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Kyoto University
Siloxane D4 Capture by Hydrophobic Microporous Materials

Yasuko Mito-oka, a Satoshi Horike, b,c Yusuke Nishitani, a Tadao Masumori, a Munehiro Inukai, d Yuh Hijikata, a Susumu Kitagawa a,b,d

a Research Center, Toyobo Co., Ltd., 2-1-1, Katata, Otsu, Shiga 520-0292, Japan
b Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan.
c PRESTO, Japan Science and Technology Agency (JST), Kawaguchi, Saitama 332-0012, Japan.
d Institute for Integrated Cell-Material Sciences (iCeMS), Kyoto University, Yoshida, Sakyoku, Kyoto 606-8501, Japan.

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ABSTRACT: Porous substances, including crystalline coordination materials and an amorphous organic polymer, were studied for their selective adsorption of siloxane D4. The investigated materials demonstrated a level of uptake comparable to that of conventional activated carbon.

Biogas generally includes methane and carbon dioxide mixtures produced by anaerobic digestion of waste materials. In biogas, the presence of impurities, such as sulfide, halide, and polysiloxane compounds, is a problem because they hinder the purification of methane, which is required for its further use. Several techniques have been developed to remove siloxane, one of the major impurities, from biogas.1 Adsorption on porous activated carbon represents a common practice. However, it is difficult to completely regenerate the activated carbon after the capture of siloxanes because of their strong binding. Furthermore, the co-adsorption of siloxanes and water occurs under humid conditions. Thus, the development of new porous adsorbents for siloxanes is significant. Among the siloxanes in biogas, octamethylcyclotetrasiloxane (siloxane D4, Figure 1a) is highly abundant. In this study, we investigated the selective capture of siloxane D4 by several organic/inorganic microporous compounds.

Porous coordination polymers (PCPs), or metal–organic frameworks (MOFs), and covalent organic frameworks (COFs) have been developed in the last decade.2 These are constructed via coordination or covalent bonds. They have a large surface area and diverse, functional chemical substituents, and are studied for gas storage, separations, and catalysis. There are many reports on the CO2 separation over CH4 by use of these materials.2,4 On the other hand, to the best of our knowledge, there are no reports on siloxane adsorption by these compounds, even though both of the separation technologies are important to purify CH4 from biogas. We focused on siloxane D4, which has a high boiling point (448 K), strong hydrophobicity, and low polarity. Here we employed [ZnO(bdc)(bpz)] (bdc, 1,4-benzenedicarboxylate; bpz, 3,3′,5,5′-tetramethyl-4,4′-bipyrazolate);3 [Al(OH)(2,6-ndc)] (2,6-ndc, 2,6-naphthalenedicarboxylate; DUT-4);4 and amorphous, porous organic framework poly(4,4′-biphenylene)silane (EOF-2) because of their hydrophobicity and large surface area. A conventional activated carbon species was also studied for comparison.

Figure 1. Structures of (a) siloxane D4, (b) [ZnO(bdc)(bpz)2], (c) [Al(OH)(2,6-ndc)] (DUT-4), and (d) poly(4,4′-biphenylene)silane (EOF-2).

Structures of the porous compounds are shown in Figure 1. We characterized the hydrophobicity of the compounds by a water vapor adsorption experiment. Each sample was activated and exposed to water vapor at 30 °C and 60% relative humidity for 3 h under the control of a thermohygrostat. We then evaluated the amount of adsorbed water from the change in weight. The amount of adsorbed water was found to be 5.2, 8.2, and 0.3 wt% for [ZnO(bdc)(bpz)2], DUT-4, and EOF-2, respectively. These levels are comparable to that of activated carbon (3.8 wt%), which was prepared under the same conditions. Only small quantities of H2O were adsorbed because of their hydrophobicity, especially in the case of EOF-2. For this species, the hydrophobic moiety poly(4,4′-biphenylene)silane is responsible for the framework’s hydrophobicity.
For the selective adsorption of siloxane D4 from biogas, co-
adsorption of not only moisture but also other gases, such as CO2
and CH4, by the adsorbents must be prevented. Adsorption iso-
therms of CO2 and CH4 at 298 K were measured. Activated carbon
shows a Langmuir-type isotherm for CO2, and the total amount
adsorbed reaches 51 mLg−1 at 101 kPa. The other three compounds
show linear type isotherms, and their adsorption levels are less than
40 mLg−1. In case of CH4, all four compounds show low levels of
adsorption (less than 20 mLg−1 at 101 kPa). Linear isotherms indi-
cate low affinity between the gases and porous frameworks at 298
K. The adsorption behavior is therefore suitable for selective ad-
sorption of siloxane D4 in the presence of the other impurities.

