



# A pillar-layer metal-organic framework for efficient adsorption separation of propylene over propane

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## ABSTRACT

Developing energy-effective alternatives for olefin/paraffin separations have been regarded as one of the most challenging separations in the petrochemical industry. In this work, a zinc-based pillar-layer metal-organic framework  $[\text{Zn}_2(5\text{-aip})_2(\text{bpy})](\text{DMF})(\text{H}_2\text{O})_2$  (**1**) is reported as a high-performance adsorbent for highly efficient separation of  $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$  mixture. The structure and properties of **1** are confirmed by various characterization techniques. Then its adsorption and separation behaviors of  $\text{C}_3\text{H}_6$  and  $\text{C}_3\text{H}_8$  are systematically investigated. Although **1** has  $\text{C}_3\text{H}_6$  adsorption capacity of 1.91 mmol/g at 100 kPa and 298 K, it exhibits preferential adsorption of  $\text{C}_3\text{H}_6$  over  $\text{C}_3\text{H}_8$  with high  $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$  adsorption selectivity up to 19.8, outperforming most widely investigated MOFs. Furthermore, breakthrough experiments demonstrate that efficient separation of  $\text{C}_3\text{H}_6$  over  $\text{C}_3\text{H}_8$  on **1** can be achieved, revealing its outstanding separation performance under dynamic conditions. In particular, this material not only can be readily regenerated at 423 K within 20 min, but also exhibits good recyclability during five consecutive adsorption-desorption cycles. Thus, such advantages as high  $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$  adsorption selectivity, easy regeneration and excellent recyclability make the pillar-layer **1** promising in practical application of  $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$  separation.

## 1. Introduction

Olefins including ethylene ( $\text{C}_2\text{H}_4$ ) and propylene ( $\text{C}_3\text{H}_6$ ) are primarily feedstocks for the manufacture of various high-value chemical products, particularly for synthetic polymers [1–6]. During the production of olefins, their saturated paraffinic counterparts of ethane ( $\text{C}_2\text{H}_6$ ) and propane ( $\text{C}_3\text{H}_8$ ) are also along with produced, leading to the olefin/paraffin mixtures [7–11]. Thus, a prerequisite separation of olefin/paraffin mixtures is inevitably required to isolate corresponding pure components from the mixtures before their following utilization [12,13]. Considering their close molecular sizes and boiling points [14,15], such as  $\text{C}_3\text{H}_6$  (kinetic diameter 4.678 Å, bp 225.46 K) and  $\text{C}_3\text{H}_8$  (kinetic diameter 4.3–5.118 Å, bp 231.02 K), olefin/paraffin separations are still commonly performed by cryogenic distillation to date, which is an energy-intensive process and accounts for over 0.3% of the global energy consumption [16]. For example, current  $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$  separation relying on cryogenic distillation is typically performed at 243 K and 30 bar to obtain high purity  $\text{C}_3\text{H}_6$  [17]. Adsorption separation is disclosed as a promising alternative that could save substantial energy, since its operation conditions can be performed at room temperature. Generally, its key closely depends on the development of new

adsorbent materials with highly efficient separation performance [18,19]. Therefore, increasing efforts have been made to explore the potential of porous materials for facilitating industrial olefin/paraffin separations [20,21].

Recently, metal-organic frameworks (MOFs), as a class of adjustable porous crystalline materials, have received considerable attention, since they can offer great opportunities for diverse applications, especially in separation and purification of gases [22–26]. Featuring properties of uniform and well-defined pore structures, ultrahigh and extraordinary porosity, controllable and tunable functionalities [27,28], these unparalleled properties have made MOFs promising candidates for high-performance separation of olefin/paraffin mixtures [29–31]. Until now, with regard to olefin/paraffin separations, especially in  $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$  separation, these efficient adsorption separations commonly follow the four mechanisms: kinetic, steric, gate-opening or equilibrium mechanisms [21], determining from the properties of the adsorbents [32]. For kinetic separation, Li and co-workers firstly reported that ZIF-8 has the capability of kinetic separation of  $\text{C}_3\text{H}_6$  and  $\text{C}_3\text{H}_8$  by utilizing the remarkable differences in their diffusion rates [33]. Steric separation, also known as molecular size exclusion or sieving effect, is based on the precise control of the pore aperture size within MOFs. It has been well

