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Supplementary Information

# HKUST-1 as an Open Metal Site Gas Chromatographic Stationary Phase – Capillary Preparation, Separation of Small Hydrocarbons and Electron Donating Compounds, Determination of Thermodynamic Data

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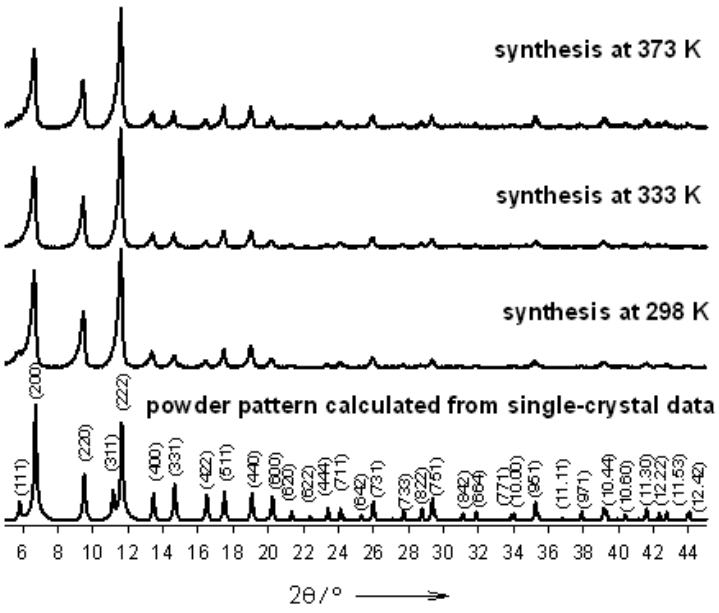
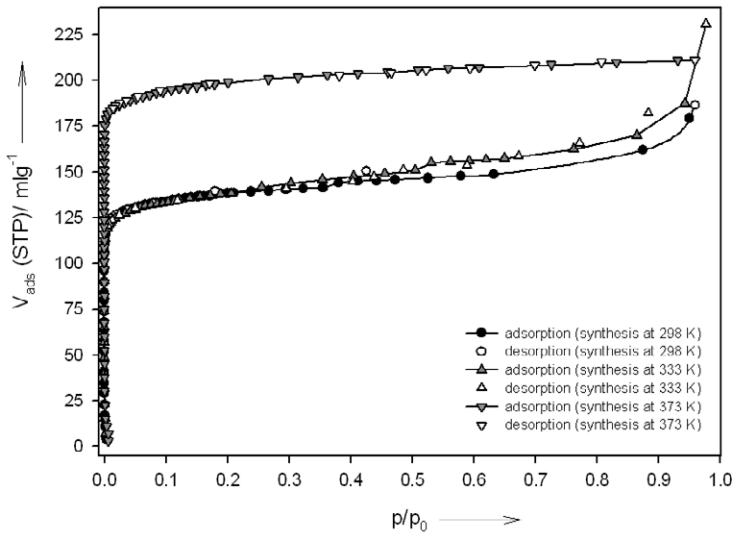
Bulk synthesis of HKUST-1 using the controlled SBU approach

General bulk synthesis at different temperatures. 0.299 g (1.5 mmol) copper(II) acetate monohydrate (Acros Organics, >98 %), called CuAc, was dissolved in 25 ml deionised water and heated to a temperature of 298 K, 333 K, and 373 K. In the next step a solution of 0.210 g (1 mmol) benzene-1,3,5-tricarboxylic acid (ABCR, 98 %), called $H_3BTC$, dissolved in 25 ml ethanol (VWR, > 99,8 %) was dropwise added to every precursor solution. Afterwards the suspension was stirred for 1 hr at the chosen temperature, cooled down to room temperature, and stirred again for 12 hrs. The blue solids were filtered off and washed with ethanol and diethyl ether (VWR, > 99,7 %). For activation the HKUST-1 material was heated at 373 K under vacuum . From the procedure described, a dark blue powder was obtained.




**Supporting Fig. 1** Powder X-ray diffractogrammes of HKUST-1 synthesised at different temperatures in comparison with the powder pattern simulated from single crystal data of HKUST-1.



