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Nanocrystals and nanomaterials of isoreticular zeolitic imidazolate frameworks

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ABSTRACT

By expanding the coordination/deprotonation modulator approach in a rational manner using different zinc salts and modulators we have developed facile high-yield room temperature syntheses of nanocrystals and nanomaterials of a microporous RHO-type zeolitic imidazolate framework (ZIF), ZIF-71. It is shown that the coordination or deprotonation modulation function of the modulator depends upon solution composition. Characterization by means of PXRD, SEM/TEM, FT-IR, TG/DTA, VT-PXRD, DLS and argon physisorption measurements revealed that the ZIF-71 nanomaterials exhibit good thermal stability in air and exist as micrometer-sized particles that consist of agglomerated nanocrystals or very small crystalline domains embedded in an amorphous phase and possess different networks of disordered meso- and macropores. The hierarchically porous structures depend upon the synthesis conditions. Further experiments indicated that the synthetic method can be expanded to produce nanomaterials of two other RHO-type ZIFs, ZIF-25 and ZIF-97. In another related ZIF system, nanomaterials synthesis is hampered by competitive formation of RHO-type (ZIF-93) and SOD-type (SIM-1) phases.

1. Introduction

Crystalline microporous zeolitic imidazolate frameworks (ZIFs), a distinctive subclass of metal organic frameworks (MOFs), are assembled from divalent metal cations and imidazolate-based linkers that possess zeolite-related topologies [1,2]. ZIFs are more versatile in their properties than zeolites because various functional substituents can be introduced at the organic imidazolate linker. Furthermore, some ZIFs exhibit good thermal and chemical stability compared to most other MOFs [3]. Therefore, ZIFs are currently extensively investigated for potential applications in various fields such as gas storage, separation, catalysis, sensing, drug delivery [4] and fabrication of advanced carbon materials [5,6].

An example of materials of current interest is provided by a series of isoreticular Zn-based ZIFs with RHO topology first synthesized by Yaghi and coworkers using imidazolate linkers that carry different substituents of various polarities at the 4 and 5 positions [7,8]. These isoreticular ZIFs with properties ranging from hydrophilic to hydrophobic have been used for systematic studies of adsorption and separation of environment and energy relevant gases (CO_2, CH_4) [8–10] as well as biofuel purification properties [11]. In particular, one member of the series, the hydrophobic ZIF-71, has provoked so far considerable attention due to its favorable properties for water/organics (*e.g.*, bioalcohol) separations [11,12] *via* membrane technologies [13–16] and as a shock absorber material [17].

For many of the above mentioned applications it is desirable to provide the ZIFs as nanocrystals with defined size and shape as, for example, molecular diffusion times to intra-micropore active sites become shorter and the number of surface active sites increases with decreasing particle size [18,19]. Also, nanocrystals are advantageous over microcrystals for the fabrication of ZIF/polymer composites such as mixed matrix membranes [15,16] and fiber mats [20]. In recent years, various colloidal chemistry routes to the production of nanoscale ZIFs have been successfully developed [4,21]. The methods comprise syntheses in organic [22–24] and aqueous media [25], including the use of additives such as coordination/deprotonation modulators [26], surfactants [27], copolymers [28] or reverse micelles [19] as well as different metal salts [18] and oxides [13,29]. An alternative to facilitate molecular diffusion is *via* introducing meso- and/or macropores in microporous solids. Such hierarchically porous MOF materials can be synthesized using cooperative supramolecular templating strategies

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[30]. Very recently, such strategies have been applied successfully to produce hierarchically porous nano- [31] and microcrystals [32] as well as nanomaterials [33] of the prototypical ZIF-8 with SOD topology.

We have recently reported a facile additive-free room temperature solution-based method that results in rapid formation of ~45 nm ZIF-71 nanocrystals. However, the method has at its current stage of development the disadvantage that the ZIF-71 nanocrystals can be recovered only with low yield [34]. It is worth noting that reports on such small ZIF nanocrystals are so far only available for ZIF-8 [19,22,24,26,27] and ZIF-7 [23] as well as for ZIF-93 [35] that is one member, besides ZIF-71, of the isoreticular RHO-type ZIFs [8]. Here, we demonstrate how our method above can be further expanded in a rational manner on the basis of the coordination/deprotonation modulator approach [26,36] towards facile high-yield syntheses of size-controlled ZIF-71 nanocrystals and hierarchically porous nanomaterials with large porosity and good thermal stability in air. In addition, the potential of further expanding the method to produce nanomaterials of other ZIFs is shown for ZIF-25 and ZIF-97 that are also members of the isoreticular RHO-type ZIFs [8]. An additional motivation of our investigations was to provide further contributions towards improving current knowledge on parameter influence in ZIF nanocrystal and nanomaterials synthesis [18,21,24,26].

2. Experimental

2.1. Materials

The following zinc salts (zinc nitrate hexahydrate: $Zn(NO_3)_2\cdot 6H_2O$, zinc acetate dihydrate: $Zn(ac)_2\cdot 2H_2O$), solvents (*n*-propanol: *n*-PrOH, methanol: MeOH, *N*,*N*′-dimethylformamide: DMF), imidazole derivatives (4,5-dichloroimidazole: Hdcim, 4-formyl-5-methylimidazole: Hfmim, 4-hydroxymethyl-5-methylimidazole: Hhmim, 4,5-dimethylimidazole: Hdmim, 1-methylimidazole: 1-mim) and amines (*n*-butylamine: *n*-$BuNH_2$, ethanolamine: EA) were purchased from commercial suppliers and used without further purification.

