

Recognition of 1,3-Butadiene by a Porous Coordination Polymer

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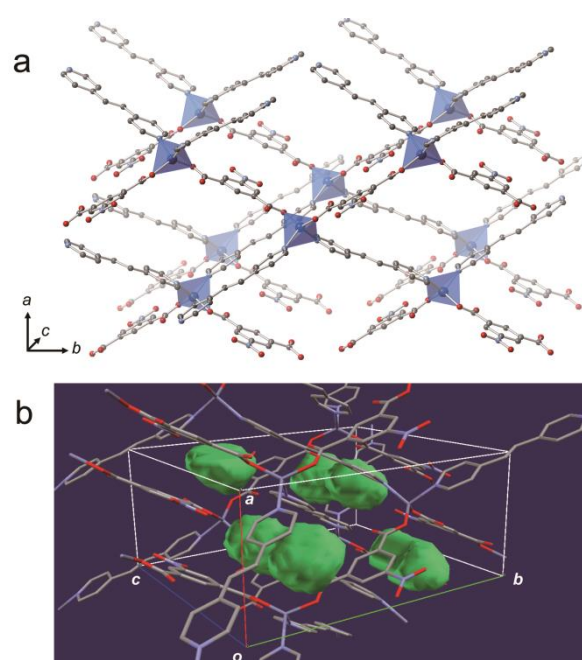
Abstract: The separation of 1,3-butadiene from C4 hydrocarbon mixtures is imperative for the production of synthetic rubbers, and there is a need for a more economical separation method, such as a pressure swing adsorption process. With regard to adsorbents that enable the C4 gas separation, $[\text{Zn}(\text{NO}_2\text{ip})(\text{dpe})]_n$ (SD-65; NO_2ip = 5-nitroisophthalate, dpe = 1,2-di(4-pyridyl)ethylene) is a promising porous material because of its structural flexibility and restricted voids, which provide unique guest-responsive accommodation. Adsorption isotherms and *in-situ* PXRD studies elucidated the 1,3-butadiene selective sorption profile of SD-65, which was further investigated using multi-gas separation and adsorption-desorption cycle experiments for its application to separation technology.

1,3-Butadiene is a major industrial chemical used in the production of synthetic rubbers. It is typically produced through extractive distillation from C4 hydrocarbons because of the similarity between the relative volatilities of C4 hydrocarbon isomers (Table S1).^[1] The extractive distillation thus requires large amounts of energy through the re-boiling of 1,3-butadiene in organic solvents. An alternative energy-efficient purification method is pressure swing adsorption (PSA) using microporous adsorbents that can separate gas molecules thermodynamically or kinetically.^[2] The former thermodynamic approach uses adsorbents containing accessible cations, such as Ag^+ and Cu^+ .^[3] This enables a strong π -complexation to 1,3-butadiene for separation; however, it requires time or energy to regenerate the adsorbent at ambient condition. The latter kinetic, size-selective separation approach has also been unsuccessful in separating 1,3-butadiene from *trans*-2-butene because of their similar molecular size, e.g. using all-silica decadodecasil 3R (DD3R)^[4] containing one-dimensional channels.^[5] Thus, adsorbents that

satisfy both 1,3-butadiene selectivity and regeneration ability are required.

Porous coordination polymers (PCPs) or metal–organic frameworks (MOFs) have attracted considerable attention because of their structural diversity.^[6] They are synthesized with metal ions and organic bridging ligands, resulting in cavities within their frameworks that can accommodate guest molecules. Although many PCPs have been proposed for separating olefin/paraffin mixtures,^[7] all these focus on identifying mono-olefin from paraffin,^[8] with no reports on separating C4 diolefin from mono-olefins and paraffins. Because of the significance of separating 1,3-butadiene and consequent chemical processes, herein, we describe the first example of a PCP for separating 1,3-butadiene from six major C4 hydrocarbons, including four mono-olefins, at ambient temperature and pressure.

