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Editor's Choice

Superuniform Molecular Nanogate Fabrication on Graphene Sheets of Single Wall Carbon Nanohorns for Selective Molecular Separation of CO_2 and CH_4

Tomonori Ohba,*[1] Hirofumi Kanoh,[1] and Katsumi Kaneko[2]
[1] *Graduate School of Science, Chiba University, 1-33 Yayoi, Inage-ku, Chiba 263-8522*
[2] *Research Center for Exotic Nanocarbons, Shinshu University, 1-17-1 Wakasato, Nagano 380-8553*

(Received July 8, 2011; CL-110582; E-mail: ohba@pchem2.s.chiba-u.ac.jp)

Superuniform nanosized gates (nanogates; 0.41 ± 0.02 nm in size) were donated on graphene sheets of single wall carbon nanohorn (SWCNH) particles by controlled oxidation. Superuniform nanogate donation confers high molecular selectivity and large adsorption capacity upon SWCNH. The molecular selectivity of CO_2 over CH_4 attains 17 below 0.01 MPa by the nanogate separation.

A new clean energy source for achieving a stable energy supply and reducing the emission of greenhouse gases such as CO_2 is in great demand. Biogas is a promising energy source for a clean and environmentally friendly fuel. The main components of biogas are 30–70% CH_4 and 20–60% CO_2.[1,2] The utilization of biogas requires the separation of CH_4 and CO_2 as well as storage of the former. In addition, CO_2 must be removed as the most common greenhouse gas. For these reasons, many studies have been performed with the aim of achieving materials with high separation ability.[3–13] Several techniques based on absorption, cryogenic distillation, membrane separation, and adsorption can be applied to intensive separation systems. Reported selectivity of CO_2 over CH_4 is 20–90 for organic polymers and 1–30 for porous media.[6–13] Basu et al. review biogas separation using membrane separation, which is used for more commercial and industrial purposes.[13] These membranes are fabricated from organic polymer and porous media. Adsorption separation processes have the advantages of high energy efficiency, easy control, and continuous operation. Typical porous media for adsorption separation include zeolites, porous carbons, and more recently, metal–organic frameworks.[3,5,7–12] These media, which possess narrow and well-defined nanopores, can separate two or more molecules according to differences in molecular size. However, they generally have a small nanopore capacity. Therefore, for these porous media to be useful in gas separation by adsorption, it is necessary that they achieve a larger nanopore capacity and uniform nanopore entrances.

Single wall carbon nanohorns (SWCNHs) have the structure of a graphene sheet rolled up into a tube.[14,15] The internal nanopores of SWCNHs are originally closed pores, although they can be opened by partial oxidation.[16] Adsorbed molecules can then pass into the internal nanopores through holes on the graphene sheets of SWCNH particles. Finely controlled oxidation techniques can donate molecule-sized holes that serve as nanosized molecular gates (nanogates), on the graphene sheets of SWCNH particles. The length of the nanogates should be similar to the thickness of graphene (i.e., 0.34 nm). On the other hand, typical carbon molecular sieves have long and narrow slit-shaped nanopores.[17–19] Hence, separation mechanisms using nanogates intrinsically differ from those of typical gas separation processes by molecular sieves. In other words, a high selectivity and large internal nanopore capacity can be achieved by nanogate-fabricated SWCNHs.

The treatment conditions for opening holes on the graphene sheets of SWCNH particles are determined by thermogravimetric analysis in an O_2 atmosphere of $100\,mL\,min^{-1}$. High-resolution transmission electron microscopy observations were carried out on the closed-, nanogate-, and open-SWCNH particles using a JEM-2100F at 120 kV (JEOL; Chiba CAC). Multimolecular probe analysis was conducted using N_2, CH_4, and SF_6 molecules. Here, the molecular sizes of N_2, CH_4, and SF_6 are 0.37, 0.42, and 0.59 nm, respectively, as estimated by the Lennard–Jones molecular diameters in a one-centered model.[16] SWCNHs were evacuated at 423 K below 10 mPa for 2 h prior to each adsorption measurement of N_2 at 77 K, CH_4 at 160 K, and SF_6 at 303 K in a volumetric system. The adsorption isotherms of CO_2 and CH_4 were also measured at 273 K after the same vacuum treatment as described above.

