

Selective Disproportionation of Alkylbenzenes Over Mordenite Molecular Sieve Catalyst

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Symmetrical trialkylbenzenes are the predominant components of the trialkylbenzene isomer mixtures at equilibrium. Over silica-alumina, X and Y faujasite-type molecular sieves, and other acid-type catalysts with sufficient isomerization activity, significant amounts of symmetrical trialkylbenzenes are formed in the disproportionation of dialkylbenzenes. However, over mordenite, symmetrical trialkylbenzenes are absent from the product of disproportionation, although the catalyst has adequate isomerization activity. This represents a special case of shape-selective kinetic control, in which the thermodynamically most favored isomer is not formed, due to the special crystal structure of the catalyst. Effective channel apertures in the acidic form of mordenite are between the minimum cross sections of the wider symmetrical trialkylbenzenes (about 8.6 Å) and the other trialkylbenzene isomers (about 8.2 Å). The shape selectivity of alkylbenzene disproportionation is not affected by thermal deactivation of the mordenite.

INTRODUCTION

Symmetrical trialkylbenzenes are the predominant components of the trialkylbenzene isomer mixtures at equilibrium. Therefore, in thermodynamically controlled, acid-catalyzed dialkylbenzene disproportionations, symmetrical trialkylbenzenes are the most abundant product isomers. This is usually the case over silica-alumina, X and Y faujasite-type molecular sieves, and other acid catalysts with sufficient isomerization activity. In a kinetically controlled reaction, such as catalysts with low isomerization activity, only certain trialkylbenzene isomers are formed. Here we report a third kind of control (which might be viewed as a special case of kinetic control), where—although the catalyst possesses adequate isomerization activity—symmetrical trialkylbenzenes are absent from the product. This reaction occurs over acidic mordenite molecular sieve. Mordenite is characterized by its high silicon:aluminum ratio (about 5:1), and its crystal structure. The basic building block of this structure is a tetrahedron consisting of one silicon or aluminum atom surrounded by four oxy-

gen atoms. The crystal is made up of four- and five-member rings of this tetrahedron. The chains are linked together to form a network of large parallel channels interconnected only by small cross channels. Rings of 12 tetrahedrons form the large channels (1). Shape selectivity in dialkylbenzene disproportionation is a consequence of the small pore size and characteristic structure of mordenite.

EXPERIMENTAL METHODS

We used Zeolon H, the acid (or "hydrogen") form of mordenite, produced by the Norton Company. Our sample contained 0.99% Na (determined by neutron activation analysis), and had a silicon:aluminum ratio of 5:1.

Two other catalysts used for comparisons were white TCC beads silica-alumina commercial cracking catalyst obtained from Socony Mobil Company, and an ammonium exchanged form of Y-type faujasite, purchased from the Linde Division of Union Carbide Company. The latter was deactivation by heating in air at 538°C.

The reactions of 1-methyl-2-ethylben-

zene were used to study transalkylation selectivity over these catalysts. The reactions of methylethylbenzenes and the reaction apparatus used has been described in detail earlier (2). Reaction conditions were liquid hourly space velocity of 16, a hydrogen:hydrocarbon molar ratio of 5, 204°C temperature, and atmospheric total pressure. The experiments were 20 min long. Reaction effluent samples were taken after 20-min catalyst onstream times. An acetone-Dry Ice condenser was used to collect liquid products. Liquid products were analyzed with a 300-ft long Ucon LBX-550 capillary gas chromatographic column. Product distributions over the mordenite catalyst are shown in Table 1.

RESULTS AND DISCUSSION

The principal reaction of 1-methyl-2-ethylbenzene over acidic catalysts (other than mordenite) is isomerization to 1-methyl-3- and 4-ethylbenzenes and dispropo-

portionation to toluene and methyldiethylbenzenes (MDEB) or ethylbenzene and dimethylethylbenzenes (DMEB) (2). Two of the six possible MDEB isomers, 1-methyl-3,4-diethylbenzene and 1-methyl-3,5-diethylbenzene, cannot be formed directly from 1-methyl-2-ethylbenzene. Their formation requires either isomerization of 1-methyl-2-ethylbenzene before the transekylation or isomerization of one of the other MDEB isomers. The situation is similar with the DMEB isomers. The isomers which cannot be formed directly from 1-methyl-2-ethylbenzene by transmethylation are 1,2-dimethyl-4-ethylbenzene and 1,3-dimethyl-5-ethylbenzene. The relative amounts of MDEB and DMEB isomers which cannot be formed directly from 1-methyl-2-ethylbenzene are related to the extent of methylethylbenzene isomerization (2). The isomerization which is needed to produce these isomers is faster than the rate of methylethylbenzene iso-

