

Cation-Type Dependences of ^1H and ^{29}Si MAS NMR Chemical Shifts and Desorption Temperatures of Water Molecules in Faujasite-Type Zeolites

ABSTRACT

In order to reveal adsorbed states of water molecules on faujasite-type zeolites (FAU) systematically, twenty five kinds of FAU were prepared in this study: Na ions in FAU with Si/Al ratios of 1.0, 1.2, 1.7, 2.4, and 3.5 were exchanged by each Li, K, Rb, and Cs ions. High-resolution solid-state ^1H NMR spectra with a magic-angle-spinning (MAS) method showed a signal which can be assigned to H atoms of water molecules adsorbed on each FAU. Complex dependences of ^1H chemical-shift (CS) value on cation types were recorded (the lowest CS value was detected in Na- or K-type FAU with each Si/Al ratio). The similar tendency was recorded on ^{29}Si MAS NMR spectra. In addition, thermogravimetry (TG) and differential-thermal-analysis (DTA) lines showed that a desorption temperature of water molecules was increased with decreasing Si/Al ratios, conversely, the temperature showed complex dependences on cation properties (the minimum temperature was recorded in Na- or K-type FAU with each Si/Al ratio). In our simulations, the similar complex relations recorded on the ^1H and ^{29}Si MAS NMR spectra were obtained by use of a supercage model.

Keywords: Faujasite, Water, Adsorption, solid-state ^1H NMR

1. INTRODUCTION

Zeolites are microporous crystalline materials and constructed by SiO_4 and AlO_4 units.

Zeolite's types are classified by crystalline structures and Si and Al ratios (Si/Al). Faujasite-type

17 zeolites (FAU) are one of the zeolites, widely used in chemical industries and scientific
 18 endeavors, because of their special structure and properties of adsorption, ion exchange, and
 19 catalysis [1-7]. The general chemical formula of FAU in an unit cell is
 20 $M_{(x/n)}(SiO_2)_{(192-x)}(AlO_2)_x \cdot yH_2O$, where M is a cation of charge $+n$. The number x of cations can
 21 vary from 0 to 96, depending on the Si/Al ratio. The number of water molecules (y) in the unit cell
 22 is depended on steam pressure. The crystalline structure of FAU as well as the position of the M
 23 cations is determined by X-ray and neutron diffraction measurements [8, 9]. The unit framework of
 24 FAU is constructed by sodalite cages combined by hexagonal prisms each other, and makes a
 25 pore (it is called as supercage). The substitution of Si with Al atoms in the FAU framework
 26 induces a net negative charge on the framework. To keep the overall framework to the neutral
 27 charge, the M ions are distributed at three kinds of specific position in FAU: Sites I (SI) are
 28 located in the center of hexagonal prism, while the sites I' (SI') are present in the sodalite cage
 29 toward the hexagonal prism, sites II (SII) is located in the six-ring windows, and sites III (SIII) and
 30 III' (SIII') are located in the center of the four-ring and twelve-ring windows of the supercages,
 31 respectively [10, 11]. It is also known that cations occupy whole SI, SI', and SII in FAU with any
 32 Si/Al ratio, in contrast, population of SIII and SIII' is increased with decreasing Si/Al ratios in a
 33 range of Si/Al ratio < 2 [9-11]. The cation at SII, SIII, and SIII' can be immediately exchanged by
 34 other cations in solutions. It is reported that the size and valence of the M ion are critically
 35 important in adsorption capacities and catalytic properties [6]. FAU with low Si/Al ratios shows
 36 hydrophilic characters because the M ions attract water molecules by strong electrostatic
 37 interactions. Therefore, the presence of water molecules in FAU cannot be avoided in many
 38 applications, especially, operating at ambient temperature. Molecular dynamics (MD) and
 39 molecular orbital (MO) simulations show informations of the water molecules and the cation sites
 40 in FAUs [10-18]. MD simulations show a three-step mechanism of water adsorption on FAU: water

41 molecules are firstly adsorbed around the M ions in FAU, the next water molecules form a
 42 monolayer on the FAU surface, the further waters (the third step) are located in the supercage
 43 [12]. In addition, another MD calculation reports that the first water molecules are adsorbed on the
 44 cations located at SI (SI') and SII in FAU with Si/Al > 2, in contrast, in a case of small Si/Al ratios,
 45 the water molecules interact with cations at the whole sites of cations [13, 14]. Based on these
 46 reports, the cations can locate at SIII and SIII' and interact with water molecules in only Si/Al < 2.
 47 Grand-Canonical-Monte-Carlo (GCMC) demonstrations explain Si/Al ratio dependences on
 48 adsorption isotherms and heats observed in Na-type FAU [10, 11, 15, 16]. These simulations are
 49 generally performed for the unit cell model of hydrated and anhydrated FAUs. In a case of MO
 50 simulations, small cluster models, which are local parts of the FAU framework, have been
 51 frequently used [17-23]. Second-order Moller-Plesset (MP2) and density-functional-theory (DFT)
 52 methods show good agreement with the experimental proton-affinities (PA) values, although
 53 small cluster models of (H₃SiO)₄AlH and AlSi₁₀O₁₄H₁₇ (three four-rings and one six-ring are
 54 combined) are employed [17]. In a case of ²⁹Si NMR methods, it is reported that Si-O-Si angles
 55 in zeolite frameworks strongly contribute to ²⁹Si chemical shift (CS) values [20-23]. Experimental
 56 studies also report that the location of these M ions plays a crucial role on the thermodynamics,
 57 molecular dynamics, catalysis, and adsorbents in FAUs. The interactions between water
 58 molecules and FAUs have been revealed by adsorption and desorption isotherms, infra-red (IR),
 59 Raman, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), NMR, and
 60 dielectric measurements, etc. [1-8, 24-36]. DRIFTS spectra reveal the formation of
 61 strongly bonded water-cation clusters in zeolites [24]. IR and Raman spectra show that bending
 62 vibrations of FAU framework are linked with the unit-cell sizes and the vibrations are influenced
 63 by the charge distribution within FAU [25]. Solid-state ²⁹Si, ²⁷Al, and ¹H NMR measurements of
 64 FAU are performed with a magic-angle-spinning (MAS) method to determine Si/Al ratios and to

65 study acid sites of FAU [27-32]. However, ^1H MAS NMR spectra with high speed MAS (>30 kHz)
66 are rarely reported as functions of Si/Al ratios and cation types in hydrated FAU. In this
67 study, TG-DTA, N_2 adsorption isotherms, and ^1H and ^{29}Si MAS NMR measurements were
68 performed in twenty five kinds of FAU with Si/Al ratios of 1.0, 1.3, 1.7, 2.4, and 3.5, in addition,
69 and with cations of Li, Na, K, Rb, and Cs, in order to reveal water molecules states in FAUs.

70

71 **2. MATERIALS AND METHODS**

72 **2.1 Sample Preparation**

73 In this study, two commercial FAUs of Na form (Tosoh Co.) with Si/Al ratio of 1.2 and
74 2.4, and three specimens (abbreviated to Sample A, B, C) prepared by modifying a recipe of the
75 previous report [37], were employed. Sample A, B, and C were synthesized by the following
76 process.

77 **2.1.1. Sample A**

78 Sodium aluminate (5.59 g), potassium hydroxide (5.38 g), sodium hydroxide (7.77 g), and
79 sodium silicate (11.50 g) were dissolved in aqueous solution (85.90 g) and mixed
80 thoroughly. Obtained aqueous solution was incubated at 342 K for 14 hours and agitated at 368 K
81 for 4 hours in vessel sealed with Teflon. After filtering, obtained specimens were washed by a
82 0.01 M sodium hydroxide solution and dried at room temperature.

