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The Reactions of 1-Methyl-2-ethylbenzene

I. Exploring the Structure of Intracrystalline Void Space and the Catalytic Properties of Molecular Sieves and Other Catalysts

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Reactions of dialkylaromatic hydrocarbons can tell one a great deal about properties of unknown catalysts by comparing the activities and selectivities over them with those over known catalysts. Minimum pore dimensions, the strength and spatial environment of acid sites, the approximate dimensions of the intracrystalline cavities in which reactions occur, the extent of diffusion limitation, and optimum activation conditions are examples of the type of information revealed by such tests. We determined methylethylbenzene reaction patterns over HY, diuturnal Y, HZSM-5, H-mordenite, and many other materials.

INTRODUCTION

High-resolution electron microscopy, scanning electron microscopy, X-ray diffraction, and neutron diffraction are some of the physical techniques used to determine the crystal structure of molecular sieves and other catalysts. The intracrystalline void space, on the other hand, is best explored by chemical reactions of certain model compounds. In addition to catalytic activity and selectivity determination, these reactions can measure the shape and size of the void space (*1*). Some examples are listed below.

Frilette *et al.* measured cracking rates of *n*-hexane and 3-methylpentane in various acidic zeolites (*2*). The so-called "constraint index" is the ratio of the logarithms of the unconverted *n*-hexane and 3-methylpentane reacted under certain specified conditions. This ratio is approximately equal to the corresponding ratio of first-order cracking rate constants. The constraint index has been useful for characterizing many new zeolites; it can show small differences between pore diameters.

Dewing has used *meta*-xylene isomerization (*3*), and Karge and co-workers (*4*) and Weitkamp and co-workers (*5*) used the transalkylation of ethylbenzene to distinguish between large-pore and medium-pore zeolites.

The *n*-decane test of Martens *et al.* has been frequently used to characterize new small-, medium-, and large-pore zeolites (*6*). The ratio of 2-methylnonane to 5-methylnonane produced correlates well with pore size and pore dimensionality.

Paraffin cracking product profiles can also distinguish between pore types and cage sizes. Miradatos and Barthomeuf have shown that the narrower and more tortuous the space available, the lower will be the product C_4/C_3 ratio (*7*).

Jacobs *et al.* used the reactions of various naphthenes to distinguish between different medium-pore zeolites. Up to 1% noble metal is added to the zeolites in these tests to minimize coke formation and deactivation. The naphthenes were cyclodecane (*8, 9*), ethylcyclohexane (*10, 12*), and other mono-, bi-, and tricyclonaphthenes (*13*).

The "spaciousness index" of Weitkamp

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et al. (*14*) characterizes the effective pore width of bifunctional zeolite catalysts with a single figure. The spaciousness index is the ratio of isobutane to *n*-butane formed in the hydrocracking of C_{10} naphthenes (e.g., butylcyclohexane or pentylcyclopentane). Unlike the constraint index, the spaciousness index is independent of temperature, and it is particularly sensitive in the transient region between medium- and large-pore zeolites.

In the absence of macropores or mesopores, sorption studies with molecules with systematically increasing diameters can also measure pore diameters. This approach follows the pioneering work of Breck (*15*).

Since 1967 we have used the reactions of 1-methyl-2-ethylbenzene (M2EB)[2] to measure acid and dehydrocyclization activities and selectivities (*16–22*). Here we describe the test and show its usefulness to characterize minimum pore dimensions, the strength and spatial environment of acid sites, the approximate dimensions of the intracrystalline void space where the reaction occurs, and the extent of diffusion limitation. In Part II we show the use of the test for bifunctional catalysts.

EXPERIMENTAL

Materials

The catalysts were commercially available samples of HY, diuturnal (ultrastabilized) Y, ZSM-5, mordenite, and offretite. The feed was M2EB.

Reaction conditions were WHSVs between 2 and 31, a hydrogen : hydrocarbon mole ratio of 5, 204–370°C, and ~1.1 atm. The hydrogen diluent minimizes catalyst deactivation. At least two experiments were made on most samples. Table 1 shows selected results.

