

Original Research Article

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 (MAS) method showed a signal which can be assigned to H atoms of water molecules adsorbed on each FAU. The chemical-shift (CS) value was increased with increasing Si/Al ratios, in contrast, complex dependences were observed on cation types (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. This model can also explain the results of N_2 adsorption isotherms and complex dependence of desorption temperatures. 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.

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

14 1.INTRODUCTION

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

16 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 endeavors,

18 because of their special structure and properties of adsorption, ion exchange, and catalysis [1-7].

19 The general chemical formula of FAU in an unit cell is $\text{M}_{(x/n)}(\text{SiO}_2)_{(192-x)}(\text{AlO}_2)_x \cdot y\text{H}_2\text{O}$, where M is a

20 cation of charge $+n$. The number x of cations can vary from 0 to 96, depending on the Si/Al ratio.

21 The number of water molecules (y) in the unit cell is depended on steam pressure. The

22 crystalline structure of FAU as well as the position of the M cations is determined by X-ray and

23 neutron diffraction measurements [8, 9]. The unit framework of FAU is constructed by sodalite

24 cages combined by hexagonal prisms each other, and makes a pore (it is called as

25 supercage). The substitution of Si with Al atoms in the FAU framework induces a net negative

26 charge on the framework. To keep the overall framework to the neutral charge, the M ions are

27 distributed at three kinds of specific position in FAU: Sites I (SI) are located in the center of

28 hexagonal prism, while the sites I' (SI') are present in the sodalite cage toward the hexagonal

29 prism, sites II (SII) is located in the six-ring windows, and sites III (SIII) and III' (SIII') are located in

30 the center of the four-ring and twelve-ring windows of the supercages, respectively [10, 11]. It is

31 also known that cations occupy whole SI, SI', and SII in FAU with any Si/Al ratio, in contrast,

32 population of SIII and SIII' is increased with decreasing Si/Al ratios in a range of Si/Al ratio < 2

33 [10-12]. The cation at SII, SIII, and SIII' can be immediately exchanged by other cations in

34 solutions. It is reported that the size and valence of the M ion are critically important in adsorption

35 capacities and catalytic properties [6]. FAU with low Si/Al ratios shows hydrophilic characters

36 because the M ions attract water molecules by strong electrostatic interactions. Therefore, the

37 presence of water molecules in FAU cannot be avoided in many applications, especially,

operating at ambient temperature. Molecular dynamics (MD) and molecular orbital (MO) simulations show information of the water molecules and the cation sites in FAUs [10, 11, 13-19]. MD simulations show a three-step mechanism of water adsorption on FAU: water molecules are firstly adsorbed around the M ions in FAU, the next water molecules form a monolayer on the FAU surface, the further waters (the third step) are located in the supercage [13]. In addition, another MD calculation reports that the first water molecules are adsorbed on the cations located at SI (SI') and SII in FAU with Si/Al > 2, in contrast, in a case of small Si/Al ratios, the water molecules interact with cations at the whole sites of cations [14, 15]. Based on these reports, the cations can locate at SIII and SIII' and interact with water molecules in only Si/Al < 2. Grand-Canonical-Monte-Carlo (GCMC) demonstrations explain Si/Al ratio dependences on adsorption isotherms and heats observed in Na-type FAU [10, 11, 16, 17]. These simulations are generally performed for the unit cell model of hydrated and anhydrous FAUs. In a case of MO simulations, small cluster models, which are local parts of the FAU framework, have been frequently used [18-24]. Second-order Moller-Plesset (MP2) and density-functional-theory (DFT) methods show good agreement with the experimental proton-affinities (PA) values, although small cluster models of (H₃SiO)₄AlH and AlSi₁₀O₁₄H₁₇ (three four-rings and one six-ring are combined) are employed [18]. In a case of ²⁹Si NMR methods, it is reported that Si-O-Si angles in zeolite frameworks strongly contribute to ²⁹Si chemical shift (CS) values [21-24]. Experimental studies also report that the location of these M ions plays a crucial role on the thermodynamics, molecular dynamics, catalysis, and adsorbents in FAUs. The interactions between water molecules and FAUs have been revealed by adsorption and desorption isotherms, infra-red (IR), Raman, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), NMR, and dielectric measurements, etc [1-8, 25-37]. DRIFTS spectra reveal the formation of strongly bonded water-cation clusters in zeolites [25]. IR and Raman spectra show that bending vibrations of FAU framework are linked with the unit-cell sizes and the

vibrations are influenced by the charge distribution within FAU [26]. Solid-state ^{29}Si , ^{27}Al , and ^1H NMR measurements of FAU are performed with a magic-angle-spinning (MAS) method to determine Si/Al ratios and to study acid sites of FAU [28-33]. However, ^1H MAS NMR spectra with high speed MAS (>30 kHz) are rarely reported as functions of Si/Al ratios and cation types in hydrated FAU. In this study, TG-DTA, N_2 adsorption isotherms, and ^1H and ^{29}Si MAS NMR measurements were 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, and with cations of Li, Na, K, Rb, and Cs, in order to reveal water molecules states in FAUs.

2. MATERIALS AND METHODS

2.1 Sample Preparation

In this study, two commercial FAUs of Na form (Tosoh Co.) with Si/Al ratio of 1.2 and 2.4, and three specimens (abbreviated to Sample A, B, C) prepared by modifying a recipe of the previous report [38], were employed. Sample A, B, and C were synthesized by the following process.

2.1.1. Sample A

Sodium aluminate, potassium hydroxide, sodium hydroxide, and sodium silicate solution were dissolved in aqueous solution and mixed thoroughly. Obtained aqueous solution was incubated at 342 K for 14 hours and agitated at 368 K for 4 hours in vessel sealed with Teflon. After filtering, obtained specimens were washed by a 0.01 M sodium hydroxide solution and dried at room temperature.

2.1.2. Sample B

Sodium hydroxide and sodium aluminate were poured in water and stirred until completely dissolved. Sodium silicate solution was added into the solution and stirred at room

86 temperature for 1 day. Another concentration of sodium hydroxide, sodium aluminate and
87 sodium silicate aqueous solution was transferred into the prepared solution and let the mixed
88 solution for 1 day after stirring for 30 minutes. After incubation of 7 hours at 373 K, obtained
89 samples were washed by water and dried at room temperature.

