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The Cause of Shape Selectivity of Transalkylation in Mordenite

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Mesitylene, hemimellitene, and 1-methyl-2-ethylbenzene were reacted over acidic mordenites and other solid acid catalysts. In the transalkylation reaction of methylethylbenzene, symmetrical trialkylbenzenes approached equilibrium faster than dialkylbenzenes. Over mordenites, however, the rate of formation of the symmetrical trialkylbenzenes is slower than the rate of dialkylbenzene isomerization. Transalkylation to form the symmetrical trialkylbenzene over mordenite is most probably inhibited because there is not enough space to form the large 1,1-diphenylalkane-type intermediate. Transition states leading to the other trialkylbenzene isomers are relatively smaller and, therefore, their formation is uninhibited. Formation of symmetrical trialkylbenzenes by intramolecular isomerization from the other trialkylbenzenes proceeds well over mordenites.

Mordenites deactivate much faster than Y faujasite, probably because diffusion through their one-dimensional pore system is easily blocked by radical ions or other strongly adsorbed molecules.

Transalkylation and isomerization are the principal acid-catalyzed reactions of polyalkylbenzenes. Transalkylation most probably involves 1,1-diphenylalkane-type intermediates as suggested by Pines and Arrigo (*1*) and Streitwieser and Reif (*2*). The formation of symmetrical trialkylbenzenes from ortho-dialkylbenzenes requires either isomerization of the dialkylbenzenes before the transalkylation or isomerization of one of the other trialkylbenzene isomers. At conditions where dialkylbenzene isomerization approaches equilibrium, the trialkylbenzenes are at equilibrium also (*3*). If the catalyst has sufficient isomerization activity (as shown by the isomerization of the parent dialkylbenzene) the thermodynamically more stable symmetrical trialkylbenzene constitutes a major part of the trialkylbenzene isomer mixture. Recently we reported a special case of shape selectivity over acidic mordenite molecular sieve in which symmetrical trialkylbenzenes were absent from the product, although the catalyst had adequate isomerization activity (*4*). Symmetrical trialkylbenzenes are about 0.5–1 Å wider than the other trialkylbenzene isomers. For example, minimum cross sections determined from Fisher–Hirschfelder–Taylor molecular models of 1,2,3-, 1,2,4-, and 1,3,5-trimethylbenzenes are 8.1, 7.6, and 8.6 Å. The crystal structure of mordenite has one-dimensional "large" channels which are interconnected with smaller channels with diameters of 2.8 Å (*5*). We attributed the absence of symmetrical trialkylbenzenes from the reaction product to the fact that they are wider than the other isomers and cannot pass through the narrower pore windows. In this case, effective channel apertures in mordenite would be between the diameters of the symmetrical and unsymmetrical trialkylbenzenes (i.e., between 8.2 and 8.6 Å). Another possible explanation was suggested to the author by Dr. P. B. Venuto (*6*). According to this explanation, symmetrical trialkylbenzenes cannot be formed in the pores of mordenite because diphenylmethane-type intermediates or transition states leading to symmetrical isomers require more space than available. Formation of the somewhat less bulky transition states leading to the other isomers will not be inhibited.

The purpose of this work is to determine the cause of shape selectivity in transalkylation over mordenite catalysts.

EXPERIMENTAL

The reactor, its operation, and the analytical procedures have been described before (*7*). Experimental reaction conditions were 204–400°C temperatures, atmospheric pressure, and an H_2-to-feed molar ratio of 3:1. In most experiments, the LHSV was 8. The experiments were 21 min long; separate liquid samples were collected at 7-min intervals.

We obtained 1-methyl-2-ethylbenzene from Columbia Organic Chemicals Company; hemimellitene (1,2,3-trimethylbenzene) from Matheson Coleman and Bell Company; mesitylene (1,3,5-trimethylbenzene) from Eastman Organic Chemicals; and *o*-xylene from Phillips Petroleum Company. The hydrocarbons were reacted over two types of synthetic acidic mordenites (Zeolon H and "pelleted" Zeolon H, an experimental sample, Norton No. 31.1-227) and natural small-pore mordenite. All three were obtained from the Norton Company. An experiment performed over H^+–Y faujasite is also shown for comparison. This catalyst was made by NH_4^+ exchanging and deamminating at 532°C a Na–Y faujasite manufactured by the Linde Division of Union Carbide Corporation. Catalysts were activated at 532°C. We used 42/60-mesh particles. Product conversion values in the tables are corrected for feed impurities.

