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High-throughput screening of synthesis parameters in the formation of the metal-organic frameworks MOF-5 and HKUST-1

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ABSTRACT

High-throughput methods were employed to study the influence of reaction parameters on the synthesis of the metal-organic frameworks MOF-5 ($Zn_4O[(OOC)_2 \cdot C_6H_4]_3$) and HKUST-1 ($Cu_3[(OOC)_3C_6H_3]_2(H_2O)_3 \cdot xH_2O$). Thus, compositional parameters (metal salt, reagent concentrations, and pH) as well as process parameters (temperature, time) were investigated in order to establish reaction trends and fields of formation. A multiclave reaction block was used to perform the investigation of 24 different solvothermal reactions at a time. Attention was focused on the phase purity and the crystal morphology of the resulting compounds. The characterization of the samples was performed by X-ray powder diffraction and high resolution scanning electron microscopy. The experimental results show that the formation, phase purity, and morphology of MOF-5 and HKUST-1 are extremely sensitive to the synthesis parameters explored in this study.

1. Introduction

Metal-organic frameworks (MOF) represent a new class of crystalline porous inorganic–organic hybrid compounds that have attracted increasing academic and industrial interest in the last few years [1–3]. Due to their fascinating properties and potential applications, derived from the combination of molecularly defined linkers and large crystalline pore spaces, metal-organic frameworks (MOFs) have stimulated numerous studies regarding both the characterization of known structures as well as the "design" of new systems [4,5]. The success of MOF syntheses is based on the concept of network design. Thus, the assembly of inorganic units (isolated metal–atoms as well as metal–oxygen clusters, chains or layers) with functionalized organic linker-molecules leads to the formation of three-dimensional extended frameworks [6]. Therefore, the incorporation of the desired structural features permits the tuning of the properties of new compounds [7]. The synthesis of MOFs proceeds mainly under solvothermal conditions. A common characteristic of these systems is their complex parameter space, where small changes in compositional or process parameters (reaction temperature, reaction time, metal salt, solvent, or pH value of the reaction solution) can have a profound impact on the structures formed and thus on their properties. In contrast, the role of at least some reaction parameters in the synthesis of the industrially important microporous materials such as zeolites is well understood [8,9]. Systematic investigations of inorganic–organic hybrid compounds are still rare [10,11]. In this context, high-throughput (HT) methods in materials science permit an accelerated, systematic investigation of the reaction parameter space while consuming small amounts of reagents [12–14]. Here we report on the systematic screening of reaction parameters of two MOFs, $Zn_4O[(OOC)_2C_6H_4]_3$ (MOF-5) [15] and $Cu_3[(OOC)_3C_6H_3]_2(H_2O)_3 \cdot xH_2O$ (HKUST-1) [16] employing HT as well as conventional methods.

2. Experimental

2.1. Chemicals

ZnO (Fluka, ⩾99.0%), $Zn(CH_3COO)_2 \cdot 2H_2O$ (Merck, *p.a.*), $ZnCl_2$ (Fluka, ⩾98.0%), $Zn(NO_3)_2 \cdot 6H_2O$ (Acros, 98%), $ZnSO_4 \cdot 7H_2O$ (Fluka, *p.a.*), 1,4-benzenedicarboxylic acid ($C_6H_4(CO_2H)_2$, H_2BDC, Aldrich, 98%), *N,N'*-diethylformamide ($(CH_2CH_3)_2NCHO$, DEF, Aldrich, 99%), mesitylene (Merck, ⩾98%), toluene (Fluka, ⩾99.7% over molecular sieve), chlorobenzene (Merck, ⩾99%), $Cu(NO_3)_2 \cdot 2.5H_2O$ (Aldrich, 98%), $Cu(CH_3COO)_2 \cdot H_2O$ (Merck, *p.a.*), $CuCl_2 \cdot 2H_2O$ (Grüssing, 99%), 1,3,5-benzentricarboxylic acid ($C_6H_3(COOH)_3$, H_3BTC Fluka, 98%), and absolute ethanol (BfB, 99.98%) were used as received.

