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# Tailoring mesoscopically structured H-ZSM5 zeolites for toluene methylation



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#### ABSTRACT

Mesoscopically structured zeolites based on H-ZSM5 were designed and synthesized as highly active and shape selective catalysts for methylation of toluene by tuning diffusion and acid site concentration of the catalysts. This was achieved by combining desilication, subsequent dealumination and chemical deposition of a mesoporous SiO<sub>2</sub> overlayer of several nanometer thickness. The decreasing effective diffusion length in zeolite crystals achieved by desilication and dealumination increased the turnover rate of toluene by favoring activation of methanol and facilitating desorption of the produced xylenes, albeit with some loss in p-xylene selectivity. The presence of the SiO<sub>2</sub> overlayer increased the p-xylene selectivity by enhancing the tortuosity of the zeolite, randomly blocking pore openings at the surface, and increasing the effective diffusion path length. The final material combines the higher catalyst utilization with enhanced selectivity leading to rates comparable to the parent zeolite, but at significantly higher selectivity.

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# 1. Introduction

The reaction of toluene with methanol to xylenes has great potential to become an important process in the chemical industry [1]. Among the three xylene isomers, p-xylene has the highest demand as a key intermediate for the production of terephthalate, which itself is an intermediate for polyester synthesis [2]. Methylation of toluene on commercially available medium pore zeolites, however, often yields thermodynamic mixtures of the xylene isomers [3–5] (i.e., ortho:meta:para xylene ratio of ~22:53:25 at 650 K [6]). As the xylene isomers have similar boiling points, energy intensive processes, such as adsorption or fractional crystallization, are required for separation [1,2].

The para-selectivity with H-ZSM5 has been reported to be enhanced by increasing the zeolite crystal size [7–9], by impregnating with phosphorous or boron compounds [4,8,10,11], and by chemical vapor (CVD) [12] or liquid deposition (CLD) [13,14] of tetraethyl orthosilicate (TEOS). In particular, TEOS deposition on the zeolite particle surface is an attractive method to increase the shape selectivity by partially blocking the pore openings as well as by reducing the concentration of Brønsted acid sites in pore mouth region [3,12,14]. The modification decreases the diffusivity

\* Corresponding author. E-mail address: Johannes.Lercher@ch.tum.de (J.A. Lercher). of o- and m-xylene, while it increases for p-xylene [15]. On the other hand, the desilication and subsequent dealumination of H-ZSM5 shorten the diffusion path length and increase the transport rates of all aromatic molecules [16,17], leading to enhanced activity [18–20], albeit with lower shape selectivity compared to the parent material [20].

In this work, the strategy to synthesize small crystal zeolites with a mesoporous  $SiO_2$  overlayer for efficient catalyst utilization and high shape selectivity is reported. The synthesis of materials structured on a meso-scale level is described, together with the characterization of intermediate and final materials, and the investigation of their catalytic impact on the toluene methylation kinetics.

## 2. Experimental

### 2.1. Materials

Zeolite H-ZSM5 (Si/Al = 36; Süd-Chemie) was used as parent material, and five different hierarchical samples were prepared by desilication (DS), subsequent dealumination (DS–DA) and by surface modification (SM) by CLD of TEOS, as shown in Scheme 1.

The desilicated DS sample was prepared by heating the parent H-ZSM5 in a 0.2 M NaOH (>98%, Sigma–Aldrich) solution (30 cm<sup>3</sup> per gram of zeolite) at 340 K under stirring for 0.75 h [21]. The solution was transferred into vials, and the solid phase was centrifuged at



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**Scheme 1.** Schematic representation and TEM images of the hierarchical samples prepared from the parent H-ZSM5 zeolite. DS = desilicated H-ZSM5, DS-DA = dealuminated DS sample, SM = surface modified sample by chemical liquid deposition of tetraethyl orthosilicate (TEOS). \*Indicates the location of extra-framework AI species (EFAI).

4000 rpm for ~0.5 h and washed with deionized water. The washing procedure was repeated three times. The sodium form of the DS zeolite was exchanged into the ammonium form in 0.2 M NH<sub>4</sub>Cl (>99.5%, Sigma–Aldrich) solution (30 cm<sup>3</sup> per gram of zeolite) at 353 K under stirring for 6 h. The solid was separated and the ion exchange with fresh 0.2 M NH<sub>4</sub>Cl solution was repeated three times. After the third ion exchange, the zeolites were separated by centrifugation, washed with deionized water and dried (at 353 K) before the sample was treated in a synthetic air (flowing at 1.7 cm<sup>3</sup> s<sup>-1</sup>; 20.5% O<sub>2</sub> in N<sub>2</sub>, Westfalen) at 823 K (heating rate of 0.05 K s<sup>-1</sup>) for 10 h to obtain the Brønsted acidic form of the zeolite.

The desilicated and dealuminated (DS–DA) sample was prepared from the DS sample in a 1 M 2,3-dihydroxybutanedioic acid (L-tartaric acid; >99.5%, Sigma–Aldrich) solution (20 cm<sup>3</sup> per gram of zeolite) at 333 K under stirring for 4 h [22]. This solution was separated, washed, and dried as described above, before it was calcined in synthetic air (flowing at 1.7 cm<sup>3</sup> s<sup>-1</sup>) at 823 K (0.05 K s<sup>-1</sup>) for 10 h.

The surface modified SM samples were prepared by heating the parent H-ZSM5, the DS or the DS–DA sample in hexane (25 cm<sup>3</sup> per gram of zeolite; 97%, Sigma–Aldrich) with TEOS (4 wt% SiO<sub>2</sub> per gram of zeolite; >99.0%, Sigma–Aldrich) at 353 K under stirring for 1 h [13]. Hexane was removed with a rotary evaporator under vacuum, and the materials were dried at 353 K, before the treatment in a synthetic air (flowing at  $1.7 \text{ cm}^3 \text{ s}^{-1}$ ) at 353 K (0.083 K s<sup>-1</sup>) for 2 h, 453 K (0.033 K s<sup>-1</sup>) for 3 h, and finally 823 K (0.033 K s<sup>-1</sup>) for 5 h. This procedure was repeated three times for all samples (i.e., H-ZSM5, DS, and DS–DA) to obtain the final material (total deposition amount of 12 wt% of SiO<sub>2</sub>).

