

## Evidence for the Presence of a Bimolecular Pathway in the Isomerization of Xylene on Some Large-Pore Zeolites

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Using deuterated *para*-xylene as a reactant we have found that more than 20% of the *meta*- and *ortho*-xylenes, obtained when using a HY zeolite as catalyst, are formed via a bimolecular mechanism. This involves, as an intermediate complex, a molecule of trimethylbenzene and another of xylene. The bimolecular process is less important in the case of mordenite, and does not occur in Zeolite Beta at low levels of conversion. The relative proportion of uni- to bimolecular mechanism depends on: reaction conditions, zeolite composition, and zeolite structure. Some of the mechanistic conclusions, reached when using xylene isomerization and transalkylation as a test reaction on faujasite zeolites, should be revised in light of these results. Finally, transalkylation between trimethylbenzenes and xylenes is proposed as a test reaction for 12 membered-ring (MR) zeolites since structural differences can be better established than when the conventional xylene isomerization-transalkylation reaction is used. © 1991 Academic Press, Inc.

### INTRODUCTION

The isomerization of *meta*-xylene and ethylbenzene to *ortho*- and *para*-xylene is one of the processes in which the introduction of zeolites as catalysts has represented a clear technological improvement. Practically all of the currently working isomerization plants are using mordenite or ZSM-5 as catalysts. The goal is to minimize the transalkylation reaction while maximizing the catalyst activity for the isomerization, especially to the *para*-isomer (1, 2).

Besides its technological interest, the isomerization of xylenes has been proposed as a test reaction for zeolites and zeolite-like catalysts (3-5). In this sense, the influence of site density, acid strength, and size and shape of the channels can be followed from the relative rates of the isomerization and transalkylation reactions, *para*- to *ortho*-xylene ratio, and distribution of prod-

ucts in the trimethylbenzene isomers (4). When the isomerization of xylenes is used as a test reaction for measuring the influence of acid site density and acid strength, it is always assumed that isomerization is a unimolecular reaction, while transalkylation is a bimolecular one. Therefore, it has been proposed that the increase in the isomerization/transalkylation ratio associated to the decrease in the Al content, can be attributed to a decrease in the density of acid sites which will affect the bimolecular reaction more than the unimolecular reaction (5). This interpretation assumes that two close acid sites are necessary for the bimolecular reaction to occur, something which is difficult to imagine from the point of view of two positive carbocations interacting. Moreover, it is also assumed that the isomerization takes place by a unimolecular 1,2 methyl-shift. The 1,2 methyl-shift mechanism which has been proved to be the only one occurring on amorphous silica-alumina (6), does not have to be the only one operating

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when the reaction takes place on confined spaces as is the case in zeolites. Indeed, Lanewala and Bolton (7) considered the possibility of xylene isomerization on faujasite zeolites occurring by a bimolecular reaction via trimethylbenzenes as intermediates.

There is no doubt that if in some zeolites isomerization takes place extensively via a bimolecular reaction, similar to the one responsible for trimethylbenzene formation, previous results and interpretations made when using xylene isomerization as a test reaction on zeolites should be reviewed.

In this work we have studied the mechanism of xylene isomerization by working at low levels of conversion, on 12 MR zeolites using deuterated xylenes. The influence of parameters such as framework Si/Al ratio and reaction conditions are also discussed.

#### EXPERIMENTAL

##### Materials

A series of ultrastable HY zeolites were prepared by steam-calcination of  $\text{NH}_4\text{NaY}$  samples followed by  $\text{NH}_4^+$  exchange (HYS), as has been reported previously (8). Another series of ultrastable faujasites (HYD) was obtained by dealumination of a NaY (SK-40, Union Carbide) using  $\text{SiCl}_4$  and following the procedure reported in the literature (9). Zeolites Beta samples with different Si/Al ratios, were synthesized following the procedure described previously (10). The activation of the Zeolites Beta was carried out by heating the samples first in a stream of  $\text{N}_2$  up to 773°K followed by calcination at 823°K in an air stream. The resultant samples were twice exchanged with  $\text{NH}_4^+$  and calcined at 823°K. Mordenite (Norton-100) was dealuminated by acid treatment at 353°K. The framework Al content of the faujasites was calculated from the unit cell parameter (ASTM-D 3942-80) and the equation given by Fichtner-Smittler (11). In the case of Zeolites Beta the framework Si/Al ratio was obtained from the  $^{29}\text{Si}$