90 **2.1.3. Sample C**

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

104 **2.1.4. Ion Exchange**

105 Ion exchanged FAUs were prepared by the following manipulation: Na-type FAU added
106 into 1M MCl aqueous solution ($M = \text{Li, K, Rb, Cs}$) and the solution was stirred at ca. 340K by 24
107 hours. After filtering of ion-exchanged specimens from the solution, M-type FAU was washed by
108 water and dried at room temperature. In this literature, M-type FAU with Si/Al ratio of x is
109 abbreviated to M_x ; e.g. $K_{2.4}$ means K-type FAU with $\text{Si/Al} = 2.4$.

110

111 **2.2.Measurement**

112 ^1H and ^{29}Si MAS NMR measurements were carried out by using a Bruker Avance 600
113 spectrometer (14.01T) with MAS accessory. Solid-state high-resolution ^1H MAS NMR spectra
114 were recorded at a Larmor frequency of 600.13 MHz with a MAS speed of 30 kHz. Powdered
115 FAU samples and a small amount of silicon lubber were packed in a ZrO rotor with an outer
116 diameter of 2.5 mm. Here, silicon lubber is aim to be inner reference of ^1H chemical shifts ($\delta =$
117 0.12 ppm). Si/Al ratios were determined by observing ^{29}Si MAS NMR spectra at 119.22 MHz with
118 a MAS ratio of 10 kHz. Powdered samples and silicon lubber were packed into a ZrO rotor with
119 an outer diameter of 4.0 mm. Here, silicon lubber is inner reference of ^{29}Si chemical shifts ($\delta =$
120 -22.59 ppm). All spectra of ^1H and ^{29}Si nucleus were obtained from free-induction-decay signals
121 which were recorded after a $\pi/2$ pulse. A pulse sequence of ^{29}Si MAS NMR was designed with a ^1H
122 decoupling pulse. Recycle times of 5 and 60 s were employed on ^1H and ^{29}Si MAS NMR
123 measurements, respectively.

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

128 TG, differential TG(DTG) and DTA curves were recorded from 293 to 673 K at heating
129 rate of 5 K min⁻¹ with a Seiko Instrument Inc. TG/DTA 6300 apparatus, where Al₂O₃ powder was
130 used for standard sample.

131 N₂ adsorption isotherms were observed at 77 K by using a Bell Japan Inc.
132 BELSORP-mini II. Before the adsorption experiments, all samples were crushed in a mortar and
133 were heated at 673 K for 5 hours in vacuum.

134

135 **2.3.Simulation**

136 Computer calculations were carried out by using a Gaussian 03 program [39] to
 137 estimate locations of water molecules, alkali-metal ions, and terminal H atoms in the FAU
 138 framework and to simulate shielding tensors of ^1H nucleus in water molecules. Since alkali-metal
 139 ions (especially Cs ion) take with many electrons, therefore, aB3LYP/LanL2DZ function was
 140 employed for optimization of water molecules and alkali-metal ions in the FAU framework.
 141 Shielding tensor estimation of ^1H nucleus was performed by an ONIOM
 142 (MP2/cc-pVDZ:HF/cep-4G) method; where shielding tensor of water molecules were estimated
 143 by the MP2/cc-pVDZ function, and the other atoms in the frameworks were done by using
 144 HF/cep-4G. In the case of ^{29}Si nucleus, shielding tensors were calculated by the
 145 B3LYP/LanL2DZ function in another framework model.

146

147 **3.RESULTS AND DISCUSSION**

148 **3.1. XRD and ^{29}Si MAS NMR Measurements**

149 XRD spectra recorded in commercial and prepared FAUs are shown in Fig.1. These
 150 powder patterns reveal that all characteristic FAU peaks are closely match with those reported in
 151 previous reports [40] and Sample C retains the FAU structure after the calcination. In addition,
 152 the XRD lines also suggest that lattice constants of the FAUs are independent on cation
 153 characters and Si/Al ratios.