#### 2.2. Catalyst characterization

The elemental composition and the crystal size distribution of the materials were determined by atomic absorption spectroscopy (AAS) using Unicam M Series Flame-AAS equipped with an FS 95 auto-sampler and a GF 95 graphite furnace and by dynamic light scattering (DLS) using a Malvern Zetasizer Nano ZS system, respectively. The powder X-ray diffraction (XRD; Philips X'Pert Pro system,  $\lambda_{CuK\alpha} = 0.154056$  nm, 40 kV/40 mA) patterns were recorded between  $2\theta$  angles of 5–70° (step size of 0.017° and a scan speed of 0.3 s per step). The signals between ~5–10° and 22–25° after background correction were integrated and compared to the parent H-ZSM5 to estimate the relative crystallinity of the hierarchical samples (see Table S1). The TEM images were taken by a Hitachi H-7100 with a maximum acceleration of 120 kV after cutting through the cross section of the sample.

The N<sub>2</sub> physisorption was carried out at 77 K on a PMI automated sorptometer after outgassing the samples under vacuum at 523 K for 2 h. The BET isotherm [23] was used to evaluate the apparent specific surface area over a relative pressure range from 0.01 to 0.1  $p/p_0$ . The micro- and meso-pore volumes were evaluated by using the  $\alpha_s$  comparative plot [24] with non-porous hydroxylated silica [25] as the reference adsorbent. The macropore volume was calculated by subtracting micro- and meso-pore volumes from the total pore volume determined at  $p/p_0$  = 0.95. The pore size distribution of the zeolites was evaluated by the DFT method (cylindrical pore, NLDFT equilibrium model).

Infrared (IR) spectroscopy (Thermo Nicolet 5700 FT-IR spectrometer, resolution  $4 \text{ cm}^{-1}$ ) with pyridine (99.8%, Sigma–Aldrich)

and 2,6-di-tert-butyl-pyridine (2,6-DTBPy; >97%, Sigma-Aldrich) as probe molecules was used to determine the total concentration of Brønsted and Lewis acid sites as well as of Brønsted acid sites located in the pore mouth regions [26], respectively. 2,6-DTBPy was used as a probe molecule to determine the concentration of Brønsted acid sites in the pore mouth regions, because the kinetic diameter of 2,6-DTBPy (1.05 nm) is much larger than the size of the H-ZSM5 micropores  $(0.51 \times 0.55 \text{ and } 0.53 \times 0.56 \text{ nm} [27])$ . All samples were pressed into self-supporting wafers (density ~0.01 g cm<sup>-2</sup>) and activated in vacuum ( $p < 10^{-7}$  kPa) for 1 h at 723 K (heating rate of  $0.17 \text{ K s}^{-1}$ ) before the spectra of the activated samples were measured. The samples were exposed to pyridine or 2,6-DTBPy at 0.01 kPa and 423 K for 0.5 h and evacuated for 1 h to desorb weakly bound molecules. The bands at  ${\sim}1545~cm^{-1}$  and  ${\sim}1450~cm^{-1}$  in the IR spectra of pyridine adsorbed were integrated to determine the total concentration of Brønsted and Lewis acid sites, respectively, Pyridine adsorbed on Lewis acid sites resulted in two bands at 1447 cm<sup>-1</sup> and at 1455 cm<sup>-1</sup>, which were deconvoluted with two Gaussian functions  $(R^2$  values were above 0.98 in all cases). The sample was subsequently heated to 723 K (0.17 K s<sup>-1</sup>) for 0.5 h in vacuum to determine the concentration of strong Brønsted and Lewis acid sites. In order to calculate the concentration of Brønsted acid sites interacting with 2,6-DTBPy, the change of  $3610 \text{ cm}^{-1}$  area of the parent H-ZSM5 sample was correlated with the integrated area of the N-H<sup>+</sup> stretching band of protonated 2,6-DTBPy at 3367 cm<sup>-1</sup> [26]. This ratio was used to relate the area of the band at 3367 cm<sup>-1</sup> to the concentration of Brønsted acid sites interacting with 2,6-DTBPy for the mesoscopically structured samples. All spectra were collected at 423 K and normalized to the overtone lattice vibration bands at 1990 and  $1870 \text{ cm}^{-1}$  for comparison of the IR spectra of different samples. Note that the acid site concentrations reported are normalized to the weight of zeolite, and the materials with an SiO<sub>2</sub> overlayer were further normalized to account for the weight of the TEOS deposited (12 wt%).

#### 2.3. Kinetic experiments

The catalyst samples (4-25 mg, 180-250 µm) diluted with silicon carbide (7 times the weight of the catalyst; F46, ESK-SiC GmbH) were held in place by quartz wool inside a quartz plug flow reactor (0.4 cm ID). All catalysts were treated at 823 K (0.17 K  $s^{-1}$ ) under flowing He ( $1.7 \text{ cm}^3 \text{ s}^{-1}$ ; 99.996%, Westfalen) for 0.5 h prior to the reaction. The temperature was measured by a type K thermocouple in external contact to the reactor. It was maintained constant by a stainless steel furnace controlled by an Eurotherm controller (Series 2416). The toluene methylation was carried out between 548 and 723 K at atmospheric pressure by flowing premixed toluene (>99.9%, Sigma-Aldrich) and methanol (MeOH; >99.8%, Sigma–Aldrich) feed ( $p_{\text{toluene}} = 6 \text{ kPa}$ ,  $p_{\text{methanol}} = 1.5 \text{ kPa}$ ) into a vaporizer filled with silicon carbide. The total flow rate was varied between 1.2 and 2.3 cm<sup>3</sup> s<sup>-1</sup>. The reactor effluent was analyzed by online gas chromatography (Agilent 7820A) equipped with a DB-WAX column (30 m  $\times$  0.32 mm  $\times$  0.5  $\mu$ m) and a flame ionization detector. All rates were normalized by the total concentration of Brønsted acid sites.

#### 3. Results and discussion

# 3.1. Chemical composition and structural characterization of mesoscopically structured materials

The chemical composition and the textural properties of the parent and mesoscopically structured materials are compiled in Table 1. The Si/Al ratios indicate that desilication selectively

removed Si, while dealumination primarily removed extra-framework Al (vide infra) from the zeolite. The surface modification by TEOS led to the deposition of a mesoporous  $SiO_2$  overlayer in the macro- and large mesoporous volume of the zeolite domains. Note that the  $SiO_2$  deposition nominally increased the Si/Al ratio.