TABLE I  
Physicochemical Characteristics of the  
Zeolites Studied

Zeolite	Pore size (Å)	$a_0$ (Å)	Al/(Al + Si) <sub>F</sub>	Crystallinity (%)
HYS-1	7.4	24.55	0.185	85
HYS-2		24.42	0.111	90
HYS-3		24.29	0.036	80
HYD-1	7.4	24.56	0.189	90
HYD-2		24.43	0.115	85
HYD-3		24.29	0.033	90
Beta-1	7.5 × 6.7		0.107	75
Beta-2	6.5 × 5.0		0.056	85
Beta-3			0.010	70
Mordenite-1	7.0		0.125	95
Mordenite-2			0.071	90
Mordenite-3			0.031	85

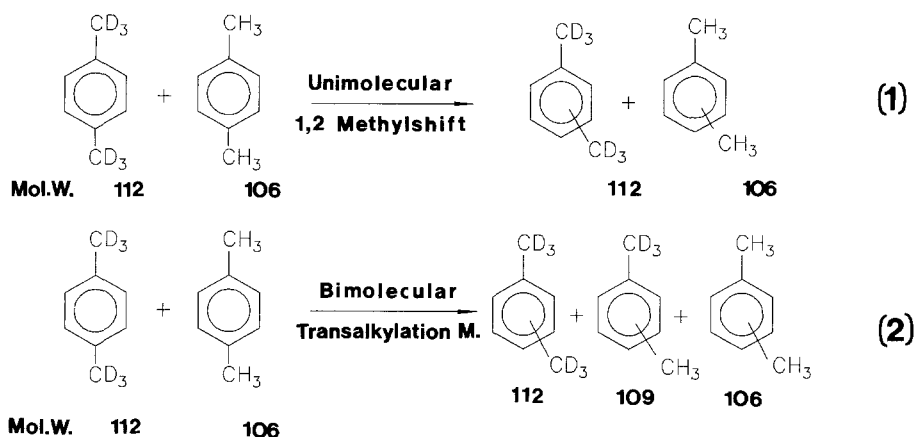
NMR MAS spectra (12), while for mordenites the value comes from chemical analysis (Table 1).

##### Catalytic Experiments

All experiments were carried out in a fixed-bed glass flow continuous reactor (4). A mixture of ≈40% hexadeuterated ( $\text{C}_6\text{H}_4(\text{CD}_3)_2$ ) and ≈60% normal ( $\text{C}_6\text{H}_4(\text{CH}_3)_2$ ) *para*-xylene was fed to the reactor by means of a positive displacement pump.  $\text{N}_2$  was added as a carrier gas with a hydrocarbon partial pressure of  $2 \times 10^4 \text{ N W} \cdot \text{m}^{-2}$ . The contact time was changed by modifying weight of catalyst (15–150 mg) and flow rate (0.20–1.40  $\text{mmol} \cdot \text{h}^{-1}$ ) trying to keep the conversion low and constant in all cases (≈5–8%). The reaction was studied at two temperatures, 493 and 673°K, and in all cases the products were accumulated between 0 and 30 s and analyzed by GC-MS.