Reaction products were analyzed by GC. We used a Varian 3700 gas chromatograph with a J&W-fused silica capillary column, a flame ionization detector, and an HP 3392A integrator for the analyses. GC retention times are shown in Table 2.

The Reactions of Methylethylbenzene

Transalkylation and isomerization are the most important acid-catalyzed reactions of M2EB.

Transalkylation by Reaction A produces monoalkylbenzenes and trialkylbenzenes from dialkylbenzenes. With M2EB, transethylation yields toluene and a methyldiethylbenzene (MDEB) isomer, and transmethylation gives ethylbenzene and a dimethylethylbenzene (DMEB) isomer. There are six possible isomers of each of these trialkylbenzene species.

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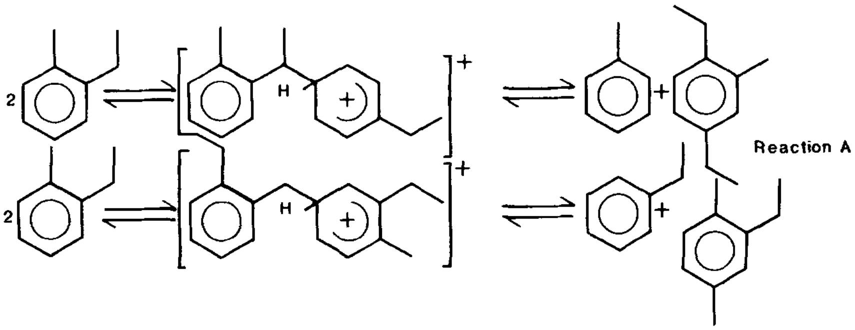
[2] Abbreviations of frequently mentioned compounds and ratios are listed in the Appendix.



Bimolecular Transalkylation

TABLE 1

Selected Results of the Reactions of 1-Methyl-2-Ethylbenzene over Different Molecular Sieves

Catalyst	Diuturnal HY	HY	H-Beta	H-Beta	Offretite	HZSM-5[g]
Maximum catalyst pretreatment temperature (°C)[a]	538	538	538	538	538	538
Test temperature (°C)	260	260	260	204	370	260
WHSV	31	31	16	16	2.1	31
Isomerization, 1-Me-3- and 4-EtBzs, % of total MEBs[b]	47.4	1.0	53.4	15.40	10[h]	2.3[i]
Transmethylation, % of total feed[c]	10.6	0.22	7.1	3.84		
Transethylation, % of total feed[d]	31.0	1.35	14.5	11.00	0.02	~0.07
Alkyl exchange, % of total feed[e]	6.0	~0.1	~2	~0.5		~0.02
Isomerization/transalkylation	0.54	0.6	1.6	0.92	50	~25
Transethylation/transmethylation	2.9	6	2	3		
Transethylation/alkyl exchange	5.2	14	7	22		
Isomer distributions[f]						
ortho-Xylene (*23*)	25		43	40	59	
1-Methyl-2,4-diethylbenzene (20.7)	25.2	48	20.5	21.3	48	40
1-Methyl-2,5-diethylbenzene (21.6)	24.2	45	21.3	23.3	44	60
1-Methyl-3,4-diethylbenzene (10.0)	8.9	3	10.1	9.7	8	
1-Methyl-3,5-diethylbenzene (47.7)	41.7	4	48.1	45.7		
Total methyldiethylbenzenes, % of feed	17.10	0.13	8.95	6.77	0.12	0.046
Total dimethylethylbenzenes, % of feed	5.91	0.80	4.0	2.15		
1,2,4-Trimethylbenzene, % of feed		0.01			0.75	0.05

[a] Reaction conditions: $H_2:HC = 5$ and 1.1 atm. Unless otherwise noted, catalysts were pretreated first at 204°C in dry H_2 for at least 3 h. After this, the temperature was gradually increased in 6 h to 538°C. The catalysts were then treated at 538°C with dry air for $\frac{1}{2}$ h, with N_2 for 5 min, and with H_2 for $\frac{1}{2}$ h. If more than one run was made over the same catalyst sample, it was regenerated between runs at 538°C with dry air for $\frac{1}{2}$ h, N_2 for 5 min, and H_2 for $\frac{1}{2}$ h.

