

High-Pressure Hydrogen Adsorption on a Porous Electron-Rich Covalent Organonitridic Framework

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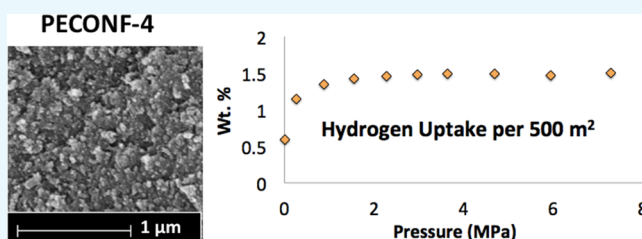
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S Supporting Information

ABSTRACT: We report that a porous, electron-rich, covalent, organonitridic framework (PECONF-4) exhibits an unusually high hydrogen uptake at 77 K, relative to its specific surface area. Chahine's rule, a widely cited heuristic for hydrogen adsorption, sets a maximum adsorptive uptake of 1 wt % hydrogen at 77 K per 500 m² of the adsorbent surface area. High-pressure hydrogen adsorption measurements in a Sieverts apparatus showed that PECONF-4 exceeds Chahine's rule by 50%. The Brunauer–Emmett–Teller (BET) specific surface area of PECONF-4 was measured redundantly with nitrogen, argon, and carbon dioxide and found to be between 569 ± 2 and 676 ± 13 m² g⁻¹. Furthermore, hydrogen on PECONF-4 has a high heat of adsorption, in excess of 9 kJ mol⁻¹.



INTRODUCTION

Hydrogen is an attractive alternative fuel that is not subject to the negative externalities of fossil fuels.^{1–4} Efficient hydrogen generation and storage would benefit mobile and stationary energy needs.^{5,6} However, both mobile and stationary applications of hydrogen energy require improvements in the volumetric energy density of stored hydrogen.^{7,8}

Hydrogen storage by physisorption on high surface area adsorbents has attracted attention because of fast cycle times, low regeneration energies, and moderate operational pressures (compared to other hydrogen storage techniques such as absorption, chemisorption, liquefaction, and extreme pressurization). A number of carbonaceous and noncarbonaceous high surface area adsorbents have been studied for their hydrogen adsorption properties, with varied results.^{9–11} Metal–organic frameworks (MOFs), in general, have been shown to adsorb 6–10 wt % of hydrogen,¹² though scalability issues and high materials costs limit potential use cases. Both MOFs and covalent organic frameworks have recently attracted attention for a variety of energy applications.^{13–16}

The capacity of an adsorbent is largely dependent on the porosity accessible to the gas (quantified by specific surface area or micropore volume) and the strength of the attractive physical interactions between the adsorbate and the adsorbent (quantified by the isosteric heat of adsorption). The optimal isosteric heat of adsorption to maximize hydrogen delivery (at standard operating conditions) is between 15 and 20 kJ mol⁻¹.^{17,18} Carbonaceous adsorbents have high specific surface areas but isosteric heats generally less than 9 kJ mol⁻¹.^{18–21}

Notable exceptions are oxygen-rich microporous carbons developed by Blankenship et al.²² and the carbide derived carbons of Yushin et al.²³ Alternative strategies to increase the isosteric heat of hydrogen adsorption have included implanting metal ions or nanoparticles and/or otherwise functionalizing the carbonaceous surface.^{24–26}

In this work, we investigated the hydrogen physisorption properties of PECONF-4, which is an inexpensive condensation product of hexachlorocyclotriphosphazene and 3,3'-diaminobenzidine (DAB) (Supporting Information, Section 1). PECONF-4 is an electron-rich compound, making it a possible candidate for improved physisorption through increased dispersion forces. In a prior study, we have shown that PECONFs have high methane and carbon dioxide uptake and exceptional selectivity for these gases over nitrogen.²⁷ PECONF-4 has a polygranular structure with grain sizes on the order of tens of nanometers, micropore diameters predominantly less than 7 Å in width, and no apparent macroporosity.

