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Kinetic Separation of Hexane Isomers by Fixed-Bed Adsorption with a Microporous Metal−Organic Framework

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A three-dimensional microporous metal−organic framework Zn(BDC)(Dabco)$_{0.5}$ (BDC = 1,4-benzenedicarboxylate, Dabco = 1,4-diazabicyclo [2,2,2]octane), having two types of intersecting pores to encapsulate linear hexane and to block branched hexanes, and thus exhibiting highly selective sorption with respect to *n*-hexane, has been successfully applied to the kinetic separation of hexane isomers by fixed-bed adsorption.

Porous metal−organic frameworks (MOFs), which are new types of zeolite analogues, have been of significant interest because of their potential applications in gas storage, separation, heterogeneous catalysis, and sensing.[1−14] Unlike traditional porous zeolite materials whose pores are confined by tetrahedral oxide skeletons and thus difficult to be tuned, the pores within MOFs can be systematically varied by the judicious choice of metal-containing secondary building units (SBUs) and/or bridging organic linkers. This superior feature is significantly important to develop novel functional materials for gas separation, which are based on their selective sorption behaviors and mainly determined by size exclusive effect in which smaller molecules can go through the microporous channels while larger substrates are blocked.

The separation of hexane isomers to boost octane ratings in gasoline has been a very important process in the petroleum industry and predominantly practiced by cryogenic distillation, although some alternative technologies such as ISOSIV process have been developed.[15] Because the distillation process is highly energy consuming, there is an increasing demand to develop novel materials and technologies as alternative processes to traditional distillation. By making use of pore space to take up and discriminate hexane isomers, the emerging porous MOFs show the promise for kinetic separation of hexane isomers by fixed-bed adsorption; however, this has never been realized. As shown in Figure 1, the kinetic diameters of *n*-hexane (nHEX), 3-methylpentane (3MP), and 2,2-dimethylbutane (22DMB) are slightly different at 4.3, 5.0, and 6.2 Å, respectively;[16] thus the micropores within MOFs need to be deliberately designed with suitable pore size/curvature for such kinetic separation. To make use of three-dimensional intersecting pores of about 7.5 Å × 7.5 Å along axis [100] and pores of 3.8 Å × 4.7 Å along axes [010] and [001] for the storage and discrimination of hexane isomers, we herein report the first example of microporous MOFs Zn(BDC)(Dabco)$_{0.5}$ (MOF **1**) (BDC = 1,4-benzenedicarboxylate, Dabco = 1,4-diazabicyclo[2,2,2]octane)[17] for kinetic separation of hexane isomers.

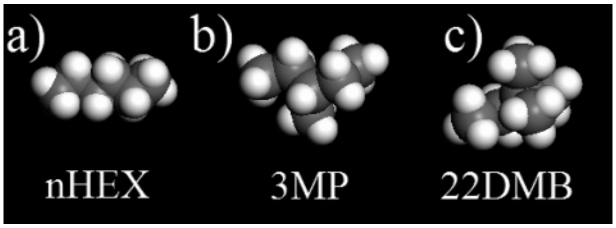

Figure 1. (a) CPK models of *n*-hexane, (b) 3-methylpentane, and **(c)** 2,2-dimethylbutane.

As revealed in the X-ray single-crystal structure by Kim et al., Zn(BDC)(Dabco)$_{0.5}$ (MOF **1**) is constructed of paddle-wheel $Zn_2(COO)_4$ clusters bridged by BDC dianions and Dabco pillar linkers to form a three-dimensional framework of a primitive cubic (α-Po) net.[17] There exist two types of intersecting channels of about 7.5 Å × 7.5 Å along the *a*-axis and channels of 3.8 Å × 4.7 Å along *b* and *c* axes, respectively (Figure 2 and Supporting Information Figure S1). It is expected that the hexane isomers nHEX, 3MP, and 22DMB can go through the channel of 7.5 Å × 7.5 Å along the *a*-axis; however, the van der Waals interactions between linear nHEX with the microporous walls will be stronger because of its more van der Waals interaction sites attributed to its long chain and small kinetic diameter. Of the most interest are the channels of 3.8 Å × 4.7 Å along *b* and *c* axes, which can take up the linear nHEX but block the branched 3MP and 22DMB, thus the hexane isomers might be kinetically separated by fixed-bed adsorption with such a simple microporous MOF.

