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Study of the Oxidative Dehydrogenation of Ethylbenzene

IV. Extension of the Reaction Mechanism to Various Solid Acid Catalysts and Its Application to Catalyst Design

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The generality of the reaction mechanism, which is presented on the Na–$SiO_2 \cdot Al_2O_3$ catalysts, has been confirmed in the oxidative dehydrogenation of ethylbenzene and cumene on various solid acid catalysts. The amount of adsorbed ethylbenzene is well correlated to the amount of effective acid sites with H_0 between 1.5 and −5.6, while the turnover frequency is well correlated to the amount of effective base sites with pK_a between 17.2 and 26.5. Thus, the effective acid and base sites can generally be considered to adsorb ethylbenzene and abstract β-hydrogen of adsorbed ethylbenzene, respectively. The strong acid sites ($-5.6 > H_0$) are thought to be active for the cracking and total oxidation reaction. This reaction mechanism provides the plan for the catalyst design. Al–P catalyst which satisfies the plan actually showed high activity and selectivity.

INTRODUCTION

In previous papers, SnO_2–P_2O_5 catalyst has been found to be the most active and selective catalyst for the oxidative dehydrogenation of ethylbenzene (EB) among various oxide catalysts, where the addition of phosphorus (the acidic component) enhanced the selectivity (*1*). The details of the catalytic behavior of SnO_2–P_2O_5 catalyst have also suggested that the activity and selectivity of this reaction are controlled by the acid and base properties of the catalyst (*2*). To confirm the role of the acid and base properties of the catalysts on the catalytic oxidation reactions, the effect of the acid and base sites has been studied in detail using a series of Na-treated SiO_2–Al_2O_3 (Na–Si·Al) catalysts (*3*). Fiedorow *et al.* (*4*) and Alkhazov and Lisovskii (*5*) have proposed that the role of the acid sites is to form a carbonaceous deposit which is active in this reaction; however, we have reached a contradictory conclusion that the acid–base sites with suitable strength ranges are the active sites (*6*). The presented roles of the above sites are as follows, and the following mechanism has been proposed on the basis of the revealed roles of the acid and base sites in a molecular aspect (*6*): (1) Ethylbenzene coordinates to the acid site of H_0 between 1.5 and −5.6 with electron-withdrawing character, and its α-hydrogen is activated. (2) The α-hydrogen of ethylbenzene is abstracted by the base site adjacent to the acid site mentioned above to form an adsorbed intermediate. These steps to adsorb ethylbenzene take place reversibly. (3) Gas-phase oxygen is activated on the base site of pK_a between 17.2 and 26.5 to form the active oxygen species, O^-, and the β-hydrogen of the adsorbed intermediate of ethylbenzene is abstracted by the O^- species to form styrene. The active site is also regenerated in this step. In this mechanism, the step to abstract the β-hydrogen determines the overall rate of styrene formation.

Recently, the methods that form the basis of the scientific design of catalysts have attracted considerable attention (*7*, *8*). Catalyst design can be regarded, in many

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ways, as a logical application of available information to the selection of a catalyst for a given reaction, and the elucidation of the reaction mechanism and its extension can play important roles in it. In order to design the effective catalysts for the oxidative dehydrogenation of ethylbenzene, the abovementioned mechanism which is proposed in the case of the Na–Si · Al system should be proved to hold generally on other catalysts.

In this study, ten types of solid acid catalysts, including SnO_2 and Sn–P, were examined in the oxidative dehydrogenation of ethylbenzene and cumene to prove the generality of the reaction mechanism which is essential for further development of the catalyst for the oxidative dehydrogenation of ethylbenzene.

EXPERIMENTAL

Catalysts

$SiO_2 \cdot Al_2O_3$(L) (Nikki Chemical Co. N632(L)) (Si · Al(L)), SiO_2–MgO (Nikki Chemical Co. X661) (Si · Mg), Al_2O_3 (Sumitomo Activated Alumina KHD and KAT-6), and SiO_2 (Fuji-Davison Chemical Ltd. microbeads silica gel 5D) were sieved and calcined at 773 K for 2 h in air. The preparation of solid phosphoric acid, SnO_2, SnO_2–P_2O_5 (Sn–P), and Na–$SiO_2 \cdot Al_2O_3$ (Na–Si · Al) catalysts was described in the previous paper (*3*). Li–$SiO_2 \cdot Al_2O_3$ (Li–Si · Al), K–$SiO_2 \cdot Al_2O_3$ (K–Si · Al), and Na–SiO_2 · MgO (Na–Si · Mg) were prepared by the ion exchange method in the same way as Na–$SiO_2 \cdot Al_2O_3$ (*3*). For Al_2O_3–P_2O_5 (Al–P) and SiO_2–P_2O_5 (Si–P), a known amount of phosphoric acid was added to the hydroxide gel of Al and Si, dried, calcined at 773 K for 2 h in air, and sieved. The hydroxide gels were prepared by either boiling tetraethylorthosilicate in H_2O + HCl or by adding $NH_4OH_{aq.}$ to the aqueous solution of $Al(NO_3)_3 \cdot 9H_2O$. Al_2O_3–B_2O_3 (Al–B) catalyst was prepared by impregnating Al_2O_3 (KAT-6) with an aqueous solution of H_3BO_3, drying, and calcining at 793 K.

