ZEOLITE SILYLATION FOR THE ENHANCEMENT OF *para*-SELECTIVITY IN TOLUENE ALKYLATION WITH ETHYLENE

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Received October 31, 1996
Accepted November 28, 1996

Dedicated to Dr Karel Mach on the occasion of his 60th birthday.

The effect of zeolite silylation using tetraethyl and tetramethyl orthosilicate on the enhancement of *para*-selectivity and of yields of *p*-ethyltoluene in toluene alkylation with ethylene was investigated for different Si loadings. It was found that zeolite silylation caused a substantial increase in the selectivity and yield of *p*-ethyltoluene. Data on changes in sorption capacity, in the number of surface and inner strong acid OH groups, in the rate of uptake of *p*-ethyltoluene together with the catalytic activity of zeolite and its deactivation indicate that the silylation is restricted to surface and subsurface zeolite layers. The enhancement of *para*-selectivity and yield of *p*-ethyltoluene are controlled predominantly by changes in geometry of pore openings and thus by transport rates of ethyltoluenes.

Key words: Zeolite silylation; Toluene alkylation; Ethylene; Tetraethyl orthosilicate; Transport of products; *para*-Shape-selectivity.

p-Dialkylaromatic hydrocarbons, namely *p*-xylene, *p*-ethyltoluene, *p*-diethylbenzene and *p*-propyl- and *p*-isopropyltoluenes, represent important starting materials for production of various polymers, pesticides, fungicides, flavours *etc.*[1–3]. When the alkylation of toluene or ethylbenzene is carried out on amorphous alumosilicates an enrichment in *ortho*- and *para*-isomers in gaseous products, due to the higher reactivity of the respective positions relative to thermodynamic equilibrium is observed[1,3]. On the other hand, when the alkylation takes place in the pores of zeolites of MFI structure (ZSM-5) possessing medium pores of the size 5.1 × 5.5 and 5.4 × 5.6 Å in three-dimensional structure, high selectivity with respect to *para*-isomers is achieved[1,4,5].

It was found, by ^{13}C MAS NMR study that in alkylation of toluene with methanol to xylenes the alkylation step inside the ZSM-5 zeolite pores results, in preferential formation of *p*- and *o*-xylenes[6], similarly as on an open reaction space of the amorphous alumo-

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silicates. Moreover, "*in situ*" FTIR studies of the alkylation of toluene with methanol to xylenes in ZSM-5 zeolite indicated an enrichment of *ortho*- and particularly *meta*-isomers in the adsorbed phase, along with a considerable enrichment of the *para*-isomer among the gaseous products[7,8]. It implies that after the alkylation step of the reaction there proceeds a positional isomerization of xylenes, followed by a fast release of the *para*-isomer from the zeolite inner volume into the gaseous phase. It means that the resulting product composition is predominantly affected by differences in the rate of diffusion of individual dialkylbenzene isomers. It was found that the ratio of diffusivities of individual xylene isomers in the temperature range of 373–473 K is about *p*- : *o*- : *m*- = 1 000 : 10 : 1 (ref.[7]).

Although *para*-selectivity can be improved by reaction conditions, its main enhancement can be achieved by tailoring the crystal structure of zeolite catalysts. Employment of large crystals of ZSM-5 or of zeolites with narrow pore diameter (as ZSM-22 with pore sizes – 4.5 × 5.5 Å, ZSM-23 – 4.5 × 5.6 Å, ZSM-48 – 5.3 × 5.6 Å) yields higher selectivities to *para*-isomers[9,10]. However, these zeolites are less resistant against deactivation by coke, formed *via* subsequent alkylation, isomerization, transalkylation and hydrogen transfer reactions leading to polyaromatic hydrocarbons. These side reactions result from a longer contact time in the narrow or long pores particularly of bulkier molecules, which are released with difficulty into the gaseous phase.

To improve zeolite *para*-selectivity, it was also suggested to block the acid sites located on the surface of zeolite crystals, on which the alkylation reaction (as well as isomerization of *para*-isomers leaving the inner zeolite pores) can proceed without any space limitations. Poisoning of the surface acid sites by bulky strong bases (*e.g.* by quinoline) which cannot enter zeolite pores was employed and resulted in an increase of *para*-selectivity[11,12]. However, organic bases are easily desorbed into a reactant stream during the reaction time-on-stream, and thus this procedure is not applicable in a large scale. Another approach which can block the surface acid sites is their silylation by bulky organosilicates, which cannot enter the zeolite pores and thus block the inner acid sites[1,13,14]. There are several papers concerned with application of this procedure either in liquid[15] or gaseous phase (so called chemical vapour deposition, CVD)[16–18], resulting in an enhancement of zeolite *para*-selectivity.

