

Supporting Information

Nanoscale Infrared Imaging of Zeolites Using Photoinduced Force Microscopy

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Section S1: Experimental Details on Materials Synthesis

A. Materials

Tetraethylorthosilicate (TEOS, 99%, Sigma-Aldrich), tetra-n-propylammonium hydroxide (TPAOH, 35 w%, Alfa Aesar), tetra-propylammonium bromide (TPABr, 98%, Sigma-Aldrich), aluminum isopropoxide (> 98%, Sigma-Aldrich), ammonium sulfate ((NH₄)₂SO₄, 99.5%, Acros organics), NH₄NO₃ (Acros Organic, 99+%), sodium silicate solution (Na₂O(SiO₂)_x·xH₂O, ~10.6% Na₂O, ~26.5%SiO₂, Sigma-Aldrich), aluminum sulfate octadecahydrate (Al₂(SO₄)₃·18H₂O, 98%, Sigma-Aldrich), sulfuric acid (H₂SO₄, 95%, reagent grade, Fischer Scientific), ethanol (CH₃CH₂OH, absolute, Biosolve) were used as received. Quartz plates (LSP Quartz B.V.) were also used as supports in this study. The supports were cleaned prior to use by immersing in a 50 wt % hydrogen peroxide solution for 45 min, then rinsed with deionized H₂O, and dried at 333 K prior to seed layer deposition. The large coffin-shaped ZSM-5 crystals (~ 20×20×100 μm³) have been provided by ExxonMobil (Machelen, Belgium) and their synthesis has been previously reported.¹ The crystals were calcined at 823 K (ramp rate of 5 K min⁻¹, 6 h hold) followed by triple ion exchange with a 10 wt% ammonium nitrate (>99%, Acros Organics) solution at 353 K. Then, the material was converted into proton form by calcination at 823 K (ramp rate of 5 K min⁻¹, 6 h hold).

B. Preparation of pure-Si MFI seeds

The preparation of pure-Si MFI crystals (2.14 × 1.34 μm²) followed the method of Yoon and co-workers.² The pure-Si MFI crystals were synthesized from a solution composition of 6 TEOS:0.9 TPAOH:620 H₂O. The synthesis solution was prepared by introducing TEOS into the solution containing TPAOH and H₂O. The mixture was transformed into a clear solution after stirring in a sealed liner for 24 h at room temperature. The clear solution was then filtered through a filter paper and charged into a Teflon-lined autoclave. The

hydrothermal reaction was carried out under rotation oven at 423 K for 12 h. The seeds crystals were calcined in an air oven at 823 K for 30 h, with a ramp rate of 1.0 K min⁻¹, to remove TPA⁺.

C. Preparation of *b*-oriented zeolite ZSM-5 thin-films

Perfectly *b*-oriented pure-Si MFI seed monolayers on a glass plate were prepared by manual assembly, following well-established techniques.³ For preparation of the thin-films using TPA⁺ as the structure-directing agent (SDA), the secondary growth media (SGM) with composition of 1 SiO₂:0.022 Al:0.2 TPAOH:200 H₂O:0.1 (NH₄)₂SO₄ was prepared by adding TEOS into the mixture of TPAOH and deionized H₂O under stirring in a sealed liner at room temperature for 4 h. Aluminum isopropoxide was added to the solution and stirred for 1 h. Then (NH₄)₂SO₄ was introduced to the solution. After 30 min of stirring, the solution was filtered and transferred to a 20 mL Teflon-lined autoclave with the seeded substrate horizontally placed at the bottom of the autoclave. The hydrothermal secondary growth was placed in a static oven at 423 K for 15 h. After the required reaction time, the autoclave was removed from the oven and quickly cooled to room temperature by immersing in cool H₂O. As-synthesized zeolite films on substrates were carefully removed from the autoclave and washed with copious amounts of deionized H₂O and dried in air at 333 K.

For preparation of the SGM using ethanol as the SDA, a solution comprising the required amount of Al₂(SO₄)₃·18H₂O for specified Si/Al ratios, 0.34 g H₂SO₄ and 33.99 g of H₂O was added to a sodium silicate solution made by mixing 4.37 g of sodium silicate and 32.67 g H₂O. Then, the 1.38 g of ethanol was added to give a resulting solution with a final composition of 1 SiO₂:X Al:1.611 Ethanol:200 H₂O, (X = 0, 0.004, 0.008 and 0.022). The solution was filtered and transferred to a 20 mL Teflon-lined autoclave with seeded substrate horizontally placed at the bottom of the autoclave. The hydrothermal secondary growth was carried out in a static oven at 453 K for 24 h. After the reaction, the autoclave was removed from the oven and quickly cooled to room temperature by immersing in cool H₂O. As-synthesized zeolite thin-films on substrates were carefully removed from the autoclave and washed with copious amounts of deionized H₂O and dried at 333 K.

