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Research paper

Part II: Quantum mechanical prediction of heats of adsorption for C_2-C_4 hydrocarbons in MOF-74-Mg/Zn periodic structures

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ABSTRACT

Periodic boundary condition models are used to investigate the interaction of small hydrocarbons (C_2-C_4) with MOF-74-Mg/Zn. In contrast to other studies where molecular cluster approaches are used, the complete chemical environment of the framework is included. This allows correcting the binding energies for basis-set superposition error, molecular lateral interaction, zero-point energy, and thermal contributions. As such, the presented results are directly comparable to experimental calorimetric values. This work discusses, for the first time, the origin of the fictitious agreement between binding energies obtained with molecular clusters and experimental heats of adsorption, identifying its origin as due to compensation of errors.

1. Introduction

In petroleum refining industries, olefin and paraffin molecules appear as the result of cracking processes of long-chain hydrocarbons. As the so obtained light hydrocarbons constitute a gas mixture, their separation is of paramount importance for their subsequent use in the production of plastics, polymers, waxes, etc. The separation task is currently achieved via an energetically and monetarily demanding procedure based on cryogenic distillation which, even for the simplest separations (ethylene from ethane, and propylene from propane) consumes around 120 trillion BTU per year [1] In addition, the use of highly refined separation methods able to uniquely isolate one specific chemical species over the other(s) is critical due to the strict requirements demanded by their use as raw materials. The attempt of mitigating both energy and capital consumptions for more efficient gas mixture separation applications is being pursued by alternative cost-effective procedures [2] Chemisorption, physisorption, and extractive distillation are among those that have attracted the most of the attention [1]

Among the alternative methods explored, selective sorption achieved by porous materials is considered to be the most promising. At first, experimental [3–5] and theoretical/computational [6] efforts were devoted to molecular sieve materials such as zeolites. In that context, a relatively new class of porous materials, metal-organic frameworks (MOFs), soon emerged as a possible alternative, receiving considerable attention over zeolites for the adsorptive separation of alkane/alkene gas mixtures [7–10]

MOFs are porous materials formed by inorganic bricks joined by organic ligands where, in some cases, partially coordinated metal atoms act as open sites for guest molecules to be adsorbed. It is known that MOFs exhibit very interesting properties for various potential applications. In fact, several MOF structures exhibit greater porosity [11] higher sorption capability and higher surface area [12] than have ever been observed in any other synthesized crystalline porous materials [13–15] Such features have made MOFs ideal candidates for a wide range of potential applications: heterogeneous catalysis [16], gas sensing [17], drug delivery [18], light gas molecules separations [19], and fuel gas storage [20]. MOFs with high density of open metal sites such as MOF-74 (also known as CPO-27) have shown a significant separation potential beyond that of other MOFs and zeolites so far investigated [8]. Structurally, MOF-74 consists of 3D hexagonal packing frameworks of helical MO_5 chains (*i.e.*, metal atom (M) not fully coordinated) connected by 2,5-dihydroxyterephthalte organic linkers (Fig. S1).

In the last decade, several computational studies have been devoted to the investigation of capturing and storage of common small gas molecules (CO, CO_2, NO, NO_2, H_2O, etc.) at the open metal sites in MOF-74-M isostructural frameworks (M = Mg, Zn, Fe, Ni,

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Co, Cu, Mn, Ti, V, and Cr) [21,20,22,23]. Several experimental investigations appearing in the last few years on the interaction of larger molecules such as light hydrocarbons with MOF-74-Mg/Co/Fe/Ni [24–27], have revealed interesting properties requiring an explanation at the electronic structure level. In this regard, MOF-74-Fe showing a differential binding energy between saturated and unsaturated hydrocarbons of ~20 kJ/mol was identified as having an appreciable potential in efficiently separating the components of light hydrocarbon mixtures [28,29].

The contribution that accurate computational investigations can provide on novel materials is to assess in detail and eventually provide guidance in enhancing the properties of already available frameworks, as well as supporting the *ad hoc* design of new, more efficient, and potentially *smart* materials. In this regard, the rigorous characterization and the understanding of the structural and binding nature of guest molecules with respect to the open metal sites, and the assessment of the different behavior of the various metal cations allow for revealing the potential on the performances of the chosen frameworks toward separation applications. In addition, acquiring knowledge about the nature of the chemistry of the host-guest complex can suggest possible structural functionalizations able to enhance (or quench) specific adsorption requirements.

