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Enhanced Thermal Conductivity in a Diamine-Appended Metal–Organic Framework as a Result of Cooperative CO₂ Adsorption

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Abstract

Diamine-appended variants of the metal–organic framework $M_2(\text{dobpdc})$ ($M = \text{Mg}, \text{Mn}, \text{Fe}, \text{Co}, \text{Zn}$; $\text{dobpdc}^{4-} = 4,4'$ -dioxidobiphenyl-3,3'-dicarboxylate) exhibit exceptional CO_2 capture properties owing to a unique cooperative adsorption mechanism, and thus hold promise for use in the development of energy- and cost-efficient CO_2 separations. Understanding the nature of thermal transport in these materials is essential for such practical applications, however, as temperature rises resulting from exothermic CO_2 uptake could potentially off-set the energy savings offered by such cooperative adsorbents. Here, molecular dynamics simulations are employed in investigating thermal transport in bare and e-2-appended $\text{Zn}_2(\text{dobpdc})$ (e-2 = *N*-ethylethylenediamine), both with and without CO_2 as a guest. In the absence of CO_2 , the appended diamines function to enhance thermal conductivity in the *ab*-plane of e-2- $\text{Zn}_2(\text{dobpdc})$ relative to the bare framework, as a result of non-covalent interactions between adjacent diamines that provide additional heat transfer pathways across the pore channel. Upon introduction of CO_2 , the thermal conductivity along the pore channel (the *c*-axis) increases due to the cooperative formation of metal-bound ammonium carbamates, which serve to create additional heat transfer pathways. In contrast, the thermal conductivity of the bare framework remains unchanged in the presence of zinc-bound CO_2 but decreases in the presence of additional adsorbed CO_2 .

Keywords: Metal-organic framework, diamine- $M_2(\text{dobpdc})$, heat transfer, CO_2 capture, phonon scattering

Introduction

Metal–organic frameworks are crystalline, porous solids that exhibit vast chemical and structural tunability, and in tandem with their extremely high internal surface areas, these properties have rendered them promising candidates for a variety of applications, including gas storage, molecular separations, and catalysis.^{1–5} Recently, diamine-appended frameworks with the formula (diamine)₂M₂(dobpdc) (also known as diamine–M₂(dobpdc); M = Mg, Mn, Fe, Co, Zn; dobpdc^{4–} = 4,4'-dioxidobiphenyl-3,3'-dicarboxylate) have been shown to capture CO₂ with unprecedented efficiency and selectivity.^{6–13} In these materials, CO₂ reacts with the metal-bound amine to form a metal-bound ammonium carbamate, which then propagates as ion-paired ammonium carbamate chains that extend along the framework channels.^{7,9,14} Single-crystal X-ray diffraction structures of Zn₂(dobpdc), e-2–Zn₂(dobpdc) (e-2 = *N*-ethylethylenediamine), and e-2–Zn₂(dobpdc)–CO₂ are shown in Fig. 1, as determined in Ref. [9]. This unique mechanism gives rise to step-shaped CO₂ uptake, and the material step temperature (isobaric conditions) or step pressure (isothermal conditions) can be tuned based on the choice of appended diamine. As such, these materials are of interest for various challenging separations in industry, including the capture of CO₂ from power plant flue emissions,^{7,9,11,15} as they can operate using much smaller pressure or temperature swings and achieve higher working capacities than traditional adsorbents.

One important practical consideration in evaluating the performance of these materials is the rate at which CO₂ can be loaded into the pores without causing a prohibitively sharp temperature increase. Indeed, adsorption of CO₂ is an exothermic process, potentially leading to a considerable increase in the local temperature that is higher than the step temperature in an adsorption isobar curve. To dissipate this heat quickly and maximize the quantity of CO₂ adsorbed, a given framework must have a high thermal conductivity. Additionally, high thermal

conductivities can reduce adsorption/desorption cycle times in practical configurations, which can lead to improvements in process efficiency. Previous investigations of thermal transport in MOFs have predominantly been limited to materials in the absence of guest molecules,^{16–22} while the few studies that have investigated heat transfer in the presence of an adsorbed gas have considered only physisorbed gases.^{23–25} Our previous studies^{23,25,26} have shown that the presence of physisorbed guests introduces new phonon scattering channels resulting from gas-framework collisions, which serve to reduce thermal conductivity. The possible effects of chemisorbed guests on thermal transport in MOFs, however, have remained unstudied.