In this paper the liquid phase silylation of the crystal surface of ZSM-5 zeolites by different organosilicates is described in detail, and its impact on the number of acid sites on the zeolite surface and in its pores, pore volume modification, uptake rate of *p*-ethyltoluene (*p*-ET), and on the function of zeolite catalyst in alkylation of toluene with ethylene to ethyltoluenes is reported.

EXPERIMENTAL

The ZSM-5 zeolite with Si/Al ratio 22.5 was supplied by the Research Institute for Oil and Hydrocarbon Gases, Bratislava. The acid form of this zeolite was prepared by ion exchange of its sodium form with 0.5 M nitric acid. The silylation procedure was following: ZSM-5 zeolite was calcined at 770 K in a dry oxygen stream for 2 h. Then the sample was cooled to ambient temperature in a dry nitrogen, a solvent (usually hexane or toluene) was added followed by a known amount of silylation agent. Tetramethyl- (TMOS) – ZSM-5/B1-B4 and tetraethyl- (TEOS) – ZSM-5/A1-A7 orthosilicates (Fluka) were used (Tables I–IV). All these steps were carried out with exclusion of air moisture. The resultant mixture was stirred for 4 h at ambient temperature and than for 7 h at 390 K. The mother liquid was then evaporated in vacuum, and the silylated sample was calcined in an oxygen stream at 770 K for 8 h. X-Ray diffraction and IR spectra of zeolite skeletal vibrations indicated that silylation does not change the structure of ZSM-5 zeolite.

The zeolite inner void volume was estimated from the sorption capacity for argon measured in a static apparatus at 13.33 kPa of argon pressure at 80 K on samples pretreated at 720 K in a vacuum of 10^{-4} kPa for 16 h. The number of strong acid sites was calculated from the high temperature peak of the temperature-programmed desorption (20 K/min) of ammonia (TPDA) performed in a helium stream (5 ml/s) on zeolites (0.3 g) pretreated at 770 K for 1 h. The zeolites were equilibrated in an ammonia stream (10% ammonia in nitrogen) at 373 K for 0.5 h and then in a helium stream at the same temperature for 0.5 h.

The number of strong acid bridging Si–OH–Al groups was also determined by FTIR spectra of hydroxyl region (Nicolet, Magna 550). Parent H-ZSM-5 zeolite exhibited 0.69 mmol/g of strong acid groups estimated from the high-temperature peak of TPD of ammonia, and the intensity of IR band at 3 612 cm^{-1} corresponding to structural bridging Si–OH–Al groups. The number of strong Lewis sites estimated from pyridine adsorption (IR band at 1 445 cm^{-1}) was lower than 5% relative to the number of bridging OH groups. In addition, the zeolite contained also some terminal Si–OH groups (IR band at 3 745 cm^{-1}), roughly 10% of the bridging OH groups, of low acidity, which do not take part in acid-catalyzed reactions. All the zeolite characteristics including toluene conversions given in Tables I–IV are related to the weight of parent ZSM-5 zeolite and not to the weight of the catalyst.

TABLE I
Characteristics of ZSM-5 zeolite (Si/Al = 22.5) modified with TEOS

Zeolite	Si added wt.%	Si–OH–Al groups[a] mmol g^{-1}	TIPB conversion[b] %	Sorption capacity (mmol g^{-1}) for		*p*-ET rel. rate
				argon[c]	*p*-ET[c]	
H-ZSM-5	0	0.69	82.5	5.26	0.63	0.27
H-ZSM-5/A1	0.1	0.57	61.5	4.77	0.58	0.20
H-ZSM-5/A2	0.5	0.67	[d]	5.05	0.62	0.22
H-ZSM-5/A3	1.0	0.63	[d]	4.91	0.61	0.23
H-ZSM-5/A4	1.5	0.66	[d]	5.08	0.61	0.23
H-ZSM-5/A5	2.0	0.63	55.3	4.84	0.59	0.22
H-ZSM-5/A6	4.3	0.65	20.0	4.85	0.62	0.20
H-ZSM-5/A7	8.4	0.74	<1.0	4.46	0.60	0.13

[a] The number of OH groups determined from TPD of ammonia; [b] after 15 min of T-O-S; [c] sorption capacities for argon and *p*-ET are related to 1 g of parent zeolite (not to the weight of silylated zeolite); [d] not determined.

