

Benzene Alkylation with 1-Dodecene over Y Zeolite

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Linear alkylbenzene (LAB) is an important intermediate used in the detergency sector. The industrial process for LAB production is based on alkylation of benzene with olefins using aluminium trichloride or hydrofluoric acid as catalyst. Due to the hazardous nature of these catalysts, efforts have been made to replace it with environmentally safer catalysts such as heteropolyacids,¹ H-ZSM-5, H-ZSM-12,² HY,³ clays⁴ and H-mordenite.^{5,6}

In this study, benzene alkylation with 1-dodecene was studied over three kinds of faujasite type zeolites from different company with different SiO₂/Al₂O₃ ratios. The effects of reaction parameters such as temperature and molar ratio of benzene to 1-dodecene were also investigated. Furthermore, emphasis was paid to relate the catalytic activity of these catalysts with their acidic properties by using NH₃-TPD.

Experimental Section

Zeolite HY (Union Carbide, SiO₂/Al₂O₃ = 4.8), USH-Y (Zeolyst, SiO₂/Al₂O₃ = 80) and DAY (Degussa, SiO₂/Al₂O₃ = 200) were used in this work. Mg-USY and Na-USY were prepared by solid-state ion exchange method: 3 g USH-Y was mixed with a calculated amount of magnesium or sodium nitrate, respectively, and ground homogeneously, then calcined at 500 °C for 5 h. The alkylation reaction was carried out in a batch reactor. Before reaction, N₂ was charged into the reactor to regulate the reaction pressure of 10 atm. The products were analyzed by GC (HP 5890 series II) using FID furnished with SE-30 30 m capillary column.

NH₃-TPD profiles were measured with a home-made apparatus and ammonia desorption was carried out from 100 °C to 600 °C at a heating rate of 10 °C/min.

The conversion and selectivity were calculated as follows. Conversion = $(M_{d0} - M_d) / M_{d0} \times 100\%$, where M_{d0} is the molar percentage of 1-dodecene before reaction, and M_d is the molar percentage of 1-dodecene after reaction. Selectivity for LAB (S_{LAB}) was defined as $S_{LAB} = M_l / M_t$, where M_l is the molar percentage of LAB in the final products, and M_t is sum of molar percentage of all products including all 1-dodecene isomers and phenyldodecane isomers.

Results and Discussion

The results of the alkylation of benzene with 1-dodecene over various catalysts are presented in Table I. The conversions of 1-dodecene over three kinds of Y zeolites and Mg²⁺ and Na⁺ ion exchanged USH-Y at benzene to 1-dodecene molar ratio of 8.7 : 1 are 100%, 90.4%, 50.7%, 38.6% and 0%, respectively, in the order of USH-Y > H-Y > DAY > Mg-USY > Na-USY. The selectivity for LAB also decreases with the decrease of conversion from 100% for USH-Y to 0% for Na-USY. Among five different positional phenyldodecane isomers, as for the reaction product, isomer content decreases with the carbon number (toward the center of the chain) and a little higher selectivity for 2-phenyl isomer were observed over all the catalysts. Selectivity for 2-phenyl isomer of 55.8%, 32.3%, 27.4%, and 25.5% with the order of Mg-USY > DAY > H-Y > USH-Y are in inverse trend with the conversions.

Generally, the acidity of a catalyst influences product distribution as well as catalytic activity. The acidic properties of various Y zeolites were studied by the thermodesorption of ammonia. All ammonia TPD profiles are presented in Figure 1. The amount of desorbed ammonia shows much difference among three Y zeolites with drastic decrease of peak intensity in the order HY > USH-Y > DAY, which corresponds to the differences of aluminum content in these samples and is in line with the number of acid sites. H-Y zeolites presents only one broad peak with the tip at 249 °C. On the other hand, USH-Y and DAY exhibit two apparent peaks around 200 °C and 400 °C. It is observed that the first peaks appear at 200 °C and 219 °C in USH-Y and DAY, respectively. The second peaks occur at 376 °C and 402 °C, respectively, for DAY and USH-Y. The distribution of acid sites among these samples varies so much. In the case of H-Y, the peak is so broad, and peak area at high temperature zone is much smaller than that at low temperature. However, in the cases of USH-Y and DAY, the high temperature peaks are almost the same size as the low temperature peaks. This reflects that weak acid sites dominate in H-Y. However, DAY and USH-Y contain higher portion of strong acid sites. Furthermore, the maximum temperature of the high-temperature peak in USH-Y is 402 °C, higher than 386 °C of DAY. Finally, from all that was observed above, Y zeolites from different company with different SiO₂/Al₂O₃ show not only the difference of number