SWCNH samples are named as follows: As synthesized SWCNH; closed-SWCNH, SWCNH oxidized for 0.5 h; nanogate-SWCNH, and SWCNH oxidized for 9 h; open-SWCNH (see Supporting Information; SI for details).[22] High-resolution transmission electron microscopy (TEM) images of closed-SWCNH, nanogate-SWCNH, and open-SWCNH particles are shown in Figure S-3 (SI[22]). Closed-SWCNH particles, which are composed of tips and tubes, assemble to form spherical structures. The internal nanopores, which have an average diameter of 3 nm,[20] are sealed by graphene sheets. Therefore, the particle density ($1.3\,g\,cm^{-3}$) is quite low compared to the graphite particle density of $2.3\,g\,cm^{-3}$ reported in previous papers.[16,17] Assemblies of nanogate-SWCNH particles have a structure similar to those of closed-SWCNHs, although many pinholes may be observed on the graphene walls. The insert in Supporting Information Figure S-3b[22] shows a side view of such a pinhole, although the image is not simply understood. These pinholes serve as nanogates. In the case of open-SWCNHs, the tips have disappeared as a result of oxidation. Thus, open-SWCNH particles have large pore entrances of about 3 nm in diameter. Therefore, we presume that closed-SWCNH particles have closed internal nanopores whereas open-SWCNH particles have perfectly open internal nanopores. However, we could not accurately estimate the nanogate sizes from the TEM images. To resolve this issue, we evaluated the nanogate size distribution by multimolecular probe analysis, which uses adsorption isotherms of gas molecules differing in size.

Figure 1 shows the adsorption isotherms of N_2 at 77 K, CH_4 at 160 K, Xe at 303 K, and SF_6 at 303 K. The adsorbed amounts of N_2 at $P = 0.06$ MPa for closed-, nanogate-, and open-SWCNHs as shown in Figure 1a were 160, 660, and 680 $mg\,g^{-1}$, respectively. Therefore, N_2 molecules can efficiently enter the internal nanopores of nanogate- and open-SWCNHs; in

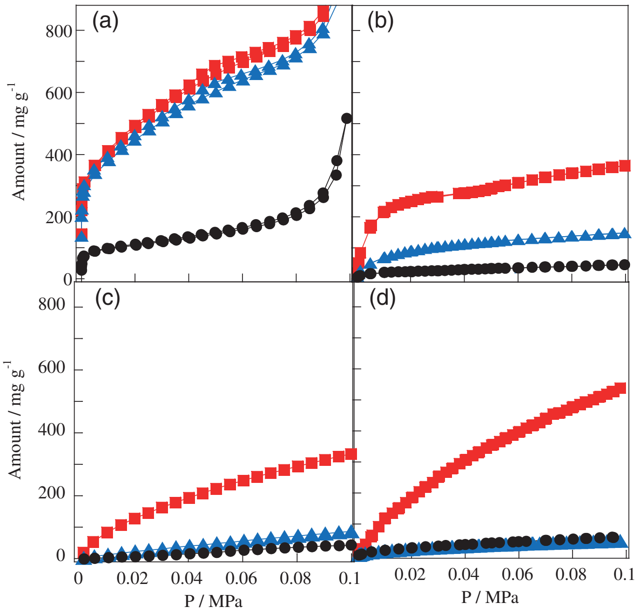

Figure 1. Adsorption isotherms of N_2 at 77 K (a), CH_4 at 160 K (b), Xe at 303 K (c), and SF_6 at 303 K (d). ●: Closed-SWCNH, ▲: nanogate-SWCNH, and ■: open-SWCNH.

