

Comparison of Cresol Transformation on USHY and HZSM-5

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The cresol (methylphenol) transformation on zeolite USHY was investigated in a flow reactor at 380°C and atmospheric pressure. The results are compared with those previously reported for HZSM-5 (*J. Catal.* 172, 307 (1997)). On USHY, the catalytic stability follows the sequence $p \geq m > o$ -cresol, the turnover numbers (TONs) are similar for all three cresol isomers, but slightly higher for p -cresol. Thus, the access to acid sites is not limited. While on HZSM-5, the cresol reactivity follows the sequence $p > m > o$ -cresol, with the TON in the ratio $p:m:o = 7:4:1$. The HZSM-5 zeolite catalytic activity is more stable and its acid sites are more active than those of USHY, for p - and m -, but not for o -cresol, which means that o -cresol's access to the active sites in HZSM-5 is limited. The cresols are transformed through two main routes, a unimolecular isomerization via a 1,2-methyl shift and a bimolecular disproportionation or transalkylation reaction. On HZSM-5, isomerization is the dominant pathway for all cresols, disproportionation being limited by the space available near the acid sites and by the acid site density; while on USHY, a large pore zeolite with a higher acid site density, disproportionation is more significant. On both zeolites, o -cresol shows the highest disproportionation selectivity, which could be due to a rapid formation of diphenylmethane intermediates via a benzylic carbocation of o -cresol. The p/o and m/o ratios obtained for m - and p -cresol transformation respectively are higher with HZSM-5 than with USHY, while the p/m ratios obtained for o -cresol transformation were similar on both catalysts. It is concluded that not only with HZSM-5 but also with USHY the selectivity of isomerization is governed by product desorption/diffusion. The cresol composition at high conversions on USHY is 44% o -cresol, 42% m -cresol, and 14% p -cresol, which contrast with the composition found on HZSM-5: 36% o -cresol, 48% m -cresol, and 16% p -cresol. The xylenol distribution is governed by rapid interconversion and differences in diffusivities. © 2000 Academic Press

Key Words: cresol; isomerization; disproportionation; USHY; HZSM-5.

INTRODUCTION

Zeolites have replaced corrosive and polluting acids as catalysts in many refining and petrochemical processes and should substitute for them in the synthesis of fine and spe-

cial chemicals. The choice of zeolite catalysts is based on their remarkable acid properties and especially to their well-defined pore structure, with apertures and cages of approximately the size of organic molecules. Cresol isomers are used in the production of antiseptics, drugs, insecticides, dyes, phenolic resins, antioxidants, and polymers (1). In the commercial synthesis of cresols the most common processes are alkaline hydrolysis of chlorotoluene, the cleavage of cymene hydroperoxide, and the alkylation of phenol with methanol. This alkylation, which is an electrophilic substitution, is strongly *ortho-para* directing (2–6). The *meta* isomer can be obtained by subsequent isomerization (7). The isomerization of various methyl aromatics (xylenes (7–12), halogenotoluenes (13), toluidines (14, 15), etc.) has been widely studied due to its industrial importance as well as its scientific interest. Some authors have reported that their data were consistent with the consecutive reversible 1,2-methyl shift mechanism (7, 8, 16), while others have proposed a triangular scheme with direct *ortho/para* interconversion (16). The interpretation of experimental data is generally complicated, for selectivity depends on various parameters: acid site density and strength and pore structure. Thus, for large pore zeolites the *ortho/para* interconversion is more significant than for amorphous silica–alumina due to transalkylation reactions. With medium pore size zeolites the selectivity is determined by the product desorption from the pores. We have previously shown on HZSM-5 (17) and on a series of HY (18) that cresols are transformed through two main reactions: isomerization and disproportionation. For HZSM-5 the isomerization rates were always higher than the disproportionation rates. The initial conversion rates were in the ratio $r_p:r_m:r_o = 20:3:1$, and the initial I/D selectivities were $(I/D)_p:(I/D)_m:(I/D)_o = 100:30:8$. The isomer equilibrium composition obtained over HZSM-5 was 36% o -cresol, 48% m -cresol, and 16% p -cresol. The m - and o -cresol transformations were investigated at a given contact time in the course of deactivation on the series of HY (Si/Al = 4.5–55). o -Cresol and m -cresol reactivities were similar on HY (4.5) but as the Si/Al ratio increased, o -cresol reactivity increased relative to that of m -cresol; however, in all cases the catalyst deactivated less for m -cresol

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TABLE 1
Catalyst Physicochemical Characteristics

