Shape-Selective Reactions with Zeolite Catalysts

IV. Alkylation of Toluene with Ethylene to Produce p-Ethyltoluene

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Reaction of toluene with ethylene over HZSM-5 zeolite gave a mixture of ethyltoluenes which contained *meta* isomer as the major product. Coking of the catalyst increased the percentage of *para* isomer in the ethyltoluenes from 29 to 47%. Over HZSM-5 modified with phosphorus and a variety of metal oxides, ethyltoluenes were produced which contained 90–99% *para* isomer. A comparison of the isomers produced by toluene disproportionation to produce *p*-xylene (and benzene) with toluene alkylation to produce ethyltoluene, revealed that with the same catalyst, ethyltoluene formation is more *para*-selective than xylene formation. It is proposed that this is due to the presence of the larger ethyl group on the aromatic ring, relative to methyl, which gives rise to enhanced steric effects and diffusional discrimination among the product isomers in the shape-selective catalysts.

I. INTRODUCTION

Previous papers of this series have described the alkylation of toluene with methanol to produce xylenes (*1*), the disproportionation of toluene to give benzene and xylenes (*2*), and xylene isomerization (*3*) over ZSM-5 class zeolite catalysts. Near-equilibrium mixtures of the xylenes were usually observed with the unmodified zeolites. When the ZSM-5 catalysts were modified to incorporate oxides of phosphorus and a variety of metals, dramatic increases in the concentration of the *para* isomer (85–97%) in the xylene product were observed (*1–3*).

The *para* isomer has the smallest minimum dimension. With these *para*-selective, modified catalysts, the ratio of rates of diffusion of *para* relative to the larger *ortho* and *meta* isomers increased about three orders of magnitude (*4*). It was proposed that the pores and channels of the *para*-selective zeolites were effectively reduced in size to favor diffusion of the smaller para isomer out of the pores. The more slowly diffusing *ortho* and *meta* isomers remaining within the zeolite isomerize to produce more *para* isomer accounting for the overall high selectivity to *p*-xylene.

Since these modified catalysts possess a high degree of shape selectivity, we have examined the effects of increasing the size of the original substituent on the aromatic ring and the size of the alkylating reagent by observing the ratio of isomers of the alkylation product produced. Results for the alkylation of toluene with ethylene to produce ethyltoluene over a variety of modified and unmodified ZSM-5 class zeolites are reported here.

II. EXPERIMENTAL METHODS

Materials

High-purity toluene and ethylene, 99+%, were used without further treatment.

Catalysts

The ZSM-5 crystals used for the unmodified catalyst (Table 1), were prepared by the general methods outlined by Argauer and

TABLE 1

Alkylation of Toluene with Ethylene-Unmodified HZSM-5

Conditions	Starting materials		Alkylation reaction			
	1 (Toluene)	2 (Ethylene)	3	4	5	6
Temp., °C	350	350	275	300	350	400
WHSV Tol. $(N_2)^a$	6.9	(0.4)	6.9	6.9	6.9	6.9
C_2H_4	0	2.6	0.5	0.5	0.5	0.5
Tol/C_2H_4 (mole)	—	—	4.5/1	4.5/1	4.5/1	4.5/1
Conversion, %						
Tol (theor. max. 22.2%)	0.7	—	9.5	17.6	20.7	20.5
C_2H_4	—	99	58.3	93.7	94.4	91.3
Selectivity to products, %						
Benzene	31.3	0.4	0.2	0.3	0.8	2.9
Ethylbenzene	—	1.3	0.3	0.9	1.4	2.0
Xylenes	34.7	8.4	0.6	1.2	1.4	4.0
p-Ethyltoluene	—	2.1	22.2	22.2	23.3	22.0
m-Ethyltoluene	—	4.6	34.8	48.9	53.3	50.1
o-Ethyltoluene	—	0.5	4.6	3.8	8.3	11.9
C_1–C_4 (gas)	34.0	51.6	3.6	2.6	1.8	1.5
Other aromatic	—	7.6	33.7^b	20.1^b	9.7	5.6
C_{5+} Aliphatic	—	23.5	—	—	—	—
Total	100.0	100.0	100.0	100.0	100.0	100.0
Ethyltoluene	$Equilibrium^c$					
Para	33.7	—	29.2	36.0	29.6	27.4	26.2
Meta	49.9	—	63.9	56.5	65.3	62.8	59.6
Ortho	16.3		6.9	7.5	5.1	9.8	14.2

^{a} Nitrogen diluent for neat ethylene feed.
^{b} May contain some C_{5+} aliphatic compounds.
^{c} At 327°C.