In this work, we use molecular dynamics (MD) simulations to investigate mechanisms of heat transfer in bare and e-2-appended $\text{Zn}_2(\text{dobpdc})$ (e-2 = *N*-ethylethylenediamine), and we apply the Green-Kubo method to predict their thermal conductivities with and without adsorbed CO_2 . Consistent with our previous studies, thermal conductivity in the bare material is diminished in the presence of (non-coordinating) physisorbed CO_2 , whereas it is unchanged in the presence of more strongly adsorbed, zinc-bound CO_2 . Importantly, however, an enhancement in thermal conductivity is observed for e-2- $\text{Zn}_2(\text{dobpdc})$ upon chemisorption of CO_2 , resulting from the introduction of new heat transfer pathways along the framework channels. This result is in contrast to the reduction in thermal conductivity that occurs in the presence of physisorbed guests and has important implications for heat management during CO_2 adsorption that is of relevance for practical separation applications.

Fig. 1. (a) Portion of the single-crystal X-ray diffraction structure of $\text{Zn}_2(\text{dobpdc})$ viewed down the framework channel (c axis); (b) a view of the primary coordination sphere of a zinc(II) node in the dominant conformation of $\text{e-2-Zn}_2(\text{dobpdc})$; and (c) crystal structure of the dominant conformation of $\text{e-2-Zn}_2(\text{dobpdc})$ following cooperative CO_2 insertion into the metal-amine bonds, which results in the formation of chains of ammonium carbamate that propagate along the channel direction. Images were adapted from Ref. [9]; light blue, red, dark blue, gray, and white spheres represent Zn, O, N, C, and H atoms, respectively. Thermal transport in all three frameworks was investigated in this work using molecular dynamics simulations.

Structures and Methodology

In our calculations, we evaluated the thermal conductivity of guest-free $\text{Zn}_2(\text{dobpdc})$ and $\text{e-2-Zn}_2(\text{dobpdc})$, $\text{e-2-Zn}_2(\text{dobpdc})$ with chemisorbed CO_2 , and $\text{Zn}_2(\text{dobpdc})$ in the presence of metal-bound and more weakly physisorbed CO_2 . In the case of $\text{Zn}_2(\text{dobpdc})$, metal-bound CO_2 molecules do not move from their initial DFT-determined locations in the pores, whereas the other more weakly associated physisorbed CO_2 molecules are those that can diffuse away from their

initial random calculated positions. The simulation cell size for each framework was set based on the DFT-relaxed lattice constants. For the interactions between atoms in $\text{Zn}_2(\text{dobpdc})$, e-2- $\text{Zn}_2(\text{dobpdc})$ and e-2- $\text{Zn}_2(\text{dobpdc})\text{-CO}_2$, we used a modified version of the DREIDING force field,²⁷ in which the equilibrium distances between atoms were adjusted to the DFT-relaxed structures. Among other general force fields, we picked DREIDING as it allows for the description of existing hydrogen bonds. The required charges on atoms were obtained using the DDEC algorithm,²⁸ wherein partial atomic charges are calculated using the electron densities obtained from DFT calculations. The CO_2 molecules loaded within $\text{Zn}_2(\text{dobpdc})$ were modeled using the TraPPE force field.²⁹ The initial atomic configurations for the MD simulations involving metal-bound CO_2 adsorbed in $\text{Zn}_2(\text{dobpdc})$ were taken from snapshots of equilibrated DFT calculations.

For the DFT calculations, we used a plane-wave basis and projector augmented-wave (PAW)^{30,31} pseudopotential with the Vienna ab-initio Simulation Package (VASP) code.^{32–35} To include the effect of the van der Waals (vdW) dispersive interactions on binding energies and mechanical properties, we performed structural relaxations with a vdW dispersion-corrected functional (vdW-DF2)³⁶ as implemented in VASP. For all calculations, a Γ -point sampling of the Brillouin zone and a 600-eV plane-wave cutoff energy were employed. We explicitly treated twelve valence electrons for Zn ($3d^{10}4s^2$), six for O ($2s^22p^4$), five for N ($2s^22p^3$), four for C ($2s^22p^2$), and one for H ($1s^1$). All structural relaxations were performed with a Gaussian smearing of 0.05 eV.³⁷ The ions were relaxed until the Hellmann-Feynman forces were less than $0.02 \text{ eV}\text{\AA}^{-1}$.

