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# Some Ion Exchange Properties of Porous Silica Beads Loaded with Semicrystalline Titanium Phosphate

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# Some Ion Exchange Properties of Porous Silica Beads Loaded with Semicrystalline Titanium Phosphate

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**Abstract:** Semicrystalline titanium phosphate, $Ti_2O_3(H_2PO_4)_2 \cdot 2H_2O$ (TiOP), has been synthesized mainly in the interior pores of porous silica beads, and some ion exchange properties of TiOP-loaded silica beads thus obtained (TiOP-$SiO_2$) and their thermally treated product at 500°C (TiOP-$SiO_2$(500)) were investigated. The degree of TiOP-loading was 16.5% on an average. As a whole, TiOP-$SiO_2$ and TiOP-$SiO_2$(500) retained the ion exchange properties including very high ion exchange rates that TiOP and its thermally treated product at 500°C obtained in the form of powders possessed.

**Keywords:** Titanium phosphate, porous silica beads, ion exchange, selectivity

## INTRODUCTION

Lithium has two naturally occurring stable isotopes, $^6$Li and $^7$Li, and both are very useful in nuclear industry, especially $^6$Li in D-T fusion power reactors through the nuclear reaction $^6$Li(n, $\alpha$)T. This necessitates separation of lithium isotopes. It is well-known that inorganic ion exchangers exhibit high selectivities for specific ions, temperature stability and inertness

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to solvents, as well as resistance to high radiation field as compared with well-developed organic ion exchange resins (1). The much more interest we have been concerned is that some inorganic ion exchangers register the high selectivity for $^6$Li (we call this property as $^6$Li-specific), in addition to the above-stated properties. Such ion exchangers include those based on manganese oxides (2–4), niobic and tantalic acids (5) and layered phosphate composites (6).

In our previous papers (7–10), we reported the synthesis of semicrystalline titanium(IV) phosphate with the layered structure, $Ti_2O_3(H_2PO_4)_2 \cdot 2H_2O$, in the form of powders, designated hereafter as $TiOP_p$, and characterization of $TiOP_p$ and its thermally treated products as cation exchangers including selectivity for the lithium isotopes. $TiOP_p$ was characterized by its high ion exchange rate; $H^+/Li^+$ ion exchange equilibrium was attained in one minute at room temperature. The thermally treated products of $TiOP_p$, at temperatures between 200 to 600°C, exhibited high selectivity for the sodium ion from among Group 1 metal ions, and was lithium-isotopically $^6$Li-specific. The selectivity for $^6$Li isotope was a slow increasing function of the temperature of the thermal treatment up to 600°C. Unfortunately, $TiOP_p$ and its thermally treated products were unsuited materials for column operation. Synthesis of TiOP onto the surfaces of acryl beads was successfully attempted, and some ion exchange properties of the TiOP-loaded acryl beads (TiOP-ac) thus obtained were examined, which was reported in a previous paper (10). A large problem on TiOP-ac was that its thermal treatment was not possible due to the very low thermal resistance of the acryl beads.

In the present study, TiOP was synthesized mainly in the interior pores of silica beads, and the ion exchange properties of TiOP-loaded silica beads, designated hereafter as TiOP-$SiO_2$, and its thermally treated product at 500°C, designated hereafter as TiOP-$SiO_2$(500), were examined. In this paper, we report the results of such experiments.

## EXPERIMENTAL

### Synthesis of TiOP onto Inner Pores of Silica Beads

Four kinds of silica beads were investigated as host material of TiOP loading. They were Micro Beads Silica Gel Grade 300 (MB-300), Micro Beads Silica Gel Grade 500 (MB-500), Micro Beads Silica Gel Grade 800 (MB-800), and Wakosil C-200. The first three beads were manufactured by Fuji Silysia Chemical Ltd, and the last one by Wako Pure Chemical Industries, Ltd. The particle diameters stated in specification were 70 to 500 μm for MB-300, MB-500 and MB-800, and 64 to 210 μm for C-200, and the average pore diameters of MB-300, MB-500, and MB-800 were 30, 50, and 80 nm, respectively. The pore diameters of MB-300, MB-500, and MB-800 by mercury penetration porosimetry were about 28, 46, and 67 nm, respectively. The pore diameter of the given beads was slightly lot-dependent. For C-200, no pore with pore diameter more than 10 nm was found.