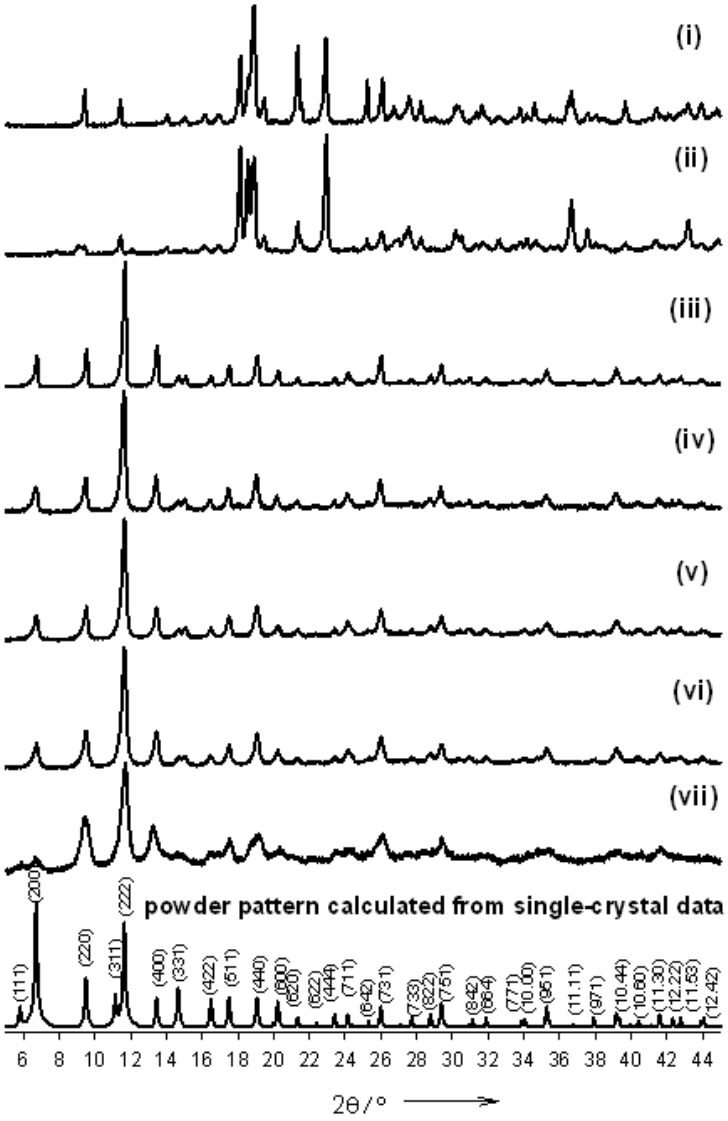

**Supporting Fig. 2** Nitrogen adsorption isotherms of different HKUST-1 materials synthesised at 298 K, 333 K, and 373 K.

**Supporting Table 1** Comparison of surface areas values of different HKUST-1 materials synthesised at 298 K, 333 K, and 373 K.

| | A(BET) in $m^2/g$ | $A(BET)_{Snurr}$ in $m^2/g$ |
|---|---|---|
| synthesis at 298 K | 418 | 547 |
| synthesis at 333 K | 435 | 540 |
| synthesis at 373 K | 603 | 804 |

Investigations of the influence of the SBU precursor concentration on HKUST-1 formation.

