

Cresol Isomerization on HZSM-5

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The cresol transformation was investigated on HZSM-5 at 380°C. Isomerization and disproportionation products were observed. Isomerization was the main reaction. The cresol isomerization rates on HZSM-5 increased from *ortho*- to *meta*- to *para*-isomer with decreasing molecular kinetic diameter. The initial conversion rates were in a ratio $r_p:r_m:r_o=20:3:1$. The isomerization product selectivity favoured molecules with the smallest kinetic molecular diameter at the onset of the reaction, and as reaction proceeded, the reaction product composition was determined thermodynamically. For *ortho*-cresol, at low conversion the *m/p* ratio slightly decreased with conversion, and at higher conversions the selectivity became insensitive to the degree of conversion, giving a *m/p* ratio equal to 3. For *meta*-cresol isomerization, the *p/o* ratio decreased steadily with conversion, and the initial *para* selectivity was associated to both transition state and product shape/size selectivity. The isomer equilibrium composition obtained was 36% *ortho*-, 48% *meta*-, and 16% *para*-cresol, in disagreement with the thermodynamically calculated composition. The isomerization rates were always greater than disproportionation rates. The isomerization rates followed the sequence $r_I(p) > r_I(m) > r_I(o)$, while the disproportionation rate sequence was $r_D(p) > r_D(m) \cong r_D(o)$. The initial *I/D* selectivities were in a ratio $(I/D)_p:(I/D)_m:(I/D)_o=100:30:8$. © 1997 Academic Press

INTRODUCTION

New concepts have been developed recently in catalysis associated with zeolite channel size and structure, such as shape and/or size selectivity to reactants, transition state, and/or products (1–5); the 10 member ring zeolites have attracted interest for their potential in fine chemicals. Industrial consumption of phenolic compounds such as cresols has increased in recent years (6–8), since they are used as feedstocks or intermediaries in the production of antiseptics, drugs, insecticides, dyes, phenolic resins, antioxidants, and polymers. The cresol natural sources have been coal tar, refinery waste stream, and coal gasification. Their industrial use depends on their purity; thus, laborious purification processes are needed. Among the alternative routes to cresols that are being explored, one is found to be phenol alkylation by methanol. The isomerization of alkylaromatics has been widely studied. Tracer studies with homo-

neous catalysts have shown that methyl group migrated on a ring by an intramolecular 1,2-alkyl shift mechanism (9), while on the other hand, higher alkyl groups like ethyl, *n*-propyl, *i*-propyl, *t*-butyl, etc., appeared to isomerize via intermolecular transalkylation (9–11). With amorphous silica alumina (12, 13), the 1,2-methyl shift was the dominant pathway, although the apparent selectivity for this mechanism was lower than that obtained with the homogeneous catalyst. With larger pore zeolites like LaY, the apparent deviation from the 1,2-methyl shift mechanism was even greater than that for amorphous silica-alumina catalysts (14, 15). Even more it has been shown that on Y zeolites a significant amount of isomerization products are formed via a bimolecular mechanism by intermolecular transalkylation (16–19). The intermediate pore size zeolite, e.g., HZSM-5, has been very successful in minimizing the transalkylation reaction while maximizing the isomerization activity particularly to *p*-isomer (20–22). The zeolite HZSM-5 has strong acid sites, and its intermediate size pores resist coke formation better than larger pore faujasites. Studies on the isomerization of heteroatom-substituted alkyl aromatics such as chlorotoluenes (23), toluonitriles (24), toluidines (25), and alkylanilines (26) have been reported in the literature. Patents describing cresol isomerization on HZSM-5 have appeared (27, 28). However, to our knowledge no work on cresol transformation by zeolites has been reported in the open literature. The present work examines HZSM-5 zeolite activity and selectivity in cresol transformation.

