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Shape-Selective Reactions with Zeolite Catalysts

II. Selective Disproportionation of Toluene to Produce Benzene and *p*-Xylene

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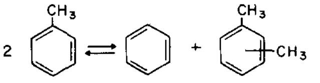
Toluene disproportionated to produce benzene and xylenes rich in the *para* isomer (70–90%) over ZSM-5 zeolites which were modified with phosphorus, boron, or magnesium compounds. A mechanism is proposed where oxides of these elements, present in the zeolites, reduce the dimensions of pore openings and channels sufficiently to favor formation and outward diffusion of *p*-xylene, the isomer with the smallest minimum dimension. This chemistry has potential for an improved process to prepare benzene and *p*-xylene from toluene.

I. INTRODUCTION

The disproportionation of toluene to produce equimolar amounts of benzene and xylenes, Eq. (1), along with other products by subsequent reactions is well known (*1*).



(1)

Equilibrium constants for this reaction are not changed significantly by shifting from liquid to vapor phase or by large changes in temperature (*2, 3*). More highly substituted methylbenzene isomers may also be produced by subsequent reactions between the primary products. This is generally defined as a transalkylation reaction. Hastings and Nicholson have calculated equilibrium concentrations to include the tri- and tetramethylbenzenes, summarized in part in Table 1 (*3*).

As a result of sustained demand for individual C_8 aromatic compounds, especially *p*-xylene and ethylbenzene, over the past three decades, better catalysts and processes have been sought for large-scale commercial plants. Although improvements have been made in the older Friedel–Crafts technology based on aluminum chloride, certain undesirable features are inherent in their use. Product streams are contaminated with corrosive compounds, catalysts cannot be regenerated at plant sites and disposal of spent catalyst wastes contributes to growing pollution problems.

A large number of patents have appeared which describe a variety of solid acidic catalysts for heterogeneous vapor/liquid phase reactions for toluene disproportionation. Mixtures of silica and alumina were impregnated with platinum (*4*) or antimony (*5*), for example. Various forms of mordenite (*6*) including dealuminized modifications (*7*) were active and had low aging rates. The faujasites exchanged with rare earth or transition metals were used for toluene disproportionation (*8*).

Oliver and Inoue have summarized a large body of early industrial research dealing with toluene disproportionation (*9*). Although catalysts were not identified, they have indicated that heterogeneous, vapor phase systems with solid catalysts have significant economic advantages. Commercial processes have been announced by Sinclair/Atlantic Richfield (*9*) and Toray Industries/Universal Oil Products (*10, 11*).

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TABLE 1[a]

Theoretical Equilibrium Concentrations of Methylbenzenes (Mole%)

Temperature (°C)	Benzene	Toluene	Xylenes	Trimethylbenzenes	Tetramethylbenzenes
27	30.0	44.0	22.2	3.6	0.2
127	30.2	43.1	22.7	3.8	0.2
227	31.2	42.2	22.6	3.7	0.3
327	31.5	41.7	22.7	3.8	0.3
427	31.9	41.1	22.7	3.9	0.4
527	32.0	40.6	23.1	3.9	0.4
627	32.3	40.6	22.7	3.9	0.5
727	32.4	40.3	22.8	4.0	0.5

[a] See Ref. (*3*).

At Mobil laboratories, new generations of high silica/alumina ratio zeolites were synthesized and evaluated for hydrocarbon transformations. Grandio, Schneider, Schwartz, and Wise have described a process for converting any isomeric mixture of xylenes to the equilibrium composition under very mild conditions of reaction (*12*). Any desired isomer, such as *p*-xylene, could be removed by established methods and the remaining isomers isomerized to the equilibrium mixture for recycline. In another case, at 260–315°C in the liquid phase or 370–540°C in the vapor phase, toluene was disproportionated to benzene and an equilibrium mixture of xylene isomers (*13*).

Many variations of process schemes for transformation of relatively low cost aromatic mixtures to desired high-value products, such as *p*-xylene, are becoming available (*14*). They are usually based on solid catalysts which disproportionate, alkylate, transalkylate, isomerize, or dealkylate various aromatic feed stocks. In most of these cases near-equilibrium concentrations of xylene isomers were produced.

An objective of the research reported here was the production of *para*-xylene in concentrations significantly higher than equilibrium by a *selective* toluene disproportionation (STDP). This is defined as the conversion of 2 moles of toluene to 1 mole each of benzene and *p*-xylene. Results of certain initial catalyst preparation and screening experiments are reported.

II. EXPERIMENTAL METHODS

Materials. High-purity toluene, 99+% was used without further purification.