contrast, there are no open internal nanopores for the closed-SWCNH. Here, the slight difference in adsorbed amounts between the nanogate- and open-SWCNHs relates to the burnout rates. Therefore, nanogate-SWCNH particles have nanogates larger than 0.37 nm (the molecular size of N_2). In the case of adsorption isotherms for CH_4, as shown in Figure 1b, the adsorbed amounts at $P = 0.06$ MPa for closed-, nanogate-, and open-SWCNHs were 40, 130, and 310 mg g^{-1}, respectively; the adsorbed amount for the nanogate-SWCNH is between the amounts for closed- and open-SWCNHs. This suggests that the nanogates have a diameter similar to the molecular size of CH_4 (0.42 nm). In the case of Xe adsorption (Figure 1c), the adsorbed amounts were 30, 60, and 250 mg g^{-1} for closed-, nanogate-, and open-SWCNHs, respectively. Thus, the nanogate diameters should be somewhat smaller than the Xe molecular size (0.46 nm). On the other hand, SF_6 could not be adsorbed in the internal nanopores of the nanogate-SWCNH. The adsorbed amounts at $P = 0.06$ MPa for closed-, nanogate-, and open-SWCNHs were 40, 40, and 400 mg g^{-1}, respectively. This suggests that the nanogate size is smaller than the molecular size of SF_6 (0.59 nm).

The molecular probe analyses above permit the evaluation of nanogate size, as shown in Figure 2. We assume that the accessibility rates of closed- and open-SWCNHs are 0 and 100%, respectively. Hence, the accessibility rate of a nanogate-SWCNH was evaluated from differences in the adsorbed amounts of nanogate- and closed-SWCNHs. The accessibility rates of N_2, CH_4, Xe, and SF_6 molecules in the internal nanopores of nanogate-SWCNH are 100, 40, 15, and 0%, respectively. These indicate that, for instance, the nanogate size is larger than 0.37 nm (the molecular size of N_2) and smaller than 0.59 nm (the molecular size of SF_6). The fact that 40% of the nanogates also admit CH_4 molecules to the internal nanopores suggests that 40% of the nanogates are larger than 0.42 nm (the molecular size of CH_4) and 60% are smaller. In the same manner, 15% of the nanogates are larger than 0.46 nm (the molecular size of Xe). The nanogate size distribution is readily evaluated from the above accessibility rate using a general Lorentzian distribution in Figure 2. The nanogate size has a sharp distribution with a mean of 0.41 ± 0.02 nm. Therefore, superuniform nanogates were donated on SWCNHs by a finely controlled pore-opening method.

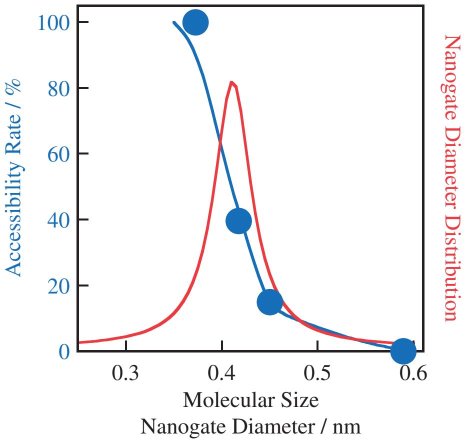

Figure 2. Accessibility to the internal nanopores and nanogate diameter distribution.

