Characterization of carbon cryogel microspheres as adsorbents for VOC

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ABSTRACT

Adsorption characteristics of carbon cryogel microspheres (CC microspheres) with controlled porous structure composed of mesopores ($2\,nm < d_p < 50\,nm$; d_p is pore diameter) and micropores ($d_p < 2\,nm$) were studied to examine their suitability as adsorbents for a volatile organic compound (VOC). The amount of toluene, as a model VOC, adsorbed on the CC microspheres could be changed by varying either the size of the mesopores or the volume of the micropores. The peak temperature of the temperature-programmed desorption profiles of toluene from the CC microspheres was higher than that from granular activated carbon (GAC) with numerous micropores, indicating that toluene is adsorbed more strongly on CC microspheres than on GAC. To permit the practical use of CC microspheres, the adsorption characteristic of moisture on CC microspheres and GAC were evaluated. The effect of adsorption of moisture on the gas permeation property of an adsorption module prepared from the CC microspheres was also examined.

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1. Introduction

Pollution of atmospheric and water environments is of growing concern worldwide. Since many VOCs cause air pollution by forming suspended particulate matter or by generating photochemical smog, the concentration of VOCs in the atmosphere is strictly controlled in many countries. To protect the environment from the pollution caused by VOCs, it is necessary, as a first step, to be able to detect such pollutants in the atmosphere or water using a simple method. Solid-phase extraction (SPE) is an efficient method of concentrating dilute pollutants from the environment, using a filter packed with an adsorbent. In SPE, tailoring the adsorbent to the target pollutant is the key to enhance adsorption efficiency, which leads to more sensitive and accurate analytical methods. Recently, the adsorption characteristics of various types of porous materials have been examined as potential adsorbents for VOCs [1–7]. Concerning the physical properties of adsorbents used in the SPE, the presence of micropores ($d_p < 2\,nm$; d_p is pore diameter), which give a large specific surface area, and mesopores ($2\,nm < d_p < 50\,nm$), which enhance intra-particle diffusion and shorten extraction time, are important components [4]. In addition to porous properties, specific interaction between the adsorbent and the target pollutants is needed to improve extraction. For example, the surfaces of multi-walled carbon nanotubes, which are composed of six-fold-ring sheets (graphene sheets) of carbon atoms, are known to be highly hydrophobic and interact strongly with the aromatic rings of organic pollutants such as dioxins, through the formation of π-bonding [8,9].

Activated carbons, which have been widely utilized as adsorbents or support materials of catalysts for environmental protection, possess numerous micropores and a large specific surface area. However, the mesoporosity of most activated carbon is poor [10]. On the other hand, porous carbons prepared from synthesized resins are more likely to have higher controllability in the physical and chemical properties favorable to the efficient adsorption of organic pollutants. A carbon gel is a carbonized form of phenolic resin which can be synthesized by the sol–gel polycondensation of phenolic compounds with aldehydes. By drying the phenolic resin in such a way as to limit the shrinkage of the porous structure, a porous carbon with developed mesoporosity can be obtained. A carbon cryogel is one of these carbon gels which can be prepared by employing freeze-drying during the drying process, and it possesses controlled porous structure suitable for specific adsorption of some organic compounds [11,12]. Especially, carbon cryogel prepared in the form of microspheres (CC microspheres) can be easily packed in a column, which is commonly used in a practical adsorption system.

In the present study, modification of the porous structure of the carbon cryogel microspheres (CC microspheres) is attempted with the aim of controlling the adsorption characteristics. Then, adsorption measurements of a VOC on the CC microspheres were examined and the effects of the porous properties of the CC microspheres on the adsorption characteristics are discussed. Finally, for the practical use of the CC microspheres,

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Table 1
Porous properties of the CC microspheres and GAC.