Catalysts. Procedures for synthesis of ZSM-5 zeolites have been described (*15*). Techniques for catalyst modification with phosphorus (*16*), boron (*17*), and magnesium (*18*) to produce *para* selectivity have also been reported.

Apparatus and procedure. Four to ten grams of catalyst was positioned in a fixed bed, continuous flow, electrically heated, cylindrical, quartz reactor, 1.1 × 15 cm, containing a centered quartz thermowell for experiments carried out at atmospheric pressure. Temperature was measured at three positions within the catalyst bed. Toluene 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

TABLE 2

Toluene Disproportionation over HZSM-5 Catalyst

	Run			
	1	2	3	4
Temperature, °C	450	500	550	600
Pressure, atm	1	1	1	1
Toluene, WHSV[a]	3.6	3.5	3.5	3.5
Conversion, %	8.2	19.9	39.8	51.6
Time on stream, hr	0–1	1–2	2–3	3–4
Product, wt%				
CH_4	0.05	0.1	0.55	2.7
$C_2 - C_4$	0	0	0.5	0.7
Benzene	3.2	9.2	18.3	25.4
Toluene	92.6	79.2	60.8	49.9
Ethylbenzene	0	0	0.05	0.1
p-Xylene	1.0	2.7	4.5	4.7
m-Xylene	2.1	5.8	9.6	10.0
o-Xylene	0.95	2.6	4.5	4.8
C_{9+} aromatic	0.1	0.4	1.2	1.7
Total	100.0	100.0	100.0	100.0
Xylene isomers, %				
para	24.7	24.3	24.2	24.1
meta	51.9	52.3	51.6	51.3
ortho	23.4	23.4	24.2	24.6

[a] Weight hourly space velocity: weight of feed per unit weight of catalyst per hour.

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.

III. RESULTS

Preliminary studies were made with various zeolite catalysts to determine potential for disproportionation of toluene, Eq. (1). The results with HZSM-5 zeolite, at various temperatures, are shown in Table 2. Toluene conversion increased in direct proportion to the temperature from 8 to over 50% in the range of 450–600°C. At the lowest temperature, the mole ratio of benzene/xylenes was 1.07, close to theoretical, 1.00. The observed ratio increased with increases in temperature to a value of 1.77 at 600°C. This was due primarily to a demethylation reaction as indicated by the corresponding increase in the yield of methane. Only a small amount of transalkylation occurred to give C_{9+} aromatic hydrocarbons. A near-equilibrium mixture of xylene isomers was obtained.

In the previous paper of this series (*19*), *para* selectivity for the alkyation of toluene with methanol to produce xylenes was enhanced by treatment and modification of ZSM-5 zeolite with phosphorus compounds. A similar type of catalyst prepared by *impregnation with trimethylphosphite* was tested for toluene disproportionation. Results are summarized in Table 3. This treatment with a phosphorus compound reduced catalyst activity for disproportionation as indicated by the low toluene conversion. However, the concentration of *para* isomer in the xylene product increased significantly over the equilibrium value.

In another experiment, HZSM-5 catalyst was impregnated with a solution of aqueous

TABLE 3

Toluene Disproportionation over ZSM-5 Catalyst Modified with Phosphorus[a]

	Run			
	1	2	3	4
Temperature, °C	550	600	650	700
Pressure, atm	1	1	1	1
Toluene, WHSV[b]	2.1	2.1	2.1	2.1
Conversion, %	0.3	0.8	2.0	4.4
Time on stream, hr	0–1	1–2	2–3	3–4
Product, wt%				
CH_4	0.05	0.10	0.34	1.51
$C_2 - C_4$	—	—	—	0.05
Benzene	0.14	0.34	0.82	1.70
Toluene	99.66	99.18	98.02	95.57
p-Xylene	0.10	0.19	0.38	0.68
m-Xylene	0.05	0.14	0.29	0.29
o-Xylene	—	0.05	0.10	0.10
C_{9+} aromatic	—	—	0.05	0.10
Total	100.00	100.00	100.00	100.00
Xylene isomers, %				
para	67	50	49	64
meta	33	37	38	27
ortho	—	13	13	9

[a] Phosphorus = 3.5 wt% after calcination in air.

