

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

Jay Thakkar,^a Winters Kexi Guo,^a Michael J. Janik^a and Xueyi Zhang ^{*a}

^aDepartment of Chemical Engineering, The Pennsylvania State University, University Park, PA
16802. *Corresponding author: xuz32@psu.edu

Electronic Supplementary Information

Table S1 Existing microporous materials for 1-butene/n-butane adsorptive separation

Material Involved	Ideal Selectivity (1-butene/n-butane)	Reference
Cu-Fe/MCM-41	2.4	Jin <i>et al.</i> ¹
ITQ-32	15	Palomino <i>et al.</i> ²
ZSM-5	1.23	Wang <i>et al.</i> ³
ZIF-7	1.38	van den Bergh <i>et al.</i> ⁴
Ag-Y	8.33	Padin <i>et al.</i> ⁵
Ag-clay	1.58-2.86	Lee <i>et al.</i> ⁶
Zeolite X	1.24	Harlfinger <i>et al.</i> ⁷

Computational details

Electronic structure method

All DFT calculations were performed using the Vienna *ab initio* Simulation Package (VASP).^[8]

The total system energy included the Perdew-Burke-Ernzerhof (PBE) exchange-correlation energy along with van der Waals vdW-DF3 dispersion corrections and Hubbard U corrections for Ni d-

states.^[8-9] A U correction value of 6.4 eV was used for Ni d-states, as this value has been shown to accurately predict the oxidation energetics of nickel oxides and is near the value (6.7 eV) determined through a self-consistent linear response approach for Ni-MOF-74.^[9,10,12] All calculations were spin polarized, and effort was taken to initialize the SCF cycle to different spins to assure a minimum spin configuration was arrived at. The projector-augmented wave approach was used with a plane wave basis set with energy cutoff of 850 eV.^[10] A $2 \times 2 \times 2$ k-points mesh was used for Brillouin-zone sampling.^[11] Structural optimization was completed with forces on all atoms less than 0.05 eV \AA^{-1} . All atoms of the MOF framework and the adsorbing gas molecules were free to move during optimizations.

Structural details

The initial structures of IRMOF-74-I were obtained from references [12] and [13]. The Ni-IRMOF-74-II structure was obtained by replacing the transition metal atom with Ni and optimizing the lattice parameters. Ni-IRMOF-74-I lattice parameters were directly obtained from reference [12]. A rhombohedral representation of the dehydrated structure containing 6 Ni atoms, one at each hexagonal corner, was utilized. Adsorption of 1-butene to Ni centers was first examined, with many conformers considered to increase the chances of locating a global minimum energy structure. The input structure for other adsorbed isomers were derived by altering the optimized 1-butene geometry. Once optimized structures were arrived at for other isomers, preferred structures were again altered (for example, by swapping H and methyl groups) to form other isomers to minimize the likelihood differences in adsorption energies arise from different sampling of possible adsorption configurations. Though we cannot guarantee all global optimum structures are located, we iteratively evaluated the adsorption of all isomers at a new geometry whenever a configuration that led to stronger binding of any isomer was located.

Binding energy calculations

Binding energies were calculated using equation 1 at monolayer coverage, i.e., each of the 6 Ni atoms in a pore is bound with a gas molecule ($1 \text{ mol}_{\text{gas}}/\text{mol}_{\text{Ni}}$).

$$\text{Binding Energy, BE} = E_{[\text{MOF} + 6 \text{ C}_4\text{isomers}]} - E_{[\text{MOF}]} - 6 * E_{[\text{C}_4]} \quad \dots (1)$$

where E_A represents the DFT energy of species A. Using this definition, the binding energies represent the energy change to adsorb 6 C_4 species to the MOF structure.

We followed a procedure similar to that used by Kim et al. to decompose the overall binding energy into a series of five individual components, as defined in equations 2-6.^[12]

$$\text{MOF Distortion, } \Delta D_{\text{MOF}} = E_{[\text{MOF} - 6 \text{ C}_4]} - E_{[\text{MOF}]} \quad \dots (2)$$

$$\text{C}_4 \text{ Distortion, } \Delta D_{\text{C}_4} = E_{[\text{C}_4 - \text{MOF}]} - E_{[\text{C}_4]} \quad \dots (3)$$

$$\text{C}_4\text{-C}_4 \text{ Interaction, } \Delta I E_{\text{C}_4\text{-C}_4} = E_{[6 \text{ C}_4 - \text{MOF}]} - 6 * E_{[\text{C}_4 - \text{MOF}]} \quad \dots (4)$$

$$\text{Dispersion, } \Delta D E = D E_{[\text{MOF} + 6 \text{ C}_4\text{isomers}]} - D E_{[\text{MOF} - 6 \text{ C}_4]} - D E_{[6 \text{ C}_4 - \text{MOF}]} \quad \dots (5)$$

$$\text{Bond+Steric, BSE} = \text{BE} - \Delta D_{\text{MOF}} - \Delta D_{\text{C}_4} - \Delta I E_{\text{C}_4\text{-C}_4} - (\Delta D E)/6 \quad \dots (6)$$

Here, $E_{[\text{MOF}+6 \text{ C}_4\text{isomers}]}$ is the combined optimized energy of MOF framework and 6 adsorbed C_4 molecules, $E_{[\text{MOF}]}$ is the optimized energy of MOF-74 prior gas adsorption, $E_{[\text{C}_4]}$ is the optimized energy of an isolated C_4 gas molecule calculated in a 2 nm cubic cell, $E_{[\text{MOF} - 6 \text{ C}_4]}$ is the single-point energy of the MOF framework in the optimized C_4 -adsorbed structure (with the 6 C_4 molecules deleted), $E_{[6 \text{ C}_4 - \text{MOF}]}$ is the single point energy of 6 C_4 molecules in their optimized

structure from adsorption to the MOF (with the MOF deleted), $DE_{[\text{MOF} + 6 \text{C}_4\text{isomers}]}$ is the combined dispersion energy of the MOF framework and 6 adsorbed C_4 molecules, $DE_{[\text{MOF} - 6 \text{C}_4]}$ is the dispersion energy from a single-point calculation of the MOF framework in the optimized structure with 6 C_4 molecules adsorbed, and $DE_{[6 \text{C}_4 - \text{MOF}]}$ is the single-point dispersion energy of 6 C_4 molecules in the optimized adsorbed structure. Ni atoms were found to be in high spin states before and after gas adsorption, and therefore, we did not include the energy contributions from changes in magnetic ordering of Ni that were included in the decomposition done by Kim et al. Our energy decomposition does not directly attempt to quantify hydrogen bonding interactions between C-H bonds and the MOF framework, as no structural indications of hydrogen bonding (elongation of C-H bonds, near-linear C-H-acceptor atom structures) were observed.

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