2.2. Characterization

X-ray diffraction was performed on a Stoe STADI P COMBI transmission X-ray powder diffractometer equipped with an image plate detector and a horizontal xy-stage for automated analysis. The

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diffraction patterns were collected in the range of 0–45° (2θ) using Cu Kα_1 radiation (λ = 154.18 pm); the duration of each measurement was 11 min. The morphology of the products was determined by scanning electron microscopy. A high resolution JEOL JSM-6500F scanning electron microscope equipped with an Oxford EDX-analysis system was used for the semi-quantitative elemental analysis.

2.3. High-throughput methods

For the HT screening a reactor block with 24 cavities containing Teflon® liners was used (Fig. 1). A multiclave system based on the 96 well-plate format was previously developed in our group and was described previously [12]. The reactor block is made of stainless steel and contains 24 reaction chambers organized in a 4 × 6-array. The miniaturized Teflon® reactors allow us to use reactant volumes of up to 2 ml per hole. The reactor block was sealed inside a stainless steel autoclave. All reaction mixtures in this study were homogenized for 10 min using small stir bars prior to the solvothermal treatment. The sealed multiclave was placed in a preheated oven for several hours. After cooling to room temperature, the reaction products were recovered by filtration and rinsed with the appropriate solvent on a vacuum filtering apparatus. The resulting product library was characterized by automated X-ray diffraction.

2.4. Synthesis parameter screening in the formation of MOF-5

The 24 reactor autoclave described above was used to study the influence of different synthesis parameters on the morphology and phase purity of MOF-5. Thus, two HT experiments were set up. The molar ratios and the exact amounts of starting materials for the reported HT-experiments are given in the supporting information. For each HT experiment, in one reference cavity the reaction mixture for MOF-5 according to the literature [15] but scaled down to the capacity of our microreactors was placed for comparison (31.8 mg (0.107 mmol) of $Zn(NO_3)_2 \cdot 6H_2O$, 9.0 mg (0.054 mmol) H_2BDC, 1 ml DEF).

In the first HT experiment, the influence of the Zn^{2+}-source and the presence of co-solvents on the final product was investigated. Therefore, in the reaction mixture described above, $Zn(NO_3)_2 \cdot 6H_2O$ was substituted by ZnO, $Zn(CH_3COO)_2 \cdot 2H_2O$, $ZnCl_2$ and $ZnSO_4 \cdot 7H_2O$ (Supplementary Table S1). These reactions were all repeated for reproducibility tests. In order to screen the influence of the co-solvents mesitylene, toluene and chlorobenzene on the synthesis of MOF-5, mixtures with a varying volume ratio DEF/co-solvent (Supplementary Table S1) were prepared. Zinc nitrate as well as zinc oxide were used as Zn^{2+}-source. After stirring the mixtures, the sealed multiclave was heated at 383 K for 48 h.

In the second HT experiment, the influence of the pH on the formation of MOF-5 was studied. The adapted literature synthesis mixture for MOF-5 described above was used and a volume of 50 µl of different aqueous solutions with a pH value between 1 and 13 was added to each mixture (with pH steps of 0.5). The alkaline and the acidic aqueous solutions were prepared by successive dilution of 1 M NaOH, and 1 M HNO_3, respectively. The reaction mixtures were stirred for 10 min using small stir bars; the multiclave was then placed in a preheated oven at 383 K for 48 h.

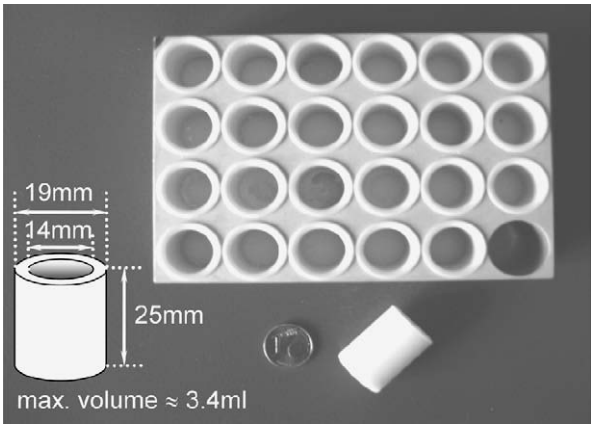

Fig. 1. Multiclave used for the screening of the influence of synthesis parameters on the formation of metal-organic frameworks. The stainless steel reactor block contains 24 reaction chambers with inserted miniaturized Teflon® reactors organized in a 4 × 6-array.

