



Kinetic separation of propylene over propane in a microporous metal-organic framework

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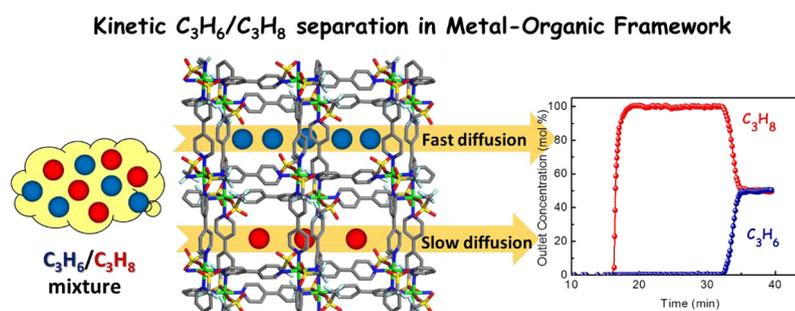
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HIGHLIGHTS

- C₃H₆/C₃H₈ mixture could be efficient separated by a microporous MOF ELM-12 via kinetic effect.
- ELM-12 exhibits faster C₃H₆ adsorption over C₃H₈ via diffusion controlled process with high kinetic C₃H₆/C₃H₈ selectivity.
- Large breakthrough time interval and fast regeneration process could be achieved in the breakthrough experiments.
- Feasible scale-up production and highly stable structure under ambient condition make this MOF practically useful.

GRAPHICAL ABSTRACT



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ABSTRACT

Propylene (C₃H₆)/propane (C₃H₈) separation is one of the most challenging as well as most energy-intensive separation processes in the petrochemical industry. Herein we report a microporous metal-organic framework ELM-12 with appropriate channels where efficient separation of C₃H₆ over C₃H₈ is achieved via the kinetic separation effect. Time-dependent kinetic adsorption, density-functional theory calculation and breakthrough experiments collaboratively demonstrate that the considerable diffusivity difference between C₃H₆ and C₃H₈ accounts for the excellent separation performance of ELM-12. The high kinetic C₃H₆/C₃H₈ separation factor (204 at 298 K), large breakthrough time interval, and easy regeneration process of this MOF, make it a promising adsorbent for this important separation task. Furthermore, this material is highly stable under ambient condition and its production can be easily scaled up, rendering it quite favorable for practical industrial application.

1. Introduction

Propylene (C₃H₆) is a major olefin raw material for petrochemical production, with a worldwide production exceeding 120 million metric tons in 2016, and its demand growth rate is over 6% per year in the past

five years. C₃H₆/C₃H₈ separation is one of the most challenging process during the C₃H₆ production, because of their very close boiling points and similar kinetic diameters [1,2]. Currently, the purification of C₃H₆ is accomplished by cryogenic distillation under harsh conditions using huge splitter column of over 100 trays [3], which is an intrinsically

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difficult and energy-intensive process due to the small difference in their condensabilities of the two components. And it is of critical importance to develop alternative, non-thermal and economically feasible technologies for C_3H_6/C_3H_8 separation.

For this purpose, adsorptive separation techniques based on porous materials have attracted extensive interest, and are believed to be very promising for substituting the traditional distillation processes due to potential tremendous energy savings [4–10]. Recent studies for adsorptive separation can be roughly categorized into three types: equilibrium separation, steric separation (molecule sieving), and kinetic separation [11]. In equilibrium separation, the separation is based on the thermodynamic affinities between different gas molecules and adsorbents [12–19]. By utilizing the π -complexation interactions, some MOFs with open metal sites (OMS) can selectively adsorb C_3H_6 over C_3H_8 on their OMS [20–24]. However, the unavoidable strong interactions between C_3H_6 and MOFs may lead to a high energy consumption in order to recover C_3H_6 from the adsorbent. In addition, some undesired olefin polymerization will occur on the OMS when applying heat to accelerate the adsorbent regeneration [25,26]. To utilize the sieving effect for C_3H_6/C_3H_8 separation, suitable porosity and channels of the adsorbent should be precisely controlled. However, considering the very similar shape of C_3H_6 and C_3H_8 , this task is particularly challenging. So far, Eddaoudi et al. reported the only MOF that can discriminatorily adsorb C_3H_6 via the molecule sieving effect [27]. This ultra-microporous MOF (KAUST-7) exhibits unexpectedly molecular exclusion of C_3H_6 from C_3H_8 at standard ambient temperature and pressure. However, the strong restriction of the pore channels might cause some problems associated with diffusion and regeneration [28]. For example, C_3H_6 adsorption is not fully reversible in NaA zeolites [29], which affects the recovery of the adsorbent and olefin products.

