

Supplementary Information JPC

Manuscript: Influence of post-synthetic surface modification on shape selective transport of aromatic molecules in HZSM-5

S. J. Reitmeier, O. C. Gobin, A. Jentys and J. A. Lercher*

*Department of Chemistry, Technische Chemie 2, Technische Universität München,
Lichtenbergstraße 4, 85747 Garching, Germany, * johannes.lercher@mytum.de*

Figure S1

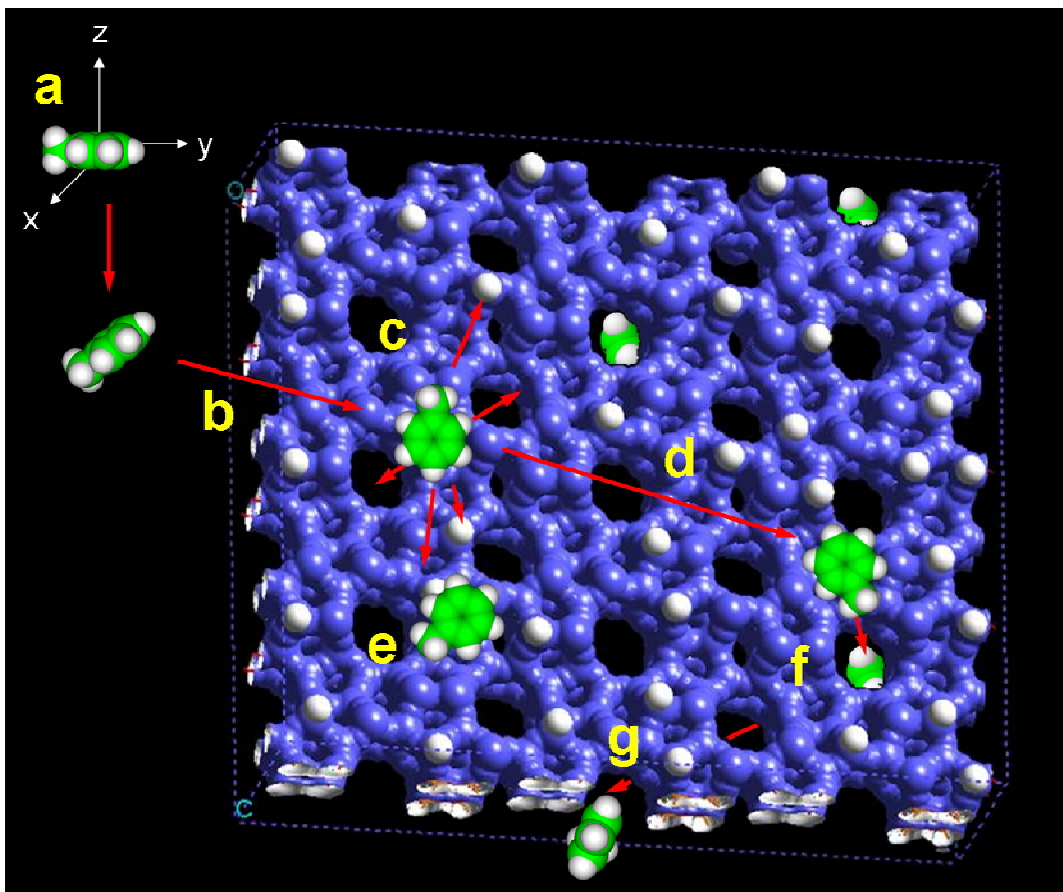


Figure S1: Scheme depicting the major elementary transport steps to the active sites of the H-ZSM5. A typical sketch of an H-ZSM5 crystal is shown with the zeolite lattice in blue and hydrogen atoms highlighted in white, respectively. Toluene molecules impinge from the gas phase with free molecular motion (a). Collision with the zeolites surface (b) are followed by trapping into a weakly-bound surface state (c), high surface mobility (d), parallel transport to the terminal hydroxyls and to the SiOHAl sites inside the pores (e, f) and finally intra-crystalline diffusion (g) are included.

