Supporting Information

Few-Unit-Cell MFI Zeolite Synthesized using a Simple Di-quaternary Ammonium Structure-Directing Agent

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Experimental procedures

1. Synthesis of the OSDA

The first step was the synthesis of bis-1,5(tributyl ammonium) pentamethylene bromides (denoted as tri-Bu-dC5(Br)2) using nucleophilic substitution of dibromopentane and tributylamine. In a typical synthesis procedure, 0.15 mol (34.491 g) of 1,5-dibromopentane (Millipore-Sigma, 97%) and 0.45 mol (83.410 g) of tributylamine (Millipore-Sigma, 99%) were dissolved in 300 mL ethanol in a three-neck 1 L flask. Ar was purged into the reactor through a sparger for a few minutes to exchange the air and kept flow at 20 mL/min during the synthesis. The flask was covered with Al foil to prevent possible degradation of the reagents. The system was heated to reflux at 90 °C for 4 days. After cooling down to room temperature, the solvent was evaporated using a rotary evaporator resulting in a semi-solid paste. Ethyl acetate was added while stirring to disperse and precipitate the solid, which was then collected using filtration to obtain white solid. One more round of rinse with ethyl acetate and filtration was performed to further purify the dibromide salts. Residual solvents were removed by rotary evaporation under vacuum. The purity of the product was checked by 1H and 13C NMR in D2O, and the results are shown in Figure S1 and Figure S3 (bottom trace), respectively.

The second step was the anion exchange of the dibromide salts to their hydroxide forms using AmberTec™ UP550 OH Anion Exchange Resin (Millipore-Sigma, 1.3 mequiv./1 mL) in a batch process. The obtained hydroxide solution was concentrated by rotary evaporation under vacuum. The concentration of the final solution was determined by titration using 0.1 M HCl and phenolphthalein as an indicator.

2. Synthesis of zeolites

Synthesis of pure-silica FDP zeolites (Si-FDP)

In a typical synthesis, aqueous solution of tri-Bu-dC5(OH)2 with a weight percentage of 30% was added into a FEP bottle followed by DI water. Tetraethyl orthosilicate (TEOS, 98%, Millipore-Sigma) was added drop-wise to the above SDA solution while stirring. The resulted solution was hydrolyzed under magnetic stirring for 24 h within a closed FEP bottle. A clear sol was formed with molar composition of 1SiO2 : x tri-Bu-dC5(OH)2 : yH2O : 4EtOH, where x varied between 0.1 to
0.25 and \( y \) varied between 8 to 38. The sol was transferred into Teflon liner and sealed into stainless steel autoclaves and heated at 120 °C for certain times while rotating. Specifically, for synthesis using high water content of \( \text{H}_2\text{O}/\text{SiO}_2 \) of 38, the heating time was 7 to 9 days, and for \( \text{H}_2\text{O}/\text{SiO}_2 \leq 13 \), the heating time was 2 to 7 days. For the study of the influence of \( \text{EtOH} \) on the crystallization, the \( \text{EtOH} \) produced from the hydrolysis of TEOS was removed by air purge during the hydrolysis. The total weight was monitored and DI water was added to compensate its loss during evaporation.

The products were washed and centrifuged until the pH was close to 7, and then dried at 70 °C overnight. Calcination was performed at 550 °C for 12 h in air in a static muffle furnace.

**Synthesis of aluminosilicate FDP zeolites (Al-FDP)**

Two aluminum sources, aluminum sulfate octadecahydrate (Millipore-Sigma, \( \geq 97\% \)) and aluminum isopropoxide (Millipore-Sigma, \( \geq 98\% \)) were used. For a typical synthesis, tri-Bu-dC5(OH)\(_2\) (30\( \% \)), DI water, NaOH and aluminum sulfate octadecahydrate were mixed and stirred to prepare a clear solution. Then, TEOS was added into the above solution drop-wise while stirring. After hydrolysis at room temperature for 24 h, a clear sol with molar composition of \( 1\text{SiO}_2 : 0.0025\text{Al}_2\text{O}_3 : 0.15 \text{tri-Bu-dC5(OH)}_2 : 0.005\text{NaOH} : 8\text{H}_2\text{O} : 4\text{EtOH} \) was obtained, which was transferred into Teflon liner and then sealed into a stainless-steel autoclave. It was heated at 120 °C while rotating in a preheated oven for 5 days, and quenched with tap water. The product was washed and centrifuged until pH was close to 7. The final cake was dried at 70 °C for 12 h. Calcination was performed at 550 °C for 12 h in air in a static muffle furnace.