RESULTS AND DISCUSSION

1-Methyl-2-Ethylbenzene

Isomerization to 1-methyl-3- and 4-ethylbenzenes, and transalkylation forming toluene and methyldimethylbenzenes or ethylbenzene and dimethylethylbenzenes are the most important reactions of 1-methyl-2-ethylbenzene over acidic catalysts (*3*). Table 1 shows product distributions over Zeolon H and the natural small-pore mordenite. The first catalyst is significantly more active than the second one. The symmetrical trialkylbenzenes (1,3-dimethyl-5-ethylbenzene and 1-methyl-3,5-diethylbenzene) cannot be formed directly from 1-methyl-2-ethylbenzene; their formation requires isomerization of either the reactant dialkylbenzene or one of the product trialkylbenzenes. Relative amounts of 1,3-dimethyl-5-ethylbenzene and 1-methyl-3,5-diethylbenzene are plotted against the extent of methylethylbenzene isomerization on

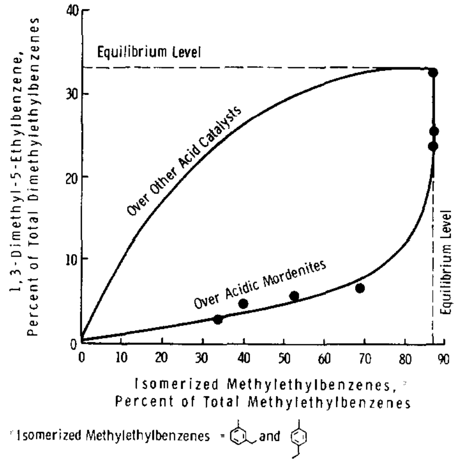

FIG. 1. Formation of 1,3-dimethyl-5-ethylbenzene in the acid-catalyzed transmethylation of 1-methyl-2-ethylbenzene.

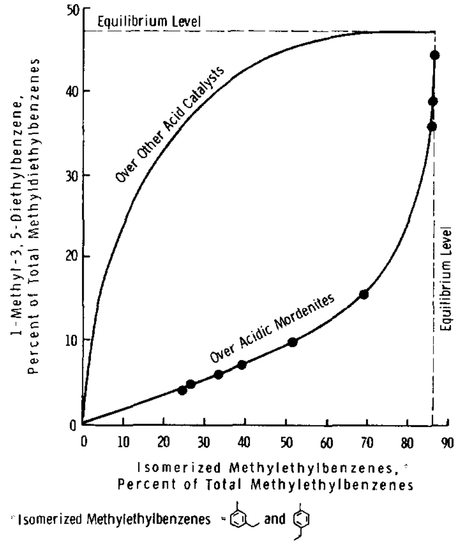

FIG. 2. Formation of 1-methyl-3,5-diethylbenzene in the acid-catalyzed transethylation of 1-methyl-2-ethylbenzene.

TABLE 1

Reactions of Methylethylbenzene over Mordenite Molecular Sieves at Atmospheric Total Pressure with an H_2:HC Molar Ratio of 3:1 and an LHSV of 8[a]