Catalyst	Si/Al overall	Formula	S_{at} (mmol of H ⁺ /g)	Ac_T (meq H ⁺ /g)	Ac_F (meq H ⁺ /g)
HZSM-5	27	H _{2.89} Na _{0.54} Al _{3.43} Si _{92.57} O ₁₉₂	0.5	0.608	0.141
USHY	2.5	H _{34.1} Na _{0.8} Al _{34.9} Si _{157.1} O ₃₈₄	2.96	1.085	0.729

Note. S_{at} , theoretical acid sites per gram of catalyst; Ac_T , total acidity measured by TPD-NH₃; and Ac_F , strong acidity (amount of NH₃ retained at $T \geq 350^\circ\text{C}$).

transformation. The disproportionation was predominant in the case of *o*-cresol. The object of the present work is to complement our two previous reports (17, 18) by studying the transformation of all three cresols over USHY, changing both the contact time and the time on stream, and comparing its activity and selectivity with HZSM-5 zeolites. The porosity of these catalysts was characterized by nitrogen adsorption.

EXPERIMENTAL

Two zeolites were tested: a HZSM-5 (PQ zeolite, CBV 5020, Si/Al = 27) and a USHY (Union Carbide, LZV-82, with a framework Si/Al = 4.5 and overall Si/Al = 2.5). They were used as powders (200–270 mesh). The physicochemical characteristics of these catalysts are given in Tables 1 and 2. The nitrogen adsorption–desorption experiments were carried out at 77 K, using a gas adsorption system ASAP 2010 (Micromeritics). Prior to the reaction, the catalysts were activated at 500°C overnight under air. The reagents (Aldrich) were used without further purification. Reactions were carried out at 380°C and at atmospheric pressure in fixed bed reactors. A detailed description of the experimental and analytical procedures have been reported elsewhere (17, 18).

RESULTS AND DISCUSSION

Adsorption Properties

The adsorption–desorption nitrogen isotherm shapes indicate the prevailing microporosity of these catalysts; however, the isotherms show a hysteresis loop closing at $P/P_0 = 0.4$, and this irreversibility has been attributed to

TABLE 2

Catalyst Crystallinity and Textural Characteristics

Catalyst	V_{tot} , cm ³ /g	V_t , cm ³ /g	V_{ultra} , cm ³ /g	V_{meso} , cm ³ /g	Crist(XRD), %	S , m ² /g
HZSM-5	0.223	0.118	0.039	0.0669	82	365
USHY	0.350	0.254	0.034	0.0620	100	649

the presence of ultramicropores and mesopores besides the normal micropores (12). The isotherms were analyzed with the Dubinin–Raduskievich (DR) equation, from which V_{DR} ($V_{DR} = V_{ultra} + V_t$) can be obtained. The *t*-plot method for the micropore volume and the BJH method for mesopores were also used. Table 2 gives the total pore volume V_{tot} (measured at $P/P_0 = 0.97$), the micropore volume given by the *t*-plot method V_t , that of ultramicropores ($V_{ultra} = V_{DR} - V_t$), that of mesopores ($V_{meso} = V_{tot} - V_{DR}$), and specific surface area. The USHY sample shows higher V_{tot} , V_t , and specific surface area, whereas V_{ultra} and V_{meso} are slightly lower. Therefore, this sample offers a higher accessibility to reactants molecules than the HZSM-5 sample. On the other hand, the space available for bimolecular reactions is restricted in the latter, which makes it more resistant to coke formation, while the former allows coke formation more easily and, consequently, deactivates more rapidly.

Activity and Catalytic Stability

Whatever the reactant cresol, both catalysts show a rapid deactivation (Fig. 1). However, as is generally observed for high-temperature gas phase reactions (19), HZSM-5 is found to be more catalytically stable than USHY.

The initial activity and catalytic stability were estimated by fitting the deactivation data by an exponential equation,

$$\text{Conversion} = C_0 \exp(-k_d \cdot t),$$

where C_0 represents the initial conversion (at time-on-

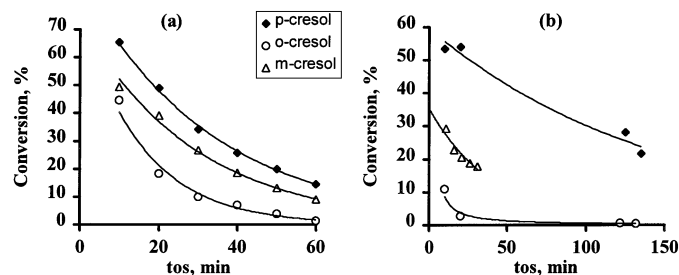


FIG. 1. Cresol conversion at 380°C, $P_{cresol} = 0.1$ bar, and $W/F = 5.15$ (gh)/mol as a function of time on stream over (a) USHY and (b) HZSM-5.