Fig. 2 Simulation box with $4 \times 4 \times 6$ unit cells (in crystallographic directions a , b and c) of (a) e-2- $\text{Zn}_2(\text{dobpdc})\text{-CO}_2$ and (b) CO_2 bound at the open Zn^{2+} sites within $\text{Zn}_2(\text{dobpdc})$. Light blue, red, blue, gray, and light gray spheres represent Zn, O, N, C, and H atoms, respectively.

The Green-Kubo method was applied to predict thermal conductivity.³⁸ This method involves calculating the instantaneous heat flux in an equilibrium MD simulation. The partial enthalpy terms required to analyze multicomponent systems were implemented as discussed in Refs. [23,25,39,40]. The MD simulations were performed using a version of the Large-scale Atomic/Molecular Massively Parallel Simulator⁴¹ software, which can correctly implement heat flux for many-body potentials.⁴² To gain further insight into the thermal conductivity predictions, we also calculated the corrected diffusivity (which is associated with molecular mobility) of metal-

bound CO₂ in Zn₂(dobpdc).⁴³ The corrected diffusivity is based on a Green-Kubo relation and is defined as the time integral of the center of mass velocity autocorrelation function for the gas component. Details of the Green-Kubo calculations for both thermal conductivity and diffusivity are provided in the Supporting Information. For determining thermal conductivity, a system size of 4×4×6 (in crystallographic directions *a*, *b*, and *c*) unit cells was used. See Fig. 2 for snapshots of the simulation cells for e-2-Zn₂(dobpdc)-CO₂ and Zn₂(dobpdc) with metal-bound CO₂. The systems were initially equilibrated under *NPT* (constant pressure-constant temperature) conditions at a temperature of 300 K and atmospheric pressure for 500,000 time steps; under *NVT* (constant volume-constant temperature) conditions at a temperature of 300 K for 300,000 time steps; and for 200,000 time steps under *NVE* (constant volume-constant energy) conditions. Finally, *NVE* simulations were run for an additional 1,000,000 time steps where the heat current was calculated every five time steps. For all cases, this procedure was performed for four simulations starting from random velocity distributions.

Results and Discussion

Predicted thermal conductivities in the crystallographic *a*, *b*, and *c* directions are shown in Fig. 3. In all cases, thermal conductivities in the *a* and *b* directions (perpendicular to the framework channels) are the same, indicating isotropy in the *ab*-plane. Relative to the bare framework, the introduction of the metal-bound diamine increases the thermal conductivity in the *ab*-plane, from 0.4 W m⁻¹ K⁻¹ for Zn₂(dobpdc) to 0.5 W m⁻¹ K⁻¹ for e-2-Zn₂(dobpdc). In contrast, thermal conductivity decreases slightly in the *c*-direction for e-2-Zn₂(dobpdc) relative to Zn₂(dobpdc). The increase in *ab*-plane thermal conductivity can be ascribed to the presence of van der Waals interactions between diamines, which create additional heat conduits between adjacent metal

nodes. However, the diamines do not interact with each other along the c -axis, and in this direction, they likely act instead as a phonon scattering source.

Fig. 3 Calculated thermal conductivities of Zn₂(dobpdc) and e-2-Zn₂(dobpdc) with and without CO₂ loading. The parameters k_a , k_b , and k_c correspond to the crystallographic a , b , and c direction as discussed in the text.

The introduction of metal-bound CO₂ in Zn₂(dobpdc) has no effect on the thermal conductivity. Molecules of CO₂ initially positioned in the vicinity of the metal nodes (suggested by DFT calculations) do not function as phonon scatterers or as agents for heat conduction. The calculated corrected diffusivities in all directions are zero, indicating that CO₂ molecules in this initial configuration do not move through the channel space. Consistent with our previous reports,^{23,25} the presence of more weakly physisorbed CO₂ results in a decrease in the thermal conductivity of Zn₂(dobpdc) in all directions, as a result of gas-framework collisions and resulting phonon scattering.

