Metal–Organic Frameworks

DOI: 10.1002/anie.200805980

Giant Pores in a Chromium 2,6-Naphthalenedicarboxylate Open-Framework Structure with MIL-101 Topology**

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Porous materials with large, regular, accessible cages and channels have attracted the interest of many researchers owing to their application in catalysis,[1] gas storage,[2,3] and gas separation.[4] In the last decade, development of crystalline inorganic–organic hybrid compounds has led to new classes of compounds, such as metal–organic frameworks (MOFs) and porous coordination polymers (PCP). Their success is based on the modular construction and the diversity of metal oxide clusters that can be connected with innumerous organic linkers. Changes of the linker size often lead to isoreticular topologies,[5] and the pore size can be adjusted. Their functionalization can be achieved by using linker molecules modified with, for example, NH_2, CH_3, or OH groups.[6,7a] Unfortunately, the use of larger or modified linker molecules for isoreticular syntheses often has a drastic affect on the reaction conditions. High-throughput methods are an efficient way to systematically investigate such complex parameter systems.[7,8]

Whereas more than one thousand different MOFs have been described, only a few have exhibited high porosity combined with high thermal and chemical stability.[3,9] One outstanding example is MIL-101, a chromium terephthalate that has been subject to a wide range of investigations, for example, in catalysis,[10] gas sorption,[11] and controlled drug release.[12]

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[**] We appreciate the support from the Deutsche Forschungsgemeinschaft (STO 643/2), Michael Fischer for calculating the theoretical pore volumes and surface areas, and Prof. Dr. A. Simon for enabling the TEM experiments.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200805980.

Herein, we report the synthesis and characterization of the chromium 2,6-naphthalenedicarboxylate MIL-101_NDC ($[Cr_3(OH)(H_2O)_2(\mu_3\text{-}O)(O_2C{-}C_{10}H_6{-}CO_2)_3]\cdot guest$; $guest = H_2O$, EtOH) with MIL-101 topology. The structure contains two kinds of extra-large cages with cavity diameters of approximately 39 and 46 Å, as well as pentagonal (13.5 Å) and hexagonal (18.2 Å × 20.3 Å) cage windows. The compound was characterized by a combination of methods: structure simulation, powder X-ray diffraction, TEM investigations, sorption experiments, optical spectroscopy, and thermogravimetric measurements.

Employing a high-throughput reactor (see the Supporting Information), we investigated the following parameters: the molar ratio of 2,6-naphthalenedicarboxylic acid (H_2NDC) to Cr^{3+}, solvent, additives (HNO_3, RCOOH), reaction temperature and time, Cr^{3+} salts ($Cr(NO_3)_3\cdot 9H_2O$, $[Cr_3(CH_3COO)_7(OH)_2]$, $CrCl_3\cdot 6H_2O$, $[Cr(acac)_3]$ (acac = acetylacetonate)), and overall concentration. More than 600 individual reactions were performed to determine the appropriate conditions for synthesis of MIL-101_NDC. The title compound is only obtained in a small parameter field. The temperature control (heating and cooling rate), starting materials, solvent, and the presence of acetic acid all play important roles.[13]

A plausible structure model of MIL-101_NDC was constructed by means of molecular simulation techniques, using lattice parameters obtained through the successful indexing of the experimental powder X-ray diffraction pattern (cubic cell, $a \approx 104.5$ Å, possible space group $Fd\bar{3}$) and the fractional coordinates of the trimeric $\{Cr_3(OH)(H_2O)_2(\mu_3\text{-}O)\}$ units of MIL-101 as the basic input parameters. Insertion of the NDC linkers and a subsequent full geometry optimization with the universal force field (UFF) gave the final structure model (Figure 1; space group $Fd\bar{3}$, $a = 104.13$ Å). The measured and calculated powder XRD patterns are in good agreement (Figure 2).[14]

