

DOI
10.31635/ccschem.021.202100789

Publication date
2022

Document Version
Final published version

Published in
CCS Chemistry

License
CC BY-NC

Citation for published version (APA):

Mengjia Yin¹, Rajamani Krishna², Wenjing Wang³, Daqiang Yuan³, Yaling Fan¹, Xuefeng Feng¹, Li Wang¹ & Feng Luo¹*

¹School of Chemistry, Biology and Materials Science, East China University of Technology, Nanchang 330013, ²Van’t Hoff Institute for Molecular Sciences, University of Amsterdam, 1098 XH Amsterdam, ³State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002

*Corresponding author: ecitluofeng@163.com

Cite this: CCS Chem. 2022, 4, 1016-1027
DOI: 10.31635/ccschem.021.202100789

The synthesis of nanoporous materials that display a combination of molecular sieving (MS) and quantum sieving (QS) effects is still a challenging task. In this work, we have demonstrated the synthesis of a nanocaged metal–organic framework (MOF), ECUT-8, that has a dual-sieving capability. ECUT-8 afforded H₂/D₂ isotope separation due to its extremely narrow window size (3.0 Å), resulting in QS. Further, the framework flexibility of ECUT-8 was exploited for the separation of butane and hexane isomers due to its MS effect. Other desirable features of ECUT-8 include high thermal, water, and chemical stability, making it suitable for practical application. Herein, these results open up an avenue to design the effects of coexistence of multiple sieving in one material.

Keywords: metal–organic framework, molecular sieving effect, quantum sieving effect, gate-opening, multiple sieving effects, isotope separation, isomer separation, thorium-based cage

Introduction

Cages or cage-based compounds present a highly desired porous material for host-guest recognition and separation due to their internal-porosity and window-size adjustment. Typically, the shape and size of the windows are expected to give molecular sieving (MS) effect, thereby allowing only the passage of smaller molecules, while excluding the entry of guest molecules that are larger than the window aperture. Additionally,
when the window size becomes small enough to distinguish the speed of diffusion of isotopes, a quantum sieving (QS) effect could be engendered.\textsuperscript{10,11} The separation of mixtures of molecules is an industrially important process.\textsuperscript{11} The current mature technique for separation is based on boiling-point-differences distillation method; however, this approach requires vast capital investment and extensive energy consumption (10–15%) worldwide.\textsuperscript{12} By contrast, the porous adsorbent-based pathway, which is relatively low-cost and energy-saving, is now receiving increasing attention.\textsuperscript{13} Recent advances reveal that for certain unique molecular separation such as \( \text{CO}_2/\text{N}_2, \text{C}_2\text{H}_2/\text{CO}_2, \text{C}_2\text{H}_4/\text{C}_2\text{H}_2/\text{C}_2\text{H}_6, \text{SO}_2/\text{CO}_2, \) and \( \text{Xe}/\text{Kr} \), both traditional adsorbents such as zeolite and porous carbon, newly developed adsorbents such as metal–organic frameworks (MOFs), cages, hydrogen-bonded frameworks (HOFs), and covalent organic frameworks (COFs) were effective.\textsuperscript{14–27}

Due to the closeness of physicochemical properties, separations of isotopic and isomeric mixtures pose peculiar challenges.\textsuperscript{28,29} However, both are needed urgently in industries as they play an essential role in resolving the energy crisis. For example, the separation of deuterium (\( \text{D}_2 \)) from \( \text{H}_2/\text{D}_2 \) isotope mixtures is of prime importance in the nuclear industry, and the separation of hexane isomers is of extreme importance in upgrading gasoline.\textsuperscript{30–32}

The kinetic diameters of both \( \text{H}_2 \) and \( \text{D}_2 \) are equal to 2.9 Å. Accordingly, the \( \text{H}_2/\text{D}_2 \) separation, as suggested by theoretical and experimental results, could be achieved from a very confined system that results in different transport between \( \text{H}_2 \) and \( \text{D}_2 \) due to their differences in de Broglie wavelength.\textsuperscript{33–40} This distinct phenomenon was defined as the QS effect.\textsuperscript{33–40} For this QS effect to be effective, the adsorbent's efficient pore size should match precisely the kinetic diameter of \( \text{H}_2 \) and \( \text{D}_2 \). However, from the viewpoint of material synthesis, the construction of materials with ultrafine pores remains a challenging issue.

