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Molecular dynamics simulation study on characterization of bis (triethoxysilyl)-ethane and bis(triethoxysilyl)ethylene derived silica-based membranes

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ABSTRACT

The virtual structures of organic–inorganic hybrid silica membranes were prepared on a computer by introducing two different types of organic functional groups into a conventional silica network. bis(triethoxysilyl)ethane (BTESE) and bis(triethoxysilyl)ethylene (BTESEthy) derived silica-based organic–inorganic hybrid microporous materials were modeled and their structures such as pore size distribution and radial distribution function were studied. Adsorbability of water and diffusivity of helium molecule was also examined. Both the hybrid silica structures showed larger pore size than pure silica. The difference in water adsorption performance and helium diffusivity was observed between two types of hybrid silica structures. BTESEthy silica showed higher loading of adsorbed water and it is expected to be a promising material for water treatment. Helium diffusivity in BTESEthy silica was greater than that in BTESE silica, which was in consistent with the micropore size.

Keywords: Molecular dynamics; Hybrid membrane; Water adsorption; Gas diffusivity

1. Introduction

A membrane separation process has attracted much attension as an energy conservation process. Inorganic microporous membranes, which have excellent thermal and chemical resistance, were in particular expected to be applied to precise separation processes of molecular mixtures such as hydrogen separation, CO_2 separation, water/alcohol separation, and water purification. Microporous amorphous silica membranes have micropores around 0.3 nm and are promising candidate for hydrogen separation membranes [1–3]. In addition, since it has excellent acid resistance, dehydration processes of organic acid solution [4,5] is another potential application of microporous silica membranes. However, rather low water resistance and moderate permeability are current issue of the performance of silica membranes. In order to overcome these problems, new types of organic–inorganic hybrid silica membranes with larger permeability and modified surface chemistry have been developed by introducing organic

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functional groups to the silica network frame [6–8]. Kanezashi et al. prepared sol–gel derived silica-based microporous membranes by using bis(triethoxysilyl) ethane (BTESE) as a precursor for colloidal sol preparation instead of ordinal tetraethoxysilane (TEOS). BTESE has an ethane group between Si–Si atoms as shown in Fig. 1. The BTESE silica membrane showed higher permeance of gases than conventional silica membranes, which suggested that BTESE silica membranes had greater effective pore size for gas separation [9]. There are so many possibilities of selecting an organic hydrocarbon group to be introduced to silicon alkoxide. By changing the organic group, it would make possible to design a variety of microporous silica-based hybrid membranes with desired characteristics for a separation process of a molecular mixture. However, the structures of these organic–inorganic hybrid microporous materials and the behaviors of guest molecules such as adsorbability and diffusivity, on which the membrane performance significantly depends, are still unclear.

On the other hand, a molecular simulation technique is very useful for studying microporous structures and dynamics of guest molecules in membranes from a view of molecular scale. Modeling of microporous structures of inorganic membranes and analysis of molecular transport through those membranes by using molecular dynamics (MD) simulations has been carried out by many research groups [10–14]. The authors have successfully modeled and reproduced conventional microporous amorphous silica structures [15,16]. The effect of microporous structures of amorphous silica membranes and membrane dynamics on gas permeation characteristics were examined through the study of temperature and molecular size dependency of gas permeance by using non-equilibrium molecular dynamics method [17,18]. Concerning organic–inorganic hybrid microporous silica-based membranes, the static structures of BTESE silica membranes and gas diffusivity in them were studied by using MD simulations and the difference in microporous structures between pure silica and BTESE silica were reported in detail in comparison with the experimental gas permeance data [19]. However, the understandings and predictions of molecular permeation properties through organic–inorganic hybrid membranes are not sufficient for design of various types of noble membranes yet.

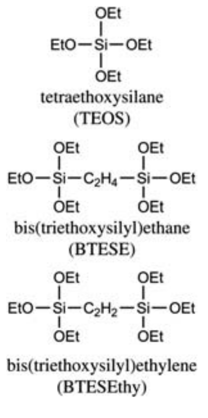

Fig. 1. Chemical formula of alkoxide as a precursor.

