated at 763 K for 3 h.

(2) About 11 kPa of hydrogen, purified by the silica gel trap at 77 K, was introduced onto the sample at 763 K for 0.5 h, then evacuated at 763 K for 0.5 h. This procedure was done once again, and then the sample was evacuated for an additional 2 h at 763 K.

(3) Vacuum-distilled oxygen, 33 kPa, was introduced onto the sample at 763 K and heated for 1 h.

(4) The sample tube was cooled down to 77 K and evacuated at 77 K for 60 s. Then the sample tube was isolated from the vacuum system by a two-way glass valve.

In some cases, the sample was treated with N_2O, instead of oxygen, as follows.

(5) Nitrous oxide (N_2O) was frozen at 77 K onto the pretreated (procedures 1 and 2) sample, then evacuated at 293 K for 30 s.

(6) Nitrous oxide was frozen onto the sample again at 77 K, evacuated at 293 K until 27 kPa, heated at 373 K for 1 h, and again evacuated at 293 K for 30 s.

(7) After procedure 6 had been repeated, the same sample was heated at 573 K for 3 h. After N_2O was introduced as in the case of procedure 6, the sample was heated at 573 K for 3 h instead of the treatment in procedure 6 and then evacuated at 293 K for 30 s.

Following these pretreatments, ESR sig-

TABLE 1

Product Distribution in the Pulse Reaction of Ethylbenzene in the Presence of Oxidants[a]

Catalyst:	Pure-SiAl	Original-SiAl	Original-SiAl
Pretreatment:	Fresh	Prereduction[b]	Prereduction[b]
Oxidant[c]:	O_2	O_2	N_2O
CO	Trace	0.090	Trace
CO_2	0.033	0.067	—[d]
Benzene	0.161	0.262	0.211
Styrene	0.134	0.154	0.130
Unrecovered ethylbenzene	1.103	1.404	1.263

[a] Measured in micromoles per gram of catalyst.

[b] Pretreated in the flow of hydrogen at 723 K for 45 min.

[c] Ethylbenzene (1 μl) and oxidant; N_2O (1 ml) or O_2 (0.5 ml) was pulsed onto the catalyst (0.200 g) at 723 K under the flow of He (100 ml/min) at the same time.

[d] The separation of CO_2 peak and N_2O peak was not sufficient.

nals were recorded at 77 and 293 K with a JEOL JES-ME-ESR-1X, X-band spectrometer. Manganese oxide in MgO was used to calibrate the *g* value. The amount of molecular oxygen species adsorbed on the catalyst was calibrated volumetrically at room temperature.

The reactivity of oxygen species was examined in the following manner. A fixed amount of ethylbenzene vapor or 1-butene was introduced onto the sample and the sample was heated under various conditions. Then the ESR signal was recorded at 77 K to measure the change of its intensity due to the reaction with the organic substance.

RESULTS

Pulse Experiments

Reaction on pure-SiAl. As shown in Table 1, a considerable amount of styrene as well as benzene and a small amount of carbon oxides were formed on pure-SiAl when ethylbenzene and oxygen were pulsed simultaneously. No hydrogen was detected. The recovery of ethylbenzene was insufficient and the unrecovery was about 1 μmol/g-cat.

To examine the physical meaning of the unrecovery of ethylbenzene, the effluents from the pulse reactor were collected for 10 min. As shown in Table 2, when effluents were collected by the trap, the amount of unrecovery was significantly less than that obtained without the trap. On the used catalyst, the amount of unrecovered ethylbenzene decreased when the effluents were collected, although the amount of styrene formed remained essentially unchanged.

When oxygen was pulsed immediately after the ethylbenzene pulse, opposite results were obtained. On the fresh catalyst, a slight amount of styrene was observed and the recovery was not changed by the trap. However, on the used catalyst, a significant amount of styrene was detected and the

TABLE 2

The Amount of ST Formed and EB Unrecovered in the Pulse Experiment with and/or without the Trap

Catalyst	Trap[a]	EB only[b]		$EB \rightarrow O_2$[e]	
		ST formed[c]	EB unrecovered[d]	ST formed	EB unrecovered
1.7Na–SiAl (fresh)	None	Nil	13.9	7.7×10^{-2}	12.1
	10.0	Nil	4.1	7.9×10^{-2}	11.5
0.0Na–SiAl (used)	None	5.3	4.4	7.9	Nil
	10.0	5.1	2.3	8.7	Nil

[a] Effluents were analyzed after being trapped at 77 K for 10.0 min.