Figure S2

^1H /MAS NMR spectroscopy was carried out on a Bruker Avance AMX-500 NMR-spectrometer with a magnetic field of 11.75 T. The samples were activated in vacuum below 10^{-2} mbar at 673 K for 2h and stored under vacuum at 373 K for 12 h before packing under dry nitrogen into a 4 mm ZrO_2 rotor. During the measurement, the rotors were spun at a frequency of 15 kHz. Spectra were recorded using a $1.6\ \mu\text{s}$ excitation pulse with 6.00 dB and adamantane acted as reference standard.

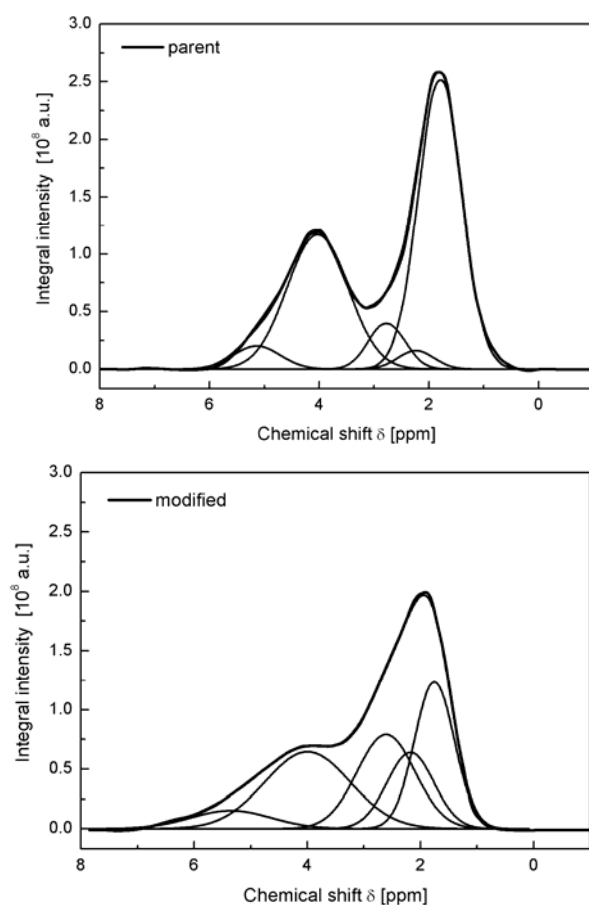


Figure S2: ^1H /MAS-NMR spectra of (top) H-ZSM5-p and (bottom) H-ZSM5-3m. Individual peaks areas were determined by a peak deconvolution formalism with Gaussian-type peaks with chemical shift of 2.0 ppm for terminal SiOH, 2.3 ppm for defect site SiOH, 2.8 ppm for extra-framework AlOH, 4.1 ppm for SiOHAl and 5.2 ppm for perturbed SiOHAl sites according to ref. ¹⁻³.