We employed $[\text{Zn}(\text{NO}_2\text{ip})(\text{dpe})]_n$ (SD-65; NO_2ip = 5-nitroisophthalate, dpe = 1,2-di(4-pyridyl)ethylene) as it possesses thermodynamic-based structural flexibility.^[9] Through coordination with two isophthalate and two dipyrindyl ligands with tetrahedral geometry, Zn^{2+} forms pseudo-diamondoid frameworks, as depicted in Figure 1a. These frameworks are triply interpenetrated and form a flexible, relatively dense coordination polymer with discrete, isolated voids (Figure 1b). Each void has a volume of 45 \AA^3 , calculated using PLATON software,^[10] and is located in the interspaces of the entangled networks. Their volume is small and cannot accommodate solvent molecules after synthesis.



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Figure 1. (a) Pseudo-diamondoid network of SD-65 along the *c* axis. Blue polyhedra, red, blue, and gray spheres represent Zn, O, N, and C atoms, respectively. (b) Isolated voids (green spheres) in the SD-65 unit cell. Probe radius for the calculation is 1.3 Å.

Single-component gas adsorption studies of the seven C₄ hydrocarbons listed in Table S1 at 25°C revealed a specific 1,3-butadiene sorption behavior of SD-65. As shown in Figures 2a and 2b, the uptakes of all butenes and butanes on SD-65 were less than 2.5 cm³ g⁻¹ at 101 kPa and 25°C. However, the uptake of 1,3-butadiene was 40 cm³ g⁻¹ at 101 kPa with a sigmoid-type sorption profile; adsorption began at 60 kPa while desorption began at 50 kPa. This profile is referred to as a gate-opening phenomenon and represents the flexible, guest-responsive nature of SD-65.^[11] This suggests that the 1,3-butadiene selective sorption stems from the structural flexibility of the framework.

As shown in Figure 3, we also investigated selected C₄ adsorption isotherms of NaX zeolite and four PCPs with flexible and non-flexible structures. The studied PCPs were [Zn(2-methylimidazole)₂] (Zn-ZIF-8),^[12] [Al(OH)(1,4-benzenedicarboxylate)] (Al-MIL-53),^[13] [Zn₂(fumarate)₂(4,4'-bpy)],^[14] and [Ca(squarate)(H₂O)].^[15] NaX zeolite, Zn-ZIF-8, Al-MIL-53 have large pores to accommodate C₄ gases, and they adsorbed not only 1,3-butadiene but also *n*-butane, and 1-butene with Type-I profiles, indicating that these pores are too large to selectively recognize 1,3-butadiene from butanes and butenes. We further examined two PCPs, flexible [Zn₂(fumarate)₂(4,4'-bpy)] and rigid [Ca(squarate)(H₂O)]. [Zn₂(fumarate)₂(4,4'-bpy)] is a doubly interpenetrated flexible structure with narrower pore opening of 1.4×1.8 Å². As shown in Figure 3d, it absorbed 1,3-butadiene with Type-1 profile at 25°C. Although this compound did not adsorb *n*-butane, it started to adsorb 1-butene at 30 kPa with a gate-opening profile, indicating that the pore opening is still too large to recognize 1,3-butadiene from butenes. [Ca(squarate)(H₂O)] has a rigid and ultra-microporous structure with pore openings of 3.4×3.4 Å² and showed selective sorption profiles for *trans*-2-butene and 1,3-butadiene over other five C₄ gases (Figure 3e). The observed selectivity is originated from molecular sieving effect like zeolite ZSM-5^[2b] and DD3R,^[4] thus, an inherent similarity of *trans*-2-butene and 1,3-butadiene makes the separation unfeasible by the molecular sieving effect, and requires cooperative structural change of the adsorbent, which we call structural flexibility, to amplify the small difference of these two gas molecules. These results indicate that SD-65 is the best candidate because of its restricted voids and structural flexibility.

