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Alkylation on Synthetic Zeolites

II. Selectivity of *p*-Xylene Formation

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The influence of the calcination temperature and the degree of cation exchange of NH_4–Y, and the addition of hydrogen chloride to Mn–Y zeolite, in relation to the selectivity of *p*-xylene formation, was studied for the alkylation reaction of toluene with methanol. It was found that within a certain range of calcination temperature (*i.e.*, 400–550°C), *p*-xylene can be obtained selectively. A proportional relation between the catalytic activity and the selectivity of *p*-xylene with the degree of cation exchange was also observed. The addition of hydrogen chloride to Mn–Y zeolite has shown a promoting effect in *p*-xylene selectivity. These behaviors of the treated catalysts can be related to Brönsted acidity.

It has also been shown that the alkylation reaction was dominant, while the isomerization reaction of the produced xylene (under the conditions employed) was depressed.

It has been established that the *p*-xylene selectivity is a function of Brönsted acidity.

INTRODUCTION

In the first part of this series we reported the data on the alkylation of toluene with methanol over synthetic Y-zeolites (*1*). It was shown that the composition of the xylene mixtures obtained deviate considerably from the thermodynamic equilibrium values, producing *p*-xylene selectively.

Thus far, most works have been devoted to classifying substituents as either para-ortho or meta orientation (*2*), and few attempts have been made to classify the para-ortho orientation (*3*). It is of interest, therefore, to examine the para-ortho orientation in the hope of predicting whether the para or the ortho isomer will be favored.

This paper describes the experiments designed to relate the selectivity of *p*-xylene with the acidity and activity of synthetic Y-zeolites.

EXPERIMENTAL

Catalyst

The various forms of NH_4–Y with different degrees of exchange and Mn–Y were prepared by conventional procedures (*4, 5*) using a warm aqueous solution of NH_4Cl and $MnCl_2$, respectively. The sample of Na–Y of Linde SK 40 (the chemical composition reported in part I) was used throughout the experiments. The degree of cation exchange was determined by flame photometry. All the samples of NH_4–Y were calcined for 3 hr at the desired temperature and Mn–Y at 300°C. All catalysts were binder free, pelletted, crushed and sized to 8/14 mesh before the calcination.