On the other hand, the isomer separation, in principle, could be achieved by exploiting the MS effects of adsorbents.\textsuperscript{29} For example, butane isomers such as linear \( n \)-butane and branched \( \text{iso}-\text{butane} \) have respective kinetic diameters of 4.7 and 5.3 Å. In a recent report, butane isomers were separated by a microporous MOF of ZU-36-Co with the pore size ranging between 3.8 and 5.2 Å, due to MS effects in such a way that the smaller linear isomer of \( n \)-butane was effectively adsorbed in this MOF, whereas the bigger branched isomer of \( \text{iso}-\text{butane} \) was excluded beyond MOF.\textsuperscript{41} Another example is the separation of hexane isomers whose kinetic diameters are: \( 3 \)-hexene (\( n \)-HEX; 4.3 Å) < 3-methylpentane (3MP; 5.0 Å) = 2-methylpentane (2MP; 5.0 Å) < 2,3-dimethylbutane (23DMB; 5.6 Å) < 2,2 dimethylbutane (22DMB; 6.2 Å), where the MS effect could be exploited using a variety of porous adsorbents such as ZIF-8 (ZIF = zeolite-like imidazole framework), \( \text{Fe}_2(\text{BDP})_3 \) (BDP = 1,4-benzene-dipyrrolylazine), \( \text{Zr-bptc} \), and \( \text{Zr-abtc} \).\textsuperscript{42–47} However, the separation of monobranched isomer from dibranched isomer was still a challenging task.

As discussed in the preceding section, the separation of \( \text{H}_2/\text{D}_2 \) in light of the QS effect demands an ideal size of \( \sim 3.0 \) Å, whereas the separation of butane and hexane isomers relying on the MS effect needed a size \( >4.0 \) Å. Clearly, the coexistence of QS and MS effects in the same material was challenging due to the pore size requirement for an MS effect for isomer separation to be achieved, precluding the QS effect for isotope separation and vice versa. In the literature, only MIL-53 (MIL = Materials from Institut Lavoisier), a flexible MOF, has been demonstrated experimentally to exhibit the coexistence effects of both QS and MS.\textsuperscript{37} Furthermore, given that the gate-opening phenomena are well-known in ZIFs\textsuperscript{48–50} due to the bending or swinging of the imidazolate ring, a similar coexistence effects of QS and MS is suggested, but this has still not been confirmed experimentally.

In this work, we use an imidazolate-derivative ligand to combine 5f and 3d metal centers, resulting in a highly rare \( [\text{Th}_8\text{Co}_8] \) nanocage-based MOF (ECUT-8) with a 3,9-connected \( ftw \) topology matrix. The effective window size, down to 3.0 Å, was observed, fully meeting the QS effect requirement. As commonly observed in ZIFs, the imidazolate-derivative ligands in ECUT-8 were flexible, leading to gate-opening and the possibility of MS effect. Both single-component adsorption tests and breakthrough experiments confirmed the isotope and isomer separation capabilities due to the coexistence effect of QS and MS.

**Experimental Section**

**Synthesis of ECUT-8**

\( \text{Co(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O} \text{ (0.034 mmol, 10 mg), 5-(1H-imidazol-1-yl)isophthalic acid (0.0646 mmol, 15 mg), and Th(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O} \text{ (0.021 mmol, 10 mg) were dissolved in a mixture of ethanol (1 mL), N,N'-dimethylformamide (DMF; 4 mL), and concentrated HNO}_3 \text{ (0.45 mL). The solution was moved into a 25 mL Teflon-lined stainless steel vessel and heated at 115 °C for 3 days, after which it was cooled down to room temperature. Red crystals were filtered and washed with 10 mL ethanol and 10 mL deionized water. The yield was 90% based on thorium (Th). Element analysis (%): Anal. Calcd for ECUT-8: C, 42.01; N, 10.49; H, 3.27. Found C, 42.08; N, 10.40; H, 3.23.**

**Stability test**

The water stability test was carried out by immersing 100 mg ECUT-8 samples in water at room temperature or in boiling water (100 °C) for 7 days. Then powder X-ray diffraction (PXRD) was used to trace the stability. A pH
stability test was performed by immersing 100 mg samples in water at pH 3.0–12 for 1 day. Then PXRD was used to trace the stability. The thermal stability test was conducted by calcining 100 mg samples in N2 at high temperature (350 °C) for 1 day. Then PXRD was used to trace the stability.