Procedure

The catalytic activity was measured in the same way as described previously (*3*). The standard reaction conditions were as follows: catalyst weight, 1.00 g; reaction temperature, 723 K; total feed rate, 290 mmol/h; partial pressures, $P_{O_2} : P_{EB} : P_{H_2O}$ = 10.1 : 14.5 : 32.6 (kPa) with N_2 balance. Reaction conditions different from the standard ones were described in the footnotes of the figures and tables. The pulse reaction was conducted by using a conventional apparatus (*2*) with some modifications. A small amount of oxygen impurity in the carrier gas was removed by the silica gel trap at 77 K immediately before the sample inlet. A sample inlet was jacketed and purged with nitrogen to prevent the introduction of oxygen into the purified carrier gas. The flow of carrier gas was split into two at the outlet of the reactor for the analysis of gaseous products and for the analysis of liquid products. The chromatographic columns were the same as those described in the previous paper (*3*). Pulses I (EB (1 mm^3) only), II (EB 10 min after O_2 (1 cm^3)) and III (EB and O_2 at the same time) were conducted onto the catalyst (0.20 g) at 723 K in the flow of oxygen-free helium (1.67 cm^3/s).

Surface Properties

The acidity and basicity of catalysts were determined by titrating with *n*-butylamine and benzoic acid, respectively, using Hammet indicators as described previously (*3*). The surface areas of the catalysts were determined by the usual BET method.

ESR Measurement of Perylene Radical on the Surface

The catalyst (0.1 g) in an ESR sample tube was evacuated at 573 K for 3 h, then the benzene solution of perylene was added into the tube through a rubber septum, and the tube was sealed. The measurement was carried out with JES-ME-ESR-1X after the sealed sample had been placed in the dark for 2 days. DPPH solution was used to calibrate the signal intensity.

RESULTS

Generality of the Role of Acid and Base Properties

The mechanism of this reaction has been proposed on Na-ion-exchanged SiAl catalysts. An adequate amount of Na promoted the catalytic activity for the formation of styrene and the effect has been correlated to the acid and base properties of the catalysts. In order to confirm the generality of this reaction mechanism, the effect of alkali ions to solid acid catalysts was studied on other series of catalysts. Li–Si · Al, K–Si · Al, and Na–Si · Mg catalysts were prepared by the same ion exchange method and tested by the pulse technique in the same way as reported previously (*3*). As shown in Table 1, the promoting effect of alkali ions was observed on all alkali–Si · Al catalysts. The amount of formed styrene at 723 K increased in the following sequence: original < Li < K < Na. The promoting effect of Na was also observed on Na-ion-exchanged Si · Mg catalyst. The activity of Li-exchanged SiAl catalysts and Na-impregnated Al_2O_3 catalysts was maximum at adequate amounts of Li and Na as has been reported on Na-exchanged Si · Al catalysts. All these results indicate that the promoting effects can be attributed to general acid and base properties of the catalysts but not to the limited effect of Na on SiAl catalyst, and that the reaction mechanism proposed previously holds in general on the solid acid and base catalysts.

TABLE 1

Amount of Styrene Formed in the Pulse Reaction (μmol/g-cat)

Catalyst	I (EB)[a]	II ($O_2 \rightarrow$ EB)[a]	III (O_2 + EB)[a]
0.0-Si · Al	Nil	Nil	0.28
8.5Na–Si · Al[b]	Nil	Nil	0.81
8.5K–Si · Al	Nil	Nil	0.73
8.5Li–Si · Al	Nil	Nil	0.31
0.0-Si · Mg	Nil	Nil	0.19
8.5Na–Si · Mg	Nil	Nil	0.29

[a] For the pulse sequence, see text.

[b] 8.5Na–Si · Al contains 8.5 μmol of Na/g-cat.

