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Functionalized MOFs for Enhanced CO₂ Capture

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ABSTRACT: Based on computational studies, we propose new metal–organic framework materials, in which the bridging ligands have been functionalized by different substituents, with the aim of improving the CO₂ adsorption capacity of the material. The materials are based on the large-pore form of MIL-53(Al³⁺), with the following functional groups: OH-, COOH-, NH₂-, and CH₃-. For each form, adsorption heats and isotherms were simulated using the Grand Canonical Monte Carlo method which were found to be consistent with DFT calculations. The study illustrates the enormous impact of the functional groups in enhancing CO₂ capture in the pressure range 0.01–0.5 bar and at room temperature. It also provides important insights into the structural factors which play a key role in the CO₂ adsorption process in the functionalized MOFs. We propose the material (OH)₂-MIL-53(Al³⁺) as an optimal candidate for improved CO₂ capture at low pressures.

The selective adsorption of CO₂ is a critical issue in many technological processes, for instance the capture of CO₂ in postcombustion flue gases from coal-fired power stations and in H₂ production.^{1,2} At present, this task is performed by amine sorbents, which require significant heating for regeneration and have high operational costs.

In the past few years, the rapidly expanding class of porous crystalline materials, metal–organic frameworks (MOFs), whose structures consist of metal oxide clusters, linked by organic molecules to form a 3D porous framework, have displayed an exceptionally rich host–guest chemistry.³ Their key features, such as very large internal surface areas and flexible chemical composition, make these materials very attractive in applications involving adsorption of strategic gases such as CO₂, CH₄, and H₂.^{5a,b} A number of feasible avenues for increasing the adsorption capacity of such materials exist, for instance ion-exchange, the introduction of open metal centers, and the use of ligand molecules with specific adsorption sites. On the last point, our recent theoretical work^{6,7} on the interaction of CO₂ with functionalized aromatic molecules (through CO₂–ligand cluster calculations) has shown the effectiveness of introducing specific polar substituent groups, e.g. –OH, –COOH or –NH₂, on the aromatic ligand in increasing the CO₂–ligand affinity. While the ability of NH₂-functionalization of MOFs to enhance CO₂ adsorption has been described in the literature,⁸ there is a dearth of experimental data on the systematic impact of functional groups such as –COOH and –OH groups on CO₂ adsorption properties and, more generally, gas separation in MOFs. However, the synthesis of such materials has certainly been shown to be feasible.⁹

Having identified the types of substituent likely to promote more effective CO₂ capture, we now build on our previous simulation work^{6,7} and report a further computational study in which we have designed functionalized versions of the MIL-53(Al³⁺) framework with –CH₃, –NH₂, –COOH, and –OH substituted ligands and compare their respective CO₂ and CH₄ adsorption properties with the nonfunctionalized framework. The nonfunctionalized MIL-53 framework shows an extraordinary flexibility (or “breathing”), oscillating between two distinct conformations called the narrow-pore (np) and the large-pore (lp) structures, resulting in a 40% cell volume variation.¹⁰ While some of us have recently proposed a thermodynamic framework that successfully rationalizes the complex phenomenon of breathing,^{11–13} we focus here exclusively on the MIL-53(lp). This choice is

motivated not only for practical computational reasons but also by the knowledge that MIL-53(lp) possesses the higher adsorption capacity in comparison to the np structure, making this structure an ideal model for exploring computationally the impact of substituted ligands on CO₂ adsorption.

Here, we predict the bulk adsorption properties of the functionalized frameworks toward CO₂ and CH₄ and, hence, capture the direct impact of molecular-level interactions on the macroscopic behavior of the crystalline MOF. We show that MIL-53(lp) functionalized with COOH- and OH-polar groups would have enhanced affinities and adsorption capacities for CO₂ compared to the original unsubstituted MIL-53(lp), in which CO₂ molecules interact most strongly with the corner-sharing hydroxyl groups of the framework rather than the ligands.^{5b} The relative thermodynamic properties of the COOH-, OH-, and NH₂-functionalized MIL-53 are contrasted.

Extracting our model from the experimentally determined crystal structure,¹⁴ we designed four periodic structures in which the BDC (benzene dicarboxylate) ligands are functionalized with the –(CH₃)₂, –NH₂, –(OH)₂, and –COOH groups. In order to optimize the position of the ligand substituents, periodic DFT calculations were performed for each structure. Next, the most favorable adsorption sites for CO₂ were identified in each structure in light of our previous cluster calculations^{6,7} and their bonding energies (BE) were computed at 0 K using periodic DFT calculations (Figure 1). Finally, CO₂ and CH₄ adsorption isotherms for the original and all substituted MIL-53(lp) frameworks were simulated at 303 K in the pressure range 0.01–0.5 atm using the Grand Canonical Monte Carlo (GCMC) method and a recently developed force field for CO₂ in MOFs.¹⁵ The GCMC calculations allow us to account for temperature, and they yield further insight into the impact of confinement and accessibility of functional groups on the thermodynamic properties. Details of the methods are given in the Supporting Information (SI).

