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Selectivity of alkali metal ion and lithium isotopes on ion exchangers prepared from $MTi_{0.5}Zr_{1.5}(PO_4)_3$ (M = Li, Na)

HIROAKI TAKAHASHI, TAKAO OI*
Department of Chemistry, Sophia University, 7-1 Kioicho, Chiyoda, Tokyo 102-8554, Japan
E-mail: t-ooi@hoffman.cc.sophia.ac.jp

Inorganic ion exchangers, H-TZP(Li) and H-TZP(Na), in the hydrogen form have been prepared by ion exchange from the precursors, $LiTi_{0.5}Zr_{1.5}(PO_4)_3$ and $NaTi_{0.5}Zr_{1.5}(PO_4)_3$, respectively. The degrees of leaching of lithium and sodium ions were 99.7% and 68%, respectively. No substantial difference in ion exchange property was observed between the two ion exchangers. Both showed high selectivity toward lithium and sodium ions, while rubidium and cesium ions showed low affinity among alkali metal ions. Isotopically, they were ^{6}Li-specific like other inorganic ion exchangers so far examined. The ^{7}Li-to-^{6}Li isotopic separation factor, *S*, was found of 1.023 to 1.025 in acidic conditions at 25°C and nearly unity in highly basic conditions (pH 12 or higher). The latter *S* value was consistent with the formation of new ion exchange sites with low isotope selectivity of lithium.

1. Introduction

Lithium is an element whose isotopes, ^{6}Li and ^{7}Li, have potentially important applications in nuclear science and industry. The largest demand for isolated or enriched lithium isotopes in the future will be in deuterium-tritium fusion reactors where compounds highly rich in ^{6}Li will be required for the tritium breeder blanket:

$$^6\mathrm{Li} + \mathrm{n} \rightarrow \mathrm{T} + {}^4\mathrm{He}.$$

Methods of lithium isotope separation have been studied and ion exchange chromatography is among promising methods. Commercially available organic ion exchangers are traditionally used as column-packing materials, and the ^{7}Li-to-^{6}Li single-stage separation factor, *S*, of up to about 1.003 is observed at room temperature [1]. The *S* value of 1.003 means that the amount of ^{6}Li taken up by 1 g of an ion exchanger is 1.003 times more than that expected when the ion exchanger shows preference for neither of the lithium isotopes. Here, *S* is defined as

$$S = \frac{(\text{amount of } ^6\text{Li in ion exchanger phase})}{(\text{amount of } ^7\text{Li in ion exchanger phase})} \times \frac{(\text{amount of } ^7\text{Li in solution phase})}{(\text{amount of } ^6\text{Li in solution phase})}.$$

This isotope separation effect is small, and the development of ion exchangers with large lithium isotope effects is hoped for.

It is reported that some inorganic ion exchangers show larger lithium isotope effects from several times to one order of magnitude than those of organic ion exchangers. They include manganese oxide-based ion exchangers [2], niobic and tantalic acids [3], and antimonic acids [4, 5], and are candidates for packing materials of column chromatography for lithium isotope separation, although each of them has a couple of drawbacks.

$HTi_xZr_{2-x}(PO_4)_3$ $(0 \leq x \leq 2)$ is another candidate. In the previous paper [6], we reported the selectivity of alkali metal ion and lithium isotopes of one end member of $HTi_xZr_{2-x}(PO_4)_3$, $HZr_2(PO_4)_3$. $HZr_2(PO_4)_3$ is lithium ion-specific among alkali metal ions and isotopically ^{6}Li-specific. It is expected that the ion exchange properties of $HZr_2(PO_4)_3$ may change with partial substitution of Zr^{4+} ions with Ti^{4+} ions due mostly to the difference in ionic radius between the two ions. In this paper, we report the selectivity of alkali metal ion and lithium isotopes of $HTi_{0.5}Zr_{1.5}(PO_4)_3$ (abbreviated as H-TZP hereafter) prepared from two precursors, $LiTi_{0.5}Zr_{1.5}(PO_4)_3$ and $NaTi_{0.5}Zr_{1.5}(PO_4)_3$. The value of $x = 0.5$ is chosen according to a report [7] that the degree of leaching of lithium ions from $LiTi_xZr_{2-x}(PO_4)_3$, a precursor of $HTi_xZr_{2-x}(PO_4)_3$, is the highest at $x = 0.5$.

