Supporting Information

Experimental Section:

Materials: NaAlO₂ (99%), sucrose (AR), tetraethyl orthosilicate (TEOS, >99%), trimethoxymethylsilane (MTS, 98%), trimethoxy(propyl)silane (PTS, 98%), trimethoxy(octyl)silane (OTS, 98%) and hexadecyltrimethoxysilane (HTS, 85%) were purchased from Aladdin, Shanghai. Tetrapropylammonium hydroxide (TPAOH, 25wt.%) and NH₄Cl (AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. Chloroform, Trihexyltetradecylphosphonium bromine ([P66614][Br]), Methyltrioctylammonium chloride ([Aliquant336][Cl]), Tributylphosphine (P444) and bromoethane, succinimide (Suc) were purchased from Sigma Alddrich. All chemicals were used without any further purification.

Synthesis of the hierarchical H-ZSM-5 zeolite: In a typical procedure, Hierarchical H-ZSM-5 samples were synthesized by pre-crystallization process using organosilanes as mesopore templates. The molar compositions of the mixtures were controlled as Al_2O_3 : SiO_2 : TPAOH: HTS: $H_2O=1.1$: 30: 6: 1.5: 750. In a typical synthesis, NaAlO₂ and TPAOH were dissolved in H₂O and stirred for 0.5 h. Then, TEOS was added into the resulting solution under vigorous stirring. This aluminosilicate gel was stirred for 3 h at room temperature, and pre-crystalized at 90 °C for 12 h. Then, HTS was added into the gel and stirred at 90 °C for 3 h. The final mixtures were transferred into an autoclave and crystallized at 170 °C for 72 h. The precipitated products were filtered and washed with distilled water. The obtained samples were dried at 110 °C for 12 h and subsequently calcined at 550 °C in air for 6 h (1 °C/min). The resulted samples were denoted as Na-ZSM-5. Then Na-ZSM-5 was converted to the H-form by three consecutive exchanges in 1.0 M NH₄Cl solution at 80 °C for 8 h. After subsequently calcined at 550 °C in air for 6 h (1 °C/min), the samples were denoted as H-ZSM-5.

Synthesis of the acylamido anion functionalized branched ionic liquid ([P4442][Suc]): The acylamido anion functionalized branched ionic liquid ([P4442][Suc]) was prepared by neutralization reaction between proton donors and a solution of phosphonium hydroxide ([P4442][OH]) in ethanol. In a typical synthesis of [P4442][Suc], equimolar succinimide was added to an ethanol solution of phosphonium hydroxide ([P4442][OH]), which was prepared from [P4442][Br] by the anion-exchange method.1,2 The mixture was stirred at room temperature for 24 h. Then, ethanol and water were distilled off at 60 °C under reduced pressure. The product dried with P₂O₅ under vacuum at 60 °C for 24 h to reduce possible traces of water.

Synthesis of the porous zeolite liquids (H-ZSM-5-liquid/[P66614][Br]): To begin with, H-ZSM-5 (0.2 g) was dispersed in 5 mL chloroform and sonicated for 20 min. Then 0.5 g [P66614][Br] was added into the above solution and stirring for 1 h to form a stable solution. Then the resulting homogeneous solution was dried on a hot plate at 50 °C and was kept at 80 °C under vacuum for at least 72 h to get the H-ZSM-5-liquid/[P66614][Br]. Na-ZSM-5-liquid/[P66614][Br] was also prepared as a reference sample in a similar route except that the starting material was Na-ZSM-5 NPs instead of H-ZSM-5 NPs. Additionally, H-ZSM-5-liquid/[Aliquant336][Cl] and H-ZSM-5-liquid/[P4442][Suc] were also prepared and measured in a similar strategy except that the liquid matrixes are [Aliquant336][Cl] and [P4442][Suc], respectively.

