High Cs$^+$ Selective Sodium Difluorotetrasilicic Mica  
—A NMR Approach—

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Abstract
Sodium difluorotetrasilicic mica (Na[Mg$_{2.5}$Si$_4$O$_{10}$F$_2$]·nH$_2$O; Na–TSM) had the highest ion-exchange selectivity for Cs$^+$ among alkali metal ions in spite of its large crystallographic ionic radius, because of its unusual cesium ion-exchange reaction with magnesium ions that were a lattice component of Na–TSM in addition to the ordinary ion-exchange reaction with Na$^+$. To elucidate the phenomenon, $^{23}$Na, and $^{133}$Cs solid NMR were applied to examine the role of Na$^+$ and Cs$^+$ in Na–TSM layer where the Na$^+$/Cs$^+$ ion-exchange reaction participates. The observed NMR spectra of $^{23}$Na and $^{133}$Cs indicated rather restricted motion of these ions and molecule. The result signified that Na$^+$ and Cs$^+$ were buried in the hexagonal cavities of basal oxygen planes of mica rather than in the interlayer space of layered gallery. When Cs$^+$ was ion-exchanged with Mg$^{2+}$ located in the skeleton of Na–TSM, Cs$^+$ was strongly sorbed into this site to keep the charge balance. These findings were well accounted for the unique hydration property of alkali metal ions that has been specified in liquid water such as hydrated ionic radii.

Key Words: Sodium difluorotetrasilicic mica, Ion exchange, Cesium ion selective, NMR.

1. Introduction
Layered inorganic materials have peculiar ion-exchange selectivity due to the swelling phenomenon of the interlayer distance. The interlayer distance changes flexibly depending on the size of intercalated molecules contrary to the three dimensional lattices such as zeolites. One of the peculiar properties of the layered materials is the accommodation of water molecules on the occasions of the ion-exchange reaction. The accommodated water molecules form definite water layers depending on the amount of water such as monolayer, bilayer, etc. The exchanged metal ions thus exist in the hydrated form in the interlayer gallery of layered lamellae. The hydration property strongly affects the ion-exchange selectivity among alkali metal ions.

Among various layered materials, Na–TSM exhibits peculiar ion-exchange affinity to cesium and rubidium ions, both having larger crystallographic ionic radii than the sodium ion. Na–TSM, on the other hand, rejects lithium ion that has the smallest crystallographic ionic radius among alkali metal ions. Proton type TSM was also hardly formed. Moreover, the ion-exchange reaction occurred with magnesium ions in addition to sodium ions. Peculiar ion-exchange property for Cs$^+$ and Rb$^+$ is definitely ascribed to the distinct interaction for the cation and lattice sorption site, hydration properties of alkali metal ions, and multi-water layer formation of the layer structure between the lattice lamellae.

It has been confirmed that NMR is one of the effective tool to study the ion-exchange property of metal ions, especially on the role of accommodated water molecules. For example, well resolved $^1$H NMR spectra indicated the partially restricted motion of water molecules corresponding to the monolayer and bilayer form in the layered transition metal disulfides. The peculiar potassium ion selectivity of cubic ammonium molybdate was accountable by the aid of $^1$H NMR study. This paper deals with NMR
study of sodium ions and cesium ions to account for the high ion-exchange selectivity for cesium ion on Na–TSM.

2. Experimental

2.1 Materials and reagents

Dihydrated Na–TSM (Na[Mg_{2.5}Si_{4}O_{10}F_{2}]·2H_{2}O; abbreviated to 2–TSM), was supplied from Topy Industry Co. Ltd.. Aqueous solution of lithium, sodium, potassium, rubidium and cesium ions were prepared from each reagent-grade chlorides (Wako Pure Chemical Industries, Ltd., Japan). Ultrapure water was prepared using PURIC system (Japan Organo Co., Ltd.) and the specific resistance was 17 MΩ cm.