#### RESULTS AND DISCUSSION

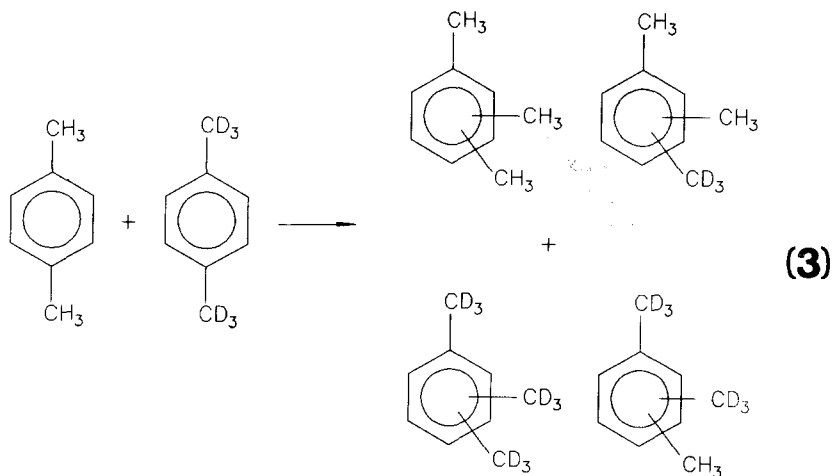
By using as reactant a mixture of deuterated and normal xylenes it is possible, following the reaction Scheme 1, to distinguish between a unimolecular and a bimolecular mechanism for xylene isomerization:



SCHEME 1

In other words, if isomerization takes place only by a unimolecular 1,2 methyl-shift, the compound with a mass of 109 should not be observed in the products. If,

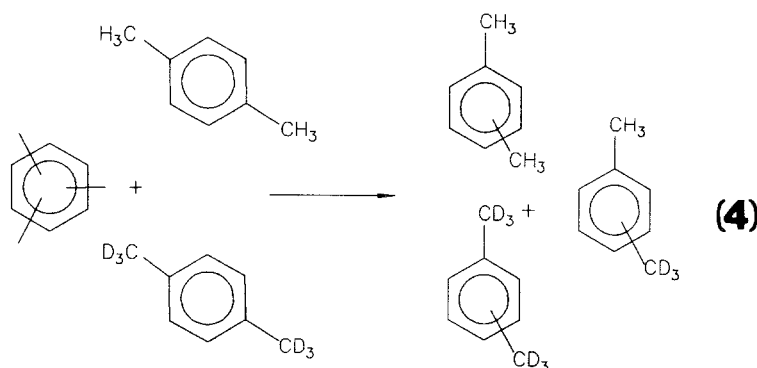
on the other hand, the trimethylbenzenes formed as primary products from the transalkylation of xylenes:



SCHEME 2

can again transalkylate with a xylene molecule before diffusing out of the pores into the gas phase, *meta*-, and *ortho*-xylene with

a molecular weight of 109 will be found even at low levels of conversion:



SCHEME 3

From kinetic experiments using normal xylenes ( $C_6H_4(CH_3)_2$ ), the possibility of reaction (4) occurring cannot be ruled out. Indeed, when feeding normal *para*-xylene, both *meta*- and *ortho*-xylene are found as primary products (Fig. 1). Since it is difficult to accept a 1,3-methyl-shift, to give *ortho*-directly from *para*-xylene, one must assume that primary products can undergo secondary reactions before passing from the zeolite pores into the gas stream.

When the isomerization reaction has been carried out using the mixture of deuterated and undeuterated xylenes on faujasite zeolites, we have found in all cases in the isomerized products, the 109 mass compound indicating that some of the xylene isomers are formed via a bimolecular mechanism involving transalkylation of methyl groups.

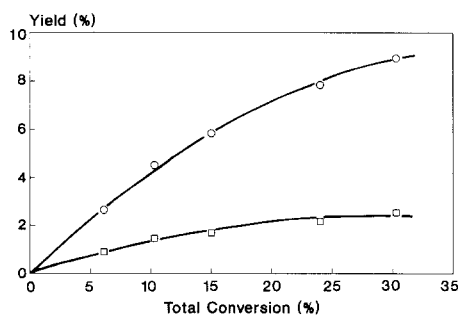


FIG. 1. Yield versus conversion for (○) *meta*- and (□) *ortho*-xylenes obtained during the isomerization of *para*-xylene at 623°K.