**Synthesis of stanosilicate FDP zeolites (Sn-FDP)**

tri-Bu-dC5(OH)\(_2\) (30\( \% \)), DI water and SnCl\(_4\)•5H\(_2\)O (Millipore-Sigma, 98\%) were mixed until a clear solution was obtained. TEOS was added drop-wise into the above solution. The mixture was stirred for 24 h to obtain a clear sol with a molar composition of \( 1\text{SiO}_2 : 0.01\text{SnO}_2 : 0.15 \text{tri-Bu-dC5(OH)}_2 : 8\text{H}_2\text{O} : 4\text{EtOH} \), which was transferred into Teflon liner and then sealed into a stainless steel autoclave. It was heated at 120 °C statically in a preheated oven for 7 days, and quenched with tap water. The product was washed and centrifuged until pH is close to 7. The final cake was dried at 70 °C for 12 h. Calcination was performed at 550 °C for 12 h in air in a static muffle furnace.
Ion-exchange of aluminosilicate FDP zeolite to proton form

The calcined aluminosilicate FDP zeolite was mixed with 1 mol/L ammonium nitrate solution to yield a 5w% suspension, which was heated at 80 °C while stirring for 5 h to exchange the Na⁺ with NH₄⁺. The product was recovered by centrifugation. This procedure was repeated 3 times. The final product was washed with DI water, dried at 70 °C and calcined at 550 °C for 6 h in air in a static muffle furnace.

Commercial MFI zeolites

Commercial aluminosilicate MFI (CBV8014) zeolite was purchased from Zeolyst.

3. Characterization

X-ray diffraction

Wide angle powder X-ray diffraction (PXRD) data of the obtained products were collected in a PANalytical X’pert X-ray diffractometer with a Cu Kα radiation (λ=1.5418 Å). Low angle PXRD data were obtained in a Bruker -AXS D5005 diffractometer with 2.2 kW sealed Cu source, the scanning range was 0.6 to 10° 2θ (0.012 °/step and duration of 20 s). The size of the crystalline domains was estimated using the Scherrer equation applied to the deconvoluted peaks at ca. 8.0°, 9.1°, 23.5° and 24.5°. The X-ray diffraction pattern of the standard LaB₆ powder was used to correct for the instrumental broadening contribution to the observed peak-profile broadening.

PDF analysis

The X-ray PDF measurements were carried out at the beamline 28-ID-1 at National Synchrotron Light Source II (NSLS-II), at Brookhaven National Laboratory. The X-ray PDF data were collected at room temperature at a wavelength of 0.16635 Å. Diffracted X-rays were detected using a PerkinElmer detector (200 μm × 200 μm pixels) with a sample-to-detector distance of 203 mm.

Fourier transform infrared

Fourier transform infrared (ATR-FTIR) spectra were collected using a ThermoNicolet Nexus 670
FTIR Spectrometer equipped with KRS-5 ATR accessory with diamond and sapphire anvil fittings and volatile sample cover.

Transmission electron microscopy

Samples for all transmission electron microscopy (TEM) investigations were prepared by grinding the samples in a quartz mortar and pestle followed by suspension in DI water. The samples were sonicated for 10 minutes and then immediately drop-casted onto a copper grid coated with holey carbon film supported on a uniform ultra-thin carbon film (Ted Pella Inc.). The grid was air-dried at room temperature. HRTEM imaging was performed on a FEI Technai G2 F30 (S)TEM operating at 300 kV using a Gatan K2 Summit camera, operated in the counting mode. Individual frames of 3710 × 3838 pixels with 0.5 s exposure were acquired, drift corrected on Digital Micrograph and summed. Additionally, HRTEM imaging was also performed on an FEI Titan at 200 keV using a 2k by 2k BM-Ultrascan CCD camera.