The BET and external surface areas, as well as the meso- and macropore volumes, increased considerably after desilication, but only marginally after subsequent dealumination. The increase in the pore volume with diameters of approximately 4–6 nm for the DS sample in Fig. 1 confirmed the generation of mesopores by desilication (see also Scheme 1), while the pore volumes did not change significantly after the subsequent dealumination. Deposition of the SiO<sub>2</sub> overlayer decreased the micropore volume, but increased the pore volume of pores with diameters <2 nm (Table 1 and Figs. S1–S3). This suggests that some of the micropores were blocked by our SiO<sub>2</sub> deposition, while the overall increase in the pore volume of pores with a diameter between 1 and 50 nm is in good agreement with a typical mesoporous oxide [28].

The XRD patterns and the relative crystallinity shown in Fig. 2 confirmed that the parent and mesoscopically structured H-ZSM5 samples maintained good crystallinity throughout the modification procedures. Note that the relative crystallinity of the SM sample decreased to 90% relative to the parent H-ZSM5, because the SiO<sub>2</sub> overlayer deposited is amorphous ( $\sim$ 12 wt%). The slight increase in the average crystal size from 120 to 140 nm (Fig. 3) after desilication, dealumination, and surface modification resulted from the removal of a small fraction of the smallest crystals after centrifugation (slightly cloudy solution even after 0.5 h of centrifugation at 4000 rpm).

#### 3.2. Acid site characterization of hierarchical materials

The IR spectra of the activated samples are shown in Fig. 4 and Figs. S4-S5 (see also Fig. S6). Two distinct bands were observed at 3745 cm<sup>-1</sup> and 3610 cm<sup>-1</sup>, characteristic for the O–H vibration of terminal silanol groups and Brønsted acid sites, respectively [29.30]. Desilication of the parent H-ZSM5 significantly increased the external surface area (Table 1), and consequently, the concentration of terminal silanol groups (3745 cm<sup>-1</sup>) increased [30]. A band at 3670 cm<sup>-1</sup> appeared after desilication, which is attributed to the OH groups of extra-framework aluminum (EFAI) species [31]. The broad band at  $3500 \text{ cm}^{-1}$  [32] decreased as a result of the silanol nest removal (see Fig. S4, left) [33]. The decrease in intensity of the band at 3670 cm<sup>-1</sup> showed that subsequent dealumination of the desilicated sample removed a part of the EFAl species. This procedure also leached some tetrahedral Al<sup>3+</sup> from the lattice and led to the formation of silanol nests (Fig. S4, left) [34], as indicated by the simultaneous re-appearance of a broad band at 3500 cm<sup>-1</sup>. Deposition of the mesoporous SiO<sub>2</sub> overlayer decreased the bands at 3745 cm<sup>-1</sup> and 3610 cm<sup>-1</sup> (terminal SiOH groups and Brønsted acid sites), while the intensity of the broad band at 3660 cm<sup>-1</sup> increased because of the presence of hydrogen bonded SiOH groups in the amorphous SiO<sub>2</sub> layer [35].

The IR spectra of adsorbed pyridine (after subtracting the spectra of activated sample) are shown in Fig. 5. The band at 1545 cm<sup>-1</sup> results from pyridinium ions formed by Brønsted acid sites [36,37] and the bands at 1447 and 1455 cm<sup>-1</sup> characterize coordinately bound pyridine molecules on OH groups and on extra-framework Al<sup>3+</sup> cations [38], respectively. The two bands characterizing coordinative bonding were quantitatively evaluated assuming similar molar extinction coefficients (Table 2). The deconvoluted IR spectra of adsorbed pyridine on H-ZSM5 and DS are shown as an example in Fig. S7.

The concentration of Brønsted and Lewis acid sites increased upon desilication (Table 2). Most of the newly formed Lewis acid sites are assigned to EFAI species (1455 cm<sup>-1</sup>), formed via O–AI

2	7	4

Table 1

infinitial composition and textural properties of the parent and mesoscopically structured materials derived non right 2005.							
Catalyst	Si/Al <sub>ratio</sub>	$S_{\rm BET}^{a}({\rm m}^2{\rm g}^{-1})$	$S_{\rm ext}^{b}({\rm m}^2{\rm g}^{-1})$	$V_{\rm pore} \ d_{\rm pore} < 1 \ {\rm nm} \ ({\rm cm}^3 \ {\rm g}^{-1})$	$V_{\rm pore} \ d_{\rm pore}$ = 1–50 nm (cm <sup>3</sup> g <sup>-1</sup> )	$V_{\rm pore} \ d_{\rm pore} > 50 \ {\rm nm} \ ({\rm cm}^3 \ {\rm g}^{-1})$	
H-ZSM5	36	435	57	0.12	0.03	0.17	
DS	27	482	96	0.12	0.05	0.23	
DS-DA	39	484	99	0.12	0.05	0.24	
SM	42	434	24	0.09	0.08	0.13	
DS-SM	36	348	41	0.06	0.08	0.14	
DS-DA-SM	47	435	84	0.08	0.06	0.20	

Chemical composition and textural properties of the parent and mesoscopically structured materials derived from H-ZSM5.

<sup>a</sup> S<sub>BET</sub> = specific surface area analyzed according to Brunauer–Emmett–Teller.

<sup>b</sup>  $S_{\text{ext}}$  = external surface area.



**Fig. 1.** Pore size distribution of the parent (H-ZSM5;  $\Box$ ), desilicated (DS;  $\Delta$ ), and subsequently dealuminated (DS-DA;  $\odot$ ) samples, analyzed by DFT method (cylindrical pore, NLDFT equilibrium model).



**Fig. 2.** Powder X-ray diffraction (XRD) patterns and relative crystallinity of the parent H-ZSM5 and the mesoscopically structured materials.

bond cleavage during the removal of tetrahedrally coordinated Si atoms from the zeolite [31]. The total concentration of acid sites



**Fig. 4.** Infrared (IR) spectra of activated samples (heated to 723 K for 1 h) measured at 423 K under vacuum ( $<10^{-7}$  kPa). The bands at 3745 cm<sup>-1</sup> and 3610 cm<sup>-1</sup> represents O–H vibration of the terminal silanol groups and the Brønsted acid sites, respectively. The spectra were normalized to the lattice vibrations.

increased significantly (from 447 to 573 µmol  $g_{zeolite}^{-1}$ ), consistent with the decrease in Si/Al ratio (Table 1). Please note here, that the concentration remained nearly constant (from 447 to 430 µmol  $g_{zeolite}^{-1}$ , see Fig. S10), if the weight loss after desilication (~25%) was accounted for, indicating that all Al<sup>3+</sup>, contributing to Lewis or Brønsted acidity, remained in the material, while the Si was removed selectively as Si(OH)<sub>4</sub>. Subsequent dealumination of the DS sample by tartaric acid decreased the concentration of Lewis and Brønsted acid sites (13%), because not only most of the EFAl species, but also some tetrahedrally coordinated lattice Al<sup>3+</sup> was removed in this step (Table 2).