Surface Properties

Typical solid acid catalysts, SnO_2, and SnO_2–P_2O_5 catalysts were used to examine further the generality of the reaction mechanism. Table 2 shows the surface properties of these catalysts. Considering the proposed reaction mechanism, the amounts of effective acid ($1.5 > H_0 > -5.6$), stronger acid ($-5.6 > H_0$), and effective base ($17.2 < pK_a < 26.5$) were measured by the acid–base titrations. Only Si · Mg catalyst had no effective acid, but all of the other catalysts had the effective acid sites. In addition, Si · Al and Al–B catalysts had the stronger acid sites. All catalysts except Si · Mg and Solid-P possessed the base sites in the effective strength range ($17.2 < pK_a < 26.5$). However, an unusual change in the color of the indicators was observed in the cases of SnO_2 and SnO_2–P_2O_5 catalysts, making it difficult to determine the basicity of the catalyst. The electron-withdrawing property of the catalysts was measured by the reaction with perylene to form the perylene cation radicals using ESR spectroscopy.

Flow Reaction

The catalytic behavior of the catalysts contained in Table 2 was examined in the oxidative dehydrogenation of ethylbenzene and cumene by the continuous flow technique. As shown in Figs. 1 and 2 the catalysts showed relatively high selectivity, especially in the reaction of ethylbenzene. The orders of activity were almost identical to each other in the reactions of cumene and ethylbenzene: Si–Al(H) ≈ Si–Al(L) ≈ Al–P > Al > Sn–P ≈ Al–B > Si–P > SnO_2 ≈ Si · Mg for ethylbenzene, and Al–P > Al ≈ Si · Al(L) ≈ Si · Al(H) > Al–B ≈ Sn–P ≈ Si–P > SnO_2 > Si · Mg for cumene.

In Fig. 3, the cracking activity of these catalysts was compared with the oxidative

TABLE 2

Surface Properties of Catalysts

Catalyst	Amount of acid (μmol/g-cat)		Amount of strong base[c] (μmol/g-cat)	Surface area (m^2/g-cat)	Amount of perylene radical (μmol/g-cat)
	Medium[a]	Strong[b]			
Si · Al(L)	100	333	250	425	10.0
Si · Mg	n.d.	n.d.	n.d.	55.8	0.04
Al_2O_3	213	n.d.	88	361	0.82
Al–P (P/Al = 1/10)	715	n.d.	93	385	1.16
Si–P (P/Si = 1/10)	406	[d]	12	246	0.01
Al–B (B/Al = 1.5/10)	356	209	77	247	4.95
Solid-P	201	n.d.	n.d.	—	0.04
SnO_2	55	n.d.	[d]	21.9	n.d.
Sn–P (P/Sn = 1/10)	117	n.d.	[d]	29.8	0.17
SiO_2	n.d.	n.d.	n.d.	210	n.d.

[a] $1.5 > H_0 > -5.6$.
[b] $H_0 < -5.6$.
[c] $17.2 < pK_a < 25.6$; stronger base of $pK_a > 26.5$ was not observed.
[d] Unusual change of color was observed.

dehydrogenation activity, in the reaction of cumene. The rate of benzene formation in the absence of oxygen is plotted against the rate of α-methylstyrene formation in the presence of oxygen. The catalysts with the effective acid sites were active in the oxidative dehydrogenation, while only the catalysts with the stronger acid sites ($-5.6 > H_0$) were active in the cracking reaction. The poisoning of Si · Al catalyst with pyridine decreased only the cracking activity, but it did not change the activity for the oxidative dehydrogenation.

In Fig. 4, the rate of styrene formation in the reaction of EB was plotted against the amount of effective acid sites. However,

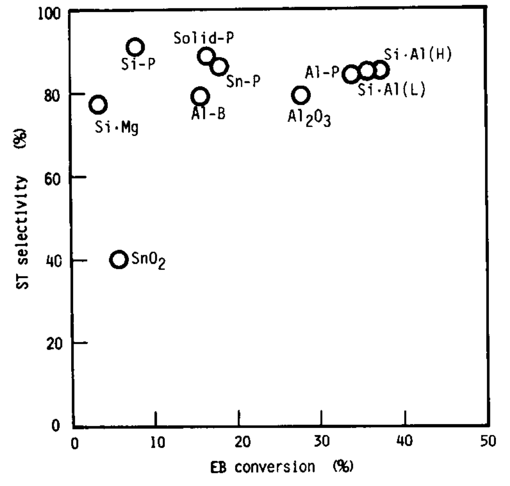

FIG. 1. Conversion and selectivity in the oxidative dehydrogenation of ethylbenzene.