[b] Ethylbenzene (1 μl) was pulsed (pulse I).

[c] Amount of styrene formed is in micromoles per gram of catalyst.

[d] Amount of ethylbenzene unrecovered is in micromoles per gram of catalyst.

[e] Ethylbenzene pulse (1 μl) was followed with O_2 pulse (2 ml). The time interval was 15 s.

TABLE 3

Effect of H_2O Pulse on EB Unrecovered[a]

Pulse interval (s)[b] EB (1 μl) → H_2O (2 μl)	EB unrecovered (μmol/g-cat)
15	5.8
30	5.3
∞[c]	13.9

[a] Catalyst used was 1.7Na–SiAl.

[b] Ethylbenzene pulse was followed by H_2O pulse with an indicated interval.

[c] H_2O was not pulsed.

recovery was complete even without the trap.

Table 3 shows the effect of the additional pulse of H_2O on the recovery of ethylbenzene. The pulse of H_2O (2 μl) was introduced after the pulse of ethylbenzene on the fresh catalyst at various time intervals. The additional H_2O pulse improved the recovery of ethylbenzene, indicating that water promotes the desorption of ethylbenzene. The same experiment using D_2O was carried out. The time intervals between the ethylbenzene and D_2O pulses were fixed at 15 s and in between this pair of pulses, 13 min was allotted. The effluents were collected by the trap at 77 K. The collected sample was analyzed by a mass spectrometer. A small amount of benzene was formed but it could be neglected in mass analysis. With the results gathered from the mass spectrum, the deuterium distribution of the effused ethylbenzene is summarized in Table 4. The deuterium distribution in C_6 ions was calibrated with the distribution of $C_6H_5^+$, $C_6H_6^+$, and $C_6H_7^+$ peaks in the spectrum of d_0-ethylbenzene (blank test).

ESR Measurement

As shown in Fig. 1, the ESR spectrum changed with each of the treatments mentioned under Experimental. The spectrum of the 17Na–SiAl after the evacuation at 763 K (procedure step 1) is shown in Fig. 1-1. A symmetrical peak at $g = 2.005$ and a broad signal at g = ca 2.1 were observed. A small signal at $g = 2.038$ was also observed. The color of the sample was still white after this evacuation. The hydrogen treatment (procedure 2) made the color of the sample gray. The treatment almost completely removed the broad and small signals and enhanced the symmetrical peak at $g = 2.005$, as shown in Fig. 1-2. The effect of the oxygen introduced (procedure 3) is shown in Fig. 1-3. The symmetrical peak at $g = 2.005$ decreased and the broad signal regenerated, as well as the small signal at $g = 2.038$. Additional new signals were observed at $g = 2.119, 2.107, 2.090, 1.976, 1.888$, and at lower values. These signals were not observed in the absence of the catalyst, indicating that they could be attributed to the adsorbed oxygen species. The new signals were sharpened by evacuating the sample at 77 K (procedure 4) but the amount of the signals did not change with the time of the evacuation. Such signals were obtained only when the measurement was made at 77 K, but were not observed at 293 K. However, the measurement at 77 K after the measurement at 293 K reproduced such signals reversibly. The evacuation at 293 K removed such signals irreversibly, as shown in Fig. 1-5. This treatment with oxygen (procedure 3) regenerated the white color of the sample but not completely.

The same results were obtained in all cases of the Na–SiAl and the original-SiAl, but the spin concentrations were different from each other. In the case of pure-SiAl,

TABLE 4

Deuterium Distribution in Recovered Ethylbenzene

Compound	Mass number[a]	Deuterium distribution (%)					
		d_0	d_1	d_2	d_3	d_4	d_5
C_8 (EB)	106	8	8	13	21	26	24
C_7	91	6	5	11	20	28	30
C_6	77	18	10	19	23	15	15

[a] Mass number of d_0 compounds.

