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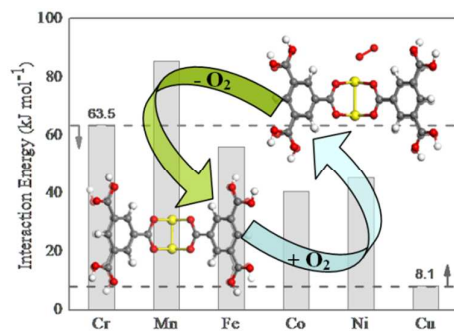
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ARTICLE TYPE

Computational study of oxygen adsorption in metal-organic frameworks with exposed cation sites: Effect of framework metal ions

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The current inefficient separation of O₂ from air is an important industrial problem. Metal-organic frameworks containing coordinatively unsaturated metal sites (CUS) have emerged as competitive new adsorbents for such targets. In this study, dispersion-corrected density functional theory calculations were performed to investigate the influence of framework metal ions on the adsorption behavior of O₂ in M₃(BTC)₂-type materials (M = Cr, Mn, Fe, Co, Ni and Cu; BTC = 1,3,5-benzenetricarboxylate acid). The results show that Ni₃(BTC)₂ can be potentially considered as promising oxygen adsorbent with relatively easier deoxygenation than Cr₃(BTC)₂. The magnitude of charge transfer from the CUS to O₂ molecule was found to have a significant impact on the interaction energies of O₂ with M₃(BTC)₂ except for the Cu version. Furthermore, it was revealed that the origin of the difference in the charge transfer can be attributed to the different electronegativity of the metals.

1. Introduction

Separation of O₂ from air is an indispensable step in industry,¹⁻³ which is currently carried out on a large scale using an energy-intensive cryogenic distillation process.⁴ Zeolites have also been used for O₂/N₂ separation, but this process is inherently inefficient because the materials used adsorb N₂ over O₂ with poor selectivity.⁵ In addition, it has been demonstrated that O₂ binding by transition-metal centers with redox-active properties can be regarded as a potentially efficient approach via the greater propensity of O₂ for accepting negative charge transferred from the metal centers than that of redox-rigid N₂.⁶ Thus, there is a clear benefit from developing new materials that can selectively adsorb O₂ based on chemical-like interactions and the deoxygenation can be operated easily near ambient temperatures; this will enable the separation to be carried out with lower energy and capital costs.

Owing to their many fascinating features, metal-organic frameworks (MOFs) have attracted a wide interest in the fields of gas storage and separation.⁷⁻¹² Among various MOFs reported in the literature, there are some materials containing coordinatively unsaturated metal sites (CUS). If these exposed cations are redox-labile transition metals, MOFs can be used to selectively adsorb O₂ with the aid of the electron transfer-driven mechanism (that is redox).¹³ Bloch et al.⁶ showed that Fe₂(DOBDC) is an adsorbent suitable for O₂/N₂ separation below 220 K, but the adsorption of O₂ is irreversible at room temperature. Cu₃(BTC)₂ (BTC = 1,3,5-benzenetricarboxylate acid), also known as HKUST-1 (HKUST: Hong Kong University of Science and Technology), is a representative of CUS-containing MOFs, in which the inorganic building unit adopts a paddle-wheel geometry with a square-

planar coordination of the metals.¹⁴ Long and co-workers¹⁵ showed that the Cr-based isostructural material, Cr₃(BTC)₂, can exhibit a loading of 14.4 wt% for O₂ adsorption at 298 K and 1 bar with an exceptional O₂/N₂ selectivity factor of 22. However, they found that the material cannot achieve a complete release of bound O₂ even heating at 323 K under dynamic vacuum. As CUS metals in MOFs have been experimentally identified as the preferential adsorption sites for O₂,¹⁵ the ability to substitute with different metals implies the potential of regulating the deoxygenation properties of the materials. Actually, both experimental and computational studies have shown that such a strategy is an effective approach to tune adsorption properties of CUS-containing MOFs toward other gases including CO₂.^{8,16-17}