RESULTS AND DISCUSSION

Specific Surface Area. The Brunauer–Emmett–Teller (BET) method is the most commonly used technique for empirically assessing the specific surface area of porous materials.²⁸ The BET theory derives from a multilayer extension of the Langmuir isotherm and the method gives a

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robust metric of specific surface area. Nonetheless, limitations occur when using the BET method to analyze microporous materials, typically resulting in an overestimation of the specific surface area.^{29,30} These limitations and the applicability of the BET method to microporous materials are discussed in the [Supporting Information](#), Section 10. Accordingly, when using the BET method to analyze PECONF-4, we have followed the consistency criteria set forth by Rouquerol et al.²⁸

Furthermore, the BET specific surface area is dependent on the selected probe molecule. Different pores are accessible to differently sized probe molecules. In this work, we measured the BET specific surface area of PECONF-4 using three different probe molecules, nitrogen, argon, and carbon dioxide at 77, 87, and 298 K. Each probe molecule offers a different advantage. Diatomic nitrogen is the original BET probe molecule, has a cross-sectional area of 16.2 Å squared, and has been through the most historical vetting with the BET method.²⁸ However, nitrogen has a quadrupole moment that may interact with surface electric field gradients, leading to alignment or other error inducing effects. Argon is slightly smaller, with a cross-sectional area of 13.8 Å squared, and as it is spherically symmetric, it only has nonspecific charge interactions.²⁸ Carbon dioxide has a cross-sectional area of 21.0 Å squared and a strong quadrupole moment, but a higher critical temperature.²⁸ In very small pores (as found in PECONF-4, [Supporting Information](#), Section 4), errors may be induced by kinetically limited equilibration times at cryogenic temperatures. Carbon dioxide BET measurements at room temperature are less susceptible to kinetic limitations than cryogenic measurements with nitrogen or argon.³¹

At least two BET isotherms were measured for each gas (nitrogen, argon, and carbon dioxide) on PECONF-4, and specific surface areas were calculated ([Table 1](#)) by two

Table 1. Specific Surface Areas as Calculated by the BET Method and the Point B Method

	N ₂	Ar	CO ₂
BET (m ² g ⁻¹)	673 ± 18	676 ± 13	569 ± 2
point B (m ² g ⁻¹)	534 ± 9	N/A	673 ± 4

methods, as described in the [Supporting Information](#), Section 11. The average BET specific surface areas of PECONF-4 as measured by nitrogen, argon, and carbon dioxide were 673 ± 18, 676 ± 13, and 569 ± 2 m² g⁻¹, respectively. The average point B specific surface areas determined using nitrogen and carbon dioxide were 534 ± 9 and 673 ± 4 m² g⁻¹, respectively. The argon isotherms were too sparse in the region of interest to apply the point B method.

Chahine's rule is based on the BET surface area and posits that the maximum excess hydrogen adsorption on a material at 77 K is 1 wt % for every 500 m² of the BET surface area.^{1,2} This rule follows from estimates of hydrogen packing on graphene and has been demonstrated empirically in numerous hydrogen adsorption studies with few exceptions.^{1,2,32–34} While initially posited only for carbonaceous adsorbents, studies have shown Chahine's rule to be more generally applicable to porous materials including MOFs.^{35–37} Several candidate materials have been hypothesized to exceed Chahine's rule by incorporating metal ions into a high surface area carbon or by other functionalization of the surface to alter hydrogen packing and densify the adsorbed phase, though most of these ideas are untested.^{24–26}

Hydrogen Adsorption Measurements. We measured hydrogen excess adsorption on PECONF-4 using Sievert's method at temperatures of 77, 87, 253, 273, and 298 K and at pressures up to 9 MPa. In calculating excess adsorption, we used gas-phase densities from the NIST REFPROP Standard Reference Database.³⁸ The highest measured excess adsorption was 10.3 mmol g⁻¹ (2.03 wt %), at 77 K. This corresponds to 1.50 wt % hydrogen uptake for every 500 m² of adsorbent surface area, 50% above the maximum posited by Chahine's rule. This value is a conservative estimate based on the highest surface area measured, 676 m² g⁻¹.