Section S2: Characterization and Testing of Zeolite Thin-Films

A. Scanning electron microscope

The images of as-synthesized seed layers and ZSM-5 films were examined by the scanning electron microscope (SEM) XL-30 (Philips) instrument operating at an acceleration voltage of 5 kV. Before measurement the surface of the film was coated with Pt of about 5 nm thickness to reduce charging effects.

B. Confocal fluorescence microscopy

The TPA⁺ and ethanol directed zeolite ZSM-5 thin-films for confocal fluorescence microscopy (CFM) measurements were synthesized on silicon wafers and quartz plates, respectively, to prevent contamination from glass. All zeolite thin-films were first treated with 0.2 M NH₄F solution for 6 h to remove the outermost amorphous silica layers that can block the channels of the thin-films.² Then the films

were calcined in an air oven at 823 K for 20 h, with a ramp rate of 1.0 K min^{-1} , to remove the organics. The calcined samples were ion-exchanged with a 1 M NH_4NO_3 solution (Acros Organic, 99+%) overnight at 343 K followed by a 7 h calcination at 823 K in an air flow oven with a ramp rate of 1.0 K min^{-1} .

The CFM measurements were conducted using a Nikon ECLIPS 90i upright confocal laser scanning fluorescence microscope with a $100\times 0.73\text{ NA}$ or a $50\times 0.55\text{ NA}$ dry objective lenses. Fluorescence microphotographs were collected using 561 nm (a 575 nm long-pass filter) laser light.

C. Photoinduced force microscopy

Details of the Photoinduced force microscopy (PiFM) can be found in the proof-of-concept paper from Molecular Vista.⁴ Typically, a commercial AFM microscope operated in dynamic noncontact mode with an integrated off-axis parabolic mirror is used. The excitation source is a tunable mid-IR quantum cascade laser (QCL) with a pulse width of 30 ns and an adjustable repetition rate that is set to the difference frequency between the first and second mechanical resonances of the AFM cantilever, approximately 1.6 MHz for this study. The AFM is operated so that the second mechanical mode detects the surface topography and the first mechanical mode detects the photoinduced force. The cantilever resonances are independent eigenmodes, allowing for the topography and PiFM to be recorded simultaneously without crosstalk. The excitation laser is focused by the parabolic mirror to an elliptical spot with a size of 2λ and 2.5λ for the short axis and long axis, respectively. An average laser power of 1.0 mW is used at the sample surface.

D. Methanol-to-Hydrocarbons on zeolite ZSM-5 thin-films and large crystals

The methanol-to-hydrocarbons (MTH) process over the assembled zeolite ZSM-5 thin-films and large crystals was performed using a Linkam cell (THMS600) equipped with a temperature controller (Linkam TMS94) and its lid is equipped with a quartz window.

For zeolite ZSM-5 thin-films, the film fabricated on a silicon wafer or quartz plate was placed on the heating stage of Linkam cell, which was further connected to cooling water. The inlet of the reactor set-up was connected to the N_2 gas line, via a methanol saturator, whereas the outlet was vented out. For each MTH reaction, a highly *b*-oriented zeolite ZSM-5 thin-film was placed on the heating stage of a Linkam cell, which was attached to a temperature controller. Prior to the MTH reaction, the previously calcined film was first heated to 393 K at a rate of 30 K min^{-1} and held at this temperature for 60 min in an N_2 atmosphere. Subsequently, after the temperature increased to 623 K, acting as the carrier gas, a constant N_2 flow (40 mL min^{-1}) was introduced to a methanol saturator for a 4 h reaction.

For large zeolite ZSM-5 crystals, single, large zeolite crystals were placed on a glass plate in the reaction cell and subsequently heated to 393 K at a rate of 30 K min^{-1} under an oxidative atmosphere with an O_2 flow of 20 mL min^{-1} . Afterwards, the temperature was increased to 773 K a rate of 5 K min^{-1} under the same flow conditions and kept at that temperature for 60 min. Then the temperature

was decreased to the reaction temperature of 623 K under N₂ atmosphere. Once the temperature had stabilized, the N₂ flow (20 mL min⁻¹) was changed to run through a room temperature bubbler containing methanol. The reaction was run for 90 min, after which time the methanol flow was removed and the reactor was cooled to room temperature under N₂ atmosphere.