Catalyst	Norton Zeolon H mordenite						Norton natural small-pore mordenite		
Reaction temp (°C)	204			315			315		
Cut (7 min each)	1	2	3	1	2	3	1	2	3
Product distribution (mole %)									
1-Methyl-2-ethylbenzene	28.30	43.64	56.30	6.15	9.22	10.16	65.30	72.96	74.32
1-Methyl-3 and 4-ethylbenzenes	62.70	47.94	37.25	38.64	55.90	62.34	32.64	25.39	24.11
Benzene	0.03	0.04	0.03	1.16	0.48	0.33	0.02	0.03	0.02
Toluene	3.92	3.28	2.46	17.02	9.67	9.46	0.91	0.72	0.65
Ethylbenzene	0.53	0.44	0.32	7.78	4.69	3.40	0.12	0.09	0.08
Xylenes	0.29	0.28	0.23	6.87	3.49	2.35	0.08	0.07	0.06
Diethylbenzenes	0.26	0.30	0.22	5.15[b]	3.08[b]	2.11[b]	0.04	0.04	0.04
Dimethylethylbenzenes	0.47	0.49	0.35	6.03	4.23	2.94	0.11	0.08	0.08
Methyldiethylbenzenes	3.38	3.44	2.67	9.37	8.43	6.56	0.71	0.57	0.52
Other[c]	0.11	0.11	0.17	1.81	0.82	0.35	0.04	0.05	0.16
Isomer distribution (%)									
1,2-Dimethyl-3-ethylbenzene	4	4	3	4	4	5	5	5	
1,2-Dimethyl-4-ethylbenzene	43	44	45	29	33	32	45	49	51
1,3-Dimethyl-2-ethylbenzene	1			1	1	2			
1,3-Dimethyl-4-ethylbenzen	23	24	25	17	18	19	26	26	27
1,3-Dimethyl-5-ethylbenzene	7	6	5	33	26	24	3		
1,4-Dimethyl-2-ethylbenzene	22	22	22	16	17	18	21	20	22
1-Methyl-2,4-diethylbenzene	34	36	38	21	23	24	37	36	36
1-Methyl-2,5-diethylbenzene	35	40	42	22	25	26	45	48	48
1-Methyl-2,6-diethylbenzene	2	1	1	1	1	1	2	2	3
1-Methyl-3,4-diethylbenzene	13	13	11	11	12	13	10	9	9
1-Methyl-3,5-diethylbenzene	16	10	7	45	39	36	6	5	4
Isomerized methylethylbenzenes (% of total methylethylbenzenes)	69.0	52.3	39.9	86	86	86	33.3	26.1	24.5

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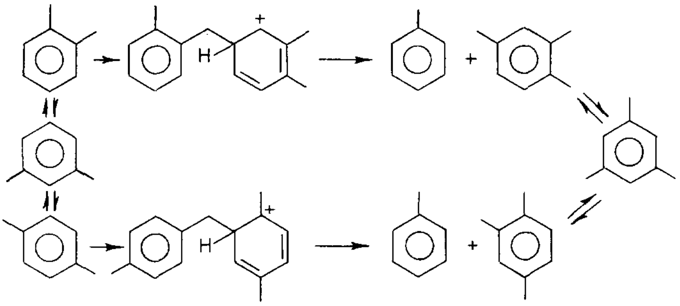
[a] Reaction conditions = 1.7 ml catalyst (42/60 mesh), pretreated first with N_2 (125 ml/min) for 1 hr at 526°C, then with H_2 (125 ml/min) another hour at the same temperature. Experiments were 21 min long.

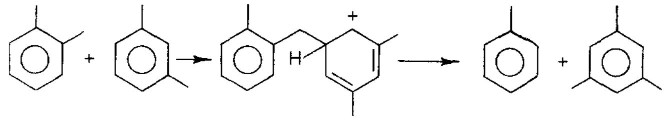
[b] Ortho:meta:para = 7:64:29.

[c] Mostly trimethylbenzenes.

Figs. 1 and 2. Figures 1 and 2 show that over most acid catalysts, symmetrical trialkylbenzenes approach equilibrium levels faster than methylethylbenzenes (*3*). However, over acidic mordenites, the rate of formation of the symmetrical trialkylbenzene isomers is significantly slower than the rate of methylethylbenzene isomerization, in good agreement with our earlier data (*4*). After sufficient time for isomerization, the symmetrical trialkylbenzenes reach equilibrium levels (e.g., over Zeolon H at 315°C during the first 7-min sample; Table 1). This suggests that in mordenites the formation of symmetrical trialkylbenzenes by transmethylation is inhibited, but they may be formed by isomerization of the other isomers. Isomerization of polyalkylbenzenes over 200°C primarily proceeds through intramolecular 1,2-shifts (*7*):



Formation of the symmetrical trialkylbenzenes proceeds by direct transalkylation over acid catalysts other than mordenites:



Hemimellitene

Zeolon H and H+–Y faujasite are much more active for the isomerization and transmethylation of hemimellitene than "pelleted" Zeolon H and the natural mordenite. Initial isomerization and transmethylation rates and isomer distributions are nearly the same over Zeolon H and H+–Y faujasite (Table 2). This shows that a symmetrical trialkylbenzene, such as mesitylene can be formed by an intramolecular isomerization reaction; and it can diffuse out of the pores.