2.2 The ion-exchange reaction

The ion-exchange reaction between H+ and MA+ seemed impossible because a proton type TSM is hardly prepared. The ion-exchange reaction with Li+, K+, Rb+ and Cs+ with Na+ was thus examined on Na–type 2–TSM. Air dried powder 2–TSM (0.2 g, about 5 × 10^{-4} mol) were mixed with 20 cm³ of 0.5 mol dm⁻³ solution of Li+, K+, Rb+ and Cs+ in a glass ampoule, and were stored at 60°C for 48 h with intermittently shaking. After equilibration, the amount of metal ions remained in the supernatant solution were determined by an atomic absorption spectrometry, abbreviated to AAS, except Li+. An atomic emission spectrometry, abbreviated to AES, was used for the determination of Li+. The amount of the metal ions sorbed in the exchanger phase was estimated from the difference between the added amount and the reminded amount of metal ions in the supernatant solution.

2.3 Preparation of staging samples

Different staging samples were prepared by varying exchanged metal ions and drying conditions. Preparation procedures and abbreviations were summarized in Table 1.

A powder X-ray diffractometer (MO3X–HF, MAC Science Co., Ltd., Japan) equipped with monochromized Cu–Kα was used for the characterization of staging materials.

2.4 NMR

$^{23}$Na and $^{133}$Cs NMR spectra were measured using NMR spectrometer (JEOL AL–300, JEOL Japan) for solid samples. Magic angle spinning (MAS) NMR of $^{23}$Na and $^{133}$Cs were carried out using AVANCE 400S NMR spectrometer (Bruker, Germany). The spinning rate was set in 7.0 kHz.

3. Results and Discussion

3.1 General aspects of the alkali metal ion-exchange

Table 2 shows the concentration of alkali metal ions in the supernatant solution before and after the ion-exchange reaction onto 2–TSM. The amount of sorbed metal ions calculated as difference between the concentration of reference metal ions and the concentration of metal ions after equilibration were also listed on Table 2. It was found that the selectivity order was K+ < Rb+ < Cs+. Li+ was hardly ion-exchanged on 2–TSM. An inquiry to the ion-exchange reaction, the ionic radius was one of the main factors behind the selectivity order. Because the ion-exchange reaction occurs in the aqueous media, the hydrated ionic radii are more important than that of the crystallographic ionic radii. The hydrated ionic radii of Na+, Li+, K+, Rb+ and Cs+ are 0.33 nm, 0.37 nm, 0.25 nm, 0.24 nm and 0.24 nm, respectively.

<p>| Table 1 Preparation of staging samples |
|-----------------|-----------------|</p>
<table>
<thead>
<tr>
<th>Ion</th>
<th>Staging (Abbreviation)</th>
<th>Procedure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na+</td>
<td>monolayer (1–TSM)</td>
<td>1–TSM supplied was used without any further preparation.</td>
</tr>
<tr>
<td></td>
<td>bilayer (2–TSM)</td>
<td>10% of 2–TSM sol supplied was prepared according to the method previously described1).</td>
</tr>
<tr>
<td></td>
<td>trilayer (3–TSM)</td>
<td>0.2 g of 2–TSM were immersed in 20 cm³ of 0.5 mol·dm⁻³ of Na+ at 60°C for 1 h. After settled time, mica was filtered with a micro filter (Ø = 5 µm) and dried for 30 min in the air.</td>
</tr>
<tr>
<td>Cs+</td>
<td>anhydrous (Ce–TSM)</td>
<td>2–TSM was filtered after ion-exchange reaction and air-dried for 24 h.</td>
</tr>
</tbody>
</table>

Amount of sorbed metal ions = (Concentration of reference metal ions) – (Concentration of metal ions after equilibration). Volume of solution: 20 cm³, weight of 2–TSM: 0.2 g.

| Table 2 The concentration of alkali metal ions in the supernatant solution and the amount of sorbed metal ion onto 2–TSM |
|-----------------|-----------------|-----------------|
| Concentration of reference metal ions /mol dm⁻³ | Concentration of metal ions after equilibration /mol dm⁻³ | Amount of sorbed metal ions /mol·mol⁻¹ TSM⁻¹ |
| Li+ | 0.462 | 0.453 | 0.39 |
| K+ | 0.368 | 0.297 | 3.1 |
| Rb+ | 0.481 | 0.170 | 13.5 |
| Cs+ | 0.434 | 0.046 | 16.9 |

Table 3 Crystallographic ion radii, hydrated ion radii and B-coefficient of alkali metal ions