**X-ray crystallography**

X-ray diffraction data of ECUT-8 were collected at 298 K on a Bruker-Apex (II) diffractometer using graphite-monochromated MoKα radiation (λ = 0.71073 Å). Data reduction included the correction for Lorentz and polarization effects, and an applied multiscan absorption correction (SADABS). The crystal structure was solved and refined using the SHELXTL program suite. Direct methods yielded all nonhydrogen atoms, which were refined with anisotropic thermal parameters. All hydrogen atom positions were calculated geometrically and were found overlapped with their respective atoms. The SQUEEZE subroutine of the PLATON software suite (~https://www.chem.gla.ac.uk/~louis/software/platon/index.html) was used to remove the scattering from the highly disordered guest molecules. CCDC 2055060 contains the supplementary crystallographic data of ECUT-8. The data are available free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. A crystallographic summarization is shown in Supporting Information Table S1.

**Results and Discussion**

**ECUT-8 structure**

The MOF with the formula of [ThCoL₃] [L₂⁻ = 5-(1H-imidazol-1-yl)isophthalate] was synthesized by the solvothermal reaction of Th(NO₃)₄, Co(NO₃)₂, and L in DMF in the presence of HNO₃ at 120 °C. The yield was up to 90% based on Th. Single-crystal X-ray diffraction revealed that ECUT-8 crystallized in the rhombohedral crystal system with R₃̅₂ space group. In the asymmetric unit, there was one crystallography-independent Th and one Co site. The Th(IV) site is coordinated by nine carboxylate oxygen atoms from six L₂⁻ ligands, while the Co(II) site held a common octahedral geometry finished by three carboxylate oxygen atoms from three L₂⁻ ligands and three nitrogen atoms from the other three L₂⁻ ligands. Each L₂⁻ ligand connects to two Th(IV) ions.

**Figure 1** | The structure of ECUT-8. (a) View of the ThCo dinuclear unit bridged by three L⁻ carboxylate groups and connects to nine L⁻ ligands. (b) View of the [Th₈Co₈] cage in a hexagonal biconical configuration with the highlighted large cavity about 0.8 nm aperture. (c) View of the narrow six-ring window (3.0 Å). (d) View of the imidazolate-derivatized L⁻ ligands. (e) The simplified three-connected triangle node. (f) The simplified nine-connected three-capped triangular prism node. (g) The simplified [Th₈Co₈] cage. (h) The overall 3,9-connected ftw topology matrix in ECUT-8.

DOI: 10.31635/ccschem.021.202100789
Corrected Citation: CCS Chem. 2022, 4, 1016–1027
Previous Citation: CCS Chem. 2021, 3, 1115–1126
Link to VoR: https://doi.org/10.31635/ccschem.021.202100789
and two Co(II) ions with one carboxylate in the chelate mode and the other in the bridging mode. The secondary building unit in ECUT-8 is the ThCo dinuclear unit, where the Th and Co center were bridged by three L\(^2\)− carboxylate groups (Figure 1a). The novel Th\(_8\)Co\(_8\) nanocage, composed of eight ThCo dinuclear units in a hexagonal biconical configuration, is shown in Figure 1b. The effective aperture, excluding the van der Waals radii of atoms, is \(\sim 8.0\) Å, with a great window size of only 3.0 Å (Figure 1c). A careful inspection of the window structure suggested a high degree of similarity with the narrow six-ring window (3.4 Å) in ZIF-8 (Supporting Information Figure S1). The unique structural feature of ZIF-8 is the framework flexibility caused by the bending or swinging of the imidazolate unit, leading to an open gating and the possibility of separation due to the MS effect. Analogously, ECUT-8, with a comparable structural feature, is expected to exhibit similar open gating and along with the MS effect. Most importantly, the very small window (3.0 Å) in ECUT-8 matches well with the kinetic diameter of H\(_2\) and D\(_2\) (2.9 Å), strongly suggesting its potential for H\(_2\)/D\(_2\) separation via the QS effect.

