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Transformation of meta- and ortho-cresol over HY

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The transformation of *m*- and *o*-cresol has been investigated on a series of HY zeolites with Si/Al ratio in the range of 4.5 to 55, at 380°C and atmospheric pressure. It was found that the zeolite activity increased but stability decreased with N_{Al} for both *m*- and *o*-cresol. For $\mathrm{Si/Al} = 4.5$ the zeolite activity was similar for both reactants, but as Si/Al ratio increased, *o*-cresol became relatively more reactive than *m*-cresol, and for all Si/Al ratios the catalysts were more stable in the *m*-cresol transformation. Both *m*- and *o*-cresol were converted mainly through two parallel reactions – isomerization and disproportionation. The disproportionation reaction was predominant, and more important in the case of *o*-cresol. The isomerization/disproportionation selectivity increased for *m*-cresol and decreased for *o*-cresol with N_{Al}. Catalyst deactivation favoured disproportionation in the case of *o*-cresol and isomerization in the case of *m*-cresol, except for *o*-cresol conversion on HY(4.5), where both reactions were equally affected. Isomerization selectivity for *m*-cresol (p/o) was found to be higher than the equilibrium value and to increase with catalyst deactivation; while for *o*-cresol, the isomerization ratio (m/p) did not change with time on stream for HY(4.5) and HY(16.6) and decreased for HY(55). Disproportionation selectivity ($\mathrm{ph}/\sum \mathrm{x}$) was equal to unity independently of Si/Al ratio or catalyst deactivation.

Keywords: cresols, transformation, isomerization, disproportionation, zeolites HY

1. Introduction

The industrial consumption of phenolic compounds such as cresols has increased in recent years [1,2], since they are used as feedstocks or intermediates in the production of antiseptics, drugs, insecticides, dyes, phenolic resins, antioxidant and polymers. Patents describing cresol isomerization on HZSM-5 have appeared [3,4]. However, very few works on cresol transformation by zeolites have been reported in the literature [5,6]. The effect of zeolite Si/Al ratio on cresol transformation has been scarcely studied [5,6]. In contrast, xylenes reactions over different catalysts – HZSM-5 [7,8], offretite [9,10], HY [11–13] – have been studied in detail. However, xylene isomerization and disproportionation mechanisms are still being debated in the literature. Contradictory reports have appeared on the effect of Si/Al ratio on selectivity. Some authors [14] have proposed that the xylenes isomerization reaction is monomolecular, while disproportionation is a bimolecular reaction, that requires adjacent acid sites, and that therefore the isomerization/disproportionation ratio (I/D) is determined by the acid site density. Corma et al. [15] and Guisnet et al. [16] have shown that there is some contribution of a bimolecular mechanism to the formation of xylene isomerization products over wide-pore zeolites. On the other hand, it has been proposed that the disproportionation reaction requires stronger acid sites than isomerization. Therefore, the I/D ratio cannot be solely controlled by site density, at least in the case of wide-pore zeolites, like faujasites. The object of the present work is to contribute to clarifying the effect of Si/Al ratio on the reaction selectivity in the case of cresol transformation over HY zeolite.

2. Experimental

The transformation of meta- and ortho-cresol (3- and 2-methylphenol) has been studied over three HY zeolite samples with framework Si/Al ratios of 4.5 (LZY82, Union Carbide), 16.6 (Conteka) and 55 (Degussa). The catalyst chemical composition is given in table 1. The catalysts were activated in nitrogen flow at 500°C overnight.

The reactions were carried out at 380°C and atmospheric pressure in fixed-bed reactors. A toluene–cresol solution (cresol/toluene molar ratio $= 9$) was fed by a positive displacement pump, at different flow rates (0.25–9 ml/h), diluted in nitrogen, $((\mathrm{N}_2 + \mathrm{T})/\mathrm{cresol} = 9$. Product samples were collected at 10 min

Table 1
Chemical compositions of the catalysts

Zeolite (Si/Al)	N_{Al}	$(\mathrm{Si/Al})f$	Formula
HY(4.5)	34.9	4.5	$\mathrm{Na_{0.8}H_{34.9}Al_{34.9}Si_{157.1}O_{384}}$
HY(16.6)	10.9	16.6	$\mathrm{Na_{0.3}H_{10.6}Al_{10.9}Si_{181.1}O_{384}}$
HY(55)	3.4	55	$\mathrm{Na_{0.2}H_{3.2}Al_{3.4}Si_{188.6}O_{384}}$

