Chemistry–A European Journal

Communication
doi.org/10.1002/chem.202101871

Chemistry Europe
European Chemical Societies Publishing

VIP

Upgrading Octane Number of Naphtha by a Robust and Easily Attainable Metal-Organic Framework through Selective Molecular Sieving of Alkane Isomers

Hao Wang+,*[a] Xinglong Dong+,[b] Jiayu Ding,[c] Kaifang Wang,[a] Liang Yu,[a] Shang Zhang,[c] Yu Han,[b] Qihan Gong,*[c] An Ma,[c] and Jing Li*[a, d]

Abstract: The separation of alkanes, particularly monobranched and dibranched isomers, is of paramount importance in the petrochemical industry for optimizing the feedstock of ethylene production as well as for upgrading the octane number of gasoline. Here, we report the full separation of linear/monobranched alkanes from their dibranched isomers by a robust and easily scalable metal-organic framework material, $Co_3(HCOO)_6$. The compound completely excludes dibranched alkanes but adsorbs their linear and monobranched isomers, as evidenced by single-component and multicomponent adsorption measurements. More importantly, the material exhibits excellent performance in separating naphtha and is capable of providing high quality feedstock for the production of ethylene and gasoline components with high octane number, making it a promising candidate for naphtha separation in petrochemical industry.

Naphtha, mainly consisting of C_5–C_{12} alkanes, cycloalkanes, and aromatic hydrocarbons, represents an important distillate during oil refinement. It is the primary raw material for the manufacture of ethylene, xylenes, gasoline, and other various chemicals.[1] For example, branched C5–C7 alkane isomers are superior components for gasoline blends with high octane number (RON), which is a standard measure of an engine or aviation gasoline capability against compression. A typical naphtha blend is composed of 30% normal alkanes, 30% branched alkanes, and the remaining are cycloalkanes and aromatics, which is subject to separation before further use (Scheme 1). Traditional separation of naphtha relies on distillations (Scheme 1, marked in red), which split the mixture into components with different carbon numbers (or boiling point). Lighter distillate are used as raw materials for the production of ethylene while the heavier counterpart will undergo catalytic reforming to produce gasoline and valuable aromatic chemicals (benzene, toluene, xylenes, etc.). However, the separation by distillation is inefficient and energy intensive. For example, linear alkanes with high carbon number are superior feedstock for ethylene production, but they are excluded from the feedstock due to their high boiling points.

Adsorptive separation of naphtha could potentially split the mixture into components according to their molecular characters, such as degree of branching, with lower energy input. This may also improve the efficiency of naphtha use. Zeolite 5A is the currently employed adsorbent in industry for the separation of alkane isomers or naphtha (Scheme 1, marked in purple). However, zeolite 5A adsorbs normal alkanes only and excludes any branched isomers.[2] This is not an optimal solution and thus limits its wider implementation. An ideal separation would be splitting normal/monobranched alkanes and other isomers with higher branching because monobranched alkanes are premium raw materials for producing ethylene but not ideal

[a] Prof. H. Wang,+ K. Wang, L. Yu, Prof. J. Li
Hoffmann Institute of Advanced Materials
Shenzhen Polytechnic
7098 Liuxian Blvd., Nanshan District, Shenzhen,
Guangdong 518055 (P. R. China)
E-mail: wanghao@szpt.edu.cn

[b] Dr. X. Dong,+ Prof. Y. Han
Advanced Membranes and Porous Materials Center
Physical Sciences and Engineering Division
King Abdullah University of Science and Technology
Thuwal 23955-6900 (Saudi Arabia)

[c] J. Ding, S. Zhang, Dr. Q. Gong, Prof. A. Ma
Fundamental Science & Advanced Technology Lab
PetroChina Petrochemical Research Institute
Beijing, 102200 (P. R. China)
E-mail: gongqihan@petrochina.com.cn

[d] Prof. J. Li
Department of Chemistry and Chemical Biology
Rutgers University
123 Bevier Road, Piscataway, NJ 08854 (USA)
E-mail: jingli@rutgers.edu

[+] These authors contributed equally to this work.