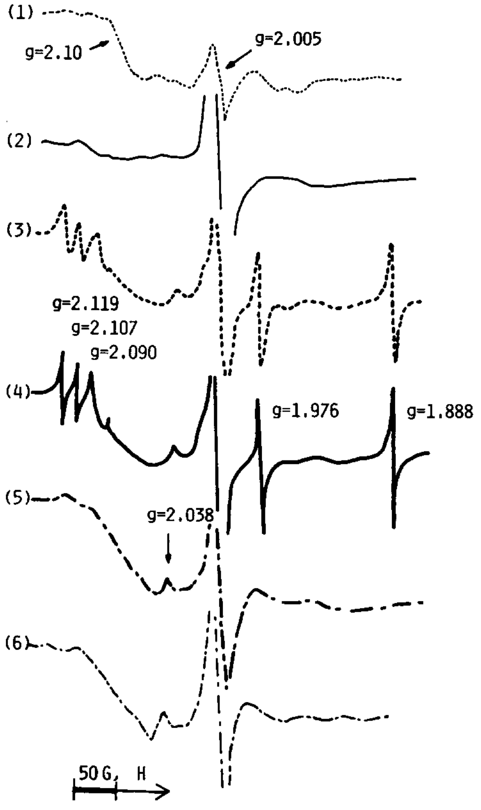

FIG. 1. ESR spectra of 17Na–SiAl measured at 77 K: (1) after evacuation at 763 K for 3 h; (2) after repeated treatment with hydrogen (11 kPa) followed by evacuation at 763 K; (3) sample (2) followed by exposure to 33 kPa of O_2 at 763 K for 1 h; (4) sample (3) followed by the evacuation at 77 K for 60 s in which additional signals in the higher fields such as 4030, 4060, 4360, 4375, 4445, 4945, 4975, 5070, 5150, and 5235 G ($=10^{-4}$ T) at 9.20 GHz were observed; (5) ESR spectrum of sample (4) measured at 293 K; (6) ESR spectrum of original-SiAl measured at 77 K after the N_2O treatment.

almost the same results were obtained as in the case of Na–SiAl, except that the broad signal at g = ca 2.1 could not be detected.

Instead of the O_2 treatment, N_2O treatment was also examined. The evacuation and the following hydrogen treatments (procedures 1 and 2) gave the same results as those mentioned above. After N_2O was frozen onto the sample at 77 K, the evacuation was performed at 293 K for 30 s. Such treatment has been reported to give O^- species on MgO samples (*25*). The signals measured at 77 K are shown in Fig. 1-6. In addition to the singlet peak at $g = 2.005$ which was observed before the N_2O addition, a signal at $g = 2.038$ and a broad signal at g = ca 2.1 appeared, but the size of these peaks was small. Such signals were enhanced by the further treatment of N_2O (procedures 6 and 7). The same signals were obtained when the measurement was made at 293 K, although the intensities of the signals had decreased. Signals which were observed after the treatment with O_2 (i.e., g = 2.119, 2.107, 2.090, 1.976, 1.888, and lower) were not detected in the case of the N_2O treatment.

Assignment. The observed ESR signals could be assigned as follows. The broad signal at $g = 2.1$ disappeared with the H_2 treatment, appeared with the O_2 treatment, and was not observed on pure-SiAl. Consequently, the signal could be attributed to the transition metal ion impurities, probably Fe^{3+}, which has been observed by Cordischi *et al.* and Arakawa and Ueda (*26*). The singlet peak at $g = 2.005$ always existed on the sample in all of the treatments, indicating that this peak should be one of the defect centers as were observed on irradiated $SiO_2 \cdot Al_2O_3$ (*27*) or zeolites (*13, 28*). Vedrine and co-workers have assigned this g value of $g = 2.005$ as a V_4 center of the Si particle formed on the γ-irradiated SiAl (*27*). As a doublet character signal, which at low Na content was a singlet, was observed at high Na content, this center is suggested to be influenced by the sodium ion. N_2O has been proposed to act as an electron sink (*29*), trapping the free electron at the surface *via* a reaction of the type,

$$N_2O + e^- \rightarrow N_2 + O^-.$$

O^- species thus formed gave signals at $g_\perp = 2.042$ and $g_\parallel = 2.002$ on MgO (*25*). The small signal at $g = 2.038$ observed both after the oxygen and N_2O treatments could be a part of the anisotropic signal of O^-. However, another part of the anisotropic signals was difficult to detect because of the large signal originating from the V-type center discussed above. The residual signals (g = 2.119, 2.107, 2.090, 1.976, 1.888, and at lower values) were observed after oxygen treatment, but not after N_2O treatment. Consequently, these signals could be assigned as adsorbed molecular oxygen species such as O_{2ad} and O^-_{2ad} (*19, 30*). Signals at higher fields (with low g values) were the characteristics of triplet radicals showing the presence of neutrally adsorbed molecular oxygen species (O_{2ad}). The signals, however, were different from those reported with gaseous molecular oxygen in the g value, strength, and number of the signals (*30*). This suggests that this oxygen species does not exist in the gas phase but is fixed on the surface. The results that the amount of the signals had not changed after the evacuation for 30 s and for 60 s at 77 K and that these signals were not observed in the absence of the catalyst also support this. After the introduction of 1-butene at 77 K, these signals of molecular oxygen species at higher g values decreased gradually. Such reactivity has been reported for the reaction of butene with molecular oxygen anion species (O_2^-) on zeolites (*23, 31*).