Fig. 3. Crystal size distribution measured by dynamic light scattering (DLS) method. left: H-ZSM5 (□), DS (Δ) and DS–DA (○), right: SM (□), DS–SM (Δ) and DS–DA (○).



**Fig. 5.** IR spectra after adsorption of pyridine at 423 K, 0.01 kPa and outgassing for 1 h under vacuum (spectra of the activated sample subtracted). The bands at 1447 and 1455 cm<sup>-1</sup> represent the coordinately bonded pyridine molecules on SiOH groups and EFAI species, respectively and the band at 1545 cm<sup>-1</sup> pyridinium ions formed on Brønsted acid sites.

Surface modification with TEOS decreased the Brønsted acid site concentration to a similar extent, whether the sample was treated by desilication or subsequent dealumination prior to deposition of SiO<sub>2</sub> overlayer ( $\Delta_{SM}$  in Table 2; loss of 30–40 µmol of Brønsted acid sites per g zeolite). Note that most of the Brønsted acid sites were strong and more than 90% of pyridine was still adsorbed on all sites even after the samples were outgassed to 723 K.

Deposition of the mesoporous SiO<sub>2</sub> overlayer onto the DS sample significantly decreased the Lewis acid site concentration, whereas it slightly increased for the H-ZSM5 and DS–DA. Hence, the surface modification procedure affects the concentration of Lewis acid sites via the removal of EFAl by reacting with the deposited SiO<sub>2</sub> (site passivation) and via generation of EFAl by mild dealumination (breaking O–Al bond). The Lewis acid site concentration for the DS–SM sample decreased, because the significant fraction of EFAl formed during desilication (DS sample) was removed during the condensation reaction of TEOS. Most of the EFAl formed during desilication was accessible to TEOS ( $\Delta_{SM}$  DS, Table 2;

see also Fig. S11) and, thus, was present at crystal boundaries. On the other hand, the EFAI concentration was affected inversely in the H-ZSM5 and DS-DA-SM sample, because the formation of EFAI species by breaking O—AI bonds was greater than their passivation by SiO<sub>2</sub> deposition. This suggests that the Lewis acid sites in these samples were most likely not accessible to react with the relatively large TEOS molecules.

Quantitative evaluation of the acid sites at the external surface and in the pore mouth of the zeolite was performed via adsorption of 2,6-DTBPy. The corresponding IR spectra are shown in Fig. 6. The concentrations of Brønsted and Lewis acid sites determined by 2,6-DTBPy adsorption are summarized in Table 2 and Fig. 7. A fraction of terminal SiOH groups (3745 cm<sup>-1</sup>) and Brønsted acid sites (3610 cm<sup>-1</sup>) interacted with 2,6-DTBPy, as shown by the decrease in the intensity of both bands. New bands appeared at 3367 cm<sup>-1</sup> and 1616 cm<sup>-1</sup>, which are assigned to the N—H<sup>+</sup> and C=C stretching vibrations of 2,6-DTBPyH<sup>+</sup>, respectively. The correlation between these bands (shown in Fig. S9) indicates that both bands can be used for quantification of the acid sites probed.

After desilication, the bands at  $3367 \text{ cm}^{-1}$  and  $1616 \text{ cm}^{-1}$  in Fig. 6 increased compared to the parent H-ZSM5. We attribute this to the fact that a substantial fraction of Brønsted acid sites became accessible to 2,6-DTBPy through the generation of mesopores, increasing in this way the concentration of Brønsted acid sites in the pore mouth region. These Brønsted acid sites were primarily removed during subsequent dealumination with tartaric acid, the kinetic diameter (0.68 nm) of which is slightly larger than the size of the H-ZSM5 micropores (~0.55 nm). The decrease in intensities of the bands at 3367 cm<sup>-1</sup> and 1616 cm<sup>-1</sup> compared to DS sample confirmed the loss of Brønsted acid sites in the pore mouth region. The surface modification by the SiO<sub>2</sub> overlayer deposition decreased only the fraction of Brønsted acid sites accessible by 2,6-DTBPy, because the kinetic diameter of TEOS (0.96 nm) is larger than the size of the H-ZSM5 micropores, and consequently, only Brønsted acid sites at the pore mouth region were affected (Fig. 7). Thus, the total loss Brønsted acid site concentration is equal to the decrease in sites accessible to 2,6-DTBPy (~30-40 umol per g zeolite).

#### 3.2.1. Toluene methylation on parent and modified H-ZSM5

The turnover rates of toluene at different reaction temperatures and the apparent energy of activation are shown in Table 3 (the conversions of reactants, turnover, and formation rates of methanol and the aromatic products are shown in Tables S3–S5). The reaction orders of toluene methylation were 0.6–0.7 with respect to methanol and 0.4 with respect to toluene under the reaction conditions used [39]. This indicates that the slow diffusing

Table 2

Concentration of Brønsted and Lewis acid sites determined by adsorption of pyridine and 2,6-di-tert-butyl-pyridine (2,6-DTBPy).

	Brønsted acid sites ( $\mu$ mol g zeolite <sup>-1</sup> )			Lewis acid sites ( $\mu$ mol g zeolite <sup>-1</sup> )				
	Total <sup>a</sup>	Strong <sup>b</sup>	2,6-DTBPy accessible <sup>c</sup>	% 2,6-DTBPy interaction <sup>d</sup>	Total	EFAl	SiOH	
H-ZSM5	380	371	90	24	67	3	64	
DS	398	370	204	51	175	102	73	
DS-DA	345	332	131	38	55	16	39	
SM	351	327	62	18	76	16	60	
DS-SM	366	331	170	47	129	72	57	
DS-DA-SM	312	293	92	29	74	28	46	
<sub>ASM</sub> H-ZSM5 <sup>e</sup>	29	44	28	_	-9	-13	4	
ASM DS <sup>e</sup>	32	39	34	-	46	30	16	
ΔSM DS-DA <sup>e</sup>	33	39	39	-	-19	-12	-7	

<sup>a</sup> After adsorption of pyridine at 423 K and outgassing for 1 h under vacuum.