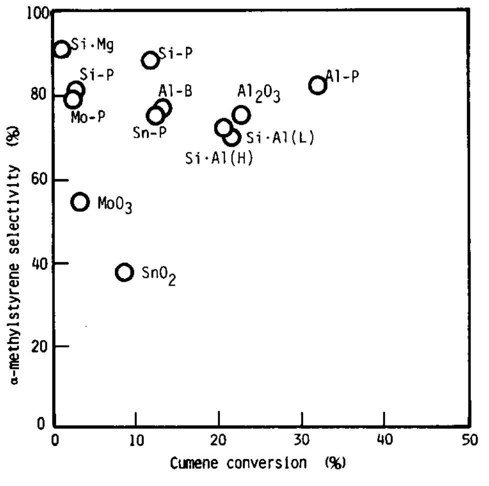

FIG. 2. Conversion and selectivity in the oxidative dehydrogenation of cumene. Partial pressures: $P_C : P_{O_2} : P_{H_2O} : P_{N_2} = 12.8 : 10.1 : 32.6 : 55.5$ (kPa).

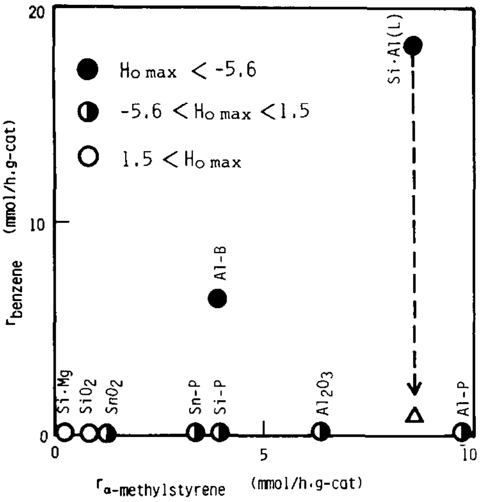

FIG. 3. Correlation between oxidative dehydrogenation activity and cracking activity in the reaction of cumene. Partial pressures: $P_C : P_{H_2O} = 12.8 : 32.6$ (kPa); $P_{O_2} = 10.1$ kPa for oxidative dehydrogenation but $P_{O_2} = 0.00$ kPa for cracking, with N_2 balance. △, Pyridine was added to the system.

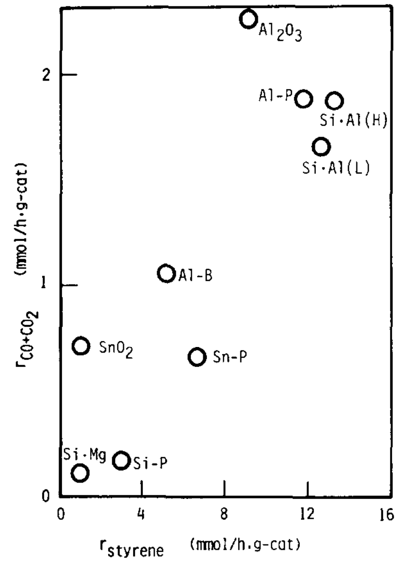

FIG. 5. Correlation between the rate of styrene formation and total oxidation in the reaction of ethylbenzene.

the correlation is not sufficient to explain the activity by only the acidic properties of the catalyst. The effect of the basic properties should be taken into account as well as the acidic properties.

Figure 5 shows the correlation between styrene (ST) formation and combustion. The increase in the rate of styrene formation results in the increase in the rate of carbon oxides formation. The same correlation between oxidative dehydrogenation and total oxidation is observed in the reaction of cumene.

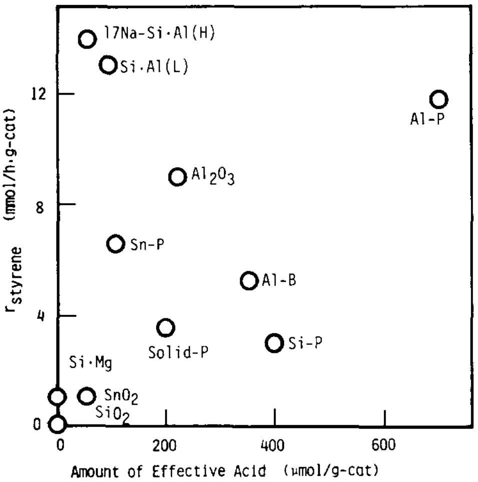

FIG. 4. Correlation between the rate of styrene formation and the amount of effective acid sites of $1.5 > H_0 > -5.6$ in the oxidative dehydrogenation of ethylbenzene.

