1. Introduction

“Second-generation” bioethanol derived from abundant and renewable lignocellulosic biomass feedstocks is considered as an attractive biofuel\(^1\)\(^-\)\(^5\). Although industrial-scale production of “first-generation” bioethanol from sugarcane and corn is already underway\(^6\), edible crops should be grown only for food to prevent food shortages as the world’s population increases. Thus, second-generation technology using inedible biomass is a more desirable and sustainable means of bioethanol production compared to the first-generation technology, and the annual production of second-generation bioethanol is increasing\(^7\). However, some specific features of lignocellulosic biomass and fermentable sugars need to be considered to maintain high efficiency of the second-generation bioethanol production processes. The first issue arises from recalcitrance of lignocellulosic biomass that prohibits polysaccharides (i.e., cellulose and hemicellulose) tightly locked in lignocellulosic biomass feedstocks from undergoing depolymerization to fermentable sugars such as glucose, fructose, which is generated via glucose isomerization, and xylose\(^4\),\(^5\). Physicochemical pretreatments disrupt such rigid structures and improve reactivity of the polysaccharides. However, lignin, a macromolecule with a complicated three-dimensional-network structure and the third largest component of lignocellulosic biomass, undergoes fragmentation to release small phenolic compounds including vanillin and syringaldehyde during the pretreatment processes\(^5\),\(^8\). The second issue is the instability of fermentable sugars under the harsh reaction conditions required for the depolymerization of polysaccharides\(^5\), even after physicochemical pretreatments. In addition to a loss of fermentable sugars, their degradation provides undesired furanic by-products, 5-hydroxymethylfurfural (HMF) and furfural (Fig. 1)\(^5\),\(^12\),\(^14\). Besides, another main component of plant cell walls, pectin, also is degraded into such furanics\(^15\). These aromatics, both phenolic and furanic compounds, significantly inhibit the fermentation processes involved in synthesizing bioethanol\(^8\),\(^9\). A previous report indicated that the activity of Saccharomyces cerevisiae was halved in the presence of only 3 mM vanillin in the fermentation broth\(^8\). Similar fermentation processes to produce biodegradable plastics, such as poly(3-hydroxybutyrate), from glucose also were reported to be inhibited by HMF\(^16\),\(^17\). To improve

---

DOI: doi.org/10.1627/jpi.63.163

* To whom correspondence should be addressed.

* E-mail: m.yabushita@tohoku.ac.jp

---

Selective Separation of Biomass-derived Sugars and Aromatics with Aromatic Domains of Metal-organic Frameworks and Surface-modified Silica

Mizuo YABUSHITA\(^1\)* and Atsushi FUKUOKA\(^2\)

\(^1\) Institute of Multidisciplinary Research for Advanced Materials, Tohoku University,
2-1-1 Katahira, Aoba-ku, Sendai 980-8577, JAPAN

\(^2\) Institute for Catalysis, Hokkaido University, Kita 21 Nishi 10, Kita-ku, Sapporo 001-0021, JAPAN

(Received February 12, 2020)

Second-generation bioethanol, which is produced from inedible lignocellulosic biomass resources, is an attractive green fuel for addressing climate change. The efficiency of fermentation processes for synthesizing bioethanol from lignocellulosic-biomass-derived sugars is drastically reduced by aromatic compounds such as 5-hydroxymethylfurfural and vanillin, which are undesirable contaminants released from lignocellulosic biomass into the fermentation broth, even at concentrations on the order of several millimolar. This review describes the selective removal of these aromatic toxins from aqueous mixtures containing sugar co-solute(s) using a variety of adsorbents involving aromatic domains as adsorption sites – metal-organic frameworks and surface-modified \(\text{SiO}_2\) without detectable adsorption of the latter compound(s). The design concept for adsorbents enabling such molecular recognition also is addressed; the surface area and shape of aromatic domains control the degree of interaction with guest molecules (i.e., sugars, furanics, and phenolics) and also are the key to achieving reversible adsorption/desorption processes.

Keywords

Adsorption, Biomass, Calixarene, Metal-organic framework, Molecular recognition, \(\pi-\pi\) interaction
overall efficiency of biorefinery processes that rely on biocatalysts, prior to fermentation steps, the aromatic toxins released from lignocellulosic biomass need to be removed selectively from aqueous solutions containing fermentable sugar co-solutes, without causing any losses of the latter compounds. This review article summarizes our recent approaches to the development of such selective adsorbents through material design.