The sorption of *p*-ethyltoluene (Fluka) over parent and silylated samples was performed to follow the effect of silylation on transport rates of *p*-ethyltoluene. Zeolite sample was evacuated in vacuum of 1.3 . 10^{-6} kPa for 3 h at 700 K. The adsorption of *p*-ethyltoluene was carried out at 373 K at *p*-ethyltoluene partial pressure of 85 Pa. The adsorption was followed at least 6 h to reach the equilibrium amount of adsorbed *p*-ethyltoluene (*p*-ET). Time intervals of 1–5 min were used to estimate the initial rate of the adsorption (Tables I and III). Within this period no isomerization of *p*-ET to *meta*-isomer occurred. The uptake rate was measured gravimetrically and calculated according to the following equation

$$r_{5-1} = (Q_5 - Q_1)/Q_\infty \quad . \tag{1}$$

Q_1 and Q_5 denote the uptakes at given time (in min), Q_∞ the uptake after equilibrium.

A relative number of external surface strong acid sites of ZSM-5 crystals was checked by the decomposition of 1,3,5-triisopropylbenzene (TIPB, Fluka), the kinetic diameter of which is too large to penetrate inside the ZSM-5 channel system. TIPB was charged into a stream of dry nitrogen via syringe pump at the concentration of 1.0 vol.%, at temperature of 570 K and WHSV of 1.0 h^{-1}. The first analysis of the reaction products was made after 15 min of time-on-stream (T-O-S), similarly as in the case of alkylation and reaction.

The toluene alkylation with ethylene was carried out in a vapour phase continuous down-flow microreactor at atmospheric pressure. Nitrogen, used as a carrier gas, was saturated with toluene at 334 K to perform kinetic runs at toluene concentration of 18.5 vol.% and WHSV of 10.0 h^{-1}. The stream of nitrogen and toluene was mixed with a stream of ethylene to reach the toluene to ethylene molar ratio of 3.8. A catalyst (weight of 0.1–0.4 g) in a granulated form (0.3–0.7 mm) was located in a microreactor (i.d. 10 mm) and pretreated in an oxygen stream at 770 K for 1 h. The reaction

TABLE II

Toluene conversion and *p*-ET selectivity in toluene alkylation with ethylene in dependence on T-O-S for H-ZSM-5 (Si/Al = 22.5) modified with TEOS

Zeolite	Si added wt.%	Toluene conversion[a] %	*p*-ET selectivity[a] vol.%	*p*-ET yield[a] %	Toluene conversion[b] %	*p*-ET selectivity[b] vol.%	*p*-ET yield[b] %
H-ZSM-5	0	96.6	33.4	32.3	93.4	34.0	31.7
H-ZSM-5/A1	0.1	74.3	52.6	39.1	74.5	56.3	41.9
H-ZSM-5/A2	0.5	77.9	45.6	35.5	78.2	52.9	41.4
H-ZSM-5/A3	1.0	74.5	74.8	55.7	73.3	83.4	61.1
H-ZSM-5/A4	1.5	74.9	82.3	61.6	65.9	86.8	57.2
H-ZSM-5/A5	2.0	72.4	93.7	67.8	54.4	95.8	52.1
H-ZSM-5/A6	4.3	75.4	94.8	71.5	43.8	96.0	42.0
H-ZSM-5/A7	8.4	59.8	95.3	56.7	38.4	97.1	37.3

[a] After 15 min of T-O-S; [b] after 135 min of T-O-S.

products were analyzed by an "on-line" gas chromatograph (Hewlett–Packard, 5890 Series II), equipped with mass spectrometric (5971A) and flame ionization detectors, using Supelcowax 10 (Supelco) high resolution capillary column (30 m length, i.d. 0.2 mm, phase thickness 0.2 μm).