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*Author to whom all correspondence should be addressed.

2. Experimental

2.1. Preparation of ion exchangers

H-TZP was prepared from two different precursors in an expectation that they may yield ion exchangers with different ion exchange properties. One precursor, $LiTi_{0.5}Zr_{1.5}(PO_4)_3$ (abbreviated as L-TZP hereafter), was prepared by heating a stoichiometric mixture of lithium carbonate, zirconyl nitrate, phosphoric acid and titanium dioxide (rutil form) at 950 °C for 10 hours in an electric furnace. $HTi_{0.5}Zr_{1.5}(PO_4)_3$ was prepared by replacing Li^+ ions in L-TZP by H^+ ions through ion exchange. For this purpose, L-TZP was treated with 1 M (1 M = 1 mol/L) nitric acid with stirring at 80 °C for two days, and the treatment was repeated twice.

The other precursor, $NaTi_{0.5}Zr_{1.5}(PO_4)_3$ (abbreviated as N-TZP hereafter), was prepared according to the similar process to that of L-TZP, starting from sodium carbonate, zirconyl nitrate, phosphoric acid and titanium dioxide, and $HTi_{0.5}Zr_{1.5}(PO_4)_3$ was obtained by treatment of N-TZP with 10 M nitric acid with stirring at 80 °C for five days. The acid treatment was repeated four times. Hereafter, $HTi_{0.5}Zr_{1.5}(PO_4)_3$ prepared from L-TZP is abbreviated as H-TZP(Li) and that from N-TZP as H-TZP(Na).

Identification of crystal phases in the ion exchangers and their precursors was carried out by the powder X-ray diffraction (XRD) method.

2.2. Characterization

The degrees of leaching of lithium and sodium ions from the precursors were determined by the $HF\text{-}HNO_3\text{-}HCl$ decomposition of aliquots of H-TZP(Li) and H-TZP(Na) followed by the determination of lithium and sodium ions in the resultant solutions by flame photometry. The specific surface areas of the precursors and the ion exchangers were measured by the Brunauer-Emmett-Teller (BET) method with a Microbetrics Flowsorb II 2300. Their scanning electron microscope (SEM) photos were taken with a Hitachi S-4500 electron microscope, and their infrared (IR) spectra were measured with a Perkin Elmer 1650 IR spectrometer. Thermogravimetry-differential thermal analysis (TG-DTA) data were recorded on a Rigaku TAS-200 TG-DTA analyzer. Gas emission during the heating of samples (TG-IR) was monitored with the system of a Perkin Elmer Spectrum 2000 IR spectrometer and a Perkin Elmer TGA7 TG analyzer. In this system, gases released from a sample on the TG analyzer was directly introduced to a gas cell of the IR spectrometer by means of a N_2 flow.

2.3. Measurements of distribution coefficient and separation factor

To examine alkali metal ion selectivity on the ion exchangers, distribution coefficient (K_d) in mL/g is calculated by the formula

$$K_d = \frac{\text{amount of cation in the 1 g ion exchanger phase}}{\text{amount of cation in the 1 mL solution phase}}$$

A 0.1 g aliquot of the ion exchanger was placed in 10 mL of a buffer solution ($0.2\ M\ NH_3 + 0.2\ M\ NH_4Cl$) of pH = 9.18 containing Li^+, Na^+, K^+, Rb^+ and Cs^+ ions of 1.0 mM at 25 °C. After equilibrium was attained between the ion exchanger and solution phases, the concentrations of the alkali metal ions were measured flame photometrically. The amounts of ions taken up by the ion exchanger were calculated from the concentration differences before and after the ion exchange equilibrium.