83 **2.1.2. Sample B**

84 Sodium hydroxide (1.48 g) and sodium aluminate (0.76 g) were poured in water (7.17
85 g) and stirred until completely dissolved. Sodium silicate solution of 27.3% (39.21 g) was added
86 into the solution and stirred at room temperature for 1 day. Another concentration of sodium
87 hydroxide (0.1%), sodium aluminate (9.1%) and sodium silicate (37.6%) aqueous solution of 92.66
88 g was transferred into the prepared solution and let the mixed solution for 1 day after stirring for

89 30 minutes. After incubation of 7 hours at 373 K, obtained samples were washed by water and
90 dried at room temperature.

91 **2.1.3. Sample C**

92 Sodium hydroxide (1.65 g) and sodium aluminate(3.64 g) were added into 15-crown-5
93 ether(2.25 g)of aqueous solution(17.75 g). Silica sol (Nissan Chemical Industries, Ltd.Snotecs
94 40)of 30.0 g was dissolved in the solution. This solution was stirred with a magnetic bar at
95 approximately 200 rpm for 1 day at room temperature. Zeolite crystals were obtained by keeping
96 it in Teflon-lined stainless steel autoclave at 383 Kfor 10 days. After washing with water until pH
97 of the filtrate solution achieved to 6, crystals were dried at room temperature overnight. In order
98 to remove template of 15-crown-5 ether from the crystal, temperature of the sample was
99 increased with 3 K min⁻¹ until 423 K and kept the same temperature for 1 hour. After this
100 manipulation, the sample was successfully heated with 3 K min⁻¹ until 643 K and kept at the
101 temperature for 3 hours. Oxygen gas was run into the oven with flow speed of 150 ml min⁻¹ for
102 the calcination. All sample preparation described above were carried out by employing an
103 AdvantecFS-605 electric drying oven with Isuzu auto tuning control system and an autoclave of
104 302AC-T304-101503(Parr Instrument Company Moline).

105 **2.1.4. Ion Exchange**

106 Ion exchanged FAUs were prepared by the following manipulation: Na-type FAU added
107 into 1M MCl aqueous solution (M = Li, K, Rb, Cs) and the solution was stirred at ca. 340K by 24
108 hours.After filtering of ion-exchanged specimens from the solution, M-type FAU was washed by
109 water and dried at room temperature.²³Na MAS NMR measurements observed at a Larmor
110 frequency of 158.75 MHz with the MAS speed of 10 kHz showed ion-exchanged ratios of 100 %
111 (Li), 100 % (Na), 100 % (K), 60 % (Rb), and 60 % (Cs), where these values have error within
112 ±5%. The low ratios recorded in Rb- and Cs-type FAU can be explained by six-ring window-size

113 of FAU frameworks: Since Rb^+ (296 pm) and Cs^+ (338 pm) have large ion-size compering with
114 the window-size of ca. 250 pm, Na^+ ions located in sodalite cages can't be exchanged.

115 In this literature, M-type FAU with Si/Al ratio of x is abbreviated to Mx; e.g. K2.4 means
116 K-type FAU with Si/Al = 2.4.

117

118 2.2.Measurement

119 ^1H and ^{29}Si MAS NMR measurements were carried out by using a Bruker Avance 600
120 spectrometer (14.01T) with MAS accessory. Solid-state high-resolution ^1H MAS NMR spectra
121 were recorded at a Larmor frequency of 600.13 MHz with a MAS speed of 30 kHz. Powdered
122 FAU samples and a small amount of silicon rubber were packed in a ZrO_2 rotor with an outer
123 diameter of 2.5 mm. Here, silicon rubber is aim to be inner reference of ^1H chemical shifts (δ =
124 0.12 ppm). Si/Al ratios were determined by observing ^{29}Si MAS NMR spectra at 119.22 MHz with
125 a MAS ratio of 10 kHz. Powdered samples and silicon rubber were packed into a ZrO_2 rotor with
126 an outer diameter of 4.0 mm. Here, silicon rubber is inner reference of ^{29}Si chemical shifts (δ =
127 -22.59 ppm). All spectra of ^1H and ^{29}Si nucleus were obtained from free-induction-decay signals
128 which were recorded after a $\pi/2$ pulse. A pulse sequence of ^{29}Si MAS NMR was designed with a ^1H
129 decoupling pulse. Recycle times of 5 and 60 s were employed on ^1H and ^{29}Si MAS NMR
130 measurements, respectively.

131 In order to confirm that crystal structures of prepared specimens constructs to FAU
132 networks, powder X-ray diffraction (XRD) patterns were measured by a Rigaku RINT 2100 and a
133 Bruker D8 ADVANCE diffratcometer in a scan range of 5 and 50 ° in steps of 0.02 ° with a Cu
134 anticathode.

135 TG, differential TG(DTG) and DTA curves were recorded from 293 to 673 K at heating
136 rate of 5 K min^{-1} with a Seiko Instrument Inc. TG/DTA 6300 apparatus, where Al_2O_3 powder was

137 used for standard sample.

138 N_2 adsorption isotherms were observed at 77 K by using a Bell Japan Inc.
139 BELSORP-mini II. Before the adsorption experiments, all samples were crushed in a mortar and
140 were heated at 673 K for 5 hours in vacuum.

141

142 **2.3. Simulation**

143 Computer calculations were carried out by using a Gaussian 03 program to estimate
144 locations of water molecules, alkali-metal ions, and terminal H atoms in the FAU framework and
145 to simulate shielding tensors of ^1H nucleus in water molecules. Since alkali-metal ions (especially
146 Cs ion) take with many electrons, therefore, a B3LYP/LanL2DZ function was employed for
147 optimization of water molecules and alkali-metal ions in the FAU framework. Shielding tensor
148 estimation of ^1H nucleus was performed by an ONIOM (MP2/cc-pVDZ:HF/cep-4G) method;
149 where shielding tensor of water molecules were estimated by the MP2/cc-pVDZ function, and the
150 other atoms in the frameworks were done by using HF/cep-4G. In the case of ^{29}Si nucleus,
151 shielding tensors were calculated by the B3LYP/LanL2DZ function in another framework model.

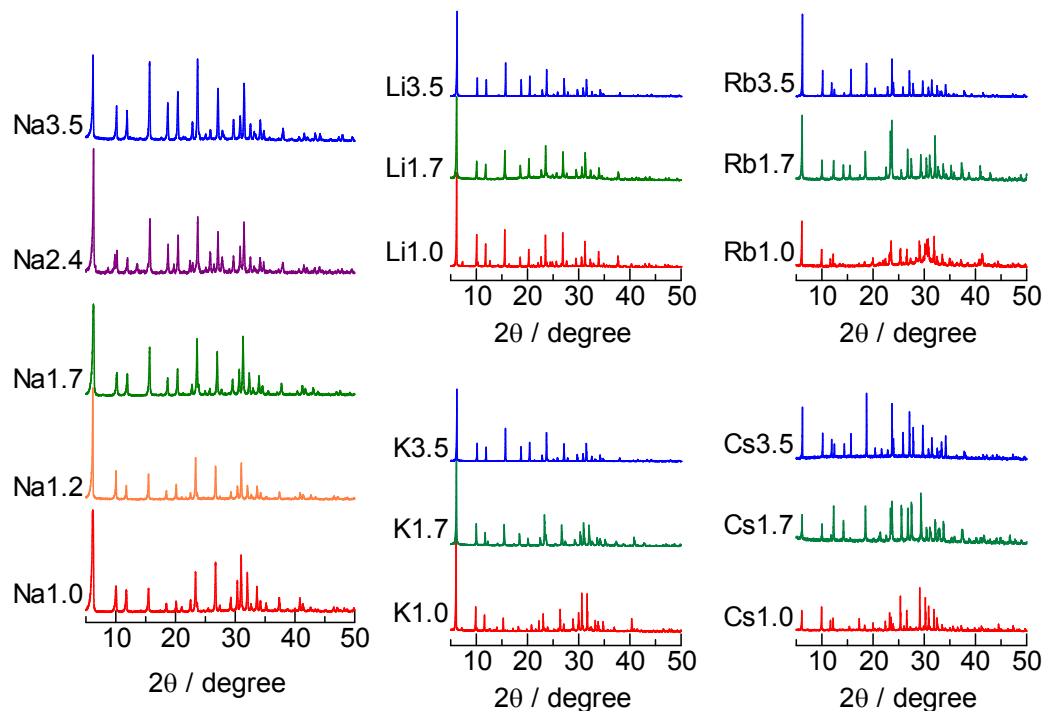
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153 **3. RESULTS AND DISCUSSION**

