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Shape-Selective Reactions with Zeolite Catalysts

V. Alkylation or Disproportionation of Ethylbenzene to Produce *p*-Diethylbenzene

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Alkylation of ethylbenzene (EB) with ethylene produces diethylbenzene (DEB) over ZSM-5 zeolite catalysts. Disproportionation of EB over these catalysts gives benzene and DEB. Less *ortho*-DEB forms than expected for equilibrium. Large-crystal ZSM-5 gives higher concentrations of *para*-DEB (PDEB) than small-crystal ZSM-5. Alkylations and disproportionation over ZSM-5 modified with magnesium and phosphorus yield 98–99+% PDEB. These observations establish the elements necessary for development of a commercial PDEB process.

INTRODUCTION

Alkylation of benzene with ethylene to produce ethylbenzene (EB), along with polyethylated benzenes, is a well-known reaction. Considerable attention has been given to this chemistry because large amounts of EB were required to satisfy growth in demand for styrene in a highly competitive market. Friedel–Crafts catalysts such as aluminum chloride (*1–4*), boron triflouride (*5*), and titanium tetrachloride (*6*); solid acids such as silica–alumina mixtures (*7, 8*) and aluminum phosphate (*9*); zeolites (*10, 11*); and super acids (*12, 13*) have been used. Higher ethylated products, including pentaethylbenzene and hexaethylbenzene (*14*) were also produced.

Following the discovery of *para*-selective zeolite catalysts (*15–18*), preparation of *p*-diethylbenzene (PDEB) was achieved by direct alkylation of EB. In the past, complex synthetic procedures were required. High-purity PDEB has been prepared by reduction of *p*-ethylacetophenone (*19, 20*) and by selective sorption of the *para* isomer from an isomeric mixture. In the latter process, X or Y zeolites, containing barium and/or potassium, were used (*19*). The sorbed PDEB was displaced and diluted with toluene to give a mixture easily separated by distillation.

EXPERIMENTAL

Materials. High-purity ethylbenzene and ethylene were used without further treatment.

Catalysts. Procedures for synthesis of ZSM-5 zeolite crystals have been described (*22*).

Modified zeolites, Mg–P–ZSM-5. HZSM-5 zeolite (60.5 g) having a crystallite size of approximately 1–2 μm containing 35 wt% alumina binder, in the form of $\frac{1}{16}$-in. extrudate, was steamed at 600°C for 1 h. It was thereafter impregnated with a solution of 38.7 g of diammonium acid phosphate in 100 ml of water, dried, and calcined at 500°C overnight in an open dish. The resulting product was cooled and impregnated overnight with a solution of 195 g of magnesium acetate tetrahydrate in 133 ml of water, dried, and calcined at 500°C for about 19 h. The final catalyst contained 4.93 wt% magnesium and 3.48 wt% phosphorus, probably present as their corresponding oxides.

Apparatus and procedures. Five to ten grams of catalyst were positioned in a fixed-bed, continuous-flow, electrically

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heated, cylindrical, quartz reactor, 1.1 × 15 cm, containing a centered quartz thermowell for experiments carried out at atmospheric pressure. The temperature was measured at three positions within the catalyst bed. Ethylbenzene was delivered by a metering pump to a vaporizer, and where appropriate, mixed with carrier gases with rates determined by mass flow meters. The reaction temperature was recorded as the highest reading in the catalyst bed. The vapor from the reactor was passed successively through cold water and Dry-Ice traps. The remaining gas was measured by a wet-test meter and collected in a tower by displacement of brine or water for subsequent analysis. The liquid in the dry-ice trap was warmed to ambient temperature and the gas evolved was collected in a Teflon bag for analysis. The remaining liquid was combined with the condensate in the water-cooled trap and analyzed by gas chromatography. A silica-gel column was used to analyze gases, and a 5% SP-1200/5% Bentone on Supelcoport column was used for the organic liquid.

Metal apparatus constructed entirely of stainless steel was used for experiments carried out at elevated pressure. Catalyst volumes up to 50 cm^3 could be used. All equipment was automated to permit continuous, unattended operation. Generally, reaction products were collected for analysis and material balances were calculated for 1- to 2-h periods after equilibrium had been established, and also for periods of up to 24 h. Material balances were calculated for most runs; overall weights of liquid and gaseous products fell well within 100 ± 2% of the weight of the starting materials.

