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Enhancing shape selectivity without loss of activity – novel mesostructured ZSM5 catalysts for methylation of toluene to *p*-xylene†

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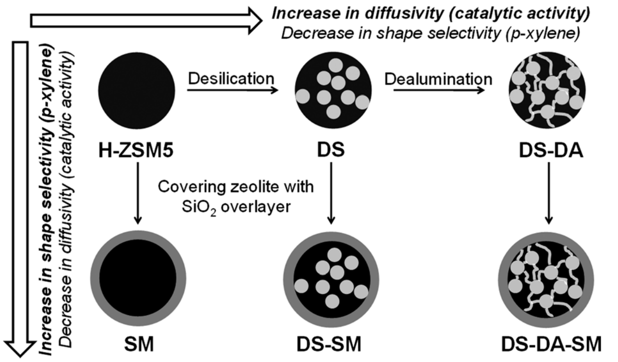
An increase in *p*-xylene selectivity was observed without losing the catalytic activity over novel mesoporous nano-sized ZSM5 crystals covered with an external SiO_2 overlayer created by deposition of tetraethyl orthosilicate.

p-Xylene is an important intermediate for the production of polyethylene terephthalate with a current capacity of 26 × 10^6 tons per year, growing at 6–8% annually.[1] It is primarily produced from steam cracking of naphtha and catalytic reforming, along with benzene, toluene and other xylene isomers.[1] Among these aromatic molecules, toluene is formed in excess and *p*-xylene in deficit relative to the market demand,[2] and, thus, the routes to convert toluene selectively to *p*-xylene, such as the acid catalyzed toluene disproportionation and methylation,[3] have been the focus of industrial and academic research for the last few decades.

Medium pore acid zeolites, such as H-ZSM5, are well-proven shape-selective catalysts,[4] because their micropore dimensions are similar to the size of the aromatic reactants and products (~0.55 nm). It has been shown that the selectivity of *p*-substituted products is enhanced (from ~25 to >80%) by impregnating the zeolites with boron or phosphorus compounds[5] as well as chemical vapor[6] or liquid deposition[7,8] of tetraethyl orthosilicate (TEOS). The modification procedures partially block pore openings and enhance the shape selectivity by increasing and decreasing the diffusivity of *p*- and *o*-/*m*-xylenes, respectively.[9] These methods, however, suffer from a lower catalyst efficiency induced by the decrease in diffusivity of bulky aromatic products, and lower concentration of Brønsted acid sites.[5–9] Alternatively, the selectivity can be enhanced by synthesizing zeolite crystals with particular shapes, thus, tailoring the diffusivity by selectively increasing the transport path length of the crystals[10–12]

We report here a novel approach towards tailored nanostructured zeolites that are able to produce *p*-xylene selectively without losing catalytic activity compared to the parent zeolite by combining the sequence of well known post-treatment procedures as follows: (i) enhancing the transport rates of molecules in the zeolite by generating mesopores and reducing the effective diffusion length *via* desilication (DS),[13] (ii) increasing the transport rates even further by selectively removing the extra-framework aluminum species from pore entrances of the modified nanocrystals (DS) *via* dealumination (DS–DA), and (iii) compensating the loss of the shape selectivity by increasing the diffusivity of *p*-xylene and decreasing that of *m*-/*o*-xylene *via* modification with a mesoporous SiO_2 overlayer (SM).[9,14]

The zeolite modification sequence is shown in Scheme 1 and the chemical composition and the textural properties are compiled in Table 1. The external surface areas and mesopore volumes increased significantly after desilication, but only marginally after subsequent dealumination. The mesopore volume also increased by the deposition of a SiO_2 overlayer, but was accompanied by a modest decrease in the micropore volume.



Scheme 1 Zeolites prepared from H-ZSM5 by desilication (DS), subsequent dealumination (DS–DA), and deposition of the SiO_2 overlayer with tetraethyl orthosilicate from H-ZSM5 (SM), DS (DS–SM) and DS–DA samples (DS–DA–SM).