Figure S3

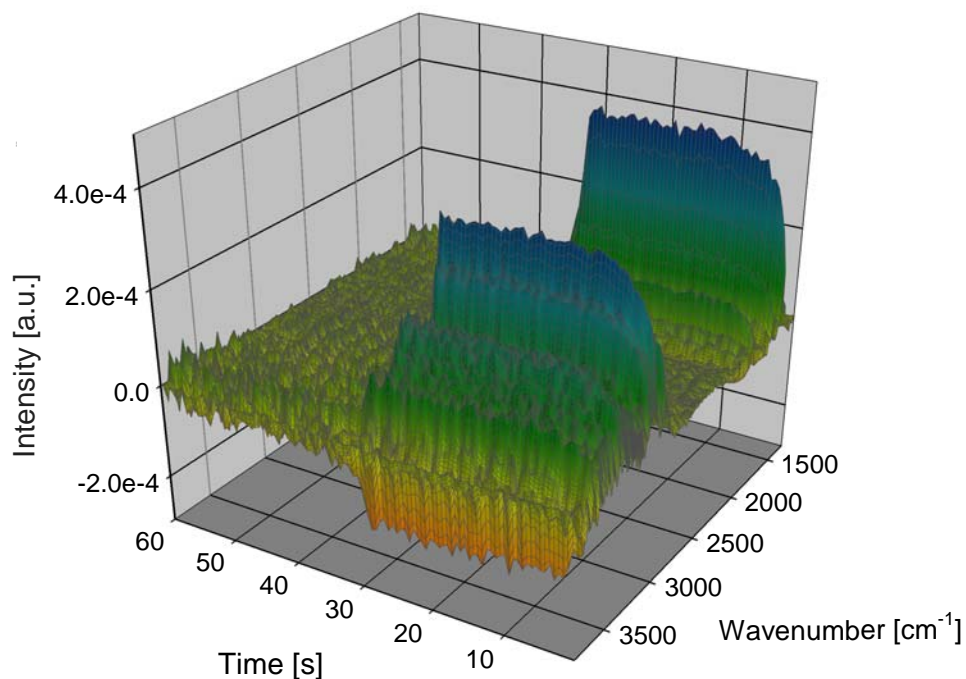


Figure S3. Series of time-resolved difference infrared spectra following the sorption and desorption of toluene on H-ZSM5-1m at equilibrium partial pressure of 0.06 mbar at 403 K. Vibrational bands increasing with time are denoted in blue, those decreasing with time in orange. The cycle time of the volume perturbation performed with a modulation frequency of 0.0167 Hz was 60 s, yielding a time resolution between individual spectra of 0.6 s.

Figure S4.

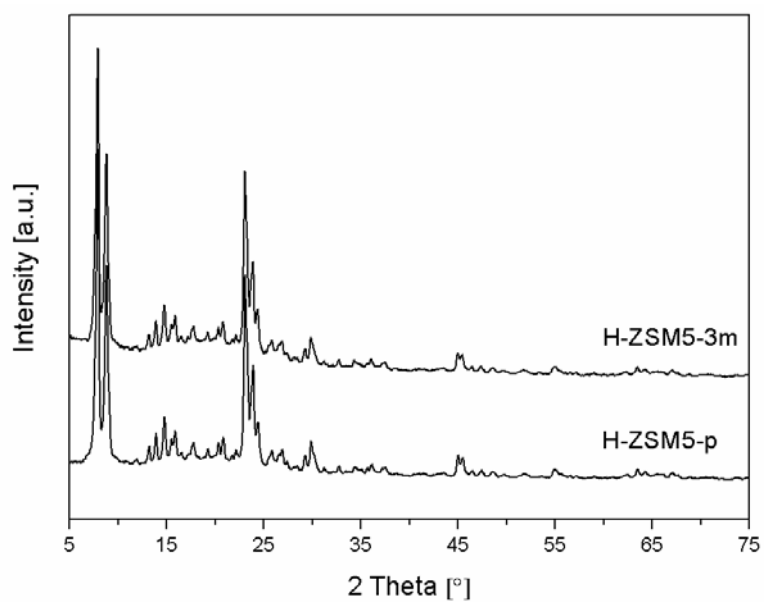


Figure S4. XRD patterns of unmodified H-ZSM5-p and modified H-ZSM5-3m measured in transmission mode using Cu-K α -radiation at a wavelength of 1.540598 Å.

Figure S5.

