Metal-organic framework (MOF) aerogels with high micro- and macroporosity†

Martin R. Lohe [a], Marcus Rose[a], and Stefan Kaskel*[a]

Department of Inorganic Chemistry, Dresden University of Technology , Mommsenstraße 6, 01069 Dresden, Germany. Fax: +49 351 463 37287; Tel: +49 351 463 35155; E-mail: Stefan.Kaskel@chemie.tu-dresden.de

Elemental Analysis

The elemental analysis was performed at the Max-Planck-Institute for Chemical Physics of Solids, Dresden. The approximate molecular formula can be described as $Fe^{(III)}{}_3O(C_6H_3(COO)_3)_2NO_3 \cdot n\ H_2O \cdot m\ EtOH$. Table 1 shows the measured result and the calculated values for n=1.1 and m=1.

Element	% (wt., measured)	% (atom., measured)	% (wt., calc.)	% (atom., calc.)	deviation (atom.-%)
C	33.3±0.3	35.08	33.10	35.52	1.24
H	2.0±0.1	25.11	1.97	25.22	0.44
O	41.4±0.5	32.74	39.91	32.15	1.85
N	1.92±0.08	1.73	1.93	1.78	2.34
Fe	23.5±0.3	5.33	23.09	5.33	0.07
	Σ= 102.12	Σ= 100.00			

Table S1: Measured and calculated values for the elemental composition of the obtained Fe-BTC gels

Magnetic Measurements

Magnetic measurements were carried out at 300 K on a vibrating sample magnetometer (VSM) by Quantum Design. In Figure 1 one can see a part of the loop for a FeBTC xerogel and a MIL-100(Fe) sample.

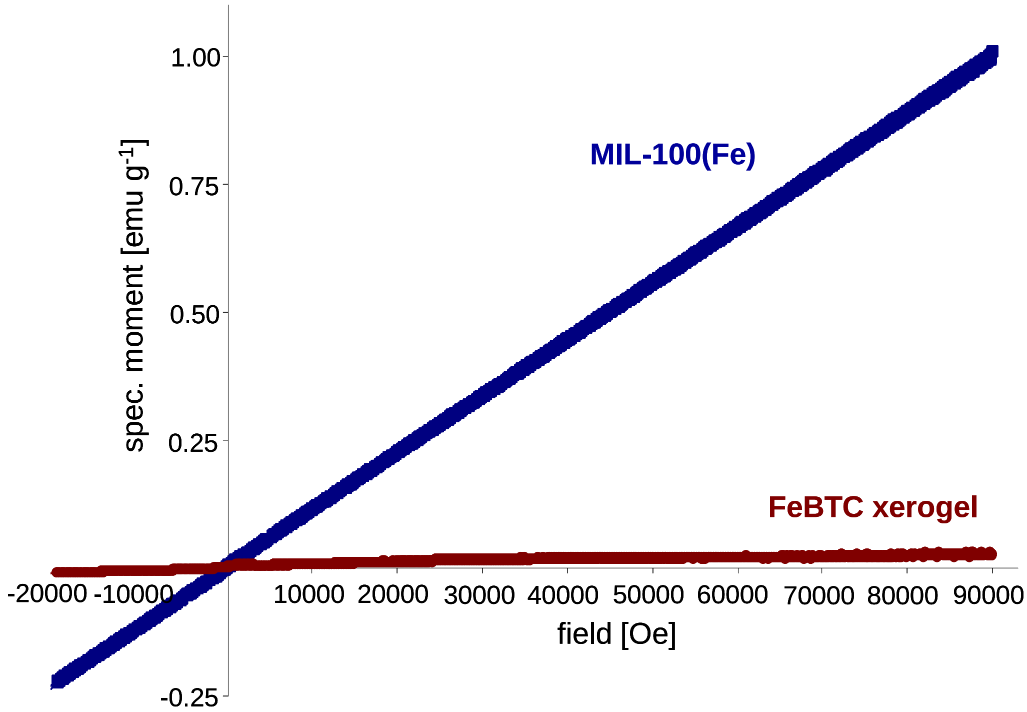

Figure S2: Specific magnetic moment of an amorphous FeBTC xerogel compared to a crystalline MIL-100(Fe) sample.