Samples for high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) were stored under vacuum (10^{-6} torr) prior to STEM experiments to minimize contamination. HAADF-STEM images and STEM-EDX maps were acquired on an aberration-corrected FEI Titan 60-300 (S)TEM, equipped with an analytical Super-Twin pole piece, CEOS DCOR probe corrector, and a SuperX EDX detector. The microscope was operated at 200 kV with a STEM incident probe convergence angle of 25.5 mrad and the HAADF detector collection angles of 39 and 200 mrad. EDX spectrum maps were acquired using the Bruker Esprit software at an electron dose rate of approximately 0.32 e/Å²s. All scans used a 9 μsec pixel dwell time with probe step size of 2 nm for sample with Si/Sn atomic ratio of 105.

Scanning electron microscopy

Samples for scanning electron microscopy (SEM) imaging were prepared by drying a droplet of suspension in DI water on a Si wafer at room temperature. The images were collected on a Thermo Fisher Helios G4 FIBSEM microscopy at 2 kV and 25 pA using a TLD detector.

Argon physisorption
Argon (-186 °C) adsorption was performed using a commercially available automatic manometric sorption analyzer (Quantachrome Instruments AutosorbiQ MP). Prior to adsorption measurements, the samples were outgassed at 300 °C for 12 h under turbomolecular pump vacuum. The cumulative pore volumes and the pore size distributions were determined by the nonlocal density functional theory (NLDFT) from the adsorption branch using the Ar on zeolites/silica cylindrical pore method.[1]

Water vapor sorption

Water vapor adsorption measurements were performed using an automatic volumetric sorption system (Quantachrome, Autosorb iQ). The vapor unit comprises of a manifold heater (50 °C) and circulation fan inside the insulated manifold compartment, plus a vapor generator and control components. The vapor generator consists of a glass vial, similar to a small Erlenmeyer flask, approximately 5.0 cm long. Double distilled water (vapor source) was filled in the vial, and the stem portion of the vial attaches to the vacuum-tight fitting. The generated vapor is supplied to the volumetric sorption unit without condensation as the manifold temperature is maintained at 50 °C. Prior to the adsorption measurements, 100-130 mg of zeolite was placed into an adsorption cell and pretreated at 300 °C for 3 h under vacuum. In the method utilized, the total amount of water vapor admitted into the system and the amount of water vapor remaining after reaching the adsorption equilibrium were determined from the results of appropriate P-V-T measurements using Quantachrome software. The sample bath temperature was maintained around 25 °C. In order to obtain a full isotherm, 20 adsorption points in the P/P₀ range 0.05-0.9 were obtained.

Solid-state nuclear magnetic resonance spectra

Solid state MAS and cross polarization MAS spectra were recorded using a Bruker 500 MHz Avance spectrometer and a Bruker 4 mm MAS probe. The operating frequencies are 99.5, 125.5, 130.3 and 186.3 MHz for ²⁹Si, ¹³C, ²⁷Al and ¹¹⁹Sn nuclei, respectively. About 50 mg of sample in powder form was packed into a 4 mm rotor at ambient conditions and spun at 8000 Hz for ²⁹Si and ¹³C MAS NMR, 12000 Hz for ²⁷Al MAS NMR and 11000 Hz for ¹¹⁹Sn MAS NMR. For ²⁹Si MAS NMR, 4 microsec-90 deg pulses was applied and the free induction decay signal was recorded under ¹H
decoupling condition and with a repetition delay time of 60 sec. 512 scans were averaged. $^{13}$C CPMAS was achieved at the similar rf power condition and with 1 ms contact time. 0.5 microsec-$\pi/18$ angle pulse was used with strong $^1$H decoupling for $^{27}$Al MAS NMR and 512 transients were averaged. Chemical shifts in ppm were calibrated externally to TMS for $^{13}$C and $^{29}$Si and 1 M aqueous solution of Al(NO$_3$)$_3$ for $^{27}$Al NMR. $^{119}$Sn chemical shift was calibrated using an external MAS NMR signal of SnO$_2$ powder at -604.3 ppm. The sample rotor was then inserted into a 5 mm glass NMR tube and attached to a vacuum gas manifold for dehydration procedure by evacuating at 150 °C for 3 hours. Dry O$_2$ gas was introduced into the dehydrated powder in order to reduce $^{119}$Sn relaxation time before MAS NMR measurement.