EXPERIMENTAL

A HZSM-5 zeolite with a molar ratio Si/Al = 27 was used. The size of nearly spherical polycrystalline zeolite particles was $\leq 1 \mu\text{m}$, as determined by scanning electron microscopy. The Langmuir specific surface area was 471 m²/g, as measured by nitrogen adsorption at liquid nitrogen temperature using an ASAP 2010 (Micromeritics), and the external surface area was 60 m²/g, as calculated by *t*-plot method. The catalysts were activated at 500°C overnight under air. As *ortho*- and *para*-cresol are solid at room temperature, it was necessary to use a solvent in order to feed the reactants to the reactor, and thus toluene was used as a solvent for

the three isomers to keep the same conditions. No toluene disproportionation products were observed. The reagents (Aldrich) were used without further purification. Reactions were carried out at 380°C and at atmospheric pressure in fixed bed reactors. A toluene cresol solution (cresol/toluene molar ratio = 9) was fed by a positive displacement pump and diluted in nitrogen ($(N_2 + T)/\text{cresol} = 9$). The reaction system was placed under fume hood to keep the laboratory as free as possible of reactant and product vapours. Different contact times were achieved by varying either the catalyst mass (0.01–0.5 g) or the reactant flow (2.25–9 ml/h). Product samples were collected at 10-min interval up to 1 h and analyzed by gas chromatography, using a FID and a capillary column WCOT fused silica 50 m \times 0.25 mm ($L \times d$) coated with CP-cresol ($df = 0.2 \mu\text{m}$).

RESULTS AND DISCUSSION

The transformation of cresol (methylphenol) isomers over HZSM-5 led mainly to isomerization products according to reaction 1 in Fig. 1. However, minor quantities of disproportionation products, i.e., phenol and xylenols (dimethylphenols), were detected, which could be formed following reaction 2 in Fig. 1. The HZSM-5 pore size favoured monomolecular (1,2-methyl shift) reaction [1], while bimolecular reaction [2] was severely inhibited.

HZSM-5 activity for cresol isomer transformation, at 10 min on stream, is compared in Fig. 2, which shows that cresol conversion rates decreases in the following order: *para* > *meta* > *ortho*-cresol. This can be explained on the basis of reactant shape selectivity. *Para*-cresol has the smallest kinetic diameter and so it diffuses inside the pores toward the active sites faster than do the other two isomers. The ZSM-5 has two types of channels, one sinusoidal with a circular pore aperture of ~ 0.54 – 0.56 nm and another straight with an elliptic pore aperture of ~ 0.52 – 0.58 nm, and the channel intersection with critical dimension of 0.9 nm; since the cresol kinetic molecular diameter should be smaller than those reported for xylenes and methylanilines (26) (see Table 1), diffusivity differences among cresols must be less marked than in the case of the for-

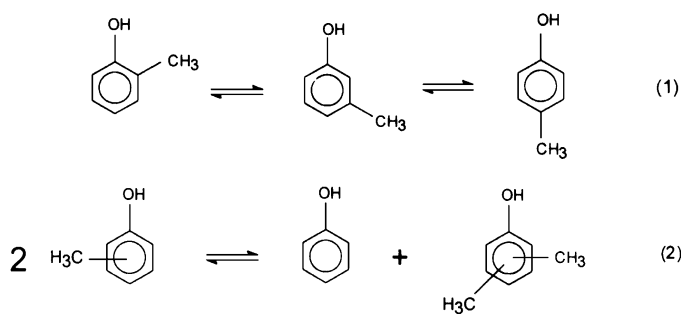


FIG. 1. Cresol reaction scheme.

