Outstanding methane gravimetric working capacity of computationally designed rhr-MOFs

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Abstract

A multi-scale approach is employed to design metal-organic frameworks (MOFs). The methane sorption properties are studied by grand canonical Monte Carlo simulations to reveal the structure-property relationship with respect to the methane total uptake and working capacity at different temperatures and pressures. We identify **rhr**-MOFs with outstanding gravimetric working capacity. For example, the **BBB** MOF (largest studied pore size) achieves a value of 60.7 wt% at 298 K and 5-65 bar.

Keywords

metal-organic framework, rhr topology, methane sorption, working capacity, design

Introduction

The material class of metal-organic frameworks (MOFs) has important applications in various fields, including gas storage¹⁻¹¹, separation¹²⁻¹⁶, catalysis¹⁷⁻²⁰, light harvesting²¹, drug delivery²², and biomedical imaging²³. MOFs consist of metal ions or clusters that are coordinated by organic ligands to produce 1D, 2D, or 3D materials. Their porous structure with tunable surface area and pore volume makes them particularly suitable for storing natural gas, which is the cleanest fossil fuel in terms of Pb, Hg, NO_x, SO_x, CO, and CO₂ pollutants²⁴. Given that methane constitutes the main part of natural gas, its *total uptake* and *working capacity* are in the focus of adsorption studies in MOFs. Both the gravimetric [wt%] and volumetric [cm³(STP)cm⁻³] values are important for storage characterization^{25,26}. The announced targets of the US Department of Energy (DoE) are a gravimetric working capacity of 50 wt% and a volumetric working capacity of 263 cm³(STP)cm⁻³ for automobile applications at 273 K, for example²⁷. Achieving these targets, however, is very challenging.

Simulation techniques can point to new directions for designing MOFs with new topologies and enhanced methane sorption properties, having demonstrated high accuracy and requiring less resources than laboratory experiments in terms of time and money²⁸⁻³². In this context, we employ molecular mechanics and density functional theory (DFT) calculations to computationally design MOFs with **rhr** topology. Methane sorption is simulated by grand canonical Monte Carlo calculations to derive the total uptakes and working capacities. We will show that several **rhr**-MOFs meet the gravimetric DoE targets and exceed the working capacities (gravimetric and volumetric) of well-known benchmarking MOFs. The family of **rhr**-MOFs likewise contains members with well balanced (gravimetric versus volumetric) working capacity.

Methodology

Review of the topologies of paddlewheel MOFs in Ref. 33 has revealed promising candidate nets for designing new compounds. Among those is the **rhr** net, which has a vertex geometry similar to the geometry of the paddlewheel cluster and is capable of forming highly porous MOFs^{34,35}. We construct **rhr**-MOFs by combining the paddlewheel cluster with a ditopic linker, following the pattern of the **rhr** topology. We first expand the **rhr** net, then place the paddlewheel clusters onto the vertices of the net, and finally place the linkers onto the edges of the net (center of linker onto center of edge; linker oriented along edge). The **rhr** net offers the great advantage that interpenetration is not possible, and the paddlewheel cluster is a very stable building unit in many compounds including MOFs and paddlewheel complexes³⁶⁻³⁸ (which indicates that the designed MOFs can be synthesized and will be stable under operation conditions). We deal with six isorecticular **rhr**-MOFs built by the ditopic dicarboxylate linkers illustrated

in Figure 1: **T**: Cu(acetylenedicarboxylic acid)₂; **B**: Cu(terephthalic acid)₂; **TT**: Cu(hexa-2,4-diynedioic acid)₂; **BB**: Cu(biphenyl-4,4'-dicarboxylic acid)₂; **BTB**: Cu(4,4'-ethyne-1,2-diylidibenzoic acid)₂; **BBB**: Cu(*p*-terphenyl-4,4''-dicarboxylic acid)₂.

Figure 1. Ditopic dicarboxylate linkers considered in this study. The names refer to the number of triple bonds (**T**) and benzene rings (**B**).

Figure 2. (a,b) Schematic representation of the **rhr** topology and (c) final structure of the **BB** MOF.

