High-throughput screening of small-molecule adsorption in MOF†

Pieremanuele Canepa, Calvin A. Arter, Eliot M. Conwill, Daniel H. Johnson, Brian A. Shoemaker, Karim Z. Soliman and Timo Thonhauser*

Using high-throughput screening coupled with state-of-the-art van der Waals density functional theory, we investigate the adsorption properties of four important molecules, H₂, CO₂, CH₄, and H₂O in MOF-74- with ¼ Be, Mg, Al, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Sr, Zr, Nb, Ru, Rh, Pd, La, W, Os, Ir, and Pt. We show that high-throughput techniques can aid in speeding up the development and refinement of effective materials for hydrogen storage, carbon capture, and gas separation. The exploration of the configurational adsorption space allows us to extract crucial information concerning, for example, the competition of water with CO₂ for the adsorption binding sites. We find that only a few noble metals—Rh, Pd, Os, Ir, and Pt—favor the adsorption of CO₂ and hence are potential candidates for effective carbon-capture materials. Our findings further reveal significant differences in the binding characteristics of H₂, CO₂, CH₄, and H₂O within the MOF structure, indicating that molecular blends can be successfully separated by these nano-porous materials.

1 Introduction

The modular building-block nature of metal organic framework (MOF) materials makes these hybrid systems very intriguing for a variety of technologically important applications, ranging from gas storage and gas sequestration to more exotic applications. The extraordinary diversity demonstrated by MOFs derives primarily from their vast range of organic linkers combined with the wide chemistry of metal atoms (or clusters), which alters their responses to many external physical and chemical stimuli and influences their flexibility, affinity toward adsorbing molecules, and intrinsic reactivity. In this regard, much progress has been made improving the adsorption properties of MOFs. For example, MOFs with unsaturated metal centers, such as MOF-74- with ¼ Mg, Mn, Fe, Co, Ni, Cu, and Zn, show improved adsorption densities for H₂ and CH₄ and faster adsorption at small partial CO₂ pressures, the latter of which is highly desirable for CO₂-capturing applications.

Although considerable experimental effort has gone into the synthesis, characterization, and study of adsorption properties of target molecules in MOFs, such work typically requires a significant amount of time, slowing down scientific progress. Thus, the help of computational material science becomes crucial, accelerating and guiding the refinement of existing materials as well as the prediction of new MOFs. High-throughput screening (HTS) is a very promising approach that screens many possible materials much faster than experiment; it is well established in the fields of pharmacology and biology and just recently was introduced into the materials science community. Excellent examples include the materials project and the material genome initiative.

In this work, we demonstrate the importance of HTS to accelerate the discovery of MOFs with better adsorption properties for gas-storage and gas-separation applications. We focus on one particular MOF, MOF-74, because of its unprecedented adsorption characteristics and specificity towards CO₂, which make it very important for separating CO₂ from CH₄ in low-quality gas, such as biogas. We start with MOF-74-Zn and use HTS to study its large configurational adsorption space and element space. Specifically, we study the adsorption properties of four important molecules: H₂, CH₄, CO₂, and H₂O in combination with 25 different metals: Be, Mg, Al, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Sr, Zr, Nb, Ru, Rh, Pd, La, W, Os, Ir, and Pt.

Note that, from this list, only eight iso-structural MOF-74- with ¼ Ti, Mg, Mn, Ni, Co, Fe, Zn, and Cu have been synthesized since 2005, attesting to the long experimental timeframe. The pioneering contribution of Park et al. in the study of CO₂ adsorption in MOF-74- (with ¼ Mg, Ca, and the first row of transition metals) constitutes a sub-set of our study and serves as a benchmark. However, that study is limited to only CO₂ adsorption; we extend the list of possible metals considerably and also study adsorption of H₂, CH₄, and H₂O. The effect of water is particularly important in that it is always present in flue gases in the form of humidity and might...
pre-adsorb at MOF unsaturated metal sites, hindering the adsorption and transport properties of other target molecules.9