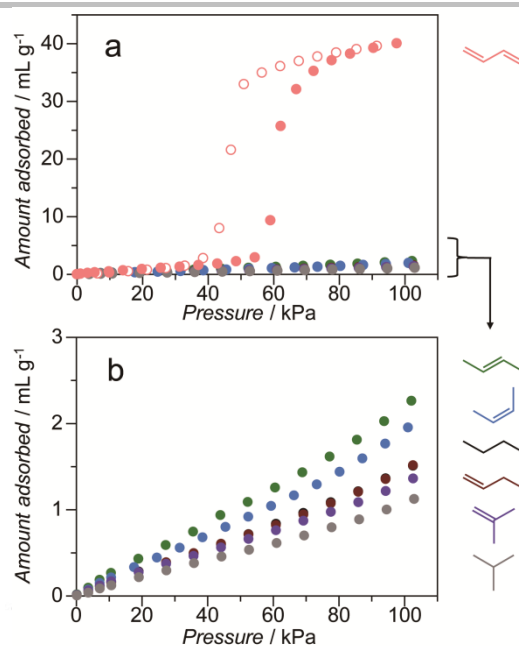


Figure 2. (a) Adsorption isotherms of SD-65 for 1,3-butadiene (pink, desorption isotherm is also shown as open circle), *trans*-2-butene (green), *cis*-2-butene (blue), *n*-butane (black), 1-butene (brown), isobutene (purple), and isobutane (gray) at 25°C. (b) Enlarged graph from 0 to 3 mL g⁻¹ of amount adsorbed.

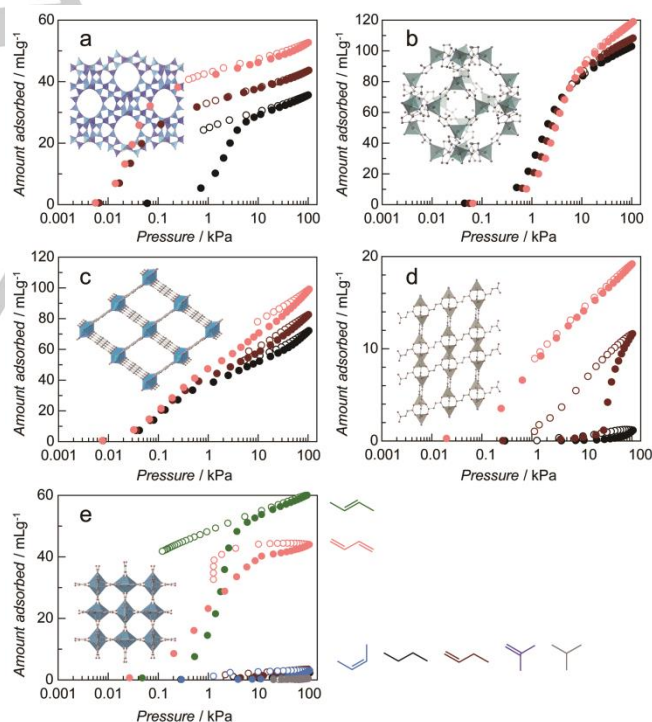


Figure 3. Isotherms of adsorption (solid circle) and desorption (open circle) at 25°C of (a) NaX zeolite, (b) [Zn(2-methylimidazole)₂] (Zn-ZIF-8), (c) [Al(OH)(1,4-benzenedicarboxylate)] (Al-MIL-53), (d) [Zn₂(fumarate)₂(4,4'-bpy)]. Pink: 1,3-butadiene, brown: 1-butene, black: *n*-butane. (e) [Ca(squarate)(H₂O)]. Green: *trans*-2-butene, blue: *cis*-2-butene, purple: isobutene, gray: isobutane are also shown.

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To investigate the structural rearrangement we measured the powder X-ray diffraction (PXRD) patterns of SD-65 under variable pressure of 1,3-butadiene. As shown in Figure 4, *in situ* PXRD studies revealed gradual, crystal-to-crystal structural transformation upon 1,3-butadiene adsorption. During the adsorption process, some diffraction peaks were diminished and new diffraction peaks emerged at 10.9, 12.3, and 25.3° of 2 θ , which could not be indexed with either the same unit cell or a combination of unit cells with SD-65 without guest molecules. However, the comparison of the PXRD pattern to that of an isorecticular compound, [Zn(NO₂ip)(dpa)]_n (dpa = 1,2-di(4-pyridyl)ethane),^[16] allowed us to establish that the framework of SD-65 expanded along the *a*-axis and contracted along the *b*-axis upon 1,3-butadiene sorption (Figure S1). The structural transformation via gas adsorption was reversible, as confirmed by the PXRD patterns upon removal of 1,3-butadiene (Figure S2).