Mesitylene

Mesitylene and hemimellitene have similar isomerization and transmethylation conversions at 315°C over Zeolon H (Table 2). Isomer distributions are also similar. Furthermore, at 315°C nearly the same amount of pseudocumene is formed from these two hydrocarbons over the much less active natural mordenite. This, too, shows that diffusion through the pores of mordenite of the symmetrical mesitylene is not seriously inhibited. A comparison of the rates of *o*-xylene and mesitylene isomerization over the natural mordenite at 315°C further substantiates this observation; the smaller *o*-xylene isomerizes slower than mesitylene (Table 2).

Mordenite Deactivation

Table 3 shows a significant difference between acidic mordenite and Y-faujasite sieves. During our 21-min experiment, hemimellitene conversions remain virtually unchanged over the H+–Y faujasite. At the same time, conversions decrease drastically over the mordenite catalyst. Figures 3 and 4 show similar fast deactivations using the other hydrocarbons over both the synthetic Zeolon H and the natural mordenite. This rapid deactivation of mordenites might be attributed to their peculiar crystal structure,

TABLE 2

Reactions of Mesitylene, Hemimellitene, and *o*-Xylene over Mordenite Molecular Sieves[a]

Feed	Hemimellitene						Mesitylene				*o*-Xylene	
Catalyst	Zeolon H	Pelleted Zeolon H		Natural Mordenite		H^+-Y faujasite	Zeolon H		Natural Mordenite		Natural Mordenite	
Reaction temp (°C)	315	315[b]	400	315	400	315	204	315	260	315	260	315
Product composition (mole %)[c]												
Benzene	0.09		0.14		0.06	0.09	0.01	0.06	0.01	0.01		
Toluene	2.25	0.22	2.53		0.12	3.39	0.02	2.37	0.01	0.01		0.01
Xylenes	20.35	1.76	15.91	0.4	1.18	25.31	0.15	19.38	0.02	0.08	100	99.98
Trimethylbenzenes	56.46	97.02	70.28	99.6	97.83	48.44	99.67	57.21	99.94	99.83		0.01
Tetramethylbenzenes	20.85	1.00	11.14		0.81	22.77	0.15	20.98	0.02	0.07		
Isomer distributions (%)[c]												
o-Xylene	22	23	24		40	22	20	22			99.9	98
m-Xylene	57	45	51		46	58	67	55			0.08	1.9
p-Xylene	21	32	25		14	20	13	23			0.003	0.1
Hemimellitene	8.1	93.4	12	92.7	73	7.6	1.3	7.7	0.05	0.5		
Pseudocumene	63.5	6.2	71	7.2	26	64.1	15.5	60.5	1.9	7.9		65
Mesitylene	28.4	0.4	17	0.1	1	28.3	83.2	31.8	98.0	91.6		35
1,2,3,4-Tetramethylbenzene							8	10		15		
1,2,3,5-Tetramethylbenzene							46	50		30		
1,2,4,5-Tetramethylbenzene							46	40		55		

[a] Reaction conditions = atmospheric pressure; an H_2-to-feed molar ratio of 3:1; and an LHSV of 8. Catalysts (1.7 ml and 42/60 mesh size) were pretreated first with N_2 (125 ml/min) for 1 hr at 532°C, then with H_2 (125 ml/min) another hour at the same temperature. Experiments were 21 min long with three 7-min cuts. Only the first cuts are shown in this table.

[b] LHSV = 16.

[c] Corrected for feed impurities.