2 Computational details

To explore the binding configurational space in terms of metal species and adsorbing molecules, we use density functional theory with the van der Waals density functional vDW-DF,46–48 as implemented in VASP.49–54 We have successfully applied vDW-DF to investigate the adsorption of small molecules in MOFs and nano-structures in numerous other studies.5–9,16,26–28,53 In particular, vDW-DF is crucial for correctly describing the binding of water.26

Due to the large unit cell of MOF-74, with 54 atoms, the total energy was sampled at the Γ-point only. Projector augmented-wave theory55,56 combined with a well-converged plane-wave cutoff of 480 eV were used to describe the wave functions. The convergence threshold for the total energy was set to 1 × 10−5 eV, ensuring accurate calculation of the adsorption energies. The internal geometry and unit cell of MOF-74–# were fully relaxed for all # using vDW-DF59 [empty and fully loaded with H2, CO2, H2O, and CH4] until the force and stress criteria of 1 × 10−3 eV Å−1 and 1 × 10−3 eV Å−3 were satisfied. To study the electronic structure of these MOF materials, we carried out the Bader analysis using the fast implementation proposed by Henkelman et al.60 Graphical manipulations were carried out using J-ICE61.

Our calculations start from the experimental trigonal structure of MOF-74–Zn with space group R3, a = 25.932 Å, c = 6.836 Å, and 54 atoms per unit cell.62 We then substitute for the Zn atoms with Be, Mg, Al, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Sr, Zr, Nb, Ru, Rh, Pd, La, W, Os, Ir, and Pt in sequence. Originally, we also considered Y, Mo, Ag, Ce, and Au, but their MOF structures are relatively unstable, preventing their convergence. Note that the main objective of this high-throughput investigation is not to accurately reproduce some properties of a small number of materials, but rather to explore at relatively high accuracy the element and adsorption configurational space of a much larger class of systems. Since some of these metals present an open-shell electronic structure, we adopted a collinear spin-corrected treatment, with an appropriate approximation for vDW-DF.63 We impose an anti-ferromagnetic alignment of the spins on the six metal ions in the unit cell, according to previous experimental64 and theoretical65 observations. Six H2, CO2, H2O, and CH4 molecules per unit cell are then adsorbed at the uncoordinated metal sites. # in the MOF nano-pores, reproducing the channel saturation observed in previous X-ray and neutron-diffraction experiments.66

3 Results

3.1 Properties of the empty MOF

We begin by commenting on the structural characteristics of the empty MOF-74. Table 1 shows the structural parameters and other relevant quantities of MOF-74 after complete structural relaxation at 0 K. Our computed data compares well with previous experimental and theoretical investigations—see Table 1 in the ESL† There is no simple explanation for the dependence of the lattice parameters on the metal species, but note that Os results in the smallest unit cell and Ca in the largest. The significant difference between them can be associated with their ionic radii: Ca2+ ≈ 1.00 Å and Os2+ ≈ 0.49 Å ions in a penta-coordinated oxygen environment (as found in MOF-74–#).67 The other metal species do not necessarily follow this simple trend, so we cannot extract a general dependence of volume on the ionic radius.

We also simulated the powder X-ray spectra of a few selected MOFs obtained throughout the HTS procedure, resulting in important fingerprints for their future synthesis (see ESI†).

The Bader charges of the metal ions in the MOF are interesting. Fig. 1 analyzes the 25 situations in Table 1 and plots the

Table 1

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<thead>
<tr>
<th>Metal</th>
<th>Z</th>
<th>a</th>
<th>c</th>
<th>V</th>
<th>Q_{M}</th>
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<tr>
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<tr>
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<td>7.210</td>
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<td>26.560</td>
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</tr>
</tbody>
</table>

Fig. 1 Number of occurrences of particular Bader charges Q_{M} in Table 1.
number of occurrences of Bader charges $Q_{e}$. We see that most of the metal species in MOF-74 display charges ranging from 1.0 to 2.0 $e$, consolidating the picture of divalent metal ions. Exceptions are Al, which carries almost a 3+ charge as expected, and Cu, which remains as Cu(I). Our findings also suggest that Rh, Pd, Os, Ir, and Pt remain weakly charged, preserving their noble metal characteristics. The local oxygen environment experienced by the metal species of MOF-74 resembles a “surface termination” of the corresponding binary oxides, explaining the charge nature of these ions. Note that the charge characteristics of such metal ions reflect their reactivity toward the adsorbates.