As with the structure of MIL-101, MIL-101_NDC is in close relationship to the augmented zeolite Mobil Thirty-Nine (MTN) structure type.[15] The structure is based on supertetrahedra (ST), which consist of trimeric $\{Cr_3(OH)(H_2O)_2(\mu_3\text{-}O)\}$ units that are linked along the edges by the naphthalenedicarboxylate ions. The free aperture of the ST windows is about 10.2 Å (as compared to ca. 8.6 Å for MIL-101). The framework is constructed of pentagonal (5 ST) and hexagonal rings (6 ST) that form two types of mesoporous cages (Figure 1). The smaller dodecahedral cage (5^{12}; 20 ST) consists only of pentagonal rings with a free diameter of approximately 13.5 Å (ca. 12 Å for MIL-101), and the diameter of the accessible cavity is about 39 Å (ca. 29 Å for

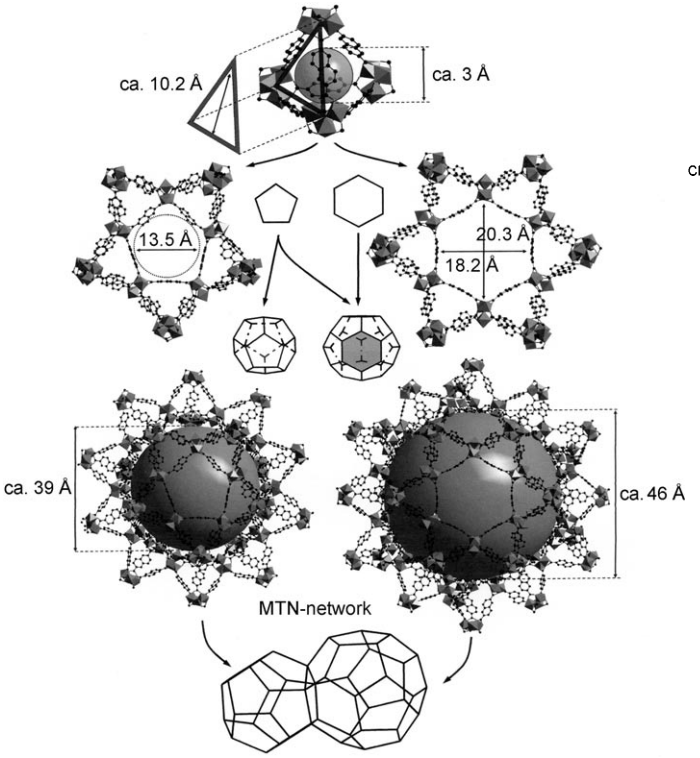

Figure 1. Bottom-up construction of the MTN-type network (MTN = zeolite Mobil Thirty-Nine) in MIL-101_NDC framework starting from supertetrahedra (top) that form rings (middle) and cages (bottom).

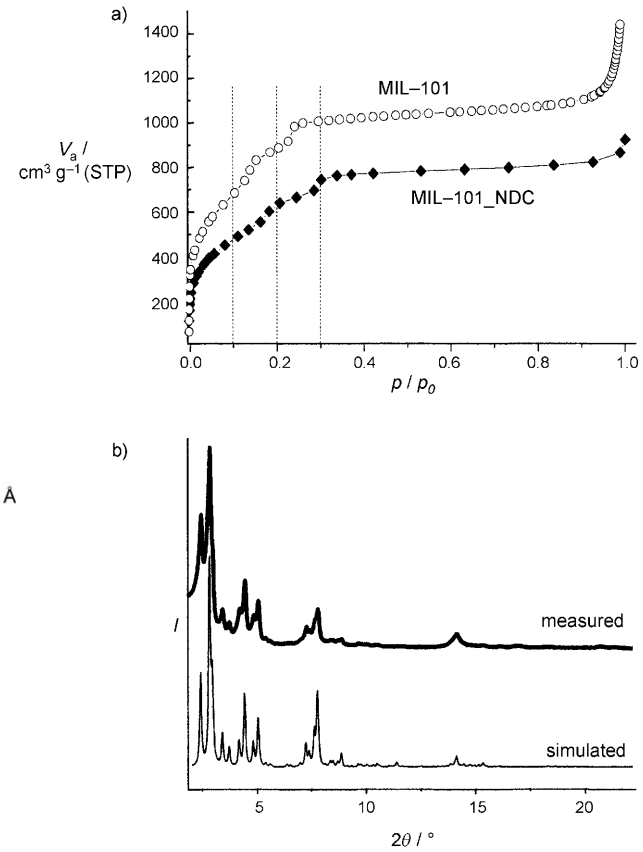

Figure 2. Characterization of MIL-101_NDC by a) nitrogen sorption at 77 K and b) powder X-ray diffraction.