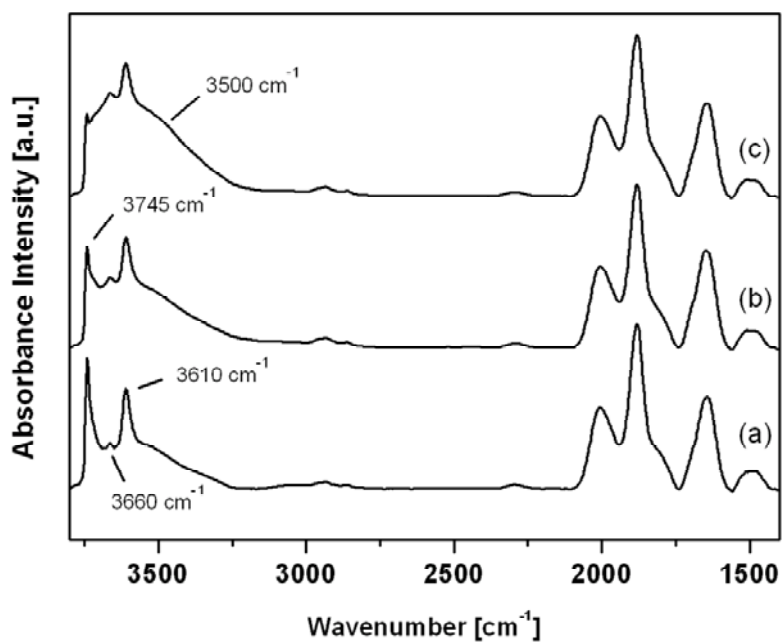


Figure S5. IR spectra of activated (a) H-ZSM5-p and modified samples (b) H-ZSM5-1m and (c) H-ZSM5-3m under vacuum (below 10^{-7} mbar) at 403 K. The three spectra are normalized to the integral of the lattice and overtone vibrations bands of ZSM-5 between 2105 and 1740 cm⁻¹.

Figure S6

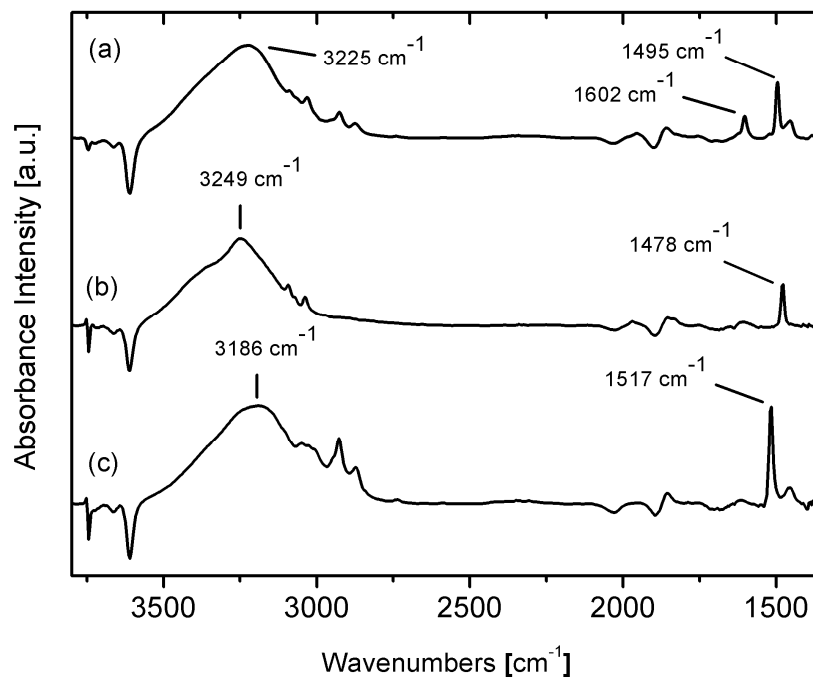


Figure S6. Difference infrared spectra of H-ZSM5-1m after adsorption of (a) toluene, (b) benzene and (c) *p*-xylene measured with partial pressure of 0.06 mbar at 403 K. The corresponding activated spectrum was subtracted and all spectra were normalized to the lattice and overtone vibrations of ZSM-5 between 2105 and 1740 cm^{-1} .

Figure S7.

