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Alkylation of benzene with ethane over platinum-loaded zeolite catalyst

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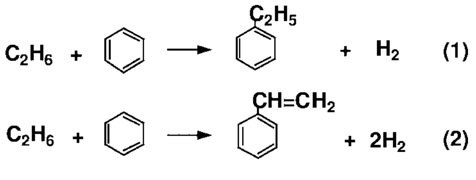
Alkylation of benzene with ethane was carried out using various zeolite catalysts at temperature ranges of 400–550 °C. Loading of platinum onto zeolite greatly enhanced the yield of ethylbenzene. Among the zeolites tested, H-ZSM5 and H-MCM22 showed catalytic activities. By contrast, mordenite did not yield ethylbenzene. Moderate acid strength distribution is the key factor of zeolite catalysts. Optimum catalyst and conditions for this reaction are as follows. The platinum-loaded H-ZSM5 catalyst containing 6.8 wt% Pt, at a reaction temperature of 500 °C, afforded ethylbenzene and styrene formation rates of 14.2 and 0.8 mmol h^{-1} g-cat^{-1}, respectively (benzene-based yields 7.3 and 0.4%). In the alkylation of benzene with ethane over platinum-loaded H-ZSM5, ethene was initially formed from ethane over the metallic platinum. Then the alkylation proceeded over the acid sites of H-ZSM5.

KEY WORDS: ethylbenzene; H-ZSM5; platinum; ethane; acid strength; dehydrogenation

1. Introduction

Catalyzed alkylation of aromatic compounds is an important industrial process. The development of a new alkylation catalyst is still of current interest. Recently, aluminum-chloride-catalyzed alkylation of benzene with ethene has been replaced by zeolite-catalyzed alkylation processes. Zeolite ZSM5 was reported to be active in the ethylation of benzene and toluene [1–3], which led to the great commercial process (Mobil-Badger). More recently a new zeolite, MCM22, has been applied in a new process of ethylbenzene production called the EB Max process [4].

In the alkylation of aromatics, alkyl halides, alcohols [5–9] and alkenes [10–14] are used as alkylating agents. Alkylation of benzene with propane catalyzed with Ga-modified H-ZSM5 has been reported [13]. Propane was transformed into a secondary propyl cation by H^- abstraction with Lewis acid. However, ethane is much less reactive than propane toward an acid catalyst. Several patents have disclosed the preparation of ethylbenzene with ethane and benzene at a high pressure in the liquid phase [15,16]. However, to our knowledge, there are no scientific papers on the alkylation of benzene with ethane in the gas phase.



We have studied the alkylation of benzene with ethane to ethylbenzene (1) and styrene (2) using various modified zeolite catalysts for the purpose of reducing the production cost, and we have found that platinum-loaded H-ZSM5 afforded ethylbenzene together with a small amount of styrene [17].

This paper deals with detailed studies on the alkylation of benzene with ethane over various modified zeolite catalysts for the purpose of reducing the production cost of styrene.

2. Experimental

2.1. Materials

H-ZSM5 ($SiO_2/Al_2O_3 = 80$), H-Y ($SiO_2/Al_2O_3 = 5.6$) and H-mordenite ($SiO_2/Al_2O_3 = 20$) were supplied by the Catalyst Society of Japan. H-ZSM5 ($SiO_2/Al_2O_3 = 21.5$–60) and H-MCM22 were prepared according to the literature [18,19]. Various metal-loaded H-ZSM5 catalysts (metal content from 1.7 to 6.8 wt%) were prepared by impregnation with $H_2PtCl_6 \cdot 6H_2O$, $RhCl_3 \cdot 3H_2O$, $RuCl_3 \cdot 3H_2O$ (Mitsuwa Pure Chemicals), $Ni(NO_3)_2 \cdot 6H_2O$ (Wako Pure Chemical Industries Ltd.), and $Ga(NO_3)_3 \cdot 3H_2O$ (Kishida Chemicals), in aqueous solutions, and the loaded catalysts were dried and calcined at 550 °C for 3 h in air.

