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A Simple Method for Determining the Relative Significance of the Unimolecular and Bimolecular Pathways of Xylene Isomerization over HY Zeolites

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The transformation of pure xylenes, of pure trimethylbenzenes (TMB), and of mixtures of *m*-xylene ($\geq$95 mol%) and 1,2,4-trimethylbenzene was carried out at 623 K on a HY zeolite with a framework Si/Al ratio equal to 16. TMB isomerization was 4 to 10 times faster than xylene isomerization. The disproportionation of 1,2,4-TMB was 4 to 7 times faster than the disproportionation of *p*-xylene and of the other TMB isomers and 30 and 55 times faster than that of *m*-xylene and of *o*-xylene. The addition of 1,2,4-TMB to the *m*-xylene reactant caused a significant increase in the formation of xylene isomers and particularly of *o*-xylene owing to a rapid transalkylation between 1,2,4-TMB and *m*-xylene. The high rate of the latter reaction rendered possible, besides the unimolecular isomerization process, a direct isomerization of *m*-xylene through two successive bimolecular reactions, *m*-xylene disproportionation followed by transalkylation between the trimethylbenzene produced and *m*-xylene. From a simple model it was shown that the *para*/*ortho* selectivity of the bimolecular *m*-xylene isomerization was very different from (much lower than) that of the unimolecular isomerization. This explains why in a series of HY zeolites with different framework Si/Al ratios the greater the disproportionation to isomerization rate ratio (*D*/*I*) the lower the *para*/*ortho* selectivity. The value of the *para*/*ortho* selectivity of the unimolecular process was determined accurately from the extrapolation at *D*/*I* = 0 of the *para*/*ortho* ratio. Low values of *D*/*I* were obtained by inhibiting selectively *m*-xylene disproportionation by adding methylcyclohexane to the reactant. It is shown that the relative proportion of unimolecular and bimolecular mechanisms can be estimated from the experimental values of the *para*/*ortho* ratio. © 1996 Academic Press, Inc.

INTRODUCTION

On acid catalysts *m*-xylene undergoes two competitive transformations, isomerization into *o*- and *p*-xylenes and disproportionation into toluene and trimethylbenzene. Three types of selectivity can be defined, isomerization selectivity (*para-*/*ortho*-xylene ratio), disproportionation selectivity (distribution of trimethylbenzene isomers), and disproportionation/isomerization selectivity (*D*/*I*). With shape-selective zeolites the *para*/*ortho* selectivity depends mainly on the diffusion path of xylenes (size of the pores, crystallite size, etc.) (1–8) hence it is a good criterion for characterizing this path. More information on the zeolite pores can be obtained from trimethylbenzene distribution, which can depend both on the diffusion path and on the space available near the acid sites, and from the *D*/*I* ratio which depends on the same parameters as well as on the zeolite acidity (5, 7, 9, 10).

m-Xylene transformation can also be used for characterizing the acidity, particularly with non-shape-selective catalysts. Indeed isomerization and disproportionation are both catalyzed by the protonic acid sites (9, 11–14). Moreover the sites active for xylene isomerization and disproportionation at 623 K must be able to retain pyridine adsorbed at least at 600 K, i.e., their acid strength is intermediate between the one necessary for *n*-hexane cracking at 673 K (pyridine adsorbed at least at 800 K) and that for 3,3-dimethyl-1-butene isomerization at 473 K (at least at 500 K) (15).

It is generally admitted that xylene isomerization involves transformation of benzenium ion intermediates through methyl shift. This transformation being the limiting step, no direct isomerization of *p*-xylene into *o*-xylene (and vice versa) can occur (9, 16).

The mechanism of xylene disproportionation is much more complex as it involves six successive steps (Fig. 1) and two different types of intermediates, benzylic carbocations and trimethyldiphenylmethane, protonated or not protonated (4, 9, 14). From an increase in the *D*/*I* ratio with the aluminium content of Y zeolites it was concluded that while the unimolecular process of isomerization required only one acid site for its catalysis, two acid sites were necessary for catalyzing disproportionation (5, 14). This seems quite possible when the mechanism in Fig. 1 is examined. Indeed two different protonic sites could be involved in step 3 (and 1, 2) and in step 4 (and 5, 6).

However recent results shows that the situation is not as simple, as this, in particular for the transformation of xylenes on zeolites. Indeed no clear relation was obtained between the *D*/*I* ratio and the density of the acid sites when a large series of zeolites (i.e., of Y zeolites) was considered