2. Separation of Aromatics and Sugars by Metal-organic Frameworks

2.1. Surface-area Effects of Aromatic Domains of Metal-organic Frameworks on Affinity for Glucose and 5-Hydroxymethylfurfural

Selective removal of aromatics from sugars necessitates the development of adsorbent materials with molecular recognition property. Our previous thermodynamic study using carbon materials, which also were used as catalysts for cellulose depolymerization [13,14,18,19], demonstrated that the adsorption of sugar molecules on the surface of a carbon material is driven by dispersion forces consisting of CH-π interactions [18–21], while another type of dispersion force, the π-π interaction, is dominant in the adsorption of aromatic compounds on carbon materials [22]. Since CH-π interactions are weaker than π-π interactions [23], discriminating between these interactions is the key to selective separation of aromatics from sugars.

In other work, we found that pyrene units involved in the metal-organic framework (MOF) NU-1000 [24] did not adsorb glucose at all, even at its saturation concentration, but showed affinity for sugar dimers such as cellobiose and lactose [25]. This discriminating behavior of NU-1000 for sugar compounds was rationalized by electronic structure calculations. The calculated interaction of a glucose molecule with the pyrene unit in water (adsorption enthalpy (ΔH_{ads}) = -14.7 kcal mol^{-1}) is weaker than that of a cellobiose molecule with the same unit (ΔH_{ads} = -21.2 kcal mol^{-1}), due to fewer CH groups present in the former sugar molecule. In addition, the small surface area of each pyrene unit of NU-1000 also could be responsible for the lack of glucose affinity, since this aromatic domain limits the number of interactions with sugar molecule CH groups (i.e., CH-π interactions). In this context, we theorized that, in stark contrast to the large and disordered graphene sheets found in carbon materials, which interact with enough sugar molecule CH groups to trigger adsorption, small and ordered aromatic domains such as the pyrene units of NU-1000 have the potential to be selective sites that do not adsorb sugars but can adsorb aromatics via π-π interactions.

To examine this theory, the surface-area effects of aromatic domain on the affinity for adsorbates were investigated initially using various MOFs, since this class of materials can be designed by tuning organic linkers as well as inorganic nodes. As illustrated in Fig. 2(A), the MOFs consisting of different linkers (i.e., phenyl units (Mg_{2}(m-dobdc)) [26], biphenyl units (mmen-Mg_{2}(dobpdc)) [27], and pyrene units (NU-1000) [24]) were tested in aqueous solution containing either glucose or HMF at an initial concentration of 16 mM (Fig. 2(B)). Three MOFs did not adsorb glucose at all, indicating that all of these aromatic domains were too small to interact well with a glucose molecule. For HMF adsorption, unlike Mg_{2}(m-dobdc) and mmen-Mg_{2}(dobpdc), both of which did not exhibit any

Compounds in solid and dotted boxes are fermentable sugars and aromatics toxic to the biocatalysts used for fermentation processes, respectively.

Fig. 1 Schematic of Second-generation Bioethanol Production
affinity, NU-1000 exhibited an HMF uptake of 146 mg g_{NU-1000}^{-1}. These results suggest that the site requirement for \( \pi-\pi \) interaction with an HMF molecule is a domain composed of at least four aromatic rings.

### 2.2. Selective Separation of Sugars and Furanics by NU-1000

In a single-component aqueous solution containing either glucose or HMF, only the latter was adsorbed on the surface of NU-1000. These results motivated us to investigate the detailed adsorption processes of HMF, another furanic compound furfural, and monomeric sugars (i.e., glucose, fructose, and xylene), all of which can be produced from lignocellulosic biomass\(^{13}\).

**Figures 3(A) and 3(B)** show the single-component adsorption isotherms for these five adsorbates over NU-1000. HMF and furfural were adsorbed on NU-1000 as a type I isotherm, indicating that the adsorption processes were enthalpically highly favorable\(^{29,30}\). The adsorption equilibrium constants (\( K_l \)) for HMF and furfural calculated from the isotherm data and the Langmuir equation were 120 \( \pm 16 \) M\(^{-1} \) and 28 \( \pm 6 \) M\(^{-1} \), respectively (see **Table 1**). The difference in affinity for aromatic compounds is discussed below. In contrast to these furanic compounds, NU-1000 showed no affinity for any of the monomeric sugars, consistent with the results shown in **Fig. 2**.

