

# EFFECT OF CATION EXCHANGE ON Y-ZEOLITE ACTIVITY IN TOLUENE ALKYLATION WITH METHANOL

Sami Matar\* and Mohamed A. Muse

Department of Chemistry,  
University of Petroleum & Minerals,  
Dhahran - 31261, Saudi Arabia.

الخلاصة :

تم دراسة تأثير التبادل الأيوني لمادة زيوليت الصوديوم مع كل من أيونات الهيدروجين - الماغنسيوم والكالسيوم على ألكلة التولوين بالميثانول عند درجات ٢٥٠ ، ٣٠٠ ، ٣٥٠ م باستخدام مفاعل ثابت صغير .  
لقد أعطى العامل الحفّاز الذي تبادل مع أيون الهيدروجين بدرجة عالية نسبة تحول أكبر للتولوين من العوامل الحفّازة الأخرى . وأعلى درجة انتقاء كانت لمركب البارازيلين وهي ٤٦,٨٪ وقد نتجت عن استخدام العامل الحفّاز الذي يحتوي على نسبة هيدروجين منخفضة .  
وعندما استعمل الزيوليت الذي يحتوي على نسبة عالية من الكالسيوم وجد أن النتائج تقارب تلك التي استخدم فيها العامل الحفّاز الذي يحتوي على نسبة هيدروجين منخفضة مما يعطي دلالة على تقارب الحامضية لهذين العاملين الحفّازين .  
كذلك وجد أنه عند استخدام زيوليت الماغنسيوم ( درجة تبادل ٦٠٪ ) فإن نتائج التفاعل تقارب تلك التي استخدم فيها زيوليت الكالسيوم ( درجة تبادل ٧٢٪ ) ولكن درجة انتقاء البارازيلين أقل .  
لقد أدت معالجة زيوليت الهيدروجين بحامض الفوسفوريك الى تعدد الألكلة ، ولكن عند استخدام فوسفات النشادر الحامضية والتي تقل حامضيتها عن حامض الفسفوريك فقد وصلت نسبة ألكلة التولوين الى ١٩,٥٪ مع انخفاض درجة انتقاء البارازيلين بنسبة ٤٪ عن العامل الحفّاز غير المعالج .

\*Address for correspondence:  
221 Gisir El-Suez Apt. # 9  
Heliopolis  
Cairo  
Egypt

## ABSTRACT

The effect of exchanging  $\text{Na}^+$  in NaY-zeolite by  $\text{H}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$  on the alkylation of toluene with methanol at 250°, 300°, and 350°C was studied using a small fixed-bed reactor. It was found that the highly-exchanged H–NaY catalyst gave the highest toluene conversion. However, the best selectivity for *p*-xylene of 46.8 wt% was obtained with the less-exchanged H–NaY catalyst. Results obtained for a highly-exchanged Ca–NaY catalyst are comparable in alkylation activity and *p*-xylene selectivity to a less-exchanged H–NaY catalyst indicating comparable acidities. Mg–NaY zeolite (60% exchange level) has shown similar alkylation activity to Ca–NaY zeolite (72% exchange level) but slightly lower selectivity to *p*-xylene. Impregnation of H–NaY zeolite with phosphoric acid resulted mainly in polyalkylation. Impregnating the same catalyst with less acidic  $\text{NH}_4\text{H}_2\text{PO}_4$  slightly increased toluene conversion to 19.5%, but selectivity to *p*-xylene was about 4% lower than the unimpregnated catalyst.

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### INTRODUCTION

*p*-Xylene is an important chemical intermediate for producing terephthalic acid. This acid is the monomer used with glycols to obtain polyesters for synthetic fiber production.

Naphtha catalytic reforming is the main process for producing C<sub>6</sub>–C<sub>8</sub> aromatics. An extraction step is used to get these aromatics from the reformat [1]. After separation of benzene, toluene, and ethyl benzene, a mixture of three xylene isomers is obtained. The ratio of the three isomers, *para*: *ortho*: *meta*, is approximately 1:1:2, which is very close to the thermodynamic equilibrium values for these isomers at the reforming temperature. Thermodynamic equilibrium values are shown in Table 1 [2].

