The binding nature of light hydrocarbons on Fe/MOF-74 for gas separation†

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The application of a metal–organic framework (MOF) has expanded into the area of heterogeneous catalysis, gas storage and separation, drug delivery, and lightweight magnets. Herein, we investigate the nature of olefin and paraffin binding on Fe/MOF-74 and identify several factors that determine separation efficiency using the first-principles calculations. The calculated binding energies and magnetic orderings are in excellent agreement with those observed in experiments. While the olefin strongly interacts with Fe atoms through a well-known π-complexation, the HOMO – 1(2) of the paraffin weakly interacts with Fe atoms without back-donation, facilitating the olefin–paraffin separation primarily. However, the mutual gas–gas interactions and magnetic transitions of the MOF host also contribute significantly to the total binding energy of each gas molecule as much as 2–28% and 6–8%, respectively, emphasizing the necessity that these subtle effects must be handled carefully when considering selective binding with small energy differences. In particular, Fe/MOF-74 is shown to be a unique system where the guest-dependent magnetic transition observed only for the olefin adsorption is a secondary reason for the high olefin–paraffin adsorption selectivity measured. The understanding of the hydrocarbon binding energetics can provide a way to modify MOFs for enhanced separation/sorption properties that can be complemented by principles of kinetic separation.

Introduction

Light hydrocarbons such as methane, ethane, propane, acetylene, ethylene and propylene are widely used as the energy resources and chemical feedstocks in diverse industries. While the application areas are different for each hydrocarbon species, they are produced all at the same time by thermal cracking of large hydrocarbons and thus separation processes are required to obtain high purity ingredients. Commercially, the separation of binary gas mixtures such as ethane–ethylene and propane–propylene is the most important but difficult process due to the similar physicochemical properties of the mixed gases. Although the cryogenic distillation has been successfully used for these separations, its operating cost is exceedingly high since low temperatures and high pressures are required, demanding the development of alternative technologies.2–3 Separation methods based on reversible chemical absorption have been investigated as a promising approach.1,3,4 In earlier attempts on the adsorptive separation, however, the low surface area (capacity) and selectivity were two major limitations.5,4 To overcome the latter problems simultaneously, a number of research studies have focused on the Ag(i) or Cu(i) cation impregnated mesoporous adsorbents and indeed, they exhibited good separation selectivities due to the π-complexation5 between the metal cations and olefins.1,4,6,7

As an extension, metal–organic frameworks (MOFs) have also been explored for olefin–paraffin separation.8–15 MOFs are composed of metal-containing clusters and organic linkers16 with extremely high surface area that enables MOFs to be used in gas manipulations such as carbon dioxide,17–25 hydrogen,26–33 and hydrocarbons.34–39 Especially MOFs with coordinatively unsaturated metal sites can strongly bind with the guest olefins. To the best of our knowledge, open Cu sites in HKUST-113 and ZJU-5,10 open Fe sites in MIL-100(Fe),14 and open M sites in M/MOF-74 (M = Mg, Mn, Fe, Co, Ni, Zn)8–12 were reported to undergo π-complexation with olefins.

Among them, the M/MOF-74 (or CPO27-M) have been studied most extensively due to their outstanding separation performance. For instance, Fe/MOF-74 shows 2–3 times higher selectivity and capacity for hydrocarbon separation compared to the zeolite-based solid adsorbents without capacity loss and hysteresis for dozens of cycles.10 While they exhibit overall good olefin–paraffin selectivity...
regardless of the particular metal species, the best separating materials are different for each case of gas mixtures. For instance, Fe/MOF-74 and Mn/MOF-74 are optimal for the separation of ethylene–ethane and propylene–propane mixtures, respectively, and Co/MOF-74 is the best for the separation of methane from a mixture of C2 hydrocarbons. To resolve such mixture-dependent adsorption performance as well as to modulate metal centers and functional groups for obtaining suitable characteristics, an atomic scale understanding is necessary.