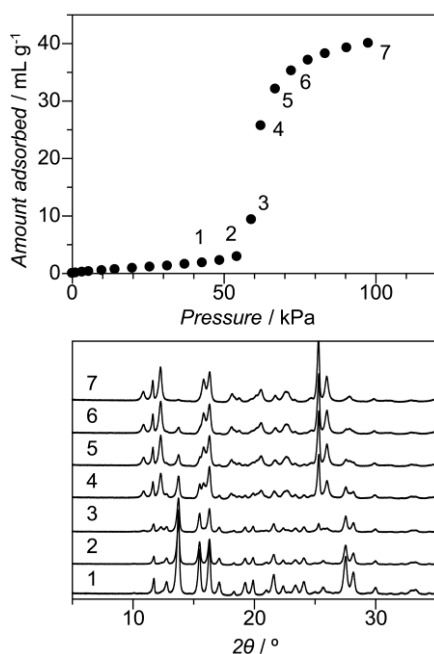


Figure 4. *In situ* PXRD patterns at each equilibrium point of 1,3-butadiene adsorption on SD-65 at 25°C.

The structural transformation is also apparent in the ¹³C MAS NMR spectra, in fact a generalized change of chemical shift was observed in the SD-65 after loading with d₆-1,3-butadiene at 96 kPa and room temperature, which corresponds to the virtually complete filling of the cavities (Figure 5a and b). In particular, the remarkable downfield shift ($\Delta=+3$ ppm) of carbon n. 4, in metha position with respect to nitrogen of the pyridine ring, is consistent with a deviation from *s-cis* planar conformation on the C3-C6 bond of dpe for the presence of butadiene. The use of hydrogen-depleted perdeuterobutadiene allowed us to highlight the efficient magnetization transfer, through dipolar coupling, from the host hydrogens to the guest CD and CD₂ carbons by cross-polarization experiments, indicating short intermolecular distances (Figure 5b). 2D ¹H-¹³C HETCOR NMR spectroscopy is the method of choice for the recognition of supramolecular arrangements and intermolecular interactions in complex systems.^[A1] Indeed, while the 2D ¹H-¹³C HETCOR NMR spectrum at 50 μ s contact time

highlights the host hydrogen assignment (Figure 5e), the 2D NMR spectrum at 0.5 ms contact time pinpoints that the H₅ hydrogen in ortho-position to nitrogen of pyridyl moiety ($\delta=8.2$ ppm) correlates with the CD₂ carbons ($\delta=113.7$ ppm), unambiguously showing the close proximity among these atoms in the host-guest structure (Figure 5d).

