Supporting Information - Fast and efficient synthesis of a host guest system: a mechanochemical approach

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January 13, 2016

Experimental part:

Since the base ($(CH_3)_4NOH$) was not used in the presented synthesis of NENU-5, the chemical composition of our product is different from the one given for NENU-5 ($[Cu_2(BTC)_{4/3}(H_2O)_2]_6[HPMo_{12}O_{40}] \cdot (C_4H_{12}N)_2 \cdot xH_2O$, with x = 25-30).[1] Taking into account the relative humidity, the reactants, and the charge balance, the formula can be given as $[Cu_2(BTC)_{4/3}(H_2O)_x]_6[H_3PMo_{12}O_{40}] \cdot yH_2O$ (x = 0-2, y = 39-41).

The ratio of the Keggin-type POM in the HKUST-1 network was confirmed by X-ray fluorescence (XRF) analysis. The values are given in Table S1. In the XRF measurements, the heavy elements were analysed. The measurements were conducted with a Niton XL3t GOLDD+ Analyzer (Themo scientific, USA) and the sample was used without further preparation.

Based on nitrogen adsorption measurements of the raw product, the specific surface area was determined to $218\,m^2\,g^{-1}$. The isotherms of the adsorption and desorption are shown in Figure S5. The measured surface area corresponds to 28.7% of the BET specific surface area of the raw product of the mechanochemical synthesis of HUKST-1 ($758\,m^2\,g^{-1}$).[2] Before the measurement, the sample was heated up to 200 °C at 5 mbar for 16 hours.

Thermogravimetric (TG) measurements showed a weight loss 15.7% in the range from room temperature to 200 °C. This weight loss corresponds to 43 molecules of water. Further heating to 300 °C results in a additional mass loss of 6.4% most propably attributed to traces of acetic acid in the pores(Figure S7).

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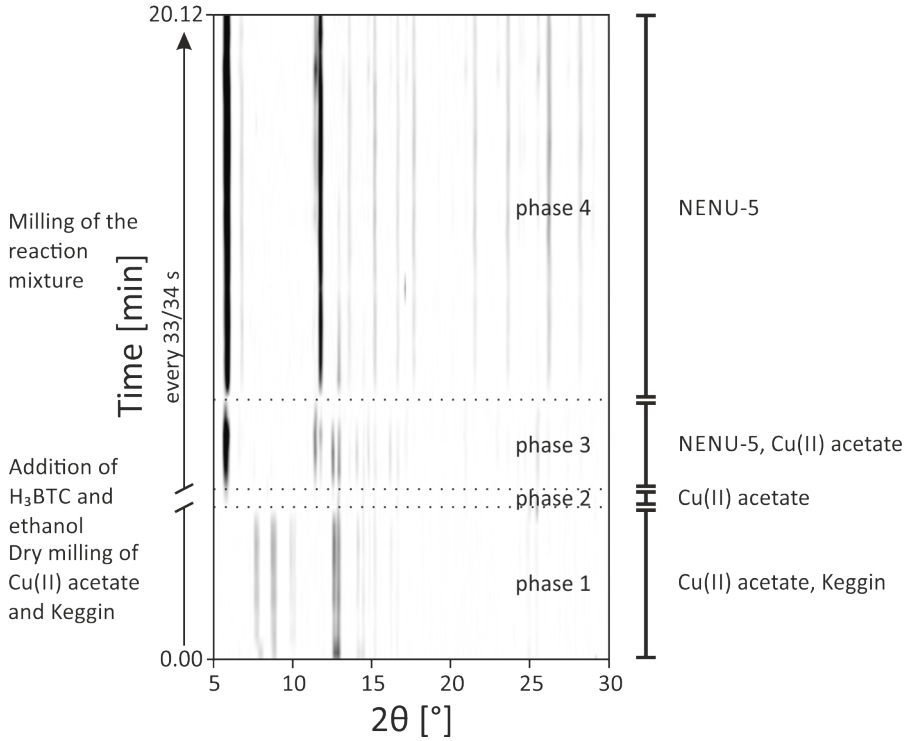

Figure S1: 2D plot of synchrotron XRD data for the mechanochemical synthesis of NENU-5 at 30 Hz including a pre-milling step (5 min) of copper(II)-acetate monohydrate and the Keggin-type POM (reaction 1). A description of the reaction procedure and the detected compounds is given; Cu(II) acetate = copper(II) acetate monohydrate, Keggin = $H_3PMo_{12}O_{40}{\cdot}13\,H_2O$, H_3BTC = 1,3,5-benzenetricarboxylic acid.