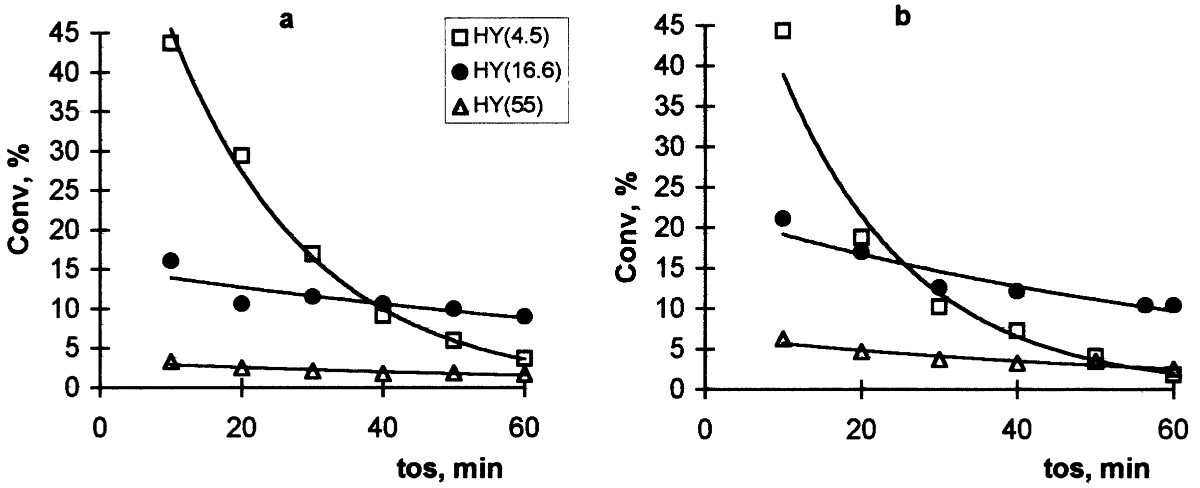

Figure 1. (a) *m*-cresol and (b) *o*-cresol conversion on HY(4.5), HY(16.6) and HY(55).

intervals up to 1 h and analysed 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 $= 0.2\,\mu$m)).

3. Results and discussion

3.1. Activity and stability

HY activity in cresol transformation increased with increasing number of framework aluminium atoms, N_{Al}, as expected for a reaction catalysed by Brønsted acid sites (see figures 1a and 1b). The observed products were cresol isomers, phenol and xylenols (dimethylphenols). Two reactions can account for the products observed, the isomerization and disproportionation reactions. These catalysts were rapidly deactivated as illustrated in figure 1. Deactivation was more important, as expected, for HY(4.5). The remaining global ($X(60)/X(10)$) ($X(t)$ represents the conversion at time on stream, t), isomerization ($I(60)/I(10)$), and disproportionation ($D(60)/D(10)$) activities, after 1 h of reaction with respect to 10 min, are reported in tables 2 and 3, for *m*- and *o*-cresol transformation, respectively. In table 3 is also given the coke percentage (weight%) after 1 h of reaction for *o*-cresol transformation. Contrary to the expected, the HY(16.6) stability was slightly higher than that for HY(55), though the carbon percentage (%C) at 60 min reaction was higher on HY(16.6) than on HY(55), as reported in table 3. The catalyst stability observed was then as follows: HY(16.6) > HY(55) > HY(4.5).

3.2. Selectivity

3.2.1. Isomerization/disproportionation (I/D) selectivity

It was observed that catalyst deactivation had a greater effect on disproportionation than on isomerization for *m*-cresol conversion probably due to the fact that the former reaction requires stronger acid sites than the latter one. This is in agreement with what has been observed by other authors for xylene transformation over HY [11–13]. Consequently, the I/D ratio increased with time on stream for all catalysts, as illustrated in figure 2a. This increase was more pronounced for HY(4.5), because of its rapid loss of strong acid sites. On the other hand, for HY(55) and HY(16.6) the $I/D < 1$, even for a deactivated catalyst, while for HY(4.5) $I/D > 1$. This difference in selectivities can be a consequence of the fact that HY(4.5) has fewer number of strong acid sites than the other two zeolites. Obviously, the deactivation process does not only affect the number of strong acid sites, but also reduces the acid site density and in some cases it may cause pore blockage [17], leading to diffusional limitations. For *o*-cresol, the I/D ratio was less than one for all catalysts as illustrated in figure 2b, indicating that the disproportionation reaction was favoured independently of Si/Al ratio. However, at simi-