As shown in **Figs. 3(C) and 3(D)**, competitive adsorption processes using NU-1000 were investigated using two different aqueous solutions containing C6 compounds (i.e., glucose, fructose, and HMF) or C5 compounds (i.e., xylene and furfural)\(^{29}\). Each furanic compound was adsorbed well on NU-1000, while no adsorption uptake of sugars was observed. The \( K_l \) values for HMF and furfural in the competitive adsorption were 96 \( \pm 21 \) M\(^{-1} \) and 26 \( \pm 5 \) M\(^{-1} \), respectively (**Table 1**), both of which are close to those in the single-component mode. This similarity indicates that the sugar co-solutes do not impact the interaction between the furanic adsorbates and pyrene units of NU-1000. Note that, although previous studies reported that activated carbons\(^{31,32}\), zeolites\(^{33}\), and hyper-cross-linked polymers\(^{34,35}\) also adsorbed furanic compounds selectively with tiny or no uptake of sugar co-solutes, the origin of high selectivity observed for these adsorbents is totally different from the molecular recognition property of NU-1000. These reported adsorbents show affinity for monomeric sugars to some extent in a single-component mode, and thus the tiny (or zero) sugar uptake in multicomponent aqueous mixtures likely arises from the occupation of adsorption sites by more dominant furanic adsorbates.

This outstanding molecular recognition property of NU-1000 was highlighted in further competitive adsorption experiments in an aqueous mixture containing 8 mM HMF and 500 mM glucose (**Fig. 4**\(^{28}\)). Even in the presence of a 63-fold excess amount of glucose co-solute, NU-1000 removed 80 % of HMF originally present in the mixture, with no observable uptake of glucose. The control adsorbents consisting of commercially available carbon materials, activated carbon (MSC-30, Kansai Coke & Chemicals) and carbon black (Black Pearl 2000, Cabot, denoted as BP2000), removed greater than 97 % of HMF, but simultaneously adsorbed more than 2.5 % of glucose from the same aqueous mixture.

### 2.3. Selective Separation of Sugars and Phenolics by NU-1000

To explore the applicability of NU-1000, the single-component adsorption of a variety of phenolic compounds (i.e., 4-hydroxybenzaldehyde, 4-hydroxybenzoic acid, vanillin, vanillic acid, syringaldehyde, and syringic acid), which are possible fragments derived from lignin\(^{38-41}\), on NU-1000 was investigated\(^{36}\). Consistent with the adsorption of furanic compounds (**Figs. 3(A) and 3(B)**), isotherms for all of the phenolics also exhibited type I behavior (**Fig. 5**), indicating that these aromatic compounds displayed high affinity for NU-1000. The \( K_l \) values for the two categories of aldehydes (i.e., 4-hydroxybenzaldehyde, vanillin, and syringaldehyde) and carboxylic acids (i.e., 4-hydroxybenzoic acid, vanillic acid, and syringic acid) gradually increased with the number of methoxy groups (**Table 2**). These trends imply the importance of surface area of aromatic adsorbates for affinity for NU-1000; this hypothesis was supported both experimentally and computationally by the direct correlation found in the parametric plots of adsorption Gibbs free energy.

---

**Note:** The original text contains references which are not included in the provided extract. For a complete understanding, these references should be consulted. The data and figures mentioned are illustrative of the selective separation and adsorption properties of NU-1000 in the context of lignocellulosic biomass processing.
\[ \Delta G^{\text{ads}} \] as a function of surface area of aromatic compounds (Fig. 6). Another important finding from this direct scaling is the lack of dependence on a class of functionalities involved in an adsorbate molecule, since a significant mismatch should be observed in these parametric plots if some functional groups showed specifically stronger (or weaker) affinity for NU-1000 than other functionalities.