[b] Corrected for 0.67 wt% 1-methyl-3- and 4-ethylbenzenes in the feed.

[c] Ethylbenzene plus dimethylethylbenzenes.

[d] Toluene plus methyldiethylbenzenes.

[e] Xylenes plus diethylbenzenes.

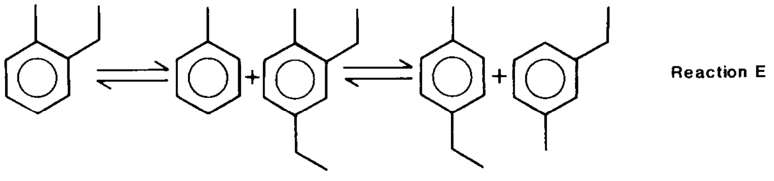
[f] Equilibrium concentration at 315°C are shown in parentheses (Ref. (*16*)).

[g] Silica/alumina = 85.

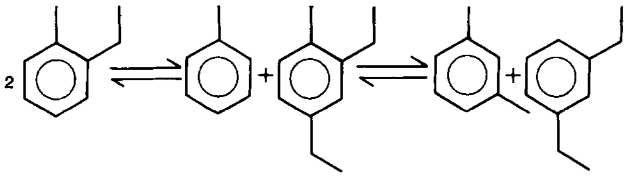
[h] 8.5% 1-Methyl-3-ethylbenzene + 1.5% 1-methyl-4-ethylbenzene.

[i] 1.6% 1-Methyl-3-ethylbenzene + 0.7% 1-methyl-4-ethylbenzene.

The reverse reactions could yield either the original M2EB or one of its other two isomers (this is the intermolecular isomerization mechanism, Reaction E) or xylene and diethylbenzene. We call this last reaction "alkyl exchange (Reaction F)."



Intermolecular Isomerization



Reaction F

Alkyl Exchange

Whenever there is enough space to accommodate a large, bimolecular transition state, transalkylation involves a 1,1-diphenylalkane-type intermediate (Reaction A). If there is not enough space for this intermediate (e.g., in HZSM-5), transalkylation might proceed by Reaction B, a different, slower reaction. Reaction B differs from Reaction A because it is a monomolecular reaction. It can occur in intermediate-pore zeolites with high silica/alumina ratios and, therefore, with very strong acid sites. Transalkylation here involves a protonated alkylphenyl ion (*23*). The alkyl group, probably associated with a very strong acid site, leaves this protonated alkylphenyl intermediate and is attached to a nearby phenyl ring (Reaction B). According to Santilli, in Reaction B, transethylation is very much more likely than transmethylation because the ethyl carbocation is more stable than the (hypothetical) methyl one (*24*). Santilli also noted that wherever there is enough space to form the diphenylalkane intermediate, transalkylation proceeds via Reaction A. This is because the diphenylalkane intermediate is better stabilized by resonance than either the protonated alkylphenyl ion or the alkyl carbocation. With MEB feed, one might distinguish between the two mechanisms by the abundance of DMEB, the products of transmethylation, relative to that of methyldiethylbenzenes (MDEBs), the products of transethylation. This is not always easy because at low overall conversion levels, even with Reaction A, the concentration of DMEBs could be very low. Fortunately, transalkylation by Reaction B has a very low rate relative to isomerization. For example, at 260°C, the isomerization/transalkylation ratios (I/TA) in diuturnal Y and HZSM-5 under comparable reaction conditions are 0.54 and 25, respectively (Table 1). Assuming equal transalkylation rates for each of the three MEB isomers, isomerization is better expressed as the percentage of the total MEBs remaining in the product. Table 1 shows these figures. Transethylation, transmethylation, and al-