Due to the difficulty in obtaining the detailed microscopic information by experiments, quantum mechanics methods are increasingly used to understand the interactions of various guest species with CUS-containing MOFs.^{8,18-21} However, the investigations related to O₂ adsorption are still very scarce up to date. As far as we know, there are only three studies that have been reported on such a topic on the basis of density functional theory (DFT) calculations. Supronowicz et al.²² and Zhou et al.²³ studied the adsorption of O₂ in Cu₃(BTC)₂, while Maximoff et al.¹³ probed the mechanism for the irreversible adsorption of O₂ in Fe₂(DOBDC). Thus, more efforts are highly necessary to have a thorough understanding of the interactions between O₂ and MOFs. For this purpose, a dispersion-corrected DFT method was employed in this work to systematically investigate the adsorption of O₂ in a series of HKUST-1 type materials, M₃(BTC)₂ with the first transition-metal elements (M = Cr, Mn, Fe, Co, Ni and Cu). We tried to find whether there is a possibility to reduce the energy required for deoxygenation by metal

substitution. Such studies can give a direct insight into the nature of the O₂-metal interactions by eliminating other potential influencing factors.¹⁷ The obtained results could provide a theoretical foundation for guiding the future design of new CUS-containing MOFs with improved O₂ separation performance.

2. Models and methods

2.1. Structures of Cluster Models

The Cu-containing cluster model adopted in our calculation was cut from the unit cell of Cu₃(BTC)₂, the crystal structure of which was constructed from the X-ray diffraction (XRD) data,²⁴ as shown in Fig. 1a. The Cu atoms in this cluster were then substituted by those selected from the first transition-metal elements (Cr, Mn, Fe, Co, and Ni). Each of such-obtained cluster models (M₂BTC₄) contains 82 atoms after saturating the carboxylate groups with H atoms, as shown in Fig. 1b and 1c. Such cluster models have been successfully used to reproduce the binding and spectroscopic properties of different small molecules interacting with them.^{22-23, 25-26}

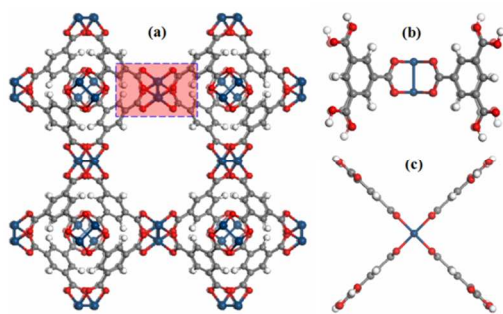


Fig. 1 (a) Illustration of the structure of M₃(BTC)₂ series (M = Cr, Mn, Fe, Co, Ni and Cu) with the dimetallic tetracarboxylate CUS, and (b, c) M₂BTC₄ cluster models used in the calculations (side view, b; top view, c) (metal, blue; C, gray; O, red H, white).

2.2. Computational details

It has been well-documented that a significant deficiency in commonly used DFT methods is the lack of a suitable treatment for dispersion interactions.²⁷ Thus, the dispersion-corrected DFT (DFT-D) calculations were used to optimize the structures of the cleaved clusters as well as their complexes with oxygen molecules, using the DMol³ module implemented in Materials Studio.²⁸⁻²⁹ The Perdew-Burke-Ernzerhof (PBE) GGA exchange-correlation functional³⁰ with the Grimme correction³¹ and the double numerical plus polarization (DNP) basis set were employed in all the calculations.^{32,33} The dispersion parameters can be found in the Supplementary Information. DFT semicore pseudopotentials (DSPP)³⁴ was used to set the type of core treatment. This core potential was developed specifically for DMol³ calculations to include some degree of relativistic effects, which is a very useful approximation for the heavier elements in our cluster models. The self-consistent field (SCF) procedure was used with a convergence threshold of 10⁻⁶ au on the energy and electron density.^{32,35} The direct inversion of the iterative subspace technique developed by Pulay was used with a subspace size 6 to speed up SCF convergence.³⁶ The convergence threshold parameters for the optimization were 10⁻⁵ Ha (energy), 2 × 10⁻³ Ha/Å (gradient), and 5 × 10⁻³ Å (displacement), respectively. The

