Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

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

John H. Ahn[†], *Robin Kolvenbach*[†], *Sulaiman S. Al-Khattaf*[‡], *Andreas Jentys*[†] *and Johannes A. Lercher*[*,†]

[†]Department of Chemistry, Technische Universität München, Lichtenbergstraße 4, 85747 Garching, Germany

[‡]Center of Research Excellence in Petroleum Refining and Petrochemicals, King Fahd University of Petroleum & Minerals, Dhahran, 31261, Saudi Arabia

*Corresponding Author: Johannes.Lercher@ch.tum.de

Experimental Section

H-ZSM5 (Süd-Chemie) was desilicated in 0.2 M NaOH (>98 %, Sigma Aldrich) solution (30 cm^3 g^{-1}) at 340 K under stirring for 0.75 hour. The sample was washed with deionized (DI) water, followed by an ammonium exchange in 0.2 M NH_4Cl (>99.5 %, Sigma Aldrich) solution (30 cm^3 g^{-1}) at 353 K under stirring for 6 hours. After repeating the ammonium exchange procedure three times, the sample was washed, dried and was treated in a synthetic air (flowing at 1.7 cm^3 s^{-1}; 20.5 % O_2 in N_2, Westfalen) at 823 K (heating rate of 0.05 K s^{-1}) for 10 hours to obtain the DS sample. The DS sample was dealuminated in a 1 M 2,3-dihydroxybutanedioic acid (L-tartaric acid; >99.5 %, Sigma Aldrich) solution (20 cm^3 g^{-1}) at 333 K under stirring for 4 hours. The sample was washed, dried and was treated in a synthetic air (flowing at 1.7 cm^3 s^{-1}) at 823 K (0.05 K s^{-1}) for 10 hours to obtain the DS-DA sample. The SM samples were prepared in a solution of hexane (25 cm^3 g^{-1}; 97 %, Sigma Aldrich) with TEOS (4 wt%; >99.0 %, Sigma Aldrich) at 353 K under stirring for 1 hour [1]. Hexane was removed with a rotary evaporator under vacuum and the materials were dried and treated in a synthetic air (flowing at 1.7 cm^3 s^{-1}) at 353 K (0.083 K s^{-1}) for 2 hours, 453 K (0.033 K s^{-1}) for 3 hours and finally at 823 K (0.033 K s^{-1}) for 5 hours. This procedure was repeated three times for all samples (i.e., H-ZSM5, DS and DS-DA) before the catalysts were tested (total deposition amount of 12 wt% of SiO_2).

Atomic absorption spectroscopy (Unicam M Series Flame-AAS equipped with an FS 95 auto-sampler and a GF 95 graphite furnace) was used to determine the elemental compositions of the materials. The N_2 physisorption measurements were evaluated by using the α_s comparative plot [2] with nonporous hydroxylated silica [3] as the reference adsorbent. The diffusion coefficients of o-xylene were measured from the uptake rates using infrared spectroscopy (Thermo Nicolet 6700 FT-IR spectrometer, resolution of 4 cm^{-1}) by flowing saturated o-xylene (0.04 kPa) onto a self-supporting wafer in a cell (1.5 cm^3), after activating the sample at 523 K (0.17 K s^{-1}) under flowing helium (2.1 cm^3 s^{-1}; 99,996%, Westfalen) for 12 hours. The spectra were collected at 403K, every 60 seconds and the data was analyzed according to Crank [4] using the same CMA evolutional strategy implemented in MATLAB [5]. The concentration of Brønsted acid sites was determined with IR spectroscopy (Thermo Nicolet 5700 FT-IR spectrometer, resolution 4 cm^{-1}) by adsorbing pyridine (99.8 %, Sigma Aldrich) onto a self-supporting wafer, activated under vacuum (<10^{-7} kPa) for 1 hour at 723 K (heating rate of 0.17 K s^{-1}). The sample was then exposed to pyridine at 0.01 kPa and 423 K for 0.5 hour, outgassed for 1 hour under vacuum to desorb weakly bound species and the band at ~1545 cm^{-1} after the adsorption was integrated to determine the total concentration of Brønsted acid sites.