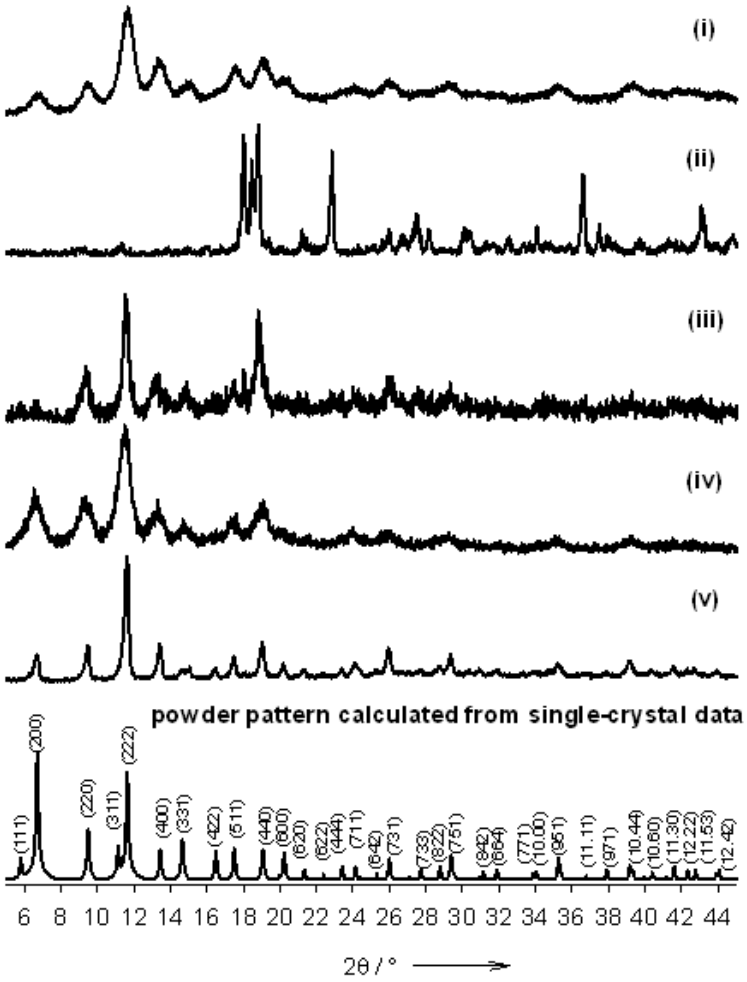
According to the protocol for the bulk synthesis above, a 0.04 mol/L solution of $H_3BTC$ in ethanol was dropwise added to a (i) 0.001 mol/L, (ii) 0.005 mol/L, (iii) 0.01 mol/L, (iv) 0.06 mol/L, (v) 0.1 mol/L, (vi) 0.15 mol/L, and (vii) 0.25 mol/L aqueous solution of CuAc at room temperature. After a stirring for 1 hr, blue crystalline material was filtered off from the mixture and activated as described in the bulk synthesis section.




**Supporting Fig. 3** Comparison of the powder X-ray diffractogrammes of materials, which were synthesised using the standard protocol (see above) for the HKUST-1 bulk synthesis with different CuAc concentrations.

Investigation of solvent effects.

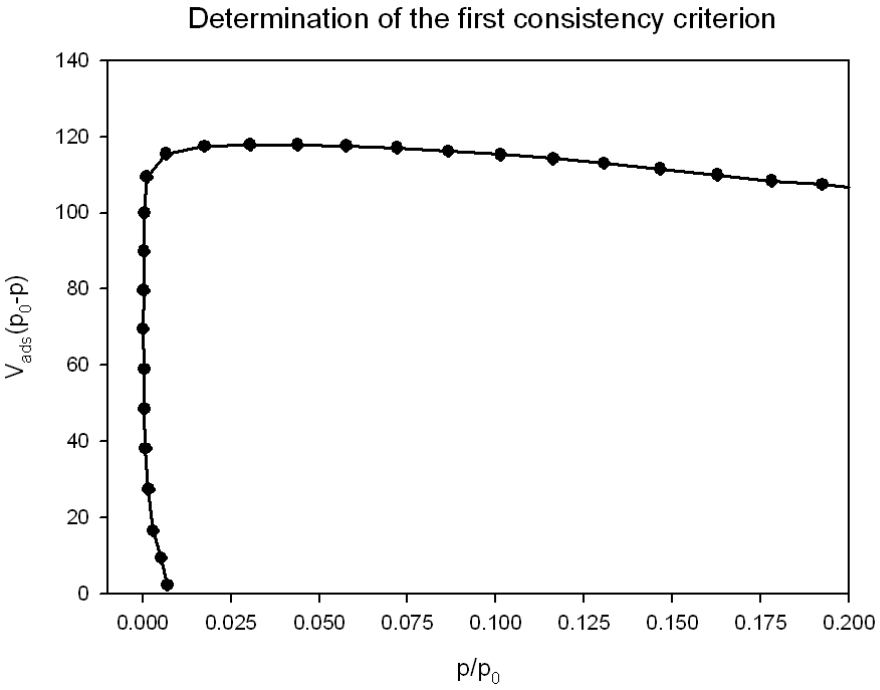
The protocol of the HKUST-1 synthesis above was altered in respect to the solvents used. In each case the linker solution was slowly added to the stirred precursor solution at room temperature. After a stirring time of 1 hr the blue solid matrial formed was filtered off from the solution. The mateial was subsequently activated. The following concentrations and solvents were used: (i) 0.06 mol/L of CuAc and 0.04 mol/L of $H_3BTC$ in dioxane (Merck, > 99 %), (ii) 0.06 mol/L of CuAc and 0.6 mmol/L of $H_3BTC$ in deionised water, (iii) 0.06 mol/L of CuAc and 0.04 mol/L of $H_3BTC$ in acetone (VWR, > 99.8 %) the addition of ethanol caused in this case the precipitation HKUST-1 material, (iv) 0.06 mol/L of CuAc and 0.04 mol/L of $H_3BTC$ in *N,N*-dimethylformamide (Carl Roth, ≥ 99.5 %) also in this case, the addition of ethanol caused the precipitation HKUST-1 material, and (v) 0.06 mol/L of CuAc in deionised water and 0.04 mol/L of $H_3BTC$ in ethanol.



