JOURNAL OF CATALYSIS 76, 418–432 (1982)

Shape Selective Reactions with Zeolite Catalysts

III. Selectivity in Xylene Isomerization, Toluene–Methanol Alkylation, and Toluene Disproportionation over ZSM-5 Zeolite Catalysts

L. B. YOUNG, S. A. BUTTER,[1] AND W. W. KAEDING

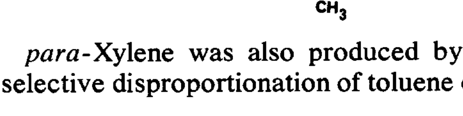
Mobil Chemical Company, Edison, New Jersey 08818

Received November 25, 1981; revised February 23, 1982

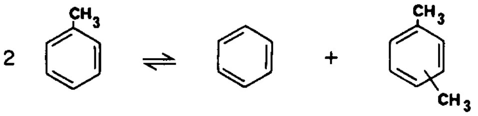
Data are presented for *para*-selective and nonselective formation of xylenes from alkylation of toluene with methanol and toluene disproportionation over ZSM-5 class zeolite catalysts. Possible mechanisms leading to *para*-selectivity are discussed. Isomerization of the pure xylene isomers has been used as a mechanistic probe. Distinctly different reaction paths (i.e., isomer composition curves) for xylene isomerization have been observed for *para*-selective in comparison to nonselective catalysts. Reaction paths followed by the *para*-selective catalysts are probably a consequence of diffusional effects possibly superimposed on the sterically altered intrinsic kinetics, both of which favor formation of the more rapidly diffusing *para* isomer.

INTRODUCTION

The selective preparation of para-substituted benzene derivatives by means of various modified zeolite catalysts has recently been reported (*1–4*). In particular, ZSM-5 class zeolites have been of considerable interest because the channel dimensions are approximately the same as the molecular dimensions of many aromatic molecules (*1, 2, 5, 6*). By altering catalyst and reaction parameters, high concentrations of *para* isomer in the xylene product have been obtained. We have recently reported the selective alkylation of toluene by methanol over various modified ZSM-5 type zeolites, which gave greater than 90% *para* isomer in the xylene product (*1*):


(1)

para-Xylene was also produced by the selective disproportionation of toluene over modified ZSM-5 catalysts. Approximately equimolar amounts of benzene and *para*-rich xylenes (70–90% *para*) were observed (*2*):


(2)

Certain shape-selective reactions catalyzed by modified ZSM-5 class zeolites have been reviewed recently (*5–8*). It has been proposed that *para* selectivity is a result of selective diffusion of the smaller *para* isomer and/or selective steric effects favoring the formation of *para*-xylene (*1, 2, 5, 6*).

We wish to report some additional data on alkylation of toluene with methanol and toluene disproportionation over ZSM-5 catalysts. In addition, reaction pathways (i.e., isomer composition curves) for isomerization of pure xylene isomers have been determined in an attempt to elucidate the reaction mechanism. An accompanying paper develops a mathematical theory for enhanced *para* selectivity (*9*).

---

[1] Present address: Air Products and Chemicals, Inc., P.O. Box 538, Allentown, Pa. 18105.

0021-9517/82/080418-15$02.00/0

EXPERIMENTAL

Catalysts. The synthesis of ZSM-5 has been reported previously (*10*). The *para*-selective catalysts modified with phosphorus, designated as PZSM-5, were made by impregnation of the hydrogen or ammonium form of ZSM-5 with solutions of trimethylphosphite, phosphoric acid, chlorodiphenylphosphine, or dichlorophenylphosphine, as previously described (*1*). Techniques for modification with boron (*1*) and magnesium (*2*) have also been reported. Catalysts (with the exception of H_3PO_4/SiO_2) were calcined at 500–550°C for 2–4 hr before use.

Apparatus and procedure. Nichrome-heated quartz or stainless-steel tubular flow reactors were packed with 5.0 g of 14/20 mesh catalyst. Temperatures were measured in a thermowell extending axially through the bed. Liquid mixtures were fed and controlled with a Milton Roy Minipump or Sage syringe pump and passed through a preheater to vaporize the charge. Analytical procedures have been described previously (*1*, *2*).

Rate calculations. Approximate relative

TABLE 1

Toluene Disproportionation over ZSM-5 Catalysts[a]

Catalyst	Temp. (°C)	WHSV[b]	Toluene conversion (%)	Xylene isomer composition (%)		
				para	*meta*	*ortho*
HZSM-5[c]	450	3.6	8	24.7	51.9	23.4
	500	3.5	20	24.3	52.3	23.4
	550	3.5	40	24.2	51.6	24.2
	600	3.5	52	24.1	51.3	24.6
HZSM-5, large crystal[d]	550	30	13.2	35	46	19
5% HZSM-5/ 95% SiO_2	600	364	0.5	49.3	38.2	12.4
	600	171	1.7	33.1	48.7	18.2
	600	38	5.8	27.5	50.6	21.9
B-ZSM-5[c]	600	2.8	20.8	28.2	50.9	20.9
	650	2.8	24.5	34.9	48.0	17.1
	700	2.8	20.2	73.0	21.1	5.9
	700	2.8	13.1	87.2	10.1	2.7
Mg-ZSM-5[c] (11.5% Mg)	500	0.9	19.0	54.9	34.6	10.5
	500	1.7	13.1	63.7	28.2	8.1
	500	7.0	3.9	82.4	14.0	3.6
	550	1.7	26.4	56.3	33.8	9.9
	550	3.5	15.8	74.3	20.2	5.4
	550	7.0	9.4	80.0	16.0	4.0
	550	9.8	4.6	88.1	9.6	2.3
	600	3.5	23.6	70.4	23.3	6.3
	600	9.8	10.9	84.6	12.3	3.1
Equilibrium[e]	427			23.5	52.1	24.4
	527			23.1	51.35	25.6
	627			22.8	50.6	26.6

[a] Atmospheric pressure.

[b] Weight hourly space velocity, g feed/g catalyst/hr.

[c] Ref. (*2*).

[d] Ref. (*3*).

[e] Ref. (*23*).

rates of the various reactions were calculated assuming first-order dependence on the aromatic and zero-order dependence on methanol (if present). Contact time was assumed to be inversely proportional to total molar feed rate.

RESULTS

Toluene Disproportionation

In general, unmodified ZSM-5 type catalysts give nearly equilibrium xylene mixtures (24% *para*) in toluene disproportionation [Eq. (2)] (Table 1) (*2, 3, 5, 11*). An exception which has been reported is the 35% *para* isomer concentration in the xylene product produced by large crystal HZSM-5 (*3*). In addition, we have observed that at very high temperatures and space velocities, xylene mixtures containing up to 50% *para* isomer are produced at low conversion of toluene over unmodified HZSM-5 (Table 1). In contrast, certain modified ZSM-5 type catalysts have been shown to disproportionate toluene to produce benzene and xylenes with the *para* isomer content greater than 80%, far in excess of the equilibrium level (Table 1) (*2*).