Measurements: Viscosities were tested on the AR-G2 instrumentation by using a steel cone and steel plate geometry with 2° cone angle and a 40 mm diameter plate. Thermo-gravimetric analysis (TGA) measurements were taken under N_2 atmosphere with a heating rate of 10 °C/min by using TGA Q50 TA instrument. Differential scanning calorimetry (DSC) measurements were taken under N_2 atmosphere with a heating rate of 10 °C/min by using TGA Q50 TA instrument. Differential scanning calorimetry (DSC) measurements were taken under N_2 atmosphere with a heating rate of 10 °C/min by using the DSC Q100 TA instrument. Nitrogen adsorption isotherms were measured at 77 K using a TriStar 3000 volumetric adsorption analyzer manufactured by Micromeritics Instrument Corp. (Norcross, GA). Before measurements, samples were degassed in vacuum at 150 °C for at least 12 h. The BrunauerEmmett-Teller (BET) method was utilized to calculate the specific surface areas. NH_3 -TPD experiments were measured on a connected thermal conductivity detector (TCD). Typically, 50 mg of the zeolite was pretreated at 500 °C in He (20 mL/min) for 2 h and then cooled to 80 °C before NH3 adsorption for 40 min. Ammonia desorption measurements were achieved in the temperature range of 80~700 °C at a ramping rate of 10 °C/min. The

distribution of Lewis and Brønsted acids was determined by infrared spectroscopy of adsorbed pyridine (Vertex 70, Bruker). The analysis of Brønsted and Lewis acid sites was carried out using the absorption at 1545 and 1454 cm-1, respectively. For scanning electron microscopy (SEM) and transmission electron microscopy (TEM) characterization, pure H-ZSM-5liquid/[P66614][Br] was transferred to lacy carbon-coated 200-mesh copper TEM grids and dried in a vacuum oven before electron microscopy analysis, which was then characterized using a Hitachi HD-200 operating in scanning TEM (STEM) mode using a secondary electron (SE) and /or bright-field STEM detector operating at 200 kV. The samples used for Positron annihilation lifetime spectroscopy (PALS) were prepared by directly evaporating a 20 µL ²²NaCl solution (~3.7*10⁵ Bq) onto the surface of one of the two disks and, after the water evaporated, then covering that disk with the other disk. This "sandwich" was then wrapped in 10 μm thick aluminium foil. PALS measurements were performed at room temperature using the PALS system established within the Low-Activation Materials Development and Analysis Lab at Oak Ridge National Lab. Gas adsorption-desorption isotherms were obtained by using an Intelligent Gravimetric Analyser (Hiden Isochema, IGA) that combines accurate computer control of pressure and temperature with high-precision measurements of sample weight changes to acquire gas isotherms. The sample was loaded into a quartz sample container and sealed in the stainless steel chamber. The sample was dried and degassed at a temperature of 80 °C and a vacuum pressure of 1 mbar for a minimum of 5 h before the dry mass was recorded. Mass measurements were then acquired at increasing CO₂ pressures up to desired pressure, taking into account the buoyancy effect on the mass. The temperature of the sample was maintained using either a constant temperature recirculating water bath for the 298 K measurement.