Superuniform nanogates could have the ability to separate similar molecules. As mentioned above, the separability of CO_2 and CH_4 has received much attention in recent years because of ecological considerations. Figure 3 shows the adsorption isotherms of CO_2 and CH_4 for closed- and nanogate-SWCNHs at 273 K and the adsorption selectivity evaluated from the ideal adsorption solution theory for equilibrium adsorption. Here the adsorption selectivity relating to the separation ability is defined as adsorption amount of CO_2 over CH_4 at a same pressure. Molecules are adsorbed only in the external nanopores for closed-SWCNHs but in the internal and external nanopores for nanogate-SWCNHs. The adsorption amounts of CO_2 and CH_4 in the internal nanopores are then obtained from differences between the adsorption amounts on closed- and nanogate-SWCNHs. All CO_2 adsorption isotherms show larger adsorbed amounts than the corresponding isotherms for CH_4, because of the stronger interaction of CO_2 with SWCNHs. Nanogate-SWCNHs adsorb a larger amount than closed-SWCNHs, given by the availability of the internal nanopores. The adsorption in the internal nanopores is actually influenced by the nanogates. The selectivity of CO_2 over CH_4 clearly demonstrates a gate effect, as shown in Figure 3b. Here, the molecular size of CH_4 is 0.42 nm, where the short and long axes of CO_2 are 0.38 and 0.57 nm, respectively.[21] Hence, CH_4 is restricted from passing through the nanogate. The selectivity for closed-SWCNHs is 2–3 in the entire pressure range, similar to typical activated carbons. The selectivity for nanogate-SWCNHs is also 2–3 above $P = 0.01$ MPa. The selectivity in the internal nanopores is over 3 below $P = 0.05$ MPa and attains 17 at $P = 0.01$ MPa. Thus, a CH_4 is judged to pass through a nanogate with an average size of 0.42 nm in the low-pressure region, whereas it is pushed into the internal nanopores in the high-pressure region. On the other hand, CO_2 can pass through a nanogate. Therefore,

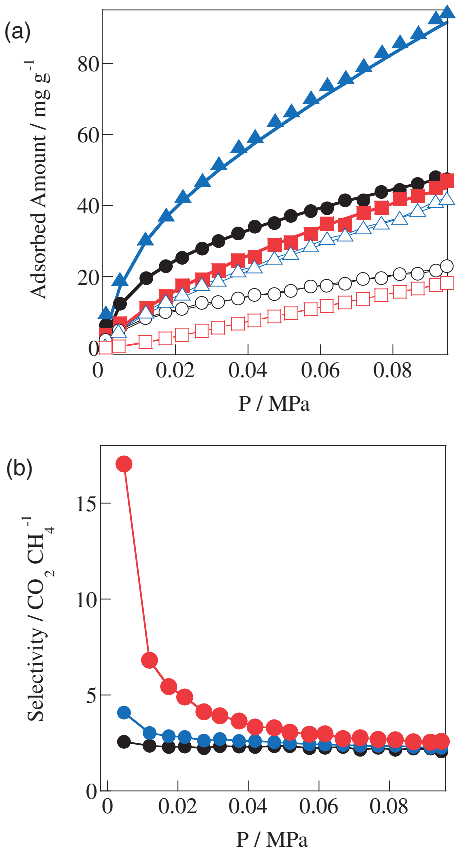

Figure 3. (a) Adsorption isotherms of CO_2 (filled symbols) and CH_4 (open symbols) on closed-SWCNH (black curves) and nanogate-SWCNH (blue curves), and in the internal nanospaces of nanogate-SWCNH (red curves) at 273 K. (b) Selectivity of CO_2 over CH_4 for closed-SWCNH (black), nanogate-SWCNH (blue), and the internal nanopores of nanogate-SWCNH (red).

the high selectivity in the low-pressure range would be strongly affected by the nanogates of SWCNHs.

In conclusion, superuniform molecular nanogates (0.41 ± 0.02 nm in size) were donated on SWCNH particles with a tubular structure resembling that of carbon nanotubes. Nanogate-SWCNHs have superuniform nanogates of molecular size and large internal nanopore capacity. Therefore, nanogate donation confers a high selectivity for CO_2 and a large adsorption capacity upon SWCNHs. Highly selective separation of other molecules and in various conditions could also be possible by further controlling the nanogate size. The nanogate separation mechanism is a novel mechanism of molecular separation.

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