

Selective Alkylation of Toluene with Methanol to Produce *para*-Xylene

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Received April 14, 1980; revised August 4, 1980

Toluene has been alkylated with methanol over ZSM-5-class zeolite catalysts to produce xylenes and water. A near equilibrium mixture containing 24% of the *para* isomer was usually observed. Production of over 90% *para* isomer in the xylene product was achieved when the catalyst was modified by impregnation with phosphorus and with boron compounds. *para*-Xylene selectivity was also enhanced by coking and coating the catalyst surface with heat-stable polymers. A controlled reduction in the effective dimensions of the catalyst pore openings, and/or channels, along with deactivation of acidic surface sites, has been proposed as a mechanism for the selective production of *p*-xylene.

I. INTRODUCTION

Toluene is the major single component produced in the catalytic reformers of petroleum refineries, the principal source for industrial aromatic hydrocarbons (1). Benzene and the C₈ aromatics, however, are presently the compounds in greatest demand. The large quantities of toluene produced are utilized primarily to prepare benzene by dealkylation or consumed as a component in gasoline to improve octane quality.

para-Xylene is a valuable aromatic compound in reformat because of demand for oxidation to terephthalic acid, a major component in polyester fibers. A relatively high cost is associated with obtaining it in the desired 99+ % purity because purification requires separation from three close boiling C₈ aromatic compounds, *m*-xylene, *o*-xylene, and ethylbenzene and subsequent isomerization of the remaining *ortho/meta* xylene isomers to the equilibrium mixture for recycle. Since the equilibrium amount

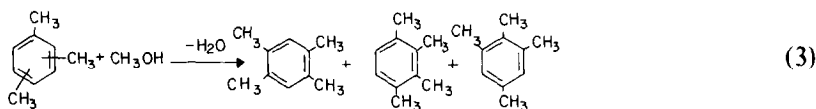
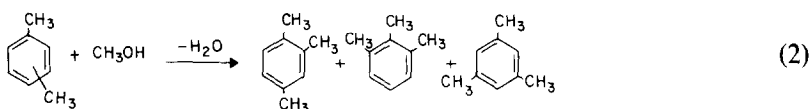
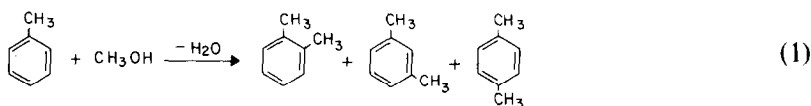
of *para* isomer in the xylenes is only about 24% of the total, separation and isomerization processes must be repeated many times. The necessary removal of ethylbenzene by isomerization and cracking is another complicating factor.

An objective of the work reported here was to identify a relatively simple and practical method for the direct alkylation of toluene with methanol to produce high yields of *p*-xylene and provide the basis for a more economical commercial process starting with toluene and methanol.

Alkylation of toluene has been studied extensively. Basic principles for electrophilic substitution reactions (2) and comparisons of a variety of Friedel-Crafts catalysts have been made with this model reaction (3). Initial *ortho/para* orientation of substituents has been established. However, isomerization under the conditions of reaction always occurred to give a mixture of all xylene isomers (Eq. (1)). The latter, in turn, may be further methylated to produce tri- and tetramethylbenzenes with a sufficient supply of methanol and more vigorous conditions of reaction (Eqs. (2) and (3)). In addition, isomerization and trans-alkylation may be superimposed on all of the primary alkylation reactions.

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In the early 1960s, the new synthetic zeolites which appeared attracted attention as alkylation catalysts because of their high acidity, freedom from corrosive substances such as halogen and volatile acids, potential for regeneration, ease of catalyst separation from reaction products, and elimination of growing problems associated with disposal of spent catalysts such as aluminum chloride. Early work with the faujasites X and Y, especially rare earth exchanged varieties, revealed effective performance in alkylation of benzene or toluene with low-molecular-weight olefins or alcohols (4). *Ortho-para* orientation of substituents was observed under relatively mild conditions of reaction. Comparisons between promoted Friedel-Crafts catalysts and these zeolites indicated similar reaction mecha-

nisms involving an electrophilic attack on the aromatic ring by carbonium ion intermediates (5).

In 1970, Yashima and co-workers focused attention on the distribution of xylene isomers produced by alkylation of toluene with methanol over a variety of cation-exchanged zeolite Y catalysts (6). The relatively high amount of *para* isomer obtained (45–50%) with certain catalysts was especially interesting (Table 1). Other exchanged Y zeolites of this series gave an isomeric xylene distribution similar to that observed by Allen and Yats in a comprehensive study of Friedel-Crafts alkylations (3). None of these catalysts, however, gave a composition very close to the calculated thermodynamic equilibrium (7) (Tables 1 and 2). In a subsequent paper, Yashima

TABLE I
Alkylation of Toluene with Methanol: Literature Values

Catalyst	Temperature (°C)	Xylene isomers (%)		
		<i>para</i>	<i>meta</i>	<i>ortho</i>
H-, Ce-, La-, Ni-, Co-, and Mn-Y zeolites ^a	225	45–50	30–22	25–28
Cd-, Ca-, Mg-, Sr-, and Li-Y Zeolites ^a	225	25–20	20–15	55–65
BF ₃ -P ₂ O ₅ ^b	60	26	14	60
Thermodynamic equilibrium ^c	227	24.1	54.8	21.1

^a Ref. (6).

^b Ref. (3).

^c Ref. (7).

