Selective adsorption of butenes over butanes on isoreticular Ni-IRMOF-74-I and Ni-IRMOF-74-II†

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The separation of butanes and butenes using MOF-74 (with two reticular MOFs with different pore sizes, Ni-IRMOF-74-I and Ni-IRMOF-74-II) was evaluated computationally using density functional theory. We identified that C₄ alkene versus alkane selectivity stems from π–d chemical interactions, whereas selectivity differences among butenes stem from steric implications.

IRMOF-74-I (or MOF-74) is a highly porous, crystalline metal–organic framework (MOF) molecular sieve with honeycomb topology and one-dimensional pore channels (~1.1 nm). The structure is comprised of divalent metal atoms (e.g. Ni²⁺, Cu²⁺, and Co²⁺), which are coordinated by 2,5-dihydroxyterephthalic acid linkers and homogeneously distributed across the three-dimensional framework (Fig. 1a). These metal atoms are accessible via pore channels and are connected to each other by sharing a corner oxygen atom. Due to these unique structural features, IRMOF-74-I provides a high concentration of identical and spatially isolated metal atoms, exhibiting long range order. Each metal atom has one axial site occupied by a solvent molecule during synthesis. Removal of the axially coordinated solvent molecule by post synthetic vacuum and/or heat treatment reveals coordinatively unsaturated metal atoms that are Lewis acid sites (Fig. 1b). These metal atoms function as binding sites and have thus been utilized for reversible adsorption and separation of hydrocarbon mixtures containing gas molecules such as C₂H₆, C₂H₄, C₂H₂, C₃H₈, and C₃H₆.

Separation of C₄ isomers (1-butene, trans-2-butene, cis-2-butene, 1,3-butadiene, n-butane, and i-butane) from one another by traditional processes is challenging. These isomers are important precursors in the synthesis of many commodity chemicals and a high purity isomer is generally desirable for process simplification. Although IRMOF-74-I and other MOFs with open metal sites have been utilized for the separation of smaller hydrocarbon molecules, separation of C₄ isomers is scarce and to the best of our knowledge only a couple of studies focus on utilizing IRMOF-74-I.  

Barnett et al. experimentally studied the effect of variation in electronic properties of the metal binding site on the separation selectivity of 1-butene over cis- and trans-2-butene. A charge dense cation (e.g. Ni²⁺) was found to favour 1-butene selectivity whereas a metal cation with comparatively lower charge density (e.g. Mn²⁺) favoured cis-2-butene selectivity. Furthermore, less adsorption selectivity towards trans-2-butene was attributed to the steric hinderance of this isomer to the metal site, whereas the increase in adsorption capacity for 1-butene compared to cis- and trans-2-butene on increasing coverage was ascribed to stabilizing effects from stronger gas–gas interactions. Similar results were obtained by Kim et al. in their density functional theory (DFT) work considering the adsorption of C₄ alkenes on Fe-IRMOF-74-I. The order of DFT-calculated binding strengths was, 1-butene > isobutene > cis-2-butene > trans-2-butene, the weaker binding for cis- and trans-2-butene was due to the increased steric hindrance experienced by these isomers on metal sites. These studies, however, did not address the interactions between IRMOF-74 and C₄ alkenes. Furthermore, no MOF design attempts were made to vary steric hindrance effects by modulating pore sizes. Additionally, Hubbard U corrections were not considered by Kim et al. while calculating the binding energies or performing energy decomposition
Hubbard U corrections are shown to improve the description of localized transition metal d states, including improved agreement with experimentally observed high spin states.\textsuperscript{15,16,18}

The work described in this paper builds on the computational results obtained by Barnett et al. and Kim et al. respectively.\textsuperscript{13,14} We utilize smaller pore-sized Ni-IRMOF-74-I and its isoreticular structure, a larger pore Ni-IRMOF-74-II, to computationally understand the effect of pore size variation on the binding of C\textsubscript{4} isomers (1-butene, \textit{trans}-2-butene, \textit{cis}-2-butene, i-butene, 1,3-butadiene, \textit{n}-butane, and i-butane) and their separation.\textsuperscript{19} The Ni form of IRMOF-74 was chosen due to the high Ni charge density, higher 1-butene adsorption capacity, and its possible role in separating C\textsubscript{4} isomers as observed in literature.\textsuperscript{13,14} DFT methods were used to calculate the binding energies and to decompose these binding energies into constituent components. The data obtained in this paper provides a connection between structure and the adsorption and separation of these C\textsubscript{4} isomers on MOF-74.

Periodic DFT calculations of C\textsubscript{4} adsorption within the Ni-IRMOF-74 structure were performed using the Vienna Ab initio Simulation Package (VASP). Spin-polarized electronic structure calculations were performed using the PBE exchange-correlation functional including the vdW-DF3 dispersion corrections, and Hubbard U corrections on Ni d states. Further details of the electronic structure methods and energy decomposition approach are given in the ESI.\textsuperscript{†}