TABLE 3

Catalyst Initial Activity and Deactivation Constants for Cresol Conversion on USHY and HZSM-5 at W/F = 5.15 (gh)/mol

Reactive	USHY			HZSM-5		
	C_0 , %	TON	k_d , min ⁻¹	C_0 , %	TON	k_d , min ⁻¹
<i>p</i> -Cresol	87.2	57.3	0.030	59.7	231.5	0.0068
<i>m</i> -Cresol	73.8	48.5	0.035	35.4	137.3	0.024
<i>o</i> -Cresol	76.8	50.5	0.064	8.04	31.2	0.023

stream, $t=0$) and k_d a constant that reflects the catalyst deactivation. As can be seen in Table 3, the USHY zeolite is more active, though less catalytically stable than HZSM-5. On USHY the catalytic stability varies for the different cresols, following the sequence $p \geq m > o$ -cresol, while on HZSM-5 the catalytic stabilities are $p \geq m \approx o$ -cresol.

The conversions ($t=10$ min) of the cresols are plotted in Fig. 2, as a function of contact time taken as W/F , the ratio between the catalyst weight and the reactant molar flow rate. On the HZSM-5 catalyst, the reactivity of cresols clearly follows the sequence $p > m > o$ -cresol, while on USHY the sequence is $p > m \approx o$ -cresol, as shown in Fig. 2. This might be associated with the *p*-isomer highest diffusivity. USHY is more active than HZSM-5, for all cresols, which can be related to its acid site higher density and accessibility (Tables 1 and 2) as well as to the extraframework aluminium species that may interact with framework protonic sites, generating a very strong acidity (12, 20–23). However, given the turnover number (TON), as the number of molecules converted per theoretical acid site (from Table 1), we find, as expected, that the acid sites on ZSM-5 are more active than on USHY, for *p*- and *m*-cresol, but not for *o*-cresol transformation (see Table 3). Therefore, there must be a strong hindrance to *o*-cresol entering the pore of HZSM-5, or if it does enter into the pore, there is not enough space for the transition state needed to be formed for its transformation. On the other hand, on USHY, whatever the reactant cresol isomer, the TONs are similar, which means that their access to the acid sites is not

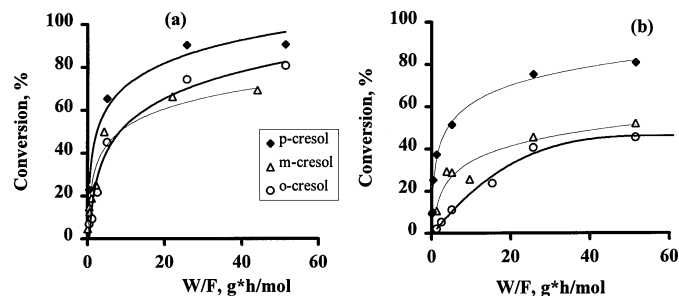


FIG. 2. Cresol conversion ($t=10$ min) as a function of contact time (W/F , (gh)/mol) on (a) USHY and (b) HZSM-5.

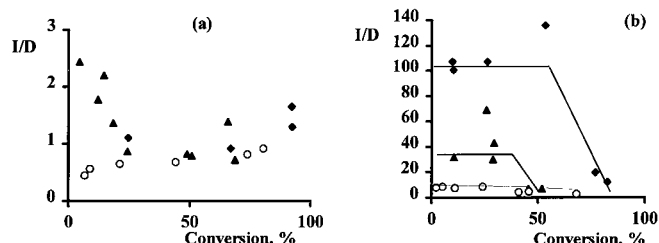


FIG. 3. I/D selectivity as a function of conversion for (a) USHY and (b) HZSM-5. Legend as in Fig. 1.

limited and that their intrinsic molecular property (polarity, basicity, etc.) differences do not seem to affect cresol reactivities on USHY, whereas on HZSM-5, the TON are quite different, indicating once again the pronounced diffusion limitations.

Selectivity

The cresols react over the zeolites mainly through two parallel reactions, isomerization (I) and disproportionation (D) (17, 18); however, the dealkylation reaction is also possible, particularly on USHY. The isomerization to disproportionation (I/D) selectivity shows a great difference between USHY (Fig. 3a) and HZSM-5 (Fig. 3b) (17). In all cases HZSM-5 is more selective in isomerization than USHY, as is observed for xylenes transformation (9). This was quite expected as the formation of the bulky diphenylmethane intermediates of disproportionation is strongly inhibited in the narrow channel intersections of HZSM-5 (≈ 8.5 Å in diameter) whereas it is not the case in the supercages of USHY (13 Å in diameter). However, there is an important difference between xylene and cresol transformations. With both catalysts, the I/D ratio is initially much lower from *o*-cresol than from the other two isomers, while it was the reverse in the case of xylenes (11), where the initial values were $I/D=1.8$ (*o*-xylene), 0.9 (*m*-xylene), and 0.3 (*p*-xylene) on USHY. This could be due to a higher stability of the benzylic carbocation formed from the *ortho* isomer, which is the first intermediate in disproportionation (11).