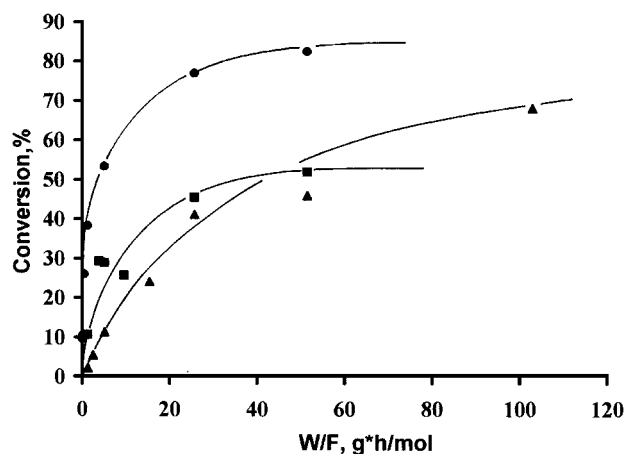


FIG. 2. Cresol conversion over HZSM-5 as a function of contact time. (●) *para*-cresol, (■) *meta*-cresol, and (▲) *ortho*-cresol.

mer compounds, but still the conversion rate differences indicate important diffusivity and/or adsorption differences. The competitive adsorption of xylenes and cresols has been investigated by various authors (29, 30). Dessau (29) found that in the competitive adsorption of *p*- and *o*-xylenes on HZSM-5 the adsorption of *p*-xylene was fairly selective at equilibrium, while it was more selective at initial stage, emphasizing kinetic diffusional effects. In the competitive adsorption of *p*- and *o*-cresols on HZSM-5 he found the adsorption of *p*-cresol slightly selective. Namba *et al.* (30) measured the competitive adsorption of the three isomers of xylenes and cresols on HZSM-5; they found that the total amount of xylenes adsorbed at equilibrium was lower and the *para* selective adsorption (Sp) higher than for cresols (for xylenes $Sp = 0.876$ and for cresols $Sp = 0.36$); they attributed this to the less bulky hydroxyl group and concluded that *p*-selectivity of HZSM-5 was low for cresols. Consequently, one should expect the rates for cresol transformation to be nearly the same for all isomers. However, it is evident from Fig. 2 that there is a clear difference between the rates of transformation for the three isomers, under the conditions of our experiments. In Table 2 are given the apparent initial rates ($\text{mol h}^{-1} \text{g}^{-1}$) for cresol transformation, estimated from the initial slopes of conversion curves on function of W/F (g h mol^{-1}). The ratio found for the global transformation rates was $r_p : r_m : r_o = 20 : 3 : 1$. These differences in rates might arise from the interaction between adsorption,

TABLE 1

Molecular Critical Diameter in Nanometers (26)

	<i>Ortho or meta</i>	<i>Para</i>
Xylenes	0.74	0.68
Methylaniline	0.652	0.598

TABLE 2
Apparent Initial Rates, mol g⁻¹ h⁻¹

	<i>Ortho</i>	<i>Meta</i>	<i>Para</i>
r	0.021	0.077	0.483
r_I	0.019	0.073	0.48
$r_D \times 10^2$	0.22	0.21	0.44

diffusion, reaction, and deactivation in the unique pore structure and surface acidity of HZSM-5 zeolite. As the points in Fig. 2 were taken at 10 min on stream, due to experimental limitations, the differences in deactivation rates for the cresols may play a significant role, but we do not believe that it can wholly account for the observed difference in rates. Therefore, the observed initial selectivity to reactants should be attributed to the intrinsic differences between isomers (in the diffusion, adsorption, reaction, and deactivation) and to the experimental conditions of the present work.