Recently, several theoretical studies have been performed on the hydrocarbon binding/separation in MOF-74. et al. analysed the ethylene and methane adsorptions on Mg/ and Zn/MOF-74 by employing cluster models. In their calculations, only a forward donation was identified for ethylene adsorption, while both forward and backward donations are observed in methane adsorption, conflicting with the common π-complexation phenomena. Sillar et al. investigated the methane adsorption on Mg/MOF-74 focusing on the lateral interactions where they showed that the mutual gas–gas interaction contributes to the total binding energy by 10–15%. Verma et al. examined the adsorption of C1–C3 hydrocarbons particularly on Fe/MOF-74. They observed notable forward and backward donations for the ethylene adsorption, but not for the ethane adsorption. While their calculated energies are qualitatively consistent with experiments, explanations for distinctive adsorption of acetylene, the binding nature of paraffin, mutual gas interactions, magnetic transitions, and their effects on the hydrocarbon separation were not addressed and still remain unclear.

In Fe/MOF-74, the intrachain magnetic ordering of Fe atoms along the c-direction (Fig. 1) is switched from ferromagnetic (FM, Fig. 1b) to antiferromagnetic (AFM, Fig. 1c) after olefin adsorption, while it remains FM for the paraffin adsorption. This selective magnetic transition can affect the adsorption strength by a different amount for each gas molecule, thereby affecting the separation selectivity.

In this paper, we investigate the binding nature of olefins and paraffins on Fe/MOF-74 using the periodic DFT calculations that can fully describe the magnetic orderings, mutual gas interactions, and their effects on the hydrocarbon separations. In particular, the present study addresses the following aspects: (1) what is the nature of a distinctive adsorption of acetylene with sp hybridization compared to olefins with sp² hybridization? (2) what is the binding nature of paraffin, is it just dispersion interactions, or are there distinct orbital interactions different from the olefin case? (3) can mutual gas–gas interactions affect the separation efficiency, and if so, to what extent? and (4) how and to what extent did the magnetic transition from ferro- to anti-ferromagnetism upon olefin adsorption observed experimentally, but not paraffin adsorption, affect the separation efficiency?

Calculation details

The periodic density functional theory (DFT) calculations were performed under the generalized gradient approximation (GGA) with dispersion corrections (D2) as implemented in the Vienna Ab initio Simulation Package (VASP). The electronic structure of bare Fe/MOF-74

The electronic structure of Fe/MOF-74 and its effects on the binding of hydrocarbons can be understood from the conventional

Results

Electronic structure of bare Fe/MOF-74

Both Perdew–Burke–Ernzerhof (PBE) and revised PBE (RPBE) exchange–correlation functionals give a qualitatively identical trend in binding energies of hydrocarbons, but RPBE + D2 provides quantitatively superior results. While we also examined Hubbard U-corrections with U_eff = 4.0 eV for Fe, the binding energies were much worse than the uncorrected results. See Table S1 in the ESI† for the comparison of calculation methods. Therefore, we adopted RPBE + D2 in all calculations. The initial structures were taken from the experiments and geometries were fully optimized until the force is less than 0.025 eV Å⁻¹. We used a plane wave basis set and the projector-augmented wave (PAW) method with an energy cutoff of 500 eV. The Brillouin zone integration was performed at the gamma point. All crystal structures were visualized using the VESTA program.