It should be remarked that at high conversion of *m*- and *p*-cresols over HZSM-5, there is a pronounced decrease in the I/D ratio (Fig. 3b). This decrease can be explained by the secondary disproportionation of *o*-cresol resulting from isomerization. This was expected, as the disproportionation selectivity from *o*-cresol is much higher than that from *p*- or *m*-cresols (17). No decrease is observed with USHY for *p*- and *o*-cresol, which is not abnormal, as the difference in the I/D ratio from the cresol isomers is more limited than that over HZSM-5. The catalysts deactivation affects both isomerization and disproportionation reactions, but the latter one is normally the most affected, as can be seen from the results given in Table 4, where the deactivation

TABLE 4

Initial Isomerization (I_0 , %) and Disproportionation (D_0 , %) and the Corresponding Deactivation Constants (k_d) for USHY(4.5) at 380°C and 5.15 (hg)/mol

	<i>o</i>		<i>m</i>		<i>p</i>	
	X_0^a	k_d	X_0^a	k_d	X_0^a	k_d
I	25.8	0.061	26.9	0.0198	32.9	0.017
D	46.2	0.062	43.4	0.0503	54.0	0.043

^a X_0 represents I_0 in the first row and D_0 in the second row.

constant k_d is usually much higher for the disproportionation reaction than for isomerization. This can be attributed to the deactivation of the stronger acid sites required for a disproportionation reaction to occur, or to the narrowing of pore diameter by coke deposition, which favours isomerization products by limiting disproportionation product diffusion, and/or to the xylenols being strongly adsorbed on the acid sites; once formed, they do not desorb immediately but continue to react, leading to the formation of coke precursors (12).

At low conversion *m*-cresol leads preferentially to the *para* isomer. This was expected over HZSM-5 owing to the shape selectivity of this medium pore size zeolite; thus, large values of the *p/o* ratio are obtained from *m*-xylene isomerization (7, 9). On the other hand, the high *p/o* ratio (>2 at zero conversion) found for USHY (see Fig. 4b) is quite unexpected, from the intramolecular mechanism of isomerization through the methyl shift, in the benzenium ion intermediates. A value close to 1 should be obtained as was the case with *m*-xylene isomerization over HFAU zeolites (9, 11). However, a high *p/o* ratio has also been observed from *m*-cresol on γ -alumina and silica-alumina (24). Therefore, it appears that even with a large pore zeolites, isomerization is limited by the product desorption. In agreement with this proposal, there is an apparent direct transformation of *o*-cresol into *p*-cresol and vice versa.

The *m/o* ratio (from *p*-cresol) and the *m/p* ratio (from *o*-cresol) are both relatively high at zero conversion (Fig. 4), as expected for consecutive reactions; however, the *m/p* ratios, on both catalysts, have the same values and are lower than the thermodynamic value. This can be explained by the *p*-cresol rapid desorption. In the case of HZSM-5, it might also be possible that *o*-cresol is directly transformed to *p*-cresol, through consecutive disproportionation and transalkylation reactions, on the external surface; there are not space limitations.

The cresol isomer distribution of the reaction products for USHY is shown in Fig. 5, 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). Also on the diagram are shown, for