154 **3.1. XRD and ^{29}Si MAS NMR Measurements**

155 XRD spectra recorded in commercial and prepared FAUs are shown in Fig. 1. Here,
156 some spectra are omitted to economize the space (Na1.2 and Na2.4 were commercial samples,
157 in contrast three specimens of Na1.0, Na1.7, and Na3.5 were prepared in this study. Therefore,
158 the spectra of samples synthesized in this study are displayed in Fig. 1. The powder patterns
159 observed in Na1.2 and Na2.4 are also shown in the figure to compare with those synthesized in
160 this study). The powder patterns reveal that all characteristic FAU peaks are closely match with

those reported in previous reports [38] (the spectra of M1.2 and M2.4 were also similar to those of Na1.2 and Na2.4, respectively) and Sample C retains the FAU structure after the calcination. The result that the similar patterns were obtained in whole FAUs suggests that lattice



constants of the FAUs are independent on cation characters and Si/Al ratios.

Fig. 1. XRD spectra of M-type faujasite zeolites (M = Li, Na, K, Rb, Cs) with Si/Al ratios of 1.0, 1.2, 1.7, 2.4, and 3.5.

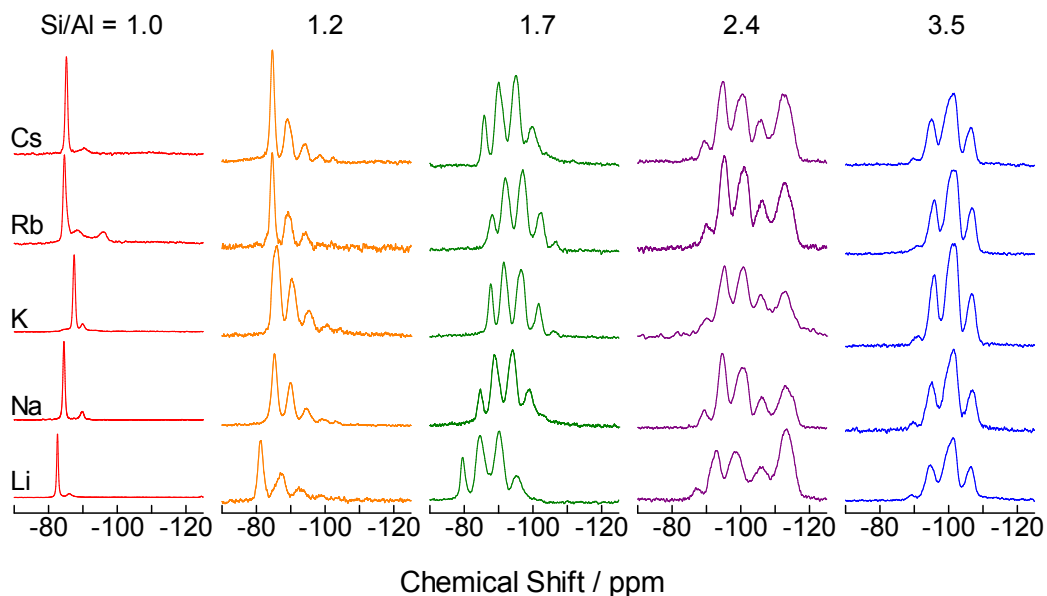
²⁹Si MAS NMR spectra observed in FAUs are displayed in Fig.2. These lines were able to be analyzed by several Gaussian functions (Lorentz functions could not be fitted well). Substituting each area obtained by fitting the Gaussian function into the following relation [27], Si/Al ratio of 1.0, 1.7 and 3.5 were obtained for Sample A, B and C, respectively, and 1.2 and 2.4 for commercial specimens. These Si/Al values could be estimated within ± 0.05 .

173

$$\text{Si/Al} = \frac{\sum A_n}{\sum 0.25nA_n} \quad (1)$$

174

175 Here, n and A_n denote the number of Al atoms bonding to a SiO_4 unit and an area of each
 176 analyzed curve, respectively. The similar line-shapes were recorded on the ^{29}Si MAS NMR
 177 spectra of the same Si/Al ratio (it is the same meaning of independent on cation types). This
 178 result suggests that the Si/Al ratio is rarely changed on cation substitutions. In contrast, complex
 179 dependences of chemical shift (CS) values on cation types were obtained: the lowest CS values
 180 were observed in K- or Rb-type FAU in the same Si/Al ratio. In reported MO simulations [21, 22],
 181 it is shown that ^{29}Si CS values are decreased with increasing angles of Si-O-Si in the zeolite
 182 framework. In contrast, our XRD spectra were rarely changed with Si/Al ratios and cation types,
 183 therefore, it can be considered that Si-O-Si angles in the FAU framework were retained by ion
 184 exchanges. In order to reveal the complex dependences recorded on the ^{29}Si MAS NMR spectra,
 185 we performed MO simulations. Results are described in section 3.5.

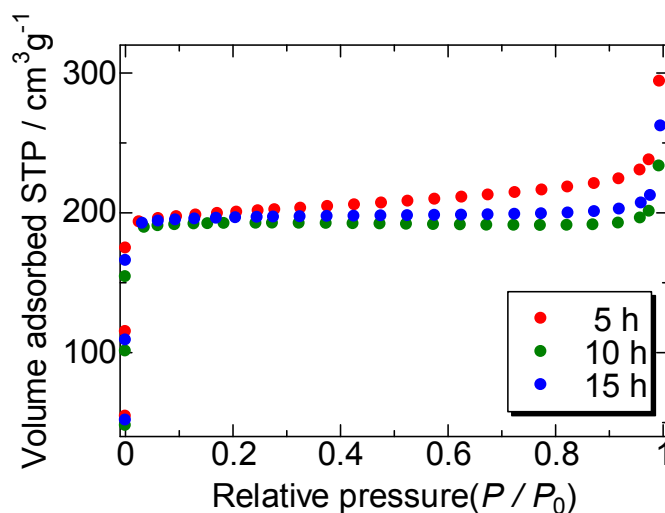


186 **Fig. 2.** Influences of Si/Al ratios on ^{29}Si MAS NMR spectra of M-type faujasite zeolites (M
187 = Li, Na, K, Rb, Cs).

188

189 3.2. N_2 Adsorption Isotherm Measurements

190 In order to reveal removing conditions of the water molecules from FAUs, N_2 adsorption
191 isotherms measurements were observed as a function of desorption times. N_2 adsorption
192 isotherms measurements of Na1.0 were carried out after degas handling at 673 K in vacuum for
193 5, 10, and 15 hours, because FAU with Si/Al ratio of 1.0 is the highest hydrophilicity in the FAUs
194 treated on the present study. Results of N_2 adsorption isothermal measurements are shown in
195 Fig. 3. Slopes at low relative pressures in these curves are linked to micropore capacities. Since
196 whole adsorption curves at low relative pressures showed the similar tendencies as displayed in
197 Fig. 3, the pre-observation condition of 5 hours at 673 K in vacuum were employed for all N_2
198 adsorption isotherm measurements in this study (Since we interested in micropore characters of



199 FAUs, the different values recorded at high relative pressure are not important in this study).

200 **Fig. 3.** N_2 adsorption isotherms of Na-type faujasite zeolites with the Si/Al ratio of 1.0
201 (Na1.0) after water molecules removed from the zeolites at 673 K for 5 (●), 10 (●), and 15 h

202 (•).