In 2009, Li et al. reported the first study illustrating kinetic C_3H_6/C_3H_8 separation on ZIF-8 and its derivatives to overcome this challenge [30]. Compared with equilibrium or steric separation, such non-equilibrium separation is more energy-efficient, in which the regeneration process can be remarkably accelerated due to the absence of strong interactions for gas molecules. After that, extensive endeavors have been put forward to MOFs for kinetic C_3H_6/C_3H_8 separation, but very few examples have been reported [31]. Very recently, Li and Eddaoudi groups evaluated several MOFs possessing good kinetic selectivities that can be utilized for C_3H_6/C_3H_8 separation [32,33]. Additionally, besides high kinetic selectivity, the ideal adsorbent materials for industrial application should also possess other favorable properties, in terms of the gas mixture separation performance, structural stability, regeneration, and scale-up of production etc.

In this work, a microporous MOFs ELM-12 with excellent kinetic selectivity was explored for separation of C_3H_6/C_3H_8 mixtures via kinetic separation effect. This MOF material has optimal channels (Fig. 1) exhibiting a remarkable diffusivity difference of C_3H_6 and C_3H_8 , and can also be easily regenerated and synthesized in large-scale.

2. Experimental

2.1. Synthesis of materials

The synthesis of ELM-12 crystals was based on a reported method [34,35] with some modifications. An ethanol solution of 4,4'-bipy (4,4'-bipyridine) (10.0 mmol/L, 10.0 mL) was carefully dropped onto an aqueous solution (10 mL) of $Cu(OTf)_2$ ($OTf^- =$ trifluoromethanesulfonate) (5 mmol/L) in a 50 mL beaker with no stirring. After that, the beaker was placed at room temperature (298 K), and blue crystals of $[Cu(bipy)_2(OTf)_2] \cdot 2EtOH \cdot H_2O$ were obtained in 5 to 7 days. The resultant crystals were filtered, washed thoroughly with H_2O /ethanol (1/1 v/v) solution, and dried in air, with a yield of $\sim 82\%$ based on 4,4'-bipy. The crystals were evacuated to 10^{-6} bar at 393 K until no further weight loss was observed to give $[Cu(bipy)_2(OTf)_2]$ (ELM-12) as a guest free structure.

Large-scale synthesis of ELM-12 was carried out as follows: Powder sample was obtained by slowly mixing an aqueous solution (5.0 L) of $Cu(OTf)_2$ (750 mmol, 275 g) with an ethanol solution (5.0 L) of 4,4'-bipy (1500 mmol, 234 g) in a glass tank (20 L), and the mixing process lasted for about one hour. Blue powder precipitate formed immediately, and the reaction got completely finished within a few hours at room temperature. The sample was then filtered, washed with H_2O /ethanol (1/1 v/v) solution, and dried under vacuum at 393 K, with a yield of ~ 421 g $[Cu(bipy)_2(OTf)_2]$ (ELM-12).

The synthesis of ELM-22 was based on a reported method [36] with some modifications as follows: An acetonitrile solution of 4,4'-bipy (20.0 mmol/L, 5 mL) was carefully layered onto an acetonitrile solution (5 mL) of $Co(OTf)_2$ (10 mmol/L) in a 20 mL vial with no stirring. After that, the vial was placed at room temperature (298 K). After three weeks, orange powder of $Co(bipy)_2(OTf)_2$ (ELM-22) was obtained, which was then collected by filtration, and washed with acetonitrile three times.

All chemical reagents and solvents were commercially available, and used without further purification.

2.2. Characterizations

Powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku Smartlab3 powder X-ray diffractometer equipped with a copper-sealed tube ($\lambda = 1.54178 \text{ \AA}$) at room temperature. SEM images were obtained using a Hitachi SU8010 scanning electron microscope.