real-space global cutoff radius was set to be 4.8 Å. All the results reported in this work were obtained using the spin-polarized calculations, where the optimal spin configurations were determined automatically by the self-consistent iterations. Our results show that the spin-state of an isolated O₂ molecule calculated is triplet, which agrees well with the spin-state nature of O₂. In addition, we tried to manually fix the spin-state of O₂ in some O₂-M₃(BTC)₂ complexes using different values, and found that the spin-states of the complexes corresponding to the lowest energies are the same as those found by the DFT code. Thus, it is a feasible way to explore the properties of the examined systems using the methodology described above. In addition, frequency calculations were performed to check whether the structural optimizations reached the global energy minimization. The optimized structures were then used for subsequent energy calculations.

The interaction energy (ΔE_{int}) of an O₂ molecule with each of the molecular cluster models at 0 K was calculated according to the following equation

$$\Delta E_{\text{int}} = E_{\text{MOF-O}_2 \text{ complex}} - E_{\text{MOF}} - E_{\text{O}_2}$$

where E represents the energy of the system after full geometry relaxation, $E_{\text{MOF-O}_2 \text{ complex}}$ is the total energy of the MOF cluster-O₂ complex, E_{MOF} and E_{O_2} are the energies of the isolated cluster structure and O₂ molecule, respectively. In such a definition, a larger negative value of ΔE_{int} corresponds to a stronger binding strength. The numerical basis sets in the DMol³ code are local basis sets, one advantage of which is the ability to minimize the effect of basis set superposition error (BSSE). Inada and Orita³⁷ have also shown that the magnitude of BSSE for the binding energies calculated using the numerical basis sets like DNP are very small. Therefore, the interaction energies were calculated without the correction of BSSE in this work.

As done by others,^{32,38} Mulliken population analysis method was used to examine the electron distribution and charge transfer mechanism in the systems considered in this work. To calculate the adsorption enthalpy (ΔH) of O₂ at 298 K, the thermal contribution, including $RT/2$ (R is the ideal gas constant) for each degree of freedom of the gas molecule and the PV term simply approximately by RT , was taken into account.³⁹ The correction of the zero-point energy (ZPE) was also considered using the harmonic approximation. Such a method has also been used to calculate the adsorption enthalpies of other gases in other adsorbents at elevated temperatures.⁴⁰

3. Results and discussion

3.1. Validation of the Method

To study the adsorption of O₂ in MOFs containing CUS, the DFT-D method adopted in this work has to be validated. We firstly compared the optimized structures of the empty and O₂-loaded Cr₃(BTC)₂ with the information obtained experimentally.¹⁵ It was found that the calculated Cr-Cr bond length is 2.127 Å in the paddle wheel of the empty structure, which is in line with the experimental value of 2.058 Å. When O₂ molecule was adsorbed on each of the two CUS metals, the Cr-Cr bond length in the optimized structure was elongated to 2.751 Å, which also agrees very well with the value of 2.790 Å

obtained from Rietveld analysis of powder neutron diffraction data. Since there are no experimental data or DFT results reported for the adsorption enthalpy of O₂ in Cr₃(BTC)₂, a comparison of this property cannot be carried out.

We further compared the calculated O₂/Cu₂BTC₄ interaction energy with the result obtained on the basis of B3LYP-D3/TZVP level.²² As far as we know, the latter is the only energetic information available in the literature related to O₂ adsorption in M₃(BTC)₂. Our calculation shows that the energy is about -8.1 kJ mol⁻¹ and is dominantly contributed from the dispersive interactions (-7.5 kJ mol⁻¹). This observation indicates that inclusion of dispersion correction in the DFT method is very important for predicting the energy of the systems with weak interactions. In addition, this result is close to the interaction energy (-9.6 kJ mol⁻¹) obtained using DFT with B3LYP-D3/TZVP in which the dispersion contribution (-9.0 kJ mol⁻¹) is also found to play a dominant role.

