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One-of-A-Kind: A Microporous Metal-Organic Framework Capable of Adsorptive Separation of Linear, Mono- and Di-branched Alkane Isomers via Temperature- and Adsorbate-Dependent Molecular Sieving

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Separation of alkane isomers represents a crucial process in the petrochemical industry in order to achieve high octane rating of gasoline. Herein, we report the first example of complete separation of linear, monobranched and dibranched alkane isomers by a single adsorbent. A calcium-based robust microporous metal-organic framework, Ca(H₂tcpb) (tcpb = 1,2,4,5-tetrakis(4-carboxyphenyl)-benzene) exhibits unique molecular exclusion behavior which enables full separation of binary or ternary mixtures of alkane isomers into pure form of each isomerate. The successful separation of monobranched and dibranched alkane isomers will not only lead to the production of higher quality gasoline with maximum possible octane numbers but also fill the gap in the current separation technology. Exploration of separation mechanism indicates that structural flexibility and adsorbate-dependent structure change of the porous framework plays a vital role for the observed temperature-dependent molecular sieving property of the adsorbent.

Chemical separations that convert chemical mixtures into pure or purer forms are energy-intensive processes, accounting for 10-15% of the global energy consumption.[1] Developing more energy-efficient separation methods is, therefore, pivotal to reduce the energy usage and suppress carbon dioxide emission. The separation of alkane isomers based on their degree of branching represents a critical yet challenging process in the petrochemical industry.[2] During oil refinement, light naphtha fraction (mostly straight-chained C5 and C6) undergoes catalytic isomerization and generates a mixture of linear, monobranched, and dibranched isomers. Isomers of a higher degree of branching usually possess higher research octane number (RON). For example, the RONs of 3-methylpentane (75) and 2,2-dimethylbutane (94) are much higher than that of their linear isomer n-hexane (25). Thus, to produce gasoline with high RON, alkane isomers with low RON need to be removed from the mixture and recycled back into the catalytic reactor. Distillation is a conventional process to separate alkane isomers. However, in light of the high energy consumption associated with heat-driven distillations, more energy-efficient adsorptive separation has been developed and employed as an alternative/supplementary technology for alkane isomers separation.

The current benchmark sorbent for the separation of alkane isomers is zeolite 5A, which behaves as a molecular sieve. Due to its suitable pore aperture, it adsorbs linear alkanes only and excludes all branched isomers, and is thereby capable of removing linear alkanes from the isomerate mixtures. The adsorbed linear alkanes are subsequently sent back to the catalytic reactor where they then undergo additional cycles. However, since zeolite 5A cannot be used to separate monobranched and dibranched isomers, new adsorbent materials that possess such capability is much needed, as separation of alkanes with different degree of branching is a critical step to produce higher quality gasoline with further improved RONs. Tremendous effort has been made to achieve this goal, including the use of a fixed bed of silicalite or zeolite membranes.[3-6] However, because of the stringent requirement on the matching pore aperture of the adsorbent and kinetic diameter of the adsorbate, it has been extremely difficult to find a suitable candidate for this process, as such, to this date adsorptive separation of monobranched and dibranched alkanes has not been implemented in real-world systems and search for ideal sorbent materials remains ongoing.[7]

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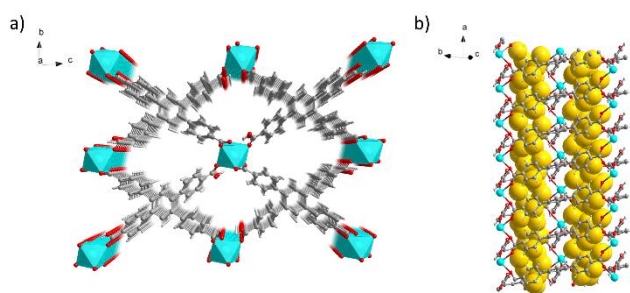
Fig. 1 (a) Crystal structure of Ca(H$_2$tcpb) showing the 1D open channels. (b) The shape of 1D channels outlined by adsorbed helium atoms. Helium adsorption simulation was performed at 1 K and 1 bar. Colour scheme: Ca: magenta, O: red, C: grey, He: gold.

