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Zeolitic Imidazolate Framework-8 Nanocrystal Coated Capillary for Molecular Sieving of Branched Alkanes from Linear Alkanes along with High-Resolution Chromatographic Separation of Linear Alkanes

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Abstract: A zeolitic imidazolate framework-8 (ZIF-8) nanocrystal coated capillary is shown not only to have a strong ability to sieve branched alkanes from linear alkane isomers owing to the narrow pore windows but also to offer excellent features for high-resolution gas chromatographic separation of linear alkanes due to van der Waals interaction between linear alkanes and the hydrophobic inner surfaces of the micropores. This makes the ZIF-8 coated capillary very promising for the specific adsorption and separation of alkanes in complicated matrices.

The large diversity in structures and pore sizes, high surface areas, adsorption affinities, and selective penetrations make metal−organic frameworks (MOFs) attractive as advanced chromatographic separation media.[1] Zeolites, a successful example of a molecular sieve, with their well-defined pore structures and pore diameters close to those of alkane molecules, are suitable adsorbents for separating alkanes based on the degree of branching.[2] Zeolitic imidazolate frameworks (ZIFs) combine highly desirable properties from both zeolites and MOFs, such as microporosity, high surface areas, exceptional thermal and chemical stability, and changeable metal clusters or organic ligands.[3] Utilization of MOFs as high efficient adsorbents for alkane adsorption and separation has been reported.[4] However, these chosen MOFs do not show the ability to be a molecular sieve. Recently, utilization of ZIFs as membranes for sieving gas molecules, such as H_2, CO_2, CH_4, has been reported.[5] As a combination of MOFs and zeolites, the potential application of ZIFs for molecular sieving together with chromatographic separation for alkanes is considerable but underexplored.

Here we report the ZIF-coated capillary for molecular sieving of branched alkanes from linear alkanes along with high-resolution gas chromatographic (GC) separation of linear alkanes. Alkanes are important constituents of raw chemicals in the petroleum and chemical industry. The separation of linear alkanes from branched isomers is a very important process in petroleum refining,[6] improving the gasoline octane number and the low temperature properties of aviation fuels. Some small pore-sized zeolites have been used to sieve branched alkanes from linear alkanes to boost the octane ratings of petrol.[7] The process and mechanism of such a separation are always of high concern.

To demonstrate the proof-of-concept, we take ZIF-8 as an example of ZIFs. ZIF-8 has the formula $Zn(mim)_2$ (mim = 2-methylimidazole) with a sodalite (SOD)-related zeolite type structure (Figure S1 in Supporting Information).[8] ZIF-8 is both chemically and thermally stable, which makes it a good medium for separation. The six-membered-ring pore windows of ZIF-8 are narrow (~3.4 Å), but the pores are much larger (~11.4 Å).[5a] The narrow pore windows of ZIF-8 are expected to be able to sieve

branched alkanes from linear alkanes. Moreover, the hydrophobic behavior of the micropores of ZIF-8 should provide an advantage for the GC separation of linear alkanes.

ZIF-8 nanocrystals are synthesized according to Cravillon et al. (Supporting Information; Figures S2−S5).[9] Methanol suspension of ZIF-8 nanocrystals is used to fabricate the ZIF-8 coated capillary with homogeneous coverage and thickness of ZIF-8 coatings via a dynamic coating method (Supporting Information; Figure S6).[10]
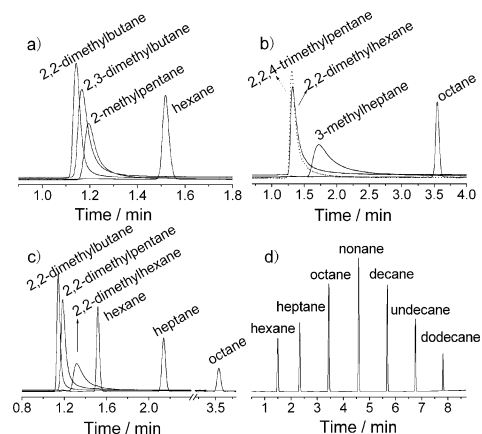

Figure 1. Chromatograms on the ZIF-8 coated capillary (20 m long × 0.25 mm i.d.) for GC separation of (a) hexane and its branched isomers; (b) octane and its branched isomers; (c) 2,2-dimethyl-branched alkanes and linear alkanes at a N_2 flow rate of 1 mL min⁻¹ under 170 °C; and (d) linear alkanes at a N_2 flow rate of 1.5 mL min⁻¹ using a temperature program: 140 °C for 1 min, then 20 °C min⁻¹ to 290 °C for the remainder.