For most selective ZSM-5 catalysts, the proportion of *para*-xylene in the xylenes has been found to increase with increasing temperature (*2*). This effect is shown in Fig. 1 and Table 1 for magnesium and boron modified ZSM-5 catalysts. Each modified catalyst is characterized by a set of toluene conversion/*para*-xylene in xylenes/temperature curves of the type shown in Fig. 1. When only the xylene isomer compositions are considered, however, *all* catalysts examined, regardless of their toluene conver-

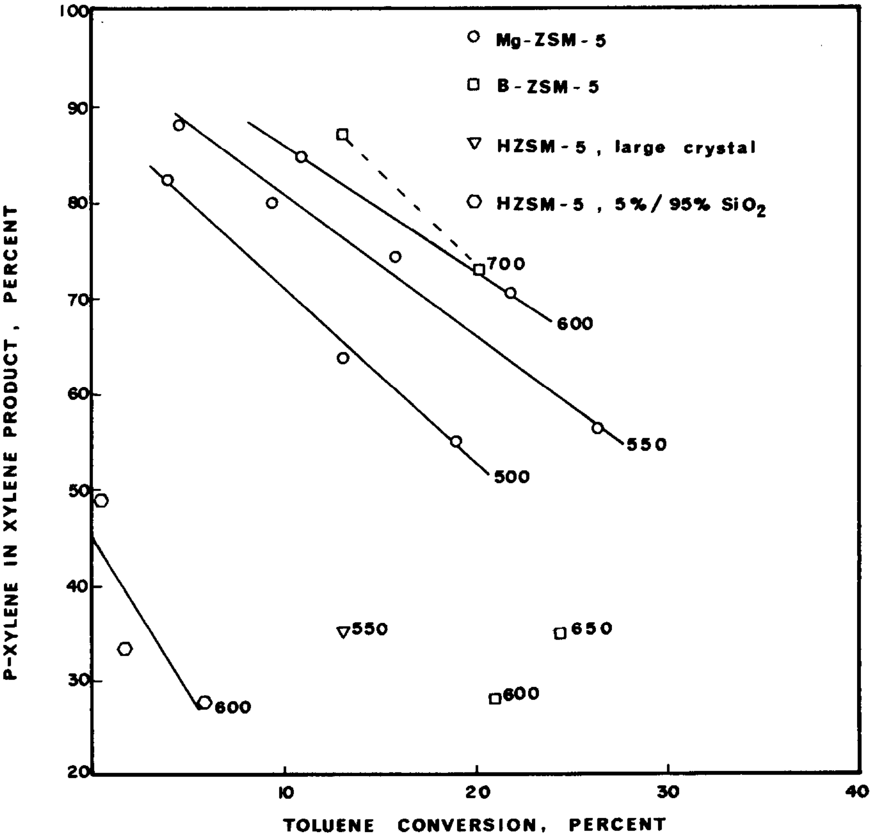


FIG. 1. Toluene disproportionation over ZSM-5 catalysts.

sion vs *para*-xylene selectivity performance, fall on the same xylene composition curve, with points falling between pure *para*-xylene and the equilibrium composition (Fig. 2). Thus the low selectivity unmodified HZSM-5 and large crystal HZSM-5 (*3*) fall on the same isomer composition curve as the highly para-selective Mg-ZSM-5 (Fig. 2). These data were obtained at widely varying temperatures, space velocities, and pressures.

Alkylation of Toluene with Methanol

In a manner similar to selective toluene disproportionation, unmodified ZSM-5 type catalysts usually give near-equilibrium xylene mixtures in the alkylation of toluene with methanol [Eq. (1)], as shown in Table 2 (*1*), although large crystal ZSM-5 has been reported to give 46% *para*-xylene in total xylenes produced (*3*). Modified ZSM-5 catalysts are capable of giving very high *para*-xylene selectivities. In fact, some catalysts have been shown to produce greater than 90% *para*-xylene in xylenes (Table 2) (*1*). In toluene alkylation by methanol as in selective toluene disproportionation, *para*-xylene selectivity generally increased with increasing temperature (Fig. 3).

In sharp contrast to toluene disproportionation, however, many different xylene isomer composition curves were observed for alkylation of toluene by methanol over a variety of selective and nonselective catalysts (Fig. 4). At low temperatures, many modified ZSM-5 type catalysts produced *ortho*-rich xylene product mixtures (Fig. 4). These xylene isomer compositions appear to approach the ratio, *ortho*/*meta*/*para* = 60/14/26, shown to be the initial xylene isomer composition in low-temperature Friedel–Crafts catalyzed methylation of tol-

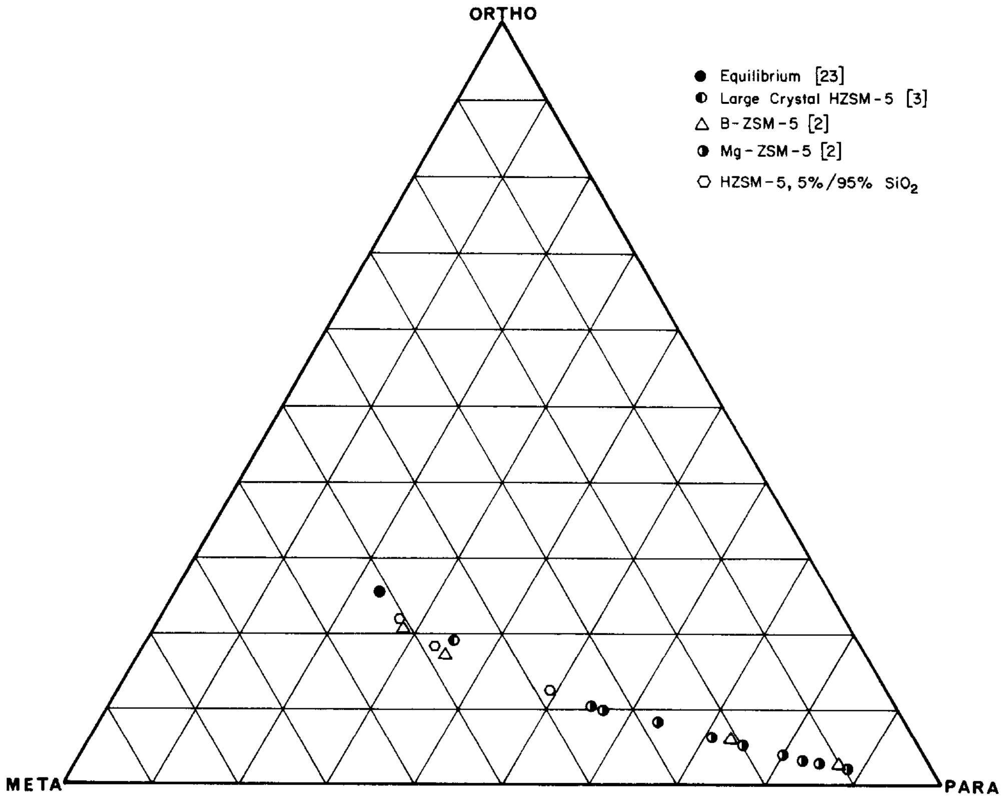


FIG. 2. Xylene isomer composition in toluene disproportionation over ZSM-5.