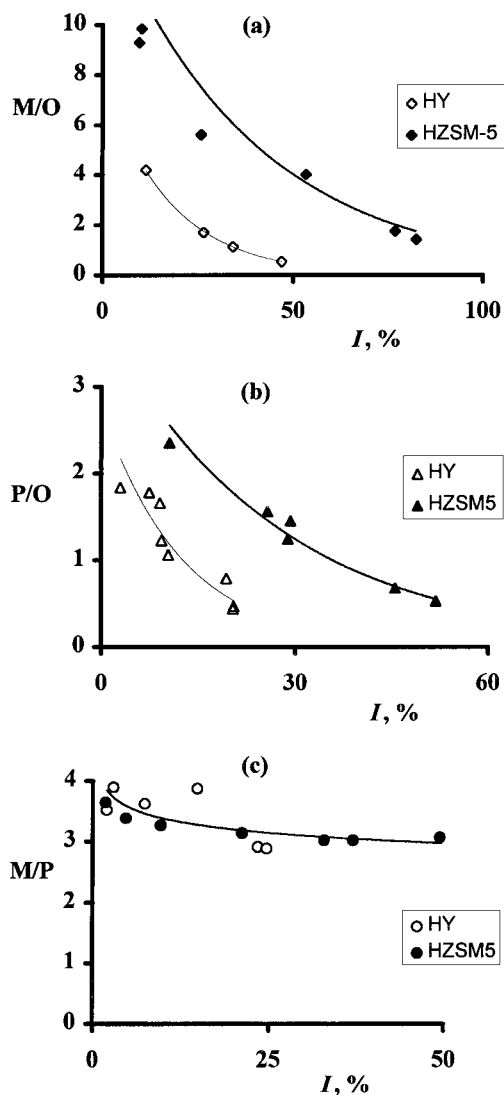


FIG. 4. Comparison of isomerization selectivities on both catalysts: (a) *m/o* from *p*-cresol, (b) *p/o* from *m*-cresol, and (c) *m/p* from *o*-cresol.

comparison, the data for HZSM-5 (17) and the calculated equilibrium composition. The compositions approached at high conversions over USHY at 380°C are given in Table 5 together with those previously reported by us for HZSM-5 (17), the thermodynamic calculated values (25), and the

TABLE 5
Equilibrium Composition of Isomer Mixtures

Compounds	<i>ortho</i>	<i>meta</i>	<i>para</i>	Ref.
Cresols	44	42	14	This work on USHY(4.5)
Cresols	36.0	48.0	16.0	(17)
Cresols	37.0	58.0	5.0	Calculated (25)
Toluidines	31.0	52.0	17.0	(15)
Toluidines	33.7	50.2	16.1	(14)
Xylenes	23.0	53.0	24.0	(26)

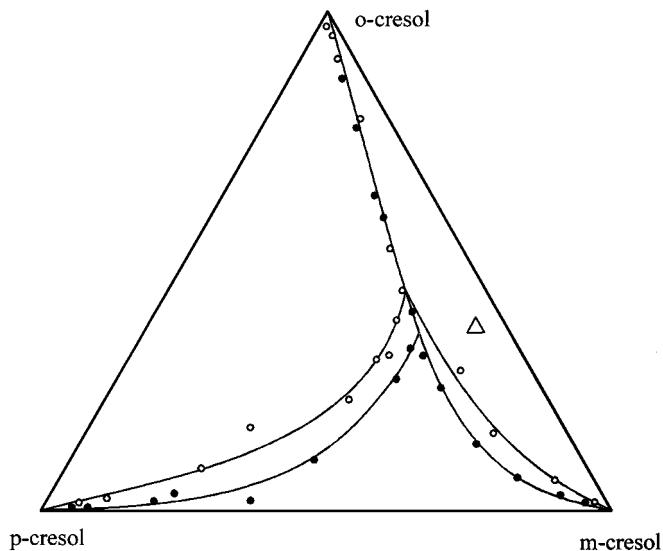


FIG. 5. Cresol triangular composition diagram for USHY and HZSM-5.

equilibrium composition obtained on HZSM-5 for xylenes (26) and toluidines (14, 15). As can be seen, our results substantially differ from the calculated values using the thermodynamic free energies of formation (25). Our experimentally found composition at high conversions was further tested using binary and ternary cresol mixtures of different compositions and in all cases the product composition shifted toward 44% *o*-cresol, 42% *m*-cresol, and 14% *p*-cresol on USHY, which are quite different from the calculated 37, 58, and 5%, respectively. Although for xylenes the experimentally found equilibrium composition agrees with the thermodynamically calculated value (26), in the case of toluidines it does not (14, 15), nor in the case of cresols, as reported for HZSM-5 in (17) and in the present work for USHY. Hardy and Davis (14), based on the similarity between their experimental equilibrium compositions for toluidines and those experimentally found for xylenes have suggested that the equilibrium value calculated from the API (27) data is incorrect. In our case on both catalysts, *para*-selective—HZSM-5—and non-*para*-selective—USHY—the experimentally found amount of *p*-cresol is substantially higher than that expected from the calculated equilibrium composition. Beyond what we have shown in previous works (17, 18), Fig. 5 clearly illustrates the shape-selectivity path toward the equilibrium from *p* and *m*-cresol, but not from *o*-cresol; here, the two catalysts show diffusion disguise kinetics since apparently *p*-cresol is formed directly from *ortho* from the very beginning. The difference in the composition at high conversions between the two catalysts and that calculated using the thermodynamic data seems to imply that the composition is sensitive to the catalyst structure; otherwise, to obtain the true equilibrium values, the experimental ones have to be corrected by a factor which

should be a function of the activity coefficient characteristic of the given system (cresol-zeolite).