TiOP was synthesized from $TiOSO_4$ and $NH_4H_2PO_4$. Various parameters such as the mole ratio of $TiOSO_4$ to $NH_4H_2PO_4$ were changed to find out the optimum conditions for the synthesis of TiOP in the pores of silica beads. The optimum procedure established for synthesizing TiOP-$SiO_2$ was as follows: To a flask containing 5 $cm^3$ of the 0.6 M $TiOSO_4$ solution was added 2 g of silica beads at 70°C. The flask was evacuated with an aspirator for 20 minutes to have the $TiOSO_4$ solution penetrate into the inner pores of the beads as much as possible, and the beads were then air-dried. At this point, the majority of the $TiOSO_4$ was incorporated into the pores of the silica beads. To these wet $TiOSO_4$-containing silica beads was added 5 $cm^3$ of 0.6 M $NH_4H_2PO_4$ solution, and the mixture was stirred at 70°C for 30 min and then allowed to stand for ten days at 100°C with occasional stirring. During these ten days, titanium phosphate was synthesized not only in the pores of the silica beads but also in the solution and on the surfaces of the beads. After ten days' standing, the TiOP-loaded silica beads were placed on a 100 mesh sieve and TiOP synthesized on the surfaces of the silica beads were removed as much as possible by softly rubbing them to the 100 mesh net of the sieve. TiOP-loaded silica beads were then washed with pure water and separated from fine powders of TiOP. Grain sizes of TiOP powders were several hundreds nm, and consequently they could be easily separated from TiOP-loaded silica beads since they went through the mesh of the sieve while TiOP-loaded silica beads did not.

TiOP-$SiO_2$ (500) was obtained by heating TiOP-$SiO_2$ at 500°C for ten hours.

## Characterization

The powder X-ray diffraction (XRD) patterns were recorded using a Rigaku RINT2100V/P X-ray diffractometer with the Cu $K\alpha$ radiation ($\lambda = 1.54056$ Å) in the $2\theta$ range of 5 to 70 degrees at room temperature. Pore size distributions of silica beads as provided and TiOP-loaded silica beads were measured with a micrometritics Pore Sizer 9320 mercury penetration porosimeter. The titanium and phosphorus contents in TiOP-$SiO_2$ and the weight ratio of TiOP in the pores of silica beads to TiOP-$SiO_2$ (the degree of TiOP loading) were determined by ICP-atomic emission spectroscopy (ICP-AES) with a Seiko Instruments SPS7700 ICP-AES spectrometer after $HNO_3$-HF decomposition of an aliquot of TiOP-$SiO_2$. The scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) analyses were carried out with a Hitachi S-4500 scanning electron microscope. Optical photographs were taken with a Keyence V-H7000 digital microscope. Concentrations of Group 1 metal ions in solution were determined by flame photometry with a Daini Seikosha SAS-727 atomic absorption spectrometer and those of other elements by ICP-AES. The specific surface areas were measured by the Brunauer-Emmett-Teller (BET) method with a Micrometrics Flowsorb II 2300.

The ion exchange properties of TiOP-$SiO_2$ and TiOP-$SiO_2$(500) were examined in three aspects, i.e., selectivity of Group 1 metal ions, ion uptakes of Group 1 elements and the $H^+/K^+$ ion exchange rate.

