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Kenta Ooi[a]; Yoshitaka Miyai[a]; Shunsaku Katoh[a]
[a] Government Industrial Research Institute Shikoku, Takamatsu-Shi, Kagawa, Japan

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Ion-Exchange Properties of Ion-Sieve-Type Manganese Oxides Prepared by Using Different Kinds of Introducing Ions

KENTA OOI, YOSHITAKA MIYAI, and SHUNSAKU KATOH
GOVERNMENT INDUSTRIAL RESEARCH INSTITUTE
SHIKOKU, TAKAMATSU-SHI, KAGAWA, JAPAN

Abstract

Three ion-sieve-type manganese oxides, HMnO(Li), HMnO(Na), and HMnO(K), were prepared by acid treatments of Li^+-, Na^+-, and K^+-introduced manganese oxides, respectively. Three oxides were obtained from γ-MnO_2 and the corresponding alkali metal hydroxides by heating at 600°C. The ion-exchange properties of the adsorbents were investigated by pH titration, K_d measurements, and the adsorption of metal ions from seawater. The selectivity sequences of alkali metal ions were $Na^+ < Cs^+ < Rb^+ < K^+ < Li^+$ for HMnO(Li) and $Li^+ \approx Na^+ < Cs^+ < K^+ < Rb^+$ for HMnO(Na) and HMnO(K). The high selectivity of Li^+ on HMnO(Li) can be ascribed to an ion-sieve effect of spinel-type manganese oxide which was produced from $LiMn_2O_4$. Since HMnO(Na) and HMnO(K) had [2 × 2] tunnels of edge-shared $[MnO_6]$ octahedra, the high selectivities of K^+ and Rb^+ on these samples were used to explain that the sizes of the [2 × 2] tunnels were suitable for filling ions of about 1.4 Å in radius in a stable configuration. The order of metal-ion uptake from seawater was $Sr^{2+} < K^+ < Mg^{2+} < Ca^{2+} < Na^+ < Li^+$ for HMnO(Li), $Li^+ < Sr^{2+} < Mg^{2+} < Ca^{2+} < Na^+ < K^+$ for HMnO(Na), and $Li^+ < Sr^{2+} < Ca^{2+} < Mg^{2+} < K^+ < Na^+$ for HMnO(K).

INTRODUCTION

The adsorption of metal ions on manganese oxides has been extensively studied for both analytical (*1–7*) and geochemical reasons (*8–14*) and for water-pollution control (*15–19*). The adsorptive properties of manganese oxides are strongly dependent on their crystal and pore structures.

Ion-sieve-type manganese oxide was first synthesized by Vol'kin et al.

from manganese hydroxide which had been saturated with lithium ions (*20, 21*). It showed a remarkably high selectivity for the lithium ion among alkali metal ions. This was explained by the presence of micropores with a suitable size for fixing the lithium ion. Alkali metal ions other than those of lithium cannot enter the micropores since their ionic radii are too large. Ion-sieve-type manganese oxide has been successfully applied to the recovery of lithium from brine or bittern (*20, 22*). Also, we showed in a previous paper that it is one of the most promising adsorbents for the recovery of lithium from seawater owing to its high capacity for lithium, ease of lithium elution, and its high stability in adsorption–elution cycles (*23*).

An ion-sieve-type manganese oxide can be prepared by the thermal crystallization of metal ion-saturated manganese hydroxide followed by the extraction of metal ions with an acid solution. Therefore, its ion-exchange properties are dependent on the kinds of metal ions introduced into the manganese hydroxide precursor (*21*). However, there have been no systematic studies on the effects of metal ions introduced during preparation regarding the ion-exchange selectivity of ion-sieve-type manganese oxide.

In the present study we investigated the ion-exchange properties of three kinds of ion-sieve manganese oxides obtained by the acid treatment of Li^+-, Na^+-, and K^+-introduced manganese oxides. By comparing the ion-exchange properties of these samples, we determined the influence on ion-exchange selectivity of the metal ions introduced.

EXPERIMENTAL

Materials

Ion-sieve-type manganese oxides were prepared in a manner similar to that described previously (*23*). 100 g of γ-type manganese oxide (I.C. No. 4) was immersed in a 2-dm^3 alkali metal hydroxide (LiOH, NaOH, or KOH) solution (1 *M*), stirred for 1 week at 25°C, filtered, and then heated at 600°C for 2 h (the samples were designated $MnO_x(M)$, where M represents the metal ion introduced. The alkali metal ion-introduced manganese oxides were treated with nitric acid solutions of known concentration until the concentration of the alkali metal ions in the supernatant was less than 10^{-4} *M*. The acid-treated samples were washed with water and dried at 70°C. The products were designated HMnO(M), where M represents the alkali metal ion introduced.