Both MOF materials show paramagnetic behavior while the specific magnetic moment of the xerogel is significantly lower than that of MIL-100(Fe).

TG/DTA Analysis

Figure S3 shows a TG curve of a FeBTC xerogel sample under air. The dried gel (dried overnight at 80°C in a cabinet desiccator) is stable up to approximately 200 degrees centigrade under oxidizing atmosphere.

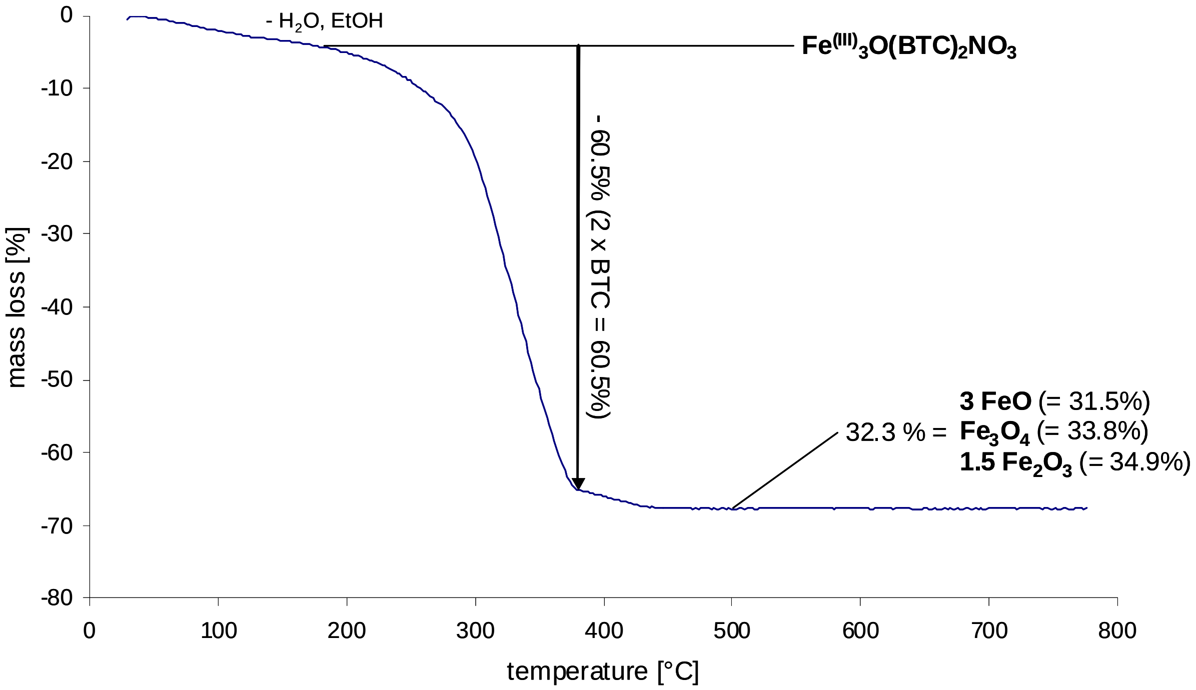

Figure S3: TG curve of a FeBTC xerogel sample measured in air.

Infrared and Raman spectroscopy

The infrared spectra were collected with an ATR (attenuated total reflection) setup. All samples (even the crystalline MOF) show a small absorption band at about 1700 cm^{-1} which can be attributed to an acid carbonyl stretching vibration. Due to many overlapping bands it was not possible to perform an accurate and reproducible fitting of the spectra of the gels. However, the amount of free carboxylic acid groups is below 10 %.