Pulse Reaction

Further study was carried out using the pulse technique. The reactants were pulsed on the catalyst (0.2 g) in the following sequences: only ethylbenzene (1 mm^3) was pulsed (pulse I), oxygen (1 cm^3) was first pulsed (pulse II′) and then ethylbenzene (1 mm^3) was pulsed 10 min later (pulse II), and oxygen (1 cm^3) and ethylbenzene (1 mm^3) were pulsed simultaneously (pulse III). Styrene, benzene, and carbon oxides were formed, and a considerable amount of ethylbenzene was not recovered. Table 3 shows the results of styrene formation and Table 4 shows the results of combustion.

As shown in Table 3, SiO_2 showed no catalytic activity. Solid-P, Al_2O_3, Si–Al, Si · Mg, and Si–P formed styrene only in pulse III (ethylbenzene and oxygen were pulsed simultaneously), indicating that the

TABLE 3

Styrene Formation by the Pulse Reaction (μmol/g)[a]

Catalyst	I (EB only)[b]	II′ (O_2)[b]	II (EB)[b]	III (O_2 + EB)[b]	III − II[b]
Al_2O_3	Trace	Nil	Trace	0.40	0.40
Al–P	0.10	Nil	0.08	1.12	1.12
Al–B	0.21	Nil	0.14	0.38	0.24
Si · Al	Trace	Nil	Trace	0.28	0.28
SiO_2	Nil	Nil	Nil	Nil	Nil
Si · Mg	Nil	Nil	Nil	0.05	0.05
Si–P	Nil	Nil	Nil	Trace	Trace
Solid-P	Trace	Trace	Nil	0.06	0.06
Sn–P	2.09	Nil	3.54	3.67	0.13
SnO_2	1.10	Nil	1.49	1.63	0.14

[a] Reaction temperature, 718 K.
[b] For the pulse sequence, see text.

oxygen species weakly adsorbed on the catalyst is active in this reaction. Al–P, Al–B, Sn–P, and SnO_2 formed styrene even in pulse I, indicating that the lattice oxygen or the strongly adsorbed oxygen species still has an activity. In the case of Sn–P and SnO_2 catalyst, the amount of styrene formed increased in the sequence I < II < III, but the difference was not so large. In the cases of Al–P and Al–B, however, the amount of formed styrene in pulse III was much greater than that in pulse I or II, showing that the contribution of weakly adsorbed oxygen species was greater than that of strongly adsorbed species or lattice oxygen on these catalysts. In order to discuss the active oxygen species of these catalysts, further investigation is necessary.

As shown in Table 4, SiO_2, Al_2O_3, Si · Al, Si · Mg, Al–P, Al–B, SnO_2, and Sn–P formed carbon oxides in the oxygen pulse II′ as well as in pulse III. Especially on Si · Al and SiO_2, the amount of carbon oxides formed in pulse II′ was very close to that formed in pulse III. But no carbon oxides were formed on the catalysts but SnO_2

TABLE 4

Total Oxidation by the Pulse Reaction (μmol/g)[a]

Catalyst	I (EB only)[b]	II′ (O_2)[b]	II (EB)[b]	III (O_2 + EB)[b]	III − II[b]
Al_2O_3	Nil	0.01	Nil	0.16	0.15
Al–P	Nil	0.02	Nil	0.05	0.03
Al–B	Nil	0.01	Nil	0.11	0.10
Si · Al	Nil	0.12	Nil	0.13	0.01
SiO_2	Nil	0.03	Nil	0.05	0.02
Si · Mg	Nil	Nil	Nil	0.09	0.09
Si–P	Nil	Nil	Nil	Nil	Nil
Solid-P	Nil	Nil	Nil	Nil	Nil
Sn–P	1.18	1.17	0.05	1.12	Nil
SnO_2	1.28	2.08	1.00	2.11	0.03

[a] Reaction temperature, 718 K.
[b] For the pulse sequence, see text.

and Sn–P in the ethylbenzene pulse in pulse I and pulse II. These results indicate that carbon oxides are formed by the combustion of carbon species strongly adsorbed on the surface in the case of these catalysts. In the cases of SnO_2 and Sn–P catalysts, on the other hand, carbon oxides were formed without gaseous oxygen in pulses I and II. Furthermore, the amount of carbon oxides formed in the oxygen pulse II′ is essentially equal to that formed in pulse III. These results indicate that the strongly adsorbed oxygen or the lattice oxygen may take part in the total oxidation of ethylbenzene on SnO_2 and Sn–P catalysts.

