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Alkylation on Synthetic Zeolites

I. Alkylation of Toluene with Methanol

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A study has been made of the catalytic activity and properties peculiar to zeolite Y in various cationic and decationized forms during the alkylation reaction of toluene with methanol. It has been shown that the activity of the cation exchanged zeolite Y is in the following order:

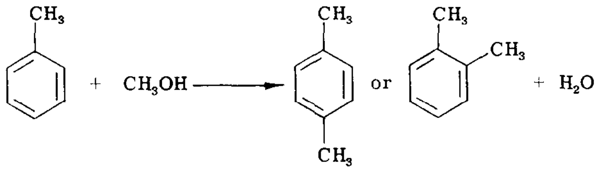
$$\text{REY} > \text{HY} > \text{divalent} > \text{monovalent}.$$

It has been found that the composition of the xylene mixture obtained deviates greatly from the thermodynamic equilibrium values. At thermodynamic equilibrium, the xylene mixture contains about 22% *p*-xylene, while in this investigation *p*-xylene comprises about 50% of the mixture. This might be due to the fact that, given our experimental conditions, the secondary isomerization reaction of the initially formed xylene was depressed in the super cage of the zeolite catalysts.

It has been established that *p*-xylene can be obtained selectively using highly active zeolite catalysts under appropriate reaction conditions.

INTRODUCTION

Synthetic zeolites have been shown to be versatile catalysts for various reactions. The catalytic properties of zeolites X and Y have been discussed by Venuto for the alkylation reaction of aromatics with a wide variety of alkylating agents (*1*). However, the data on the alkylation of toluene with methanol are very scanty (*2*). In the alkylation of toluene with methanol, substitution of the methyl group of toluene is para/ortho orientation and the first stage reaction products are supposed to be para and ortho isomers. But due to the fact that alkylation and isomerization reactions of Eqs. 1 and 2 occur successively or almost simultaneously on acidic catalysts, a product results which corresponds closely to thermodynamic equilibrium as calculated by Taylor (*3*) and is shown in Table 1.



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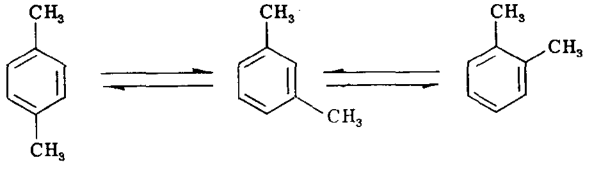

(2)

TABLE 1
THERMODYNAMICAL EQUILIBRIUM COMPOSITION OF C_8-AROMATICS [DATA FROM TAYLOR (3)]

Aromatics	Composition (%) 200°C	300°C	500°C
p-Xylene	21.8	21.1	18.9
o-Xylene	20.6	21.6	23.0
m-Xylene	53.5	51.1	47.1
Ethylbenzene	4.1	6.2	11.0

Hanson and Engel have reported the kinetics of xylene isomerization over a silica-alumina catalyst (*4*). They have shown that *p*-xylene and *o*-xylene do not directly interconvert; that is, the migrating methyl group moves around the benzene ring in steps of one ring position at a time. This is represented schematically in Eq. 2. In the case of zeolite catalysts the reaction takes place within the super cage of the zeolite crystal, as reported by many workers (*5, 6*). It is assumed that the occurrence of the secondary movement of the methyl group within the super cage would be difficult. Thus, the isomerization reaction of Eq. 2 most probably would be depressed and the alkylation reaction of Eq. 1 would be favored to produce *p*- and *o*-xylene selectively.

The purpose of this study of the alkylation reaction of toluene with methanol is to obtain *p*- or *o*-xylene selectively and to compare the catalytic activity of the various cation exchanged forms of zeolite Y in relation to this alkylation reaction.

EXPERIMENTAL

Materials

Catalyst. Throughout the experiment, the sample was NaY zeolite, Linde SK 40 (Na/Al atomic ratio 0.84, SiO_2/Al_2O_3 molar ratio 4.7). The chemical composition of NaY is shown in Table 2.