Supporting information for this article is available on the WWW under https://doi.org/10.1002/chem.202101871

←-------|-------→ Adsorptive separation by zeolite 5A

Composition of a typical naphtha blend (wt%)						
	Normal alkanes	Monobranched alkanes	Other branched alkanes	Cycloalkanes	Aromatic hydrocarbons	Total
C_5	4.27	1.36	0.00	0.49	0.00	6.12
C_6	5.20	3.78	0.68	3.68	0.82	14.16
C_7	5.21	4.63	1.16	7.60	1.73	20.33
C_8	5.14	3.32	2.29	9.25	3.70	23.70
C_9	5.01	2.36	2.97	6.65	2.64	19.63
C_{10}	3.36	2.22	3.11	2.35	0.28	11.32
C_{11}	0.26	0.63	1.79	0.02	0.00	2.70
C_{12}	0.19	0.29	1.55	0.01	0.00	2.04
Total	28.64	18.59	13.55	30.05	9.17	100.00

Traditional distillation

←-------|-------→ Adsorptive separation proposed in this work

Scheme 1. Solutions for the separation of naphtha.

gasoline components due to its relatively low RON. ZSM-5 is a well-known zeolite adsorbent that shows separation of monobranched and dibranched alkanes, but its low adsorption capacity limits its separation efficiency.[3]

Metal-organic frameworks (MOFs) are particularly promising for the separation of hydrocarbons in light of their diverse structure types, highly tunable pore size, pore shape and functionality.[4,5,6,7] A number of MOF materials that can well separate alkane isomers have been reported over the past few years.[8,9] The representative examples include $Fe_2(BDP)_3$,[10] ZIF-8,[11] Y-fum,[12] Zr-bptc,[13] and Zr-abtc,[13] to name a few. However, none of these materials are capable of separating monobranched alkanes and their dibranched isomers with high efficiency. We recently reported two MOF-based splitters, $Ca(H_2tcpb)$[14] and Al-bttotb,[15] that separate monobranched and dibranched alkanes through selective molecular sieving. Nevertheless, they are both built on relatively complicated linkers, making their scale-up synthesis difficult/expensive. In this work we report the full sieving of monobranched and dibranched alkanes by a robust, simple, and easily achievable MOF, $Co_3(HCOO)_6$ (denoted as Co-fa). More importantly, in the separation of naphtha, Co-fa outperforms the benchmark zeolite and other MOF materials, such as ZSM-5 and Al-bttotb, making it a promising candidate for industrial separation of naphtha.

Co-fa is built exclusively on Co^{2+} and formate ($HCOO^-$). It features a three-dimensional (3D) framework containing one-dimensional (1D) channels with pore diameter of 5.5 Å (Figure 1), falling right between the molecular sizes of monobranched and dibranched alkanes.[16] The compound was synthesized via solvothermal reactions following reported recipe with modifications. Notably, hundred-gram scale-up synthesis can be easily performed in lab and the materials were characterized by powder X-ray diffraction (PXRD) and thermogravimetric analysis (TGA) (Figure S1–S2). Additionally, Co-fa is structurally robust. Its framework is well retained upon heating in open air or exposure to moisture.

We re-examined the porosity of Co-fa by nitrogen adsorption measurements at 77 K which yielded a BET surface area of 365 m^2/g (Figure S3), consistent with reported values. Single-component adsorption experiments of alkane isomers were conducted on a Quantachrome Vstar volumetric vapor adsorption analyzer. The compound adsorbs similar amounts of linear and monobranched alkanes (1.5–1.7 mmol/g) but fully excludes their dibranched isomers (Figure 2a). Thus it represents a rare example of rigid framework that is capable of separating monobranched and dibranched alkanes through selective molecular sieving. The adsorption behavior of Co-fa correlates well with its pore dimensions. The separation capability of the compound is further confirmed by multicomponent column breakthrough measurements of an equimolar ternary mixture of nHEX, 3MP, and 22DMB. As shown in Figure 2b, 22DMB eluted out from the column at the first minute without any retention. This is not unexpected as Co-fa adsorbs essentially no dibranched alkanes. In contrast, 3MP and nHEX were retained in the column until the 36th and 51st minute, consistent with their substantial adsorption by the adsorbent. The aforementioned results confirm that Co-fa is capable of fully separating linear/monobranched alkanes from their dibranched isomers through selective molecular exclusion.