<sup>b</sup> After subsequently heating the samples to 723 K for 0.5 h.

<sup>c</sup> Total concentration of Brønsted acid sites (both strong and weak) located in the pore mouth region. After adsorption of 2,6-DTBPy at 423 K and outgassing for 1 h under vacuum.

<sup>d</sup> Defined as% of 2,6-DTBPy interacting with total Brønsted acid sites.

<sup>e</sup> Difference between before and after the deposition of SiO<sub>2</sub> overlayer.



**Fig. 6.** Changes in IR spectra after adsorption of 2,6-di-tert-butyl-pyridine (2,6-DTBPy) at 423 K, 0.01 kPa and outgassing for 1 h in vacuum (spectra of activated samples are subtracted). The characteristic bands at 3367 cm<sup>-1</sup> (N–H<sup>+</sup> vibration) and 1616 cm<sup>-1</sup> (C=C vibration) appear from 2,6-DTBPy interaction with the zeolite.



**Fig. 7.** Concentration of internally and externally accessible Brønsted as well as Lewis acid sites per gram of a zeolite. White represents Lewis acid sites, gray and black the Brønsted acid site accessible and not accessible by bulky 2,6-DTBPy, respectively.

molecules formed by multiple alkylations accumulate in the zeolite crystals. As this degree of accumulation varies with the partial pressure of methanol and toluene, the competitive adsorption of higher substituted products reduces the increase in the coverage of both reactants (Eq. (1)) causing a rate dependence lower than one with respect to the pressure of toluene and methanol.

In general, desilication and subsequent dealumination increased and surface modification decreased the toluene turnover rates. This trend was especially pronounced at lower temperatures. The apparent activation energy for toluene methylation decreased slightly with desilication and dealumination, but increased with surface modification by an external SiO<sub>2</sub> overlayer deposition, e.g., from 81 to 101 kJ mol<sup>-1</sup> with H-ZSM5 and after surface modification, respectively (Arrhenius plot shown in Fig. S12).

The reaction of toluene methylation is concluded to be controlled by the accumulation of larger reaction products within the pores, because the turnover rates were affected by changes in the mesoporosity and the transport path length in the catalyst (Table 3). The Weisz–Prater criterion [40] (Table S6) suggests that the reaction is influenced by the transport of large aromatic products, while the transport of the main product (p-xylene) and of the reactants (toluene, methanol) is not likely influencing the reaction rate. Thus, a simplified toluene turnover rate can be formulated by using a competitive Langmuir formalism for the adsorption of methanol and toluene [47] neglecting the disproportionation of toluene (<1%) in Eq. (1):

$$r_{\text{TM}} \propto k_{\text{TM}} \frac{K_{\text{Tol}} p_{\text{Tol}}}{1 + K_{\text{Tol}} p_{\text{Tol}} + \sum_{i=1}^{n} K_n p_n} \frac{K_{\text{MeOH}} p_{\text{MeOH}}}{1 + K_{\text{MeOH}} p_{\text{MeOH}} + \sum_{i=1}^{n} K_n p_n}$$
with  $p_n = f(p_{\text{MeOH}}, p_{\text{Tol}})$  (1)

where  $K_{\text{TM}}$  is the reaction rate constant,  $K_{\text{MeOH}}$  and  $K_{\text{Tol}}$  are the adsorption equilibrium constant of toluene and methanol,  $p_{\text{MeOH}}$ and  $p_{\text{Tol}}$  are the partial pressures of methanol and toluene, while  $K_n$  and  $p_n$  are the adsorption constant and partial pressure of the products. Eq. (1) indicates that a higher concentration of o- and m-xylene as well as of multiple alkylated products inside the zeolite pores reduces both the local concentration of toluene and the surface coverage of methanol. The measured concentration of these adsorbed bulky aromatic products was much higher than the predicted coverage at equilibrium [41], emphasizing their importance in reducing the steady-state concentrations of toluene and methanol.

After desilication and subsequent dealumination, the increase in the toluene turnover rates is attributed to the decrease in the effective diffusion length ~45% and 63% (based on o-xylene, see Table S7), thereby reducing the steady-state concentrations of oxylene, m-xylene, and multiple alkylated reaction products [41]. The increase in turnover rate and the decrease in effective path length after dealumination (DS–DA) indicate that EFAl species contribute to the retention of bulky aromatic molecules inside the pores. Consequently, their removal (Fig. 7) also decreases the concentration of these molecules inside the pores. EFAl (Table 2) species formed upon desilication decrease the transport rate by either physically blocking pore openings or by chemically interacting with the aromatic molecules.

The partial blocking of the pore openings by the SiO<sub>2</sub> overlayer significantly increased the diffusion path length, especially for the large aromatic molecules (>70%, see Table S7) [15]. *In situ* IR spectroscopy (Fig. S1 of Ref. [41]) showed that the relative concentration of larger aromatic products with respect to toluene increased after surface modification by 30%, which results in a lower concentration of the reactants inside the zeolite pores because of competitive adsorption (Eq. (1)). Thus, we conclude that o-xylene, m-xylene and multiple aromatic products accumulate toward the steady-state concentration, while the reaction to p-xylene is (neither externally nor internally) diffusion limited on any of the investigated catalysts. Hence, the differences in the activity of the catalysts are attributed to differences in the (surface) chemistry inside the pores rather than to varying effectiveness factors.

The alkylation reaction proceeds via the activation of methanol to either a methoxonium ion or a methyl carbenium ion and the subsequent reaction with an aromatic molecule. The concentrations of adsorbed xylene and trimethylbenzene after leaching decreased and after surface modification with SiO<sub>2</sub> increased, which leads to the discussed variation in the concentration of toluene and methanol inside the pores (Eq. (1)).

In addition, the significant presence of aromatic products from toluene methylation in the zeolite pores [42] increased, consequently, the probability of competitive methylation reactions, i.e., methylation of xylene to TriMB and of TriMB or tetramethylbenzene (TetraMB). The latter (xylene and TriMB) methylation

turnover fates of toluene at unreferit reaction temperatures and the apparent energy of activation for toluene methylation.								
	573 K	623 K	673 K	723 K	723 K			
	Toluene turnover rate <sup>a</sup> (10 <sup>-2</sup> mol [s mol H] <sup>-1</sup> )	Toluene turnover rate $(10^{-2} \text{ mol } [\text{s mol } \text{H}]^{-1})$	Toluene turnover rate $(10^{-2} \text{ mol } [\text{s mol } \text{H}]^{-1})$	Toluene turnover rate $(10^{-2} \text{ mol } [\text{s mol } \text{H}]^{-1})$	$E_{app}^{b}$ (kJ mol <sup>-1</sup> )			
HZSM5	2.1	7.5	14	20	81			
DS	2.7	8.9	16	20	75			
DS-DA	3.7	11	19	25	68			
SM	0.84	4.5	12	19	101			
DS-SM	0.92	4.2	12	20	90			
DS-DA-SM	15	65	15	24	87			

Turnover rates of toluene at different reaction temperatures and the apparent energy of activation for toluene methylation.

