Porous Materials

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# A Highly Porous Metal–Organic Framework with Open Nickel Sites**

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*Dedicated to Professor Rüdiger Kniep on the occasion of his 65th birthday*

Metal–organic frameworks (MOFs) have emerged as a new class of crystalline porous materials with extraordinary high adsorption capacities and pore sizes exceeding those of traditional porous materials.[1] MOFs are considered as promising specific catalysts[2] and hydrogen storage materials[3] because of the presence of open, accessible metal centers. These active sites can be generated, for example, in square paddle-wheel units $\{M_2(O_2C)_4\}$ (M = Cu, Ni, Zn, Co, Mo)[4,5] and trigonal $\{M_3(\mu_3\text{-}O)(O_2C)_6\}$ clusters (M = Sc, Cr, Fe, Ni, Al, In).[6–8] Such clusters act as nodes or secondary building units (SBUs) connected through multifunctional carboxylate linkers, resulting in highly porous three-dimensional networks, such as HKUST-1,[4] MIL-100,[7] or MOF-14.[9] For zinc-containing MOFs, the octahedral $\{Zn_4O(O_2C)_6\}$ SBU is a common motif,[10] resulting in materials with very high porosity and exceptional hydrogen-storage properties.[11] However, the metal sites are coordinatively saturated in these structures.

Herein, we present the synthesis, structure, and properties of the new porous material DUT-9 (DUT = Dresden University of Technology) formed by btb linkers (btb = benzene-1,3,5-tribenzoate) and $\{Ni_5(\mu_3\text{-}O)_2(O_2C)_6\}$ clusters, which is a novelty in MOF chemistry. $\{Ni_5O_2(btb)_2\}$ has a high concentration of open metal sites per cluster and a very high porosity that is unknown for nickel-containing MOFs to date.[12]

DUT-9 was obtained by solvothermal reaction of $Ni(NO_3)_2{\cdot}6H_2O$ and $H_3$btb in *N*,*N*-dimethylformamide (DMF) or *N*,*N*-diethylformamide (DEF; see Experimental Section for details). Elemental analysis revealed an overall composition of the as-made material of $[Ni_5O_2(btb)_2(def)_{21}(H_2O)_{21}]$. The phase purity and stability of the compound was monitored by PXRD analysis (Supporting Information, Figure S6).

The crystal structure of DUT-9 (space group $R\bar{3}$) contains a $\{Ni_5(\mu_3\text{-}O)_2(CO_2)_6(L)_4(H_2O)_4\}$ (L = DMF, DEF) cluster (distorted octahedral SBU). Five octahedrally coordinated nickel atoms are bridged by two $\mu_3$-O atoms and six carboxylate groups (Figure 1 a). The five nickel atoms are coplanar. The central nickel atom Ni1 is coordinated by four carboxylate oxygen atoms and the two $\mu_3$-O atoms. Ni2 and Ni3 and their symmetry equivalents Ni2* and Ni3* (* $1-x$, $-y$, $-z$), are linked to three carboxylate oxygen atoms, an oxygen atom of formamide, a water oxygen atom, and a $\mu_3$-O atom. The four DMF/DEF and four water molecules can be removed to create accessible metal sites in the structure (Supporting information, Figure S2). The SBUs are arranged in parallel Kagome nets stacked in the ABC sequence perpendicular to the *c* direction (Supporting Information, Figure S4 and S5). Each SBU is connected to four ligands within a layer and to two additional linkers belonging to the two adjacent layers each (up and below a given layer), thus forming a structure with the topology of a (3,6)-connected net, which is unknown to date (for details, see the Supporting Information).

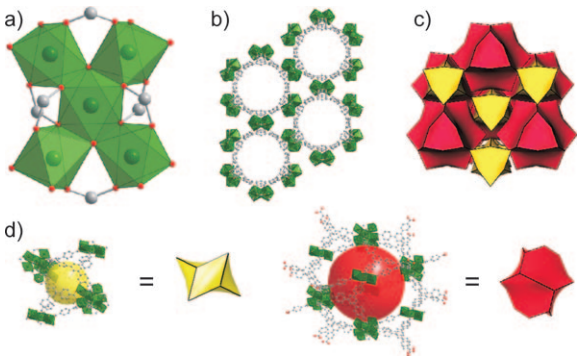


***Figure 1.*** Crystal structure of DUT-9. a) $\{Ni_5(\mu_3\text{-}O)_2(CO_2)_6(O_L)_8\}$ cluster ($O_L$ = oxygen of solvent molecules); C gray, Ni green, O red. b) View along [001]. c) Topology of DUT-9 (view along [001]). d) The two different types of pores are represented by yellow and red (view along [100]). Additional coordinated solvent molecules were omitted for clarity in all cases.