3.2 Adsorption characteristics

Our discussion now moves to the analysis of the adsorption energies, which determine whether molecular adsorption is favorable. We define the adsorption energy as in eqn (1)

$$\Delta E = E_{\text{MOF+M}} - E_{\text{MOF}} - E_{M(g)},$$

where $E_{\text{MOF+M}}, E_{\text{MOF}},$ and $E_{M(g)}$ is the total energy of MOF with molecules adsorbed in its nano-pore, the energy of the empty MOF, and the energy of the molecule in its gas-phase geometry, respectively. Note that throughout the manuscript, we will also refer to adsorption energies as binding energies. Two interesting deformation contributions $\delta E_M$ and $\delta E_{\text{MOF}}$, which are clearly connected to the adsorption process, are defined in eqn (2) and (3):

$$E_M = E_{\text{MOF+m}} - E_{M(g)},$$

$$\delta E_{\text{MOF}} = E_{\text{MOF+M+m}} - E_{\text{MOF}},$$

where $E_{\text{MOF+M+m}}$ and $E_{\text{MOF+M+m}}$ are the energies of the molecule and the MOF in their adsorption geometries. $\delta E_M$ and $\delta E_{\text{MOF}}$ express the energy cost both adsorbate and MOF have to pay during the adsorption process. The $\delta E_M$ term also contains the lateral interactions between adjacent molecules, which, in turn, depend on their positions and the electronic characteristics of each. Note that both $\delta E_M$ and $\delta E_{\text{MOF}}$ contributions maximize the binding interaction in relation to the rearrangement of the molecular and MOF geometries. $\delta E_M$ and $\delta E_{\text{MOF}}$ are obtained by partitioning the adsorption energy, and thus, are naturally included in the definition of $\Delta E$ in eqn (1). Finally, an adsorption quantity $\Delta E^C$ can be defined without deformation contributions:

$$\Delta E^C = \Delta E - \delta E_M - \delta E_{\text{MOF}}.$$  

Table 2 is the main result of this paper and collects the calculated values for the quantities defined in eqn (1)–(4).

When molecules are adsorbed in their structures, the pore size and volume of the MOFs decrease (see Table 1 in the ESI†). The extent of the volume change depends on the size of the adsorbing molecules and the nature of the adsorption interactions in Table 2. For example, the MOF nano-pore clogs when six CH4 molecules are concomitantly adsorbed, increasing lateral molecule-to-molecule interaction, as demonstrated by the $\delta E_M$ in Table 2. Large, attractive $\delta E_M$ values “unphysically” lower the overall $\Delta E$. Fig. 2 shows the perturbation in the volume of MOF-74 after six CH4 molecules are introduced in its cavity. This trend is not directly correlated to $\Delta E$, but rather to $\delta E_M$ (Table 2), which combines the molecular deformations and the lateral interactions the molecules experience during adsorption. In the case of CH4, the intermolecular interactions are strong, and keep the MOF structure from “swelling apart,” which might occur otherwise, given the substantial volume of six CH4 molecules in such a small pore (diameter ~13 Å). Similar conclusions can be drawn for H2, CO2, and H2O, although, the effect on their respective volume changes is smaller. The variance in volume change due to the diversity of the MOF/molecule interactions and the molecular volume again reflects the high structural flexibility of these porous materials. In other words, the MOF structure responds differently to different molecules, and the significant and unprecedented molecular recognition effects can be exploited for sensor applications, which will be investigated in a forthcoming publication.