E. Assignment of IR spectra

Most references base the assignment of the broad band centered around 1100 cm⁻¹ to asymmetric stretching of internal tetrahedral atoms based on the original assignment⁵⁻¹⁰, and state that an increase in framework Al content will cause a shift to lower wavenumbers due to the longer Al-O bond compared to the Si-O bond¹¹ as well as the lower mass of Al compared to Si,¹⁰ though it is known that the shift is also sensitive to cations and pretreatments, so care needs to be exercised in interpreting shifts of the band.^{10,11} In the present work, a gradual shift of the band around 1100 cm⁻¹ and its eventual split into two bands were observed by studying a series of zeolite with a wide range of Si/Al ratios from 45 to ∞ , consistent with the previous infrared spectroscopy research on ion exchanged zeolites with increasing contents of cations larger than than Si.¹² The weaker shoulder at ca. 1000 cm⁻¹ has been assigned to a vibration involving \equiv Al-OH nests due to cation vacancies.⁹ The complexity of the assignment of the IR bands for zeolites requires further investigations using advanced spectroscopy techniques with high sensitivity, like PiFM, etc., and accurate simulation methods.

Section S3: Supplementary information Figures S1-S5

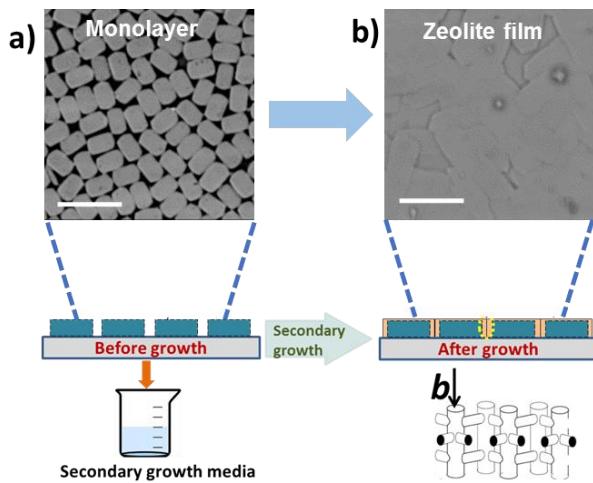


Figure S1. Schematic of the procedure for the fabrication of zeolite ZSM-5 thin-films using the secondary growth method. A pure-Si MFI a) monolayer was prepared using manual assembly method, and a continuous b) zeolite ZSM-5 thin-films formed by immersing the monolayer into secondary growth media for a specified time for secondary growth using tetrapropylammonium hydroxide or ethanol as the structure-directing agents. Note that the white scale bar represents 5 μm .

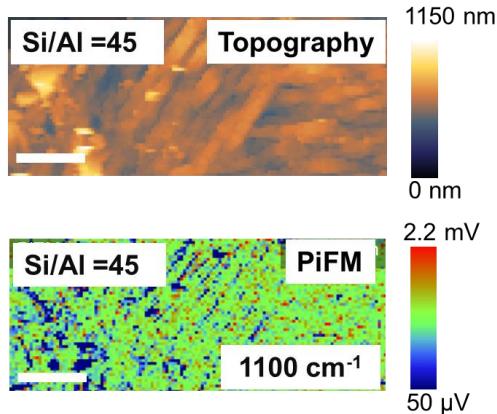


Figure S2. Measurement of Tetrapropylammonium (TPA^+) -directed zeolite ZSM-5 thin-films with $\text{Si/Al} = 45$ using Photoinduced force microscopy (PiFM). Top and bottom are the topography and the corresponding framework vibration observed by PiFM at 1100 cm^{-1} of the zeolite ZSM-5 thin-film grown in a secondary growth media with $\text{Si/Al} = 45$. Note that the white scale bar represents 1 μm . The results show that the TPA-directed zeolite ZSM-5 thin-film grown in the secondary growth media with $\text{Si/Al} = 45$ has significant overgrowth with needle-like zeolite crystal features.¹³