<sup>a</sup> Measured based on the toluene consumption (*p*toluene = 6.0 kPa, *p*methanol = 1.5 kPa, 10 mg of catalyst and total flow rate = 2.3 cm<sup>3</sup> s<sup>-1</sup>).

<sup>b</sup> Apparent energy of activation based on the toluene turnover rates measured between 548 and 623 K.

reaction was more significant for zeolites with higher diffusion constraints, e.g., SM compared to H-ZSM5, leading to lower toluene turnover rates. Note that the methylation of larger aromatic products is also favored compared to toluene, because the activation energy of methylation reactions of the benzene ring decreases with number of methyl substitutions ( $\sim$ 10 kJ mol<sup>-1</sup> difference between xylene and toluene methylation [43,44]), and therefore, the differences in the rates are more pronounced at lower reaction temperatures [45] (Table 3, see also Section 3.2.2).

Table 3

In the reactions studied, one would assume the apparent energy of activation to increase with a decreasing intra-particle diffusion limitation; however, the opposite has been observed. The energy of activation increases linearly with the diffusion path length as shown in Fig. 8 and Table 3, which reflects the increasing coverage of the large aromatic products competing for the active sites with the reactants (methanol and toluene). Therefore, the activation energy is a measure for the temperature dependence of the coverage of the heavy alkylated products compared to the reactant molecules. As the concentration of adsorbed reactants (toluene and methanol) decreases, the increasing concentration of heavier products inside the pores increases the apparent activation energy. As the concentration of the latter increase with pore length, the apparent activation energy increases simultaneously. Note that in the absence of competitive product adsorption, the activation energy for the reaction would be identical for all catalysts, because both the local steric environment at the reactive sites and the chemical composition are not affected by the modification.

In summary, the differences in the catalytic activity are attributed to the change in the relative concentration of adsorbed species in the pores caused by the competitive adsorption of large aromatic products leading to a lower concentration of the reactant molecules at the active sites. Consequently, the toluene turnover rates increased with DS and DS–DA samples (vice versa for the samples with SiO<sub>2</sub> overlayer).

# 3.2.2. Influence of the mesoscopically structured pores and reaction temperature on methanol usage

The methanol used for alkylating toluene, the aromatic products and for the formation of light hydrocarbons (LH), was discussed previously as a function of the zeolite framework type [39]. The *fraction of MeOH for LH formation* was defined as follows:

Fraction of MeOH for LH formation

$$=\frac{2 \times C_2 + 3 \times C_3 + 4 \times C_4 + \dots}{\text{Methanol}_{\text{in}} - (\text{Methanol} + 2 \times \text{DME})_{\text{out}}}$$
(2)

Methanol and dimethyl ether (DME) were treated as one reactant (accounting for the stoichiometry of 1/2 for DME), because methanol is reversibly dehydrated to DME and both are able to methylate aromatic molecules via a similar mechanism [46,47]. A fraction of unity would indicate that methanol was used only for the formation of light hydrocarbons and none for the methylation or the formation of aromatics.



**Fig. 8.** Apparent activation energy of toluene methylation (from Table 3) vs. the estimated pore length, calculated from the o-xylene uptake rates with IR Spectroscopy at 403 K [41]. These values were estimated by assuming that the intrinsic diffusion coefficients were the same between the samples and that the changes were caused by the differences in the effective diffusion lengths. The filled symbols represent surface modified samples (SM ( $\blacksquare$ ), DS–SM ( $\blacktriangle$ ) and DS–DA–SM ( $\bigcirc$ )) and unfilled the non-modified samples (parent H-ZSM5 ( $\Box$ ), DS ( $\Delta$ ) and DS–DA ( $\bigcirc$ )).

The fraction of *MeOH for LH formation* on the catalysts studied here is summarized in Table 4. Surprisingly, by decreasing the reaction temperature, the fraction of methanol used for light hydrocarbons formation increased from 0.21 at 723 K to 0.48 at 573 K for the parent H-ZSM5 (Table 4). Aromatic products, such as xylenes and TriMBs, are methylated further and light hydrocarbons are dealkylated from these highly methylated aromatics [48,49], as these molecules cannot exit the pores. Under these conditions, dealkylation becomes favorable over methylation. (Scheme 2) [39]. The methylation of xylenes or TriMBs was favored at lower reaction temperatures relative to toluene methylation, because the activation energy of toluene methylation was higher than that of xylenes or TriMBs. This in turn led to higher probability for the formation of light hydrocarbon via dealkylation from highly methylated aromatic molecules.

The methanol usage toward formation of light hydrocarbons also increased as the effective diffusion length became longer, i.e., the *MeOH for LH formation* fraction increased from 0.30 to 0.48 to 0.75, at 573 K with DS–DA, H-ZSM5, and SM samples, respectively (Table 4). We attribute this to a longer residence time of the highly substituted aromatic molecules in the zeolite pores, which resulted in a higher probability for product methylation and eventual dealkylation to form light hydrocarbon (Scheme 2).

# 3.2.3. Influence of the pores structured on a mesoscale level and the reaction temperature on selectivities

The selectivities of xylene isomers and TriMBs in the aromatic products are shown in Table 5. The selectivity to p-xylene decreased with desilication and dealumination, but increased significantly

with the deposition of an external  $SiO_2$  overlayer and in general on all catalysts with the reaction temperature. Note that the xylenes and TriMBs selectivities in aromatics did not change significantly with the zeolite modifications or with reaction temperatures.

The overall impact of the structural changes on a mesoscale level with respect to the p-xylene selectivity as a function of the toluene turnover rates at 723 K is shown in Fig. 9, left and as a function per weight of zeolite in Fig. 9, right. Desilication and subsequent dealumination increased the toluene turnover rate by  $\sim$ 5% and 30%, respectively, but decreased the p-xylene selectivity within xylenes from  $\sim$ 65% to 55% and 50%. Deposition of the SiO<sub>2</sub> overlayer on these materials decreased the toluene turnover rate by  $\sim$ 5%, but increased p-xylene selectivity significantly (from 50–65% to 75–85%).