To check the size effects of the used cluster models, we compared the calculation results on the basis of an O₂-loaded cluster and periodic models by taking Cr₃(BTC)₂ as an example. In the periodic calculations, the k-point sampling was performed at the G-point due to the large cell. It was found that the interaction energy of the CUS Cr with O₂ obtained from the periodic calculation is -66.8 kJ mol⁻¹, and the Cr–O distance and O–O bond length are 1.874 and 1.268 Å, respectively. These values are in good agreement with those calculated using the cluster model (see Table 1), while the calculation time increases significantly using the periodic model. The above comparison demonstrates that the cluster models adopted in this work are acceptable and thus can be adopted for further exploration.

3.2. Interaction Energies and Geometries

Table 1 Comparison of the metal–O₂ (d_{M-O}) distances, bond lengths (d_{O-O}) of the adsorbed O₂ molecule, charges transferred (CT) from the M₃(BTC)₂ to O₂, interaction energies (ΔE_{int}), dispersion contributions (ΔE_{disp}) to the interaction energies, and adsorption enthalpies of O₂ at 298 K

Metals	d_{M-O} (Å)	d_{O-O} (Å)	CT (e)	ΔE_{int} (kJ mol ⁻¹)	ΔE_{disp} (kJ mol ⁻¹)	ΔH (298 K) (kJ mol ⁻¹)
Cr	1.881	1.266	0.19	-63.5	-11.4	-65.4
Mn	1.858	1.285	0.23	-85.3	-12.3	-85.5
Fe	1.835	1.262	0.14	-56.0	-12.2	-61.6
Ni	1.955	1.249	0.05	-45.2	-7.1	-44.0
Co	2.043	1.245	0.01	-40.5	-10.1	-35.4
Cu	2.279	1.235	0.01	-8.1	-7.5	-5.1

3.2.1. Adsorption of O₂ in Cr₃(BTC)₂. Among the M₃(BTC)₂ series considered in this work, Cr₃(BTC)₂ is the only material that have been experimentally proved to exhibit a high O₂ loading and exceptional O₂/N₂ selectivity.¹⁵ Thus, we began with examining the adsorption mechanism of O₂ in this material.

As shown in Fig. 3, O₂ molecule is angularly adsorbed on the Cr center through one oxygen end and the adsorption does not induce significant change of the MOF structure. One can observe from Table 1 that the interaction energy between O₂ and Cr₃(BTC)₂ is -63.5 kJ mol⁻¹. The CUS metal acts as a Lewis-base site due to the higher electronegativity of oxygen, and thus there is a charge of 0.19 e transferred from Cr₃(BTC)₂ to O₂. To explore the influence of charge transfer on the adsorption behavior, we artificially tuned the charge state of the CUS site (Cr) by adding an extra electron to or removing an electron from the cluster

During our calculations, we have tried to put O₂ molecule on the different sites in the structure of cluster models. By comparing the calculated interaction energies, it was observed that the CUS metals are the preferential sites for O₂ adsorption. Actually, such observations have already been found for the adsorption of many different guest species in CUS-containing MOFs. Thus, the following comparisons were made only using the interaction energies calculated for the systems with an O₂ molecule adsorbed on the CUS. The results are shown in Fig. 2 and summarized in Table 1. It can be found that the dispersion energies are comparable among the structures with CUS metals of Cr, Mn, Fe, and Co. Although the dispersion energies are similar between the Ni- and Cu-containing systems, the contribution to the total interaction energy in the former is much smaller than that in the latter.

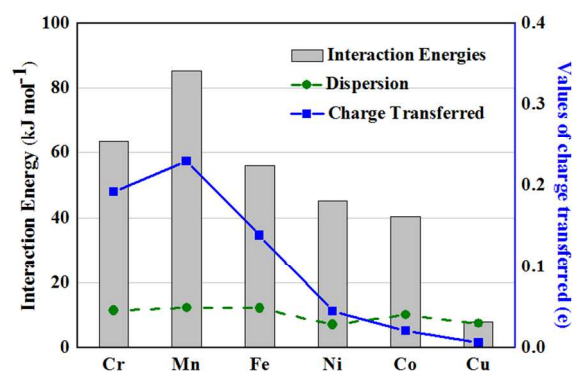


Fig. 2 The O₂ interaction energies (gray bar), the charge transferred from the M₃(BTC)₂ to O₂ (blue line against the y-axis on the right) and long-range dispersion correction to interaction energies (green dash line).