In-Situ IR spectroscopy

The catalyst were tested in a quartz plug flow reactor (0.4 cm ID) after treating the sample (180-250 μm) diluted with silicon carbide (7x catalyst weight; F46, ESK-SiC GmbH) at 823 K (0.17 K s^{-1}) under flowing helium (1.7 cm^{3} s^{-1}; 99,996%, Westfalen) for 0.5 hour. Premixed toluene (> 99.9 %, Sigma Aldrich) and methanol (MeOH; >99.8 %, Sigma Aldrich) feed ($p_{toluene}$ = 6 kPa, $p_{methanol}$ = 1.5 kPa) or 1,2,4-trimethylbenzene (98 %, Sigma-Aldrich) with methanol ($p_{1,2,4\text{-TriMB}}$ = 1.2 kPa, $p_{methanol}$ = 0.3 kPa) was fed into a vaporizer filled with silicon carbide for the reaction testing in atmospheric pressure and the products were analyzed by on-line gas chromatography (Agilent 7820A) equipped with a DB-WAX column (30 m x 0.32 mm x 0.5 μm) and a flame ionization detector. The toluene consumption rates were normalized by the weight of zeolite, i.e., rates of the materials with SiO_2 overlayer were multiplied by 1.12 because the total SiO_2 deposition was 12 weight % of the zeolite.The in-situ infrared (IR) spectroscopy of toluene methylation with H-ZSM5 and SM samples was measured at 573 K using Thermo Nicolet 6700 FT-IR spectrometer (resolution of 4 cm^{-1}; cell volume of 1.5 cm^{3}). The catalyst in a self-supported wafer (~5 mg) was activated at 573 K (heating rate of 0.17 K s^{-1}) for 1.5 hours under flowing helium (2.2 cm^{3} s^{-1}; 99,996%, Westfalen). After collecting the spectra of activated samples, the reaction mixtures were introduced by flowing saturated toluene (2.4 kPa, 2.0 cm^{3} s^{-1}) and methanol (9.9 kPa, 0.11 cm^{3} s^{-1}) at 288 K with helium (0.20 cm^{3} s^{-1}). The spectra were measured every 60 seconds during the reaction and the spectra of H-ZSM5 and SM after activation and ~0.5 hour after introducing the reaction mixtures is shown in Figure S1. The gas product distributions (<15 %) and rates (all within factor of 2) trends were similar to the ones obtained from plug flow reactor at similar conditions. The areas of the O-H vibration region of Brønsted acid (~3610 cm^{-1}) in Figure S1 were integrated to estimate the changes of surface coverage in the zeolites. About 20 and 40 % of Brønsted acid sites interacted with H-ZSM5 and SM samples, respectively (determined by change in the area counts of dashed from solid spectra in 3610 cm^{-1} region in Figure S1).