Isosteric Heat of Adsorption. To assess the isosteric heats of hydrogen adsorption on PECONF-4, we simultaneously fitted excess adsorption isotherms at multiple temperatures using a superposition of Langmuir isotherms (dual-Langmuir method, [Supporting Information](#), Section 12) ([Figure 1](#)). The robustness of this fitting procedure has been

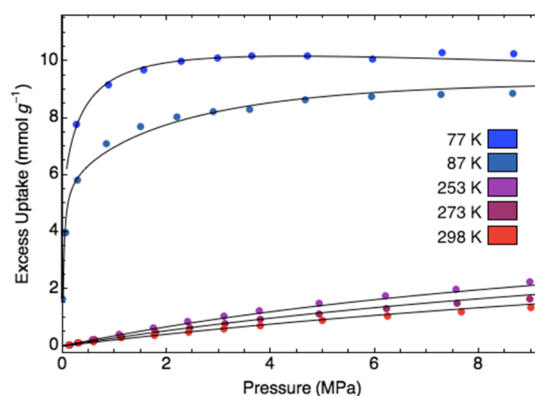


Figure 1. Dual-Langmuir fit of hydrogen excess adsorption data on PECONF-4 at 77, 87, 253, 273, and 298 K.

previously demonstrated with multiple gases,^{39–42} and here allows for a simultaneous fit of all our hydrogen adsorption data with average residual squared errors of 0.0213 (mmol g⁻¹)² per point. This fitting technique was adapted from work by Mertens⁴³ and was modified for the nonideal gas regime. In particular, this fitting procedure relies on the physically relevant Langmuir equation, avoids ideal gas assumptions and the common (though false) assumption that the adsorbed phase has negligible volume, and recognizes that excess adsorption cannot be used to approximate absolute adsorption at high pressures. This methodology is detailed in the [Supporting Information](#), Section 12, and gives the isosteric heats of adsorption as opposed to the isoexcess heats of adsorption as is typically reported.

The isosteric heats of hydrogen adsorption on PECONF-4 at different temperatures are plotted as functions of pressure in [Figure 2](#). The low-pressure values are in the range of 9.5–10.5 kJ mol⁻¹ for cryogenic temperatures (77–87 K), significantly higher than their moderate temperature (253–298 K) counterparts. Temperature dependence of the isosteric heats is expected from surface heterogeneity.⁴⁴ As a redundant check, we also calculated the low temperature isosteric heats of hydrogen adsorption on PECONF-4 using only data from the 77 and 87 K isotherms. This redundant check yielded results similar to [Figure 2](#) (see [Supporting Information](#), Section 13).

For comparison, the isoexcess heat of hydrogen adsorption on PECONF-4 was also calculated from the isotherm data without relying on any fitting procedure. This method,

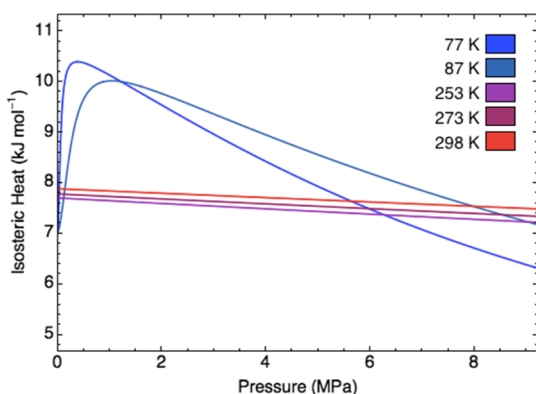


Figure 2. Isosteric heats of hydrogen adsorption on PECONF-4 as calculated by the dual-Langmuir fitting procedure.

described in the [Supporting Information](#), Section 14, relies on a number of assumptions that make it less accurate than the dual-Langmuir method. In particular, this isoexcess method assumes ideal gas conditions and negligible adsorbed-phase volume and does not differentiate between excess and absolute adsorption. Results from this method are plotted in [Figure 3](#).