2.2. Apparatus and procedure

The reaction was carried out with a fixed-bed flow type quartz reactor (350 × 10 mm) at atmospheric pressure. 50 mg of the catalyst was placed in the reactor using a quartz glass wool plug. The metal-loaded zeolite catalyst was reduced with hydrogen *in situ* at 500 °C for 1 h just before use. The alkylation reaction was carried out at 350–550 °C for 0.5–5 h.

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Benzene was fed to the reactor by passing ethene or ethane through the benzene saturator thermostatted at 20–60 °C. The effluent from the reactor was condensed in a trap containing heptane, and externally cooled in an ice water bath.

The reaction products (benzene, toluene, ethylbenzene, xylene, styrene and cumene) were analyzed by a Shimadzu GC 14A equipped with FID and using a CPB1, 0.53 mm × 25 m capillary column, with an internal standard substance. Analyses of C_2H_4 and C_2H_6 were carried out with a Shimadzu model GC14B gas chromatograph equipped with FID and using a 3 mm × 3 m column packed with Porapak Q. Analysis of H_2 was carried out with a Shimadzu model GC 8A gas chromatograph equipped with TCD and using a 3 mm × 2.5 m column packed with activated carbon.

Catalytic activities were evaluated by space time yield of products (STY; mmol h^{-1} g-cat^{-1}). The STY was defined as follows: cumulative products obtained in mmol divided by the reaction time (h) per unit gram of the catalyst.

2.3. Characterization of catalysts

Catalysts were characterized by means of powder X-ray diffraction using a Shimadzu model XRD-6000 diffractometer with monochromated Cu Kα radiation. The surface area of the catalysts was measured with a BET method using nitrogen as the adsorbate with an automatic Micromeritics Gemini model 2375. The acidity and acid strength distribution of zeolites were measured by the NH_3-TPD method using a BEL Japan, Inc., model TPD-1-AT. The catalyst was evacuated at 100 °C, and NH_3 was adsorbed at 100 °C with a partial pressure of 2.7 kPa. The excess NH_3 was evacuated at the same temperature for 1 h. The NH_3-adsorbed catalyst was heated at a heating rate of 20 °C/min under flowing He, and desorbed NH_3 was monitored by a quadrupole mass spectrometer.

X-ray photoelectron spectra were recorded on a Jeol model JPS 9000 with Mg Kα irradiation.

3. Results and discussion

3.1. Alkylation of benzene with ethene

Table 1 shows the product yields of alkyl aromatics in the alkylation of benzene with ethene over H-mordenite, H-Y and H-ZSM5, conducted under the same reaction conditions, in order to compare ethylation of benzene with ethene and ethane. Becker et al. reported that H-mordenite afforded a high yield of ethylbenzene under He-diluted reaction conditions, using an excess of benzene [10]. However, H-mordenite and H-Y exhibited only slight catalytic activities (runs 1 and 2). On the other hand, H-ZSM5 afforded the highest values of ethylbenzene and styrene yields, 32.9 and 1.4%, respectively, at 450 °C (run 5).

The effects of the reaction temperature on the yield of C_8 aromatics in the reaction with H-ZSM5 are shown in runs 3–6. Yields of C_8 aromatics increased with an increase in the reaction temperature from 350 to 450 °C. On the other hand, the yield of C_8 aromatics decreased at the higher temperature of 550 °C. Since the reaction was carried out at high temperatures, toluene and xylene were formed due to cracking or isomerization of ethylbenzene, but diethyl and polyalkylated benzenes were hardly observed.

3.2. Alkylation of benzene with ethane

3.2.1. Activity of various metal-loaded zeolite catalysts

Table 2 summarizes the results of bare and various metal-loaded H-ZSM5 in the alkylation of benzene with ethane, which was conducted at a higher reaction temperature (500 °C) than that with ethene. Unloaded H-ZSM5, which exhibited the highest catalytic activity in the reaction with ethene, afforded very small amounts of C_8 aromatics and ethene (run 7). Ga/H-ZSM5, which was reported to be an active catalyst in the alkylation of benzene with propane [13], showed only slight activity in the reaction with ethane (run 8).