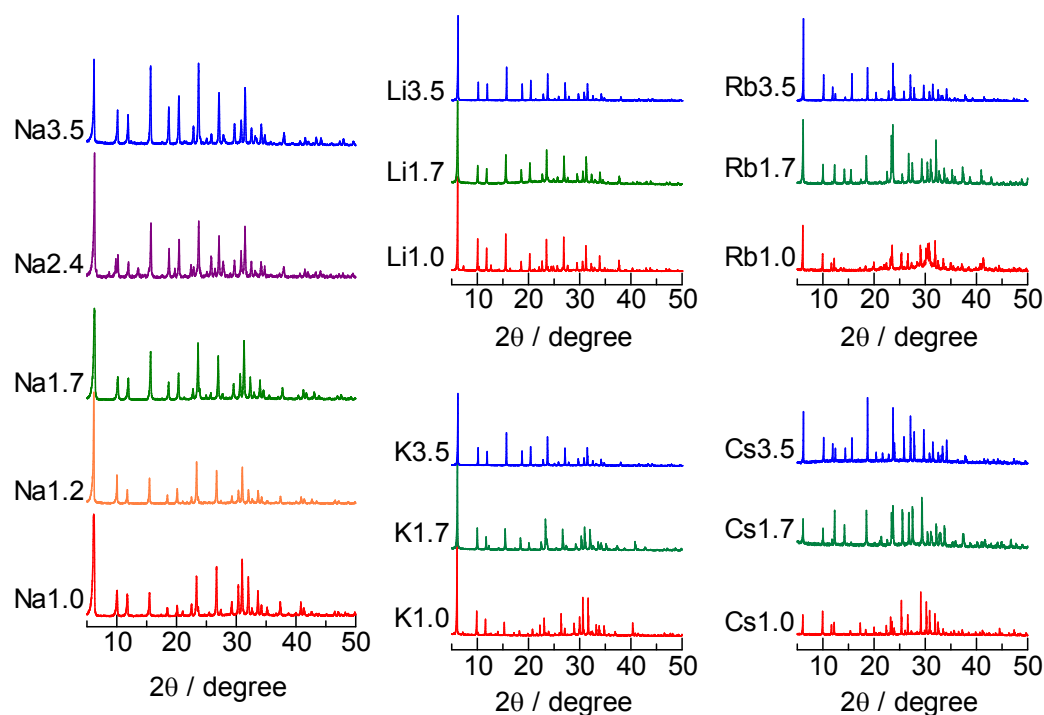


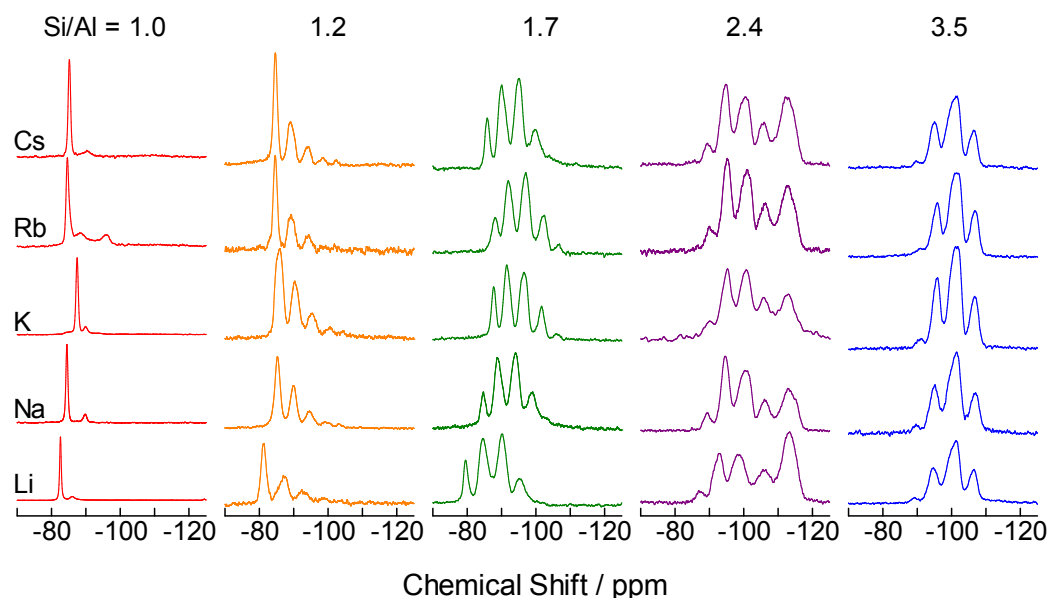
Fig. 1. XRD spectra of M-type faujasite zeolites (M = Li, Na, K, Rb, Cs) with Si/Al ratios of 1.0, 1.2, 1.7, 2.4, and 3.5.

²⁹Si MAS NMR spectra observed in FAUs are displayed in Fig.2. These lines were able to be analyzed by several Gauss functions. Substituting each area obtained by fitting the Gauss function into the following relation [28], 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.

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

Here, n and A_n denote the number of Al atoms bonding to a SiO_4 unit and an area of each analyzed curve, respectively. The similar line-shapes were recorded on the ²⁹Si MAS NMR spectra of the same Si/Al ratio (it is the same meaning of independent on cation types). This

166 result suggests that the Si/Al ratio is rarely changed on cation substitutions. In contrast, complex
 167 dependences of chemical shift (CS) values on cation types were obtained: the lowest CS values
 168 were observed in K- or Rb-type FAU in the same Si/Al ratio. In reported MO simulations [22, 23],
 169 it is shown that ^{29}Si CS values are decreased with increasing angles of Si-O-Si in the zeolite
 170 framework. In contrast, our XRD spectra were rarely changed with Si/Al ratios and cation types,
 171 therefore, it can be considered that these CS dependences caused by other origins. Detail



172 discussions are shown in section 3.5.

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

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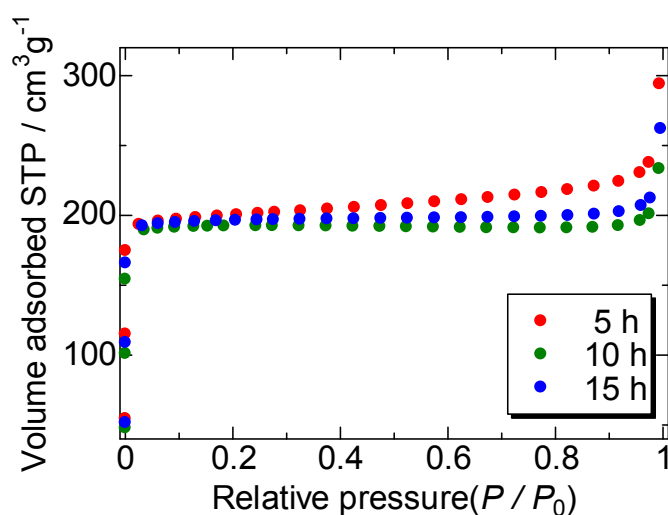
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180 3.2. N₂ Adsorption Isotherm Measurements

181 In order to reveal removing conditions of the water molecules from FAUs, N₂ adsorption
 182 isotherms measurements were observed as a function of desorption times. N₂ adsorption
 183 isotherms measurements of Na1.0 were carried out after degas handling at 673 K in vacuum for



184 5, 10, and 15 hours, because FAU with Si/Al ratio of 1.0 is the highest hydrophilicity in the FAUs
 185 treated on the present study. Since whole adsorption curves showed the similar tendencies as
 186 displayed in Fig. 3, the pre-observation condition of 5 hours at 673 K in vacuum were employed for
 187 all N₂ adsorption isotherm measurements in this study.