The contrasting affinity of NU-1000 for these six phenolic compounds and glucose again provided an opportunity to examine competitive adsorption. In this experiment, the separation selectivity of NU-1000 was elucidated using an aqueous mixture containing these seven solutes (500 mM glucose and 3 mM of each phenolic compound), which imitates actual fermentation broths. NU-1000 adsorbed 171 mg g NU-1000–1 of phenolic compounds in total (corresponding to 99 % of the six phenolics originally present in the aqueous mixture), while glucose uptake was not detected. Under the same conditions, the activated carbon material MSC-30 removed almost all phenolic compounds along with 226 mg gMSC-30–1 of glucose.

The high selectivity of NU-1000 observed in competitive adsorption clearly demonstrated this MOF material to be a unique adsorbent possessing molecular recognition that can sequester aromatic and sugar compounds, even in the presence of a greater excess amount of sugar compounds in the same aqueous solution. In contrast, this adsorbent has the drawback of incomplete regeneration via extraction of adsorbed aromatic compounds.

Dashed lines are isotherms replicated using Langmuir parameters.

Fig. 3 Adsorption Isotherms of Furansics and Sugars on NU-1000 at 297 K in Both Single and Competitive Modes

---

Table 1 Adsorption Equilibrium Constants \( (K_L) \) for Each Adsorbate in Both Single-component and Competitive Modes on NU-1000 at 297 K

| Adsorbate | Single \( [M^{-1}] \) | Competitive \( [M^{-1}] \) |
|-----------|-------------------|-------------------|
| Glucose   | N/A \(^{a)} \)   | N/A \(^{a)} \)   |
| Fructose  | N/A \(^{a)} \)   | N/A \(^{a)} \)   |
| HMF       | 120 ± 16          | 96 ± 21           |
| Xylose    | N/A \(^{a)} \)   | N/A \(^{a)} \)   |
| Furfural  | 28 ± 6            | 26 ± 5            |

\(^{a)}\) Adsorption equilibrium constant, determined from the Langmuir equation.

\(^{b)}\) Not determined, due to no detectable adsorption.
because of its excessively strong interaction with aromatic molecules, reflected by their large $K_L$ values (see Table 2). This implies that the adsorption capacity of NU-1000 decreases upon repeated use for separation of aromatics and sugars due to accumulation of the former compounds. Thus, control of the degree of interaction for enabling extraction of guest molecules while maintaining high separation selectivity is necessary.

Table 2  Adsorption Equilibrium Constants ($K_L$) for Each Adsorbate on NU-1000

| Adsorbate              | Surface areaa) [Å²] | $K_L$b) [M⁻¹] |
|------------------------|---------------------|--------------|
| Furfural               | 109.1               | 28 ± 6       |
| HMF                    | 136.0               | 120 ± 16     |
| 4-Hydroxybenzaldehyde | 133.6               | 443 ± 79     |
| 4-Hydroxybenzoic acid | 139.9               | 2431 ± 653   |
| Vanillin               | 159.2               | 8017 ± 1680  |
| Vanillic acid          | 165.5               | 20407 ± 5251 |
| Syringaldehyde         | 185.3               | 17947 ± 3974 |
| Syringic acid          | 191.6               | 42639 ± 6229 |

a) Estimated from the optimized geometry by electronic structure calculations (see the supporting information of Ref. 35).
b) Adsorption equilibrium constant, determined from the Langmuir equation.

---

**Fig. 4** Competitive Adsorption of Glucose and HMF on Various Adsorbents at the Initial Concentrations of Glucose (500 mM) and HMF (8 mM)

**Fig. 5** Single-component Adsorption Isotherms of Phenolics on NU-1000

Dashed lines are isotherms replicated using Langmuir parameters.

J. Jpn. Petrol. Inst., Vol. 63, No. 4, 2020
3. Surface-modified SiO₂ Adsorbents for Selective Separation of Aromatics and Sugars

A prerequisite for development of selective and regenerable adsorbents is the precise control of the degree of host-guest interactions. As opposed to the conjugated aromatic pyrene units of NU-1000, we assumed that a hydrophobic pocket consisting of calixarene, which is a macrocyclic molecule composed of phenolic units linked by methylene groups and has been previously reported to encapsulate hydrocarbons in aqueous solutions, would exhibit a suitable degree of interaction with guest molecules for both adsorption and desorption processes. Therefore, a variety of modifiers, including p-t-butylcalix[4]arene, were grafted onto the surface of SiO₂ to elucidate the affinity of each modifier for aromatic adsorbates in aqueous solution.