Isomerization selectivities represented by *meta* to *para* (*m/p*), *para* to *ortho* (*p/o*), and *meta* to *ortho* (*m/o*) ratio, for *ortho*-, *meta*-, and *para*-cresol isomerization, respectively, are shown in Fig. 3 as a function of isomerization percentage, obtained either by changing the contact time or in the course of deactivation experiments. As these two sets of points lie on the same curve, one may conclude that the deactivation effect on isomerization product distribution is equivalent to the change in contact time. For *ortho*-cresol isomerization, the *m/p* ratio (Fig. 3a) attained the experimental equilibrium value very soon and consequently was practically constant, which appears to suggest that *para*-cresol is formed directly from *ortho*-cresol, representing a straight line path to the equilibrium in Fig. 6. These results agree with those reported in the patent literature (28), where the *m/p* ratio was found almost constant and around 3 for different conditions of temperatures (250–380°C), pressures (15–60 atm), time on stream (1–40 h), liquid hourly space velocities (1–3 h⁻¹), and atmosphere (N₂, H₂). A similar result has been reported for *o*-toluidine on HZSM-5 at 400°C (25), but no explanation was given for this. We believe, as suggested by one of the reviewers, that this is a clear case of diffusion disguise of the true reaction path (31). For *meta*- and *para*-cresol isomerization, the *p/o* and *m/o* ratios decreased with increasing conversion (see Figs. 3b and 3c). In the case of *meta*-cresol isomerization, the *p/o* ratio is initially kinetically controlled, and as transformation proceeds it becomes thermodynamically controlled. One may argue that the initial isomerization selectivity can be explained on the basis of the stability of the intermediate σ -complex (carbonium ion resonance hybrid). As anything which will increase the stability of the intermediate will also lower the activation energy necessary to attain it, and since the products are kinetically and not thermodynamically con-

trolled at the beginning, the formation of the intermediates is dependent on the activation energy necessary to form them and not on the thermodynamic stability of the products; moreover, as the intermediate once formed is rapidly converted to products, its relative stability is a measure of product ratio and vice versa. Figure 4 illustrates a possible mechanism for *meta*-cresol isomerization into *ortho*- and *para*-cresol. A comparison of the intermediates involved shows that (a) in Fig. 5 is a canonical form with an *ortho*-quinonoid structure, while (b) has a *para*-quinonoid structure, more stable than the former (32). It is reasonable then to assume structure (b) to be more stable than structure (a) and therefore to contribute more to the hybrid increasing its stability in comparison with the *ortho*-intermediate. However, since the σ -complex of the starting reactive, *m*-cresol, actually has a much higher energy than those of the products, their relative stabilities have little influence on the product selectivity. A more reasonable explanation for the initial product selectivity in *m*-cresol isomerization is that it is product diffusion controlled, *p*-cresol diffusing

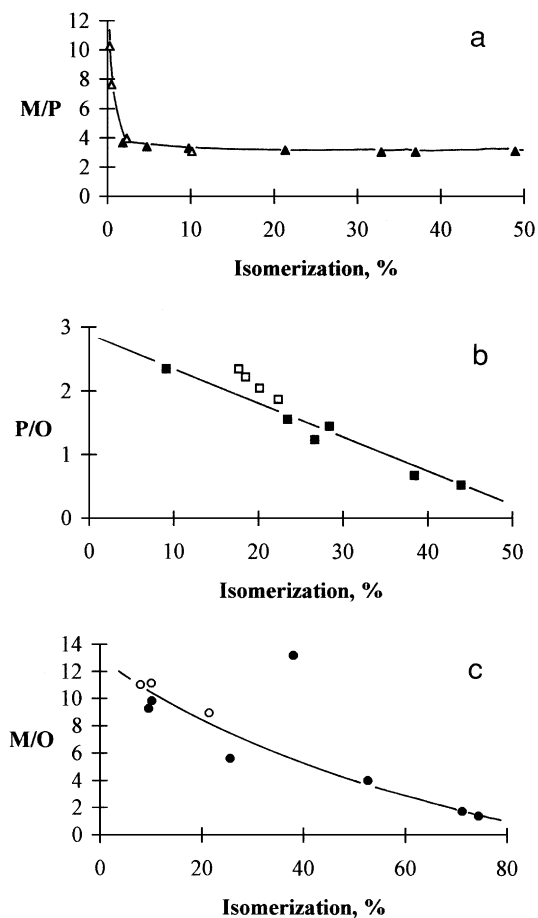
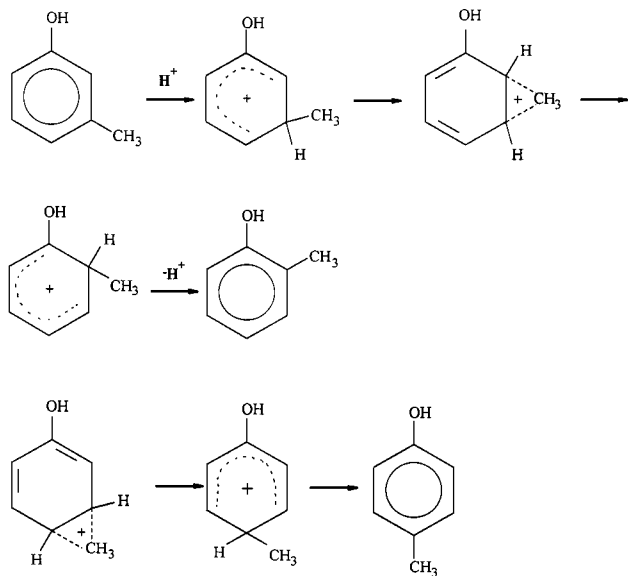
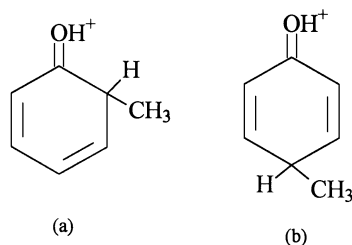