To address the ground state magnetic orderings for each gas adsorbed structure, we adopted supercells containing 36 adsorption sites to describe AFM ordering along the 1D chain of Fe/MOF-74 as shown in Fig. 1. We assumed that gas molecules occupy all unsaturated Fe sites. For each gas adsorption, we examined three different magnetic orderings that are observed in experiments: (i) intrachain FM and interchain antiparallel (Fig. 1b), (ii) intrachain AFM and interchain antiparallel (Fig. 1c), and (iii) intrachain FM and interchain parallel (magnetized).
ligand field theory. Fig. 2a shows the projected density of states (DOS) for each d-orbital of Fe and that for oxygen, where the top and bottom sides correspond to the up- and down-spin electrons, respectively. From the geometric viewpoint, each Fe ion has a square pyramidal coordination of oxygen atoms (Fig. 1 and 2b) and one coordination site is empty toward the tunnel to afford one more ligand. The highest and second highest energy levels of d_{xy}, d_{yz}, and d_{z^2} orbitals, respectively, are largely in agreement with the energy splitting by the square pyramidal coordination of ligands. However, the d_{xy}, d_{yz}, and d_{z^2} orbitals, namely d_{3z^2-R} orbitals, are more similar in energy than typical five-coordinate systems as noted with the splitting shown in (i) in Fig. 1, since the neighboring Fe atoms are located close together at 2.79 Å along the diagonal direction (Fig. 2b), disturbing the orbital symmetry.

One down-spin electron in d^6 of Fe(II) occupies the aforementioned d_{3z^2-R} orbitals that are located just below the Fermi level (Fig. 2a–(i)), so it is the highest occupied molecular orbital (HOMO) of bare Fe/MOF-74. Fig. 2c shows an isosurface of electron density at the HOMO level as noted with (i) in Fig. 2a.

![Fig. 2](image-url) (a) The decomposed DOS for Fe and oxygen ions in bare Fe/MOF-74. The dotted and solid lines in the lower part of the figure indicate the relative positions of HOMO and LUMO levels for isolated paraffin (Ma = methane, Ea = ethane, Pa = propane) and olefin (Ay = acetylene, Ey = ethylene, Py = propylene) gas molecules. (b) Local geometries with Fe–O distances, Fe–Fe distance, Fe–O–Fe angle. (c) The electron density isosurface at the HOMO level as noted with (i) in Fig. 2a.

Olefin adsorption

The binding nature of olefin–metal complexes has been explained well in organometallic chemistry by employing the \( \sigma(\pi) \)-bonding and \( \pi \)-backbonding concepts, namely \( \pi \)-complexation, where the outermost shell of a metal and the HOMO of an olefin are involved. The HOMO of a free olefin gas is the \( \pi \)-bonding molecular orbital which is placed at 2–3 eV below the Fermi level of bare Fe/MOF-74 as shown in Fig. 2a. Instead of an isotropic 4s orbital in the olefin–Ag(i) or –Cu(i) complexation, the 3d orbitals participate in the olefin–Fe/MOF-74 complexation as the outermost shell, owing to the open geometry of MOF-74. Therefore, the spatial direction and phase of Fe-3d orbitals should match well with the interacting orbitals of the olefin to form a complex.

For the acetylene (Ay) adsorption, for example, the projected DOS and corresponding electron density isosurfaces at several relevant energy levels are presented in Fig. 3a and b, respectively. The most significant orbital overlap appears at the energy level of (i), which is attributed to the bonding between the d_{xy} orbital of Fe and the HOMO of Ay, which locates in the z-direction, namely \( \pi \)-HOMO. We denote this \( \sigma \)-type orbital interaction as the \( \pi \)-d_{xy} bonding (Fig. 3b–(i)).

In contrast to ethylene (Ey) and propylene (Py) that belong to the sp^2 hybridization group, the sp hybridized Ay has two degenerate HOMOs, \( \pi_x \) and \( \pi_y \), rather than one. This additional \( \pi \)-HOMO can interact with the Fe–d_{xy} orbital, namely \( \pi \)-d_{xy} bonding, as shown in Fig. 3a–(ii) and b–(ii). Although this \( \pi \)-type overlap of \( \pi \)-d_{xy} bonding is much smaller than that of \( \pi \)-d_{z^2} bonding, it increases the binding strength between Ay and Fe/MOF-74 compared to the other olefins to some extent.