The lithium isotope selectivity was estimated as S values measured batchwise. A 0.1 g aliquot of H-TZP was placed in a lithium ion-containing aqueous solution with the Li^+ ion concentration of 0.1 M for a week at 25 °C. The solution was then separated from the ion exchanger phase by filtration, and the pH and Li^+ ion concentration were measured. The lithium isotopic ratios, $^7Li/^6Li$, in the solution before and after the equilibrium were measured by the surface ionization technique with Varian Mat CH-5 mass spectrometer in a usual procedure described previously [1]. From the experimental data in the solution phase, S was calculated using the following equation,

$$S = [r(1+r)C_0 - r(1+r_0)C]/[r_0(1+r)C_0 - r(1+r_0)C],$$

where C_0 and C are the Li^+ ion concentrations before and after the ion exchange equilibrium, and r_0 and r are the lithium isotopic ratios before and after the equilibrium, respectively. The solution phase consist of 10 mL of 0.1 M lithium hydroxide solution, 4 mL of 0.1 M lithium acetate solution or 3 mL of lithium chloride solution.

3. Results and discussion

3.1. Characterization of L-TZP and H-TZP(Li)

The XRD pattern of L-TZP is shown in Fig. 1a. It agrees with the one recorded by Mizuhara *et al.* [7] except that

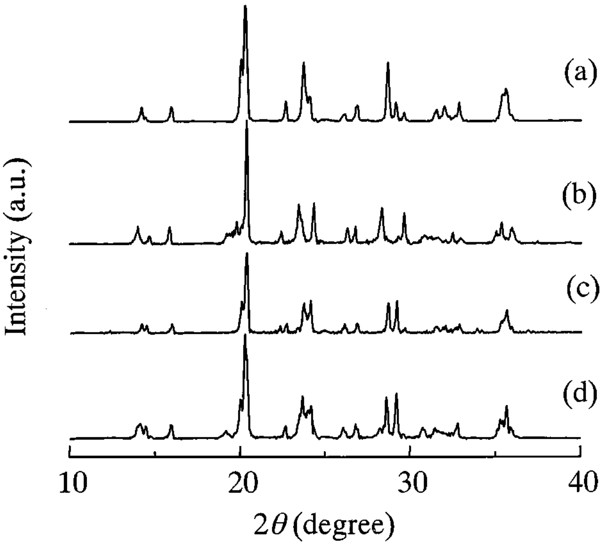

Figure 1 XRD patterns of (a) L-TZP, (b) H-TZP(Li), (c) H-TZP(Li) after Li^+ ion uptake from aqueous lithium hydroxide solution, and (d) H-TZP(Li) after Li^+ ion uptake from aqueous lithium acetate solution.

no peak assignable to impurities is observed in our pattern while a ZrP_2O_7 (JSPDS No. 29-1399) impurity peak was detected at around $2\theta = 21.6^\circ$ in their pattern. The calcining temperature is 950 °C in our experiments and 1000 °C in experiments by Mizuhara *et al.* [7]. We found that a high temperature tends to result in the formation of impurities. As for the crystal system of L-TZP, Mizuhara *et al.* [7] claimed that it was monoclinic. The XRD pattern of the L-TZP is in fact very similar to that of $LiZr_2(PO_4)_3$ reported by Casciola *et al.* [8] whose crystal system is monoclinic. No weight loss of L-TZP is observed up to 500 °C by TG-DTA and TG-IR measurements, which shows the nonexistence of water of crystallization in L-TZP.