Organic Reactants

Toluene, methanol, *p*-xylene and *o*-xylene

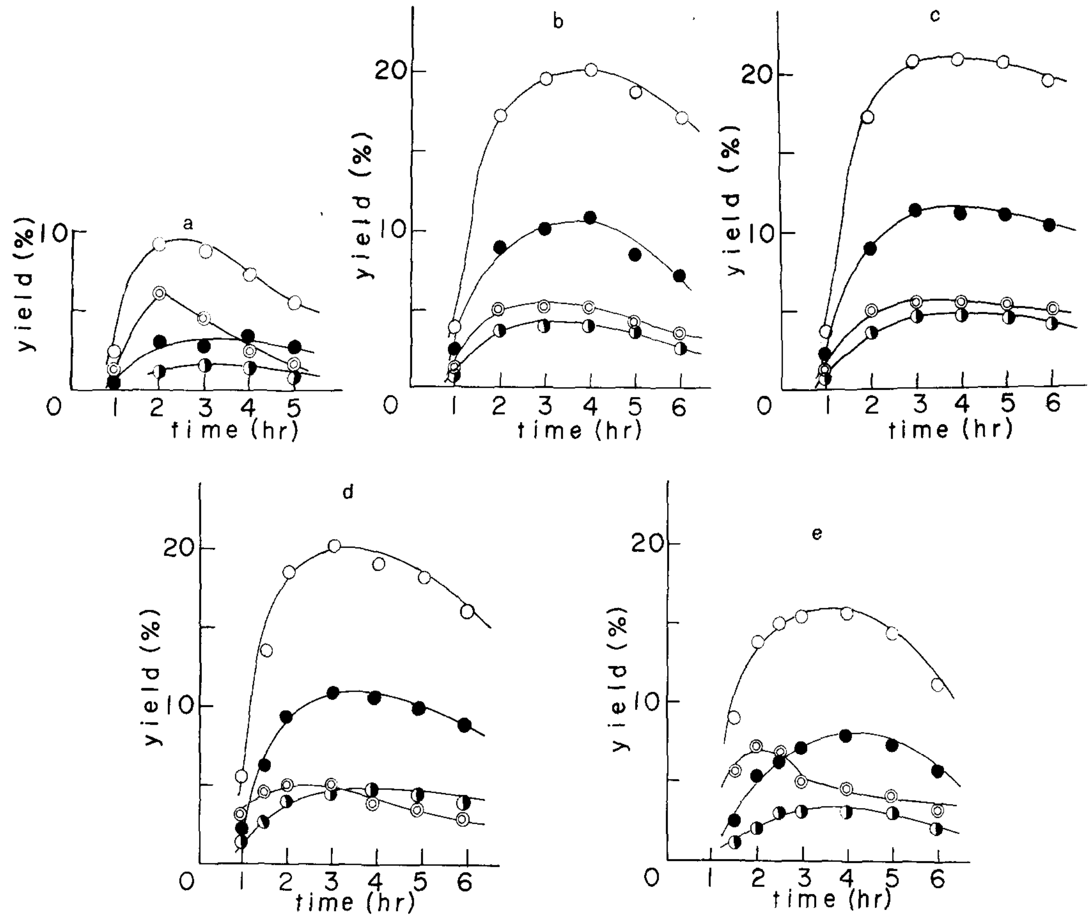


FIG. 1. (a) Activity of NH_4-Y calcined at 300°C; O, total xylene; ●, p-xylene; ◎, o-xylene; and ◑, m-xylene. Conditions: $W/F = 120$(g/mole hr); temp = 225°C; toluene/methanol = 2. (b) Activity of NH_4-Y calcined at 400°C; O, total xylene; ●, p-xylene; ◎, o-xylene; and ◑, m-xylene. Conditions, $W/F = 120$(g/mole hr); temp = 225°C; toluene/methanol = 2. (c) Activity of NH_4-Y calcined at 500°C; O, total xylene; ● p-xylene; ◎, o-xylene; and ◑, m-xylene. Conditions: $W/F = 120$(g/mole hr); temp = 225°C; toluene/methanol = 2. (d) Activity of NH_4-Y calcined at 600°C; O, total xylene; ●, p-xylene; ◎, o-xylene; and ◑, m-xylene. Conditions: $W/F = 120$(g/mole hr); temp = 225°C; toluene/methanol = 2. (e) Activity of NH_4-Y calcined at 700°C; O, total xylene; ●, p-xylene; ◎, o-xylene; and ◑, m-xylene. Conditions: $W/F = 120$(g/mole hr); temp = 225°C; toluene/methanol = 2.

were obtained from standard commercial sources with a purity of 99.5%.

Analysis

Reaction mixtures were analyzed by gas chromatography. The conditions for analysis have been reported in part I.

Apparatus and Procedure

The same flow system apparatus as described in part I was used (*1*).

The experimental procedure has also been reported as in part I. The catalysts were calcined in the electrically heated quartz reactor, and were used for the reaction *in situ*. In the case of Mn–Y, hydrogen chloride was introduced to the catalyst bed along the carrier gas (N_2).

Samples of the products were collected periodically for analysis using an ice trap.

The content of NH_4 in the zeolite, after various temperature pretreatments, *i.e.*, 300°, 400°, 450°, 500°, 550°, 600°, and 700°C, was measured by entrapping the NH_3, resulting from the decomposition of NH_4-Y into $HY + NH_3$, in a standard solution of HCl. The remaining HCl was then titrated with a standard solution of NH_4OH.

Reaction Conditions

$W/F = 120$ (g/mole hr)
Reaction Temp = 225°C
Toluene/Methanol = 2 (mole/mole)

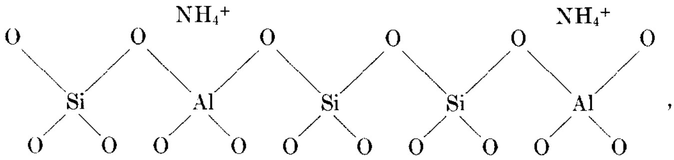
The above reaction conditions were employed throughout this experiment (unless otherwise specified).