TABLE 2

Gas Chromatographic Retention Times of Selected Polyalkylaromatics

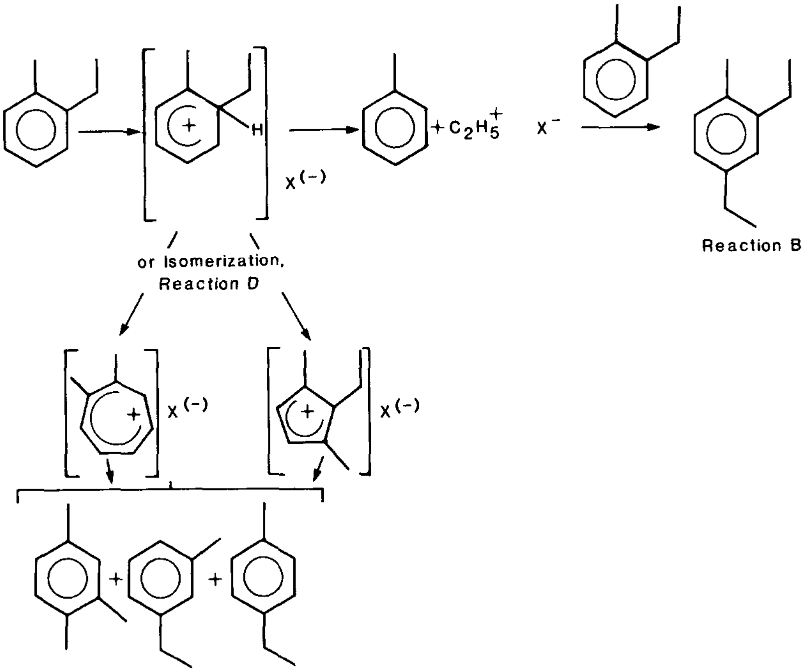
Compound	BP (°C)	Relative retention time
Toluene	110.625	1.000
Ethylbenzene	136.186	1.32
p-Xylene	138.351	1.35
m-Xylene	139.103	1.35
o-Xylene	144.411	1.42
1-Methyl-4-ethylbenzene	161.989	1.66
1-Methyl-3-ethylbenzene	161.305	1.66
1-Methyl-2-ethylbenzene	165.153	1.72
1,2,4-Trimethylbenzene	169.351	1.77
Indan	177.82	1.89
1,3-Diethylbenzene	181.102	1.94
1,4-Diethylbenzene	183.752	1.957
1,2-Diethylbenzene	183.423	1.98
1,3-Dimethyl-5-ethylbenzene	183.58	1.99
1,4-Dimethyl-2-ethylbenzene	186.83	2.01
1,3-Dimethyl-4-ethylbenzene	188.20	2.05
1,2-Dimethyl-4-ethylbenzene	189.48	2.07
1,3-Dimethyl-2-ethylbenzene	190.01	2.09
1,2,4,5-Tetramethylbenzene	196.80	2.18
1-Methyl-3,5-diethylbenzene	200.70	2.19
1-Methyl-3,4-diethylbenzene	203.6	2.23
1-Methyl-2,4-diethylbenzene	205.0	2.26
1-Methyl-2,5-diethylbenzene	207.1	2.27

Note. Retention times were measured on a J&W-fused silica capillary column. Values vary with temperature-programming conditions, flow rate, and the age of the column.

kyl exchange are shown as percentages of feed. The I/TA ratios use "percentage of feed" isomerization and transalkylation values.

If the catalyst does not contain any hydrogenation component, the presence of trimethylbenzenes (TMB), usually the 1,2,4-isomer, might be another indication of acid sites strong enough to protonate a phenyl ring.