Further analysis of the topology of this MOF revealed that each of the L\(^2\)− ligands was connected to three identical ThCo dinuclear units, while each ThCo dinuclear unit was connected to nine L\(^2\)− ligands. Given the connectivity of the L\(^2\)− ligands and ThCo dinuclear units, they were simplified as forming three-connected triangle nodes (Figures 1d and 1e) and nine-connected three-capped triangular prism nodes (Figure 1f), respectively. Subsequently, a simplified nanocage was obtained as shown in Figure 1g, rendering an overall 3.9-connected \(ftw\) topology matrix (Figure 1h) with the short topology symbol, \((4^6)(4^62^8)\).\(^{51}\)

### ECUT-8 stability and porosity

The thermal stability of ECUT-8 was initially investigated by thermogravimetric analysis (TGA), resulting in the loss of solvent molecules before 340 °C (Supporting Information Figure S2). Notably, this MOF displayed ultrahigh thermal and chemical stability; for example, calcining at 350 °C for 24 h, stable after immersion in water or boiling water for 7 days, as well as immersion in acidic or alkaline solution at pH 3–12 for 24 h. This was confirmed by PXRD, shown as representative photographs of the samples in Figures 2a and 2b). After methanol exchange, the activated ECUT-8 samples were obtained by raising the temperature to 150 °C under vacuum. A type I profile of N\(_2\) adsorption at 77 K was observed for the activated samples (Supporting Information Figure S3). The Brunauer–Emmett–Teller (BET) surface area and pore volumes were 760 m\(^2\)/g and 0.34 cm\(^3\)/g, respectively. Besides, a narrow pore size distribution at 0.76 nm was observed, consistent with the aperture (0.8 nm) of [Th\(_8\)Co\(_8\)] cage.

### H\(_2\)/D\(_2\) Separation

Recent advances disclose that H\(_2\)/D\(_2\) separation could be achieved through the QS effect.\(^{33–40}\) Accordingly, two dominating methods emerged to obtain the QS effect, viz, designing ultramicroporous materials with windows or apertures of \(\sim 3.0\) Å and constructing porous materials with open-metal sites. Additionally, a very recent discovery disclosed that flexible MOFs could be effective candidates.\(^{37}\) Moreover, in a recent report, the combined QS effects were attested to be effective.\(^{39}\) In the literature, both the cryogenic thermal desorption spectroscopy (TDS) measurements and breakthrough experiments have been employed to confirm the actual separation ability of porous materials. By contrast, only limited cases were investigated through breakthrough experiments to be effective, presenting a commonly used method for evaluating separation.\(^{36}\)

The extremely narrow window in ECUT-8 exactly matches with the kinetic diameter of H\(_2\) and D\(_2\), suggesting that it might be suitable for H\(_2\)/D\(_2\) isotope separation. As shown in Figure 3a, ECUT-8 enabled high D\(_2\)
adsorption capacity up to 208 cm$^3$/g at 1 bar and 77 K. By contrast, H$_2$ uptake under the same condition was 186 cm$^3$/g, lower than D$_2$ uptake, which was $\sim$22 cm$^3$/g, indicative of selective adsorption of D$_2$ than H$_2$. These results in conjunction with the narrow window (3.0 Å) obtained in ECUT-8, implied a strong relationship between H$_2$/D$_2$ separation and the QS effect. To evaluate the binding energy between the MOF framework and hydrogen isotopes, we further carried out calculation of adsorption enthalpies ($Q_{st}$) for D$_2$ and H$_2$ applying the virial equation of state, with the use of the unary adsorption isotherm data at 77 and 87 K (Supporting Information Figure S4), giving 8.4 kJ/mol for D$_2$, stronger than the 7.9 kJ/mol obtained for H$_2$ at zero coverage (Figure 3b). The selective adsorption of D$_2$ over H$_2$ was then evaluated by the ideal adsorption solution theory (IAST), giving D$_2$/H$_2$ selectivity of 1.38 for an equimolar D$_2$/H$_2$ mixture at 77 K and 1 bar (Figure 3c). To further confirm its actual D$_2$/H$_2$ separation performance, the dynamic breakthrough experiment was performed using an ECUT-8 column set at 77 K and 1 bar with an H$_2$/D$_2$/Ne (10/10/80, vol %) mixture. Remarkably, H$_2$ was first eluted through the packed column after 19 min/g, whereas the retention time for D$_2$ was after 23 min/g, suggesting complete D$_2$/H$_2$ separation (Figure 3d).