**Table 1. Thermodynamic Equilibrium Composition of C<sub>8</sub> Aromatics at Three Temperatures**

| Aromatics wt %   | Composition |       |       |
|------------------|-------------|-------|-------|
|                  | 200°C       | 300°C | 500°C |
| <i>p</i> -Xylene | 21.8        | 21.1  | 18.9  |
| <i>o</i> -Xylene | 20.6        | 21.6  | 23.0  |
| <i>m</i> -Xylene | 53.5        | 51.1  | 47.1  |
| Ethylbenzene     | 4.1         | 6.2   | 11.0  |

To separate the *p*-xylene isomer from the mixture, an adsorption column is used followed by isomerization of the remaining *ortho/meta* forms to an equilibrium mixture and then recycling to the adsorption column [3]. In this way, pure *p*-xylene is obtained. If the *ortho* isomer is needed, a second adsorption column could be used. The *ortho* isomer is also a valuable precursor for plasticizers [4].

A study of the alkylation of toluene with methanol using shape-selective zeolites to obtain pure *p*-xylene or a mixture of *p*- plus *o*-xylene having a higher percentage of both isomers than that obtained from reforming may be of interest as an alternate route to the currently used method [5]. Venuto and others had shown that acidic faujasites, rare-earth exchanged X- and Y-zeolites and H–Y zeolite are effective alkylation catalysts [6]. Their work created interest in studying the alkylation reaction of toluene with alcohols by other investigators [5,7,8].

Toluene produced is always in excess of demand

for chemical use, and the major part is essentially dealkylated to benzene or disproportionated to benzene and xylene mixture. It is worth mentioning that Saudi Arabia is currently producing more methanol than needed for local consumption. If the export market becomes unfavorable, new outlets for methanol could be sought. A possible one could be the alkylation of toluene with methanol.

### EXPERIMENTAL

#### Preparation of K–NaY, Mg–NaY, and Ca–NaY Zeolites

Zeolites used for the investigation were prepared by ion exchange of NaY zeolite with a fixed amount of 10% solutions of the chlorides of the corresponding cations. After four hour of stirring at 60°C the mixture was cooled, decanted, and washed several times with deionized water till completely free from ions. Decanted solution plus the washing was analyzed for Na<sup>+</sup> and also the cation used for the exchange by the atomic absorption technique. The percent exchange was determined. For the higher exchange level, the same procedure was repeated for another four hours using fresh chloride solution.

#### Preparation of H–NaY Zeolite

A similar procedure to that mentioned above was used except the chloride solution was NH<sub>4</sub>Cl. After completing the exchange as above, the prepared catalyst was dried in an oven at 105°C for one hour, and then heated to 450°C for three hours to complete the deamination reaction. For the more highly-exchanged catalyst, a second exchange was made for another four hours. Impregnation of the catalyst was made by using aqueous solutions of P<sub>2</sub>O<sub>5</sub> and NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>.

#### Catalyst Conditioning

Before any one of the prepared catalysts was used for the alkylation reaction, it was calcined in a stream of air for three hours at 400°C, then in a stream of dry nitrogen for another hour. An IR spectrum was taken for NaY before the ion exchange and for the prepared calcined catalysts to ensure that the unit cell has not been affected.

### Toluene Alkylation

A fixed-bed tubular reactor system was used for the study. A quartz tube having a length of 180 mm and internal diameter 12 mm served as the reactor. Heating was done by the use of a tubular furnace. The bed temperature was adjusted to the required value at least one hour before starting the reaction. A thermocouple was used to measure the bed temperature at two points. A thermometer was also used for the same purpose. Reactants (toluene:methanol mole ratio 2:1) were introduced to the bed by a small feeding pump and the flow was measured by a wet flow-meter. Products were collected in two traps, an ice-cooled trap followed by an acetone-dry-ice trap. The last trap was connected to a drying tube filled with Drierite.

After completing the reaction (approximately one hour), a slow stream of dry nitrogen was passed through the bed to drive off liquids entrapped in the catalyst. Both traps were weighed to determine the mass of the products. The liquid in the first trap had two layers, an aqueous layer containing methanol and water, and the upper hydrocarbon layer containing the products and unreacted toluene. In a few experiments, some unreacted methanol was found in this layer. The aqueous layer was analyzed by using a capillary-tube technique to determine the percent of methanol. A standard curve using known amounts of methanol-water mixture was made for this calculation. The determined values were used for calculating methanol conversion.

GLC analyses of the hydrocarbon layer were made by the use of a 6 m by 0.5 inch internal diameter stainless steel column packed with 5 wt % bentone and 15 wt % didecylphthalate on 80/100 mesh acid-washed Chromosorb P. A Varian 3700 model with TCS and temperature programming between 70°C and 140°C has a good separation for the xylene isomers.