Platinum-modified H-ZSM5 is known to be an active catalyst in the aromatization of alkanes [17]. Platinum-loaded Al_2O_3 is known to be a good catalyst for the dehydrogenation of alkane in petroleum refinery. However, a fresh H_2PtCl_6-loaded and calcined H-ZSM5 afforded a slightly higher level of activity to the ethylation of benzene than that without platinum (run 9).

On the other hand, the ethene formation rate increased in the course of the alkylation reaction for 3 h. This seemed to be due to the reduction of the initially loaded platinum species to metallic platinum by the hydrogen produced. We examined the effect of hydrogen reduction of the fresh catalyst before the reaction. As seen in run 10, ethylbenzene

Table 1
Alkylation of benzene with ethene over various zeolite catalysts.[a]

Run	Catalyst	SiO_2/Al_2O_3	Reaction temp. (°C)	Product yield (%)				
				Toluene	Ethylbenzene	Xylene	Styrene	Cumene
1	H-mordenite	20	450	0	0.2	0	0	0
2	H-Y	5.6	450	0.2	3.5	0	0	0
3	H-ZSM5	80	350	4.6	25.2	0	0	3.1
4	H-ZSM5	80	400	7.2	31.6	3.6	1.2	2.0
5	H-ZSM5	80	450	8.6	32.9	3.6	1.4	1.1
6	H-ZSM5	80	500	5.4	30.9	3.7	1.1	0.6

[a] Reaction conditions: catalyst 50 mg, reaction time 0.5 h, benzene $C_2H_4 = 10:50$ mmol/h, product yield benzene-based.

Table 2
Comparison of various metal-loaded zeolites in the alkylation of benzene with ethane.[a]

Run	Catalyst	SiO_2/Al_2O_3	Metal (wt%)	Space time yield ($mmol\,h^{-1}$ g-cat^{-1}) Ethylbenzene	Styrene	C_2H_4	H_2
7	H-ZSM5[b]	80	–	0.2	0	0	0.1
8	Ga/H-ZSM5	80	1.7	0	0.2	1.2	4.6
9	Pt/H-ZSM5[b]	80	4.9	1.4	0	6.0	7.8
10	Pt/H-ZSM5	80	4.9	8.5	0.6	25.4	35.5
11	Pt/H-ZSM5	21.5	6.8	14.3	0.8	26.8	55.9
12	Ni/H-ZSM5	21.5	2.1	0.7	0.4	0.8	9.1
13	Rh/H-ZSM5	21.5	3.6	0.5	0	0.4	17.9
14	Ru/H-ZSM5	21.5	3.5	0.3	0	0	6.8
15	Pt/H-Y	5.6	6.8	0	0	24.9	42.0
16	Pt/H-gallosilicate	(45)[c]	6.8	2.3	1.1	31.8	42.9
17	Pt/H–Al-MCM22	25	6.8	5.9	0.4	35.4	44.9
18	Pt/H-mordenite	20	6.8	0.3	0	12.1	24.8
19	Pt/H–Ga-MCM41	(65)[c]	6.8	0	0	23.7	26.2

[a] Reaction conditions: catalyst 50 mg, 500 °C, 0.5 h, benzene : C_2H_6 = 10 : 50 $mmol\,h^{-1}$, pretreatment H_2, 500 °C, 1 h.

[b] Without the pretreatment hydrogen reduction.

[c] SiO_2/Ga_2O_3.

