Electronic supporting information (ESI)
MIL-100(Al, Fe) as water adsorbents for heat hransformation purposes – a promising application

Felix Jeremias,[a,b] Anupam Khutia,[b] Stefan K. Henninger*[a] and Christoph Janiak*[b]

[a] *Dept. Thermally Active Materials and Solar Cooling, Fraunhofer Institute for Solar Energy Systems ISE, Heidenhofstr. 2, 79110 Freiburg, Germany. Fax: +49 761 4588 9000; Tel: +49 761 4588 5104; E-mail: stefan.henninger@ise.fraunhofer.de*
[b] *Institut für Anorganische Chemie und Strukturchemie, Universität Düsseldorf, 40204 Düsseldorf, Germany. Fax: +49 211 8112287; E-mail: janiak@uni-duesseldorf.de*

Additional E-mails
Felix Jeremias: felix.jeremias@ise.fraunhofer.de
Anupam Khuta: anupam.khutia@uni-duesseldorf.de

Synthesis and Activation

MIL-100(Fe): MIL-100(Fe) was prepared as reported in the literature (*Chem. Commun.*, **2007**, 2820-2822). For activation, the light orange solid product was centrifuged off and was heated (110°C) with 40 mL DMF for 4h. Then the powder was centrifuged off and mixed with 40 ml ethanol. The ethanol suspension was stirred at 60°C for 5h and then centrifuged. Finally the solid was stirred with 40 ml water at 100°C overnight (12h). Then it was centrifuged off and dried at room temperature.

*MIL-100(Al):*1.8 mmol (0.6659 g) of $Al(NO_3)_3$* 9 H_2O (Sigma-Aldrich, 98%), 1.2 mmol (0.3025 g) of trimesic acid trimethyl ester (Sigma-Aldrich, 98%), 4 mmol (0.4 ml) of 65 % nitric acid and 311 mmol (5.6 ml) of deionized water were placed in an autoclave and heated under static conditions for 72 h and 210°C. The resulting, white solid was centrifuged off, washed with deionized water and dried in air to yield MIL-100(Al)AS (as synthesized).
For activation, the MIL-100(Al)AS was dispersed in 30 ml of DMF (extra pure, Carl Roth), stirred for 1h, centrifuged off, redispersed again in 30 ml of DMF, stirred overnight, centrifuged off, dispersed in 30 ml of redistilled ethanol, stirred for 1 h, centrifuged off, redispersed again in 30 ml of redistilled ethanol, stirred overnight, centrifuged off, and finally dried in air at 60°C for 12 h. Overall yield was 260 mg of MIL-100(Al), activated.

Description of the Analytic Methods

Samples were vacuum-degassed at 120°C for 17h before the measurements. Nitrogen sorption isotherms were obtained on a Quantachrome® Nova. Water sorption isotherms were obtained volumetrically on a Quantachrome® Hydrosorb. For cycling measurements and calorimetric heat of adsorption measurements, the TGA/DSC apparatuses Setaram® Setsys Evolution 1750 and Setaram® TGADSC111 were used, both equipped with humidifiers of the Setaram® WetSys type. Powder X-ray diffractograms (PXRDs) were obtained on a Bruker® D8-Advance using a flat sample holder, with Cu-K_α radiation (40 kV/40 mA) and a Lynxeye® detector. Step size $\Delta 2\theta = 0.02°$, time per step = 4 s.