TABLE 2
Equilibrium Concentrations of Xylene Isomers^a

Temperature (°C)	<i>para</i>	<i>meta</i>	<i>ortho</i>
27	23.82	59.80	16.38
127	24.24	56.82	18.94
227	24.07	54.77	21.16
327	23.81	53.24	22.95
427	23.45	52.12	24.43
527	23.09	51.35	25.56
627	22.81	50.58	26.61
727	22.49	50.06	27.45

^a Ref. (7).

obtained a 50% concentration of *para* isomer in the xylene product with Mn-Y catalyst; however, no details were reported on the conversion of toluene or methanol or reaction products other than the xylenes (8).

The pioneering work by Weisz and Fritelte (9) and by Chen, Miale, and others on the shape-selective characteristics of certain zeolite catalysts, with reactions of aliphatic hydrocarbons, as reviewed by Csicsery (10), is fundamental to our thinking on the appearance of relatively high concentrations of *para* isomer in the xylene product. These principles, in effect, state that reactions which occur within the pores of zeolites may have steric restrictions imposed on the reacting molecules, during their approach to various possible transition states, which will give a product mixture entirely different from that of the same reaction occurring in solution or the surface of a catalyst where these constraints are not in effect.

Chen and co-workers have studied alkylation of toluene with methanol over several new-generation Mobil zeolites with high silica/alumina ratios (>12/1), such as ZSM-5 (11). They found that using microcrystalline catalyst samples resulted in an equilibrium mixture of xylenes (24–25% *para*). However, when relatively large crystals of ZSM-5 were used, about 46–48% of the xylene product was the *para*

isomer. They also found that treatment of the zeolite with alkylchlorosilane or certain organic bases, presumably to deactivate the external surface, gave a catalyst which produced as much as 81% of the *para* isomer in the xylene product (11). This was a clear indication of shape selective catalysis with an aromatic substrate.

Techniques for producing *para* selectivity in zeolite catalysts for various reactions have recently been reported (12). Several zeolite catalyst modification procedures which gave high selectivity to *p*-xylene when toluene was alkylated with methanol are described in this paper.

II. EXPERIMENTAL

Materials

Methanol, methyl ether, and toluene were high-purity reagents (99+%) and were used without further purification.

Catalysts

All of the zeolite catalyst crystals utilized in this study were prepared by members of the Catalyst Research and Development Group, Mobil Research and Development Corporation (13). Procedures for synthesis of ZSM-5 (14) and ZSM-11 (15) have been described. Modifications of the catalysts used in alkylation reactions to increase selectivity to the *para* isomer were achieved by impregnation with solutions of the corresponding salts or compounds in aqueous or organic solutions. Subsequent evaporation of the solvent and then controlled calcination in air to produce the corresponding oxides gave the final, *para*-selective, modified catalysts used. With phosphorus compounds, for example, phosphoric acid or ammonium phosphate in water could be used. Diphenylphosphinous acid, triphenylphosphine or phosphorus trichloride dissolved in methylene chloride, carbon tetrachloride, or benzene could also be used. A carborane-siloxane polymer (16) dissolved in chloroform could be applied to the catalyst. Boron compounds

such as boric acid, trimethylborate, boron hydrides, or triphenylborane could be applied when dissolved in suitable, inert solvents and subsequently dried and calcined.

Apparatus and Procedure

Two to ten grams of catalyst was positioned in a fixed-bed, continuous-flow, electrically heated, cylindrical, 1.1×15 -cm quartz reactor, containing a quartz thermowell in the center. Experiments were carried out at atmospheric pressure. Temperature was measured at a minimum of three positions within the catalyst bed. Solutions of methanol and toluene, in desired molar ratios, were delivered by a metering pump to a vaporizer and, where appropriate, mixed with carrier gases, with rates deter-

mined by mass flow meters. The reaction temperature was recorded as the highest reading in the catalyst bed.

The vapor from the reactor was cooled successively in cold water and dry ice traps. Noncondensable gas was measured by a wet test meter and collected for subsequent analysis in a tower by displacement of brine or water. The liquid in the dry ice trap was warmed to ambient temperature. Evolved gas was collected in a Teflon bag for analysis. The remaining liquid was combined with the condensate in the water-cooled trap, and the organic and water phases were separated, weighed, and analyzed by gas chromatography. A silica gel column was used to analyze gases, a 5% SP-1200/5% Bentone-34 on Supelcoport

TABLE 3
Alkylation of Toluene with Methanol over HZSM-5 Catalyst^a

	1	2	3	4
Conditions				
Temperature (°C)	600	600	600	600
Toluene/methanol (mole ratio)	2/1	2/1	2/1	2/1
WHSV ^b	5.2	5.3	5.3	5.3
Time on stream (hr)	0-0.8	0.8-1	1-17.5	17.5-18
Conversion (%)				
Toluene ^c	51	36	30	30
Methanol	100	100	100	100
Organic product (wt%)				
Benzene	14.4	3.9	1.4	1.7
Toluene	47.9	61.4	67.1	66.9
Ethylbenzene	0.3	0.1	—	—
Xylene <i>para</i>	7.3	8.0	9.0	9.1
<i>meta</i>	15.8	15.4	12.9	13.0
<i>ortho</i>	7.5	7.2	5.8	5.9
Ethyltoluene	2.4	0.4	0.3	0.3
Mesitylene	1.0	0.3	—	—
Pseudocumene	2.3	2.8	2.9	2.8
Other aromatics	1.1	0.5	0.6	0.3
Total	100.0	100.0	100.0	100.0
Xylene composition (%)				
<i>para</i>	24	26	32	33
<i>meta</i>	52	50	47	46
<i>ortho</i>	24	24	21	21

^a Reaction at atmospheric pressure; only traces of gas were formed.

^b Weight of toluene and methanol feed mixture per hr per unit weight of catalyst.