Definitions

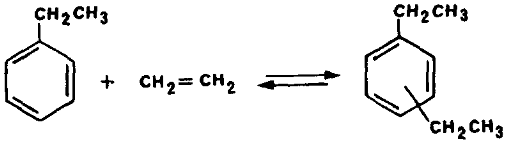
Weight–hourly space velocity (WHSV): weight of reactor feed per unit weight of catalyst per hour. Selectivity to products: weight of each product obtained divided by the weight of starting materials consumed, normalized to 100%. Conversion: weight of starting material consumed divided by weight of starting material normalized to 100%. *para*-Selective catalysts: catalysts which give more than twice the thermodynamic equilibrium amount of *para* isomer in the product for alkylation, disproportionation, etc.

RESULTS AND DISCUSSION

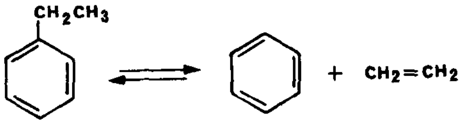
Reactions

Diethylbenzene was prepared by alkylation of ethylbenzene with ethylene over a variety of ZSM-5 zeolite catalysts (Eq. (1)). It was also produced from EB by disproportionation (Eq. (3)). Under more vigorous conditions, higher temperatures or contact times, disproportionation occurs during alkylation. Fortunately, the desired product is formed in both reactions.

Alkylation/Dealkylation

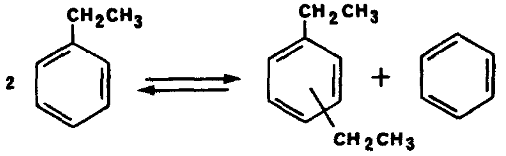


(1)



(2)

Disproportionation



(3)

Unmodified, Unselective Catalysts

Results for the alkylation reaction with small-crystal (0.02–0.2 μm) HZSM-5 catalyst, SiO_2/Al_2O_3 ratio 70/1, are summarized in Table 1. At low temperatures, diethylbenzene was the major product (Eq. (1)). At higher temperatures, benzene was also a significant product; this indicates greater

TABLE 1

Alkylation of Ethylbenzene with Ethylene over ZSM-5

Run No.	SiO_2/Al_2O_3 ratio 70/1						SiO_2/Al_2O_3 ratio 1600/1		
	1	2	3	4	5	6	7	8	9
Conditions									
Temp. (°C)	250	250	300	300	350	350	350	350	350
WHSV									
EB	7.2	7.2	6.9	6.9	7.1	7.1	7.9	7.2	7.2
C_2H_4	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.6
EB/C_2H_4 (mole)	4.0/1	4.0/1	3.8/1	3.8/1	4.0/1	4.0/1	4.1/1	3.5/1	3.1/1
TOS[a] (h)	0–1	18–19	0–1	18–19	0–1	22–23	0–1	2–18	19–22
Conversion (wt%)									
EB	19	5	50	48	53	56	15	11	6.4
C_2H_4	86	3	92	83	68	67	27	15	9.7
Selectivity to products (wt%)									
Benzene	3.5	0.5	18.9	19.0	28.1	30.1	8.1	6.6	5.6
Toluene	1.7	6.6	1.8	1.5	2.8	4.0	2.4	2.7	5.3
Xylene	2.1	6.9	1.5	1.5	0.5	0	0.8	1.0	1.3
Ethyltoluene	1.3	1.8	2.1	1.5	0	0	0.5	0.4	1.1
Diethylbenzene	77.4	71.8	70.1	72.3	53.7	45.4	86.1	86.3	82.0
Other aromatics	9.4	9.7	2.3	2.8	9.1	12.9	1.7	2.6	3.9
Gas	4.6	2.7	3.3	1.4	5.8	7.6	0.4	0.4	0.8
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Diethylbenzene									
Para	35.5	51.1	31.1	30.6	28.9	28.7	36.9	41.1	51.1
Meta	60.2	46.5	62.3	64.5	61.4	60.8	62.1	58.3	48.9
Ortho	4.3	2.4	6.6	4.9	9.7	10.5	1.0	0.6	0

[a] Time on stream.

participation of the disproportionation mechanism (Eq. (3)). The increasing selectivity to gaseous products with higher temperatures shows that dealkylation is also a factor (Eq. (2)).