Alkane isomers are the main components of naphtha, thus they are commonly used as model mixtures to evaluate the capability of an adsorbent for naphtha separation (hexane isomers are used in most cases). In order to obtain more

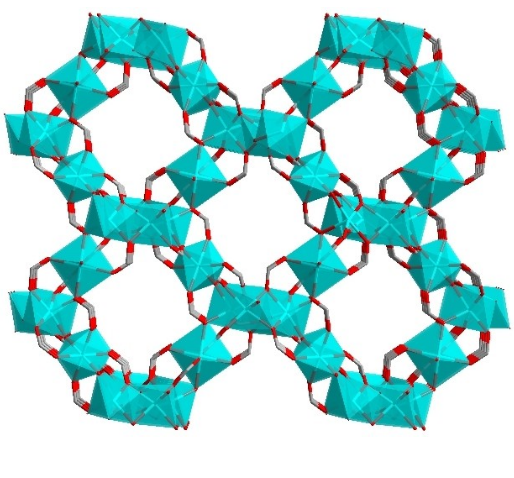
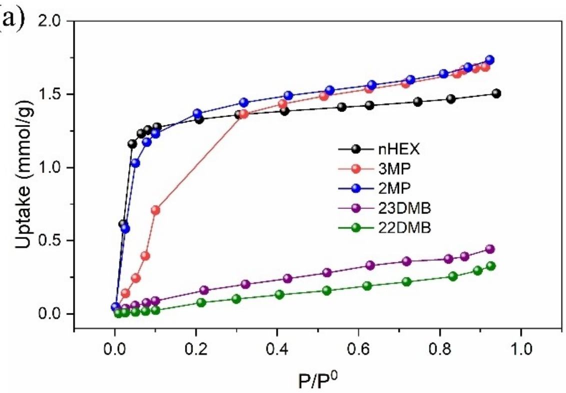


Figure 1. Crystal structure of $Co_3(HCOO)_6$. Colour scheme: cyan polyhedra: Co, red: O, grey: C.

(a)



(b)

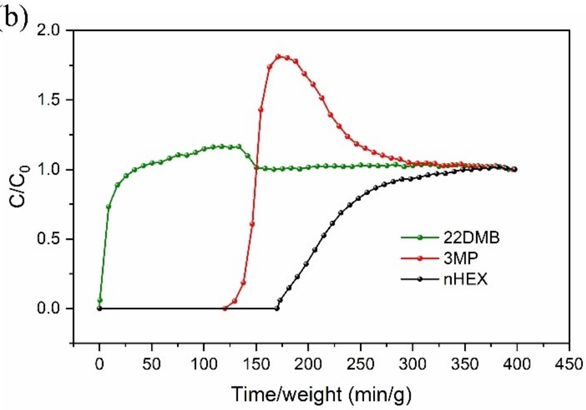
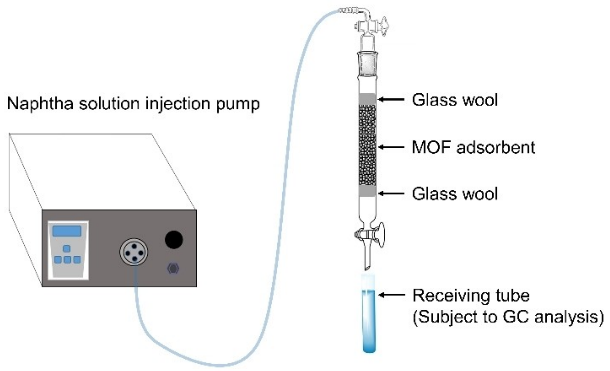