In this work, we have tried to model two different types of organic–inorganic hybrid silica-based microporous structures by molecular simulations, and adsorption and diffusion simulations of guest water molecule were carried out for characterization of the hybrid structures as the first step of prediction of membrane performance. BTESE silica and bis(triethoxysilyl)ethylene (BTESEthy) silica was adopted for examination of organic–inorganic hybrid structures. We focused on the effect of an organic functional group on the material structures such as radial distribution function (RDF) and pore size distribution (PSD). The RDF and PSD of hybrid materials were compared with those of pure silica structures. Adsorbability of guest water molecule and diffusivity of guest helium molecule were also examined for BTESE silica and BTESEthy silica as well. The difference in hydrophilicity for those hybrid materials was studied.

2. Theoretical method

The preparation and characterization of virtual microporous structures and MD simulations of water adsorption and helium diffusion were conducted by using MATERIALS STUDIO software supplied by Accelrys, Inc. We adopted the well-known pcff force-field [20] as the basis of our potential function in this work. The pcff force-field is one member of the *ab initio* consistent force-field family, composed of CFF91, CFF, pcff, and COMPASS (Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies) force-field, with the same functional form. The modified hybrid-pcff (h-pcff) computational model was applied to accurately construct the silica-based organic–inorganic hybrid membrane. The details of the h-pcff force-field and its parameters were described elsewhere [21].

2.1. Membrane structure construction

A virtual organic–inorganic hybrid structures were prepared by replacing about 25% of oxygen atoms in a conventional pure silica glass structure with organic groups. All ethoxy groups of alkoxides shown in Fig. 1 are replaced with siloxane group through the ideal hydrolysis and polymerization reaction for a real

Table 1
Unit cell property of each virtual silica

Precursor	Density (g/cm^3)	Size (Å)	The number of atoms			
			Si	O	C	H
TEOS	2.2	42.7	1,728	3,456	0	0
BTESE	1.74	47.7	1,728	2,659	1,594	3,188
BTESEthy	1.74	47.4	1,728	2,659	1,594	1,594

silica-based polymer. Therefore, it should be noted that a silicon atom is connected to only one organic group in the replacing operation for model structure construction. The density, cell size, and the number of atoms of virtual hybrid structures are summarized in Table 1.

2.2. Characterization of structures

2.2.1. Pore size distribution

PSD of each structure was calculated for quantitative estimation of void structures of virtual microporous membrane models. In the PSD calculation, an atom was treated as a sphere with hard core whose size was equal to the size parameter, σ of Lennard-Jones (LJ) potential. A guest molecule was assumed to be not able to access to the inside of the spherical region in a distance of $\sigma/2$ from the center of an atom that constituted the organic–inorganic silica-based polymer network. The local size of the accessible volume was defined as the pore diameter.

The LJ size parameters of atoms in the membrane structure used in this work are summarized in Table 2. The shape of –CH_2– group in BTESE silica and –CH– group in BTESEthy silica were assumed to be sphere with the denoted LJ diameter [22,23].

2.2.2. Radial distribution function

The static ordered or disordered sub-nano scale structures can be estimated by calculating the RDF defined by Eq. (1). We can see a local density of a solid or liquid structure of interest from RDF, and it reflects the possibility of existence of another atom located at a distance from an atom.

Table 2
Size parameter of each atom

Precursor	σ parameter of LJ potential (Å)			
	Si	O	C	H
TEOS	0.41	2.70	–	–
BTESE	0.41	2.70	3.207	–
BTESEthy	0.41	2.70	3.207	–

$$g(r) = \frac{1}{\rho}\frac{n(r)}{4\pi r^2 \Delta r} \quad (1)$$

ρ and $n(r)/(4\pi r^2 \Delta r)$ are the averaged number density of atom of the whole MD cell and the local number density of atom in a shell located at a distance from r to $r + \Delta r$ from the center of an atom, respectively. Since $g(r)$ is a normalized local density by ρ, we can see some characteristic peaks corresponding to the localized atoms at some distances in particularly at shorter distances. For the case of liquid or amorphous structures, the value of RDF approaches to unity at long enough distances of r.

2.3. Adsorption simulation

The SORPTION module of MATERIALS STUDIO was utilized to estimate the amount of adsorbed water for two different organic–inorganic microporous structures, BTESE silica and BTESEthy silica. A grand canonical Monte Carlo (GCMC) simulation method was adopted for the adsorption simulations. The maximal calculation step was 1,000,000, and the last 10,000 steps of equilibrated state were used to calculate the amount adsorbed. Adsorption isotherms at 298.15 K were obtained and the hydrophilicity of those hybrid structures was examined.