At 250°C, rapid catalyst aging occurred as indicated by the decrease in conversion of starting materials with time on stream. This may be due to slow desorption of products. At higher temperatures, steady-state performance was observed with minimal catalyst aging.

When a less active, highly siliceous ZSM-5 was tested, SiO_2/Al_2O_3 ratio 1600/1 (Table 1), conversion was reduced and the DEB product selectivity increased as expected. Comparison with the 70/1 catalyst at similar EB conversions, Runs 1 and 7 (Table 1), show that side reactions consuming ethylene were reduced with the 1600/1 catalyst.

A large-crystal (1–2 μm) ZSM-5, SiO_2/Al_2O_3 ratio 70/1, was also tested over a broad temperature range (Table 2). Conversions of ethylene and EB increased with temperature, and DEB selectivity reached a maximum (80%) at 325°C. In Run 6, we maintained Run 5 conditions except for the weight–hourly space velocity which was increased from 7.4 to 22.2. EB conversion decreased from 38 to 14%, DEB selectivity increased from 62 to 83%, and by-products were reduced. However, comparison of Run 6 with Run 4 at different conditions shows similar EB conversion and DEB selectivity. A competition between the vari-

TABLE 2

Alkylation of Ethylbenzene with Ethylene: Large-Crystal HZSM-5 (1–2 μm) SiO_2/Al_2O_3 ratio 70/1

	Run No.							
	1	2	3	4	5	6	7	8
Conditions								
Temp. (°C)	250	275	300	325	350	350	375	400
WHSV								
EB	6.9	6.9	6.9	6.9	6.9	20.8	6.9	6.9
C_2H_4	0.5	0.5	0.5	0.5	0.5	1.4	0.5	0.5
EB/C_2H_4 (mole)	3.8/1	3.8/1	3.8/1	3.8/1	3.8/1	3.9/1	3.8/1	3.8/1
Conversion								
EB	0.6	1.2	3.3	15	38	14	39	42
C_2H_4	0.1	5.1	22	85	94	60	89	77
Selectivity to products (wt%)								
Benzene	2.2	4.3	0.8	1.7	13.3	3.1	15.1	20.1
Toluene	6.0	0.8	0.4	0.6	3.5	1.2	2.9	2.7
Xylene	0.9	23.5	7.2	2.1	2.6	2.3	2.9	2.7
Ethyltoluene	3.6	3.0	2.3	2.1	3.7	1.2	3.1	2.7
Diethylbenzene	45.3	39.1	66.8	80.0	62.1	83.2	63.0	57.5
Other aromatics	8.2	12.8	11.9	8.8	6.7	4.8	6.2	5.5
C_5–C_9	22.4	9.4	4.3	2.4	4.0	2.0	3.6	3.6
Gas	11.4	7.1	6.3	2.3	4.1	2.2	3.2	5.2
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Diethylbenzene								
Para	49.3	64.5	80.2	75.7	54.2	87.2	50.3	50.2
Meta	50.7	35.5	19.8	24.3	45.7	12.8	49.6	49.6
Ortho	0	0	0	0	0.1	0	0.2	0.2

ous reactions and intermediate products in the catalyst bed complicates the optimization process.

Comparison of DEB Isomer Ratio with Thermodynamic Equilibrium

The ratio of isomers observed departs considerably from the calculated thermodynamic equilibrium values (Table 3) (*23*). Furthermore, large changes are observed with moderate changes in reaction conditions. This is in sharp contrast with xylene produced by either alkylation of toluene with methanol or toluene disproportionation (*16, 17*). Wide variations in crystal size and SiO_2/Al_2O_3 ratio all gave near-equilibrium mixtures of xylene isomers with unmodified ZSM-5.

TABLE 3

Thermodynamic Equilibrium of Diethylbenzene Isomers[a]

Temp., (°C)	*Para*	*Meta*	*Ortho*
50	34.3	55.3	10.4
100	33.2	54.7	12.1
200	31.3	53.7	15.0
300	29.8	52.7	17.5
400	28.5	52.0	19.5
500	27.5	51.3	21.2
600	26.7	50.7	22.6

[a] Calculated by M. M. Wu with a computer program prepared by F. H. Krambeck and J. C. V. Kuo. Pressure has no effect on isomer composition.