Meanwhile, the lowest unoccupied molecular orbital (LUMO) of the olefin gas locates at 3–4 eV above the Fermi level of bare

![Fig. 3](image-url) (a) The decomposed DOS for the acetylene (Ay) adsorbed Fe/MOF-74. (b) (i) The bonding between the d_{xy} orbital of Fe and the \( \pi \)-HOMO of Ay; (ii) bonding between the d_{z^2} orbital of Fe and the \( \pi \)-HOMO of Ay; (iii) the \( \pi \)-backbonding between the d_{xy} orbital of Fe and LUMO of Ay. (c) The Fe–O distances, Fe–O–Fe angle, and Fe–Fe distance are increased by Ay adsorption.
Fe/MOF-74 and it accepts electrons from the Fe-d_{yz} orbital by forming the π-backbonding as shown in Fig. 3a–(iii) and b–(iii). These bondings and backbonding synergistically contribute to the strong adsorption of olefins on Fe/MOF-74, not only by way of typical electron donation–backdonation, but also from a geometric viewpoint as follows.

Upon the Ay adsorption, an Fe atom is pulled out toward the channel direction, with an increase of the coordination number from five to six by forming a bond with Ay. While the strong π-d_{yz} bonding mainly induces the pulling and bond formation, the π-backbonding additionally helps the binding strength, where it diminishes Fe–Fe attractions by drawing electrons from the HOMO that are responsible for direct Fe–Fe interactions. Indeed, the slightly delocalized HOMO bands (Fig. 2a–(i)) in bare MOF disappear after the Ay adsorption, indicating the disappearance of the direct interaction between Fe atoms. Instead, all the down-spin electrons are localized in the d_{yz} orbital and participate in the π-backbonding with Ay molecule (Fig. 3a–(iii)). This π-backbonding orbital is the HOMO of Ay adsorbed Fe/MOF-74.

As a result, Fe–O bond distances increase by 0.08 Å on average, and the distance between neighboring Fe atoms increases from 2.79 to 3.31 Å. The Fe–O–Fe bond angle also increases up to 107.1°. These geometric evolutions can be the origin of the observed magnetic transition along the 1D chain of Fe atoms for the olefin adsorption.33–35 The C–C distance of gas molecules, the Fe–Fe distance, and bond angles before/after the adsorption that can be a measure of complexity, are summarized in the ESI† (Table S2).

**Paraffin adsorption**

Hereafter, the notation [mol]_geom indicates that the geometry was taken from the complex denoted as “geom”, and the part (or whole) of the complex under consideration is denoted as “mol”. For example, [MOF + Pa]_{MOF+Pa} denotes the fully optimized structure of the propane (Pa) adsorbed MOF (both host and guest included), [MOF]_{MOF+Pa} denotes the MOF host only, whose geometry is extracted from the fully optimized MOF + Pa, and [MOF]_{MOF} denotes the optimized structure of the bare Fe/MOF-74. Similarly, [Pa]_{MOF+Pa} denotes the Pa guest molecules only, whose geometries were taken from the fully optimized MOF + Pa. [1Pa]_{MOF+Pa} denotes a single gas molecule taken from MOF + Pa. These notations are illustrated in Fig. S3 in the ESI† for clarity.

Fig. 4a shows the projected DOS of Fe atoms for [MOF + Pa]_{MOF+Pa}, [MOF]_{MOF+Pa} and [MOF]_{MOF}. The overall DOS change of Fe atoms due to the Pa adsorption is negligible to that due to the olefin adsorption (Fig. 4b). To be more specific, the change in electronic structure due to the structural change of the MOF host upon Pa adsorption (from green [MOF]_{MOF} to blue [MOF]_{MOF+Pa}) is exceedingly small, consistent with small geometry changes for paraffin adsorptions (Table S2, ESI†). Moreover, the additional changes by adding Pa molecules to the distorted MOF (from blue [MOF]_{MOF+Pa} to black [MOF + Pa]_{MOF+Pa}) are also small, indicating that the electronic interactions between Pa and Fe/MOF-74 are insignificant compared to the olefin cases where the gas adsorption also induces a noticeable alteration in the electronic structure of the host MOF as shown in Fig. 4b. The most significant changes in electronic structure for Pa adsorption are marked with (i)–(iv) and they are discussed below.

