

Thermodynamics of Methane Adsorption on Copper HKUST-1 at Low Pressure

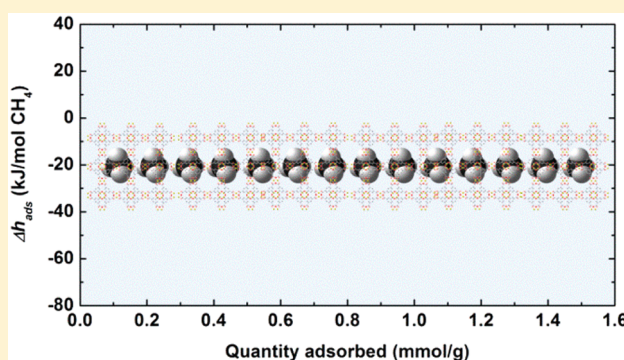
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ABSTRACT: Metal–organic frameworks (MOFs) can be engineered as natural gas storage materials by tuning the pore structures and surface properties. Here we report the direct measurement of CH₄ adsorption enthalpy on a paddlewheel MOF (Cu HKUST-1) using gas adsorption calorimetry at 25 °C at low pressures (below 1 bar). In this pressure region, the CH₄–CH₄ intermolecular interactions are minimized and the energetics solely reflects the CH₄–MOF interactions. Our results suggest moderately exothermic physisorption with an enthalpy of -21.1 ± 1.1 kJ/mol CH₄ independent of coverage. This calorimetric investigation complements previous computational and crystallographic studies by providing zero coverage enthalpies of CH₄ adsorption. The analysis of the new and literature data suggests that in initial stages of adsorption the CH₄–HKUST-1 interaction tends to be more sensitive to the pore dimension than to the guest polarizability, suggesting a less specific chemical binding role for the open Cu site.



Increasing CO₂ release from the burning of fossil fuels is a major environmental concern.^{1,2} Numerous alternative strategies for effective and environmentally friendly energy sources are being explored. Natural gas (primarily CH₄) has shown several significant advantages, including relatively low carbon emission per unit energy produced, fewer smog-forming pollutants, and abundant, underutilized natural reserves.^{3,4} Typically, natural gas has to be stored under pressure to optimize volumetric energy density for further transport, delivery, and application. Traditional methods emphasize high-pressure multistage compression or low-temperature liquefaction; however, these require complex equipment, consume considerable energy, and are costly and energy inefficient. Over the past few decades, porous materials have shown significant promise as natural gas storage media at room temperature and moderately high pressure. The two major groups of materials investigated include porous carbons⁵ and zeolites.⁶ Recently, metal–organic frameworks (MOFs) have attracted global attention for their outstanding performance in catalysis,⁷ molecular sensing,⁸ energy storage,^{9,10} as well as selective gas storage/adsorption/separation.^{8,11,12} MOFs are constructed by coordinating metal cations and rigid organic linkers in three dimensions.¹³ They can have intricate open pore structures and chemically functionalized surface sites. Developed by Chui et al.,¹⁴ HKUST-1 features a 3D open framework with three types of cages (Figure 1), namely, the small tetrahedral pocket (0.4 nm), the medium cuboctahedral

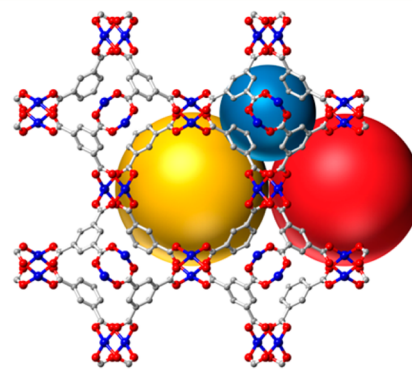


Figure 1. Structure of Cu HKUST-1. The blue sphere indicates the 0.4 nm tetrahedral cages, while yellow and red spheres show the 1.0 and 1.1 nm pores, respectively.

cage (1.0 nm), and the large cuboctahedral pore (1.1 nm). There are unsaturated Cu nodes, which are only accessible from the largest pores. The open Cu node and the small 0.4 nm cages are considered to be the primary binding sites for CH₄ storage at high pressure.^{15–17} So far, Cu HKUST-1 is one of the very few MOFs that approaches or meets the new

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volumetric storage target at 298 K and 65 bar, 263 cc(STP)/cc, set by the U.S. Department of Energy (DOE) if the CH₄ packing efficiency loss is not considered.^{3,18,19} Most previous investigations on HKUST-1 focused on the adsorption capacity and calculation of isosteric heat of adsorption from high-pressure isotherms (up to 100 bar),^{3,18–21} the details of which are summarized by Long et al.¹⁸ in a perspective article, whereas the energetics of binding at zero coverage, which directly reflects CH₄–MOF interactions, has not yet been experimentally documented. Although different binding sites are identified for fully loaded HKUST-1,^{15–17} the site specificity and energetics of CH₄ molecules when they first enter the freshly activated empty framework remain unclear. These questions set our motivation for the present research.