203

204 The result of N₂ adsorption isothermsineach FAU are shown in Fig. 4. These figures reveal that

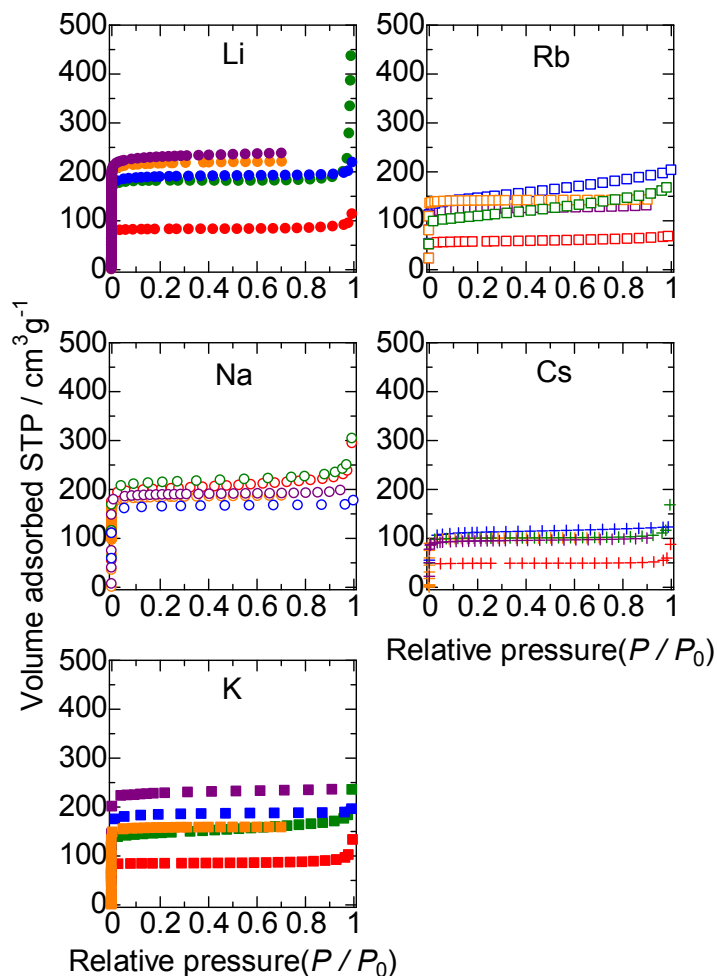
205 whole FAUs manipulated in this study take the I-type adsorption curve of the IUPAC

206 classification: N_2 molecules adsorb in micro and macro pores of FAUs in the range of low and

207 high relative pressures, respectively. The isotherm curves also show small amount of N_2

208 molecules adsorbing on Rb- and Cs-type FAUs comparing with those of the other types, as

209 displayed in Fig. 4, although the similar lattice constants were recorded by our XRD



210 measurements. These dependences are similar to reported tendencies [38]. Pore size
 211 distribution curves can be generally obtained by N₂ adsorption isotherm measurements, however,
 212 low resolution spectra were obtained. Therefore, only tendencies can be discussed for pore
 213 sizes in this study. These N₂ adsorption results can be considered that the majority of a large ion
 214 is shared in a part of the super cage space: ca. 250 pm of windows size of six-ring is smaller than
 215 296 (Rb⁺) and 338 pm (Cs⁺) in diameter, and similar to 266 pm (K⁺), and larger than 120 (Li⁺) and
 216 190 pm (Na⁺) [39]. Other discussions are described in section 3.5.
 217 **Fig. 4. N₂ adsorption isotherms of faujasite zeolites as a function of Si/Al ratios of 1.0**

218 (red), 1.2 (orange), 1.7 (green), 2.4 (purple), and 3.5 (blue).

219

220 **3.3.TG/DTA Measurements**

DTA, TG, and DTG curves obtained in each FAU are shown in Fig. 5. The endothermic

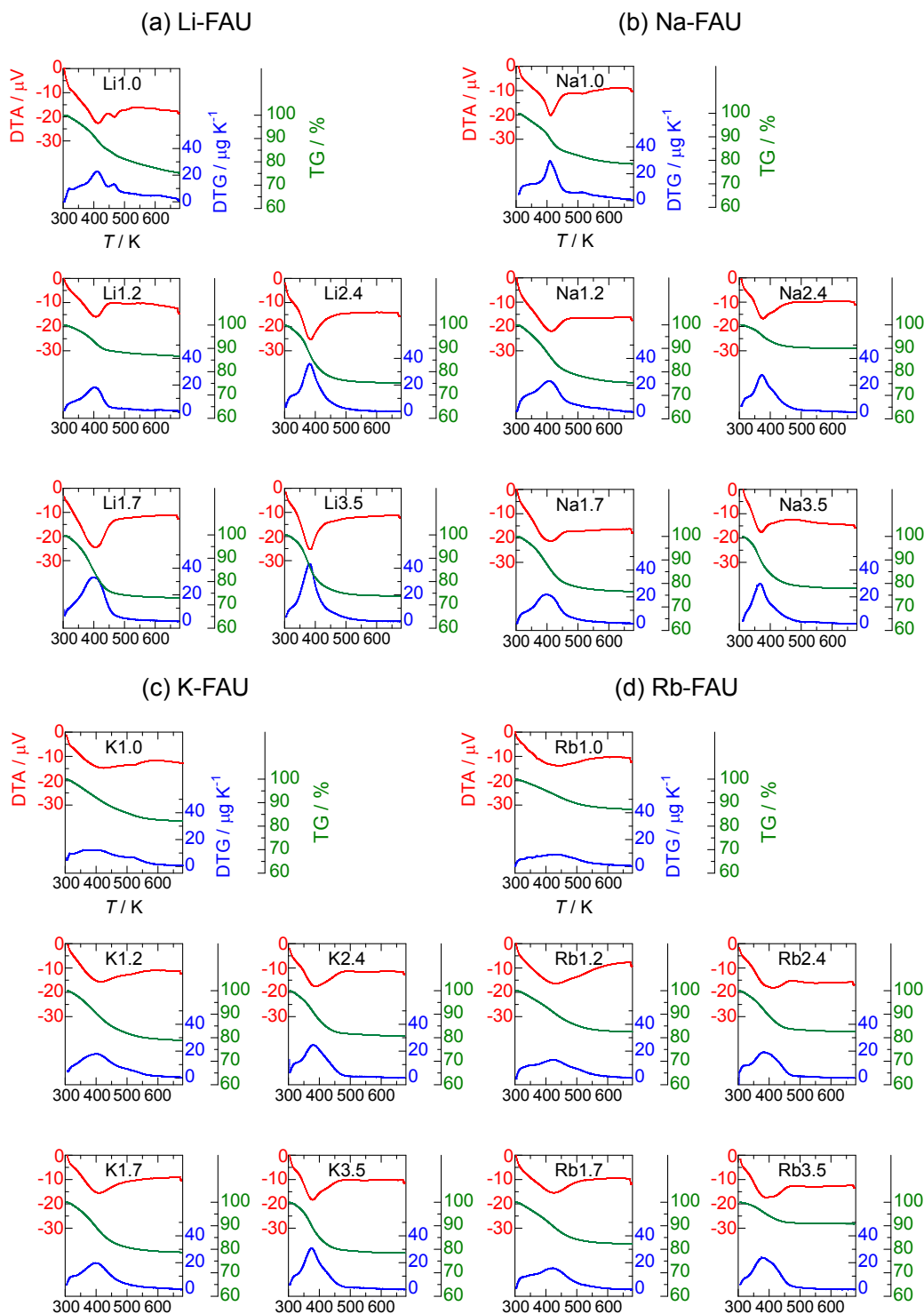
222 peak were observed at around 400 K. Since weight loss was also recorded at the temperature,