The formation of 124TMB (Reaction D) might also involve the protonated polyalkylphenyl intermediate of transalkylation (Reaction B) discussed above. This positively charged intermediate can either dissociate to an alkylbenzene molecule and an alkyl carbocation, as discussed above, or undergo ring contraction to a five-membered ring (or ring expansion to a seven-membered ring), Reaction D:



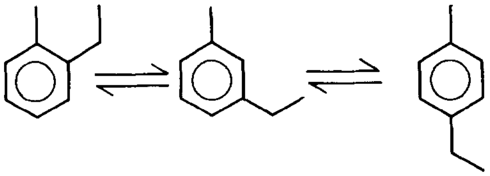
Monomolecular Transalkylation and Intermolecular "Ring Contraction–Expansion" Isomerization

Ring expansion of the five-membered ring (or ring contraction if the intermediate was a seven-membered ring) to a six-membered ring may restore the original skeleton or one of the other MEB isomers or form a TMB isomer.

Thus, part of the protonated phenyl intermediates may form other MEB isomers and TMBs (through consecutive ring enlargement–ring contraction steps: Reaction D), and the other part may lose an ethyl group which (probably as a $C_2H_5^+$ carbocation solvated by very strong acid sites of the catalyst) reacts with another MEB to form MDEBs. The presence of TMBs at low overall conversions suggests that transalkylation may have occurred by Reaction B which involves the same protonated phenyl intermediate as Reaction D. At present, we have no evidence to support or refute this hypothesis. One should be aware, however, that (especially at high overall conversion levels) other reactions can also yield TMBs. We have observed 1,2,4-trimethylbenzene (124TMB) at low conversion levels only over HZSM-5, offretite (at 370°C only), and HY.

Isomerization produces 1-methyl-3- and 1-methyl-4-ethylbenzenes (M3EB and M4EB).

Acid-catalyzed isomerization may proceed by either an intramolecular (Reactions C and D) or an intermolecular (Reaction E) mechanism


Reaction C

Intramolecular "Around-the-Ring" Isomerization

The intramolecular reaction proceeds either by 1,2 shifts (Reaction C) or by consecutive ring contraction–ring enlargements (Reaction D) discussed above. Transalkylated intermediates (see above) are involved in intermolecular isomerization (Reaction E). Under the reaction conditions of our test, isomerization could proceed by all three mechanisms. The acid-catalyzed reactions are summarized in Table 3.

What Can the Test Tell Us?

The MEB test can reveal the following:

- Minimum pore dimensions.
- The space available around acid sites.

TABLE 3

Summary of Acid-Catalyzed Reactions

Reaction	Transition state	Products
Transalkylations		
A. Intermolecular	1,1-Diphenylalkane	Methyldiethylbenzenes, dimethylethylbenzenes, toluene + ethylbenzene
B. $C_2H_5^+$ transfer	Phenyl protonated by very strong acid + solvated $C_2H_5^+$ ion	1-Methyl-2,4-diethylbenzene + toluene
Intramolecular (= unimolecular) isomerizations		
C. "Around-the-ring" isomerization	Phenyl ring protonated by medium strong acid	1-Methyl-3-ethylbenzene 1-Methyl-4-ethylbenzene
D. Ring contraction or ring enlargement	Phenyl- or cyclopentadienyl or cycloheptadienyl ring protonated by very strong acid	1-Methyl-3-ethylbenzene 1-Methyl-4-ethylbenzene 1,2,4-Trimethylbenzene
E. Intermolecular (= bimolecular) isomerization	1,1-Diphenylalkane + mono- and trialkylbenzenes	1-Methyl-3-ethylbenzene 1-Methyl-4-ethylbenzene
Alkyl exchange		
F. Intermolecular	1,1-Diphenylalkane + mono- and trialkylbenzenes	Xylenes + diethylbenzenes

- The strength of acid sites.
- Diffusion effects.
- Optimum activation conditions.
- Dehydrocyclization and hydrogenolysis activities.

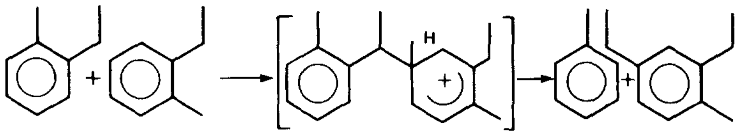
These are explained in detail below.