Adsorbent	S_{total} [a] (m^2/g)	V_{total} [a] (cm^3/g)	d_{peak} [b] (nm)	S_{mes} [a] (m^2/g)	V_{mes} [a] (cm^3/g)	S_{mic} [a] (m^2/g)	V_{mic} [a] (cm^3/g)
CCM200[c]	604	0.43	3.8	293	0.30	311	0.13
CCM400[c]	589	0.68	6.2	305	0.56	284	0.12
CCM800[c]	617	1.04	13.8	276	0.89	341	0.15
CCM400-AC[d]	813	0.85	7.1	341	0.64	472	0.21
CCM400-IM[e]	291	0.59	8.1	283	0.58	8	0.01
GAC	1308	0.57	ND[f]	ND[f]	ND[f]	1308	0.57

[a] Determined by using the α_s-plot [10]: total specific surface area (S_{total}), specific surface area of mesopores (S_{mes}), specific surface area of micropores (S_{mic}), total pore volume (V_{total}), volume of mesopores (V_{mes}) and volume of micropores (V_{mic}).
[b] Peak diameter of pore size distribution determined by using the Dollimore–Heal method [14].
[c] CC microspheres prepared under the condition of $R/C = 200$, 400 and 800, respectively.
[d] CCM400 modified by CO_2 activation.
[e] CCM400 modified by impregnation of phenolic resin.
[f] Not detected.

a tubular-type adsorption module was fabricated and its gas permeation property was examined in the presence of moisture.

2. Experimental

2.1. Preparation of adsorbents

A resorcinol-formaldehyde (RF) aqueous solution, which contains sodium carbonate (Na_2CO_3) as the catalyst for the sol–gel polycondensation, was prepared in the same manner as previously reported [11]. The molar ratio of resorcinol to formaldehyde was fixed at 0.5. The molar ratio of resorcinol to sodium carbonate was changed in the range of 200–800, while the ratio of resorcinol to water was fixed at $0.25\,g\,cm^{-3}$. The CC microspheres were prepared by inverse emulsion polymerization, followed by freeze-drying and carbonization in a N_2 atmosphere. For comparison, granular activated carbon (GAC) derived from petroleum pitch and obtained from Kureha Chemical Industry, Japan was also tested.

With the aim of modifying the porous structure of the CC microspheres, the CO_2 activation and impregnation of phenolic resin were respectively examined in a following manner. In the CO_2 activation, the CC microspheres were exposed to a nitrogen gas flow containing 5 vol.% of CO_2 at 1073 K for 2 h. In the impregnation method, 0.75 g of phloroglucinol as a precursor of the phenolic resin and 1.0 g of Pluronic F127 amphiphilic triblock copolymer (BASF Japan Ltd.) were dissolved in 20 ml of ethanol. The solu-

tion was continuously stirred at room temperature for 24 h until the color of the solution had turned a transparent reddish-brown. Then, 75 mg of the CC microspheres was immersed in the solution and gently agitated for 2 h until air bubbles released from the CC microspheres were no longer observed, indicating that the CC microspheres had been impregnated thoroughly with the phenolic resin. The CC microspheres were then filtered and dried overnight in an oven at 353 K. Finally, the microspheres were heated in a N_2 atmosphere at 1073 K to carbonize the impregnated phenolic resin.

A tubular-type adsorption module was prepared as follows. First, 50 mg of the CC microspheres were dispersed in 10 ml of water containing 1 wt.% of polyvinylpyrrolidone (average molecular weight = 360,000; Wako Pure Chem., Japan) under the irradiation of ultrasound. Then, a tubular silica membrane (diameter 10 mm, length 100 mm; SPG Tech. Co., Ltd.) with mean pore diameter of 100 nm was dipped into the solution. The dipping was repeated for 10 times to completely cover the surface of the silica membrane with the CC microspheres. Finally, the membrane loaded with the CC microspheres was sufficiently dried in an oven at 673 K in a nitrogen gas flow to obtain the adsorption module.

2.2. Characterization of adsorbents

The intra-particle structure of the CC microspheres was observed using a transmission electron microscope (TEM) (HF-2000; Hitachi Ltd.) and the Raman spectrum of the CC microspheres was measured by a Raman spectrophotometer (NRS-2100; JASCO Corp.).