Xylenol Distribution

Whatever the catalyst, in the case of *o*-cresol, at low conversions the primary xylenols are as expected: 2,4-, 2,5-, and 2,6-xylenol, but as shown in Fig. 6, as the conversion increases, all other xylenols are formed via a rapid interconversion, according to the scheme shown in Fig. 7. However, some differences may be worth noting: on one hand, the percentage of 2,4-xylenol is higher on USHY than on HZSM-5, while the reverse is true for 2,5-xylenol, for a low level of disproportionation; on the other hand, over HZSM-5 the percentage of 2,4- and 2,5-xylenol initially are similar and from about 2.5% disproportionation, 2,5-xylenol predominates over 2,4-xylenol, whereas on USHY the percentage of 2,4- is clearly higher than that of 2,5-xylenol up to about 15% disproportionation. Since 2,4-xylenol should be kinetically favoured due to the stronger *para*-directing effect of

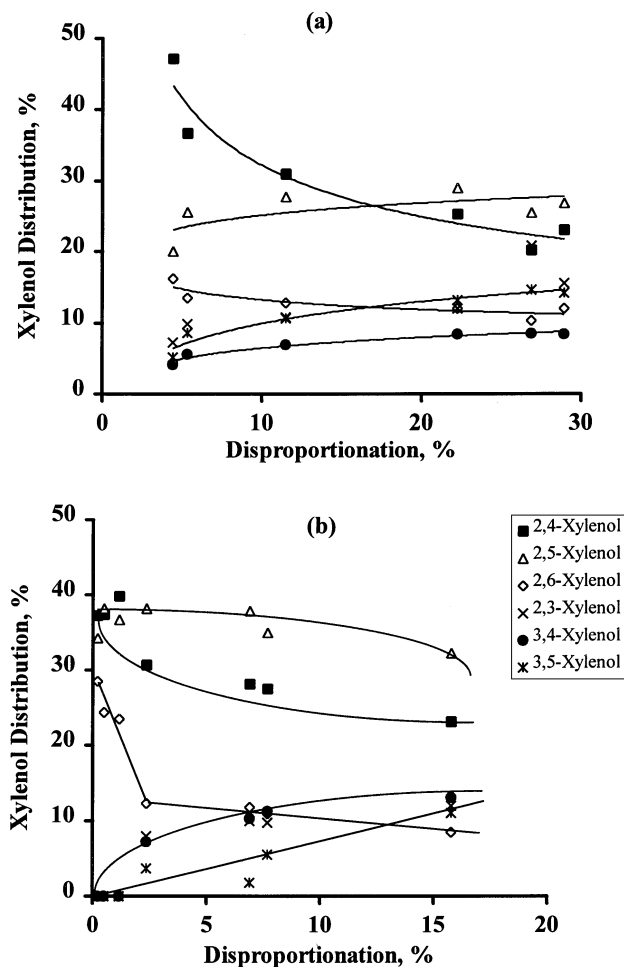


FIG. 6. Xylenols distribution from *o*-cresol disproportionation (a) on USHY and (b) on HZSM-5.