Table 2
Stability for meta-cresol transformation on HY

Catalyst	$X(60)/X(10)$	$I(60)/I(10)$	$D(60)/D(10)$
HY(4.5)	0.085	0.13	0.039
HY(16.6)	0.56	0.70	0.50
HY(55)	0.52	0.58	0.50

Table 3
Stability and coke percentage for ortho-cresol transformation on HY

Catalyst	$X(60)/X(10)$	$I(60)/I(10)$	$D(60)/D(10)$	Coke (wt%)
HY(4.5)	0.042	0.039	0.035	12.45
HY(16.6)	0.49	0.38	0.59	9.79
HY(55)	0.40	0.13	0.42	7.31

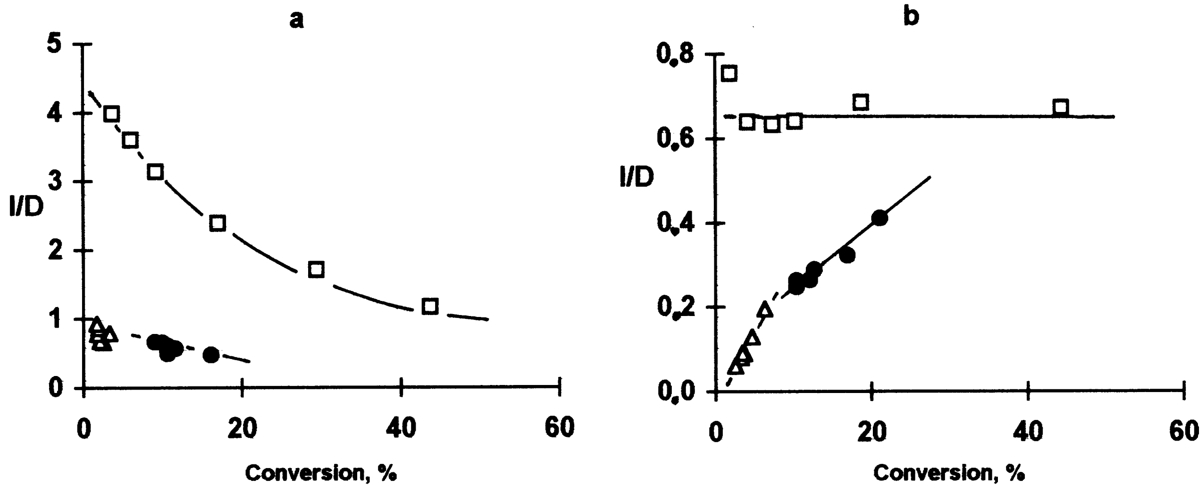

Figure 2. (a) *m*-cresol and (b) *o*-cresol *I/D* selectivity on HY(4.5), HY(16.6) and HY(55). Legends as in figure 1.

lar conversion levels *I/D* was found higher for HY(4.5) zeolite than for HY(16.6) and HY(55), respectively. The effect of deactivation on *I/D* ratio depended on the Si/Al ratio (see figure 2b). While for a Si/Al = 4.5, this ratio was constant in the whole range of conversions, for a Si/Al = 16.6 the *I/D* ratio showed a moderate increase and for a Si/Al = 55 the increase was pronounced. In the case of *o*-cresol transformation on HY(4.5), the catalyst deactivation seemed to affect both isomerization and disproportionation to the same extent, but as the Si/Al ratio increases the catalyst deactivation affects the isomerization reaction to a larger extent than the disproportionation. This means, contrary to the expected, that the decrease in the number or strength of acid sites, brought about by the catalyst deactivation, mainly affects the "unimolecular" isomerization reaction. This can be explained, if it is postulated that the xylenols, once formed, may participate in bimolecular transalkylation reactions, as represented in figure 3, with an *o*-cresol molecule to give a cresol isomer and another xylenol molecule that may require stronger acid sites. The data on HY(55), the low-activity catalyst and kinetically most

