A comparison of the ethylation of ethylbenzene and toluene on acid, cationic and silylated ZSM-5 zeolites

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The Fe, Mn and Al ion-exchanged H-ZSM-5 zeolites exhibit a slightly lower para-selectivity in the alkylation of ethylbenzene with ethylene compared to that of the parent H-ZSM-5, in contrast to the alkylation of toluene with ethylene, where an increase in para-selectivity was observed. It is concluded that the presence of metal cations changes the rates of competitive reactions (alkylation or disproportionation compared to isomerization) but do not substantially contribute to the steric hindrances, which should be more pronounced with bulkier diethylbenzenes. A deposition of silica on the zeolite surface, which evidently increases the hindrance in the diffusional transport of the isomer leads to an increase in the zeolite para-selectivity in the alkylation reactions of both ethylbenzene and toluene.

Keywords: Ethylation of ethylbenzene; ethylation of toluene; small crystals of H-ZSM-5; surface silylation; zeolite para-selectivity; metal ion-exchanged zeolites

1. Introduction

Although the para-selectivity of several medium pore zeolites such as ZSM-5, -22, -23, -48 and -50 and of their modified forms has been extensively studied, this property has still not been thoroughly elucidated [1–8]. It is evident that diffusional effects contribute significantly to the over-equilibrium concentrations of para-isomers, achieved in synthesis of xylenes, ethyltoluenes and diethylbenzenes [2,9,10]. However, together with transport phenomena, competition between the alkylation and isomerization reaction or disproportionation and isomerization reaction can play an important role in the resulting para-selectivity of the zeolite.

We reported that the presence of Fe, Mn and Al cations located in zeolite channels increased the zeolite para-selectivity in the toluene alkylation with ethylene; moreover, the metal cations exhibiting redox properties contributed to an easier coke removal during the zeolite catalyst regeneration process [8].

This paper deals with the effect of the presence of metal cations in the inner zeolite channels and of silylation of the zeolite surface on the activity and para-selectivity of H-ZSM-5 zeolites in ethylbenzene disproportionation and alkylation with ethylene. Attention is also paid to the deactivation of the zeolites during reaction and to comparison of the para-selectivity of modified zeolites in reactions of ethylbenzene and toluene.

2. Experimental

The H-ZSM-5 zeolites (prepared from their Na forms by an ion-exchange with 0.5 M HNO_3) with Si/Al ratios from 22.5 to 600 and crystal size in the range from 0.5 to 2.5 μm were supplied by the Research Institute for Oil and Hydrocarbon Gases, Czechoslovakia. The ion-exchange of Fe^{3+}, Mn^{2+} and Al^{3+} ions into H-ZSM-5 (abbreviated as MeH-ZSM-5) was carried out at 330 K using 0.5 M $FeCl_3$, $Al(NO_3)_3$ and $MnCl_2$ at conditions (pH = 3) during which precipitation of hydroxo-oxidic species was suppressed. The surface silylated zeolites were prepared by suspending the H-ZSM-5 zeolite in *n*-hexane containing a calculated amount of tetraethyl orthosilicate resulting in addition of 1 and 10 wt% of Si to the original zeolite (abbreviated as Si_1H-ZSM-5 and Si_{10}H-ZSM-5, respectively); for details see ref. [8]. The presence of some amount of extra-crystal amorphous silica in silylated zeolites cannot be excluded.

The characteristics of the zeolites, which have already been published (cf. ref. [8]), are given in table 1. The zeolite void volume was checked on the basis of the argon sorption capacity and the number of strong acid sites was estimated

Table 1
Characteristics of zeolites

Zeolite	Si/Al	OH groups [a] (mmol/g)	Sorption capacity (mmol Ar/g)	Coke [b] (wt%)
H-ZSM-5	22.5	0.69	4.87	0.4
FeH-ZSM-5	22.5	0.64	4.77	3.7
AlH-ZSM-5	22.5	0.65	4.76	1.9
MnH-ZSM-5	22.5	0.62	4.77	3.5
Si_1H-ZSM-5	22.5 [c]	0.62 [d]	4.92 [d]	–
Si_{10}H-ZSM-5	22.5 [c]	0.60 [d]	4.48 [d]	–
H-ZSM-5A	45.0	0.30	5.80	–
H-ZSM-5B	600	0.02 [e]	5.90	–

[a] Estimated by means of temperature-programmed desorption of ammonia.