<table>
<thead>
<tr>
<th>Ions</th>
<th>Crystallographic ion radii /nm</th>
<th>Hydrated ion radii /nm</th>
<th>B-coefficient /kg mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li+</td>
<td>0.068</td>
<td>0.37</td>
<td>+0.150</td>
</tr>
<tr>
<td>Na+</td>
<td>0.097</td>
<td>0.33</td>
<td>+0.086</td>
</tr>
<tr>
<td>K+</td>
<td>0.133</td>
<td>0.25</td>
<td>-0.007</td>
</tr>
<tr>
<td>Rb+</td>
<td>0.152</td>
<td>0.24</td>
<td>-0.030</td>
</tr>
<tr>
<td>Cs+</td>
<td>0.170</td>
<td>0.24</td>
<td>-0.045</td>
</tr>
</tbody>
</table>

(71)
respectively, as listed on Table 3 together with B-coefficient of the viscosity\(^9\). The positive and the negative in B-coefficient indicate the construction and the destruction of the ice-structure of water molecules in the second hydration shell in aqueous solution. Hydrated Rb\(^+\) and Cs\(^+\), which show high ion-exchange selectivity on 2-TSM, have rather small hydrated ionic radii and the negative B-coefficients. Low ion-exchange selectivity was observed to K\(^+\) even the hydrated ionic radius is small (0.25 nm). Because of its B-coefficient is nearly zero, the ice-structure was kept during the ion-exchange reaction, low ion-exchange selectivity was result comparing to Rb\(^+\) and Cs\(^+\).

In addition to the large hydrated ionic radius, the positive B-coefficient for Li\(^+\) means strong affinity of hydrated state on the occasion of the ion-exchange reaction. Therefore the Na\(^+\)/Li\(^+\) ion-exchange reaction hardly occurred. This aspect was supported by the selectivity order, which was obtained on the experiment.

### 3.2 \(^{23}\)Na and \(^{133}\)Cs NMR spectra of TSMs

The ion-exchange reaction of Mg\(^2+\)/M\(^+\) (M\(^+\)=K\(^+\), Rb\(^+\), Cs\(^+\)) was observed on 2-TSM in addition to the ion-exchange reaction of Na\(^+\)/M\(^+\) as previously reported\(^1\). A solid NMR was applied to investigate the ion-exchange mechanism. In NMR theory, static NMR spectra for solid samples show line broadening, which eliminate or obscures the characteristic sharp individual signals of NMR. One type of line broadening for solids is caused by dipolar interactions between adjacent nuclei or chemical shift anisotropy. This problem is eliminated by the magic angle spinning (MAS) technique, which involves rotating solid samples rapidly at a frequency greater than 2 kHz in a special sample holder that is maintain at an angle of 57.4 deg with respect to the external field\(^10\). Fig. 1-1 shows static \(^{23}\)Na NMR spectra of (a) 3-TSM, (b) 2-TSM and (c) 1-TSM. Fig. 1-2 shows MAS \(^{23}\)Na NMR spectra of (a) 2-TSM, (b) 1-TSM and (c) Cs-TSM. Fig. 2 shows MAS \(^{133}\)Cs spectrum. These NMR spectra will be interpreted according to the type of multilayer water molecules as follows.

**Trilayer**

\(^{23}\)Na: A sharp signal and a relatively wide signal are observed on static \(^{23}\)Na NMR as seen in Fig. 1-1 (a). Sharp one has the half line width of 2.0 kHz and it is almost same as the signal of NaCl solution, which means 3-TSM has at least a kind of Na\(^+\) with rapid motion similar to hydrated Na\(^+\) in aqueous solution. In general, the transverse relaxation time (\(T_2\)) becomes longer at very high mobility of spins, and the narrow spectrum results. This phenomenon is called “Motional Narrowing”\(^11\). Thus Na\(^+\) attributed to this sharp signal is rather mobile state and locates in the large interlayer space of 3-TSM in which the interlayer distance is about 0.9 nm. Left signal with half line width of 11.0 kHz shows restricted Na\(^+\) compare to that of right one and it is assigned to non-exchangeable Na\(^+\) as discussed later.