Selectivity for Group 1 metal ions was investigated by measuring the distribution coefficients, $K_d$, in $cm^3 \cdot g^{-1}$, defined by the formula,

$$K_d = \frac{\text{Amount of cation in 1 g solid phase}}{\text{Amount of cation in 1 cm}^3\text{ solution phase}}$$

For the measurement of $K_d$ values under the basic condition, 0.4 g aliquot of the ion exchanger was placed in 5 $cm^3$ of $NH_3$-$NH_4Cl$ buffer solution of pH 9.2 containing 1 mM of $Li^+$, $Na^+$, $K^+$, $Rb^+$, and $Cs^+$ ions at 25°C for one day. The period of one day was long enough to equilibrate the solid phase with the solution phase. The two phases were then separated by filtration, and concentrations of the ions in the solution phase were analyzed. The amount of an ion taken up by the ion exchanger was calculated from the concentration difference in the solution phase before and after the ion exchange equilibrium. The measurement under the acidic condition was carried out in a similar manner except that the buffer solution was changed to acetic acid-acetate of pH 5.3.

The $Li^+$ ion uptake under the basic condition was measured by placing 0.3 g aliquot of the ion exchanger in 4 $cm^3$ of the mixed solution of LiOH and LiCl of pH 12.3 with the lithium ion concentration of 0.1 M at 25°C for one day. The $Li^+$ ion uptake per 1 gram of the ion exchanger was calculated from the concentration difference in the solution before and after the ion exchange equilibrium. Similar experiments were carried out for sodium and potassium ions. The $Li^+$ ion uptake under the acidic condition was measured by equilibrating 0.3 g aliquot of the ion exchanger with 4 $cm^3$ of the acetic acid-lithium acetate buffer solution of pH 5 with the lithium ion concentration of 0.1 M at 25°C. The $Li^+$ ion uptake per 1 gram of ion exchanger was calculated from the concentration difference in the solution before and after the ion exchange equilibrium. Similar experiments were also carried out for sodium, potassium, rubidium, and cesium ions.

The rate of the $H^+/K^+$ ion exchange was examined under acidic and basic conditions at 25°C. The measurement under the basic condition was as follows: 0.3 g aliquot of the ion exchanger was immersed in 4 $cm^3$ of the mixed solution of KOH and KCl of pH 12.3 with the potassium ion concentration of 0.1 M, and ion exchange between hydrogen ions in the ion exchanger and potassium ions in the solution commenced immediately. An aliquot of the solution was sampled by filtration with a disk filter when the predetermined experimental time elapsed, and the potassium concentration was measured. The amount of potassium ions taken up by the ion exchanger was calculated from the concentration difference in the solution phase before the start of the experiment and after the predetermined reaction time elapsed. Similar measurements were carried out in the acidic condition using the acetic acid-potassium acetate buffer solution of pH 5.1 with potassium ion concentration of 0.1 M.

## RESULTS AND DISCUSSION

### Synthesis and Characterization

Our previous study on the synthesis of TiOP in solution showed that the grain sizes of flake-like shaped TiOP powders synthesized from $TiOSO_4$ and $NH_4H_2PO_4$ were several hundreds nm (9). So, it was preferable to use silica beads, whose pores diameter were several hundreds nm or larger, large enough to accommodate TiOP powders with such grain sizes in their inner pores. Unfortunately, we could not find such porous silica beads on the market.

Figure 1 shows the EDX images of Ti and P on the cross-sections of a TiOP-loaded MB-300 bead (Figs. 1a and 1b), a TiOP-loaded MB-500 bead (Figs. 1c and 1d) and a TiOP-loaded MB-800 bead (Figs. 1e and 1f) after