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elucidated by the fluorinated KAUST-7 in which  $C_3H_6$  molecules can be adsorbed into the pores while the larger  $C_3H_8$  molecules are blocked [2]. In terms of gate-opening mechanism that typically occurs for flexible MOFs associated with structural transitions, our group recently reported the case of flexible CPL-1 for the separation of  $C_3H_6$  over  $C_3H_8$  through an unique gate opening adsorption behavior for  $C_3H_6$  but not for  $C_3H_8$  under the same conditions [15]. Currently, the development of equilibrium separation  $C_3H_6/C_3H_8$  mixture is the most common and effective method within MOFs among the four mechanisms [21].

For equilibrium separation, it is mainly achieved by the specific interactions between the  $\pi$ -bonding orbital in olefin molecules with the vacant s-orbital of the unsaturated metal sites [15,21], such as MIL-100(Fe) [18,34], Cu-BTC [35], the series of MOF-74 materials [17,36–38]. For example, Long's group has systematically investigated the series of MOF-74 materials for separating  $C_3H_6/C_3H_8$  mixture. MOF-74 materials show preferential  $C_3H_6$  over  $C_3H_8$  owing to their high density of unsaturated metal sites, which could selectively interact with  $C_3H_6$  molecules to form stronger interaction compared with those of  $C_3H_8$  [36]. Among other M-MOF-74 materials, Mn-MOF-74 has the highest  $C_3H_6/C_3H_8$  selectivity of 16.6. Very recently, Bae et al. [18] reported that the uptakes of  $C_3H_6$  and  $C_3H_8$  in MIL-100(Fe) are 4.6 and 3.9 mmol/g at 323 K and 100 kPa, and the IAST selectivity for equimolar  $C_3H_6/C_3H_8$  mixture is still below 5 at 100 kPa, despite the partial reduction of coordinatively unsaturated Fe(III) in MIL-100(Fe) frameworks to Fe(II) by activating at 523 K. To date, most reports on the adsorption selectivity of  $C_3H_6/C_3H_8$  are still quite low and cannot satisfy the demand of efficient separation. Thus, it is challenging yet highly urgent to further explore the high-performance MOFs adsorbents with high adsorption selectivity of  $C_3H_6/C_3H_8$  to achieve the target of efficient separation.

For these purposes, we reported a zinc-based MOF, **1**, with the formula of  $[Zn_2(5\text{-aip})_2(\text{bpy})]\cdot(\text{DMF})\cdot(\text{H}_2\text{O})_2$  (5-aip, aminoisophthalic acid; bpy, 4,4'-bipyridine), having moderate  $C_3H_6$  uptake and satisfactory adsorption selectivity of  $C_3H_6/C_3H_8$ . **1** is constructed with two-dimensional layer composed of Zn(II) metal center and 5-aip, in which further connected by an  $N,N'$ -donor linker bpy acting as a pillar linker to form the pillar-layer MOF with one-dimensional channels of dimension  $\sim 5.9 \times 8.1 \text{ \AA}^2$ . Neogi and co-workers firstly reported **1** for  $\text{CO}_2$  capture with excellent moisture stability under humid conditions [39]. Apart from its superior moisture and thermal stability, **1** also has proper aperture size and unsaturated metal site of Zn(II) center, making it a commendable candidate for  $C_3H_6/C_3H_8$  separation. Moreover, the adsorption selectivity of  $C_3H_6/C_3H_8$  is among the highest for MOFs materials to date. In this work, highly efficient separation of  $C_3H_6/C_3H_8$  mixture was well achieved by exploiting the equilibrium mechanism in **1** at room temperature, demonstrating it a promising alternative for industrial  $C_3H_6/C_3H_8$  separation.

## 2. Experimental

### 2.1. Materials

Zinc nitrate hexahydrate  $[Zn(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}]$  (99%) was purchased from Guangzhou Chemicals Co. Ltd. The organic ligands 5-aminoisophthalic acid (5-aip, 98%) and 4,4'-bipyridine (bpy, 98%) were obtained from Aladdin.  $N,N$ -dimethylformamide (DMF, 99.5%) and ethanol (EtOH, 99.7%) were got from Guangdong Guanghua Sci-Tech Co. Ltd.

