Alkylation of Benzene with Ethane over Platinum-loaded H-ZSM5 Catalyst

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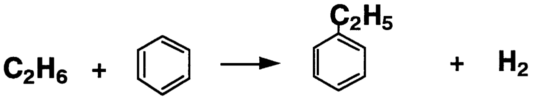
Ethylbenzene was prepared from benzene and ethane, using platinum-loaded H-ZSM5 catalyst at 500 °C, giving the ethylbenzene and styrene space time yields of 14.2 and 0.8 mmol h^{-1}• g^{-1} of catalyst, respectively (benzene-based yields 6.9 and 0.4%).

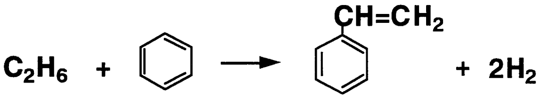
Increasing demand for styrene prompted us to investigate one step synthesis of it, by using an alkylation and dehydrogenation dual functional catalyst. Recently old mineral acid catalyzed alkylation of benzene with ethene is replaced by zeolite catalyzed alkylation process.[1] Among zeolites, ZSM5 type one is reported to be active in the alkylation of benzene and substituted benzenes.[2]

Alkylation of benzene with propane catalyzed with Ga-modified H-ZSM5 catalyst was reported.[3] However, the mechanism of the reaction with propane cannot readily be extended to that with ethane. Ethane is much less reactive as compared to propane toward acid catalyst. Several patents disclosed preparation of ethylbenzene with ethane and benzene at high pressure in liquid phase.[4,5] However, to our knowledge, no scientific papers on the alkylation of benzene with ethane in gas phase were seen.

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



(1)



(2)

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 from the Catalyst Society of Japan. H-ZSM5 (SiO_2/Al_2O_3 = 21.5) was prepared according to the literature.[6] Gallium and platinum-loaded H-ZSM5 catalysts were prepared by the impregnation method, and the loaded catalysts were dried and calcined at 550 °C for 3 h in air. The reaction was carried out with a fixed-bed flow type quartz reactor (350 x 10 mm) at an atmospheric pressure, and the products were analyzed by gas chromatography.

Table 1 shows the space time yields (STY ; average for the reaction time from 0 to 30 min) of ethylbenzene and styrene in the alkylation of benzene with ethene or ethane over various zeolite and gallium or platinum-loaded H-ZSM5 catalysts. The reaction of ethene was 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 excess of benzene.[7] 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 STY of 61.4 and 2.5 mmol h^{-1}• g^{-1}-cat, respectively at 450 °C (Run 3). These values corresponded to the total yield of 30% based on benzene feed. Since the reaction was carried out at a high temperature, toluene was formed due to cracking of ethylbenzene but diethyl and polyalkylated benzenes were only slightly observed.

The reaction with ethane 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, and gallium-loaded H-ZSM5 afforded very small amounts of C_8 aromatics and ethene (Runs 4 and 5).

Platinum modified H-ZSM5 is known to be an active catalyst for aromatization of alkane.[8] Platinum-loaded Al_2O_3 is well known to be a good catalyst for the dehydrogenation of alkane in petroleum refinery. However, a fresh platinum-loaded H-ZSM5 afforded slightly higher activity to ethylation of benzene than that without platinum (Run 6).

On the other hand, ethene formation rate increased in the course of the alkylation reaction for 3 h. This seemed to be due to the reduction of initially loaded platinum species to metallic platinum by the hydrogen formed. We have examined hydrogen pretreatment of the fresh catalyst before the reaction. As seen in Run 7, ethylbenzene and ethene formation rates increased greatly However, powder X-ray diffraction analyses of the fresh and H_2 reduced catalysts did not show differences in the diffraction angles of respective peaks. On the other hand, peak width ascribed to the metallic platinum broadened some extent after reduction with H_2. X-ray photo electron spectroscopic analyses again revealed that platinum species on the fresh catalyst would be metallic. From these results, platinum species on the H-ZSM5 could be metallic, even the catalyst was calcined in air. During hydrogen treatment prior to the reaction, platinum species on the H-ZSM5 could be redistributed to highly dispersed states to give a higher catalytic activity.

The ethene STY slightly increased from 25.4 to 29.2 mmol h^{-1}• g^{-1} with increasing the loading level of platinum from 4.9 to 8.8wt% (Runs 7-9). However, the total C_8 aromatics STY was the highest at the loading level of 6.8wt% (Run 8). Although the loading level of platinum increased to 8.8wt% (Run 9), the total C_8 aromatics formation rate decreased and that of styrene increased.