DISCUSSION

Reaction Mechanism

In the previous study on Sn–P (*2*) and Na–SiAl (*6*) catalysts, a considerable amount of ethylbenzene has not been recovered in the pulse reaction. Such an unrecovery has been correlated to the reversible absorption of ethylbenzene on the catalyst surface. The adsorption state has also been confirmed to be dissociated at the α-position from the isotope exchange study (*6*). The correlation between the amount of reversibly adsorbed ethylbenzene and the amount of acid sites ($1.5 > H_0 > -5.6$) leads to the conclusion that the active site to adsorb ethylbenzene is the acid sites of H_0 between 1.5 and −5.6 (effective acid sites). The turnover frequency, calculated from the rate of styrene formation and the amount of effective acid sites, was well correlated to the base site of pK_a between 17.2 and 26.5. This leads to the conclusion that the abstraction of β-hydrogen to form the adsorbed intermediate of ethylbenzene occurs on the base site of pK_a between 17.2 and 26.5 (effective base sites). The role of effective base sites has also been determined to be to adsorb gaseous oxygen to form O^- species.

In this study, such an insufficient recovery of ethylbenzene was observed in the pulse reaction. As the flow rate of carrier gas was increased from 0.74 to 1.67 cm^3/s the absolute value of the unrecovery was not the same as that reported in the previous study. The amount of adsorbed ethylbenzene is plotted against the amount of effective acid sites in Fig. 6. As the effective acid sites increase, the amount of adsorbed ethylbenzene increases, showing that the acid sites of H_0 between 1.5 and −5.6 adsorb ethylbenzene, perhaps, in the dissociated state as in the proposed reaction mechanism mentioned above.

The turnover frequency of this reaction is calculated by assuming that the active site to adsorb ethylbenzene is the effective acid sites:

$$\text{turnover frequency} = \frac{\text{the rate of styrene formation in the flow reaction at 723 K}}{\text{the amount of effective acid sites } (1.5 > H_0 > -5.6)}.$$

In Fig. 7, the calculated turnover frequency is plotted against the amount of effective base ($26.5 > \mathrm{p}K_a > 17.2$) together with the turnover frequency on Na–Si · Al catalysts reported in the previous paper (*6*). The turnover frequency is well correlated to the amount of effective base sites, indicating that β-hydrogen is abstracted from the adsorbed ethylbenzene under the function of the effective base sites.

As shown in Table 3, the formation of styrene was observed in the case of pulse III on almost all of the catalysts, showing that the weakly adsorbed oxygen on the catalyst surface is active in the abstraction of β-hydrogen of adsorbed ethylbenzene. This also agrees well with the conclusion obtained in the pulse reaction on Na–Si · Al catalysts (*6*). The intrinsic effect of such weakly adsorbed oxygen can be represented by the difference in the styrene yield between pulse III and pulse II (Table 3, the

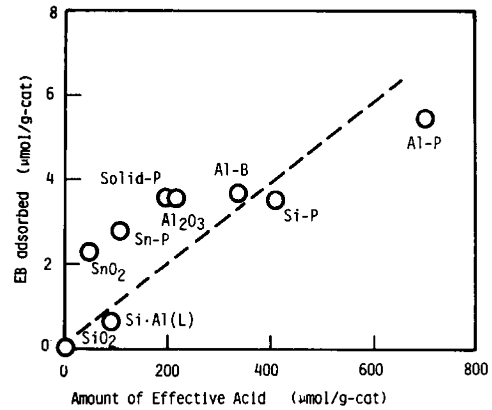

FIG. 6. Correlation between the amount of ethylbenzene adsorbed and that of effective acid sites. Reaction temperature, 718 K.

last column). The effect decreases as follows: Al–P > Al_2O_3 > Si · Al ≈ Al–B > SnO_2 ≈ Sn–P > Solid-P ≈ Si · Mg ≈ Si–P. This tendency almost agrees with the tendencies obtained by the continuous flow reaction, suggesting that the same reaction mechanism can hold both in the flow and pulse reactions.

Fiedorow *et al.* (*4*) and Alkhazov and Lisovskii (*5*) proposed that the active site of this reaction is the carbonaceous deposit formed on the acid sites; however, the direct correlation of the acid and base sites with this reaction discussed above leads to the conclusion that the effective acid and base sites are the active sites for the oxidative dehydrogenation of ethylbenzene.