Determination of Alkali Metal Ion Content

The alkali metal ion contents of $MnO_x(M)$ and HMnO(M) were determined by atomic absorption spectrometry after the samples were dissolved in a mixed solution of concentrated HNO_3 and HCl.

X-Ray Analysis

A powdered x-ray diffraction analysis was made on a Rigaku Denki x-ray diffractometer (model RAD II) with Ni-filtered CuK_α radiation (graphite monochrometer).

Distribution Coefficients (K_d)

K_d values of the alkali metal ions were determined by the batch method. The HMnO(M) (0.10 g) were immersed in 10 mL of a solution containing 10^{-4} M each of Li^+, Na^+, K^+, Rb^+, and Cs^+ at different pH values. These values were adjusted by using a hydrochloric acid solution or 10^{-4} M alkali metal hydroxide solutions. The concentrations of the metal ions in the exchanger and solution were determined from the concentrations relative to the initial concentrations in the solution. The concentrations of metal ions were determined by atomic absorption spectrometry. The K_d values were calculated using

$$K_d\,(\mathrm{mL/g}) = \frac{\text{amounts of metal ions in exchanger}}{\text{amounts of metal ions in solution}} \times \frac{\text{mL solution}}{\text{g exchanger}}$$

The pH Titration Curves

A weighed amount (0.10 g) of HMnO(M) was immersed in 10 mL of a mixed solution of varying ratios of (LiCl + LiOH) or (KCl + KOH) with intermittent shaking for about 30 days at 25 ± 0.1°C. The ionic strength in the mixed solution was adjusted to 0.1. After attaining equilibration, the pH of the supernatant solution was measured with a Horiba Model M8s pH meter in a nitrogen atmosphere.

Adsorption from Seawater

The HMnO(M) (0.05 g) was immersed in 2 L of seawater and stirred at 25°C. After stirring for 7 days, the HMnO(M) was collected by filtration and dried at 70°C. The collected HMnO(M) was dissolved in a mixed solution of concentrated HNO_3 and HCl; then the concentration of metal ions was determined by atomic absorption spectrometry. The metal ion uptake from the seawater was calculated by subtracting the metal ion content of HMnO(M).

RESULTS AND DISCUSSION

Preparation of HMnO(M)

The alkali metal contents of the alkali metal ion-introduced manganese oxides (MnO_x(M)) were 3.21, 1.29, and 1.44 meq/g for MnO_x(Li), MnO_x(Na), and MnO_x(K), respectively. The extractability of alkali metal ions from MnO_x(M) was examined by using nitric acid solutions with different concentrations. The fractions of alkali metal ions extracted from MnO_x(M) are plotted as a function of nitric acid concentration in Fig. 1. The extractability followed the order $K^+ < Na^+ < Li^+$. The lithium ion could be extracted to more than 90% at HNO_3 concentrations of only 0.01 *M*. On the other hand, the extractabilities of the sodium and potassium ions were 75 and 35%, respectively, even at an HNO_3 concentration of 10 *M*. From these results we carried out an acid treatment with a 1 *M* HNO_3 solution for MnO_x(Li) and 10 *M* HNO_3 solutions for MnO_x(Na) and MnO_x(K). The alkali metal ion contents of the products (HMnO(M))

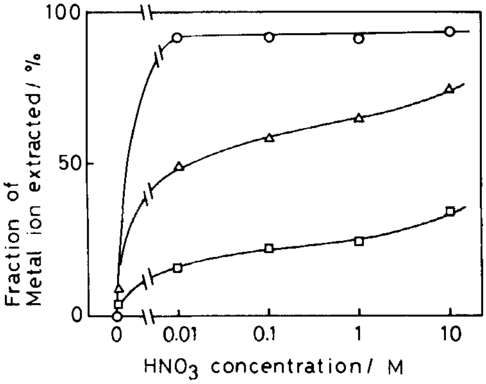

FIG. 1. Effect of HNO_3 concentration on the extractability of alkali metal ions. (○) Li^+-introduced manganese oxide, (△) Na^+-introduced manganese oxide, (□) K^+-introduced manganese oxide. Adsorbent: 50 mg. Total volume: 50 mL. 25°C.

were 0.03, 0.50, and 1.15 meq/g for HMnO(Li), HMnO(Na), and HMnO(K), respectively.