#### *Influence of the Reaction Temperature on the Mechanism of Isomerization*

In Fig. 2 the product distribution obtained at 493 and 673°K of reaction temperature with Zeolites HYS-1,2,3 is given. These data show that for all catalysts, a higher proportion of the isomer with molecular weight of 109 is obtained at the highest reaction temperature. This observation would indicate that the isomerization via transalkylation has a higher activation energy than the isomerization via 1,2 methyl-shift; a fact that agrees with the well known fact that transalkylation of xylenes to give toluene and trimethylbenzenes requires 3–4 Kcal.mol<sup>-1</sup> more than the isomerization.

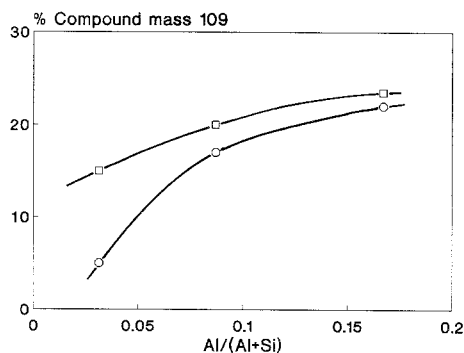


FIG. 2. Percentage of the *ortho*-xylene with 109 molecular weight obtained in the *ortho*-xylene fraction, at 493°K (○) and 673°K (□) at levels of conversion in the range 5.5–7.5%.

These results suggest that when the isomerization of xylenes is carried out on zeolite catalysts in which both the uni- and bimolecular mechanisms are simultaneously operating, if the activation energy must be used to compare catalysts from different workers, one must be sure that the same range of temperature has been chosen to compare the activation energy values. Our observation also limits the usefulness of xylene isomerization as a test reaction, if zeolite catalysts of different intrinsic activity are compared by modifying the reaction temperature in order to keep constant conversion. It must be pointed out that these considerations are limited only to those zeolites for which both types of isomerization mechanisms apply.

#### *Influence of the Conversion Level*

The results from Fig. 3 show that for faujasite zeolites, when increasing the level of conversion, the selectivity to the 109 isotope increases. This is not surprising since the selectivity to trimethylbenzenes increases with conversion, and the isomerization via transalkylation involves trimethylbenzene intermediates. Again, these results show that in the isomerization of xylene, special care should be taken in working at the same level of conversion in order to achieve a

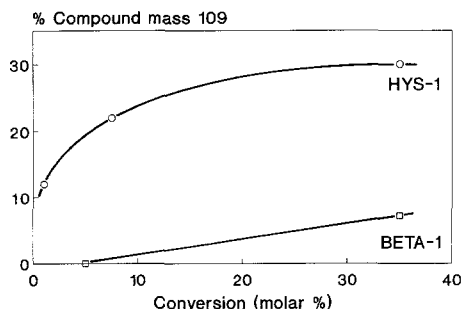


FIG. 3. Influence of the level of conversion on the proportion of *ortho*-xylene with molecular weight 109 formed, in the *ortho*-xylene fraction, during the isomerization of *para*-xylene at 493°K on HYS-1 and Beta-1 zeolites.

reliable comparison of the activity and selectivity of zeolites.

#### *Influence of the Framework Si/Al Ratio*

The isomerization results on ultrastable Y zeolites with different framework Si/Al ratios (Fig. 2), clearly show that the amount of the xylene isomer with 109 molecular weight formed, decreases when decreasing the framework Al content. This observation correlates well with the fact that the selectivity for transalkylation of xylenes to give toluene and trimethylbenzenes decreases when decreasing the framework Al content of ultrastable Y zeolites (13). Several hypotheses can be formulated to explain why bimolecular reactions are more affected by dealumination than the competing unimolecular ones. One hypothesis (5) assumes that the bimolecular transalkylation is carried out on two close acid sites probably by a Langmuir–Hinselwood type reaction. It is obvious that such formulation cannot involve two Wheland's complexes within close interaction, and should be better regarded as the interaction between one Wheland complex and another molecule in its close vicinity and "retained" by the strong electric fields present into the zeolite cavities. From this point of view the presence of charged extraframework Al species (EFAL) can play a significant role by influencing the adsorption properties.