223 this endothermic signal can be attributed to water desorption from each FAU. The origin of the

224 broad signal of DTA and successive decreasing of TG curves can be considered that there are

225 some states of water molecules in FAU: some ones interact with FAU frameworks, others are

226 affected by cation, and the others are located around the center of supercage in FAU [12]. Since it
 227 is difficult to determine desorption temperature of water molecules uniquely, a temperature with
 228 the largest slope on TG curves (T_{DTG}) was introduced. Here, T_{DTG} is a peak temperature of each



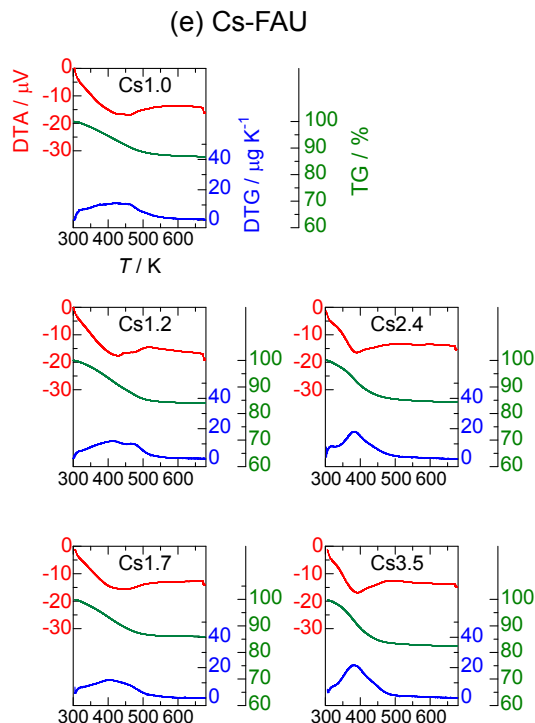


Fig. 5. DTA, TG, and DTG curves observed in M-type faujasite zeolites as a function of temperatures. M = (a) Li, (b) Na, (c) K, (d) Rb, (e) Cs.

DTG curve and means a temperature at which abundant water molecules are removed from FAU. Each T_{DTG} value estimated is listed in Table 1. Based on these values, the higher T_{DTG} is obtained in the lower Si/Al ratios. Since it is well known that cations in zeolites attract water molecules by strong electrostatic interactions, this tendency can be explained by hydrophilicity of FAU (the lower Si/Al ratio results in the higher concentration of cations in FAU). It means that the T_{DTG} value links to a factor of strength of hydrogen bonding among water molecules and cations in FAU. In the case of cation-type dependencies, complex tendencies were recorded: The smallest T_{DTG} was obtained in K- or Na-type FAU as shown in Table 1. This tendency is similar to those observed in the ^{29}Si NMR CS values. Detail discussion about this tendency is described in section 3.5.

248

249 **Table 1. Temperatures with the largest slope on each TG curve (T_{DTG}) of hydrated FAU.**250 **Unit is in K. Errors of temperatures are within 1 K, in the case of K1.0, Rb1.0, Cs1.0, and**251 **Cs1.7, those are within 3 K.**

252

Si/Al Ratio	Li	Na	K	Rb	Cs
1.0	411	408	398	443	419
1.2	405	406	397	418	413
1.7	400	398	397	423	403
2.4	380	371	378	381	384
3.5	380	366	374	375	383

260

261

262 **3.4. ^1H MAS NMR Chemical Shift**263 ^1H MAS NMR spectra observed with a MAS ratio of 30 kHz are shown in Fig. 6. Two

264 Lorentz-type signals were recorded on each spectrum. Peaks observed at 0.12 ppm and around

265 5 ppm can be assigned to H atoms in silicon rubber (inner reference) and in water molecules

266 adsorbing on each FAU, respectively. Since very small amount of silicon rubber was added into

267 the sample tubes, the enlarged spectra at around 0 ppm were also displayed in Fig. 6. Since

268 only one signal was detected at around 5 ppm, it can be considered that spin-exchange rates

269 among the H atoms of water molecules adsorbing on each cation and those linking with other

270 water molecules in the supercage are fast enough. Based on this result, it can be considered that

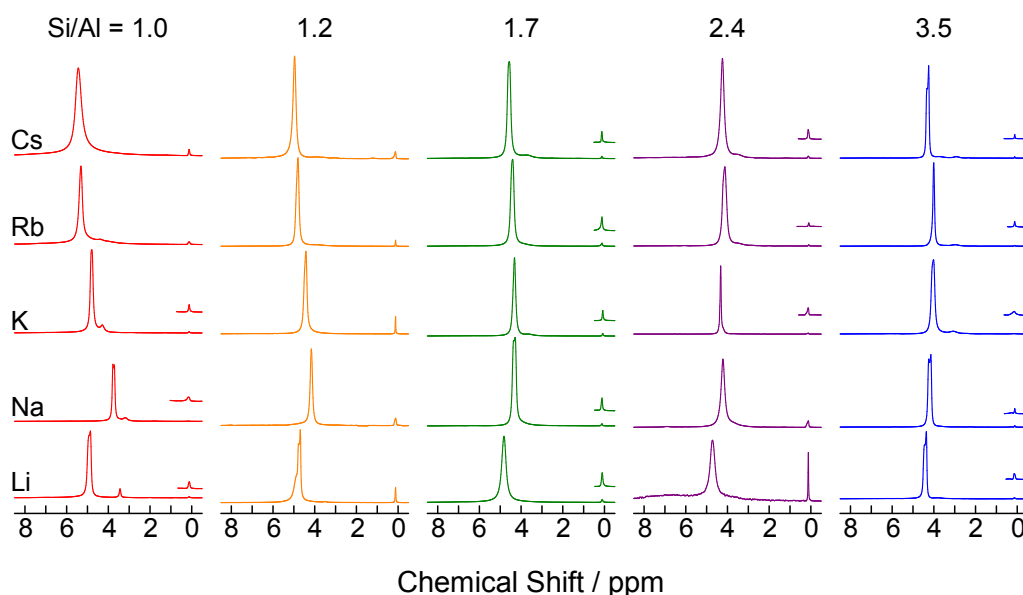
271 whole water molecules are linked each other and we can consider only partial water molecules

272 instead of whole ones in FAU. The CS values recorded on the ^1H MAS NMR spectra are listed in

273 Table 2. The similar CS dependencies on cation types were obtained as those recorded on the

274 ^{29}Si NMR spectra, i.e. large CS values were detected in Li- or Cs-type FAU. Since it is reported275 that the larger ^1H CS values are detected in H atoms forming the stronger H-bond [45], it can be

276 considered that H-bonds among water molecules and the FAU frameworks are attractive in Li-
 277 and Cs-FAUs, and an origin of the complex dependencies of T_{DTG} and ^1H CS values is the same.
 278 In addition, shielding tensors of ^1H nuclei are almost determined by diamagnetic terms rather
 279 than paramagnetic components [46], therefore, it can be regarded that electron densities of H
 280 atoms in water molecules adsorbing on Li or Cs ions in the FAU framework are low. In order to
 281 reveal reasons why electron densities of water molecules are low in Li or Cs-type FAU, CS
 282 simulation was carried out.