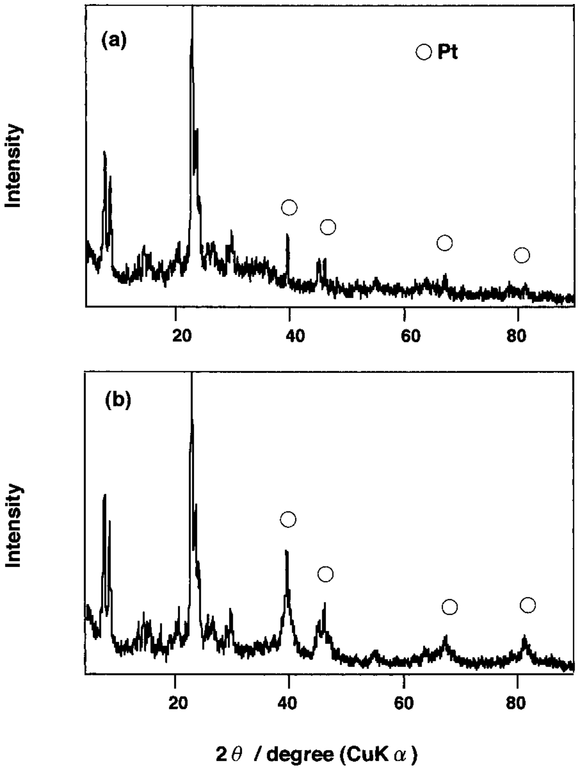

Figure 1. X-ray diffraction patterns of platinum-loaded H-ZSM5 catalyst: (a) fresh catalyst after calcination at 550 °C in air and (b) hydrogen-reduced catalyst at 500 °C for 1 h.

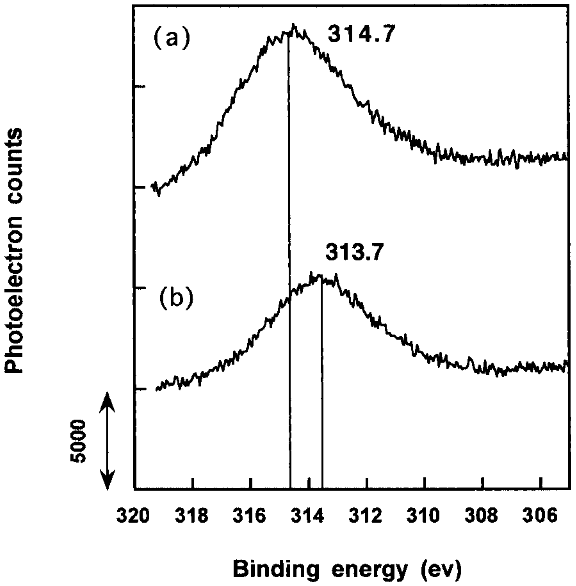

Figure 2. Pt $4d_{5/2}$ X-ray photoelectron spectra of fresh (a) and hydrogen-reduced Pt-loaded H-ZSM5 catalyst (b).

and ethene formation rates increased greatly and, in addition, a small amount of styrene was detected.

X-ray diffraction patterns of the fresh and H_2-reduced Pt-loaded H-ZSM5 are presented in figure 1. The powder X-ray diffraction analyses of these catalysts did not reveal any differences in the diffraction angles of the respective peaks. However, the peak width ascribed to the metallic platinum broadened to some extent after reduction by H_2. XPS results are shown in figure 2. The binding energy of Pt $4d_{5/2}$ shifted from 314.7 to 313.7 eV after hydrogen treatment. These results indicate that platinum oxide on the fresh catalyst which seems to be highly dispersed (no diffraction peaks were assignable to platinum oxide by XRD) would be reduced to metallic platinum by H_2 and, as a result, the ethene STY would be increased.

Dehydrogenation of alkane could possibly be promoted with other transition metals. Ni, Rh, and Ru-loaded H-ZSM5 were prepared by impregnating respective solutions of salts at the same loading level (in moles) as platinum (6.8 wt%, 0.35 mmol g^{-1}), but they exhibited only slight catalytic activities (runs 12–14). The smaller catalytic activities of these metal-loaded catalysts are ascribed to smaller amounts of ethene. These findings demonstrate that dehy-

Table 3
Comparison of acidity of various zeolites.

Catalyst	SiO_2/Al_2O_3 (SiO_2/Ga_2O_3)[a]	Acidity ($\times 10^{-1}$ mmol g^{-1})			
		∼300[b]	310[b]	350[b]	∼400[b]
H-Y	5.6	4.1	0	0	0
H-gallosilicate	(45)	1.2	4.9	0	0
H–Al-MCM22	25	6.1	0	10.0	0
H-ZSM5	21.5	4.2	0	7.9	0
H-mordenite	20	2.0	0	4.5	14.0
H–Ga-MCM41	(65)	3.3	0	0.2	2.8

[a] Numerals in parentheses indicate SiO_2/Ga_2O_3.
[b] NH_3 desorption peak temperature (°C).

drogenation of ethane to ethene is the key reaction in the ethylation of benzene.