Some additional experiments will be necessary for the precise assignment of these signals; however, it is noteworthy that the SiAl catalyst is proven to adsorb and activate oxygen. The adsorption and the activation occurred only with the hydrogen pretreatment but required no irradiation treatment, indicating that such a type of oxygen activation could occur in the oxidative dehydrogenation of ethylbenzene.

Amount of adsorbed oxygen species. The amount of adsorbed oxygen species was varied with the sodium content of the catalyst. The amounts of O^- and O_{2ad} increased until 17 μmol of Na/g-cat and remained at a stationary level above 17 μmol of Na/g-cat. This relationship with Na content is similar to that of the amount of base sites of pK_a between 17.2 and 26.5. Figure 2 shows the correlation of the amount of adsorbed oxygen species to the amount of base sites of pK_a ~17.2-26.5. The amount of O_{2ad} was calibrated volumetrically and since the large signal of the V center made it difficult to determine the amount of O^- species, the relative amount was displayed. As shown in Fig. 2, an approximate linear relationship exists between the amount of adsorbed oxygen species and the amount of effective base sites.

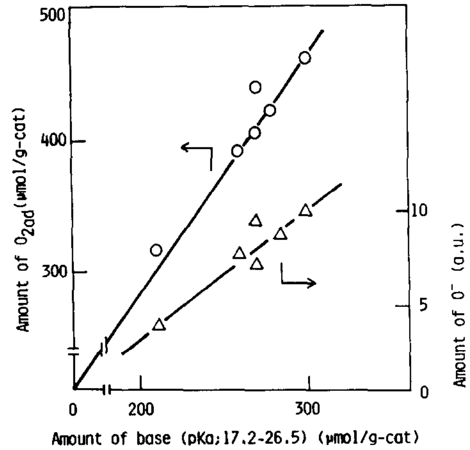

FIG. 2. Correlations between the amount of base (pK_a; ~17.2–26.5) and the amount of O_{2ad} formed (○) and O^- formed (△) after the exposure to 33 kPa of O_2 at 763 K for 1 h.

The amount of O^- species also changed with the treatment temperature of the catalyst with oxygen. The effect of the treatment temperature on the amount of O^- formed is shown in Fig. 3. Oxygen, 27 kPa, was introduced onto the sample which had been pretreated (procedures 2 and 3) and then evacuated at 77 K. The ESR signal at 77 K was obtained after the sample was heated under each condition shown in Fig. 3 and quenched immediately at 77 K.

DISCUSSION

Activation of Ethylbenzene

As shown in Table 1, a significant amount of styrene was formed only when ethylbenzene and oxygen were pulsed at the same time, while molecular hydrogen could not be observed on pure-SiAl. The same results

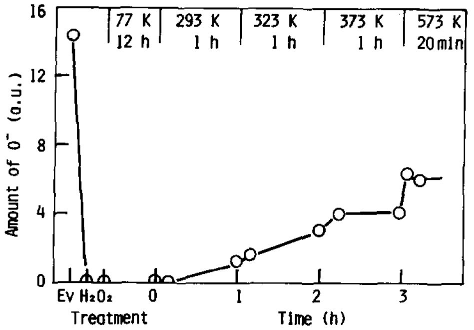

FIG. 3. Change of the amount of O^- species on 17Na–SiAl with treated temperature in the presence of oxygen. The sample was evacuated at 763 K (Ev), treated with hydrogen at 763 K (H_2), followed by brief evacuation and the sample was quenched to 77 K immediately after the introduciton of 33 kPa of O_2 at 293 K. ESR spectra were obtained at 77 K.