TABLE 4

Alkylation of EB with Ethylene: Large-Crystal Mg-P-ZSM-5 Catalyst

	Run No.		
	1	2	3
Conditions			
Temp. (°C)	400	425	525
Pressure (psig)	100	100	100
WHSV			
EB	29.7	30.31	30.21
C_2H_4	1.16	1.16	1.16
H_2	0.24	0.24	0.24
$EB/C_2H_4/H_2$ (mole)	6.77/1/3	6.9/1/3	6.9/1/3
Conversion			
EB	11.4	12.6	16.6
C_2H_4	51.1	37.4	28.8
Selectivity to Products (wt%)			
Benzene	8.0	15.2	58.0
Toluene	1.0	2.1	1.6
Xylene	0.4	0	0.4
Ethyltoluene	1.1	0.8	3.8
Diethylbenzene	88.4	79.7	32.7
Other aromatics	0.6	1.2	0.4
Light gas	0.5	1.0	3.1
Diethylbenzene			
Para	99.2	99.9	99.6
Meta	0.8	0.1	0.4
Ortho	0	0	0

Unmodified, large-crystal ZSM-5 differs from the corresponding small-crystal variety in two important aspects. First, formation of *ortho*-DEB is virtually eliminated. Second, *para*-DEB selectivity increases significantly at the expense of the *meta* isomer.

para-Selective Catalysts

para Selectivity was increased in large-crystal ZSM-5 by impregnation with phosphorous and magnesium salts, which were subsequently converted to their oxides by calcination. Screening tests for alkylation of EB with ethylene, at 100 psig pressure, in the presence of 3 moles of hydrogen per mole of ethylene, are summarized in Table 4. The use of hydrogen decreased catalyst aging. Furthermore, ethylene was not reduced to ethane! Diethylbenzene was the major product at 400–425°C. A remarkable 99.2–99.9% *para* isomer in the diethylbenzene product was obtained with this catalyst.

Dealkylation, Disproportionation and Olefin Oligomerization

As indicated by Eqs. (2) and (3), dealkylation and disproportionation of EB lead to production of benzene and ethylene. Furthermore, ethylene reacts with itself over ZSM-5 to form other olefins, paraffins, and even benzene and substituted benzenes (Table 5, Run 1). Thus, benzene in the product could originate from at least three different reactions and be consumed by others to give xylenes, ethyltoluene, etc.

To gain insight to conditions, primarily temperature, which may affect the various reaction possibilities, ethylbenzene was passed over unmodified ZSM-5. In Runs 3 and 4, Table 5, approximately equimolar amounts of benzene and diethylbenzene were isolated. This indicates that disproportionation was the favored reaction. At 350+°C, the product mixture was more complex. Benzene and gas (ethylene equivalent) increased in regular steps with temperature indicating that dealkylation (Eq. (2)) was significant. Toluene, EB, xylene, and ethyltoluene selectivity increases, reaches a maximum at 400°C, and then decreases. This suggests that these compounds are made from ethylene and are in turn dealkylated to give more gas and benzene. The gas was a mixture of C_1–C_4 hydrocarbons resulting from oligomerization of ethylene, cracking, and subsequent dealkylation. The *para* isomer was favored at low temperatures giving way to *meta* isomer at high temperatures.

When a *para*-selective, large-crystal ZSM-5 catalyst was used with EB as the feed, a 99.3–99.8% *para* isomer in the DEB product was observed at all temperatures, Table 6. This result is similar to that found for selective alkylation (Table 3). Only the *para* isomers, with a small minimum dimension, are able to rapidly diffuse out of the