We estimated the adsorption capacity of these compounds for si-
loxane D4 by a TGA study. Since siloxane D4 has low volatility,
we could not use conventional gas adsorption instruments. TGA
profiles for samples that were activated and exposed to siloxane D4
vapor at 30 °C for 3.5 h were measured. Activated carbon adsorbs
approximately 20 wt% siloxane D4, and desorption is observed in
the temperature range 200–300 °C. The other compounds show
various sorption characteristics. DUT-4 adsorbs 15 wt% of siloxane
D4. This framework strongly confines the molecules, and its re-
lease temperature is over 250 °C. Such stable confinement is not
amenable to the desorption of siloxane D4 using a low regeneration
energy. On the other hand, [Zn2O(bdc)(bpz)2] and EOF-2 show
gradual release beginning near room temperature, and adsorption
uptakes of 30 wt% for [Zn2O(bdc)(bpz)2] and 13 wt% for EOF-2 are
observed. XRD pattern of [Zn2O(bdc)(bpz)2] after removal of the
adsorbed siloxane D4 was same as the initial state, and it indi-
cates its crystallinity is retained via the sorption of siloxane D4.
The BET surface area of activated carbon is 1050 m2g−1, and those of
[Zn2O(bdc)(bpz)2], DUT-4, and EOF-2 are approximately 1500,
1300, and 1000 m2g−1 respectively. The total uptake of siloxane D4
is dependent on the surface area. Consequently, we confirmed
strong hydrophobicity, low adsorption of CO2 and CH4 gases, and
satisfactory siloxane D4 uptake for [Zn2O(bdc)(bpz)2] and EOF-2.
These two compounds release adsorbed siloxane D4 at a tempera-
ture lower than that of activated carbon, and are promising materi-
als with regard to both selectivity and energy consumption for re-
generation. During the siloxane adsorption and desorption exper-
iments, these structures did not change, as determined by powder X-
ray diffraction and solid state NMR measurements.

To investigate the spectral properties of the adsorbed siloxane
D4 in the porous compounds, we performed solid state 29Si NMR
measurements (Figure 2). The peak for bulk siloxane D4 appears at
−19.2 ppm.9 The chemical shift of the Si atoms in EOF-2 is ob-
served at −14.9 ppm, whereas in the original report, it was observed
at −17.9 ppm.6 The difference in the chemical shift is due to the
amorphous nature of the framework. The peak for siloxane D4
adsorbed in these compounds is sharp because of isotropic motion.
The chemical shift of this peak varies among EOF-2, [Zn2O(bdc)(bpz)2],
and DUT-4 (−19.2, −21.6, and −24.5 ppm, respectively). The peak in EOF-2 is the same as that in bulk siloxane
D4, which indicates a weak host–guest interaction. A higher up-
field shift corresponds to an increase in this interaction, thus indi-
cating that DUT-4 has the highest affinity for siloxane D4. This
coresponds to the TGA result, which showed that the release tem-
perature for DUT-4 was the highest of all compounds. The DUT-4
spectrum also shows a small fractional shoulder at −23 ppm. This
is attributed to the variable environment of siloxane D4 in the pores.

Figure 2. Solid state 29Si MAS NMR spectra of (a) EOF-2 framework
exclusively and frameworks with adsorbed siloxane D4: (b) EOF-2, (c)
[Zn2O(bdc)(bpz)2], and (d) DUT-4.

