

The Different Adsorption Behavior of Ethanol and Water on Pure Silica Zeolites and MCM-41 Modified with Trimethylsilyl Group

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Selective permeation of ethanol from aqueous ethanol solution through pure silica MFI membrane is promising as applying to efficient concentration technique in a field of biomass fermentation. However, other pure silica zeolites, which have different minute pore structures in crystals from MFI, have not yet been studied about the ability as separation membrane very much. In this paper, adsorption isotherm measurements of ethanol, water and nitrogen for crystal powders of MFI, MEL, MTT, and MTW prepared according to the literatures were carried out, and the adsorption properties will be discussed. The amount of vapor of ethanol or water adsorbed per a specific surface area, V_A (vapor), was estimated from the results obtained by nitrogen adsorption isotherms. The V_A (EtOH) values for the zeolites indicated almost the same. These zeolites showed different V_A (H₂O) values. ²⁹Si MAS NMR results suggested V_A (H₂O) was influenced by the silanol group on the surface of the zeolite crystal but V_A (EtOH) was not influenced. The similar results were also obtained in the case of MCM-41 before and after the hydrophobic modification with trimethylsilyl group.

Key Words: zeolite, adsorption isotherm, specific surface area, ethanol, water.

1. INTRODUCTION

The production of ethanol from biomass fermentation is very important technology because the produced fuel is CO₂ neutral and does not increase the CO₂ concentration in atmosphere. The separation process of ethanol from ethanol aqueous solution is the most energy consuming and costly process. Therefore, membrane separation and pervaporation, PV, of ethanol have been studied. Particularly, it has been well-known that pure silica MFI (Silicalite) membrane had good ethanol selectivity and large flux [1-3]. Nevertheless, this has shown not enough performance to apply the PV process. On the other hand, it has been considered that the zeolites consisting of high Si content exhibited the ethanol selectivity from the study about MFI powders of different Si/Al ratios [4]. Therefore, the pure silica zeolite except for MFI such as MEL, MTT and MTW would have the possibility to apply to the ethanol selective PV process. Each zeolite crystal has the unique minute pore structure and pore size, as summarized in table I. In addition, amorphous MCM-41 would be also a candidate in the viewpoint of a pure silica material. However, the behavior of adsorption of ethanol or water has not been revealed for these pure silica materials. The adsorption isotherm of nitrogen gas

reflect the specific surface area involving the minute pore has been recognized as a fundamental characterization to structure. Considering the difference of the specific surface area for each pure silica material, not only the comparison of the amount of an absorbed gas, but that of the amount normalized by the specific surface area is important to estimate the latent ability as an ethanol selective membrane. In this paper, adsorption isotherms of ethanol, water and nitrogen were measured for crystal powders of MFI, MEL, MTT and MTW, and for amorphous powder of MCM-41 partially modified with or without a hydrophobic trimethylsilyl, TMS, group [9]. The normalized adsorption behavior of ethanol or water will be discussed. Additionally, the influence of the silanol group on the material surface on the adsorption behavior was studied by means of ²⁹Si MAS NMR measurement.

2. EXPERIMENTAL

Pure silica zeolites were prepared according to the literatures [1, 5-8]. SDAs using for the sake of constructing regular crystal structures were also prepared according to the literatures, as shown in table I. The conditions of the preparations of pure silica zeolites were summarized in table II.

A powder of MCM-41 was prepared from a gel composition of {tetraethyl orthosilicate : HCl : EtOH : H₂O : tetradecyltrimethylammonium bromide} = {1 : 0.02 : 10 : 5 : 0.15} by mol ratios [10]. The mixture was stirred for 3 h at room temperature to cast on the glass substrate. The obtained powder was calcined at 823 K for 24 h. MCM-41 partially modified with trimethylsilyl group, TMS, was obtained by two manners. The powder

Table I Pore structures of pure silica zeolites, and structure directing agents, SDA, for their preparations

Zeolite	Pore structure	SDA
MFI	Crossing 3-directional, 10MR	TPAB ^{a)}
MEL	Crossing 2-directional, 10MR	DDPO ^{b)}
MTT	1-Directional, 10MR	DIIO ^{c)}
MTW	1-Directional, 12MR	pDAB4OH ^{d)}

a) tetrapropylammonium bromide. b) 3,5-dimethylpiperidinium hydroxide [5]. c) N,N-diisopropylimidazolium hydroxide.[6] d) polyammonium hydroxide, refer to the literatures [7,8].