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Two different types of pores are present in the structure of DUT-9 (Figure 1c,d): a smaller pore approximately 13 Å in diameter and a larger pore with a diameter of approximately 25 Å (see also Supporting Information, Figure S3). Both pores are arranged in an alternating fashion along to the *c* axis (Figure 1c), giving rise to hexagonal channels throughout the whole crystal structure (Figure 1b).

According to thermal analyses, DUT-9 is stable at least up to 200 °C (Supporting Information, Figure S14). During the conventional solvent removal procedure of heating in vacuum, DUT-9 partially collapses, as revealed by the low porosity and the significantly changed PXRD pattern (Supporting Information, Figures S7, S10). Furthermore, the framework cannot be restored by resolvation with DEF (Supporting Information, Figure S7). Even the exchange of high-boiling solvents by dichloromethane caused pore collapse (Supporting Information, Figures S7, S10). Supercritical drying (SCD) using $CO_2$ was recently proposed to remove the solvent without collapse of the framework.[13] Judging from the PXRD patterns before and after supercritical drying of DUT-9 (DUT-9-SCD), this method turned out to be essential for obtaining the framework in a solvent-free manner.

The extremely high permanent porosity of DUT-9-SCD was confirmed by gas- and liquid-phase adsorption measurements (Supporting Information, Figure S11). The specific pore volume calculated from the nitrogen adsorption isotherm at −196 °C (Figure 2, inset) is 1.77 $cm^3 g^{-1}$ ($p/p_0 = 0.91$).

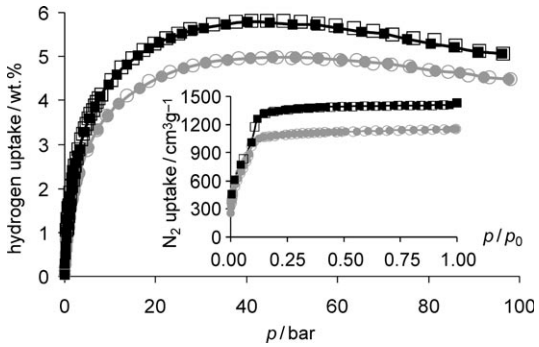


***Figure 2.*** Hydrogen high-pressure excess adsorption isotherms −196 °C. Inset: nitrogen physisorption isotherms (−196 °C) of DUT-9-SCD (gray circles) and DUT-9, additionally activated at 120 °C (black squares). Closed symbols: adsorption; open symbols: respective desorption.

As it was not possible to determine a linear range of the BET plot, in this case the method is not suited to compute the specific surface area of DUT-9. The thermal analysis of the supercritically dried sample (Supporting Information, Figure S15) reveals that solvent molecules remain coordinated during this activation procedure.

Additional activation of DUT-9-SCD by heating in vacuum leads to a partial removal of coordinated solvent molecules, thus giving rise to a significantly increased nitrogen uptake (1406 $cm^3 g^{-1}$ in saturation) and a pore volume of up to 2.18 $cm^3 g^{-1}$. To the best of our knowledge, this value is among the highest values reported for MOFs to date[8,14,15] and is unique for nickel-containing MOFs.

Analysis of the pore size distribution of DUT-9-SCD based on low-pressure nitrogen adsorption isotherms (Supporting Information, Figures S8, S9) revealed two maxima at 16–17 Å and at 22–23 Å, which are in good agreement with the pore diameters estimated from the crystal structure of DUT-9. Furthermore, an increase of the pore sizes after additional activation in vacuum at 100 °C could be observed, which is additional evidence for the increase of the accessible pore volume.