The emergence of metal-organic frameworks (MOFs) offers new opportunities for industrially challenging chemical separations given their highly tunable pore size, pore shape, and surface functionality.[8, 9] Indeed, MOFs have shown enormous advantages and outperformed traditional sorbents in a number of industrially relevant separations including CO$_2$ capture,[10, 11] propane/propylene separation,[12, 13] and acetylene/ethylene separation,[14] to name a few. Extensive research on MOFs has revealed their usefulness for the separation of alkane isomers.[15, 16] While several MOFs can efficiently separate linear and monobranched alkanes with comparable or even better performance with respect to zeolite 5A, an ideal MOF for discriminating monobranched and dibranched isomers has yet to be discovered. Long et al. Reported the thermodynamic separation of hexane isomers by Fe$_2$(BDP)$_3$, a microporous MOF with triangular channels.[15] While all isomers can be adsorbed due to the relatively large pore size, they show different adsorption affinity and thus the adsorbent can discriminate linear, monobranched, and dibranched isomers from a ternary mixture. Y-fum and ZIF-8 are two representative MOFs that show excellent separation of linear and monobranched alkanes,[7, 16] but like zeolite 5A, they cannot separate monobranched and dibranched isomers. Adsorbents that show dicrimination between mono- and di-branched alkanes include zeolite BETA,[17] MFI,[18] Zn$_2$(HBDC)$_2$(dmtrz)$_2$,[19] Fe$_2$(BDP)$_3$,[15] and Fe$_3$O(6FDCA)$_3$,[20] to name a few, however, the separation by these materials is achieved by moderate differences in either adsorption affinity or rates, which leads to relatively low selectivity and efficiency. In this work we demonstrate, for the first time, that the separation of monobranched and dibranched alkane isomers can be achieved by a microporous MOF, Ca(H$_2$tcpb), through selective molecular exclusion.[21, 22] More importantly, using temperature programming this compound is capable of separating a ternary mixture of linear, monobranched, and dibranched alkanes into pure components through temperature- and adsorbate-dependent size sieving.

Ca(H$_2$tcpb) was synthesized via solvothermal reactions of CaCl$_2$ and H$_4$tcpb in ethanol at 100 °C for 3 days (See Supporting Information for synthesis details).[22] In its crystal structure, Ca^{2+} ions are six-coordinated by carboxylate oxygen atoms, and the CaO$_6$ octahedra are connected through H$_2$tcpb^{2-} linkers to form a three-dimensional (3D) framework with 1D open channels

running along the crystallographic *a*-axis (Fig. 1). The material has a BET surface area of ~ 220 m^2 g^{-1}, and the pore size distribution shows the size of the 1D channel is 5.5-6 Å (Fig. S2), consistent with the pore diameter measured from the as-synthesized crystal structure (~5.5 Å, distance between H-H, excluding Van der Waals radii). This pore size is close to the kinetic diameters of branched alkanes (5.0-6.2 Å). Additionally, this compound was selected as a candidate for the separation of alkane isomers because it is thermally robust (Fig. S3), and it retains its crystallinity after 3 years on a shelf (Fig. S4). More importantly, it exhibits high moisture stability and hydrophobic character.[22] The activated structure does not adsorb water moisture after exposure to open air for 5 days (Fig. S5).

