Chinese Chemical Letters xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Chinese Chemical Letters

journal homepage: www.elsevier.com/locate/cclet

Communication

Two-dimensional cobalt metal-organic frameworks for efficient C_3H_6/CH_4 and C_3H_8/CH_4 hydrocarbon separation

Weidong Fan, Yutong Wang, Zhenyu Xiao, Zhaodi Huang, Fangna Dai*, Rongming Wang, Daofeng Sun*

State Key Laboratory of Heavy Oil Processing, College of Science, China University of Petroleum (East China), Qingdao 266580, China

ARTICLE INFO

Article history:
Received 31 August 2017
Received in revised form 12 November 2017
Accepted 14 November 2017
Available online xxx

Keywords:
Metal-organic frameworks
Microporous
Two-dimensional
Selective separation

ABSTRACT

A Co-based two-dimensional (2D) microporous metal-organic frameworks, $[Co_2(TMTA)(DMF)_2(H_2O)_2]\cdot NO_3^-\cdot DMF$ (UPC-32) has been synthesized based on 4,4′,4″-(2,4,6-trimethylbenzene-1,3,5-triyl) tribenzoic acid (H_3TMTA). UPC-32 features a 2D microporous framework exhibits high adsorption of H_2 (118.2 cm^3/g, 1.05 wt%, at 77 K), and adsorption heat (Q_{st}) of CO_2 (34–46 kJ/mol). UPC-32 with narrow distance between layers (3.8 Å) exhibits high selectivity of C_3H_6/CH_4 (31.46) and C_3H_8/CH_4 (28.04) at 298 K and 1 bar. It is the first 2D Co-MOF that showed selective separation of C3 hydrocarbon from CH_4.

C1 to C3 light hydrocarbons (CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_6 and C_3H_8) are important energy resources and raw chemicals. For example, natural gases, whose main component is CH_4, have been considered as the most promising alternative fuel for future vehicle transportation, while C_3H_8 are important chemical for the manufacture of fine chemicals such as acrylonitrile, acrylic acid, allyl alcohol, propylene oxide, isopropanol, glycerol as well as other organic chemicals. In order to fully utilize these light hydrocarbons, high quality and purity of them are essential [1–3], thus, separations of these light hydrocarbons, especially the separation of C2 and C3 hydrocarbons from CH_4 are very important industrial processes [4,5]. The traditional separation technology such as the cryogenic distillation and the pressure swing adsorption, which are based on their different vapor pressures and boiling points, are energy-intensive. Compared to the traditional separation technologies, adsorptive separation is one of the most promising low-cost and energy-efficient route. However, the traditional adsorbents, such as zeolites, have low separation coefficient owing to their less-varying porosity and low surface area. Hence, developing new-type and more effective adsorbents is critical for the effective separation of light hydrocarbons [6–9].

Metal-organic frameworks (MOFs), which are comprised of metal ions or clusters coordinated with organic ligands, have been regarded as a novel class of crystalline microporous materials with periodic network structures [10,11]. Owing to the pores within such porous MOFs can be adjusted to maximize their size-selective sieving effects and the pore surfaces can be functionalized to direct specific recognition of small molecules, porous MOFs have been intensively investigated for applications in traditional gas storage and separation, such as N_2, H_2, CO_2, and so on [12–16]. Recently, MOFs start to show ability in separation of light hydrocarbons [17–20]. For example, FJI-C1 [21] and FJI-C4 [22] have been reported to display high C_3H_8/CH_4 separation performance (78.7 and 293.4). The sizes and shapes of the pores in MOFs sorbents are the foremost for their separation performance. The pore size of an adsorbent which is comparable to or slightly larger than the kinetic diameters of the adsorbate will significantly promote the separation selectivity of these light hydrocarbons. Hence, the design and synthesis of MOFs with narrow pores close to 4.0 Å are crucial for the separation of light hydrocarbons (C1-C3) as their kinetic diameters range from 3.3 Å to 4.4 Å. In addition, based on the adsorbate-surface interactions, tailoring pore surface function, such as the immobilization of polar functional groups is another effective strategy to improve the MOFs' separation.

In this communication, we present an unprecedented 2D cobalt MOF, $[Co_2(TMTA)(DMF)_2(H_2O)_2]\cdot NO_3^-\cdot DMF$ (denoted as UPC-32) by using a functional 1,3,5-tris(4-carboxyphenyl)benzene ligands H_3TMTA. UPC-32 exhibits 2D layered structure with permanent porosity, high adsorption of H_2, and high adsorption heat (Q_{st}) of CO_2. In addition, UPC-32 shows porosity-dependent C_3H_6 and C_3H_8 uptakes and selective C_3H_6 and C_3H_8 adsorption over CH_4.