FIG. 3. Isomerization ratio as a function of isomerization percentage. (a) (\blacktriangle) *m/p* for *o*-cresol, (b) (\blacksquare) *p/o* for *m*-cresol, and (c) (\bullet) *m/o* for *p*-cresol. Open symbols represent the respective ratio in course of deactivation.

FIG. 4. A mechanism for *meta*-cresol isomerization.

out of the zeolite crystal much more rapidly than the more bulky *o*-cresol. This is consistent with the results of *o*-cresol isomerization, discussed above, where the secondary isomerization product, *p*-cresol, appears to be formed in apparent parallel reaction with the primary product, *m*-cresol. Similar results have been reported for toluidines (25) and for xylenes (18, 33). In all these cases, it has been observed that *m*-isomer is converted to the *p*-isomer at a faster rate than it is converted to *o*-isomer. For example, for *m*-xylene isomerization, *p/o* ratios of 2 (33) and 2.9 (34) have been reported; for *m*-toluidine values of 2.5 (25) and 3.3 (26) have been reported; from our results by linear extrapolating the data, in Fig. 3b, to 0% of isomerization, one obtains a value of 2.8. If the diffusion were the only controlling factor and as the molecular critical diameters decrease from xylene to toluidine to cresol, one should expect the *p/o* selectivity to follow the same trend, i.e., to decrease together with molecular critical diameters, but because this is not the case, there must be another factor, which might be a transition state shape/size selectivity. Lercher *et al.* (33) found for *m*-xylene isomerization on HZSM-5 that *p/o* ratio was constant and equal to 2 in the temperature range 473–573 K;

FIG. 5. Intermediate σ -complexes.

the authors concluded that the apparent activation energy for *o*- and *p*-xylene formation from *m*-xylene was identical and suggested a restricted transition state selectivity to explain their results. Similarly, Corma *et al.* (34) have suggested that *m*-xylene isomerization might be subjected to transition state shape selectivity to explain the *p/o* selectivity on 12-member ring zeolite; consequently this should not be disregarded in the smaller channels of 10-member ring zeolites. For *para*-cresol isomerization, *meta* is formed in a primary reaction, while *ortho*-cresol is formed out of *meta*-cresol in a secondary reaction, and as reaction proceeds the isomerization ratio decreases towards its equilibrium value. The fall in *p/o* and *m/o* ratios, with increasing conversion, may also be explained by the transalkylation reactions either between the reacting cresol and a xylenol to give a cresol isomer and another xylenol, or between phenol and xylenol to give cresol isomers; the former reaction does not affect the *I/D* ratio, but it might change the isomerization ratio. In the case of the latter reaction both the *I/D* ratio and the isomerization ratio are affected, in such a way that *I/D* increases. But these bimolecular reactions are inhibited inside the HZSM-5 pores by the space constraint; also, the amount of xylenols is too small to contribute much to the change in the product distribution. Therefore this fall must be the result of product thermodynamic stability.