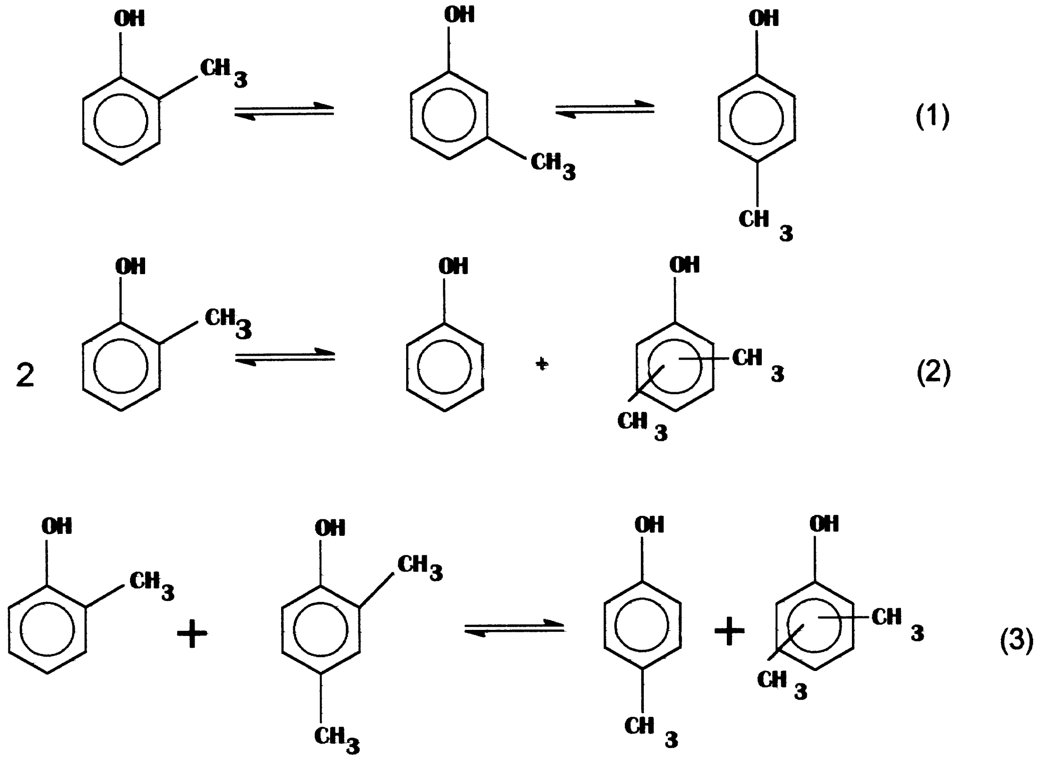

Figure 3. Scheme of reactions.

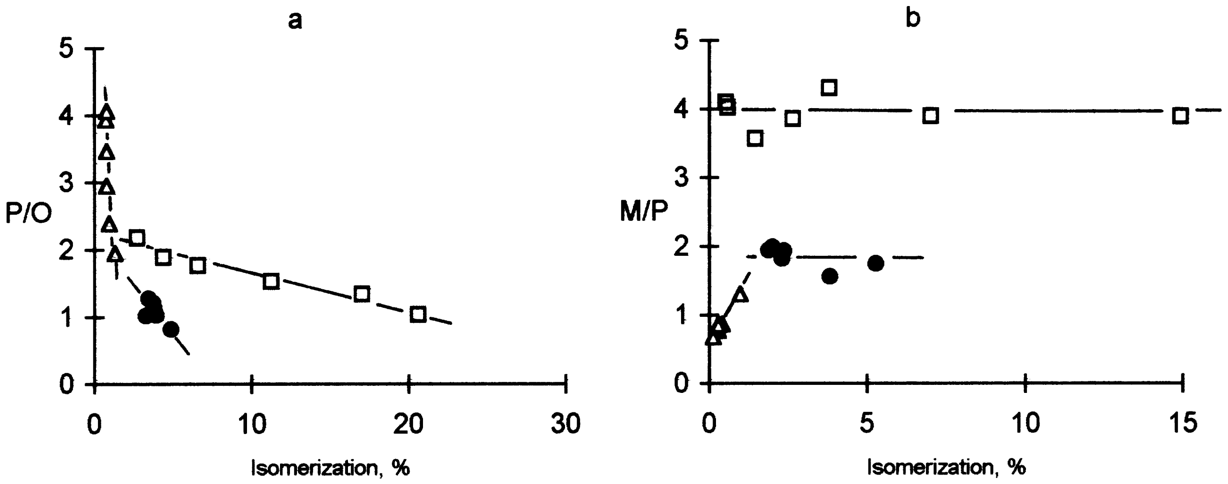

Figure 4. (a) *m*-cresol and (b) *o*-cresol isomerization selectivity on HY(4.5), HY(16.6) and HY(55). Legends as in figure 1.