### RESULTS AND DISCUSSION

Alkylation of toluene with methanol using zeolites has previously been investigated [7,8]. Results had shown that the selectivity for *p*-xylene is optimized when the pore diameter is just enough to allow the reactant molecules to enter the supercage of the zeolite but is small enough to allow *p*-xylene to diffuse out more selectively than the other two isomers. The effect of exchange of certain cations for Na<sup>+</sup> in Y-zeolite, and of the extent of that exchange,

on the alkylation activity and selectivity for *p*-xylene as well as for *o*-xylene was not well investigated.

In this work, the effect of exchanging Na<sup>+</sup> in NaY zeolite for K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, and H<sup>+</sup> was studied at three temperatures, 250, 300, and 350°C. Two different exchange levels were used for each cation. For K-NaY zeolite, only one exchange level was used since it has shown a very low alkylation activity. The effect of impregnating H-NaY catalyst with some phosphorus compounds, on the alkylation activity was also investigated. Kaeding and others have shown that such impregnation for ZSM-5 resulted in higher *p*-xylene selectivity [9].

In a preliminary investigation, Na-Y zeolite was tested for the alkylation reaction at 250 and 350°C. No alkylation activity was observed for this catalyst as evidenced from the absence of xylenes or polyalkylated products. The amount of nonaromatic hydrocarbon products for the 250°C reaction was only 2.6 wt % of the hydrocarbon mixture which contained only unreacted toluene and some methanol. When the reaction was run at 350°C, the nonaromatic hydrocarbons increased to 12.8 wt % and benzene resulting from toluene dealkylation was 2.1 wt %. These results indicated that this catalyst is not suitable for the alkylation reaction but may be suitable for dehydration of methanol. It has been observed that the dehydrated NaY zeolite does not show strong OH bands indicating low protonic character [10].

When 57% Na<sup>+</sup> ions were exchanged by K<sup>+</sup> ions and the alkylation reaction tried at 250, 300, and 350°C, no alkylation activity was noticed except for the 350°C reaction. However, toluene conversion was only 1.8% and selectivity for *p*-xylene was very low (10.5%). This catalyst has shown a lower methanol dehydration activity than NaY zeolite and the amount of nonaromatic hydrocarbons was only 2.4 wt %. No further investigation of this catalyst was pursued.

Investigating Mg-NaY zeolite was done for two levels, a low 46% and an intermediate 60% exchange level. Results of the investigation at 300 and 350°C are shown in Table 2. The lower level magnesium catalyst was found to exhibit a low alkylation activity at the two temperatures. However, selectivity for *p*-xylene was 45.5% at 300°C.

The intermediate magnesium catalyst has shown a much higher alkylation activity only at 350°C, as evidenced from toluene conversion of 14.6%. The

**Table 2.** Alkylation of Toluene with Methanol using Mg–NaY Zeolites

| Experiment Number                       | 2    | 3    | 8    | 9    |
|---|------|------|------|------|
| <u>Reaction Conditions</u>              |      |      |      |      |
| Catalyst exchange level                 | 46   | 46   | 60   | 60   |
| Temperature, °C                         | 300  | 350  | 300  | 350  |
| Time on Stream, h                       | 0.8  | 1.0  | 1.0  | 1.0  |
| WHSV, h <sup>-1</sup>                   | 3.2  | 3.9  | 1.2  | 1.4  |
| <u>Conversion %</u>                     |      |      |      |      |
| Toluene                                 | 2.3  | 2.8  | 2.1  | 14.6 |
| Methanol                                | 37.8 | 38.0 | 37.0 | 47.3 |
| <u>Hydrocarbon Layer, Analysis wt %</u> |      |      |      |      |
| Benzene                                 | –    | –    | –    | 3.2  |
| Toluene                                 | 95.7 | 94.9 | 96.9 | 83.6 |
| Ethylbenzene                            | –    | –    | –    | –    |
| Xylenes                                 | 2.6  | 3.0  | 2.2  | 11.9 |
| Polyalkylates                           | –    | –    | –    | –    |
| Others (nonaromatic hydrocarbons)       | 1.6  | 2.0  | 0.8  | 1.4  |
| <u>Xylene Composition</u>               |      |      |      |      |
| <i>Para</i>                             | 42.3 | 39.8 | 45.5 | 35.6 |
| <i>Ortho</i>                            | 30.8 | 23.4 | 22.7 | 21.0 |
| <i>Meta</i>                             | 26.9 | 36.8 | 31.8 | 43.4 |
| <i>Para plus ortho</i>                  | 73.1 | 63.2 | 68.2 | 56.6 |
| <u>Aqueous Layer, Analysis wt %</u>     |      |      |      |      |
| Water                                   | 36.2 | 36.7 | 45.5 | 65   |
| Methanol                                | 63.8 | 63.3 | 54.5 | 35   |