The degree of leaching of lithium ions from L-TZP is 99.7%. This value is higher than the value of 91.4% by Mizuhara *et al.* [7]. The reason for the substantial difference between the two groups may be ascribable to the difference in leaching conditions; our acid treatment with stirring was carried out twice at 80 °C while their acid treatment is performed only once without stirring at room temperature. The XRD pattern of H-TZP(Li) is shown in Fig. 1b. Mizuhara *et al.* [7] claimed that the crystal system of H-TZP(Li) was rhombohedral. However, our crystal structure analysis using a JADE 4.0 program provided by Materials Data Inc. indicates it is monoclinic rather than rhombohedral. The topotactic ion exchange from L-TZP to H-TZP(Li) thus occurs.

The SEM photograph of H-TZP(Li) is shown in Photo 1a. It is roughly in the form of pillars with heights of about 2 μm. Some aggregation of particles is observed. The specific surface area of H-TZP(Li) is 1.4 m^2/g, larger than 0.28 m^2/g of the precursor.

A 0.27% weight loss was observed up to 250 °C in the TG-DAT measurement of H-TZP(Li), which is ascribed to the release of water. Thus, the chemical formula of H-TZP(Li) is $HTi_{0.5}Zr_{1.5}(PO_4)_3 \cdot 0.07H_2O$. The theoretical ion exchange capacity of H-TZP(Li) is then 2.23 meq./g, assuming that H^+ ions of $HTi_{0.5}Zr_{1.5}(PO_4)_3$ alone contribute to ion exchange.

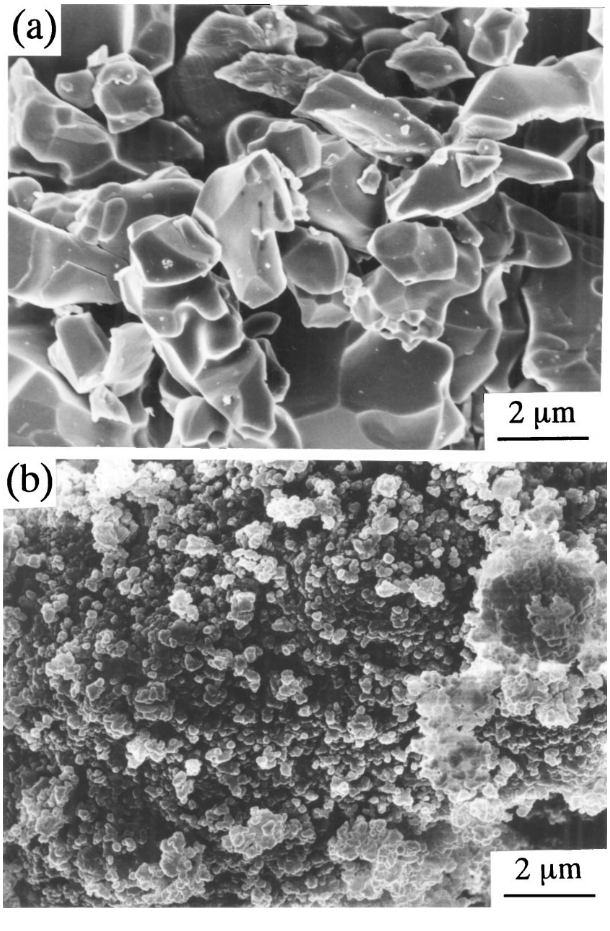

Photo 1 SEM photographs of (a) H-TZP(Li) and (b) H-TZP(Na).

3.2. Characterization of N-TZP and H-TZP(Na)

The XRD pattern of N-TZP is shown in Fig. 2a. It is very similar to that of $NaZr_2(PO_4)_3$ (JSPDS No. 33-1312) and hence its crystal system is probably rhombohedral. No weight loss of N-TZP was observed up to 500 °C in the TG-DTA chart.

Contrary to L-TZP, the degree of leaching of sodium ions is only 68% despite the fact that much concentrated acid is used for the acid treatment of N-TZP than that for L-TZP (10 M vs. 1 M). N-TZP thus has much higher acid resistibility and may be structurally more stable than L-TZP. The XRD pattern of H-TZP(Na) is shown in Fig. 2b. H-TZP(Na) retains the rhombohedral structure the precursor possesses and is similar to that of $HZr_2(PO_4)_3$ (JSPDS No. 38-0004). However, peaks assignable to N-TZP due to the low sodium ion extractability are observed, in addition to an unknown peak at around 18.1° that is absent in the pattern of N-TZP.

