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Uptake of Zinc Ion by Hydrous Manganese (IV) Oxide

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Synopsis. The uptake of zinc ion by hydrous manganese(IV) oxide in ammonium chloride solution containing zinc ion was investigated. The uptake of zinc ion was found to be proportional to the potassium content in the hydrous manganese(IV) oxide, the molar ratio of the sorbed Zn^{2+} to the released K^+ being *ca.* 1 : 2.

Adsorption studies of zinc ion on various kinds of anhydrous manganese(IV) oxides have been carried out in a 2 M[†] NH_4Cl solution containing zinc ion. An adsorption mechanism was postulated in order to explain the ion exchange reaction based on a surface chelation on the hydrated oxide.[1,2] Investigations have been carried out on the mode of metal adsorption by natural and synthetic manganese(IV) oxides as regards the characterization of oxides,[2,3] catalysis[4] and oceanology.[5] However, the effect of the chemical composition of manganese(IV) oxides on the mode of adsorption still remains unclarified.

Hydrous manganese(IV) oxide obtained by reduction and disproportionation of alkaline manganate(V), (VI), and (VII) solution usually contains a large amount of alkali and chemically bound water, exhibiting unusual properties differing a great deal from the anhydrous manganese(IV) oxides prepared by pyrolysis or oxidation of manganese(II) in acid solutions.[6]

In this study, the uptake of zinc ion by hydrous manganese(IV) oxide was investigated and the results were discussed in relation to the replacement of potassium ion present in the sorbent.

Experimental

The measurement of the uptake of zinc ion by hydrous manganese(IV) oxide was carried out in a way similar to that described by Kozawa.[1] The hydrous manganese(IV) oxide was dried by heating at 110 °C. 0.1 g of the sample was then added to 50 ml of zinc solution prepared by dissolving 0.01 M ZnO in 1.5 M NH_4Cl (pH 6.8). The hydrous manganese(IV) oxide suspended in an Erlenmeyer flask was stirred magnetically for 18 h at room temperature and then centrifuged. The supernatant layer was analyzed for zinc ion by titration. The uptake of zinc ion by the hydrous manganese(IV) oxide was calculated from the zinc ion concentrations in solution before and after the uptake was affected.

The preparation and characterization of the hydrous manganese(IV) oxide sample were the same as reported.[6]

Results and Discussion

The zinc ion uptake data and the chemical composition of hydrous manganese(IV) oxides are given in Table 1, together with those of manganese(IV) oxides of other types.

The uptake of zinc ion by typical amorphous and hydrous manganese(IV) oxides (Table 1, 1—4 and 7) was extremely high as compared to that of anhydrous manganese(IV) oxides (12—14). The hydrous manganese(IV) oxides prepared in a solution of high pH showed an approximately constant composition with the formula $K_2O \cdot 4MnO_2 \cdot 4H_2O$. Variation in chemical

TABLE 1. ZINC ION UPTAKE DATA AND CHEMICAL COMPOSITION OF THE MANGANESE (IV) OXIDES

No.	Preparation			Composition[a]				Zn^{2+} sorbed
	Procedure	pH	Temp °C	MnO_2 wt%	x in MnO_x	K_2O wt%	H_2O wt%	mol/g × 10^4
1	H_2O_2 reduction of $KMnO_4$ soln[b]	12.8	30	69.4	1.99	16.9	13.7	18.68
2	K_2SO_3 reduction of $KMnO_4$ soln[b]	12.6	50	68.2	1.98	18.4	13.4	20.39
3	KNO_2 reduction of $KMnO_4$ soln[b]	12.1	30	70.1	1.98	15.8	14.1	20.24
4	Disproportionation of K_2MnO_4 soln[b]	13.0	30	68.8	1.99	17.7	13.5	20.89
5	Disproportionation of K_2MnO_4 soln[b]	4.1	50	80.5	1.94	8.8	10.7	9.91
6	Disproportionation of K_2MnO_4 soln[b]	2.5	50	87.1	1.91	4.7	8.2	5.71
7	Disproportionation of K_3MnO_4 soln[c]	>13	50	66.1	2.01	19.2	14.8	21.74
8	2M HNO_3 treatment of sample No. 1	<1	30	87.9	1.89	4.0	8.1	5.76
9	Heating of sample No. 1	—	200	71.0	1.97	17.5	11.5	11.52
10	Heating of sample No. 1	—	300	73.8	1.94	17.7	8.0	6.71
11	Heating of sample No. 1	—	700	76.4	1.87	18.3	5.3	2.99
12	(α-MnO_2)			89.3	1.97	6.8	3.9	0.53
13	(β-MnO_2)			99.5	2.00	0	0.5	0.31
14	(γ-MnO_2)			97.8	1.97	0	2.2	1.69