Single-component breakthrough experiments were carried out initially to examine the feasibility and capability of MOF **1** for

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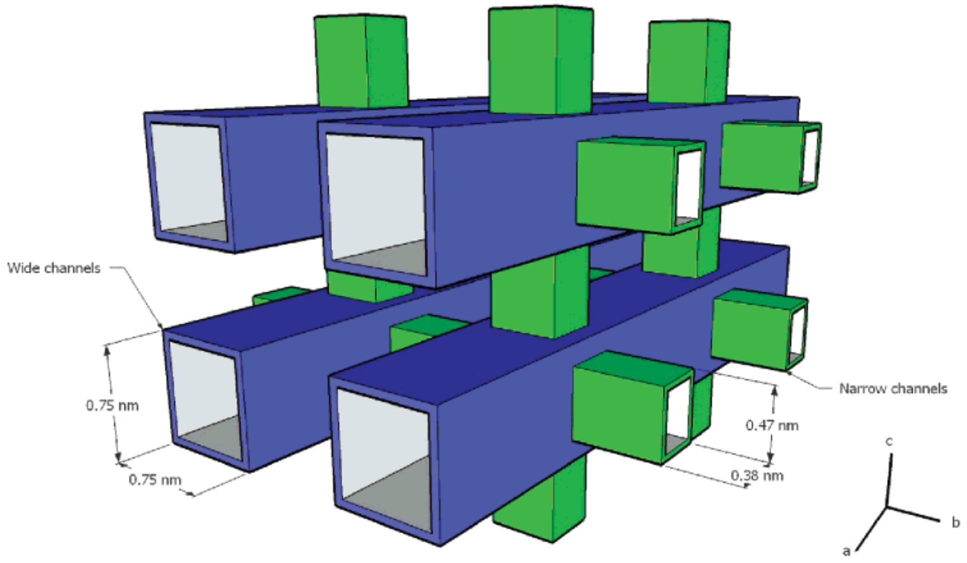

Figure 2. Perspective illustration of 3D intersecting channels in the X-ray crystal structure of Zn(BDC)(Dabco)$_{0.5}$ of 7.5 Å × 7.5 Å along *a*-axis, and 3.8 Å × 4.7 Å along *b* and *c* axes.

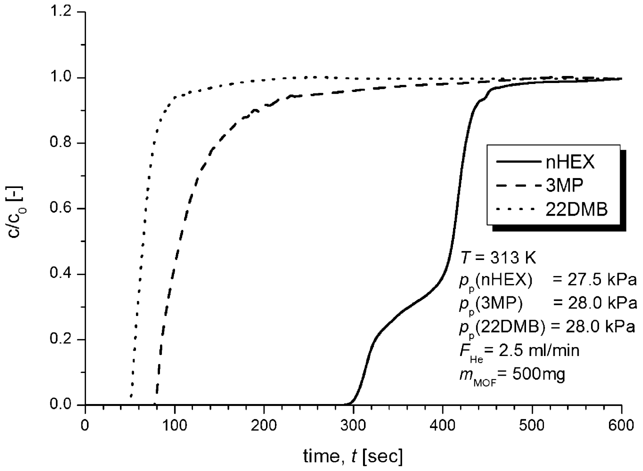

Figure 3. Pure component breakthrough curves for 22DMB, 3MP, and nHEX at $T = 313$ K and $p = 28$ kPa.