[b] Amount of coke related to the zeolite weight after ethylbenzene alkylation with ethylene for TOS of 175 min.

[c] Si/Al concerns the parent zeolite; 1 wt% or 10 wt% of Si was added during silylation process.

[d] Note, per gram of silylated zeolite.

[e] Calculated value from Si/Al ratio.

from the high-temperature peak of the temperature-programmed desorption of ammonia (for details see refs. [8,11]).

The ethylbenzene reactions were performed in a vapour phase, continuous glass down-flow microreactor at atmospheric pressure. Nitrogen used as a carrier gas was saturated with ethylbenzene at 355 K to a level of 18.5 vol%. The ethylene feed was fixed at an ethylbenzene to ethylene molar ratio of 3.8. A catalyst (0.4 g) in granulated form (0.3–0.7 mm) was located in a microreactor bed (inner diameter, 10 mm) and pretreated in an oxygen stream at 770 K for 1 h. Then the sample was cooled to a preset reaction temperature (520, 570 or 620 K). The reaction products were analyzed by means of an on-line gas chromatograph (Hewlett-Packard 5890 series II) using the Supelcowax 10 capillary column (30 m length, inner diameter 0.2 mm, phase thickness 0.2 μm). The reaction course was followed for 175 min. The ethylbenzene conversion and para-diethylbenzene (*p*-DEB) selectivity at a reaction time-on-stream (TOS) equal to 15 min were used for comparison of variously modified zeolites. The amount of coke formed in the course of the ethylbenzene alkylation with ethylene (after TOS of 175 min) was evaluated by its combustion in an air stream and by determination of the amount of CO, CO_2 and H_2O released (table 1).

3. Results and discussion

The alkylation of ethylbenzene with ethylene was accompanied by ethylbenzene disproportionation in the temperature range 570–670 K, in contrast to the alkylation of toluene with ethylene, where the toluene disproportionation pro-

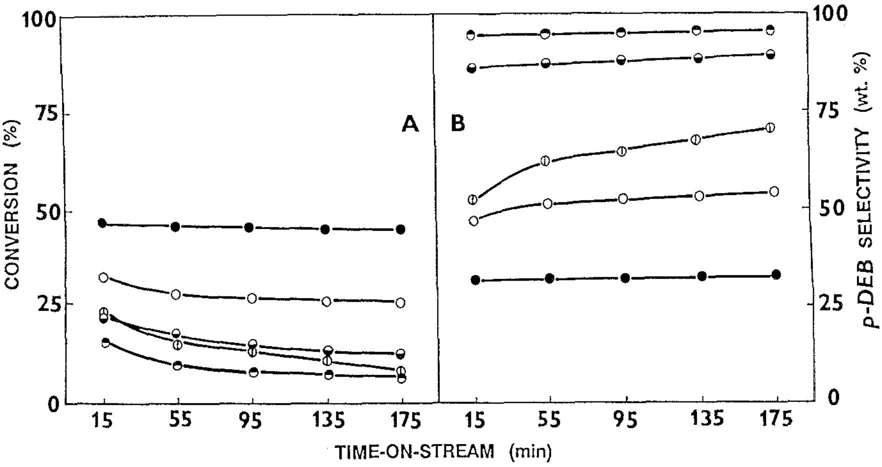

Fig. 1. Time-on-stream dependence of ethylbenzene conversion (A) and para-diethylbenzene selectivity (B) in ethylbenzene alkylation with ethylene at 570 K and WHSV 10 h^{-1}. (○) H-ZSM-5 (570 K), (●) H-ZSM-5 (620 K), (⦶) FeH-ZSM-5, (◒) Si_1H-ZSM-5, (◓) Si_{10}H-ZSM-5.