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† Electronic supplementary information (ESI) available: Experimental details, concentration of acid sites, *in situ* IR spectra obtained during toluene methylation and estimation of surface coverage. See DOI: 10.1039/c3cc46197a

Table 1 Chemical composition, textural and diffusional properties of the samples

	H-ZSM5	DS	DS–DA	SM	DS–SM	DS–DA–SM
Si/Al ratio	36	27	39	42	36	47
$S_{\text{ext}}{}^{a}$ ($m^2\ g^{-1}$)	57	96	99	24	41	84
$V_{\text{mi}}{}^{b}$ ($cm^3\ g^{-1}$)	0.12	0.12	0.12	0.09	0.06	0.08
$V_{\text{meso}}{}^{b}$ ($cm^3\ g^{-1}$)	0.03	0.05	0.05	0.08	0.08	0.06
$D_{o\text{-x}}{}^{c}$ ($10^{-18}\ m^2\ s^{-1}$)	6.1	23	63	1.8	8.6	15
$D_{p\text{-x}}{}^{d}$ ($10^{-18}\ m^2\ s^{-1}$)	10	11	23	17	18	26

[a] S_{ext} = external surface area. [b] V_{mi} and V_{meso} correspond to the micro- and meso-pore volume of the zeolite, respectively. [c] $D_{o\text{-x}}$ = apparent diffusion coefficient of *o*-xylene at 403 K, from infrared spectroscopy uptake rates. [d] $D_{p\text{-x}}$ = apparent diffusion coefficient of *p*-xylene at 403 K, from zero length column measurements.

The *p*-xylene selectivity as a function of the toluene consumption rate during the toluene methylation at 723 K is shown in Fig. 1. The rates are normalized to the net weight of the zeolite phase after modifications. Desilication and subsequent dealumination increased the toluene consumption rates by 6 and 16% relative to parent H-ZSM5, respectively. The fact that these modifications led to higher reaction rates in parallel to an increase in the diffusivity of xylenes (Table 1) suggests that the reaction is diffusion limited (see also ESI† and below). Note that the apparent diffusion coefficients of *p*-xylene in Table 1 are underestimated compared to the *o*-xylene values and were listed only to show the relative trends (see ESI†).

The deposition of a mesoporous SiO_2 overlayer on these materials led to a decrease in the toluene consumption rate by approximately 12–18%, mainly because the concentration of Brønsted acid sites decreased by approximately 10% after these modifications (ESI†). The apparent diffusion coefficient of bulky aromatic molecules such as *o*-xylene (Table 1) also decreased after deposition of the SiO_2 overlayer, leading in turn to a significant increase in the concentration of these molecules in the pores. The higher concentration is deduced from the fact that the intensity of the band of the bridging OH groups at 3610 cm^{-1} (Brønsted acid sites) decreased by a factor of two more strongly during toluene methylation with the SM materials compared to parent H-ZSM5 (ESI†). The higher concentration of more substituted products leads to a higher probability in the methylation of these aromatic products than of toluene. Assuming that the coverages are in the linear portion of the isotherm, the ratio of toluene to all other higher substituted aromatics decreased from 5/95 with parent H-ZSM5[15] to 2.5/97.5 for the SM sample. The competition between toluene and the various substituted aromatic molecules causes its conversion rate to decrease in proportion to its relative concentration. The high abundance of bulky aromatic products[15] should in turn lead also to a lower fraction of chemisorbed methanol (which also should account for a decrease of a factor of two, because of the similar adsorption constants of the two reactants) because of competitive adsorption on Brønsted acid sites. This should proportionally reduce the overall rate of methylation to all aromatic species in the pores. Both effects combined would account for an approximate decrease by a factor of four in the forward rate. The much lower impact of the modification on the rate is attributed to the high conversion of methanol (see Fig. 1, legend). Thus in summary, the SiO_2 overlayer causes the reduction of the toluene methylation rate by a lower coverage of activated methanol and by a lower probability of toluene methylation in the presence of increasing concentrations of bulky aromatic molecules (*vice versa* for DS and DS–DA samples because of the lower concentration of bulky aromatic products in the pores).