model. Previous studies²³ have shown that the electron will diffuse throughout the entire framework when an electron is added to or removed from the Cr₃(BTC)₂ cluster. In this work, after structural optimization for the neutral, negatively and positively charged Cr₃(BTC)₂, it was found that the Mulliken atomic charges of the Cr ions are +0.53 e , +0.43 e and +0.58 e , respectively. When Cr₃(BTC)₂ gains an extra electron, the structure is compressed with the Cr–Cr distance in the paddle wheel shortened to 1.890 Å from 2.127 Å. In contrast, for Cr₃(BTC)₂ losing an electron, the structure is expanded with the Cr–Cr distance elongated to 2.215 Å. These changes can be attributed to the fact that the interaction between Cr ions is enhanced when gaining extra electrons and decreased while losing electrons.

In addition, when adding one electron to Cr₃(BTC)₂, O₂

molecule was found to interact strongly with the CUS Cr with an interaction energy of $-102.7 \text{ kJ mol}^{-1}$. Mulliken charge population analysis shows that there is $0.36e$ charge transfer from the $\text{Cr}_3(\text{BTC})_2$ to O_2 molecule. In contrast, after removing one electron from $\text{Cr}_3(\text{BTC})_2$, the energy is decreased to $-59.9 \text{ kJ mol}^{-1}$, slightly smaller than $-63.5 \text{ kJ mol}^{-1}$ of the neutral $\text{Cr}_3(\text{BTC})_2$. The charge transferred is $0.07e$ which is also less than the value of $0.19e$ calculated for the neutral one. These observations demonstrate that the interaction energy of O_2 can correlate well with the magnitude of the charge transferred from $\text{Cr}_3(\text{BTC})_2$ to O_2 . As a result, reducing the energy required for deoxygenation can be realized through controlling the magnitude of charge transfer. For this purpose, one feasible approach is to weaken the donor strength of bridging organic ligands by adding electron-donating/withdrawing substituents.¹⁵ In current study, we put the emphasis on exploring the influence of metal substitution.

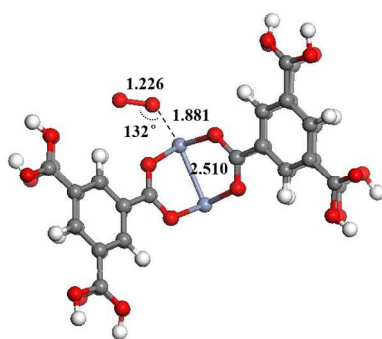


Fig. 3 The optimized structure of O_2 -loaded $\text{Cr}_3(\text{BTC})_2$ (Cr, blue; C, gray; O, red; H, white) (distances in Å).

3.2.2. Adsorption of O_2 in other $\text{M}_3(\text{BTC})_2$. The charge transferred between other $\text{M}_3(\text{BTC})_2$ and the adsorbed O_2 molecule are listed in Table 1. It can be found that the transfer magnitude varies from $0.01e$ to $0.23e$, depending on the nature of the metal ions. Compared to the bond length (1.225 Å) of a free O_2 molecule, the O-O bond length increases from 1.235 Å in $\text{Cu}_3(\text{BTC})_2$ to 1.285 Å in $\text{Mn}_3(\text{BTC})_2$. As a result, the magnitude of charge transfer can also be reflected from the bond length change of the adsorbed O_2 molecule.

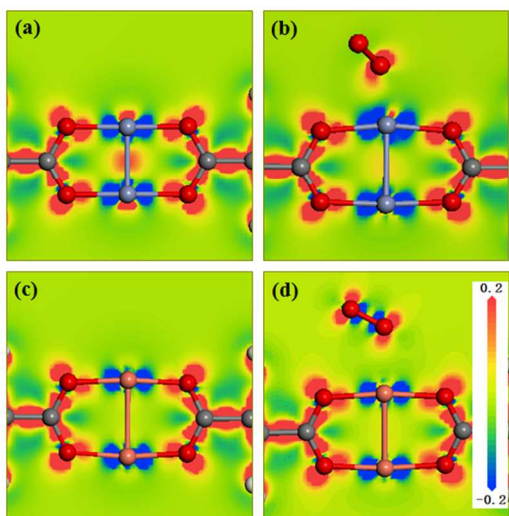


Fig. 4 The electron density differences for: (a) empty $\text{Cr}_3(\text{BTC})_2$, (b) O_2 -

$\text{Cr}_3(\text{BTC})_2$ complex, (c) empty $\text{Cu}_3(\text{BTC})_2$, and (d) O_2 - $\text{Cu}_3(\text{BTC})_2$ complex.