significant, may indicate a consecutive reaction scheme, with disproportionation being the primary reaction, while the I/D ratio on HY(4.5), the most active catalyst and the most coked, seemed to be affected by diffusion disguise of the true reaction path. Thus, an important amount of cresol isomerization products on HY zeolites may come via bimolecular reactions, at least in the case of *o*-cresol transformation; however, for *m*-cresol one cannot rule out this possibility. Furthermore, this reaction needs stronger acid sites than does the disproportionation between reactant molecules. The predominance of the disproportionation reaction in cresol transformation on HY zeolites could be due to the strong electric field inside the pores and to the space available nearby the acid sites that allows the bulky transition state to be formed. A transition state selectivity must be playing a role in determining the easiness of *o*-cresol disproportionation with respect to *m*-cresol. As seen above, the catalyst deactivation had opposite effects on I/D ratio for *m*- and *o*-cresol. In the former, deactivation favoured isomerization reactions, in contrast in the latter it favoured the disproportionation reaction (except for Si/Al = 4.5). This can be attributed to a greater contribution of a bimolecular mechanism to the formation of cresol isomers from *o*-cresol than from *m*-cresol.

3.2.2. Isomerization selectivity

For *m*-cresol isomerization, the p/o ratio increased with time on stream, i.e. with catalyst deactivation, as shown in figure 4a. This para-selectivity may be associated to a relatively higher electronic density on the para- than on the ortho-position, which makes the 1,2-methyl shift to the para-position relativily easier, and therefore the isomerization to the ortho-position requires slightly stronger acid sites. However, this increase was greater for HY(55). In all cases the p/o ratio was higher than the equilibrium value 0.15.

In the case of *o*-cresol, the Si/Al ratio had an effect

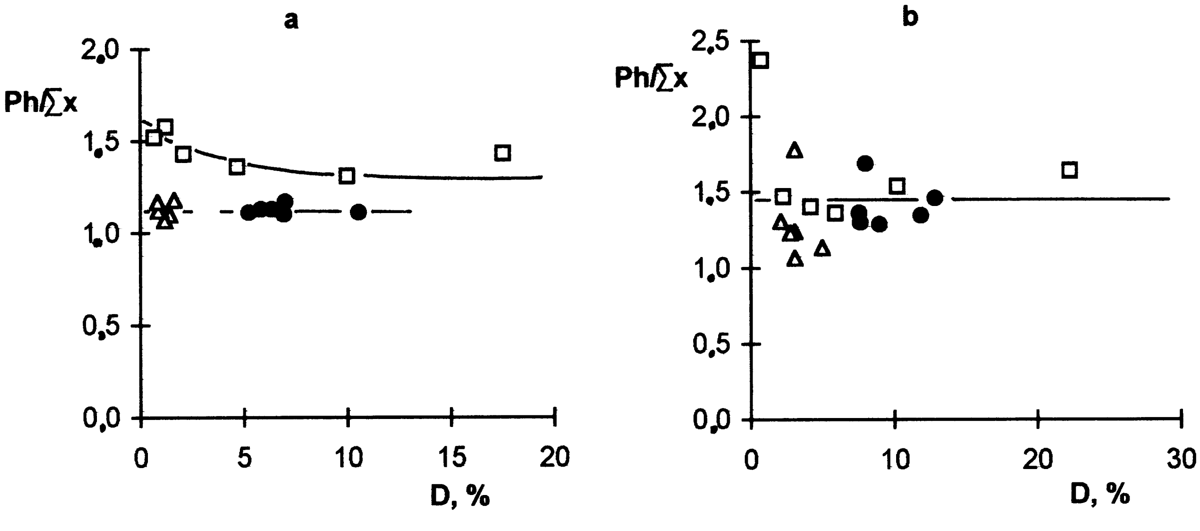

Figure 5. Disproportionation (ph/∑x ratio) selectivity. Legends as in figure 1.

on the isomerization selectivity. Figure 4b shows that for HY(4.5), the m/p ratio was constant at about 4, while for HY(16.6) its value resulted close to 1.75, and in contrast for HY(55) this ratio decreased with deactivation. At increasing Si/Al, the m/p ratio was observed to decrease; this cannot be explained on the basis of consecutive unimolecular isomerization, nor can it explain the apparent direct formation of *p*-cresol from *o*-cresol. Therefore, some *p*-cresol must be formed via transalkylation, as proposed in reaction 3, figure 3.