TABLE 1
REACTIONS^a OF 1-METHYL-2-ETHYLBENZENE OVER THE HYDROGEN FORM OF "ZEOLON" MORDENITE^b

Temperature of pretreatment, in dry H ₂ (°C):	482	593	842	842
Reaction temp (°C):	204	204	204	343
Product distribution, (mole %)				
Unreacted 1-Methyl-2-ethylbenzene	78.40	85.00	99.88	84.10
1-Methyl-3-, and 4-ethylbenzenes	20.48	14.25	0.04	15.73
Benzene	0.016	0.003		0.012
Toluene	0.450	0.317	0.03	0.085
Ethylbenzene	0.117	0.070		0.011
Xylenes	0.017	0.011		0.002
1,2,4-Trimethylbenzene	0.001			
Diethylbenzenes	0.022	0.009		
1,3-Dimethyl-5-ethylbenzene	0.0003			
Other Dimethylethylbenzenes	0.106	0.054		0.006
1-Methyl-3,5-diethylbenzene	0.0013	0.0012		0.0004
Other Methyldiethylbenzenes	0.389	0.284	0.05	0.054
Isomerized methylethylbenzenes (%) of total methylethylbenzenes	20.71	14.37	0.04	15.8
Disproportionation by ethyl transfer (mole %)	0.78	0.57	0.09	0.108
Disproportionation by methyl transfer (mole %)	0.21	0.11		0.012
Isomerization/disproportionation by ethyl transfer	26	25	0.4	146

^a Reaction conditions: An LHSV of 16, atmospheric total pressure, and an H₂: hydrocarbon ratio of 5. The experiments were 20 min long. The catalyst was regenerated at 482°C with air for 20 min before the hydrogen pretreatment.

^b Prepared by the Norton Company. Silicon: aluminum ratio about 5:1. Approximate composition (H, Na)₂ Al₂Si₉O₂₂·6H₂O.

merization. At a methylethylbenzene isomerization level of about only 40%, the relative concentration of the MDEB and DMEB isomers approaches the equilibrium distribution. [The equilibrium distribution of the MDEB isomers in Ref. (2) did not include 1-methyl-2,3-diethylbenzene and 1-methyl-2,6-diethylbenzene. These two isomers (expected only at a low relative concentration) were not detected. Recently, however, with an improved chromatographic apparatus, these isomers were determined. Table 2 shows the corrected equilibrium distributions of the MDEB isomers.]

At equilibrium, the symmetrical trialkylbenzene, 1-methyl-3,5-diethylbenzene, is the main component of the MDEB isomer

mixture (46.8% at 315°C). Similarly, 1,3-dimethyl-5-ethylbenzene is the most prevalent DMEB isomer (33.5% at 315°C). Over silica-alumina, decationized Y-type faujasite molecular sieve, and other acid-type catalysts, relatively high concentrations of these isomers are formed even at low (i.e., 11%) methylethylbenzene isomerization levels (Table 2). However, practically none of these symmetrical trialkylbenzenes are produced over the "hydrogen" mordenite molecular sieve (Table 2).

The crystal structure of sodium mordenite has one-dimensional channels with a diameter of 6.6 Å. These channels are interconnected with smaller channels with a diameter of 2.8 Å (3). The channel aperture of the "hydrogen" mordenite is some-