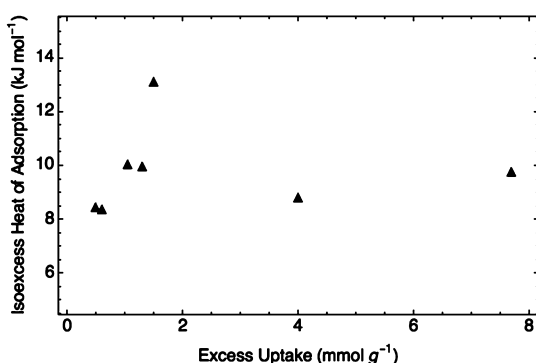


Figure 3. Isoexcess heat of hydrogen adsorption on PECONF-4, determined without fitting the adsorption data.

As expected, the isoexcess heat of adsorption differs in detail from [Figure 2](#) and has more scatter because of noise. Nonetheless, the results of this isoexcess method suggest that PECONF-4 has a high isosteric heat, likely in the range of 8.5–10 kJ mol⁻¹, in approximate agreement with the results of the dual-Langmuir method.

PECONF-4 has a high isosteric heat compared to other experimentally measured microporous carbons.^{19,24,45,46} This result can in part be attributed to the small pore sizes of PECONF-4 ([Supporting Information](#), Section 4), in which overlapping wall potentials increase the overall dispersion interactions. Schindler and LeVan have calculated that slit-pore carbons with 4–6 Å pores can have Henry's law regime isosteric heats of 7–10 kJ mol⁻¹.⁴⁷ However, in practice, very few carbonaceous materials have been reported to have isosteric heats of hydrogen adsorption in excess of 9 kJ mol⁻¹, even when pore sizes are comparable to PECONF-4.^{19–21,34} Notable exceptions have been reported for microporous carbons with uniquely functionalized surfaces such as oxygen-rich microporous carbons and carbide-derived carbons.^{22,23} It is possible that the electron-rich nature of PECONF-4 contributes to its high isosteric heat and exceptional hydrogen uptake. PECONF-4 is electron-rich

because of its electron-donating NH₂ groups, wherein the electron lone pair at the nitrogen can participate in the backbone pi bonding. The dispersion forces for physisorption are expected to increase with electron density in the adsorbent. Charge transfer interactions with the adsorbed hydrogen may be possible, but these usually give much higher enthalpies of adsorption. Although important details need clarification, the electron-rich nature of PECONF-4 is believed to contribute to its large isosteric heat of hydrogen adsorption, much like for carbon dioxide.²⁷

CONCLUSIONS

In conclusion, PECONF-4 has an exceptionally high hydrogen uptake relative to its specific surface area. A conservative analysis shows that at 77 K, PECONF-4 adsorbs 1.50 wt % of hydrogen per 500 m² of surface area, which exceeds Chahine's rule by 50%. This also corresponds to a high isosteric heat of adsorption, in excess of 9 kJ mol⁻¹, possibly resulting from interactions between adsorbed hydrogen and the electron-rich backbone of PECONF-4. These properties make PECONF-4 an interesting new candidate for hydrogen storage and separation. Further work to increase the specific surface area while maintaining the unique surface chemistry of PECONF-4-like materials could make them important as materials for hydrogen storage.

METHODS

PECONF-4 was synthesized from DAB and hexachlorocyclo-triphosphazene in a simple polycondensation reaction. Additional details on this synthesis can be found in the [Supporting Information](#), Section 1. Gas adsorption isotherms were measured on PECONF-4 using both a Micromeritics Tristar II 3020 apparatus and a custom high-pressure Sieverts apparatus. Additional details on the gas adsorption measurements can be found in the [Supporting Information](#), Section 2. Additional microscopy and spectroscopy characterizations of PECONF-4 are described in the [Supporting Information](#).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the [ACS Publications website](#) at DOI: 10.1021/acsomega.8b03206.

Materials synthesis; experimental methods; skeletal density; pore-size distribution; transmission electron microscopy; pore-size distribution; transmission electron microscopy; MAS NMR spectroscopy; X-ray diffraction; Fourier transform infrared spectroscopy; differential thermogravimetry and thermogravimetric analysis; the BET method, its limitations and applicability; the point B method for determining specific surface area; dual-Langmuir fitting; dual-Langmuir fits with only 77 and 87 K isotherms; and a method for estimating isoexcess heat of adsorption without fitting the data ([PDF](#))

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Notes

The authors declare no competing financial interest.

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