RESULTS AND DISCUSSIONS

The silylation, depending on the amount and type of silylating agent (TEOS, TMOS), was accompanied by changes in the overall number of strong acid sites (inner and on external surface), in sorption capacity of *p*-ET, an inner zeolite volume (reflected in the sorption capacity of argon) and in relative number of strong acid sites located on the surface of silylated zeolite crystals with respect to the parent zeolite, as estimated by the degree of dealkylation of 1,3,5-triisopropyltoluene (see Tables I and III).

It was found that with increasing amount of TEOS added to the zeolite, the number of strong acid OH groups as well as the sorption capacity of *p*-ET decreases by 5–7 rel.%. The same trend was also observed for adsorbed argon. Similarly to increasing amount of Si in the zeolite, the sorption capacity and relative rate of *p*-ET uptake decrease by *ca* 10–20%. Interestingly, all these values are lower compared to the parent zeolite, but do not differ substantially in increasing Si loading (with the exception of sample ZSM-5/A7). The exception in the series is the zeolite silylated with the Si amount equal to 0.1 wt.%, which shows greater decrease in values for all the zeolite characteristics studied.

Similar results have been obtained also for the series of silylated zeolites when TMOS was employed. However, the higher decrease in all the above characteristics was observed for zeolite with added 0.1 and 1.0 wt.% Si, while at the higher Si loadings (2.0 and 4.3 wt.% Si), comparable values of the corresponding characteristics of the zeolite silylated with TEOS (at loadings higher than 1.0 wt.% Si) were found.

TABLE III
Characteristics of ZSM-5 zeolite (Si/Al = 22.5) modified with TMOS

Zeolite	Si added wt.%	Si–OH–Al groups mmol g^{-1}	TIPB conversion[a] %	Sorption capacity (mmol g^{-1}) for		*p*-ET rel. rate
				argon[c]	*p*-ET	
H-ZSM-5	0	0.69	82.5	5.26	0.63	0.27
H-ZSM-5/B1	0.1	0.52	[b]	4.78	0.53	0.19
H-ZSM-5/B2	1.0	0.59	[b]	4.79	0.61	0.17
H-ZSM-5/B3	2.0	0.66	81.6	5.17	0.63	0.22
H-ZSM-5/B4	4.3	0.58	60.7	5.05	0.64	0.22

[a] After 15 min of T-O-S; [b] not determined.

Surprisingly, the conversion of triisopropylbenzene (TIPB) indicated that not all strong acid bridging OH groups on the surface of the zeolite crystals were consumed by silylation up to such high loadings as 4.3 wt.% of Si. This implies that hydrolysis of TEOS or TMOS does not take place preferentially on the strong acid OH groups, but also low acid (Si–OH) sites are involved. Moreover, formation of some SiO_2 phase outside the zeolite crystals can be expected.

Toluene conversion and selectivity to *p*-ethyltoluene (together with *p*-ET yield) in toluene alkylation with ethylene at times-on-stream of 15 and 135 min (to estimate zeolite deactivation) are compared for parent samples and the zeolites silylated by TEOS and TMOS in Tables II and IV, respectively. It is seen that there is a dramatic decrease in conversion (compared to the parent zeolite) for 0.1 wt.% of added Si for TEOS and 0.1–1.0 wt.% of added Si for TMOS. Then, depending on Si loading, the conversion slightly increases (0.5 wt.% Si for TEOS and 2.0 wt.% for TMOS), being followed by further conversion decrease with increasing Si loading, particularly at the highest value of Si loading (H-ZSM-5/A7). For all the zeolites investigated, some deactivation in T-O-S took place which was caused by zeolite coking. It was much higher compared to the parent zeolite for Si loadings above 1.5 wt.% Si (TEOS), but for the zeolites silylated by TMOS the deactivation was nearly not observed. However, some coking did take place, as the selectivity and yield were higher at T-O-S for 135 min in comparison with those for 15 min.