TABLE 5

Ethylbenzene Disproportionation: Large-Crystal HZSM-5

	Run No.							
	1	2	3	4	5	6	7	8
Conditions								
Temp. (°C)	350	200	250	300	350	400	450	500
WHSV								
EB	0	3.5	3.5	3.5	3.5	3.5	3.5	3.5
C_2H_4	2.6	0	0	0	0	0	0	0
Conversion								
EB	—	0.8	3.5	20.4	50.4	72.2	83.3	89.6
C_2H_4	99	—	—	—	—	—	—	—
Selectivity to products (wt%)								
Benzene	0.4	36.9	29.9	33.6	40.5	51.0	58.0	60.8
Toluene	0	0	0	0.6	6.0	12.5	12.6	10.4
Xylenes, EB	9.7	0	2.2	0.9	2.8	4.0	4.1	3.9
Ethyltoluene	7.2	0.5	0.4	0.4	4.1	4.3	2.1	1.1
Diethylbenzene	—	37.3	60.4	61.7	38.0	8.8	2.4	1.8
Other aromatics	7.6	0	1.9	1.1	3.6	6.0	5.4	4.1
C_5–C_9	23.5	2.1	0.6	0.6	2.0	3.0	2.4	1.9
Gas	51.6	23.2	4.6	1.1	3.0	10.4	13.0	16.0
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Diethylbenzene								
Para	—	85.5	63.5	46.8	36.8	29.8	29.4	33.3
Meta	—	14.5	36.5	50.1	62.5	68.6	68.1	65.0
Ortho	—	0	0	0.1	0.7	1.6	2.5	1.7

pores by comparison with the larger *ortho* and *meta* isomers. Isomerization to the *para* form or dealkylation are favored with the latter.

DISCUSSION AND SUMMARY

Substituents on the benzene ring have been progressively increased from dimethyl (*17*) to methylethyl (*18*) to diethyl in alkylation and disproportionation reactions over ZSM-5 catalysts. Thermodynamic equilibrium mixtures of xylene isomers were obtained with unmodified catalysts. However, much lower amounts of *ortho* isomers were produced with ethyltoluene and DEB. Departures were also observed from the equilibrium ratio of the *meta*/*para* isomers. In zeolite catalysts, reactants must come together to form the transition complex within the restricted volume of the pore system. Increasing the size of starting materials and products increases the difficulty. The *ortho* position, for example, because of the adjacent large methyl group compared with hydrogen, requires more space or more restricted geometry to reach the transition state than the *meta* or *para* position. The zeolite pores and residence times of reactants and products are much longer in large-crystal ZSM-5 than in small-crystal catalysts. *Ortho* and *meta* isomers have more time to isomerize to the *para* analog. *Para*-DEB with the smallest minimum dimension diffuses out of the catalyst more rapidly than *ortho* or *meta* isomers. Large crystals have fewer surface sites for nonselective reactions than small crystals. Modifying reagents and coke may selectively de-

TABLE 6

Selective EB Disproportionation: Large-Crystal Mg-P-ZSM-5

	Run No.		
	1	2	3
Conditions			
Temp. (°C)	425	475	525
Pressure (psig)	100	100	100
WHSV			
EB	30.2	30.2	30.2
H_2	0.24	0.24	0.24
TOS (h)	429–430	520–521	538–539
Conversion			
EB	14.7	18.9	22.5
Selectivity to Products (wt%)			
Benzene	42.7	50.4	62.4
Toluene	2.5	1.6	1.3
Xylene	0	0	0
Ethyltoluene	0.8	0.9	0.6
Diethylbenzene	46.1	31.7	15.4
Other aromatics	1.2	2.1	2.7
Light gas	6.7	13.3	17.6
Total	100.0	100.0	100.0
Diethylbenzene			
Para	99.8	99.6	99.3
Meta	0.2	0.4	0.7
Ortho	0	0	0

activate surface sites because of their greater accessibility. Any of these factors would contribute to enhanced *para* selectivity.

Haag and Olson have recently presented an impressive and comprehensive discussion of general principles which account for *para* selectivity in zeolite catalysts (*24*). Selective/unselective xylene isomerization and toluene disproportionation are compared. Quantitative tests were developed for measurement of diffusion and reaction rates. *para* Selectivity is quantitatively described in terms of catalyst activity, crystal size, and rates of diffusion. These same general principles also apply to ethyl substituents on the benzene ring. Alkylation/dealkylation/disproportionation reactions occur with greater ease (lower temperatures) than with methyl groups. The larger size of the ethyl groups magnifies the difference in size between the smaller *para* isomer and the *ortho* and *meta* isomers. This accounts for the high *para*-DEB selectivity observed.

Mixed diethylbenzenes have been produced with a large number of catalysts. However, separation and purification of the individual isomers has been impractical because of their close boiling points. The *para*-selective ZSM-5 zeolite catalysts described here provide the basis for developing a commercial *p*-DEB process for industry.

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