Landolt (5). Preparation of the acid form required ion exchange with aqueous ammonium chloride or nitrate after calcination followed by washing and a final calcination.

Phosphorus modification. The ammonium form of ZSM-5 containing 35% alumina binder was added to an aqueous solution of diammonium hydrogen phosphate at about 90°C. After standing for 2 h, the zeolite was filtered, dried at 105°C, and then calcined at a final temperature of 500°C. The recovered P-ZSM-5 zeolite contained 3.4 wt% phosphorus, present as the oxide.

Calcium/phosphorus modification. The P-ZSM-5 catalyst prepared above was suspended in a solution of calcium acetate monohydrate in water at 90°C for a period of 2 h. The zeolite was separated by filtration, dried at 90°C overnight, and calcined up to 500°C to give Ca-P-ZSM-5 catalyst. Analysis indicated the presence of 3.6 wt% phosphorus and 6.0% calcium present as the oxides.

Manganese/phosphorus modification. In a similar manner, P-ZSM-5 was suspended in a solution of manganese acetate tetrahydrate in water for 2 h at 90°C, removed by filtration, dried at 90°C for 2 h, and calcined at 500°C. Analysis revealed 6.4 wt% manganese and 3.5 wt% phosphorus, present as the corresponding oxides.

Boron/phosphorus modification. The am-

monium form of ZSM-5 was suspended in a solution of boric acid and phosphoric acid in water at 85°C. After standing overnight, the entire contents was poured into a dish and placed in an oven at 110°C to remove the water. The dish was placed in an oven at 500°C overnight, then cooled to give a modified catalyst containing 4% boron and 1% phosphorus, present as the oxides.

Boron/magnesium modification. In a similar manner, the ammonium form of ZSM-5 was suspended in a solution of magnesium acetate tetrahydrate and boric acid in water at 90°C overnight. The entire contents was poured in a dish, the water evaporated, heated at 500°C in air overnight to give a catalyst containing 10 wt% Mg and 1 wt% B, present as the oxides.

Silicon modification. HZSM-5 was modified with a high-boiling methyl- or phenyl-substituted silicone oil. The composite was heated and subsequently calcined in air to decompose the reagent and convert it to the oxide.

para Selectivity over coked catalyst. A metal pressure reactor unit described previously (*1*) was used for this series of reactions. The model reactions used for measurement of *para* selectivity of various levels of coke deposition were

(a) Toluene alkylation: Mixtures of toluene/ethylene/hydrogen at a weight hourly space velocity, WHSV (g feed/g catalyst/h) of 29.6/1.15/0.25, respectively, molar ratio 7.8/1/3, at 425°C and 100 psig pressure were passed over a *para*-selective catalyst to produce ethyltoluene.

(b) Toluene disproportionation: Mixtures of toluene/hydrogen, WHSV 29.6/0.25, mole ratio 7.8/3, at 550 and 600°C, 100 psig pressure were passed over the *para*-selective catalyst to produce xylenes and benzene.

A rapid shift from alkylation to disproportionation was achieved by turning the ethylene off or on and adjusting the temperature. The latter was done to obtain similar toluene conversions. Liquid samples were collected for 15-min intervals before and af-ter each reaction change (alkylation/disproportionation) to permit comparison of products at the same level of coke on the catalyst. Intervals of 5–25 h for each reaction were used before shifting to the other. Toluene conversion varied from about 8–11% for alkylation and 4–10% for disproportionation. When the conversion was reduced to roughly half the original value, the catalyst was regenerated with air to remove coke and restore the original performance. Coke on catalyst ranged from 0 to 10%.