TABLE 2

Reaction of Toluene with Methanol over ZSM-5 Catalysts

Catalyst	Temp. (°C)	WHSV[a]	Toluene/ methanol(mole)	Toluene conversion (%)	Xylene isomer composition (%)			Xylenes in aromatic product (wt%)
					para	*meta*	*ortho*	
HZSM-5	400	3.7	1.5	38	24	54	22	
	450	5.4	1.4	44	24	53	23	
HZSM-5, large crystal[b]	500	6.6	2.0	39	46	36	18	88[c]
PZSM-5	400	28.2	1.4	9.1	35.1	24.4	40.5	86.7
(ϕ2PCl, 2.9% P)	450	28.3	1.4	8.1	46.0	22.8	31.2	77.1
	500	28.3	1.4	12.4	56.1	20.9	23.0	78.5
	550	28.3	1.4	15.9	72.5	15.3	12.2	84.6
	600	11.3	1.4	8.3	91.2	4.7	4.1	90.0
PZSM-5	250	5	0.5	1.8	29.1	21.4	49.5	91
(3.2% P)	300	5	0.5	11.9	30.9	23.4	45.7	83
	350	5	0.5	33.9	32.5	26.4	41.1	77
	400	5	0.5	42.6	38.0	34.0	28.0	75
PZSM-5	550	22.2	1	20.4	83.0	9.4	7.6	86
(5.4% P)	550	9.8	1	32.0	83.1	11.4	7.5	86
	550	4.4	1	38.1	71.2	19.2	9.6	86
PZSM-5	550	16.5	1	32.6	70.3	16.9	12.8	80
(3.3% P)	550	8.3	1	45.1	54.6	28.9	16.5	78
PZSM-5	550	16	1	45.9	49.8	32.6	17.6	80
(2.9% P)	550	34	1	39.1	57.4	25.5	17.1	82
PZSM-5	550	17	1	9.9	92.6	4.4	3.0	91
(5.6% P)	550	5	1	25.8	91.2	5.5	3.3	91
PZSM-5	550	16	1	48.1	36.4	44.0	19.6	81
(2.4% P)	550	34	1	45.7	48.2	34.6	17.2	81
PZSM-5	550	21	1	15.7	81.1	10.2	8.7	82
(6.0% P)	550	9	1	28.8	80.1	11.6	8.3	84
	550	4	1	34.7	75.1	15.7	9.2	84

[a] Weight hourly space velocity, g feed/g catalyst/hr.

[b] Ref. (*3*).

[c] 4.3 wt% benzene in aromatic product.

uene (*12*). The xylene product compositions obtained at low temperatures over modified ZSM-5 are also similar to those produced by silica–alumina catalyst (Fig. 4). At higher temperatures, selective catalysts tend toward 100% *para*-xylene, whereas less selective catalysts generally tend toward the equilibrium xylene composition as shown in Fig. 4. At a temperature of 550°C, several phosphorus-modified ZSM-5 catalysts generated xylene isomer compositions which fall on one curve leading from 100% *para* to equilibrium. The isomer composition curves discussed above are representative of the general types observed for selective alkylation of toluene with methanol. However, many more were observed, depending on catalyst modification and reaction conditions.

Isomerization of Pure Xylene Isomers

In order to better understand the reaction mechanisms which lead to the variety of isomer composition curves illustrated above for toluene disproportionation and alkylation of toluene with methanol (Figs. 2 and 4), isomerization experiments were carried out starting with the pure xylene iso-

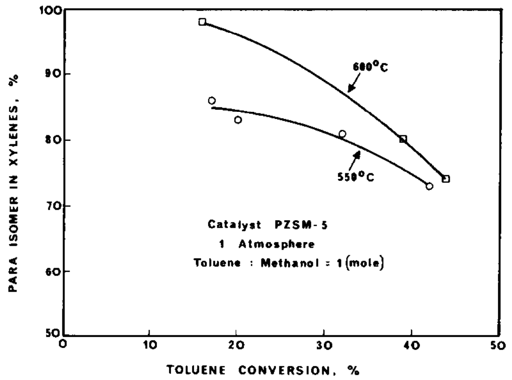


FIG. 3. Alkylation of toluene with methanol over PZSM-5.

mers using *para*-selective and nonselective zeolite catalysts (Table 3). A graphical representation of the data for the pure xylene isomers (Fig. 5), shows that at least two reaction paths (isomer composition curves) exist for each xylene isomer. One set of curves (A,B,C) defines reaction paths for the nonselective catalysts, while a second set (A′,B′,C′) defines paths for the *para*-selective zeolite catalysts. The selective path A′ for *ortho*-xylene which deviates to the *para* side of the straight-line 100% *ortho*-to-equilibrium path appears to be unprecedented in the literature. Even at low *ortho*-xylene conversions, *para*-xylene is formed in excess of *meta*-xylene. The implications of this will be discussed later. An intermediate curve was observed for *ortho*-xylene isomerization over unmodified HZSM-5 which was only slightly *para*-selective in toluene disproportionation (Fig. 5). This curve (A″) was generated using feeds of pure *ortho*-xylene, *ortho*-xylene/methanol, and *ortho*-xylene/water.