Because of the remarkable pore volume and the presence of open metal sites and regarding to the need for efficient energy storage materials, the storage capacities of DUT-9-SCD for different gases were investigated. Cheetham and coworkers showed in 2006 that $[NaNi_3(OH)(sip)_2]$ (sip = 5-sulfoisophthalate) strongly binds hydrogen at coordinatively unsaturated nickel sites.[16] This was shown by inelastic neutron scattering spectroscopy and temperature-programmed desorption experiments. According to hydrogen adsorption measurements, $[NaNi_3(OH)(sip)_2]$ stores 0.94 wt % hydrogen at 1 bar and −196 °C.

The Gibbs excess hydrogen physisorption isotherms of DUT-9-SCD are presented in Figure 2. Owing to a better comparability between different materials, and because of the assumptions necessary for conversion, the excess data were not converted into absolute values. DUT-9-SCD shows a maximum hydrogen excess uptake of 4.99 wt % (52 mg $g^{-1}$) at 45 bar. A remarkable increase of the gas uptake up to 5.85 wt % (62 mg $g^{-1}$) at 40 bar and −196 °C could be achieved by additional thermal activation in vacuum after supercritical drying. The amount adsorbed by the new MOF material (DUT-9-SCD) at 1 bar and −196 °C is 1.33 wt % and 1.66 wt % for the additionally activated material.

The storage capacity of additionally activated DUT-9-SCD is among the highest reported for MOFs at −196 °C to date,[17] and comparable to that of MIL-101 (6.1 wt % at 60 bar),[18] DUT-6 (5.64 wt % at 50 bar),[14] or $Cu_2$(tptc) and $Cu_2$(qptc) (tptc = terphenyl-3,3″,5,5″-tetracarboxylate, qptc = quaterphenyl-3,3‴,5,5‴-tetracarboxylate; 6.06 wt % and 6.07 wt % at 20 bar).[19] Only MOF-177 has a higher storage capacity of 7.5 wt % at 70 bar.[20] CPO-27-Ni stores 1.8 wt % at 70 bar.[12d]

Methane Gibbs excess physisorption (Figure 3) reveals a maximal excess uptake of 188 mg $g^{-1}$ (at 100 bar and 25 °C) for

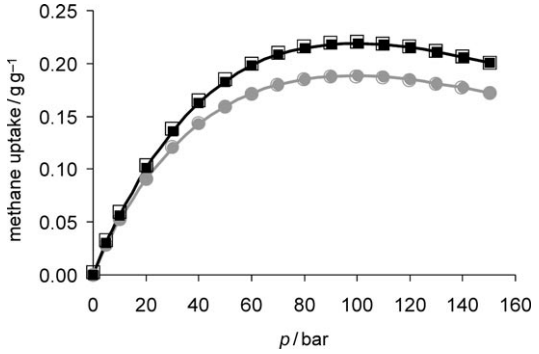


***Figure 3.*** Methane high-pressure excess adsorption isotherms (25 °C) of DUT-9 (gray circles) and DUT-9 activated at 120 °C (black squares). Closed symbols: adsorption; open symbols: corresponding desorption.

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DUT-9-SCD, which increased to 219 mg g$^{-1}$ (at 100 bar and 25°C) after additional evacuation at 120°C. As well as the observed hydrogen storage capacity, the gravimetric methane uptake of DUT-9-SCD at room temperature is among the leading materials, which include MIL-101 (239 mg g$^{-1}$ at 80 bar),[21] DUT-6 (230 mg g$^{-1}$ at 100 bar)[14] and COF-102 (243 mg g$^{-1}$ at 85 bar).[22] Furthermore, it significantly exceeds the methane storage capacity of CPO-27-Ni, a reference MOF with open nickel sites and a methane uptake of 135 mg g$^{-1}$ at 50 bar.[23]

Due to the low crystallographic densities (0.467 g cm$^{-1}$ for DUT-9-SCD and 0.358 g cm$^{-1}$ for the solvent-free framework), the maximal volumetric methane storage capacities amount to only 124 cm$^3$ cm$^{-3}$ and 112 cm$^3$ cm$^{-3}$, respectively. The values are comparable to DUT-6 (126 cm$^3$ cm$^{-3}$), which also has a low crystallographic density. With a volumetric methane storage capacity of 220 cm$^3$ cm$^{-3}$, PCN-14 is one of the best storage materials regarding the volumetric uptake.[24]

