Supporting information

Solvent polarity-induced pore selectivity in H-ZSM-5 catalysis

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Experimental details:

Materials: H-ZSM-5-880 sample was prepared according to method (V) from the paper of Müller and Unger, with gel composition 8TPABr/123(NH₂)₂O/Al₂O₃/1460SiO₂/2280H₂O and crystallization for 7 days at 180 °C.¹ H-ZSM-5-82 sample was prepared according to method (IV) from the same paper, with gel composition 8TPABr/123(NH₂)₂O/Al₂O₃/80SiO₂/2280H₂O and crystallization for 7 days at 180 °C.¹ H-ZSM-5-75 sample was prepared according to a method described by Chen et al. with intended Si/Al = 94.² Medium-silica H-ZSM-5-27 sample (NH₄-form, Si/Al ratio = 27, supplier name SM-55) was obtained from AI-Si-Penta Zeolithe GmbH. 98% pure furfuryl alcohol (Sigma-Aldrich) was additionally purified by vacuum distillation prior to experiments. 1,4-dioxane (99.8%) was purchased from Sigma-Aldrich. 2-butanol was obtained from Acros Organics. MilliQ water was obtained from water purification system Synergy UV (Merck Millipore).

CLS microscopy: Prior to the catalytic staining and microscopy experiments, samples were deposited in small vials and calcined in an ashing furnace LVT 3/11 (Nabertherm) in three stages. First the samples were heated to 80°C (1°C/min) and kept at this temperature for 1 h in order to remove easily desorbing molecules. Next, they were heated to 120°C (1°C/min) and kept at this temperature for 1 h to remove physiosorbed water, minimizing undesirable hydrothermal dealumination. Finally, the samples were heated to 450°C (1°C/min) and subsequently kept at this temperature for 50 h to remove fluorescent contaminants. After allowing samples to cool, they were immediately used in catalytic staining experiments to prevent re-adsorption of fluorescent contaminants from the environment. Furfuryl alcohol oligomerization was used as a fluorogenic reaction. Portions of 0.5 mg zeolite samples were added to 1 ml of an appropriate solvent-furfuryl alcohol mixture (furfuryl alcohol content 10% vol) and left to react for 65 hours under magnetic stirring at room temperature. Stained zeolite samples were spin-coated on a clean #1 cover glass and sealed to polytetrafluoroethylene container via a silicone rubber gasket. As immersion media, 1 ml of the respective solvent was added. Confocal fluorescence images were acquired using a Fluoview FV1000 (Olympus) with an oil immersion objective lens (100X, 1.4 NA, Olympus) and λ exc = 532 nm, λ em = 545-645 nm. Further image analysis and processing was performed with Imagel v.1.49i software (NIH).

Elemental analysis: A Varian 720-ES (simultaneous ICP-OES with axially viewed plasma) (Varian Inc.) supplied with double-pass glass cyclonic spray chamber, concentric glass nebulizer SeaSpray (Glass Expansion) and “high solids” torch was used. The instrument features a Cooled Cone Interface, echelle monochromator and custom-designed Vistachip CCD detector (Agilent) mounted on a triple-stage Peltier device and cooled to -35°C. The instrument provides true simultaneous measurements and full wavelength coverage from 167 to 785 nm, given its ability to determination of a series of elements from one single run. Solutions were presented to the spectrometer using the Varian SPS3 Sample Preparation System (Varian Inc.).

TGA: H-ZSM-5-88050 mg samples were catalytically stained with 20 ml of 10% vol furfuryl alcohol-water/1,4-dioxane mixture for 65 hours under magnetic stirring at room temperature. After they were dried at 40°C for 30 minutes and analyzed in TGA Q500 V6.7 Build 203 (TA instruments) with platinum pan. The TGA method was the following: 5°C/min heating ramp to 800 °C in O2 atmosphere.