effect of increasing the temperature for both catalysts was generally a decrease in *p*-xylene selectivity and a decrease in *p*- plus *o*-xylene. For the intermediate level catalyst, *para*- plus *ortho*- decreased from 68.2% obtained at 300°C to 56.6% at 350°C. Some dealkylation activity was also noticed for this catalyst at 350°C, as evidenced by the presence of 3.2 wt % benzene. However, nonaromatic hydrocarbons were generally low.

Results of the alkylation using two calcium exchange levels (59 and 72%) are shown in Table 3. The investigation of the intermediate level was done only at 350°C. By comparing the results with those for the intermediate Mg–NaY at the same temperature, Ca–NaY has shown a lower alkylation activity. However, the selectivities for *p*-xylene were

**Table 3.** Alkylation of Toluene with Methanol using Ca–NaY Zeolites

| Experiment Number                       | 10   | 11   | 12   | 18   |
|---|------|------|------|------|
| <u>Reaction Conditions</u>              |      |      |      |      |
| Catalyst exchange level                 | 72   | 72   | 72   | 59   |
| Temperature, °C                         | 250  | 300  | 350  | 350  |
| Time on Stream, h                       | 1    | 1    | 1    | 1    |
| WHSV, h <sup>-1</sup>                   | 1.4  | 1.6  | 2.12 | 1.74 |
| <u>Conversion %</u>                     |      |      |      |      |
| Toluene                                 | 3.1  | 5.8  | 12.2 | 10.1 |
| Methanol                                | 41.3 | 65.0 | 60.0 | 50.7 |
| <u>Hydrocarbon Layer, Analysis wt %</u> |      |      |      |      |
| Benzene                                 | –    | –    | 0.3  | 1.2  |
| Toluene                                 | 94.3 | 89.7 | 83.7 | 88.3 |
| Ethylbenzene                            | –    | –    | –    | –    |
| Xylenes                                 | 1.0  | 3.8  | 8.8  | 10.0 |
| Polyalkylates                           | 2.8  | 3.0  | –    | –    |
| Others (nonaromatic hydrocarbons)       | 2.0  | 3.6  | 4.1  | 0.5  |
| <u>Xylene Composition</u>               |      |      |      |      |
| <i>Para</i>                             | 40   | 34.2 | 41.2 | 36.9 |
| <i>Ortho</i>                            | 40   | 47.4 | 26.0 | 27.1 |
| <i>Meta</i>                             | 20   | 18.4 | 32.8 | 36.0 |
| <i>Para plus ortho</i>                  | 80   | 81.6 | 67.2 | 64.0 |
| <u>Aqueous Layer, Analysis wt %</u>     |      |      |      |      |
| Water                                   | 40.9 | 64.9 | 59.5 | 46.3 |
| Methanol                                | 59.1 | 35.1 | 40.5 | 53.7 |

similar.

The alkylation activity for the higher Ca–NaY catalyst however was low at 250°C but increased at 350°C as shown from toluene conversion, which increased from 3.1 to 12.2% respectively. The selectivity for *p*-xylene was 40% at 250°C, lowered to 34.2% at 300°C then increased to 41.2% at 350°C. However *para*- plus *ortho*-xylenes were about 80% and did not change much from reacting at 250 and 300°C but decreased to 67.2% at 350°C. This behavior probably indicates the superimposition of isomerization and a mass-transfer factors. The results obtained for this catalyst also indicate a higher methanol dehydration activity than the intermediately exchanged Ca–NaY and Mg–NaY.

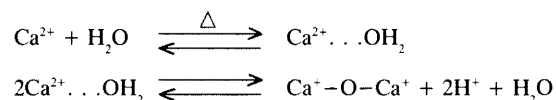
Investigating H–NaY zeolite at two exchange