**Bronsted acid sites evaluation**

The steady state pyridine and 2,6-DTBP titrations during ethanol dehydration were performed in a upflow packed bed reactor. The reactor consisted of a 4 mm I.D. quartz U-tube which was loaded with ca. 50 mg of catalyst pressed and sieved to size fraction of 106-250 μm. The catalyst bed was placed between two plugs of inert quartz wool, above which the void volume was reduced using inert quartz chips (SiO$_2$, 850-4750 μm, Sigma Aldrich). Temperature measurements were made using a 1/16” type-K thermocouple (Omega) placed directly above the catalyst bed, while a second thermocouple was placed in the furnace used to control the temperature using a PID temperature controller (OMEGA, CN-7800). Prior to introducing any reactant, the catalyst bed was calcined in-situ at 400 °C at 3 °C min$^{-1}$ and held for 1 hour under a 40 mL STP/min stream of air. The catalyst bed was then cooled down to the desired reaction temperature and flushed with a stream of He (60 mL STP/min) prior to introducing the vapor phase reactant stream. Analysis of the vapor phase products was performed using an online gas sampling gas chromatograph (Agilent, 7890A) equipped with a quantitative carbon detector (QCD, POLYARC) in conjunction with a flame ionization detector (FID). Separation of the various products and reactant in the GC were performed using an HP-PLP Q column (Agilent, 19091P-QO4).

Liquid ethanol was fed into a vaporization section through a 1/16” PEEK capillary line (0.01” ID), where a syringe pump (Cole Parmer 74905) series equipped with a gas tight syringe (SGE) controlled the liquid flow rate (fixed at 1 μl/min). The vaporization section consisted of resistively
heated and temperature-controlled aluminum tube, inside which the liquid feed was vaporized and swept with a helium carrier gas regulated by a mass flow controller (Brooks, 5850S). Helium flow rates were fixed in these experiments at 60 mL STP/min. The vaporized stream of ethanol in helium was then passed through a switching section, consisting of a heated 6-port valve (Vici Valco, DL6UWE), from which the stream could be sent either directly to the analysis section (GC, Agilent 7890A) or through the reactor first. Analysis of the vapor stream as it by-passed the reactor and sent directly to the analysis section, allowed the verification of the molar flow rate carbon into the reactor. Once a steady stream of ethanol was ascertained through bypass gas-sampling injections, the 6-port valve was switched, allowing the vaporized ethanol stream to contact the catalyst bed. Subsequent gas-sampling injections allowed for the quantification of different reaction parameters, and it was found that DEE was the only reaction product observable at maintained conversions (< 0.7%). Once the initial transients subsided and a steady-state was achieved, an instantaneous switch was made from an ethanol feed to the one containing pyridine (molar EtOH/Pyridine ~503) or DTBP (molar Ethanol/DTBP~808). Both switches led to a drop in DEE formation rates; while pyridine was able to quench the rates entirely, the rates under DTBP reduced but did not drop to zero. Reaction turnover frequencies were calculated as the slope of the mass-normalized ethanol turnover rate vs. cumulative pyridine uptake [mol/g] (Eq.1):

\[ TOF = \frac{\text{rate before titrant introduction [mol EtOH/g cat./min]}}{\text{cumulative Pyridine uptake to completely quench rates [mol/g cat.]}} \]  

Eq. 1

The fraction of external acid sites was calculated using two different criteria, given by Eq.2, and Eq.3, respectively:

\[ f_{ext} = 1 - \frac{\text{rate after DTBP saturation}}{\text{rate prior to DTBP introduction}} \]  

Eq. 2

\[ f_{ext} = \frac{\text{cumulative uptake of DTBP}}{\text{cumulative uptake of pyridine}} \]  

Eq. 3

The values obtained using the two different methods were found to be in good general agreement, validating the accuracy of the measurements.

Infrared spectroscopy using pyridine as a base probe

Infrared (IR) spectrum was collected on a Nicolet™ iS50 Fourier-transform infrared spectroscopy (FTIR) spectrometer with a Hg-Cd-Te (MCT, cooled to -196 °C by liquid N2) detector by averaging
128 scans at 2 cm\(^{-1}\) resolution in the 4000 – 600 cm\(^{-1}\) range and were taken relative to an empty cell background reference collected under dynamic vacuum (< 0.01 Torr) at 150 °C, 225 °C and 300 °C. Detailed procedure has been reported in a previous work.\(^2\)

UV/Vis spectroscopy

UV/Vis spectrum was collected from a Varian Cary 4000 UV-vis spectrometer in diffuse reflectance mode.

