Size- and Stereo-specific Accommodation of Alkanes and Alkenes in Calixarene-based Microporous Solids

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Hydrophobic micropores created in the crystal lattice of a calix[4]arene–polyoxometalate hybrid (C2-PW) selectively accommodated heptane rather than the branched homologues. The sorption properties were tunable by slight modification of the calixarene unit, whereby the recognition of E–Z stereochemistry of 2-heptene was achieved.

Porous materials have attracted continuing interests in relation to separation, storage, and catalysis technologies.[1,2] Especially, shape-selective sorption of simple hydrocarbons is an important and challenging subject, but successful examples have been quite limited to date.[3] We have recently reported the microporosity of an ionic crystal composed of hydrophobic calix[4]arene–Na^+ complex and Keggin polyoxometalate ($(C2\text{-}Na)_3[PW_{12}O_{40}]$) (C2-PW, Figure 1), and demonstrated a hydrophobic character of the pore environment in the preferential adsorption of alcohols rather than water.[4] Herein, we report that the micropore of C2-PW selectively accommodates linear alkane and alkene rather than the branched homologues. We also demonstrate that a subtle modification of the calixarene unit drastically affects the sorption properties, and provide an example of facile recognition of E–Z stereochemistry of 2-alkene.

The calixarene components we used in addition to C2 are those with isopropyl (IC3) and butyl (C4) ester-substituents, from which corresponding hybrid crystals (IC3-PW and C4-PW) were prepared similarly to C2-PW.[4] Powder X-ray diffraction (PXRD) profiles of these crystals (S-Figure 1 in Supporting Information)[5] were almost similar to that of C2-PW whose structure has been determined by single-crystal X-ray crystallography (Figure 1), indicating that they also take similar packing structures with micropores.

Vapor sorption of heptanes (heptane, 2-methylhexane, and 2,2-dimethylpentane) and (*E*)-/(*Z*)-2-heptenes towards C2-PW was investigated at 25 °C (Figure 2a).[6] The binding isotherms for heptane and 2-heptenes (○, ▲, ▼) showed clear rise at low equilibrium pressures (P_e), indicating that they were efficiently accommodated in the microchannel.[7] From the PXRD profiles before and after the sorption, the original framework was essentially retained during the accommodation process. On the other hand, hindered 2-methylhexane (■) and 2,2-dimethylpentane (◆) were reluctant to penetrate into the pores. Thus, C2-PW selectively traps linear molecules. Since the pore opening size was estimated to be ca. 4 × 8 Å, this result is quite reasonable considering the steric bulk of the isopropyl group of 2-methylhexane and *tert*-butyl group of 2,2-dimethylpentane.

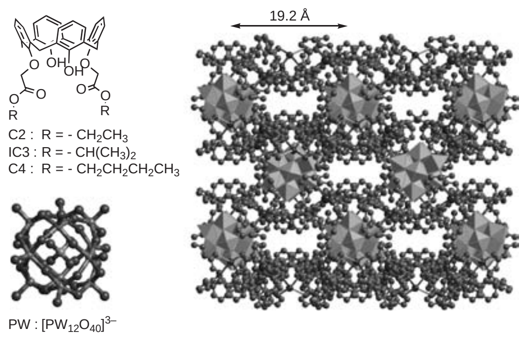

Figure 1. Building units of porous crystals (left) and the crystal structure of C2-PW viewed along the 101 direction with hydrogen atoms and solvent molecules omitted (right).

The efficient uptake of heptane and 2-heptenes, thus observed, was considered driven primarily by the attractive van der Waals and/or CH···π interaction of the guest alkyl chains with the hydrophobic pore surface. Actually, negligible accommodations of N_2 and Ar were observed at −196 and 25 °C with high pressure (up to 5 MPa), despite their small molecular sizes (S-Figure 2 in Supporting Information).[5] The important role of the weak interaction involving alkyl chains was further supported by the sorption profile of methane: The binding isotherm was characteristic of the accommodation in the pore but the P_e required for saturation (ca. 2 MPa) was much higher than those of heptane and 2-heptenes (ca. 4 kPa, Figure 2a).

The interaction involving the alkyl chains was further investigated by means of IR spectroscopy. The C–H stretching vibration bands of free heptane at 2967, 2931, and 2872 cm^{-1} (Figure 3a (i)) showed remarkable shifts to lower energies (2952, 2921, and 2853 cm^{-1}) after being trapped in the pores of C2-PW (ii). Such shifts have been reported when long alkyl

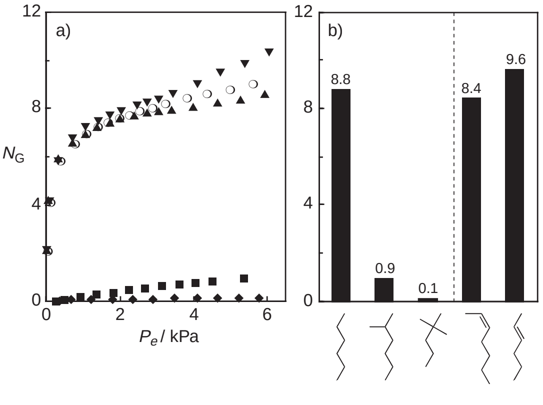

Figure 2. a) Sorption isotherms of heptane (○), 2-methylhexane (■), (*Z*)-2-heptene (▲), (*E*)-2-heptene (▼) (25 °C) and 2,2-dimethylpentane (◆) (20 °C) to C2-PW. Plots of the number of guest molecules trapped in a single unit cell (N_G) versus P_e. b) N_G at P_e = 5 kPa.