The variation in p-xylene selectivity with catalyst modification is the result of the combination of several pathways. During toluene methylation, the p-xylene isomer can be generated by toluene methylation, xylene isomerization, and dealkylation of highly methylated aromatic molecules [39]. Thus, the p-xylene formation rate can be formulated assuming that neither the reactants nor pxylene are diffusion limited and a certain concentration of o-, mxylene, and higher alkylated products is present according to Eq. (3). Disproportionation reaction can be neglected, as it is slow under these reaction conditions, i.e., <1% of the toluene converted underwent disproportionation.

$$r_{pX} \propto r_{\rm TM} + r_{\rm mXiso} + r_{\rm Dealk}$$
 (3)

$$r_{pX} \propto k_{\text{TM}} \frac{K_{\text{Tol}} p_{\text{Tol}}}{1 + K_{\text{Tol}} p_{\text{Tol}} + \sum_{i=1}^{n} K_{n} p_{n}} \frac{K_{\text{MeOH}} p_{\text{MeOH}}}{1 + K_{\text{MeOH}} p_{\text{MeOH}} + \sum_{i=1}^{n} K_{n} p_{n}} S_{\text{TM}}$$

$$+ k_{\text{iso}} \theta_{mX} + k_{\text{De}} \theta_{\text{HAP}}$$
(4)

Here,  $K_{\text{TM}}$ ,  $K_{\text{iso}}$ , and  $k_{\text{De}}$  are the reaction rate constants of the toluene methylation, the m-xylene isomerization, and the dealkylation, respectively and  $S_{\text{TM}}$  is the intrinsic selectivity for the formation of p-xylene via methylation of toluene.  $\theta_{mx}$  and  $\theta_{\text{HAP}}$  are the surface coverages of m-xylene and higher alkylated products. The toluene conversion for the surface modified samples with SiO<sub>2</sub> overlayer was generally lower by ~1–4% compared to the non-modified catalysts (see Table S4) at the same reaction conditions (space velocity, temperature, partial pressures, and similar C<sub>1</sub> conversions). This is attributed to the higher concentration of large aromatic products in the pores, which results in a lower local concentration of toluene and adsorbed methanol at the active sites. Moreover, the higher rate for the methylation of the products compared to that of toluene further lowers the toluene turnover rate (Section 3.2.1).

The overall selectivity of p-xylene decreased as the toluene conversion increased. For the surface modified materials (SM, DS–SM, and DS–DA–SM), the selectivity to p-xylene was clearly higher at the same toluene conversion level (Fig. 10, at 723 K; p-xylene

#### Table 4

Fraction of methanol (MeOH) used for the formation of light hydrocarbons (LH)<sup>a</sup> at different reaction temperatures during toluene methylation for the parent H-ZSM5 and its mesoscopically structured samples.

	573 K	623 K	673 K	723 K
H-ZSM5	0.48	0.42	0.30	0.21
DS	0.36	0.32	0.26	0.22
DS-DA	0.30	0.28	0.20	0.15
SM	0.75	0.57	0.46	0.35
DS-SM	0.68	0.54	0.45	0.35
DS-DA-SM	0.60	0.52	0.40	0.31

<sup>a</sup> Defined in Eq. (2). Data was measured during toluene methylation at  $p_{toluene} = 6.0$  kPa,  $p_{methanol} = 1.5$  kPa, 10 mg of catalyst and total flow rate = 2.3 cm<sup>3</sup> s<sup>-1</sup>.



**Scheme 2.** Methylation and dealkylation of light hydrocarbons during the reaction of toluene with methanol inside H-ZSM5 zeolites. Toluene and p-xylene are not diffusion limited, while larger aromatic molecules, such as m- and o-xylenes, Tri- and TetraMBs are accumulated inside the pores. Most of the light hydrocarbons are formed from highly methylated aromatic products before leaving the zeolite pores as less-methylated aromatic molecules.

selectivity vs.  $C_1$  conversion shown in Fig. S14). Note that the p-xylene selectivity decreased more pronounced at toluene conversion levels above ~15% (compared to the lower toluene conversion levels) for the H-ZSM5 sample (Fig. 10, empty square), because the methanol was nearly depleted at this point (methanol conversion >90%). Under these conditions, the isomerization became the dominant reaction and the p-xylene selectivity started to approach the thermodynamic equilibrium.

The relative contribution of dealkylation compared to the other two pathways can be evaluated by comparing the fraction of methanol used for LH formation with the p-xylene selectivity (Fig. 11) as both were produced simultaneously in the dealkylation of multiple alkylated aromatics. The slope of the linear correlation observed increased with temperature and confirmed the decrease of the dealkylation rate relative to the methylation and isomerization rates. It was discussed in the previous section that the rate of toluene methylation decreased with surface modification, while it is shown here that the p-xylene formation rate increased as the temperature increased from 573 to 723 K (Table 5). Hence, the isomerization is concluded to be the most dominant pathway in controlling the selectivity of the xylenes formed [41,50]. Likewise, the p-xylene selectivity increased significantly after the surface modification with the mesoporous SiO<sub>2</sub> layer, because the effective diffusion path length increased resulting in a strong increase in the concentration of o-, m-xylene, and higher alkylated products inside the pores. This situation led to an increase in the rate of both isomerization and dealkylation, which over-compensated the decrease in the toluene methylation rate leading to the increased p-xylene formation rate observed.