The cresol isomer distribution of the reaction products is shown in Fig. 6, in a triangular composition diagram, where each symbol represents an experimental value, obtained by varying the contact time or reaction time on stream (catalyst decay); the calculated equilibrium composition is also shown. The composition of the equilibrium mixture experimentally obtained over HZSM-5 at 380°C is given in Table 3 together with the thermodynamic calculated value

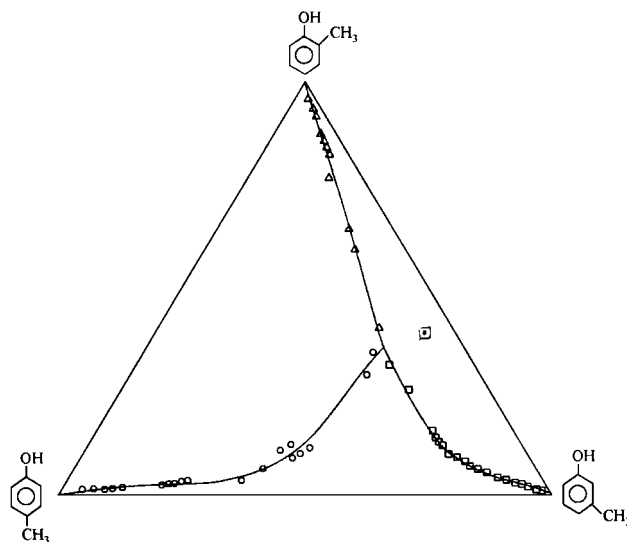


FIG. 6. Triangular composition diagram of cresols on HZSM-5 at 380°C.

TABLE 3
Equilibrium Composition of Isomer Mixtures

Compounds	<i>Ortho</i>	<i>Meta</i>	<i>Para</i>	Ref.
Cresols	36.0	48.0	16.0	This work
Cresols	37.0	58.0	5.0	Calculated (35)
Toluidines	31.0	52.0	17.0	(26)
Toluidines	33.7	50.2	16.1	(25)
Xylenes	23.0	53.0	24.0	(36)

(35) and the equilibrium composition obtained on HZSM-5 for xylenes (36) and toluidines (25, 26). As can be seen, our result substantially differs from the calculated using the thermodynamic free energies of formation (35). Our experimentally found equilibrium composition was further tested using binary and ternary cresol mixtures of different compositions and in all cases the product composition shifted towards 36% *ortho*, 48% *meta*-, and 16% *para*-cresol, which is quite different from the calculated, 37, 58, and 5%, respectively. Although for xylenes the experimentally found equilibrium composition agrees with the thermodynamically calculated value (36), in the case of toluidines it does not (25, 26), nor in the case of cresols, as reported in the present work. Hardy and Davis (25) based on the similarity between their experimental equilibrium composition for toluidines and the experimentally found for xylenes have suggested that the equilibrium value calculated from the API (37) data is incorrect.