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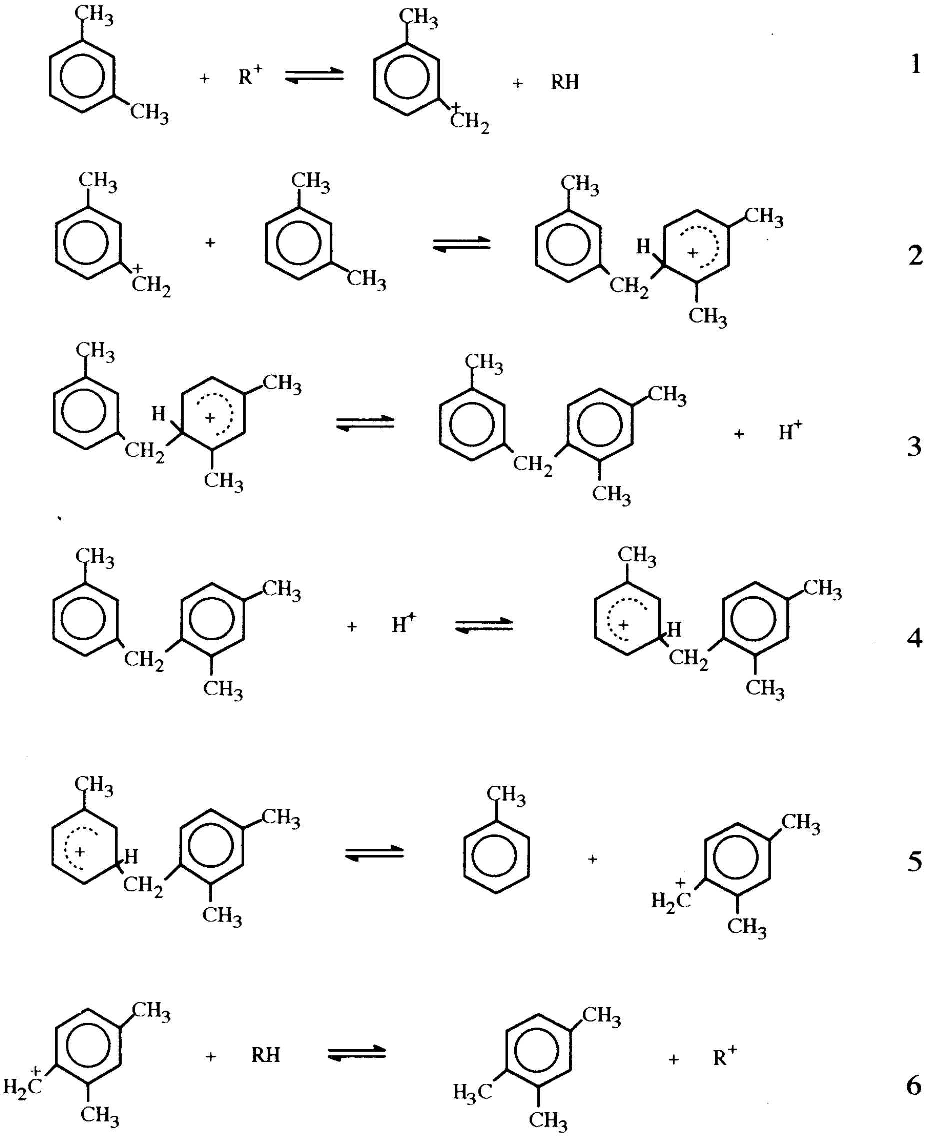


FIG. 1. Mechanism of *m*-xylene disproportionation. RH: xylenes, trimethylbenzenes, toluene, R^+, the corresponding benzylic carbocations.

(17, 18). Furthermore the presence of a bimolecular pathway in the isomerization of xylene on some large pore zeolites, first proposed by Lanewala and Bolton (19), has been recently confirmed (20, 21) by the investigation of the transformation of a mixture of hexadeuterated ($C_6H_4(CD_3)_2$) and of nondeuterated *p*-xylene. This bimolecular isomerization would occur through two successive steps, disproportionation of the xylene reactant followed by a transalkylation reaction between trimethylbenzene and the reactant. The existence of a *direct* bimolecular isomerization of xylenes requires that the kinetic rate constant of the second step of transalkylation be greater than that of disproportionation.

In this work we discuss the possibility of a direct bimolecular isomerization pathway by comparing the rate of xylene and trimethylbenzene transformations. Moreover a simple method is proposed to estimate the relative percentages of the mono- and bimolecular isomerization pathways.

EXPERIMENTAL

1. Catalysts

Five of the six HY zeolite samples used were supplied by PQ Zeolites B.V. (CBV series), the sixth by Union Carbide (LZY 82). Table 1 gives the unit cell parameters a_0 determined through the ASTM-D 3942-80 method, the framework Si/Al ratio calculated from a_0 with the equation given by Breck and Flanigen (22), and the relative crystallinity estimated from XRD (ASTM-D 3906-80 method) and from

TABLE 1

Physicochemical Characteristics of HY Zeolite Samples

Sample	Framework Si/Al ratio	a_0 (Å)	Crystallinity (%) XRD	Crystallinity (%) Adsorption
HY-1	3.9	24.53	100[a]	100[a]
HY-2	13.6	24.35	73	
HY-3	16.0	24.29	70	87
HY-4	19.2	24.27	50	92
HY-5	30.2	24.25	50	87
HY-6	4.5	24.49	100	

[a] Reference.

nitrogen adsorption; in the latter case the crystallinity is taken as the ratio between the micropore volumes of the zeolite and of the reference sample (23).

2. *Catalytic Experiments*

Xylene and trimethylbenzene transformations were carried out in a flow reactor under the following conditions: 623 K, $p(\text{Hydrocarbon}) = 0.0625$ bar, $p(N_2) = 0.9375$ bar, WWH (weight of reactant per hour and per weight of catalyst) = 20 to 1200 h^{-1}. Prior to being used, the zeolite samples were calcined *in situ* at 773 K under dry air flow (3.6×10^3 ml h^{-1}) for 10 h, the samples being kept under nitrogen flow during cooling to reaction temperature. In order to limit the zeolite deactivation, short values of time-on-stream were used and the catalysts were regenerated under dry air flow at 773 K for 4 h after each experiment. This regeneration treatment allows one to keep a constant activity value for at least ten experiments. The analysis of the effluents was carried out for time-on-stream long enough (15 to 65 s depending on the reactant flow rate) to obtain steady state conditions: constant value of the GC peak area hence a constant value of the reactant pressure, conversion and product distribution quite similar to those obtained from extrapolation of these data at zero time-on-stream and practically no change in these data for longer time-on-stream values in the case of a stable zeolite, toluene/trimethylbenzene ratio close to 1, showing the absence of chromatographic effects.

