Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information for

Ethanol & Water Vapor Adsorption in Methanol-Derived ZIF-71

Ryan P. Lively*[a], Michelle E. Dose[b], Joshua A. Thompson[b], Benjamin A. McCool[a], Ronald R. Chance[a,b], and William J. Koros[b]

[a]*Algenol Biofuels, 28100 Bonita Grande Drive, Bonita Springs, FL 34315, USA.*

[b]*School of Chemical & Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA*

* Corresponding Author

Experimental

MeOH ZIF-71 Synthesis:

A solution of zinc acetate (0.0734 g, 0.40 mmol) in 15 mL of methanol and a solution of 4,5-dichloroimidizole (0.2192 g, 1.60 mmol) in 15 mL of methanol, were combined in a sealed vial and let stand at room temperature for 24 hrs. The methanol was then removed from the vial using a pipette and the remaining crystals were soaked in chloroform (3 x 20 mL) for three days. To recover the crystals, the solution was centrifuged for 5 minutes at 8000 rpm and the chloroform was decanted. The crystals were then dried under vacuum at 50°C for 24 hrs to remove any of the remaining solvents from the crystals. Yield: 0.137 g, >90% based on zinc acetate.

Powder X-ray Diffraction

Powder X-ray diffraction patterns were obtained on a PAnalytical X'pert diffractometer operating with Cu Kα radtion and equipped with an X'celerator detector.

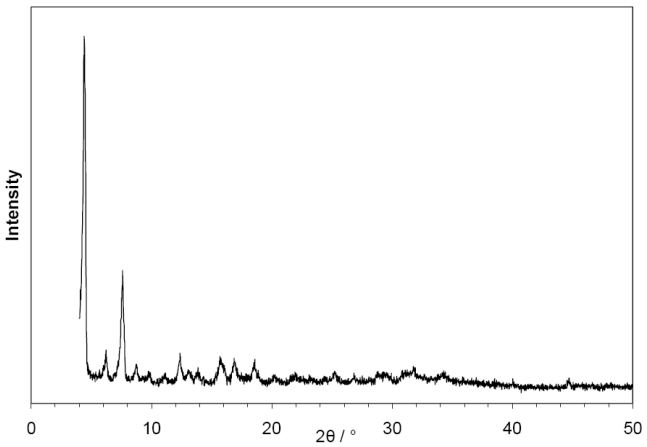

Fig.S1 PXRD pattern of ZIF-71 synthesized in methanol at room temperature. PXRD was taken after solvent exchange and drying at 50°C under vacuum for 24 hours.

SEM Imaging

Scanning electron microscopy (SEM) was used to evaluate the synthesized ZIF-71 crystal size. After solvent exchange and drying, the ZIF crystals were sputter-coated with a 10-20nm thick gold coating (Model P-S1, ISI, Mountain View, CA), and transferred to a high resolution Field Emission Scanning Electron Microscope, Leo 1530 (Leo Electron Microscopy, Cambridge, UK). Figure S1 shows a representative SEM image of ZIF-71.

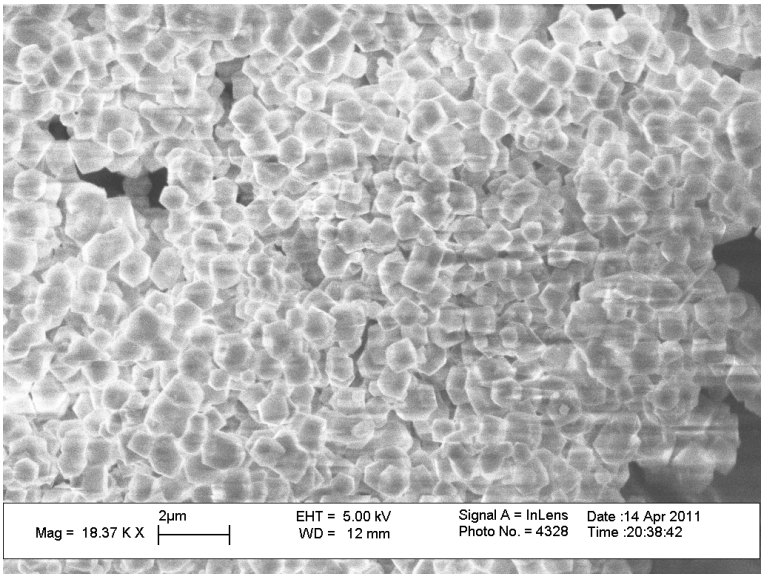

Fig. S2: SEM image of ZIF-71 synthesized in methanol at room temperature.