The *p*-ET yields together with conversions within T-O-S for 135 min indicate that for the zeolites silylated by TEOS up to *ca* 1.5 wt.% Si no dramatic deactivation occurs, and the yields of *p*-ET are substantially increased. It is necessary to note that with Si loadings higher than 2.0 wt.%, a comparison of selectivity (yield) for the silylated zeolites is not straightforward as the selectivity reaches values between 95 and 100%, and

TABLE IV

Toluene conversion and *p*-ET selectivity in toluene alkylation with ethylene depending on T-O-S for H-ZSM-5 (Si/Al = 22.5) modified with TMOS

Zeolite	Si added wt.%	Toluene conversion[a] %	*p*-ET selectivity[a] vol.%	*p*-ET yield[a] %	Toluene conversion[b] %	*p*-ET selectivity[b] vol.%	*p*-ET yield[b] %
H-ZSM-5	0	96.6	33.4	32.3	93.4	34.0	31.8
H-ZSM-5/B1	0.1	70.3	55.0	38.7	71.6	61.9	44.3
H-ZSM-5/B2	1.0	64.2	80.1	51.4	64.9	85.2	55.3
H-ZSM-5/B3	2.0	79.7	54.9	43.8	80.1	65.7	52.6
H-ZSM-5/B4	4.3	75.0	76.6	57.5	74.6	85.2	63.6

[a] After 15 min of T-O-S; [b] after 135 min of T-O-S.

therefore it is no more sensitive to further changes of this property. For the zeolites silylated by TMOS also a decrease in conversion compared to the parent zeolite was observed. However, the increase in the *p*-ET yield at the same amount of added Si was lower compared to the zeolites silylated by TEOS.

It follows that silylation of H-ZSM-5 zeolite results in a substantial increase in the selectivity and the yield of *p*-ET. Its yields increase with Si loadings. Simultaneously, the decrease in conversion and particularly the increase in the zeolite deactivation by coke at higher Si loadings indicate changes in the number of strong acid sites and/or considerable changes in pore openings.

For the zeolites silylated by TEOS and TMOS (0.1 and 0.1–1.0 wt.% Si, respectively) a decrease in overall number of strong acid sites is unexpectedly high and, by contrast, a decrease in the number of surface acid centres is very low (*cf*. Tables I and III). The number of surface sites for crystal sizes around 1 μm was estimated not to be greater than 5% of the total number of strong acid Si–OH–Al groups. This indicates that silylation inside pores has to take place. As the kinetic diameter of TEOS and TMOS molecules (*ca* 8.9 Å) is greater compared to channel openings (5.1 × 5.5 and 5.4 × 5.6 Å for ZSM-5) it is supposed that dealkylation of silylating agents proceeds to some extent, and the rest of molecules penetrate inside the pores particularly during the zeolite calcination. Also the sorption capacities for argon and *p*-ET confirm this suggestion.

On the other hand, at higher loadings of Si it is supposed that silylation proceeds exclusively on the external surface or subsurface layers, and the interior of the channels is not affected. The total number of strong acid OH groups does not change significantly by the zeolite silylation with TEOS (above 0.1 wt.% Si) and TMOS (above 1.0 wt.% Si). This follows from their estimation by ammonia desorption and equilibrium sorption of *p*-ET, which both reflect the number of strong acid sites. Similarly, the sorption capacity for argon indicates that the inner volume of zeolite channels is not significantly decreased by Si.

There are different views in the literature on the effect of silylation on the zeolite structure and catalytic activity. From one side it is considered that surface strong acid Si–OH–Al sites, which are assumed to play a dominant (negative) role in *para*-selectivity, are blocked by silylation[15]. The others prefer the effect of narrowing of the channel pore openings by silylation[16–18], and, thus the changes in diffusivities, or better, increased differences among transport rates of *para*-, *meta*- and *ortho*-isomers.

In our previous paper[19] it has been shown that the surface sites can hardly play a key role in the zeolite *para*-selectivity as the “coked” zeolite possessing no free surface sites (evidenced by a negligible TIPB conversion) did not exhibit higher *p*-ET yield compared to the parent zeolite. It is reported here that with silylated zeolites a substantial increase in both the selectivity and yield to *p*-ET were obtained although the samples contained a high number of strong acid sites on the zeolite surface, reflected in a high degree of dealkylation of TIPB relative to the parent zeolite (*cf*. Table II, 0.1–2.0

wt.% Si added and Table IV, whole range of Si added). This indicates that surface sites do not contribute substantially to the isomerization of *p*- to *m*-ethyltoluene or to nonselective alkylation. Therefore, their function in the catalytic reaction can hardly be dominant.