TABLE 2
CHEMICAL COMPOSITION OF ZEOLITE Na-Y

	SiO_2	Al_2O_3	Na_2O	H_2O
wt%	47.2	17.2	8.8	26.8

The cationic and HY forms of zeolite were prepared by conventional cation exchange procedures (*7, 8*) using aqueous solutions of the chloride salt of the corresponding metal. The degree of cation exchange was determined by flame photometry. The degree of cation exchange was about 80% in most cases. HY zeolite was obtained by deamination of NH_4Y calcining at 500°C for 3 hours. All cation exchanged zeolites were calcined for 3 hours at 300°C, pelleted binder free, crushed, and sized to 8–14 mesh before activation.

Organic Reactants. The toluene and methanol were obtained from standard commercial sources having a purity of 99.5%.

Analysis

The reaction mixtures were analyzed by gas chromatography, using a 4-meter stainless steel column having a diameter of 4 mm with stationary phase Celite-545 (60–80 mesh) containing 7 parts of Benton-34 and 5 parts of DNP with respect to 100 parts of solid support. The carrier gas was H_2 (80 ml/min) and the analysis temperature was 90°C.

Apparatus and Procedure

The experiment was carried out in a fixed bed type apparatus with a continuous flow system at atmospheric pressure.

The uncalcined catalyst was placed in the electrically heated quartz reactor and was purged with nitrogen. The calcination was carried out for 3 hours at the desired temperature which was then brought to the reaction temperature without transferring the catalyst or exposing it to the atmosphere. The mixture of toluene and methanol in the desired molar ratio (toluene in excess) was then fed into the catalyst bed by a microfeeder. The samples of the products were collected periodically for analysis using an ice trap.

All calculations were done with respect to methanol and the yield was defined as follows:

$$\text{Yield} = \frac{\text{moles of xylene produced}}{\text{moles of methanol fed}} \times 100\ (\%)$$

RESULTS AND DISCUSSION

Reaction Conditions

The effect of W/F (see below), the temperature, and the molar ratio of the reactants on the yield of reaction products, especially *p*-xylene, has been studied, using HY zeolite (obtained from deamination of NH_4Y zeolite by calcining at 500°C) up to 300°C.

The results of toluene alkylation experiments, taken at the highest alkylation activity which usually occurred within 3 or 4 hours on stream time, are presented in Figs. 1, 2, and 3. The W/F has been defined as follows:

$$W/F = \frac{\text{weight of the catalyst (g)}}{\text{feed rate (mole/hr)}}$$

The results in Fig. 1 show that the largest yield of xylene is obtained at $W/F \geqq 120$. Above this W/F there is no noticeable effect on the yield or on the selectivity of *p*-xylene.

Fig. 2 shows the effect of the reaction temperature. It is clear that with the rise of temperature, the total yield increases and there is also an increase of *m*-xylene and a decrease of *p*- and *o*-xylene. This is evidently due to the isomerization of *p*- and *o*-xylene at a high temperature. At 225°C the *p*-xylene is maximum in the mixture of xylenes (i.e., 51%).

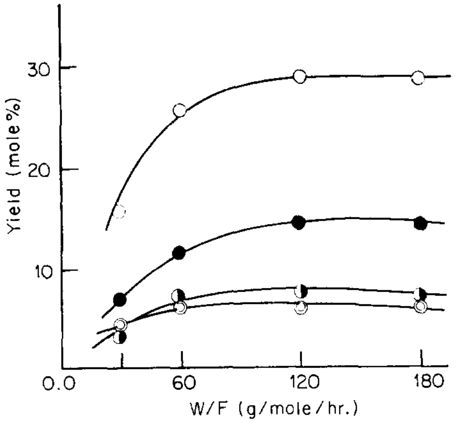

FIG. 1. Effect of change of W/F; conditions: temp. = 225°C, toluene/methanol = 2. ○, total xylene; ●, *p*-xylene; ◎, *o*-xylene; ◑, *m*-xylene.