have been obtained on commercial SiAl (original-SiAl) in the preceding study (*1*). This shows that styrene is formed on the SiAl surface but not on the impurities which may exist in commercial SiAl (i.e., Fe^{3+}) and that styrene is formed through an oxidative dehydrogenation process but not the simple dehydrogenation process. In this pulse reaction, a significant amount of ethylbenzene was not recovered. The same results were observed in the case of original- and Na–SiAl catalysts, and this incomplete recovery has been related to the acidity of H_0 between 1.5 and −5.6 (*1*). Such unrecovery has been assumed to be caused by the reversible adsorption of ethylbenzene (*1, 12, 32*). To confirm the reversibility of the adsorption of ethylbenzene, the effluent was collected by a silica gel trap at 77 K. The results shown in Table 2 indicate that the incomplete recovery is due to the reversible adsorption of ethylbenzene or, in other words, due to the gradual desorption of ethylbenzene. Table 2 also shows that such a site which adsorbs ethylbenzene is still active even after carbonaceous compounds have deposited on the surface. Consequently, the amount of unrecovered ethylbenzene represents the ability of the catalysts to adsorb ethylbenzene. The correlation between the amount of unrecovery and that of the acid sites (*1*), indicates that the active site which adsorbs ethylbenzene reversibly is the acid site of H_0 between 1.5 and −5.6.

The water pulse following the ethylbenzene pulse promoted the desorption of ethylbenzene, as shown in Table 3. Then the role of H_2O on the desorption of ethylbenzene was studied in the deuterium exchange experiments. The first column in Table 4 shows that about 90% of the ethylbenzene treated with D_2O at 723 K was exchanged by deuterium. Even at maximum, the number of deuteriums exchanged was five per one ethylbenzene. The deuterium distribution in molecular ions and that in C_7 ions were the same within the experimental errors. As the C_7 fragment of ethylbenzene has been reported to be produced by the cleavage of the C–C bond between the α-C and β-C of the side chain (*33*), the comparison of molecular ions with the C_7 ions shows the nature of the terminal methyl group. The similarity in deuterium distribution of these ions proves that the terminal methyl group is inactive for the H–D exchange from the above results. The deuteration of the aromatic ring has also been suggested. In spite of the fact that the C_6 ions are said to be formed not simply by dealkylation, the results obtained by Meyerson *et al.* (*33*) have shown that the C_6 ions have a nature of an aromatic ring preferentially. Consequently, the difference between the deuterium distribution in C_7 ions and that in C_6 ions should suggest the different nature of the hydrogen at the side chain. The deuterium distribution in the C_6 ions was lower than those in the C_7 and C_8 ions. Although the calibration performed on the C_6 ions to obtain the third column of Table 4 was not complete, a more precise correction would lower the amount of deuterium exchanged. These results show that the deuterium exchange should occur preferentially on the hydrogen at the α-carbon of the side chain(α-hydrogen). For example, the d_0 ion in C_6 ions was about 18%, on the other hand, those in C_7 and C_8 ions were about 8%, indicating that about 10% of ethylbenzene is deuterated at only the α position of the ethyl group but is not deuterated at the benzene ring. These results show that the β-hydrogen of the terminal methyl group is unexchangeable; however, the α-hydrogen and the hydrogen on the benzene ring are exchangeable. Moreover, the exchange on the α-hydrogen is predominant to that on the aromatic ring. Thus, the adsorbed species can be regarded as being dissociated reversibly at the α position of ethylbenzene. α-Hydrogen will be abstracted by the basic site, or in other words, perhaps by the OH group adjacent to the acid site which has been identified as an adsorption site of ethylbenzene (*1*). These conclusions explain the inhibiting effect of the α-hydrogen in alkylbenzenes observed in the competitive reaction with ethylbenzene on Sn–P catalyst (*12*).

It is concluded from quantum calculations that acid sites withdraw the electron of the aromatic ring to enhance the acidic property of the α-hydrogen, and its interacts with the OH group near the acidic site (*35*). This dissociative adsorption of ethylbenzene should be the case, and the mechanism of the activation of ethylbenzene is summarized in Fig. 4. It is noteworthy that ethylbenzene is reversibly adsorbed in the dissociated state at the α position and that the active site is the acid site distributed in the range of H_0 between 1.5 and −5.6. The electron-withdrawing character of such an acid site is confirmed by the following two experimental results. (1) When 1.6 kPa of pyridine was adsorbed on the sample at 373 K, which had been evacuated at 743 K, the characteristic ir spectra of L-Py was observed at 1620 and 1455 cm^{-1}. This shows that Lewis acid sites are present on the surface of the catalysts. (2) The introduction of benzene solution of perylene at 293 K onto the sample which had been evacuated at 623 K results in the formation of perylene cation radicals, the amounts of which are varied with the Na content of the catalyst and correlate with the amount of the acid sites stronger than $H_0 = 1.5$. These results show that all or a part of the acid sites stronger than $H_0 = 1.5$ possess an electron-withdrawing character. Danforth has reported that such Lewis acid sites are generated on the aluminum ion by the Na treatment (*34*).