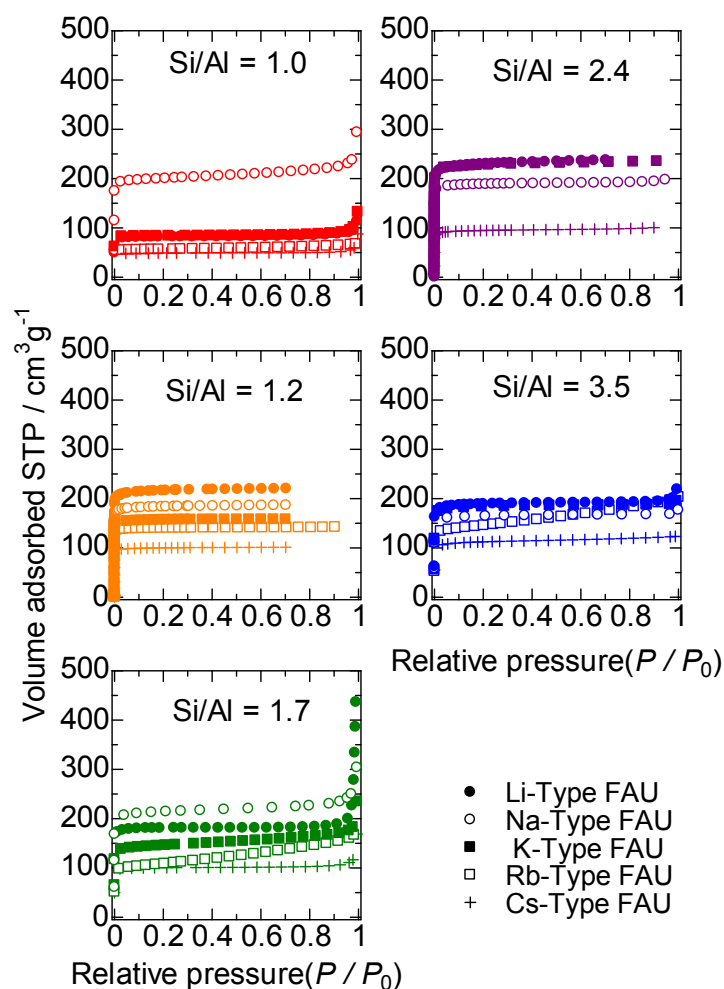
188 **Fig. 3. N₂ adsorption isotherms of Na-type faujasite zeolites with the Si/Al ratio of 1.0**
 189 **(Na1.0) after water molecules removed from the zeolites at 673 K for 5 (●), 10 (●), and 15 h**
 190 **(●).**

191

192 The result of N₂ adsorption isotherms in each FAU as a function of Si/Al ratios and cation
 193 types are shown in Figs. 4 and 5, respectively. These figures reveal that whole FAUs manipulated

194 in this study take the I-type adsorption curve of the IUPAC classification: N₂ molecules adsorb in

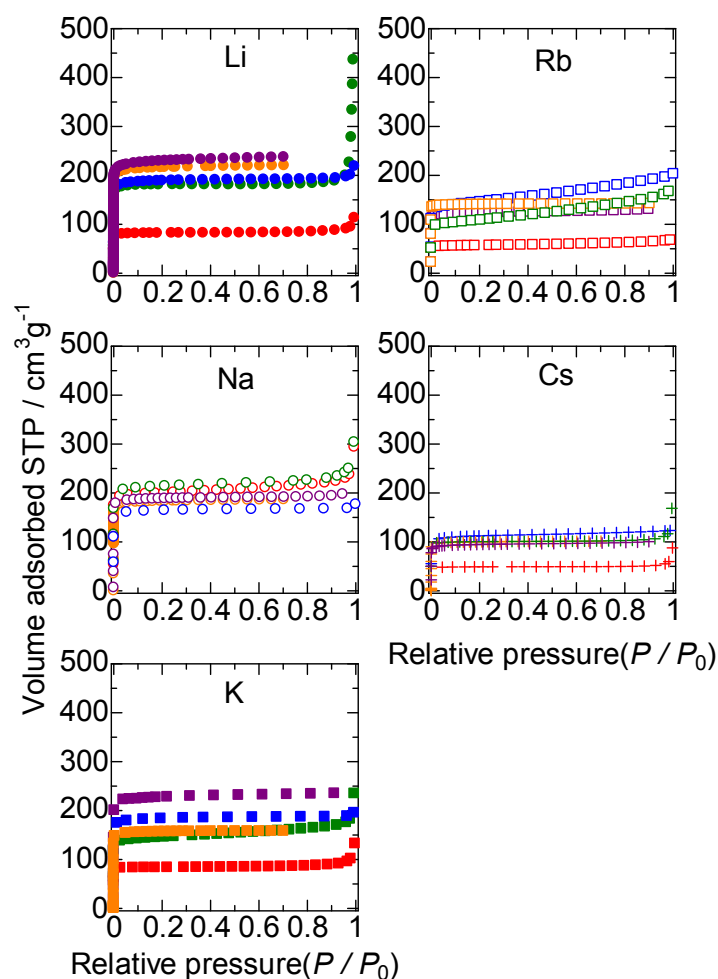
195 micro and macro pores of FAUs in the range of low and high relative pressures, respectively. The
 196 isotherm curves also show small amount of N_2 molecules adsorbing on Rb- and Cs-type
 197 FAUs comparing with those of the other types, as displayed in Fig. 4, although the similar lattice
 198 constants were recorded by our XRD measurements. These dependences are similar to
 199 reported tendencies [40]. These N_2 adsorption results can be considered that the majority of a
 200 large ion is shared in a part of the super cage space: ca. 250 pm of windows size of six-ring is



201 smaller than 296 (Rb^+) and 338 pm (Cs^+) in diameter, and similar to 266 pm (K^+), and larger than
 202 120 (Li^+) and 190 pm (Na^+) [41].

