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The Influence of Additives on the Decomposition of an Alkaline Manganate(VII) Solution

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Synopsis. The decomposition of manganate(VII) in an alkaline solution was significantly enhanced by the addition of hydrous manganese(IV) oxide or metal ions, such as Ni(II) and Co(II). On the other hand, the inhibitive effect of the tellurate(VI) ion on the decomposition was found even in the presence of the additives described above.

The decomposition of manganate(VII) in alkaline solutions, which yields manganate(VI) and oxygen, has been extensively studied and has been shown to be complex. It is well-known that the rate of the decomposition increases with increases in the temperature and alkali concentration.[1,2] In addition, some workers have shown that the decomposition is a function of the surface area of glass[1,3] and the presence of metal oxides, such as MnO_2, SnO_2, and PbO_2.[1,4] Till recently, it has been thought that the decomposition of manganate(VII) in alkaline solutions could be explained by the oxidation of the OH^- ion by manganate(VII) to $OH^{\cdot}$ radicals, which afterwards react to produce oxygen.[1,2,5] However, Vepřek-Šiška and Ettel[6] have recently shown that the kinetic analysis of the earlier workers is invalid because of the presence of traces of Ni(II) and Co(II) ions in the solution, those ions actively assist the decomposition.

Recently some new industrial techniques utilizing a high oxidation potential of manganates have been developed in the field of pollution control. The present authors have also developed the removal of nitrogen oxides from waste gas by using alkaline manganates(VI and VII) solutions.[7] In the course of this development, further information about the decomposition of alkaline manganate(VII) solution was necessary.

This study will deal with the stimulative effect of various kinds of hydrous manganese(IV) oxides (abbreviated as hydrous MnO_2) and of nickel and cobalt ions, and the inhibitive effect by the tellurate(VI) ion on the decomposition of manganate(VII) in an alkaline solution.

Experimental

A 0.5-dm^3 four-necked flask equipped with a reflux condenser, a thermometer, and a stirrer was used as the reaction vessel. Potassium hydroxide was dissolved in distilled water. Then, the concentrated solution of potassium manganate(VII) was added to the alkali solution and the total volume of the reaction solution was immediately adjusted to 200 cm^3 with distilled water. The additives, such as hydrous MnO_2 and metal sulfates, were added, together with distilled water, at the end. At all times the solution was vigorously stirred. The basic conditions were: $KMnO_4$; 0.05 mol dm^{-3}, KOH; 6 mol dm^{-3}, temperature; 80 °C. All the reagents used were commercial, extra pure reagents, and they were used without further purification. The decomposition of manganate(VII) was determined by pipetting 5 cm^3 of the reaction solution from the flask at regular time intervals, filtering out the insoluble matter, and chemically analyzing the manganates(VI and VII) in the filtrate.[8] The analysis of the chemical composition of the insoluble matter was done in the manner previously reported.[9] The amount of the tellurate(VI) ion adsorbed by the hydrous MnO_2 was calculated from the tellurate(VI) ion concentrations in the solution before and after the adsorption was affected. The tellurate(VI) ion was analyzed according to the method of Kishioka *et al.*[10]

Results and Discussion

Stimulative Effect of Hydrous MnO_2 and Ni(II), Co(II) Ions. The decomposition of manganate(VII) in alkaline solutions is well-known to be accelerated by the presence of manganese(IV) oxide, but there remains a lack of understanding of the relationship between this effect and the chemical composition of the manganese(IV) oxide. In this study, several kinds of hydrous MnO_2 (shown in Table 1) were prepared, and their stimulative effects on the decomposition (Eq. 1) were investigated by the addition of 0.05—0.06 g (5×10^{-4} mol Mn) of the hydrous MnO_2 to the alkaline manganate(VII) solution. The hydrous MnO_2 substances are amorphous, and their surface areas range from 140 to 160 $m^2\,g^{-1}$. The results given in Fig. 1 show that the stimulative effect of the hydrous MnO_2 increased with an increase in the content of MnO_2. That is, the hydrous MnO_2 with many manganese atoms on its surface became effective in stimulative action. The significant stimulative effect of the hydrous MnO_2 could be similarly explained by the electron-transfer mechanism proposed by Vepřek-Šiška and Ettel,[6] which was previously used to explain the stimulative effect of transition metal ions.

$$4MnO_4^- + 4OH^- = 4MnO_4^{2-} + O_2 + H_2O \qquad (1)$$

Figure 2 shows the stimulative effect of Ni(II) and Co(II) ions in concentrations of 2.5×10^{-3} mol dm^{-3}

TABLE 1. CHEMICAL COMPOSITION OF THE MANGANESE(IV) OXIDES USED IN THE EXPERIMENTS

MnO_2 sample No.	pH of formation	Composition			
		x in MnO_x	MnO_2 (wt%)	K_2O (wt%)	H_2O (wt%)
1[a]	8.1	2.00	68.4	16.4	15.2
2[a]	4.2	1.94	80.7	8.4	10.9
3[a]	3.2	1.92	83.2	7.7	9.1
4[b]	<1	1.90	86.5	5.2	8.3

a) Disproportionation of 0.6 mol dm^{-3} K_2MnO_4 solution by the addition of 1 mol dm^{-3} H_2SO_4. b) 0.5 mol dm^{-3} H_2SO_4 treatment of Sample No. 1.