The product selectivities are compared in Table 4 at similar levels of conversion for the three cresols, where isomerization (*I*) is defined as the sum of produced isomers, in molar percentage, from each cresol, and disproportionation (*D*) is defined as twice the total amount of xylenols

TABLE 4
Selectivities of Cresol Transformations on HZSM-5

	Reactant						
	<i>p</i> -Cresol		<i>m</i> -Cresol		<i>o</i> -Cresol		
Conv. (%)	10.4	26	10.6	25.7	2.15	11.2	24.0
Isom./Disp.	101	107	32.1	30.1	7.78	7.62	8.31
<i>R</i>	9.85	5.62	2.35	1.56	3.64	3.27	3.14
Req.	1.57		0.14		11.6		
Disp. (%)	0.102	0.24	0.286	0.34	0.24	1.28	2.57
Phenol/Xyls	1.33	1.59	1.87	1.76	1.43	1.30	1.09
2,6-Xylenol	0.00	0.00	0.00	0.00	29.8	22.1	11.9
2,4-Xylenol	56.9	38.3	0.00	22.4	36.5	40.5	31.7
2,5-Xylenol	43.1	61.7	53.2	62.4	33.7	37.4	39.5
2,3-Xylenol	0.00	0.00	16.1	0.00	0.00	0.00	7.32
3,5-Xylenol	0.00	0.00	0.00	0.00	0.00	0.00	3.39
3,4-Xylenol	0.00	0.00	30.8	15.3	0.00	0.00	6.10

Note. *R* = *m/o*, *p/o*, or *m/p* for the transformation of *p*-, *m*-, or *o*-cresol, respectively. Req., the respective equilibrium ratio calculated using the free energies of formation (35).

observed (2 Σ xylenols). In all cases the isomerization reaction was the main path in cresol conversion. However, our results clearly show that at low degree of conversion, the ratio of *I/D* increases from *ortho*- (~8) to *meta*- (~30) to *para*-cresol (~100). This is a consequence of the differences in the rates of isomerization and disproportionation of cresols, as we have obtained, the isomerization and disproportionation rates decrease from *para* to *meta* to *ortho*, though isomerization rate is always greater than disproportionation rate for each cresol:

$$r_I(p) > r_I(m) > r_I(o)$$

$$r_D(p) > r_D(m) \cong r_D(o)$$

$$r_I(p) > r_D(p), \quad r_I(m) > r_D(m), \quad r_I(o) > r_D(o).$$

This fact can be understood on the basis of transition state shape selectivity. On the one hand, the transition states needed for the disproportionation are bulkier than those needed for isomerization; on the other hand, the transition states needed for the disproportionation of *o*-cresol and of *m*-cresol are probably somehow bulkier than those of *p*-cresol. In addition, although the external surface area is low (60 m²/g) with respect to the internal (410 m²/g), the possibility of disproportionation occurring on the external surface cannot be disregarded. For low and moderate conversion levels the *I/D* ratios are nearly constant for each cresol, as can be seen in Table 4 and Fig. 7. For higher conversions the disproportionation became significant as isomerization declined, this result is clearly shown in Figs. 8a and 8b.

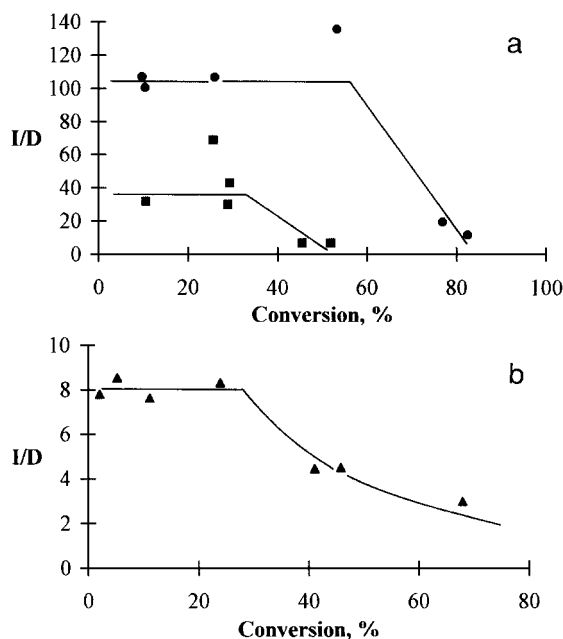


FIG. 7. Reaction selectivity as function of conversion: (a) (●) *para*- and (■) *meta*-cresol; (b) (▲) *ortho*-cresol.

