

Study of Mn^{2+} and MnO_4^- products interaction in alkaline solution

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Interaction of Mn^{2+} ions with MnO_4^- in alkaline medium is considered. The main component of this interaction is manganese oxyhydroxide $MnO(OH)$ and not manganese dioxide, that is revealed by means of X-ray diffraction analysis, IR-spectrometry and chemical analysis. It is demonstrated that decomposition of $MnO(OH)$ occurs in the wide temperature range (60–550°C), that results in mixture of Mn_2O_3 and MnO_2 oxides formation.

Keywords: manganese (III) oxyhydroxide, synthesis, decomposition.

Рассмотрено взаимодействие ионов Mn^{2+} с MnO_4^- в щелочной среде. По результатам РСА, ИК-спектроскопии и химического анализа установлено, что в качестве основного компонента образуется оксигидроксид марганца $MnO(OH)$, а не диоксид марганца. Показано, что разложение $MnO(OH)$ происходит в широком интервале температур (60–550°C), в результате которого образуется смесь оксидов Mn_2O_3 и MnO_2 .

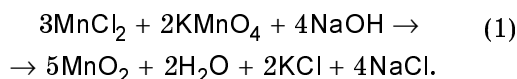
Дослідження продуктів взаємодії Mn^{2+} та MnO_4^- у лужному середовищі. *Д.С.Софронів, О.М.Одноволова, С.М.Десенко, Л.В.Гудзенко, П.В.Матейченко, Л.В.Руденко, О.М.Лебединський.*

Розглянуто взаємодію іонів Mn^{2+} та MnO_4^- у лужному середовищі. За результатами РСА, ІК-спектроскопії й хімічного аналізу встановлено, що в якості основного компонента утворюється оксигідроксид марганцю $MnO(OH)$, а не диоксид марганцю. Показано, що розкладання відбувається у широкому інтервалі температур (60–550°C), у результаті якого утворюється суміш оксидів Mn_2O_3 та MnO_2 .

1. Introduction

Oxides of manganese are of interest for use as a sorption material for extracting radionuclides and heavy metal ions from aqueous solutions. The interaction of Mn^{2+} and MnO_4^- ions in alkaline medium accord-

ing to reaction 1 [1] is a well known and simple method for obtaining of manganese dioxide from aqueous solutions:



Various authors have obtained particles with different morphological characteristics according to this reaction, and, as is known, functional properties of materials are largely determined by size and shape of the particles. Thus, particles of δ - MnO_2 were obtained with specific surface of $273.5 \text{ m}^2 \cdot \text{g}^{-1}$ and an average size of 450 nm [2]. The authors [3] have obtained α - MnO_2 particles in the form of needles with the size less than 100 nm. However, the similar reaction is used for birnesite production [4], mineral in which manganese enters in two forms — (III) and (IV). The data given in [5] also indicate the formation of a mixture of manganese oxides.

Particles obtained by such method in [1] were spherical from 0.1 to 1 μm in diameter with specific surface area $73 \text{ m}^2 \cdot \text{g}^{-1}$. One month later the specific surface area of these particles became $49 \text{ m}^2 \cdot \text{g}^{-1}$ but identification of the product obtained in this work was not carried out and it was preliminary called — MnO_2 .

However, it was found in [6] that mixture of compounds is formed during the obtaining of MnO_2 particles process according to reaction 1. This mixture includes Mn (III) as the main substance (36–40 wt.% in terms of Mn_2O_3), Mn (IV) (no more than 7 wt.% in terms of MnO_2), and Mn (II) (no more than 2 wt.% in terms of MnO). These values do not correspond to the literature data according to which MnO_2 can be formed. According to the IR spectrometric analysis data, only absorption bands at 443 and 505 cm^{-1} were disclosed in these samples obtained [7]. These absorption bands correspond to the Mn–O bond vibrations in $MnO(OH)$.

Results of sorption properties of $MnO(OH)$ particles study showed that they can extract cerium, europium, copper with the high efficiency (more than 95 %) in a wide range of pH 4–9. Moreover, these $MnO(OH)$ particles possess sorption capacity to cerium, europium, strontium and cobalt — 100, 50, 45 and 20 mg/g at pH 5.0 (for cobalt pH is 6.5), respectively. Thus, the study of interaction process of Mn^{2+} and MnO_4^- ions in alkaline medium and the interaction products identification is of interest to practical and scientific purposes.

Thereby, the detail study of products of interaction of Mn^{2+} and MnO_4^- ions in alkaline medium is an aim of the current paper.