The gas adsorption calorimetry system developed by Ushakov and Navrotsky²² features a Calvet-type microcalorimeter combined with an accurate gas dosing system. Our previous studies mainly focused on hydration enthalpies of nanoparticles.^{23–25} Recently, we expanded the application of this system to CO₂ adsorption on a green MOF (CD-MOF-2) made with sugar,²⁶ in which strong zero coverage enthalpy of adsorption was observed and different binding sites were distinguished and correlated to specific surface chemistry. This work demonstrated that direct gas adsorption calorimetry could accurately detect the energy of binding at very low molecular coverage. Here we implement this methodology to study the enthalpy of CH₄ adsorption on Cu HKUST-1 at pressure well below 1 bar. By direct experimental observations, we are able to quantify the enthalpy of CH₄ adsorption at zero coverage and 25 °C. We discuss trends in the zero coverage differential enthalpy of gas adsorption on HKUST-1 for guest molecules of different sizes. We generalize the trend of enthalpy of CH₄ adsorption as a function of the size of the smallest accessible pores of the MOF by combining our experimental data with results in the literature.

The CH₄ adsorption isotherms and their corresponding calorimetric traces are plotted in Figure 2A,B. In the pressure range investigated, CH₄ adsorption on HKUST-1 results in a linear isotherm (Henry's adsorption isotherm²⁷) as a function of pressure, which suggests the CH₄ uptake is proportional to the pressure of the gas. Such isotherms are typically seen for adsorption at very low surface coverage, at which the molecule–surface binding dominates and the molecule–molecule interactions are negligible. The height and area of calorimetric peaks generated by adsorption of each CH₄ dose are nearly identical (Figure 2B). Accordingly, the differential enthalpy of adsorption (Figure 2C) appears to be constant, -21.1 ± 1.1 kJ per mole of CH₄, which falls in the range of physisorption, suggesting that the CH₄–HKUST-1 interaction is homogeneous in the pressure range investigated and independent of the coverage. Moreover, the isotherms and differential enthalpy of adsorption curves for the first and second round of adsorption are entirely overlapping, confirming reversible adsorption upon regeneration.

Adsorption on porous materials is governed by both the physical and chemical characteristics of both the framework and adsorbate molecule.²⁸ At the initial section of the isotherm (Henry's Law region, with constant slope) for nonpolar adsorbents, the size selectivity based on the steric constraints defined by the pore geometry and the diameter of the adsorbate is a dominant factor.²⁹ Therefore, it is important to evaluate the steric effects (zero coverage enthalpy of adsorption) for the same MOF with molecules with varying kinetic diameters and

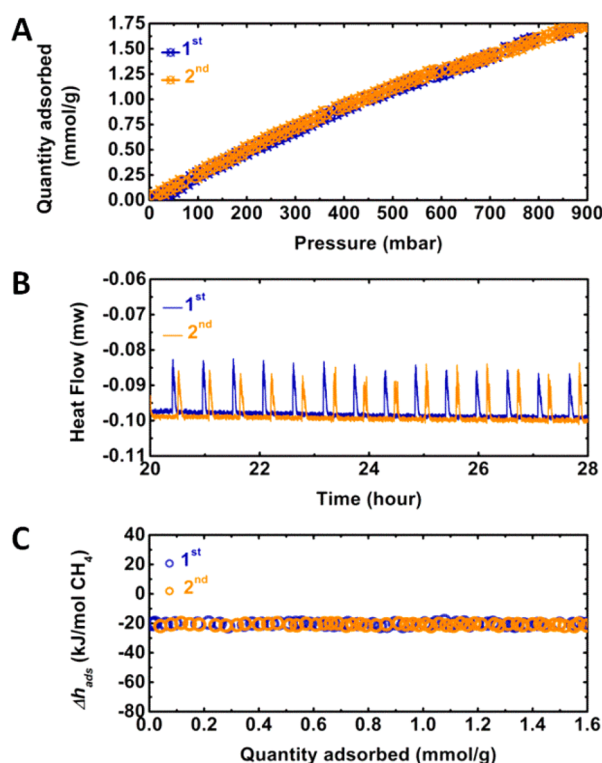


Figure 2. (A) CH₄ adsorption isotherms, (B) corresponding calorimetric signals, and (C) differential enthalpies at 25 °C for the first (navy) and second (orange) round of CH₄ adsorption on the same sample of Cu HKUST-1.