203

204 **Fig. 4. Influences of cation types on N₂ adsorption isotherms of faujasite zeolites with**
 205 **Si/Al ratios of 1.0, 1.2, 1.7, 2.4, and 3.5.**



206 **Fig. 5. N₂ adsorption isotherms of faujasite zeolites as a function of Si/Al ratios of 1.0**
 207 **(red), 1.2 (orange), 1.7 (green), 2.4 (purple), and 3.5 (blue).**

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209 3.3.TG/DTA Measurements

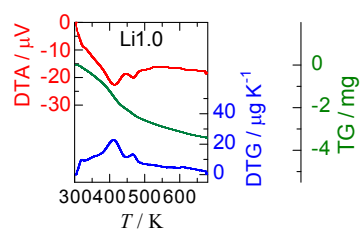
210 DTA, TG, and DTG curves obtained in each FAU are shown in Fig. 6. The endothermic
 211 peak were observed at around 400 K. Since weight loss was also recorded at the temperature,
 212 this endothermic signal can be attributed to water desorption from each FAU. The origin of the
 213 broad signal of DTA and successive decreasing of TG curves can be considered that there are

214 some states of water molecules in FAU: some ones interact with FAU frameworks, others are
 215 affected by cation, and the others are located around the center of supercage in FAU [13]. Since it
 216 is difficult to determine desorption temperature of water molecules uniquely, a temperature with
 217 the largest slope on TG curves (T_{DTG}) was introduced. Here, T_{DTG} is a peak temperature of each
 218 DTG curve and means a temperature at which abundant water molecules are removed from FAU.
 219 Each T_{DTG} value estimated is listed in Table 1. Based on these values, the higher T_{DTG} is obtained
 220 in the lower Si/Al ratios. Since it is well known that cations in zeolites attract water molecules by
 221 strong electrostatic interactions, this tendency can be explained by hydrophilicity of FAU (the
 222 lower Si/Al ratio results in the higher concentration of cations in FAU). It means that the T_{DTG}
 223 value links to a factor of strength of hydrogen bonding among water molecules and cations in FAU.
 224 In the case of cation-type dependencies, complex tendencies were recorded: The smallest T_{DTG}
 225 was obtained in K- or Na-type FAU as shown in Table 1. This tendency is similar to those
 226 observed in the ^{29}Si NMR CS values. Detail discussion about this tendency is described in
 227 section 3.5.

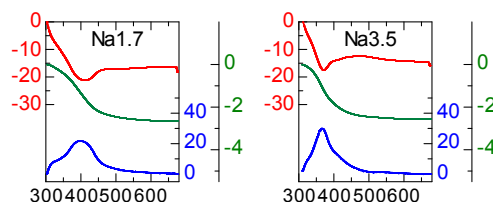
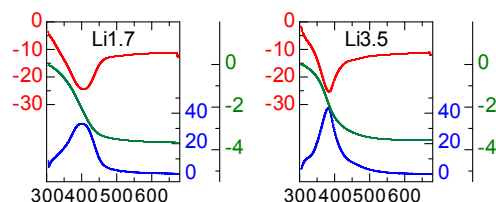
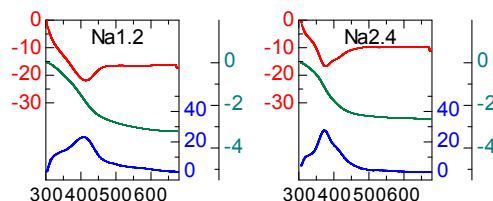
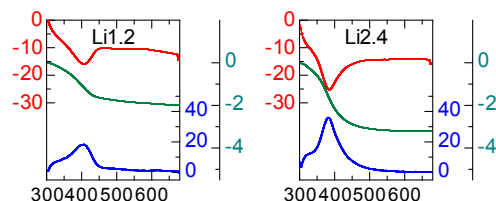
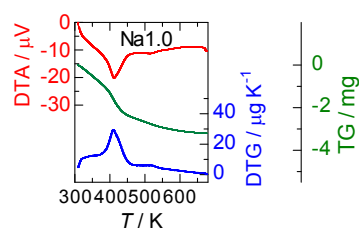
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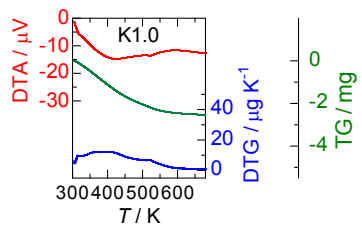
(a) Li-FAU



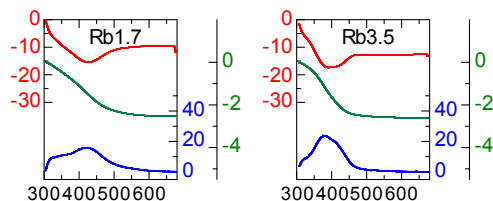
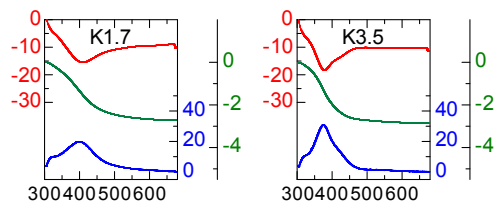
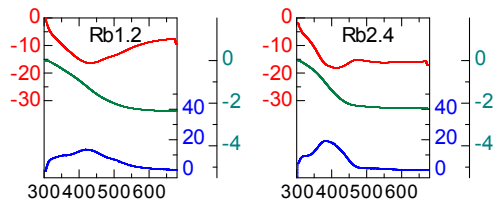
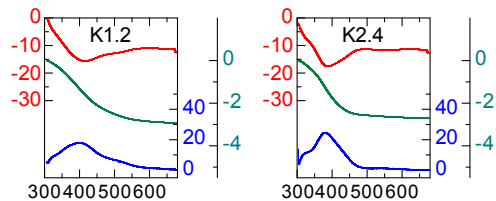
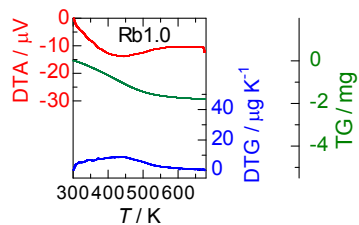
(b) Na-FAU