The key interactions in the paraffin adsorbed Fe/MOF-74 can be categorized as follows, for example, in the case of Pa.

1. Paraffin–Fe interaction: since the HOMO of Pa gas resembles a π*-antibonding orbital (composed of C–H σ-bonds), it can interact with the in-phase d_{xy} and d_{yz} orbitals of Fe atoms instead of the d_{xz} orbital. To do that, the Pa gas should withdraw a sufficient amount of electrons from d_{xy} that forms the Fe–Fe direct interaction. However, the latter interaction cannot be so strong since the HOMO of Pa is a combination of the localized σ-orbitals that are far below the Fermi level of Fe/MOF-74 (Fig. 2a). Indeed, the Fe–Fe distance increases only by 0.02 Å after the Pa adsorption (see the ESI† for detailed geometries), contrast to the 0.52 Å increment for the Ay adsorption. Instead, the HOMO – 2 of Pa is a σ-resembled orbital close to the unsaturated Fe atoms, and hence instead

![Fig. 4](image-url)
This HOMO – 2 interacts with the d_{pz} orbital of Fe atoms as shown in Fig. 4a–(i) and c–(i). In the same manner, the HOMO – 1 of ethane (Ea) can interact with Fe atoms. Note that the π-backbonding to the paraffin is not allowed, and the above overlap between HOMO – 2(1) of paraffin and Fe/MOF-74 is much smaller than that for the olefins, both leading to a weak adsorption of the paraffin in Fe/MOF-74.

(2) Paraffin–ligand interaction: the short distances between H in Pa and O in Fe/MOF-74 (2.59 Å in calculation, 2.48 Å in experiment) allow the interaction between Pa and the ligands of Fe/MOF-74 at the energy level of (ii), for example, in Fig. 4a. This type of interaction is also available for the olefin cases.

(3) Mutual gas interaction: in the DOS of Pa (shaded in Fig. 4a), the band splitting in the multiple gas molecules [[Pa]_{MOF-74}] compared to a single isolated gas molecule [[1Pa]_{MOF-74}] implies the interaction between gas molecules. Since the band split is attributed to the in-phase interaction (iii) and out-of-phase interaction (iv), it depends on the spatial shape of the molecular orbitals. Note that the extent of DOS splitting, or mutual gas interaction, decreases as the molecular size decreases (Pa > Ea > Ma). Consistently, the calculated gas–gas interaction energies for Ay, Ey, Py, Ma, Ea, and Pa in the Fe/MOF-74 framework are 0.9, 2.1, 5.5, 1.8, 4.3, and 8.0 kJ mol\(^{-1}\), respectively, whose magnitudes are in accord with the Ma–Ma interaction in Mg/MOF-74 (2.4 kJ mol\(^{-1}\)).\(^{42}\) This dispersion-dominant interaction is stronger for larger molecules since their polarizabilities are higher and intermolecular distances are closer within the confined volume. In addition, the mutual gas interaction is smaller in olefins since the gas–gas intermolecular distances are further apart, the molecular sizes and polarizabilities are smaller, and the polarizable HOMO electrons are in large part delocalized through the bonding with open metal sites in Fe/MOF-74 (shaded in Fig. 4b).

Binding energies

The binding energy is calculated between the fully optimized geometries/energies under the ground state magnetic orderings for each structure. Consistent with experiments,\(^{10}\) Fe/MOF-74 shows a clear olefin–paraffin selectivity in binding energies: it binds olefin gases (45–50 kJ mol\(^{-1}\)) and paraffin gases (15–30 kJ mol\(^{-1}\)) (Fig. 5).

For olefins, the exact order of calculated binding energy (Py > Ay > Ey) is different from the Bloch’s experiments (Ay > Ey > Py) but the same as another measurement using the same experimental method,\(^{12}\) indicating that the energy differences (within 5 kJ mol\(^{-1}\)) are perhaps in the error range of measurements. For comparison, the binding energies in the absence of mutual gas interactions are considered. As mentioned above, Ay has an additional π\(_x\)-bonding that contributes weakly to the adsorption and hence, Ay shows a stronger gas–MOF interaction (white bar) than Ey and Py by \(\sim 3\) kJ mol\(^{-1}\) as shown in Fig. 5. The mutual gas interactions in olefins, however, are largest in the Py, perhaps as expected.