The purple block-shaped crystals of UPC-32 were synthesized by the solvent thermal reaction of $Co(NO_3)_2\cdot 6H_2O$ and H_3TMTA. The synthesis details are shown in Supporting information. Single

---

* Corresponding authors.
E-mail addresses: fndai@upc.edu.cn (F. Dai), dfsun@upc.edu.cn (D. Sun).

https://doi.org/10.1016/j.cclet.2017.11.020
1001-8417/© 2017 Chinese Chemical Society and Institute of Materia Medica, Chinese Academy of Medical Sciences. Published by Elsevier B.V. All rights reserved.

Please cite this article in press as: W. Fan, et al., Two-dimensional cobalt metal-organic frameworks for efficient C_3H_6/CH_4 and C_3H_8/CH_4 hydrocarbon separation, Chin. Chem. Lett. (2017), https://doi.org/10.1016/j.cclet.2017.11.020

crystal X-ray diffraction (SCXRD) of UPC-32 revealed that it crystallizes in the monoclinic system with the $P2_1/c$ space group. There are two Co^{2+} ions (Co1 and Co2), one $TMTA^{3-}$ ligand, two coordinated DMF molecules and two coordinated water molecules in the asymmetric unit of UPC-32. Co1 and Co2 are connected by three carboxylic groups to form a $Co_2(COO)_3$ paddle-wheel cluster (Fig. 1a). The Co1 is coordinated by three oxygen atoms from three different carboxylic groups and one oxygen atom from water molecule with the average Co1-O bond length of 2.024 Å. The Co2 is coordinated by three oxygen atoms originating from three $TMTA^{3-}$ ligands, two oxygen atoms from coordinated DMF molecules and one oxygen atom from coordinated water molecule with the average Co2-O bond length of 2.039 Å. The $Co_2(COO)_3$ clusters are connected by three carboxylic groups of $TMTA^{3-}$ ligands to form a 2D double-layer framework. The single neighboring layer of UPC-32 stack on top of each other by π-π interactions (3.8 Å) (Fig. 1b) to form a 3D supramolecular architecture with large pores ($15.8 \times 15.8 \times 3.8$ Å^3) (Fig. 1c). The potential void calculated by the PLATON [23] software is 53.7% of the total volume (2395.5 Å^3 out of the 4456.3 Å^3 unit cell volume). The phase purity for the bulk materials of UPC-32 has been confirmed by the PXRD analysis (Fig. S1 in Supporting information). Thermogravimetric analysis (TGA) curve display approximately 30.1% weight loss in the temperature range from 40 °C to 308 °C (Fig. S2 in Supporting information), which are assigned to the release of two coordinated DMF molecules, two coordinated water molecules and one guest DMF molecule for UPC-32. Above 308 °C, the frameworks start to decompose.

The establishment of permanent porosity is one of the important goals in MOF research [24]. The as-synthesized crystals of UPC-32 were solvent exchanged three times with dry acetone, then the samples were degassed at 298 K for one night and at 353 K for 12 h with the outgas rate of 5 mmHg/min to produce the activated samples for the gas adsorption measurements. The active phases are highly crystalline, and remain almost the same as its as-synthesized phase (Fig. S1 in Supporting information). The N_2 gas adsorption curve of UPC-32 at 77 K is recorded to check their porosity (Fig. 2). UPC-32 show type I N_2 adsorption isotherms, suggesting permanent micro-porosity. The N_2 gas uptake is 332 cm^3/g at 77 K and 1 bar. The pore volume calculated is 0.41 cm^3/g, which is smaller than the theoretical pore volume (0.50 cm^3/g) owing to the structural contractions during the activation. The Brunauer-Emmett-Teller (BET) surface area calculated is 1345 cm^2/g.

The H_2 adsorption experiments show 118.2 cm^3/g (1.05 wt%) and 83.6 cm^3/g (0.75 wt%) uptakes around 1 bar at 77 and 87 K, respectively (Fig. 3a). The moderate H_2 uptake for UPC-32 at 77 K is comparable to PCN-131 (0.84 wt%) and PCN-19 (0.95 wt%) [25,26]. Moreover, the adsorption heat of H_2 calculated by the Clausius-Clapeyron equation is 8.5 kJ/mol at zero coverage and decreases slowly with increasing H_2 loading (Fig. 3c). These values are higher than those of some famous MOF materials, such as HKUST-1 (6.6 kJ/mol) [27], MOF-5 (5.2 kJ/mol) [28], and NOTT-122 (6.0 kJ/mol) [29].

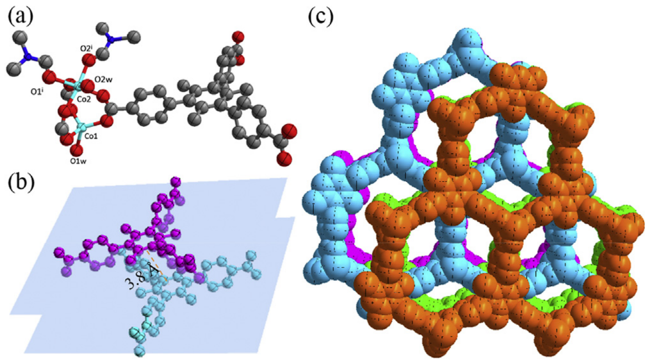

Fig. 1. Structure of UPC-32: (a) The $TMTA^{3-}$ ligand and Co cluster. (b) The distance between the two layers. (c) ABAB stacking of 2D layers.