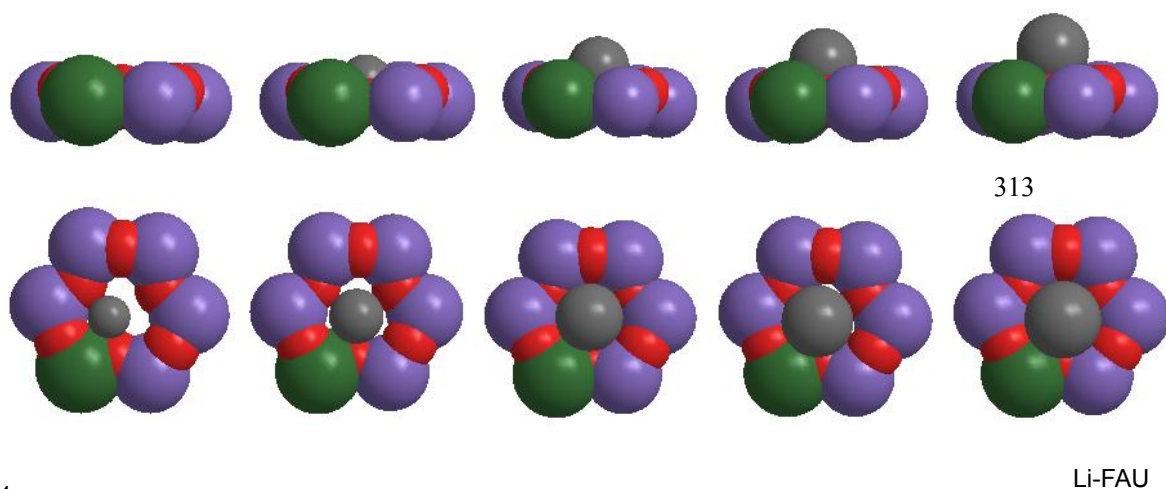
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 284 **Fig. 6. ^1H MAS NMR spectra observed in M-type faujasite zeolites (M = Li, Na, K, Rb, Cs)**
 285 **with Si/Al ratios of 1.0, 1.2, 1.7, 2.4, and 3.5. Inner reference of silicon rubber is observed**
 286 **at 0.12 ppm (enlarged spectra are displayed).**

Table 2. Chemical shift (CS) values recorded on the ^1H MAS NMR spectra. Unit is in ppm.

	Si/Al Ratio				
	1.0	1.2	1.7	2.4	3.5
Cs	5.44±0.08	4.97±0.05	4.57±0.05	4.23±0.05	4.25±0.04
Rb	5.32±0.05	4.80±0.04	4.40±0.05	4.13±0.05	4.00±0.03
K	4.80±0.03	4.42±0.04	4.31±0.04	4.32±0.02	4.02±0.05
Na	4.16±0.07	4.16±0.03	4.28±0.05	4.22±0.05	4.14±0.05
Li	4.86±0.08	4.69±0.06	4.82±0.06	4.72±0.06	4.36±0.05

3.5.Simulation

On the results of ^1H and ^{29}Si MAS NMR, and TG measurements, the lowest CS and T_{DTG} values were obtained for K- or Na-type FAU in the same Si/Al ratio. The N_2 adsorption isotherm curves reveal that absorbable space of N_2 molecules on Rb- and Cs-type FAU is smaller than the others with the same Si/Al ratio, although the similar lattice constants among them were detected by our XRD measurements. The smaller absorbable volumes in Rb- and Cs-type FAU can be explained by the six-ring window-size of FAU frameworks: Rb^+ (296 pm) and Cs^+ (338 pm) have large ion-size competing with the window-size of ca. 250 pm, therefore majority parts of the ions are shared a part of supercage space as displayed in Fig. 7. In this figure, coordinates of each cation were optimized by a B3LYP/LanL2DZ function. The similar illustrations are reported for Li, K, Mg, and Ca-type zeolites [19].



314

315 **Fig. 7. Estimated locations of the cations on the six-ring windows. Si, O, Al, H, and**
 316 **cation are shown by purple, red, green, and gray, respectively.**

317

318 Based on this figure, we can consider a model in which number of water molecules coordinating
 319 to cations is depended on cation's size: small cations of Li^+ (120 pm) and Na^+ (190 pm) can insert
 320 into the FAU frameworks, therefore a few water molecules can adsorb on them, in contrast,
 321 Rb^+ and Cs^+ are located on frameworks, therefore several water molecules can link to the cations.
 322 In order to estimate coordination number of water molecules on each cation, we introduced a
 323 supercage model with chemical formula of $\text{MAiSi}_{47}\text{O}_{73}\text{H}_{48}$, ($\text{M} = \text{Li, Na, K, Rb, Cs}$). Since a
 324 reported simulation with MP2 and DFT methods in local structure models ($\text{AlSi}_7\text{O}_{14}\text{H}_{12}$,
 325 $\text{AlSi}_{10}\text{O}_{14}\text{H}_{17}$, $\text{Si}_{11}\text{O}_{24}\text{H}_{16}$, etc.) of supercage shows a good agreement with experimental values
 326 [17, 20-23], our model of $\text{MAiSi}_{47}\text{O}_{73}\text{H}_{48}$ is suitable to simulate CS values. In our supercage
 327 model, reported coordinates of Si (Al) and O atoms were used and the Al atom was inserted into
 328 a part of six-ring, because experimental and theoretical reports show that whole SII is occupied
 329 by cations with a Si/Al range from 1 to 5, and occupancies of SIII and SIII' are gradually
 330 increased with decreasing Si/Al ratios in $\text{Si/Al} < 2$ [9, 11, 40-44]. In our simulation, positions of
 331 each alkali cation, terminal H atoms of the framework, and H and O atoms in water molecules

332 were optimized by a function of B3LYP/LanL2DZ. The coordination number of water molecules
 333 was estimated by the following process for each M-type FAU: one water molecule was initially
 334 put on the origin of this model (center of the supercage) and, then, coordinates of the water
 335 molecules and the cation and terminal H atoms were optimized. At the next step, the second
 336 water molecule was located at the origin and converged positions of two water molecules and the
 337 cation were simulated by the same function. If both water molecules can adsorb on the cation,
 338 then the same process was continued until any water molecule can't link directly to each
 339 cation. The result of coordination number of water on each cation is listed in Table 3 and illustrated
 340 in Fig. 8. This simulation showed different numbers of water molecules adsorbing on each cation.

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346 **Table 3. The number and ^1H chemical shift (CS) values of adsorbed water molecules on**
 347 **each cation in FAU estimated by MP2/cc-PVDZ function in the super cage model. Values**
 348 **are in a case of one water molecule adsorbing on each cation.**

Cation	CS / ppm		
	Number of Water Molecules	One Water	Waters
Li	1	0.8506	0.8506
Na	2	1.0873	0.4394
K	3	1.1897	1.0634
Rb	3	1.2286	1.1346
Cs	3	1.2639	1.1482

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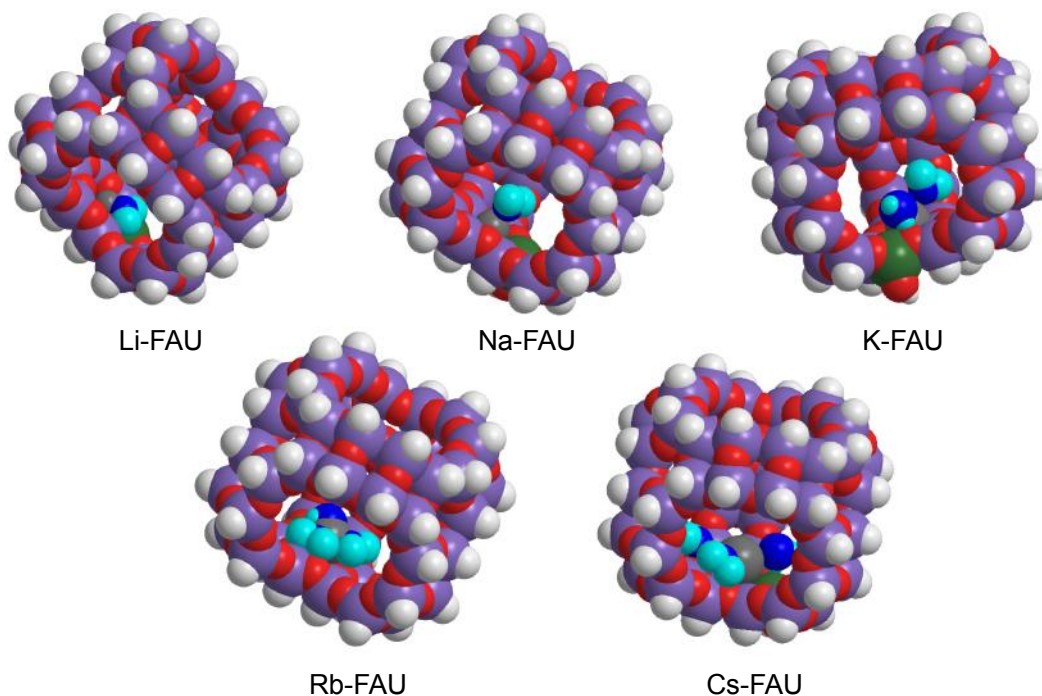