Among the catalysts which fit the nonselective curves (A,B,C) are AP zeolite (*13*), nickel/silica–alumina (*14*), partially rare

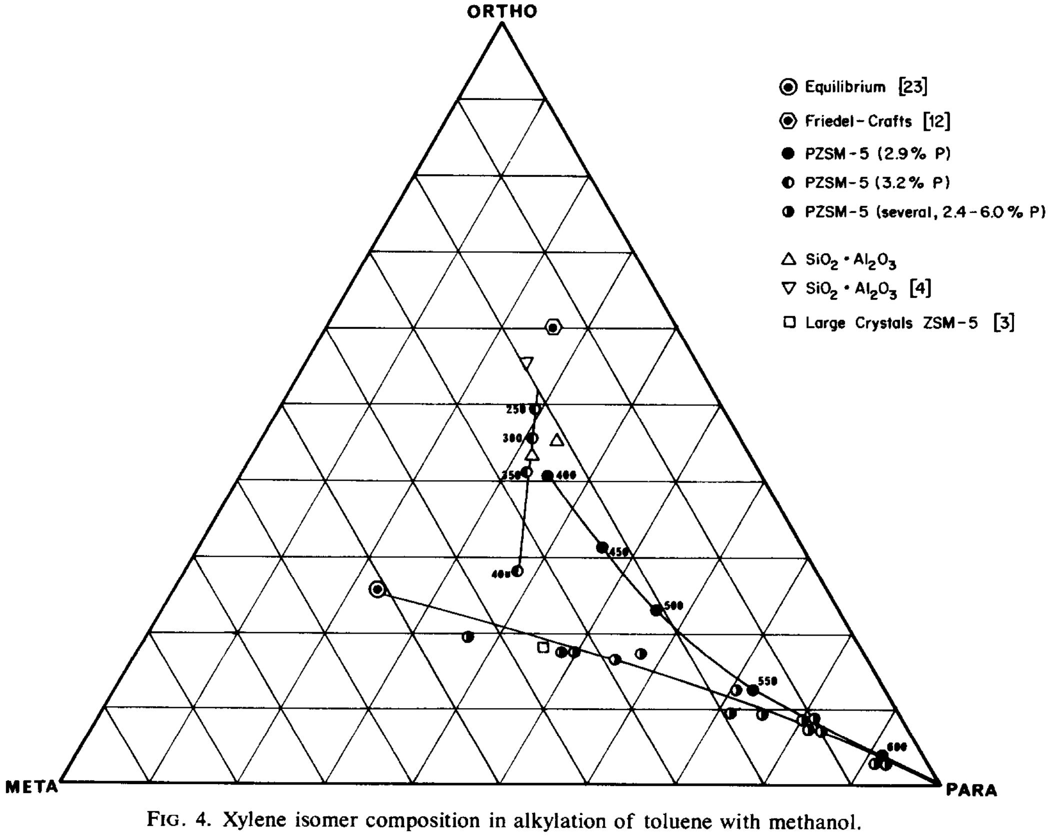


FIG. 4. Xylene isomer composition in alkylation of toluene with methanol.

TABLE 3

Xylene Isomerization over ZSM-5 Catalysts

Catalyst	Feed	Temp. (°C)	WHSV[a]	Xylene isomer composition (%)			Xylenes in aromatic product (wt%)
				para	*meta*	*ortho*	
PZSM-5 (3.9% P)	*o*-Xylene	550	13	10.1	12.2	77.7	
		550	6	16.0	23.5	60.5	
		550	3	20.3	37.2	42.5	
		550	3	21.3	40.7	38.0	
PZSM-5 (2.9% P)	*m*-Xylene	550	3	3.9	94.1	2.0	
		500	3	5.6	91.5	2.9	
PZSM-5 (1.2% P)	*p*-Xylene	500	22	93.1	5.3	1.6	
		410	22	97.6	2.0	0.4	
		410	3	81.0	15.5	3.5	
MgZSM-5 (9.4% Mg)	*o*-Xylene	550	3	8.6	10.2	81.2	
		550	7	5.3	4.5	90.2	
		550	14	3.2	2.2	94.6	
		550	29	1.7	1.1	97.2	
H_3PO_4/SiO_2	*o*-Xylene	550	1.9	1.6	7.9	90.6	
		550	1.9	3.0	16.2	80.8	
		550	0.7	2.2	12.3	85.5	
		550	0.7	0.6	1.7	97.5	
		550	0.3	0.75	1.7	97.5	
		550	0.2	1.2	2.5	96.2	
HZSM-5	*o*-Xylene	300	26	2.8	8.8	88.4	99.8
		300	19	10.2	25.6	64.3	99.6
		300	13	15.1	36.0	48.9	99.1
		300	13	9.4	21.5	69.1	99.4
	o-Xylene/water[b]	300	13[c]	4.5	14.8	80.7	99.5
		300	13[c]	9.2	27.0	63.8	98.4
	[d]	300	13[c]	8.7	24.0	67.3	97.8
	o-Xylene/methanol[e]	300	12[c]	0.3	2.2	97.4	98.0
		300	12[c]	1.2	5.1	93.8	97.3
		300	24[c]	0.3	1.2	98.5	97.3
PZSM-5 (7.1% P)	*p*-Xylene	600	8.3	90.9	6.8	2.3	
	p-Xylene/methanol[f]	600	7.7[g]	86.2	10.3	3.5	
		600	5.2[g]	81.7	13.5	4.9	
		600	3.4[g]	71.8	20.5	7.6	
	p-Xylene/water[h]	600	5.7[g]	83.7	12.0	4.3	

[a] Weight hourly space velocity, g · feed/g · catalyst/hr.

[b] *o*-Xylene : H_2O = 3.2 (mole).

[c] WHSV of *o*-xylene.

[d] *o*-Xylene : H_2O = 0.082 (mole).

[e] *o*-Xylene : methanol = 4.0 (mole).

[f] *p*-Xylene : methanol = 4.0 (mole).

[g] WHSV of *p*-xylene.

[h] *p*-Xylene : water = 4.9 (mole).

earth-exchanged Y zeolite (*15*), and phosphoric acid on kieselguhr (Table 3). The *para*-selective catalysts which generated the new selective curves (A′,B′,C′) were phosphorus and magnesium-modified ZSM-5 zeolites (Table 3). The data for AP catalyst were generated at 260°C for liquid phase reaction. As will be discussed later, the reaction path for AP catalyst has been shown to shift somewhat toward the selective