Molecular Dynamics Simulation: Classical molecular dynamics (MD) simulations were carried out with the LAMMPS package.¹ The [P66614][Br] ionic liquid is modeled with the general Amber force field (GAFF)² and the atomic charges are fitted from the restrained electrostatic potential (RESP) at the B3LYP/6-31+G* level in Gaussian 09 package.³ The H-ZSM-5 zeolite is parameterized based on the INTERFACE force field⁴ with Al atoms occupying the T7, T8 and T12 sites to reach a Si/Al ratio of 31. The Lorentz-Berthelot rules were applied to the cross pairs of atoms of ion liquid/ion liquid and ion liquid/zeolite. The cutoff distance of 10 Å is chosen for the Lennard-Jones potential and the real-space part of the electrostatic potential. Long-range electrostatics is calculated with the 3D particle-particle-particle mesh (PPPM) algorithm. To model the interface between ion liquid and the zeolite, we use the slab model under periodic boundary conditions, consisting of four 1×2 pentasil layers cut along the [100] surface and 2×1 [010] surfaces of H-ZSM-5 unite cell built from the experimental lattice parameters of MFI type zeolite in general (20.09×19.74×13.14 Å³).⁵ Additional hydrogens are added to saturate the dangling Si-O bonds on the surface as the silanol groups and to create the Brønsted site on the oxygen of Al-O-Si bridge. Ten pairs of [P66614][Br] ion liquid molecules are inserted in the vacuum space of 40 Å in the perpendicular direction between slabs. The straight and sinusoidal channels of our model are longer than 40 Å to ensure enough space for the insertion of the longest alkyl chain of the [P66614][Br] ion liquid (about 20 Å). The geometry of the whole system is first optimized by 10000 steps followed by 5 ns equilibration in NPT ensemble at 298 K and ambient pressure with the time step of 1 fs. Another 5 ns NVT simulation is performed for production with the Nosé-Hoover thermostat corresponding to 100 fs.⁶

References

1. S. Plimpton. J. Comput. Phys. **1995**, 117, 1-19.

2. J. Wang; R. M. Wolf; J. W. Caldwell; P. A. Kollman; D. A. Case. J. Comput. Chem. 2004, 25, 1157-1174.

M. J. Frisch; G. W. Trucks; H. B. Schlegel; G. E. Scuseria; M. A. Robb; J. R. Cheeseman; G. Scalmani; V. Barone; B. Mennucci; G. A. Petersson; H. Nakatsuji; M. Caricato; X. Li; H. P. Hratchian; A. F. Izmaylov; J. Bloino; G. Zheng; J. L. Sonnenberg; M. Hada; M. Ehara; K. Toyota; R. Fukuda; J. Hasegawa; M. Ishida; T. Nakajima; Y. Honda; O. Kitao; H. Nakai; T. Vreven; J. A. Montgomery Jr; J. E. Peralta; F. Ogliaro; M. Bearpark; J. J. Heyd; E. Brothers; K. N. Kudin; V. N. Staroverov; R. Kobayashi; J. Normand; K. Raghavachari; A. Rendell; J. C. Burant; S. S. Iyengar; J. Tomasi; M. Cossi; N. Rega; J. M. Millam; M. Klene; J. E. Knox; J. B. Cross; V. Bakken; C. Adamo; J. Jaramillo; R. Gomperts; R. E. Stratmann; O. Yazyev; A. J. Austin; R.

Cammi; C. Pomelli; J. W. Ochterski; R. L. Martin; K. Morokuma; V. G. Zakrzewski; G. A. Voth; P. Salvador; J. J. Dannenberg; S. Dapprich; A. D. Daniels; Ö. Farkas; J. B. Foresman; J. V. Ortiz; J. Cioslowski; D. J. Fox. *Gaussian 09, Revision B.01*, Gaussian, Inc.: Wallingford CT, 2010.

4. F. S. Emami; V. Puddu; R. J. Berry; V. Varshney; S. V. Patwardhan; C. C. Perry; H. Heinz. *Chem. Mater.* **2014**, *26*, 2647-2658.

5. Ch. Baerlocher; L. B. McCusker. Database of Zeolite Structures. <u>http://www.iza-structure.org/databases/</u> (accessed May 04 2018).

6. (a) S. Nosé. J. Chem. Phys. 1984, 81, 511-519; (b) W. G. Hoover. Phys. Rev. A 1985, 31, 1695-1697.

 S_{BET} , S_{micro}, S_{meso}, V_{total} , V_{micro}, V_{meso}, Sample cm³·g⁻¹ m²∙g⁻¹ m²∙g⁻¹ m²∙g⁻¹ cm³·g⁻¹ cm³·g⁻¹ H-ZSM-5 zeolites 362.7 134.3 0.304 0.119 0.165 228.5

Table S1 Physical properties of the hierarchical H-ZSM-5 zeolites.