The somewhat higher STY of hydrogen as compared to the sum of STY of ethene, ethylbenzene, and styrene (×2) may be ascribed to coke deposition and the aromatization and polymerization of ethene.

Ethylbenzene and styrene were not detected in the reaction with Pt-loaded H-Y and H–Ga-MCM41 (runs 15 and 19). Platinum-loaded H-mordenite afforded just a small amount of ethylbenzene (run 18). Platinum-loaded H-MCM 22 and H-gallosilicate produced a large amount of C_8 aromatics (runs 16 and 17). The MCM22 type zeolite has been reported to be an active catalyst for ethylbenzene synthesis in the liquid phase [5]. H-MCM22 afforded an ethylbenzene and styrene STY of 5.9 and 0.4 mmol h^{-1}g-cat^{-1}, respectively. H-gallosilicate, which has the same structures as ZSM5, yielded a smaller amount of total C_8 aromatics as compared to H-ZSM5 and H-MCM22. On the other hand, the styrene STY had the highest value of 1.1 mmol h^{-1} g-cat^{-1}. Bradley et al. reported that Ga-modified monomorillonite is a good catalyst for the dehydrogenation of cumene [20]. The relatively large amount of styrene would be produced due to the dehydrogenation activity of the gallium species.

Table 3 shows the acidity and acid strength distribution of various unloaded zeolites used in this study. The acidity was calculated from the amount of desorbed NH_3. H-Y had the weakest acid strength (NH_3 desorption below 300 °C). NH_3 desorption appeared above 400 °C (peak at 450 °C) for H-mordenite and H–Ga-MCM41. H-ZSM5 and H-MCM22 had an NH_3 desorption peak at 350 °C. H-gallosilicate exhibited a desorption peak at 310 °C.

Ethylbenzene and styrene were not detected in the reaction with H-Y and H–Ga-MCM41. H-mordenite afforded a very small amount of ethylbenzene. Among these zeolites, H-ZSM5 exhibited the highest yield of total C_8 aromatics. On the other hand, H-gallosilicate, which has the same structure as ZSM5, afforded the highest styrene yield of 1.1%.

From these findings, it is clear that the catalytic activity of zeolites is related to both the structure and acid strength of the zeolites. Moderate acid strength (NH_3 desorption at 310–350 °C) is essential for this reaction. However, a strong acid site may decompose at a high temperature once it has formed ethylbenzene.

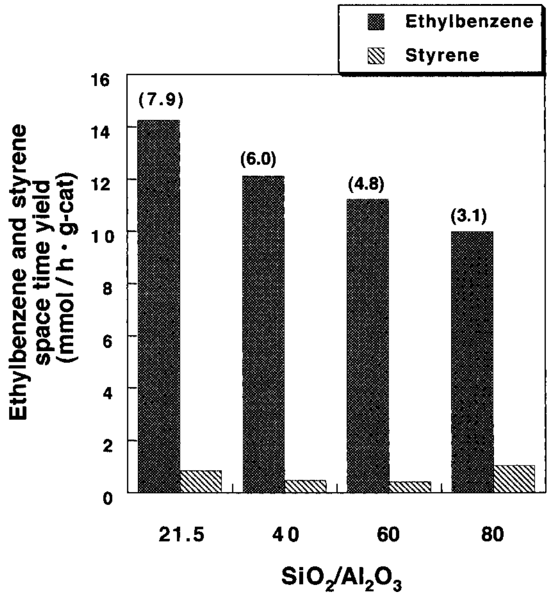

Figure 3. Effect of SiO_2/Al_2O_3 on the STY of ethylbenzene and styrene. Numerals on the bar indicate acidity of H-ZSM5 ($\times 10^{-1}$ mmol g^{-1}), Pt (6.8 wt%)/H-ZSM5 = 50 mg, benzene/ethane = 10/50 (mmol h^{-1}), reaction temperature 500 °C.