2.3. Kinetic and equilibrium adsorption measurement

Kinetic and equilibrium adsorption were measured with the Intelligent Gravimetric Analyzer (IGA001, Hiden, UK), which uses a gravimetric technique to accurately measure the gas sorption on materials under diverse operating conditions. For each test, about 50 mg of MOF sample was loaded into the sample cell, then the system was out-

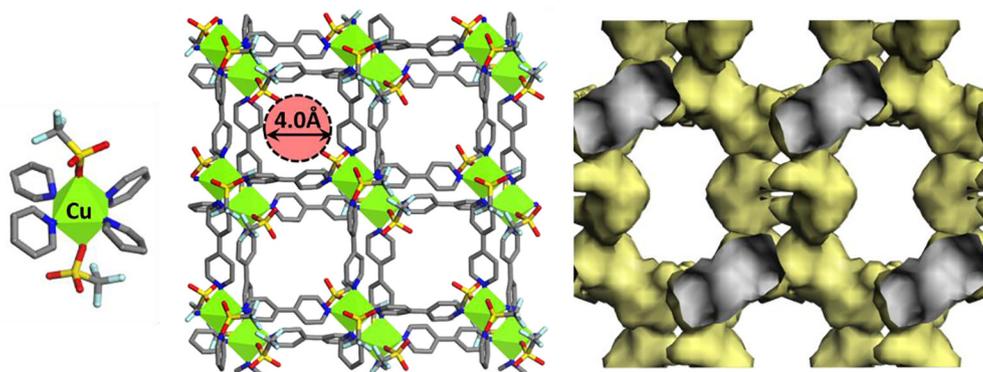


Fig. 1. Illustration of the crystal structure and two-dimensional zigzag channels in ELM-12 [32], with the inner surface of channels shown in gray. Hydrogen atoms are omitted for clarity (Cu, green; O, red; F, light blue; S, yellow; N, blue; C, gray). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

gassed at 393 K for 2 h prior to the gas sorption measurements. All the gases used (C_3H_6 , C_3H_8 , and He) were of 99.99% purity.

2.4. Breakthrough experiment

The breakthrough experiments for C_3H_6/C_3H_8 (50/50 v/v) mixtures were carried out at a flow rate of 4 mL/min (298 K, 1.01 bar). Activated MOF particles (ELM-12, 4.122 g; ELM-22, 4.217 g) with dimensions of ~ 200 – $300 \mu\text{m}$ were packed into $\phi 9 \times 150 \text{ mm}$ stainless steel column under N_2 atmosphere, respectively. After each separation test, the adsorption bed was regenerated by He flow (20 mL/min) for 30 min at 298 K.

2.5. Density-functional theory calculation

Density-functional theory (DFT) calculations were performed using the Quantum-Espresso package [37]. A semi-empirical addition of dispersive forces to conventional DFT was included in the calculation to account for van der Waals interactions. We used Vanderbilt-type ultrasoft pseudopotentials and the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) exchange correlation. The structure of ELM-12 was first optimized, which agrees well with the reported ELM-12 (guest-free) structure. Then, C_3H_6 or C_3H_8 gas molecules were introduced to various locations of the MOF, followed by full structural relaxations.

3. Results and discussion

3.1. Structure analysis and kinetic adsorption

By mixing raw chemical material $Cu(OTf)_2$ and common ligand precursor 4,4'-bipy under different conditions, both large crystal and powder samples of ELM-12 can be synthesized at room temperature (Fig. S1). The guest-free structure of ELM-12 consists of a rigid square-grid copper bipyridine scaffold with dynamic OTf^- groups. ELM-12 possesses 2D zigzag channels with pore window around 4.0 \AA (Fig. 1), which matches better with the size and shape of C_3H_6 ($6.5 \text{ \AA} \times 4.0 \text{ \AA} \times 3.8 \text{ \AA}$) as compared to C_3H_8 ($6.8 \text{ \AA} \times 4.2 \text{ \AA} \times 3.8 \text{ \AA}$), suggesting a potential application for C_3H_6/C_3H_8 separation.

Time-dependent C_3H_6 and C_3H_8 kinetic adsorptions of ELM-12 were measured at 298 and 308 K, respectively, up to 1 bar (Fig. 2). ELM-12 shows considerably faster uptake of C_3H_6 than C_3H_8 at both temperatures, and C_3H_6 reaches the adsorption equilibrium very fast, implying a high kinetic selectivity of C_3H_6 over C_3H_8 .

To quantify the kinetic selectivity of ELM-12, the diffusional time constants ($D' = D/r^2$) for C_3H_6 and C_3H_8 were calculated respectively, and the kinetic selectivity $D'(C_3H_6)/D'(C_3H_8)$ was obtained (Fig. S2). As

Table 1
Summary of the equilibrium uptakes and kinetic C_3H_6/C_3H_8 selectivities in selected MOFs.