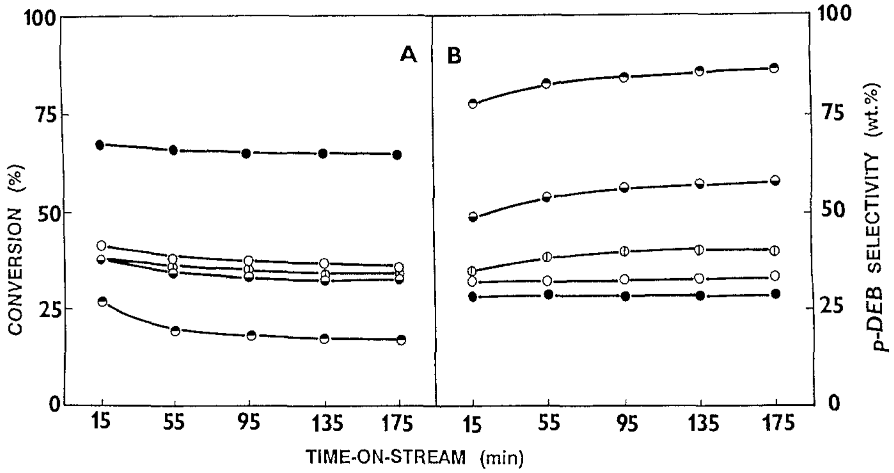

Fig. 2. Time-on-stream dependence of ethylbenzene conversion (A) and para-diethylbenzene selectivity (B) in ethylbenzene disproportionation at 570 K and WHSV 10 h^{-1}. (○) H-ZSM-5 (570 K), (●) H-ZSM-5 (620 K), (⌽) FeH-ZSM-5, (◒) Si_1H-ZSM-5, (⊖) Si_{10}H-ZSM-5.

ceeded to a very low extent (cf. ref. [8]). At a temperature of 520 K, when the disproportionation of ethylbenzene was suppressed, the H-ZSM-5 zeolite exhibited conversion of ethylbenzene, in alkylation of ethylbenzene with ethylene, of 12.0% with selectivity to *p*-DEB of 61.7 wt%. However, a rapid deactivation of the zeolite in TOS took place, making it difficult to use these conditions for comparison of different zeolites. This deactivation was probably caused by a "low-temperature coke", consisting mainly of ethylene oligomers [12] and/or adsorbed reaction products; according to Kaeding [2], the desorption of DEBs at 520 K is very slow, causing rapid deactivation of the zeolite catalyst.

On the other hand, when a decrease in ethylbenzene conversion in TOS was very low at a temperature of 620 K, the *p*-DEB selectivity approached the thermodynamic equilibrium value (fig. 1, conversion 46.7%, *p*-DEB selectivity 31.8 wt%); moreover, the conversion in ethylbenzene disproportionation reached a high level (fig. 2). Therefore, a higher temperature region is also not suitable for comparison of the conversion-selectivity of various zeolites. For this reason, the catalytic activity and para-diethylbenzene selectivity of parent and modified H-ZSM-5 zeolite were investigated at 570 K (figs. 1, 2, tables 2, 3).

With the increasing Si/Al ratio of the unmodified H-ZSM-5 zeolite and, thus, with a decreasing number of strongly acid OH groups, the conversion of ethylbenzene decreased and, on the other hand, the selectivity to *p*-DEB increased for both reactions (fig. 3). For the disproportionation reaction, the *p*-DEB selectivity approached the equilibrium composition under the given condition. The ethylbenzene to ethylene ratio used for the alkylation reaction was 3.8. As can be seen from table 2 and fig. 1, the conversion of ethylbenzene for H-ZSM-5 (Si/Al 22.5) was substantially higher than the theoretical conver-

Table 2
Alkylation of ethylbenzene with ethylene on H-ZSM-5 and modified zeolites ($T = 570$ K, WHSV $= 10\ h^{-1}$, ethylbenzene to ethylene molar ratio 3.8); thermodynamic equilibrium composition of diethylbenzene isomers at 570 K: para – 29.8%; meta – 52.7%; ortho – 17.5%