2.5. Synthesis parameter screening in the formation of HKUST-1

The synthesis mixture for HKUST-1 as described in the literature [16] was scaled down to a total volume of liquids of 2 ml (69.8 mg (0.03 mmol) $Cu(NO_3)_2 \cdot 2.5H_2O$ and 35.7 mg (0.17 mmol) of H_3BTC, and 2 ml of a 1:1 mixture of absolute ethanol and doubly distilled water (Millipore)).

2.5.1. Influence of metal salt on HKUST-1 synthesis

In a second HT experiment, the influence of different copper(II) salts and salt mixtures on the formation of HKUST-1 was investigated. Thus, 12 different molar ratios $Cu(NO_3)_2 \cdot 2.5H_2O$/$Cu(OAc)_2 \cdot H_2O$, six different molar ratios $CuCl_2 \cdot 2H_2O$/$Cu(OAc)_2 \cdot H_2O$, and six different molar ratios $Cu(NO_3)_2 \cdot 2.5H_2O$/$Na(OAc) \cdot 2H_2O$ were investigated in this study. $Na(CH_3COO) \cdot 3H_2O$ was used for tuning the pH of the starting mixtures. The total amount of Cu^{2+} ions in each reaction mixture was kept constant at 0.3 mmol. The detailed composition of the different reaction mixtures is reported in Supplementary Table S2. The sealed multiclave was treated at 423 K for 20 h. In order to study the influence of the reaction temperature, the same experiment was repeated at 348 K.

2.5.2. Influence of temperature and time on the synthesis of HKUST-1

The typical synthesis procedure for the synthesis of HKUST-1 described in the literature proceeds under solvothermal conditions at 453 K [16]. However, at these conditions a significant amount of Cu_2O is obtained as by-product [17]. For many applications, such as catalysis, the purity of the product is a fundamental criterion. We therefore studied the influence of the synthesis temperature at 453, 423, 393, and 348 K. The solvothermal syntheses were performed in conventional autoclaves (Parr) with a maximum internal volume of 25 ml. In a typical reaction mixture, 0.427 g (1.8 mmol) of $Cu(NO_3)_2 \cdot 2.5H_2O$ were dissolved in 6 ml doubly distilled water and mixed with an ethanolic solution (6 ml abs. EtOH) of trimesic acid (0.221 g, 1.0 mmol). Additionally, the relative yield of HKUST-1 at 348 K was studied as a function of the synthesis time. The reaction product was filtered off, rinsed with d.d. water, and weighed out after storing in water-saturated atmosphere over night. The relative yield was calculated assuming a molar mass of 947.7 g mol^{-1} corresponding to the water content of a fully re-hydrated material ($Cu_3[(OOC)_3C_6H_3]_2(H_2O)_3 \cdot 16H_2O$) [9]. The water content was estimated from the weight loss in TGA measurements.

2.5.3. Effect of concentration on HKUST-1 crystal morphology

The influence of the concentration of the reaction mixture on the morphology of HKUST-1 was studied in a third HT experiment. The reaction mixtures were prepared by multiplying the molar amounts of $Cu(NO_3)_2 \cdot 2.5H_2O$ and H_3BTC in the adapted recipe described above by a concentration factor "x" (with x = 0.1, 0.25, 0.5, 0.75, 1.0, 1.3, and 1.75). To test reproducibility, the same mixture compositions were repeated at different positions in the 24-reactors array. The multiclave was sealed and treated for 24 h in a preheated oven at 348 K (Supplementary Table S3).