The binding energies $\Delta E$ of H2, CO2, CH4, and H2O in MOF-74 also show diverse molecular recognition (see Table 2). In general, we find that the $\Delta E$ of these molecules differ in magnitude by tens of kJ mol$^{-1}$ and follow a precise and expected trend H2O $\geq$ CO2 $\geq$ CH4 $\geq$ H2, confirming previous experimental and theoretical findings (see Tables 2 and 3 in the ESI†). The consistent gap between the adsorption energies of different molecules indicates that MOFs can be used in filters to efficiently separate blended gases. According to the electrostatic complementarity principle (donor–acceptor), the metal species of the MOF structures act as a Lewis acid, lacking in electrons, while the adsorbing counterparts (in general oxygen atoms) behave as a Lewis base, providing electrons. In the case of H2O, the driving force dictating the molecular adsorption at the metal site is its strong dipole moment; adsorption of H2, CO2, and CH4 relies on weak van der Waals forces as demonstrated by the $\Delta E$ in Table 2. Water clearly remains the preferred molecule for the metal sites, with the exception of some noble metals—Rh, Pd, Os, Ir, and Pt—implying that moist environments could hinder gas-storage applications. Scarcely documented in the literature, the presence of water in these nano-porous materials remains a major operational problem; it partially explains why non hydro-soluble MOFs, such as fluorinated MOFs, are being developed.

Also note the different adsorption energy contributions, $\delta E_M$, $\delta E_{\text{MOF}}$, and $\Delta E^C$ in Table 2. As anticipated, the negative sign of the $\delta E_M$ is due to intermolecular attraction and its magnitude depends only on molecular size and the extent of pore reconstruction, which is connected to the nature of the metal ions. On the other hand, with very few exceptions, the sign of the $\delta E_{\text{MOF}}$ is positive indicating that the MOF undergoes an unfavorable reconstruction when the molecule is adsorbed. In most cases the $\delta E_M$ is larger than $\delta E_{\text{MOF}}$.

In general, the calculated $\Delta E$ of Table 2 are in good agreement with previous experimental and computational data. Our data reproduce the $\Delta E$ order established for.
CO₂ in MOF-74-Mg < MOF-74-Ni < MOF-74-Co, consistent with experiment (see Tables 2 and 3 in the ESI†). The adsorption energies calculated for most of the molecules are slightly overestimated by 2–5 kJ mol⁻¹ from the experimental data (where available), which is typical for the vdW-DF functional. Nevertheless, including the zero-point energy (ZPE) and thermal correction via phonon calculations (not performed in this study) can slightly lower the ΔE by few kJ mol⁻¹ (3–6 kJ mol⁻¹) and bring them in better agreement with experiment, but these corrections would not alter the qualitative results. Previous work in this field has demonstrated that changes in the molecular frequencies due to adsorption are generally very small (from 5 to 20 cm⁻¹), consistent with the weak nature of the molecule-MOF interaction. Furthermore, the molecular vibrations and those of the MOF scaffold fall into different frequency ranges, so they remain highly decoupled. ΔEₕ, rather than ΔE, is more appropriate for comparison with experimental data, as it is not affected by the spurious lateral interactions introduced by the high-loading regimes imposed in our simulations (six molecules per cell).

3.3 Adsorption of H₂ and CH₄

Somewhat surprisingly, the data in Table 2 demonstrate that for most cases, the adsorption energies of H₂ in MOF-74 only marginally change with the metal species. It follows that the currently synthesized MOF-74-Mn, MOF-74-Fe, MOF-74-Co, MOF-74-Ni, and MOF-74-Zn are already optimal for hydrogen storage. A loading of six molecules in MOF-74-ₚ per unit cell corresponds to a hydrogen-storage capacity of 1.6 mass% and 4.9 g H₂ L⁻¹. Although not investigated here, MOF-74 has secondary binding sites, and the unit cell can hold 12H₂ molecules under high pressure, corresponding to theoretical values of 3.2 mass% and 9.9 g H₂ L⁻¹ volumetric uptake. These numbers are in the middle range of physisorption-based, nanoporous hydrogen-storage materials. Again, H₂O in the MOF environment is a problem for hydrogen-storage applications; its large binding energy compared to H₂ degrades the storage...
capacity further. Note that the sign of $\Delta E$ for H$_2$ in MOF-74-Ti suggests that this adsorption is thermodynamically prohibited.