Reaction of Adsorbed Ethylbenzene with Oxygen

In the formation of styrene from adsorbed ethylbenzene, the abstraction of a hydrogen at the terminal methyl group (β-hydrogen) is necessary. As shown in Table 2, the oxygen pulse onto the adsorbed ethylbenzene produces an observable amount of styrene. This shows the ability of oxygen species to abstract β-hydrogen. The site to oxidize the adsorbed intermediate of ethyl-

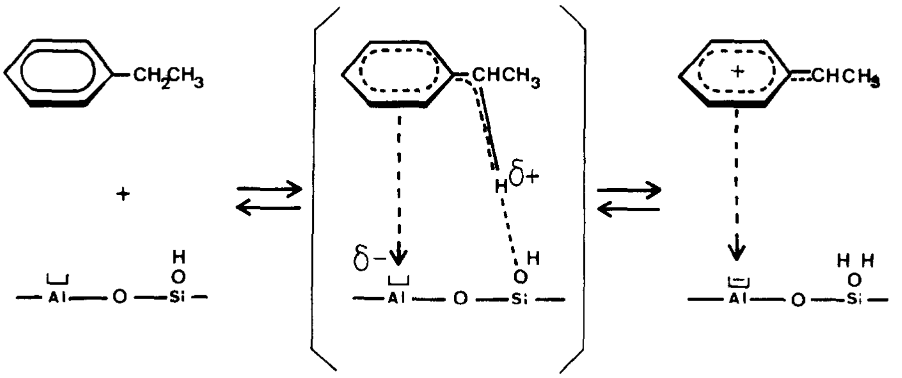

FIG. 4. Reaction scheme for the adsorption of ethylbenzene.

benzene has been shown to be base sites of pK_a between 17.2 and 26.5 in the preceding paper (*1*). As shown in Table 2, the styrene formed from adsorbed ethylbenzene is irreversibly adsorbed on the fresh catalyst to form coke but not on the used catalyst. This shows that the coke formed in the flow reaction covers and deactivates the site to polymerize styrene and that the active site to abstract the β-hydrogen is still effective even after coke formed on the catalyst. These conclusions explain well the time course of the flow reaction (*1*).

Activation of Oxygen

In this study, the ability of SiAl catalysts to activate gaseous oxygen is confirmed. It is worth noting that such adsorption and activation of oxygen occur only with a simple hydrogen pretreatment and require no irradiation pretreatment. Such hydrogen treatment and the following evacuation will produce an anion vacancy by the addition of a hydrogen to the OH group and the subsequent desorption of the surface H_2O species formed. In a similar manner, the same site can be produced by the adsorption of ethylbenzene as shown in Fig. 4, followed by the desorption of the surface water. Thus, oxygen can be adsorbed during the oxidative dehydrogenation of ethylbenzene.

Figure 2 shows the correlation of the amount of adsorbed oxygen species to the amount of base sites of pK_a ~17.2–26.5. The amounts of O_{2ad} and O^- are proven to be proportional to the amount of base on the sample. These results show that the amount of adsorbed oxygen species is controlled by the Na content and that the active site to form O_{2ad} and O^- is the base site of pK_a between 17.2 and 26.5. Such a base site is proposed to be produced adjacent to the acid site of H_0 between 1.5 and −5.6 by the inductive effect of Na–SiAl catalyst, whereas an adjacent base site exists on the original-SiAl catalyst only by chance (*1*).

Figure 3 shows the effect of the treatment temperature on the amount of O^- formed on the catalyst with gaseous oxygen. The adsorbed molecular oxygen species (O_{2ad}) formed easily at 77 K, while the formation of O^- species was not observed at 77 K in 12 h, and the amount of O^- species gradually increased with time at 293 and 323 K. Above 373 K, the amount of O^- increased steeply and soon reached a stationary state. These results show that at high temperatures such as reaction temperatures above 723 K, the amount of O^- will quickly reach a stationary state.

All these results suggest that O^- is formed on the base site of pK_a between 17.2 and 26.5 through the well-known scheme to activate oxygen (*19*, *36*).

$$O_{2gas} \rightleftharpoons O_{2ad} \rightleftharpoons (O_{2ad}^-) \rightarrow 2O^- \quad (1)$$

base site (pK_a ~17.2–26.5).

As the hyperfine structure resulted from Al ion was not observed, these oxygen species may be adsorbed on the Si ion.