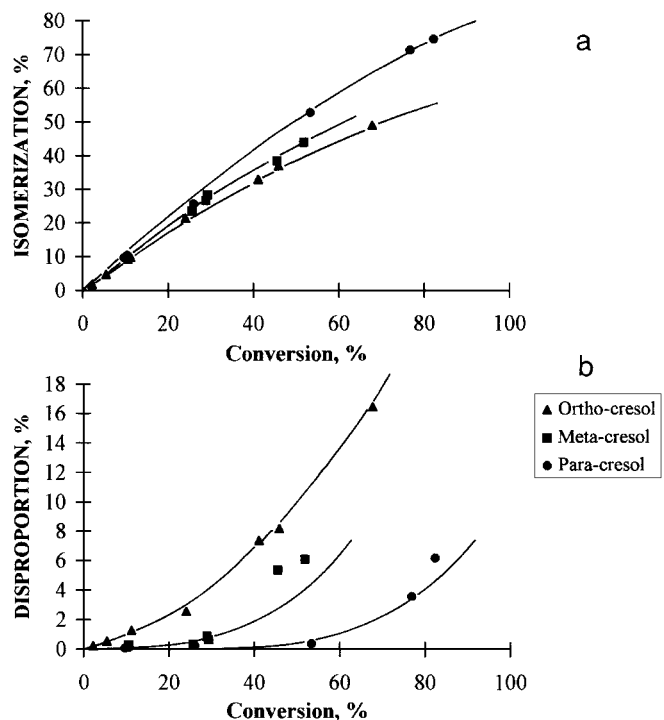


FIG. 8. (a) Isomerization. (b) Disproportionation as function of conversion. (●) *para*-, (■) *meta*-, and (▲) *ortho*-cresol.

In spite of the small disproportionation contribution to the cresols transformation on HZSM-5, our GC analysis was capable of detecting very small amount of xylenols and so allowed us to follow the changes in xylene distribution with more or less good accuracy. Thus, for *para*-cresol, the main product of disproportionation expected was the 2,4-, which should be formed by intermolecular transfer of a methyl group to an *ortho*-position to the -OH; at low and moderate conversions the 2,4- and 2,5-isomers were observed. Therefore, 2,4-xylene rapidly isomerizes to 2,5-xylene, which desorbs very rapidly as soon as formed. For *meta*-cresol, at low conversions the observed isomers coincide with expected, but at moderate conversion the 2,3-xylene disappeared, the 3,4-xylene decreased as 2,5-xylene increased and 2,4-xylene appeared. In the case of *ortho*-cresol, the detected xylenols, at low conversions, were the same as expected and as conversion increased all other xylenols were observed. According to the reaction scheme, reaction 2 in Fig. 1, the ratio $\text{phenol} / \sum \text{xylenols}$, should be equal to unity, in agreement with the observed value (Table 4). The slight discrepancies could be due to the fact that phenol diffuses faster than xylenols and some dealkylation may also occur.

CONCLUSIONS

The isomerization via 1,2-methyl shift is the main pathway in the cresol transformation on HZSM-5. The appar-

ent initial reaction rates are in a ratio of $r_p : r_m : r_o = 20 : 3 : 1$. The initial isomerization product distribution is determined by transition state and product shape/size selectivities. The *ortho*-cresol isomerization product ratio is nearly equal to the equilibrium from the beginning of the reaction, as a result of diffusion disguise of the true reaction path. The initial isomerization selectivity for *m*-cresol is controlled by product diffusion and by transition state shape/size selectivity. The *meta* and *para* isomerization ratios decrease toward the respective equilibrium value as conversion increases. The equilibrium composition found was *ortho*, 36%; *para*, 16%; and *meta*, 48%. The disproportionation reaction is practically negligible. However, the *I/D* selectivity ratio increases from *ortho* to *meta* to *para*. It is constant at low conversions but decreases as conversion increases.

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