In our case, we have considered that dealumination results not only in changes of the total number and density of acid sites (and hence of the frequency factor and kinetic rate constant ( $k$ ) through the concentration of active sites  $[S_0]$ ) since:

$$k = k_0[S_0]$$

but also of the adsorption characteristics ( $K$ ) of the zeolite.

It seems therefore that if the adsorption capacity and adsorption selectivity change upon dealumination, the relative rate of bimolecular to unimolecular reactions will also change independent of the number of active sites involved in the event.

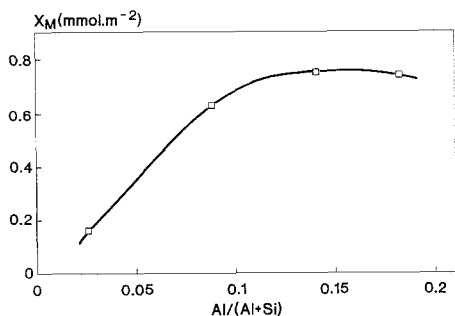


FIG. 4. Amount of xylene adsorbed on HYS samples with different framework Al contents, from the equilibrium isotherms obtained at 473°K.

In order to check this hypothesis, the adsorption of *meta*-xylene has been carried out on a series of HYS samples with different framework Si/Al ratio and the results are given in Fig. 4. It appears that upon dealumination the amount of adsorbed xylene strongly decreases on samples with less than  $\approx 20$  Al/U.C. This behavior is quite similar to the evolution of the amount of 109 isomer with the framework Al content of the zeolite (Fig. 2). In conclusion, it appears that changes in the adsorption characteristics of the zeolite will produce changes in the relative rate for uni- and bimolecular reactions in general, and on the uni- and bimolecular type of isomerization in particular.

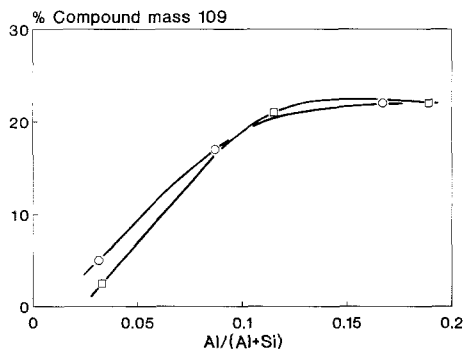


FIG. 5. Percentage of *ortho*-xylene with 109 molecular weight obtained on HYS (○), and HYD (□), at 493°K reaction temperature at levels of conversion in the range 5.5–7.5%.

In order to study the possible influence of the dealumination procedure, the product distribution during the isomerization of the xylene mixture containing the deuterated compounds has also been studied on  $\text{SiCl}_4$  (HYD) dealuminated zeolites. Results from Fig. 5 show a similar behavior for the two set of samples.

#### *Influence of the Zeolite Structure*

It has been shown (4) that the ratio isomerization/transalkylation is strongly dependent on zeolite structure. Indeed, the inhibition of the transalkylation of dimethylbenzenes in ZSM-5 zeolite has been used as a typical example of transition state shape selectivity (14). On this zeolite the bimolecular reaction is much more space constricted than unimolecular isomerization,