Although being simpler and computationally less demanding, the use of molecular cluster models to assess light hydrocarbon separation encounters the risk of not always providing an accurate and realistic description of the interaction of the molecules at the open metal centers. In a previous recent work [30], we have discussed the influence that the chemical environment of the framework has on the assessment of molecular binding energies, indicating how a minimal cluster model was not able to properly describe the intermolecular interaction of larger hydrocarbons with the open metal sites. The outcome of that assessment was quite dramatic, indicating differences in the binding energies as large as 12 kJ/mol per metal site. As a further step, in this present work, density functional theory (DFT) is applied to full 3D periodic structures of MOF-74-Mg and MOF-74-Zn in order to investigate the role that basis set superposition error (BSSE) [31], zero-point energy (ZPE), and thermal corrections have in contributing to the accurate calculation of binding energy results that can then be used in determining heats of adsorption. These calculated heats of adsorption are then directly comparable with experimental results. In addition, the role of the molecular lateral interaction is also addressed.

This work therefore addresses at a fundamental level the effect that the chemical environment of the frameworks, the several physicochemical contributions (*i.e.*, lateral interaction, ZPE, and thermal corrections) and the inevitable corrections arising from the application of theoretical approximations (*i.e.*, from the semi-empirical treatment of dispersion forces to BSSE) have on the structure and on the binding nature of C_2-C_4 molecules adsorbed in MOF-74 treated as 3D periodic structures. The intent of this investigation is to provide an accurate and refined description of the proposed problem with the results being directly comparable with experimental data. In addition, this work aims at providing a better understanding of the efficiencies that MOF-74-Mg/Zn can have for the separation of C_2-C_4 mixtures in petroleum refining processes.

2. Theoretical and computational details

Linear combination of atomic orbital (LCAO, all-electron Gaussian-type basis sets) DFT calculations were performed with the Crystal14 code [32,33]. The hybrid-GGA B3LYP [28,34] functional *a posteriori* corrected with a semi-empirical contribution able to account for the long range $1/r^6$ dispersion term was employed [35] where the original Grimme parametrization for the molecular species was modified to include the effect of periodic boundary conditions as implemented in the Crystal program [36]. The motivation for choosing these theoretical approaches lays in their efficiency, and capability of providing reliable quantitative information about the nature of the long range interactions characterizing the addressed problem. The adopted values for the modified atomic parameters are listed in the ESI (Table S1). Following previous works [21,30,37], TZV and TZVP basis sets were chosen for Zn and Mg atoms, respectively. For H, C, and O, the standard Ahlrichs TZP basis sets were adopted [38]. Throughout all the calculations, the numerical integration task was achieved by applying an XLGRID pruned-grid [32].

Full 3D periodic boundary condition (PBC) dynamic geometry relaxations (*i.e.*, simultaneous relaxation of both lattice parameters, and atomic positions) were performed on the 3D bulk structures of MOF-74-Mg/Zn starting from the experimentally refined geometry of MOF-74-Mg for both the systems [39]. After full geometry relaxation, vibrational frequency calculations were performed to ensure the stability of the solutions, and to account for the zero-point, and thermal energy contributions, which then allow for correcting the binding energies to provide heats of adsorption. SCF convergence thresholds were set to 10^{-8} and 10^{-10} Hartrees for geometry optimization and vibrational frequency calculations, respectively. The Monkhorst-Pack [40] shrinking factors for the reciprocal space sampling were set to 2 corresponding to four k-points in the reciprocal space.

The energetic interaction between the adsorbed molecule and the open metal sites in the MOFs was obtained by applying Hess's law

$$\Delta E = (E_{MOF+Mol} - (E_{MOF} + nE_{Mol}))/n \qquad (1)$$

where $E_{MOF+Mol}$ is the calculated total energy of the MOF and adsorbed molecule system, E_{MOF} is the calculated total energy of the MOF, E_{mol} is the calculated total energy of the adsorbed molecule in the gas phase, and n (=1, 3, and 6) indicates the number of molecules adsorbed within the framework. We shall refer to the different molecular loadings as low (1 molecule), medium (3 molecules), and high (6 molecules).

Binding energies are corrected for basis set superposition error (BSSE) using the counterpoise correction method [31]. Vibrational frequency calculations were performed at the Γ point, and normal modes were determined from mass-weighed Hessian matrix derivatives [41]. The zero-point vibrational energy E_{ZPV} and the thermal contribution to the enthalpy $H(T)$ at a given temperature T and standard pressure P^0 were calculated for molecules in the gas phase as:

$$H^0(T) = E_{trans}(T) + E_{rot}(T) + E_{vib}(T) + RT \qquad (2)$$

where E_{trans}, E_{rot}, and E_{vib} are the translational, rotational, and vibrational contributions respectively, while RT is the correction arising from the P^0V term (*i.e.*, ideal gas approximation). The corresponding value for T was taken to be 298.15 K. For the pure bulk with or without an adsorbed molecule

$$H^0(T) = E_{vib} \qquad (3)$$

and the enthalpy of adsorption at the given temperature T was calculated as:

$$H^0_T = \Delta E + E_{ZPV} + H^0(T) \qquad (4)$$

which can be directly compared to the heat of adsorption observed experimentally:

$$Q_{ads}(T) = -H^0_T \qquad (5)$$