While the yield of H-TZP(Li) from L-TZP is 99%, that of H-TZP(Na) from N-TZP is 63%, indicating that part of the formed H-TZP(Na) is dissolved by 10 M nitric acid. The XRD measurement of the evaporation residue of the leachate identifies $Zr(HPO_4)_2 \cdot H_2O$ (JSPDS No. 22-1022) as shown in Fig. 2c.

The SEM photograph of H-TZP(Na) is shown in Photo 1b. H-TZP(Na) is in the form of roughly spherical particles with diameter of about 0.2 μm. Like in the case of H-TZP(Li), some aggregation of particles is observed. The specific surface area is 5.6 m^2/g.

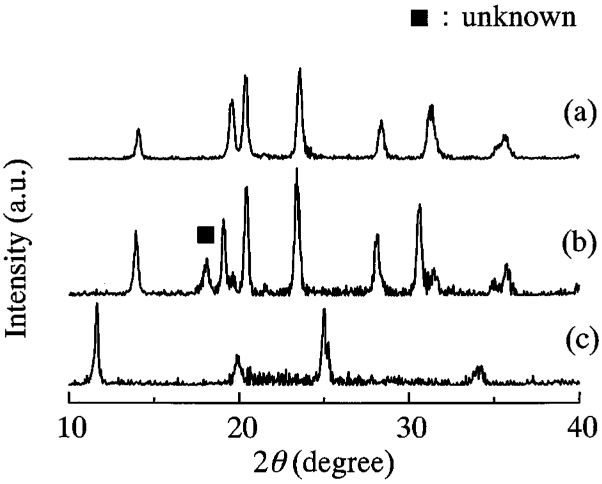

Figure 2 XRD patterns of (a) N-TZP, (b) H-TZP(Na), and (c) the evaporation residue of the leachate.

TG-DTA and TG-IR measurements of H-TZP(Na) show a 2.2% weight loss due to the release of water up to 250°C. Therefore, the exact chemical formula of H-TZP(Na) should be $H_{0.68}Na_{0.32}Ti_{0.5}Zr_{1.5}(PO_4)_3 \cdot 0.56H_2O$. The theoretical ion exchange capacity of H-TZP(Na) is 1.47 meq./g, assuming that H^+ ions of $H_{0.68}Na_{0.32}Ti_{0.5}Zr_{1.5}(PO_4)_3$ alone contribute to ion exchange.

3.3. Alkali metal ion selectivity of H-TZP(Li) and H-TZP(Na)

In Fig. 3, alkali metal ion selectivity of the ion exchangers expressed in terms of K_d values is depicted. Trends in affinity toward alkali metal ions are similar to each other between the two ion exchangers; no substantial difference in ion exchange selectivity to alkali metal ions is observed. They both show high affinity toward lithium and sodium ions. Judging from the experimental errors of flame photometric measurements, K_d values for those two ions must be higher than 1×10^4 mL/g. Contrary to lithium and sodium ions, rubidium and cesium ions are hardly taken up by the ion exchangers. Those results indicate that the two ion exchangers have ion exchange sites whose sizes are fit for lithium and sodium ions; rubidium and cesium ions are too large to be taken up by the ion exchangers (ion sieve effect).

A close comparison of the plots for H-TZP(Li) and H-TZP(Na) reveals that K_d values of H-TZP(Na) is higher than those of H-TZP(Li) for each of K^+, Rb^+ and Cs^+ ions. This is probably attributable to the difference in specific surface area between the two ion exchangers. H-TZP(Na) has a larger specific surface area than H-TZP(Li) (5.6 m^2/g vs. 1.4 m^2/g). This means that the former has a large amount of ion exchange sites on the surfaces of particles that show no ion sieve effect, compared to the latter, which leads to higher K_d values for H-TZP(Na) than for H-TZP(Li).