**ECUT-8 flexibility**

It is well known that ZIF series constructed from imidazole or imidazolate-like ligands based on the local flexibility of imidazole or imidazolate-like ligands such as bending or swinging or rotating movement. This property often enables flexible adsorption, viz, the so-called gate opening, endowing the ZIF series to effectively adsorb molecules that show bigger size than the window of ZIF materials, consequently leading to the MS separation effect. For example, ZIF-8 displays a narrow six-ring window of $\sim$3.4 Å and a large cage of $\sim$11.4 Å, which is theoretically expected to separate hydrogen (2.9 Å kinetic diameter) from larger molecules like methane (3.8 Å) and nitrogen (3.6 Å). However, selective adsorption of larger molecules, as evidenced by experimental results and theoretical calculation, was observable mainly due to gate opening. This phenomenon of flexible adsorption was also observed in MIL-53. In ECUT-8, imidazolate-like ligands were used with a narrow window, which is expected to separate hydrogen from larger molecules such as methane and nitrogen.
six-ring narrow window analogous to ZIF-8; thus, flexible adsorption was also expected with this fabrication. In this regard, we first tested CO$_2$ adsorption, which showed a kinetic diameter of 3.3 Å, slightly larger than the window size (3.0 Å). As shown in Figure 4a, almost "step-shaped" adsorption and evident hysteresis were observed for CO$_2$ at 298 and 273 K, implying the existence of gate opening in ECUT-8.50 We confirmed this gate opening phenomenon further by exploring the effective aperture size in ECUT-8 using a series of probe molecules including C$_3$H$_4$ (4.2 Å), C$_2$H$_6$ (4.4 Å), and C$_3$H$_6$ (4.7 Å). The results are shown in Figures 4b–4d. Interestingly, in contrast to CO$_2$ molecules, C$_3$H$_4$ molecules afforded clearer "step-shaped" adsorption. Impressively, increasing the molecule size resulted in an observation of "two-step" gate opening for C$_2$H$_6$ (4.4 Å) and C$_3$H$_6$ (4.7 Å) molecules, where the first and second "step-shaped" transitions occurred at pressures of $\sim$1.2 kPa and $\sim$10 kPa, respectively. These results indicated that the flexibility of ECUT-8 allowed the adsorption of larger molecules. For molecular sizes in the 3.3–4.2 Å range, the framework showed "one-step" adsorption profiles. To enable the passage of molecules larger than 4.2 Å, a "two-step" gate opening was necessary, and to the best of our knowledge, such gate-opening phenomenon is not observable in ZIF series.

Butane and hexane isomer separation

Separation of the linear isomer from the branched isomers is necessary for the production of high-quality commodities in the petrochemical industry. For example, enhancing the research octane number (RON) and the subsequent upgrade of gasoline.32 For both butane and hexane isomers, their linear isomer and branched isomers showed similar physical and chemical properties, especially their comparable molecule size; thus, creating a major challenge for separation. More importantly, hexane isomer contains three components, namely, linear, monobranched, and dibranched isomers. Most porous adsorbents could separate the linear isomer from the monobranched isomer effectively; however, complete separation of the linear, monobranched, and dibranched isomers remains a challenging task.42–47
As discussed above, the flexibility in ECUT-8 permits it to exhibit a “two-step” gate opening effect, thereby allowing for the adsorption of large molecules. In this regard, ECUT-8 was presumed to enable the MS effect for butane and hexane isomer. First, we tested the adsorption of butane isomers (n-butane/n-C4H10 vs iso-butane/iso-C4H10), as shown in Figure 5a. The linear isomer of n-C4H10 gave the kinetic diameter of 4.7 Å, comparable with C3H6. Thus, a “two-step” gate opening was expected for n-C4H10. Indeed, this was observed for n-C4H10, where the pressures for the “two-step” gate opening were ∼1.2 and 6.3 kPa, respectively. The adsorption capacity of n-butane at 298 K and 100 kPa was as high as 3.5 mmol/g. This value exceeded that observed for most reported porous adsorbents such as ZU-36-Co (2.1 mmol/g),41 Y-fum-fcu-MOFs (2.0 mmol/g),52 and commercial 5A zeolite (1.3 mmol/g).41 By contrast, a new “one-step” gate-opening profile was observed for larger molecules like iso-butane (5.3 Å), with the corresponding gate-opening pressure of ∼6.3 kPa; thus, significantly reducing the iso-butane uptake to 1.2 mmol/g at 298 K and 100 kPa. These results indicated higher selective adsorption of n-butane over iso-butane due to the MS effect, resulting from the flexibility of the MOF framework.