We further analyzed the electron density differences calculated for the empty and O_2 -loaded structures of $\text{M}_3(\text{BTC})_2$. Such electron density differences are the deformation density, which can be calculated as the total electron density of the system with the corresponding density of the isolated atoms subtracted. The results for the $\text{Cr}_3(\text{BTC})_2$ and $\text{Cu}_3(\text{BTC})_2$ systems are given in Fig. 4 as an example. For the empty $\text{Cr}_3(\text{BTC})_2$, Fig. 4a and 4b indicates that the exposed Cr ions can serve as an electron donor. After O_2 adsorption, the electron depletion of Cr site is enhanced (Fig. 4b) with a remarkable electron transfer from Cr ion to O_2 . In contrast, for the case of $\text{Cu}_3(\text{BTC})_2$ loaded with O_2 , there is almost no charge redistribution on the CUS Cu (Fig. 4d) compared to the empty one (Fig. 4c). The charge transferred from $\text{Cu}_3(\text{BTC})_2$ to O_2 is $0.01e$ and thus is nearly negligible. The origin of the different charge transfer between the various $\text{M}_3(\text{BTC})_2$ and O_2 can be attributable to the different electronegativity of the metals, as demonstrated in Fig. 5. Obviously, the magnitudes of charge transfer correlate well with the electronegativities of the CUS metals. The larger the electronegativity, the more difficulty for O_2 accepting negative charge transferred from the metal center, resulting in a decrease in the magnitude of charge transferred.

From Fig. 2 it can be found that the overall increasing trend of the charge transfer from $\text{M}_3(\text{BTC})_2$ to O_2 is in line with the changing trend of the calculated interaction energies. This could be expected because the weak bond between the metal and O_2 molecule resulted from partial transfer of electrons is a significant contribution to the O_2 - $\text{M}_3(\text{BTC})_2$ interactions. With regard to $\text{Cu}_3(\text{BTC})_2$, the calculated interaction energy without dispersion contribution is only -0.6 kJ mol^{-1} , which is the weakest among the $\text{M}_3(\text{BTC})_2$ series due to a negligible charge transfer from $\text{Cu}_3(\text{BTC})_2$ to O_2 .

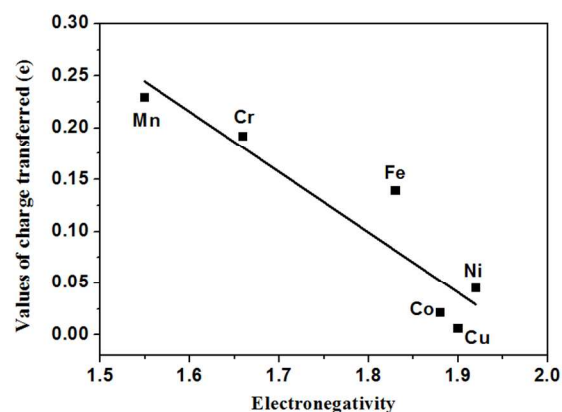


Fig. 5 Correlation between the charges transferred from $\text{M}_3(\text{BTC})_2$ to O_2 and the Pauling electronegativities of the metals.