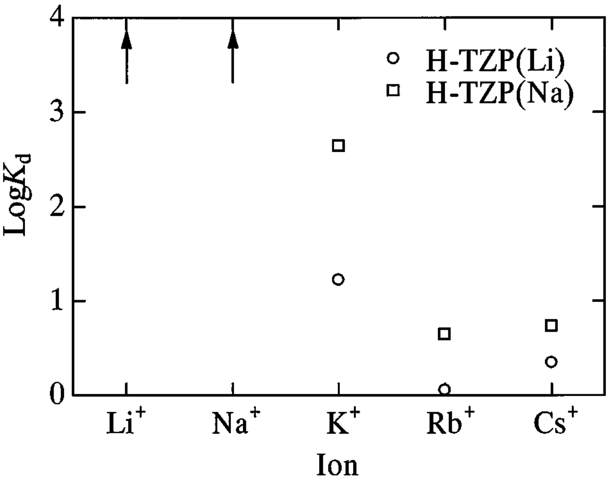

Figure 3 K_d values for alkali metal ions. The arrows mean the K_d values for lithium and sodium ions are above 1×10^4 both for H-TZP(Li) and H-TZP(Na).

3.4. Lithium isotope selectivity of H-TZP(Li) and H-TZP(Na)

Experimental conditions and results are summarized in Table I. Each datum of the results is the average of the data obtained in two independent experiments. S values, amounts of Li^+ ions taken up by the ion exchangers, and specific surface areas measured after the Li^+ ion uptake are plotted against pH of the solution phase measured after the ion exchange equilibrium in Fig. 4a, b and c, respectively. The S values are larger than unity, showing that H-TZP(Li) and H-TZP(Na) are isotopically ^{6}Li-specific. This trend is the same as those observed for inorganic ion exchangers so far examined [2–6] and also for organic ion exchangers [1]. The sum of forces acting on lithium ions are thus larger in the solution phase than in the ion exchanger phase, based on the theory of isotope effects [9].

The two ion exchangers seem to give similar S-values at a given pH-value against our expectation that different precursors might result in ion exchangers with different lithium isotope selectivity.

The pH dependence of S-value is observed in Fig. 3a. When the pH value is below 6, the S-value is 1.023 to 1.025, while at pH 12 or higher, it is nearly unity, that is, H-TZP does not show affinity toward either of the lithium isotopes in highly basic conditions. This observation is best understood by assuming that ion exchange sites that show little lithium isotope selectivity are newly formed in those conditions, which makes the overall lithium isotope selectivity small. The assumption is supported by the data shown in Figs. 4b and c. It is seen in Fig. 4b that the amounts of Li^+ ions taken up by the ion exchangers exceed the theoretical ion exchange capacities at pH 12 or higher. This is a strong supporting evidence of the revelation of new ion exchange sites. It is seen in Fig. 4c that the specific surface area becomes quite large after the ion exchangers are used in highly basic conditions, which can be

TABLE I Experimental conditions and results on lithium isotope selectivity and related measurements

Ion exchanger	Solution phase[a]	Temp (°C)	pH[b,c]	S[c]	Li^+ ion uptake (mmol/g)[c]	Specific surface area (m^2/g)[b,c]
H-TZP(Li)	0.1 M LiOH	25	12.6	1.003	6.43	27.7
H-TZP(Li)	0.1 M CH_3COOLi	25	4.56	1.025	1.99	0.5
H-TZP(Li)	0.1 M LiCl	25	1.51	1.023	1.56	1.1
H-TZP(Na)	0.1 M LiOH	25	12.0	1.000	1.65	26.3
H-TZP(Na)	0.1 M CH_3COOLi	25	5.09	1.023	0.942	5.7
H-TZP(Na)	0.1 M LiCl	25	2.58	—	0.0982	7.4

[a] Original composition.