The porous properties of the adsorbents were evaluated using the volumetric gas adsorption method. After outgassing the adsorbents at 523 K for 4 h in a vacuum, the adsorption and desorption isotherms of nitrogen were measured at 77 K using an automatic gas adsorption and desorption apparatus (Belsorp-mini, BEL Japan, Inc.). The adsorption and desorption isotherms of toluene were also measured using an automatic gas adsorption and desorption apparatus (Belsorp 18; BEL Japan, Inc.) at 298 K, after outgassing the adsorbents at 573 K in a vacuum for 4 h prior to the measurements.

Temperature-programmed desorption (TPD) profiles of toluene from the adsorbents were measured using a TPD apparatus (Belcat; BEL Japan, Inc.) equipped with a thermal conductivity detector (TCD). After outgassing the adsorbents at 673 K in a He gas flow for 2 h, standard He gas containing 400 ppm of toluene was introduced to 50 mg of the adsorbents packed in a quartz sample tube, which was thermally controlled at 313 K, at a constant flow rate of $30\,cm^3/min$ for 30 min. During the measurements, the temperature of the cell was raised from 313 K to 673 K at a constant heating rate of 2.5 K/min. Then, desorbed toluene was detected by the TCD which was directly connected to the exit of the sample tube.

The adsorption isotherms of moisture on the adsorbents and the differential heat of adsorption were also measured at 298 K using a
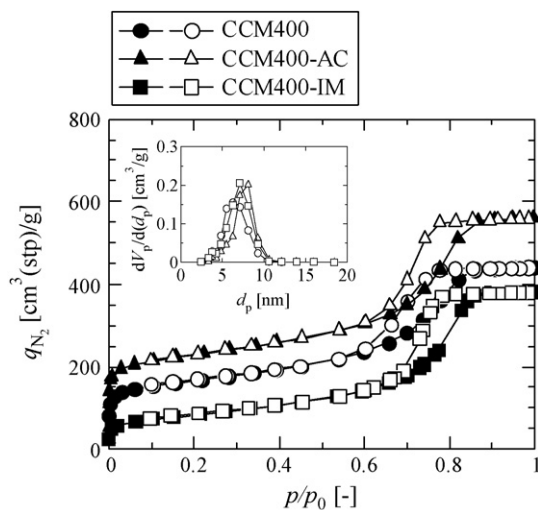