All the aromatic reactants were supplied by Fluka (>99.5 wt% pure for xylenes and >98 wt% pure for 1,2,4- and 1,3,5-TMB and >95 wt% for 1,2,3-TMB). They were percolated on a silica gel column so as to eliminate traces of peroxides which have a strong inhibiting effect on aromatic transformations (24).

Analysis of reaction products was performed on-line by gas chromatography using a 30-m fused silica J&W DB WAX capillary column. The temperature programme was as follows: 308 K for 17 min followed by temperature increase at 6 K min^{-1} to 383 K and keeping at this temperature for 10 min.

RESULTS AND DISCUSSION

1. *Possibility of a Direct Isomerization of Xylenes Through Disproportionation Products*

Figure 2 shows that on the HY-3 zeolite *o*-xylene appears as a primary product of *p*-xylene transformation. This observation cannot be explained by the monomolecular mechanism. Therefore part of isomerization occurs most likely through a bimolecular pathway involving as successive steps the reactions

$$2X_R \rightleftharpoons T + TMB \qquad [1]$$

$$TMB + X_R \rightleftharpoons \underset{(o,m,p)}{X} + TMB, \qquad [2]$$

where X_R, T, and X(o, m, p) are the xylene used as a reactant, toluene, and xylene mixture respectively.

As shown in Section 2.1, reaction [2] can lead to all the xylene isomers, which explains the apparent direct interconversion of the *para* and *ortho* isomers. It can be noticed that disproportionation of trimethylbenzenes could also participate, in addition to reaction 2, in transformation of xylenes.

$$2\,TMB \rightarrow \underset{(o,m,p)}{X} + TTMB, \qquad [3]$$

where TTMB denotes tetramethylbenzenes.

For *o*-xylene to appear as a primary product of *p*-xylene transformation reaction 2 or/and reaction 3 must be much faster than reaction 1. To verify this point the rates of reactions 1 and 3 were determined accurately from the initial slopes of the curves giving the conversion of the three xylene isomers and of the trimethylbenzene isomers into their disproportionation products. Simultaneously the rates of isomerization of the xylene and trimethylbenzene isomers were measured. Examples of the curves, conversion vs contact time, are given in Fig. 3. Table 2 gives the initial rates of disproportionation and isomerization of the

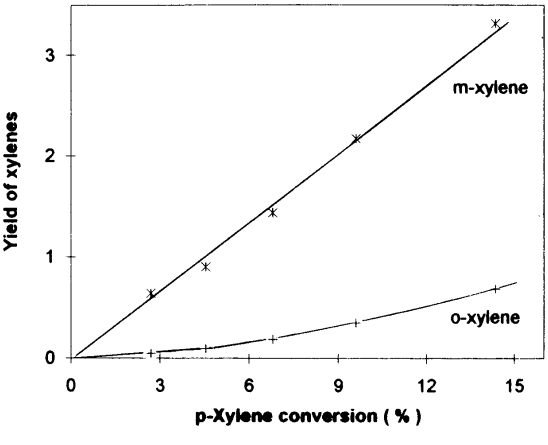


FIG. 2. *p*-Xylene transformation on the HY-3 sample; Yields of *m*- (∗) and *o*- (+) xylenes produced versus *p*-xylene conversion.

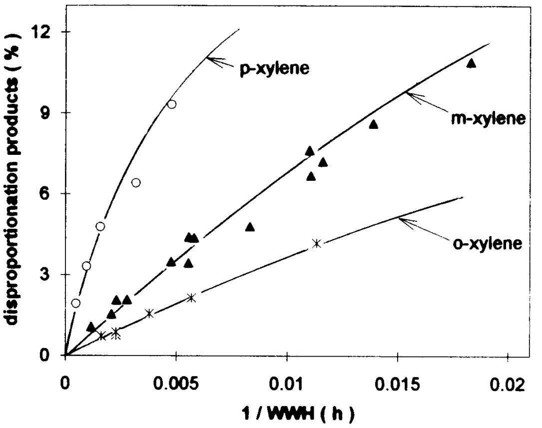


FIG. 3. Effect of contact time (1/WWH) on the yields in disproportionation products resulting from *o*-, *m*-, and *p*-xylene transformations.

various xylene and trimethylbenzene isomers as well as the average turnover frequencies (based on the theoretical density of the protonic acid sites calculated from the unit cell formula). It should be remarked that all the kinetic values (except those related to 1,2,3-TMB transformation due to 5% isomers in the reactant) are obtained with a good accuracy (± 2–3%).

The rate of disproportionation depends very much on the reactant. The rate of 1,2,4-TMB disproportionation which is the fastest reaction, is about 60 times greater than the slowest one (*o*-xylene disproportionation). Large differences exist in the rates of disproportionation of xylene isomers (*p*-xylene disproportionation is about nine times faster than *o*-xylene disproportionation) or of trimethylbenzene isomers (1,2,4-TMB disproportionation is about 4 times faster than the disproportionation of 1,2,3 or 1,3,5 isomers). However the disproportionation of all of the trimethylbenzenes (reaction 3) is faster than that of xylenes (reaction [1]).