1. Minimum pore dimensions. M2EB requires pores with dimensions of at least about 5.1 × 5.4 Å to enter; and one of the products of isomerization, 1-methyl-3-ethylbenzene (M3EB), requires even wider pores. If reaction rates are sufficiently high to discount reactions used by "outside" surfaces, the presence of the *meta* isomer shows that a substantial fraction of the pores is at least about 5.5 Å wide.

2. The space available (the "cavity") around the acid site. The absence of symmetrical trialkylbenzenes in the reaction product at low conversion levels indicates that the cross section of the space around the acid site (the "cavity") is most likely smaller, or at least not much larger, than about 6.7 × 7 Å. This is the cross section of the pores of H-mordenite (*25*). In intermolecular transalkylation (Reaction A) in H-mordenite symmetrical trialkylbenzenes cannot form as primary products because there is not enough space to form the necessary transition state next to the acid site. Therefore, in H-mordenite, 1,2,3- and 1,2,4-trialkylbenzenes are the only primary transalkylation products (i.e., only these isomers are formed at low conversion levels) (Tables 1 and 2 of Ref. (*21*)). The thermodynamically most stable isomers, the symmetrical trialkylbenzenes, are absent from the product. [At high conversion levels, intramolecular isomerization (Reaction C) forms symmetrical trialkylbenzenes from the other isomers (Table 1 of Ref. (*22*)).]

3. Acid strength. The transethylation/transmethylation ratio (TE/TM) in intermolecular transalkylation (Reaction A) decreases with increasing acid strength in most cases because stronger acids discriminate less between ethyl and methyl transfers than weaker ones (Tables 2 and 3 of Ref. (*20*).

In large-pore zeolites and in amorphous catalysts, transalkylation proceeds by a bimolecular mechanism. Pines and Arrigo (*26*) and Streitwieser and Reif (*27*) suggested that the reaction involves 1,1-diphenylalkane-type intermediates (Reaction A). According to Ward, the reaction is catalyzed by Brønsted acid sites (*28*).



The strength and number of acid sites determine isomerization and transalkylation *rates*. The TE/TM, however, probably depends on the strength of the acid sites but not on their number. Transmethylation has a higher activation energy than transethylation (Fig. 3 of Ref. (*19*)). Weaker acid sites will, therefore, discriminate more between these two reactions than stronger ones. Thus, a lower TE/TM will indicate a stronger acid site. A comparison of diuturnal Y with HY illustrates this: TE/TMs are 2.9 and 6, respectively (Table 1). We would expect this because the concentration of framework alumina is less in diuturnal Y than in HY. In Y (and most other) zeolites, acid strength is inversely proportional to the concentration of framework aluminum up to about a silica/alumina ratio of 10. As another example, the TE/TM's over weaker acids, like MgY and amorphous silica–alumina, are 25+ and 40, respectively (Tables 1 and 3 of Ref. (*20*)).

If transalkylation occurs by Reaction B, a low TE/TM does not indicate weak acidity. The presence or absence of TMBs (at low conversion levels!) may tell whether transalkylation occurred by the bimolecular Reaction A or by the monomolecular Reaction B.

The I/TA ratio is affected by many variables, including the type of the zeolite, the type of the cation, the partial pressure of water during catalyst pretreatment and during the MEB test, etc. (Table 3 of Ref. (*20*)). In addition, temperature and hydrocarbon partial pressure have large effects on the I/TA. Raising the temperature increases intramolecular isomerization (Reaction C) rates much faster than transalkylation (Reaction A) rates because the activation energy of the former reaction is much larger than that of the latter (Figs. 2, 6, and 7 of Ref. (*20*)). Raising hydrocarbon partial pressure increases transalkylation rates relative to isomerization rates because transalkylation (Reaction A) is usually bimolecular, whereas intramolecular isomerization (Reaction C) is monomolecular (*19*). Therefore, the I/TA's should always be compared at identical temperatures and hydrocarbon partial pressures. However, I/TA is almost unaffected by space velocity and by the conversion level up to perhaps 10–15% transalkylation conversion levels (Fig. 1 of Ref. (*20*). The I/TA also depends on the contribution of intermolecular isomerization (Reaction E) to total isomerization and on the steric environment around the acid site. Zeolites with different structures, therefore, should not be compared with each other by the I/TA ratio.