To show the molecular sieving power of ZIF-8, we apply the ZIF-8 coated capillary for GC separation of linear alkanes and their different sized branched isomers. In the case of C-6 and C-8 groups, both hexane and octane achieve baseline separation from their respective branched isomers though the branched isomers could not be well separated from each other (Figure 1a,b). To test whether the separation is determined by a molecular sieving effect, we choose hexane, heptane, octane, and their 2,2-dimethyl-branched isomers (critical diameter 6.3 Å) as targets for separation. The typical elution sequence of alkane isomers on traditional stationary phases such as (5%-phenyl)-methylpolysiloxane usually follows the order of boiling points, which also happens on GC columns packed by MOF-508[4a] or MOF-5 with large pore channels without the molecular sieving effect (Figure S7). Nevertheless, the elution order is somewhat reversed for branched alkanes on our ZIF-8 coated capillary. The branched alkanes elute much earlier than their linear alkane isomers (Figure 1c; Figure S8). Moreover, 2,2-dimethyl-hexane (bp 107 °C) even elutes earlier than hexane (bp 69 °C) and heptane (bp 99 °C) though the former has a higher boiling point.

The above results reveal that our ZIF-8 coated capillary is highly capable in separating branched alkanes from their linear alkane isomers. Although the size of the pore window in ZIF-8 is estimated to be ~3.4 Å from crystallographic data, previous reports show that the framework structure of ZIF-8 is in fact more flexible rather than static in its nature and there is no sharp cutoff at 3.4 Å, and even larger molecules such as CH_4 (critical diameter ~3.8 Å) can enter the pore network.[5a,11] However, more bulky branched alkanes (critical diameter >5.4 Å) are not able to pass the narrow pore windows of ZIF-8, leading to their shorter retention time.

Our ZIF-8 coated capillary also gives high resolution and selectivity for the separation of linear alkanes with a broad range of boiling points and their elution sequence in the order of the carbon numbers (Figure 1d). Low boiling point constituents of linear alkanes (hexane, heptane, octane, nonane) are also baseline separated without temperature-programmed control, even at a temperature much higher than their boiling points (Figure S9).

The selectivity of the ZIF-8 coated capillary for the separation of linear alkanes mainly arises from the van der Waals interaction between linear alkanes and the hydrophobic inner surfaces of the micropores in ZIF-8. The relatively stronger van der Waals interaction between linear alkanes and the inner walls of the pores makes linear alkanes well separated from each other. Meanwhile, the relatively weaker van der Waals interaction between branched alkanes and the outer walls of the pores makes the separation of branched alkanes difficult (Table 1). In addition, the branched alkanes are not totally unretained with small differences in retention time on the ZIF-8 coated capillary mainly because of the differences in the length of the linear part of these branched alkanes and/or the numbers of carbon atoms.
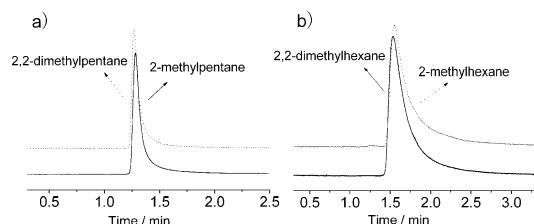
Figure 2. Comparison of 2-methyl-monosubstitute and 2,2-dimethyl-multisubstitute in retention time and peak shape on the ZIF-8 coated capillary (20 m long ×0.25 mm i.d.) at 150 °C under a N_2 flow rate of 1 mL min^{-1}: (a) 2,2-dimethylpentane and 2-methylpentane; (b) 2,2-dimethylhexane and 2-methylhexane.