Fig. 1. Isotherms of nitrogen on the CC microspheres at 77 K: closed symbol, adsorption; open symbol, desorption. (The inset shows the pore size distribution of the microspheres.)
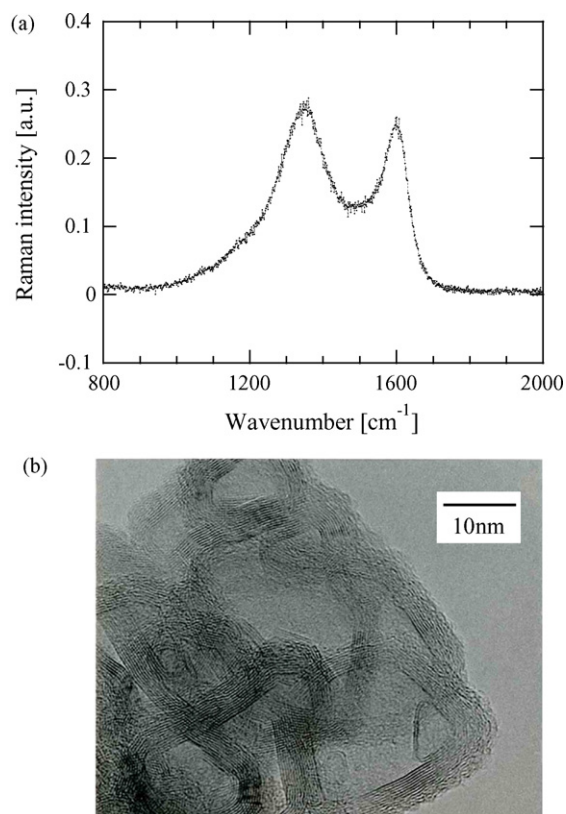
Fig. 2. (a) Raman spectrum of the CC microspheres and (b) TEM image of the primary particles formed in the CC microspheres.
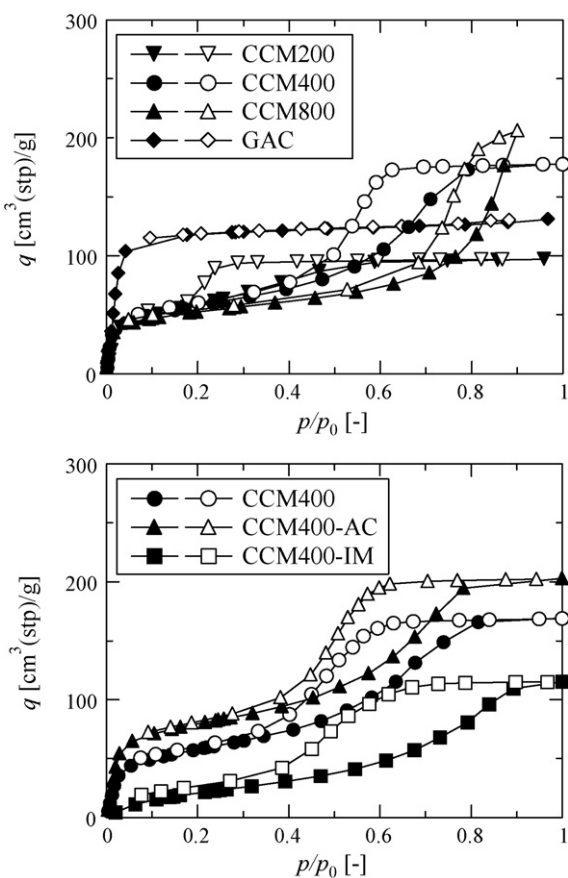

Fig. 3. Isotherms of toluene on the CC microspheres and GAC at 298 K: closed symbol, adsorption; open symbol, desorption.

twin-conduction-type calorimeter (Tokyo Riko Co., Ltd.) after outgassing the adsorbents at 523 K for 4 h in a vacuum. The calorimeter is equipped with two cells, i.e. a sample cell and a reference cell, which were placed in a thermostated air bath [13]. After introducing a controlled amount of moisture from gas storage to the cells, the heat of adsorption was recorded as a difference of the heat evolved in the two cells. Adsorption isotherm of moisture was also determined from the relation between equilibrium vapor pressure and adsorbed amount.

Gas permeability of the adsorption module was evaluated using helium as a probe gas. The adsorption module was set in a sample cell and was outgassed in a helium gas flow at 473 K prior to the measurement. Then, helium gas containing a controlled amount of moisture or hexane as an adsorptive was introduced to the cell, which was set at 313 K, and the permeation flux of helium through the module was measured using a bubble-type flowmeter. The relative concentration of the adsorptive was varied in the range of 0–80%.

3. Results and discussion

3.1. Porous properties of CC microspheres

Table 1 summarizes the porous properties of the adsorbents examined in this study. It is clear that the CC microspheres possess a high degree of mesoporosity, which depends on the molar ratio (R/C) of resorcinol to catalyst used in the sol–gel polycondensation of the RF solution. For instance, the average size of the mesopores formed in the CC microspheres can be changed by varying the R/C ratio. On the other hand, the microporosity of the CC microspheres is not as great as that of GAC, since the volume of micropores in the CC microspheres is less than 25% of that in GAC.