2.4. Diffusion simulation

Diffusivity of helium molecule in the virtual structures was examined by calculating the mean squared displacement (MSD) of helium molecules using constant NVT-ensemble MD simulation, where N is the number of molecules, V is the volume and T is the temperature. Helium molecules were placed at some locations in unit cell of each structure and the trajectories of them were traced as a function of time. The Einstein equation given by Eq. (2) was used to estimate diffusivity coefficient, D from an MSD curve plotted against time. The value of D could be easily obtained from a slope of the curve.

$$\mathrm{MSD(t)} = \frac{1}{N}\sum_{i=1}^{N}\left\langle [r_{\mathrm{i}}(t_0+t) - r_{\mathrm{i}}(t_0)]^2 \right\rangle = B + 6D \times t \quad (2)$$

N is the number of traced molecules, $r_{\mathrm{i}}(t_0+t)$ and $r_i(t)$ the location of the ith atom at $t_0 + t$ and t, respectively.

3. Results and discussion

3.1. Characterization of hybrid structures

Fig. 2 shows the pore size distribution of pure silica, BTESE silica and BTESEthy silica structures.

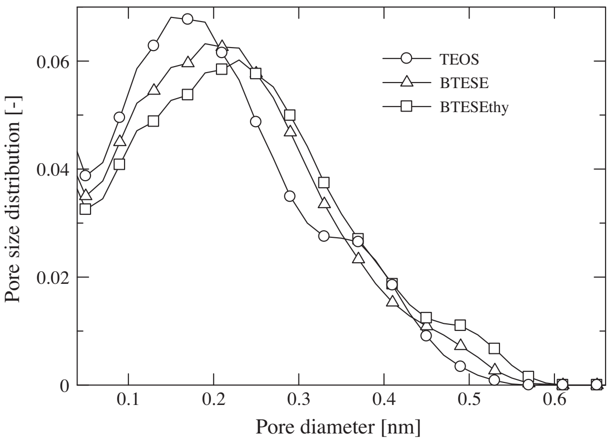

Fig. 2. Comparison of pore size distribution.

Both the organic–inorganic hybrid structures had a broader distribution than pure silica, and the location of peak of hybrid structures shifted to the greater size. The volume ratio of pores whose size was larger than 0.5 nm was higher for hybrid structures than pure silica. The existence of an organic functional group instead of an oxygen atom between Si–Si might cause slight expansion of polymer network and increase the pore size.

Fig. 3 shows the radial distribution functions for Si–O covalent bonding and Si–C covalent bonding in each structure. The Si–O bonding lengths are nearly identical and this length might not affect the difference in these pure silica and hybrid structures. On the contrary, a significant shift of Si–C bonding length of both the BTESE silica and BTESEthy silica from the Si–O bonding length to the longer length was observed. A polymer network ring that is including Si–C covalent bonding can be larger than a network ring composed of only Si–O covalent bonding.

The distribution of non-bonding Si–Si atom distance of three different structures was shown in Fig. 4. The peaks of Si–Si for both the BTESE silica and BTESEthy silica obviously located at longer distances than Si–Si of pure silica structure. Since the distance between non-bonding Si–Si indicates the diagonal distance in a polymer network ring, the longer distance can be one of the evidences for enlargement of the polymer network ring in organic–inorganic hybrid structures. This was in good agreement with the results of PSD, therefore an organic functional group inserted between two Si atoms instead of an oxygen atom contributed to the increase in pore size and it is expected to improve gas permeance.

3.2. Water adsorption

Fig. 5 shows adsorption isotherms of water for BTESE silica and BTESEthy silica. A significant difference in amount of adsorbed water was observed between two hybrid materials. As shown in Fig. 6, BTESEthy silica showed nearly three times higher amount of adsorbed water than BTESE silica. The total pore volume of BTESE silica was 58.34 nm^3/cell and that of BTESEthy silica was 58.61 nm^3/cell. The size of water molecule is said to be 0.265 nm [24] or around 0.3 nm [25]. Therefore, the observed large difference in water loading for these structures was not be explained by the difference in neither pore volume nor pore size. One of the possible reasons of this difference would be attributed to the difference in hydrophilicity between $–C_2H_4–$ group and $–C_2H_2–$ group. The $–C_2H_2–$ group in BTESEthy silica has a