Table 1: Ratio of copper and molybdenum in the mechanochemical synthesised NENU-5 (XRF analysis).

measurement	ratio Cu [%]	ratio Mo [%]
1	48.7	51.1
2	48.7	51.1
3	48.8	51.0

References

[1] C. Y. Sun, S. X. Liu, D. D. Liang, K. Z. Shao, Y. H. Ren and Z. M. Su, *J. Am. Chem. Soc.*, 2009, **131**, 1883–1888.

[2] M. Klimakow, P. Klobes, K. Rademann and F. Emmerling, *Microporous Mesoporous Mater.*, 2012, **154**, 113–118.

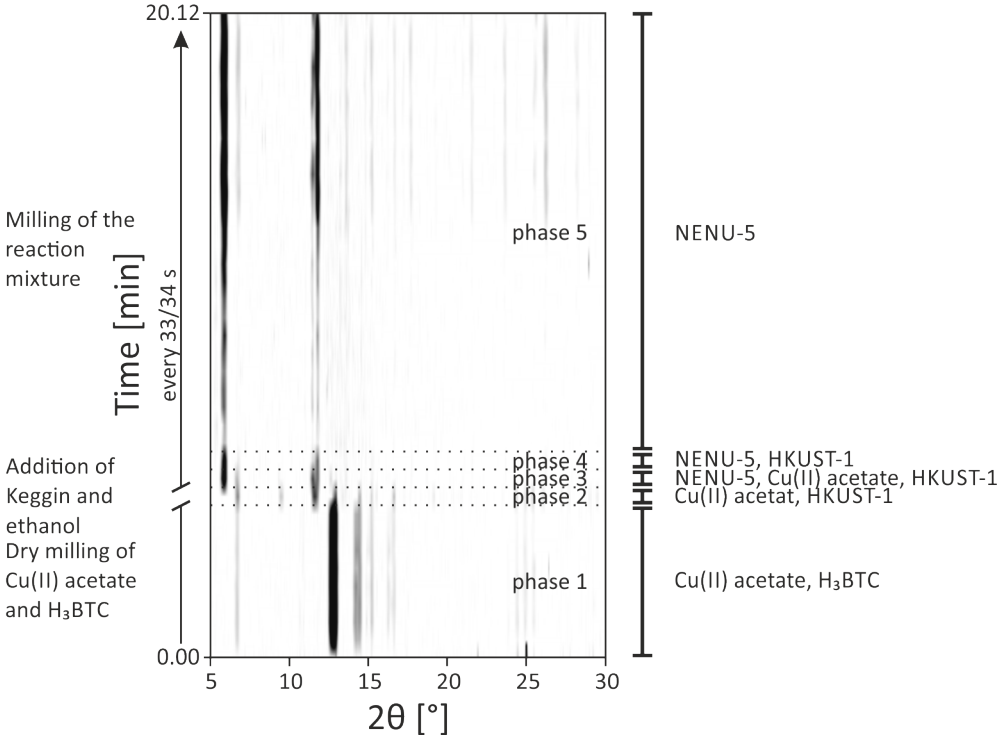

Figure S2: 2D plot of synchrotron XRD data for the mechanochemical synthesis of NENU-5 at 30 Hz including a pre-milling step (5 min) of copper(II)-acetate monohydrate and BTC (reaction 2). A description of the reaction procedure and the detected compounds is given; Cu(II) acetate = copper(II) acetate monohydrate, Keggin = $H_3PMo_{12}O_{40}{\cdot}13\,H_2O$, H_3BTC = 1,3,5-benzenetricarboxylic acid.