Table II Conditions of reaction and calcination for zeolite

Process	MFI [1]	MEL [5]	MTT [6]	MTW [8]
Composition of sol soln. (mol ratio)	Si ₂ O ₃ ; 1 ^{a)} Na ₂ O; 0.05 ^{c)} H ₂ O; 80 SDA; 0.1	Si ₂ O ₃ ; 1 ^{a)} KOH; 0.05 H ₂ O; 18 SDA; 0.25	Si ₂ O ₃ ; 1 ^{a)} Na ₂ O; 0.043 ^{c)} H ₂ O; 24 NaF; 0.016 SDA; 0.2	Si ₂ O ₃ ; 1 ^{b)} Na ₂ O; 0.1 ^{c)} H ₂ O; 36.5 SDA; 0.08
Reaction ^{d)} temp. (time)	448 K 4 days	443 K 14 days	423 K 15 days	423 K 6 days
Calcination temp. (time)	773 K 24 hours	873 K 24 hours	873 K 24 hours	773 K 24 hours

a) colloidal silica. b) silica-gel. c) added as a NaOH. d) reacted in a Teflon-lined stainless autoclave.

of MCM-41 (1.0 g) evacuated at 383 K for 24 h was added into 100 ml of toluene under N₂ flow, then hexamethyldisilazane (0.54 ml, 2.62 mmol) or trimethylchlorosilane (0.33 ml, 2.62 mmol) was added. The mixture was heated at reflux for 3 h. The partially modified powder was filtered and washed by toluene and ethanol, then evacuated at 383 K for 24 h. From the result of ²⁹Si NMR, 14 ppm of peak arising from a fixed silyl group was found to afford the MCM-41 partially modified with TMS.

Powder X-ray diffractometry, XRD, was conducted at room temperature by using a RIGAKU RINT 2000 diffractometer in the range of 2θ from 2 to 50°. All diffraction patterns were in good agreement with the literatures [10, 11]. Nitrogen adsorption isotherms at 77 K, water and ethanol adsorption isotherms at 298 K were measured using conventional volumetric apparatus, which was BEL Japan BELSORP 28SA and BELSORP-18 after evacuated at 573 K for 5 h. The ²⁹Si (79.49 MHz) NMR spectra were obtained on a Bruker DRX-400 FT-NMR spectrometer equipped with magic-angle spinning accessory. The peaks were divided by the Gaussian dispersion fitting program WINFIT (Bruker Biospin).

3. RESULTS AND DISCUSSION

3.1 Nitrogen Adsorption Isotherms: The adsorption isotherms of N₂ on pure silica materials are shown in Fig. 1. The specific surface areas calculated by the Langmuir and the multilayer BET adsorption equations are shown in table III. The specific surface areas of MFI and MTW are almost the same value as the published data of pure silica types. [12, 13]. However, the specific surface area of pure silica MEL and MTT had not been reported up to now. In the references, the specific surface areas of these zeolites containing other elements, such as Al, are shown in table III [14-17].

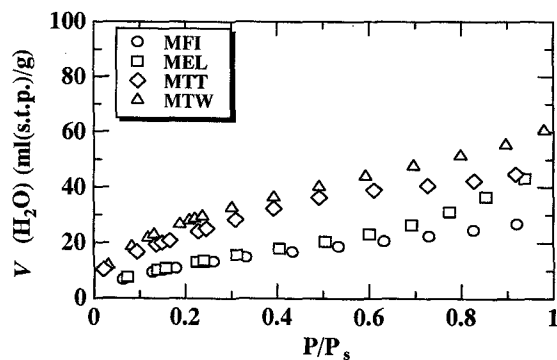


Fig. 3 The adsorption isotherms of water on pure silica zeolites.