3.2.3. Phenol/$\sum$xylenols (ph/$\sum$x) ratio

As expected from the disproportionation reaction stoichiometry, the ph/$\sum$x ratio resulted to be approximately equal to 1 for all catalysts and was not greatly affected by catalyst deactivation (see figure 5). However, for HY(4.5) its value was slightly higher than for the other two, probably as a result of some side reactions like dealkylation or even to a minor diffusional limitation due to the important coke formation on this zeolite. The fact that the ph/$\sum$x ratio was close to one and not affected by deactivation means, on the one hand, that there was not another source of phenol, i.e., that there was little, if any, dealkylation, and, on the other hand, that the disproportionation reaction products were not subjected to diffusional limitations; i.e., either the coke formed did not block the pores, causing diffusional limitations, and only affecting the number and the mean strength of the remaining acid sites, or the disproportionation occurred on the external surface free of diffusional limitations.

3.2.4. Xylenol distribution

For *m*-cresol, the obtained results showed a clear influence of both Si/Al ratio and of catalyst deactivation on xylenol distribution. Figure 6 represents the percentage of each xylenol as a function of disproportionation for all catalysts. As can be seen, the primary products: 2,5-, 3,4- and 2,3-xylenol were favoured at higher Si/Al ratio, while the formation of secondary products 3,5-, 2,4- and 2,6-xylenol was enhanced on lower Si/Al ratio zeolites. This is a consequence of the increasing probability of secondary reactions on decreasing Si/Al ratio.

From *o*-cresol, the primary disproportionation products expected are 2,6-, 2,3-, 2,5- and 2,4-xylenol, while 3,4- and 3,5-xylenol should be formed in secondary reactions via isomerization of the primary formed xylenols. In fact this was observed, as shown in figure 7, which represents the xylenols distribution as function of disproportionation percentage (D, %) for the three zeolites tested. The xylenols distribution obtained was affected by the Si/Al ratio. Thus, the apparent primary products 2,5- and 2,3- were favoured on HY(4.5), as were the secondary 3,4- and 3,5-; while 2,6- seemed not to be particularly affected by the ratio, except that for HY(16.6) its value seems slightly higher than for HY(4.5) and HY(55); in contrast, 2,4- was enhanced by higher Si/Al ratio. As one can see on HY(4.5) the apparent primary products are 2,5-, 2,4- and 2,6-xylenol, while 2,3-xylenol was expected also to be a primary product; its evolution suggests that it may come from the xylenol isomerization, either by a unimolecular process or by a bimolecular transalkylation with a reactant molecule of *o*-cresol. As the catalyst deactivates, the percentage of the primary formed xylenol either keeps constant or increases, as a consequence of the decrease in the percentage of the xylenols formed in secondary reactions. On HY(16.6), 2,5- and 2,6-xylenol percentages do not change much – they are practically constant – while 2,4-xylenol increases with time on stream. On HY(55), 2,4-xylenol increases, 2,5- decreases and 2,6-xylenol keeps constant. 2,6-xylenol as seen is approximately constant and around 15% for HY(55) and HY(4.5); for HY(16.6) its percentage is slightly higher, around 20%, but constant; therefore its percentage in the xylenol fraction is clearly not affected by the catalyst deactivation. The finding that 2,6-xylenol percentage is independent of deactivation may be explained as either its formation takes place on the external surface or if it does occur in the interior of the channels, the coke deposition does not lead to diffusional limitations, affecting only the number and the mean strength of the acid sites. If this is so, then the 2,6-xylenol formation neither is affected by the change in the number nor by the mean strength of sites remaining available for reaction. 2,4-xylenol increases with deactivation for all catalysts and its increase changed with Si/Al ratio, being greater as the N_{Al} decreases. 2,5-xylenol was fairly constant on HY(16.6) and close to 17%; while for HY(4.5) it was close to 30%, and for HY(55) it decreased to nil, therefore, contrary to what was observed with 2,4-xylenol, 2,5-xylenol formation was favoured by higher N_{Al}. Also it is interesting to note, that for HY(4.5) the percentage of coke was the highest, however it did not affect 2,5-xylenol; on the contrary, the coke percentage on HY(55) was less but it did have a tremendous effect on 2,5-xylenol, which may be caused by the need of a minimum number of acid sites with a certain strength.

