Gram-scale, high-yield synthesis of a robust metal–organic framework for storing methane and other gases†

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We have synthesized and characterized a new metal–organic framework (MOF) material, NU-125, that, in the single-crystal limit, achieves a methane storage density at 58 bar (840 psi) and 298 K corresponding to 86% of that obtained with compressed natural gas tanks (CNG) used in vehicles today, when the latter are pressurized to 248 bar (3600 psi). More importantly, the deliverable capacity (58 bar to 5.8 bar) for NU-125 is 67% of the deliverable capacity of a CNG tank that starts at 248 bar. (For crystalline granules or powders, particle packing inefficiencies will yield densities and deliverable capacities lower than 86% and 67% of high-pressure CNG.) This material was synthesized in high yield on a gram-scale in a single-batch synthesis. Methane adsorption isotherms were measured over a wide pressure range (0.1–58 bar) and repeated over twelve cycles on the same sample, which showed no detectable degradation. Adsorption of CO₂ and H₂ over a broad range of pressures and temperatures are also reported and agree with our computational findings.

Broader context

Natural gas is a promising alternative to petroleum-based fuels for vehicles. However, it is a challenge to store natural gas at sufficiently high densities to satisfy driving range requirements. One solution is to store natural gas at very high pressures (245 bar), which is the approach used by most natural gas powered vehicles in the United States today. Another potential solution is to use a porous material to adsorb natural gas, leading to higher densities at lower pressures. In this work we describe a novel adsorbent, the metal–organic framework NU-125, which is able to store at 58 bar 86% as much methane as an empty cylinder would store at 248 bar. We also show that NU-125 can be synthesized at gram scales and can withstand multiple adsorption/desorption cycles, which demonstrates potential for future use in adsorbed natural gas (ANG) tanks.

There has been increasing interest in the use of natural gas as a transportation fuel for vehicles, especially in countries that import significant amounts of oil.1–3 However, adoption of natural gas vehicles (NGVs) has been hindered by technical and economic barriers imposed by the high pressures required (typically 248 bar in the USA) to achieve energy densities (~9.3 MJ L⁻¹) for reasonable driving ranges.4 The compressed natural gas (CNG) fuel tanks in current use need to be heavily reinforced, which increases their cost and weight, and they cannot be designed to conform to the shape of the vehicle as with traditional gasoline tanks. Additionally, the refueling-station infrastructure required to transport, store, and compress natural gas to such high pressures requires significant capital, which deters the investment required to build a natural gas vehicle economy.4

A possible solution is to use porous materials that can store natural gas within their pores in high concentration but at relatively low pressures.5 However, porous materials that are available commercially, such as activated carbon, do not have sufficiently high storage capacities and, to date, no suitable material has been commercialized.4

In response to this important technological challenge, the scientific community has recently reported many novel porous materials specifically for use in NGVs with ever increasing...
methylene storage capacities.\textsuperscript{6–12} Many of these materials belong to a versatile class of materials known as metal–organic frameworks (MOFs) that are synthesized by the self-assembly of modular molecular “building blocks” into stable, highly porous crystals.\textsuperscript{13,14} Due to the modularity of the building blocks, an enormous number of MOF materials are possible, which has led to large-scale computational screening approaches to identify MOFs that would be optimal for methane storage.\textsuperscript{15,16}

While these reports are helpful in understanding the design principles for high-capacity methane storage materials, identifying a practical material of potential commercial interest requires taking many technical considerations into account (i.e., besides total capacity). The adsorbent material must have a high deliverable capacity (amount adsorbed at the highest pressure minus amount adsorbed at the lowest pressure), which in turn requires one to design a material around a relevant operating pressure range. A typical two-stage compressor can rapidly fill fuel tanks up to pressures in the \( \sim 60 \) to \( 70 \) bar range, but higher pressures require additional compression stages.\textsuperscript{17,18} Therefore, reducing the compression pressure from \( 248 \) bar to \( \sim 60 \) to \( 70 \) bar would drastically reduce the capital cost of refueling stations, while further reductions in pressure may only provide marginal benefits. The lowest pressure is constrained by the fuel injection requirements of typical internal combustion engines (\( \sim 5 \) to \( 8 \) bar).\textsuperscript{19} Thus, a practical porous material for NGVs should have a high deliverable capacity between \( \sim 5 \) and \( 8 \) bar and \( \sim 60 \) to \( 70 \) bar. Additionally, the porous material must be synthesized in high yield and be robust enough for repeated storage/release cycles.