3.2.2. *Effect of SiO_2/Al_2O_3 ratio on C_8 aromatics STY*

Figure 3 shows the effect of the SiO_2/Al_2O_3 ratio on the ethylbenzene and styrene STY. The catalytic activity increased with a decrease in the SiO_2/Al_2O_3 ratio of H-ZSM5 from 80 to 21.5. The acidity of H-ZSM5 measured by NH_3-TPD increased from 0.31 to 0.79 mmol g^{-1} with the decrease in the SiO_2/Al_2O_3 ratio, indicating that not only the acid strength of the zeolite but also the total acidity played an important role in the ethylation of benzene. The highest C_8 aromatic yield was obtained with the Pt (6.8 wt%)-loaded H-ZSM5 with a SiO_2/Al_2O_3 ratio of 21.5. The yields of ethylbenzene and styrene corresponded to 7.3 and 0.4% based on benzene, whereas the benzene conversion was 8.3%. The ethylbenzene selectivity and yield were higher than that of the liquid phase reaction at 390 °C, 6.1 MPa [15].

3.2.3. *Effects of loading level of platinum on C_8 aromatics and ethene STY*

The effects of the loading level of platinum on the ethylbenzene, styrene and ethene STY is shown in figure 4. At a loading level of 3.0 wt%, a small amount of ethylbenzene

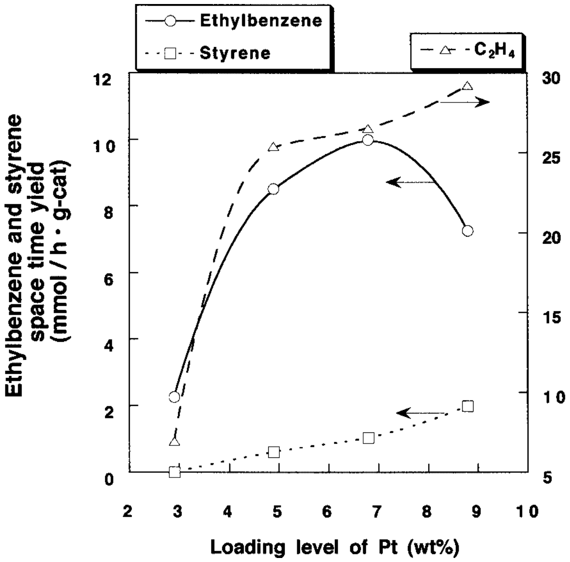

Figure 4. Effect of loading level of Pt in Pt/H-ZSM5 on the STY of ethylbenzene, styrene and ethene. H-ZSM5 $SiO_2/Al_2O_3 = 80$, other conditions are the same as in the caption to figure 3.

was produced because of the low ethene STY. Ethene STY increased with an increase in the loading level of Pt from 3.0 to 4.9 wt%, and as a result, the C_8 aromatics STY greatly increased. The ethene STY slightly increased from 25.4 to 29.2 $mmol\,h^{-1}\,g^{-1}$ with an increase in the loading level of platinum from 4.9 to 8.8 wt%. However, the total C_8 aromatics STY was the highest at the loading level of 6.8 wt%. Although the total aromatics STY decreased with an increase in the loading level of platinum to 8.8 wt%, the styrene yield increased, possibly because of the dehydrogenation of ethylbenzene.

3.2.4. *Effects of reaction temperature on C_8 aromatics STY*

The effect of the reaction temperature on the ethylation of benzene with ethane is shown in figure 5. The rate of dehydrogenation of ethane increased markedly from the reaction at 450 to that at 500 °C. The largest amount of ethylbenzene was obtained at 500 °C, and a further increase in the reaction temperature to 550 °C greatly decreased the STY of ethylbenzene. The STY of ethene was constant above 500 °C. In the reaction with ethene, the C_8 aromatics yield had the highest value at 450 °C. This was probably due to the higher reaction temperature required for the dehydrogenation of ethane to ethene.