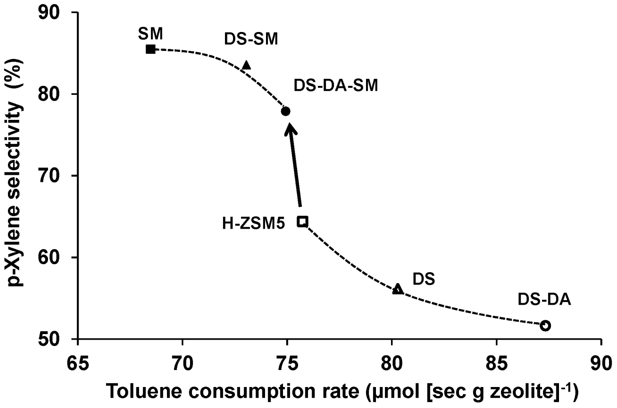

Fig. 1 Selectivity of *p*-xylene within xylenes *vs.* toluene consumption rate during toluene methylation at 723 K (p_{toluene} = 6.0 kPa, p_{methanol} = 1.5 kPa, 10 mg of catalyst, C_1 (MeOH and dimethyl ether) conversion = 82–89%, total flow rate = 2.3 $cm^3\ s^{-1}$). The filled symbols represent samples with deposition of the SiO_2 overlayer (SM (■), DS–SM (▲) and DS–DA–SM (●)) and unfilled symbols without (parent HZSM5 (□), DS (△) and DS–DA (○)). The arrow highlights the overall effect of the modification.

Desilication and subsequent dealumination decreased the *p*-xylene selectivity (from 64 to 52%), while it increased significantly with the deposition of a SiO_2 overlayer (to 78–85%). During the methylation of toluene, the selectivity of *p*-xylene is determined by the rates of three different reaction pathways, *i.e.*, toluene methylation, xylene isomerization and dealkylation of highly-methylated aromatic molecules.[16] The rate of the first reaction increases with increasing diffusivity, albeit to a relatively modest degree. As methanol is certainly not diffusion limited, we conclude that its concentration adsorbed on Brønsted acid sites changes at least by 25% (from SM to DS–DA samples). Interestingly, the rate of *p*-xylene formation was constant for all three samples with the SiO_2 overlayer (SM, DS–SM and DS–DA–SM) and the three without (H-ZSM5, DS and DS–DA), with the former being larger by *ca.* 30% (Fig. 2). This strongly suggests that the changes in the selectivity observed are primarily caused by the relative rates of diffusion of the bulkier molecules. The higher rate of *p*-xylene formation with the SiO_2 overlayer indicates that the combination of dealkylation and isomerization provides a higher contribution to the rate of *p*-xylene formation in the three surface modified than the unmodified samples.

In order to determine the significance of these reaction pathways in the xylene selectivities, methanol was co-fed with toluene (represents toluene methylation) or 1,2,4-trimethylbenzene (TriMB; represents dealkylation reaction) at low (573 K) and high (723 K) reaction temperatures. The product distribution at lower reaction temperature represents the reaction controlled products, as the reaction is operated more at the reaction limited regime and *vice versa*, the diffusion controlled products at high temperatures

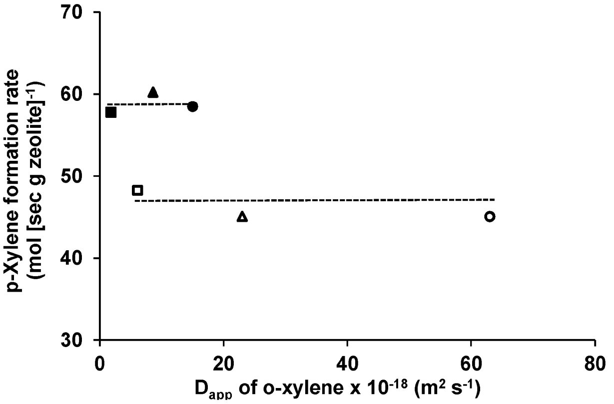

Fig. 2 *p*-Xylene formation rate *vs.* apparent diffusion coefficient of *o*-xylene during toluene methylation at 723 K ($p_{toluene}$ = 6.0 kPa, $p_{methanol}$ = 1.5 kPa, 10 mg of catalyst, C_1 (MeOH and dimethyl ether) conversion = 82–89%, total flow rate = 2.3 cm^3 s^{-1}). The filled symbols represent samples with deposition of the SiO_2 overlayer (SM (■), DS–SM (▲) and DS–DA–SM (●)) and unfilled without (parent HZSM5 (□), DS (△) and DS–DA (○)).