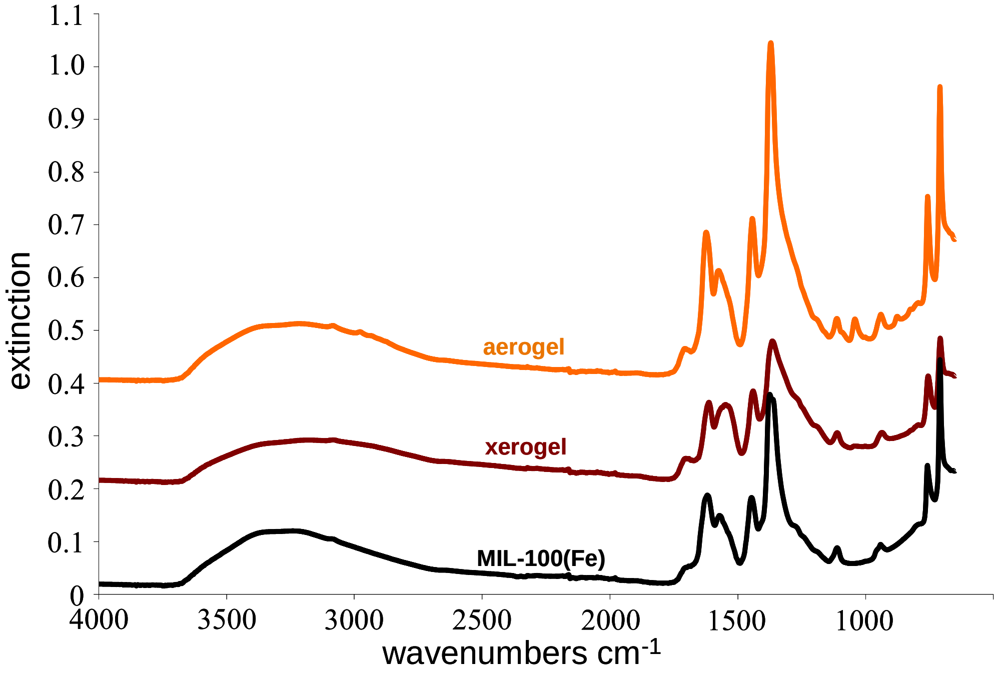

Figure S4: Infrared spectra of a xerogel (offset: 0.2), an aerogel (offset: 0.4) and a MIL-100(Fe) sample.