However the differences in reactivity of TMB and of xylenes (less than 2 to 60) seem too small to explain the apparently direct intertransformation of *o*- and *p*-xylenes. Indeed at low conversion the amount of TMB being very low, their bimolecular disproportionation occurs very slowly. This was verified by one experiment using a very low pressure of 1,2,4-TMB (3.3×10^{-3} bar), which would correspond to about 5 mol% of 1,2,4-TMB in *m*-xylene. The disproportionation rate is equal to about 9.7×10^{-6} mol s^{-1} g^{-1}, i.e., quite comparable to the rate of *o*- or *m*-xylene disproportionation measured under the standard conditions (Table 2). It can thus be concluded that at least at low conversion the participation of reaction [3] in the bimolecular isomerization of xylene is very limited.

This is not the case for reaction [2] for the partial pressure of one reactant (xylene) is high. In order to verify the role of this reaction in xylene isomerization we have investigated the effect the addition of small amounts (2.5 and 5 mol%) of 1,2,4-TMB to *m*-xylene has on the formation of the products. A relatively significant increase in the formation of xylenes (particularly of *o*-xylene) and of toluene is observed as well as a small increase in the formation of TTMB and of TMB. The increase in the formation of xylenes is in agreement with the mechanism of xylene isomerization which involves trimethylbenzene intermediates. On the other hand reactions [1–3] cannot explain the supplementary formation of toluene which results most likely from reaction [4], i.e., transalkylation between TMB and *m*-xylene;

$$\mathrm{mX} + \mathrm{TMB} \rightarrow \mathrm{T} + \mathrm{TTMB}. \qquad [4]$$

As indicated above, reaction [3] is most likely negligible compared to reaction [2] and also to reaction [4], which involves *m*-xylene (the main component in the feed) as a reactant. With reactions [2] and [4], the formation of toluene must be identical to that of tetramethylbenzene. This is not the case (Table 3): the increase in the percentage of tetramethylbenzene is 2–3 times lower than the increase in the percentage of toluene. This observation can be explained by admitting that a part of tetramethylbenzene is consumed, for instance by transalkylation with *m*-xylene, e.g.,

$$\mathrm{TTMB} + \mathrm{mX} \rightarrow 2\mathrm{TMB}. \qquad [5]$$

The percentage of tetramethylbenzene consumed through this reaction is equal to the difference between the supplementary formations of toluene and of tetramethylbenzene, e.g., with the addition of 5% of 1,2,4-TMB, 0.36% of TTMB (0.59–0.23%) results from reaction [5] with the formation of twice more TMB, e.g., 0.72%. From which it is possible to

TABLE 2

Rates of Disproportionation (*D*) and of Isomerization (*I*) of the Xylene and Trimethylbenzene Isomers (10^{-6} mol s^{-1} g^{-1}) on the HY-3 Zeolite and Average Turnover Frequencies (10^{-3} s^{-1}) in Brackets

Reactant	*D*	*I*	*D/I*
o-xylene	10.6 (11.1)	19.2 (20.1)	0.55
m-xylene	19.4 (20.4)	17.8 (18.7)	1.1
p-xylene	93.1 (97.6)	27.2 (28.6)	3.4
1,2,3-Trimethylbenzene	140–180 (146–189)	140–194 (146–204)	0.93–1.2
1,2,4-Trimethylbenzene	597 (627)	97 (102)	6
1,3,5-Trimethylbenzene	149 (156)	135 (141)	1.1

TABLE 3

Transformation of *m*-Xylene on the HY-3 Zeolite: Influence of the Addition of 1,2,4-TMB to the Formation of Toluene, Xylenes, Trimethylbenzenes and Tetramethylbenzenes (Yield, mol%)

TMB (mol%): Product	0	2.5	5.0
Toluene	3.0	3.20 (0.20)	3.59 (0.59)
Xylenes	5.01	5.32 (0.31)	5.61 (0.60)
Trimethylbenzenes	2.88	2.93 (0.05)	3.09 (0.21)
Tetramethylbenzenes	0.07	0.17 (0.10)	0.30 (0.23)

calculate the amount of TMB consumed from reaction [4]:

$$0.72 - 0.21 = 0.51\%$$

This amount is close to that of toluene formed (0.59%, Table 3) which indicates that reactions [2], [4], and [5] explain the effect of the addition of 1,2,4-TMB to *m*-xylene, confirming that reaction [3] is negligible. The bimolecular isomerization of xylenes therefore involves only the successive reaction [1] and [2].

2. *Determination of the Percentage of Bimolecular Isomerization*

The percentage of bimolecular isomerization can be estimated from the transformation of the mixture of labelled and normal xylenes, for instance $C_6H_4(CD_3)_2$ and $C_6H_4(CH_3)_2$ (20, 21). However this method is relatively difficult to use requiring analysis of the products through GC/MS coupling. Moreover because of the difficulty in xylene chromatographic separation, *p*-xylene is used as a reactant and only *o*-xylene can be accurately analyzed. Hence the estimation is very favorable for the bimolecular process, particularly at low conversion, for if *o*-xylene is a secondary product of the monomolecular process it is a primary product of the bimolecular process. Hence the percentage of bimolecular isomerization in the formation of *o*-xylene from *p*-xylene should be close to 100% at very low conversion. Consequently this method can allow only to conclude on the existence of a bimolecular process and to compare its significance at a given conversion on various catalysts. Therefore this method which is difficult to use does not give more information than the initial selectivity of *p*-xylene isomerization.