Several computational studies have investigated the interaction of CH$_4$ with MOF-74, often using plain LDA functionals that incorrectly describe the dominating van der Waals interactions relevant to the adsorption.$^6$ Note that here we employ an exchange-correlation functional that is not parametrized and hence can capture the diverse nature of the molecular interactions with all metals. On the other hand, the empirical method DFT$^+$$D$ (ref. 76) works well only for a few metals where the empirical parameters (the $C_6$ coefficients) are extracted from ab initio data, which is not appropriate for metals whose $C_6$ coefficients are extrapolated from lighter elements along the group.$^{77-78}$ Consequently, Park et al.$^{45}$ obtained very similar $\Delta E$ for the metal ions of the first transition metal row. Furthermore, the $C_6$ obtained by Grimme et al.$^7$ were derived for atomic species and not ions and do not reflect the nature of the metal ions in MOF-74 as demonstrated by the Bader charges in Table 1 and Fig. 1.

### 3.4 Competition of H$_2$O and CO$_2$ adsorption

We can also compare the computed binding energies for CO$_2$ and H$_2$O. The top panel of Fig. 3 shows that in most cases, the $\Delta E$ for CO$_2$ in MOF-74-$\mathcal{M}$ oscillate between 40 and 60 kJ mol$^{-1}$. However, when MOF-74-Al, MOF-74-La, and MOF-74-Nb adsorb CO$_2$, we observe its complete chemi-adsorption at the metal site, sharing electrons with the MOF structure, and causing a steep increase in the adsorption energies. From a practical point of view, strong chemi-adsorption prevents re-use of MOFs, as the molecule is fully integrated in the MOF structure and its chemical identity cannot be recovered. In the ESI† we show the irreversible structural and molecular changes in MOF-74-Al and MOF-74-La loaded with CO$_2$.

In contrast, in MOF-74-Be, -Ca, and -Cr, we observe complete desorption of CO$_2$ molecules from the metal sites, despite the considerable adsorption energies reported in Fig. 3. MOF-74-Be is thus a special case, and we do not list it together with the other noble metals that have a strong affinity for CO$_2$. To quantify this effect, we report the molecule/metal distances in Table 2 of the ESI†. The slight affinity of CO$_2$ for the metal species Be, Ca, and Cr causes the molecules to draw closer, establishing strong intermolecular attractions, and decreasing the overall $\Delta E_M$ (see ESI†). The large binding energy shown by water in MOF-74-Ca (i.e. $-87$ kJ mol$^{-1}$) is an indication of the expected high reactivity of Ca toward H$_2$O, resulting in important implications for the practical synthesis and usage of the MOF itself. As mentioned, large values of $\Delta E_M$ spuriously affect the final magnitude of $\Delta E$, whereas the $\Delta E^C$ are more appropriate as a reference for further comparisons. CO$_2$ behavior with some metal ions, such as Ti, Zr, and W, is similar but less pronounced.

The bottom panel of Fig. 3 shows the binding energy of CO$_2$ relative to that of H$_2$O. In most of the metals investigated, water binds more strongly than CO$_2$, occasionally reaching more than 100 kJ mol$^{-1}$ as in MOF-74-Al, -Sc, -V, -Fe, -Sr, -Nb, -La, and -W. Recently, Planas et al.$^{79}$ attempted to increase CO$_2$ affinity compared to water by functionalizing the metal species of MOF-74-Zn with amines and increasing the adsorption energy of CO$_2$, but the reactivity of water was not tested. A closer look at the adsorption geometries for these models explains the reasons of such high $\Delta E$ values—we observe the incipient formation of strong hydrogen bonds with oxygen atoms that coordinate the metal ions and explain the large structural deformation subsequent to adsorption ($\Delta E_{MOR}$ in Table 1). For these latter cases, we have plotted the density of states (DOS) of both MOF and water molecules before and after the adsorption, demonstrating the nature of the chemi-adsorption (see ESI†). Although the DOS indicates injection of some molecular states in the MOF band structure, the geometry of the adsorption conformation does not assist in water dissociation, in contrast to what is observed for surfaces of the respective metal-oxides.