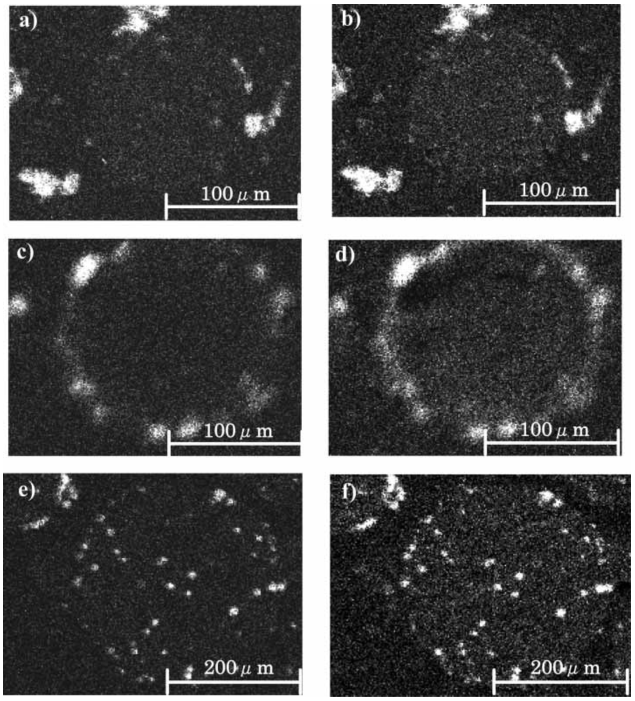

***Figure 1.*** The EDX images of a) Ti and b) P on MB-300, those of c) Ti and d) P on MB-500 and those of e) Ti and f) P on MB-800.

ten days' standing. A comparison of Figs. 1a, c, and e, and b, d, and f, reveals, albeit not very clearly, that silica beads with larger pore diameters can accommodate larger amounts of titanium and phosphorus. No appreciable peaks of Ti and P were observed on C-200, which showed that the pore sizes of the C-200 beads were so small that TiOP could not form inside their pores. From these results, in addition to the above-mentioned preferable property of silica beads as host material of TiOP loading, we judged MB-800 was the best among the four kinds of silica beads tested, albeit not very satisfactory, and decided to use TiOP-loaded MB-800 (TiOP-$SiO_2$) for various measurements. Figures 1e and 1f also show that Ti and P are nearly uniformly dispersed inside the MB-800 bead.

The best ratio of the weight of silica beads used for the synthesis to the volume of the 0.6 M $TiOSO_4$ solution was about 0.4 $g/cm^3$. At this ratio, the added the solution nearly completely penetrated into the inner pores of silica beads. When the volume of $TiOSO_4$ solution was in excess of 0.4 $g/cm^3$, the relative amount of TiOP synthesized outside the pores of the silica beads tended to increase. When the ratio was below this value, the amount of TiOP synthesized inside the pores of the beads tended to decrease. These were monitored by EDX analysis.

The exact formation mechanism of TiOP is unclear. Even in the best-studied silicon alkoxides systems of the sol-gel method, much of the reaction mechanisms remain unsolved. It would be necessary to detect some reaction intermediates to understand the formation mechanism of TiOP, which is certainly beyond the scope of the present study. A possible scheme may be that titanium phosphate in the ammonia form was first synthesized from $TiOSO_4$ and $NH_4H_2PO_4$ and eventually converted to the one in the hydrogen form by washing with water.

XRD patterns of the silica beads (MB-800) as provided and TiOP-loaded silica beads are given in Fig. 2. The peak at around $2\theta = 9^\circ$ shows the layered structure of TiOP (7). Note that the XRD pattern of TiOP-$SiO_2$ after ten days' standing was taken after TiOP synthesized on the surfaces of the silica beads were removed as much as possible, while no such treatment was conducted for the other TiOP-$SiO_2$. As is seen in Fig. 2, TiOP crystals were already observed after one day's standing and in three to five days, crystal growth was almost finished. We sometimes experienced, however, that the completion of the crystal growth of TiOP took a longer time even under similar conditions. So, we decided to allow the mixture of $TiOSO_4$-containing silica beads and the 0.6 M $NH_4H_2PO_4$ solution to stand for ten days.