We collected adsorption isotherms of three C6 alkane isomers with different degree of branching on Ca(H$_2$tcpb) at various temperatures (30, 60, 90, 120, and 150 °C, Fig. 2a-c). The isotherms of n-hexane (nHEX) at 30-120 °C show uptake capacities comparable to those of zeolite 5A and other reported MOFs. However, its isotherm at 150 °C exhibits a dramatic decrease in uptake amount. For 3-methylpentane (3MP), high uptake is also achieved at 30 °C but as the temperature increases to 60 and 90 °C, the adsorbed amount decreases significantly. At 120 and 150 °C there is essentially no adsorption up to ~ 120 torr. Strikingly, the MOF compound adsorbs negligible 2,2-dimethylbutane (22DMB) at all temperatures examined except 30 °C. It is worth to mention that full adsorption equilibrium was reached for each pressure point during the collection of these isotherms and no diffusional restriction was observed. Undoubtedly, the observed highly temperature- and adsorbate-dependent adsorption is not solely thermodynamically controlled, but should be partially attributed to the framework flexibility of the MOF adsorbent, as discussed in more detail below.

The anomalous adsorption phenomena observed here are interesting as they suggest a considerable potential for separating alkanes as a function of branching using this MOF adsorbent. As seen from the adsorption isotherms shown in Fig. 2d-e, at 60 °C the compound adsorbs nHEX and 3MP but excludes 22DMB while at 120 °C it adsorbs only the linear isomer. To the best of our knowledge, this is the first example where a sorbent shows complete size sieving toward monobranched and dibranched alkanes. It is noteworthy to mention that the adsorption of nHEX and 3MP at 60 and/or 120 °C shows fast kinetics, reaching equilibrium within 1-2 minutes (Fig. 2d-e, inserts). We thus designed a two-column system for breakthrough experiments, aiming at separating a ternary mixture of nHEX, 3MP, and 22DMB into chemically pure components. Fig. 2f depicts a schematic representation of the separation setup. The rationale is as follows: When the ternary mixture passes through the first column packed with MOF powder at 120 °C, nHEX will be adsorbed and retained in the column while the branched isomers (3MP and 22DMB) will be eluted out without retention. The eluted binary mixture is subsequently directed to the second column packed with MOF powder at 60 °C where 3MP will be retained but not 22DMB. Hence the initial ternary mixture can be separated into three chemically pure and individual components.
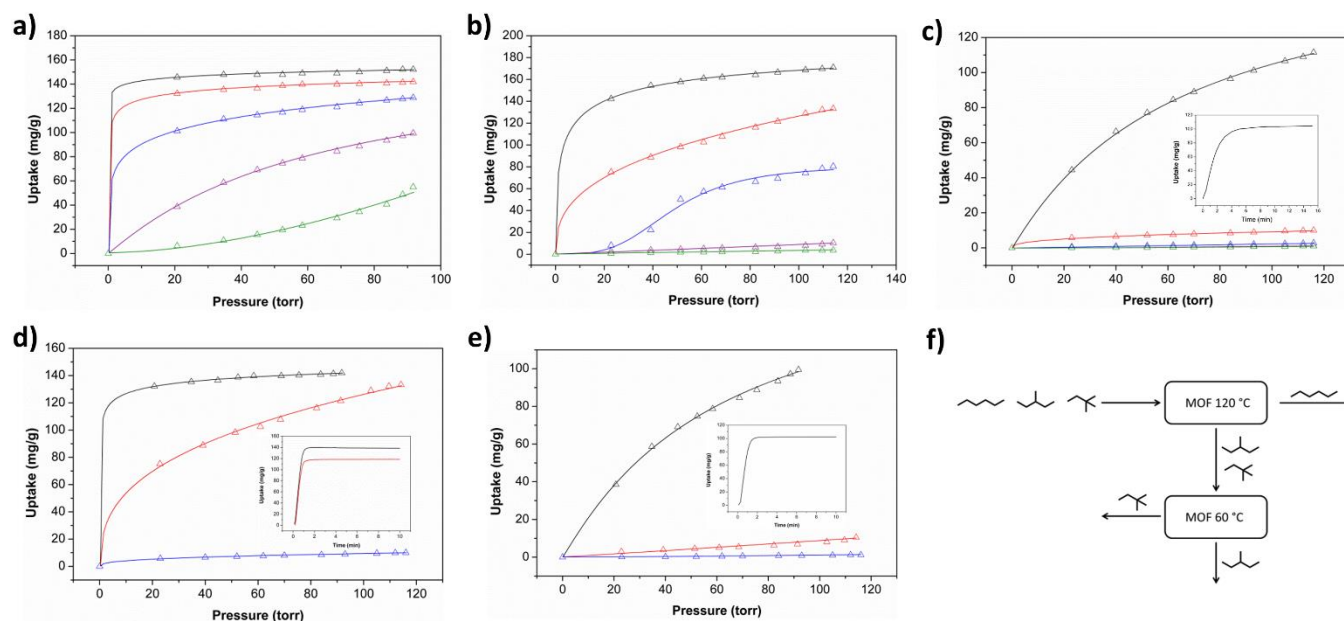
Fig. 2 Adsorption isotherms of (a) nHEX, (b) 3MP, and (c) 22DMB (insert: adsorption rate of 22DMB at 30 °C) at 30 °C (black), 60 °C (red), 90 °C (blue), 120 °C (purple), and 150 °C (green). Comparison of adsorption of nHEX (black), 3MP (red), and 22DMB (blue) at (d) 60 °C and (e) 120 °C (inserts: adsorption rates of the corresponding isomers at 100 torr). (f) Schematic representation of the proposed temperature programmed separation of C6 alkane isomers.