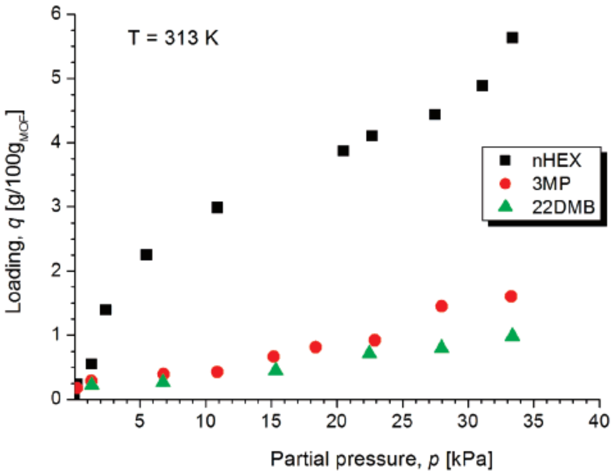

Figure 4. Pure-component adsorption isotherms of 22DMB (green), 3MP (red), and nHEX (black) at $T = 313$ K.

kinetic separation of hexane isomers at 313 K. As shown in Figure S2 (Supporting Information) and Figure 3, their breakthrough times are quite different, from 100 s for 22DMB to 200 s for 3MP and to 900 s min for nHEX at partial pressure near 6 kPa. When the partial pressure is increased to 28 kPa, their breakthrough times are systematically reduced to 60 s for 22DMB, to 100 s for 3MP, and to 400 s for nHEX, respectively. The different breakthrough times of the order nHEX > 3MP > 22DMB indicate that the adsorption strengths of the hexane isomers to MOF **1** decrease as the degree of branching increases simply because of their different van der Waals interactions with the microporous walls and the confinement of nHEX within the small pores. nHEX can have the access to all three intersecting channels, thus its interaction with MOF **1** is significantly stronger than other two isomers. The pure component breakthrough curve of nHEX at a temperature of 313 K (Figure 3) clearly indicated that there exist two types of interaction sites of nHEX with MOF **1**, which are attributed to two types of intersecting channels for the access of nHEX in the MOF **1**.

To figure out the kinetic separation condition with the aim to optimize and maximize the separation selectivity and capacity of MOF **1** for binary and ternary hexane isomers, pure-component adsorption isotherms were established from single breakthrough curves. As shown in Figure 4 and Figure S3 (Supporting Information), the adsorption capacities of MOF **1** for nHEX reach to 5.5 wt % at 313 K and 33 kPa, and 4.0% at 343 K and 33 kPa, respectively, which are not saturated. As both 22DMB and 3MP have the only access to the channels of 7.5 Å × 7.5 Å along the *a*-axis, the adsorption capacities of MOF **1** for 22DMB and 3MP are significantly lower than those for nHEX. 3MP is longer than 22DMB, which leads to its slightly higher sorption capacities.

The potential of MOF **1** for kinetic separation of hexane isomers by fixed-bed adsorption was finally realized by binary and ternary breakthrough experiments. At low partial pressure of 0.7 kPa, the mixture of 22DMB and 3MP can be easily separated with breakthrough time of 500 and 1200 s, respectively (Figure S4a). The separation efficiency decreases when the partial pressure increases with breakthrough time of 180 and 320 s, respectively, at 4.8 kPa (Figure S4b). As the interaction of nHEX with MOF **1** is significantly stronger than those of 22DMB and 3MP with MOF **1**, the monobranched 3MP and dibranched 22DMB hexane isomers can be readily separated from linear nHEX isomer, as clearly shown in their binary breakthrough curves of 3MP/nHEX (Figure S4e) and 22DMB/nHEX (Figure 5) with a moderate loading of nHEX up to 2.98 wt %. MOF **1** is also potentially applicable to the kinetic