For paraffin, the order of calculated binding energy is consistent with two independent experiments, Pa > Ea > Ma.\(^{10,12}\) This order is completely consistent for all aforementioned binding components: (1) the molecular orbitals of paraffins that are able to interact with Fe are placed higher in energy in the order of Pa > Ea > Ma, (2) the paraffin–ligand dispersion interaction is higher for larger and more polarizable molecules, and (3) the strength of the gas–gas interaction is in the order of Pa > Ea > Ma. A consistent slight underestimation of the binding energy for paraffins is probably due to the overestimation of the distance between gas molecule and Fe/MOF-74 (2.59 Å in calculation, 2.48 Å in experiment for Pa) and the consequent underestimation of gas–MOF interactions, as well as the limitations of the present density functionals used. Also, the partial occupancy that depends on the loading can alter the binding strength of gas molecules.

The binding energy can be further decomposed into contributions from the geometric distortion, magnetic transition, mutual gas interaction, and electronic effects. Fig. 6 shows relative energies for each gas adsorption state. By using the same [mol] notations as in the previous section, state (i) is [MOF]_{MOF-gas} with intrachain FM ordering and 36 free gas molecules (isolated MOF and gas molecules in each ground state, i.e. a reference energy state); state (ii) is [MOF]_{MOF-gas} with intrachain FM ordering and...
36 \([\text{gas}]_{\text{MOF-gas}}\) (distorted MOF and gas molecules without magnetic transition); state (iii) is \([\text{MOF}]_{\text{MOF-gas}}\) in ground state magnetic ordering and 36 \([\text{gas}]_{\text{MOF-gas}}\) (same distorted geometries as state (ii) but in ground state magnetic ordering); state (iv) is \([\text{MOF}]_{\text{MOF-gas}}\) with ground state magnetic ordering and \([\text{gas}]_{\text{MOF-gas}}\) (MOF host is the same as state (iii) but mutual gas interactions are included); and state (v) is \([\text{MOF+gas}]_{\text{MOF-gas}}\) (fully electronically relaxed gas adsorbed MOF, i.e., the final adsorption state). Therefore, the numbers between each state are, from left to right, the binding energy contributions of the geometric distortion, magnetic transition by MOF host (Mag.h), mutual gas interaction (gas–gas), and total electronic effects. The total electronic effects include all interactions between MOF and gas molecules such as charge transfer, polarization and dispersion, as well as the additional magnetic transition effect by electronic interaction (Mag.e). Note that the total contribution of magnetic transition is the sum of Mag.h and Mag.e.

The olefin adsorption (solid lines) induces distortion energy penalties for both the MOF host and gas molecules of 40–50 kJ \(\text{mol}^{-1}\) and 6–17 kJ \(\text{mol}^{-1}\), respectively. This distortive energy penalty is most significant for Ay adsorption as expected from the extent of geometry changes (Table S2 in the ESI†). This large distortion is stabilized by the magnetic transition (total 2.8–3.3 kJ \(\text{mol}^{-1}\)), mutual gas interaction (0.9–5.5 kJ \(\text{mol}^{-1}\)), and mostly by electronic interactions between MOF and gas (90–110 kJ \(\text{mol}^{-1}\)). The strength of electronic interactions is notably larger for Ay adsorption, consistent with the distinctive orbital interaction picture of Ay as described in the previous section.