The adsorption selectivity for equimolar n-butane/iso-butane mixtures was calculated to be 130.5 at 100 kPa and 298 K (Supporting Information Figure S5). This result

![Figure 5](image_url) **Figure 5** | Butane separation research. (a) The adsorption isotherms of n-butane and iso-butane at 298 K. The highlighted section is the “step-shaped” gate opening. (b) The breakthrough experiments on ECUT-8 column for n-butane and iso-butane at 298 K.

![Figure 6](image_url) **Figure 6** | The vapor adsorption of hexane isomers upon ECUT-8 at 298 K. (a) The adsorption isotherms of hexane isomers. (b) The adsorption kinetics of hexane isomers.
implied its outstanding potential in n-butane/iso-butane separation. Further, to confirm the actual separation potential, breakthrough experiments on the ECUT-8 column were carried out for an equimolar n-butane/iso-butane mixture at 298 K (Figure 5b). As anticipated, iso-butane flowed through the column almost immediately, suggesting that the iso-butane adsorption was excluded by ECUT-8, owing to the MS effect, fully consistent with the adsorption results and structural analysis. By contrast, n-butane was retained in the ECUT-8 column for a very long time, up to 70 min/g. The n-butane adsorption capacity is as high as 3.25 mmol/g, equal to 97% of the theoretical adsorption capacity (3.35 mmol/g at 0.5 bar). This value by far exceeded that of the benchmark material of ZU-36-Co (0.89 mmol/g).41 The productivity of the ECUT-8 long time, up to 70 min/g. The productivity of the ECUT-8 was as high as 68 mL/g, also by far exceeding the benchmark material of ZU-36-Co (17.5 mL/g).45 These results strongly suggested that ECUT-8 is superior regarding its application in C4 isomer separation.

As discussed above, with ECUT-8, the adsorption of a guest molecule with a size below 4.4 Å occurred through a “one-step” gate-opening mechanism, while the uptake of a guest molecule with a size of ~4.4–4.7 Å occurred through a “two-step” gate opening. As the size of guest molecules continued to increase, there was a significant reduction of guest molecule uptake due to the MS effect. In this regard, the flexibility in ECUT-8 could expand its effective window aperture to 4.7 Å. However, when the sizes of guest molecules were larger than the enhanced aperture, no adsorption was guaranteed due to the MS effect. The kinetic diameter of iso-butane was 5.3 Å and, therefore, was excluded from the pores, as demonstrated in the breakthrough experiments in Figure 5. The linear isomers of n-HEX had a kinetic diameter of 4.3 Å, close to the criterion required for an occurrence of “one-step” gate opening. The monobranched isomers of 3MP and 2MP had a larger kinetic diameter of 5.0 Å, a slightly larger size than that achievable with iso-butane. Accordingly, due to the MS effect, a reduced uptake for monobranched isomers was expected. As for the dibranched isomers of 23DMB and 22DMB, they afforded the largest kinetic diameter in the range of 5.6 and 6.2 Å, far exceeding all tested molecule probes; thus, no adsorption due to the MS effect was expected. In this regard, a complete separation of hexane isomer was achieved.

Figure 6a presents the results of hexane vapor adsorption at 30 °C. Ultrahigh n-HEX adsorption capacity up to 209 mg/g was observed that exceeded most top-performing adsorbents for this task,42–47 including Al-bttotb (151 mg/g),46 Ca-tcpb (150 mg/g),45 MIL-53(Fe)-(CF3)2 (32 mg/g),44 and Fe2(BDP)3 (113 mg/g).43 By contrast, the uptake of monobranched isomers was relatively lower, yielding 93.2 and 93.8 mg/g for 3MP and 2MP, respectively. Impressively, almost no adsorption (1.0 mg/g) and extremely low adsorption of 10.7 mg/g were observed for the dibranched isomers, 22DMB and 23DMB, respectively. These results were consistent with our expectations and suggested a potential for complete separation of a mixture of linear, monobranched, and dibranched isomers. Additionally, we performed an investigation on the adsorption kinetics of ECUT-8. As shown in Figure 6b, ECUT-8 shows high n-HEX uptake, moderate 2MP, and 3MP uptakes, low 23DMB uptake, and no uptake of 22DMB, agreeing well with the adsorption isotherms data. These differences in adsorption kinetics also implied its potential for total separation of hexane isomers.