The interaction between siloxane D4 and the framework depends
on the porosity of the structures. The framework of [Zn2O(bdc)(bpz)2] has 3-D connected channels with a bottle-and-
neck-type shape, and DUT-4 has 1-D straight channels with a
rhombic shape. We assume that the stronger interaction of siloxane
D4 with DUT-4 results from a more uniform match between the
shapes of the guest molecule and the pore. We studied the adsorp-
tion mechanism of siloxane D4 in the pore by molecular mechanic
calculations (Figures S6 and S7). Even though we employed vari-
ous conformations as the initial structure, the methyl groups of
siloxane D4 preferably directed to the corners of the rhombic pore
shape of DUT-4 in all the optimized structures. We then considered
that the rectangular shape of siloxane D4 could fit to the pore shape,
generating strong interactions. On the other hand, in
[Zn2O(bdc)(bpz)2], siloxane D4 has a more isotropic nature, con-
sistent with the observation of gradual desorption from lower tem-
peratures.

We studied the selective adsorption properties of the frameworks
under not only gas equilibrium conditions but also kinetic (gas
flowing) conditions. The gas comprising siloxane D4 (5 ppm) in air
at 50% relative humidity and 25 °C was used to evaluate the selec-
tive sorption properties. Breakthrough curves of the compounds are
shown in Figure 3. The gas mixture (pressure, 101 kPa and flow
rate, 0.5 L min−1) was passed through a column filled with 100 mg
of activated powder samples. We monitored the time-dependent
concentration of siloxane D4 in the outlet gas to estimate the effi-
ciency of removal. All the compounds show over 95% removal
efficiency initially, and this level gradually decreases as the amount
of adsorbed material increases. The EOF-2 framework shows a
profile similar to that of activated carbon, and the observed removal
efficiency is reduced to approximately 70% at 500 min. On the
other hand, [Zn2O(bdc)(bpz)2] and DUT-4 show better performance.
The decays of removal efficiency after 300 minutes for these com-
ounds are smaller than that of EOF-2. Even after 1000 min, the
observed efficiencies are over 70%, which indicates their effective
adsorption of siloxane D4. If the compounds preferably adsorb water vapor than siloxane D4, the removal efficiency would decay more rapidly because of water adsorption. The retention of the high efficiency of siloxane D4 removal by [Zn$_2$O(bdc)(bpz)$_2$] and DUT-4 suggests that they have strong selectivity for siloxane D4 even under high humidity conditions. The high level of selectivity is attributed to their strong hydrophobicity and optimal chemical interaction with siloxane D4, leading to high uptake. The EOF-2 framework also exhibits high hydrophobicity; however, the breakthrough curve shows a rapidly decreasing profile because of its weaker interaction with siloxane D4, as suggested by TGA and NMR studies.

In conclusion, we investigated three microporous compounds, [Zn$_2$O(bdc)(bpz)$_2$], DUT-4, and EOF-2, to evaluate their selective adsorption of siloxane D4. Results for their adsorption of water, CO$_2$, and CH$_4$, which are found in biogas, suggested the hydrophobic nature of these frameworks and further indicated that they have only weak interactions with these gases under ambient temperature and pressure. Both equilibration and kinetic studies of the selective adsorption of siloxane D4 indicated that these frameworks have a level of efficiency comparable with that of conventional activated carbon. Among these compounds, [Zn$_2$O(bdc)(bpz)$_2$] is one of the best candidates for the selective adsorption of siloxane D4 at ppm levels under gas flowing conditions. As a future work, we will employ the mixture gas having the exactly same composition of biogas to evaluate the performance of the selectivity for these compounds. These results encourage further studies toward the design of new porous materials for selective removal of various volatile organic compounds, including the family of siloxane molecules, from biogas mixtures under humid conditions.

ASSOCIATED CONTENT

Synthesis of compounds, gas adsorption experiments, TGA, XRD, molecular mechanics calculation.

Figure 3. Breakthrough curves of siloxane D4 for [Zn$_2$O(bdc)(bpz)$_2$] (pink), DUT-4 (blue), EOF-2 (purple), and activated carbon (green) at room temperature. The flue gas composition is siloxane D4 (5 ppm) in air at 50% relative humidity and 298 K. The flow rate is 0.5 L min$^{-1}$, and the space velocity is 100,000 h$^{-1}$.

REFERENCES


AUTHOR INFORMATION

Corresponding Author

Prof. Susumu Kitagawa
E-mail address: kitagawa@iicems.kyoto-u.ac.jp
Fax: +81-75-383-2732; Tel: +81-75-383-2736

Author Contributions

The manuscript was written through contributions of all authors.

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