to summarize the general trends of confinement effects from different frameworks for the same guest molecule.

Two major conclusions were reached by previous studies using neutron powder diffraction (NPD) and grand canonical Monte Carlo (GCMC) simulation on the CH₄–HKUST-1 system.^{15–17} First, at full CH₄ loading (very high pressure) there appear to be two major binding locations, the small cages and the Cu nodes.^{15–17} Second, it was suggested that without considering the impact of Cu nodes, CH₄ molecule went into the small cages first.^{15,16} In addition, the estimated magnitude for the CH₄–small pore interactions (potential energy from GCMC) was approximately -20 kJ per mole of CH₄.¹⁶ On the other hand, the isosteric heat ($-Q_{st}$) fitted from high-pressure CH₄ sorption isotherms (up to 100 bar) was found to be around -17 kJ per mole of CH₄.³ These studies described possible adsorption locations at very high loading (high pressure), potential filling sequence, and the average binding energy for CH₄–HKUST-1 interactions. The present calorimetric data complement the existing reports by providing directly measured zero coverage enthalpy of CH₄ adsorption in HKUST-1 (-21.1 ± 1.1 kJ per mole of CH₄). The measured enthalpy profile suggests that below 1 bar Δh_{ads} is constant and not a function of CH₄ loading. Such behavior is rarely observed for adsorption calorimetry. It indicates that at zero coverage CH₄ has only one type of interaction with HKUST-1 or that interactions of multiple types are energetically undistinguishable.

Pore confinement is governed mainly by van de Waals interactions, while metal site binding relies on Coulombic forces.¹⁷ This means that the same framework may interact differently as the size or polarizability of the guest molecule varies. Therefore, we selected CH₄, CO₂, Kr, and Xe as

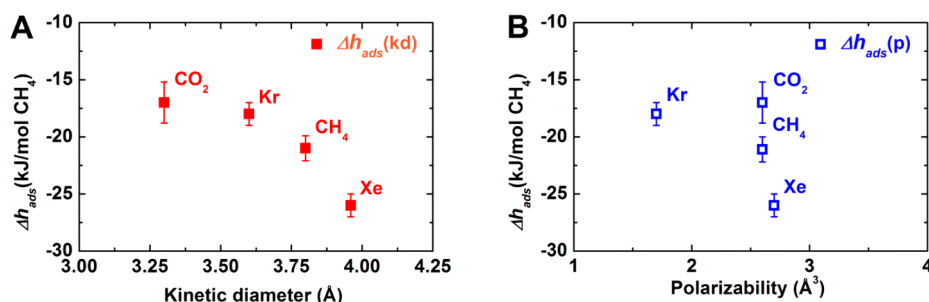


Figure 3. Zero coverage differential enthalpy of adsorption for CH₄, CO₂, Kr, and Xe as a function of their respective (A) kinetic diameter and (B) polarizability.^{30–34,39}

molecular probes, which are different in dimensions and polarizability. Their directly measured zero coverage enthalpies³⁵ of adsorption on HKUST-1 are plotted versus kinetic diameter (Figure 3A) and polarizability (Figure 3B). Interestingly, Δh_{ads} appears to have a roughly exponential dependence on the kinetic diameter. It becomes more exothermic as the size of adsorbate increases regardless of the polarizability; however, no detectable dependence between Δh_{ads} and polarizability was observed. Although the polarizabilities of CH₄, CO₂, and Xe are nearly identical, they present distinct zero coverage Δh_{ads} ranging from -16 to -26 kJ per mole of adsorbate (Figure 3B). Such behavior suggests that the guest–host interaction in HKUST-1 at zero coverage appears to be more sensitive to the size of guest molecules than to the polarizability. In other words, at pressure below 1 bar, the chemical specificity of the open Cu site in its interactions with the guest molecules may be subordinate to steric (size) effects.