The Forcite program of the Accelrys Materials Studio v6.1 package is used for pre-optimization of the constructed structures³⁹. The strong covalent bonds are described by the Universal Force Field (UFF)⁴⁰. The Smart algorithm of Forcite with convergence thresholds of 10^{-4} kcal/mol, $5 \cdot 10^{-3}$ kcal/mol/Å, $5 \cdot 10^{-3}$ GPa, and $5 \cdot 10^{-5}$ Å for the energy, force, stress, and atomic displacements, respectively, is employed. In the pre-optimization step we relax the atomic positions only, keeping the unit cell parameters fixed. The unit cell is optimized by a series of DFT calculations at different volumes, followed by fitting of the obtained free energies to the Birch-Murnaghan equation of state⁴¹. The bulk modulus is derived from the second derivative of the free energy as a function of the volume (at equilibrium volume). The DFT calculations are carried out using the SIESTA code⁴², the Perdew-Burke-Ernzerhof exchange-correlation functional, norm-conserving pseudopotentials with the electronic configurations $3d^{10} 4s^1 4p^0$ (Cu), $2s^2 2p^4$ (O), $2s^2 2p^2$ (C), $1s^1$ (H), and a double- ξ polarized basis sets. We account for spin-polarization with opposite

spins on interacting Cu atoms. Because of the large unit cells of the **rh**r-MOFs, Γ -point calculations turn out to be sufficient. At the end the atomic positions are relaxed by DFT calculations with a force convergence criterion of 0.02 eV/Å. To ensure accurate atomic forces, an energy cutoff of 600 Ry is used for calculating charge densities. As an example, the obtained structure of the **BB** MOF is shown in Figure 2.

Grand canonical Monte Carlo simulations are employed to study the sorption properties. Simulation parameters for methane (modeled as united atom) are obtained from the TraPPE force field⁴³ (with $\sigma = 3.73$ Å, $\varepsilon/k_B = 148$ K), as Refs. 9, 26, and 32 have shown that this approach leads to excellent agreement of the theoretical and experimental methane sorption isotherms. In addition, we have tested that the TraPPE-EH force field (explicit hydrogen) gives very similar results. The MOFs are described by the DREIDING force field⁴⁴ and the sorption parameters for Cu are taken from the UFF. Lennard-Jones potentials are employed to describe the van der Waals interactions (cut-off 12.8 Å). The MOFs are assumed to be rigid. We use the MUSIC⁴⁵ package ($2.5 \cdot 10^7$ steps for equilibration as well as for production). The Peng-Robinson equation of state is adopted to calculate the fugacity coefficients⁴⁶.

Results and Discussion

The geometric surface areas (N probe), pore volumes (He probe), and framework densities of the designed MOFs, as calculated by the Poreblazer program⁴⁷, are summarized in Table 1. We observe that longer linkers lead to larger geometric surface areas and pore volumes, but to smaller framework densities. The same trend is reported in Ref. 48, for example, for a number of experimentally realized MOFs. There is convincing agreement between the unit cell parameters obtained by the molecular mechanics and DFT calculations, see Table 1. As expected (see Ref. 49, for example), the bulk modulus decreases when the length of the linker increases.

Table 1: Comparison of the isorecticular **rh**r-MOFs.

	unit cell parameters UFF (Å)	unit cell parameters DFT (Å)	Bulk Modulus (GPa)	geometric surface area (m ² /g)	pore volume (cm ³ /g)	framework density (g/cm ³)	heat of adsorption (kJ/mol)
T	31.17	31.53	10.8	3780	1.83	0.462	9.6
B	37.94	37.37	6.2	4284	2.64	0.332	10.1
TT	40.27	40.49	6.7	5218	3.75	0.244	5.8
BB	52.20	52.29	2.7	5034	5.12	0.183	7.4
BTB	61.11	61.21	3.5	7109	8.35	0.114	5.9
BBB	67.15	67.25	2.8	6985	9.63	0.100	6.0

Figure 3. Methane sorption isotherms of the designed **rhr**-MOFs in the pressure ranges from 0 to 90 bar (a-h) and from 0 to 5 bar (i-p).