MOFs	Uptakes at 1 bar (mg/g)		Kinetic selectivity	Temperature [K]	Ref.
	C_3H_6	C_3H_8			
ZIF-8	160	155	125	303	28
[Zn(2-cim) ₂]	95	105	60	303	28
Zn(ox) _{0.5} (trz)	98	/	860	303	30
Zn(ox) _{0.5} (atrz)	72	/	175	303	30
DBTO	62	50	11	298	29
BTO	32	31	12	298	29
ELM-12	62	60	204	298	This work
ELM-12	59	56	971	308	This work

shown in Fig. 2, the diffusion rate for both C_3H_6 and C_3H_8 increases with increasing temperature, and the kinetic C_3H_6/C_3H_8 selectivity is up to 204 at 298 K and 971 at 308 K. For comparison, we investigated the equilibrium adsorption (Fig. S3) of C_3H_6 and C_3H_8 on ELM-12, and derived the adsorption heat (Fig. S4) and IAST (ideal adsorbed solution theory) selectivity (Fig. S5) under equilibrium condition. In fact, ELM-12 has close equilibrium adsorption amount for both C_3H_6 (62 mg/g) and C_3H_8 (60 mg/g), similar adsorption heat (C_3H_6 , 30 kJ/mol; C_3H_8 , 28 kJ/mol) and low IAST selectivity (1.5). Therefore, the main separation driving force for C_3H_6/C_3H_8 mixture on ELM-12 should be attributed to the kinetic effect as indicated by the large diffusivity difference of the two molecules. The kinetic C_3H_6/C_3H_8 separation performances of previously reported MOFs were summarized in Table 1. Although ELM-12 has relatively low equilibrium adsorption capacity for C_3H_6 and C_3H_8 at 298 K, its C_3H_6/C_3H_8 kinetic selectivity (204) is significant higher than DBTO (11) and BTO (12), and even higher than that of ZIF-8 [28], [Zn(2-cim)₂] [28], and Zn(ox)_{0.5}(atrz) [30] at 303 K.

3.2. Density-functional theory calculation

The excellent kinetic C_3H_6/C_3H_8 selectivity prompted us to further investigate the gas adsorption mechanism in ELM-12. As a useful method for understanding the adsorption behavior under equilibrium conditions, DFT calculations were performed to reveal the adsorption position of C_3H_6 and C_3H_8 in this MOF structure. As shown in Fig. 3, C_3H_6 and C_3H_8 molecules are uniformly distributed in the 2D channels of ELM-12, and both C_3H_6 and C_3H_8 molecules exhibit interactions with the OTf^- sites ($H \cdots O$ 2.7–2.8 Å) (Fig. S6). The relatively long $H \cdots O$ distance indicating a weak interaction with the framework, which is consistent with the low adsorption heat found in ELM-12 [10]. The

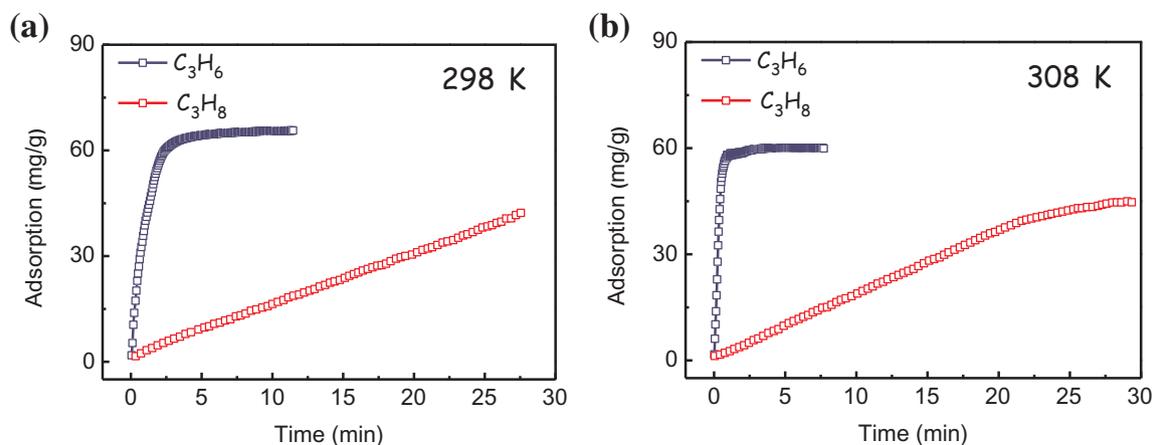


Fig. 2. Kinetic adsorption profiles of C_3H_6 and C_3H_8 for ELM-12 at 298 K (a) and 308 K (b).