Another intriguing phenomenon demonstrating the molecular sieving mechanism is the similarity in retention time of different substitute branched isomers with the same length of linear chain and the resemblance of their chromatographic peak shapes. The branched isomers with the same linear chain almost elute simultaneously (Figure 2a,b). Both the asymmetric factor and peak width show a close relationship with the length of the linear part of the branched alkanes, and they increase synchronously with the length of the chain (Figure S10). The short linear end of the branched isomers is difficult to enter into the pores because of the steric effect of the substitutes, thereby giving a smaller asymmetric factor and peak width. In contrast, the long linear end of the branched isomers is apt to enter into the pores due to hydrophobic adsorption but cannot go through the pores because of the branched sides. Thus, the resistance of the pore windows results in the long-chain-branched alkanes having a delayed elution and broader peaks (Figure 2b vs Figure 2a). Possessing the same length of linear carbon chains, 2-methyl-branched and 2,2-dimethyl-branched alkanes give similar retention times and peak shapes under a specific temperature (Figure 2a,b).

Table 1. Experimental Adsorption Enthalpies of the Nine Alkanes on ZIF-8 Coated Capillary

|		T_{boil} (°C)	t_R[a] (min)	$-\Delta H_{ads}$[b] (kJ/mol)
C-6	2,2-dimethylbutane	50	1.14	7.7 ± 0.4
	2-methylpentane	60	1.20	18.9 ± 1.2
	hexane	69	1.52	29.5 ± 0.5
C-7	2,2-dimethylpentane	79	1.19	13.7 ± 0.8
	2-methylhexane	90	1.35	24.2 ± 1.2
	heptane	99	2.14	38.1 ± 0.5
C-8	2,2-dimethylhexane	107	1.32	20.7 ± 1.2
	2-methylheptane	116	1.87	29.7 ± 1.7
	octane	126	3.55	43.8 ± 0.6

[a] Obtained from the gas chromatograms at a N_2 flow rate of 1 mL min^{-1} under 170 °C. [b] Calculated from the slope of the van't Hoff plots with a temperature range of 130−170 °C for the C-6 group, 150−190 °C for the C-7 group, and 170−210 °C for the C-8 group.

To illustrate the energy effect on the interaction between analyte and ZIF-8, the adsorption enthalpies are calculated from the van't Hoff plot[12] (Figure S11) and summarized in Table 1. On the ZIF-8 coated capillary, branched alkanes are more weakly retained than their linear isomers (Figure 1a−c), while shorter chain linear alkanes are more weakly retained than longer chain linear alkanes (Figure 1d). This is also reflected in the adsorption enthalpies of the isomers. The adsorption enthalpies increase with carbon numbers. For the alkanes with the same number of carbon atoms, the more branched alkanes give the smaller adsorption enthalpies, showing a lower energetic interaction with the ZIF-8, while the linear alkanes show the largest adsorption enthalpies. The adsorption enthalpy results provide a good explanation for the order of retention times and the elution sequence of the hydrocarbons from an energetic point of view.

To demonstrate that the pore window size and pore size of ZIF-8 is appropriate for the linear alkanes, we use ZIF-7 for comparison. ZIF-7 has smaller pore window size (2.9 Å) and pore size (4.3 Å)[13] than the critical diameter of linear alkanes and ZIF-8. ZIF-7 and ZIF-8 have the same SOD zeolite type (Figure S1). The difference in pore and pore window size is derived from the difference of organic ligands, 2-methylimidazole in ZIF-8 and benzimidazole in ZIF-7. ZIF-7 nanocrystals were synthesized according to Li et al. (Supporting Information; Figures S12−S15).[5b] The ZIF-7 coated capillary does not offer a baseline separation of hexane, heptane, octane, and nonane, and the retention times of these linear alkanes are all within 1.6 min (Figure S16). To show that the poor separation of these linear alkanes on the ZIF-7 coated capillary does not result from GC separation conditions, the contribution of temperature and N_2 flow rate to column efficiency is investigated. As a result, the theoretical plate number does not change greatly with temperature and flow rate (Figures S17 and S18). These results indicate that these two variables do not make a significant contribution to the poor separation of the linear alkanes. Thus, the inaccessible pores of ZIF-7 should be the reason for the unfavorable separation of hexane, heptane, octane, and nonane. The selectivities of the linear alkane and branched alkanes on the ZIF-8 and ZIF-7 coated capillaries are compared in Tables S1 and S2.