The optical photographs of silica beads (MB-800) as provided and TiOP-$SiO_2$ are shown in Figs. 3a and 3b respectively. It can be seen that part of the surfaces of TiOP-$SiO_2$ are covered with TiOP crystals in spite of our endeavors to remove TiOP synthesized on the surfaces of the silica beads as much as possible. Figures 3c and 3d are the SEM images of the surface of a silica bead as provided and a TiOP-loaded silica bead, respectively. TiOP synthesized on the surface can be clearly seen in Fig. 3d.

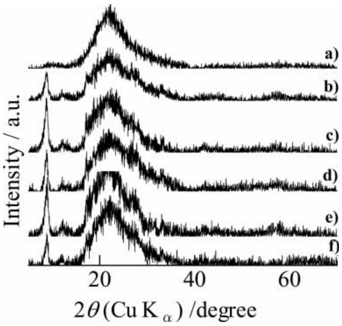

***Figure 2.*** The XRD patterns of a) MB-800 silica beads as provided, b) TiOP-loaded MB-800 after 1 day's standing, c) b) TiOP-loaded MB-800 after 3 days' standing, d) TiOP-loaded MB-800 after 5 days' standing, e) TiOP-loaded MB-800 after 7 days' standing and f) TiOP-loaded MB-800 after 10 days' standing

The mole ratio of Ti : P in TiOP-$SiO_2$ was 1 : 1.09, determined after decomposing an aliquot of TiOP-$SiO_2$. Thus, TiOP-$SiO_2$ contained slightly excessive phosphorus relative to titanium expected from its stoichiometry of 1 : 1, which indicated that phosphorus compounds with no titanium content might be synthesized as impurities. The average degree of TiOP loading on

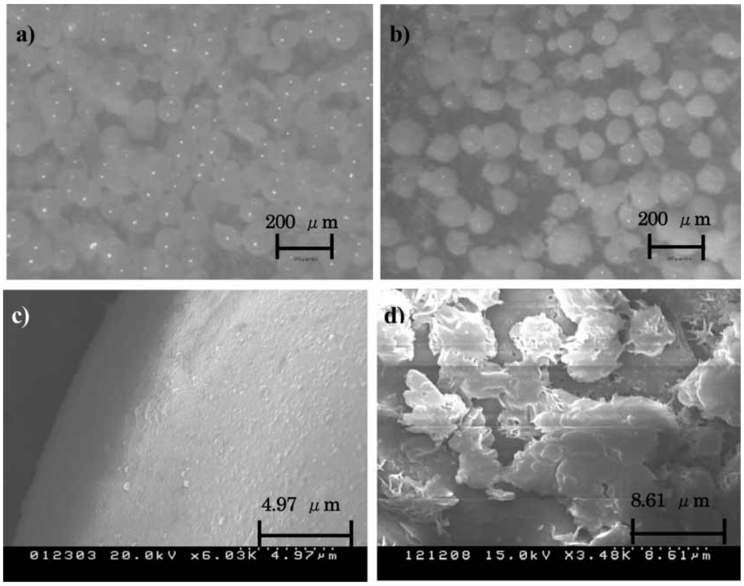

***Figure 3.*** Optical photographs of the surfaces of a) silica beads (MB-800) as provided and b) TiOP-$SiO_2$, and SEM images of c) the surface of a silica bead (MB-800) as provided and d) a TiOP-loaded silica bead.

silica beads was 16.5% based on the Ti content. Hereafter, the degree of TiOP loading is specified in the parenthesis after TiOP-$SiO_2$, whenever necessary.

The specific surface areas of silica beads (MB-800) as provided, TiOP-$SiO_2$(16.5%) and $TiOP_p$ were 46.3, 49.5, and 59.2 $m^2/g$, respectively. The specific surface area of TiOP-$SiO_2$(16.5%) would have been 48.4 $m^2/g$, if it had been given as the weighted average of those of MB-800 and $TiOP_p$. It was actually slightly larger than the "theoretical" value, which corresponded to the fact that the average crystal size of TiOP synthesized in pores of silica beads was smaller than that of $TiOP_p$.