The adsorbed geometries and the computed binding energies for the adsorption of C\textsubscript{4} isomers on open Ni metal sites at complete coverage (i.e., 1 mol gas per mol Ni) for both MOFs are presented in Fig. 2 and Table 1. The order of binding energy (and in turn the binding strength and or affinity) of C\textsubscript{4} isomers for Ni-IRMOF-74-I is, 1-butene (strongest binding) > \textit{cis}-2-butene > i-butene > 1,3-butadiene > \textit{trans}-2-butene > \textit{n}-butane > i-butane. For the larger pore Ni-IRMOF-74-II, the order changes to, i-butene = 1-butene > 1,3-butadiene > \textit{trans}-2-butene > \textit{cis}-2-butene > i-butane = \textit{n}-butane. These trends in binding energies for the adsorption of C\textsubscript{4} isomers are also roughly translated in the metal (Ni) to isomer distances (Fig. 2), where generally the isomer with the stronger interaction is located closer to binding site. Additionally, based on the adsorbed geometries of the C\textsubscript{4} molecules, the closest atoms to the Ni site for alkenes are the double bonded carbons, whereas for alkanes, the closest adsorbate atom to Ni is hydrogen. Similar geometrical observations have been reported for smaller hydrocarbon alkane and alkenes.\textsuperscript{20} Binding \textit{via} the C–C double bond is due to the higher electron density of double bond and the resulting π-complexation with the open metal site, generating stronger interactions with alkanes as is reported in Table 1.\textsuperscript{20} The weaker interactions of the alkane stems from the weak electron donation from the σ orbital of the C–H bond to the unsaturated metal site.\textsuperscript{20} Alkenes, irrespective of the pore size, exhibit stronger binding energies compared to alkanes.

In order to further investigate, analyse and compare the binding energies of each individual C\textsubscript{4} isomer, energy decomposition analysis similar to that in Kim et al., was performed and is depicted in Fig. 3.\textsuperscript{14} Binding and consequently the adsorption capacity of a specific molecule is a combination of the stabilizing molecule–molecule interactions, dispersion interactions and the binding affinity towards the Lewis acid metal sites. To facilitate these attractive interactions, destabilizing MOF framework and C\textsubscript{4} molecule geometry distortions occur, as well as steric repulsions induced during adsorption. The adsorption of C\textsubscript{4} isomers on Ni sites generate significant MOF framework distortions, with alkane causing positive distortion energies of greater than 30 kJ mol\textsuperscript{−1} whereas alkenes cause significantly less MOF distortion. Non-dispersion interactions among C\textsubscript{4} adsorbates in the adsorbed structure are attractive in the Ni-IRMOF-74-I small pore size structure, contributing –10 to –15 kJ mol\textsuperscript{−1} to the binding energy. The dispersion stabilization, including both gas–gas interactions and gas–MOF interactions, contributes significantly to the overall binding energy, however, are comparable for both alkane and alkenes and irrespective of the MOF pore size. Dispersion interactions, therefore, do not contribute significantly to dictating the selectivity for adsorption among the various C\textsubscript{4} species. For example, in Ni-IRMOF-74-I, the dispersions interactions are –53.06 and –47.39 kJ mol\textsuperscript{−1} for 1-butene and \textit{n}-butane, respectively. However, the large difference in framework distortion (49.18 and 8.23 kJ mol\textsuperscript{−1} for 1-butene and \textit{n}-butane) and the bond and steric interactions (–62.46 kJ mol\textsuperscript{−1} and –0.46 kJ mol\textsuperscript{−1} for 1-butene and \textit{n}-butane) mainly dictate the difference in binding energy between the alkane and alkene. The combination of bond and steric interactions is

### Table 1: Binding energy of C\textsubscript{4} isomers for Ni-IRMOF-74-I and Ni-IRMOF-74-II at complete Ni coverage

| C\textsubscript{4} isomer | Binding energy (kJ mol\textsuperscript{−1}) | Ni-IRMOF-74-I | Ni-IRMOF-74-II |
|--------------------------|------------------------------------------|----------------|----------------|
| 1-Butene | –79.53 | –66.45 |
| i-Butene | –76.72 | –66.77 |
| \textit{cis}-2-Butene | –78.10 | –53.73 |
| \textit{trans}-2-Butene | –67.99 | –60.61 |
| 1,3-Butadiene | –74.13 | –64.65 |
| i-Butane | –51.60 | –48.41 |
| \textit{n}-Butane | –56.08 | –48.14 |

Fig. 2 Adsorbed geometries of C\textsubscript{4} isomers on Ni-IRMOF-74-I (top) and Ni-IRMOF-74-II (bottom). Black dotted lines represent Ni–C distances, while green dotted lines represent Ni–H distances. Distances are labelled in Angstrom.
interactions with the adsorbing C4 alkenes, thus weaker addition of an extra benzene ring in the linker, imparts weaker Lewis acidity of the Ni metal sites in Ni-IRMOF-74-II, due to the reduced Lewis acidity of the Ni-IRMOF-74-II sites.

Comparing the factors that dictate the relative binding of butene isomers is not straightforward, as the binding energies are comparable, and the decomposition does not provide reliable nor straightforward explanations for the differences. There is some difference in the binding energies of 1-butene and i-butene from cis-2- and trans-2-butene in Ni-IRMOF-74-II, suggesting that the separation of these isomers might be possible using the larger pore Ni-IRMOF-74-II.

Conclusions

This study computationally investigated the adsorption of C4 alkanes and alkenes on IRMOF-74-I and its isoreticular IRMOF-74-II with larger pores. This study set up computational models for hydrocarbon adsorption on IRMOF-74 series, which also detailed different types of interactions contributing to the adsorption. We applied periodic DFT to reliably represent the extended MOF structure, and provided a detailed binding energy decomposition analysis to explain the mechanistic source of binding energy differences between alkenes and alkanes and with the variation in MOF pore size. The results indicate that C4 isomers can be separated in both IRMOF-74. C4-C4 interactions in IRMOF-74-I are stronger. Although the adsorption strength of C4 hydrocarbons on IRMOF-74-II is weaker, there is still obvious difference in adsorption energies, especially among alkenes.

Author contributions

Jay Thakkar: writing – original draft, methodology, investigation; Winters Kexi Guo: investigation; Michael J. Janik: writing – review & editing, supervision, resources; Xueyi Zhang: writing – review & editing, supervision, conceptualization.

Conflicts of interest

There are no conflicts to declare.

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