Finally, materials proposed as candidates for commercialization must be validated by accurately measuring the high-pressure volumetric gas storage, which has previously been shown to critically depend on the assumed equation of state, as well as other criteria.\textsuperscript{20}

We sought to create a material that met the multitude of constraints mentioned above and now report a new porous material, the NU-125 MOF, that is robust, can be made in high yield on the gram-scale, and importantly, can achieve storage densities nearly as high (86%) as existing CNG tanks but at less than 1/4 the pressure. NU-125 is synthesized from Cu\textsuperscript{II} \( \text{ salt and a new hexa-carboxylic acid linker (see LH}_6 \text{ in Scheme 1). The synthesis and characterization of LH}_6 \text{ is described in the ESI.} \textsuperscript{\dagger}

Briefly, LH\(_6\) was obtained \textit{via} saponification of the corresponding hexaester precursor, which, in turn, was obtained \textit{via} click chemistry involving 2 and 3. (Not explored here, but clearly important for actual commercialization, are: (a) acceptable manufacturing-scale materials cost, and (b) material resilience with regard to anticipated chemical impurities.)

We investigated the scalability of this synthesis by using successively larger vessels (from a 1 dram vial up to a 1 L jar, concentrations of solvents and reagents were scaled proportionally, see Fig. 1A). In each case, we obtained NU-125 in high yield (the smallest vial yielded 20 mg of MOF while the 1 L jar yielded 2 g of MOF). (Clearly any practical commercial use of a MOF would require upward scaling by additional orders of magnitude.) A sample from each crystalline precipitate was characterized by powder X-ray diffraction (PXRD). The measurement confirmed that the same product was obtained in each case (see Fig. 1B).

X-ray diffraction (XRD) analysis of single crystals of NU-125 revealed a non-catenated structure with an \( \text{i/A/m} \) space group in which the framework nodes consist of Cu\textsuperscript{II} units coordinated by the carboxylates of L\(_6\) in paddlewheel fashion (see Fig. 2). The experimental structure has unit cell dimensions of \( a = b = 31.31 \) Å and \( c = 44.81 \) Å at \( 225 \) K. The solvent-free NU-125 structure has a density of 0.578 g cm\(^{-3}\), which is used in converting the measured methane storage capacity to volumetric units.\textsuperscript{23} NU-125 has an \textit{rht} topology, which was pioneered by Eddaoudi\textsuperscript{22} and has since been used by us and many other groups.\textsuperscript{23–27} NU-125 has four distinct cages, as shown in Fig. 2. The relationship between the framework topology and the

![Scheme 1](image) Synthesis of hexa-carboxylic acid strut used to construct NU-125 (LH\(_6\)).

![Fig. 1](image) Investigating the scalability of NU-125 synthesis by using (A) successively larger vessels and (B) validating samples from each vessel via PXRD measurements. Indicated volumes refer to vessel size, not the amount of solvent used. Total MOF yield from each vessel is indicated in grams.
The structure of the NU-125 framework as revealed by X-ray analysis is shown in Fig. 2. Large purple, orange, green, and blue spheres indicate the largest spheres (24, 16, 15, and 11 Å, respectively) that can fit into the four distinct cages, depicted as polyhedra of the corresponding color. Small gray, white, red, blue, and cyan spheres represent carbon, hydrogen, oxygen, nitrogen, and copper atoms, respectively. Coordinated water molecules have been removed to better represent the activated structure.

The geometry of the four cages has been discussed in detail recently for another MOF of rht topology, NU-111. The XRD-derived crystal structure was subsequently used to simulate N$_2$/CH$_4$/CO$_2$/H$_2$ gas adsorption (see ESI† for simulation details). To simulate electrostatic interactions, the atoms of the NU-125 structure were assigned partial charges using a recently described charge equilibration method. As shown in Fig. 3, NU-125 has an absolute methane storage capacity at 298 K of 228 v$_{STP}$/v at 58 bar, which corresponds to 86% of the methane stored in a CNG tank at 248 bar. Ultimately, the deliverable capacity determines the driving range of NGVs. Here, it is as important for a porous material to have low capacity in the 5–8 bar range as it is for the material to have high capacity in the 60–70 bar range. Hence, NU-125 benefits from a careful balance of strong binding sites and weakly binding surfaces, resulting in an adsorption isotherm that is not too steep at low pressures. Taking 5.8 bar as a specific lower pressure limit and 58 bar as the upper limit, Fig. 3 shows that the deliverable capacity of NU-125 is 174 v$_{STP}$/v at 298 K. When compared to a CNG tank operating on the same lower pressure limit, a tank filled with NU-125 could, in principle, deliver 67% as much fuel (although this does not take into account the powder packing density, which would necessarily reduce capacity). However, it is clear that CH$_4$ adsorption does not plateau at 58 bar (see Fig. 3), so that if incrementally higher pressures were attainable without incurring significant cost (i.e., still using low-cost compressors), higher deliverable capacities could be obtained.