This is why we have attempted to develop a more simple and more accurate method for determining the relative significance of the mono- and bimolecular isomerization pathways. This method is based on the simple information obtained during the transformation of *m*-xylene carried out on a series of Y zeolites with different framework composition, namely that the greater the disproportionation/isomerization rate ratio (*D/I*) the lower the *para-/ortho*-xylene ratio (*para/ortho*) (Fig. 4). This could indicate (and it is demonstrated in Section 2.1) that the bimolecular isomerization process whose significance increases with *D/I* is more selective to *o*-xylene than the monomolecular process. The percentage of bimolecular isomerization of *m*-xylene can therefore be estimated from the experimental value of the *para/ortho* ratio provided however the values of this ratio for the mono- and for the bimolecular isomerizations are determined.

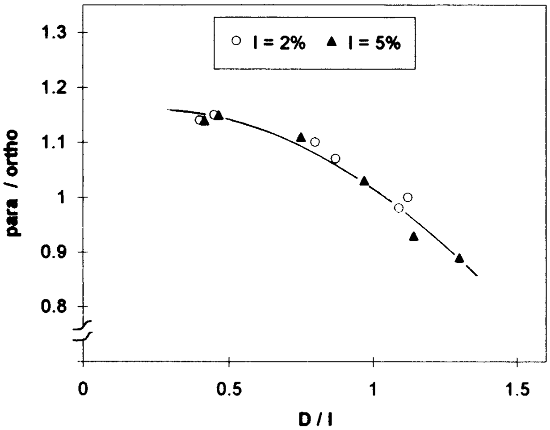
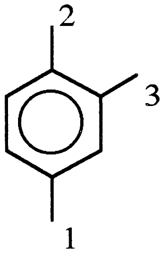


FIG. 4. Transformation of *m*-xylene on a series of HY zeolite samples. *Para-/ortho*-xylene selectivity versus disproportionation/isomerization rate ratio (*D/I*) for 2% and for 5% of isomerization.

2.1 Estimation of the para/ortho selectivity of the bimolecular isomerization of m-xylene. The various steps involved in this bimolecular process are indicated in Fig. 5. *m*-Xylene disproportionation (reaction [1]) leads to toluene and to 1,2,3-, 1,2,4-, or 1,3,5-trimethylbenzenes; transalkylation of TMB and *m*-xylene (reaction [2]) can occur through six different steps. The TMB distribution obtained from reaction [1] is practically independent of the conversion (Fig. 6) and of the catalyst (25). This distribution, 1,2,3-TMB, 7.0%; 1,2,4-TMB, 65.5%, 1,3,5-TMB, 27.5%, is very close to that at thermodynamic equilibrium (26), 7.7, 65.7, and 26.6%.

The relative rates of the six steps of reaction [2] can be estimated from the rates and selectivities of TMB disproportionation. The distribution of xylenes resulting from 1,2,4-TMB disproportionation is practically constant up to 6% conversion (Fig. 7). Whatever the Y zeolite employed the distribution is the following: 45% of *o*-, 42% of *m*-, and 13% of *p*-xylene. The nucleophilic attack of 1,2,4-TMB occurs therefore at 45% in position 1, at 42% in position 2, and at 13% in position 3 (these positions corresponding to the position of the positive charge in the benzylic carbocation).