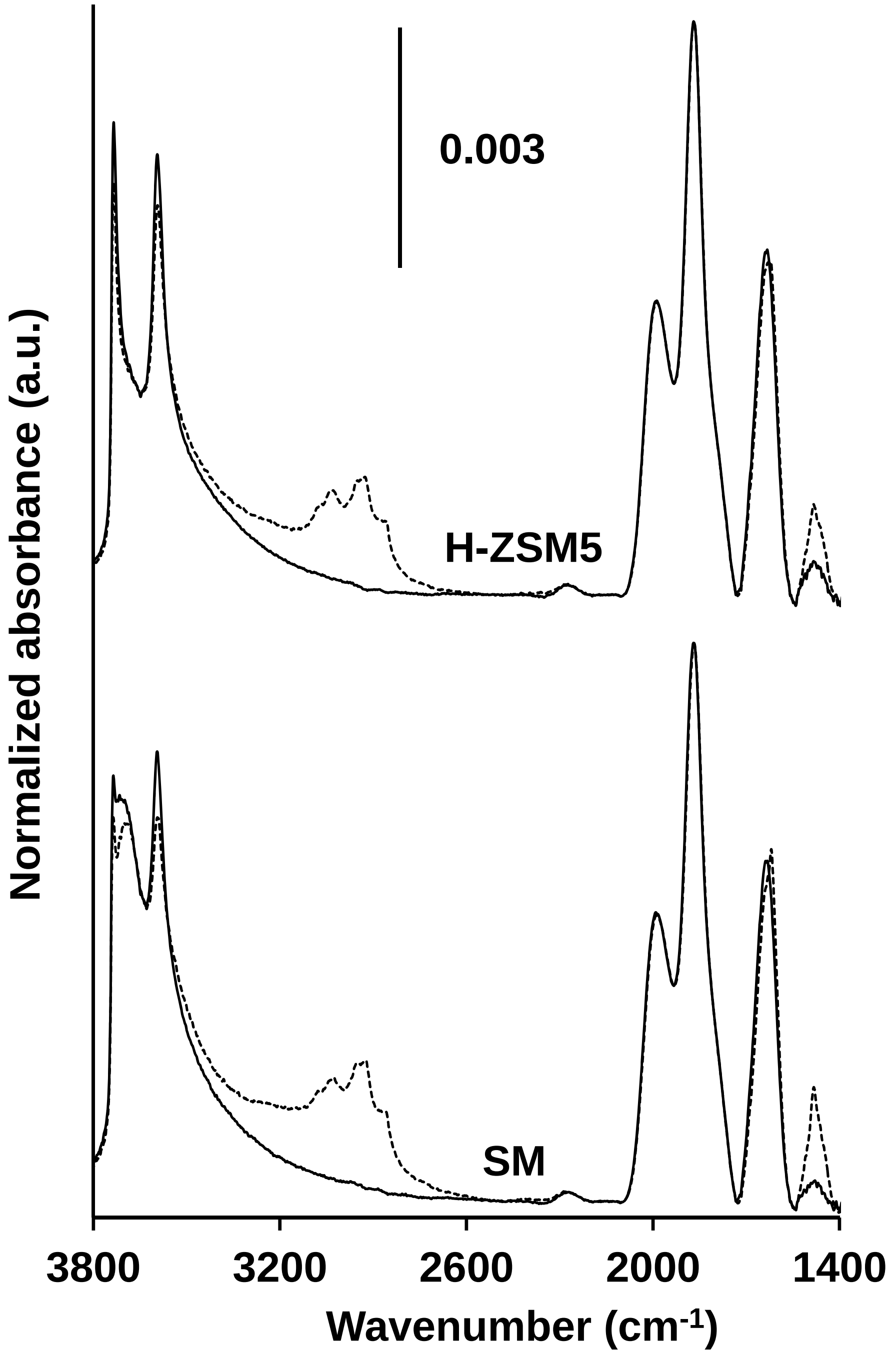

Figure S1: Infrared spectra before (solid) and during the reaction of toluene methylation (dashed, after ~0.5 hour) at 573 K with H-ZSM5 (top) and SM (bottom; surface modified sampled derived from H-ZSM5 by depositing SiO_2 overlayer from tetraethyl orthosilicate) samples. The areas of O-H vibration region corresponding to Brønsted acid (~3610 cm^{-1}) were integrated to estimate the surface coverage in the zeolites.

Surface coverage estimation

The coverage in the zeolite was estimated by assuming a Langmuir isotherm, where the definition is given by the equation below:

$$\theta = \frac{K \times p}{1 + K \times p}$$

where Θ is the coverage, K is the equilibrium constant and p is the partial pressure. The equilibrium constant of toluene and p-xylene was calculated by using the standard enthalpy and entropy from [6] and the partial pressure of 0.02 was used to agree with the in-situ IR experimental condition above. The surface coverage by using these assumptions was ~6 % for toluene and <<1 % for p-xylene. Note that the actual surface coverage was ~20 and 40 % for the H-ZSM5 and SM samples (vide supra). Much higher surface coverage than the equilibrium value suggest that the reaction (toluene methylation) is diffusion limited by large aromatic products in the zeolite pores.

References

[1] S. Zheng, H.R. Heydenrych, H.P. Röger, A. Jentys, J.A. Lercher, Top. Catal. 2003, 22, 101-106.

[2] M. Kruk, M. Jaroniec, J. Choma, Carbon 1998, 36, 1447-1458.

[3] S. J. Gregg, Adsorption Surface Area and Porosity, 2nd ed., Academic Press Inc.: New York, 1982.

[4] J. Crank, The Mathematics of Diffusion, Oxford University Press, New York, 1979.

[5] J. A. Lozano, P. Larranaga, I. Inza, E. Bengoetxea, Towards a New Evolutionary Computation: Advances on Estimation of Distribution Algorithms, Springer, New York, 2006.

[6] R. R. Mukti, A. Jentys, J.A. Lercher, J. Phys. Chem. C 2007, 111, 3973-3980.