^c Theoretical conversion of toluene is 50% due to the limiting methanol concentration.

column was used for the organic liquid, and a Porapak QS column was used for the aqueous phase.

Metal apparatus constructed entirely of stainless steel was used for experiments carried out at elevated pressure. Catalyst volumes up to 50 cm³ could be used. All equipment was automated to permit continuous, unattended operation. Generally, reaction products were collected for analysis and material balance calculations for 1 to 2-hr periods after equilibrium had been established and also for periods of up to 24 hr. Material balances were calculated for most runs reported with overall weights of liquid and gaseous products falling well within 100 ± 2% of the weight of the starting materials.

III. RESULTS

A. Unmodified Zeolite Catalysts

The alkylation of toluene with methanol was studied initially with samples of ZSM-5 catalyst which had been calcined, ion exchanged with ammonium nitrate or chloride to remove sodium, and then calcined at 500°C to obtain the active acid form by expulsion of ammonia. A reaction occurred to give a mixture of xylene isomers as the principal products (80+ %); Eq. (1). Results for a typical experiment are summarized in Table 3. The catalyst was very active initially as indicated by the high toluene conversion (51%). The large amount of benzene observed initially resulted from toluene disproportionation,

TABLE 4
Alkylation of Toluene with Methanol over HZSM-5 Catalyst^a

	1	2	3	4
Conditions				
Temperature (°C)	490	495	400	400
Toluene/methanol (mole ratio)	1.5	1.5	1.5	1.5
WHSV ^b	20.6	20.2	20.6	3.7
Time on stream (hr)	0.5	1.2	1.7	2.6
Conversion (%)				
Toluene	39	40	33	38
Methanol	99+	99+	99+	99+
Organic Product, wt%				
Benzene	1.9	1.7	0.8	1.6
Toluene	57.0	56.4	63.0	58.6
Ethylbenzene	0.2	0.3	0.4	0.5
Xylene <i>para</i>	7.6	7.9	5.8	6.7
<i>meta</i>	17.1	17.7	12.8	15.2
<i>ortho</i>	7.8	7.9	5.5	6.4
Ethyltoluene <i>para</i>	1.0	1.1	2.8	1.5
<i>meta</i>	2.3	2.4	4.8	3.8
<i>ortho</i>	1.0	0.3	0.3	0.9
Mesitylene	0.7	0.5	0	0.2
Pseudocumene	2.7	3.4	3.0	4.7
Other aromatics	0.7	0.5	0.8	0
Total	100.0	100.0	100.0	100.0
Xylene composition (%)				
<i>para</i>	23	24	24	24
<i>meta</i>	53	53	53	54
<i>ortho</i>	24	23	23	22

^a Atmospheric pressure, only traces of gas were formed.

^b Weight of toluene and methanol feed mixture per hr per unit weight of catalyst.

which will be discussed in detail in the next paper of this series. After an hour of reaction, however, catalyst activity and toluene disproportionation were reduced, probably as a result of coke formation. The ratio of xylene isomers initially observed was similar to that calculated for the equilibrium mixture, Table 2. With time on stream, however, a small but significant increase in the proportion of *para* isomer was observed.

In another experiment with HZSM-5 zeolite at lower temperature, near-equilibrium mixtures of xylenes were also observed (Table 4). Somewhat larger amounts of ethyltoluene were produced at the lower temperature.

In a similar manner, the alkylation of toluene with methanol was studied with HZSM-11 zeolite catalyst (Table 5). In this

series, the weight hourly space velocity was varied from 5.4 to 39.5 hr⁻¹. Even at the highest space velocity, the methanol conversion remained at 100%. This illustrates the very high activity of the ZSM-5 class of zeolites. The amount of *para* isomer in the xylene product (24–31%) was somewhat higher than the equilibrium value (23.3%). Two trimethylbenzene isomers were also identified, mesitylene (1,3,5-trimethylbenzene) and pseudocumene (1,2,4-trimethylbenzene) with HZSM-5 (Table 4) and with HZSM-11 (Table 5). Pseudocumene with the smaller minimum dimension was produced in significant excess.

B. Catalyst Modified with Coke

In the previous section we observed that with HZSM- catalyst the amount of *para* isomer in the xylene product increased

TABLE 5
Alkylation of Toluene with Methanol over HZSM-11 Catalyst^a

	1	2	3
Conditions			
Temperature (°C)	450	450	450
Toluene/methanol (mole ratio)	1.4/1	1.4/1	1.4/1
WHSV ^b	5.4	17.1	39.5
Conversion (%)			
Toluene	44	40	38
Methanol	100	100	100
Organic product (wt%)			
Benzene	0.64	0.3	0.1
Toluene	51.6	54.0	56.4
Ethylbenzene	0.1	0.1	0.04
Xylene <i>para</i>	8.7	8.8	10.1
<i>meta</i>	18.9	17.3	15.7
<i>ortho</i>	8.3	7.5	6.9
Ethyltoluene	2.6	2.5	2.1
Mesitylene	0.6	0.2	0.1
Pseudocumene	6.6	6.3	6.2
Other aromatics	0.4	0.3	0.3
Total	100	100	100
Xylene composition (%)			
<i>para</i>	24	26	31
<i>meta</i>	53	52	48
<i>ortho</i>	23	22	21

^a Atmospheric pressure; only traces of gas were formed.

^b Weight of toluene and methanol feed mixture per hr per unit weight of catalyst.

modestly with time on stream at the expense of other isomers (Table 3). A corresponding decrease in toluene conversion also occurred. We believe this was due to coke deposition on the catalyst. Initial activity could be restored by controlled calcination with air diluted with nitrogen to remove these deposits by conversion to carbon oxides.