Fig. 8. Molecular arrangements of water molecules adsorbed on cations in the FAU supercage. H and O atoms of water molecules are shown by cyan and blue, respectively. Si, O, Al, H, and cation in the framework are illustrated by purple, red, green, and gray, respectively.

In order to estimate CS values of water molecules, a method of ONIOM (MP2/cc-pVDZ : HF/cep-4G) was employed, where the former function of MP2/cc-pVDZ was applied for H and O atoms in water molecules and the latter was used for each cation and Si, O, Al, H atoms in the framework. The MP2/cc-pVDZ function also applied for shielding tensor estimation of a tetramethylsilan (TMS) molecule, where all coordinates of atoms were optimized by a B3LYP/6-31G** method. Subtracting shielding tensors of H atoms in the water molecules from that of TMS, ^1H CS values in the water molecules were immediately obtained as listed in Table 3. The CS values simulated in the model showed the similar tendency to those observed in ^1H MAS NMR measurements, i.e., the smallest CS value is recorded for Na-type FAU (since demonstrated ^1H CS values are rarely agreed with experimental values and CS is relative values,

only tendencies are discussed in this study). Conversely, assuming another model in which only one water molecule adsorbed on each cation, CS values were monotonously increased with cation sizes, as displayed in Table 3. Therefore, it can be regarded that the difference of coordination number of water molecules influences on the complex dependences recorded on the NMR spectra. Based on our ^1H MAS NMR and TG-DTA results, it can be concluded that water molecules form weak hydrogen bonds in Na- and K-type FAU with high Si/Al ratios. In Li, Na, K Rb, and Cs ions, charge density on each surface is decreased with increasing ion radius, therefore, it can be regarded that water molecules form weaker hydrogen bonds with the larger cations. In contrast, since abundant parts of the large ions can't insert in the FAU framework, several water molecules can contact to the larger cations. Based on these two factors, the result that middle size ions of Na and K form weak hydrogen bonds with water molecules in FAU can be explained.

We also attempted to simulate the complex dependences of ^{29}Si MAS NMR CS values on cation types as displayed in Fig. 2. The supercell model was also employed in this simulation. Applying a HF/CEP-4G function to whole atoms in the model, calculated ^{29}Si CS values with respect to silanes [47] were obtained as listed in Table 4. The simulated CS values show the similar complex tendencies to those recorded on the ^{29}Si MAS NMR spectra, therefore, it can be considered that cation positions also influence on ^{29}Si CS values.

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402 **Table 4.** ^{29}Si chemical shift (CS) values estimated by HF/CEP-4G function in the super
403 cage model.

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414 **4. Conclusion**

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Cation	CS / ppm
Li	-125.17
Na	-125.44
K	-125.63
Rb	-125.50
Cs	-125.24

In order to reveal adsorbed states of water molecules on faujasite-type zeolites (FAU), Na-type FAU with five different Si/Al ratio were prepared. In addition, Na ions in these five FAUs were exchanged by Li, K, Rb, or Cs ions. XRD and ^{29}Si MAS NMR spectra showed that FAU frameworks were rarely changed by ion exchanges. High-resolution solid-state ^1H MAS NMR spectra showed a signal which can be assigned to H atoms of water molecules adsorbed on each M-type FAU. Complex dependences of ^1H NMR signal on cation types were observed (the lowest CS value was recorded in Na- or K-type FAU with each Si/Al ratio). The similar tendencies were detected in TG-DTA measurements: a desorption temperature of water molecules showed complex dependences on cation properties (the minimum temperature was recorded in Na- or K-type FAU with each Si/Al ratio). In order to reveal the complex tendencies of ^1H NMR CS values, computer simulations were attempted in a supercage model. In our simulations, it was revealed that the different coordination number of water molecules to each cation results in the complex CS dependencies on cation types. The different coordination number can be accepted,

428 because ion sizes of Li and Na ions are smaller than that of six-rings windows in the FAU
429 framework, conversely, Rb and Cs ions are larger, i.e. abundant parts of Rb and Cs ions are
430 occupied a part of the supercage.

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433 **COMPETING INTERESTS**

434 Authors have declared that no competing interests exist.

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References

1. Breck DW. Zeolite Molecular Sieves: Structure, Chemistry, and Use. John Wiley: New York; 1974.
2. Rabo JA. Zeolite Chemistry and Catalysis. American Chemical Society: Washington; 1976.
3. Bekkum H, Flanigen EM, Jansen JC. Introduction to Zeolite Science and Practice. Elsevier: Amsterdam; 1991.
4. Auerbach SM, Carrad KA, Dutt PK. Handbook of Zeolite Science and Technology. Marcel Dekker: New York; 2003.
5. Yang RT. Adsorbents: Fundamentals and Applications. John Wiley & Sons: New York; 2003.
6. Baerlocher C, McCusker LB, Olson DH. Atlas of Zeolite Framework Types, 6th ed. Elsevier: New York; 2007.
7. Xu R, Pang W, Yu J, Huo Q, Chen J. Chemistry of Zeolites and Related Porous Materials: Synthesis and Structure. John Wiley & Sons: Singapore; 2007.
8. Fitch AN, Jobic H, Renouprez A. Localization of benzene in sodium-Y-zeolite by powder neutron diffraction. J. Phys. Chem. 1986;90(7):1311-1318.
9. Vitale G, Mellot CF, Bull LM, Cheetham AK. Neutron Diffraction and Computational Study of Zeolite NaX: Influence of SIII' Cations on Its Complex with Benzene. J. Phys. Chem. B. 1997;101(23):4559-4564.
10. Beauvais C, Boutin A, Fuchs AH. A Numerical Evidence for Nonframework Cation Redistribution Upon Water Adsorption in Faujasite Zeolite. ChemPhysChem. 2004;5(11):1791-1793.
11. Beauvais C, Boutin A, Fuchs AH. Adsorption of water in zeolite sodium-faujasite: A molecular simulation study. C. R. Chim. 2005;8(3-4):485-490.
12. Shirono K, Endo A, Daiguji H. Molecular Dynamics Study of Hydrated Faujasite-Type Zeolites. J. Phys. Chem. B. 2005;109(8):3446-3453.
13. Coasne AB, Maurin G, Henn F, Jeffroy M, Boutin A. Cation Behavior in Faujasite Zeolites upon Water Adsorption: A Combination of Monte Carlo and Molecular Dynamics Simulations. J. Phys. Chem. C. 2009;113(24):10696-10705.
14. Abrioux C, Coasne B, Maurin G, Henn F, Boutin A, Lella AD, Fuchs AH. A molecular simulation study of the distribution of cation in zeolites. Adsorption. 2008;14(4-5):743-753.
15. Lella AD, Desbiens N, Boutin A, Demachy I, Ungerer P, Bellatc JP, Fuchs AH. Molecular simulation studies of water physisorption in zeolites. Phys. Chem. Chem. Phys. 2006;8:5396-5406.
16. Caillieza F, Boutinb A, Demachyb I, Fuchs AH. Thermodynamic study of water confinement in hydrophobic zeolites by Monte Carlo simulations. Molecular Simulation. 2009;35(1-2):24-30.