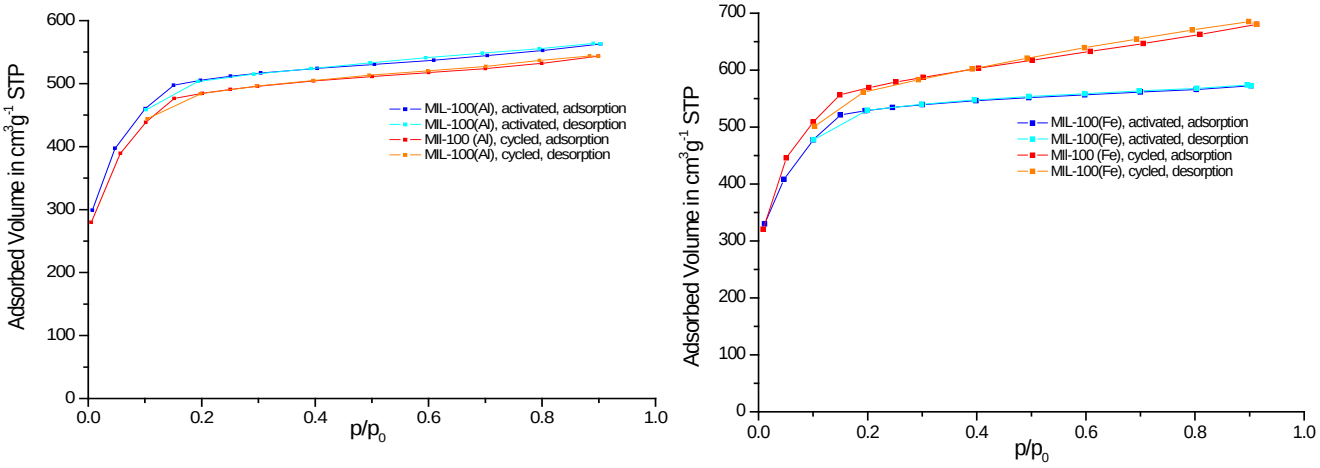

Fig. S1 Nitrogen sorption isotherms for MIL-100(Al) (left) and MIL-100(Fe) (right).

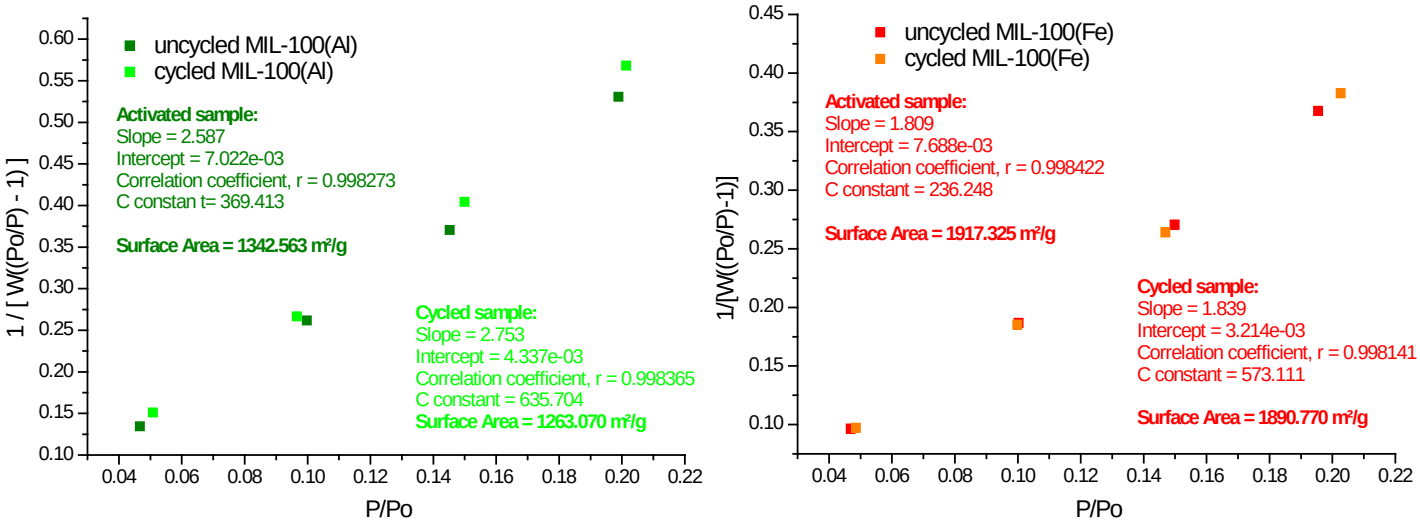

Fig. S2 BET plots for MIL-100(Al) (left) and MIL-100(Fe) (right) from N_2 sorption isotherms in Fig. S1.

Error bars in Fig. 4:

For the differential heat of adsorption graph (Fig. 4), errors have been calculated according to the Gaussian law of error propagation, assuming the following errors for each measured variable:

$\Delta T_1 = \Delta T_2 = 0.1$ K

$\Delta p_1 = 1$ % of measured value

$\Delta p_2 = ½$ of the respective interpolation interval (see following graph).