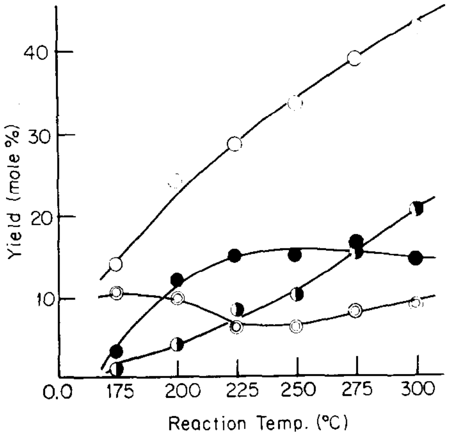

FIG. 2. Effect of reaction temperature; W/F = 120, toluene/methanol = 2 (symbols defined in Fig. 1).

The effect of the molar ratio of the reactants is shown in Fig. 3. The total yield increases with the decrease of methanol in the reactant mixture, but the *p*-xylene decreases in the product correspondingly. At molar ratio 2, there is an appropriate yield about 29% and the *p*-xylene comprises 51% of the xylene mixture.

Small amounts of such by-products as trimethylbenzene and ethyltoluene were formed under the severe conditions. Ethylbenzene was not detectable. The experimental conditions were so chosen that xylene (especially *p*-xylene) was the main product and the by-products were only at

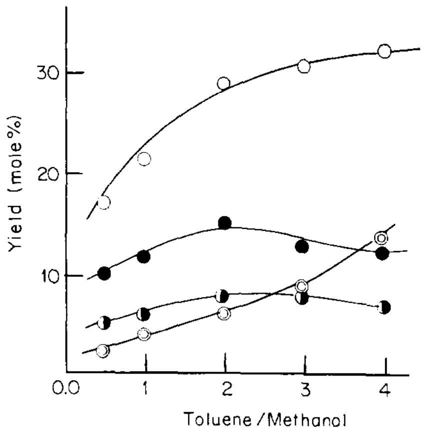

FIG. 3. Effect of change of molar ratio; temp. = 225°C, W/F = 120 (symbols defined in Fig. 1).

TABLE 3
ACTIVITY OF ZEOLITE Y
Conditions: $W/F = 120$ (g/mole hr^{-1}); temp. = 225°C; toluene/methanol = 2

Catalyst	% Na^+ exchanged	Yield[a] (mole %)	Xylene composition (%) *p*-	*m*-	*o*-
HY	82.5	28.9	51.0	26.7	22.3
CeY	84.2	37.5	48.5	30.6	20.9
LaY	76.3	42.8	41.5	38.6	19.9
NiY	80.3	26.3	44.7	22.3	33.0
CoY	75.8	24.7	45.5	24.0	30.5
MnY	72.7	21.1	46.6	22.7	30.7
CdY	80.3	10.2	21.7	13.5	64.8
CaY	82.5	8.7	21.4	15.8	62.8
MgY	68.4	7.5	19.7	13.6	66.7
SrY	80.5	4.4	22.6	18.5	58.9
LiY	65.3	1.1	22.9	29.2	47.9
NaY	100.0	0.0	—	—	—
Sil-Al	—	0.7	25.1	19.3	55.6

[a] The yield listed in Table 3 is taken at the highest alkylation activity that usually occurred within 3 or 4 hours on stream time.

the trace level. The chosen optimum conditions are as follows:

$W/F = 120$ (g/mole hr^{-1})
Reaction temperature = 225°C
Toluene/methanol = 2

Further investigations have been made under the above condtions or otherwise mentioned conditions.