In stark contrast to both scenarios for bare $\text{Zn}_2(\text{dobpdc})$, chemisorption of CO_2 in ϵ -2- $\text{Zn}_2(\text{dobpdc})$ results in a 100% *increase* in thermal conductivity in the c -direction, to $0.5 \text{ W m}^{-1} \text{ K}^{-1}$. Here, the newly-formed hydrogen-bonded ammonium carbamate chains (see Fig. 1c) provide an additional heat transfer pathway along the framework channels. The thermal conductivity of ϵ -2- $\text{Zn}_2(\text{dobpdc})\text{-CO}_2$ is notably 2-3 times higher than that of conventional activated carbon⁴⁴ and comparable to that of zeolites MFI and MEL,^{45,46} which are extensively deployed in gas storage and separation applications. Importantly, as a result of this enhanced thermal conductivity upon CO_2 adsorption, less active cooling of ϵ -2- $\text{Zn}_2(\text{dobpdc})$ would be required in a practical separations process. Thus, in addition to the other advantages offered by diamine-appended MOFs compared to traditional adsorbents, these materials are capable of reducing unwanted thermal effects by quickly dissipating heat generated during adsorption.

It is important to note that the thermal conductivity enhancements reported here were observed for the MOF single crystal. Changes in thermal conductivity upon chemisorption of CO_2 for corresponding bulk powder or pellet samples are expected to differ due to the presence of voids between individual crystallites which reduce thermal conductivity by introducing interfacial thermal resistance between crystallites. Future studies would benefit from an evaluation of the differences in thermal conductivity in single crystal, powder, and pellet samples upon chemisorption of CO_2 . We also note that the substantial increase in thermal conductivity observed here for the diamine-appended $\text{Zn}_2(\text{dobpdc})$ upon CO_2 uptake is a phenomenon that is more likely to be observed for frameworks with larger pores, wherein suitable void space remains even upon incorporation of appended diamines and chemisorption products, such that there is no significant enhancement in crystal gas collisions that diminish thermal conductivity.²⁵ Indeed, $\text{Zn}_2(\text{dobpdc})$ has much larger pores and also a lower thermal conductivity than denser MOFs such as $\text{Cu}_3(\text{BTC})_2$

(also known as HKUST-1; $\text{BTC}^{3-} = 1,3,5\text{-benzenetricarboxylate}$)²⁶ and $\text{Zn}_4\text{O}(\text{BDC})_3$ (also known as IRMOF-1 or MOF-5; $\text{BDC}^{2-} = 1,4\text{-benzenedicarboxylate}$)¹⁷, and therefore the introduction of diamines and ammonium carbamates along the *c*-axis is anticipated to result in more pronounced changes to thermal conductivity.

Conclusion

In summary, we have used MD simulations to investigate thermal transport in the frameworks $\text{Zn}_2(\text{dobpdc})$ and $\text{e-2-Zn}_2(\text{dobpdc})$ both without and with CO_2 as a guest. We find that in the presence of CO_2 , the unique chemisorption mechanism in $\text{e-2-Zn}_2(\text{dobpdc})$ serves to enhance the thermal conductivity in the direction of the framework channels, whereas adsorption of CO_2 in the bare material has no effect on or decreases the thermal conductivity. These results point to enhanced thermal management as an additional advantage of these diamine-appended materials for practical applications. Indeed, upon CO_2 uptake, most diamine- $\text{M}_2(\text{dobpdc})$ frameworks follow a similar mechanism of ammonium carbamate chain formation. However, we note that certain other appended diamines, such as 2,2-dimethyl-1,3-diaminopropane, have been shown to react with CO_2 via a more complex mechanism that also involves the formation of carbamic acid pairs.¹¹ In the future, we plan to investigate the effects of these differing chemisorption mechanisms on thermal transport in diamine- $\text{M}_2(\text{dobpdc})$ frameworks.

Notes

The authors declare the following competing financial interest: J.R.L. has a financial interest in Mosaic Materials, Inc., a start-up company working to commercialize metal-organic frameworks of the type investigated here for CO_2 separations.

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Supporting Information. Additional information on simulation methodology.

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