(c) K-FAU



(d) Rb-FAU



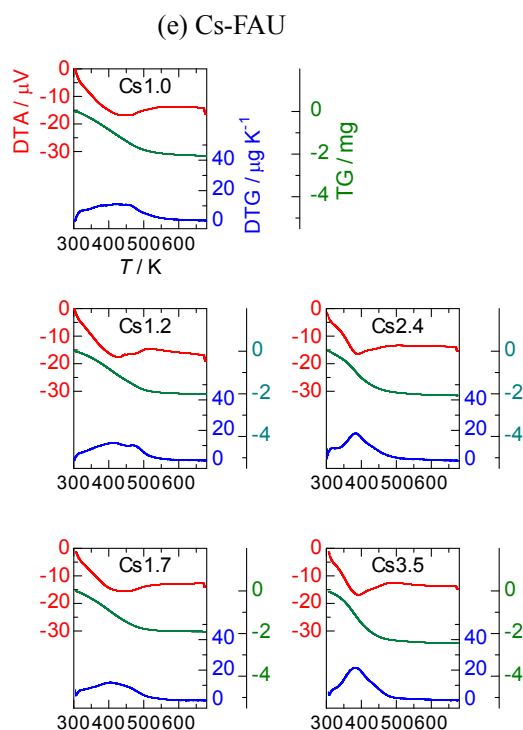


Fig. 6. DTA, TG, and DTG curves observed in M-type faujasite zeolites as a function of temperatures. M = (a) Li, (b) Na, (c) K, (d) Rb, (e) Cs.

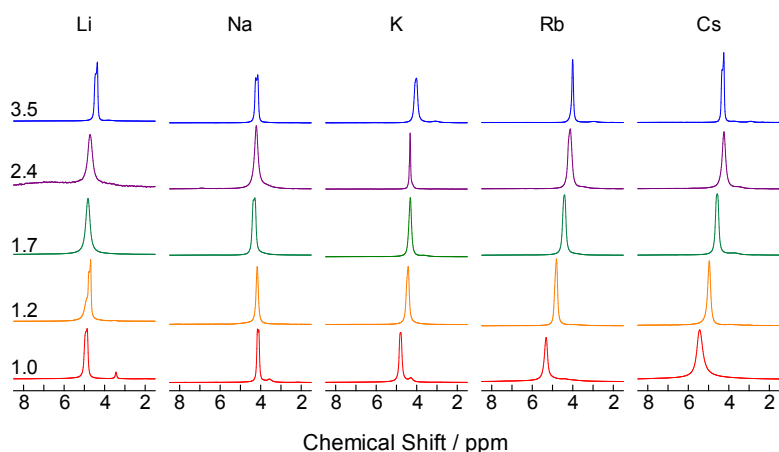
Table 1. Temperatures with the largest slope on each TG curve (T_{DTG}) of hydrated FAU. Unit is in K

Si/Al Ratio	Li	Na	K	Rb	Cs
1.0	411.0	408.1	358.1	442.8	419.0
1.2	405.0	406.3	397.2	418.0	412.8
1.7	399.5	397.5	396.8	423.0	403.3
2.4	380.4	370.7	378.1	380.8	383.6
3.5	380.0	365.5	373.7	374.6	382.8

3.4. ^1H MAS NMR Chemical Shift

Si/Al ratio dependencies of ^1H MAS NMR spectra observed with a MAS ratio of 30 kHz

are shown in Fig. 7. Only one Lorentz-type signal was recorded on each spectrum (This signal recorded at around 5 ppm can be assigned to H atoms in water molecules adsorbing on each FAU), hence it can be considered that spin-exchange rates among the H atoms of water molecules adsorbing on each cation and those linking with other water molecules in the supercage are fast enough. Based on this result, it can be considered that whole water molecules are linked each other and we can consider only partial water molecules instead of whole ones in FAU. In the ^1H MAS NMR spectra, the peaks were shifted to higher field (the same meaning as lower CS value) with increasing Si/Al ratios for each alkali-metal-type FAU. This tendency can be explained by hydrophobicity of FAU frames: Since the larger Si/Al ratio results in the larger hydrophobicity, water molecules form weak interaction with FAU frameworks. This model is the same as explaining Si/Al ratio dependences of the T_{DTG} . The large shifts of the ^1H CS value were recorded in Cs- and Rb-type FAUs, in contrast, little shifts were obtained in Li- and Na-type FAUs as shown in Fig. 7. This result suggests that interactions among water

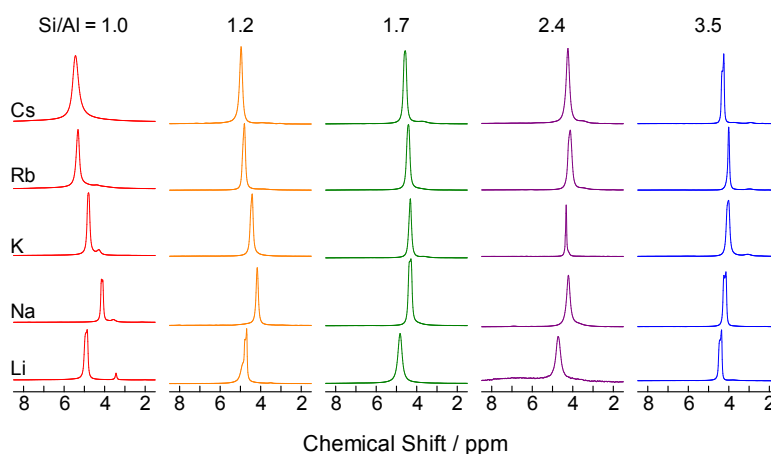


molecules and FAU frameworks are dependent on cation's characters.

Fig. 7. Si/Al ratios dependences of ^1H MAS NMR spectra observed in M-type faujasite zeolites (M = Li, Na, K, Rb, Cs).

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265 In order to show the cation-size dependences of ^1H MAS NMR CS values, the same spectra
 266 were re-plotted as a function of cation's types. The similar tendencies to those obtained on the
 267 ^{29}Si NMR spectra and T_{DTG} were obtained as displayed in Fig. 8. Since it is reported that the
 268 larger ^1H CS values are detected in H atoms forming the stronger H-bond [47], it can be
 269 considered that H-bonds among water molecules and the FAU frameworks are attractive in Li-
 270 and Cs-FAUs, and an origin of the complex dependencies of T_{DTG} and ^1H CS values is the
 271 same. In addition, shielding tensors of ^1H nuclei are almost determined by diamagnetic terms
 272 rather than paramagnetic components [48], therefore, it can be regarded that electron densities
 273 of H atoms in water molecules adsorbing on Li or Cs ions in the FAU framework are low. In order
 274 to reveal reasons why electron densities of water molecules are low in Li or Cs-type FAU, CS
 275 simulation was carried out.