RESULTS AND DISCUSSION

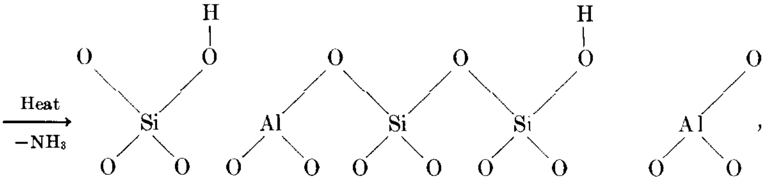
The Influence of Calcination Temperature

The selectivity of *p*-xylene has been studied for NH_4–Y zeolite after calcination over a range of temperatures between 300 and 700°C. The results are shown in Fig. 1 (a, b, c, d, and e) at 300°, 400°, 500°, 600°, and 700°C, respectively. For the samples calcined below 400 and above 550°C, *o*-xylene was produced from the start of the reaction, as is clear from the results in Fig. 1 (a, d and e). For the sample calcined at 300°C, the orientation was reversed with the time on stream producing a *p*-xylene rich product after 3.5 hr. And for the samples calcined at 400–550°C, a *p*-xylene rich product was obtained from the start of the reaction. Raising the temperature from 550 to 600°C and 700°C, again a change was observed in the product composition with the time on stream; this change, however, for the sample at 600°C is after 1.5 hr and for 700°C after 3 hr of the time on stream. The reaction time at which the yield of *p*-xylene goes over that of *o*-xylene versus the calcination temperature has been plotted in Fig. 2.

Ward (*6*) has reported the influence of calcination temperature on the hydroxyl groups and the acidity of stabilized H–Y. He has shown that the concentration of B-acid increases as the calcination temperature is increased from 300 to 425°C. It remains constant as the calcination temperature is increased to 600°C and then declines sharply as the temperature is increased to 800°C. The Lewis acidity remains almost constant until the calcination temperature reaches 550°C, and then increases rapidly as the temperature increases. The interpretation of this phenomenon has been given by the following equations:

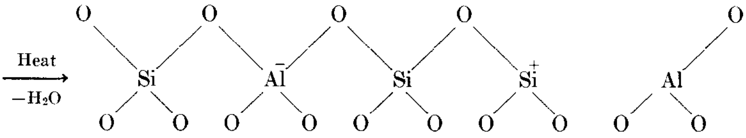


(1)



(2)

and



(3)

In our experiment the results of the deamination after various temperature pretreatments are shown in Fig. 3. It is clear that with the rise of pretreatment temperature the NH_4 content decreases and falls almost to zero at 550°C. Thus the NH_4–Y converts into H–Y + NH_3, which is repre-

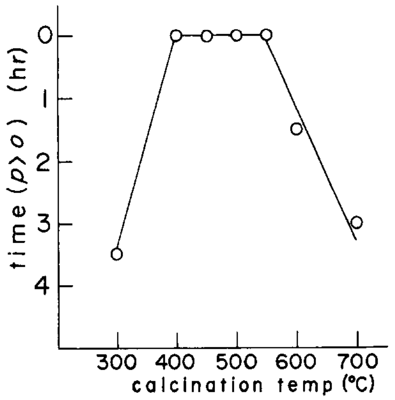


FIG. 2. Relation of calcination temperature and the time at which para isomer goes over ortho isomer; Conditions: W/F = 120(g/mole hr); temp = 225°C; toluene/methanol = 2(mole/mole).

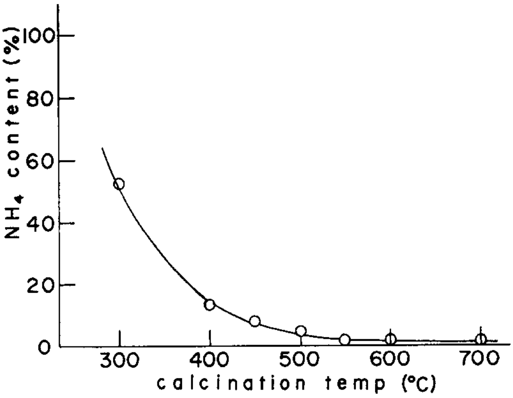


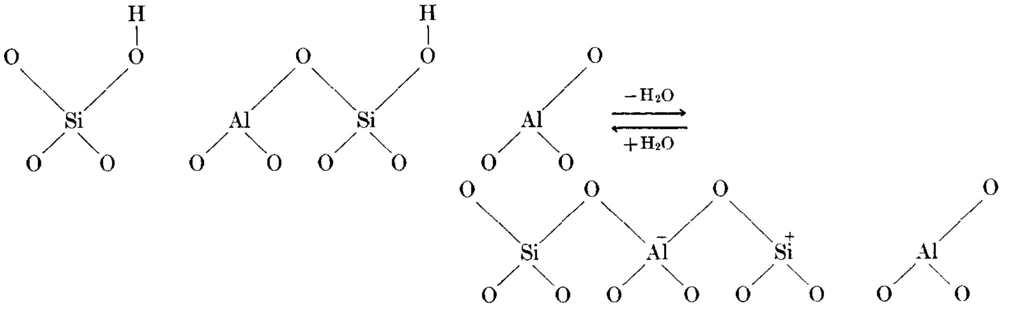
FIG. 3. NH_4 content at various calcination temperatures (the degree of exchange of the sample used is 76.6%).