Time (min)	H-ZSM-5		FeH-ZSM-5		Si_{10}H-ZSM-5	
	15	174	15	175	15	175
conversion (%)	32.9	26.2	23.8	8.1	15.4	5.6
selectivity (wt%)						
C_1–C_4[a]	9.6	12.9	1.0	2.0	3.0	1.3
benzene	4.5	2.9	6.1	2.4	4.1	2.1
toluene	2.0	1.6	2.5	4.2	2.8	4.0
p-xylene	0.7	0.5	0.8	–	1.0	–
isopropylbenzene	–	–	0.9	–	–	–
p-ethyltoluene	1.8	1.3	1.8	1.9	3.0	1.8
m-ethyltoluene	1.3	0.7	1.1	–	–	–
p-diethylbenzene	35.6	41.6	42.5	60.0	76.8	85.6
m-diethylbenzene	39.1	34.4	38.3	24.7	4.7	3.5
o-diethylbenzene	0.8	0.6	0.6	–	–	–
C_{10+}	4.6	3.5	4.4	4.8	4.6	1.7
diethylbenzene selectivity (%)						
para	47.2	54.4	52.2	70.8	94.2	96.1
meta	51.7	44.8	47.0	29.2	5.8	3.9
ortho	1.1	0.8	0.8	–	–	–

[a] Without ethylene.

sion, which can be attained for the alkylation reaction (26.3%). Thus, the ethylbenzene disproportionation leading to the diethylbenzenes and benzene proceeds simultaneously and was not completely suppressed by the ethylene presence. There is a substantial difference in the temperatures at which the conversion of toluene and ethylbenzene attain the comparable level in disproportionation reactions (of about 200 K higher for toluene than for ethylbenzene). It supports the assumption that the disproportionation reactions of both toluene and ethylbenzene on H-ZSM-5 zeolite proceed via a dealkylation–alkylation mechanism and not via biphenyl methane (ethane) transition complexes, which are too bulky (especially for diethylbenzene molecules) to be accommodated in the H-ZSM-5 zeolite channel intersections. The complete product composition for both reactions on H-ZSM-5, FeH-ZSM-5 and Si_{10}H-ZSM-5 are given in tables 2 and 3. For comparison of different zeolites only the conversion and para-selectivity data are used.

The ion exchange of Al, Fe and Mn ions resulted in a decrease in the number of strong acid OH groups and a slight decrease in the zeolite void volume reflected in argon sorption capacity (table 1). However, preliminary results [13], concerning the rate of uptake of *p*-ethyltoluene on H- and MeH-forms of

Table 3
Ethylbenzene disproportionation on H-ZSM-5 and modified zeolites ($T = 570$ K, WHSV = 10 h^{-1})

Time (min)	H-ZSM-5		FeH-ZSM-5		Si$_{10}$H-ZSM-5	
	15	175	15	175	15	175
conversion (%)	40.9	36.4	28.0	23.4	26.8	17.5
selectivity (wt%)						
C_1–C_4	1.8	1.2	0.8	0.6	3.4	1.4
benzene	40.1	38.9	38.9	38.0	41.3	38.4
toluene	2.3	2.3	2.0	2.2	4.7	3.4
p-xylene	0.2	0.3	–	–	1.0	0.5
m-xylene	0.3	0.3	–	–	0.2	–
p-ethyltoluene	0.7	0.5	0.4	0.4	2.3	1.7
m-ethyltoluene	1.2	0.8	0.7	0.5	0.9	0.7
p-diethylbenzene	16.6	18.1	19.9	23.1	35.4	45.5
m-diethylbenzene	35.0	36.4	36.0	34.8	10.0	7.5
o-diethylbenzene	1.1	0.5	0.4	–	–	–
C_{10+}	0.7	0.7	0.9	0.4	0.8	0.9
ethyltoluene selectivity (%)						
para	31.6	33.0	35.3	39.8	77.9	85.8
meta	66.4	66.1	63.9	60.2	22.1	14.2
ortho	2.0	0.9	0.8	–	–	–

ZSM-5 zeolites, do not indicate a significant decrease in this rate for metal ion exchanged zeolites. When the zeolite surface was deposited by SiO_2 (Si$_1$H- and Si$_{10}$H-ZSM-5) a decrease in the number of strong acid OH groups corresponded