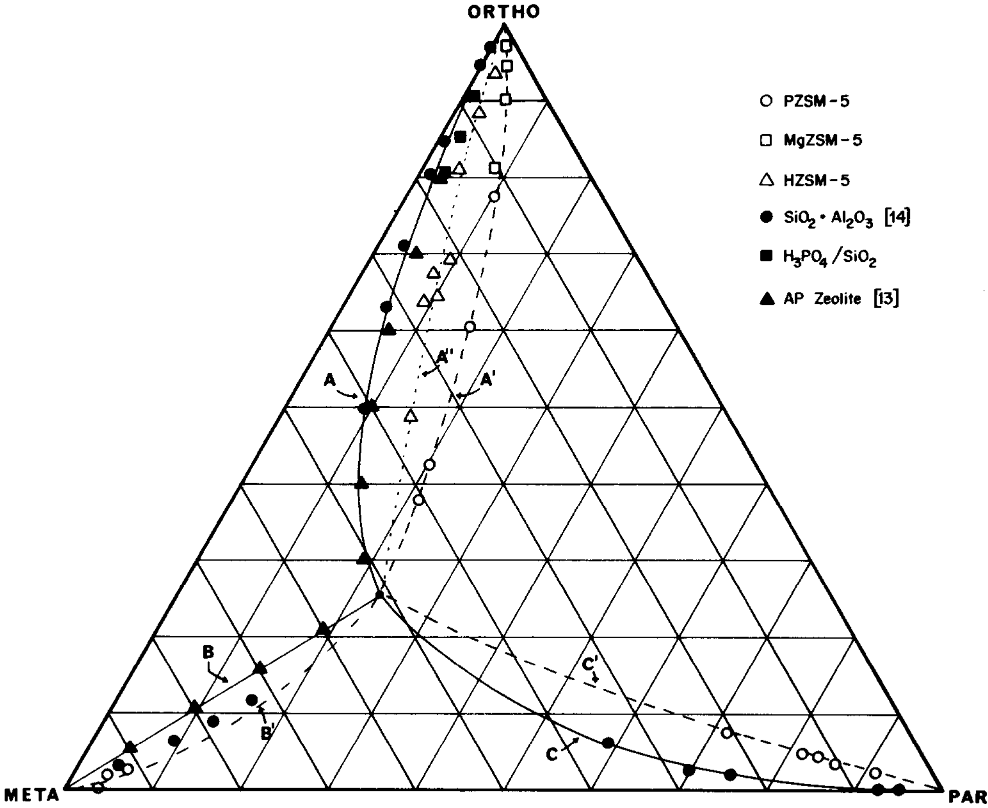


FIG. 5. Reaction paths for isomerization of pure xylene isomers. Paths A,B,C, nonselective catalysts; paths A', B', C', selective ZSM-5 catalysts.

curve (A') with increasing temperature and crystal size (*13*).

Relative Reaction Rates

A comparison was made of relative rates of isomerization of *ortho-*, *meta-*, and *para*-xylene in the presence of methanol over a *para*-selective PZSM-5 catalyst. Methanol was cofed in order to simulate toluene–methanol alkylation conditions where the presence of water or surface OCH_3, or isomerization via trimethylbenzenes (alkylation/dealkylation) might influence the apparent reaction paths. The results in Table 4 show that the relative reactivities of the xylene isomers are in the order: *para-* > *meta-* > *ortho*-xylene. The major reaction in each case was isomerization although in the case of *para*-xylene, a significant amount of further alkylation to 1,2,4-trimethylbenzene (pseudocumene) was observed. In addition, it may be noted that isomerization of *ortho*-xylene gives *para*-xylene in excess of *meta*-xylene, and isomerization of *meta*-xylene gives *para*-xylene in large excess over *ortho*-xylene.

The relative rate of alkylation of toluene by methanol was also calculated for the same PZSM-5 catalyst used for isomerization (Table 4). This catalyst was highly *para* selective for alkylation (>90% *para*). The observed rate of alkylation (k_a) was about three times the rate of isomerization of *para*-xylene and 7–15 times the rates of isomerization (k_i) of *meta-* and *ortho*-xylenes. A comparison of toluene–methanol alkylation and xylene isomerization rates was also made using an unmodified HZSM-5 catalyst (Table 5). With this catalyst the opposite was found: the observed

TABLE 4

Xylene Isomerization in the Presence of Methanol[a] over PZSM-5

Feed	*p*-Xylene/ methanol	*m*-Xylene/ methanol	*m*-Xylene/ methanol	*o*-Xylene/ methanol	Toluene/ methanol
Feed rate (mmol/hr/g cat)					
Aromatic	73	73	22	22	82
Methanol	18	18	6	6	20
	91	91	28	28	102
Temperature (°C)	600	600	600	600	600
Product composition (mole %)					
Benzene	0.38	0.33	0.41	0.45	0.07
Toluene	0.56	—	0.23	—	85.56
p-Xylene	93.14	1.67	3.56	1.68	12.62
m-Xylene	2.76	97.64	94.79	0.63	0.74
o-Xylene	0.75	0.05	0.19	96.51	0.39
p-Ethyltoluene	0.29	—	—	—	0.08
1,2,4-Trimethylbenzene	2.11	0.31	0.83	0.72	0.53
Relative rates[b]					
Isomerization	5.0	2.4	1.6	1.0	
Total loss	6.5	2.2	1.5	1.0	16

[a] 4 : 1 (mole) aromatic : methanol.

[b] Assumed that reaction is first order in aromatic, zero order in methanol, and contact time is inversely proportional to total molar feed rate.

rate of isomerization was 10–15 times faster than alkylation.

para-selective ZSM-5 catalyst $k_a > k_i$
Unmodified ZSM-5 catalyst $k_a < k_i$

DISCUSSION

To put these results in perspective, the relative rates of xylene isomerization, toluene disproportionation, and alkylation of toluene with methanol over HZSM-5 zeolite catalysts were estimated. The results shown in Table 5 indicate that *ortho*-xylene isomerization is about 13 times faster than alkylation of toluene with methanol for the parent (unmodified) HZSM-5 catalyst. An estimate of the relative rates of toluene disproportionation and alkylation of toluene with methanol can be made from the data in Tables 1 and 2. For toluene disproportionation over unmodified HZSM-5, the toluene conversion was 8% at 450°C, 3.6 WHSV, for alkylation of toluene with methanol the toluene conversion was 44% (theoretical = 71% because of limiting methanol) at 450°C, 5.4 WHSV. This gives a rate ratio, toluene alkylation/disproportionation, of about 10. Thus the reactivity order over unmodified HZSM-5 is

Xylene isomerization		Toluene–methanol alkylation		Toluene disproportionation
	>		>	
k_i		k_a		k_d
~100	:	10	:	1

This is roughly consistent with the rate ratio of xylene isomerization/toluene disproportionation, k_i/k_d, of ~1000 reported by Haag and Dwyer for HZSM-5 (*5, 6, 11, 16*) which apparently reflects the difficulty of achieving the bimolecular transition state required for transalkylation (disproportionation) within the ZSM-5 structure. This has been termed "restricted transition state selectivity" (*6*) and is believed to be the ma-

TABLE 5

Xylene Isomerization and Toluene Alkylation with Methanol over Unmodified HZSM-5

Feed	*o*-Xylene/ water	Toluene/ methanol/ water
Feed rate (mmol/hr/g cat)		
Aromatic	80	82
Water	967	533
Methanol	—	20
	1047	635
Temperature (°C)	300	300
Product compositon (mole %)		
Benzene	0.19	—
Toluene	0.70	94.97
p-Xylene	8.53	1.48
m-Xylene	23.47	1.34
o-Xylene	65.94	1.41
p-Ethyltoluene	—	0.05
1,2,4-Trimethylbenzene	1.14	0.63
Others	—	0.12
	99.97	100
Relative rate[a]	13	1

[a] Assumed that reaction is first order in aromatic, zero order in methanol, and contact time is inversely proportional to total molar feed rate.

jor factor responsible for the high selectivity in the ZSM-5 isomerization process (*5*, *16*). Over larger pore zeolites such as zeolite Y (faujasite), k_I/k_d is about 10–20 (rather than 1000) which leads to much poorer xylene selectivity in xylene isomerization (*5*, *16*). Bolton has reported that xylene isomerization over zeolite Y proceeds via a bimolecular (i.e., transalkylation) mechanism involving a diphenylmethane-type transition state and that the degree of isomerization is proportional to the amount of transalkylation (*15*). In the 1-methyl-2-ethylbenzene/zeolite Y system, Csicsery has found that isomerization occurs by both intramolecular and intermolecular (transalkylation) mechanisms (*17*).