TABLE 3

DEACTIVATION OF CATALYSTS IN THE REACTION OF HEMIMELLITENE AT 315°C, AT ATMOSPHERIC PRESSURE, WITH AN H_2:HC MOLAR RATIO OF 3:1

Catalyst	H⁺-Y faujasite			Zeolon H		
Cut (7 min each)	1	2	3	1	2	3
Product composition (mole %)						
Toluene	3.4	2.6	1.9	2.3	0.7	0.1
Xylenes	25.3	23.5	23.6	20.4	9.3	0.9
Trimethylbenzenes	48.4	50.0	50.6	56.5	79.7	98.2
Tetramethylbenzenes	22.8	23.9	23.9	20.8	10.2	0.8
Trimethylbenzene isomer distribution (%)						
Hemimellitene	7.6	7.8	8.5	8.1	13.5	76.5
Pseudocumene	64.1	65.4	67.9	63.5	72.5	22.8
Mesitylene	28.3	26.8	23.6	28.4	14.0	0.7

consisting of parallel pores which are not interconnected. The diffusing molecules cannot pass each other because their diameter is only slightly less than the cross section of the pores. If one molecule along the pore becomes strongly adsorbed, it will prevent the diffusion of the other molecules in that pore. Radical ions, easily formed over the strong acid sites of mordenite, could adsorb very strongly, as shown by Katzer (*8*). Our deactivation data are in good agreement with Katzer's observation that diffusion coefficients decrease in mordenites with increasing saturation time. Strong adsorption of only a few radical ions will not severely affect reaction and diffusion rates in Y faujasite which has a three-dimensional pore structure.

CONCLUSIONS

1. The rate of formation of symmetrical trialkylbenzenes from dialkylbenzenes over acidic mordenites is slower than the isomerization of dialkylbenzenes. The opposite holds over other acid catalysts.

2. The formation of symmetrical trialkylbenzenes by transalkylation is strongly inhibited in mordenites because there is not enough space to form the transition state.

3. Symmetrical trialkylbenzenes may be

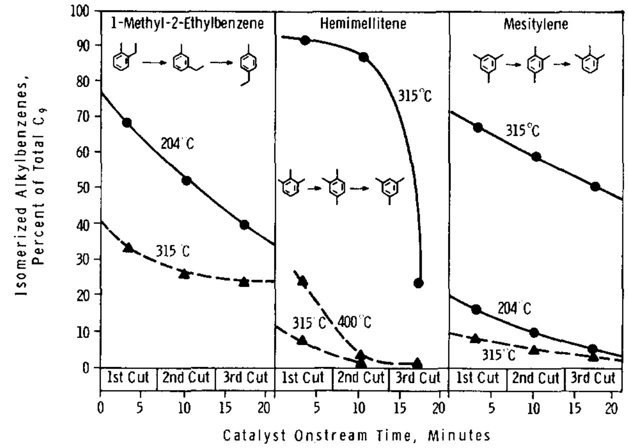


FIG. 3. Isomerization of three C_9 alkylaromatic hydrocarbons over Norton Zeolon H mordenite (solid line) and Norton natural small-pore mordenite (dashed line) with a H_2:HC molar ratio of 3:1 and an LHSV of 8.

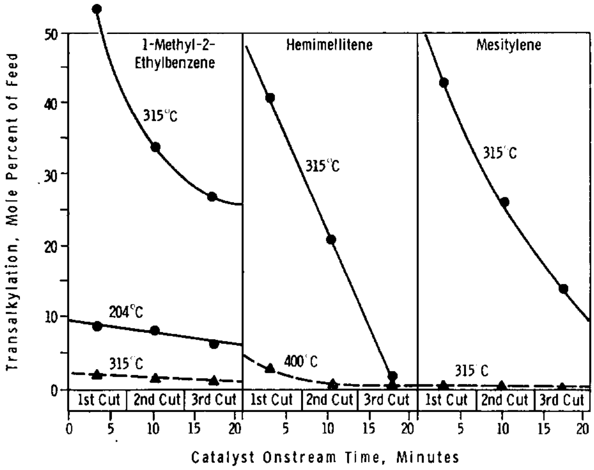


FIG. 4. Transalkylation of three C_9 alkylaromatic hydrocarbons over Norton Zeolon H mordenite (solid line) and Norton natural small-pore mordenite (dashed line) with a H_2:HC molar ratio 3:1 and an LHSV of 8.

formed over mordenites from the other trialkylbenzene isomers via intramolecular isomerization.

4. Mordenites deactivate much faster than H^+–Y faujasite because their one-dimensional pore system can be blocked much more easily by radical ions or other strongly adsorbed molecules than the three-dimensional network of the faujasite.

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