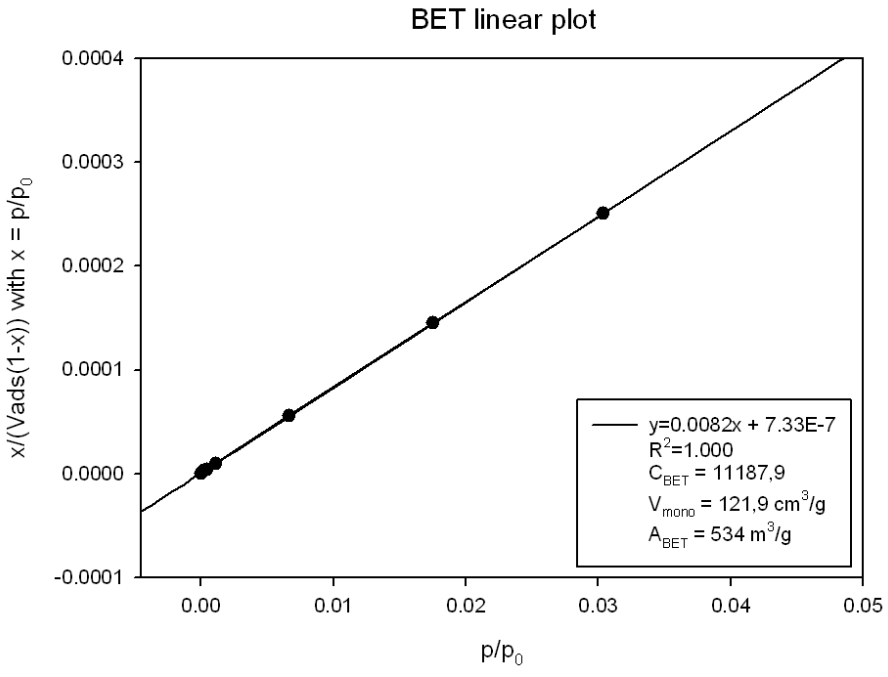

**Supporting Fig. 4** Comparison of the powder X-ray diffractogrammes of materials, which were synthesised using different solvents.

Evaluation of the consistency criterion according to Y.-S. Bae, A. O. Yazaydin and R. Q. Snurr, *Langmuir*, 2010, 26, 5475.

BET consistency plot based on the 77 K $N_2$ adsorption isotherms of HKUST-1. A positive slope was found in the $p/p_0$ range from app. 0.005 to 0.03.




**Supporting Fig. 5a**




**Supporting Fig. 5b**