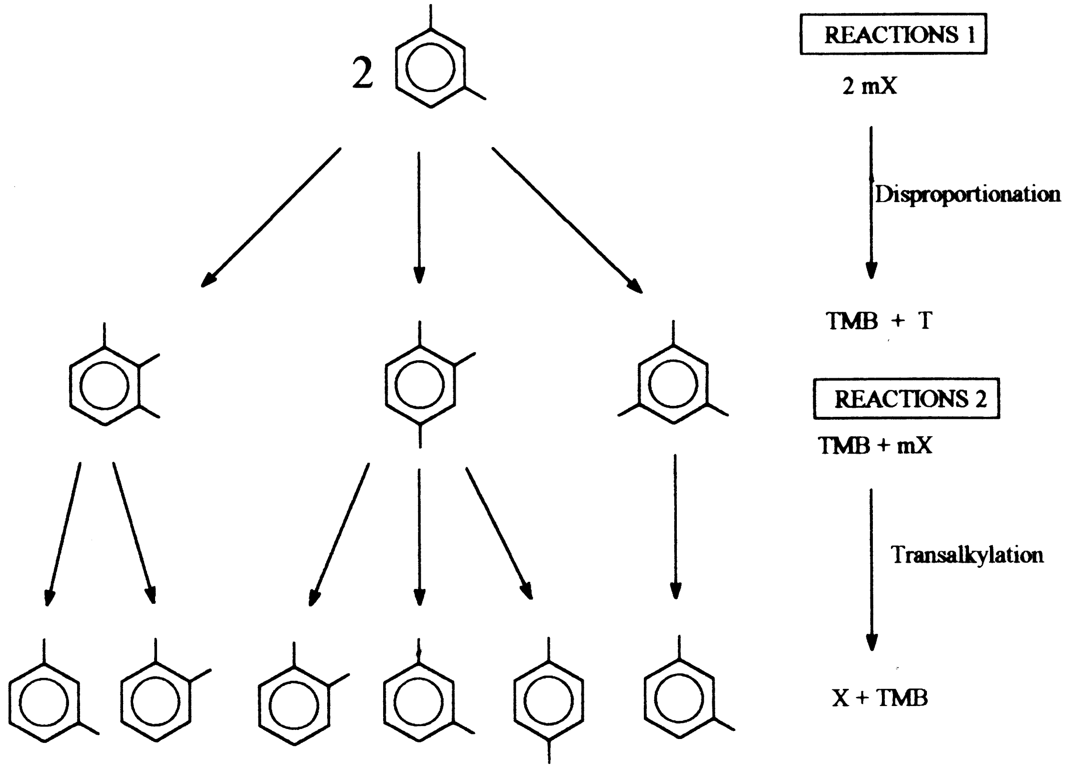


FIG. 5. Bimolecular isomerization of *m*-xylene. Reaction scheme.

The constant xylene distribution confirms that 1,2,4-TMB disproportionation is much faster than xylene isomerization (20 to 35 times (Table 2)). The experiments carried out with the mixtures of *m*-xylene and of 1,2,4-TMB confirm that the nucleophilic attack of 1,2,4-TMB by *m*-xylene in position 1 (with formation of *o*-xylene) is like that by 1,2,4-TMB, faster than in position 3 (formation of *p*-xylene).

The distribution of xylenes resulting from 1,2,3-TMB disproportionation changes slightly with the conversion (Fig. 8) but for a given conversion is independent of the zeolite (25). Only *m*-xylene (23%) and *o*-xylene (77%) are initially formed. We have verified by investigating the transformation of *m*-xylene + 1,2,3-TMB mixtures that the increase in xylene formation caused by transalkylation is due only to *o*-xylene. The slight change with 1,2,3-TMB conversion in the xylene distribution confirms that xylene isomerization is not much lower than 1,2,3-TMB disproportionation (5–10 times, Table 2.)

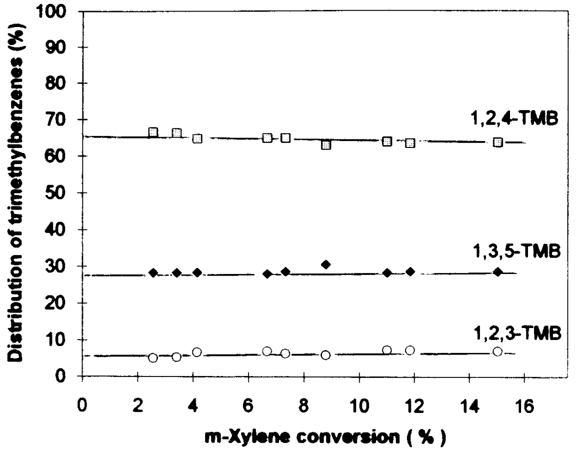


FIG. 6. *m*-Xylene transformation on the HY-3 sample. Distribution of trimethylbenzenes versus *m*-xylene conversion.

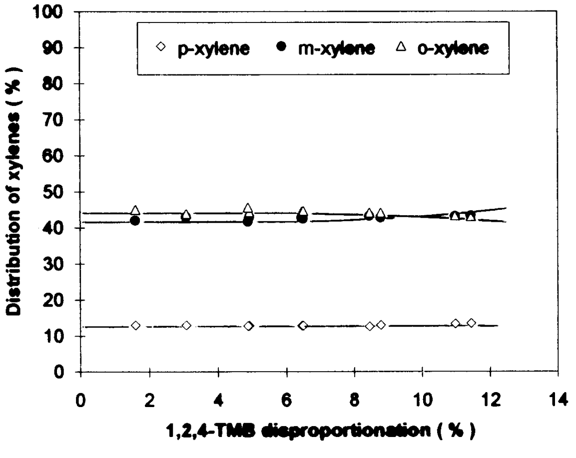


FIG. 7. 1,2,4-Trimethylbenzene transformation on the HY-3 sample. Distribution of xylenes versus the percentage of 1,2,4-trimethylbenzene disproportionation.

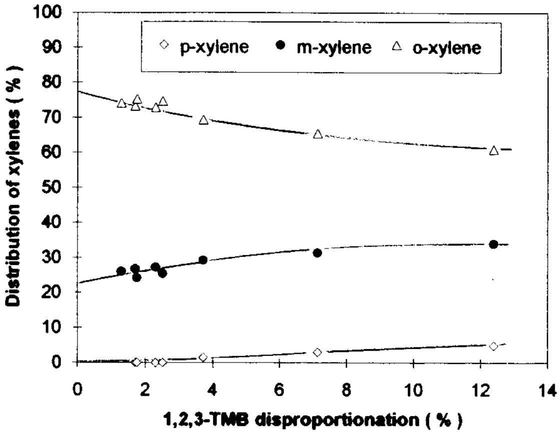
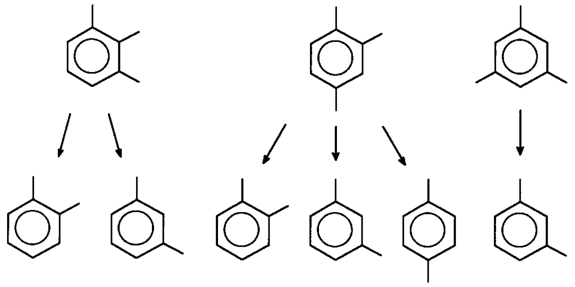


FIG. 8. 1,2,3-Trimethylbenzene transformation on the HY-3 sample. Distribution of xylenes versus the percentage of 1,2,3-trimethylbenzene disproportionation.