Fig. S1. a) Chemical structure of [BMIM][NTf₂] and b) CO₂ adsorption-desorption isotherms of [Bmim][NTf₂] and ZSM-5-liquid/[Bmim][NTf₂] collected at 298 K, respectively.



Fig. S2. XRD pattern of the hierarchical H-ZSM-5 zeolites.



Fig. S3. N_2 adsorption-desorption isotherms of the hierarchical H-ZSM-5 zeolites.



Fig. S4. NH₃-TPD patterns of the hierarchical H-ZSM-5 synthesized using hexadecyltrimethoxysilane.

The hierarchical H-ZSM–5 samples exhibited two peaks at approximately 200 °C and 450 °C in Figure S4, which represented weak (150.2 μ mol/g) and strong acidity (61.2 μ mol/g), respectively [Ind. Eng. Chem. Res. 2004, 43, 2610]. It was reported that the acid sites located on the external/mesopore surface have a lower acid strength than those inside the micropore system. Thus, in this work the acid located almost in the micropore system.



Fig. S5. Py-FTIR spectra of hierarchical H-ZSM–5 synthesized using hexadecyltrimethoxysilane: pyridine (up) anddimethyl pyridine (below).

We also measured the Py-FTIR spectra of hierarchical H-ZSM–5 to study the distribution of Brønsted (1545 cm⁻¹) and Lewis acidity (1450 cm⁻¹) in micropores (pyridine) and mesopores/macropores (dimethyl pyridine) as shown in Figure S5. For all the profiles, normalization processing to 1 g of catalyst is carried out. It was found that the hierarchical H-ZSM–5 not only showed high amount of Lewis acidity but also showed a certain amount of Brønsted acidity for both strong and weak acidity [Appl. Catal. B: Environ., 2015, 166-167, 327]. However, for acidity detected by dimethyl pyridine, it was found that no Brønsted/Lewis acidity in mesopores/macropores.



Fig. S6. (a) Chemical structure of the branched ionic liquid ([P66614][Br]), (b) MD snapshots showing the side alkyl chains preventing the ionic liquid from further filling the sinusoidal channel and (c) straight channel of H-ZSM-5 zeolite.



Fig. S7. The conditions to form hydrogen bonding are not satisfied in a) H-ZSM-5 NPs and b) Na-ZSM-5-liquid/[P66614][Br].



Fig. S8. Photographs of pure H-ZSM-5-liquid/[P66614][Br] at room temperature.



Fig. S9. The viscosity versus temperature trace of [P66614][Br].



Fig. S10. TGA traces of the H-ZSM-5-liquid/[P66614][Br] and [P66614][Br] at air atmosphere, respectively.



Fig. S11. a) SEM (scale bar =150 nm) and b) TEM images (scale bar = 100 nm) of H-ZSM-5 NPs.



Fig. S12. XRD pattern of [P66614][Br].



Fig. S13. Positron annihilation lifetime spectroscopy (PALS) of H-ZSM-5-liquid/[P66614][Br].

The annihilation lifetime of o-Ps (refer to the period between the generation and annihilation of o-Ps) can be correlated to the average pore size in the materials by the Tao-Eldrup model as following:

$$\tau_3 = 0.5 \times \left[1 - \frac{R}{R + \Delta R} + \frac{1}{2\pi} \sin\left(\frac{2\pi R}{R + \Delta R}\right) \right]^{-1}$$

Where au_3 refer to the o-Ps lifetime (ns), and ΔR is the empirical electron thickness that is generally taken to be 0.166 nm.



Fig. S14. Chemical structure of a) [Aliquant336][Cl] and b) [P4442][Suc].



Fig. S15. CO₂ adsorption-desorption isotherms of H-ZSM-5-liquid/[P4442][Suc] and H-ZSM-5-liquid/[Aliquant336][Cl] collected at 298 K, respectively.