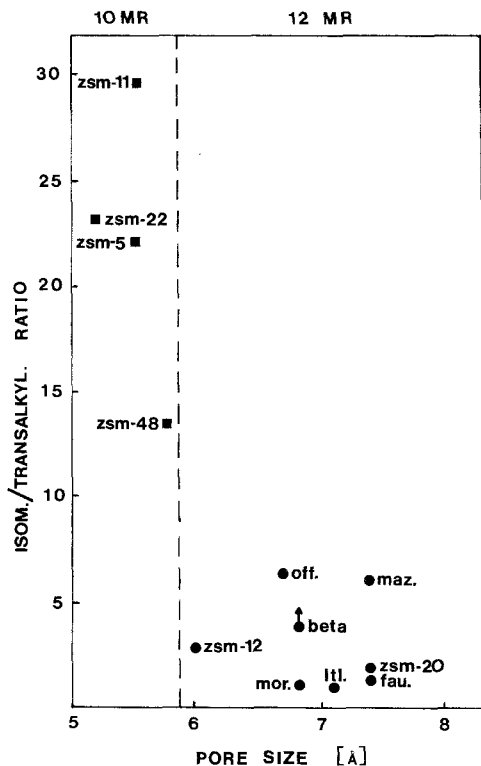


FIG. 6. Isomerization to transalkylation ratio as a function of pore diameter for 10 and 12 MR zeolites, observed during the isomerization of *meta*-xylene at 623°K and low levels of conversion (4–8%).

TABLE 2

Percentage of *Ortho*-Xylene with a 109 Molecular Weight, Obtained during the Isomerization of *Para*-Xylene at 493°K

Zeolite	Conversion (%)	109/106 + 109 + 112 ( $\times 10^2$ )	Selectivity TMB (%)
HYS-1	<1	12	21
HYS-1	7.5	22	24
HYS-1	35	30	29
HYS-2	6.0	17	24
HYS-3	5.5	5	22
HYD-1	6.0	22	23
HYD-2	8.5	21	25
HYD-3	5.5	2.5	21
Beta-1	5.0	—	8
Beta-1	35	7.2	17
Beta-2	7.5	—	6
Beta-3	7.0	—	5
Mordenite-1	4.5	6.8	25
Mordenite-2	7.5	1.2	23
Mordenite-3	7.0	—	18

and therefore a small amount of trimethylbenzenes are formed. Figure 6 shows the isomerization to transalkylation ratio as a function of the zeolite pore diameter, at a constant level of conversion of  $\approx 6\%$ , and a clear difference between 10 and 12 MR zeolites is observed (15).

Since transalkylation of xylenes is strongly hindered in medium-pore zeolites, it should be expected that only the unimolecular isomerization process should take place in these zeolites. Indeed, when the experiments were carried out using deuter-

ated *para*-xylene on H-ZSM-5 (Si/Al = 18), partially deuterated (MW 109) products were not found, which would agree with the strong geometrical restrictions for bimolecular reactions inside the pores of the ZSM-5 zeolite. However, in the case of 12 MR zeolites, transalkylation can take place extensively, and one could expect on these zeolites that the isomerization of xylenes would take place by both a uni- and a bimolecular process.

In Table 2 the percentage of the 109 isomer is given for three large-pore zeolites, i.e., faujasite, Beta, and mordenite, within various framework Si/Al ratio. The results obtained show that, while in faujasite zeolites more than 20% of the total isomerization can take place via transalkylation, none of the isomerization occurs via a bimolecular mechanism in the case of Beta zeolite at low levels of conversion. In the case of mordenite, the bimolecular mechanism for isomerization takes place, but it is much more impeded than in Zeolite Y.

In the case of Zeolite Beta the transalkylation reaction between two xylene molecules to give toluene and trimethylbenzene is strongly hindered geometrically in the sinusoidal channels of the Beta structure (16) (Fig. 7), and would only take place in the rectilinear ones. The geometrical restrictions in the sinusoidal channels would explain the relatively high isomerization to transalkylation ratio observed with Zeolite Beta in comparison with faujasite or mordenite (Fig. 6). However, one must take into account that the formation of xylene iso-