Over *para*-selective PZSM-5, the reactivity order observed was (Table 4)

Toluene–methanol alkylation		Xylene isomerization
	>	
k_a		k_I
16	:	1–7

This is a reversal of the reactivity order observed for unmodified HZSM-5 (Table 5). In order for *net para*-xylene isomerization to occur, the larger, more slowly diffusing *meta*- and *ortho*-xylene isomers [diffusivity of *para*-xylene is ~1000 times greater than that of *meta*- and *ortho*-xylenes (*3*)] formed within the pores must escape from the zeolite crystal. This becomes increasingly more difficult as modification of the ZSM-5 crystal increases the diffusional resistance.

With the alkylation reaction, which is essentially nonreversible, the smaller molecules of toluene and methanol easily diffuse into the crystal and react, and the larger product xylenes must diffuse out of the zeolite crystal. If the net alkylation rate is mainly controlled by the rate of reaction of toluene and methanol, and not by the rate of diffusion of the product xylenes, then the alkylation will be slowed less than xylene isomerization by increasing diffusional resistance of the catalyst.

Diffusional discrimination between xylene isomers ["reactant selectivity" (*6*)] is illustrated by the relative rates of isomerization of the three xylene isomers over a highly *para*-selective PZSM-5 catalyst (Table 4). The relative rates of isomerization were

para-xylene:*meta*-xylene:*ortho*-xylene
~5:2.5:1

This is consistent with the more rapid diffusion of the smaller *para* isomer into the zeolite pores, followed by the interconversion to the other xylene isomers.

Xylene isomerization paths over the non-shape-selective catalysts, SiO_2–Al_2O_3, H_3PO_4/SiO_2, and AP zeolite (at 260°) (paths A,B,C, Fig. 5) appear to be consistent with stepwise intramolecular methyl shifts [Eq. (3)]. This mechanism has been confirmed

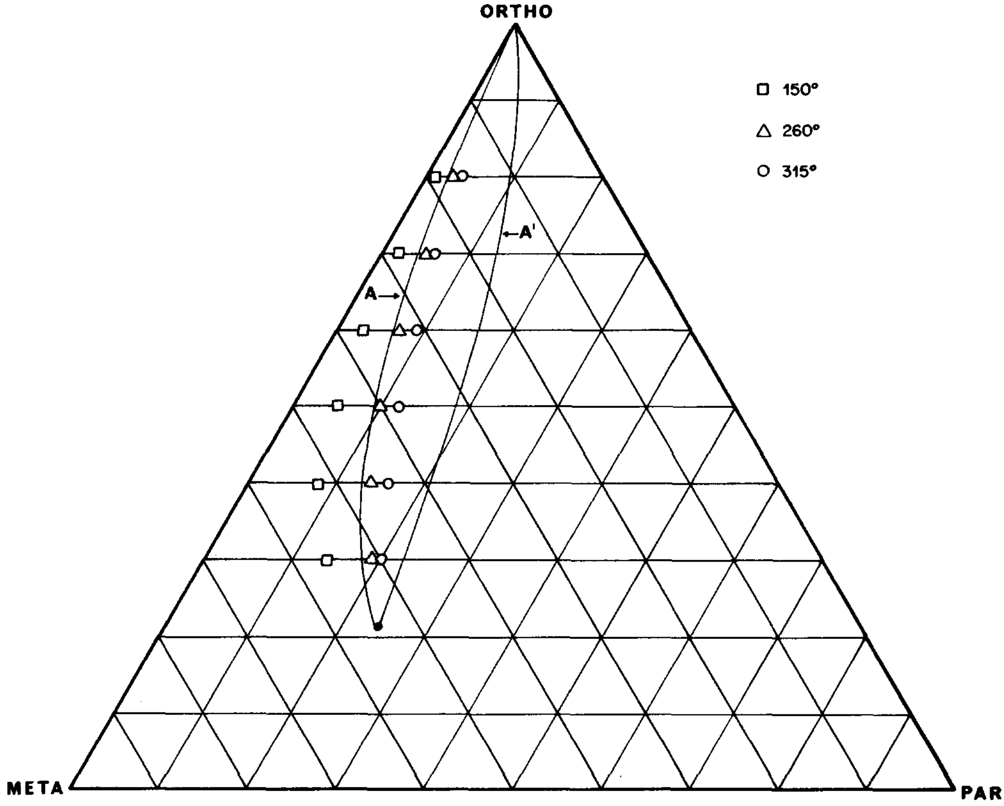
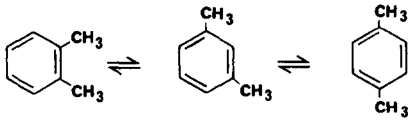


FIG. 6. Reaction paths for isomerization of pure xylene isomers over AP zeolite (*13*). Path A, nonselective catalysts; path A′, selective ZSM-5 catalysts (see Fig. 5).

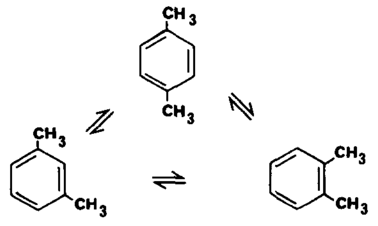
by labeling of the methyl groups for xylene isomerization over SiO_2–Al_2O_3 catalyst (*14*). The kinetics observed for xylene isomerization over small crystal AP catalyst at lower temperatures were also consistent with this mechanism (*13*).