An experiment of longer duration with HZSM-5 catalyst at 550°C was carried out to determine the degree to which ordinary coke deposition would affect the amount of *para* isomer in the xylene product and toluene conversion during the alkylation of toluene with methanol. Results are illustrated in Fig. 1.

Steady operation was observed during the first 30 hr with high toluene conversion (74%) and an equilibrium mixture of xylene product. Catalyst activity decreased during the next 30 hr as indicated by a decrease in toluene conversion from 74 to 3%. The

concentration of *para* isomer in the xylene product increased to 50%. During the remaining 24 hr of operation, toluene conversion decreased to 1.5% and *p*-xylene concentration increased to 64% after a total of 84 hr of operation.

Coke deposition in the catalyst accounted for a 77 wt% increase after the reaction. The coked catalyst was partially regenerated with a slow stream of air at 550°C for 3.5 hr. Alkylation of toluene with methanol over this partially regenerated catalyst gave 49.5% *para* isomer in the xylene mixture at 60% toluene conversion. Further calcination of the catalyst to remove all of the coke gave an equilibrium mixture of xylene isomers in the alkylation product.

C. Catalyst Modified with Polymer

During our studies concerned with various catalyst modifications for enhancement of *para* selectivity, HZSM-5 was

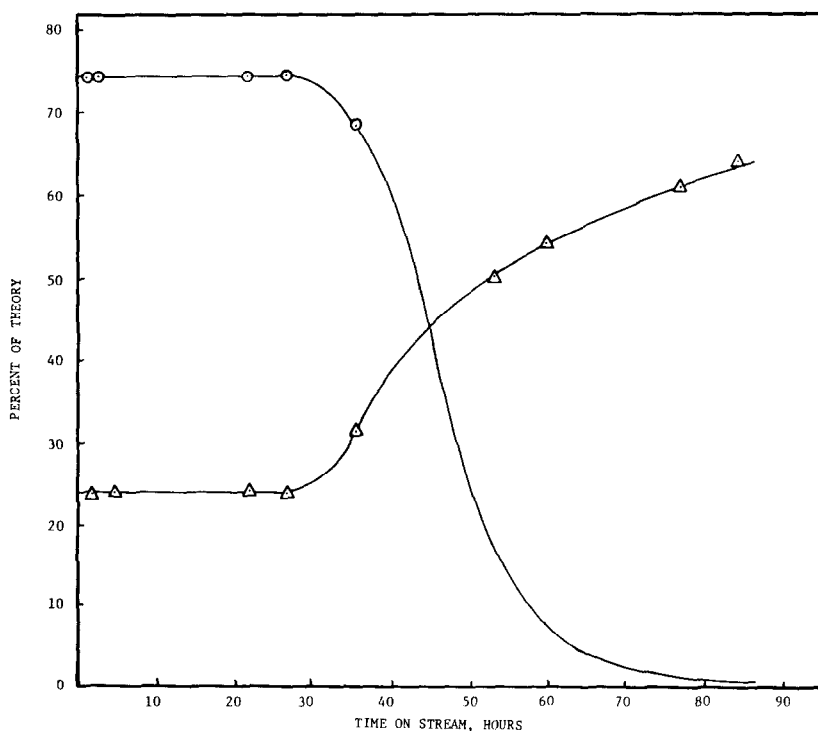


FIG. 1. Alkylation of toluene with methanol, HZSM-5 catalyst. Legend: ○—Toluene conversion; △—*para* isomer in xylene product. Conditions: temp., 550°C; atmospheric pressure; WHSV, 5; Tol/MeOH molar feed ratio, 1.4.

coated with Dexsil 300, dissolved in chloroform (16). This material is a polymer composed of *meta*-carborane units connected by siloxane groups and has outstanding high temperature stability. The molecular weight range was about 9,000–20,000. We speculated that this material might cover and deactivate the external surface of the zeolite, reducing the potential for isomerization of products formed within the pore structure without significantly blocking diffusion of molecules in and out of the catalyst. Results with toluene and methanol are summarized in Table 6. At the lowest temperature, 350°C, after 1 hr of operation, the concentration of *para* isomer in the xylene product was 37%, a modest increase over the equilibrium value (Table 6, Run 1). After 4 hr of operation under various condi-

tions of reaction, the temperature had been increased to 450°C, toluene conversion had decreased from 14 to 4%, and *p*-xylene had increased to 43% of the xylene product. This small increase in *p*-xylene selectivity was probably due to coke formation accompanied by a decrease in toluene conversion. After a total of about 6 hr of operation at a maximum temperature of 470°C conversion was reduced to <1%. The catalyst was calcined with air at this point at 450°C to remove coke. The toluene conversion at 450°C immediately following the calcination, increased to 19% and the *para* isomer in the xylene product increased to 93% (Table 6, Run 3).

D. Catalyst Modified with Phosphorus

The acid or ammonium forms of the

TABLE 6
Alkylation of Toluene with Methanol over Carborane–Silicone^a Coated HZSM-5

	1	2	3 ^c
Conditions ^b			
Temperature, (°C)	350	450	450
Toluene/methanol (mole ratio)	1.4	1.4	1.4
WHSV ^d	15	15	15
Time on stream (hr)	1	4	0.5
Toluene conversion (%)	14	4	19
Organic Product (wt%)			
Benzene	0	0.2	0.4
Toluene	84.3	95.6	78.8
Ethylbenzene	—	—	0.2
Xylene <i>para</i>	4.3	1.6	16.6
<i>meta</i>	3.8	1.0	1.0
<i>ortho</i>	3.5	1.1	0.3
Ethyltoluene	1.2	—	2.4
Mesitylene	—	—	—
Pseudocumene	2.3	0.6	0.3
Others	0.6	—	—
Total	100.0	100.0	100.0
Xylene composition (%)			
<i>para</i>	37	43	93
<i>meta</i>	33	27	5
<i>ortho</i>	30	30	2

^a Dexsil 300, supplied by Supelco, Inc., Bellefonte, Pa. 16823.