The previously described analysis leads to further discussion of the energetics of CH₄ adsorption in frameworks with different pore sizes. The near-zero coverage CH₄ adsorption enthalpies, extrapolated from reported isosteric heat curves,^{3,36} for Cu-based MOFs³ and covalent-organic frameworks (COFs)³⁶ are plotted versus the size of the smallest accessible pore/cage of a specific structure, R_s (see Figure 4). All of the

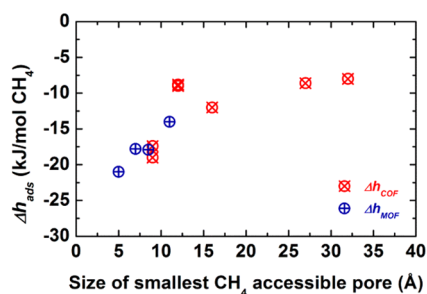


Figure 4. Near-zero coverage enthalpies (Δh_{ads}) of CH₄ adsorption on Cu-based metal–organic frameworks (MOFs) and covalent organic frameworks (COFs) as a function of their size of the smallest CH₄ accessible pore.^{3,36}

MOFs have open Cu nodes, while the COFs have no metal components. Interestingly, Δh_{ads} exhibits a monotonic and roughly exponential trend as a function of R_s . Interaction energies with a similar profile were also observed in our previous study on the confinement of a rigid organic molecule in a set of porous silicas with different pore sizes.³⁷ For the present plot, once R_s is identical to the kinetic diameter of CH₄, as seen for the small cage (0.4 nm) of HKUST-1 and CH₄, the pore/cage may confine CH₄ tightly, resulting in a strongly

exothermic heat effect. Δh_{ads} is less exothermic as the pore expands. When the pore dimension is significantly greater than the size of the CH₄ molecule, the 3D cage constraint becomes negligible. Then, each CH₄ molecule may only interact with the surface and/or the metal sites at one point. This indicates that regardless of the chemical properties of the framework, maximizing the accessible cages around 0.4 nm (the same as CH₄ diameter) may hold the key to achieving the new DOE volumetric storage target. A recent adsorption study suggests that the optimal $-Q_{st}$ at low loading for maximum CH₄ delivery is around -20 kJ per mole of CH₄,¹⁹ which is the enthalpy we have observed in this study of Cu HKUST-1.

Direct CH₄ adsorption calorimetry on Cu HKUST-1 quantified the binding enthalpy as a function of loading, tested the adsorption reproducibility, and discussed the possible binding preference of CH₄ at very low pressure. In the initial, low-pressure range, the differential enthalpy of CH₄ adsorption is constant and appears to be more sensitive to the size of the smallest accessible pore of the framework than to the polarizability of the guest molecule. In a broader context, the present study provides valuable insights for future optimization of natural gas storage materials. Rational design and development of MOF structures with well-balanced open porosity and a large fraction of accessible small cages with size comparable to that of CH₄ may enhance storage performance.

EXPERIMENTAL METHODS

The detailed chemical and structural analyses of Cu HKUST-1 used in the present work, including powder X-ray diffraction patterns, nitrogen adsorption–desorption isotherms, and thermal analysis have been published elsewhere,³⁸ so we do not repeat them here. The adsorption enthalpy measurements were performed by gas adsorption calorimetry at 25 °C using a commercial gas dosing system (Micromeritics ASAP 2020) coupled to a Calvet-type microcalorimeter (Setaram Sensys).²² The preactivated HKUST-1 sample (~ 20 mg) was placed in one side of a custom-made silica glass forked tube, the other side of which remained empty serving as a reference. This tube was inserted into the twin chambers of the microcalorimeter, conducted to the gas dosing manifold and degassed under vacuum ($<10^{-3}$ Pa) for 12 h at 180 °C to remove any initial adsorbates. The gas dosing system was programmed in incremental dosing mode (10 μ mol per dose). The waiting period between each dose was 0.5 to 1.0 h to ensure equilibration. The adsorption isotherm and associated heat effects were recorded simultaneously. The differential enthalpy of adsorption, Δh_{ads} (kJ per mole of CH₄), of each dose was calculated by dividing the observed heat effect by the amount of

gas adsorbed for that specific dose. All adsorption calorimetry experiments were repeated at least once.

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Notes

The authors declare no competing financial interest.

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