4. *Diffusion limitation.* Distributions of products of consecutive reactions can tell the extent of diffusion limitation. At equal total conversion levels, the ratio of primary-to-secondary reaction products depends on the ratio of the corresponding rate constants and on the extent of diffusion constraint. The mathematics for the effects of diffusion on primary and secondary product ratios has been worked out by Wei (*29*).

Zeolite pore dimensions are frequently similar to the dimensions of the diffusing molecules. When the structural dimensions of the zeolite catalyst approach those of the reacting or product molecules, even subtle changes in the dimensions of the molecules can result in large changes in diffusivity.

Reactant- and product-type shape selectivities are caused by diffusional constraint and, therefore, they are affected by crystallite size. If the shape selectivity is unaffected by the size of the catalyst crystals, it is due to transition-state restrictions (restricted transition-state type selectivity).

Transalkylation produces mono- and trialkylbenzenes from diethylbenzenes (Reaction A). If these mono- and trialkylbenzene products react with each other in a consecutive transalkylation step, the products are dialkylbenzenes (or benzene and a tetraalkylbenzene).

In the case of MEB, the products of such secondary or consecutive transalkylation are either MEB isomers (products of the so-called bimolecular isomerization reaction—Reaction E) or diethylbenzenes plus xylenes ("alkyl exchange" or Reaction F). It is obvious that alkyl exchange should be proportional to bimolecular isomerization. In the absence of diffusion limitations, the ratio of primary-to-secondary reaction products of consecutive reactions depends only on the overall conversion level and on the relative rate constants of the first and second reactions. If diffusion is rate limiting, the relative concentrations of secondary products will be higher than those measured over a catalyst where diffusion is not rate limiting. With MEB, the ratio of transethylation to the sum of xylenes and diethylbenzenes is a good and practical measure of alkyl exchange. Thus, at similar conversion levels, a higher transethylation/alkyl exchange ratio (TE/AE) suggests less diffusion limitation; and vice versa, a lower TE/AE suggests more diffusion limitation.

Thus, the TE/AE is related to the effectiveness factor. (Note, however, that if there is a hydrogenolysis catalyst component, *o*-xylene could also be produced from M2EB through hydrogenolysis of the C–C bond of the ethyl side chain.)

The points above are useful to show differences of diffusional limitations between different zeolites.

If transalkylation occurs by Reaction B, transalkylation and alkyl exchange conversions are probably too low to permit meaningful conclusions.

Diffusion limitation could have more than one cause. Slow diffusion through long and/or narrow pores or in a one-dimensional pore system could be one of them; long adsorption of feed and/or product molecules on strongly adsorbing sites could be another. Phenomena like the "cage" or "window" effect described for *n*-octane in erionite are also possible (*30–32*). The test cannot distinguish among these cases.

5. *Optimum activation conditions.* Conversions measured after pretreating the catalyst at different temperatures or under different conditions can indicate optimum activation temperatures (*18*), optimum water vapor pressures, the type of gas to be used during pretreatment, and other conditions.

6. *Dehydrocyclization activity.* Cyclization to indan and indene and subsequent ring opening to *n*-propylbenzene may be used to test platinum-type dehydrocyclization activity. Since these reactions are consecutive, changes in the ratio of the bicyclic products to *n*-propylbenzene could be used to detect diffusion limitations. (The ratio is a function of the overall conversion level and the effectiveness factor.)