Table III Specific surface areas of pure silica materials

Pure silica materials	Specific surface area (m ² /g)				
	Langmuir ^{a)}	BET ^{b)}	Literatures ^{c)}		
			Pure	[lit.]	Others [lit.]
MFI	450.4	302.4	337 ^{d)}	[12]	358 ^{e)} [14]
MEL	332.8	232.8	-	-	344 [15]
MTT	297.1	193.5	-	-	275 [16]
MTW	281.5	185.3	201	[13]	310 [17]
MCM-41	1451	874.7	1058	[23]	-
MCM-41-HMDS	946	557.0	-	-	-
MCM-41-TMCS	1116	661.7	-	-	-

a) calculated in the range of 0 < P < 500 (Torr). b) in the range of 0.05 < P/Ps < 0.35. c) calculated by the BET theory though the range was unknown, except for MFI type. d) calculated by the finite layer BET theory (n=1.55). e) in the range of 0.05 < P/Ps < 0.3.

As reasonable results, the specific surface areas of the zeolites having unidirectional pore structures were the smallest, and increased in the order of 2-directional, 3-directional. From the N₂ isotherms, the difference between 10MR of MTT and 12MR of MTW could not be found. The amorphous MCM-41 type showed higher value than the zeolites.

3.2 Ethanol and Water Adsorption Isotherms of the Zeolites: The adsorption isotherms of ethanol and water on pure silica zeolites are shown in Figs. 2 and 3, respectively. The amount of ethanol adsorbed, V (EtOH), on the pure silica zeolites decreased in the order of MFI > MEL > MTW ≈ MTT. On the other hand, the amount of adsorbed water, V (H₂O), increased in the order of MFI ≈ MEL < MTT < MTW. Therefore, MFI is the most suitable adsorbent for selective adsorption and separation of ethanol among these pure silica zeolites.

3.3 Ethanol and Water Adsorption Isotherms Normalized by the Specific Surface Area of the Zeolites: The adsorption isotherms of ethanol and water normalized by the specific surface area for the BET model are shown in Figs. 4 and 5, respectively.

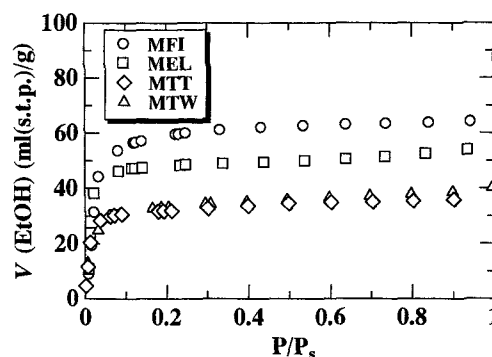


Fig. 2 The adsorption isotherms of ethanol on pure silica zeolites.

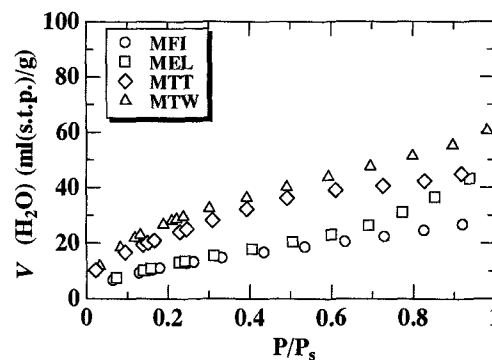


Fig. 3 The adsorption isotherms of water on pure silica zeolites.

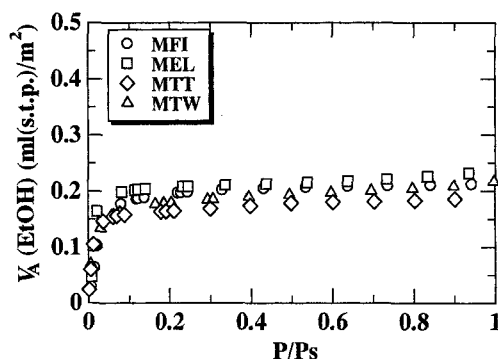


Fig. 4 The adsorption isotherms of ethanol on the specific surface area.