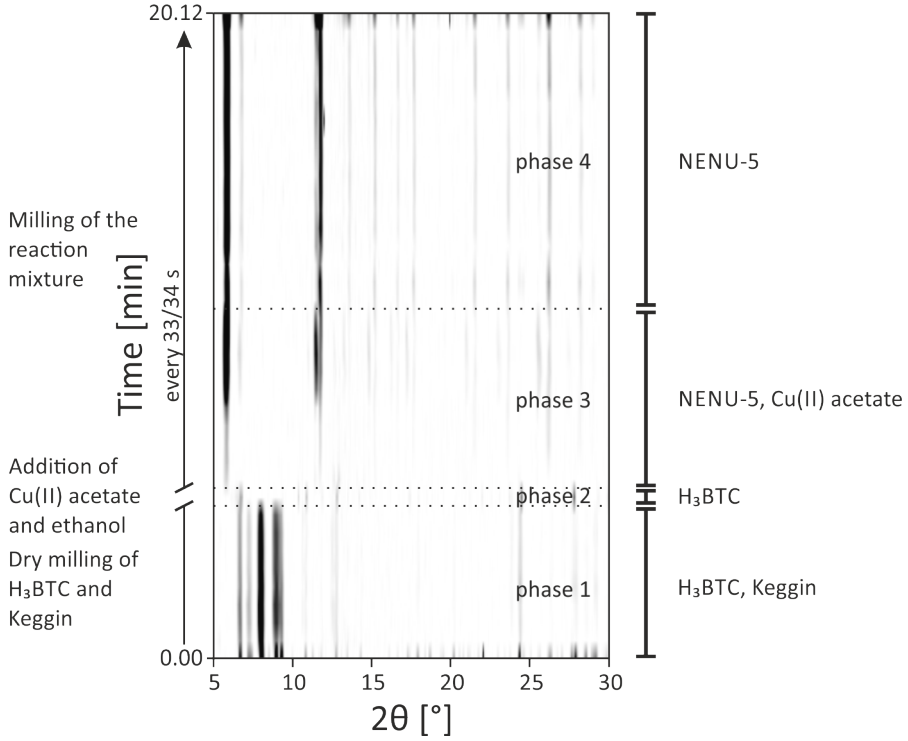

Figure S3: 2D plot of synchrotron XRD data for the mechanochemical synthesis of NENU-5 at 30 Hz including a pre-milling step (5 min) of BTC and the Keggin-type POM (reaction 3). A description of the reaction procedure and the detected compounds is given; Cu(II) acetate = copper(II) acetate monohydrate, Keggin = $H_3PMo_{12}O_{40}{\cdot}13\,H_2O$, H_3BTC = 1,3,5-benzenetricarboxylic acid.

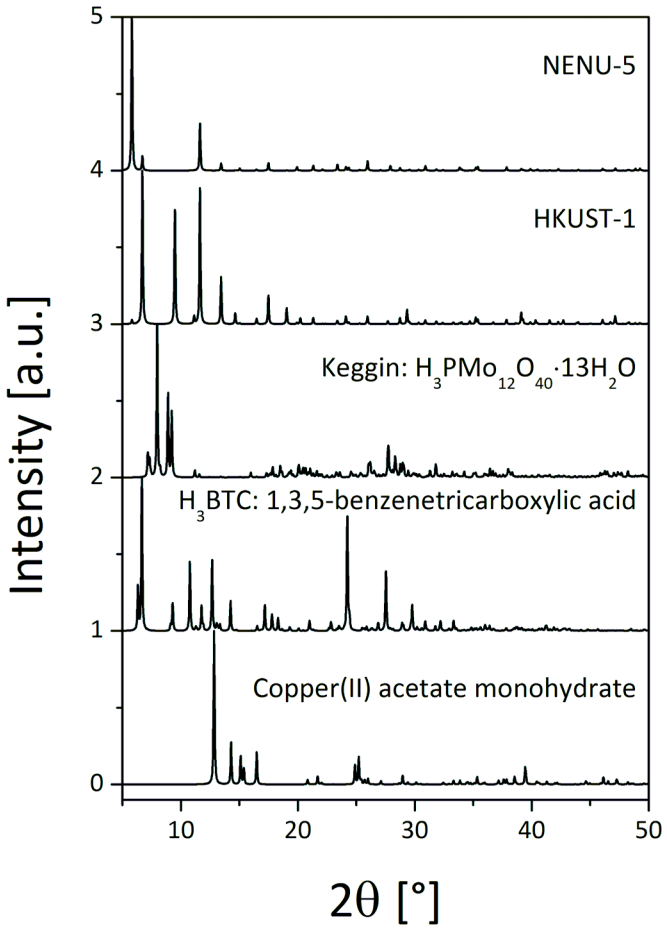

Figure S4: Calculated diffraction patterns of NENU-5, HKUST-1, the Keggin-type POM $H_3PMo_{12}O_{40}\cdot 13\,H_2O$, 1,3,5-benzenetricarboxylic acid, and copper(II) acetate monohydrate.