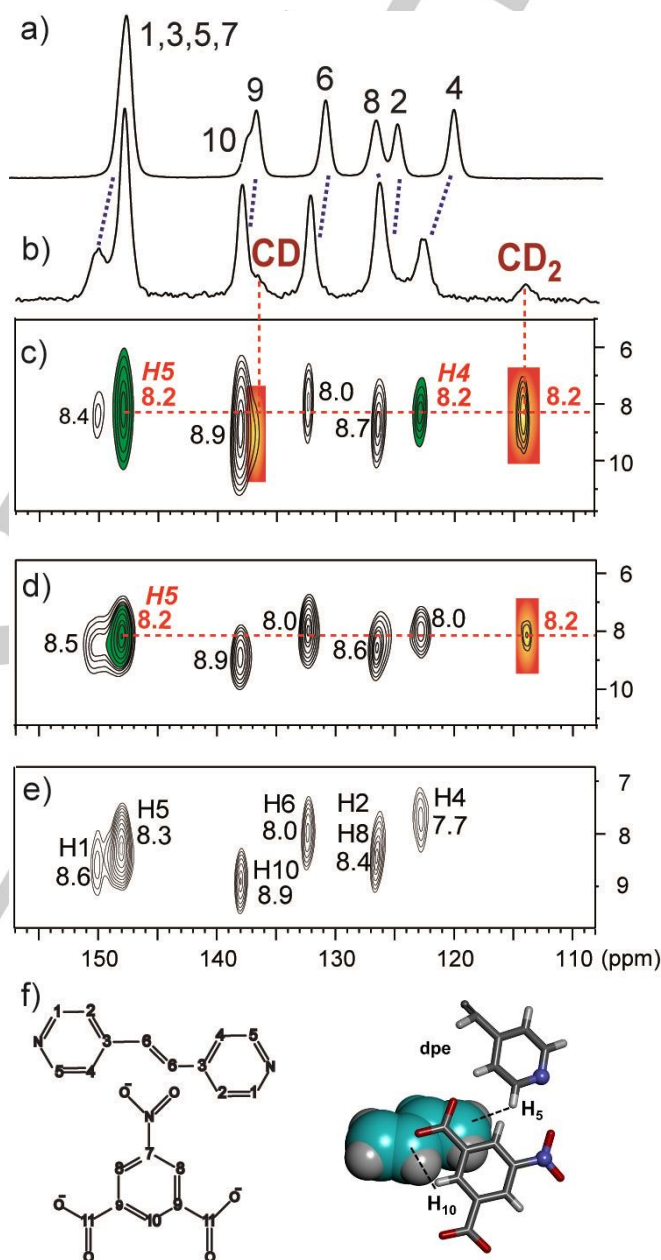


Figure 5. (a) ¹³C CP MAS NMR spectrum of SD-65 and (b) SD-65 accommodating d₆-1,3-butadiene. 2D ¹H-¹³C HETCOR spectra of SD-65/d₆-1,3-butadiene compound at 50 μ s (c), 0.5 ms (d) and 2 ms (e). (f) Numbering of chemical structures and schematic representation of the intermolecular interactions between host and guest.

At a longer contact time of 2 ms also the H₄ hydrogen participates in the same spin system H₅-CD₂, confirming that the CD₂ group selectively interacts with one side edge of the pyridyl ring (Figure 5c). At this contact time, CD carbon receives the magnetization from H₁₀ hydrogen of nitroisophthalatebenzene resonating at

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$\delta=8.9$ ppm, such a high value of ^1H chemical shift indicates an acidic aromatic proton which can favorably interact with the electron rich system of butadiene. Collectively, the distance constraints, derived by 2D NMR spectroscopy, reveal the location of the guest molecule in the cage. A representation of intermolecular interactions between the guest and host molecules is depicted in Figure 5f. The tight fitting of butadiene in the cavity suggests a restricted mobility of the guest in the structure, consistently with the long ^{13}C T_1 spin-lattice relaxation times of more than 150 s. This conclusion is enforced by variable temperature ^2H spin-echo NMR which is sensitive to the motional behavior of C-D vectors:^[A2] at low temperature the lineshape singularities are separated by 120 kHz indicating a quasi static arrangement of the C-D bonds while on increasing temperature only moderate librations about the equilibrium position occur, reducing and modulating the separation between singularities (Figure S11).

We further measured the adsorption isotherms at various temperatures to give insight into the flexibility-based separation of 1,3-butadiene (Figure S3). The gate-opening pressure for 1,3-butadiene decreased with decreasing operating temperature, i.e., from 60 kPa at 25°C to 20 kPa at 15°C to 10 kPa at 0°C. The amount adsorbed at 0°C and 97 kPa ($P/P_0 = 0.80$) reached $52\text{ cm}^3\text{ g}^{-1}$, which corresponds to one molecule per void in the structure in Figure 1b. However, the volume of each void (45 \AA^3) is smaller than the van der Waals volume of 1,3-butadiene, 70 \AA^3 .^[17] As suggested by the *in situ* PXRD study, SD-65 transforms its structure such that 1,3-butadiene can diffuse into the isolated, small voids and be accommodated. The isosteric heat for 1,3-butadiene, as calculated by the Clausius-Clapeyron equation, was 40 kJ mol^{-1} (Figure S4), which is significantly smaller than that of Ag^+ containing zeolite Y ($100\text{--}122\text{ kJ mol}^{-1}$)^[3b] and identical to that of charge-neutral zeolite DD3R (39 kJ mol^{-1}).^[5] The voids of SD-65 have no accessible metal sites for guest molecules, indicating that the interaction between SD-65 and 1,3-butadiene is based on weak interactions, such as electrostatic and dispersion interaction. Considering the size of the adsorbates, bulky molecules, such as isobutene, *cis*-2-butene, 1-butane, and isobutane cannot diffuse into the discrete voids of SD-65 and are excluded. From the viewpoint of the physical parameters of C4 hydrocarbons (Table S1), the difference in the interaction between the adsorbent and C4 hydrocarbons would be derived mainly from the difference in quadrupole moment of these gaseous molecules; -5.5 D\AA for 1,3-butadiene, -2.3 D\AA for *trans*-2-butene, and -1.9 D\AA for 1-butene. The larger quadrupole moment of 1,3-butadiene exclusively induces structural change of the framework and is small enough to diffuse into the voids, leading to the selectivity of SD-65. Therefore, SD-65 displays selectivity for 1,3-butadiene based on size difference and adsorbent–adsorbate interactions.