It was previously reported that the concentration of Brønsted acid sites located in the pore mouth region does not affect the pxylene selectivity significantly [3,12,14], which was confirmed by comparing the Brønsted acid site concentrations (Table 2) with the selectivities (Table 5). A correlation between the p-xylene selectivity and the concentration of Brønsted acid sites located in the pore mouth region was not found. The DS-SM sample with the highest p-xylene selectivity observed within the series of catalysts studied has also the highest concentration of acid sites

Table 5		
Selectivity of xylene isomers in xylenes, xylenes and trin	methylbenzenes (triMBs) in a	aromatics during toluene methylation. <sup>a</sup>
		<b>.</b>

	573 K (6–15%) <sup>b</sup>		623 K (31-46%	1–46%) <sup>b</sup> 673 k		673 K (65–75%) <sup>b</sup>		723 K (82–89%) <sup>b</sup>	
	Xylene selectivity p:m:o [%]	Xylenes (TriMBs) [mol%] <sup>c</sup>							
H-ZSM5	38:28:35	90 (5.8)	51:25:24	89 (8.3)	60:24:16	88 (9.2)	64:24:12	89 (8.8)	
DS	33:29:38	92 (5.9)	42:29:29	87 (9.1)	52:29:19	86 (9.7)	56:30:14	87 (9.1)	
DS-DA	33:28:39	92 (5.1)	41:29:31	90 (8.0)	49:29:22	89 (9.2)	52:31:17	89 (9.0)	
SM	47:25:28	87 (8.0)	70:17:13	88 (7.3)	81:13:6	89 (6.5)	85:11:4	92 (5.3)	
DS-SM	41:27:32	86 (8.8)	60:21:18	85 (9.9)	76:15:9	87 (8.6)	84:12:5	90 (6.4)	
DS-DA- SM	40:27:33	87 (8.0)	57:23:20	86 (9.8)	71:18:11	87 (9.2)	78:16:7	89 (7.6)	

<sup>a</sup> Measured at  $p_{toluene} = 6.0$  kPa,  $p_{methanol} = 1.5$  kPa, 10 mg of catalyst and total flow rate = 2.3 cm<sup>3</sup> s<sup>-1</sup>.

<sup>b</sup> C<sub>1</sub> (methanol and DME) conversion (Table S3).

<sup>c</sup> mol% within aromatics; rest is detected as 1,2,4,5-tetraMB.



**Fig. 9.** Selectivity of p-xylene within xylenes vs. toluene turnover rate (left, per mole of Brønsted acid site) and consumption rate (right, per gram of zeolite) during toluene methylation at 723 K ( $p_{toluene} = 6.0$  kPa,  $p_{methanol} = 1.5$  kPa, 10 mg of catalyst, total flow rate = 2.3 cm<sup>3</sup> s<sup>-1</sup>). The filled symbols represent surface modified samples (SM ( $\blacksquare$ ), DS-SM ( $\blacktriangle$ ) and DS-DA-SM ( $\bigcirc$ )) and unfilled the non-modified samples (parent HZSM5 ( $\Box$ ), DS ( $\Delta$ ) and DS-DA ( $\bigcirc$ )).



**Fig. 10.** p-Xylene selectivity vs. the conversion of toluene during toluene methylation, measured at 723 K ( $p_{toluene} = 6.0 \text{ kPa}$ ,  $p_{methanol} = 1.5 \text{ kPa}$ , 4-25 mg of catalyst, total flow rate =  $1.2-2.3 \text{ cm}^3 \text{ s}^{-1}$ , C<sub>1</sub> (methanol and DME) conversion = 40-99%). The filled symbols represent surface modified samples (SM ( $\blacksquare$ ), DS–SM ( $\blacktriangle$ ) and DS–DA–SM ( $\bullet$ )) and unfilled the non-modified samples (parent H-ZSM5 ( $\Box$ ), DS ( $\Delta$ ) and DS–DA ( $\bigcirc$ )).

accessible for 2,6-DTBPy (152  $\mu$ mol g<sup>-1</sup>) compared to the parent H-ZSM5 and DS-DA samples (90 and 131  $\mu$ mol g<sup>-1</sup>, respectively) with a lower p-xylene selectivity.

In conclusion, the series of these zeolite modifications, i.e., desilication, dealumination, and deposition of mesoporous SiO<sub>2</sub>



**Fig. 11.** p-Xylene selectivity vs. fraction of MeOH for LH formation during toluene methylation, measured at 573 K ( $\bigcirc$ ), 623 K ( $\triangle$ ), 673 K ( $\bigcirc$ ) and 723 K ( $\square$ ) ( $p_{toluene} = 6.0 \text{ kPa}, p_{methanol} = 1.5 \text{ kPa}, 10 \text{ mg of catalyst, total flow rate = 2.3 cm<sup>3</sup> s<sup>-1</sup>}).$ 

overlayer, simultaneously enhanced the p-xylene selectivity and toluene turnover rate (Fig. 9; maintained the activity in per weight of zeolite basis). Desilication and dealumination prior to SiO<sub>2</sub> deposition resulted in decreased transport path length of bulky aromatic products by more than  $2 \times$  (Table S7 [41]) reducing the amount of large reaction products and, consequently, led to a more efficient usage of the active sites and higher toluene turnover rates. SiO<sub>2</sub> deposition enhanced the isomerization and dealkylation rate

by increasing the local concentration of larger reaction products and, in turn, increased the p-xylene selectivity.

### 4. Conclusions

Tailoring H-ZSM5 zeolites with a series of well-known modification steps enabled synthesis of a new generation of catalysts that combine high activity and high selectivity to p-xylene via methylation of toluene. The desilication (DS) and dealumination (DA) with NaOH and tartaric acid, respectively, and deposition of a mesoporous SiO<sub>2</sub> overlayer onto the zeolite surface were used to modify the materials by reducing the size of the crystal domains and maintaining their shape selectivity. The Lewis and Brønsted acid site concentrations in the pore mouth region (accessible by 2,6-ditert-butyl-pyridine) increased substantially after desilication, but these sites were effectively removed by subsequent dealumination with tartaric acid, without causing major changes to the mesoporosity. The surface modification by deposition of a mesoporous SiO<sub>2</sub> overlayer further decreased the concentration of Brønsted acid sites at the pore entrance and increased transport path length of the bulkier o- and m-xylene isomers.

The turnover rate of toluene and p-xylene selectivity was concluded to be strongly influenced by the presence of large aromatic products inside the pores and increased simultaneously at relatively high reaction temperatures (>673 K) with H-ZSM5 after desilication, dealumination, and subsequent SiO<sub>2</sub> overlayer deposition. Increasing the relative concentration of these species by the SiO<sub>2</sub> overlayer reduced the toluene conversion rate, because the higher concentration of bulky aromatic products (increase by 30%) led to a decreased concentration of toluene and adsorbed methanol at the active site as well as a lower probability of alkylating toluene. By shortening the effective diffusion length via desilication/dealumination (decrease by 63%) prior to SiO<sub>2</sub> deposition, the steady-state concentration of bulky aromatic molecules in the pores could be decreased. This new material increased p-xylene selectivity and toluene turnover rates from 64% to 78% and by  $\sim$ 20%, respectively (and maintained the catalytic activity in per weight of zeolite basis), however, with the drawback of a slightly lower selectivity of methanol usage.

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#### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2013.12.003.

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