Catalyst Activation

To compare the catalytic activity of a catalyst, it is obvious that the catalysts with a similar method of preparation and similar analyses must be compared. It is equally important that similar methods of activation (temperature, time, atmosphere, and pressure) be employed prior to use. This procedure has been demonstrated above; i.e., the same reaction conditions and methods of preparation were employed in the preparation of the catalyst. It was difficult, however, to maintain the same degree of cation exchange. The calcination temperature for REY, divalent, and monovalent cations was 300°C, while for HY it was 500°C, because the HY zeolite was obtained by deamination of NH_4Y.

The activity of the cation exchanged zeolite Y differs under different conditions; for example, calcination, reaction temperature, and degree of cation exchange. Under the conditions in which we performed this experiment, the catalytic activity of the cation exchanged zeolite Y is in the following order, as shown in Table 3.

$$\text{Na} < \text{silica-alumina} < \text{Li} \ll \text{Sr} < \text{Mg} < \text{Ca} < \text{Cd} \ll \text{Mn} < \text{Co} < \text{Ni} < \text{H} \ll \text{Ce} < \text{La}$$

In other words, monovalent < divalent < HY < REY.

The results obtained in this study are consistant with Pickert and Rabo's results reported on the cracking and isomerization of hydrocarbons (*9*), and show that the catalytic action is noticeably different depending on the cation forms of zeolite.

The cation in the zeolite catalyst plays the determining role in its catalytic activity. In other words, the catalytic activity of zeolites changes with the polarizing effect of the cation. The higher the charge and the smaller the radius of the cation, the greater is its polarizing ability and, therefore, the catalyst is more active. SrY, as shown in Table 4, has the lowest activity in the divalent series. This is explained by the largeness of the Sr^{++} cation and, consequently, has a low polarizing ability. MgY also shows a lower activity while possess-

TABLE 4

Comparison of the Activity of Divalent Cations

Conditions: W/F = 120 (g/mole hr^{-1}); temp. = 225°C; toluene/methanol = 2

Cation	Ni	Co	Mn	Cd	Ca	Mg	Sr
Ionic Radius (Å)	0.74	0.78	0.83	0.97	0.99	0.64	1.27
Na^+ exchanged (%)	80.3	75.8	72.7	80.3	82.5	68.4	80.5
Yield (%)	26.3	24.7	21.1	10.2	8.7	7.5	4.4

ing the same ionic radius, that of Co^{++}. This again can be explained by its lower degree of exchange.

The results obtained from a silica-alumina catalyst, as compared with the results from the zeolites, reveal that all of the zeolites give a much larger yield of xylene. The zeolite catalysts also possess an induction period. At a relatively high reaction temperature, the zeolite catalysts produce the mixture of xylene which corresponds closely to thermodynamic equilibrium values. A silica-alumina catalyst has a substantial effect above 450°C and gives an equilibrium mixture of xylene.

p-Xylene Selectivity and Catalytic Activity

The substitution of a methyl group of toluene is known to be a para/ortho orientation; therefore, the first stage products of the reaction of toluene with methanol are considered to be para and ortho isomers. But at thermodynamic equilibrium, as reported by Taylor (*3*), the xylene mixture contains *m*-xylene in excess. Amemiya and coworkers (*10*) have also reported their results, obtained using solid acid catalysts. They have shown an excess of *m*-xylene in the mixture. On the contrary, the results we have obtained in our experiment, using cation exchanged zeolite Y, deviate greatly from the above results. Our experiment produced *p*-xylene in excess, and at a comparatively high reaction temperature, *m*-xylene rich products have been found. This is evidently due to the isomerization of para and ortho isomers.