Reaction of Adsorbed Oxygen with Ethylbenzene

The reactivity of the adsorbed oxygen species was examined by the method described under Experimental. About 12 μmol of ethylbenzene/g-cat was introduced onto the sample which had adsorbed O_{2ad} and O^-. The amount of O_{2ad} was unchanged at 293 K even after 120 h from the introduction of ethylbenzene, while the amount of O^- decreased gradually and reached a stationary state at 3 h. The amount of O_{2ad} decreased gradually at above 323 K. The reaction of O^- which had been produced by the N_2O treatment with ethylbenzene was also studied on original-SiAl. Even at 77 K the amount of O^- species gradually decreased with the introduction of ethylbenzene as shown in Fig. 5. At 293 K, a rapid decrease of O^- species was observed.

Styrene was formed in the pulse reaction of ethylbenzene with N_2O on the pretreated (similar to procedures 2 and 3 in the helium gas flow) SiAl catalyst. As shown in Table 1, the amount of styrene is comparable to

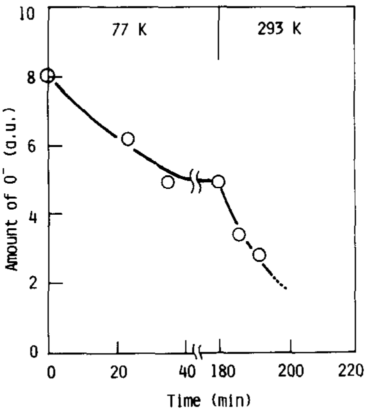

FIG. 5. Reaction of O^- species with ethylbenzene on the original-Si · Al catalyst pretreated with N_2O along with the procedure (7) as is shown under Experimental.

that in the reaction with oxygen, while the combustion was suppressed. These results show that the active oxygen species of this reaction is O^- species.

Many studies have been devoted to the reactivity of O^-. Bohme and Young showed that the oxygen ion adds only in the case of ethylene and it abstracts a hydrogen atom or a proton from higher olefins (*37*). For the simple alkanes, hydrogen atom abstraction was the only observed reaction (*38*). Neta and Schuler (*39*) have demonstrated that the addition of O^- to double bonds and aromatic systems is relatively slow so that in most cases abstraction dominates. Kazansky and co-workers (*40*) have also determined that the reaction of O^- with hydrocarbons is initiated by the abstraction of hydrogen by O^- to form the OH^- species. More recent work has demonstrated that O^- initiates hydrogen atom abstraction from alkanes and alkenes (*41*) resulting in the formation of alkenes and alkadienes, respectively. Thus, the O^- species on the catalyst surface can cause the oxidative dehydrogenation of hydrocarbons. In fact, such a mechanism has been proposed previously to explain the kinetic data on the activity of ferrite for the dehydrogenation of butenes (*10, 11, 15, 17*). A similar role of O^- species can be expected in the present reaction, that is, the O^- species abstracts the β-hydrogen of the adsorbed intermediate of ethylbenzene to form surface OH group and styrene.

Figure 6 shows the effect of Na content on the amount of O^- species and on the turnover frequency. The turnover frequency was calculated from the results obtained by the flow reaction based upon the number of acid sites of H_0 between 1.5 and 5.6 which have been proven to form the adsorbed reaction intermediate of ethylbenzene. This turnover frequency represents the ability to abstract the β-hydrogen of the intermediate. The dependence of the amount of the O^- species on Na content is very similar to that of the turnover frequency on Na content, indicating that the role of the O^- species in the flow reaction is to abstract the β-hydrogen of the adsorbed reaction intermediate.

Reaction Mechanism of Oxidative Dehydrogenation of Ethylbenzene

As mentioned above, the oxidative dehydrogenation of ethylbenzene proceeds through the adsorption of ethylbenzene (Fig. 3), the activation of oxygen (Eq. (1)), and the abstraction of β-hydrogen of adsorbed ethylbenzene with O^-. The revers-

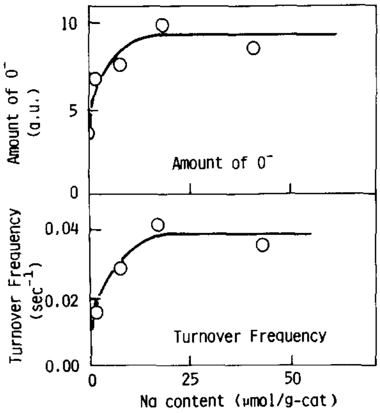

FIG. 6. Effect of Na on the amount of O^- species and on the turnover frequency.