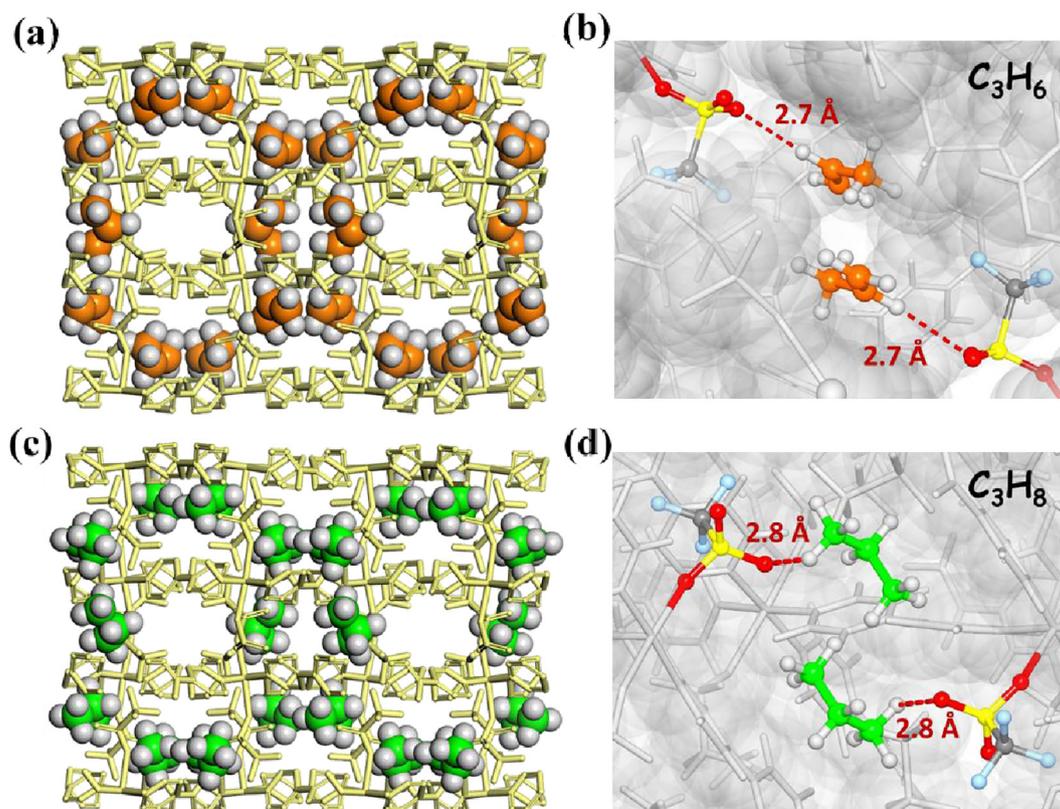


Fig. 3. DFT-calculated (a, b) C_3H_6 and (c, d) C_3H_8 adsorption locations in ELM-12. Color scheme: framework, light yellow; C in C_3H_6 , orange; C in C_3H_8 , green. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