X-Ray Analysis

The x-ray diffraction patterns of HMnO(M) are given in Fig. 2. The diffraction peaks corresponding to $LiMn_2O_4$ (ASTM 18-736), $Na_2Mn_8O_{16}$ (ASTM 29-1244), and KMn_8O_{16} (ASTM 20-908) remained after acid treatments with HNO_3 solutions. This indicates that the $LiMn_2O_4$, $Na_2Mn_8O_{16}$, and KMn_8O_{16} structures, which were formed by the heat treatment, were scarcely damaged by the removal of alkali metal ions with acid. $LiMn_2O_4$ has a spinel structure with lithium at the tetrahedral sites and manganese(III) and manganese(IV) at the octahedral sites of a cubic close-packed oxygen framework (*24*). $Na_2Mn_8O_{16}$ and KMn_8O_{16} have a tetragonal structure with sodium and potassium in [2 × 2] tunnels of edge-shared $[MnO_6]$ octahedra (*25*). Therefore, micropores are formed at the tetrahedral sites of *ccp* oxygen in HMnO(Li), while there are [2 × 2] tunnels of $[MnO_6]$ octahedra in HMnO(Na) and HMnO(K). The weak peaks at 2θ = 22, 43, and 56° in Fig. 2 suggest the presence of small amounts of unreacted γ-MnO_2.

Selectivity of Alkali Metal Ions

The equilibrium K_d values of alkali metal ions on HMnO(M) are plotted as a function of solution pH in Fig. 3. The logarithms of the K_d

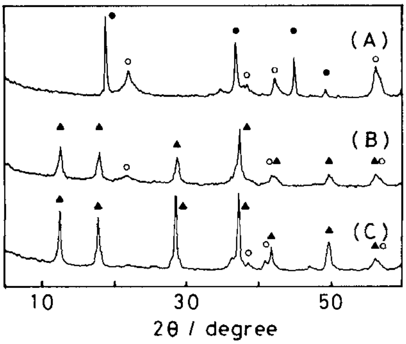

FIG. 2. X-ray diffraction patterns. (A), HMnO(Li); (B), HMnO(Na); (C) HMnO(K). (●) Peaks of $LiMn_2O_4$, (○) peaks of γ-MnO_2, (▲) peaks of $Na_2Mn_8O_{16}$ or KMn_8O_{16}.

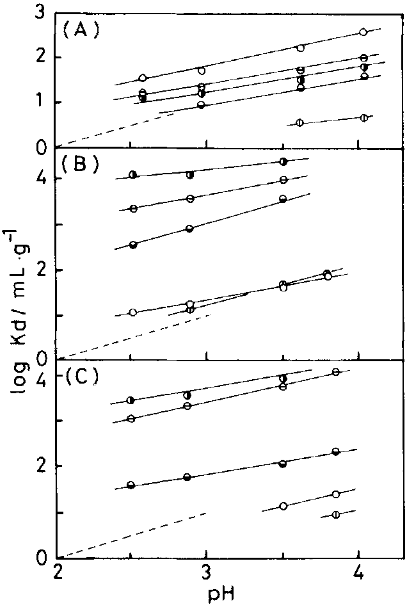

FIG. 3. Plots of log K_d against the solution pH. (A): HMnO(Li), (B): HMnO(Na), (C): HMnO(K). ○, Li^+; ⦶, Na^+; ⊖, K^+; ◐, Rb^+; ◒, Cs^+. Initial concentration of metal ions: 10^{-4} *M*. Total volume: 10 mL. Adsorbent: 0.1 g. 25°C. Dotted lines indicate straight lines of slope 1.

values linearly increased upon increasing the pH. However, the slopes of $d \log K_d/d$ pH were in most cases lower than that expected for an "ideal 1:1" ion-exchange reaction (slope = 1). We think that the deviation from a slope of 1 is due to the influence of self-dissociation of the protons on HMnO(Li) in the range above pH 3.