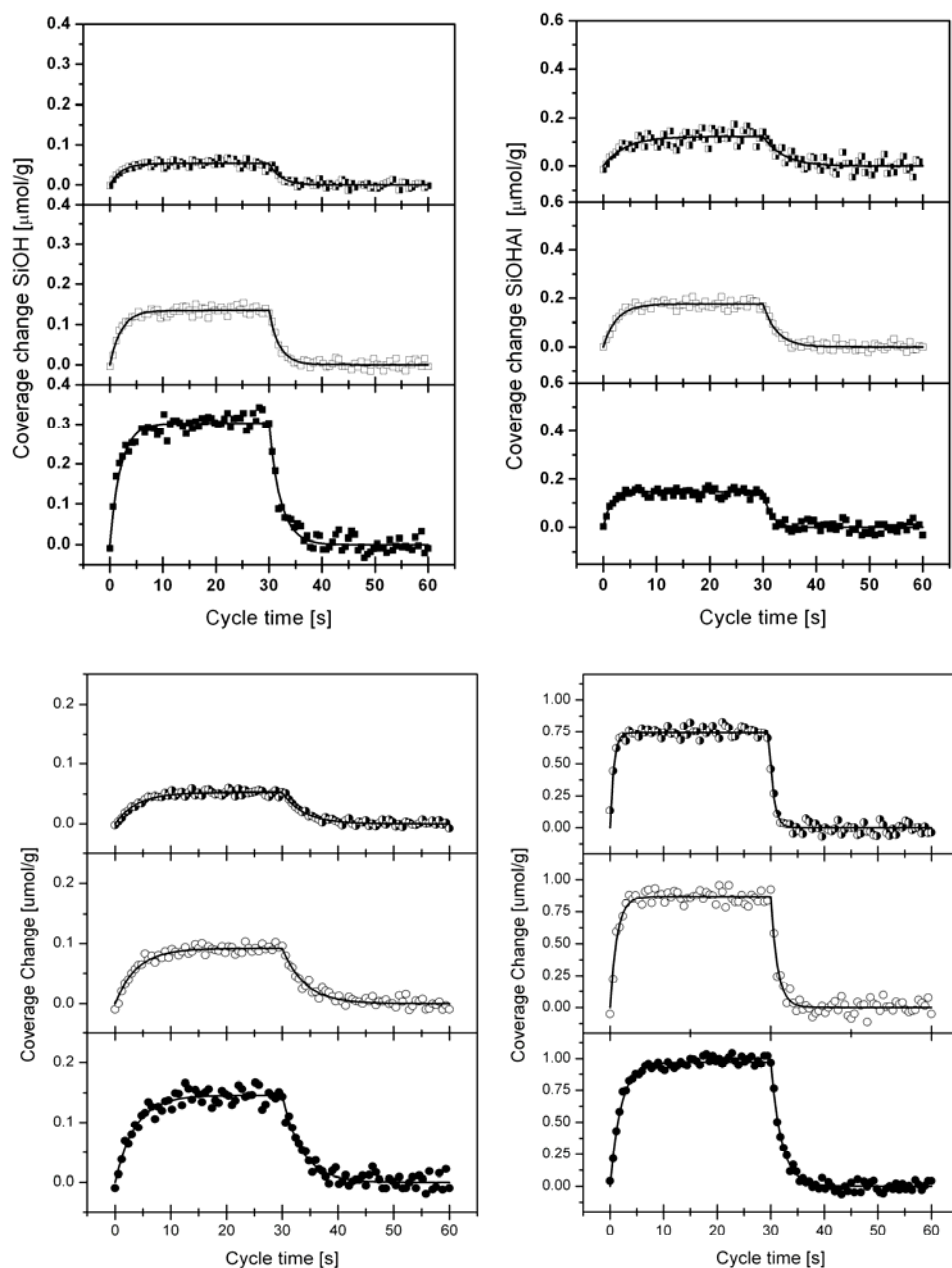


Figure S7. Coverage change profiles at 403 K for the sorption of *p*-xylene (top) and benzene (bottom) on the (left) terminal SiOH and (right) SiOHA1 groups of (■) H-ZSM5-p, (□) H-ZSM5-1m and (●) H-ZSM5-3m during a volume perturbation of $\pm 5\%$ around equilibrium pressure of 0.06 mbar.

Figure S8.

We wish to emphasize at this point, that the experimental results are to the best of our knowledge free of experimental artifacts generated e.g., by a complete blockage of a whole fraction of the pore network due to the overlayers. To ensure the accessibility of the full zeolite micropore volume and therefore all potentially available SiOHAl groups after the modification, the uptakes $\Delta c_{eq,OH}$ (at the typical pressure difference of the rapid scan experiment according to Equation 1) and uptake Δc_{OH} , calculated from the corresponding infrared sorption isotherm at these pressures, are compared. The experimental and theoretical values are in perfect agreement.