The results from the periodic DFT calculations are compared with their related cluster calculations in terms of BE (Figure 2). It is apparent that the positive effect of introducing functional groups on the CO₂–ligand interactions is maintained and even enhanced in the crystalline environment. COOH-MIL-53(lp) is the most illustrative case (Figure 1a): not only is the adsorption site geometry of CO₂ previously observed in the cluster calculation^{6,7} preserved, with a similar O_(CO₂)···H_(COOH) hydrogen bond (2.0 Å), but additional interactions are gained from C=O groups of neighboring ligands. These cooperative effects yield an enhanced lone pair polarization of the CO₂ electron density, highlighting the impact of the specific pore geometry of

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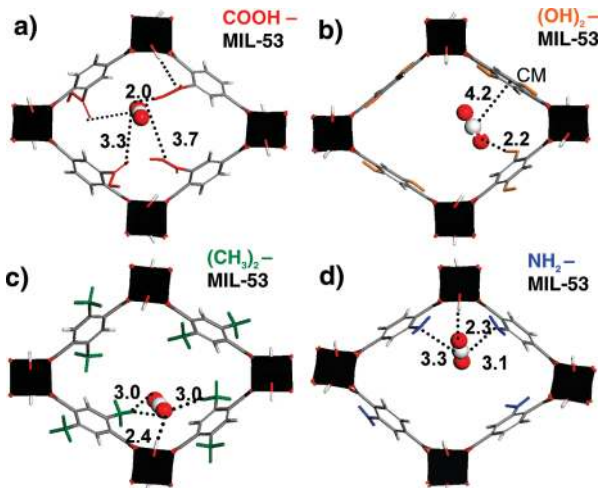


Figure 1. Most stable adsorption site for CO₂ in substituted lp forms of MIL-53(Al³⁺), calculated by DFT at 0 K: (a) COOH₂; (b) (OH)₂; (c) (CH₃)₂; (d) NH₂. Distances are reported in angstroms.

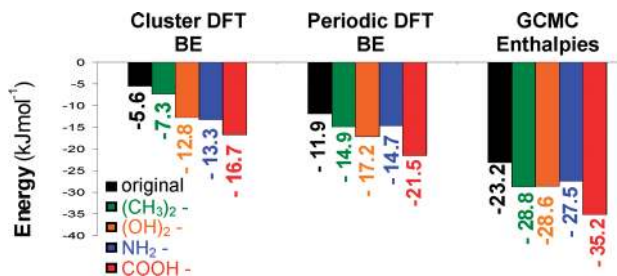


Figure 2. Histograms of the CO₂ binding energies (BE) in which the BE derived from cluster and periodic DFT calculations are compared with CO₂ adsorption enthalpies calculated by GCMC for the original MIL-53 and its functionalized forms. GCMC enthalpies are at 0.01 bar.

MIL-53(lp) and the resulting confinement. Similar cooperative effects with multiple ligand interactions are observed for CO₂ in the NH₂, (OH)₂, and (CH₃)₂-MIL-53(lp) structures (Figure 1d, b, and c respectively).

Interestingly, the ranking of CO₂ BE is slightly altered in the crystal structures when compared to CO₂-ligand clusters (Figure 2), with NH₂-MIL53(lp) having a lower affinity for CO₂ than expected from the cluster calculations. In this case, the optimal orientation of CO₂ toward the N lone pair of NH₂- is inhibited in the crystal due to the corner-sharing OH group of the inorganic subnetwork (itself the main binding site in the original material) (Figure 1d). This illustrates that, in the crystal structure, steric constraints may hinder the optimal CO₂-ligand binding geometries.

Finally, we can observe a variation in the orientation of the functionalized ligand, when compared with that in the original material (Figure S1 in the SI). This is mainly due to the presence of intraframework interactions of the substituent groups, as typically illustrated by the case of COOH-MIL-53(lp) (Figure 1a), where an hydrogen-bond-like interaction occurs between the oxygen of the COOH substituent and the hydrogen of the corner-sharing OH group.

Turning now to the GCMC calculations, we find the calculated enthalpies of adsorption of CO₂ and CH₄ at zero coverage in original MIL-53(lp) (about 24 kJ·mol⁻¹ and 17 kJ·mol⁻¹, respectively) are in excellent agreement with the experimental values^{5a} (21 kJ·mol⁻¹ and 17 kJ·mol⁻¹). Furthermore, the calculated CO₂ adsorption isotherm, in the range 0–25 bar, of the original structure at 303 K reproduces the experimental CO₂ uptake curve