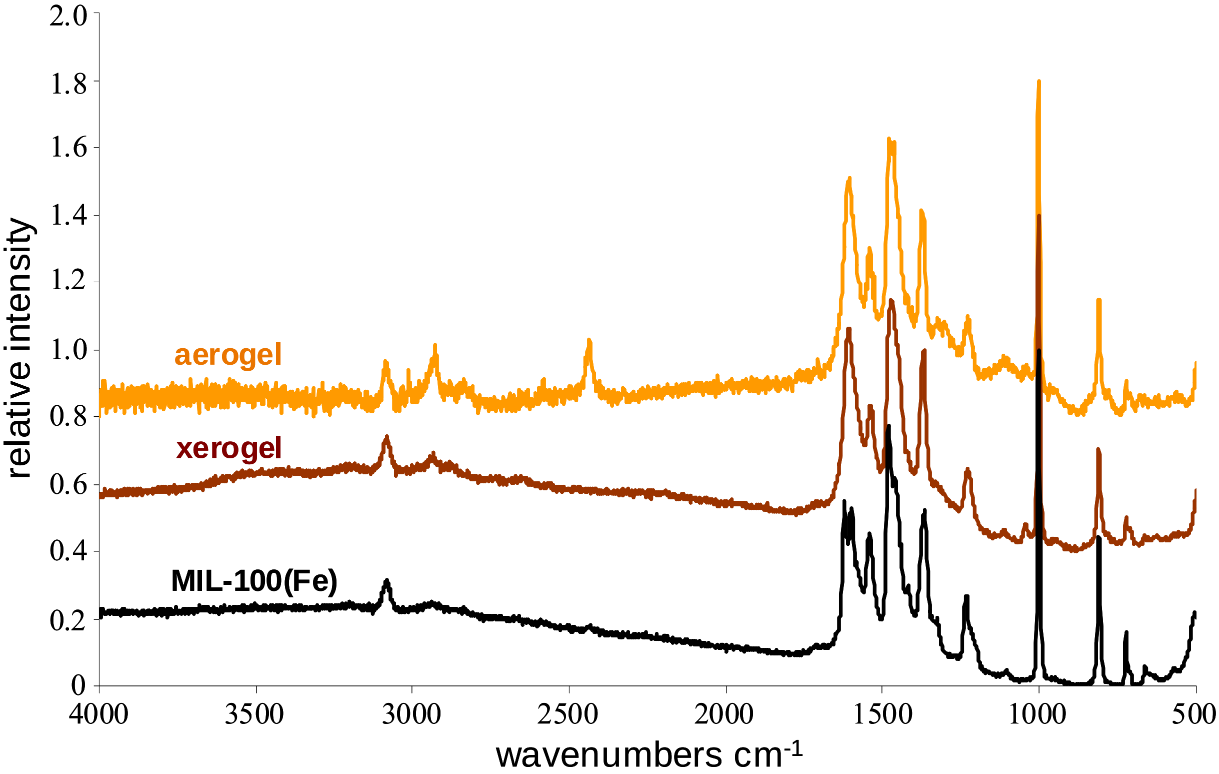

Figure S5: Raman spectra of a xerogel (offset: 0.4), an aerogel (offset: 0.8) and a MIL-100(Fe) sample.

Low pressure nitrogen physisorption measurements

The low pressure adsorption measurements were performed on an Autosorb device by Quantachrome Instruments at 77 K.