TABLE 2
DISTRIBUTION OF DIMETHYLETHYLBENZENE AND METHYLDIETHYLBENZENE ISOMERS

Catalyst	"Hydrogen" mordenite			White TCC beads		Decat-	Equi-
				silica-alumina		ionized	
Catalyst pretreatment temp (°C):	482	593	842	538	538	Y-fauja-	distribu-
Reaction temp (°C):	204	204	343	315	400	site	tion at
						204	315°C
Dimethylethylbenzenes							
1,2-Dimethyl-3-ethylbenzene	2.72			3.3	2.97	2.76	3.2
1,2-Dimethyl-4-ethylbenzene	66.14	68.7	47.28	8.9	7.87	5.17	20.9
1,3-Dimethyl-2-ethylbenzene				2.8	3.69	3.28	1.9
1,3-Dimethyl-4-ethylbenzene	18.53	21.0	26.00	28.6	29.90	27.59	16.4
1,3-Dimethyl-5-ethylbenzene	0.24		4.50	19.6	18.10	16.08	33.7
1,4-Dimethyl-2-ethylbenzene	12.37	10.3	22.22	36.8	37.47	45.12	23.9
Methyldiethylbenzenes							
1-Methyl-2,3-diethylbenzene	0.40						0.8
1-Methyl-2,4-diethylbenzene	37.24	37.15	40.30	30.7	30.7	32.23	20.3
1-Methyl-2,5-diethylbenzene	55.33	58.81	50.26	28.9	32.3	29.44	21.2
1-Methyl-2,6-diethylbenzene	1.82		2.28				1.1
1-Methyl-3,4-diethylbenzene	4.86	3.63	6.34	9.8	9.4	7.02	9.8
1-Methyl-3,5-diethylbenzene	0.35	0.41	0.82	30.6	27.6	31.31	46.8
Isomerized methylethylbenzenes ^a (% of total methylethylbenzenes)	20.7	14.4	15.8	11.0	14.9	18.6	
Total dimethylethylbenzenes (mole % of feed)	0.11	0.05	0.006	0.03	0.04	0.54	
Total methyldiethylbenzenes (mole % of feed)	0.39	0.28	0.054	0.45	0.25	10.50	
Expt.	1	2	3	4	5	6	

^a 1-Methyl-3-, and 4-ethylbenzenes.

what larger. The symmetrical trialkylbenzenes are about 0.5 to 1 Å wider than the other trialkylbenzene isomers (Table 3). The minimum cross section of 1,3-dimethyl-5-ethylbenzene is about 8.6 Å. If symmetrical trialkylbenzene isomers are formed inside the pores, they cannot diffuse out the pore windows. (The small amount of symmetrical trialkylbenzene isomers found could have formed on acid sites exposed on the external surface of the catalyst particles.) The other trialkylbenzene isomers (with cross sections below 8.2 Å) are able to diffuse out of the pores. Thus, effective channel apertures of a "hydrogen" mordenite are between 8.2 and 8.6 Å. This is considerably less than the 10 Å suggested by Sand (4). Shape-discriminating catalytic reactions over 5A molecular sieves

have been shown previously by Weisz and co-workers (5).

Our technique may also be applied to study catalyst deactivation. Molecular sieves may deactivate either by elimination of acid sites without recrystallization or by recrystallization and sintering. The peculiar selectivity observed with trialkylbenzenes allows us to determine which of these two processes predominate with mordenite. If deactivated by the first mechanism, the selectivity of trialkylbenzene formation should not change. However, if the crystal lattice is destroyed (i.e., mordenite is changing to an amorphous silica-alumina-like structure), the symmetrical trialkylbenzenes will no longer be absent from the reaction product. We deactivated "hydrogen" mordenite at 842°C to an activity level which was about 0.03% of its original activity (Table 1). Since, at this low activity, conversions are too small, we reacted methylethylbenzene at 343°C instead of 204°C. Isomerization conversion at this temperature is similar to that over the active catalyst at 204°C (Table 2). The catalyst still maintains its selectivity; i.e., the amount of symmetrical alkylbenzenes is still very much less than observed under similar circumstances over other catalysts. This suggests that catalyst deactivation occurs by successive elimination of sites and not by a complete transformation of the structure. The remaining few active sites—although representing less than 0.03% of the original number—still have essentially the same selectivity as before deactivation.

TABLE 3
MINIMUM CROSS SECTION OF ALKYL
AROMATICS

Hydrocarbon	Minimum cross ^a section (Å)
Benzene	7.0
Toluene	7.0
Ethylbenzene	7.0
<i>o</i> -Xylene	7.6
<i>m</i> -Xylene	7.6
<i>p</i> -Xylene	7.0
1-Methyl-2-ethylbenzene	7.7
1-Methyl-3-ethylbenzene	7.6
1,2,3-Trimethylbenzene	8.1
1,2,4-Trimethylbenzene	7.6
1,3,5-Trimethylbenzene	8.6
1,2-Dimethyl-3-ethylbenzene	8.1
1,2-Dimethyl-4-ethylbenzene	7.6
1,3-Dimethyl-2-ethylbenzene	8.1
1,3-Dimethyl-4-ethylbenzene	7.6
1,3-Dimethyl-5-ethylbenzene	8.6
1,4-Dimethyl-2-ethylbenzene	7.6
1-Methyl-2,3-diethylbenzene	8.2
1-Methyl-2,4-diethylbenzene	7.6
1-Methyl-2,5-diethylbenzene	7.7
1-Methyl-2,6-diethylbenzene	8.2
1-Methyl-3,4-diethylbenzene	7.7
1-Methyl-3,5-diethylbenzene	8.7

^a Determined from Fisher-Hirschfelder-Taylor molecular models.

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