Fig. 1 shows the isotherms of nitrogen adsorbed on the CC microspheres ($R/C = 400$) modified by CO_2 activation and impregnation. CCM200, CCM400 and CCM800 denote the CC microspheres prepared under the condition of $R/C = 200$, 400 and 800, respectively. CCM400-AC and CCM400-IM indicate the CCM400 modified by CO_2 activation and those modified by impregnation of phenolic resin, respectively. In a relative pressure range of $0.6 < p/p_0 < 0.8$, the isotherms show a clear hysteresis loop associated with capillary condensation and evaporation, which is typically observed for mesoporous materials [10]. (The effect of CO_2 activation or impregnation on the isotherms of nitrogen on the CC microspheres prepared under the different condition ($R/C = 800$) is shown in the supplementary material S1.) As shown in Fig. 1 and Table 1, the porous properties of the mesopores are changed by CO_2 activation or by impregnation. However, the change in the porous properties of the mesopores of the CC microspheres was smaller than that of the micropores, indicating that CO_2 activation or impregnation modified micropores rather than mesopores. Focusing on the isotherms in the relative pressure range of $p/p_0 \approx 0$, the amount of nitrogen adsorbed increases by activation due to the formation of the micropores. On the other hand, the micropore volume of the CC microspheres was significantly diminished by the impregnation. This is because the phenolic resin was mainly loaded on the micropores of the CC microspheres. Consequently, after carbonization, the micropores can be selectively filled with the carbonized resin.

A typical example of the Raman spectrum of the CC microspheres is shown in Fig. 2(a). Both D-band (1357 cm^{-1}) and G-band (1582 cm^{-1}), which correspond to the disordered graphite structure and single hexagonal crystal graphite, respectively, are clearly appeared [15]. Interestingly, it was confirmed that the CC microspheres possess a unique porous structure, which is composed of primary particles having amorphous (disordered) inner part and graphitic pore surface. As shown in Fig. 2(b), we found that the

stacked sheets of graphite layers are partially formed close to the surface of the primary particles. This indicates that the porous surface of the CC microspheres can be more easily graphitized than the inner parts. As a result of the TEM observation, the mesopores of the CC microspheres are likely to be formed between the primary particles, whereas the micropores are mostly formed inside the primary particles. (The SEM image of the cross-section of the CC microspheres is shown in supplementary material S2.)

3.2. Adsorption characteristics of CC microspheres for a VOC

Fig. 3 shows the adsorption and desorption isotherms of toluene on adsorbents with different porous structure. The isotherms on the CC microspheres could be classified into type IV. The hysteresis loop appearing in the isotherms is type H2, which is observed in porous solids composed of interconnected networks of pores of different sizes and shapes [10]. It can be seen that the relative pressure at which capillary condensation or evaporation occurs increases with the increase in the size of mesopores in the CC microspheres. It should be noted that the amount of toluene adsorbed on CCM400 and CCM800 at a high relative pressure ($p/p_0 \approx 1.0$) is greater than that adsorbed on GAC due to the presence of numerous mesopores. In addition, the relative pressure at which capillary condensation or evaporation occurs depends on the size of the mesopores. The mesopores in the CC microspheres effectively enhance the intraparticle diffusion of VOCs, which will improve the efficiency of the SPE procedure. At a low relative pressure ($p/p_0 \approx 0$), the amount of toluene adsorbed on the CC microspheres is approximately half as much as that on GAC. However, this does not indicate that the performance of the CC microspheres as adsorbents for VOCs is less than GAC: it proves that toluene is more strongly adsorbed on CC micro-

spheres than on GAC, since the peak temperature of the TPD profile of toluene desorbed from the CC microspheres is markedly higher than that from GAC, as shown in Fig. 4. This is because the affinity of toluene for the surfaces of the CC microspheres is higher than that for GAC. Here, it should be noted that adsorbed toluene can be desorbed from the CC microspheres without thermal decomposition (supplementary material S3).