MIL-101). The larger hexacaidecahedral cage ($5^{12}6^4$; 28 ST) incorporates pentagonal and hexagonal rings with a free aperture of the hexagonal windows of approximately 18.2 Å by 20.3 Å (ca. 14.7 by 16 Å for MIL-101) and an accessible cage diameter of approximately 46 Å (ca. 34 Å for MIL-101). The two types of cages are present in a small/large ratio of 2:1. Theoretical calculations (based on grand-canonical Monte Carlo simulations)[14] gave values of $V_p = 2.35\ cm^3\,g^{-1}$ and $S = 3850\ m^2\,g^{-1}$ for MIL-101_NDC and $V_p = 1.61\ cm^3\,g^{-1}$ and $S = 3210\ m^2\,g^{-1}$ for MIL-101, respectively (V_p = specific pore volume, S = specific surface area).

TEM investigations of activated MIL-101_NDC showed the presence of thin (less than 100 nm) plates (Figure 3), consisting of a crystalline MIL-101_NDC core (average diameter ca. 100 nm) and an X-ray-amorphous shell (thickness ca. 25 nm). The bright-field contrast and, particularly, Fourier transforms calculated inside selected areas demonstrated the crystalline and amorphous nature of core and shell, respectively. EDX analyses indicated the constituent elements (Cr, C, O) and the strong contrast of the amorphous shell supported the presence of heavy Cr.[16] Estimations based on a cylindrical model suggested that approximately 60 wt % of the sample consists of shell material. The Fourier transforms (Figure 3b and c) were calculated inside the marked areas. They are consistent with the zone-axis orientation [110], and the high-resolution contrast exhibits the appropriate symmetry *c*2*mm*. In this case, the lattice parameter in the single-domain region was determined from the Fourier transform to be $a \approx 104$ Å. The Fourier transform also shows considerable splitting of the peaks, as expected for the coexistence of twinned domains (Figure 3c, A and B).

The porosity of the compound was investigated by nitrogen sorption experiments at 77 K. The isotherm is of type IV, with pore-filling steps at $p/p_0 \approx 0.2$ and $p/p_0 \approx 0.3$, characteristic of the presence of two types of narrow mesopores (Figure 2a). Compared to MIL-101, these pore-filling steps are shifted to higher relative pressures, which indicates that, in MIL-101_NDC, the accessible mesopore cages have larger pore diameters than MIL-101. This result is also in agreement with the pore-size distributions calculated from the nitrogen adsorption isotherms by applying various methods (see the Supporting Information for details). The evaluation of the specific surface area should be similar to values of MIL-101 ($S_{BET} = 4100(200)\ m^2\,g^{-1}$). However, a smaller surface area of $S_{BET} = 2100(100)\ m^2\,g^{-1}$ was measured for the activated sample.[13] This reduced surface area can be explained by the presence of the X-ray amorphous shells.

In conclusion, access to highly porous and stable MOFs has been demonstrated. Further increases of pore diameter by isoreticular synthesis, using even larger organic linkers, will involve establishing the appropriate synthesis conditions, which can be accomplished by employing high-throughput