In addition to gas selectivity, regeneration of the adsorbent is another important factor for determining the applicability in PSA systems. Figure 6a shows the results of the 1,3-butadiene pressure swing adsorption-desorption cyclic study of SD-65 at 25°C (pressure profiles are in Figure S5). The 1,3-butadiene adsorption capacity of SD-65 for the first run was $26\text{ cm}^3\text{ g}^{-1}$ at 125 kPa and 25°C for 5 min. Minimal deterioration in the adsorption capacity was detected during four cycles of measurement, indicating good regeneration ability of SD-65 for 1,3-butadiene. This is because the selectivity is based only on weak adsorbent–adsorbate interactions. Conversely, a repeated

sorption study for NaX zeolite, $\text{Na}_{86}[(\text{AlO}_2)_{86}(\text{SiO}_2)_{106}]$, revealed a significant decrease in the amount adsorbed from $48\text{ cm}^3\text{ g}^{-1}$ in the first run to $10\text{ cm}^3\text{ g}^{-1}$ in the second run. This decrease was only slightly improved when the desorption time was prolonged from 3 to 60 minutes per cycle, suggesting strong interaction between the 1,3-butadiene molecules and the cationic framework of the zeolite. The amounts of adsorbed (ca. $10\text{ cm}^3\text{ g}^{-1}$) for second to fourth cycles are because of the physisorbed gases. These results demonstrate the advantage of flexible coordination polymers over traditional adsorbents for separating 1,3-butadiene in a PSA process with regard to the small energy of adsorption.

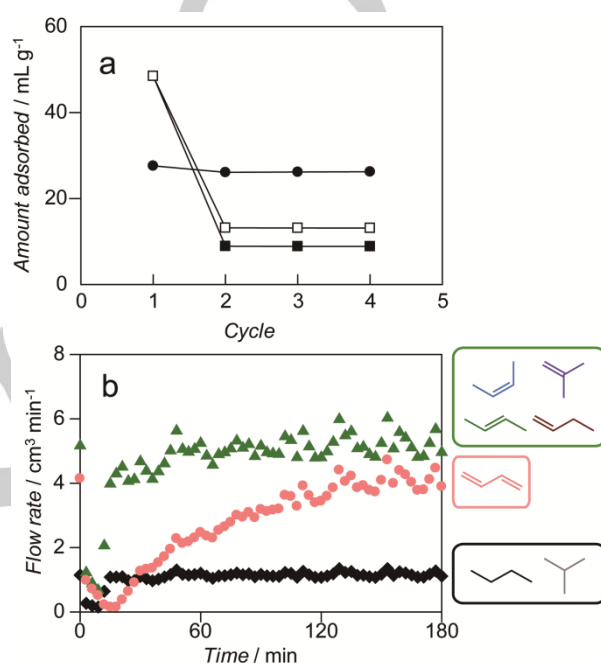


Figure 6. (a) Cycle tests of 1,3-butadiene adsorption (125 kPa for 5 min) and desorption (below 1 kPa for 1 min or for 60 min). SD-65 by 1 min of desorption (solid circle) and NaX zeolite by 1 min (solid square) and 60 min (open square) of desorption at 25°C. (b) Breakthrough curves of 1,3-butadiene (pink circle), butenes (1-butene, 2-butenes, and isobutene; green triangle), and butanes (*n*-butane and isobutane; black diamond) on SD-65 at 25°C with a total pressure of 230 kPa and a total flow rate of $10\text{ cm}^3\text{ min}^{-1}$.