**Table 4. Alkylation of Toluene with Methanol using H-NaY Zeolites**

| Experiment Number                       | 19   | 20   | 21   | 40   |
|---|------|------|------|------|
| <b>Reaction Conditions</b>              |      |      |      |      |
| Catalyst exchange level                 | 54   | 54   | 54   | 82   |
| Temperature, °C                         | 250  | 300  | 350  | 300  |
| Time on Stream, h                       | 1    | 1    | 1    | 1    |
| WHSV, h <sup>-1</sup>                   | 1.7  | 1.2  | 3.4  | 3.6  |
| <b>Conversion %</b>                     |      |      |      |      |
| Toluene                                 | 13.3 | 15.9 | 1.5  | 18.3 |
| Methanol                                | 55   | 61   | 68   | 76.5 |
| <b>Hydrocarbon Layer, Analysis wt %</b> |      |      |      |      |
| Benzene                                 | —    | —    | 0.3  | 1.8  |
| Toluene                                 | 86.3 | 83.5 | 91.3 | 79.8 |
| Ethylbenzene                            | —    | —    | —    | —    |
| Xylenes                                 | 13.3 | 15.5 | 1.2  | 16.7 |
| Polyalkylates                           | —    | —    | —    | —    |
| Others (nonaromatic hydrocarbons)       | 0.4  | 0.9  | 8.2  | 1.7  |
| <b>Xylene Composition</b>               |      |      |      |      |
| <i>Para</i>                             | 46.8 | 42.6 | 39.0 | 37.7 |
| <i>Ortho</i>                            | 25.4 | 22.7 | 26.0 | 22.8 |
| <i>Meta</i>                             | 27.8 | 34.7 | 35.0 | 39.5 |
| <i>Para plus ortho</i>                  | 72.2 | 65.3 | 65.0 | 60.5 |
| <b>Aqueous Layer, Analysis wt %</b>     |      |      |      |      |
| Water                                   | 54.3 | 58.6 | 66.9 | 50.4 |
| Methanol                                | 45.7 | 41.4 | 32.1 | 49.4 |

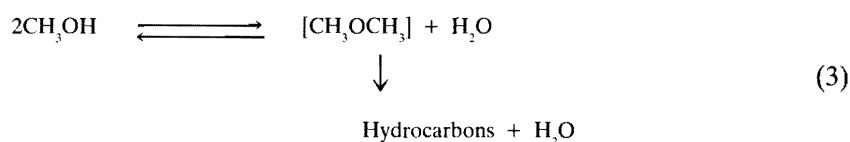
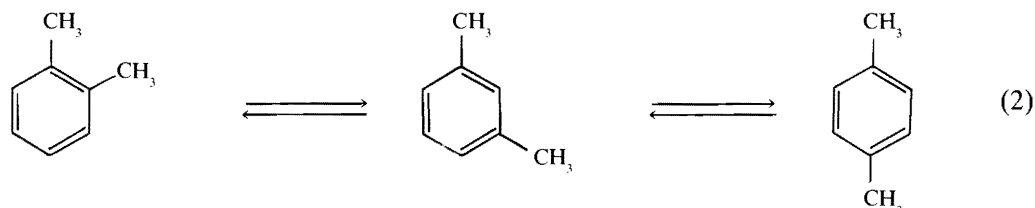
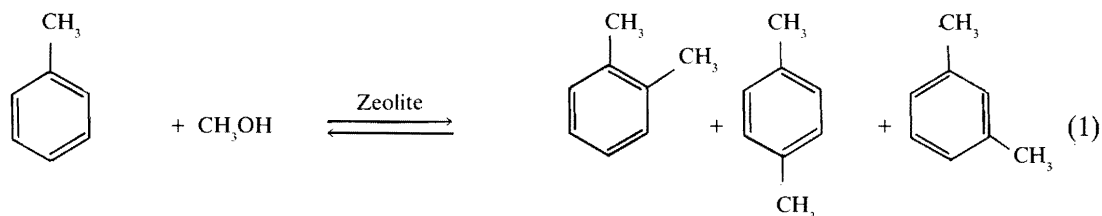
levels (54 and 82%) was done at the three temperatures for the low level and at only 300°C for the high level catalyst. The results which are shown in Table 4, indicate that increasing the acidity of the catalyst (by increasing the exchange level) increased both toluene and methanol conversion. However, the increased acidity lowered *p*-xylene selectivity from 42.6% to 37.7%. The highest selectivity for *p*-xylene (46.8%) was obtained when the low exchanged catalyst was used at 250°C. When the alkylation reaction was run at 350°C, toluene conversion was lowered to 8%. Also polyalkylation has taken place. This may be due to coke formation which was noticed at this temperature. It appears from the results of alkylation using the ion-exchanged catalysts, that the extent of exchange has a direct

effect on the catalytic activity. With Na<sup>+</sup> and K<sup>+</sup> the acidities of the catalysts were not strong enough to affect the alkylation reaction. However, the acidity of NaY was enough to effect some methanol dehydration. When Na<sup>+</sup> was exchanged by the divalent cations Mg<sup>2+</sup> and Ca<sup>2+</sup>, the acidity of the catalysts increased to the extent that alkylation was the major reaction. It has been shown that when CaY zeolite is heated above 300°C, Ca<sup>2+</sup> ions react with water produced in the reaction creating H<sup>+</sup> ions.