[b] Weight hourly space velocity: weight of feed per unit weight of catalyst per hour.

boric acid, dried, calcined, and tested for its ability to disproportionate toluene. The results are summarized in Table 4. During the first four runs, the temperature was increased successively from 500 to 700°C. Toluene conversions increased with temperature to 24.5% at 650°C and then declined. The concentration of *para* isomer in the xylene product increased gradually until the highest temperature was reached, 700°C, where a substantial increase to 73% *para* was observed. In Run 5, Table 4, following calcination with air, the high *para* selectivity was maintained at 600°C. This was a considerable increase over the 28.2% *p*-xylene observed in Run 2, also at 600°C. The high-temperature treatment of the impregnated catalyst caused a change in the catalyst which produced high *para* selectivity and decreased activity.

Boron modified catalysts of the type used for disproportionation were also tested for alkylation of toluene with methanol (*19*). The concentration of *para* isomer in the xylene product was in the 75–95% range.

Samples of ZSM-5 zeolite catalysts were also modified by impregnation with various magnesium compounds. After calcination, to convert the latter to the oxide, the modified catalyst was evaluated for the disproportionation of toluene. Runs were made at atmospheric pressure and various combinations of temperature and space velocity. Results with a catalyst which contained about 11 wt% magnesium, present as the oxide, are shown in Fig. 1. Toluene conversion at each temperature was varied by changing the space velocity. The amount of *para* isomer in the xylene product decreased in direct proportion to space velocity. Perhaps the additional residence time in the catalyst bed led to isomerization of the primary products. In all cases, however, the *p*-xylene concentration exceeded

TABLE 4

Toluene Disproportionation over ZSM-5 Catalyst Modified with Boron

	Run						
	1	2	3	4[a]	5	6	7
Temperature, °C	500	600	650	700	600	650	700
Pressure, atm	1	1	1	1	1	1	1
Toluene, WHSV[b]	2.8	2.8	2.8	2.8	2.8	2.8	2.8
Conversion, %	4.4	20.8	24.5	20.2	5.4	9.7	13.1
Time on stream, hr	1.0	0.7	1.2	1.0	1.0	1.0	1.0
Liquid product, wt%							
Benzene	2.2	10.8	13.5	12.7	2.9	5.4	8.4
Toluene	95.6	79.2	75.6	79.8	94.6	90.4	86.85
p-Xylene	0.65	2.8	3.7	5.3	1.85	3.1	3.9
m-Xylene	1.1	5.0	5.1	1.5	0.5	0.8	0.45
o-Xylene	0.45	2.1	1.8	0.4	0.15	0.2	0.1
C_{9+}	0	0.1	0.2	0.3	0	0.1	0.3
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Gaseous product, ml[c]	0	10	130	295	10	50	290
Xylene isomers, %							
para	29.4	28.2	34.9	73.0	73.8	74.2	87.2
meta	50.5	50.9	48.0	21.1	20.5	20.2	10.1
ortho	20.1	20.9	17.1	5.9	5.7	5.6	2.7

[a] Catalyst calcined at 600°C with air for 2 hr between runs 4 and 5.

[b] Weight hourly space velocity: Weight of toluene per unit weight of catalyst per hour.

[c] Five grams of catalyst used.

the equilibrium value (24%) by a substantial amount. The points at 600°C and 7 WHSV, Fig. 1, show successive 1-hr runs where some coking occurred. This resulted in lower conversion and higher *p*-xylene selectivity with time on stream.

The observed enhancement of *para* selectivity with boron and magnesium catalysts with increases in temperature is unusual. More information regarding this phenomenon will be reported in the future.

IV. DISCUSSION

In the previous paper of this series, it was shown that *p*-xylene was the major product obtained in the alkylation of toluene with methanol over ZSM-5 class zeolite catalysts which had been modified by various chemical and physical treatments (*19*). It was proposed that the zeolite pores and openings were reduced in size so that the *para* isomer, with the smallest minimum dimension, was able to diffuse out of the pores at a much more rapid rate than the *ortho* and *meta* isomers (*20*). The latter could also isomerize to para within the catalyst pore structure and also contribute to higher yields of *p*-xylene.

A similar mechanism is proposed for selective toluene disproportionation. The selective catalysts, with channels reduced in size, may favor transfer of the methyl group to the least hindered position of toluene, and the resultant *p*-xylene formed diffuses out of the pores at a relatively fast rate. In addition, *ortho* and *meta* isomers within the pores would isomerize to *para* as the latter concentration is reduced by rapid outward diffusion.