1H MAS NMR spectroscopy: 1H NMR experiments were performed at 298 K (BCU II) using a standard bore Bruker AVANCE III HD spectrometer operating at 500.87 MHz with a H/X/Y CP-MAS probe. Data collection was performed at spinning speeds of 10 kHz, using a π/2 flip angle, a repetition delay of 5s and chemical shift referencing with respect to TMS, using adamantane (chemical shift δ = 1.773 ppm) as secondary reference. To exclude fast-relaxing background signals originating from the probe, linear back-prediction of the FID-signal was performed using Bruker Topspin 3.5 software. The evolution of the 1H NMR spectra of H-ZSM-5-880 with increasing water and dioxane content are shown in Figures S8 and S9 respectively. The 1H NMR spectra were deconvoluted using DMFit software and quantified according to the method described by Houlleberghs et al.³

SRS microscopy: The H-ZSM-5-880 crystals were spin-coated on a clean cover glass #1 from an aqueous suspension. The zeolite-loaded cover glasses were theramly treated using the same procedure used for fluorescence microscopy experiments. The samples at 450°C were quickly transferred, while hot, into a cleaned desiccator under nitrogen. After being cooled down to room temperature, the desiccator was opened to briefly add a few drops of liquid benzonitrile (99%, Sigma-Aldrich) to the samples. After 24 h and prior to measurements, the desiccator was put under vacuum (1x10⁻¹ mbar) at 150°C in order to remove the excess of nitrile. The benzonitrile adsorbed in the H-ZSM-5-880 zeolites was
imaged using SRS microscopy.\textsuperscript{4,5} The experimental setup used for SRS imaging has been described elsewhere.\textsuperscript{4}
Figure S1. CLS micrographs of furfuryl alcohol oligomers accumulated at different depth within H-ZSM-5-27 crystals (lying on the [010] facet) using water (left) or 1,4-dioxane (right) as a solvent. Transmission image is presented for 1,4-dioxane based experiment. False color scale shows the observed fluorescence intensity adjusted for each slide; green arrow indicates the excitation light polarization orientation; scale bar: 5 μm.

Figure S2. CLS micrographs of furfuryl alcohol oligomers accumulated at different depth within H-ZSM-5-27 crystals (lying on the [100] facet) using water (left) or 1,4-dioxane (right) as a solvent. Transmission image is presented for 1,4-dioxane based experiment. False color scale shows the observed fluorescence intensity adjusted for each slide; green arrow indicates the excitation light polarization orientation; scale bar: 5 μm.

Figure S3. CLS micrographs of furfuryl alcohol oligomers accumulated at different depth within H-ZSM-5-82 crystals (lying on the [010] facet) using water (left) or 1,4-dioxane (right) as a solvent. Transmission image is presented for 1,4-dioxane based experiment. False color scale shows the observed fluorescence intensity adjusted for each slide; green arrow indicates the excitation light polarization orientation; scale bar: 10 μm.

Figure S4. CLS micrographs of furfuryl alcohol oligomers accumulated at different depth within H-ZSM-5-82 crystals (lying on the [100] facet) using water (left) or 1,4-dioxane (right) as a solvent. Transmission image is presented for 1,4-dioxane based experiment. False color scale shows the observed fluorescence intensity adjusted for each slide; green arrow indicates the excitation light polarization orientation; scale bar: 10 μm.
Figure S5. CLS micrographs of furfuryl alcohol oligomers accumulated at different depth within H-ZSM-5-75 crystals (lying on the [010] facet) using water (left) or 1,4-dioxane (right) as a solvent. Transmission image is presented for 1,4-dioxane based experiment. False color scale shows the observed fluorescence intensity adjusted for each slide; green arrow indicates the excitation light polarization orientation; scale bar: 5 μm.

Figure S6. CLS micrographs of furfuryl alcohol oligomers accumulated at different depth within H-ZSM-5-75 crystals (lying on the [100] facet) using water (left) or 1,4-dioxane (right) as a solvent. Transmission image is presented for 1,4-dioxane based experiment. False color scale shows the observed fluorescence intensity adjusted for each slide; green arrow indicates the excitation light polarization orientation; scale bar: 5 μm.

TGA investigation results:
To prove that concentrations of adsorbed solvent, reagent, and product are relevant for the catalysis, we used TGA to estimate the amounts of furfuryl alcohol and solvents adsorbed by the zeolite after being subjected to catalytic staining procedure. With TGA we have found that H-ZSM-5-880 crystals absorb up to 9.7% wt (water), 8.1% wt (dioxane), 9.3% wt (furfuryl alcohol and its oligomers, reaction in water), 3.2% wt (furfuryl alcohol and its oligomers, reaction in dioxane) (Figure S7). Hence we conclude that amounts of solvents, reactants and products absorbed are relevant to catalysis.