The catalytic activity increased with decreasing SiO_2/Al_2O_3 ratio of H-ZSM5 from 80 to 21.5 (Run 11). The highest C_8 aromatic yield was obtained with the Pt (6.8wt%)-loaded H-ZSM5 with SiO_2/Al_2O_3 ratio of 21.5. The yields of ethylbenzene and styrene corresponded to 6.9 and 0.4% based on benzene where benzene conversion was 7.8%. The ethylbenzene selectivity and yield were higher than that of liquid phase reaction at 390 °C, 60 atm.[5] The platinume-loaded H-ZSM5 was

Table 1. Alkylation of benzene with ethene or ethane over various zeolites and platinum-loaded H-ZSM5[a]

		SiO_2/Al_2O_3	Loading level of Ga or Pt	Reaction temp.	Space time yields / mmol h^{-1}-g^{-1}-cat			
Run	Catalyst	-	wt%	°C	Ethylbenzene	Styrene	C_2H_4(Toluene)[b]	H_2(Xylene)[c]
1	H-Mordenite[d]	20	-	450	0.4	0	(0)	(0)
2	H-Y[d]	5.6	-	450	6.8	0	(0.4)	(0)
3	H-ZSM5[d]	80	-	450	61.4	2.5	(16.0)	(1.9)
4	H-ZSM5[e]	80	-	500	0.2	0	0	0.1
5	Ga/HZSM5	80	1.7	500	0	0.2	1.2	4.6
6	Pt/HZSM5[e]	80	4.9	500	1.4	0	6.0	7.8
7	Pt/HZSM5	80	4.9	500	8.5	0.6	25.4	35.5
8	Pt/HZSM5	80	6.8	500	10.0	1.0	26.5	41.1
9	Pt/HZSM5	80	8.8	500	7.3	2.0	29.2	44.4
10	Pt/HZSM5	21.5	6.8	450	10.8	0.5	7.4	25.7
11	Pt/HZSM5	21.5	6.8	500	14.2	0.8	26.8	55.9
12	Pt/HZSM5[f]	21.5	6.8	500	2.6	0.1	2.1	4.8
13	Pt/HZSM5	21.5	6.8	550	5.8	0.7	27.2	56.7
14	Pt/HZSM5[g]	21.5	6.8	500	-	-	29.0	53.9
15	Pt/Al_2O_3[g]	-	1.0	500	-	-	25.4	49.8
16	Pt/Al_2O_3 + H-ZSM5[h]	21.5	1.0	500	6.2	0.5	4.1	24.7

a Catalyst 50 mg. Reaction time ; 30 min
Composition of the feed ; benzene : C_2H_6 = 10 : 50 mmol h^{-1}
Pretreatment ; H_2, 500 °C, 60 min
STY ; average for 0-30 min

b,c numerals in parentheses indicate STY of toluene and xylene in the reaction with ethene, respectively

d C_2H_4 was fed. composition of the feed ; benzene : C_2H_4 = 10 : 50 mmol h^{-1}

e without pretreatment

f average for 2-3 h

g feed ; C_2H_6 = 50 mmol h^{-1}

h Pt/Al_2O_3 : H-ZSM5 = (50 + 50) mg, C_2H_4 STY based on Pt/Al_2O_3

deactivated during the reaction by carbon deposition (Run 12). However, the deactivated catalyst could be regenerated by calcination with O_2 at 500 °C.

Effect of the reaction temperature on the ethylation of benzene with ethane was examined. The results are shown in Runs 10, 11,and 13. Rate of dehydrogenation of ethane increased markedly from the run at 450 °C to 500 °C. However, a considerable amount of ethylbenzene was obtained at 450 °C, a further increase in the reaction temperature to 550 °C greatly decreased formation rate of ethylbenzene. STY of ethene was constant above 500 °C.

Much higher formation rate of hydrogen as compared to the sum of STY of ethene and ethylbenzene would be ascribed to coke deposition and the aromatization and polymerization of ethene.

Platinum-loaded Al_2O_3 afforded a similar activity to dehydrogenation of ethane as platinum-loaded H-ZSM5 (Runs 14 and 15). However, ethene STY decreased in the presence of benzene in the feed, indicating that the surface of platinum-loaded Al_2O_3 is covered with benzene and as a result platinum-loaded Al_2O_3 and H-ZSM5 mixed catalysts system showed a lower STY of ethylbenzene than platinum-loaded H-ZSM5 having the same SiO_2/Al_2O_3 (Run 16).

In the reaction with propane over gallium-loaded H-ZSM5, Ivanova et al. reported that the reaction proceeds through carbenium ions as an intermediate.[4] On the other hand, in the reaction with propane over platinum-loaded H-ZSM5 only a very small amount of cumene was produced. From these findings, in the alkylation of benzene with ethane over platinum-loaded H-ZSM5, ethene would be initially formed from ethane over the metallic platinum. Then the alkylation would proceed over the acid sites of H-ZSM5.

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