Figure 3(a-h) shows the methane sorption isotherms obtained at 240 K, 258 K, 273 K, and 298 K. Zoomed views for the low pressure range are given in Figure 3(i-p). All the **rhr**-MOFs exhibit comparably high gravimetric total uptake and low volumetric total uptake (at each temperature considered), which is explained by their low density. At 298 K and 80 bar, we obtain for the **T** MOF (smallest unit cell) the lowest value of 26.7 wt% and for the **BBB** MOF (largest unit cell) the highest value of 79.4 wt%, exceeding the performance of typical benchmarking MOFs. For example, Al-**soc**-MOF-1 has one of the most advanced gravimetric uptakes of 46.7 wt%³², for MOF-5 a value of 23.4 wt% has been reported⁵⁰, and MOF-205 achieves 38.6 wt%⁵¹. The wide range in the values obtained for the designed MOFs is explained by huge differences in the porosity, see Table 1 (pore size distributions in Figure S1). In addition, this range grows when the temperature is lowered (at 80 bar, for example, we have: 33.3-96.3 wt% at 273 K, 37.8-110.1 wt% at 258 K, and 44.1-133.5 wt% at 240 K). The same temperature trends (growing values and growing spread between the MOFs) govern the volumetric total uptakes. At 80 bar, the **T** and **BBB** MOFs exhibit the highest and lowest values, respectively. We notice that the gravimetric total uptake of the **T** MOF develops at

reduced temperatures, see particularly Figure 3(g), a high pressure plateau due to the fact that the pore volume here is fully saturated by methane molecules.

Figure 4. Methane total uptake (a,c,e,g) and working capacity (b,d,f,h) of the computationally designed **rhr**-MOFs compared to well-known benchmarking MOFs.

We present in Figure 4 a comparison of the methane sorption properties obtained for the family of **rhr**-MOFs to a selection of well-known benchmarking MOFs (Al-**soc**-MOF-1³², IRMOF-6⁵⁰, MOF-5⁵⁰, MOF-177⁵¹, MOF-205⁵¹, MOF-210⁵¹, MOF-519²⁵, PCN-14^{52,53}, Ni-MOF-74^{53,54,55}, HKUST-1^{36,53,54}, UTSA-76⁵⁶, NU-111⁵⁷, NOTT-101a⁵⁸) for different thermodynamic conditions in order to evaluate a wide parameter space. At 298 K, the gravimetric total uptakes (35, 65, and 80 bar) and working capacities (5-35, 5-65, and 5-80 bar) of the **BB**, **BTB**, and **BBB** MOFs exceed those of most benchmarking MOFs (Figure 4a-f). In particular, the working capacities of the **BTB** and **BBB** MOFs satisfy the DoE target (at 5-65 bar) for automobile applications. On the other hand, all the volumetric values obtained for the **rhr**-MOFs remain below those of the benchmarking MOFs. For applications in trucks, however, the gravimetric working capacity is more critical than the volumetric working capacity, as it determines the weight of the vehicle. The **TT** MOF provides the best balance between the gravimetric and volumetric working capacities. These findings are confirmed for a reduced temperature of 273 K, see Figure 4(g,h). In this case also the **BB** MOF

satisfies the DoE target for the gravimetric working capacity. Figure 5 presents a comparison between theoretical (obtained by exactly the same methodology as used for the **rhr**-MOFs) and experimental values of the gravimetric total uptake for benchmarking MOFs.^{52,53,56-58} Excellent agreement demonstrates high accuracy of the methodology employed in the present study.

Figure 5. Comparison between theoretical and experimental values of the gravimetric total uptake for benchmarking MOFs.

Currently no MOF reaches the DoE cost target of US\$10 per kg for mass production. Ref. 59 rather has estimated a range of 33-72 US\$ per kg, out of which typically 70% are material costs. Similarity of the designed MOFs with HKUST-1 and MOF-5 indicates that they currently also fall in this range. Cost reduction would require increased yield, lower metal salt price, and/or lower linker price. As compared to solvothermal methods for industrial-scale manufacturing of MOFs, significant reduction of the total costs could be achieved through high-volume synthesis by liquid assisted grinding methods and aqueous solution chemistry.

Conclusions

We have identified MOFs with **rhr** net topology that show excellent methane sorption characteristics, several of them achieving gravimetric working capacities which satisfy the DoE targets for automobile applications. The total uptakes and working capacities outperform benchmarking MOFs such as PCN-14, Ni-MOF-74, and HKUST-1. For example, the **BBB** MOF achieves a gravimetric working capacity of 60.7 wt% at 298 K and of 73.8 wt% at 273 K (5-65 bar). The **TT** MOF provides the most balanced working capacity of 30.2 wt%, 101.7 cm³(STP)cm⁻³ at 298 K and of 38.8 wt%, 130.8 cm³(STP)cm⁻³ at 273 K.

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