Hydrogenolysis of the C–C bond of the

TABLE 4

Potential Uses of the Methylethylbenzene Test

Catalyst property evaluated	Product or product ratio measured	Relationship[a]	Test limitations
Activity	Conversion level	↑ ↑	Only above 5-Å pore diameter
Larger than 6.7 × 7 Å space around the active site	Symmetrical trialkylbenzenes		
Acid strength (for closely related systems)	TE/TM	↑ ↓	Transalkylation must occur by Reaction A
	Trimethylbenzene	↑ ↑	Total conversion level must be kept low
Reaction "B"	Trimethylbenzene		Total conversion level must be kept low
Dehydrocyclization	Indan, indene, *n*-propylbenzene	↑ ↑	
Hydrogenolysis	*o*-Xylene, xylenes	↑ ↑	Must be corrected for xylenes made by alkyl exchange
Diffusion constraint	TE/AE	↑ ↑	Applies only if transalkylation occurs by Reaction A
Diffusion constraint	Indan/*n*-propylbenzene	↑ ↑	For dehydrogenation catalysts only

[a] ↑ ↑, direct relationship; ↑ ↓, inverse relationship.

ethyl side chain may be used to measure hydrogenolysis activity.

Potential uses of the MEB test are summarized in Table 4.

What the Test Cannot Tell Us

The test cannot tell whether the sample is homogeneous or a mixture of catalytically active and inactive components. (However, in combination with X-ray diffraction, adsorption (*15*), and other measurements, this question might be answered.) Neither can the test reveal much about zeolites with less than about 5-Å pore diameters, because the feed molecules cannot penetrate such pores.

RESULTS

The reactions of M2EB over Y-type and mordenite molecular sieves have been described earlier (*16–22*).

H-Beta

MEB reaction patterns suggest the following (Table 1): The activity of H-Beta, as measured by the overall conversion level, and its acid strength, as measured by TE/TM, are similar to those of diuturnal Y.

Di- and trialkylaromatic hydrocarbons can diffuse through the pores, indicating that pore diameters are larger than about 6 Å. The space around the acid sites, or at least around a substantial part of acid sites, is larger than about 6.7 × 7 Å (*2*), as shown by the formation of symmetrical trialkylbenzenes.

I/TA is higher over H-Beta than over diuturnal Y (1.6 versus 0.6). Steric environments of acid sites in the two materials may differ, and/or the two materials may have different acid site densities.

HZSM-5

The HZSM-5 sample we tested has a silica-to-alumina ratio of 85.

HZSM-5 has low MEB isomerization activity compared to diuturnal Y and almost no transalkylation activity (Table 1). Differences in pore dimensions (5.1 × 5.6 versus 7.4 Å) explain this slower isomerization rate. In HZSM-5, the space around the acid sites (which are located at the intersections of pores) is not large enough for transalkylation by Reaction A. The very small amount of transethylation observed probably occurred via Reaction B. The presence of 124TMB supports this assumption. Lack of substantial transalkylation makes HZSM-5 the catalyst of choice for commercial xylene isomerization (*33, 34*). Its ability to convert ethylbenzene to xylenes (by the same reaction MEB is converted to TMB in Reaction D) is an additional advantage in the xylene isomerization process.

Offretite

Offretite is an intermediate-pore zeolite with about a 6.4-Å pore diameter. In many offretite samples, erionite intergrowths, stacking faults, block a large part of the pores. Offretite has very low activity in the MEB test; isomerization conversion at 370°C and 2.1 WHSV was only 10% (Table 1). The very small level of transalkylation and the presence of relatively large amounts of 124TMB suggest that transalkylation proceeds by Reaction B.

APPENDIX: ABBREVIATIONS

Abbreviation	Name
	I. Compounds
MEB	Methylethylbenzene
M2EB	1-Methyl-2-ethylbenzene
M3EB	1-Methyl-3-ethylbenzene
M4EB	1-Methyl-4-ethylbenzene
DMEB	Dimethylethylbenzene
13DM5EB Etc.	1,3-Dimethyl-5-ethylbenzene
MDEB	Methyldiethylbenzene
M35DEB, etc.	1-Methyl-3,5-diethylbenzene
TMB	Trimethylbenzene
124TMB	1,2,4-Trimethylbenzene
	II. Ratios
I/TA	Isomerization/transalkylation
TE/TM	Transethylation/transmethylation
TE/AE	Transethylation/alkyl exchange

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