4. Conclusions

The Si/Al ratio of HY zeolites has an important effect on the activity, stability and selectivity in the transformation of *m*- and *o*-cresol. The HY activity increases with increasing N_{Al} per unit cell, but the stability decreases. The cresols are transformed on HY giving isomerization and disproportionation products, that may be formed via uni- or bimolecular mechanisms. The I/D, m/p and p/o selectivities seem to be related to acid site strength and so is the xylenols distribution. The HY zeolites, in cresol transformation, have higher disproportio-

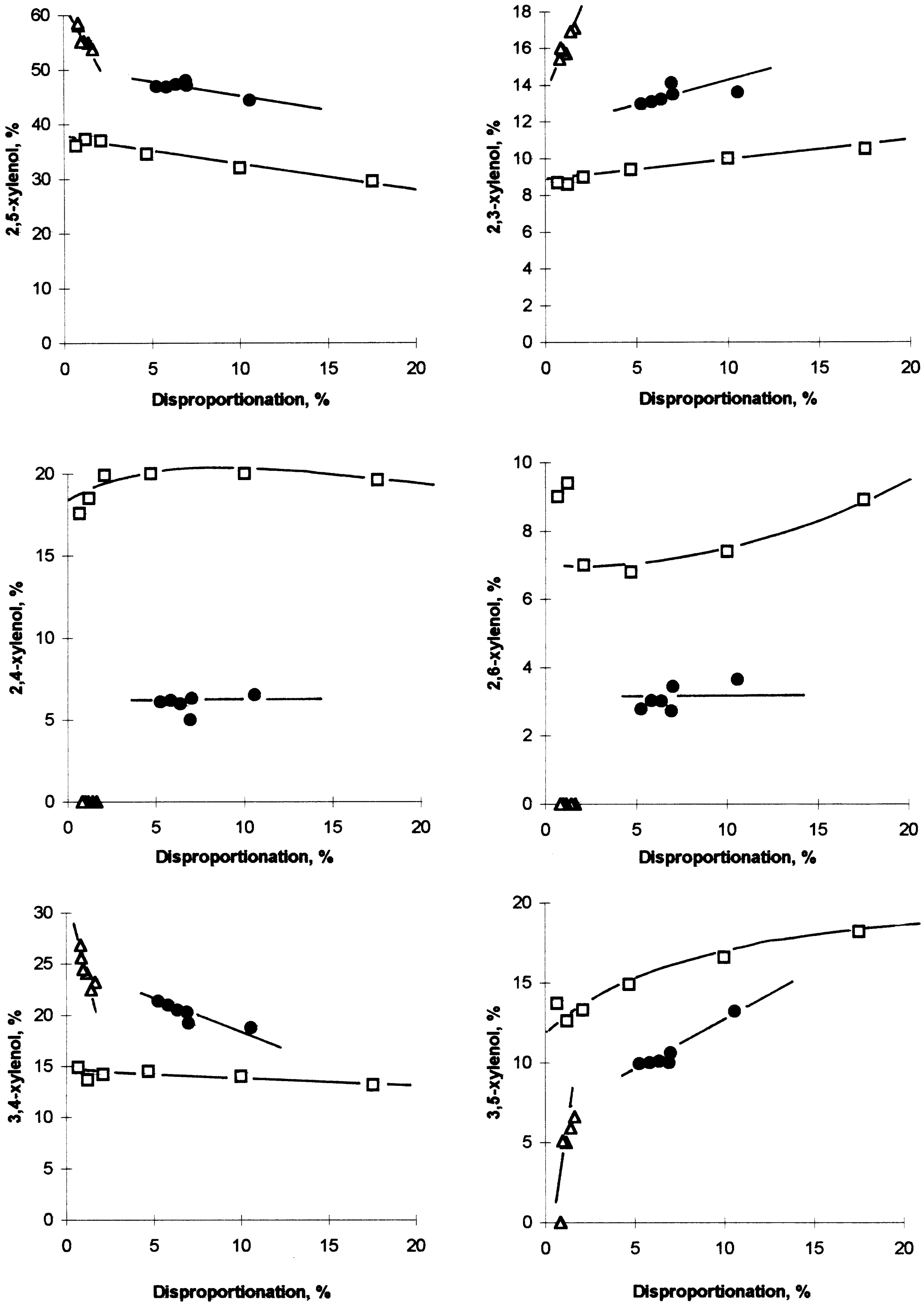

Figure 6. Xylenol distribution for *m*-cresol disproportionation. Legends as in figure 1.