2. Experimental

Materials. $MnCl_2 \cdot 4H_2O$, $KMnO_4$ produced by Merck (Germany) were used in the work. Sodium hydroxide was supplied by Reachim. All used reagents had chemically pure qualification. Distilled water was used to prepare the solutions.

Equipments. Crystal structure of the synthesized powders was determined by X-ray diffraction in the Bragg-Brentano geometry (graphite monochromator on the primary beam, $CuK\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$)). IR spectra were taken on Perkin Elmer Spectrum One Fourier transform IR spectrophotometer using samples pressed with KBr. Manganese content measurements in solutions after separation of various forms were carried out with atomic absorption spectrometer ICE 3500 (Thermo Scientific, USA) [8]. Thermal analysis was performed with a Q-1500D derivatograph. α - Al_2O_3 powder was used as a reference material.

Particle Preparation. Interaction of manganese chloride (II) with potassium permanganate in alkaline medium was carried out according to the following procedure [2]: 2.40 g of NaOH were added to 37.5 ml of 0.8 M $KMnO_4$ solution, and then 37.5 ml of a 1.2 M $MnCl_2$ solution was added dropwise with the constant stirring. The components molar ratio of the reaction mixture $KMnO_4$, NaOH and $MnCl_2$ is 2: 4: 3, respectively. Precipitation was carried out under temperatures 20, 60 and 80°C ($\pm 2^\circ\text{C}$). The resulting mixture was stirred on a magnetic stirrer during 60 min under the predetermined temperature. After that the precipitate obtained was filtered out, then it was washed several times with distilled water and dried under the room temperature during 24 h.

Determination of manganese content and its valence state in powders. The chemical phase analysis method was used to determine the manganese content and its valence state in the synthesized samples. This method is based on sequential processing of an analyzed material sample with solvents. Each of solvents can transfer only one of element forms into solution. MnO is soluble in ammonium salts unlike other manganese oxides. $Mn(II)$ extraction was performed with solution under 70 – 80°C during 1–1.5 h. The solution containing manganese (II) was separated from powder by centrifugation. Trivalent manganese was separated using its property to form metaphosphoric acid complex with metaphosphoric acid.

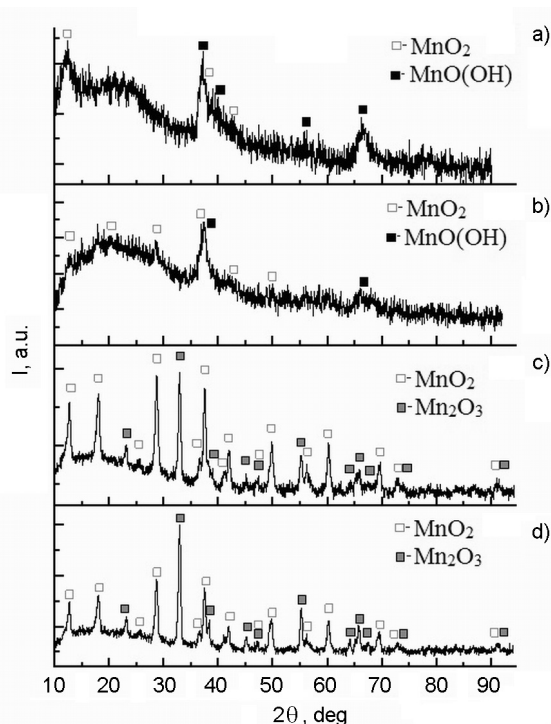


Fig. 1. X-ray diffraction patterns of synthesized powders samples: a) deposited at $T = 80^{\circ}\text{C}$; b) annealed under $T = 300^{\circ}\text{C}$ during 1 h; c) annealed under $T = 400^{\circ}\text{C}$ during 1 h; d) annealed under $T = 700^{\circ}\text{C}$ during 1 h.

This complex is stable in sulfuric acid solutions [9]. The content of total manganese amount in the samples obtained was determined after their complete dissolution in aqueous solution of oxalic and sulfuric acids mixture.

3. Results and discussion

Powders of brown color were obtained as a result of synthesis. Color of the samples obtained suggests the presence of manganese oxide (IV), regardless of the deposition temperature.