^b Reaction at atmospheric pressure.

^c After calcination at 450°C in air.

^d Weight of toluene and methanol feed mixture per hr per unit weight of catalyst.

zeolite catalyst were modified by treatment with solutions of various phosphorus compounds, dried, and calcined in air prior to use (17). In a representative case with HZSM-5, diphenylphosphinous acid, $(C_6H_5)_2POH$, dissolved in toluene, was used to impregnate a catalyst to incorporate about 5% of phosphorus after calcination in air.

When this catalyst was used for alkyla-

tion of toluene with methanol, a dramatic increase in the proportion of *para* isomer in the xylene product was observed. Results are summarized in Table 7 in which the toluene/methanol molar feed ratio was varied from 1 to 8. Only a small change was observed in the high concentration of *para* isomer (84–90%) in the xylene product. However, the conversion of toluene and production of alkylation products were

TABLE 7
Alkylation of Toluene with Methanol over HZSM-5 Catalyst Modified with Phosphorus^a

	1	2	3	4
Conditions ^b				
Temperature (°C)	600	600	600	600
Toluene/methanol (mole ratio)	1/1	2/1	4/1	8/1
WHSV ^c	10.3	10.5	10.5	10.4
Conversion (%)				
Toluene				
Observed	39.8	28.9	17.4	9.2
(Th-Max)	(100)	(50)	(25)	(12.5)
Methanol	96.4	99.3	99.9	100
Organic product (wt%)				
MeOH	0.9	0.1	0	0
MeOMe	1.5	0.2	0.05	0
H ₂ O	13.1	7.7	2.5	1.7
HCHO	0.15	0	0	0
CO, CO ₂	0.1	0.05	0.0	0
CH ₄	0.9	0.4	0.15	0.1
C ₂ H ₄	2.5	1.1	0.4	0.2
C ₃ H ₆	1.3	0.2	0.05	0
C ₄	0.3	0	0	0
Benzene	0.05	0.2	0.3	0.3
Toluene	45.0	61.2	76.4	86.7
Xylene <i>para</i>	25.4	22.3	14.8	8.9
<i>meta</i>	1.9	2.6	2.0	1.2
<i>ortho</i>	0.9	1.2	0.9	0.5
<i>p</i> -Ethyltoluene	0.5	0.3	0.1	0.1
Pseudocumene	2.2	1.2	0.3	0.1
Hemimellitene	0.2	0.1	0.05	0.0
Other	3.0	1.2	1.8	0.2
Total	99.9	100.45	99.8	100.00
Xylene composition (wt%)				
<i>para</i>	90	85	84	84
<i>meta</i>	7	10	11	11
<i>ortho</i>	3	5	5	5

^a Diphenylphosphinous acid reagent: 5.08 wt% phosphorus in catalyst after calcination.

^b Reaction at atmospheric pressure.

^c Weight of toluene and methanol feed mixture per hr per unit weight of catalyst.

significantly reduced since methanol was the limiting reagent.

Methanol is very reactive over zeolite catalysts and by itself is easily converted to a broad spectrum of hydrocarbons, both aromatic and aliphatic, containing up to 10 or 11 carbon atoms per molecule (18). In the present study, production of olefinic side reaction products was greatest at 1/1 molar feed ratios of toluene/methanol and diminished in direct proportion to the de-

crease in the alcohol component. Ethylene and propylene produced in this manner will also react with the toluene by alkylation to form undesired aromatic compounds. Therefore, a balance must be reached between efficient use of starting materials and a reasonable conversion. Fortunately, the desired alkylation reaction is dominant and favors production of xylene as the major product.

In other experiments, aqueous phos-

TABLE 8
Alkylation of Toluene with Methanol over HZSM-5 Catalyst Modified with Phosphorus^a

	1	2	3	4
Conditions^b				
Temperature (°C)	600	600	600	600
Toluene/methanol (mole ratio)	1/1	2/1	4/1	8/1
WHSV ^c	10.3	10.4	10.5	10.5
Conversion (%)				
Toluene				
Observed	18.6	20.8	15.8	9.0
(Th-Max)	(100)	(50)	(25)	(12.5)
Methanol	75.2	91.7	99.2	99.7
Organic product (wt%)				
MeOH	6.4	1.3	0.05	0
MeOMe	4.7	0.4	0.05	0
H ₂ O	8.6	6.9	4.1	2.1
HCHO	0.1	0.1	0	0
CO CO ₂	0.2	0.15	0.05	0
CH ₄	1.0	0.7	0.3	0.1
C ₂ H ₄	1.3	0.7	0.3	0.1
C ₃ H ₆	0.7	0.1	0.05	0
Benzene	0.05	0.05	0.1	0.2
Toluene	60.6	68.1	77.5	87.0
Xylene <i>para</i>	13.6	18.9	15.6	9.5
<i>meta</i>	0.3	0.4	0.6	0.5
<i>ortho</i>	0.2	0.2	0.3	0.2
<i>p</i> -Ethyltoluene	0.7	0.25	0.1	0.1
Pseudocumene	0.5	0.5	0.3	0.1
Hemimellitene	0.15	0.15	0.05	0
Other	1.1	1.1	0.5	0
Total	100.2	100.0	99.95	99.9
Xylene composition (%)				
<i>para</i>	97	97	95	93
<i>meta</i>	2	2	4	5
<i>ortho</i>	1	1	1	2

^a Aqueous phosphoric acid reagent; 8.51 wt% phosphorus in catalyst after calcination.