3.3. Adsorption Thermodynamics

The previous comparisons are based on the interaction energies under the conditions of 0 K. For practical applications, it is more useful to compare the interaction strengths at room temperature. Thus, we performed further calculations to obtain the adsorption enthalpies of O_2 at 298 K and the results are tabulated in Table 1. The calculated adsorption enthalpy for O_2 with $\text{Cr}_3(\text{BTC})_2$ is -

65.4 kJ mol⁻¹, and such a high adsorption affinity can be used to account for the incomplete deoxygenation problem mentioned previously. Owing to a higher adsorption enthalpy toward O₂ (-85.5 kJ mol⁻¹), it can be deduced that Mn₃(BTC)₂ would also have the difficulty in deoxygenation. Wang et al.⁴⁴ experimentally reported that the adsorption of O₂ in Cu₃(BTC)₂ is nearly negligible. In this work, the adsorption enthalpy in Cu₃(BTC)₂ is found to be only -5.1 kJ mol⁻¹, which is well consistent with their observations. In addition, Table 1 shows that Fe₃(BTC)₂, Co₃(BTC)₂ and Ni₃(BTC)₂ have lower adsorption affinities for O₂ (-61.6, -35.4 and -44.0 kJ mol⁻¹, respectively) than Cr₃(BTC)₂. These results suggest that the three MOFs could be considered as more promising adsorbents with a relatively easier deoxygenation for practical O₂ separation applications.

3.4. Potential Capability for O₂/N₂ Separation

To evaluate the potential capability of M₃(BTC)₂ for O₂/N₂ separation, we conducted further calculations to obtain the interaction energies for N₂ with the cluster models, as tabulated in Table S2 (see ESI†). For Cu₃(BTC)₂, our calculated value (-18.9 kJ mol⁻¹) agrees well with the result (-19.3 kJ mol⁻¹) obtained at the B3LYP-D3/TZVP level.²² N₂ has a stronger adsorption affinity with this material than that of O₂, which is also in good agreement with the experimental observation that the Henry's constant of the former is larger than that of the latter.⁴¹ For practical air separation, it would be desirable to extract O₂ rather than the main component N₂ due to the limited number of CUS metals in M₃(BTC)₂. This will greatly reduce the separation cost because of the requirement of less adsorbent amount. Since Fe₃(BTC)₂ and Co₃(BTC)₂ show stronger adsorption interactions toward N₂ compared to O₂, the two MOFs are not the preferential materials for the separation of interest. For Cr₃(BTC)₂, the interaction energy of N₂ is significantly lower than that of O₂, and thus this material can exhibit a high O₂/N₂ selectivity (~22) as reported by Long and co-workers.¹⁵ However, as described previously, Cr₃(BTC)₂ cannot achieve a complete release of bound O₂ due to too high adsorption affinity toward O₂. This will lead to the recycle issue, which is also the case for Mn₃(BTC)₂. Interestingly, Ni₃(BTC)₂ shows 11 kJ mol⁻¹ higher interaction energy toward O₂ than that of N₂, and the adsorption affinity toward O₂ is much weaker than Cr₃(BTC)₂. This demonstrates that the O₂/N₂ selectivity of Ni₃(BTC)₂ may be lower than that of Cr₃(BTC)₂, but the former material could potentially achieve complete release of the adsorbed O₂ under near room temperature. As a result, Ni₃(BTC)₂ is predicted to be the more promising adsorbent for O₂/N₂ separation with easier deoxygenation.

4. Conclusions

Dispersion-corrected DFT calculations were performed in this work to investigate the adsorption behaviors of O₂ on a series of CUS-containing MOFs M₃(BTC)₂ (M = Cr, Mn, Fe, Co, Ni and Cu). The results show that the interaction energy of O₂ with M₃(BTC)₂ can be tuned in a wide range by metal substitution. The magnitudes of charge transfer from CUS metals to O₂ correlate very well with the interaction energies of O₂ with M₃(BTC)₂. Cu₃(BTC)₂ has the lowest adsorption affinity toward O₂ among the considered systems due to a negligible charge transfer. Furthermore, this work suggests that Ni₃(BTC)₂ could be

regarded as the promising adsorbent for O₂ capture and separation. Since the separation of O₂ is a challenging topic at the moment, the knowledge obtained might provide a helpful guidance for future efforts on the synthesis of new materials with improved performance for O₂ separation.

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Notes and references

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 † Electronic Supplementary Information (ESI) available: The dispersion parameters and the interaction energies of N₂ molecules with M₃(BTC)₂. See DOI: 10.1039/b000000x/
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