It is known that the gas separation performance of PCPs showing structural flexibility from gas mixture is not always correlated with the results of adsorption isotherms of single component gases. The 1,3-butadiene selectivity of SD-65 was examined by a breakthrough experiment with a C4 hydrocarbon mixture (Figure 6b). We used crushed pellets of SD-65 to reduce dead volume in the apparatus and avoid unnecessary pressure drop in the measurement. As the gas mixture, we employed a C4 fraction comprised of 40% 1,3-butadiene, 49% butene mixture, and 11% butane mixture. The breakthrough curves at 25°C and 230 kPa showed the 1,3-butadiene selective sorption profiles, while the outlet gas contained unadsorbed 1,3-butadiene at the breakthrough point because of low 1,3-butadiene uptake in the low-pressure region. The dead volume between the PCP sample tube and gas chromatography led to the breakthrough curves where the gas flow rates started from non-zero rates. The insufficient S/N ratio for each profile is because of the scale of our apparatus, and the improvement of the ratio requires larger scale-

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based evaluation. After the breakthrough point, although the calculated outflow rates of butenes and butanes reached to the inflow rates of those gases, the outflow rate of 1,3-butadiene kept increasing, indicating no replacement of adsorbed butenes and butanes by 1,3-butadiene, and slow but selective sorption of 1,3-butadiene from the C4 gas mixture. A material balance calculation based on the saturated conditions, at 180 min, revealed that the amount of 1,3-butadiene, butenes, and butanes adsorbed on SD-65 were 28, 6, and 0.4 cm³ g⁻¹, respectively, and the 1,3-butadiene selectivity was 6.6. The SD-65 is highly hydrophobic, and shows negligible amount of H₂O uptake under the saturated vapor pressure at 25°C.^[9] With this hydrophobic character, the preferential adsorption of 1,3-butadiene from the C4 fraction and low energy consumption for regeneration of SD-65 are promising characteristics for application in naphtha crackers.

In conclusion, we have developed an adsorbent-based separation of 1,3-butadiene from a C4 hydrocarbon mixture under ambient conditions using a triply interpenetrated flexible PCP, SD-65, containing discrete voids. By considering the crystal structures and adsorption behaviors, we have deduced that specially isolated voids of SD-65 selectively captured 1,3-butadiene molecules by expanding their overall structure and excluding other C4 resembling isomers. Despite the small difference in physical properties of C4 hydrocarbons, SD-65 can separate 1,3-butadiene from C4 hydrocarbon mixtures and readily release adsorbed 1,3-butadiene under the expected PSA condition. From the viewpoint of material design for specific gas separation under ambient conditions, this work suggests that the key is to combine both narrow voids and structural flexibility for use with other light gas mixtures.

Acknowledgements

This work was partially supported by the New Energy and Industrial Technology Development Organization (NEDO). We acknowledge Dr. Ryotaro Matsuda and Dr. Hiroshi Sato for measuring the *in situ* XRPD of SD-65 under the presence of 1,3-butadiene and Dr. M. Negroni for assistance in MAS NMR spectroscopy.

Keywords: gas separation • porous coordination polymer • 1,3-butadiene • host-guest systems • microporous materials

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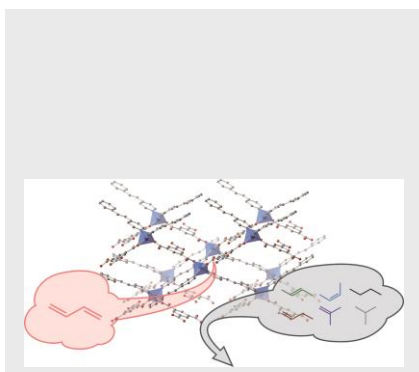
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