Propane/propylene separation in ion-exchanged zeolite-like metal organic frameworks

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ABSTRACT

Propane/propylene separation performances of zeolite-like metal organic frameworks with rhombic and sodalite topologies (*rho-* and *sod-*ZMOFs) were estimated via Monte Carlo simulations over a wide range of pressure in order to evaluate their potential use in pressure swing adsorption applications. Extra-framework cation locations of the "as-synthesized" ZMOFs were identified based on the available experimental data. Selectivities and working capacities before and after the ion exchange of ZMOFs with Li^+, Na^+, and K^+ ions were compared, by considering partially and completely ion-exchanged structures. Results showed that the difference in the dipole moments of propane and propylene is the dominant factor in separation and ion-exchanging enhances the propylene selectivity of ZMOFs. The enhancement is especially significant in *sod-*ZMOF structures for which a ten-fold increase in the selectivities was obtained, although their working capacities remained lower than those of *rho-*ZMOF structures.

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1. Introduction

Propylene is one of the most commercialized petrochemical products in the world nowadays, and polypropylene (PP), isopropyl alcohol, propylene oxide, acrylonitrile, cumene, phenol, oxo-alcohols are the commercial derivatives. The products of the fluid catalytic cracking (FCC) of petroleum hydrocarbons are gasoline, dry gas, decanted oil, coke and liquefied petroleum gas (LPG) in which light olefins are dominant. In the United States 4.9×10^6 barrels per day of feedstock were processed in the FCC units [1]. Dehydrogenation of propane is another propylene production method where the unique product is propylene. Since propylene produced via FCC is not pure enough and the conversion of propane to propylene in dehydrogenation reaction is not ideal the separation of propylene from its paraffin form, propane, is required. However, propane/propylene separation is still a challenging problem due to their similar physico-chemical properties, such as boiling points, kinetic radii, polarizabilities, as summarized in Table 1. The conventional method used widely is cryogenic distillation. Because of the close relative volatilities of propane and propylene ($T_{b,propane}$ = -47.6 °C and $T_{b,propylene}$ = -42.1 °C), cryogenic distillation process is energy intensive and expensive. Therefore, extensive studies have been carried out to develop new energy-efficient methods, such as adsorptive separation, which, unlike cryogenic distillation, does not require high energy demand since no phase change occurs during separation. An attractive adsorption-based process is the Pressure Swing Adsorption (PSA), in which gas separation takes place at high pressures via solid adsorbents and the process then swings to lower pressures to regenerate the adsorbents.

The performances of adsorption processes depend significantly on the choice of solid adsorbents. Conventional solid adsorbents such as Zeolite 13X [3] or ITQ-12 [4], lack adsorption selectivity. Therefore, the need for enhanced gas separation beyond that obtained via zeolites in which the gas separation is based on the molecular sieving, is targeting to develop novel adsorbents. Newly developed solid adsorbents, metal organic frameworks (MOFs), can be good candidate in propane/propylene separation due to their higher surface area, tunable pore structures, and favorable host–guest interactions. Lamia et al. [5] studied experimentally the adsorption of propane and propylene gases on CuBTC and predicted the preferential adsorption sites via Molecular simulation methods. Their simulated and experimental results were slightly different at high pressures due to the difficulties of obtaining true equilibrium because of the slow transport of gas molecules. Jorge et al. [6] continued the study of Lamia et al. [5] and they calculated the adsorption isotherms of binary propane/propylene gas mixtures in CuBTC. Rubes et al. [7] also studied theoretically and experimentally the adsorption of propane and propylene in CuBTC. They concluded that at high loading the heat of adsorption for propane was higher than that for propylene, thus Cu-BTC was not a good candidate for propane/propylene adsorptive separation.

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Table 1
Physical properties of propane and propylene [2].

	C_3H_8	C_3H_6
Kinetic diameter [Å]	4.3–5.118	4.678
Polarizability [10^{25}/cm^3]	62.9–63.7	62.6
Dipole moment [10^{18}/esu cm]	0.084	0.366
Boiling point (°C)	−47.6	−42.1

Studies showed that the metal center in MOFs has a key importance in gas separation processes [8,9]. The effect of the metal center of MOFs on propane/propylene separation was investigated by Geier et al. [8]. They performed experimental propane/propylene separation studies at different temperatures by using M_2(dobdc)-type MOFs, where M signifies different metal centers. They concluded that the Mn_2(dobdc) showed the highest propane/propylene separation performance among other M_2(dobdc) MOFs. Similarly, Bae et al. [9] investigated adsorptive propane/propylene selectivity in MOF-74 frameworks with different metal centers, Co, Mn, and Mg. Their results revealed that Co-MOF-74 had the highest selectivity of propylene over propane.

He et al. [10] performed studies in order to calculate the performance of some MOFs in PSA processes for separation of equimolar propane/propylene gas mixtures. They evaluated 19 different microporous MOFs (MMOFs) as adsorbent and concluded that MMOF-74 (M = Fe, Co, Mg) showed relatively higher C_3H_6 productivities in PSA adsorber than NaX and FeMIL-100.

Zeolitic Imidazolate Frameworks (ZIFs) have also been studied as alternative solid adsorbents. Two ZIF materials having sodalite topology, ZIF-8 and ZIF-7 were evaluated for adsorptive alkane/alkene separation [11,12] and were reported to have propylene selectivities slightly over than unity. On the other hand, Pan et al. [13] and Kwon et al. [14] showed that ZIF-8 may exhibit high propylene separation performance when used as membrane materials.