**Bilayer**

\(^{23}\)Na: Three signals are observed in Fig. 1-1(b). There
are also three signals in MAS NMR spectrum as seen in Fig. 1-2(a). The sharp center signal in Fig. 1-2(a) indicated the high mobility of Na\(^+\) and located in the interlayer space of 2-TSM (The interlayer distance is about 0.6 nm) same as the case of 3-TSM. This signal disappeared after the ion-exchanged with Cs\(^+\) as seen in Fig. 1-2(c). It is obvious that all of Na\(^+\) in this site are exchangeable, even the gross number of Na\(^+\) is small. The left signal in Fig. 1-1(b), which corresponds to the left signal in Fig. 1-2(a), is very strong with wide half line width of about 8 kHz. The narrow width with the smaller quadrupole splitting definitely indicates the higher coordination symmetry\(^{12}\) and the tightly restricted Na\(^+\), however, detailed accommodation site is unknown within the limited of present study. Nevertheless, this site of Na\(^+\) was non-exchangeable because the left signal in Fig. 1-2(a) remained after the ion-exchange reaction as seen in Fig. 1-2(a). Na\(^+\) ascribed to the right signal in Fig. 1-2(a) has restricted motion in a similar manner to non-exchangeable Na\(^+\) concerning on its wide half line width. Comparing with Fig. 1-2(c), about half amount of these Na\(^+\) were found to be ion-exchanged with Cs\(^+\). This Na\(^+\) seems to be accommodated in the hexagonal cavities of basal oxygen plane\(^{13}\) coordinated with water molecules.

Monolayer

\(^{23}\)Na: 1-TSM showed three signals as seen in Fig. 1-1(c). The center signal is strong and has large half line width of about 14 kHz that was similar to Na\(^+\) in sodium glass. The left and the right signals are weak and narrower than the center signal. MAS NMR spectrum in Fig. 1-2(b) also shows three signals. On account of the center signal in Fig. 1-2(b) corresponds to the right signal of Fig. 1-2(a), Na\(^+\) attributed to this signal locates in the hexagonal cavities of basal oxygen plane as mentioned above. The right signal with half line width of 1.5 kHz in Fig. 1-2(b) is strong. This signal was extinguished completely after ion-exchanged with Cs\(^+\) in a similar manner to the center signal in Fig. 1-2(a). Since the interlayer distance of 1-TSM is about 0.3 nm, Na\(^+\) located in this site has less mobility than that of 2-TSM or 3-TSM. As a result, it con-
cluded that Na⁺ related to this signal accommodated to the interlayer space of 1-TSM.

Anhydrous

¹³³Cs: MAS NMR spectrum in Fig. 2 shows a single signal with the line width about 0.3 kHz. The single signal indicates the only magnetic atmosphere for Cs⁺ with symmetric coordination. The ion-exchanged Cs⁺ is accommodated in the hexagonal cavities of basal oxygen plane as shown in Fig. 3 with restricted state, so that the reverse ion-exchange reaction hardly occurred.

In conclusion, two ion-exchange sites for the Na⁺/Cs⁺ ion-exchange reaction were confirmed by the NMR study, one had the high mobility of Na⁺ and the other had rather restricted Na⁺. There are large hemispherical holes surrounded by six tetrahedrons of Si-O matrices that are suitable for dehydrated Cs⁺ on the surface of 2-TSM. This phenomenon seems to the origin of the high ion-exchange selectivity of Cs⁺ on 2-TSM.

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References

特集「無機イオン交換体の新展開」

高セシウム選択性 Na 型合成雲母
—NMR 法による考察—

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要 旨

Na 型合成雲母（Na-TSM）のセシウムイオン交換反応は、層間のナトリウムイオンとの交換に加え八面体層に位置するマグネシウムイオンともイオン交換をするため、アルカリ金属イオンの中でセシウムイオンに対し高いイオン交換選択性を示す。この現象を解明するために 23NaNMR および 133CsNMR で Na-TSM 層における Na⁺, Cs⁺ の状態を考察した。得られた NMR スペクトルの解析によりそれらのイオンは束縛された状態で存在し、層間よりは格子側の底面酸素六員環に位置することが示唆された。また、Mg²⁺/Cs⁺ の交換では電荷バランスを保つためにこの底面酸素六員環の空隙に強く吸着されていると考えられた。