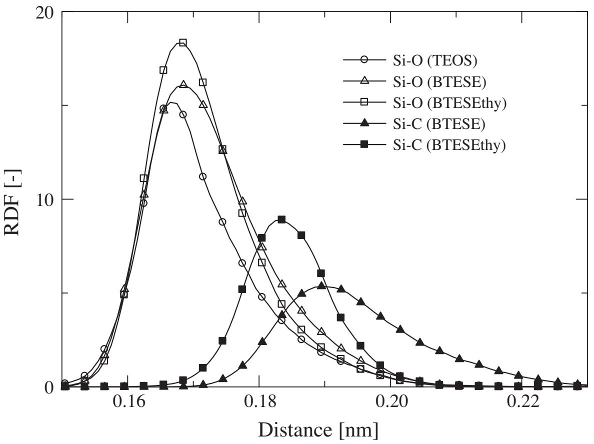

Fig. 3. RDF of Si–O and Si–C covalent bonding on virtual hybrid silica.

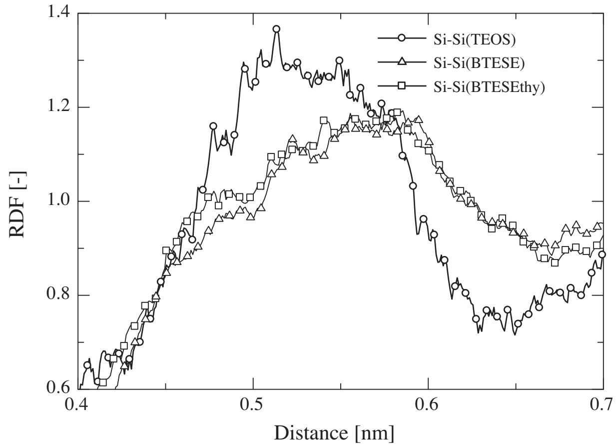

Fig. 4. RDF of Si–Si non-bonding on virtual hybrid silica.

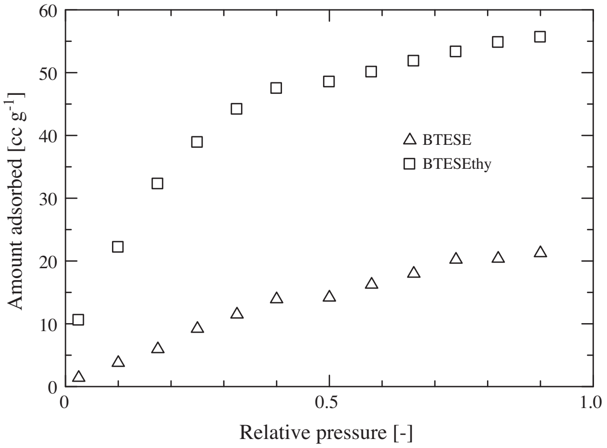

Fig. 5. Adsorption isotherm of H_2O on virtual hybrid silica.

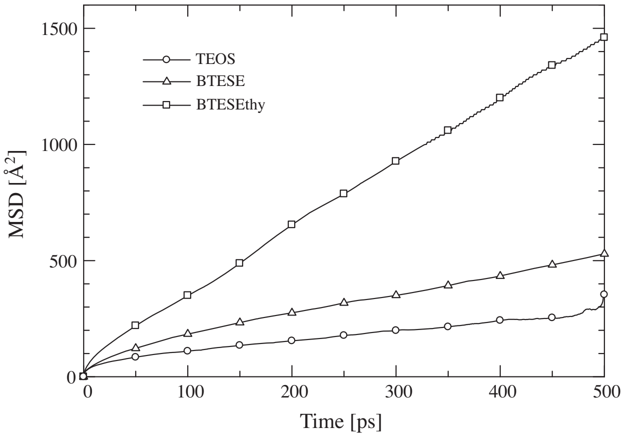

Fig. 7. Comparison of MSD of helium on virtual silica-based structures at 773 K.