Xylene isomerization over AP zeolite generated several reaction paths which were dependent on temperature and crystal size (Fig. 6) (*13*). As temperature and crystal size were increased, reaction paths for *ortho*-xylene isomerization were observed to shift somewhat toward the "*para*-selective" reaction path observed for *para*-selective ZSM-5 zeolite catalysts (A′, Figs. 5 and 6). It was found that at 200°C, small crystal zeolite AP catalyst exhibited kinetics entirely consistent with stepwise 1,2-methyl shifts:



(3)

However, with increased crystallite size and temperature, the apparent kinetics required a small contribution for a direct *ortho*-xylene to *para*-xylene path:



(4)

These results were explained in terms of a diffusional alteration of the intrinsic kinetics whereby in the larger crystallites, molecules remain in the zeolite pores long enough for several isomerization steps to occur. The observed products are thus partially the result of multistep reactions. Since *para*-xylene diffuses much faster than *meta*- and *ortho*-xylene, enhancement of *para*-xylene will occur. Thus as Wei has shown, in the presence of diffusional effects, the apparent kinetics may change from that of a single series reaction [Eq. (3)] to the more complex reaction scheme [Eq. (4)] which incorporates an *apparent* direct 1,4-methyl shift (*ortho*- to *para*-xylene) (*18*). The temperature effect on reaction paths for AP catalyst (Fig. 6) has also been explained in terms of a diffusional alteration of the intrinsic kinetics (*13*). For the usual case where the activation energy for reaction exceeds that for diffusion, diffusional effects increase with increasing temperature (*19*).

It has not been determined whether xylene isomerization over ZSM-5 catalysts is intramolecular or bimolecular. However, because of severe steric restrictions to formation of a bimolecular transition state within the ~6Å channels of ZSM-5, as shown by the high k_I/k_d as discussed above, we suggest that xylene isomerization occurs primarily via stepwise intramolecular 1,2-methyl shifts [Eq. (3)]. The unusual reaction path observed for *ortho*-xylene isomerization over highly *para*-selective ZSM-5 zeolites (curve A′, Fig. 5) may then be explained by diffusional effects much more pronounced than those observed for AP zeolite. This results in multistep interconversions within the zeolite cavity along with a diffusional selection highly in favor of the smaller *para* isomer. The net effect is an apparent direct *ortho*- to *para*-xylene conversion pathway [Eq. (4)]. Even at low *ortho*-xylene conversion over a highly *para*-selective PZSM-5 catalyst, these effects resulted in preferential formation of *para*-xylene, rather than the stepwise isomerization product, *meta*-xylene (Table 4). The various other reaction pathways for xylene isomerization over ZSM-5 (curves B′,C′, and A″, Fig. 5) are also consistent with the occurrence of extensive diffusional selection among isomers, which results in the apparent reaction scheme described by Eq. (4).

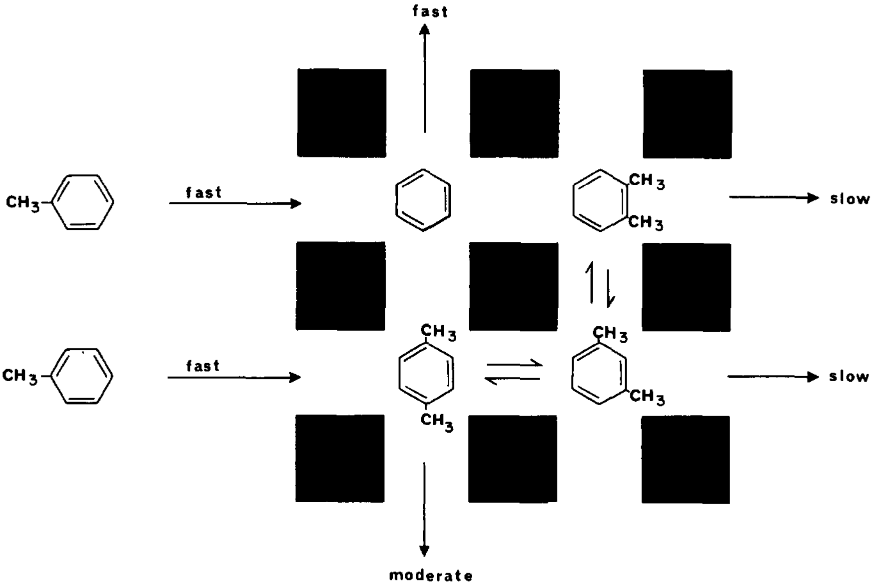
Selective Toluene Disproportionation

As discussed above, xylene isomerization is about 1000 times faster than toluene disproportionation in ZSM-5 catalysts (*3*). We suggest that toluene disproportionation to give high selectivity to *para*-xylene occurs as shown in Scheme 1 (*2, 3*).

The transalkylation reaction to form benzene and xylenes within the pores is relatively slow. Benzene diffuses out of the pores rapidly. The xylenes isomerize rapidly within the pores. *para*-Xylene diffuses out moderately fast while the *ortho* and *meta* isomers move within the pores relatively slowly and further convert to the *para* isomer before escaping from the channel system. Zeolite-mediated steric effects in the xylene-forming transition state may also enhance the amount of *para* isomer formed initially within the pores.

Further evidence for diffusion control of *para*-xylene selectivity in toluene disproportionation over ZSM-5 catalysts has been described by Olson and Haag (*20*). They have reported that for several ZSM-5 catalysts including large crystallite and inorganic-modified ZSM-5, a good correlation exists between a diffusion-related parameter (the sorption rate of *ortho*-xylene) and the *para*-xylene selectivity in toluene disproportionation (*5, 20*).

The increase in *para*-xylene selectivity with increasing temperature can be explained in terms of changes in the parameter $k(R^2/D)$ (*20*). It is expected that selectivity between species of differing diffusivities will increase as the modulus $k(R^2/D)$ increases, where k is a reaction rate, R is the crystallite radius, and D is the diffusivity (*5, 20*). The activation energies for diffusion of *meta*- and *ortho*-xylene have been reported to be in the range of 9–14 kcal/



SCHEME 1

mole (*5*, *21*). The activation energy for toluene disproportionation can be estimated from the data in Fig. 1 and Table 1 to be >20 kcal/mole. Since the activation energy for reaction (k) is greater than the activation energy for diffusion (D), the modulus $k(R^2/D)$, and consequently the diffusional effects, are expected to increase with increasing temperature. Thus the enhanced *para*-xylene selectivities observed for toluene disproportionation at elevated temperatures are consistent with the diffusion mechanism discussed (Scheme 1).

The relative amounts of *meta*- and *ortho*-xylene isomers generally observed for toluene disproportionation over *para*-selective ZSM-5 catalysts, *meta*-xylene > *ortho*-xylene (Table 1) are also consistent with diffusional control of product selectivity. Gorring has found that activation energies for diffusion of *meta*-xylene and *ortho*-xylene in Na-ZSM-5 are 14 and 9 kcal/mole, respectively (*5*, *21*). From these data and the observation that sorption rates of *meta*- and *ortho*-xylene are similar at 120°C (*22*), it seems reasonable to speculate that at elevated reaction temperatures the diffusivity of *meta*-xylene > *ortho*-xylene and thus the diffusivity of *para*-xylene ≫ *meta*-xylene > *ortho*-xylene.