The results of mercury porosimetry are depicted in Fig. 4. It can be seen that most of the pore diameters of TiOP-$SiO_2$ were between 50 to 90 nm, and that, while no substantial change in pore diameter was observed between the silica beads as provided and TiOP-$SiO_2$, the pore volume was evidently reduced by the formation of TiOP.

## Ion Exchange Properties

Uptakes of Group 1 metal ions are plotted in Fig. 5. The ion uptake of Group 1 metals by TiOP-$SiO_2$(16.5%) under the acidic condition is a slow increasing function of the atomic number from lithium towards rubidium and the uptake of the cesium ion is nearly equal to that of the rubidium ion, which suggests that those ions are trapped by the ion exchange sites of TiOP by the electrostatic force like in the cases of usual organic ion exchangers. Such a tendency is not clearly observed on TiOP-$SiO_2$(500). Contrary to the

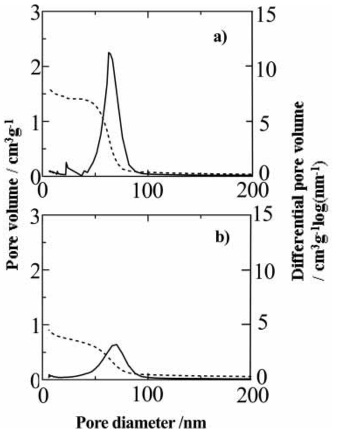

*Figure 4.* Plots of the pore volume (left vertical axis) and the differential pore volume (right vertical axis) against the pore diameter for a) silica beads (MB-800) as provided and b) TiOP-$SiO_2$. The continuous line stands for the differential pore volume, and the dotted line pore volume.

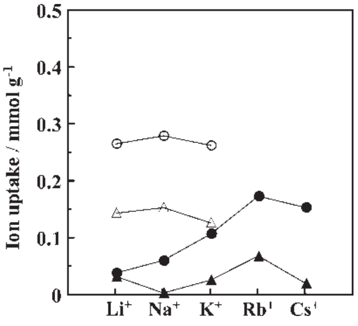

***Figure 5.*** Uptakes of Group 1 metal ions by TiOP-$SiO_2$ under the acidic condition (●) and under the basic condition (○) and by TiOP-$SiO_2$(500) under the acidic condition (▲) and under the basic condition (Δ) at 25°C. No data are available for rubidium and cesium under the basic condition due to low solubilities of their hydroxides.

tendency in the acidic condition, the lithium, sodium, and potassium ion uptakes are nearly equal both by TiOP-$SiO_2$(16.5%) and TiOp-$SiO_2$(500) under the basic condition. It is also seen in Fig. 5 that the ion uptake under the basic condition is larger than under the acidic condition for any metal ions examined both for TiOP-$SiO_2$(16.5%) and TiOp-$SiO_2$(500). This is probably due to the fact that, while about one half of dissociable hydrogen ions of the $H_2PO_4$ moiety of TiOP-$SiO_2$ are actually dissociated under the acidic condition (around pH 5), all the dissociable hydrogen ions are dissociated under the basic condition. In addition, for a given ion under the fixed condition, the uptake by TiOP-$SiO_2$(16.5%) is larger than by TiOP-$SiO_2$(500). This is consistent with the partial condensation of the $H_2PO_4$ moiety by the thermal treatment at 500°C (8). Although the ion uptakes by TiOP-$SiO_2$ are much smaller than those by $TiOP_P$, the uptakes per gram of TiOP in TiOP-$SiO_2$ are nearly equal to that of $TiOP_P$.