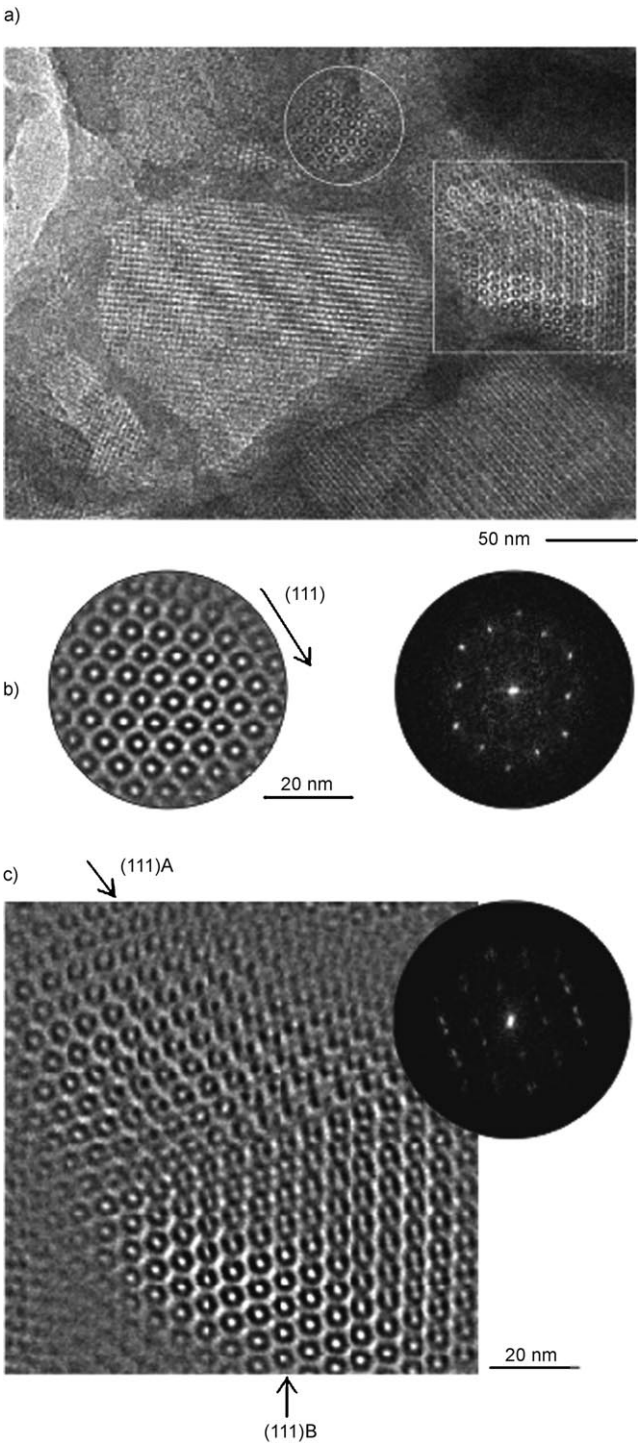

Figure 3. a) HRTEM micrograph recorded on an aggregate of crystals. Enlarged sections with Fourier transforms, calculated from indicated regions in (a): b) single domain; c) twinned area (domains A and B) in zone axis orientation [110]. Arrows indicate the systematic orientations of (111) layers.

methods and using highly sophisticated characterization methods in combination with computer simulations.

Received: December 8, 2008
Published online: February 4, 2009

Keywords: high-throughput methods · mesoporous materials · metal–organic frameworks · solvothermal synthesis · structure simulation

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[13] MIL-101_NDC was synthesized in our 24-high-throughput reactor containing teflon inserts with a maximum volume of 3 mL. 2,6-naphthalenedicarboxylic acid (43.2 mg, 0.2 mmol), 1.0 M aqueous $Cr(NO_3)_3 \cdot 9H_2O$ (200 μL, 0.2 mmol), 2.0 M acetic acid (200 μL, 0.4 mmol), and H_2O (954 μL) were homogenized for 20 min by stirring. The following temperature program was used: heating to 200 °C over 3 h, holding the temperature for 5 h, cooling to room temperature over 3 h. The reaction product MIL-101_NDC-as (as = as synthesized) was activated three times by treating with EtOH (10 mL) at 160 °C for 30 min under microwave heating. This treatment led to an increase in the specific surface area (see the Supporting Information). Thermogravimetric analysis in air revealed that MIL-101_NDC is stable up to 260 °C.

[14] All molecular simulations were carried out with software package *Materials Studio* Version 4.3, *Accelrys Inc.*, San Diego, CA, **2008**. For details, see the Supporting Information.

[15] Available at http://www.iza-structure.org/databases/.

[16] IR and Raman spectroscopy gave no information on the existence of aliphatic C–H vibrations. Thus, the incorporation of acetate groups could be ruled out (see the Supporting Information).