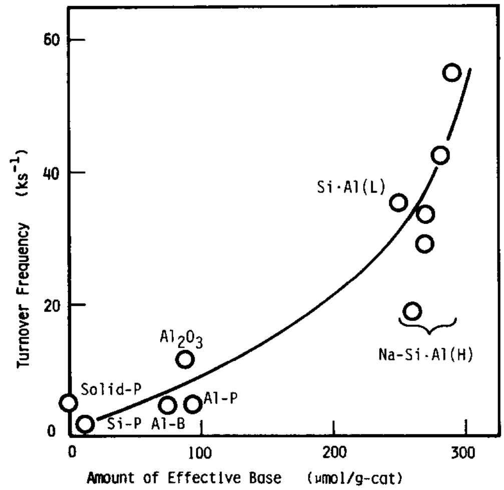

FIG. 7. Correlation between turnover frequency and the amount of effective base sites.

All these discussions agree well with those on the Na–Si · Al systems. Consequently, the mechanism proposed previously (*6*) is not limited to the Na and Si · Al system, but can hold generally for various catalysts.

Side Reactions

Carbon oxides are the predominant byproducts in this reaction. On Sn–P catalyst, the selectivity of styrene was extrapolated to 100% at zero contact time. This indicates that carbon oxides are formed by the subsequent oxidation of styrene though, on SnO_2 catalyst which is less selective, carbon oxides appear to be formed also by the oxidation of ethylbenzene (*2*).

In part II of these studies, it is suggested that the strong acid site ($-5.6 > H_0$) forms carbonaceous materials in the flow reaction and that carbon oxides are formed by the subsequent combustion of the carbonaceous materials thus formed (*3*).

As shown in Fig. 3, a strong acid site ($-5.6 > H_0$) is active in the formation of benzene which is a less predominant byproduct. Only Si · Al and Al–B catalysts with the strong acid sites show the cracking activity, and the other catalysts without strong acid sites show no cracking activity. SiO_2 and Si · Mg catalysts which contain only weak acid sites ($1.5 < H_0$) are inactive for both cracking and oxidative dehydrogenation. It can be concluded from these results that the strong acid sites are active in the cracking reactions and that the effective acid sites are inactive in the benzene formation although they are active in the oxidative dehydrogenation. As shown in Fig. 3, the poisoning with pyridine reduced the catalytic activity on the cracking, but it did not change the activity in the oxidative dehydrogenation. Although considerable amounts of benzene were observed in the cracking of cumene on Si–Al(L) and Al–B

(Fig. 2), in the steady state of the oxidative dehydrogenation of cumene the rates of benzene formation are reduced to 5.6 and 0.1 mmol/h · g-cat, respectively. This agrees well with the previously reported results that the strong acid sites become inactive in the steady state of the flow reaction because of the deposition of carbonaceous materials on them. The yields of carbon oxides in each of the pulses I, II, II′, and III are summarized in Table 4. All the catalysts formed carbon oxides in the oxygen pulse of pulse II′, except Si · Mg, Solid-P, and Si–P. This shows that the origin of carbon oxides is completely or partly attributable to the carbon species deposited in pulse I on the catalyst surface. Carbon oxides are formed also in pulse III on each catalyst, but the effect of the co-presence of ethylbenzene with oxygen, which can be evaluated from the difference between pulse II′ and pulse III, is small on SiO_2, Solid-P, Si · Al, Al–P, SnO_2, Sn–P, and Si–P catalysts. Then the combustion reactions can be attributable to the oxidation of carbonaceous compounds deposited on the catalyst surface at least on these catalysts. In the case of Sn-containing catalysts, the combustion reaction occurs in the ethylbenzene pulse (pulse I), which makes it difficult to determine the origin of carbon oxides. It should be noted, however, that only a small amount of carbon oxides is formed in the ethylbenzene pulse of pulse II on Sn–P catalyst. This suggests that, in the steady-state condition, most of the carbon oxides are formed by the subsequent combustion of deposited carbon. The flow reaction on Sn–P catalyst (*2*) also suggested the same reaction paths. Good correlation was obtained between the rates of combustion and styrene formation as shown in Fig. 5. Considering the above discussions, the amount of carbon oxides formed may depend on the amount of carbonaceous materials, and the amount of carbonaceous materials formed may depend on the amount of styrene or α-methylstyrene. These may result in the correlation shown in Fig. 5. It is well known that the carbonaceous materials are formed on the acid sites (*4, 9, 10*). Moscou and Moné pointed out that this can occur on the strong acid site such as H_0 about -8.2 (*9*). The dependence of the rate of combustion on the coke concentration formed on zeolite catalysts has also been observed (*11*). The subsequent combustion of coke formed on acid sites was observed in the oxidative dehydrogenation of ethylbenzene (*4*). These discussions lead to the following conclusion that the combustion reactions occur by the oxidation of carbonaceous compound formed on the strong acid sites (around $-5.6 > H_0$) by the subsequent reaction of styrene on most of the solid acid catalysts. However, further investigation is indispensable to clarify the details of the side reactions.