The logarithms of $K_d$ values of Group 1 metal ions are plotted in Fig. 6. As a whole, neither TiOP-$SiO_2$(16.5%) or TiOP-$SiO_2$(500) showed specific selectivity towards any of Group 1 metal ions under the acidic or basic condition.

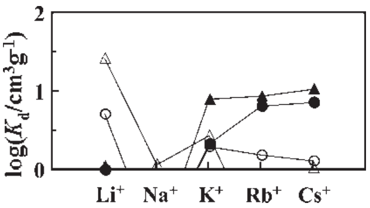

***Figure 6.*** The log $K_d$ values of Group 1 metal ions on TiOP-$SiO_2$ under the acidic condition (●) and under the basic condition (○) and on TiOP-$SiO_2$(500) under the acidic condition (▲) and under the basic condition (Δ) at 25°C.

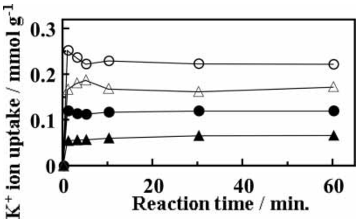

***Figure 7.*** Plots of the potassium ion uptake by $TiOP\text{-}SiO_2$ under the acidic condition (●) and under the basic condition (○) and by $TiOP\text{-}SiO_2$(500) under the acidic condition (▲) and under the basic condition (Δ) against the ion exchange reaction time at 25°C.

The largest difference between $TiOP\text{-}SiO_2$(500) and $TiOP_p$(500) was seen in the $K_d$ value of the sodium ion. While $TiOP_p$(500) showed the specifically high selectivity for the sodium ion (10), $TiOP\text{-}SiO_2$(500) had no such selectivity. Actually, the concentration of the sodium ion after the equilibrium was slightly higher than that before the equilibrium in the batch experiment. This may indicate that the silica beads (MB-800) as provided contained a small amount of sodium ion and part of it was dissolved out to the solution phase in the batch experiment (11).

The potassium ion uptakes are plotted against the reaction time in Fig. 7. It was nearly constant in the range of the ion exchange reaction time between 1 and 60 minutes both for $TiOP\text{-}SiO_2$(16.5%) and for $TiOP\text{-}SiO_2$(500) under any solution condition at examined 25°C. This means the $H^+/K^+$ ion exchange rate was very high and the $H^+/K^+$ ion exchange equilibrium was attained within one minute under any condition examined. Thus, TiOP and TiOP(500) formed in the pores of silica beads retained their ion exchange property of the very fast ion exchange rate.

## CONCLUSION

In conclusion we would like to say that semicrystalline titanium phosphate (TiOP), $Ti_2O_3(H_2PO_4)_2 \cdot 2H_2O$, was synthesized in inner pores of porous silica beads, as well as on their surfaces. The TiOP-loaded silica beads ($TiOP\text{-}SiO_2$) and its thermally treated product at 500°C ($TiOP\text{-}SiO_2$(500)) basically have the ion exchange properties similar to TiOP in the form of powders ($TiOP_p$) and its thermally treated product at 500°C ($TiOP_p$(500)), respectively. The largest difference in ion exchange properties was observed in the selectivity for the sodium ion between $TiOP\text{-}SiO_2$(500) and $TiOP_p$(500). While $TiOP_p$(500) showed very high selectivity towards the sodium ion from among Group 1 metal ions, no such property was observed on $TiOP\text{-}SiO_2$(500) in the present batch experiment. Both $TiOP\text{-}SiO_2$ and

TiOP-$SiO_2$(500) possessed very high ion exchange rates like $TiOP_p$ and $TiOP_p$(500).

## ACKNOWLEDGEMENT

Micro Beads Silica Gel Grade 300 (MB-300), Micro Beads Silica Gel Grade 500 (MB-500), Micro Beads Silica Gel Grade 800 (MB-800) were kindly donated to us by Fuji Silysia Chemical Ltd.

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