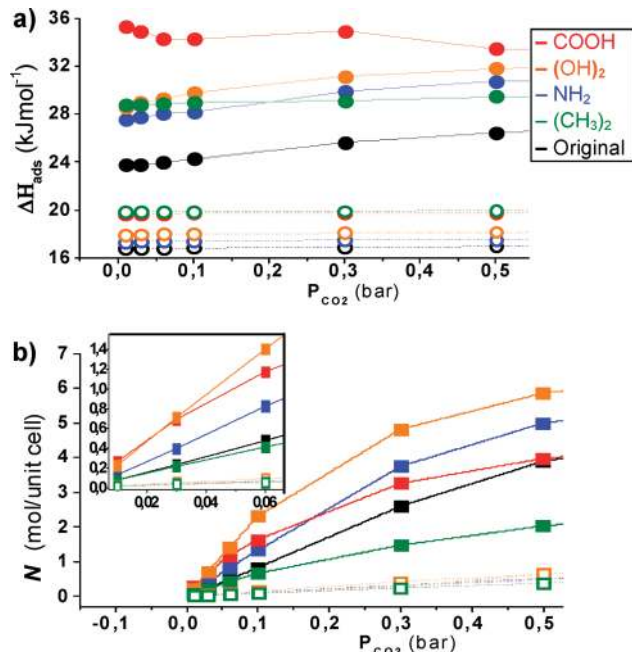


Figure 3. (a) GCMC calculated enthalpies of adsorption and (b) isotherms for CO₂ (full squares and circles, respectively) and CH₄ (empty squares and circles, respectively), in original and substituted MIL-53(Al³⁺), at 303 K and in the range 0.01–0.5 atm.

for the lp form of MIL-53(Al³⁺), as shown in the SI. These results on the original material provide validation for our method.

When considering the substituted materials, the GCMC calculations predict a systematic enhancement of CO₂ adsorption enthalpies at zero coverage in comparison with the case of the original MIL-53(lp), with the following ranking: –COOH > –(OH)₂ ~ –(CH₃)₂ > –NH₂ (Figure 2, right). It is noteworthy that this ranking is very similar to that found in periodic DFT, especially regarding NH₂-MIL53(lp). All substituted MIL-53(lp) outperform the original MIL-53(lp) in terms of adsorption enthalpy across the whole pressure range studied (Figure 3a). Among them, the COOH-MIL-53(lp) outperforms the others, having an enthalpy of adsorption of CO₂ about 14 kJ·mol⁻¹ greater than that of the original form. As expected, CH₄ adsorption enthalpies are only moderately affected by the ligand substituents (Figure 3a).

With the exception of the (CH₃)₂ substituted MIL-53(lp), the calculated isotherms all show a significant enhancement in the CO₂ uptake with respect to the original form (Figure 3a full squares) with a different ranking: –(OH)₂ > –NH₂ > –COOH at pressures above 0.2 bar. This reflects the impact of the ligand substitutions on the accessible volumes, with the bulkier substituent COOH significantly reducing the pore volume. This also accounts for the capacity of the (CH₃)₂ form being notably lower than the original form across the pressure range. Regarding CH₄ adsorption, the calculated isotherms are hardly modified upon ligand substitution (Figure 3b). On the basis of the simulated CO₂ and CH₄ isotherms at 303 K, we estimate a value for CO₂/CH₄ selectivity as the ratio of their respective uptakes at 0.1 bar, a pressure at which steric effects have not yet become visible in the isotherms and also representing the partial pressure of CO₂ in flue gas. It is noteworthy that the substituted COOH- and (OH)₂-MIL-53(lp) (together with the NH₂, as expected) exhibit enhanced CO₂/CH₄ selectivities when compared to the original MIL-53(lp), in the range of 15–17 compared to ~7 in the original material (Table S2 in the SI).

Overall, this case study on MIL-53(lp) explores the dramatic impact of ligand functionalization on CO₂ and CH₄ adsorption properties. The three different computational methods used—DFT on CO₂-ligand clusters, periodic DFT, and GCMC—offer

a high degree of consistency, which adds weight to our findings. First, CO₂ binding energies are systematically enhanced in the crystalline system, as compared to an isolated molecular cluster,^{6,7} which we rationalize due to confinement effects and multiple interactions: simulations clearly identify how the CO₂ molecule is involved in cooperative ligand interactions (Figure 1). Second, a ranking for the impact of the ligand substitution upon CO₂ adsorption enthalpies from GCMC in MIL-53(lp) at very low coverage is presented: COOH > (OH)₂ ~ (CH₃)₂ > NH₂ (Figure 2). Interestingly, the underperformance of the NH₂-MIL-53(lp) material when contrasting this ranking to that of DFT clusters suggests that CO₂ adsorption near NH₂ groups is inhibited by the presence of metal coordinated OH groups. Finally, turning to isotherms, ligand substitution significantly enhances the CO₂ uptake at low pressure. Our calculations point to (OH)₂-MIL-53(lp) and (COOH)₂-MIL-53(lp) as the best candidates (Figure 3) in terms of capacity and CO₂/CH₄ selectivity, evidencing the crucial role of polar groups in CO₂ capture and the particularly penalizing impact of bulky nonpolar groups.

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Supporting Information Available: Detailed discussion of the methodology as well as additional graphs and comments. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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