Conversion is defined as weight of starting material fed to the reactor minus weight recovered (products normalized to 100%) divided by the weight of starting materials. Selectivity is defined as weight of product divided by weight of total starting materials consumed (products normalized to 100%). Material balances were usually ±2–3%.

Apparatus and Procedure

For experiments carried out at atmospheric pressure, 4 to 10 g of catalyst, diluted with 4 vol of low-surface-area quartz chips, was positioned in a fixed-bed, cylindrical quartz reactor, 1.1 × 15 cm, containing a centered thermowell. Toluene was delivered by a metering pump to a vaporizer and mixed with ethylene at rates determined by a mass flow meter. The reaction temperature recorded was the highest reading in the catalyst bed.

The vapor from the reactor was passed successively through cold water and dry-ice traps. The noncondensed 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 34 on Supelcoport column was used for the organic liquid. Material bal-

ances and product yields were calculated with the aid of computer programs.

III. RESULTS

A. Unmodified Zeolite Catalyst

An extension of previous work where methanol was used as the alkylating agent (*1*), is use of ethanol, the next higher homolog. Preliminary experiments revealed, however, that ethanol was very rapidly dehydrated to ethylene at relatively low temperatures over ZSM-5:

$$CH_3CH_2OH \rightarrow CH_2{=}CH_2 + H_2O \quad (1)$$
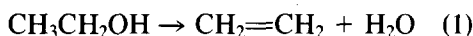
The olefin is also an effective ethylating agent. Although the facile dehydrogenation of ethanol suggests that ethylene is the primary alkylation reagent
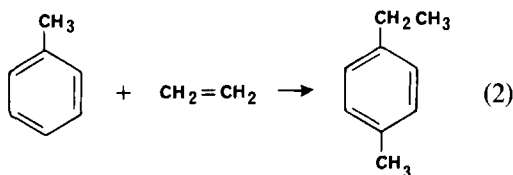
some of the product could result from direct alkylation with alcohol (*6, 7*). In any event, it was advantageous to start with ethylene to simplify the reaction and because of its lower cost. The need to separate and analyze a water phase in the hydrocarbon products was eliminated. The results which follow are based on early catalyst screening results to establish conditions and products of reaction, and indicate the variety of salts which may be used to induce *para* selectivity.

Since each starting material is known to undergo reactions over ZSM-5, the individual reagents were tested independently. At 350°C, toluene was relatively inert as indicated by low conversion, 0.7% (Run 1, Table 1). The presence of benzene and xylenes indicated that disproportionation was the major reaction (*2*). This probably accounts for the small amount of these products formed during the alkylation reaction.

By contrast, neat ethylene was very reactive at 350°C over HZSM-5 giving 99% conversion to products (Run 2, Table 1). A small amount of ethyltoluene was produced directly from ethylene. The major products were a mixture of C_1–C_{10} olefins and paraffins.

Because of the high reactivity of ethylene, it was advantageous to dilute it with excess toluene to reduce self-reaction and promote the desired alkylation (Eq. (2)). Results with unmodified HZSM-5 catalyst are summarized in Table 1. With a molar feed ratio of toluene/ethylene of 4.5/1, the theoretical maximum conversion of toluene to ethyltoluenes is 22.2%. Conversion increased with temperature and leveled out at 350°C to values approaching theoretical amounts. Mixed ethyltoluenes were the major products observed. Side reaction products were reduced significantly at the higher temperatures (350–400°C).

With the unmodified HZSM-5 zeolite catalyst, near-equilibrium ratios of the *meta* and *para*-ethyltoluene isomers were observed (Table 1). However, lower than equilibrium amounts of *o*-ethyltoluene were produced. By contrast, when methanol was used as the alkylating reagent with toluene for production of xylenes, nearly equilibrium concentrations of *o*-xylene were produced in every case (*1*).