The range of isomer contents generally shows a preference for the para isomer at low reaction temperature for highly active cation exchanged zeolite Y catalysts. We have succeeded in classifying the cation exchanged zeolite Y catalysts, with respect

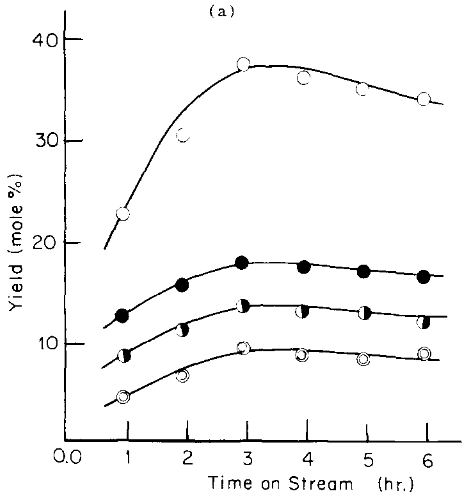

Fig. 4(a). Activity of CeY; conditions: temp. = 225°C, W/F = 120, tolune/methanol = 2 (symbols defined in Fig. 1).

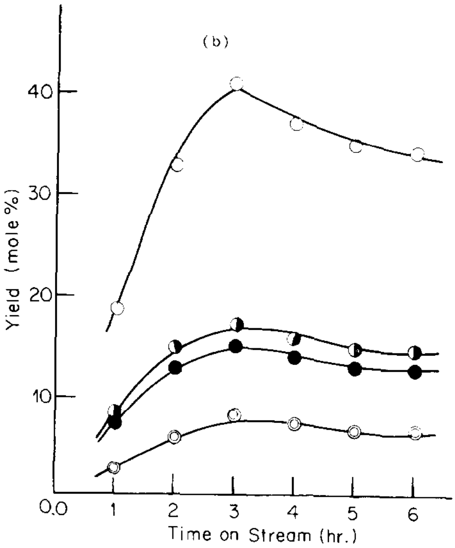

Fig. 4(b). Activity of CeY; conditions: temp. = 250°C, W/F = 120, toluene/methanol = 2 (symbols defined in Fig. 1).

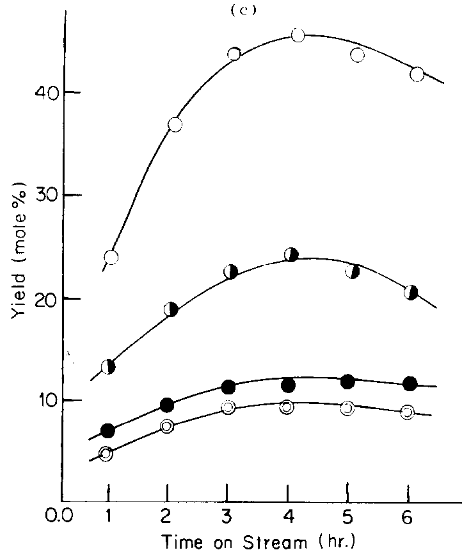

FIG. 4(c). Activity of CeY; conditions: temp. = 300°C, W/F = 120, toluene/methanol = 2 (symbols defined in Fig. 1).

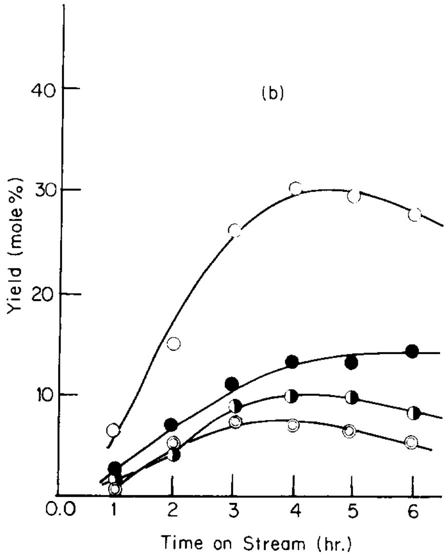

FIG. 5(b). Activity of NiY; conditions: temp. = 250°C, W/F = 120, toluene/methanol = 2 (symbols are defined in Fig. 1).

to their behavior for xylene orientation, into the following three types:

(1) The first type of catalysts are HY, LaY, and CeY. They are highly active zeolites, giving *p*-xylene in excess from the start of the reaction. To demonstrate this, the results of CeY are given in Fig. 4(a,b,c) at 225°C, 250°C, and 300°C, respectively. It is clear that at 225°C the mixture is rich in *p*-xylene and, with the rise of temperature (that is, at 250°C and 300°C), *m*-xylene increases, there is corresponding decrease in *p*-xylene, and there is no significant change in *o*-xylene.