sented in Eq. 2. On raising the temperature above 550°C, the possibility of Eq. 3 results, which shows an increase in the Lewis acidity. The results of Fig. 2 and Fig. 3 are consistant with the results reported by Ward (*6*) on the calcination of NH_4–Y. It can be said that the catalyst is rich in Brönsted acid sites between the calcination temperature of 400 and 550°C. The p-xylene selectivity in our study remains constant for the calcination temperature between 400 and 550°C. Thus this selectivity can be related to the Brönsted acidity.

Again, the change in the composition of the product mixture with the time on stream for the catalysts calcined at 600°C and above indicates that the L-acid site formed at high calcination is converted to B-acid site by the action of water formed during the reaction, as seen from the following equation:

The influence of water adsorbed on the zeolite catalyst is shown in Fig. 4. For this experiment NH_4–Y was calcined for 3 hr at 700°C and then contacted with water vapor at room temperature for two days. After this treatment, it has been recalcined at 500°C for 3 hr. A comparison of the results of Fig. 1 (e) and Fig. 4 clearly demonstrates the role of Brönsted acid sites, formed by the action of water on the catalyst system calcined at high temperatures, for the selectivity of p-xylene.

The reverse orientation with the time on stream for the catalyst calcined at 300°C may probably be explained by the fact that the amount of water in the zeolite frame was not removed completely as reported by Ward (*6*) and Benesi (*7*). It is well considered that the removal of the water gives a rise to Brönsted acidity and consequently an enhancement in the p-xylene selectivity. For this sample, however, the produced water has no significant role.



(4)

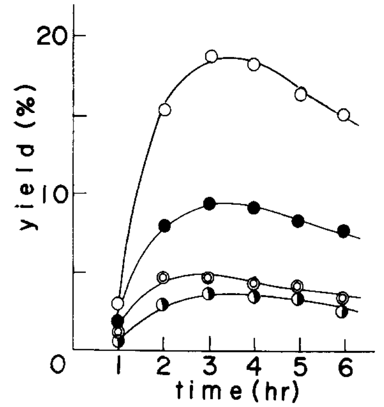


FIG. 4. Effect of H_2O adsorbed on the zeolite catalyst calcined at 700°C; ○, total xylene; ●, *p*-xylene; ◎, *o*-xylene; and ◑, *m*-xylene. Conditions: $W/F = 120$(g/mole hr); temp = 225°C; toluene/methanol = 2. Catalyst calcined at 700°C, contacted with water vapor and recalcined at 500°C for 3 hr.

Influence of the Degree of Cation Exchange

The results of the degree of cation exchange and the activity and selectivity of *p*-xylene are shown in Table 1. It is clear that with the increase of the degree of cation exchange, the activity of the catalyst increases and causes an increase in *p*-xylene selectivity. However, the absolute yield of *o*-xylene remains constant at about 5%. Thus, the yield of *o*-xylene seems to be independent of the degree of exchange.

For zeolite catalysts the activity generally increases with the increase of cation exchange. In the case of NH_4^+, with an increase of the degree of NH_4^+, the Brönsted acid sites are obviously increased. This interpretation suggests that the *p*-xylene formation is a function of Brönsted acidity.

Influence of Hydrogen Chloride

The influence on the selectivity of *p*-xylene by the introduction of hydrogen chloride to a Mn–Y zeolite catalyst was studied. This catalyst, as reported in part 1, shows reverse orientation with the time on stream at 225°C (*1*). The results on the addition of hydrogen chloride to Mn–Y zeolite catalyst are shown in Fig. 5. Hydrogen chloride was added in the carrier gas (N_2).