[b] The value measured after Li^+ ion uptake.

[c] Average of two independent experiments.

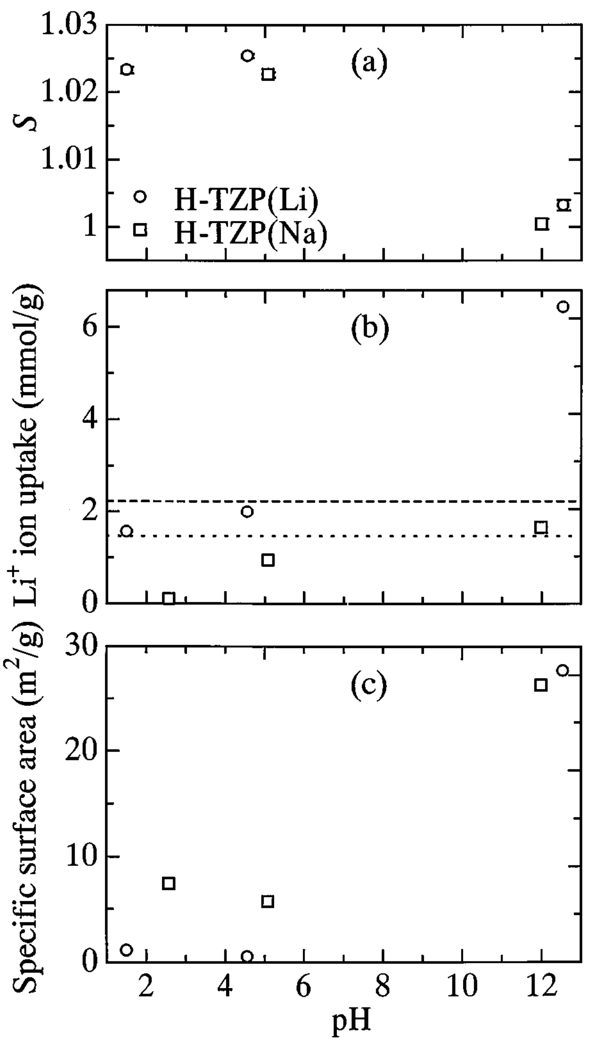

Figure 4 Plots of (a) S value, (b) amount of Li$^+$ ions taken up, and (c) specific surface area measured after Li$^+$ ion uptake. Open circles, H-TZP(Li); Open squares, H-TZP(Na). --- in (b), theoretical ion exchange capacity of H-TZP(Li); ··· in (b), theoretical ion exchange capacity of H-TZP(Na).

understood as a result of the formation of new ion exchange sites.

The XRD patterns of H-TZP(Li) after the Li$^+$ ion uptake from aqueous lithium hydroxide and lithium acetate solutions are shown in Figs. 1c and d, respectively. They are very similar to each other and to the pattern of the precursor, L-TZP. Thus, although the formation of new ion exchange sites in highly basic conditions affects the specific surface area and lithium isotope selectivity, it does not lead to the change in crystal system.

4. Conclusions

To summarize, we make the following statements:

No substantial difference in ion exchange property is observed between H-TZP(Li) and H-TZP(Na) prepared, respectively, by the acid treatment of LiTi$_{0.5}$Zr$_{1.5}$(PO$_4$)$_3$ and NaTi$_{0.5}$Zr$_{1.5}$(PO$_4$)$_3$. Both ion exchangers show high selectivity for lithium and sodium ions among alkali metal ions. Isotopically, they are ^{6}Li-specific like other inorganic ion exchangers so far examined. The S value is found of 1.023 to 1.025 at 25 °C when the pH of the solution phase is below 6, while low isotopic preference of lithium is observed in highly basic conditions. This is consistent with the formation of new ion exchange sites with low isotope selectivity of lithium.

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