Fig. 5 shows the adsorption isotherms of moisture on the CC microspheres and GAC, and the corresponding differential heat of adsorption (H_{ads}). For comparison, the experimental results obtained by using hydrophilic zeolite (A-4; purchased from Tosoh Corp.) were also shown. In a low relative pressure range ($0 < p/p_0 < 0.3$), the amount of moisture adsorbed on the CC microspheres and GAC is much smaller than that on A-4. As shown in Fig. 5(b), the initial value of H_{ads} (at $p/p_0 \approx 0$), which reflects the strength of interaction between adsorptive and adsorbent, on both CC microspheres and GAC is significantly lower than that on A-4 or the heat evolved by condensation (44 kJ/mol as indicated by a dashed line in Fig. 5(b)) of bulk moisture at 298.15 K. This result indicates that both CC microspheres and GAC possess highly hydrophobic pore surface. On the other hand, in a relatively high pressure range ($0.5 < p/p_0 < 1.0$), due to the cluster formation of water molecules, the steep adsorption uptake of moisture was observed in both adsorption isotherms on the CC microspheres and GAC. Under the saturated vapor pressure, the pore filling fraction of GAC with water is 0.65, whereas that of the CC microspheres is as small as 0.20, in spite of their larger pore volume than GAC. This is probably due to the difference in the structure of water clusters formed in the hydrophobic pores of activated carbon with a different pore size, as clarified by Iiyama et al. [16,17]. In the case
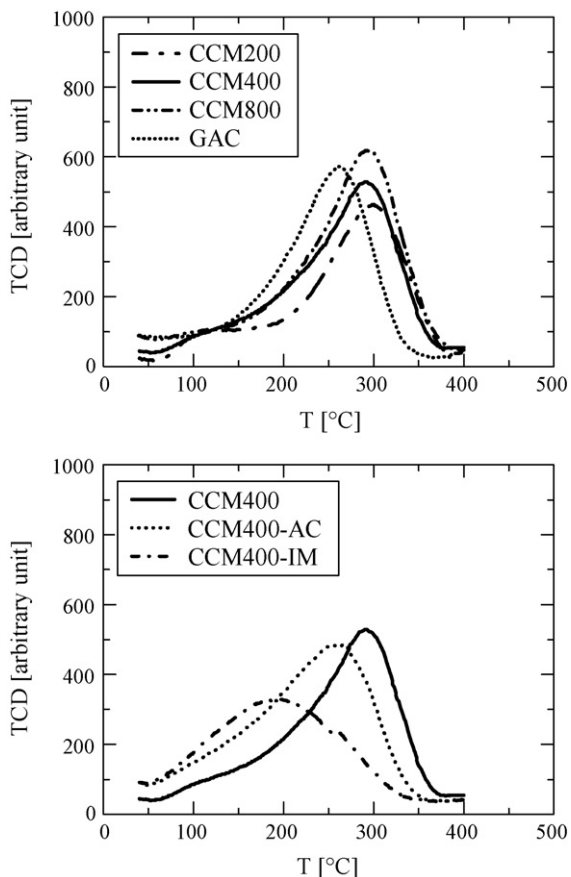

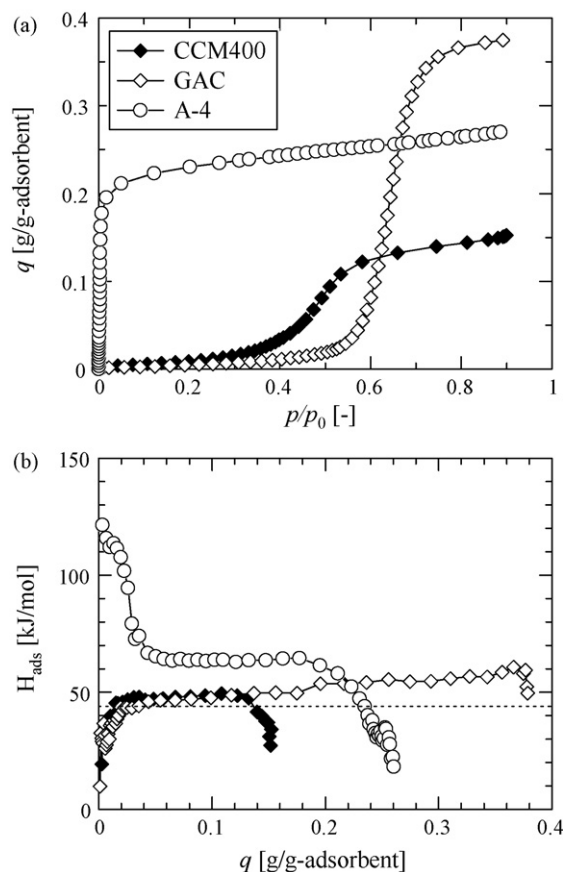Fig. 4. TPD profiles of toluene desorbed from the CC microspheres and GAC.