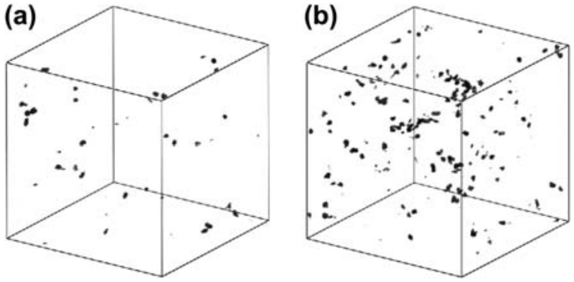

Fig. 6. Comparison of H_2O adsorption sites on (a) BTESE silica and (b) BTESEthy silica at $p/p_s = 0.1$ and $T = 298$ K.

Table 3
Diffusivity of He on hybrid silica

	Diffusivity[$m^2 s^{-1}$]
TEOS	6.99×10^{-10}
BTESE	1.38×10^{-9}
BTESEthy	4.65×10^{-9}

double bond and the carbon atoms form sp2 hybridized orbital. The electrons in the orbital easily work to form a charge-transfer complex with a guest water molecule [26,27], which is reasonably assumed to cause hydrophilicity of BTESEthy silica and its larger amount of adsorbed water. On the other hand, the $-C_2H_4-$ group in BTESE silica has a covalent single bond of sp3 hybridized orbital without a specific charge-transfer interaction. Therefore, the BTESE silica material might show rather hydrophobic property compared with the BTESEthy silica.

3.3. Helium diffusion

Sixteen helium atoms were put in each pure silica, BTESE silica and BTESEthy silica MD cell for calculation of MSD of helium. Fig. 7 shows the change of MSD along with time for each silica-based structure model at 773 K. The values of calculated diffusivity from the slope of those three curves in Fig. 6 using Eq. (2) are summarized in Table 3. The helium diffusivity in BTESEthy silica structure was greater than that in BTESE silica by nearly three times. As shown in Fig. 2, the pore size was in the order of (pure silica) < (BTESE silica) < (BTESEthy silica), and the calculated diffusivity of helium showed good agreement with the pore size order. Since helium molecule had little interaction with a membrane framework, the microporous geometrical structures might possibly affect the gas diffusivity. The rather slight difference in pore size or pore size distribution in the range around 0.4–0.5 nm of these structures seems to result in the significantly different gas diffusivity.

4. Conclusions

In this work, we prepared the virtual pure/hybrid silica structures and they were characterized by molecular simulations. Organic–inorganic hybrid silica had a larger pore than pure silica. This is due to the stretching of distance between structural framework atoms. Much more water molecules adsorbed on BTESEthy silica than BTESE silica. It indicated that difference in organic functional group greatly affected hydrophilicity of the silica structure. Helium diffusivity in BTESEthy silica was greater than that in BTESE silica, which was in consistent with the microporous geometrical structures shown in pore size distribution. BTESEthy silica can be expected to be a promising candidate for a material for high performance membranes for water treatment and gas separation.

References

[1] G.R. Gavalas, C.E. Megris, S.W. Nam, Deposition of H_2-permaelective SiO_2 films, Chem. Eng. Sci. 44 (1989) 1829–1835.

[2] S. Kitao, H. Kameda, M. Asaeda, Gas separation by thin porous silica membrane of ultra fine pores at high temperature, Maku (Membrane) 15 (1990) 222–227.

[3] N.W. Ockwig, T.M. Nenoff, Membranes for hydrogen separation, Chem. Rev. 107 (2007) 4078–4110.

[4] M. Asaeda, M. Ishida, T. Waki, Pervaporation of aqueous organic acid solutions by porous ceramic membranes, J. Chem. Eng. Jpn. 38 (2005) 336–343.

[5] M. Ishida, Y. Tasaka, M. Asaeda, A study on vapor permeation and pervaporation of acetic acid/water mixtures by porous membranes, J. Chem. Eng. Jpn. 38 (2005) 903–907.

[6] M. Kanezashi, K. Yada, T. Yoshioka, T. Tsuru, Design of silica networks for development of highly permeable hydrogen separation membranes with hydrothermal stability, J. Am. Chem. Soc. 131 (2009) 414–415.

[7] H.L. Castricum, A. Sah, R. Kreiter, D.H.A. Blank, J.F. Vente, J.E. ten Elshof, Hybrid ceramic nanosieves: Stabilizing nanopores with organic links, Chem. Commun. (2008) 1103–1105.

[8] H.L. Castricum, A. Sah, R. Kreiter, D.H.A. Blank, J.F. Vente, J.E. ten Elshof, Hydrothermally stable molecular separation membranes from organically linked silica, J. Mater. Chem. 18 (2008) 2150–2158.