On the addition of hydrogen chloride, an enhancement of selectivity of *p*-xylene was observed. When stopping the addition of hydrogen chloride the selectivity falls to the lowest point as seen from Fig. 5. Readdition of hydrogen chloride shows a promoting effect in the *p*-xylene selectivity, however, the yield of *o*-xylene remains constant. Thus, the yield of *o*-xylene seems to be independent of the addition of hydrogen chloride. Now, if it can be postulated that the action of hydrogen chloride for zeolite contributes to the formation of active Brönsted acid, the role of Brönsted acidity for the selectivity of *p*-xylene can be suggested. Matsumoto and Morita (*8*) have suggested that the active centers of a zeolite catalyst may be formed by reversible interaction between hydrogen chloride and zeolite cations as follows:

$$\overset{+}{\mathrm{Me}}\ \overset{-}{\mathrm{Z}} + \mathrm{HCl} \rightleftharpoons \overset{\overset{\delta-}{\mathrm{Cl}}}{\overset{\downarrow\delta+}{\mathrm{Me}}}\quad \overset{\overset{+}{\mathrm{H}}}{\overset{-}{\mathrm{Z}}}\ \cdot \tag{5}$$

Thus the addition of hydrogen chloride to the cation exchanged zeolite results in the

TABLE 1

ACTIVITY AND $\%NH_4^+$ EXCHANGED ON Y-ZEOLITE[a]

		Xylene Isomer Composition (%)		
$\%NH_4^+$ Exchanged	Yield (mole%)	*p*-	*m*-	*o*-
31.5	7.5	19.7	13.6	66.7
48.6	17.0	52.9	20.4	26.7
62.9	22.9	49.4	26.2	24.4
76.2	25.0	49.7	27.8	22.5
82.5	28.9	51.0	26.0	22.3

[a] *Conditions:* $W/F = 120$(g/mole hr); Reaction Temp = 225°C; Toluene/Methanol = 2 (mole/mole); Pretreatment Temp = 500°C.

TABLE 2
ISOMERIZATION OF o- AND p-XYLENE ON Y-ZEOLITE (%)

Catalyst		H	Ce	La	Ni	Mn	Si-Al
(p-Xylene)	p-	94.1	81.8	80.3	96.5	98.1	55.5
Product composition	m-	3.5	12.4	13.2	2.6	1.6	37.8
	o-	2.4	5.8	6.5	0.9	0.3	6.7
(o-Xylene)	p-	0.5	0.5	0.6	0.6	0.2	5.6
Product composition	m-	1.5	5.5	5.8	0.7	0.3	27.3
	o-	98.0	94.0	93.6	98.7	99.5	67.1

[a] *Conditions;* $W/F = 120$(g/mole hr); Reaction Temp = 225°C (Reaction temperature for Si-Al was 450°C); Pretreatment Temp = 300°C for Ce, La, Ni and Mn; 500°C for NH_4.

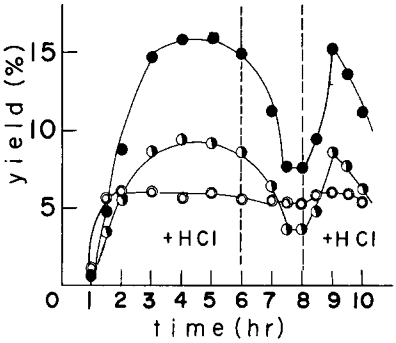


FIG. 5. Effect of the addition of HCl to Mn-Y; ●, p-xylene ◎, o-xylene; and ◑, m-xylene. Conditions: $W/F = 120$(g/mole hr); temp = 225°C; toluene/methanol = 2; calcination temp = 300°C.

formation of protonic acid. Applying this interpretation to our results, it strongly suggests the role of the Brönsted acidity in the selectivity of p-xylene, and it also shows that the Brönsted acidity has no significant effect on the yield of o-xylene.

Isomerization

Venuto (*9*) has reported that the conditions for alkylation are also favorable for isomerization of di- (or poly-) substituted alkylbenzenes such as xylenes. We performed this experiment for the isomerization of o- and p-xylene under the conditions employed for alkylation. The results are shown in Table 2. The results show that under the conditions employed, the isomerization reaction is not remarkable, while the alkylation reaction under these conditions is dominant. This may be due to the fact that the secondary movement of the methyl group is hindered within the super cage of the zeolite crystal, thus depressing the isomerization reaction and favoring the selective alkylation reaction.

The isomerization reaction has not shown a change in the product mixture, that is, the reverse orientation of o-xylene to p-xylene and vice versa with the time on stream does not occur. This suggests that the change with the time on stream of o-xylene to p-xylene is not resulted from the isomerization reaction but by the change of acid sites in the zeolite catalyst. The increase in the p-xylene selectivity by the addition of proton donors, *i.e.*, hydrogen chloride and water, to the catalyst system strongly suggests the significant role of Brönsted acidity in the selectivity of p-xylene.

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