The good selectivity, resolution, and precision for the separation of linear alkanes along with the molecular sieving effect make the ZIF-8 coated capillary a promising candidate for specific separation of linear alkanes (Tables S1−S3). An increase in analyte mass results in a linear increase of chromatographic peak area but almost no change in retention time, and thereby stable capacity factor (Figure S19). Moreover, the adsorption and separation process does not significantly change the structure and morphology of the ZIF-8 coating on the capillary (Figure S20), thereby giving reproducible

chromatograms (Figure S21). The ZIF-8 coated capillary gives a similar height equivalent to a theoretical plate (HETP) (Figure S22) to the classical HP-5 column for hexane (Figure S23). These features of the fabricated ZIF-8 coated capillary are favorable for its application to both qualitative and quantitative analysis. However, the small pore window in ZIF-8 leads to peak broadening for bulky branched alkanes due to slow diffusion, which could negatively affect separation performance, especially for bulk scale separations.
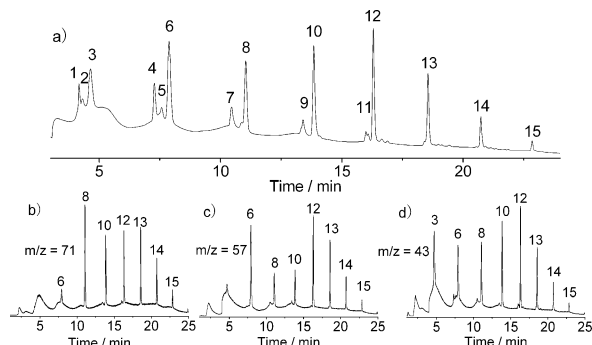
Figure 3. Chromatograms of a petrol sample on the ZIF-8 coated capillary (20 m long ×0.25 mm i.d.) at a He flow rate of 1 mL min^{-1} using a temperature program: 40 °C for 1 min, then 10 °C min^{-1} to 290 °C. (a) Total ion chromatogram monitored at m/z = 41, 43, 55, 57, 71, and 84 by GC-MS; (b, c, and d) Extracted ion chromatograms at a specific m/z of 71, 57, and 43, respectively (1: 1,2-dimethylcyclopropane; 2: pent-2-ene; 3: pentane; 4: hex-3-ene; 5: hex-2-ene; 6: hexane; 7: hept-3-ene; 8: heptane; 9: oct-3-ene; 10: octane; 11: non-3-ene; 12: nonane; 13: decane; 14: undecane; 15: dodecane).

The separation power of the ZIF-8 coated capillary column is further revealed by separating a real petrol sample. Alkanes and alkenes in the petrol sample are separated by the ZIF-8 coated capillary and identified by mass spectrometry. The branched alkanes or alkenes elute much earlier than linear isomers or under the baseline, while the linear alkanes or alkenes give sharp peaks (Figure 3). The results show the ability of ZIF-8 not only to sieve linear alkanes and alkenes from their branched isomers but also to well separate linear alkanes and alkenes with a broad range of boiling points in a complicated matrix.

In summary, the fabricated ZIF-8 coated capillary not only demonstrates a high capability in sieving linear alkanes from branched alkanes but also offers the excellent feature of high-resolution GC separation of linear alkanes from each other according to boiling points. The molecular sieving effect and host−guest interaction make ZIF coated capillary columns very promising for specific recognition and separation in high-resolution GC. ZIFs may also bring a bright future for the specific adsorption, extraction, and separation of special shaped or sized molecules in complicated matrices.

Supporting Information Available: Experimental procedures, additional figures and tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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