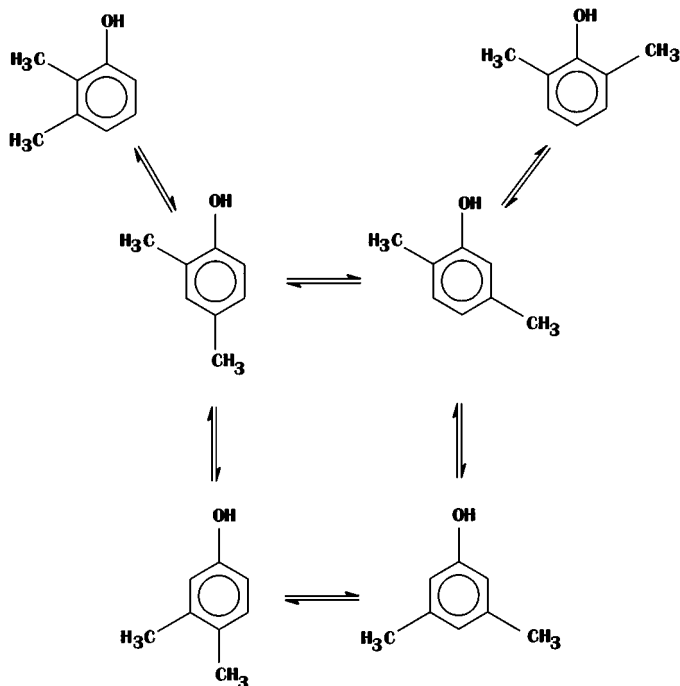


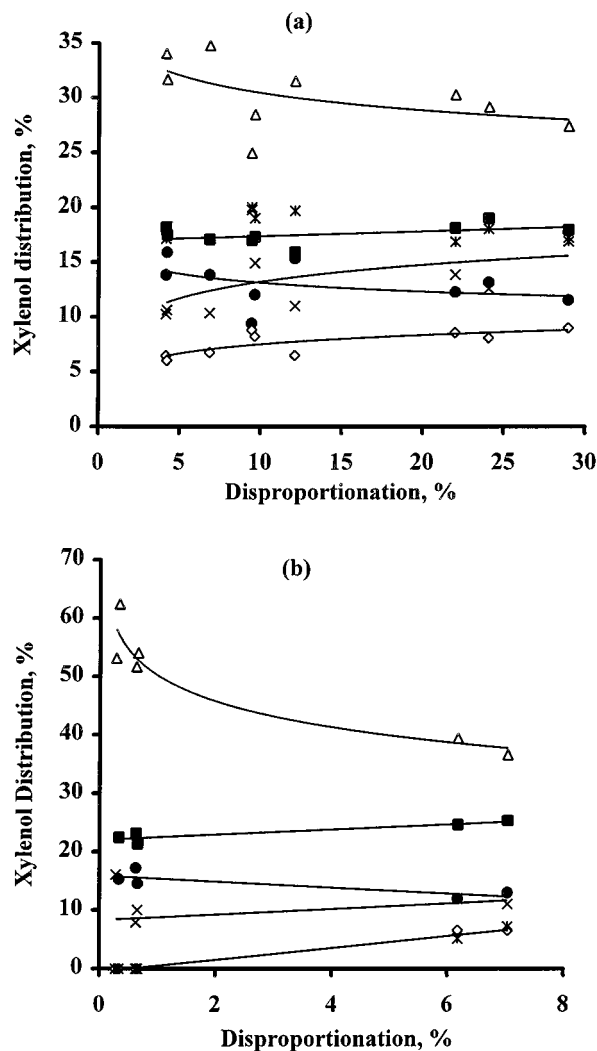
FIG. 7. Xylenols interconversion scheme.

the -OH group in relation to that of the -CH₃ group, the fact that it is not so in the case of HZSM-5 has to be associated with a diffusion disguised kinetics, which implies that 2,5-xyleneol diffuses faster than 2,4-xyleneol. In the case of secondary-formed xylenols, 2,3- and 3,4-xyleneols can only be directly formed from 2,4-xyleneol, and their formation involves a -CH₃ shift to a position which is *ortho* to a methyl group and *meta* to the -OH group, so they are formed in approximately the same proportion on HZSM-5. The third secondary xyleneol is the 3,5-xyleneol, which can only be formed directly from the 2,5-xyleneol by a methyl shift to the unfavored *meta* position to both -OH and -CH₃ groups, and whose formation is further limited, due to its size and shape, inside the HZSM-5 channels. Therefore, the secondary-formed xylenols follow the sequence 2,3- \approx 3,4- > 3,5-xyleneol, as shown in Fig. 6b; in contrast, on USHY the order is 2,3- > 3,5- > 3,4-xyleneol (see Fig. 6a).

For *m*-cresol, at low conversions the observed isomers coincide with the expected ones; among the primary-formed xylenols 2,5-xyleneol is the most favored on both zeolites because it is formed by alkylation in a position, which is *ortho* to the -OH group and *para* to the -CH₃ group, for *meta*-cresol disproportionation. The other two primary xylenols, although favored because one (3,4-xyleneol) is *ortho* to the methyl group and *para* to the -OH group and the other (2,3-xyleneol) is *ortho* to both, face sterical hindrance, particularly the latter one. Consequently, their sequence is 2,5-xyleneol > 3,4-xyleneol \geq 2,3-xyleneol (see Fig. 8). The secondary-formed xylenols on HZSM-5 follow 2,4- >

2,6- \approx 3,5-xyleneol (see Fig. 8b), while on USHY they follow 2,4- \approx 3,5- > 2,6-xyleneol (see Fig. 8a). The rapid xyleneol isomerization explains why the 2,4-xyleneol, a secondary-formed product, is found in greater proportion than the primary-formed 3,4- and 2,3-xyleneol.