^b Reaction at atmospheric pressure.

^c Weight of toluene and methanol feed mixture per hr per unit weight of catalyst.

phoric acid was used to impregnate ZSM-5 to give a catalyst containing 8.5% phosphorus after calcination. Typical results are summarized in Table 8. In these runs, toluene conversion was lower than that observed in the previous case, but the concentration of *para* isomer in the xylene product was over 95%.

The effects of temperature on the conversion of toluene and concentration of *para* isomer in the xylene product for another ZSM-5 catalyst modified with chlorodiphenylphosphine, $(C_6H_5)_2PCl$, are summarized in Table 9. It is evident that selectivity to *p*-xylene increased in direct proportion to temperature. This was an unexpected result which was observed repeatedly. This unusual effect will be discussed in a future publication.

The effect of modest increases in pressure on the alkylation of toluene with methanol was also studied. The space velocity was increased with pressure to maintain constant superficial contact time. Results summarized in Table 10 indicate that no significant effects were observed on toluene conversion or selectivity to *p*-xylene in the 0- to 45-psig pressure range.

E. Catalyst Modified with Boron

The acid or ammonium forms of the zeolite catalysts were modified by treatment with solutions of various boron com-

TABLE 10
Alkylation of Toluene with Methanol over HZSM-5 Catalyst Modified with Phosphorus: Effect of Pressure at Constant Contact Time^a

Pressure (psig)	WHSV	Toluene conversion (%)	<i>para</i> isomer in xylene product (%)
0	10	14.9	86
15	20	14.2	88
30	30	14.0	87
45	40	14.1	89

^a HZSM-5 catalyst modified with phosphorus, P = 8.58 wt%; conditions: temp., 600°C, toluene/methanol molar feed ratio 4/1.

pounds, dried, and calcined in air prior to use. In a representative case, HZSM-5 was impregnated with an aqueous solution of orthoboric acid. When toluene was alkylated with methanol at 600°C, atmospheric pressure, xylene was the principal product and the *para* isomer in the xylene products varied from 78 to 94% (Table 11). Under the reaction conditions, conversion decreased steadily with time from 24 to 13% in a period of 6 hr, probably due to coke deposition. Calcination with air restored activity and catalyst performance to the initial values. A steady increase in selectivity to the *para* isomer in the xylene product was also observed with time. This is a general phenomenon associated with coke deposition on the catalyst.

TABLE 9

Alkylation of Toluene with Methanol^a over HZSM-5 Catalyst Modified with Phosphorus: Effect of Temperature

Temperature (°C)	Conversion (%)		<i>para</i> in xylene product (%)	Xylenes in total aromatic product (%)
	Toluene	Methanol		
400	9.2	89	64	86
450	13.1	93	74	89
500	18.7	95	79	91
550	23.9	97	83	91
600	29.4	99	81	93

^a HZSM-5 catalyst modified with phosphorus; P = 5.37 wt%; Conditions: toluene/methanol molar feed ratio 2/1; WHSV = 9; atmospheric pressure.

IV. DISCUSSION

Zeolites provide a unique medium for chemical reactions. It is generally accepted that the transformations occur within the confines of the pore system and are catalyzed at cationic sites that are part of the framework structure. The interconnected channels formed by ten-membered rings of oxygen, such as in ZSM-5 and ZSM-11 (19), are especially interesting because they have dimensions similar to those of many substituted benzene derivatives. The shapes of the various molecules determine

TABLE 11
Alkylation of Toluene with Methanol over Boron-Modified HZSM-5 Catalyst^a

	1	2	3	4	5	6
Temperature, (°C)	600	600	600	600	600	600
Time on stream (hr)	0-1	1-2	2-3	3-4	4-5	5-6
Toluene conversion (%)	24	23	20	18	16	13
Organic product (wt%)						
Benzene	3.6	2.4	1.6	1.2	0.8	0.5
Toluene	74.4	75.4	77.8	80.2	82.7	85.0
Ethylbenzene	0.1	0.05	0.05	0.03	0	0
Xylene <i>para</i>	16.4	17.7	17.1	15.9	14.5	13.0
<i>meta</i>	3.8	2.6	1.7	1.2	0.8	0.5
<i>ortho</i>	0.8	0.8	0.7	0.6	0.5	0.4
C ₉ ⁺	0.9	1.05	1.05	0.9	0.7	0.6
Total	100.0	100.0	100.0	100.0	100.0	100.0
Xylene composition (%)						
<i>para</i>	78	84	88	90	92	94
<i>meta</i>	18	12	9	7	5	4
<i>ortho</i>	4	4	3	3	3	2

^a Toluene/methanol molar feed ratio = 2/1; WHSV = 3.8; atmospheric pressure.

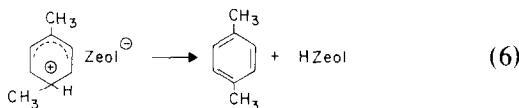
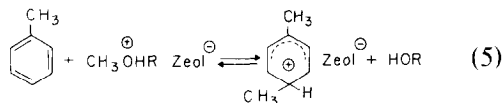
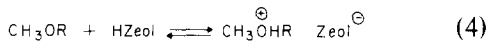
whether they are able to diffuse into the pores to a catalytic site, assume the transition state, undergo a reaction, and then diffuse out.