- 475 17. Limtrakul J, Treesukol P, Ebner C, Sansone R, Probst M. Structures and potential energy
476 surface of Faujasitic zeolite/water. *Chem. Phys.* 1997;215(1):77-87.
- 477 18. Belarbi H, Haouzi A, Giuntini JC, Devautour-Vinot S, Kharroubi M, Henn F. A DFT-based
478 model for water adsorption at aluminosilicate surfaces. Comparison with experimental data
479 extracted from dielectric relaxation spectroscopy. *J. Non-Crystalline Solids.*
480 2010;356(11-17):664-668.
- 481 19. Vayssilov GN, Rosch N. Influence of Alkali and Alkaline Earth Cations on the Brønsted Acidity
482 of Zeolites. *J. Phys. Chem. B.* 2001;105(19):4277-4284.
- 483 20. Bussemer B, Schroder KP, Sauer J. Ab initio predictions of zeolite structures and ^{29}Si NMR
484 chemical shifts. *Solid. State Nuc. Magn. Reson.* 1997; 9(2-4):155-164.
- 485 21. Valerio G, Goursot A, Vetrivel R, Malkina O, Salahub DR. Calculation of ^{29}Si and ^{27}Al MAS
486 NMR Chemical Shifts in Zeolite- β Using Density Functional Theory: Correlation with Lattice
487 Structure. *J. Am. Chem. Soc.* 1998;120(44):11426-11431.
- 488 22. Valerio G, Goursot A. Density Functional Calculations of the ^{29}Si and ^{27}Al MAS NMR Spectra
489 of the Zeolite Mazzite: Analysis of Geometrical and Electronic Effects. *J. Phys. Chem. B.*
490 1999;103(1):51-58.
- 491 23. Ricchiardi G, Sauer J. Influence of Ti substitution on the ^{29}Si NMR spectra of silicalite. A
492 computational study. *Z. Phys Chem.* 1999;209(1):21-32.
- 493 24. Beta IA, Bohlig H, Hunger B. Structure of adsorption complexes of water in zeolites of different
494 types studied by infrared spectroscopy and inelastic neutron scattering. *Phys. Chem. Chem.*
495 *Phys.* 2004;6:1975-1981.
- 496 25. Kathoh M, Koide R, Yamada K, Yoshida T, Horikawa T. IR SPECTROSCOPIC ANALYSIS OF
497 THERMAL BEHAVIOR OF ADSORBED WATER ON Y-TYPE ZEOLITE. *International J.*
498 *Mod. Phys.* 2012;6:437-442.
- 499 26. Ferwerda R, Maas JH. The influence of adsorbed molecules on the framework vibrations of
500 Na-Faujasites studied with FT Raman spectroscopy. *Spectrochimica Acta*
501 *A.* 1995;51(12):2147-2159.
- 502 27. Duer MJ. *Solid-State NMR Spectroscopy: Principles and Applications.* Blackwell
503 Science: Tokyo; 2002.
- 504 28. Fitzgerald JJ. *Solid-State NMR Spectroscopy of Inorganic Materials.* American Chemical
505 Society: Washington; 1999.
- 506 29. Semmer-Herle'dan V, Heeribout L, Batamack P, Dore'mieux-Morin C, Fraissard J, Gola A,
507 Benazzi E. Comparison of the acid strength of dealuminated H-faujasites determined by ^1H
508 NMR after water adsorption. *Microporous Mesoporous Mater.* 2000;34(2):157-169.
- 509 30. Freude D, Hunger M, Pfeifer H. Study of Brønsted acidity of zeolites using high-resolution
510 proton magnetic resonance with magic-angle spinning. *Chem. Phys. Lett.*

1982;91(4):307-310.

31. Freude D, Hunger M, Pfeifer H, Schwieger W. ^1H MAS NMR studies on the acidity of zeolites. *Chem. Phys. Lett.* 1986;128(1):62-66.

32. Freude D, Kilinowski J, Hamdan H. Solid-state NMR studies of the geometry of brønsted acid sites in zeolitic catalysts. *Chem. Phys. Lett.* 1988;149(4):355-362.

33. Jelinek R, Ozkar S, Pastore H, Malek A, Ozin GA. Guest-host interactions in sodium zeolite Y: structural and dynamical ^{23}Na double-rotation NMR study of water, trimethylphosphine, molybdenum hexacarbonyl, and $\text{Mo}(\text{CO})_4(\text{PMe}_3)_2$ adsorption in Na56Y. *J. Am. Chem. Soc.* 1993;115(2):563-568.

34. Legras B, Polaert I, Estel L, Thomas M. Mechanisms Responsible for Dielectric Properties of Various Faujasites and Linde Type A Zeolites in the Microwave Frequency Range. *J. Phys. Chem. C.* 2011;115(7):3090-3098.

35. Iwai Y, Oka N, Yamanishi T. Influence of framework silica-to-alumina ratio on the water adsorption and desorption characteristics of MHI-CaX/CaY zeolite. *J. Phys. Chem. Solids.* 2009;70(5):881-888.

36. Yang H, Ping Z, Niu G, Jiang H, Long Y. TG/DTG/DTA Study on Interaction between the Framework of High Silica Hydrophobic FAU Zeolite and Adsorbed Organics. *Langmuir.* 1999;15(16):5382-5388.

37. Robson H. *Verified syntheses of zeolite materials*: Elsevier Science Ltd.; 2001.

38. Yang S, Navrotsky A. Energetics of formation and hydration of ion-exchanged zeolite Y. *Microporous Mesoporous Mater.* 2000;37(1-2):175-186.

39. Lia YQ. Crystal radii and effective ionic radii of the rare earth ions. *J. Solid State Chem.* 1991;95(1):184-187.

40. Eulenberger GR, Shoemaker DP, Keil JG. Crystal structures of hydrated and dehydrated synthetic zeolites with faujasite aluminosilicate frameworks. I. The dehydrated sodium, potassium, and silver forms. *J. Phys. Chem.* 1967;71(6):1812-1819.

41. Jiráček Z, Vratilav S, Bosáček V. A neutron diffraction study of H, Na-Y zeolites. *J. Phys. Chem. Solids.* 1980;41(10):1089-1095.

42. Olson DH. The crystal structure of dehydrated NaX. *Zeolites.* 1995;15(5):439-443.

43. Zhu L, Seff K. Reinvestigation of the Crystal Structure of Dehydrated Sodium Zeolite X. *J. Phys. Chem. B.* 1999;103(44):9512-9518.

44. Porcher F, Souhassou M, Dusauroy Y, Lecomte C. The crystal structure of a low-silica dehydrated NaX zeolite. *Eur. J. Miner.* 1999;11(2):333-343.

45. Honda H. ^1H -MAS-NMR Chemical Shifts in Hydrogen-Bonded Complexes of Chlorophenols (Pentachlorophenol, 2,4,6-Trichlorophenol, 2,6-Dichlorophenol, 3,5-Dichlorophenol, and

546 *p*-Chlorophenol) and Amine, and H/D Isotope Effects on ^1H -MAS-NMR Spectra
547 Molecules.2013;18(4):4786-4802.
548 46. Gerstein BC, Dybowski CR. Transient Techniques in NMR of Solids. Academic Press : New
549 York ; 1985.
550 47. Heine T, Goursot A, Seifert G, Weber J. Performance of DFT for ^{29}Si NMR Chemical Shifts of
551 Silanes. J. Phys. Chem. A. 2001;105(3):620-626.