For *p*-cresol, the main product of disproportionation expected is 2,4-xyleneol, which should be formed by intermolecular transfer of a methyl group to a position *ortho* to the -OH. On USHY (see Fig. 9a) both 2,4- and 3,4-xyleneol decrease with conversion, while the rest (secondary-formed xylenols) increase. In contrast, on HZSM-5 at low conversions the only xylenols observed were the 2,4- and 2,5-xyleneol isomer, as shown in Fig. 9b. Therefore, 2,4-xyleneol rapidly isomerizes to 2,5-xyleneol, which desorbs very rapidly as soon as it is formed; this result once again confirms our previous statement in the sense that 2,5-xyleneol should diffuse faster than 2,4-xyleneol within the

FIG. 8. Xylenols distribution from *m*-cresol disproportionation. Legend as in Fig. 6.

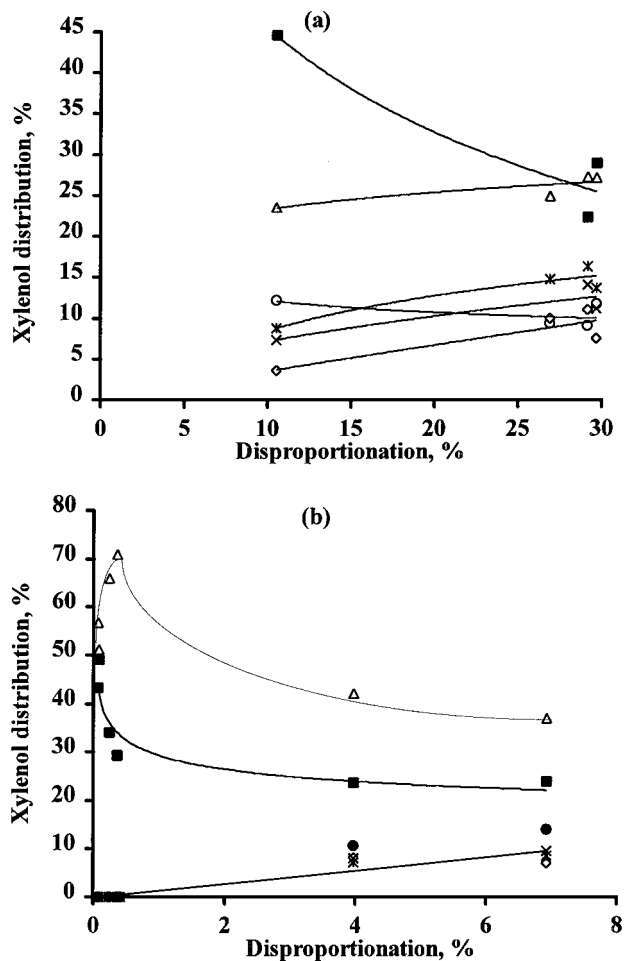


FIG. 9. Xylenols distribution from *p*-cresol disproportionation. Legend as in Fig. 6.

HZSM-5 channel system. As conversion increases, the rest of the xylenols are formed in approximately the same proportion, while 2,5-xylene decreases.

CONCLUSIONS

The transformation of cresols has been studied over USHY and compared with HZSM-5, with different pore size, structure, and different acidity; their catalytic stability, activity, and selectivity were compared at 380°C and a reactant partial pressure of 0.1 bar. Under the experimental conditions investigated HZSM-5 is more catalytically stable, though less active than USHY, in terms of moles converted per gram of catalyst; however, in terms of molecules converted per acid site, the HZSM-5 is more active than USHY, except for *o*-cresol. The cresol TON for USHY are pretty similar, whereas on HZSM-5 the cresol reactivities follow the sequence *p*->*m*->*o*-cresol. The cresols react over the zeolites mainly through two parallel reactions, isomerization and disproportionation, whose rela-

tive importance depends on the catalysts characteristics (pore structure and acidity), on the reacting cresol itself, and on the reaction conditions (temperature, total pressure, reactant partial pressure, etc.). The USHY selectivity toward the monomolecular isomerization reaction is by far lower than that of HZSM-5, due to its size/shape selectivity. On both USHY and HZSM-5 catalysts, the *o*-cresol shows higher disproportionation selectivity than the other two cresol isomers, this disproportionation occurring via diphenylmethane intermediates. On USHY the *I/D* selectivities are similar for all cresols at medium- and high-conversion levels, but for low conversions *m*-cresol shows higher isomerization selectivity than *o*-cresol. Moreover, even on a large pore zeolite like USHY, the cresol isomerization selectivity is limited by product desorption. The cresol isomer composition at high conversions on USHY is 44% *o*-cresol, 42% *m*-cresol, and 14% *p*-cresol. Once formed, xylenols undergo a rapid isomerization.

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