B. Modified Catalysts

ZSM-5 zeolite was modified by impregnation with solutions of a considerable variety of organic and inorganic reagents. After removal of the solvent by evaporation, the catalyst was dried and calcined in air to decompose the salts and convert the metal components to the corresponding oxides. Results from catalysts modified with a variety of reagents are shown in Table 2. A designation of PB-ZSM-5, for example, indicates that the catalyst was modified with phosphorus and boron.

Under the conditions of reaction re-

TABLE 2

Alkylation of Toluene with Ethylene-Modified Catalysts

Catalyst	P-ZSM-5	Si-ZSM-5	Si-ZSM-5	PB-ZSM-5	PB-ZSM-5	BMg-ZSM-5	BMg-ZSM-5	CaP-ZSM-5	MnP-ZSM-5
Analysis, wt%[a]	P = 5.6	SiO_2 = 13	SiO_2 = 13	B = 4, P = 1	B = 4, P = 1	B = 1, Mg = 10	B = 1, Mg = 10	Ca = 6.0, P = 3.6	Mn = 6.4, P = 3.5
Conditions									
Temp., °C	300	350	400	350	350	350	350	400	400
WHSV Tol	6.9	6.9	6.9	6.9	3.5	6.9	3.5	7	7
C_2H_4	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Tol/C_2H_4 mole	4.5/1	4.3/1	4.3/1	4.5/1	2.2/1	4.5/1	2.2/1	4.2/1	4.2/1
Conversion, wt%									
Tol	9.7	15.3	16.8	13.3	24.5	8.7	8.6	22.8	18.7
C_2H_4	63.2	71.2	73.1	63.0	64.3	49.9	38.2	—	—
Selectivity to products, %									
Benzene	0.1	0.5	1.0	0.2	0.1	0.4	0.2	1.3	0.3
Ethylbenzene	0.7	0.8	1.9	0.5	0.9	1.6	0.8	2.4	1.0
Xylenes	1.5	0.8	2.5	0.6	0.8	1.9	1.3	3.2	1.4
p-Ethyltoluene	52.5	90.6	77.0	78.3	69.1	75.0	71.1	81.3	94.5
m-Ethyltoluene	15.5	2.8	13.0	17.1	20.8	4.2	4.5	7.2	1.5
o-Ethyltoluene	0.1	0	0.7	0	0	0	0	0	0
Other[b]	21.8	2.6	1.1	1.0	5.5	4.1	4.2	4.6	1.3
C_1–C_4 (gas)	7.8	1.9	2.8	2.3	2.8	12.0	17.9	[c]	[c]
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Ethyltoluene									
Para	77.0	97.0	84.9	82.0	76.8	94.8	94.0	91.9	98.3
Meta	22.8	3.0	14.3	17.9	23.1	5.2	5.9	8.1	1.7
Ortho	0.2	0	0.8	0.1	0.1	0	0.1	0	0

[a] Present as their oxides.
[b] Aromatic and C_{5+} aliphatic compounds.
[c] Not measured and not included.

	Time on stream, h			
	1	5	10	28
Conversion, %				
Toluene	19.9	20.3	20.5	19.8
C_2H_4	95.6	95.6	95.6	88.7
Selectivity to				
ethyltoluene, %	85.6	86.1	86.3	95.2
Ethyltoluene, %				
Para	28.9	30.8	32.0	46.8
Meta	69.0	67.8	66.8	52.4
Ortho	2.1	1.4	1.2	0.8

[a] Conditions: 350°C, atmospheric pressure, WHSV Tol/C_2H_4 6.9/0.5, mole ratio 4.5/1.

ported, ethyltoluene was the primary product. A dramatic increase in selectivity to the para isomer (up to 98%) was observed by comparison with the unmodified catalyst. A corresponding decrease in meta isomer and virtual elimination of o-ethyltoluene was also observed.

In general, conversion of the aromatic starting material was lower with modified catalysts. This was probably due to partial blockage and reduction in size of the zeolite channel system and deactivation of some catalyst sites. By-products, especially molecules with larger dimensions, were significantly reduced because of greater steric constraints within the catalyst.