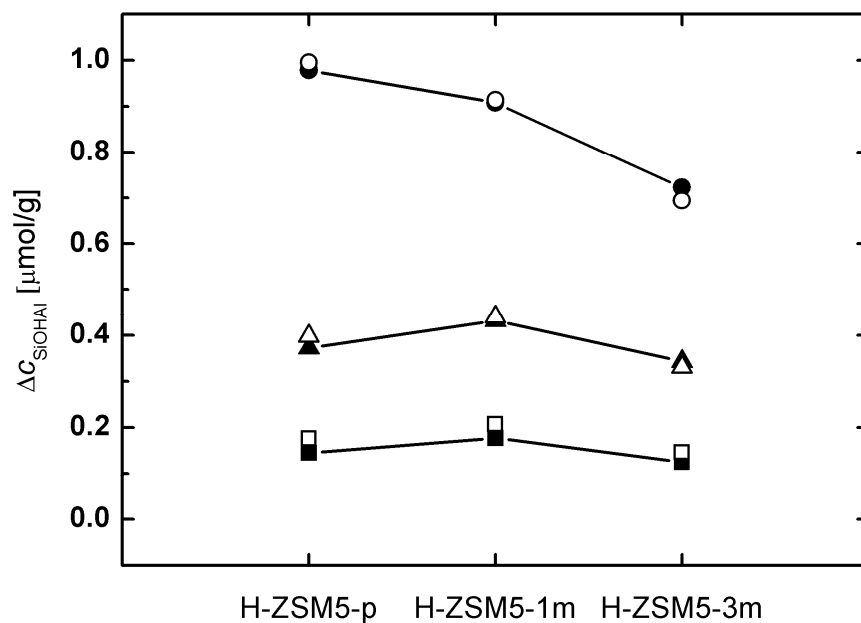


Figure S8. Equilibrium coverage changes $\Delta c_{eq,OH}$ (full symbol) for benzene (●), toluene (▲), and *p*-xylene (■) during a pressure modulation of 0.06 mbar. Open symbols represent the theoretic coverage changes estimated from the corresponding sorption isotherm data at 403 K.

Figure S9.

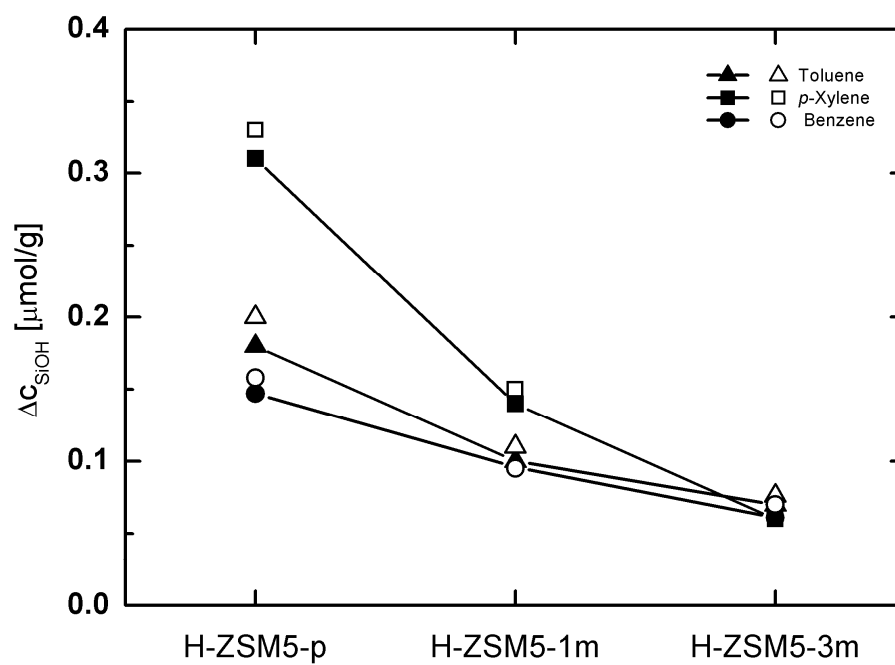


Figure S9. Comparison of the equilibrium coverage changes on the terminal SiOH groups $\Delta c_{eq, \text{SiOH}}$ (solid symbol) during the time-resolved scan measurement in rapid scan mode for the series of aromatic molecules with theoretically expected values (open symbol) calculated from the corresponding infrared sorption isotherms.