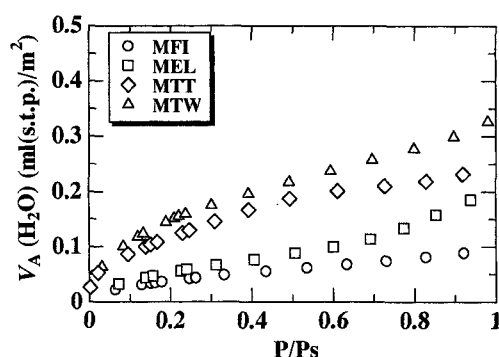


Fig. 5 The adsorption isotherms of water on the specific surface area.

In the case of the Langmuir model, the normalized amount of adsorbed gas, V_A , only changes relatively.

The V_A (EtOH) of the pure silica zeolites are almost the same values though these zeolites have different minute pore sizes and structures. This coincidence indicates that the capacity of ethanol adsorption is constant, and independent of those pore structures of pure silica zeolites. On the other hand, V_A (H_2O) values increase in the order of MFI \approx MEL < MTT < MTW. These results suggest that the adsorption mechanism on the surface of pure silica zeolites is different between ethanol and water. If the pore size affects the adsorption behavior of water, the V_A (H_2O) of MFI, MEL, and MTT for 10MR would be the same order because of the normalization. But these values are different. If the pore structure affects the adsorption behavior, the V_A (H_2O) of MTT and MTW for unidimensional structure should give constant value. In actual, it doesn't. Therefore, it is considered that the density of silanol group on the surface might affect the adsorption behavior of water in no relation to its own structure of zeolite. The strong correlation between the density of the surface silanol and the adsorbed water-molecules for MFI containing the other element (ZSM-5) had been reported by Sano *et al* [18]. So the ^{29}Si MAS NMR spectra were collected to investigate the surface silanol.

3.4 The Correlation between Adsorption Properties and the Surface Silanol: The Q3/Q4 ratios were calculated from the ^{29}Si NMR spectra of pure silica zeolites which peaks were assigned according to the literatures [19-21]. The all spectra showed several Q4 peaks and one Q3 peak. For the all cases, the peak arising

Table IV The Q3/Q4 ratio of pure silica zeolites.

Zeolite	Calcination	Amplitude (a.u.)		Ratio (%) of Q3/Q4
		[Chemical shift, ppm]		
		Q3	Q4*	
MFI	Before	152.9	5294.8	2.89
	After	Not found	13570.4	0
MEL	Before	157.4	781.0	20.2
	After	Not found	11091.9	0
MTT	Before	36.6	658.9	5.5
	After	89.9	11762.2	0.76
MTW	Before	134.1	970.9	13.8
	After	22.9	1396.9	1.6

* Determined by the total integral amplitude of Q4 sites. Chemical shift was about the Q4 peak given the largest integral amplitude as a typical data.

from Q3 site decreased by means of the calcinations of zeolites, and the peaks arising from Q4 sites increased. However, for MTW, these changes unambiguously appeared less than the cases of the other zeolites. The integral amplitudes and chemical shifts of Q3 and Q4 sites, and the ratios of Q3/Q4 were listed in table IV.

The Q3/Q4 ratios of the pure silica zeolites after calcinations increased in the order of MFI \approx MEL < MTT < MTW. This order coincides with that of the V_A (H_2O) values. The reason why MTT and MTW after the calcinations had relatively many silanol group is ambiguous. The crystallinity of zeolite after the hydro-thermal reaction or the condition of calcination would not be suitable for the adsorption behavior as an ideal crystal zeolite. However, it must be emphasized that the V_A (EtOH) of the pure silica zeolites is constant, and the V_A (H_2O) depends on the amount of residual silanol group. Therefore, the similar discussion about MCM-41s having different densities of silanol groups will be carried out.