TABLE 4

Rates of Trimethylbenzene Disproportionation into Xylenes R_1 (10^{-6} mol s^{-1} g^{-1}) and of the Bimolecular Isomerization of *m*-Xylene R_2 (10^{-6} mol s^{-1} g^{-1}), and Distribution of Xylenes Resulting from *m*-Xylene Bimolecular Isomerization X_b (%)



61.6	18.4.	134.3	125.4	38.8	74.5	R_1
4.3	1.3	88	82.1	25.4	20.5	R_2
1.9	0.6	39.7	37.1	11.5	9.2	X_b (%)

Initially 1,3,5-TMB leads only to *m*-xylene. However there is later formation of *o*- and *p*-xylenes through isomerization, this reaction not being much slower than 1,3,5-TMB disproportionation (5–10 times, Table 2).

The rates of TMB disproportionation into the various xylenes were calculated by multiplying the rates of TMB disproportionation into xylenes (1/2 of the rate of TMB disproportionation given in Table 2) by the initial xylene distribution. The values obtained (R_1) are given in Table 4. Transalkylation of TMB and *m*-xylene occurs through similar steps as in TMB disproportionation and hence with the same relative rates. Therefore the rates of bimolecular isomerization (through reactions [1] and [2]), R_2 can be considered as the product of R_1 by the distribution of TMB formed from *m*-xylene disproportionation. The distribution of xylenes X_b (Table 4) formed through bimolecular isomerization can be calculated from R_2. Table 4 shows that bimolecular isomerization occurs mainly (about 90%) through 1,2,4-TMB formation and transalkylation and that *o*-xylene is very favoured in comparison to *p*-xylene (*para/ortho* ratio equal to 0.275). A quasi-identical value of *para/ortho* (0.29) can be obtained directly from the selectivity of 1,2,4-TMB disproportionation (the formation of the ortho isomer from 1,2,3-TMB being neglected).

2.2 Estimation of the para/ortho selectivity of the monomolecular isomerization of m-xylene. This selectivity can be estimated from the extrapolation at a value of *D/I* equal to zero of the curve in Fig. 4. However, this extrapolation is not very precise because the smallest value of *D/I* found with samples of Y zeolite is equal to 0.4.

We have already shown (27) that adding isoparaffins to xylenes allows to decrease the disproportionation rate without affecting isomerization. This technique was therefore employed to obtain the *para/ortho* selectivity at very low values of *D/I*. Methylcyclohexane was chosen as an additive and used with three Y zeolites. Figure 9 shows on the example of the HY-3 zeolite that the addition of methylcyclohexane to *m*-xylene (whose partial pressure and flow rate are kept constant) decreases significantly the conversion into disproportionation products and has no effect on the conversion into isomers, hence decreases the *D/I* ratio. Values of *D/I* lower than 0.1 can be obtained and a precise value of the *para/ortho* selectivity can be obtained by extrapolation of the curve in Fig. 10 at $D/I = 0$. It must be noticed that the addition of methylcyclohexane has no direct effect on the *para/ortho* selectivity: the experimental points with methylcyclohexane are located on the curve obtained from experiments without methylcyclohexane (Fig. 10). From this method the value of the *para/ortho* ratio of the monomolecular isomerization of *m*-xylene is found to be equal to 1.18 ± 0.01. This value is slightly greater than the one measured at thermodynamic equilibrium, 1.07 (25).

2.3 Determination of the percentage of mono- and bimolecular isomerizations. The percentage of mono- and bimolecular isomerizations of *m*-xylene can be easily estimated from the experimental value of the *para/ortho* ratio and from the value of this ratio for the monomolecular process (1.18) and the bimolecular process (0.275). Thus for HY-3, which has a *para/ortho* selectivity at 5% conversion equal to 1.00 ± 0.01, the percentage of bimolecular isomerization *y* is deduced from the following equation:

$$1.0 \times 100 = 0.275y + 1.18(100 - y) \quad y = 19.9\%.$$

The percentage of monomolecular isomerization is therefore equal to about 80%. Quasi-identical values of these percentages can be obtained by using the approximate