In contrast, the paraffin adsorption (dashed lines) does not alter the geometry of the MOF host and gas molecules significantly; thereby distortive energy penalties are below 1 kJ \(\text{mol}^{-1}\). The magnetic transition does not occur for the paraffin adsorption and thus its contribution is zero. While the adsorbed paraffins are mostly stabilized by electronic effects as in the olefins (12–21 kJ \(\text{mol}^{-1}\), the mutual gas interactions (1.8–8.0 kJ \(\text{mol}^{-1}\)) become a more important factor in paraffins as compared to the olefin cases. Also, we identified in the previous section that the charge transfer between paraffin and host MOF is insignificant, consistent with Verma’s charge analysis results,\(^\text{43}\) implying that the electronic effects in paraffin adsorption is largely attributed to the long-range interactions.

Table 1 shows the total binding energies with and without the consideration of experimentally observed magnetic transition.

Table 1  The calculated binding energies with/without the consideration of magnetic transition for each gas adsorption

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>Binding energy (kJ (\text{mol}^{-1}))</th>
<th>Ground state</th>
<th>w/o Mag. Tr.</th>
<th>Experiments(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetylene</td>
<td>46.4</td>
<td>43.2</td>
<td>47</td>
<td></td>
</tr>
<tr>
<td>Ethylene</td>
<td>44.4</td>
<td>41.1</td>
<td>45</td>
<td></td>
</tr>
<tr>
<td>Propylene</td>
<td>48.1</td>
<td>45.3</td>
<td>44</td>
<td></td>
</tr>
<tr>
<td>Methane</td>
<td>14.1</td>
<td>14.1</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Ethane</td>
<td>22.5</td>
<td>22.5</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>Propane</td>
<td>28.1</td>
<td>28.1</td>
<td>33</td>
<td></td>
</tr>
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</table>

\(^a\) Ref. 10.

Note that the intrachain magnetic ordering of the paraffin adsorbed Fe/MOF-74 is identical to that of bare Fe/MOF-74 (Fig. 1b), while the olefin adsorption overturns it from FM to AFM (Fig. 1b and c)\(^1\). By including this magnetic transition, the binding energies of Ay, E and P by increase by 3.3, 3.2 and 2.8 kJ \(\text{mol}^{-1}\), respectively, where the increments are not negligible (6–8%). More importantly, since the magnetic transition appears only for the olefin adsorption, i.e., guest-dependent, it can be another reason for the high olefin–paraffin selectivity in Fe/MOF-74.

Conclusion

We fully investigated the nature of hydrocarbon binding on Fe/MOF-74 with resultant magnetic transitions observed in experiments, and identified the factors that determine the separation efficiency. The following findings are noteworthy:

1. The \(\sigma(\pi)\)-bonding and \(\pi\)-backbonding between the olefin and Fe/MOF-74 synergistically enhance the olefin adsorption in both electronic and geometric ways. Especially, two degenerated HOMOs of acetylene increase its interaction with Fe/MOF-74, compared to the other olefins.

2. For the paraffins, the HOMO does not interact, but instead the HOMO – 2 (or HOMO – 1) weakly interacts with the MOF framework. This different binding nature mainly enables Fe/MOF-74 to separate olefins from paraffins, and vice versa.

3. We show that the mutual gas interactions (1–8 kJ \(\text{mol}^{-1}\)) must also be considered carefully when evaluating the total binding energies of gas molecules in Fe/MOF-74, in particular when considering the selective binding within small energy differences.

4. The magnetic transition of Fe/MOF-74 appears only for the olefin adsorption, increasing the binding strength of olefins by \(\sim 3\) kJ \(\text{mol}^{-1}\), but not for the paraffins. This selective magnetic transition and associated energy scale are not negligible but contribute sizably to the olefin separation performance of Fe/MOF-74.

The present understanding and characterization of the deciding factors for hydrocarbon separation using MOF-74 as a prototype example give us hints to the way of tuning MOFs for improved hydrocarbon separation/sorption properties. For example, more electronegative functional groups in the organic linker can selectively increase binding strength for olefins, especially acetylene, due to the increased forward donation to the more electron deficient Fe atoms owing to the electron drawing from the linkers. Modifying framework morphology or steric groups may also be utilized to further aid kinetic separation in conjunction with the present thermodynamic guideline.

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Notes and references