A subclass of MOFs, zeolite-like metal organic frameworks (ZMOFs), have anionic structures and extraframework cations compensating charge neutrality. Particularly, ZMOFs with rhombic and sodalite topology, *rho*- and *sod*-ZMOFs [15], respectively, may exhibit customized gas separation performances due to their ion exchanging capabilities. They are also stable in the presence of water. Our previous study on CO_2/CH_4 separation capabilities of *sod*-ZMOFs showed that host–guest electrostatic interactions dominate the separation performance of these materials [16]. Hence, ZMOFs may be potential candidates to separate gas pairs, such as propane and propylene, which have similar physico-chemical properties but different electrostatic charge distributions.

In this study we focused on the propane/propylene adsorptive separation properties of ZMOFs via molecular simulation methods. The adsorption capacities of pure propane/propylene and mixed gas for "as-synthesized", partially and completely ion-exchanged *rho*- and *sod*-ZMOFs were calculated via Grand Canonical Monte Carlo (GCMC) simulation method. Working capacity, which is the key parameter in PSA process, was evaluated for each structure. The effects of the cation type and ion-exchange ratio were determined on the propane/propylene separation.

2. Model and simulation method

ZMOFs are constituted of Indium (In) metal centers and four imidazoledicarboxylic acid connected to an indium (In) atom as ligands. Six-coordinated In atoms of the framework are connected to four nitrogen and two oxygen atoms forming the six-coordinated molecular building block in *sod*-ZMOFs having sodalite topology with a cubic unit cell of dimension of 36.045 Å. In

atoms in *rho*-ZMOFs of cubic geometry with dimensions of 31.062 Å are connected to four nitrogen and four oxygen atoms, forming eight-coordinated molecular building block. The "as-synthesized" *sod*- and *rho*-ZMOFs contain 96 and 48 imidazolium (Im$^+$) cations, respectively, for charge compensation of the anionic framework.

The *sod*- and *rho*-ZMOF crystal structures were taken from Cambridge Structural Database (CSD) [17] and refined. The atomic partial charges of the *sod*-ZMOF were reported in our previous study [16]. The same procedure was followed to calculate the framework charges of *rho*-ZMOF and the charges were reported in Fig. S1.

The extraframework cations, Im$^+$, Li$^+$, Na$^+$, and K$^+$ ions were located via Monte Carlo (MC) optimization using the *Locate* task of the *Sorption* module of Materials Studio 5.0 (Accelrys, San Diego, CA) simulation package. The Universal Force Field (UFF) [18] was used at this step. According to the procedure, the temperature was increased up to 1×10^6 K in order to enable the access of cations to the cages, which are inaccessible at low temperatures due to the steric hindrance. The final structure having the lowest energy selected among 10 configurations generated after 12×10^6 Monte Carlo steps was then relaxed to 303 K. During the MC simulations the positions of the framework atoms were kept fixed.

The united atom propane and propylene models used in this study were taken from Dubbeldam et al. [19] and Sevillano et al. [4], respectively. While the propane model was uncharged, a charged dummy atom (D) was placed between the C1 and C2 atoms of the propylene molecule in order to reproduce the experimental dipole moment value. The D–C1 bond length was set to 0.704 Å, while the bond length between C1 and C2 atoms was 1.74 Å. The LJ parameters and partial electrostatic charges are reported in Table 2.

The experimentally reported ion-exchange ratios in *rho*-ZMOF [20] are 70%, 84% and 80% for Li$^+$, Na$^+$ and K$^+$, which correspond to 34 Li$^+$, 40 Na$^+$ and 38 K$^+$ cations, respectively. Moreover, 26 Li$^+$, 21 Na$^+$, and 27 K$^+$ cations correspond to 27%, 22%, 28% for Li$^+$, Na$^+$ and K$^+$ ion-exchanged *sod*-ZMOF, respectively [21]. Completely ion-exchanged structures were also investigated for propane/propylene separation. Due to the lack of the experimental propane/propylene adsorption isotherms on *sod*- and *rho*-ZMOFs, the force-field was validated by comparing the calculated CO_2 adsorption isotherms to the experimental data available in the literature [20]. Next, the validated structures were used for propane/propylene separation simulations. The validation of the structures is important because the adsorption capacity and gas separation performance of ZMOFs depend on the cation location as well as on the cation type, as reported in our recently published study [16].

Pairwise additive models were used for the van der Waals and electrostatic interactions among the gas molecules, ZMOF framework and extraframework cations. The 12–6 Lennard Jones (LJ) parameters for CO_2, extraframework cations and ZMOFs were taken from UFF. CO_2 molecule was modeled as rigid linear molecule with the partial atomic charges $q_O = -0.8$ and $q_C = 0.4$ and the C–O bond length was 1.196 Å [22]. The Lorentz–Berthelot mixing rule was implemented for unlike atom interactions. The cut-off distance, the half-length of one side of the cubic unit cells

Table 2
LJ parameters and partial charges of propane and propylene molecules.

	σ (Å)	ε/k_B (K)	q (e)	Refs.
D (dummy atom)	–	–	−1.74	[4]
C1	3.685	93	0.87	[4]
C2	4.000	51	0.87	[18]
C3	3.760	108	–	[18]
C4	3.960	56	–	[18]