Experimental measurements confirmed the feasibility of the proposed separation process (See Supporting Information for column breakthrough measurements details). As shown in Fig. 3a and 3d, when an equimolar ternary mixture of nHEX, 3MP, and 22DMB was injected into the two-column system, a clean separation was observed for the three components. nHEX was retained in the columns for the longest time of 156 minutes while 3MP broke at the 62nd minute, indicating adsorption of both nHEX and 3MP but the adsorbed amount of the former was much more substantial than that of the latter. This is consistent with the single component adsorption isotherms and our design rationale as 3MP was only adsorbed at 60 °C (not 120 °C). In contrast, 22DMB eluted out from the system immediately without any retention, confirming that adsorption did not occur at either 60 or 120 °C. This is significant since the MOF sorbent is not only capable of separating 3MP and 22DMB through size sieving, but more importantly, it offers a clean separation of all three isomers (linear, monobranched, and dibranched) via selective molecular sieving. To further confirm that the separation occurrs in compliance with the proposed mechanism, we broke down the two-column system into two single-column setups. We first performed a breakthrough experiment with an equimolar binary mixture of nHEX and 3MP at 120 °C, as shown in Fig. 3b. The results show that 3MP breaks at the 2nd minute while retention of nHEX lasts for as long as 58 minutes (Fig. 3e). This is in good agreement with the single component adsorption isotherms since Ca(H$_2$tcpb) adsorbs ~88 mg/g of nHEX but negligible amount of 3MP at 120 °C and 72 torr (partial pressure under dynamic breakthrough measurement). The other single-column breakthrough

measurement was conducted with an equimolar binary mixture of 3MP and 22DMB at 60 °C as shown in Fig. 3c. A clean separation between these two components was observed where 22DMB eluted out from the column immediately while retention of 3MP in the column lasted for 38 minutes before breaking (Fig. 3f). Again, this is in good agreement with the single-component adsorption results where the material uptakes a substantial amount of 3MP but no 22DMB at 60 °C. Results from multicomponent breakthrough experiments confirm that, different from the aforementioned adsorbents that have been studied for the separation of mono- and di-branched alkanes via thermodynamic mechanism (as in all cases both adsorbates are adsorbed), the neat separation of mono- and di-branched alkanes by Ca(H$_2$tcpb) is through a size exclusion mechanism, which renders it a very high separation selectivity. Accordingly, we confirm that temperature-programmed selective molecular exclusion can be applied to achieve separation of the ternary mixture.