The observation of a single isomer composition curve for toluene disproportionation over a variety of ZSM-5 catalysts (Fig. 2) is consistent with a slow transalkylation of toluene to form benzene and xylenes (of unknown composition), followed by rapid interconversion of the xylenes with diffusional selection among the xylene isomers (Scheme 1). If the rate of interconversion of the xylenes is fast compared to the rate of diffusion out of the crystal, then the composition of the initially formed xylenes will not be important, and the product selectivity will be primarily controlled by relative diffusion rates.

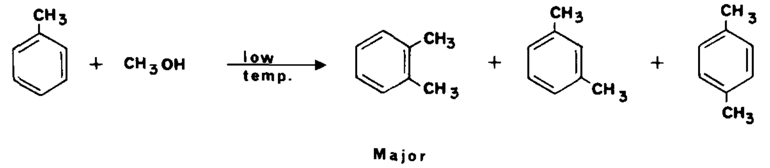
Selective Alkylation of Toluene by Methanol

Alkylation of toluene by methanol over various selective and nonselective ZSM-5 catalysts generated a number of different xylene isomer composition curves in contrast to the single curve observed for selective toluene disproportionation (Fig. 4 vs

Fig. 2). At low temperatures, the xylene product compositions are *ortho* rich, approaching those of non-shape-selective catalysts such as silica–alumina, and similar to the calculated primary product distribution for low temperature Friedel–Crafts methylation of toluene (Fig. 4) (*12*). At high reaction temperatures (>550°C), the reaction path becomes similar to those observed for *para*-xylene isomerization and selective toluene disproportionation over *para*-selective catalysts (Fig. 4) (*1*, *2*).

As discussed above, the apparent rate of alkylation of toluene by methanol is about one-tenth that of *ortho*-xylene isomerization over unmodified HZSM-5 at 300°C (Table 5). For a *para*-selective PZSM-5 catalyst, however, alkylation was about twice as fast as isomerization of *para*-xylene (Table 4). This has been discussed above in terms of increased diffusional resistance in the *para*-selective catalyst which restricts the entry and exit of the larger xylene isomers from the zeolite crystal, and thus decreases the rate of isomerization. It is apparent that depending on the ZSM-5 catalyst chosen, the alkylation rate can be similar to the isomerization rate.

Thus at low temperature, the rate of alkylation of toluene by methanol may be greater than the rate of xylene isomerization and can be carried out under conditions where the modulus (see above, $k(R^2/D)$, is sufficiently small that the diffusional effects are small (*5*). Under these conditions, *ortho*-rich product compositions approximating the primary product formed within the pores can be observed (Fig. 4):



As temperature is increased, reaction rates increase and diffusional resistance increases to the point where the xylene product distribution is determined mainly by diffusional effects as in selective toluene disproportionation (Scheme 1).

It is also possible that positional selectivity of the initial alkylation ("transition state selectivity") changes at higher temperature to favor formation of the *para* isomer. However, it is not necessary to invoke this to explain the observed reaction paths.

SUMMARY AND CONCLUSIONS

Appropriately modified ZSM-5 class zeolites are capable of generating uniquely selective product compositions. Intrinsic reactivities and selectivities are considerably altered with these modified catalysts. A large amount of data for xylene isomerization, selective toluene disproportionation, and selective alkylation of toluene by methanol is consistent with diffusional control of product selectivities.

ACKNOWLEDGMENTS

We are indebted to P. J. Yannich and J. M. Klosek for assistance with the experimental work, to J. A. Baran for preparation of the manuscript, and to A. B. Schwartz and F. G. Dwyer for providing samples of zeolite crystals. Appreciation is also expressed to our colleagues at Mobil Research and Development Corporation for many stimulating discussions. Early work by B. Weinstein and discussions with D. H. Olson and W. O. Haag were very helpful to our understanding of *para* selectivity. We are especially indebted to Professor J. Wei for his early help and encouragement in this area.

REFERENCES

1. Kaeding, W. W., Chu, C., Young, L. B., Weinstein, B., and Butter, S. A., *J. Catal.* **67**, 159 (1981).

2. Kaeding, W. W., Chu, C., Young, L. B., and Butter, S. A., *J. Catal.* **69,** 392 (1981).
3. Chen, N. Y., Kaeding, W. W., and Dwyer, F. G., *J. Amer. Chem. Soc.* **101,** 6783 (1979).
4. Yashima, T., Ahmad, H., Yamazaki, K., Katsuta, M., and Hara, N., *J. Catal.* **16,** 273 (1970); Yashima, T., Yamazaki, K., Ahmad, H., Katsuta, M., and Hara, N., *J. Catal.* **17,** 151 (1970).
5. Weisz, P. B., *Pure Appl. Chem.* **52,** 2091 (1980).
6. Derouane, E. G., *in* "Catalysis by Zeolites" (B. Imelik *et al.*, Eds.), p. 5. Elsevier, Amsterdam, 1980.
7. Naccache, C., and Taarit, Y. B., *Pure Appl. Chem.* **52,** 2175 (1980).
8. Venuto, P. B., *in* "Catalysis by Zeolites" (B. Imelik *et al.,* Eds.), p. 1. Elsevier, Amsterdam, 1980.
9. Wei, J., *J. Catal.* **76,** 433 (1982).
10. Argauer, R. J., and Landolt, R. G., U.S. Patent 3,702,866 (1972).
11. Meisel, S. L., McCullough, J. P., Lechthaler, C. H., and Weisz, P. B., "Recent Advances in the Production of Fuels and Chemicals over Zeolite Catalysts." Leo Friend Symp., 174th Am. Chem. Soc. Mtg., Chicago, Ill., Aug., 1977.
12. Allen, R. H., and Yats, L. D., *J. Amer. Chem. Soc.* **83,** 2799 (1961).
13. Chutoransky, P., and Dwyer, F. G., *Adv. Chem. Ser.* No. 121, 540 (1973).
14. Cortes, A., and Corma, A., *J. Catal.* **51,** 338 (1978).
15. Lanewala, M. A., and Bolton, A. P., *J. Org. Chem.* **34,** 3107 (1969).
16. Haag, W. O., and Dwyer, F. G., "Aromatics Processing with Intermediate Pore Size Zeolite Catalysts." AIChE Ann. Mtg., Boston, MA, Aug., 1979.
17. Csicsery, S. M., *J. Org. Chem.* **34,** 3338 (1969).
18. Wei, J., *J. Catal.* **1,** 526 (1962).
19. Weisz, P. B., and Prater, C. D., *in* "Advances in Catalysis," Vol. 6, p. 143. Academic Press, New York, 1954.
20. Haag, W. O., and Olson, D. H., U.S. Patent 4,117,026 (1978).
21. Gorring, R. L., unpublished data.
22. Young, L. B., unpublished data.
23. Taylor, W. J., Wagman, D. D., Williams, M. G., Pitzer, K. S., and Rossini, R. D., *J. Res. Nat. Bur.* **37,** 95 (1946).