X-ray diffraction pattern of the powders obtained at 80°C is shown in Fig. 1. The X-ray diffraction patterns of the powders synthesized in this work under different temperatures are similar. As follows from Fig. 1a manganese oxyhydroxide $MnO(OH)$ and manganese dioxide (IV) MnO_2 are present in the powders obtained. Absorption bands at 443 and 505 cm^{-1} are observed in IR-spectra of the powders (Fig. 2a). These bands are corresponding to vibrations of $Mn-O$ bond in $MnO(OH)$ [7]. The absorption bands in $3000-3600\text{ cm}^{-1}$ region with a maximum at 3400 cm^{-1} and absorption

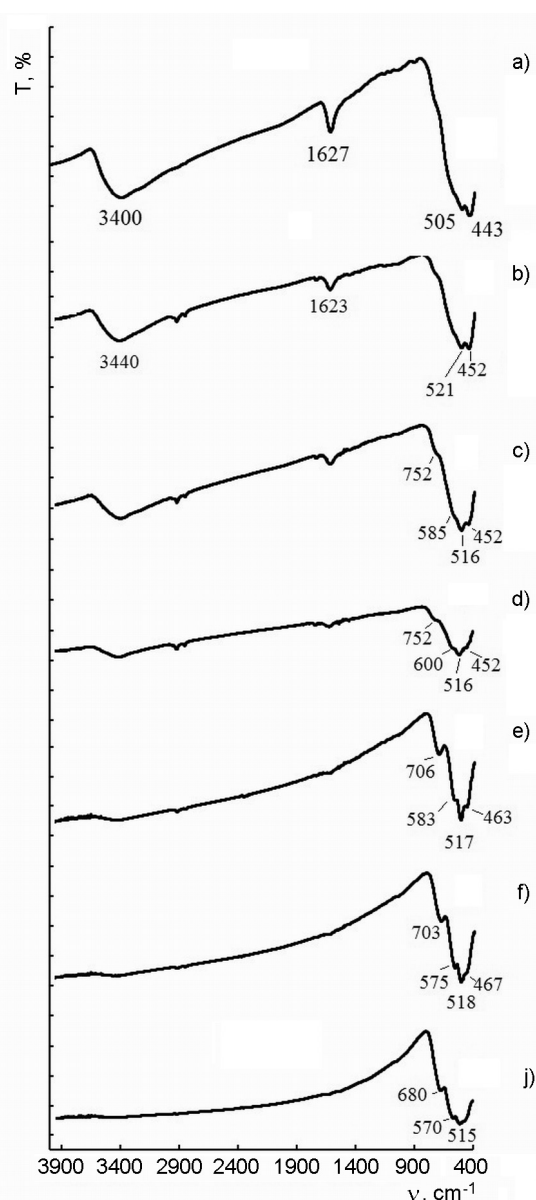


Fig. 2. IR-spectra of samples: a) deposited at 20°C ; annealed under 100 (b), 200 (b), 300 (d), 400 (e), 500 (f) and 700°C (g) during 1 h.

band at 1627 cm^{-1} are associated with valence and deformation vibrations of water molecules adsorbed on surface of the fine-dispersed particles, respectively [10, 11].

Results of content determination of manganese various forms in the synthesized samples are presented in Table 1 ($V_{total} = 75\text{ ml}$; $T_{syn} = 20^{\circ}\text{C}$ (No. 1), and $T_{syn} = 80^{\circ}\text{C}$ (No. 2)). $Mn(III)$ (37–40 % by weight) is mainly present in the samples obtained, and also $Mn(II)$ and $Mn(IV)$ appear in a small amount (not more than 2 % and 3 % by weight, respectively) according to the chemical analysis results.

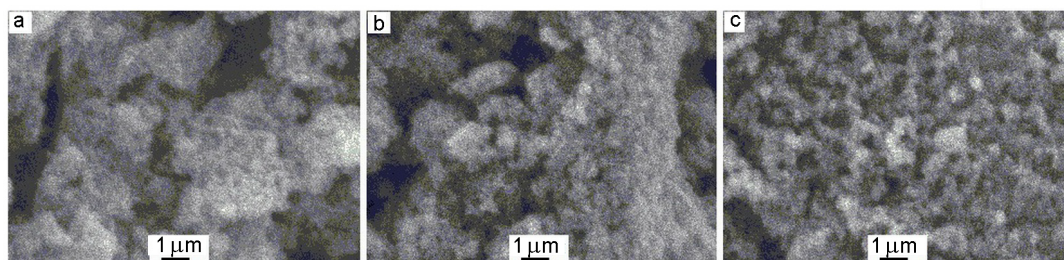


Fig. 3. Micrograph of particles deposited under different temperatures: a — 20°C; b — 60°C; c — 80°C.