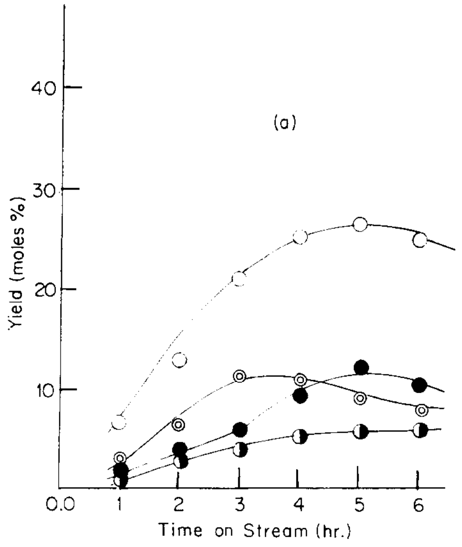

FIG. 5(a). Activity of NiY; conditions: temp. = 225°C, W/F = 120, toluene/methanol = 2 (symbols defined in Fig. 1).

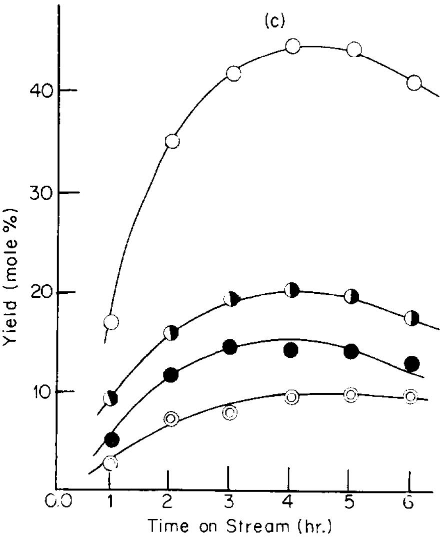

FIG. 5(c). Activity of NiY; conditions: temp. = 300°C, W/F = 120, toluene/methanol = 2 (symbols defined in Fig. 1).

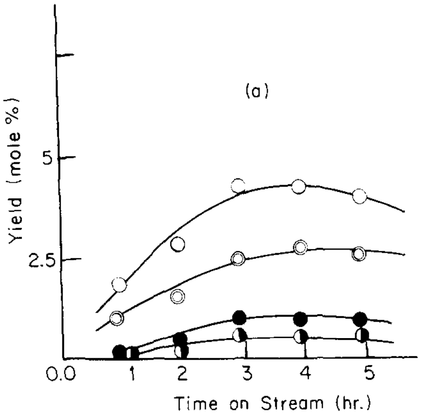

FIG. 6(a). Activity of SrY; conditions: temp. = 225°C, W/F = 120, toluene/methanol = 2 (symbols defined in Fig. 1).

(2) The second type of cation exchanged zeolites are NiY, CoY, MnY, CdY, MgY, and CaY. These catalysts give a reverse orientation with the time on stream. The results of NiY are shown in Fig. 5(a,b,c) at 225°C, 250°C, and 300°C, respectively. It is seen that p-xylene increases while o-xylene decreases with the time on stream at 225°C, and there is no significant change in m-xylene. Similar results have been obtained with CoY, MnY, CdY, MgY, and CaY. The reaction temperature for CdY and MgY, however, is 250°C and for CaY it is 300°C. At a relatively high reaction temperature, all these