Apart from the storage of energy sources, such as hydrogen and methane, the removal of carbon dioxide from exhaust gas is of increasing interest. As shown by Dietzel and co-workers, CPO-27-Ni is a suitable storage material for carbon dioxide because of its open nickel sites.[25] As compared to CPO-27-Ni (1.04 g g$^{-1}$ at ca. 30 bar and 25°C),[23] the Gibbs excess carbon dioxide physisorption isotherms (Supporting Information, Figure S12) of DUT-9-SCD reach higher maximal excess uptakes of 1.11 g g$^{-1}$ and 1.64 g g$^{-1}$ (both at 47 bar and 25°C) after additional activation in vacuum at 120°C. Thus, DUT-9 even surpasses MOF-177 (1.47 g g$^{-1}$ at 42 bar and ambient temperature), which is one of the best materials to date for carbon dioxide storage with respect to capacity.[26]

The *n*-butane physisorption isotherm was obtained at 20°C under atmospheric pressure and dynamic conditions (Supporting Information, Figure S13). According to this measurement, DUT-9-SCD stores up to 0.70 g g$^{-1}$ *n*-butane. This value surpasses that obtained for HKUST-1 (0.22 g g$^{-1}$) significantly and even that of the large-pored MOF MIL-101 (0.64 g g$^{-1}$).[27] Although exhibiting a comparable pore volume of 2.02 cm$^3$ g$^{-1}$, DUT-6 shows a *n*-butane storage capacity of 1.1 g g$^{-1}$.[14]

In conclusion, we have synthesized and characterized a new, highly porous metal–organic framework. DUT-9 has open nickel sites, exhibits remarkable adsorption properties, large pores of up to 25 Å wide, a new network topology, and has high potential for gas storage, $CO_2$ separation, and catalytic applications.

## Experimental Section

The solvothermal synthesis of DUT-9 can be performed in DMF as well as in DEF. The crystal structure of DUT-9 was determined from a crystal grown in DMF. Further analytical investigations were performed with material obtained from a reaction carried out in DEF. For a typical synthesis, $H_3$btb (180 mg, 0.41 mmol) and Ni$(NO_3)_2 \cdot 6H_2O$ (366 mg, 1.26 mmol) were dissolved in DEF (10.5 mL). The solution was heated in a Pyrex tube at 120°C for 20 h. The resulting pale green crystals of DUT-9 were collected by filtration under argon, washed twice with DEF, and dried in an argon flow at room temperature. Yield: 412 mg (54% with respect to the amount of $H_3$btb used). Elemental analysis (%) for $[Ni_5O_2(btb)_2(DEF)_{21}(H_2O)_{21}]$ (3698.68 g mol$^{-1}$: found ± σ: C 51.0 ± 0.3, H 7.56 ± 0.09, N 8.7 ± 0.2, O 23.6 ± 0.5, Ni 8.5 ± 0.2; calcd: C 51.6, H 8.26, N 8.0, O 24.2, Ni 7.9.

Crystal data: $Ni_5C_{66}H_{57}O_{22}N_4$, $M_r = 1551.71$, rhombohedral, $R\bar{3}$ (No. 148), $a = 35.411(5)$, $c = 45.691(9)$ Å, $V = 49618(14)$ Å$^3$, $Z = 9$, $\rho = 0.467$ g cm$^{-3}$, $\lambda = 0.88561$ Å, $T = 20$°C, $2\theta_{max} = 66.38$°, reflections collected/unique 37398/18956, $R_{int} = 0.0498$, $R_1 = 0.0918$, $wR_2 = 0.2833$, largest difference peak/hole 1.781/−0.662 e Å$^{-3}$. CCDC 768845 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The topology of the networks has been examined with the program packages TOPOS[28] and Gavrog Systre (http://gavrog.sourceforge.net/)

Adsorption experiments: $N_2$ physisorption isotherms were measured at −196°C up to 1 bar using a Quantachrome Autosorb 1C apparatus. High-pressure $H_2$ adsorption measurements at −196°C up to 100 bar were performed using approximately 0.7 g sample on a volumetric BELSORP-HP apparatus. High-pressure $CH_4$ adsorption was studied at 25°C using a magnetic suspension balance (Rubotherm). The buoyancy corrections are performed as described earlier.[29] High-purity gases were used ($N_2$ 99.999%, $H_2$ 99.999%, $CH_4$ 99.5%).

Additional details of the crystal structure determination, topological analysis and the SCD process, additional X-ray data, TA curves, IR spectra, and further adsorption measurements are given in the Supporting Information.

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