Taking into consideration of the hydrophobic feature of the MOF channels, we further performed a column breakthrough experiment with a binary mixture of 3MP and 22DMB in the presence of moisture (50% RH) to explore the influence from competitive adsorption of water (Fig. S13). The dynamic 3MP adsorption capacity is 55.4 mg g^{-1} (compared to 57 mg g^{-1} under dry and equivalent conditions), indicating that Ca(H$_2$tcpb) is capable of retaining its separation ability under humid conditions. It is of great importance for a compound to possess such a crucial property since competitive adsorption of water poses a common and challenging issue that often greatly impedes the adsorption/separation ability of MOFs.[23, 24]
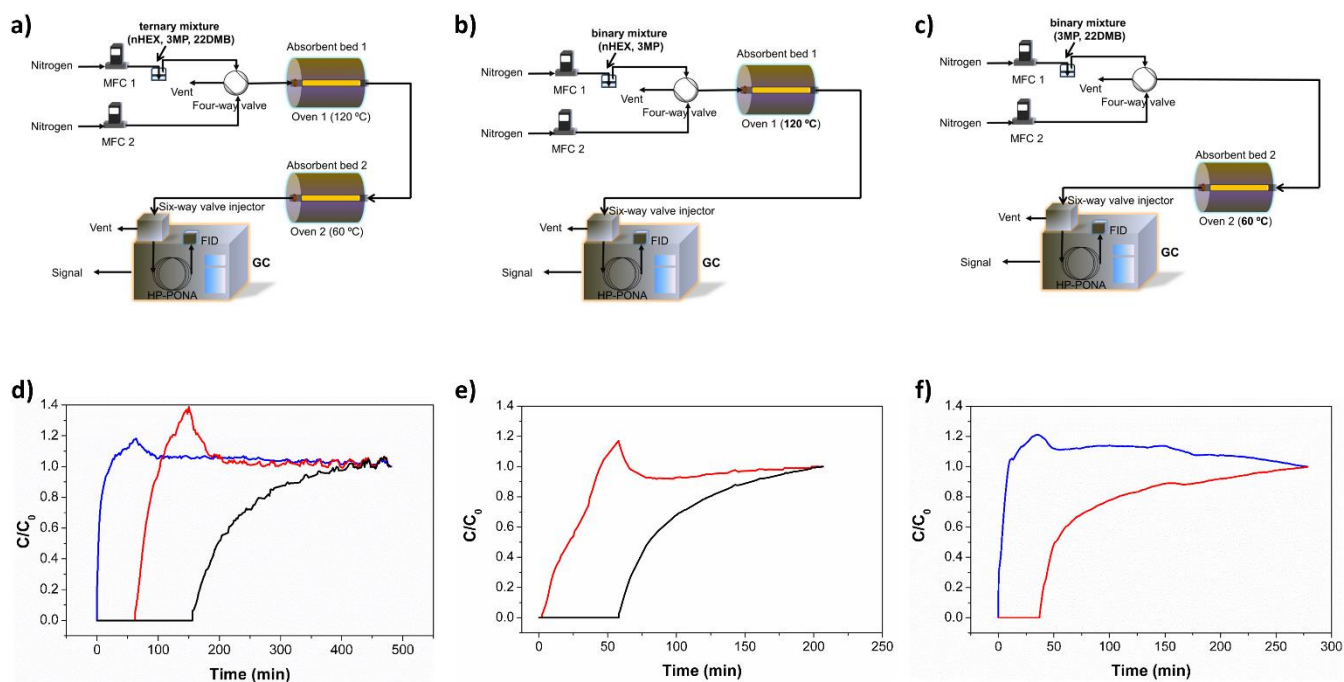
Fig. 3 Schematic setup (top row) and results (bottom row) of the multicomponent column breakthrough experiments for the ternary mixture of nHEX, 3MP, and 22 DMB (a and d), binary mixture of nHEX and 3MP (b and e), and binary mixture of 3MP and 22DMB (c and f). Colour scheme: black (nHEX), red (3MP), blue (22DMB).