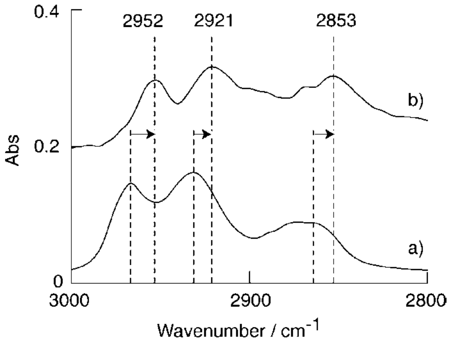

Figure 3. IR spectra (KBr pellet) of (a) heptane and (b) heptane trapped by C2-PW. For (b), the spectrum of C2-PW was subtracted from the raw spectrum.

chains were closely packed via alkyl–alkyl van der Waals force.[8] Therefore, considering also the absence of complimentary long alkyl chains in the pore surface, it is suggested that the attractive interaction between guest alkyl chains is one of the important factors for the efficient accommodation of linear molecules.

As we have shown, C2-PW accommodates linear alkane via weak attractive interaction. Since several ethyl ester groups of C2-PW are extended to lie on the pore wall, the sorption properties would be affected by the steric bulk of ester substituents. Actually, when the ethyl esters of C2-PW were replaced with butyl esters (C4-PW), the amount of trapped heptane was significantly dropped (Figure 2a vs 4a, ○). On the other hand, IC3-PW derived from calixarene with isopropyl esters sorbed heptane similarly to C2-PW (Figure 4b, ○), implying that the guest molecule can avoid the steric bulk at the pore edge due to its conformational flexibility.

The sorption isotherms in Figure 2 show that C2-PW has apparently similar affinities to heptane and 2-heptenes. However, evident differences were found in Dubinin–Radushkevich potential energies estimated from the initial stage of the sorption (S-Figure 3 in Supporting Information).[5,9] The energies for the sorption of 2-heptenes (14.0 and 13.0 kJ/mol for (Z) and (E) isomers, respectively) were definitely larger than that of heptane (11.6 kJ/mol), suggesting the involvement of additional interaction associated with the olefinic π-functionality (C–H$\cdots\pi$, π–π). The preference for alkenes was observed in the adsorption isotherms towards C4-PW, where nearly perfect selectivity was achieved (Figure 4a, ▲, ▼ vs ○).

On the other hand, the difference in the potential energies of (*Z*)- and (*E*)-2-heptenes suggested that analogous materials can potentially recognize the stereochemistry of 2-heptene in adsorption. When C4-PW was used as the sorbent, the amount of trapped (Z) isomer was only slightly larger than that of (E) isomer (Figure 4a, ▲ vs ▼). In contrast, when IC3-PW was employed, the preference for (Z) isomer was notably pronounced. When going from C2-PW to IC3-PW, a significant drop of the uptake was observed only for (E) isomer (Figures 2a and 4b, ▼), where the amount of sorbed (Z) isomer was approximately four times larger than that for (E) isomer at $P_e = 5$ kPa (Figure 4b, ▲ vs ▼). This selectivity may result from the steric repulsion between the rigid isopropyl group located at the pore edge and geometrically restricted olefinic moiety of (E) isomer.

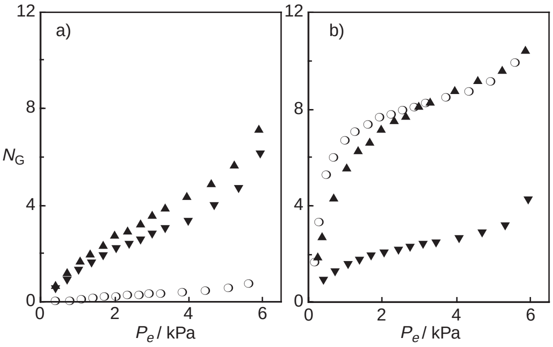

Figure 4. Sorption isotherms of heptane (○), (*Z*)-2-heptene (▲), (*E*)-2-heptene (▼) to (a) C4-PW and (b) IC3-PW at 25 °C.

In conclusion, we have shown that the calix[4]arene-based crystals provide tunable hydrophobic micropores for the facile recognition of the shape of simple alkanes and alkenes.

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5 Supporting Information is available electronically on the CSJ-Journal web site, http://www.csj.jp/journals/chem-lett/index.html.

6 Saturated vapor pressures: heptane, 6.10 kPa (25 °C); 2-methylhexane, 8.79 kPa (25 °C); 2,2-dimethylpentane, 11.2 kPa (20 °C); (*E*)-2-heptene, 6.56 kPa (25 °C); (*Z*)-2-heptene, 6.45 kPa (25 °C).

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