As mentioned, the noble metals Rh, Pd, Os, Ir, and Pt are special in that they invert the trend of the adsorption energies for CO$_2$ and H$_2$O. In their adsorption conformation water molecules are in contact with the metal species. But, this conformation is immediately disrupted due to the redox nature of those metals, which act as donors, competing with the oxidizing oxygen of water and leading to unfavorable interactions such as repulsions. After complete structural relaxation, the oxygen atoms of H$_2$O molecules are found far from the noble metal. Water molecules are entirely displaced from the original binding pocket, assuming a new binding conformation that favors hydrogen bonding with atoms of the linkers (Fig. 4). We did not observe strong interactions between the protons of H$_2$O molecules and the metal sites, which would be extremely favorable in simpler systems, such as water on platinum surfaces and other noble metals.$^{80-82}$ Analysis of the Bader charges of the metal ions explains the interaction intuitively. Once the water molecules make contact with MOF-74-$\mathcal{M}$ (with $\mathcal{M}$ = Rh, Pd, Os, Ir, and Pt), they do not directly perturb the metal ion, and its charge is unaltered. Although for Rh, Pd, Os, Ir, and Pt, the $\Delta E$ of CO$_2$ adsorption are always larger than those

![Fig. 3](image-url) (top) $\Delta E$ for CO$_2$ adsorption (in kJ mol$^{-1}$) in MOF-74-$\mathcal{M}$. (bottom) Magnitude of the adsorption energy of CO$_2$ relative to H$_2$O. A positive value in this plot means that CO$_2$ binds more strongly than H$_2$O.
for H2O, the CO2 molecules remain slightly separated from the metal ions (see ESI†) compared to other transition metals, demonstrating that such noble metals prefer a reducing environment. While noble metals in MOF-74 seem to be very promising for CO2 adsorption, they remain very expensive and unsustainable for practical applications. It is conceivable that similar adsorption/catalytic properties can be achieved with less expensive transition metals by altering the nature of the linkers. A viable strategy could be to replace the oxygen atoms of the linkers with more reductive species, increasing the concentration of electrons near the metal sites.

4 Conclusions

In this study, we sample the adsorption configurational space of small molecules in MOF-74. We use high-throughput screening to investigate the adsorption properties of H2, CH4, CO2, and H2O in MOF-74- with \( M \equiv \) Be, Mg, Al, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Sr, Zr, Nb, Ru, Rh, Pd, La, W, Os, Ir, and Pt. We demonstrate that HTS can reveal important information about these systems and accelerate the engineering and improvement of existing metal organic frameworks for hydrogen storage, carbon capture, and gas-separation.

Independent of metal species, we find a consistent gap between the adsorption energies of different molecules, i.e. from strongest to weakest \( H_2O > CO_2 > CH_4 > H_2 \). We conclude that these materials can be efficiently used in filters for separating blended gases. Furthermore, H2O is always present in the form of humidity in the operational environment of MOFs, and we find that it can significantly decrease the adsorption and transport properties of target molecules. We further find that metal species at the left of the periodic table are less effective in capturing CO2, displaying a larger affinity for H2O, which indicates that these MOFs are susceptible to moist environments. Our analysis suggests that CO2 affinity increases as we move right along the transition metal series. On the other hand, our data do not suggest a systematic trend in each group.

The redox characteristics of noble metals, such as Rh, Pd, Os, Ir, and Pt, increase the interaction with CO2 in MOF-74, while the affinity for water is almost suppressed. Thus, such metals are interesting candidates for novel MOFs that are less susceptible to humidity, with direct use in carbon-capture applications.

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