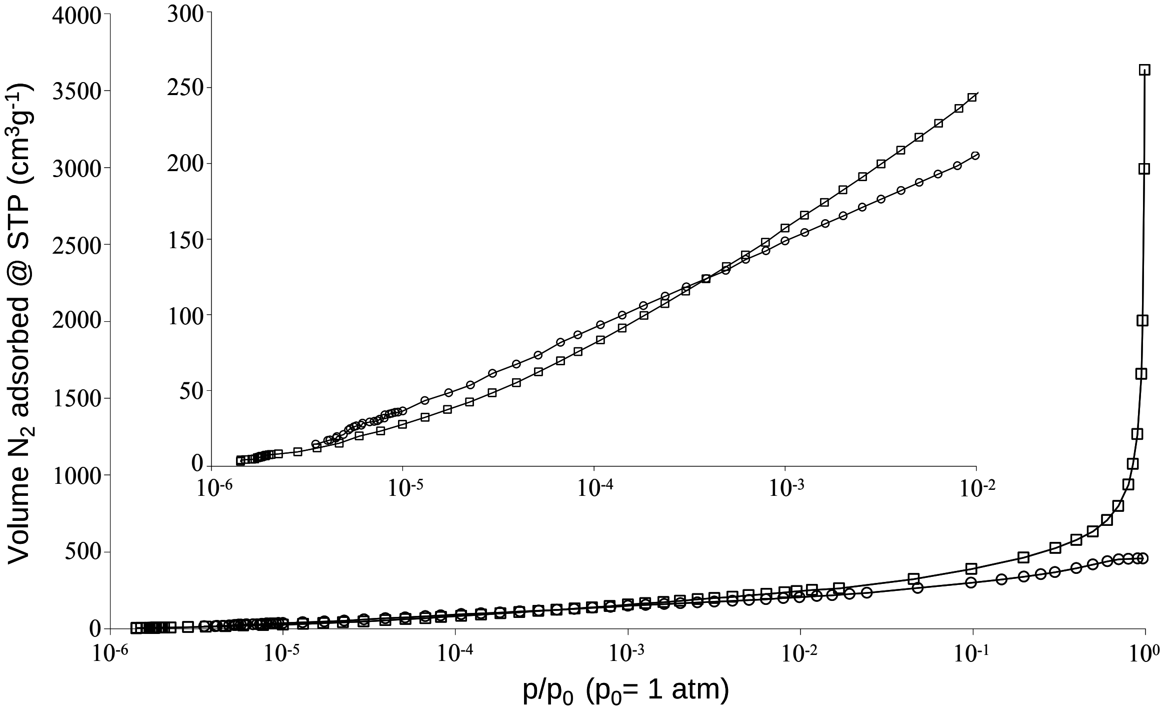

Figure S6: Low pressure nitrogen adsorption isotherms of a xerogel (○) and an aerogel (□) sample measured at 77 K.

X-ray diffraction data

Transmission powder diffraction measurements we carried out on a STOE Stadi-P diffractometer with Cu-Kα1 radiation at room temperature. The patterns shown in Figure S7 do not show significant differences for as synthesized samples and materials treated at 200°C. Further heating to 600 °C destroys the gels, leading to iron oxide.

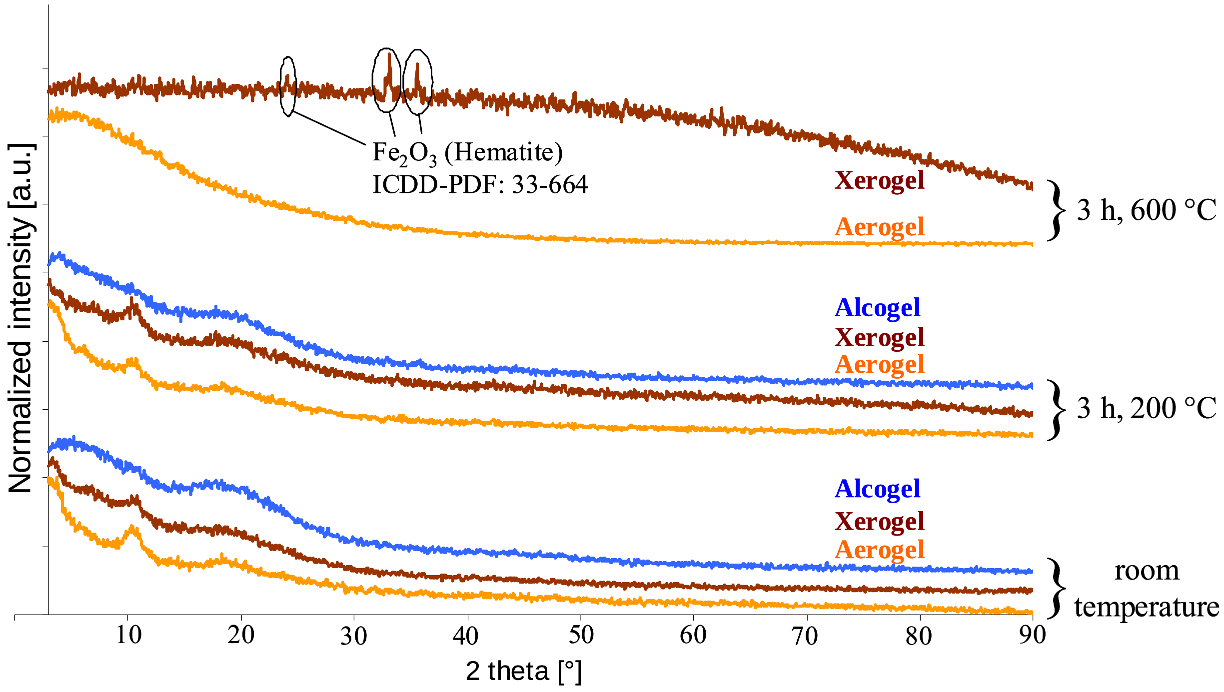

Figure S7: Powder diffraction patterns of different as synthesized and heat treated samples

High pressure methane adsorption

The Gibbs excess adsorption isotherms in Figure S8 show that the adsorbed amount in the aerogel is about 40 % lower than for the crystalline MOF at room temperature due to the significantly lower amount of micropores per volume.