ibility of the adsorption of ethylbenzene shows that the rate-determining step of this reaction is not at the adsorption of ethylbenzene but at the oxidation of the adsorbed intermediate of ethylbenzene. In this study, it is also clarified that the reaction of O^- with ethylbenzene is relatively rapid but requires an activation energy, as shown in Fig. 5. As the reaction of O^- species with hydrocarbons is said to require little activation energy, and the rate is said to be governed by the transport of hydrocarbon (*40, 41*), the activation energy mentioned above can be attributed to the further activation of the adsorbed intermediate of ethylbenzene. The formation of O^- species also requires some activation energy, as shown in Fig. 3, but the rate of it is considered to be large at high temperature. The reaction order of this reaction was fractional in both ethylbenzene and oxygen (*1*), indicating that the activation of oxygen, as well as that of ethylbenzene, has a contribution to the rate of this reaction. However, the contribution of the activation of oxygen is considered to be small in the case of Na-SiAl catalysts, because the order in oxygen was small compared to the order in ethylbenzene. Consequently, the rate-determining step of the overall reaction is proposed to be the reaction of O^- with the adsorbed intermediate of ethylbenzene to abstract the β-hydrogen.

Finally the overall reaction mechanism shown in Fig. 7 is proposed for the oxidative dehydrogenation of ethylbenzene.

(1) First, ethylbenzene coordinates to the acid site of H_0 between 1.5 and 5.6, and then the ring electron is donated to the acid site, which makes the acidic nature of the α-hydrogen pronounced.

(2) The basic OH group adjacent to the acid site mentioned above abstracts the α-hydrogen from the coordinated ethylbenzene on the acid site to give a relatively stable adsorbed species.

(3) The water formed by the abstraction of α-hydrogen desorbs to give an anion vacancy which can activate oxygen.

(4) Reversibly adsorbed surface oxygen

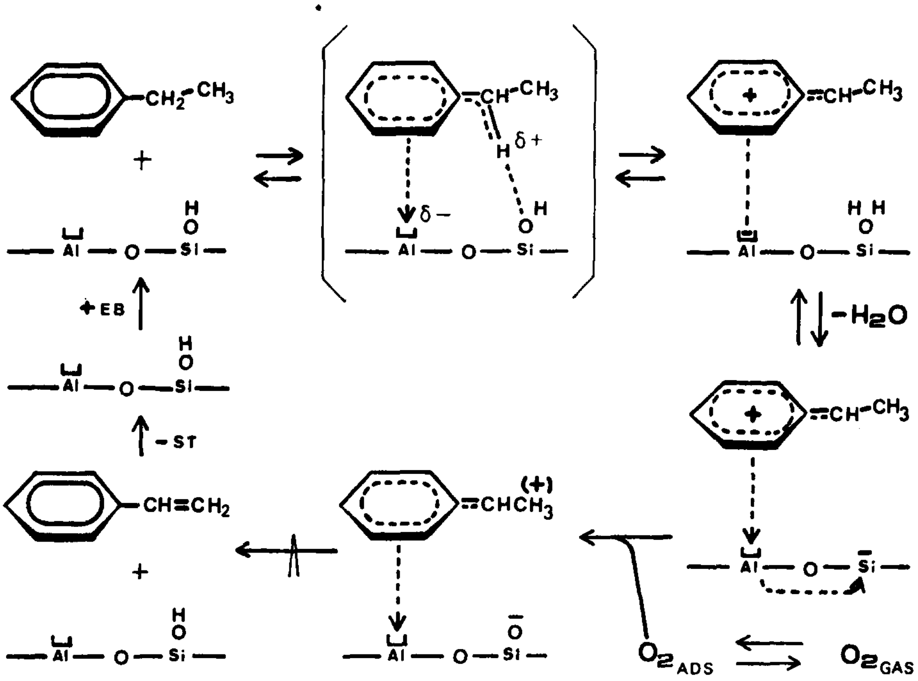

FIG. 7. Reaction mechanism proposed for the oxidative dehydrogenation of ethylbenzene.

is converted to O^- species on the site mentioned above, with the strength of such an active site from 17.2 to 26.5 in pK_a value.

(5) The reversibly adsorbed intermediate of ethylbenzene is activated and its β-hydrogen is abstracted by the O^- species to give styrene and basic OH, which regenerates the active site. This step determines the overall rate of this reaction on Na–SiAl catalysts.

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