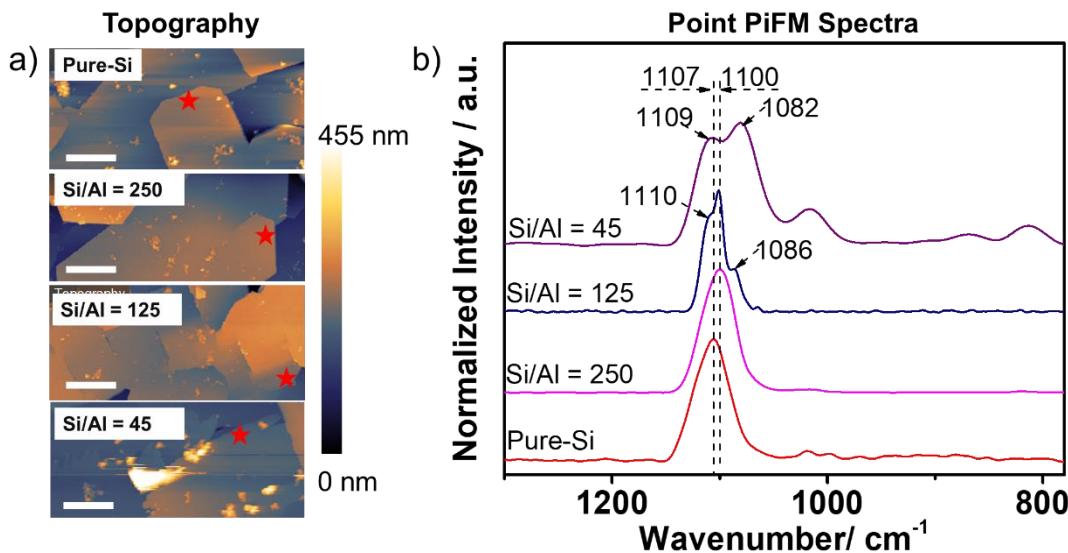


Figure S3. Point spectra measurement of zeolite thin-films with various Si/Al ratios using Photoinduced force microscopy (PiFM). a) AFM topography of zeolite thin-films grown in secondary growth media solutions with various Si/Al ratios. b) The corresponding framework vibration observed by PiFM in the locations highlighted in a) with red stars. Note that the white scale bar represents 1 μ m. The results show a gradual red shift to lower wavenumbers and finally split in the asymmetric vibration band in four different films with increasing Al content, demonstrating the influence of increasing the content of the framework Al^{3+} .

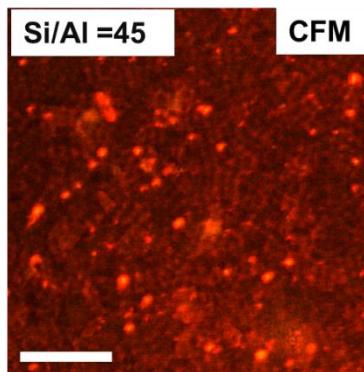


Figure S4. Image of ethanol-directed zeolite ZSM-5 thin-film with Si/Al = 45 using confocal fluorescence microscopy (CFM). The result shows honeycomb-like fluorescence structures from hydrocarbons, that formed in the catalytically active regions located in the inter-crystal spaces between the siliceous seed crystals. Note that the white scale bar represents 20 μ m.

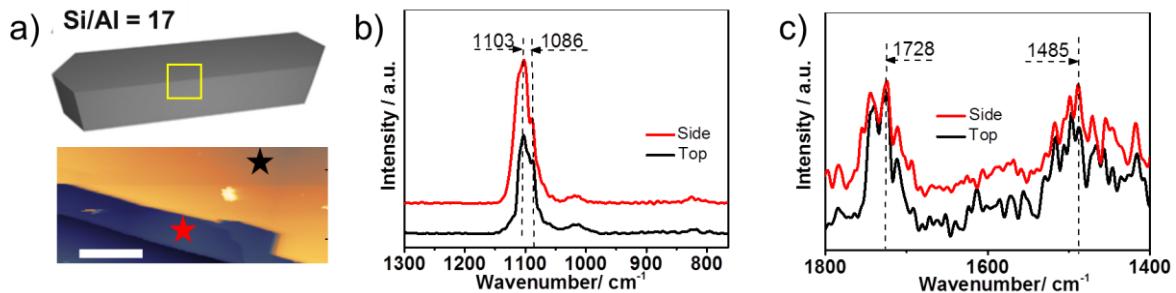


Figure S5. Point spectra measurement of large zeolite crystal using Photoinduced force microscopy (PiFM). a) Schematic model (top) and AFM topography (bottom) of the highlighted area in the large zeolite crystal with a bulk Si/Al ratio of 17. b-c) The corresponding b) framework vibration and c) hydrocarbon observed by PiFM in the locations highlighted in a). Note that the white scale bar represents 1 μm . The results show that PiFM is also sensitive to large zeolite crystal, demonstrating the possibility of PiFM for studying functional materials.

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