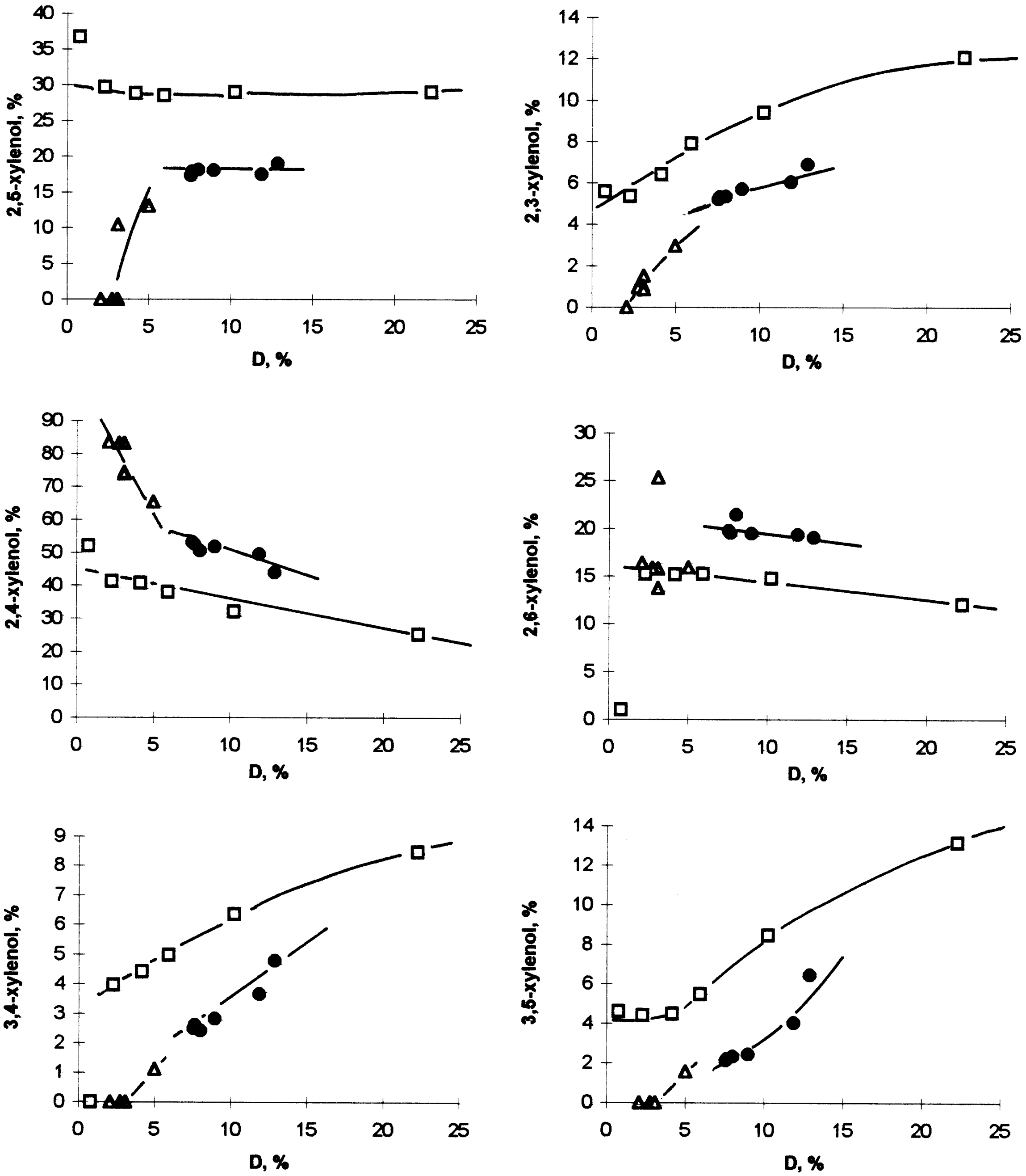

Figure 7. Xylenol distribution for *o*-cresol disproportionation. Legends as in figure 1.

nation than isomerization activity. In the case of *o*-cresol this selectivity is even more pronounced than for *m*-cresol transformation. *o*-cresol can be isomerised to *p*-cresol directly through a bimolecular transalkylation reaction.

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