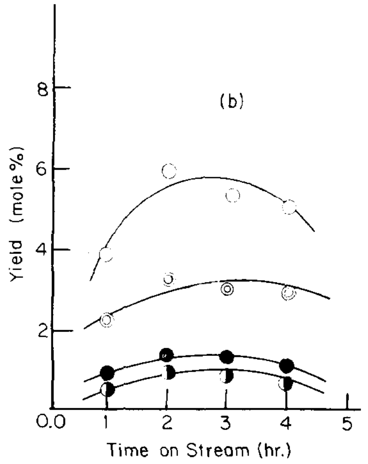

FIG. 6(b). Activity of SrY; conditions: temp. = 250°C, W/F = 120, toluene/methanol = 2 (symbols defined in Fig. 1).

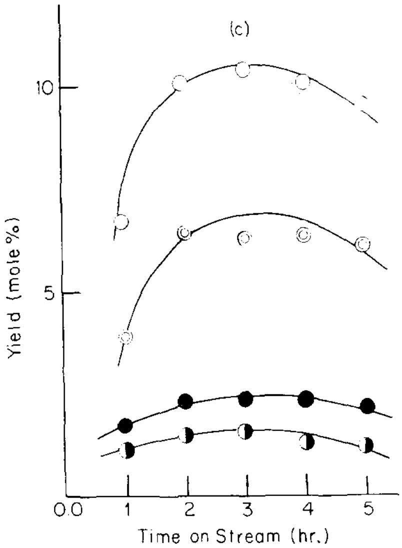

FIG. 6(c). Activity of SrY; conditions: temp. = 300°C, W/F = 120, toluene/methanol = 2 (symbols defined in Fig. 1).

forms give a product rich in p-xylene, as is clear from the results of NiY at 250°C and 300°C, but above a certain reaction temperature the product becomes rich in m-xylene.

(3) The third type are the zeolites with low activity. In this category are NaY, LiY, and SrY. These zeolites produce an excess of o-xylene. To show this, the results of SrY at 225°C, 250°C, and 300°C are given in Fig. 6(a,b,c), respectively. It is clear that o-xylene is present in large quantity at all temperatures.

From the above results it is suggested that p-xylene can be obtained selectively using highly active zeolite catalysts under appropriate reaction conditions.

GENERAL DISCUSSION

From the experimental results, the para/ortho ratio of xylene shows a preference for p-xylene. It does suggest that there is some operation of general orientation effect in the intrazeolitic environment at least under these conditions.

In the case of zeolite catalysts, the active sites for alkylation have been considered as a Brönsted acid type by many workers (*1*, *11*). It has also been reported by Hattori and Shiba (*12*) that zeolite catalysts can be classified into three types, i.e.,

(1) The strong Brönsted acid center type
(2) The interim Brönsted acid center type
(3) The weak Brönsted acid center type

Reviewing the experimental results shows that the catalysts HY, LaY, and CeY, which give *p*-xylene selectively at the start of the reaction, are of the first type. The catalysts NiY, CoY, MnY, CdY, MgY, and CaY, which reverse orientation with the time on stream, and LiY, NaY, and SrY, which do not give *p*-xylene selectively, fall in the second and third categories, respectively.

The B-acid site plays a significant role in the selectivity of *p*-xylene. The promoting effect of water has been reported by many workers (*1*, *13*). The influence of water which is formed in the reaction cannot be discounted. It seems possible that the catalysts which give reverse orientation with the time on stream are affected more and a change occurs in the acid site; i.e., probably the L-acid site changes to a B-acid site (*12*), and this produces a change of *o*-xylene to *p*-xylene.

The idea of isomerization is not suggested on the ground that direct isomerization of *o*-xylene to *p*-xylene and vice versa does not occur, as has been reported by many workers (*4*, *13*, *14*). Moreover, the experimental results of isomerization of *o*-xylene over a NiY catalyst have shown no significant yield of *p*-xylene, though *m*-xylene has been formed to some extent.

A comprehensive study on the selectivity of *p*-xylene will be discussed in a subsequent paper.

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