**Table 5. Alkylation of Toluene with Methanol over Modified H-NaY Zeolite Impregnated with Phosphorus Compounds**

| Modifying Agent                         | P <sub>2</sub> O <sub>5</sub> | NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub> | NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub> |
|---|-------------------------------|--|--|
| Experiment Number                       | 22                            | 23   | 24   |
| <b>Reaction Conditions</b>              |                               |  |  |
| Catalyst exchange level                 | 82                            | 82   | 82   |
| Temperature, °C                         | 450                           | 300  | 500  |
| Time on Stream, h                       | 1                             | 1  | 1  |
| WHSV, h <sup>-1</sup>                   | 2.1                           | 2.3  | 4.2  |
| <b>Conversion %</b>                     |                               |  |  |
| Toluene                                 | 9.0                           | 19.5   | 8.0  |
| Methanol                                | —                             | 60   | 61   |
| <b>Hydrocarbon Layer, Analysis wt %</b> |                               |  |  |
| Benzene                                 | trace                         | 2.2  | trace  |
| Toluene                                 | 84.4                          | 75.8   | 87.4   |
| Ethylbenzene                            | trace                         | —  | trace  |
| Xylenes                                 | 0.24                          | 20.4   | 0.07   |
| Polyalkylates                           | 9.4                           | 1.0  | 8.61   |
| Others (nonaromatic hydrocarbons)       | 3.7                           | 3.6  | 3.9  |
| <b>Xylene Composition</b>               |                               |  |  |
| <i>Para</i>                             | —                             | 38.0   | 14.3   |
| <i>Ortho</i>                            | —                             | 20.6   | 14.3   |
| <i>Meta</i>                             | —                             | 41.4   | 71.4   |
| <i>Para plus ortho</i>                  | —                             | 58.6   | 28.6   |
| <b>Aqueous Layer, Analysis wt %</b>     |                               |  |  |
| Water                                   | —                             | 37.3   | 43.9   |
| Methanol                                | —                             | 62.7   | 56.1   |

\*This sample contained 2.4 wt % unreacted methanol.



The  $\text{Mg}^{2+}$  ionic radius is smaller than  $\text{Ca}^{2+}$  and accordingly the charge density is higher. The associated electrostatic field for  $\text{Mg}^{2+}$  ions would have a higher ability to dissociate the coordinatively bound water molecules compared to  $\text{Ca}^{2+}$  ions [11].

The alkylation activities of both Ca–NaY (high level) and Mg–NaY (intermediate level) zeolites at 350°C are nearly comparable to that of low H–NaY zeolite at 300°C. However the selectivities for *p*-xylenes using these catalysts were not comparable. This is probably a manifestation of the effect of isomerization activity and the difference in diffusivities of the xylenes within these catalysts. The different reactions taking place are summarized in Equations (1–3). At low temperatures *ortho*, *para* orientation prevails. However as the temperature is increased, the isomerization reaction is favored, decreasing the selectivity for *p*-xylene. Increasing the strong acidity as in the case of high H–NaY decreases the selectivity for *p*-xylene for the same reason mentioned above. It appears that there could be an optimum acidity for the highest *p*-xylene selectivity.

To test for the effect of increasing the acidity on the catalyst activity and selectivity, H–Y high level catalyst was impregnated with 10 wt % phosphoric acid. The same catalyst was also impregnated by using 10 wt % of the less acidic  $\text{NH}_4\text{H}_2\text{PO}_4$ . The results which are shown in Table 5 indicate that impregnation with phosphoric acid favored reaction

(3) as well as reaction (1). However, further alkylation of the xylenes to polyalkylated benzene has taken place. Impregnation with less acidic  $\text{NH}_4\text{H}_2\text{PO}_4$  has increased toluene conversion to 19.5%. However, *p*-xylene selectivity was comparable to that of the unimpregnated catalyst.

In conclusion, it appears that the extent of acidity as well as the number of acid sites associated with the electrostatic fields of the cations has a direct effect on the alkylation activity of the catalyst. However, the observed selectivity is due to the multiple effect of the acidity and relative diffusivity of the xylene isomers.

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