Brief Method for Estimation of Activity

In the design of catalysts for this reaction, it is important to estimate the acidity and basicity but it is difficult to do this by titration in the case of colored samples using color indicators. Then a brief method to estimate the activity is needed. The nature of the active site is the electron-withdrawing acid site with a suitable strength range and such an active site can abstract the electron from the polyaromatics (i.e., perylene). The ESR spectra obtained by the reaction of perylene with catalyst are the same as those reported (*12, 13*) and are ascribable to perylene cation radical. The amount of the radical formed was nearly the same as those reported (*12–15*). In Fig. 8, the rate of styrene formation is plotted against the amount of perylene radical formed, together with the maximum acid strength of the catalysts. The activity is well related to the amount of perylene radical, except for Si · Al(L), Si · Al(H), and Al–B catalysts which possess stronger acid sites. Thus, it is empirically shown that the activity of the catalyst without stronger acid sites ($-5.6 > H_0$) can be predicted by the ability to form perylene cation radical.

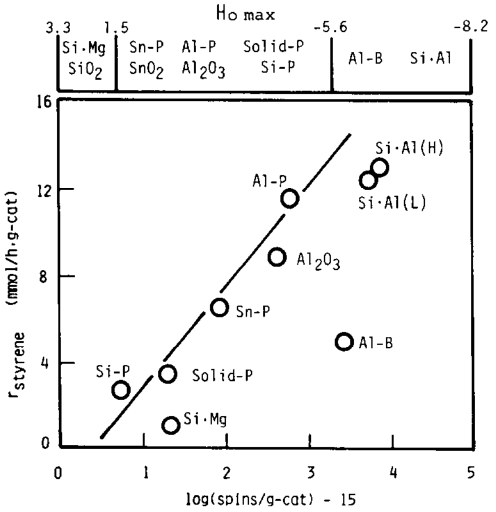

FIG. 8. Correlation between the rate of styrene formation and the amount of perylene radical formed on the catalysts.

Design of the Catalyst for the Oxidative Dehydrogenation of Ethylbenzene

In order to design the catalyst, the active site to form desired products should be increased and the site for the side reactions should be decreased. The above-mentioned reaction mechanism provides the following plans of the catalyst design for the oxidative dehydrogenation of ethylbenzene. The active sites to form styrene should be increased while the sites for cracking and total oxidation should be decreased. For the former, the acid sites of H_0 between 1.5 and −5.6, as well as the base sites of pK_a between 17.2 and 26.5, should be increased. For the latter, the strong acid sites ($-5.6 > H_0$) are undesirable. As shown in Table 2, the effective acid sites decrease in the sequence Al–P > Si-P > Al–B > Al_2O_3 > Solid-P > Sn–P > Si · Al(L) > SnO_2. The effective base sites decrease in the sequence Si · Al(L) > Al–P > Al_2O_3 > Al–B > Si–P ≫ SnO_2, Sn–P. However, Si · Al(L) and Al–B possess strong acid sites. Then, the above-mentioned plans for the catalyst design give the conclusion that Al–P catalyst will be the best catalyst for the present reaction. Al–P catalyst, actually, showed high conversion and selectivity. Si · Al catalysts also showed high activity, although they have many strong acid sites and fewer medium acid sites. The strong acid sites are considered to be covered by carbonaceous deposits (*3*). Thus, Si · Al catalysts have fewer weak acid sites and many base sites under the reaction condition. High activity is due to the large amount of effective base as shown in Fig. 7. However, some residual strong acid sites seem to be active for the formation of condensation products. The liquid products on Si · Al were significantly colored, indicating the formation of a significant amount of condensation products. Taking this into account, Al–P seems to be superior to Si · Al.

CONCLUSION

In order to design the catalysts, the active site to form the desired products should be increased while the site for the side reactions should be decreased. For this purpose, it is important to confirm the general reaction mechanism considering the active sites. The difference in the adsorption of ethylbenzene is explained by the difference in the effective acid sites ($1.5 > H_0 > -5.6$) and the turnover frequency is correlated to the effective base sites ($17.2 < \mathrm{p}K_a < 26.5$), for various kinds of catalysts. The total oxidation is suggested to occur on the strong acid site ($-5.6 > H_0$) by the combustion of the coke deposited on the catalyst, which is formed by the subsequent reaction of styrene once formed. This reaction mechanism gives the plan of the catalyst design: the catalyst which possesses a large amount of effective acid sites and effective base sites but not strong acid sites will be a good catalyst for the present reaction. Actually, Al–P which satisfies the plan showed high activity and selectivity.

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