Figure 8 represents the isotherms for single-component adsorption of glucose and HMF on each surface-modified SiO₂ adsorbent. No adsorption was observed for glucose onto any surface-modified SiO₂ adsorbents, while HMF was adsorbed onto the surfaces of calix/SiO₂ and DMPS/SiO₂ (see Fig. 7 for sample denotations). The affinity of calix/SiO₂ for HMF elucidated from Henry’s law constant (\( K_H \)) was 1.2 ± 0.0 g g⁻¹ M⁻¹, which is 4.1-fold greater than the \( K_H \) value of DMPS/SiO₂ (0.29 ± 0.01 g g⁻¹ M⁻¹), probably due to the presence of four phenolic units on the former adsorbent, which surround a cavity and interact simultaneously with a guest molecule. Meanwhile, the interaction between HMF and calix/SiO₂ was 35-fold weaker than that between HMF and NU-1000 (\( K_H = 42 \) g g⁻¹ M⁻¹), which could be beneficial to guest desorption. A lack of HMF adsorption over the control adsorbents, bare SiO₂ and TMS/SiO₂, indicates that aromatic domains are required for interaction with the aromatic adsorbate. In competitive adsorption experiments using glucose and HMF, calix/SiO₂ possessed molecular recognition and adsorbed HMF, but only with a \( K_H \) value of 1.2 ± 0.0 g g⁻¹ M⁻¹, which is consistent with the value observed in the single-component adsorption experiment. The observed adsorption performance of calix/SiO₂—a weaker interaction with HMF compared to NU-1000 and molecular recognition property—prompted an investigation to determine whether this adsorbent could be used repeatedly for separation of HMF from aqueous mixtures containing glucose. Figure 9 shows the reusability of calix/SiO₂ for competitive adsorption of glucose and HMF; in these experiments, the adsorbent was reused after being washed with deionized water in each cycle. The fresh adsorbent exhibited an...
HMF uptake of 2.9 mg g<sub>adsorbent</sub>⁻¹, while no glucose uptake was observed. Although HMF uptake decreased to 1.7 mg g<sub>adsorbent</sub>⁻¹ in the second cycle, calix/SiO<sub>2</sub> maintained this adsorption performance up to the fourth cycle, without causing glucose adsorption in any cycles. This observed change in the HMF uptakes indicates the presence of both reversible and irreversible adsorption sites on calix/SiO<sub>2</sub>; the former sites can release guest molecules upon water washing and are reusable for next cycle, but the latter binds guest molecules too tightly to release them upon washing. As demonstrated here, the precise control of degree of host-guest interactions achieved by molecular-level design of adsorption sites is of great importance for adsorption/desorption processes as well as reusability of adsorbents.

4. Conclusions

This review article summarizes our recent researches on the development of adsorbents that enable the selective sequestration of undesired aromatic compounds from aqueous mixtures containing desirable sugar compounds. The degree of host-guest interactions was controlled successfully by altering the nature of the adsorption sites (i.e., aromatic domains in MOFs and grafted species on a surface of SiO<sub>2</sub>) and the impact on molecular recognition properties highlights the importance of precise material design. Such controlled host-guest interactions also are beneficial to achieving reversible sorption processes. The adsorbents introduced in this review article and/or the ones developed in the future based on the material design concept described here could pave the way for efficient use of lignocellulosic biomass feedstocks and contribute to addressing climate change.

Acknowledgments

We appreciate the financial support provided by the Advanced Low Carbon Technology Research and Development Program (ALCA) of the Japan Science and Technology Agency (JST), a Grant-in-Aid for Fellows of the Japan Society for the Promotion of Science (KAKENHI, 14J01171), and a Grant-in-Aid for Young Scientists (19K15355). We also are grateful to our collaborators, Prof. Alexander Katz, Dr. Nicolás A. Grosso-Giordano, Prof. Jeffrey R. Long, Dr. Kathleen A. Durkin, Dr. David Small (University of California, Berkeley), Prof. Omar K. Farha, Dr. Peng Li (Northwestern University), Prof. Laura Gagliardi, Dr. Varinia Bernales (University of Minnesota), and Dr. Hirokazu Kobayashi (Hokkaido University) for their contributions regarding material design, material syntheses, and electronic structure calculations.
References