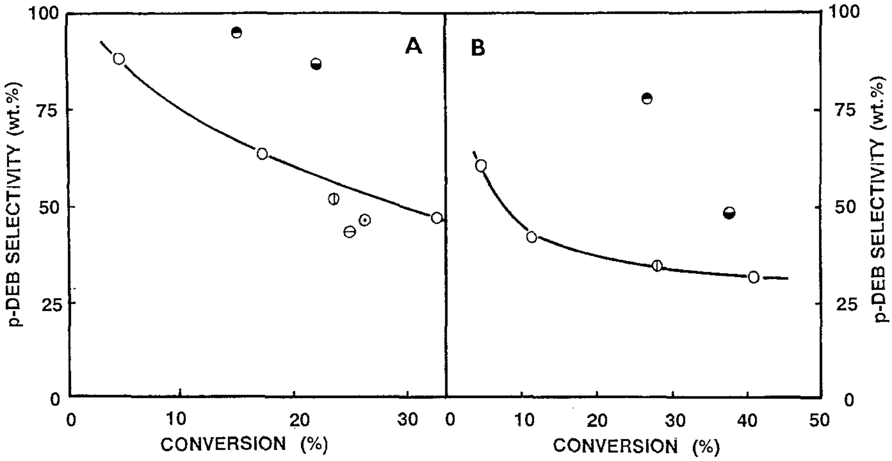

Fig. 3. The relationship para-selectivity versus ethylbenzene conversion for alkylation of ethylbenzene with ethylene (A) and disproportionation of ethylbenzene (B) at 570 K and WHSV 10 h^{-1}. (○) All H-ZSM-5, (⦶) FeH-ZSM-5, (⊙) MnH-ZSM-5, (⊖) AlH-ZSM-5, (◒) Si$_1$H-ZSM-5, (●) Si$_{10}$H-ZSM-5.

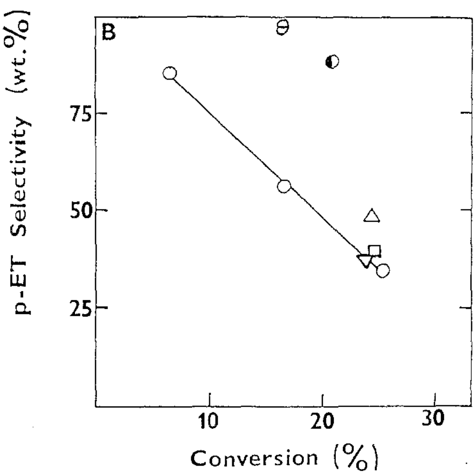

Fig. 4. The relationship para-selectivity versus toluene conversion for alkylation of toluene with ethylene at 620 K and WHSV 10 h^{-1}. (○) All H-ZSM-5, (△) FeH-ZSM-5, (□) MnH-ZSM-5, (▽) AlH-ZSM-5, (◐) Si_1H-ZSM-5, (⊖) Si_{10}H-ZSM-5.

roughly to 10–15% of the total amount of these OH groups and of sorption capacity. In fact, when these values are related to the zeolite content in the silylated material, they do not decrease. It is in agreement with the assumption of selective surface interaction of silylating agents with the zeolite OH groups eliminating the surface strong acid sites and decreasing only the free diameter of the channel windows.

The ethylbenzene conversion in the alkylation reaction with MeH-ZSM-5 zeolites was lower compared with that of the parent H-ZSM-5, in agreement with the lower number of strongly acid hydroxyl groups (cf. table 1). However, the increase in the para-selectivity was only apparent (cf. figs. 1 and 3). Taking into consideration the conversion versus para-selectivity relationships (fig. 3), the para-selectivity of MeH-ZSM-5 in the alkylation of ethylbenzene with ethylene was in fact comparable or slightly lower than that for H-ZSM-5. It has already been reported that the location of Mn^{2+}, Fe^{3+} and Al^{3+} metal cations at the cationic positions in the zeolite channel intersections has a positive effect on the resulting zeolite para-selectivity in toluene alkylation with ethylene (fig. 4) [8]. This effect was attributed to the higher para-selectivity in the first alkylation step and/or larger differences in the diffusivities of individual ethyltoluene isomers in metal ion-exchanged zeolites [6,8]. However, in the case of alkylation of ethylbenzene with ethylene, the presence of metal cations has a surprisingly slightly negative effect on the resulting para-selectivity. As the DEB molecules are larger than those of ethyltoluenes and, therefore, the differences in diffusivities of individual isomers should be expected to be higher, this finding can be explained only by the enhancement of the isomerization reaction, compared to the alkylation reaction by Fe, Mn and Al cations located in the H-ZSM-5 zeolite.