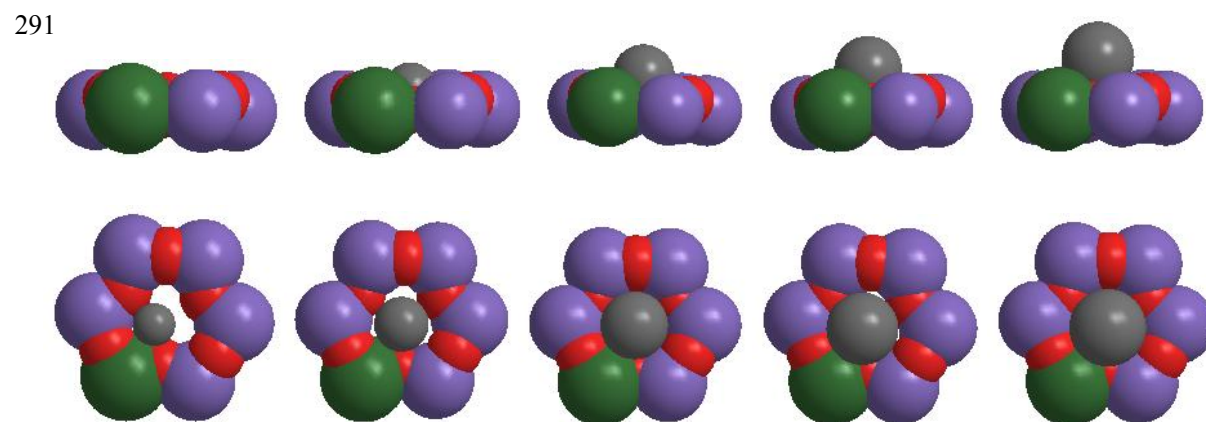
276 **Fig. 8. Influences of M cation types on ^1H MAS NMR spectra observed in faujasite**
 277 **zeolites with Si/Al ratios of 1.0, 1.2, 1.7, 2.4, and 3.5.**

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279

280 3.5.Simulation

281 On the results of ^1H and ^{29}Si MAS NMR, and TG measurements, the lowest CS and
 282 T_{DTG} values were obtained for K- or Na-type FAU in the same Si/Al ratio. The N_2 adsorption
 283 isotherm curves reveal that absorbable space of N_2 molecules on Rb- and Cs-type FAU is
 284 smaller than the others with the same Si/Al ratio, although the similar lattice constants among them
 285 were detected by our XRD measurements. The smaller absorbable volumes in Rb- and Cs-type
 286 FAU can be explained by the six-ring window-size of FAU frameworks: Rb^+ (296 pm) and Cs^+ (338
 287 pm) have large ion-size competing with the window-size of ca. 250 pm, therefore majority parts of
 288 the ions are shared a part of supercage space as displayed in Fig. 9. In this figure, coordinates of
 289 each cation were optimized by a B3LYP/LanL2DZ function. The similar illustrations are reported
 290 for Li, K, Mg, and Ca-type zeolites [20].



292
 293
 294 **Fig. 9. Estimated locations of the cations on the six-ring windows. Si, O, Al, H, and cation**
 295 **are shown by purple, red, green, and gray, respectively.**

296
 297 Based on this figure, we can consider a model in which number of water molecules coordinating
 298 to cations is depended on cation's size: small cations of Li^+ (120 pm) and Na^+ (190 pm) can insert
 Li-FAU Na-FAU K-FAU Rb-FAU Cs-FAU

299 into the FAU frameworks, therefore a few water molecules can adsorb on them, in contrast,
 300 Rb^+ and Cs^+ are located on frameworks, therefore several water molecules can link to the cations.
 301 In order to estimate coordination number of water molecules on each cation, we introduced a
 302 supercage model with chemical formula of $\text{MAISi}_{47}\text{O}_{73}\text{H}_{48}$, ($\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}$). Since a
 303 reported simulation with MP2 and DFT methods in local structure models ($\text{AlSi}_7\text{O}_{14}\text{H}_{12}$,
 304 $\text{AlSi}_{10}\text{O}_{14}\text{H}_{17}$, $\text{Si}_{11}\text{O}_{24}\text{H}_{16}$, etc.) of supercage shows a good agreement with experimental values
 305 [18, 21-24], our model is suitable to simulate CS values. In our supercage model, reported
 306 coordinates of Si (Al) and O atoms were used and the Al atom was inserted into six-ring, because
 307 experimental and theoretical reports show that whole SII is occupied by cations with a Si/Al range
 308 from 1 to 5, and occupancies of SIII and SIII' are gradually increased with decreasing Si/Al ratios
 309 in $\text{Si/Al} < 2$ [9, 11, 42-46]. In our simulation, positions of each alkali cation, terminal H atoms of the
 310 framework, and H and O atoms in water molecules were optimized by a function of
 311 B3LYP/LanL2DZ. The coordination number of water molecules was estimated by the following
 312 process for each M-type FAU: one water molecule was initially put on the origin of this model
 313 (center of the supercage) and, then, coordinates of the water molecules and the cation and
 314 terminal H atoms were optimized. At the next step, the second water molecule was located at the
 315 origin and converged positions of two water molecules and the cation were simulated by the same
 316 function. If both water molecules can adsorb on the cation, then the same process was continued
 317 until any water molecule can't link directly to each cation. The result of coordination number of
 318 water on each cation is listed in Table 2 and illustrated in Fig. 10. This simulation showed different
 319 numbers of water molecules adsorbing on each cation.

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324 **Table 2.** The number and ^1H chemical shift (CS) values of adsorbed water molecules on
 325 each cation in FAU estimated by MP2/cc-PVDZ function in the super cage model. Values
 326 are in a case of one water molecule adsorbing on each cation.