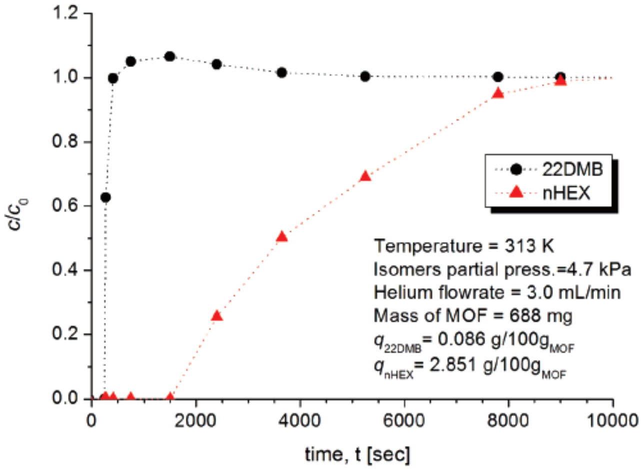

Figure 5. Binary breakthrough curve for an equimolar mixture of 22DMB/nHEX at $T = 313$ K. Points are experimental data, and doted lines are for clarity.

separation of the three hexane isomers 22DMB, 3MP, and nHEX (Figure S4f), although it is not as good as the well-established zeolite beta in terms of its separation efficiency for separation of dibranched 22DMB from monobranched 3MP.[18−19] Such low efficiency is mainly because of the large channels of 7.5 Å × 7.5 Å along the *a*-axis, which exhibit slightly different van der Waals interactions between the microporous walls with these two isomers. The most interesting feature is that MOF **1** is magnificent for its kinetic separation of linear nHEX from monobranched 3MP and dibranched 22DMB hexane isomers, apparently attributed to the narrow channels of 3.8 Å × 4.7 Å along *b* and *c* axes, which play the crucial roles to retain linear nHEX. This superior property is very important for its potential industrial application in the total isomerization process (TIP), a process of separating branched hydrocarbons from linear components to enhance octane number.

In conclusion, we present the first example of microporous MOFs for the kinetic separation of hexane isomers by fixed-bed adsorption, establishing the feasibility of the emerging microporous MOFs for their potential applications in this very important industrial process. By making use of the narrow channels of about 3.8 Å × 4.7 Å to exclusively take up linear nHEX, while to block branched hexane isomers, MOF **1** exhibits extraordinary separation selectivity to separate branched hexane isomers from linear nHEX. The exact and subtle control of the microporous channels within MOFs has played the determining roles for their discrimination of hexane isomers. Unlike most of microporous MOFs, which are very sensitive to water and moisture, MOF **1** is not only thermally stable but also very stable in the air. In fact, MOF **1** is easily reactivated and reused. The ideal microporous MOFs for the kinetic separation of ternary 22DMB/3MP/nHEX mixtures will be those having two types of micropores, one of about 4.3 Å to differentiate linear nHEX from branched 3MP and 22DMB, and another one of about 5.5 Å to discriminate monobranched 3MP from dibranched 22DMB. In practice, it might be also possible to develop step-by-step processes to separate linear isomer from branched isomers and to separate monobranched isomers from dibranched isomers, respectively, by utilizing two different types of microporous MOFs. With the availability of a number of microporous MOFs of variable microchannels together with the power to tune these channels rationally by the judicious choice of secondary building units (SBUs) and/or bridging organic linkers, the emerging microporous MOFs show bright promise for their practical applications on the kinetic separation of hexane isomers.

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Supporting Information Available: X-ray crystal structure of Zn(BDC)(Dabco)$_{0.5}$, pure component breakthrough curves for 22DMB, 3MP, and nHEX at $T = 313$ K and $p = 6$ kPa, pure-component adsorption isotherms of 22DMB, 3MP, and nHEX at 343 K, multicomponent breakthrough curves for equimolar mixtures of 22DMB/3MP, 3MP/nHEX, and 22DMB/3MP/nHEX at $T = 313$ K, experimental setup and procedure, determination of experimental adsorption equilibrium isotherms. This material is available free of charge via the Internet at http://pubs.acs.org.

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