Fig. 5. (a) Adsorption isotherms of moisture on the CC microspheres, GAC and hydrophilic zeolite (A-4) at 298 K and (b) differential heat of adsorption with amount adsorbed; the dashed line indicates the condensation heat of bulk water at 298 K.
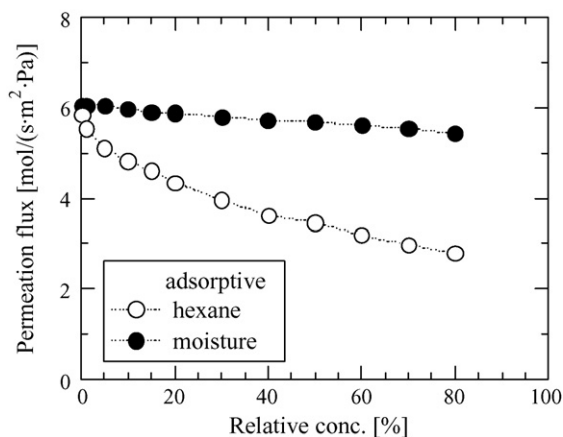
Fig. 6. Permeation flux of helium through the adsorption module at a different concentration of moisture and hexane.

of GAC having a smaller pore, H_{ads} is close to 60 kJ/mol indicating the formation of more ordered structure of water molecules in the micropores, whereas H_{ads} is less than 50 kJ/mol in the case of the CC microspheres having a larger pore. Based on the result, clustering of water molecules is more likely to occur in the pore of GAC than in the CC microspheres. Consequently, since moisture adsorbs on the CC microspheres less favorably than on GAC, it can be considered that adsorption of VOC on the CC microspheres is less influenced by the moisture in a humid environment.

Fig. 6 shows the result of a permeability test of the adsorption module prepared from the CC microspheres. As an adsorptive contained in helium gas, moisture or hexane, as a model VOC, is used. As can be expected from the above experimental result, permeation flux of helium is hardly influenced by the presence of moisture in the practical humidity range ($0 < R_H < 80\%$). On the other hand, permeation flux of helium steadily decreases with increasing the concentration of hexane, due to the adsorption of hexane on the CC microspheres.

Based on the results obtained in this study, we conclude that the CC microspheres possess moderate mesoporosity and surface properties that are suitable adsorbents for the solid-phase extraction of a VOC or its adsorption removal in the presence of moisture.

4. Conclusion

The adsorption characteristics of CC microspheres with controlled porous structure were studied for their use as adsorbents for a VOC. The adsorption efficiency of the CC microspheres and commercial GAC was investigated with regard to the difference in the mesoporosity and microporosity. It was shown that the amount of adsorbed toluene on the CC microspheres could be changed depending on the size of mesopores or the volume of micropores. The temperature required for desorption of toluene from the CC microspheres proved to be higher than that from GAC, indicating that toluene has a stronger affinity with the CC microspheres than with GAC. Since the amount of adsorbed moisture and its differ-

ential heat of adsorption on the CC microspheres were less than those on GAC, CC microspheres were more useful adsorbents than GAC for VOC removal in the presence of humidity. It was confirmed that adsorption performance of the VOC adsorption module, which was prepared from the CC microspheres, was hardly influenced by moisture.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2009.12.036.

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