4. Catalytic reactions

Methanol to hydrocarbons

Methanol conversion reaction data were obtained using a quartz, packed-bed reactor (4 mm inner diameter). Quartz wool was placed below the catalyst bed to hold it in place. The reactor temperature was maintained using a tube furnace equipped with a Watlow temperature controller and a K-type thermocouple. Prior to reaction, 22.2 mg of the catalyst was heated in helium (Praxair, 99.999%) flowing at 30 mL/min to 550 °C for 30 min before it was cooled to the reaction temperature.

In a typical experiment, 0.42 mL/h methanol (Sigma-Aldrich, HPLC, ≥99.9%) was introduced into a He (Praxair, 99.999%) stream using a syringe pump (KD Scientific, Legato 100 series). Product streams were analyzed by gas chromatography using an Agilent 6890A GC fitted with a Plot-Q capillary column (30 m × 0.32 mm × 0.25 μm) and a flame ionization detector.

The methanol conversion (\(X\)) is defined as:

\[
X = \left[1 - \left(\frac{C_{\text{eff}}}{C_{\text{feed}}}\right)\right] \times 100 \% \quad \text{Eq. 4}
\]

where \(C_{\text{eff}}\) is the carbon-based molar concentration of both methanol and dimethyl ether (DME) in the effluent and \(C_{\text{feed}}\) is the concentration of methanol in the feed. The selectivity (\(S_i\)) of hydrocarbon product \(i\) is defined as:

\[
S_i = \left(\frac{C_i}{C_{\text{eff}}}\right) \times 100 \% \quad \text{Eq. 5}
\]

where \(C_i\) is the carbon-based molar concentration of hydrocarbon \(i\) in the effluent and \(C_{\text{eff}}\) is the total carbon-based molar concentration of hydrocarbons in the effluent.

Glucose isomerization

The catalytic reactions of Sn-FDP were carried out at 90 °C. In a typical reaction, 16 mg of catalyst,
1 mL of ethanol, and 8 mg of D-[\textsuperscript{13}C-C\textsubscript{1}]-glucose were added into a 20-mL thick-walled glass reactor sealed with a crimp top (PTFE/silicone septum) from VWR. The reactor was placed in an oil bath. At specific reaction times, the reactor was quenched in an ice bath, and samples were collected. The catalyst was filtered out of the solution, and the solvent was evaporated using a rotavapor at 65 °C. Sugars were then solubilized with D\textsubscript{2}O (2.00 g), following the hydrolysis step for 24 h at 100 °C. The product distribution was quantified by \textsuperscript{13}C NMR (512 scans) using inverse gate coupling for accurate quantification in a Bruker 400 MHz NMR spectrometer.

For the stability test, the catalyst was recovered after each reaction for 24 h and washed three times with water and three times with ethanol. The material was then dried at 100 °C for 4 h. A total of three cycles were performed. Rate constants were determined assuming first order kinetics (see Figure S20).

\[
-\ln \left( \frac{C_{\text{glucose}}}{C_{\text{glucose,0}}} \right)_w = k t \quad \text{Eq. 6}
\]

Although deactivation occurs (Table S2), the selectivity to fructose remains the same.
Figures and Tables