With the system studied here the two starting reagents, toluene and methanol, readily enter the pores of ZSM-5 class zeolites. Each by itself will undergo reaction under the conditions used. Methanol is relatively reactive by comparison with toluene, and is converted to methyl ether and water under mild conditions and to hydrocarbons and additional water at higher temperatures over HZSM-5 (18). With neat toluene, more severe conditions of reaction are needed to induce disproportionation to benzene and xylenes. Under the conditions used for alkylation, protonation of methanol or methyl ether to form the corresponding oxonium ion is proposed as the initial step (Eq. (4)). This is followed by transfer of the methyl group to the aromatic ring (Eq. (5)), and transfer of a proton back to a catalyst site, (Eq. (6)). Less steric hindrance for alkylation at the *para* position within the confines of the catalyst pores is

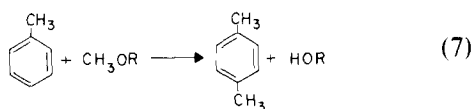
predicted by comparison with the *meta* and *ortho* positions. These same acid sites, however, can also rapidly isomerize any xylene isomer formed initially as it diffuses out of the zeolite, especially in the larger spaces where channels intersect, to give the near-equilibrium mixtures observed (Tables 4 and 5). A recent paper by Anderson and co-workers describes the relative ease of exchange of aromatic vs side chains hydrogens by deuterium labeling, over HZSM-5 catalyst (20). They show that methyl groups remain intact while hydrogens on the aromatic ring are easily exchanged under alkylation conditions. These results are consistent with the mechanism proposed.

Isomerization may also occur by interaction with acid sites on the external surface. It has been shown that unmodified, large crystal zeolites with relatively small external surface areas give *p*-xylene concentrations in the xylene product that are significantly higher than equilibrium values (11). This suggests that some isomerization does occur on the surface at higher temper-

atures, especially with small crystal varieties.



NET



R = H or CH₃

When toluene was alkylated with methanol over HZSM-5 or HZSM-11 catalysts, xylene was the major product. A small but significant amount of trimethylbenzene was also formed. The pseudocumene molecule has a smaller minimum dimension than mesitylene and was produced in 4- to >100-fold excess. This is consistent with the isomer expected for reactions occurring within a confined space such as the pore structure of a zeolite. Mesitylene, by contrast, is a substantial isomer present at thermodynamic equilibrium usually obtained with reactions in the liquid phase utilizing aluminum halide catalysts (21). Csicsery has demonstrated the relationship between the space required for transition state formation and products produced within the confines of a zeolite pore (22). Insufficient space for reacting molecules to reach the transition state configuration prevents formation of the corresponding products.

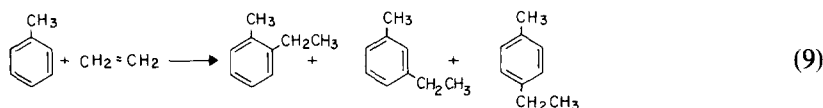
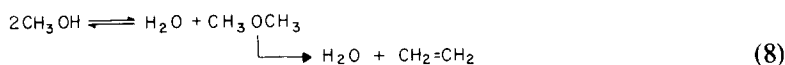
With unmodified HZSM-5 catalyst, the amount of *para* isomer in the xylene product increased modestly from 24 to 33% over 18 hr of operation (Table 3). This was

probably due to coke deposition within the catalyst or on the exterior surface, gradually reducing the pore dimensions, thereby favoring the *para* isomer with the smallest minimum dimension (Table 12). A more dramatic change was observed with the corresponding relative amounts of trimethylbenzene isomers produced as a function of time on stream. Pseudocumene with a minimum dimension of 7.6 Å was present in approximately constant amounts (Table 3). However, the yield of mesitylene, 8.6 Å, decreased rapidly during the first hour and could not be detected in the product for the remaining 17 hr of operation. Similar trends were observed under different conditions of reaction (Table 4) and with HZSM-11 (Table 5).

With catalysts which were coated with polymer (Table 6) or treated with phosphorus (Tables 7 and 8) or boron (Table 11) to induce high selectivity for *p*-xylene, mesitylene could not be detected in the products. Furthermore, relatively small amounts of pseudocumene were produced. These results demonstrate the shape-selective characteristics of ZSM-5 class of zeolites when they were tailored to produce the isomers with the smallest dimension.

The appearance of ethyltoluene in the reaction product mixture (Table 4) suggests that ethylene or ethyl alcohol was generated from methanol by a side reaction in the system and subsequently reacted with toluene (Eqs. (8) and (9)). This supports the contention that ethylene is the initial hydrocarbon product of reaction of neat methanol over zeolites (17).

When the zeolites were treated with phosphorus compounds and calcined in air, an interaction occurred that permanently altered the catalyst, resulting in reduced activity and a dramatic increase in the amount of *para* isomer in the xylene product. It was proposed that the phosphorus reagent reacts with the zeolitic acid sites to firmly attach phosphorus to the zeolite via framework oxygen (17). In addition, the phosphorus with bonded oxygen atoms,



retained from the impregnating reagent or produced by calcination in air, was uniformly distributed over the acidic sites associated with the framework aluminum atoms. Formation of high concentrations of *para* isomer in the xylene product is evidence that a reduction in effective pore size occurred in the zeolite channels, in the larger cavities formed by channel intersections, and/or in the pore openings. We believe that this has resulted in a modified

catalyst, where discrimination based on differences in the minimum dimension of the xylene isomers is much more important for determination of the relative rates of diffusion (12) and the relative steric access of the methanol alkylation reagent to the *ortho*, *meta*, and *para* positions of the toluene substrate. Alkylation at the *para* position would be favored within the more confined cylindrical pore of the modified catalysts and isomerization would be hin-

TABLE 12
Minimum Dimension of Certain Molecules and Zeolite Pores

	Zeolite pore openings (Å)	
	Crystallographic ^a calculations	Csistry ^b model
HZSM-5	5.4 × 5.6 5.1 × 5.5	6.9–7.2
HZSM-11	5.5 × 5.5	7.0–7.1
Mordenite	6.7 × 7.0 2.9 × 5.7	8.2–8.6
Minimum molecular dimension	FHT ^c hard spheres	
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	
1,2,4-Trimethylbenzene	7.6	
1,3,5-Trimethylbenzene	8.6	
1,3-Dimethyl-5-ethylbenzene	8.6	
1,2-Dimethyl-4-ethylbenzene	7.6	

^a See Ref. (23).