3.5 The Adsorption Behavior of Ethanol and Water Adsorbed on the Specific Surface Area on MCM-41 Modified with Trimethylsilyl Group: The adsorption isotherms of ethanol and water for MCM-41, MCM-41-HMDS and MCM-41-TMCS normalized by the specific surface areas are showed in Figs. 6 and 7, respectively. Furthermore, the (Q2+Q3)/Q4 ratio of each sample estimated from the ^{29}Si NMR spectra of MCM-41 type, whose peaks were assigned according to the literature [22], is listed in table V. Generally speaking, the Q2 and Q3 sites correspond to silanol group in the case of meso-porous silica materials.

Interestingly, the V_A (EtOH) values for MCM-41 type are also constant, besides approximately coincide with those for pure silica zeolites. This result suggests that the adsorption ability of ethanol is constant per a specific surface area for not only pure silica zeolites but for pure silica materials as usual. On the other hand, the MCM-41s showed various V_A (H_2O) values. Considering the (Q2+Q3)/Q4 ratio in table V, the order of V_A (H_2O) values (MCM-41-HMDS < MCM-41-TMCS < MCM-41) markedly correlates with the density of the residual surface silanol.

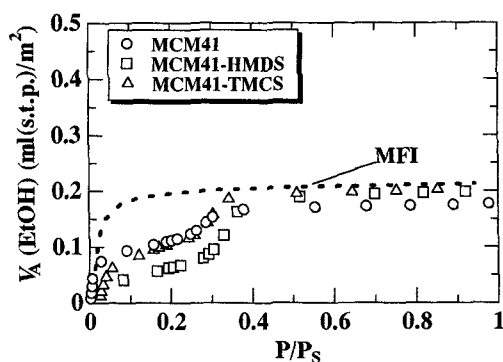


Fig. 6 The adsorption isotherms of ethanol on the specific surface area for MCM-41 type.

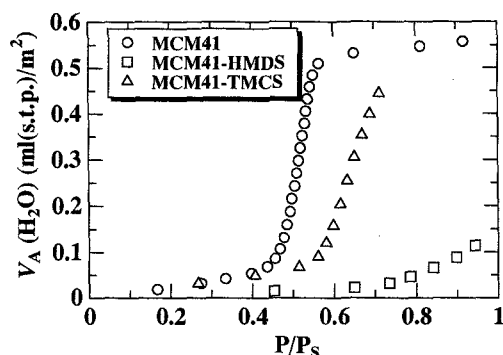


Fig. 7 The adsorption isotherms of water on the specific surface area for MCM-41 type.

Table V The (Q2+Q3)/Q4 ratios of MCM-41 type

MCM-41 type	Amplitude (a.u.) [Chemical shift, ppm]			Ratio (%) of (Q2+Q3)/Q4
	Q2	Q3	Q4	
MCM-41	25.32 [-92]	115.82 [-102]	218.99 [-111]	64.5
MCM-41-HMDS	Not found	421.71 [-104]	845.07 [-110]	49.9
MCM-41-TMCS	40.98 [-91]	207.86 [-101]	440.02 [-110]	56.5

4. CONCLUSION

As pure silica materials, four kinds of zeolites and three kinds of meso-porous MCM-41s controlled the density of silanol group by surface modifications were prepared according to the literatures. For these powder samples, the adsorption isotherms of N₂, ethanol and water were measured. The normalized amounts of adsorbed ethanol and water were estimated from the calculations of the specific surface areas against N₂ adsorption based on multi-layered adsorption of BET theory. In addition, the density of residual silanol group was investigated by ²⁹Si MAS NMR spectroscopy, in order to obtain the correlation with water adsorption.

The amount of adsorbed ethanol after normalization gave constant value of about 0.2 ml/m² in no relation to the minute pore structure and size. That is, it was found that the latent ability as ethanol-selective adsorption equaled for pure silica materials. On the other hand, the water adsorption was significantly influenced by the residual surface silanol in pure silica materials.

Consequently, if possible to control the density of residual silanol group and to solve problems on the

preparation and engineering, pure silica materials superior to MFI would be applied to ethanol-selective PV membrane.

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(Received December 21, 2002; Accepted February 19, 2003)