Figure 2. a) Single-component vapor adsorption isotherms of C6 alkane isomers on Co-fa at 30 °C. b) Column breakthrough results of an equimolar ternary mixture of nHEX, 3MP, and 22DMB at 30 °C.

insights into the separation ability of Co-fa, we performed a proof of concept separation test of naphtha using Co-fa as the adsorbent, and compared its performance with that of ZSM-5 and Al-bttotb, the representative zeolite and MOF adsorbents for the separation of alkanes. The naphtha used was from PetroChina refinery, which contains C_5–C_{12} alkanes, cycloalkanes, and aromatic hydrocarbons (see Table S1 for detail composition) and has an initial RON value of 69.41. Experimental setup of naphtha separation is shown in Scheme 2. The column was filled with Co-fa pallets (18.0 g) and a naphtha mixture was added to the column. The eluted product was collected in the receiving tube and was subject to GC analysis. The first drop of eluted product gave a RON of 85.69, meeting and exceeding the industrial standard for refined hexane blends (RON = 83).[10] It should be noted that here the feed is a real naphtha mixture with 185 components (See Table S1), rather than hexane mixtures with 3—5 isomers, which have been used in all previous studies. The RON value of the eluted products stayed above 83 until a total amount of 3.26 g of product was collected, indicating the capability of Co-fa in effectively upgrading the RON of naphtha. Parallel experiments were carried out under identical conditions for ZSM-5 and Al-bttotb. With the same amount of adsorbent, RON values of the first drop of eluted product were 84.23 and 84.10 for ZSM-5 and Al-bttotb, respectively, lower than that for Co-fa (Table 1). More importantly, the amounts of products collected with RON > 83 for ZSM-5 and Al-bttotb are notably lower than that of Co-fa. These results suggest that Co-fa outperforms ZSM-5 and Al-bttotb for naphtha separation with respect to adsorption efficiency, which can be attributed to the optimal pore structure of Co-fa.



Scheme 2. Schematic illustration of the setup for naphtha separation test.

Table 1. Results for the separation of naphtha by ZSM-5, Al-bttotb, and Co-fa.

	ZSM-5	Al-bttotb	Co-fa
Sample amount [g]	18.0	18.0	18.0
Density [g/cm^3][a]	1.05	1.04	1.20
RON of first drop eluted	84.23	84.10	85.69
Products collected[b] [g]	0.94	2.08	3.26

[a] Crystal density of adsorbents. [b] Products with RON > 83.

The following factors should be considered when developing an ideal adsorbent for industrial separation: adsorption efficiency (capacity and selectivity), framework stability, synthesis scalability, and cost. 1) Single-component vapor adsorption and multicomponent column breakthrough measurements suggested that Co-fa represents a rare example for full separation of monobranched and dibranched alkanes through selective molecular exclusion. The separation capability of Co-fa was further evaluated by naphtha separation test and the results indicate that Co-fa is superior in terms of separation efficiency and outperforms the benchmark zeolite ZSM-5 and Al-bttotb. In addition, Co-fa has a lower density than those of these two adsorbents, implying that its separation efficiency by volume could be even higher. This is also an important parameter for industrial implementation. 2) Co-fa demonstates excellent thermal and moisture stability, meeting the requirement for industrial separation of naphtha. 3) Co-fa can easily be synthesized at hundred-gram scale in one reaction in lab, indicating its easy scalability. 4) Co-fa is synthesized from Co(II) salts, formic acid, and DMF, without use of delicate organic linkers or addition of expensive templates/modulators, making it one of the most easily available and inexpensive MOF adsorbent materials.

In this work, we have demonstrated the separation of alkane isomers by Co-fa. The material adsorbs linear and monobranched alkanes only and fully excludes dibranched isomers. Further evaluation by naphtha separation measurements indicates that the compound is capable of separating naphtha efficiently for RON upgrading. Considering its facile synthesis, good stability, and low cost, Co-fa holds particular promise for industrial separation of naphtha.