All investigations in the published literature used multicomponent column breakthrough measurements with hexane vapor mixtures to test the separation capability of various MOFs in the partition of hexane isomers.42–47 From the standpoint of energy efficiency, it is preferable to carry out hexane isomer separation in the liquid phase because the boiling points of hexane isomers were above room temperature in the range of 323–341 K. Next, we confirmed the practical separation capability using a series of batch experiments with binary or ternary or quaternary mixtures in the liquid phase (Table 1 and Supporting Information Figures S6–S15). In each case, the activated ECUT-8 samples were immersed initially in the liquid-phase mixture. Subsequently, the adsorbed

Table 1 | A Summary of Hexane Separation Upon ECUT-8

<table>
<thead>
<tr>
<th>Entry</th>
<th>n-HEX</th>
<th>2MP</th>
<th>3MP</th>
<th>22DMB</th>
<th>Product</th>
<th>Purity (%)</th>
<th>Capacity (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td></td>
<td>n-HEX</td>
<td>&gt;99.9%</td>
<td>150</td>
</tr>
<tr>
<td>2</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td></td>
<td>n-HEX</td>
<td>&gt;99.9%</td>
<td>160</td>
</tr>
<tr>
<td>3</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td></td>
<td>n-HEX</td>
<td>&gt;99.9%</td>
<td>130</td>
</tr>
<tr>
<td>4</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td></td>
<td>3MP</td>
<td>&gt;99.9%</td>
<td>58</td>
</tr>
<tr>
<td>5</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td></td>
<td>2MP</td>
<td>&gt;99.9%</td>
<td>38</td>
</tr>
<tr>
<td>6</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td></td>
<td>3MP</td>
<td>&gt;99.9%</td>
<td>46</td>
</tr>
<tr>
<td>7</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td></td>
<td>n-HEX</td>
<td>&gt;99.9%</td>
<td>140</td>
</tr>
<tr>
<td>8</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td></td>
<td>3MP</td>
<td>&gt;99.9%</td>
<td>60</td>
</tr>
<tr>
<td>9</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>n-HEX</td>
<td>&gt;99.9%</td>
<td>110</td>
</tr>
</tbody>
</table>
contents were extracted using n-butyl acetate from the samples after drying naturally. Impressively, 100% pure linear n-HEX was recovered from the binary linear/monobranched or linear/dibranched mixtures. Also, a complete separation of monobranched isomers from monobranched/dibranched mixtures was realized. Even more remarkably, 100% pure 3MP was also separated from the 2MP/3MP binary mixtures. Further, sharp separation peaks were obtained with the ternary mixtures, with 100% recovery of pure n-HEX from n-HEX/3MP/22DMB mixtures, and 100% 3MP was recovered from 3MP/2MP/22DMB mixtures. Moreover, 100% n-HEX was recovered from a quaternary n-HEX/3MP/2MP/22DMB mixture. Collectively, these results strongly suggest that the complete separation of hexane isomer with 100% pure linear or 100% monobranched product is feasible, with attractive productivity. For example, 160, 140, and 110 mg/g pure n-HEX were recovered from the n-HEX/3MP, n-HEX/3MP/22DMB, and n-HEX/3MP/2MP/22DMB mixtures, respectively, while 46 mg/g pure 3MP was recovered from the n-HEX/3MP/2MP/22DMB mixture.

Figure 7 | The breakthrough research of hexane isomers upon ECUT-8 column at 298 K.

Figure 8 | (a) The time-dependent CO2 uptake profiles with the insert of the diffusivity calculation. (b) The recycle tests of breakthrough experiments on the separation of n-butane and iso-butane mixtures at 298 K (n-butane: 50%, iso-butane: 50%, flow rate of 2 min/L). (c) A comparison of n-butane and 1,3-butadiene adsorption isotherms at 298 K. (d) The breakthrough experiments on the separation of n-butane, iso-butane, and 1,3-butadiene mixtures.
recovered from a 3MP/22DMB mixtures. Even with 3MP/2MP mixtures, a high 3MP recovery of 58 mg/g was realized. To further confirm the practical separation capability, we also, for the first time, carried out direct separation via multicomponent column breakthrough measurements with a four-component liquid-phase mixture (Figure 7). The results show that ECUT-8 was capable of separating hexane isomers into individual components. 22DMB broke first from the ECUT-8 column after 24 s/g, with the retention times for 2MP, 3MP, and n-HEX being 42, 58, and 72 s/g, respectively.