We postulate that the framework flexibility and adsorbate-dependent structure change play an important role in the unique adsorption behavior of Ca(H$_2$tcpb). The pore-opening of the activated compound is governed by a cooperative interaction between a specific adsorbate molecule and the framework which is also temperature dependent. This phenomenon is similar to the breathing effect reported for several MOFs.[25-28] Structural flexibility can be advantageous for molecular separation.[27, 29] The material may be suitable for multicomponent separation when its framework breathing is temperature- and adsorbate-dependent. In such a case, when one adsorbate triggers pore opening at a given temperature, other adsorbates in the mixture cannot diffuse into the pores, resulting in high adsorption selectivity. Ca(H$_2$tcpb) represents a good example of such nature. As shown in Fig. 2b, the structural breathing (gate-opening) is evident in the isotherm at 90 °C as indicated by the step at ~ 40 torr. Appreciable adsorption takes place after this point. At higher temperatures (120 and 150 °C), the material takes up negligible amount of 3MP, as the pressure applied (up to ~120 torr) is insufficient to induce the pore opening at these temperatures. For 22DMB, on the other hand, essentially no adsorption takes place at temperature as low as 60 °C. A clear trend can be deduced based on these observations: at a given temperature, the larger the adsorbate molecule, the higher pressure (driving force) is required to open the pores. Likewise, the larger the adsorbate molecule, the lower temperature is required to open the pores. This behavior is retained in their binary mixture and is confirmed by the breakthrough results shown in Fig. 3f, where at 60 °C only 3MP

is being adsorbed and 22DMB is excluded. Similarly, the breakthrough results plotted in Fig. 3e for a nHEX/3MP binary mixture, and in Fig. 3d for a nHEX/3MP/22DMB ternary mixture further confirm that the sorbate- and temperature-dependent adsorption of Ca(H$_2$tcpb) applies to all three adsorbate molecules.
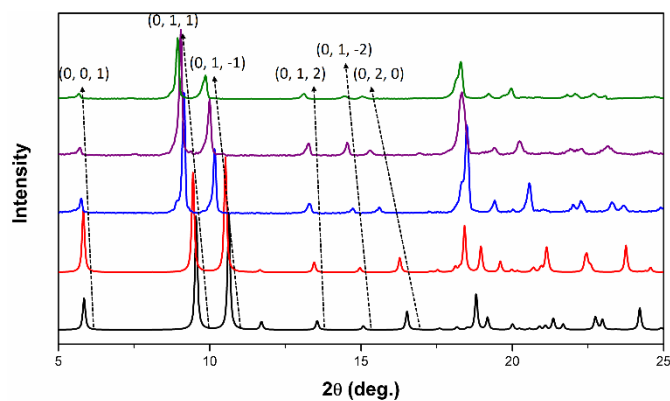
Fig. 4 PXRD patterns of various forms of Ca(H$_2$tcpb). Several important diffraction planes are indicated in the figure. From bottom to top: black (activated), red (as synthesized, loaded with H$_2$O), blue (loaded with nHEX), purple (loaded with 3MP), green (loaded with 22DMB).

To provide additional support to the above hypothesis and to better understand the correlation between the changes in the structure and observed unique adsorption behavior, we performed structural analysis on the MOF samples loaded with different alkane isomers. Our attempts to determine alkane

loaded structures by single-crystal X-ray diffraction were unsuccessful, as the alkane loading causes cracking of the single crystals, which resulted in poor diffraction data. However, the powder samples remain highly crystalline and the crystal strucutre was not affected upon alkane loading, as evident from the PXRD pattens taken after the adsorption experiments (Fig. 4, Figs. S7, S9, S11 and S16b).