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Table 1. Benzene alkylation with 1-dodecene over various catalysts^a

Catalyst ^b	B/D ^c	Temp. (°C)	Conv. (%)	Sel. _{LAB} (%)	Sel. for positional isomer phenyldodecane (%)				
					2-ph	3-ph	4-ph	5-ph	6-ph
H-Y (2.46)	8.7	140	90.4	95.0	27.4	18.9	17.5	20.9	15.3
USH-Y (80)	8.7	140	100	100	25.5	20.3	16.5	18.8	18.7
DAY (200)	8.7	140	50.7	70.8	32.3	20.6	15.5	16.6	15.1
Mg-USY (1.5 wt% Mg)	8.7	140	38.6	29.2	55.8	24.1	11.6	8.50	0
Na-USY (1wt% Na)	8.7	140	0	0	–	–	–	–	–
USH-Y (80)	4.0	140	53.6	20.0	67.9	19.7	6.60	3.40	2.40
USH-Y (80)	4.0	180	97.8	99.0	25.9	20.5	16.7	15.5	21.4
USH-Y (80)	4.0	220	92.1	95.3	26.8	20.3	16.4	15.0	21.6

Reaction condition: 10 atm, 3 h. ^aTemp. = temperature. Conv. = conversion, Sel._{LAB} = selectivity for linear alkyl benzene. ^bNumbers in the bracket represent SiO₂/Al₂O₃. ^cB:D = molar ratio of benzene to 1-dodecene

of the acid sites of the zeolites, but also their distribution and strength as well.

The alkylation of benzene with olefins goes through a carbonium ion mechanism which involves two steps. Firstly, alkene interacts with the acid catalyst to form an alkyl-carbenium ion and it undergoes a rapid rearrangement in varying degrees. The second step is the attack of benzene ring by alkylcarbenium to form phenyldodecanes, which can also isomerize to form other phenyldodecane isomers. In the case of dodecene, six carbonium ions are possible. The relative stabilities of carbonium ions increase as the C-number increases, for example, the least stable being the primary ion (1-position). In fact, due to its very low stability, the 1-phenyl isomer is not detected in the product. On the basis of the relative stabilities of the other carbonium ions (all secondary), it is expected that the isomer content will increase with the carbon number (toward the center of the chain). This is found to be so in the cases of HF, in which thermodynamic equilibrium is probably reached. However, in the cases of Y zeolites, the content of 2-phenyl isomer is greater, suggesting the non-attainment of thermodynamic equilibrium. In our previous work, it has been found by pyridine adsorption FT-IR study that both strong Bronsted and Lewis acid sites are closely related to the conversion in benzene alkylation with 1-dodecene over H-mordenite zeolite.⁷ So it is suggested that the strong acid sites are responsible for this reaction. Although the acid concentration of H-Y is much higher than that of USH-Y, the high ratio of strong acid sites in USH-Y may explain why it shows higher conversion of 1-dodecene than that of H-Y in which weak acid sites dominate. In addition, in comparison with H-Y, relatively bigger pore openings of USH-Y, which make it easier for the diffusion of reagents and products, are also attributed to its higher conversion. With very high SiO₂/Al₂O₃, the density of acid sites in DAY is low, which makes it lack sufficient strong acid sites to catalyze this reaction.