The mechanism of alkylation reactions catalyzed by various Friedel–Crafts catalysts was extensively studied in the 1950s. Interactions between aromatic hydrocarbons and aluminum halides to produce π complexes (*21*) and between alkyl and aluminum halides to explain isomerization without ionization of the alkyl group (*22*) were studied to identify initial events in the alkylation reaction. The combination of halogen acids and catalyst, such as $AlCl_3$ and HCl (*23*) or BF_3 and HF (*24*) to produce the hypothetical $HAlCl_4$ and HBF_4 acids was proposed as a key step for generation of the alkylating agent for disproportionation, Eq. (2). The proton from this "acid" was attracted by the π electron cloud of the aromatic ring and then at-

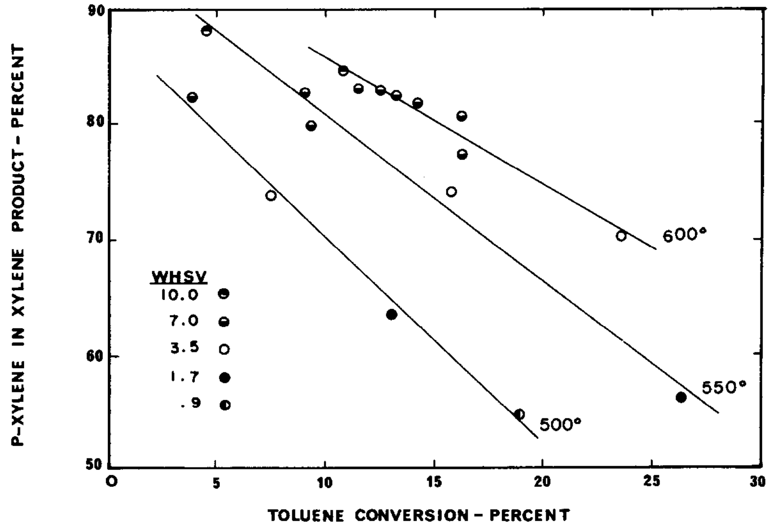
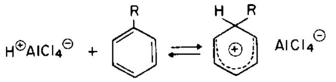


FIG. 1. Toluene disproportionation; ZSM-5 catalyst modified with magnesium oxide (Mg = 11 wt%).

tacked a ring carbon atom to form a carbonium ion salt, Eq. (3). The alkyl group could then be transferred to a second aromatic ring

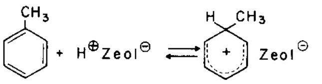
$$\mathrm{HCl} + \mathrm{AlCl_3} \rightleftharpoons \mathrm{H^{\oplus}AlCl_4^{\ominus}} \qquad (2)$$



(3)

in the transalkylation step. It was demonstrated that a *n*-propyl group (R = *n*-propyl), Eq. 3, maintained its configuration to produce the corresponding *n*-propyl derivative (*25, 26*). A key feature of this mechanism is the attack of the proton on the aromatic ring bearing the alkyl substituent to be transferred.

The zeolite catalysts which are effective for alkylation or transalkylation also contain strong, protonic acid sites. We propose that an analogous mechanism operates during the toluene transalkylation reaction described here. To summarize, the proton from the acid form of the zeolite, $\mathrm{H^+Zeol^-}$, attacks a toluene molecule at the *ipso* position, Eq. (4). This weakens the carbon–methyl bond, Eq. (5), and initiates transfer to a second toluene molecule, Eq. (6). Since this reaction occurs within the zeolite pores, the *para* position is least hindered by the snug fit of the aromatic rings and consequently would be most available to attack. Transfer of a proton back to an anionic site in the catalyst from the protonated xylene gives the xylene product and regenerates the acid site in the catalyst, Eq. (7). *ortho*- and *meta*-xylene also isomerize to the *para* isomer within the zeolite pores. Although this mechanism is speculative and conditions depart significantly from the reactions in solution, we believe it is consistent with a large body of data developed for Friedel–Crafts catalysts, the known general acidic properties of zeolites and the products observed.



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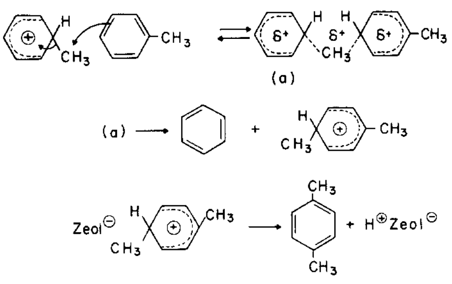

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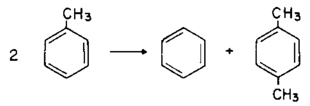

(8)

Techniques have been described for modification of Mobil ZSM-5 class zeolite catalysts by certain chemical and physical treatments to give *para*-substituted benzene derivatives in alkylation and disproportionation reactions. These new *para*-selective catalysts provide potential for a significant improvement in toluene disproportionation technology by increasing the yield of the desired *p*-xylene isomer.

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