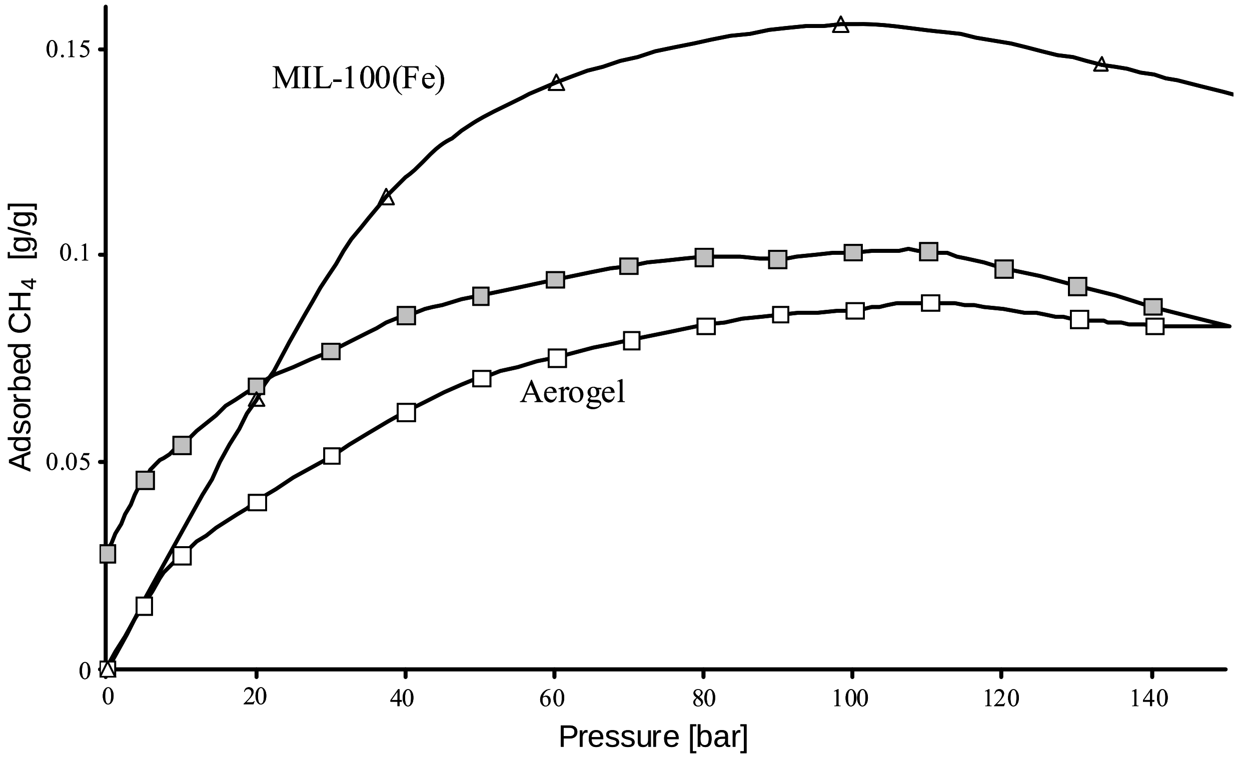

Figure S8: high pressure gravimetric methane adsorption isotherms of an aerogel (□) and a MIL-100(Fe) (Δ) sample measured at 303 K.