Table 1. Results of determination of manganese disparate forms content in the synthesized samples

No.	$T_{\text{synthesis}}, ^\circ\text{C}$	Content, %		
		Mn(II)	Mn(III)	Mn(IV)
1	20	1.8	39.5	44.0 (2.7)
2	80	0.9	37.5	41.0 (2.6)

Microphotographs of the particles obtained are shown in Fig. 3. As follows from Fig. 3, the powders are formed by spherical particles with dimensions less than 150 nm, which possess tendency to agglomeration. According to the data obtained the shape and size of synthesized particles are stable but the size of the agglomerates is changed with synthesis temperature raise. For example the agglomerate size varies in the range from 0.5 to 5 μm at deposition temperature of 20°C, and at 80°C it varies from 4 to 50 μm . Such agglomeration of the particles may result in substantial change in the material specific surface when it used as a sorbent. This can affect its absorption properties deeply.

The powders obtained were thermally annealed in air. X-ray diffraction patterns of annealed powders are shown in Fig. 1b–d. According to X-ray data the powders annealing in air under temperature $\leq 300^\circ\text{C}$ does not lead to a noticeable change in the diffraction pattern Fig. 1a,b (X-ray diffraction patterns of the powders annealed under 100°C and 200°C are not depicted in Fig. 1 in consequence of their identity to the diffraction patterns of the original samples). The samples annealing under temperatures $\geq 400^\circ\text{C}$ leads to disappearance of reflexes from manganese oxyhydroxide MnO(OH) and appearance of reflections from of manganese (III) oxide Mn₂O₃ crystallographic planes (Fig. 1d).

The results of chemical analysis of the annealed sample No. 2 (Table 1) are shown

Table 2. Results of determination of manganese various forms content during annealing of the powder obtained by precipitation under 80°C

$T, ^\circ\text{C}$	Content, %		
	Mn(II)	Mn(III)	Mn(IV)
100	1.2	37.5	48 (9.3)
200	2.2	37.5	51.5 (11.8)
300	2.5	26	55 (26.5)
400	2.2	24	60 (33.8)
500	6.4	20.5	61.5 (34.6)
700	6.8	25	63.5 (31.7)

in Table 2. As follows from the data obtained, during the annealing under temperature $\leq 200^\circ\text{C}$ the Mn(III) content in the sample remains constant, but the total manganese content increases. The total content of manganese in the sample is increased in the whole temperature range (100–700°C) at the same time. The heating above 300°C results in the Mn(III) content significant decrease (up to 20 % wt. under 500°C), and to the Mn(II) content increase (up to 6.4 wt.%). The Mn(III) content increasing is observed for the sample annealed under 700°C.

The IR-spectra of powders annealed under different temperatures are shown in Fig. 2. The IR-spectra of powders annealed under temperature 100–300°C (Fig. 2b–d) are practically identical. The weak absorption bands in the form of a shoulder at 752 and 585 cm^{-1} , as well as absorption bands at 516 and 453 cm^{-1} can be observed in these spectra. The absorption band at 453 cm^{-1} is attributed to Mn–O bond in MnOH. The absorption band at 516 cm^{-1} is typical for Mn–O bond vibrations in Mn₂O₃ [12], and the absorption band at 585 cm^{-1} is associated with Mn–O bond vibrations in Mn₂O₃ or MnO₂ [12–14]. The absorption band at 752 cm^{-1} is also probably conse-

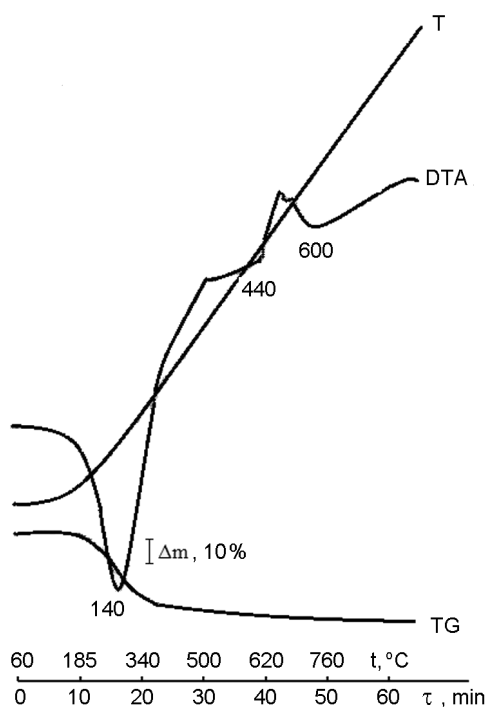


Fig. 4. Derivatogram of a dried sample of a the powder deposited from a manganese solution under $T = 80^\circ\text{C}$.