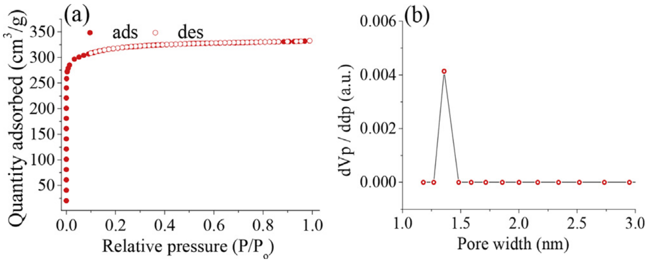

Fig. 2. (a) The N_2 sorption isotherms at 77 K, and (b) pore size distribution for UPC-32.

Since CO_2 is a dominant component of greenhouse gas and a main contaminant of natural gas, it is meaningful to investigate the capacity for CO_2 and selectivity of CO_2/CH_4. Low pressure CO_2 adsorption isotherms are also measured at 273 K and 298 K (Fig. 3b). The amount of CO_2 uptake for UPC-32 is 102.8 cm^3/g (20.2 wt%) and 65.7 cm^3/g (12.9 wt%) under 1 bar at 273 K and 298 K, respectively. Compared with the enormous MOFs, the amount of MOFs which exhibit over 20.0 wt % CO_2 uptakes at 273 K and 1 bar is relatively small [30,31]. The Q_{st} for CO_2 in UPC-32 is 46 kJ/mol calculated by the Clausius-Clapeyron equation (Fig. 3c and Table S1 in Supporting information). The predicted CO_2/CH_4 selectivity (for equimolar gas-phase mixtures) by IAST at 298 K under 1 bar are calculated as 6.6 for UPC-32 (Fig. 3d and Table S2 in Supporting information). It should be noted that these values are lower than Mg-MOF-74 (CO_2/CH_4: 105), UTSA-16 (CO_2/CH_4: 30) [32] and SIFSIX-3-Zn (CO_2/CH_4: 231) [33], but still comparable to ZIF-79 (CO_2/CH_4: 5.4) [34], SIFSIX-2-Cu (CO_2/CH_4: 5.3) and PCN-88 (CO_2/CH_4: 5.3) [35], making it qualified considerable candidate for CO_2 capture and separation from natural gas.

Considering the small pore size and intrinsic permanent porosity of UPC-32, we have investigated its potential application for light hydrocarbons adsorption and separation. Although many MOFs with excellent gas sorption capacity (such as H_2, CO_2 and CH_4) have been reported, only a few MOFs show high adsorption capacity and selectivity toward light hydrocarbons. To examine the adsorption and separation of light hydrocarbons for UPC-32, single component gas adsorption isotherms of UPC-32 for various light hydrocarbons (CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_6, and C_3H_8) are performed at both 273 K and 298 K. As expected, UPC-32 can uptake a high amount of C_3H_8 (104.3 cm^3/g), C_3H_6 (110.1 cm^3/g), C_2H_6 (80.2 cm^3/g), C_2H_4 (74.1 cm^3/g), and C_2H_2 (85.0 cm^3/g), but a relatively lower amount of CH_4 (31.3 cm^3/g) at 273 K and 1 bar (Fig. 4a). It should be noted that the sorption capacity of UPC-32 for C_3H_8 (84.9 cm^3/g), C_3H_6 (98.2 cm^3/g), C_2H_6 (66.1 cm^3/g), C_2H_4 (57.2 cm^3/g), C_2H_2 (60.6 cm^3/g), and CH_4 (18.9 cm^3/g) at 298 K and 1 bar are higher than those of UTSA-35a and UTSA-36a (Fig. 4b and Fig. S5 in Supporting information) [36,37]. The magnitude of the adsorption heats reveals the affinity of the pore surface toward adsorbents, which plays a significant part in determining the adsorptive selectivity [38]. To evaluate the affinity of such light hydrocarbons in UPC-32, the adsorption heats are calculated by the Clausius-Clapeyron equation. The Q_{st}s for CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_6, and C_3H_8 are 13.1, 6.3, 8.3, 6.6, 13.3, and 13.8 kJ/mol at zero coverage, respectively (Fig. 4c).

The C3 light hydrocarbons with higher adsorption heat may provide stronger affinity with a skeleton, which results in these

Please cite this article in press as: W. Fan, et al., Two-dimensional cobalt metal-organic frameworks for efficient C_3H_6/CH_4 and C_3H_8/CH_4 hydrocarbon separation, Chin. Chem. Lett. (2017), https://doi.org/10.1016/j.cclet.2017.11.020