The equilibrium K_d values of alkali metal ions on HMnO(M) and γ-MnO_2 at pH 3.5 are plotted as a function of the ionic radius (*26*) of alkali metal in Fig. 4. HMnO(Li) showed a selectivity sequence of $Na^+ < Cs^+ < Rb^+ < K^+ < Li^+$. The highest selectivity for lithium ions can well be explained by the ion-sieve effect of spinel-type manganese oxide which was obtained from $LiMn_2O_4$. The selectivity sequence of the other alkali metal ions was the same as that on γ-MnO_2. Therefore, the relatively high selectivities of Rb and K may be due to the presence of γ-MnO_2 in HMnO(Li).

The γ-MnO_2 contained irregular intergrowths of pyrolusite [1 × 1] and ramsdellite [1 × 2] units (*25*), causing γ-MnO_2 to have extensive defects and vacancies. Since an alkali metal ion cannot enter the [1 × 1] and [1 ×

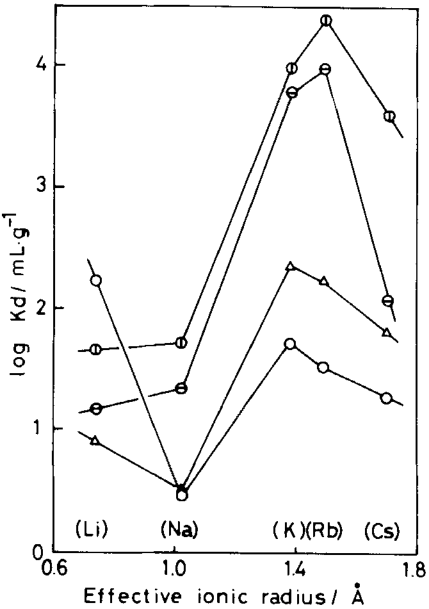

FIG. 4. Plots of log K_d at pH 3.5 against the effective ionic radius of an alkali metal ion. (○) HMnO(Li), (⦶) HMnO(Na), (⊖) HMnO(K), (△) γ-MnO_2.

2] tunnels, the selectivity on γ-MnO_2 may correspond to alkali metal ion exchanges at the defects and vacancies.

The selectivity sequences were the same ($Li^+ \approx Na^+ < Cs^+ < K^+ < Rb^+$) for both HMnO(Na) and HMnO(K). The K_d values were higher on HMnO(Na) than on HMnO(K) for all of the alkali metal ions. The larger K_d values on HMnO(Na) were due to the presence of stronger acid sites in HMnO(Na); this can be described in terms of the pH titration study mentioned below. The selectivity sequence agreed comparatively well with that on cryptomelane-type manganese oxide in a 0.1 *M* HNO_3 solution ($Li^+ < Na^+ < Cs^+ < K^+ < Rb^+$) (*7*). The cryptomelane-type manganese oxide also has [2 × 2] tunnels and has shown remarkably high selectivities for metal ions about 1.4 Å in ionic radius (K^+, Rb^+, and Ba^{2+}). From analogy with the cryptomelane-type manganese oxide, the remarkably high selectivities of Rb^+ and K^+ on HMnO(Na) and HMnO(K) can be explained by the fact that the [2 × 2] tunnels of edge-shared [MnO_6] octahedra are just suitable to make a stable fit of these ions. Cs^+ may suffer steric hindrance because of its larger ionic radius compared to the radius of the tunnels. Li^+ and Na^+ may be bound more weakly because of the shielding of electrostatic attraction due to the presence of water molecules between the cation and ion-exchange site.

The pH Titrations

The pH titration curves of HMnO(M) for (LiCl + LiOH) and (KCl + KOH) systems are given in Fig. 5. The adsorption sequence of alkali metal ions on HMnO(Li) was $K^+ < Li^+$ over the pH range studied; the lithium uptake was about 4 times larger than the potassium uptake. This indicates that HMnO(Li) has high lithium selective properties over the range from a microamount to a macroamount of ion exchange.

The pH titration curves of HMnO(Na) and HMnO(K) resembled each other. In both there were reversals of the adsorption sequence of alkali metal ions: $Li^+ < K^+$ below pH 7 while $K^+ < Li^+$ above pH 7. The higher selectivity for the lithium ion at pH > 7 may be due to lower steric repulsions among ion-exchanged lithium ions owing to the smaller ionic radius. The lithium ion uptakes at pH 10 were nearly the same (0.84 meq/g) for both HMnO(Na) and HMnO(K), while the uptake at pH 7 was 1.5