In order to understand the role of acid sites with different strength in this reaction, USH-Y was modified by Na⁺ and Mg²⁺ ion exchange. As shown in Table 1, Na⁺ ion exchange results in complete loss of conversion of 1-dodecene. Figure 1 indicates that Na⁺ ion exchanged USH-Y has only one low temperature peak at 214 °C, which means the weak acid sites

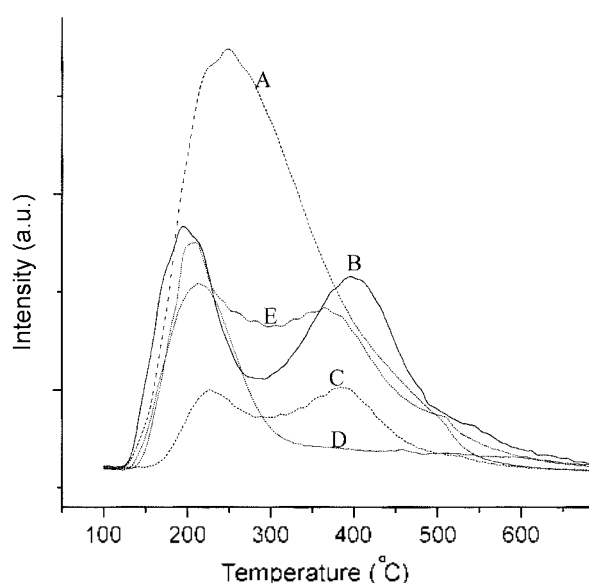


Figure 1. NH₃-TPD profiles of (A) H-Y, (B) USH-Y, (C) DAY, (D) Na-USY and (E) Mg-USY.

can't catalyze this reaction. And even the absence of other dodecene isomers demonstrates that these weak acid sites can't catalyze isomerization of 1-dodecene, either. Mg²⁺ ion exchanged sample exhibits two peaks at 206 °C and 364 °C. Compared to USH-Y, the low temperature peak shifts to a little higher temperature of 206 °C and peak area shows no big difference. However, the intensity of high temperature peak was reduced and the maximum temperature of the high-temperature peak shifts from 402 °C in USH-Y to 364 °C in Mg-USY. It is observed in Table 1 that Mg²⁺ ion exchange results in drastic decrease of conversion to 38.6% from 100% over USH-Y. It is the same case as Na-USY, weak acid sites corresponding to low temperature peak at 206 °C in Mg-USY do not play any role in this reaction. So it is the decrease of strength of strong acid sites indicated by high-temperature peak shifts from 402 °C in USH-Y to 364 °C in Mg-USY, which leads to the decrease of conversion. Furthermore, Table 1 exhibits that selectivity for LAB over Mg-USY is very low of only 29.2%, much lower than 100% over USH-Y. Strong acid sites in Mg²⁺ ion exchanged USH-

Y, whose strength is reduced in comparison with USH-Y, as indicated by the shift of the maximum temperature of the high-temperature peak from 402 °C of USH-Y to 364 °C in Mg-USY, can catalyze isomerization of 1-dodecene smoothly. However, it is not strong enough, as that in USH-Y for the alkylation of benzene ring by formed alkylcarbenium, which results in decreasing of selectivity for LAB markedly from USH-Y's 100% to 29.2% over Mg-USY.

Increment of 1-dodecene content in the reactants from benzene to 1-dodecene molar ratio of 8.7 : 1 to 4 : 1 results in drastic decrease of conversion of 1-dodecene over USH-Y from 100% to 53.6%. Furthermore, selectivity for LAB decreases drastically from 100% to 20.0%. High content of 1-dodecene in reactants reduces the opportunity for formed alkylcarbenium to attack benzene ring and it easily undergoes secondary rearrangement to form other alkene isomers. That is the reason why selectivity for LAB decreases drastically. Nevertheless, as the increase of reaction temperature to 180 °C, the conversion can reach up to 97.5% at this high content of 1-dodecene in the mixture, further increase of temperature to 220 °C results in decrease of conversion up to 92.1% due to dealkylation at high temperature.

In conclusion, benzene alkylation with 1-dodecene was studied over three Y zeolites with different SiO₂/Al₂O₃ ratios and over Na⁻ and Mg²⁺ ion exchanged USH-Y. It has been found that USH-Y with SiO₂/Al₂O₃ ratio of 80 shows the highest conversion, up to 97.8% conversion for 1-dodecene

at benzene to 1-dodecene molar ratio of 4 : 1. Furthermore, modification of USH-Y by metal ion (Na⁺, Mg²⁺) exchange enhanced the selectivity for 2-phenyl dodecane and lowered down the conversion of 1-dodecene as well. The acid properties of the zeolites were characterized by NH₃-TPD, and it was observed that strong acid sites were responsible for the reaction.

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