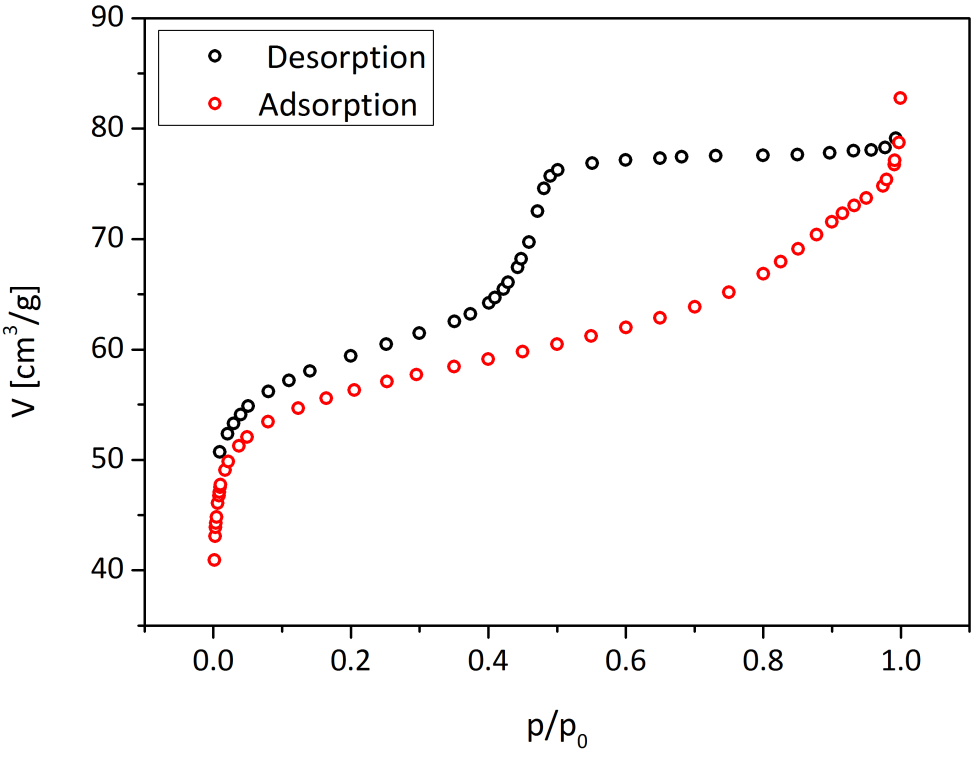

Figure S5: Adsorption and desorption isotherms for nitrogen at 77 K of mechanochemically synthesised NENU-5.