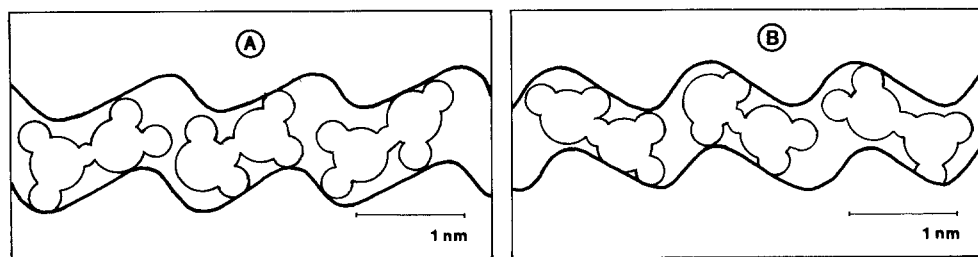


FIG. 7. Transalkylation of a methyl group between two xylene molecules inside the rectilinear (A), and the sinusoidal channels (B) of a Beta zeolite.

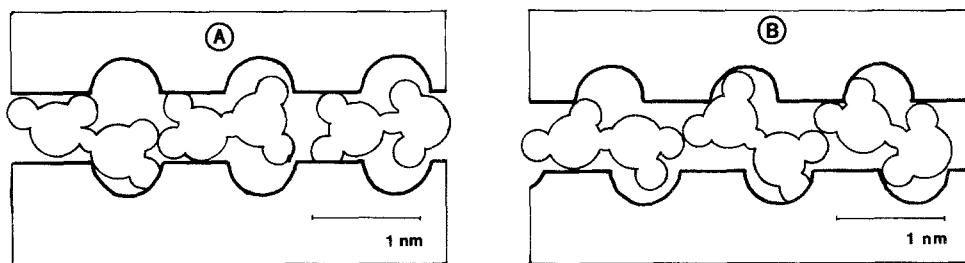


FIG. 8. Transalkylation of a methyl group between a xylene and a trimethylbenzene molecules inside the rectilinear (A) and the sinusoidal channels (B) of a Beta zeolite.

mers via the bimolecular process can be even more hindered since one molecule of trimethylbenzene and another of xylene must be accommodated in the intermediate complex. Figure 8 clearly shows that this complex is very difficult to accommodate in either the rectilinear or the sinusoidal channels. Therefore, due to geometrical constraints, Zeolite Beta behaves, from the point of view of the isomerization process, as 10 MR zeolites. Therefore, none of the isomers are formed by a bimolecular process; all are formed by a 1,2 methyl-shift.

#### CONCLUSIONS

It has been shown that during the isomerization of xylenes in the large-pore zeolites which can accommodate, as an intermediate complex, a molecule of trimethylbenzene and a molecule of xylene, a part of the xylene isomers is formed by a bimolecular mechanism involving the transalkylation of a methyl group. In those cases, isomerization takes place by both a uni- and a bimolecular mechanism. The relative proportion of these two mechanisms depends on reaction conditions (contact time, temperature), zeolite composition (framework Si/Al ratio), and geometrical characteristics of the zeolite. In this way it has been seen that when the framework Al content decreases, the adsorption capacity of the Y zeolite decreases, and the ratio of uni- to bimolecular isomerization increases. On the 12 MR zeolites studied, faujasite can produce more than 20% of the total isomerization via the bimo-

lecular mechanism. This percentage falls by a third when using mordenite. It is remarkable that, on Zeolite Beta, the xylenes are only isomerized by 1,2-methyl-shift due to geometrical restrictions to accommodate the bimolecular intermediate complex, formed by a trimethylbenzene and a xylene molecule.

From this study, it becomes apparent that if xylene isomerization is to be used as a test reaction, it cannot be assumed in some of the 12 MR zeolites that all the isomers are formed by a unimolecular reaction, with all the corresponding implications on kinetic models, activation energies, turnover frequencies, and hypotheses on the influence of the density of framework Al.

Finally, based on this work we propose the transalkylation between trimethylbenzenes and xylenes, using deuterated compounds, as a test reaction, which allows one to establish structural differences between 12 MR zeolites. These differences cannot be as clearly established by using the conventional xylene isomerization and transalkylation as a test reaction.

#### ACKNOWLEDGMENTS

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