[9] M. Kanezashi, K. Yada, T. Yoshioka, T. Tsuru, Organic–inorganic hybrid silica membranes with controlled silica network size: Preparation and gas permeation characteristics, J. Membrane Sci. 348 (2010) 310–318.

[10] D.A. Newsome, D.S. Sholl, Molecular dynamics simulations of mass transfer resistance in grain boundaries of twinned zeolite membranes, J. Phys. Chem. B 110 (2006) 22681–22689.

[11] H. Takaba, A. Yamamoto, S. Nakao, Modeling of methane permeation through a defective region in MFI-type zeolite membranes, Desalination 192 (2006) 82–90.

[12] J.M.D. MacElroy, Molecular simulation of the kinetic selectivity of a model silica system, Mol. Phys. 100 (2002) 2369–2376.

[13] W. Chang, T.Y. Lee, Molecular dynamics simulation of gas permeation phenomena in a microporous silica membrane, Chem. Eng. Sci. 61 (2006) 3974–3985.

[14] I.V. Kaganov, M. Sheintuch, Nonequilibulium molecular dynamics simulation of gas-mixtures transport in carbon-nanopore membranes, Phys. Rev. E: Stat. Nonlin. Soft Matter Phys. 68 (2003), doi: 046701/1046701/7.

[15] T. Yoshioka, A. Yasumoto, K. Kishi, T. Tsuru, MD simulation studies for effect of membrane structures and dynamics on gas permeation properties through microporous amorphous silica membranes, Desalination 233 (2008) 333–341.

[16] T. Yoshioka, T. Tsuru, M. Asaeda, Molecular dynamics study of gas permeation through amorphous silica network and inter-particle pores on microporous silica membranes, Mol. Phys. 102 (2004) 191–202.

[17] H. Takaba, E. Matsuda, B.N. Nair, S. Nakao, Molecular modeling of gas permeation through an amorphous microporous silica membrane, J. Chem. Eng. Jpn. 35 (2002) 1312–1321.

[18] T. Yoshioka, T. Tsuru, M. Asaeda, A molecular dynamics simulation of pressure-driven gas permeation in a micropore potential field on silica membrane, J. Membr. Sci. 293 (2007) 81–93.

[19] K.S. Chang, T. Yoshioka, M. Kanezashi, T. Tsuru, K.L. Tung, A molecular dynamics simulation of a homogeneous organic–inorganic hybrid silica membrane, Chem. Commun. 46 (2010) 9140–9142.

[20] J.R. Hill, J. Sauer, Molecular mechanics potential for silica and zeolite catalysts based on *ab initio* calculations. 2. aluminosilicates, J. Phys. Chem. 99 (1995) 9536–9550.

[21] K.S. Chang, T. Yoshioka, M. Kanezashi, T. Tsuru, K.L. Tung, Molecular simulation of micro-structures and gas diffusion behavior of organic–inorganic hybrid amorphous silica membranes, J. Membr. Sci. 381 (2011) 90–101.

[22] C.R.A. Catlow, C.M. Freeman, B. Vessal, S.M. Tomlinson, M. Leslie, Molecular dynamics studies of hydrocarbon diffusion in zeolites, J. Chem. Soc. Faraday Trans. 87 (1991) 1947–1950.

[23] T. Oie, G.M. Maggiora, R.E. Christoffersen, D.J. Duchamp, Development of a flexible intra- and intermolecular empirical potential function for large molecular systems, Int. J. Quan. Chem. Quan. Bio. Sym. 20 (1981) 1–47.

[24] D.W. Breck, Zeolite Molecular Sieves, Wiley, New York, NY, 1974.

[25] T. Tsuru, R. Igi, M. Kanezashi, T. Yoshioka, S. Fujisaki, Y. Iwamoto, Permeation properties of hydrogen and water vapor through porous silica membranes at high temperatures, AIChE J. 57 (2011) 618–629.

[26] T.J. Bandosz, Analysis of silica surface heterogeneity using butane and butene adsorption data, J. Colloid. Interface Sci. 193 (1997) 127–131.

[27] S.K. Parida, S. Dash, S. Patel, B.K. Mishra, Adsorption of organic molecules on silica surface, Adv. Colloid Interface Sci. 121 (2006) 77–110.