^b Obtained by adding 1.5–1.6 Å to the crystallographic dimensions.

^c Fisher-Hirschfelder-Taylor hard sphere molecular models. See Ref. (22).

dered. In addition, a bulky phosphorus compound partially blocking pore openings could also greatly favor outward diffusion of the *para* isomer relative to *meta* and *ortho*. The effective residence time inside the catalyst pores of the more bulky *ortho* and *meta* isomers would be increased, thus favoring isomerization to the *para* isomer. Phosphorus on the external surface could also cover strong acid sites located there and prevent rapid surface isomerization of the *p*-xylene which has emerged from the pore. The net result of any or all of these factors in a phosphorus-modified catalyst would be to favor selective production and preservation of the *para*-xylene isomer. The boron modified catalyst probably functioned in a manner similar to that described for phosphorus with bonding to cationic sites associated with framework aluminum.

Csicsery has studied the selective disproportionation of ethyltoluene over hydrogen mordenite (22). The 1,3,5-trialkylbenzenes, the major isomers present at thermodynamic equilibrium, were produced in only trace amounts. The 1,2,4-trialkylbenzenes with smaller minimum dimensions (measured by hard sphere models) were predominant. He also related the sizes of zeolite channel openings obtained by crystallographic measurements to the minimum dimension of the various substituted benzene molecules which could be produced by the disproportionation reaction under study, summarized in Table 12. To rationalize the experimental results, the "effective channel apertures" of mordenite were estimated to be 8.2–8.6 Å, 1.5–1.6 Å larger than values calculated from crystallographic measurements. Thus, the 1,2,4-substituted molecules could readily diffuse out of the pores while the larger 1,3,5-isomers could not.

The dynamics of organic molecules and catalysts at the relatively high temperatures of chemical reactions are very complex and the dimensions reported are speculative. Nevertheless, this is an interesting ap-

proach toward understanding the product selectivity observed with certain zeolite catalysts and may lead to more definitive studies in the future. Application of Csicsery's treatment to ZSM-5 and ZSM-11 (Table 12) indicates that *p*-xylene could readily diffuse out of the catalyst while the *o* and *m* isomers could not. In fact, an equilibrium xylene mixture was obtained with these two unmodified catalysts (Tables 3, 4, and 5). *Para* selectivity was observed only when the catalysts were modified. Perhaps more precise relationships between zeolite pores and molecular dimensions of product molecules will be determined in the future.

Deposition of coke, a relatively inert material, on the catalyst led to reduced conversion and increased selectivity (Fig. 1). This suggests a physical alteration of the catalyst. The most accessible surface acidic sites could be covered to reduce isomerization. In addition, coke deposits at the pore mouth and/or within the catalyst may reduce the effective channel dimensions, resulting in a tighter fit of the molecules and permit a finer discrimination between the xylene isomers.

This coking phenomenon also occurred with a catalyst which had been modified by impregnation with chemical reagents such as boron as shown in Table 11. *Para* selectivity increased from an initial level of 78 to 94% after 6 hr of operation as a result of coke formation. Calcination to remove coke restored the initial catalyst performance.

In a similar manner, the carborane-silicone polymer could cover the surface acidic sites and partially block pore openings to account for an increase in the amount of *p*-xylene product. Increased temperature and operation time (Table 6, Run 2) resulted in a modest increase in *para* selectivity but at a reduced conversion, reminiscent of coking. Prior to Run 3, however, the catalyst had received a treatment with air at 450°C, which resulted in a profound change in the carborane-silicone

polymer coating to dramatically increase selectivity to 93% *para* isomer. Perhaps partial oxidation resulted in polymer cleavage and redistribution, thereby permitting a tighter packing of smaller fragments, to reduce the size of pore openings and channels favoring outward diffusion of the *para* isomer.

In summary, it has been demonstrated that toluene can be alkylated with methanol to give water and xylenes with concentrations of the *para* isomer greatly exceeding the equilibrium value by modification of the ZSM-5 class of zeolite catalysts with various reagents or treatments. The catalyst can be permanently altered to maintain *para* selectivity and may be regenerated with air in a conventional manner to remove coke deposits and restore initial high catalyst activity. Early versions of the catalyst have been operated continuously for several days between regenerations. Modest increases in pressure at similar contact times have little effect on catalyst performance. Principles have been established for chemical modification of zeolite catalysts to produce and increase *para* selectivity for alkylation reactions. The results obtained establish the basis for a novel, useful, and practical method for preparing *p*-xylene from toluene and methanol.

ACKNOWLEDGMENTS

We are indebted to Mr. A. B. Schwartz and Dr. F. G. Dwyer for providing samples of the various zeolite crystals for this work, to Mr. P. J. Yannich and Mr. J. M. Klosek for assistance with the experimental work, to Ms. J. A. Baran for assistance with the manuscript, to Dr. D. D. Phillips for his advice and encouragement, and to Professor O. L. Chapman for many helpful and stimulating discussions.

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