On the other hand, the conversion and selectivity data indicate that the reaction is affected by transport processes which undergo changes by silylation. Both the selectivity and yield to *p*-ET are dramatically improved, however, at very high Si loadings zeolite deactivation by coke takes place. We have shown by FTIR spectroscopy that at higher loadings of Si the diffusivity of the bulkier ethyltoluene molecules is decreased, and thus significantly longer contact times and higher coverage of strong acid bridging OH groups inside the zeolite channels by *ortho*- and *meta*-isomers are obtained[20]. This results in the enhancement of the rate of isomerization reflected in a higher *para*-selectivity and in the decreased rate of the alkylation, because a significant part of catalytically active bridging OH groups is blocked by adsorbed ethyltoluene molecules. The application of TMOS has been shown to provide silylated zeolites which exhibited better stability of toluene conversion with T-O-S without substantial deactivation and producing high yields of *p*-ET. Zeolites silylated with TEOS reached at higher Si loadings the selectivity to *p*-ET above 90%. However, they exhibited faster deactivation. As surface strong acid sites do not affect significantly the catalyst selectivity, the contribution of transport properties changed by zeolite silylation is suggested to play a dominant role for both zeolite *para*-selectivity and stability in conversion.

There is still lack of information on the structure of grown SiO_2 phase on the zeolite. Some information concerning the silylation of silica with methyl-(trimethoxy)silane was already reported[21,22], suggesting mono- and bifunctional interaction with Si–OH groups of silica. This is in line with our assumption of the simultaneous interaction of TMOS or TEOS molecules with both strong acid Si–OH–Al groups and terminal Si–OH groups. The presence of a considerable number of strong acid sites on the surface of silylated zeolites indicates that TEOS and TMOS do not interact preferentially with these sites, but their hydrolysis takes place also *via* terminal Si–OH groups. Further step can be polymerization of the alkoxide. On the other hand, TMOS preferable interacts with surface OH groups and its hydrolysis is faster than that of TEOS, which prevent formation of polymeric layer. The kinetic diameter of TMOS molecule is about 8.9 Å (ref.[23]) being significantly larger compared to ZSM-5 channel openings. However, during the subsequent calcination at 770 K, methyl and ethyl groups can be dealkylated, and some SiO_2 particles can penetrate into the inner volume. This process seems to occur with low concentration of TEOS (0.1 wt.% Si) and TMOS (0.1–1.0 wt.% Si), which is reflected in a decrease in the number of OH groups, sorption capacities, the rate of *p*-ET adsorption as well as in the toluene conversion (*cf*. Tables I–IV). Although Niwa *et al*.[23] suggested the use of TMOS for fine control of narrowing of ZSM-5 channel openings, according to our results we prefer the blocking or plugging of zeolite openings and prolonging, thus, diffusion pathways inside the zeolite crystals. However, at higher concentrations of alkoxides the polymerization is probably much faster and only surface, and subsurface zeolite layers are attacked during the silylation process.

CONCLUSIONS

The results of ZSM-5 zeolite silylation with tetraethyl and tetramethyl orthosilicates can be summarized as follows:

1. A significant increase in *p*-ET selectivity and yield of ZSM-5 zeolite has been found after the zeolite silylation.

2. This increase in *p*-ET selectivity is probably caused by differences in diffusivities of individual ethyltoluene isomers. Moreover, after silylation the bulkier isomers spend longer time inside the zeolite pores and can isomerize to *p*-ET, increasing thus the *p*-ET selectivity.

3. A higher *p*-ET selectivity and *p*-ET yield were found with silylation in the range of Si loadings from 0.1 to 4.3 wt.%, despite the presence of a substantial amount of active sites on the “external” surface of zeolite crystals. This indicates that the blocking of active sites can hardly play a dominant role in the enhancement of the *para*-selectivity.

4. It can be assumed that under silylation conditions tetramethyl orthosilicate tends to hydrolysis much more easily than tetraethyl orthosilicate exhibiting a higher tendency to polymerization. This results in penetration of individual SiO_2 species into the inner zeolite volume during the calcination, which is particularly evident at low Si loading.

5. The detailed investigation of the effect of zeolite silylation on the enhancement of *para*-selectivity confirms our previous results emphasizing the positive role of diffusivity on the *para*-selectivity. However, a mutual effect of blocking of active sites on the “external” surface cannot be fully excluded.

This work was supported by the Academy of Sciences of the Czech Republic (Grant No. A4040707).

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