Figure S1. $^1$H NMR of tri-Bu-dC5 dibromide salt in D$_2$O. The numbers denote the corresponding position of the protons in the SDA dication as illustrated above the resonance peaks.
Figure S2. (a) XRD pattern and (b) SEM image of Si-MFI zeolite synthesized at 150 °C for 7 days using tri-Bu-dC5(OH)2 as SDA and a sol composition of 1SiO2 : 0.25 tri-Bu-dC5(OH)2 : 38H2O : 4EtOH. Scale bar in (b) is 2 μm.
Figure S3. Solid state $^{13}$C{$^{1}$H} CP MAS NMR spectrum of as-made Si-FDP (1) zeolite (top) and liquid $^{13}$C NMR spectrum in D$_2$O of pristine tri-Bu-dC5 dibromide (bottom). The resonances of carbon atoms in the as-made Si-FDP (1) zeolite are consistent with the resonances of the pristine tri-Bu-dC5 dibromide salt, confirming the integrity of the SDAs during crystallization process.
Figure S4. PDF patterns of (black) Si-FDP (4), (red) Si-FDP (1), (blue) Si-SPP and (orange) F-MFI. The Si-SPP was prepared according to our previous work,[3] and F-MFI was synthesized from fluoride medium using a reported procedure.[4]
Figure S5. FTIR spectra of calcined Si-FDP (1) and F-MFI zeolites. The presence of the characteristic absorbance band at 550 cm\(^{-1}\) confirmed that Si-FDP is consistent with the MFI topology. The band at 950 cm\(^{-1}\), an indicator of structural defects, was observed in FDP zeolites and absent in F-MFI.
Figure S6. Ar adsorption and desorption characterization of FDP zeolites in comparison with SPP zeolite. (a) pore size distributions; (b) NLDFT cumulative pore volumes and (c) isotherms.
Figure S7. SEM and TEM images of Si-FDP (2) zeolite synthesized under high SDA content as shown in Table 1. (a) Low magnification SEM and TEM (inset) images. (b) Wiener-filtered HRTEM of individual MFI-nanoparticle oriented near the [001] zone axis. Scale bar in (a) is 5 μm, in (a, inset) is 1 μm, in (b) is 10 nm and in (b, inset) is 1 nm⁻¹.
Figure S8. HRTEM images of the nano-crystalline domains for Si-FDP (1) zeolite (see Table 1). Red and orange rectangles in (c) and (d) indicate domains size of ca.10 nm. Scale bars are: (a) 100 nm, (b) 50 nm (Inset FFT 1 nm\(^{-1}\)), (c) and (d) 20 nm, and (e) and (f) 2 nm.
Figure S9. XRD patterns (a and b) and TEM images of the FDP zeolites synthesized at low water contents: (c and d) Si-FDP (3) and (e and f) Si-FDP (4). Scale bars in (c) and (e) are 200 nm and 100 nm, in (d) and (f) are 10 nm, and in (d and f, FFT inset) are 2 nm\(^{-1}\).
Figure S10. Thermal stability of Si-FDP zeolite determined at different calcination temperatures. (a) XRD patterns and (b) Ar adsorption and desorption isotherms. Calcination was performed at the indicated temperatures in a crucible placed in a static Muffle furnace in air for 6 h (heating and cooling rates were 4.5 °C/min).
Figure S11. (a) Solid-state $^{27}$Al MAS NMR spectrum of Al-FDP zeolites. (b) Solid-state $^{29}$Si MAS NMR spectra of Al-FDP zeolites. (c) XRD patterns of calcined Al-FDP zeolites synthesized under low water content.
Figure S12. EDX mapping and spectra of Al-FDP zeolites in proton form: (a) H-Al-FDP (1); (b) H-Al-FDP (2); (c) H-Al-FDP (3); (d) H-Al-FDP (4) and (e) H-Al-FDP (5).
Figure S13. TEM images of Al (a and c) and Sn (b and d) containing FDP zeolites with Si/Al and Si/Sn ratios of 157 (Al-FDP (1)) and 105 (Sn-FDP), respectively. Scale bars are 100 nm in (a and b), and 50 nm in (c and d).
Figure S14. IR spectrum of pyridine adsorbed on Al-FDP zeolite after saturation at 150 °C. The absorption band at 1545 cm$^{-1}$ is typical of pyridine interacting with Brønsted acid sites, and the absorption band at 1455 cm$^{-1}$ is assigned to the Lewis acid sites.
Figure S15. UV-Vis (a) and $^{119}$Sn MAS NMR (b) spectra of Sn-FDP with Si/Sn of 105. The absorption band at 210-220 nm region in the UV-Vis spectrum (a) originates from the framework Sn atoms.$^5$ The black trace in (b) is for calcined sample exposed to ambient conditions. The red trace in (b) is after dehydration treatment under dynamic vacuum at 150 °C for 3 h.