3.2.5. *Effect of C_2H_6/benzene ratio on C_8 aromatics STY*

Figure 6 shows the effect of the C_2H_6/benzene ratio on the C_8 aromatics yield. The C_8 aromatics yield and ethene STY was almost constant when the C_2H_6/benzene ratio was above 5. On the other hand, the C_8 aromatics yield decreased below a ratio of 5 due to the decrease in ethene STY. The platinum active site for the dehydrogenation of ethane was most likely covered with benzene at a higher benzene partial pressure.

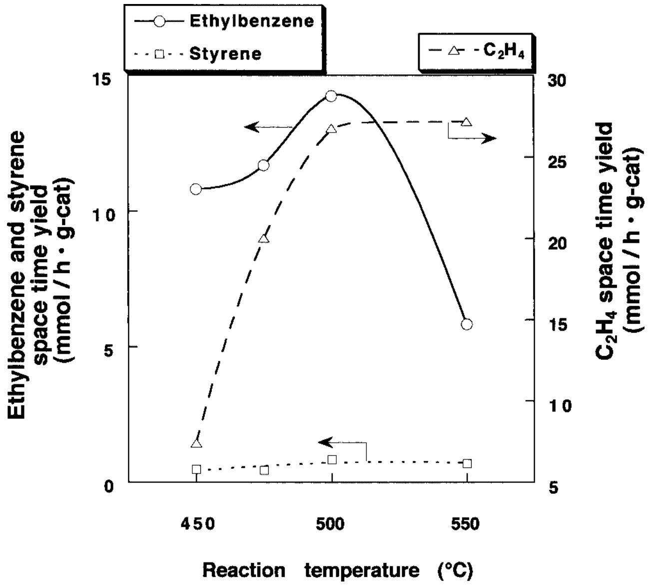

Figure 5. Effects of reaction temperature on the STY of ethylbenzene, styrene and ethene. H-ZSM5 $SiO_2/Al_2O_3 = 21.5$, other conditions are the same as those mentioned in the caption to figure 3, except the reaction temperature.

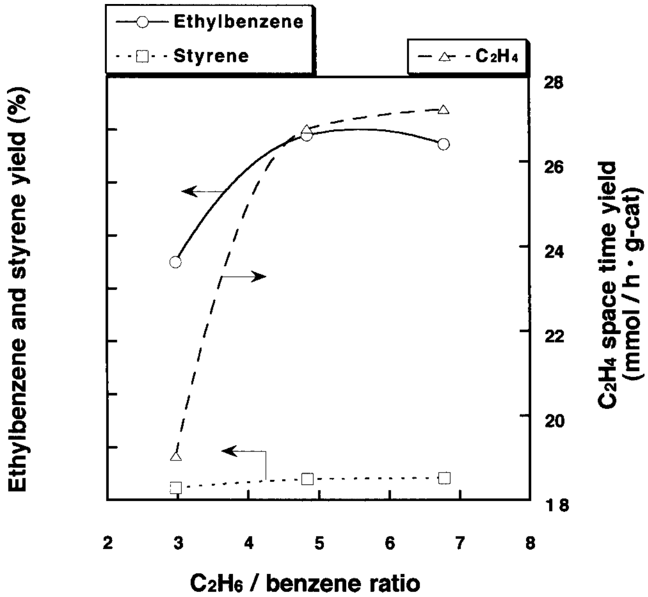

Figure 6. Effect of C_2H_6/benzene ratio on the STY of ethylbenzene, styrene and ethene. H-ZSM5 $SiO_2/Al_2O_3 = 21.5$, other conditions are the same as those mentioned in the caption to figure 3.

3.2.6. *Effects of reaction time on stream on the C_8 aromatics STY*

The platinum-loaded H-ZSM5 catalyst was deactivated by coke deposition during the reaction. However, the deactivated catalyst could be regenerated by calcination with O_2 at 500 °C. In order to reduce coke deposition, the addition of H_2 in the feed was examined. The result is shown in figure 7. Due to the shift in equilibrium among ethane, ethene and hydrogen to the ethane side, the ethene STY decreased markedly. As a result, the ethylbenzene yield was