1) Wyman, C., “Handbook on Bioethanol: Production and Utilization,” Taylor & Francis, Washington, DC (1996).
2) Goldemberg, J., Science, 315, (5813), 808 (2007).
3) Service, R. F., Science, 345, (6201), 1111 (2014).
4) Yabushita, M., Kobayashi, H., Fukuoka, A., Appl. Catal. B: Environ., 145, (1) (2014).
5) Liu, C.-G., Xiao, Y., Xia, X.-X., Zhao, X.-Q., Peng, L., Srinophakun, P., Bai, F.-W., Biotechnol. Adv., 37, (3), 491 (2019).
6) Ethanol Producer Magazine—The Latest News and Data About Ethanol Production, http://www.ethanolproducer.com/plants/listplants/US/Existing/All (accessed February 11, 2020).
7) 2019 Ethanol Industry Outlook by Renewable Fuels Association, https://ethanolrfa.org/wp-content/uploads/2019/02/RFA2019Outlook.pdf (accessed February 11, 2020).
8) Delgenes, J. P., Moletta, R., Navarro, J. M., Enzyme Microb. Technol., 19, (3), 220 (1996).
9) Klinke, H. B., Thomsen, A. B., Ahring, B. K., Appl. Microbiol. Biotechnol., 66, (1), 10 (2004).
10) Almeida, J. R. M., Modig, T., Peterson, A., Hahn-Hägerdal, B., Lidén, G., Gorwa-Grauslund, M. F., J. Chem. Technol. Biotechnol., 82, (4), 340 (2007).
11) Mhlongo, S. I., den Haan, R., Viljoen-Bloom, M., van Zyl, W. H., Enzyme Microb. Technol., 81, 16 (2015).
12) Kobayashi, H., Komanoya, T., Hara, K., Fukuoka, A., ChemSusChem, 3, (4), 440 (2010).
13) Kobayashi, H., Yabushita, M., Komanoya, T., Hara, K., Fujiya, I., Fukuoka, A., ACS Catal., 3, (4), 581 (2013).
14) Yabushita, M., Kobayashi, H., Hara, K., Fukuoka, A., Catal. Sci. Technol., 4, (8), 2312 (2014).
15) Martens, D. A., Loeffelmann, K. L., Soil Biol. Biochem., 34, (10), 1393 (2002).
16) Matsumoto, K., Kobayashi, H., Ikeda, K., Komanoya, T., Fukuoka, A., Taguchi, S., Bioresour. Technol., 102, (3), 3564 (2011).
17) Nduko, J. M., Suzuki, W., Matsumoto, K., Kobayashi, H., Ooi, T., Fukuoka, A., Taguchi, S., J. Biosci. Bioeng., 113, (1), 70 (2012).
18) Chung, P.-W., Yabushita, M., To, A. T., Bae, Y., Jankolovits, J., Kobayashi, H., Fukuoka, A., Katz, A., ACS Catal., 5, (11), 6422 (2015).
19) Yabushita, M., Techikawara, K., Kobayashi, H., Fukuoka, A., Katz, A., ACS Sustainable Chem. Eng., 4, (12), 6844 (2016).
20) Yabushita, M., Kobayashi, H., Hasegawa, J., Hara, K., Fukuoka, A., ChemSusChem, 7, (5), 1443 (2014).
21) Chung, P.-W., Charmot, A., Click, T., Lin, Y., Bae, Y., Chu, J.-W., Katz, A., Langmuir, 31, (26), 7288 (2015).
22) Ania, C. O., Parra, J. B., Piu, J. J., Fuel Process. Technol., 77-78, 337 (2002).
23) Singh, N. J., Min, S. K., Kim, D. Y., Kim, K. S., J. Chem. Theory Comput., 5, (3), 515 (2009).