Figure S7. TGA of catalytically stained H-ZSM-5-880 sample.

1H MAS NMR spectroscopy investigation results:
1H MAS NMR spectroscopy investigation revealed a significant concentration of silanol groups in H-ZSM-5-880, which are strongly interacting with water already at low loadings as indicated by the significant impact of exchange phenomena on the spectra shown in Figure S8. Although dioxane does not exhibit exchange interactions with water or silanols, even in presence of dioxane the silanol signal is impacted by exchange (Figure S9), but less extensively. Whereas in water, the silanol signal disappears due to exchange after addition of 2 mg of water to a rotor containing 47 mg of zeolite, the silanol peak was still observable as a shoulder (shifted and broadened) after addition of 15.6 mg of dioxane. The latter demonstrates that the traces of water present in dioxane and in the calcined zeolite are still in exchange with silanol and thus chemically interact with it, even when the water is strongly diluted in dioxane.

Using the calibration curve determined for water in H-ZSM-5-880 (Figure S10), the concentration of silanol defects was estimated from the spectrum of the calcined zeolite sample. In the 1H NMR spectrum for this sample (Figure S8, green trace), two peak envelopes corresponding to silanol (~2 ppm) and water (~4.5 ppm) are visible. Quantifying the silanol-derived signal provides an estimated minimal concentration of 0.194 mmol OH per gram zeolite, which corresponds to a Si/SiOH ratio of about 82.
**Figure S8.** $^1$H NMR of H-ZSM-5-880 with standard addition of water (2.0, 4.6, 6.5, 8.9, 10.8, 15.8 mg H$_2$O added to a rotor containing 47.4 mg zeolite). The spectrum of the calcined sample without water added (green trace) was magnified with by a factor 128.

**Figure S9.** $^1$H NMR of H-ZSM-5-880 with standard addition of 1,4 dioxane (2.0, 3.6, 5.6, 7.6, 9.9, 15.6 mg 1,4 dioxane added to a rotor containing 49.3 mg zeolite). Blue trace: calcined sample. The inset shows the impact of exchange on some traces, using the same colors as the main figure.

**Figure S10.** Calibration curve for quantification of water in H-ZSM-5-880. The linear correlation (dotted line) has an $R^2 = 0.9994$. The calibration curve was generated and analysed according to the method described by Houlleberghs et al."
**SRS microscopy investigation results:**

The vacuum treatment used during the preparation of the samples allowed to eliminate the excess of liquid benzonitrile without removing the molecules physisorbed within the pores of the zeolite crystals. The geometrical constraints of the MFI framework lead to an anisotropic orientation of the remaining adsorbed benzonitrile molecules that are tightly fitting inside the ZSM-5 pores. This well-defined orientation of the adsorbed molecules has been highlighted for ZSM-5 zeolites loaded with toluene, where the molecules are either located at the intersection of the straight and sinusoidal channels along the former, or in the sinusoidal channels. We assume that benzonitrile displays a similar behavior since its dimensions are close to those of toluene. Thus, the dependence of the Raman signal associated with the stretching of the nitrile function on the orientation of the incident light polarization can be used to assess the arrangement of adsorbed benzonitrile molecules and thereby provides insights into the local pore organization. Highly sensitive chemical imaging by stimulated Raman scattering (SRS) microscopy allows to obtain this information in a spatially resolved manner.

The chemical mapping of benzonitrile molecules adsorbed in H-ZSM-5-880 lying on its [010] facets at various depths is presented in **Figure S11** on the right. Two distinct regions can be observed for zeolite crystals in this orientation. The central region, corresponding to an intergrowth, where the intensity of the SRS signal is the strongest due to the presence of benzonitrile molecules along the straight channels, parallel to the incident polarization.

The chemical mapping of benzonitrile adsorbed in H-ZSM-5-880 crystals lying on their [100] face is in agreement with the results presented above (**Figure S11**, left). In this case, the main crystal body shows a strong signal originating from the benzonitrile molecules located along the straight channels parallel to the incident polarization.

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