Diffusion, recycling, stability, and other applications of ECUT-8

The diffusivity of a gas molecule that passes through porous adsorbents is another critical factor for the separation application. For ECUT-8, the diffusivity was investigated using a CO₂ molecule. Figure 8a shows the time-dependent CO₂ uptake profiles, revealing a fast adsorption equilibrium within 10 min. The diffusivity was calculated to be 3.1 x 10⁻¹⁰ m²/s, comparable with that observed in other porous adsorbents.²² Besides, investigating recycling and stability properties of nanocaged MOF materials after breakthrough experiments is also crucial in determining their application in materials' separation. Thus, we investigated the recycling capability of ECUT-8 using breakthrough experiments for the separation of n-butane and iso-butane mixture at 298 K. After three repetitions of the process, there was no apparent decrease in separation performance (Figure 8b). The maintenance of framework integrity was further confirmed by PXRD patterns obtained from the samples after completing the breakthrough experiments (Supporting Information Figure S16). Moreover, the separation of C₄ isomers was extended further to 1,3-butadiene. The adsorption isotherm of 1,3-butadiene at 298 K showed a “one-step” gate-opening profile (Figure 8c). The uptake at 298 K and 1 bar was up to 3.3 mmol/g, comparable with the uptake of n-butane (3.5 mmol/g), but far higher than the uptake of iso-butane (1.2 mmol/g). Breakthrough experiments for n-butane, iso-butane, and 1,3-butadiene mixtures at 298 K were carried out to evaluate the actual separation capacities. Interestingly, complete separation of n-butane, iso-butane, and 1,3-butadiene mixtures were observed (Figure 8d), with a breakthrough time of 4.7 min/g for n-butane, 44 min/g for iso-butane, and 90 min/g for 1,3-butadiene, respectively. The separation of 1,3-butadiene from iso-butane was due to the selective adsorption of 1,3-butadiene over iso-butane. Although ECUT-8 showed comparable adsorption of 1,3-butadiene from n-butane; however, the real separation of 1,3-butadiene from n-butane might have resulted from the differences in the adsorption type such as “one-step” gate opening for 1,3-butadiene versus “two-step” gate opening for n-butane.

Conclusion

In this work, we report the synthesis, structure, and adsorption properties of a rare and highly rare 3d-5f bimetal cage-based MOF called ECUT-8, which exhibited a combination of QS and MS characteristics. ECUT-8 contained a unique [Th₆Co₆] nanocage with 3.0 Å windows, fulfilling the criterion to demonstrate the QS effect for H₂/D₂ separation. Additionally, due to the flexibility of imidazolate-derivative ligands observable in ZIFs, the effective aperture of ECUT-8 was expandable, and consequently, molecules with kinetic diameters <5.6 Å could pass through the window of ECUT-8 utilizing “one-step” or “two-step” gate-opening mechanisms. This afforded the MS property necessary for isomer separation. Breakthrough experiments have provided convincing evidence for ECUT-8 to perform clear separations of both H₂/D₂ isotopes and butane/or hexane isomers due to the distinctive feature of coexistence of both QS and MS effects in ECUT-8.

Supporting Information

Supporting Information is available and includes experiments in detail, Figures S1–S16, and Table S1.

Conflict of Interest

There is no conflict of interest to report.

Preprint Acknowledgment

The research presented in this article was posted on a preprint server prior to publication in CCS Chemistry. The corresponding preprint article can be found here: https://doi.org/10.21203/rs.3.rs-99357/v1

Acknowledgments

This work was supported financially by the National Natural Science Foundations of China (nos. 21966002, 21871047, and 21861017), the Natural Science Foundation of Jiangxi Province of China (no. 20181ACB20003), and the Training Program for Academic and Technical Leaders of Major Disciplines in Jiangxi Province (no. 20194BCJ22010).

References


Fluorinated MOF for Enhancing H2 Desorption Temperature

Exploiting Dynamic Opening of Apertures in a Partially