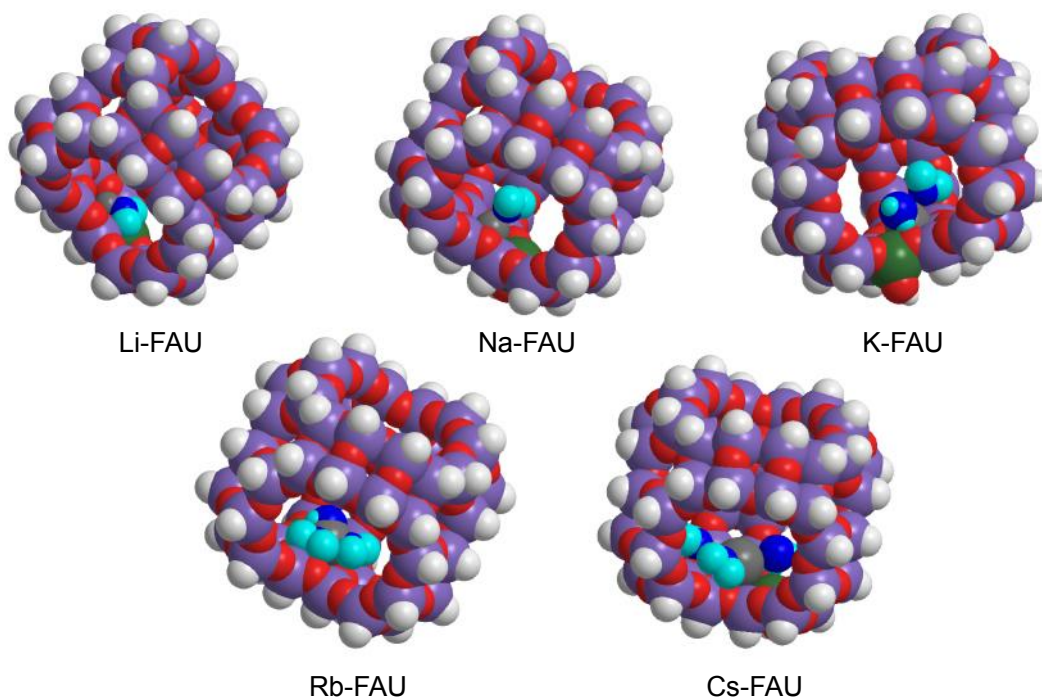
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Cation	CS / ppm		
	Number of Water Molecules	One Water	Waters
Li	1	0.8506	0.8506
Na	2	1.0873	0.4394
K	3	1.1897	1.0634
Rb	3	1.2286	1.1346
Cs	3	1.2639	1.1482

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340 **Fig. 10.** Molecular arrangements of water molecules adsorbed on cations in the FAU
 341 supercage. H and O atoms of water molecules are shown by cyan and blue, respectively.
 342 Si, O, Al, H, and cation in the framework are illustrated by purple, red, green, and gray,

343 **respectively.**

344 In order to estimate CS values of water molecules, a method of ONIOM
345 (MP2/cc-pVDZ : HF/cep-4G) was employed, where the former function of MP2/cc-pVDZ was
346 applied for H and O atoms in water molecules and the latter was used for each cation and Si, O,
347 Al, H atoms in the framework. The MP2/cc-pVDZ function also applied for shielding tensor
348 estimation of a tetramethylsilan (TMS) molecule, where all coordinates of atoms were optimized
349 by a B3LYP/6-31G** method. Subtracting shielding tensors of H atoms in the water molecules
350 from that of TMS, ^1H CS values in the water molecules were immediately obtained as listed in
351 Table 2. The CS values simulated in the model showed the similar tendency to those observed in
352 ^1H MAS NMR measurements, i.e., the smallest CS value is recorded for Na-type FAU (since
353 demonstrated ^1H CS values are rarely agreed with experimental values and CS is relative values,
354 only tendencies are discussed in this study). Conversely, assuming another model in which only
355 one water molecule adsorbed on each cation, CS values were monotonously increased with
356 cation sizes, as displayed in Table 2. Therefore, it can be regarded that the difference of
357 coordination number of water molecules influences on the complex dependences recorded on
358 the NMR spectra. Based on our ^1H MAS NMR and TG-DTA results, it can be concluded that
359 water molecules form weak hydrogen bonds in Na- and K-type FAU with high Si/Al ratios. In Li,
360 Na, K Rb, and Cs ions, charge density on each surface is decreased with increasing ion radius,
361 therefore, it can be regarded that water molecules form weaker hydrogen bonds with the
362 larger cations. In contrast, since abundant parts of the large ions can't insert in the FAU framework,
363 several water molecules can contact to the larger cations. Based on these two factors, the result
364 that middle size ions of Na and K form weak hydrogen bonds with water molecules in FAU can
365 be explained.

366 We also attempted to simulate the complex dependences of ^{29}Si MAS NMR CS values

on cation types as displayed in Fig. 2. The supercage 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 [49] were obtained as listed in Table 3. 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.

Table 3. ^{29}Si chemical shift (CS) values estimated by HF/CEP-4G function in the super cage model.

4. Conclusion

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. Its CS value was increased with increasing Si/Al ratios, in contrast, complex dependences on cation types were observed (the lowest CS value was recorded in Na- or K-type

393 FAU with each Si/Al ratio). The similar tendencies were detected in TG-DTA measurements: a
 394 desorption temperature of water molecules was increased with decreasing the Si/Al ratios,
 395 conversely, the temperature showed complex dependences on cation properties (the minimum
 396 temperature was recorded in Na- or K-type FAU with each Si/Al ratio). In order to reveal these
 397 complex tendencies, computer simulations were attempted in a supercage model. In our
 398 simulations, it was revealed that the different coordination number of water molecules to each
 399 cation results in the complex CS dependencies on cation types. The different coordination
 400 number can be accepted, because ion sizes of Li and Na ions are smaller than that of six-rings
 401 windows in the FAU framework, conversely, Rb and Cs ions are larger, i.e. abundant parts of Rb
 402 and Cs ions are occupied a part of the supercage. This result was consistent with those obtained
 403 in N₂ adsorption measurements. Since the larger ¹H CS values are observed in the stronger
 404 H-bonds [47], the complex T_{DTG} dependencies on cation types can be explained by the same
 405 origin.

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408 **COMPETING INTERESTS**

409 Authors have declared that no competing interests exist.

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414 **References**

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