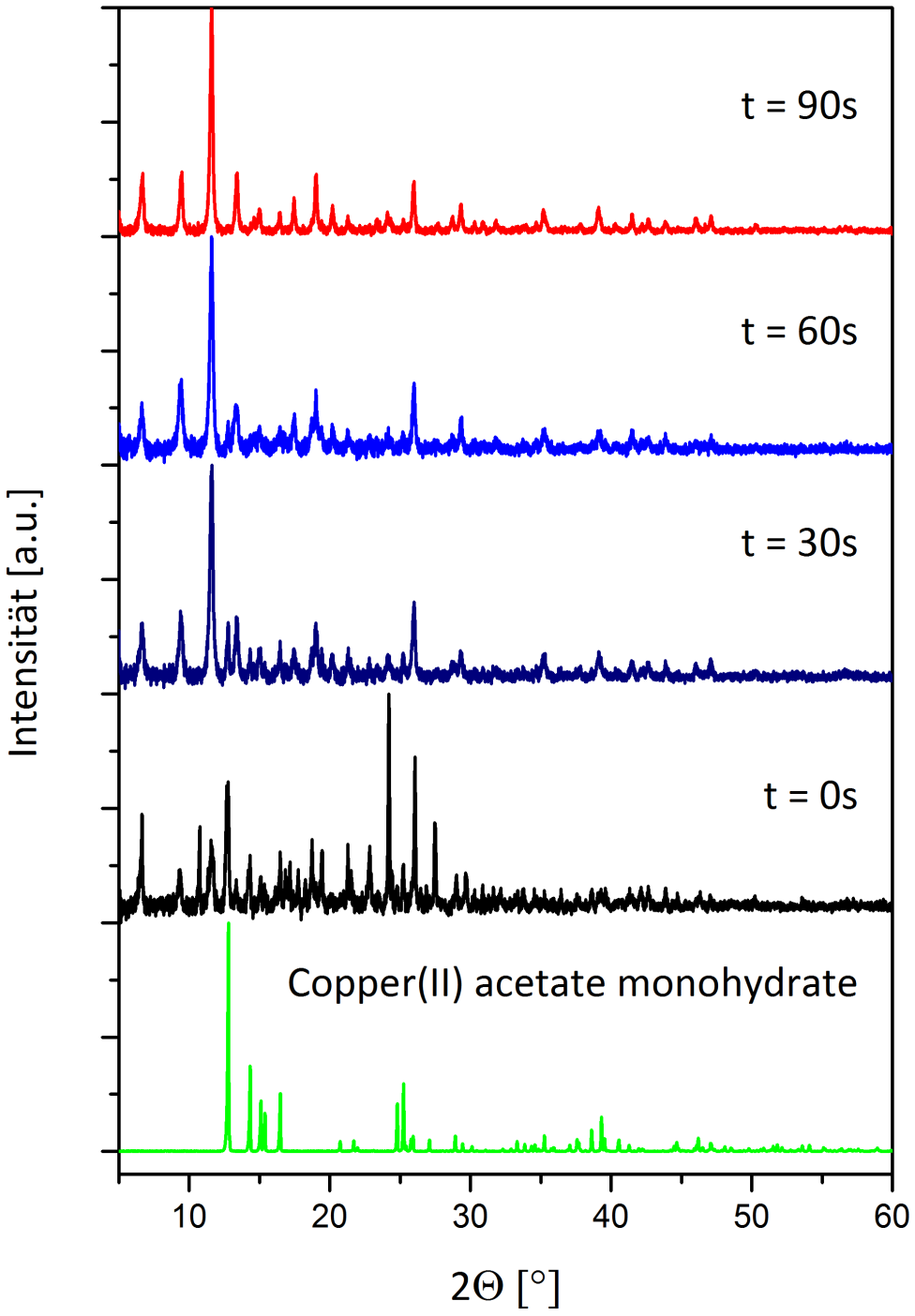

Figure S6: Diffraction pattern of the *ex situ* investigation of the mechanochemical synthesis of HKUST-1 including a pre-milling step of copper(II) acetate monohydrate.

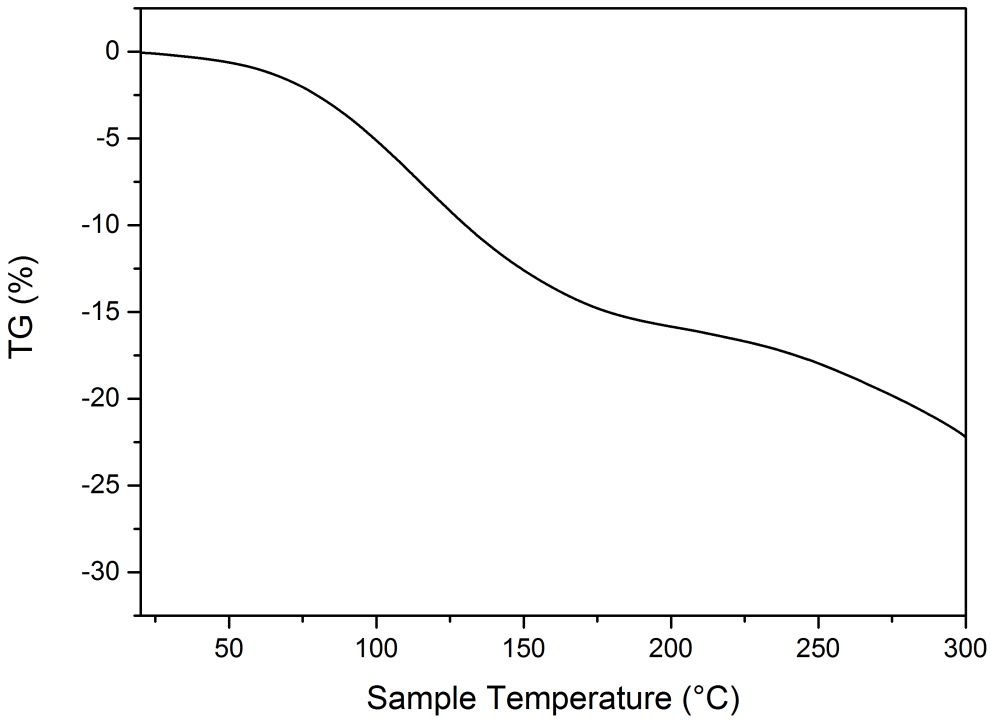

Figure S7: Plot of the thermogravimetric analysis of the mechanochemically synthesised NENU-5.