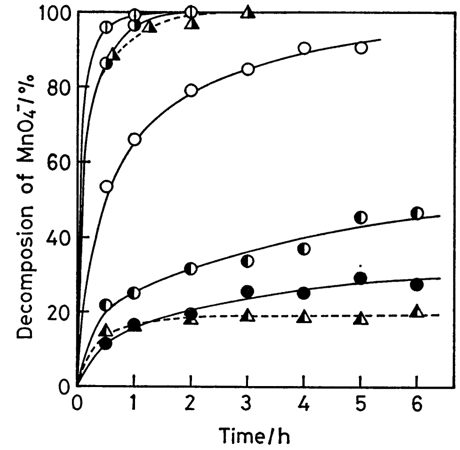

Fig. 1. Effect of several kinds of hydrous manganese (IV) oxides on the decomposition of manganate(VII).

MnO_2 sample No.	TeO_4^{2-} none	TeO_4^{2-} addition
none	●	—
1	◐	◭
2	○	—
3	◑	◮
4	⦶	—

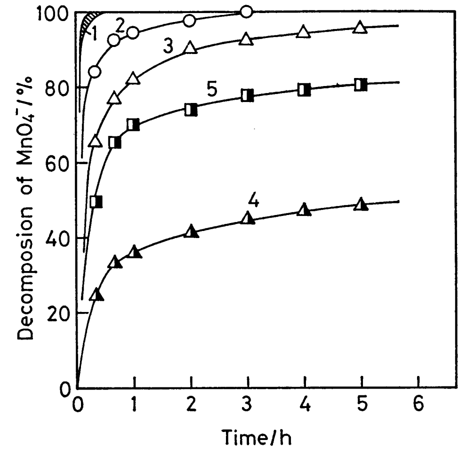

Fig. 2. Effect of metal ions on the decomposition of manganate(VII).
1: Ni^{2+}, Co^{2+}, oxides (Sample Nos. 1 and 3 in Table 1), 2: $Ni(OH)_2$, 3: Ni^{2+} and TeO_4^{2-},
4: Ni^{2+}, 5: Co^{2+} } MnO_4^- was finally added after sufficient mixing of hydroxide suspension containing TeO_4^{2-}.

on the decomposition. It was found that the decomposition was markedly accelarated by the addition of these ions; this agreed well with the result obtained by Veprek-Šiška and Ettel.[6] Therefore, the resulting precipitates obtained after the decomposition was analyzed here. The results indicate these precipitates were peroxides with a higher oxidation state than trivalent, having potassium and chemically bonded water (*e.g.*, $0.17K_2O \cdot NiO_{1.98} \cdot 2.30H_2O$; $0.04K_2O \cdot CoO_{1.71} \cdot 1.45H_2O$).

Inhibitive Effect of the Tellurate(VI) Ion. According to Issa *et al.*,[11] the inhibitive effect of the tellurate(VI) ion could be explained by the mechanism that the manganese(IV) ion formed by the decomposition of manganate(VII) forms a complex with the tellurate(VI) ion prior to precipitation as MnO_2 and before the stimulation action becomes effective. On the other hand, another mechanism, in which the inhibitive effect is caused by the adsorption of the tellurate(VI) ion on the surface of the metal oxide originating from the impurities in the reagent and on the reaction vessel wall, was also observed in this preliminary experiment.

Figure 1 shows the inhibitive effect of the tellurate(VI) ion on the decomposition in the presence of the hydrous MnO_2 (1 and 3). It was found that the tellurate(VI) ion exhibited a remarkable inhibitive effect on the hydrous MnO_2(1), but not on the hydrous MnO_2(3). The adsorption data of the tellurate(VI) ion on the hydrous MnO_2 obtained under the same conditions as that of the decomposition except that no manganate(VII) ion was present were as follows: hydrous MnO_2(1)—3.85×10^{-4}, (3)—1.96×10^{-4} mol Te(VI) adsorbed/g. The results show that the hydrous MnO_2(1), with a large amount of potassium, adsorbed more of the tellurate(VI) ion than did the hydrous MnO_2(3).[12] This tendency was correlated to the results of the decomposition experiments. These results indicate that the tellurate(VI) ion becomes effectively inhibiting by its adsorption on the surface of the hydrous MnO_2.

Figure 2 shows the similar inhibitive effect of the tellurate(VI) ion on the decomposition in the presence of Ni(II) and Co(II) ions. On changing the addition order of the reagents, namely, by adding the manganate(VII) after a sufficient contact of Ni(II) and Co(II) hydroxides with the tellurate(VI) solution, the inhibitive effect remarkably increased. The inhibitive effect of the tellurate(VI) ion in the presence of the cobalt precipitate was smaller than that in the presence of the nickel precipitate. It was thought to depend upon the small content of potassium in the cobalt precipitate, which caused the less adsorption of the tellurate(VI) ion on it.

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