N_2 Physisorption

Brunauer-Emmett-Teller (BET) surface areas and micropore volumes (t-plot method) were calculated from N_2 physisorption measurements performed on an ASAP 2020 (Micromeritics). The sample was degassed at 200°C for 18 hours within the N_2 physisorption apparatus. Figure S2 shows the N_2 physisorption isotherm.

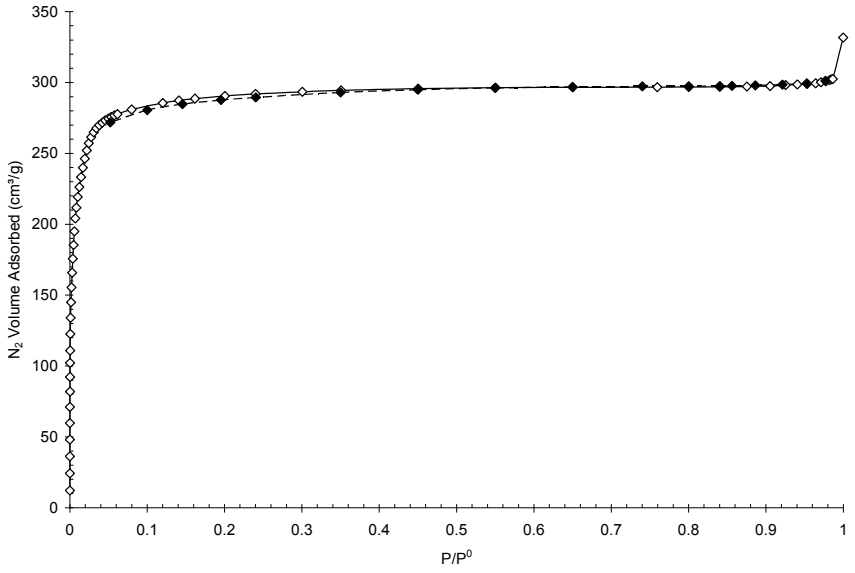

Fig. S3 N_2 physisorption isotherm on ZIF-71. Open symbols are adsorption, closed symbols are desorption.

TGA

A Netzsch STA 409 TGA was used, which could be programmed to control heating and cooling ramp rates and thermal soak times. The temperature program was: 10°C/min ramp to 700°C, air atmosphere at 50 mL/min. Buoyancy corrections were run before the ZIF-71 sample. The mass loss and the derivative of the mass loss is plotted in Figure S3.

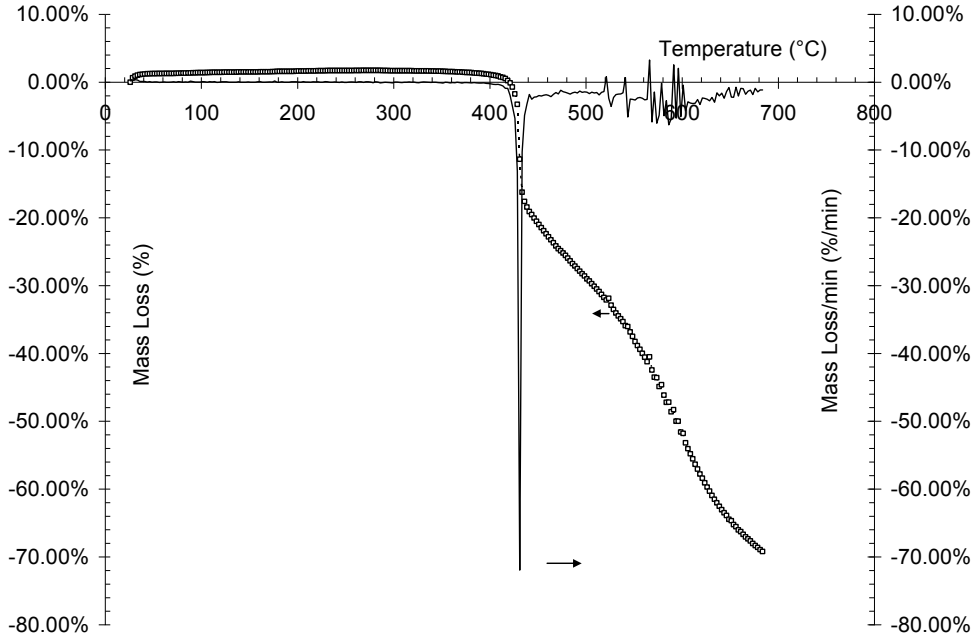

Fig. S4 TGA on ZIF-71.