### 2.2. Synthesis of $[Zn_2(5\text{-aip})_2(\text{bpy})]\cdot(\text{DMF})\cdot(\text{H}_2\text{O})_2$ (**1**)

**1** was synthesized according to the previous literature [39]. Typically,  $Zn(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$  (44 mg, 0.148 mmol), 5-aip (13.4 mg, 0.074 mmol), and bpy (11.6 mg, 0.074 mmol) were dissolved in a DMF/ $\text{H}_2\text{O}$  mixture (8 mL, 3:1, v/v) in a 20 mL Pyrex vial. The resulting mixture was sonicated for 5 min and then heated at 90 °C for 72 h to

obtain the as-synthesized **1**. The resulting powder was collected by filtration, rinsed with EtOH, and then immersed in 20 mL of EtOH for 3 days at 60 °C to replace lattice guest molecules. The supernatant solution was decanted, and 20 mL of fresh EtOH were added, during which this process was repeated six times. Finally, the resulting activated powder was collected by filtration and heated at 150 °C under dynamic vacuum for 6 h.

### 2.3. Characterizations

Powder X-ray diffraction (PXRD) patterns were recorded with a Bruker D8 Advance X-ray diffractometer operating at 40 kV and 40 mA, using Cu K $\alpha$  radiation in the range of  $2\theta = 5\text{--}40^\circ$  in  $0.02^\circ$  steps at a scan speed of  $0.02^\circ/\text{s}$ . Scanning electron microscopy (SEM) images were taken on a Hitachi SU8220 instrument. Before the measurement, the powder was sputter-coated with a thin layer of gold. Thermogravimetric analysis (TGA) was performed under  $\text{N}_2$  atmosphere and heated from room temperature to 700 °C at a heating rate of  $10^\circ\text{C}/\text{min}$  using a Netzsch TG 209F3 instrument.

### 2.4. Adsorption experiments

$C_3H_6$  and  $C_3H_8$  adsorption experiments were measured with a 3Flex Surface Characterization Analyzer (Micromeritics, USA) at 278, 288 and 298 K. The temperature was precisely controlled by a water bath in which the sample tube was immersed. Prior to each measurement, 80–100 mg of activated **1** sample was evacuated at 423 K for 6 h to remove the guest molecules. The gas adsorption isotherm was obtained as a function of pressure up to 100 kPa. Ultrahigh purity grade  $C_3H_6$  (99.99%) and  $C_3H_8$  (99.99%) were used throughout the adsorption measurements.

### 2.5. Breakthrough experiments

Breakthrough experiments of  $C_3H_6/C_3H_8$  mixture was performed using a custom-built breakthrough apparatus at 298 K, as presented in Fig. S1. Prior to the dynamic separation experiment, 200 mg of activated **1** sample was heated at 423 K for 60 min under vacuum and then packed into a stainless steel column with a length of 280.0 mm and an inner diameter of 4.0 mm, in which the void space of the two ends was filled by glass wool. Then the stainless steel column packed into **1** sample was purged under a flow of He gas (20 mL/min) for 60 min. Afterward, a premixed  $C_3H_6/C_3H_8$  (50:50, v/v) mixture was attached to a mass flow controller for the control of gas flow, with a total flow at 2 mL/min. The composition of effluent through the packed bed at the outlet was monitored by a gas chromatography (GC-9560, Shanghai Wuhao, China) with a flame ionization detector (FID). Finally, dynamic separation performance of **1** sample was verified by the breakthrough curves of  $C_3H_6/C_3H_8$  binary mixture.

## 3. Results and discussion

### 3.1. Characterization of **1**

The phase purity and crystallinity of **1** with pillar-layer framework are determined by PXRD analysis. As illustrated in Fig. 1, the experimental PXRD patterns of both as-synthesized and activated samples are in good agreement with the simulated pattern from the single-crystal structure **1** [39], indicating that well-defined crystal structure of **1** is successfully synthesized with high purity. Meanwhile, it is noted that the resulting activated product retains its crystallinity and structural integrity upon solvent-exchange treatment, as assessed by the comparison of PXRD patterns.

SEM images are collected for activated **1** to determine its crystal morphology. As shown in Fig. 2, the SEM images unambiguously demonstrate that the crystals of **1** have a relatively uniform lamellate

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