Figure S10.

Correlation of the thermodynamically expected and experimentally measured coverage changes for all sorption processes, samples, sorbate molecules and active sites resulted in a straight line with slope of 1.04, presented in Figure S1. It can be concluded, that the trends in sorption rates to internal hydroxyls are not generated by a lower total concentration of accessible sites.

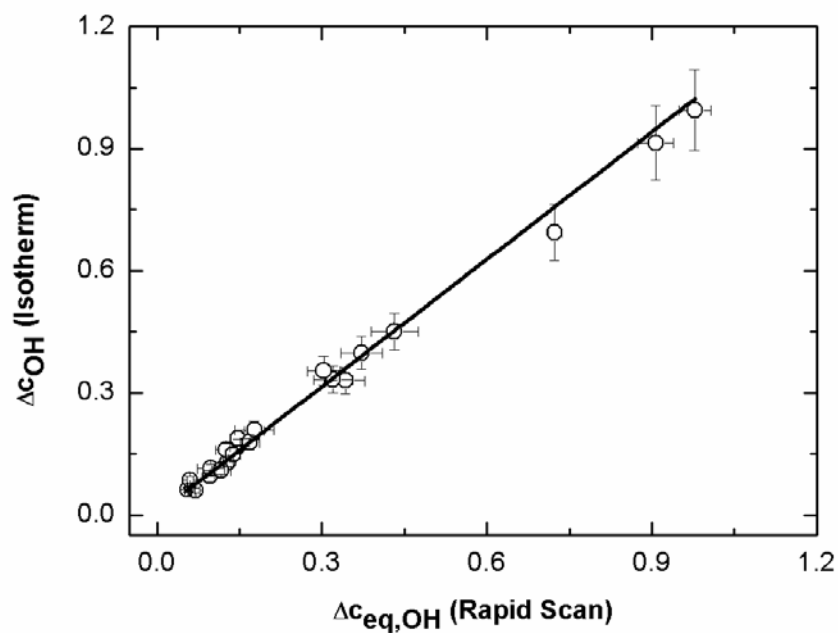


Figure S10. Correlation of the experimental equilibrium $\Delta c_{eq,OH}$ and the thermodynamic coverage changes Δc_{OH} derived from evaluation of the sorption isotherms. Symbols represent the resulting values for the series of aromatic sorbate molecules on H-ZSM5-p, -1m and -3m at 403K. The least-square fit resulted in a straight line with a slope of 1.04, confirming that the data gathered by equilibrium thermodynamics is in perfect agreement to the dynamic experiments.

Table T1.

Table T1. Inverse of the time constants for a series of H-ZSM5 samples for the sorption of aromatic molecules on the SiOH and SiOHAl groups, determined by fast time-resolved infrared spectroscopy at 403 K

1/ τ [s]	H-ZSM5-p		H-ZSM5-1m		H-ZSM5-3m	
	SiOH	SiOHAl	SiOH	SiOHAl	SiOH	SiOHAl
Benzene [*]	0.29	0.48	0.27	0.83	0.28	1.43
Toluene	0.40	0.52	0.40	0.59	0.40	0.77
<i>p</i> -Xylene	0.45	0.71	0.48	0.40	0,45	0.27

* Values for benzene are adopted from Reitmeier et al.⁴

References

- (1) Freude, D.; Hunger, M.; Pfeifer, H. *Zeitschrift für Physikalische Chemie* **1987**, 171.
- (2) Hunger, M. *Catal. Rev.* **1997**, 39, 345.
- (3) Hunger, M.; Freude, D.; Frohlich, T.; Pfeifer, H.; Schwieger, W. *Zeolites* **1987**, 7, 108.
- (4) Reitmeier, S. J.; Gobin, O. C.; Jentys, A.; Lercher, J. A. *Angew. Chem. Int. Ed.* **2009**, 48, 533.