Quartz-Spring Vapor Sorption

A McBain quartz-spring sorption system with an optical level reader (cathetometer) was used to measure vapor sorption into the ZIF-71 samples. This is a gravimetric technique which involves supporting the sample upon a calibrated quartz spring (GE Sensing, Houston, TX) within a temperature controlled chamber. The quartz spring can support a max load of 50 mg with a maximum extension of 200 mm. The cathetometer/spring combination has a measurement accuracy of 1.25μg The sample was held at 35°C, the manifold leading to the sample was held at 45°C to prevent condensation, and the vapor donor chamber was held at 22°C. After evacuating the chamber for 2 days (leak rate was less than 1 torr per day) and taking a reference point on the scale, the sample was isolated and the ethanol was degassed via a freeze-pump-thaw cycle (at least 5 cycles were used). Ethanol vapor was then introduced to the sample chamber by opening the valve to the vapor donor chamber, allowing the pressure to increase a few torr for each measurement. For each measurement, the time, temperature, pressure, and the reading on the cathetometer were recorded. With knowledge of the spring constant and the elongation of the spring, the total mass sorbed can be estimated.

After sorption was complete, the valve to the vapor donor chamber was closed and the vacuum pump was turned on. The vacuum valve was then slowly opened, allowing the pressure in the sample chamber to decrease by a few torr for each measurement. As in the sorption experiment, time, temperature, pressure, and scale reading were recorded for each point.

Comparison of water uptake into ZIF-71 with water uptake into silicalite-1

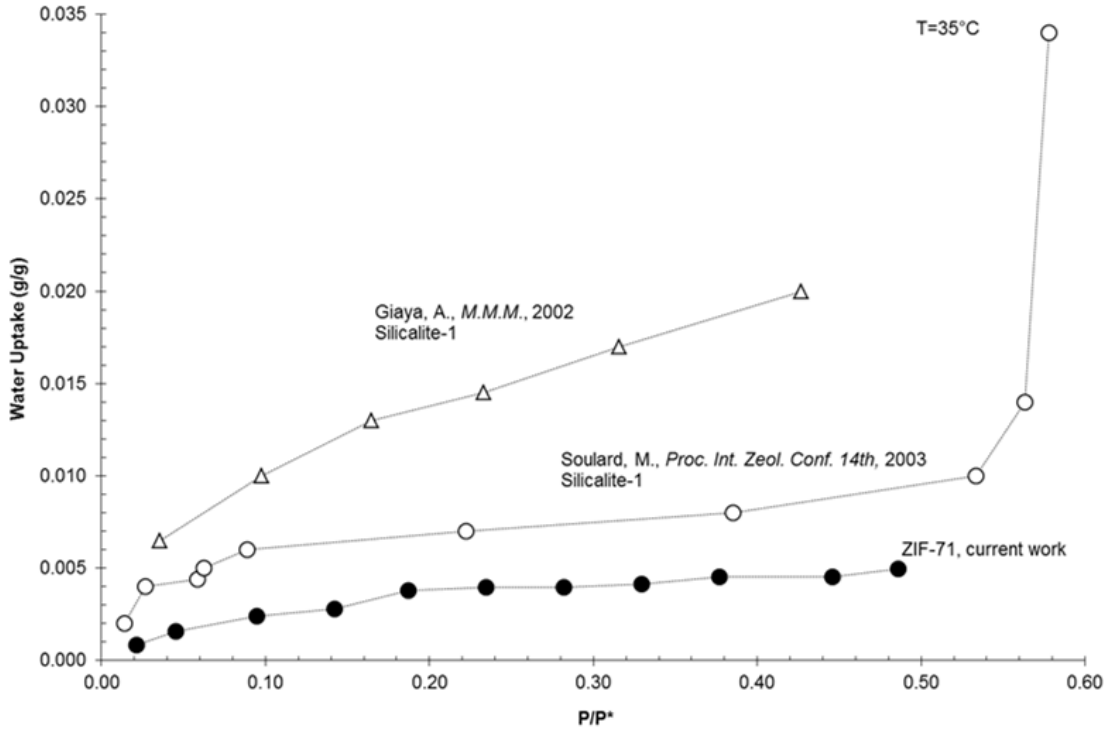

Fig. S5 Water uptake into ZIF-71 and silicalite-1 at 35°C