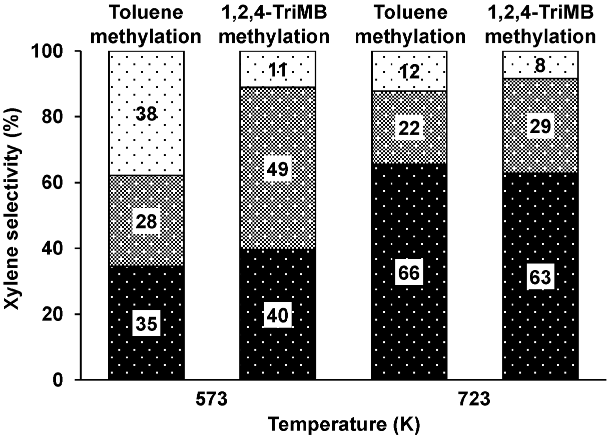

Fig. 3 Selectivity of xylene isomers within xylenes at 573 and 723 K with H-ZSM5. The reaction of toluene and methanol ($p_{toluene}$ = 6.0 kPa, $p_{methanol}$ = 1.5 kPa, 4–10 mg) or with 1,2,4-TriMB and methanol ($p_{1,2,4\text{-}TriMB}$ = 1.2 kPa, $p_{methanol}$ = 0.3 kPa, 9–25 mg) with total flow rates of 1.2–2.3 cm^3 s^{-1}, C_1 (methanol and DME) conversion = 47–55%, toluene conversion = 4–7% and 1,2,4-TriMB conversion = 2–3%. Black, grey and white represent *p*-, *m*- and *o*-xylene selectivities.

as the reaction becomes more diffusion limited. Fig. 3 shows that reaction controlled products (573 K) were quite different along these two reaction pathways, *i.e.*, 28 *vs.* 49% *m*-xylene selectivity. Despite these differences, however, similar xylene selectivities were observed at high reaction temperatures and this suggests that at relatively high temperatures (723 K) the xylene selectivity is most significantly controlled by xylene isomerization, in agreement with ref. 17.

Thus, we show here that by adjusting the size of the primary crystal domain *via* desilication–dealumination and using a mesoporous overlayer to modify the pore entrance, it is possible to increase the selectivity to *p*-xylene considerably (from 64 to 78%) without significant loss in the rate of toluene consumption. This has been made possible because the insight into the mechanistic details of methylation allowed designing catalysts that maintain methanol reactivity despite the severe product diffusion limitations. With the conventional ZSM-5 catalyst, the rate decreases after deposition of the SiO_2 overlayer, because the higher concentration of bulky aromatic products leads to the lower availability of acid sites to activate methanol and because the high abundance of aromatic products lowers the probability to methylate toluene. As the size of the primary crystal domains is decreased from 122 to 68 and 45 nm for the parent, desilicated and subsequently dealuminated samples (calculated from the diffusion coefficients of *o*-xylene, Table 1), respectively, the concentration of the aromatic molecules retained decreased. This suggests that the relative rates of transport out of the pores is maintained using the small crystal domains, while the lower concentration of aromatic molecules in the pores allows for higher alkylation rates. We would like to emphasize that such effects can only be obtained for nano-sized zeolite crystals, where the rate for the pore entrance step is part of the rate determining step due to the short diffusional path length of the pores and the significant fraction of the external surface. While the current system is certainly not yet optimized, it highlights a new strategy for enhancing the selectivity without losing the catalytic activity and these modification concepts should be applicable to many reactions that are diffusion limited and require transport induced shape selectivity.

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