a) The calculated chemical composition of the $K_2O \cdot 4MnO_2 \cdot 4H_2O$ formula is 18.3 K_2O, 67.7 MnO_2 and 14.0 H_2O(wt%), (1—8: amorphous, 9—11: tetramanganese dipotassium octaoxide[7]). b) The procedure is given in detail in a previous paper.[6] c) The reaction was performed by dilution of a (0.2M K_3MnO_4+10M KOH) solution with large amount of distilled water.

[†] 1 M=1 mol dm^{-3}.

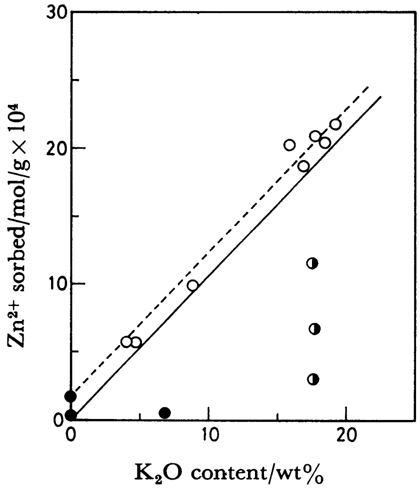

Fig. 1. Relationship between the uptake of Zn^{2+} and the K_2O content of MnO_2 substances.
○: Hydrous MnO_2 (Sample Nos. 1—10), ◑: Heated substances (Sample Nos. 9—11), ●: Crystalline MnO_2 (Sample Nos. 12—14). ——: (Zn^{2+} sorbed/K^+ content) m.r. = 0.5.

composition remarkably influenced the zinc ion uptake. For example, the reduction in the K_2O content in the hydrous manganese(IV) oxides prepared by disproportionation (5 and 6) and by acid treatment (8) gave rise to the reduction of the uptake capacity of zinc ion. Potassium in the hydrous manganese(IV) oxide is responsible for the zinc ion uptake. It seems that potassium ions are replaced by zinc ions *via* ion-exchange mechanism. After the uptake reaction, the hydrous manganese(IV) oxide was found to be free from potassium. Figure 1 shows a linear relation between the zinc uptake and the K_2O content in the hydrous manganese(IV) oxide samples. The molar ratio, sorbed Zn^{2+}/released K^+, is slightly higher than 0.5. This can be attributed to the coexistence of H^+ with K^+ on the surface of the hydrated manganese(IV) oxide. γ-MnO_2 contains only H^+ and no K^+ (14).

At pH 6.8, under which most of the Zn^{2+} uptake reactions took place, ammonium ion dominates according to

$$\frac{a_{NH_3}}{a_{NH_4^+}} = 10^{(pH-9.27)}$$

Under these conditions, we see that $(ZnCl_4)^{2-}$ is the most stable zinc ion. It seems that the tetrachlorozincate ion acts on the hydrous manganese(IV) oxide as a bindetate as in the case of a previous study[1] in which H^+ instead of K^+ was the major concern.

On heating, the hydrous manganese(IV) oxide gradually crystallized into tetramanganese dipotassium octaoxide,[7] $K_2Mn_4O_8$ (9—11). This caused decrease in the uptake capacity of zinc ion. The same trend was found in the case of α-MnO_2 (12), showing a low uptake capacity due to its high crystallinity.

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