C. Effect of Coke Formation

Decomposition reactions of organic compounds occur within the catalyst pores to produce high-molecular-weight carbonaceous material ("coke"), which gradually accumulates in the catalyst. This deposition of coke covers certain reactive sites, reduces the effective size of the zeolite channels, and alters the diffusional characteristics of the zeolite. This serves to magnify the differences in relative rates of diffusion

between the smaller para isomer and the larger ortho and meta isomers. Furthermore, the ortho and meta isomers, with larger activated complexes than the para isomer, may be selectively inhibited from being formed initially (8). All of these factors result in the selective production of the para isomer.

The effect of coking is illustrated in Table 3 with unmodified ZSM-5. Over a period of 28 h, the amount of para isomer in the ethyltoluene product increased from 29 to 47% as a result of coke deposition (about 2%) within the catalyst. This is a significant increase considering the small amount of coke and slight reduction in conversion.

When a para-selective catalyst was used, a similar enhancement in para-selectivity by coking was also observed except at higher relative concentrations of the para isomers. A series of comparisons were made between (a) percentage of para isomer in the xylene product produced from disproportionation of toluene to xylenes and benzene and (b) percentage of para isomer in the ethyltoluene product produced by alkylation of toluene with ethylene at a given coke level.

As coke was gradually deposited on the catalyst, the rates of toluene conversion decreased for each reaction and selectivity to the para isomer increased. The catalyst was regenerated periodically to restore the original activity and selectivity. Results are summarized in Fig. 1.

A higher percentage of para isomer in ethyltoluene, compared with xylene, was always observed. We believe this is due to the larger size of the ethyl group compared with methyl and is consistent with expectations for a shape-selective catalyst.

IV. DISCUSSION

para Selectivity was induced by impregnation of HZSM-5 zeolite catalyst with metal salts and phosphorus compounds which were subsequently decomposed and oxidized by heating in air and by deposition
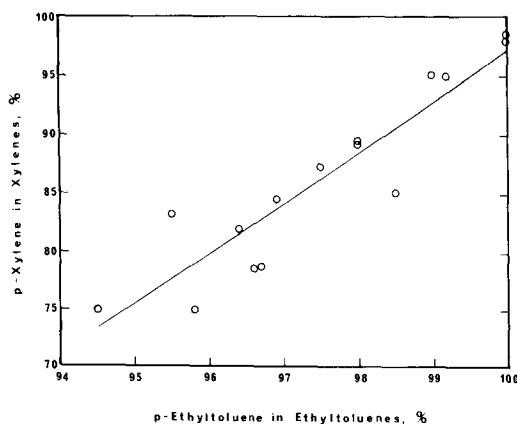
FIG. 1. Comparison of percentage of *para* isomer in the xylene product produced by disproportionation of toluene to benzene and xylene with percentage of *para* isomer in ethyltoluene produced by alkylation of toluene with ethylene at a given amount of coke for each point over a *para*-selective catalyst.

of coke. These catalyst modifications resulted in a magnification of the difference in diffusion rates between the smaller *para* isomer compared with the *ortho* and *meta* isomers. As the alkyl groups increased in size from methyl to ethyl, *para* selectivity also increased. This is consistent with predictions for reactions which take place within the sterically constrained zeolite pores. Further increases in substituent sizes should result in further enhancement of *para*-isomer selectivities.

Ethyltoluenes may be converted to the corresponding vinyltoluene monomers by catalytic dehydrogenation. The vinyltoluene product of commerce consists of a mixture of approximately 35% *para*/65% *meta* isomers. This ratio is fixed by the isomer mixtures obtained during the alkylation step with an aluminum chloride catalyst (9). The boiling points are too close to permit a practical separation by distillation.

The use of zeolite catalysts offers considerable flexibility in altering the ratio of *para/meta* isomers produced during alkylation. Nearly 100% concentrations of the *para* isomer may be obtained by direct alkylation. In addition, production of the unwanted *ortho* isomer can be virtually eliminated. An account of the new process for production of 97% *p*-methylstyrene (PMS) monomer and properties of the corresponding polymers has appeared (*10*).

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