24) Mondloch, J. E., Bury, W., Faren-Mijenez, D., Kwon, S., DeMarco, E. J., Weston, M. H., Sarjeant, A. A., Nguyen, S. T., Stair, P. C., Snurr, R. Q., Farha, O. K., Hupp, J. T., J. Am. Chem. Soc., 135, (28), 10294 (2013).
25) Yabushita, M., Li, P., Bernalas, V., Kobayashi, H., Fukuoka, A., Gagliardi, L., Farha, O. K., Katz, A., Chem. Commun., 52, (44), 7094 (2016).
26) Kapelewski, M. T., Geier, S. J., Hudson, M. R., Stück, D., Mason, J. A., Nelson, J. N., Xiao, D. J., Hulvey, Z., Gilmore, E., FitzGerald, S. A., Head-Gordon, M., Brown, C. M., Long, J. R., J. Am. Chem. Soc., 136, (34), 12119 (2014).
27) McDonald, T. M., Lee, W. R., Mason, J. A., Wiers, B. M., Hong, C. S., Long, J. R., J. Am. Chem. Soc., 134, (16), 7056 (2012).
28) Yabushita, M., Li, P., Kobayashi, H., Fukuoka, A., Farha, O. K., Katz, A., Chem. Commun., 52, (79), 11791 (2016).
29) Sing, K. S. W., Everett, D. H., Haul, R. A. W., Moscou, L., Pierotti, R. A., Rouquérol, J., Siemieniewska, T., Pure Appl. Chem., 57, (4), 603 (1985).
30) Thommes, M., Kaneko, K., Neimark, A. V., Olivier, J. P., Rodriguez-Reinoso, F., Rouquérol, J., Sing, K. S. W., Pure Appl. Chem., 87, (9-10), 1051 (2015).
31) Vinke, P., van Bekkum, H., Starch/stärke, 44, (3), 90 (1992).
32) Dornath, F., Pan, W., Micropor. Mesopor. Mater., 191, 10 (2014).
33) Ranjan, R., Thust, S., Gounaris, C. E., Woo, M., Foudas, C. A., von Keitz, M., Valantzas, K. I., Wei, J., Tsapatsis, M., Micropor. Mesopor. Mater., 122, (1-3), 143 (2009).
34) Deitoni, C., Gierlich, C. H., Rose, M., Palkovits, R., ACS Sustainable Chem. Eng., 2, (10), 2407 (2014).
35) Schute, K., Rose, M., ChemSusChem, 8, (20), 3419 (2015).
36) Yabushita, M., Li, P., Durkin, K. A., Kobayashi, H., Fukuoka, A., Farha, O. K., Katz, A., Langmuir, 33, (17), 4129 (2017).
37) Notestein, J. M., Katz, A., Iglesia, E., Langmuir, 22, (9), 4004 (2006).
38) Thompson, A. B., Cope, S. J., Swift, T. D., Notestein, J. M., Langmuir, 27, (19), 11990 (2011).
39) Thompson, A. B., Scholes, R. C., Notestein, J. M., ACS Appl. Mater. Interfaces, 6, (1), 289 (2014).
40) Yabushita, M., Grosso-Giordano, N. A., Fukuoka, A., Katz, A., ACS Appl. Mater. Interfaces, 10, (46), 39670 (2018).
要 旨

金属有機構造体や表面修飾シリカの芳香族ドメインを用いたバイオマス由来糖化合物と芳香族化合物の選択的吸着分離

嶋下 瑠帆†1, 福岡 淳†2

†1 東北大学多元物質科学研究所，980-8577 仙台市青葉区片平2丁目1番1号
†2 北海道大学炭媒科学研究所，001-0021 札幌市北区北21条西10丁目

非可食バイオマスから製造される第二世代バイオエタノールは、環境低負荷なガソリン添加剤としてその利活用が世界的に進められている。バイオエタノール製造における重要工程は、リグノセルロースを解重合して得られた糖化合物を原料に用いた発酵プロセスである。本プロセスは、バイオマス由来の副生成物（主に5-ヒドロキシメチルフルフラールやバニリン等の芳香族化合物）がわずかにでもきょう難していると著しく吸着率が低下することが知られている。本稿では、このような芳香族化合物を糖化合物水溶液で高選択的に吸着・分離するために我々が開発してきた、芳香族ドメインを有する吸着剤（金属有機構造体や表面修飾シリカ）について概説する。特に、芳香族ドメインの大きさや形状が各吸着質との相互作用の強さに与える影響について言及し、分子認識能の発現に必要な材料の性状ならびに設計指針を述べる。