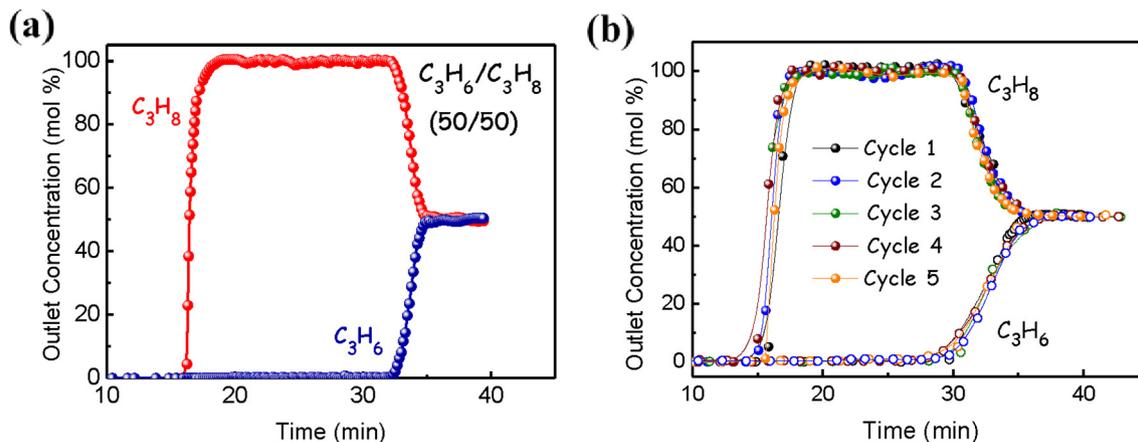


Fig. 4. (a) Experimental breakthrough curves and (b) breakthrough cycling test for C_3H_6/C_3H_8 (50/50 v/v) mixture through a bed of ELM-12 material at 298 K and 1.01 bar.

modeling results also indicate similar thermodynamic affinities of ELM-12 toward both gas molecules, which are well consistent with their equilibrium adsorption behaviors found experimentally.

3.3. Breakthrough experiments for C_3H_6/C_3H_8 mixture on ELM-12

Although many previous reports have stated that kinetic separation mechanisms are good choices for C_3H_6/C_3H_8 separation, it should be noted that such expectations have been based on inspection of their pure-component kinetic adsorption curves or associated with computational simulations. The most direct evidence for C_3H_6/C_3H_8 mixture separation in MOFs via kinetic selectivity was only reported on a rare-earth-based MOF (ftw-MOF-ABTC) [31]. Therefore, the actual

breakthrough experiment for C_3H_6/C_3H_8 (50/50 v/v) mixture on ELM-12 was carried out in this work, to further confirm the validity of kinetic effect for C_3H_6/C_3H_8 separation.

As shown in Fig. 4a, C_3H_8 firstly broke through the adsorption bed and yield a high purity gas, whereas C_3H_6 slowly eluted after 17 min and then reached equilibrium immediately. The productivity of C_3H_8 separated from the C_3H_6/C_3H_8 (50/50) mixture in ELM-12 is up to 457 mmol per liter. The long breakthrough time interval between C_3H_6 and C_3H_8 suggests that ELM-12 is quite effective for practical C_3H_6/C_3H_8 separation. Next, desorption breakthrough experiments were performed at 298 K in a total He flow of 20 mL/min (Fig. S7). C_3H_8 was desorbed very quickly, and after a period of time, C_3H_6 desorption was observed, the concentration of C_3H_6 at the outlet is higher than C_3H_8