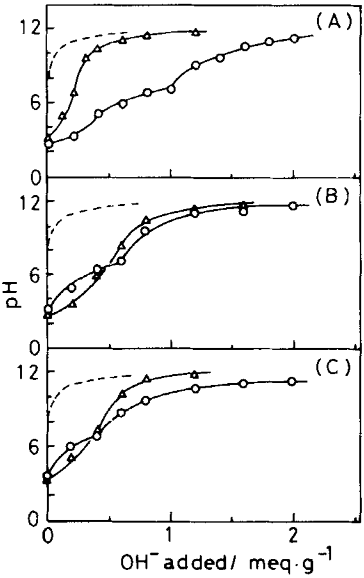

FIG. 5. pH titration curves. (A), HMnO(Li); (B), HMnO(Na); (C), HMnO(K). Solution: 0.1 *M* [MNO_3 + MOH], M = Li (O) or K (Δ). Adsorbent: 0.1 g. Total volume: 10 mL. 25°C. Dotted lines indicate blank titrations.

times larger on HMnO(Na) (0.60 meq/g) than on HMnO(K) (0.40 meq/g). This indicates that HMnO(Na) has a larger number of stronger acid sites than HMnO(K).

Adsorption from Seawater

The uptakes of alkali metal and alkaline earth metal ions from seawater are given for HMnO(M) in Table 1. The uptakes of rubidium and cesium ions were found to be below 1×10^{-3} meq/g for all of the samples. The metal ion uptake by HMnO(Li) followed the order $Sr^{2+} < K^+ < Mg^{2+} < Na^+ < Ca^{2+} < Li^+$. This is similar to that given in a previous paper (*23*). The lithium ion uptake was found to be slightly smaller in the present study. The difference in the lithium uptake might have been caused by a difference in the acid-treatment conditions during the preparation of the adsorbent. The total metal ion uptake (0.80 meq/g) was slightly smaller than the ion-exchange capacity of pH 8 (1.0 meq/g); this was evaluated from the pH titration data in the (LiCl + LiOH) system.

The uptakes of metal ions by HMnO(Na) and HMnO(K) followed the orders

$$Li^+ < Sr^{2+} < Mg^{2+} < Ca^{2+} < Na^+ < K^+ \text{ for HMnO(Na)}$$

TABLE 1
Enrichment of Elements in Seawater on HMnO(M)[a]

Element	Metal ion uptake (meq/g)		
	HMnO(Li)	HMnO(Na)	HMnO(K)
Li	0.425	0.003	<0.001
Na	0.099	0.165	0.160
K	0.043	0.252	0.102
Mg	0.082	0.090	0.096
Ca	0.146	0.148	0.094
Sr	0.006	0.008	0.004
Total	0.801	0.666	0.456

[a] Adsorption: 2 L of seawater per 50 mg at 25°C. Metal ion uptakes were calculated by subtracting the metal ion contents before adsorption experiment.

and

$$Li^+ < Sr^{2+} < Ca^{2+} < Mg^{2+} < K^+ < Na^+ \text{ for HMnO(K)}$$

It should be noticed that both HMnO(Na) and HMnO(K) do not adsorb rubidium ions from seawater in spite of the fact that they show the highest selectivities for rubidium ions among the alkali metal ions. Since the molar concentration of rubidium is 7000 times lower than that of potassium in seawater (C_K = 97.4 m*M*, C_{Rb} = 0.0014 m*M*), the ion-exchange sites for rubidium ions may be covered by potassium ions in seawater because of the low separation factor between them (α_K^{Rb} = 1.16 and 1.56 for HMnO(Na) and HMnO(K), respectively). The total uptakes by HMnO(Na) and HMnO(K) were calculated to be 0.666 and 0.456 meq/g, respectively; this agreed well with their ion-exchange capacities at pH 8 (0.68 and 0.50 meq/g for HMnO(Na) and HMnO(K), respectively).

Balistrieri et al. reported that the quantity of δ-MnO_2 sites bound by particular ions in seawater at pH 8 follows the order $K^+ < Na^+ < Ca^2 < Mg^{2+} \ll H^+$ (*14*). Compared with this result, HMnO(M) in the present study shows high selectivity for monovalent alkali metal ions.

CONCLUSION

The selectivity of ion-sieve-type manganese oxide is strongly dependent on the kind of metal ions introduced during its preparation. The difference in selectivity can be explained based on the difference in the size of the micropores or tunnels formed by the introduction/extraction reaction of the metal ion; their size varies depending on the kind of metal ions introduced.

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