We were able to obtain useful information by comparing the structures of the as-synthesized (Ca(H$_2$tcpb)·xH$_2$O) and activated (Ca(H$_2$tcpb)) form (Table S1).[22] Upon activation, the as-synthesized compound underwent a framework contraction, due to the removal of water molecules in the channels.[30] By analyzing their crystallographic data, we found that the main differences between the as-synthesized and activated structures lie in the b-axis and β angle. The length of b-axis reduces from 11.0274 to 10.8715 Å and the angle of β decreases from 87.657 to 85.982°. Changes associated with other unit cell parameters are negligible. We also noted a reduction of unit cell volume from 856.57 to 831.37 Å^3. A reverse structural variation was observed when the activated sample was loaded with alkane molecules at 30 °C. Based on the powder X-ray diffraction data (Fig. 4, Fig. S7, S9 and S11), a nice correlation can be drawn between the changes of the crystallographic parameters (expansion of b and β) and the pore size/shape of the MOF (Fig. S12). Clearly the observed structure changes from Ca(H$_2$tcpb) to Ca(H$_2$tcpb)·y(alkane) (primarily increase in the b-axis of the unit cell, Fig. S12b) are directly associated with the increase in the effective pore size of the MOF (Fig. S12c).[31] This structural change is reversible, continuous, and adsorbate-dependent. The extent of such changes also depends on the adsorbate size: the larger the molecualr size, the more significant the change. In addition, we examined the adsorption affinity of the isomers by temperature-programmed desorption and the results confirmed the follow order: nHEX > 3MP > 22DMB for this MOF, (Figure S19). The desorption energies are 78.9 and 74.8 kJ/mol, for nHEX and 3MP, respectively, in good agreement with the fact that it requires a lower pressure for nHEX to induce the structral change than that of 3MP at the same temperature.[32] This is also in accordance with previous reported results that channel-like pores show stronger adsorption affinity toward linear alkanes over their branched isomers due to more sufficient contact. Thus, the observed unique temperature- and adsorbate-dependent adsorption behavior can be attributed to the combined effect of molecular size of the alkane isomers and the extent of their interaction with the MOF: Having smallest size and strongest binding with the adsorbent, nHEX is capable of opening the pore sufficiently large to allow it to enter at a significantly higher temperature (120°C), while a lower temperature (60 °C) is required for larger-sized and less-binding 3MP to enlarge the pore window further for it to diffuse in. For the largest and least-binding 22DMB, this can be achieved only at a much lower temperature (30 °C).

To explore the generality of the adsorption behaviors toward alkanes by Ca(H$_2$tcpb), we conducted additional adsorption measurements with some other readily available alkanes including C5 and C7 isomers n-pentane (nPEN), 2-methylbutane (2MB), and n-heptane (nHEP) which are also components of gasoline. Their adsorption profiles are similar and follow the same trend as C$_6$ alkane isomers (Fig. S14 and 15). In order to evaluate the recyclability of the adsorbent, we carried out recyclability tests for both single-component adsorption experiments and ternary mixture breakthrough measurements with 12 and 5 cycles, respectively. The results (Figs. S16 and S17) demonstrate that no loss of adsorption capacity or separation capability was observed during these tests and the structural integrity of the adsorbent was well maintained after all cycles. In addition, we also performed a breakthrough test with pure hydrocarbon as a feed (a binary liquid mixture of 3MP and 22DMB) without using a carrier gas, where the mixture was pumped directly into the adsorbent bed. The results show the separation capbility of the adsorbent is well retained (Figure S18). These results further confirm the capability of Ca(H$_2$tcpb) to separate alkane isomers having different degree of branching. In light of its high stability, hydrophobicity, and excellent separation performance toward alkane isomers, Ca(H$_2$tcpb) holds great promise for RON upgrading of gasoline.

Adsorptive separation of similar molecules is challenging as it requires precise control of the pore structure and/or functionality of the adsorbent. In this work, we show, for the first time, separation of monobranched and dibranched alkanes can be attained through selective molecular sieving by a microporous MOF. In addition, a ternary mixture of linear, monobranched, and dibranched alkane isomers can be separated into chemically pure individual components by the same MOF adsorbent through temperature programming. Such processes will not only produce high quality gasoline with the maximum possible RON but also fill the gap in the current adsorption-based separation technology. Another rare yet highly desirable property is that the MOF retains its separation performance in the presence of moisture, most likely due to its hydrophobic nature. This is required for real-world separation technology. X-Ray diffraction analysis provides direct evidence correlating the flexibility of the framework and adsorbate-dependent strucutre change to the selective adsorption of the MOF.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Notes and references

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