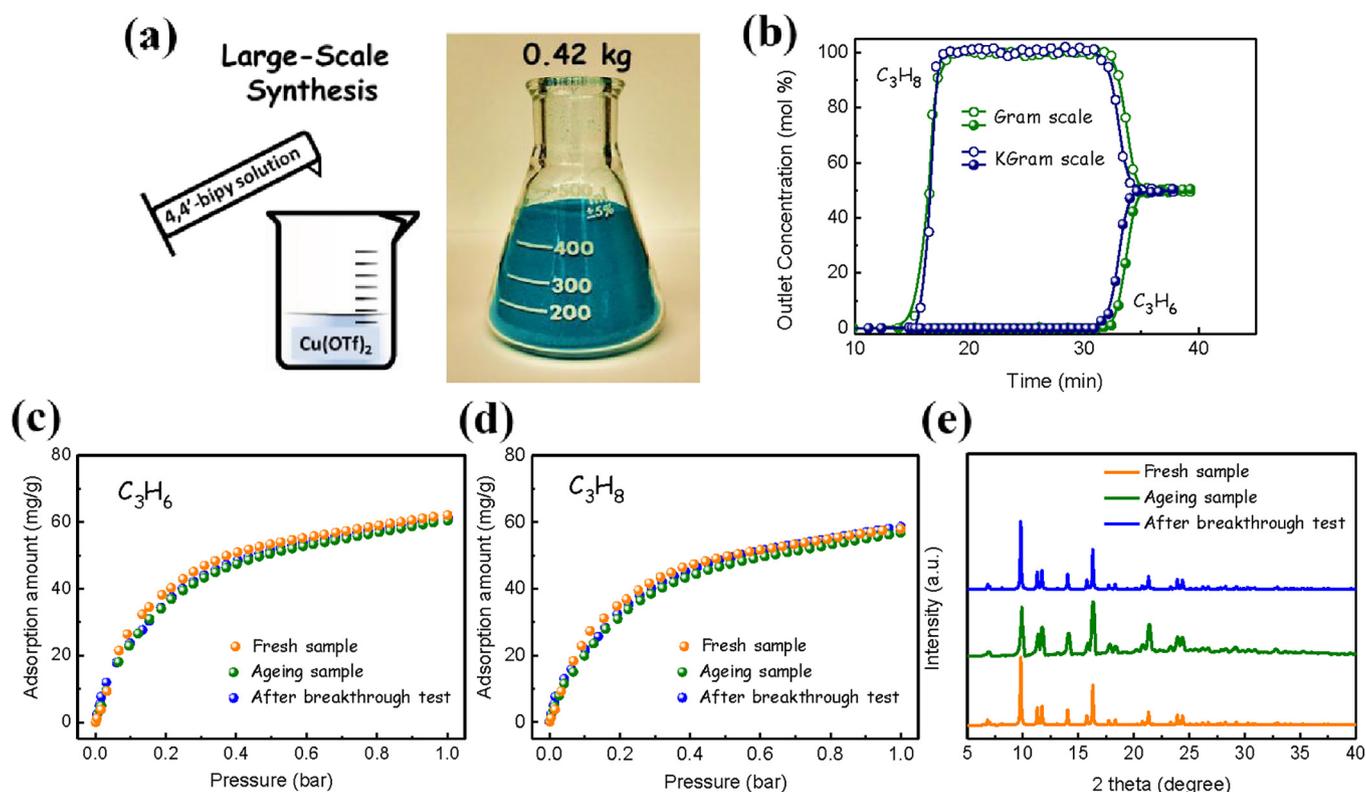


Fig. 5. (a) Kilogram-scale synthesis of ELM-12. (b) C_3H_6/C_3H_8 (50/50 v/v) breakthrough curves of ELM-12 from different scales at 298 K and 1.01 bar. (c to e) Multiple cycles of C_3H_6 and C_3H_8 adsorption isotherms and PXRD experiments showing the good structural stability of ELM-12.

during the whole desorption process, which indicated much more C_3H_6 molecules were adsorbed than C_3H_8 in ELM-12 material. Concentrated C_3H_6 can be quickly recovered within 15 min with a purity exceeding 82% during the regeneration step, benefitting from its low adsorption heat. Afterwards, cycling breakthrough experiments on ELM-12 were carried out under the same conditions. The breakthrough curves for C_3H_6/C_3H_8 mixtures in 5 cycles (Fig. 4b) are largely overlapping, showing that this material has a good durability. Furthermore, similar kinetic C_3H_6/C_3H_8 separation performance could be found in an analogous MOF (ELM-22) [37], as shown in Fig. S8.

3.4. Large scale synthesis and structural stability of ELM-12

For many years, the large gap between laboratory production and that required for commercial application has created a strong imperative in producing MOFs at large scale. The synthesis of ELM-12 can be easily scaled up at room temperature without any use of expensive metal salts or ligands. Its large-scale synthesis process is very practical. As a demonstration, 0.42 kg materials were obtained in a few hours through mixing of an aqueous solution of $Cu(OTf)_2$ with an ethanol solution of 4,4'-bipy (Fig. 5a). The breakthrough experiments in Fig. 5b revealed that the large-scale synthesized sample maintains the same C_3H_6/C_3H_8 separation productivity under aforementioned operating condition. Moreover, gas adsorption and PXRD measurements show that ELM-12 can retain its structure integrity and gas uptake capacity over 3 years of storage under ambient conditions (Fig. 5c–e).

4. Conclusion

In summary, we have revealed that microporous MOF ELM-12 is an excellent adsorbent candidate to address the challenging task of C_3H_6/C_3H_8 separation based on the kinetic mechanism. Benefiting from the zigzag 2D channels and suitable pore apertures, ELM-12 exhibits a much faster C_3H_6 adsorption over C_3H_8 under kinetic adsorption

process, giving a high kinetic C_3H_6/C_3H_8 adsorption selectivity at room temperature. The diffusivity induced separation for C_3H_6/C_3H_8 mixture on this MOF has been clearly demonstrated by the breakthrough experiments. The highly efficient separation results indicate that this MOF, with stable structure and easily scaled-up production, might be potentially applicable for the industrially important C_3H_6/C_3H_8 separation.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.cej.2018.08.108>.

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