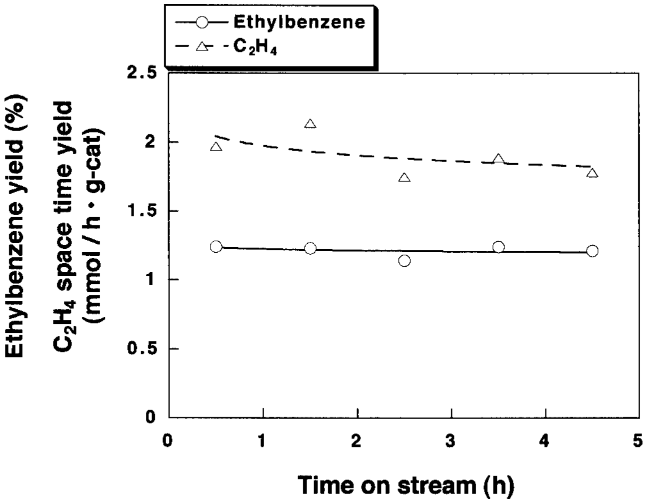

Figure 7. Effects of time on stream on the STY of ethylbenzene and ethene, Pt (6.8 wt%)/H-ZSM5 $SiO_2/Al_2O_3 = 21.5$, benzene/C_2H_6/H_2 = 6/30/20 (mmol h^{-1}).

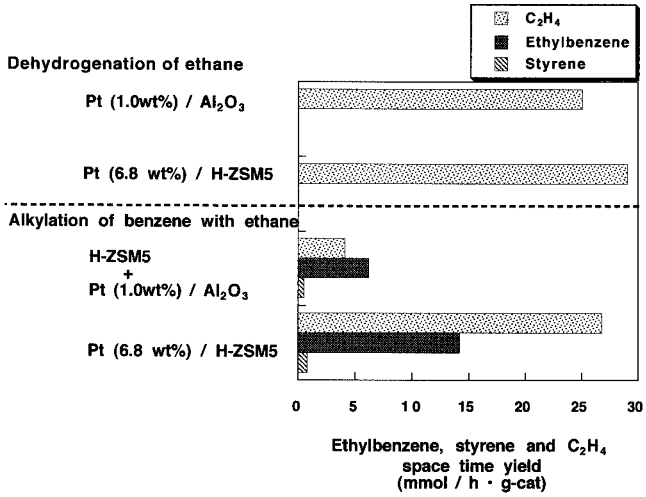

Figure 8. Comparison of Pt/Al_2O_3–H-ZSM5 mixed catalyst and Pt/H-ZSM5. Pt/Al_2O_3 + H-ZSM5 = 50 mg + 50 mg, Pt/H-ZSM5 = 50 mg.

much lower than that without hydrogen. However, the ethylbenzene yield and ethene STY were nearly constant during the run for 5 h.

3.2.7. Comparison of Pt–H-ZSM5 catalyst and Pt/Al_2O_3–H-ZSM5 mixed catalyst

Figure 8 shows the comparison of platinum-loaded H-ZSM5 with a platinum-loaded Al_2O_3/H-ZSM5 mixed catalyst. Platinum-loaded Al_2O_3 exhibited a similar activity in the dehydrogenation of ethane as that of platinum-loaded H-ZSM5. However, the ethene STY markedly decreased in the presence of benzene in the feed, indicating that the surface of platinum-loaded Al_2O_3 was covered with adsorbed benzene, and as a result, the platinum-loaded Al_2O_3/H-ZSM5 mixed catalyst system showed a lower STY of ethylbenzene than platinum-loaded H-ZSM5 with the same SiO_2/Al_2O_3.

4. Conclusion

Ethylbenzene was produced from benzene and ethane using a platinum-loaded H-ZSM5 catalyst at 500 °C, which yielded ethylbenzene and styrene space time yield of 14.2 and 0.8 mmol h^{-1} g-cat^{-1}, respectively (benzene-based yields 7.3 and 0.4%).

Platinum-loaded H-ZSM5, H-MCM22 and H-gallosilicate showed catalytic activity in the alkylation of benzene with ethane. The acid strength of zeolites may be one of the most important factors for high catalytic activity in this reaction. Moderate acidity seems to be preferred.

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