Figure S16. XRD pattern of the calcined Sn-FDP zeolite with Si/Sn of 105.
Figure S17. EDS spectrum of calcined Sn-FDP zeolite with Si/Sn of 105.
Figure S18. Crystallization of FDP zeolites. XRD patterns (a, c, e and g) and crystallization curves (b, d, f and h) of Si-FDP (a and b), Si-FDP synthesized without EtOH (c and d), Al-FDP (e and f) and Sn-FDP (g and h). The compositions used were as follows: (a and b): $\text{1SiO}_2 : 0.15 \text{ tri-Bu-dC5(OH)}_2 : 13\text{H}_2\text{O} : 4\text{EtOH}$; (c and d): $\text{1SiO}_2 : 0.15 \text{ tri-Bu-dC5(OH)}_2 : 15\text{H}_2\text{O}$; (e and f): $\text{1SiO}_2 : 0.01\text{Al}_2\text{O}_3 : 0.15\text{tri-Bu-dC5(OH)}_2 : 0.025\text{Na}_2\text{O} : 13.5\text{H}_2\text{O} : 4\text{EtOH}$; (g and h): $\text{1SiO}_2 : 0.01\text{SnO}_2 : 0.15 \text{ tri-Bu-dC5(OH)}_2 : 13.7\text{H}_2\text{O} : 4\text{EtOH}$. Synthesis was performed at 120 °C in a rotating (for a to f) or static (for g, h) autoclave using ca. 5 g of sol. The relative crystallinity is defined by the total integrated peak area at time t, over total integrated peak area at the longest time indicated for the corresponding graph; same amount of sample was used for each XRD pattern, and patterns were collected using identical scan parameters in the same instrument. Yield is defined based on the amount of zeolite collected at the longest time indicated for the corresponding graph. All materials in this figure were washed and centrifuged until the pH was close to 7, and then dried at 70 °C overnight. The zeolite yield with respect to the total silica present in the sol was also determined using the calcined (550 °C for 12 h in air in a static muffle furnace) product from the longest crystallization times shown in b, f and h and it was found to be ca. 70, 80 and 70%, respectively.
Figure S19. Particle size distribution of Si-FDP zeolites obtained at different crystallization times at 120 °C under rotation. The synthesis sol composition was 1SiO$_2$ : 0.15 tri-Bu-dC5(OH)$_2$ : 13H$_2$O : 4EtOH.
Figure S20. Fitting $-\ln(C_{\text{glucose}}/C_{\text{glucose,0}})/W$ versus time assuming first-order reaction in glucose.
Table S1. Textural properties of calcined FDP and SPP zeolites.

| Material   | Surface area (m²/g) | Pore volume (cm³/g) |
|------------|---------------------|---------------------|
|            | $S_{\text{total}}$ | $S_{\text{micro}}$ | $S_{\text{ext}}$ | $V_{\text{total}}$ | $V_{\text{micro}}$ | $V_{\text{meso}}$ |
| Si-FDP (1) | 605.9               | 164.5               | 441.4            | 0.824             | 0.066             | 0.758             |
| Si-FDP (3) | 640.9               | 102.3               | 538.6            | 0.842             | 0.030             | 0.812             |
| Al-FDP (2) | 666.7               | 102.5               | 564.2            | 0.975             | 0.028             | 0.947             |
| Si-SPP     | 628.6               | 102.5               | 526.1            | 0.978             | 0.029             | 0.949             |

[a] BET surface area determined from the adsorption data of P/P₀ between 0.1 and 0.3. [b] t-plot micropore surface area. [c] t-plot external surface area. [d] Total pore volume calculated from P/P₀ of 0.99. [e] t-plot micropore volume. [f] $V_{\text{meso}} = V_{\text{total}} - V_{\text{micro}}$. [g] Single unit cell pure silica SPP zeolite obtained by previously reported method. Note: the t-plot method was performed using the adsorption data of P/P₀ between 0.2 to 0.5.
Table S2. Stability of Sn-FDP for glucose isomerization in ethanol.

| Reaction cycle | k (g⁻¹ s⁻¹) | Selectivity to fructose (%) |
|----------------|-------------|-----------------------------|
| 1st            | 5.8         | 66                          |
| 2nd            | 3.9         | 61                          |
| 3rd            | 2.7         | 67                          |

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