2.2. Syntheses

All syntheses using various reagents and molar ratios were performed at room temperature in an analogous manner. The reagent compositions of the syntheses are provided in the Results and discussion section. To demonstrate the procedure one example is given below.

Synthesis of ZIF-71 nanocrystals using $Zn(ac)_2\cdot 2H_2O$ and 1-mim as modulator (total molar ratio Zn/Hdcim/1-mim/*n*-PrOH = 1:4:1:1000): 88.1 mg (0.401 mmol) of $Zn(ac)_2\cdot 2H_2O$ was dissolved in 15 mL (200.665 mmol) of *n*-PrOH. A second solution was prepared by dissolving 219.9 mg (1.605 mmol) Hdcim and 32.0 μL (0.401 mmol) of 1-mim in 15 mL (200.665 mmol) of *n*-PrOH. The latter clear solution was poured rapidly in the former clear solution under stirring with a magnetic bar at room temperature. Stirring was stopped after 10 s. The white precipitate was left unstirred for 1 h at room temperature and then recovered by centrifugation. The product was washed and centrifuged twice with *n*-PrOH and afterward once with MeOH. Drying was carried out at 70 °C under reduced pressure. The yield was 86% based on Zn.

In addition to the nanocrystal syntheses a microcrystalline ZIF-71 sample was prepared solvothermally and taken as a well crystalline reference material. The reaction was carried out using $Zn(ac)_2\cdot 2H_2O$ without modulator (total molar ratio Zn/Hdcim/*n*-PrOH = 1:4:1000): 88.1 mg (0.401 mmol) of $Zn(ac)_2\cdot 2H_2O$ was dissolved in 15 mL (200.665 mmol) of *n*-PrOH. A second solution was prepared by dissolving 219.9 mg (1.605 mmol) Hdcim in 15 mL (200.665 mmol) of *n*-PrOH. The latter solution was poured rapidly in the former solution under stirring. The glass tube was sealed and heated unstirred at 120 °C for 24 h. After cooling to room temperature the white precipitate was recovered by centrifugation. The product was washed and centrifuged twice with *n*-PrOH and afterward once with MeOH. Drying was carried out at 70 °C under reduced pressure. The yield was 78% based on Zn (see PXRD pattern and SEM image in Fig. S1).

2.3. Methods of characterization

Powder X-ray diffraction (PXRD) patterns were recorded using a Stoe STADI-P transmission diffractometer equipped with a sealed Cu X-ray tube, curved Ge(111) monochromator (delivering $CuK_{\alpha 1}$ radiation) and a linear position-sensitive detector. The instrumental Bragg peak broadening contribution, needed for estimation of average crystalline domain size by Scherrer's equation, was determined using a microcrystalline silicon sample. For estimating crystallinity of ZIF-71 nanomaterials PXRD measurements were performed in reflection geometry using a Stoe Theta–Theta diffractometer equipped with a sealed Cu X-ray tube and a secondary graphite monochromator (CuK_{α} radiation). The samples were slowly step-scanned in the range 2–10° 2θ. The PXRD pattern of the microcrystalline ZIF-71 sample was measured under the same conditions and taken as a reference of 100% crystallinity. Variable-temperature (VT) PXRD patterns were recorded in Debye-Scherrer geometry using a Stoe STADI-P diffractometer ($CuK_{\alpha 1}$ radiation) equipped with a Stoe high-temperature oven. The samples were contained in thin-walled silica glass capillaries (diameter 0.5 mm) during the measurements between room temperature and 400 °C. The capillaries were left unsealed (air atmosphere).

Scanning electron microscopy (SEM) was performed on a Jeol JSM-6700F instrument with a field emitter as the electron source using a low accelerating voltage of 2 kV. Transmission electron microscopy (TEM) images were taken on FEI Tecnai G2 F20 TMP and Jeol JEM-2100F-UHR field emission instruments operated with 200 kV. Methanolic dispersions were dropped on Cu grids with 400 mesh and dried under reduced pressure overnight. The latter instrument was used for selected area electron diffraction (SAED) measurements.

Dynamic light scattering (DLS) measurements were performed using a Zetasizer NanoZS from Malvern Instruments. Samples were dispersed in the respective solvent under ultrasound treatment for 20–30 min using a VWR Ultrasonic Cleaner with a frequency of 45 kHz and a power of 60 W. The dispersions were subsequently transferred into polystyrene (MeOH solvent) or quartz (DMF solvent) cuvettes. Scattering data were evaluated using the Zetasizer software from Malvern. The refractive index of ZIF-8 (1.39) [37] was used for data evaluation.

Thermogravimetry (TG) and difference thermal analysis (DTA) measurements were performed simultaneously using a Netzsch 429 thermoanalyzer. Samples were filled in alumina crucibles and heated in a flow of air with a ramp of 5 $°C\cdot min^{-1}$ from 35 °C up to 1000 °C.

For argon physisorption measurements at −186 °C a Quantachrome Autosorb-1-MP apparatus was used. Samples were outgassed in dynamic vacuum at 70 °C for *ca.* 48 h before start of the sorption measurements. Surface areas were estimated by applying the Brunauer–Emmett–Teller (BET) equation. The “Micropore BET Assistant” implemented in the ASiQwin 2.0 software from Quantachrome was used to determine the maximum relative pressure for the BET plot. It determines the BET range according to the criteria of Rouquerol, which was shown to be appropriate for different MOF materials [38]. Mesopore size distributions were