A substantially higher para-selectivity was observed for silylated SiH-ZSM-5 zeolites (Si_{10}H-ZSM-5 > Si_1H-ZSM-5), than would correspond to the conversion versus para-selectivity relationships (figs. 1 and 3). A similar high para-selectivity in the alkylation of ethylbenzene with ethylene was also achieved using large crystals of ZSM-5 zeolites and/or after zeolite modification with phosphorus, boron and magnesium compounds [2]. Note that lower conversions of ethylbenzene were found with the silylated SiH-ZSM-5 zeolites than would correspond to the number of strongly acid OH groups. It can be inferred that some part of the strongly acid OH groups of silylated ZSM-5 zeolites is accessible only for small ammonia molecules and not for reactants and/or that slower diffusion of the reactants decreases the overall rate of the alkylation reaction. The para-selectivity increase for silylated H-ZSM-5 can be caused by a decrease in the free diameter of zeolite entering channel windows resulting in lower diffusivities of individual isomers [13], even though the annihilation of active sites on the external surface of the zeolite crystals can also contribute to the higher para-selectivity. However, the estimation of the number of strong acid OH groups in silylated zeolites indicates that the number of surface sites is considerably lower than that inside the channels (when related to the weight of the zeolite).

The deactivation of zeolites in TOS is enhanced both by the presence of metal cations and by the deposition of silica on the zeolite surface compared to the parent H-ZSM-5 (figs. 1, 2, tables 1–3). The decrease in conversion is higher in all cases for the alkylation of ethylbenzene with ethylene than for ethylbenzene disproportionation. This is connected with a higher concentration of ethylene in the alkylation reaction, which can undergo oligomerization and subsequent aromatization reactions, leading to bulkier products which cannot easily diffuse out of the zeolite channels. Moreover, it should be noted that with TOS in the alkylation reaction, considerable changes in the product distribution were found, in contrast to ethylbenzene disproportionation (cf. tables 2 and 3). An increase in the zeolite coking (cf. tables 1 and 2) with MeH-ZSM-5 compared to parent H-ZSM-5 can be explained by an electron-acceptor function of the isolated cations which results in enhancement of the oligomerization and aromatization reactions [14]. On the other hand, an increased coking found with surface silylated zeolites is a result of narrowing or even plugging of the zeolite channel mouths and hindrances in transport of the products from the inner void volume of the zeolite crystal.

4. Conclusions

(i) Depending on the reaction conditions, small crystals of H-ZSM-5 zeolites can exhibit para-shape-selective properties in ethylbenzene disproportionation and alkylation with ethylene resulting in a higher concentration of para-diethylbenzene than that corresponding to thermodynamic equilibrium.

(ii) The deposition of silica on the outer crystal surface, causing an increased contribution to diffusional effects, leads to a considerably higher zeolite para-selectivity in the alkylation of both the toluene and ethylbenzene. Moreover, simultaneous annihilation of surface strong acid sites by silylation can also contribute to some extent to the zeolite para-selectivity. On the other hand, Fe, Al and Mn cations in the H-ZSM-5 zeolite channel intersections decrease the zeolite para-selectivity in the ethylbenzene alkylation in contrast to the toluene alkylation. Thus, the metal cations have a rather different effect on the competition of the alkylation versus isomerization reactions for ethylbenzene and toluene. As the diethylbenzene molecule is larger than ethyltoluene, it follows that the changes in the zeolite para-selectivity caused by the Fe, Mn and Al cations do not result from steric hindrances and diffusional effects.

(iii) Fe^{3+}, Al^{3+} and Mn^{2+} cations located at cationic sites in the zeolite channel intersections as well as silica supported on the zeolite crystal surface contribute to faster zeolite coking.

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