In addition to performing multiple cycles at the same conditions, we also measured high pressure CH$_4$ adsorption over a wide range of temperatures on the same sample (see Fig. 4A). Such temperature-dependent adsorption isotherm measurements, in particular those at low temperatures, are discussed in the ESI†. As shown in Fig. 3, NU-125 is isothermally stable over a wide range of temperatures.
indispensable because they provide information on the maximal gas storage capacity of the material. For NU-125, we obtained about 400 v_{STP}/v methane uptake at 125 K, which effectively corresponds to the upper limit for the amount of gas that can be adsorbed under very large external pressures at ambient temperature. The observed maximum CH4 uptake is very close to the upper limit of 440 v_{STP}/v as obtained from taking the nitrogen-based pore volume and assuming liquid methane density at 125 K. This suggests that methane is able to access most of the pores available in NU-125 that are accessible to nitrogen at 77 K.

We also measured CO2 and H2 adsorption over similarly wide pressure and temperature ranges (see Fig. 4B and C). The maximum excess H2 uptake at 77 K is about 6 wt% (Fig. S21†), which is in close agreement to what we expect from “Chahine’s rule” (i.e., 1 wt% for every 500 m² g⁻¹). This empirical rule is observed for most carbon (or carbon-rich) nanoporous materials in which van der Waals interactions are the dominant mechanism for adsorption. At room temperature, we observe 1 wt% (absolute) hydrogen uptake at 65 bar. NU-125 also exhibits significant CO2 uptake at high pressures. The maximum CO2 uptake at 220 K is about 32 mmol g⁻¹, which is in good agreement with the upper limit of 34.4 mmol g⁻¹ as estimated from the nitrogen pore volume and liquid density of CO2 at this temperature. The CO2 uptake at room temperature and 30 bar is about 25 mmol g⁻¹, corresponding to filling 80% of the total pore volume. At 0.15 bar and 298 K (i.e., a condition that is close to flue gas from coal power plants), the CO2 uptake is about 3 wt%, which is lower than open-metal MOF-74 but higher than many MOFs reported in a recent CO2 screening survey.38

Fig. 4 also shows our simulated isotherms, which are in excellent agreement with experiments and give further confidence to the results reported here. The agreement between theory and measurement is particularly good near room temperature, at which the interactions with open-metal sites are likely less important. For all gases, there is a small but systematic over-prediction of adsorption at lower temperatures.

In order to get better insight into the nature of the adsorption sites and interactions in NU-125, we extracted isosteric heats of adsorption (Qst) from the temperature-dependent isotherms shown in Fig. 4 using the Clausius–Clapeyron equation.20 (All isotherms were used; see ESI† for further details.) The results are summarized in Fig. 5. The magnitudes of the Qst values are consistent with other Cu-based paddlewheel MOFs. For both CH4 and H2, the Qst value is high initially and then drops after ~4 mmol g⁻¹ are adsorbed.39 Interestingly, this corresponds closely with the amount of gas required to populate the open Cu sites: 3.1 mmol g⁻¹. However, the density of C2N3 rings in NU-125 is the same as open Cu sites; hence, it is not clear from Qst data which of these two sites binds guest molecules first. The behavior of Qst with CO2 loading is quite different. CO2 shows an initial slight decrease, as in the case of H2 and CH4, but then begins to increase. We attribute this
increase to attractive CO$_2$–CO$_2$ interactions, which become important at higher loading. We are planning to carry out detailed neutron scattering studies to determine the binding sites in NU-125 and will publish those results in due course.

In conclusion, we have synthesized and characterized a stable, robust, and promising material for potential use in natural-gas powered vehicles. We have demonstrated that the synthesis is scalable to the gram level and that the deliverable CH$_4$ capacity, under reasonable operating pressure range assumptions (but neglecting particle packing inefficiencies), is 67% of what can be delivered by CNG tanks in use today but at only 23% of the pressure. Our computational simulations agree very well with measurements over a wide pressure and temperature range. We have also shown that this material may be useful in high-pressure CO$_2$ and H$_2$ related applications.

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References

21 It should be noted that this is the density of the ideal crystal and thus does not take into account the imperfect packing of the crystalline powder.
34 For the scaled-up sample, the BET surface area (3225 m$^2$ g$^{-1}$) is in even closer agreement with the result from simulations. Note that the close agreement rules out the possibility that a
significant fraction of poorly adsorbing amorphous material is also present.


36 The definition of STP used in this paper is the IUPAC definition: 273 K and 1 bar. If pure methane were stored in a CNG tank at 298 K and 248 bar, the molar density of the gas would be 11.67 mol L⁻¹, whereas at 273 K and 1 bar the molar density of methane is 0.0442 mol L⁻¹. Taking the ratio of the two leads to a storage capacity of 264.3 v_STP/V, of which NU-125 is able to capture ~86%.


39 If the H₂ isotherms at 30 and 50 K are not used in evaluating Qₑₑ, the step near 4 mmol g⁻¹ is no longer clearly observed (see ESI, Fig. S23†).