Acknowledgements

We thank the financial support from the National Natural Science Foundation of China (21901166), the Guangdong Natural Science Foundation (2019A1515010692), Shenzhen Science and Technology Program (No. JCYJ20190809145615620, RCYX20200714114539243), and PetroChina (2019A-1809-3).

Conflict of Interest

The authors declare no conflict of interest.

Keywords: alkane isomers · hydrocarbon separation · metal-organic frameworks · naphtha · octane number

[1] R. A. Myers, *Handbook of Petroleum Refining Processes*, McGraw-Hill, New York **2004**.
[2] D. Peralta, G. Chaplais, A. Simon-Masseron, K. Barthelet, G. D. Pirngruber, *Ind. Eng. Chem. Res.* **2012**, *51*, 4692–4702.
[3] A. F. P. Ferreira, M. C. Mittelmeijer-Hazeleger, A. Bliek, *Adsorption* **2007**, *13*, 105–114.
[4] R.-B. Lin, L. Li, H.-L. Zhou, H. Wu, C. He, S. Li, R. Krishna, J. Li, W. Zhou, B. Chen, *Nat. Mater.* **2018**, *17*, 1128–1133.

[5] L. Li, R.-B. Lin, R. Krishna, H. Li, S. Xiang, H. Wu, J. Li, W. Zhou, B. Chen, *Science* **2018**, *362*, 443–446.
[6] D.-D. Zhou, P. Chen, C. Wang, S.-S. Wang, Y. Du, H. Yan, Z.-M. Ye, C.-T. He, R.-K. Huang, Z.-W. Mo, N.-Y. Huang, J.-P. Zhang, *Nat. Mater.* **2019**, *18*, 994–998.
[7] P.-Q. Liao, N.-Y. Huang, W.-X. Zhang, J.-P. Zhang, X.-M. Chen, *Science* **2017**, *356*, 1193–1196.
[8] H. Wang, J. Li, *Acc. Chem. Res.* **2019**, *52*, 1968–1978.
[9] W.-G. Cui, T.-L. Hu, X.-H. Bu, *Adv. Mater.* **2020**, *32*, 1806445.
[10] E. D. Bloch, W. L. Queen, R. Krishna, J. M. Zadrozny, C. M. Brown, J. R. Long, *Science* **2012**, *335*, 1606–1610.
[11] A. F. P. Ferreira, M. C. Mittelmeijer-Hazeleger, M. A. Granato, V. F. D. Martins, A. E. Rodrigues, G. Rothenberg, *Phys. Chem. Chem. Phys.* **2013**, *15*, 8795–8804.
[12] A. H. Assen, Y. Belmabkhout, K. Adil, P. M. Bhatt, D.-X. Xue, H. Jiang, M. Eddaoudi, *Angew. Chem. Int. Ed.* **2015**, *54*, 14353–14358; *Angew. Chem.* **2015**, *127*, 14561–14566.
[13] H. Wang, X. Dong, J. Lin, S. J. Teat, S. Jensen, J. Cure, E. V. Alexandrov, Q. Xia, K. Tan, Q. Wang, D. H. Olson, D. M. Proserpio, Y. J. Chabal, T. Thonhauser, J. Sun, Y. Han, J. Li, *Nat. Commun.* **2018**, *9*, 1745.
[14] H. Wang, X. Dong, E. Velasco, D. H. Olson, Y. Han, J. Li, *Energy Environ. Sci.* **2018**, *11*, 1226–1231.
[15] L. Yu, X. Dong, Q. Gong, S. R. Acharya, Y. Lin, H. Wang, Y. Han, T. Thonhauser, J. Li, *J. Am. Chem. Soc.* **2020**, *142*, 6925–6929.
[16] H. Wang, K. Yao, Z. Zhang, J. Jagiello, Q. Gong, Y. Han, J. Li, *Chem. Sci.* **2014**, *5*, 620–624.

Manuscript received: May 28, 2021
Accepted manuscript online: June 26, 2021
Version of record online: July 16, 2021