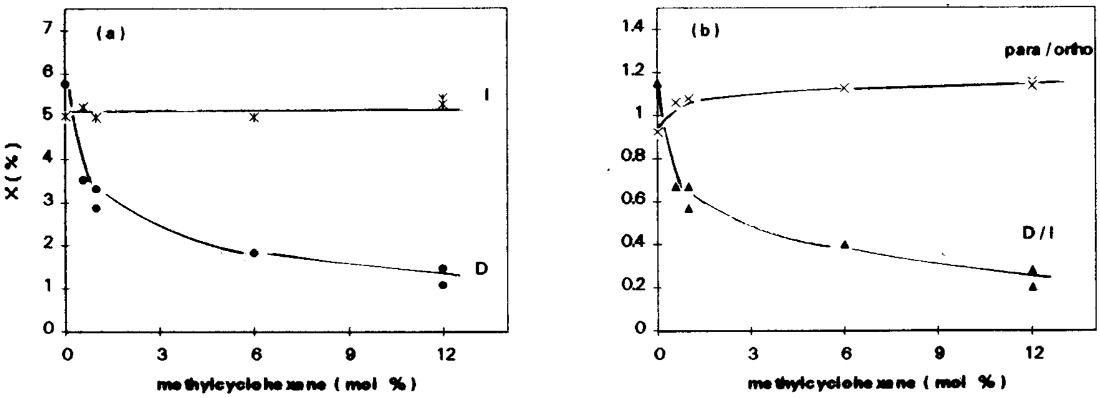


FIG. 9. *m*-Xylene transformation on the HY-3 sample. Influence of the percentage of methylcyclohexane added to *m*-xylene (a) on the conversion *X* (%) into the isomers (*I*) and into disproportionation (*D*) products (b) on the *para/ortho* and disproportionation/isomerization (*D/I*) selectivities.

value of the *para/ortho* ratio of the bimolecular process drawn from the selectivity of 1,2,4-TMB disproportionation.

Figure 11 shows that the percentage of bimolecular isomerization increases as a function of the *D/I* ratio. All the experimental points obtained on the series of Y zeolites, with or without adding methylcyclohexane and whatever the conversion of *m*-xylene (in the range 1 to 15%), are located on the same curve. This confirms that the *para/ortho* selectivity is determined by the ratio between the rates of disproportionation and isomerization.

CONCLUSION

On Y zeolites *m*-xylene isomerization can occur not only through the classical monomolecular mechanism but also through a “bimolecular” mechanism which involves two successive steps, disproportionation of *m*-xylene followed by transalkylation of trimethylbenzenes and *m*-xylene into a mixture of xylenes and trimethylbenzenes. The transalkylation step is faster than *m*-xylene disproportionation, which explains why xylenes resulting from the bimolecular mechanism can appear as primary products. The *para/ortho* selectivity of the bimolecular process is completely different from that of the monomolecular process (0.275 instead of 1.18). The selectivity of the monomolecular isomerization is the value obtained for a disproportionation/isomerization ratio equal to zero, i.e., when the bimolecular isomerization which involves the *m*-xylene disproportionation as a first step does not occur. This value can thus be determined by extrapolating the curve giving the *para/ortho* ratio as a function of the *D/I* ratio, low values of this latter ratio being obtained by adding methylcyclohexane (which is an inhibitor of disproportionation) to *m*-xylene. The *para/ortho* selectivity of the bimolecular isomerization can be estimated from a simple model. Its value is close to the *para-/ortho*-xylene selectivity of 1,2,4-trimethylbenzene disproportiona tion.

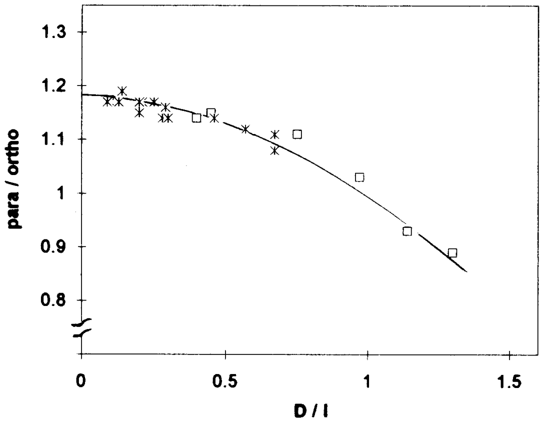


FIG. 10. *m*-Xylene transformation on a series of Y samples. *Para-/ortho*-xylene selectivity versus disproportionation/isomerization rate ratio for 5% of isomerization. Values obtained from experiments with (□) and without (∗) addition of methylcyclohexane.

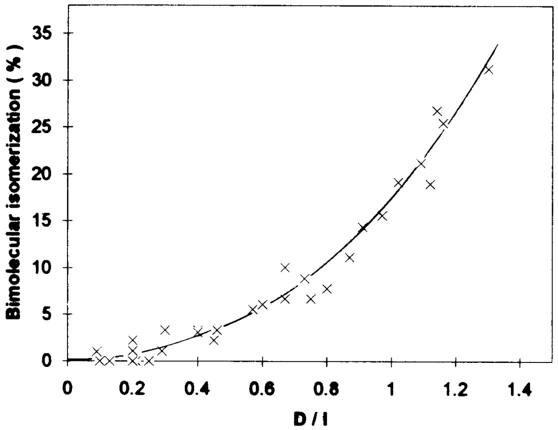


FIG. 11. Percentage of bimolecular isomerization for *m*-xylene transformation at low conversion (1 to 15%) on a series of Y zeolites versus the disproportionation/isomerization (*D/I*) rate ratio.

The *para/ortho* selectivities of the mono- and bimolecular isomerization processes being very different, the percentages of these processes can be determined accurately from the *para/ortho* selectivity of the concerned zeolite measured at low conversion values. A maximum value of 20% (at 5% *m*-xylene conversion) is found for the bimolecular isomerization on Y zeolites, which confirms that *m*-xylene isomerization can be used as a model reaction for the characterization of the acidity of solid catalysts. Moreover it is now possible from the *para/ortho* selectivity to distinguish between the mono- and bimolecular processes and to obtain the true value of the monomolecular isomerization rate.

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