quence of Mn–O bond oscillation. The absorption bands at 706–703, 585, 516, and 463 cm^{-1} are appeared in the IR-spectra during annealing temperature raising up to 400–500°C. The absorption band at 706–703 cm^{-1} can be attributed to Mn–O bond oscillation in MnO_2 [14]. It can be noted that intensity of the absorption band at 463 cm^{-1} decreases and this band appears in the IR spectrum of the sample annealed under 500°C in the shoulder form. The absorption band of 463 cm^{-1} which is characteristic for the Mn–O bond in MnOH is absent in the IR-spectra of the samples annealed under 700°C (Fig. 2g). As it can be seen, the absorption bands at 680, 570, and 515 cm^{-1} are only present in such IR-spectra (Fig. 2g). The absorption band at 680 cm^{-1} is associated with Mn–O oscillations in MnO_2 [15], and the absorption band at 570 cm^{-1} can be attributed to Mn–O bond vibration in Mn_2O_3 or MnO_2 .

The results of thermogravimetric analysis of the samples are shown in Fig. 4. The main mass loss (24 wt.%) is observed at 140°C maximum in the temperature range of 60–350°C. The mass loss can be caused by either adsorbed water removal from the particles surface directly or partial decomposition of manganese oxyhydroxide according to reactions 2 and 3 [16]:

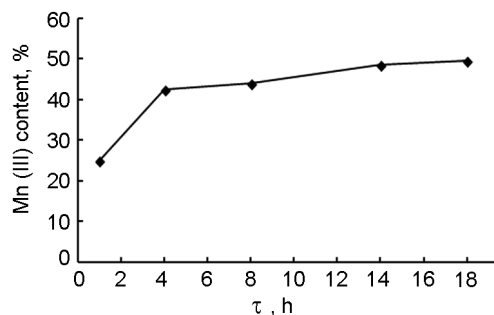
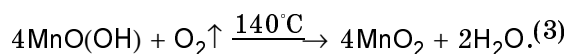
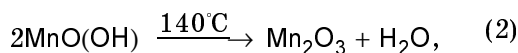


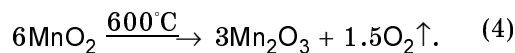
Fig. 5. Mn(III) content dependence on the heat treatment time.



Thus, according to the chemical analysis data (Table 2) a significant increase in the total manganese content was observed during annealing in the temperature range of 100–200°C, on the one hand. It can be a result of adsorbed water removal. And on the other hand, Mn(IV) content increase in the samples took place too, that was connected with reaction 3. As a result, the absorption bands at 752 and 585 cm^{-1} are observed in the IR-spectra of samples annealed at 200°C (Fig. 2c).

The appearance of absorption band peaked at 516 cm^{-1} in the IR-spectra points to reaction 2. A gradual loss of the sample mass is recorded on the curve of thermogravimetric analysis during the temperature increase more than 200°C. There is a thermal peak with a maximum at 440°C in the temperature range of 350–550°C (4 wt.% loss) in the DTA curve, which is associated with the decomposition continuation of manganese oxyhydroxide according to reaction 3.

Moreover, according to the chemical analysis data (Table 2), Mn(IV) content increasing is observed, and intensification of the absorption bands at 703 and 575 cm^{-1} are recorded in the IR-spectra. 453 cm^{-1} absorption band associated with the vibrations of Mn–O bond in $\text{MnO}(\text{OH})$ is attenuated at the same time. The thermal peak with a maximum at 600°C in the temperature region of 550–800°C (the mass loss of 2 %) caused by manganese dioxide decomposition according to the following reaction 4:



This reaction leads to Mn(III) content increase in the samples. However, there is no transition of Mn(IV) total amount to Mn(III) even after heating during 18 h (Fig. 5).

Thus, MnO(OH) is the main product of Mn²⁺ and MnO₄²⁻ interaction in the alkaline medium. MnO(OH) decomposition leads to formation of Mn₂O₃ and MnO₂ oxides mixture.

4. Conclusions

Interaction of Mn²⁺ ions with MnO₄²⁻ in alkaline medium has been studied. It has been ascertained that manganese oxyhydroxide MnO(OH) is the main component of this interaction. It was found that the thermal decomposition of MnO(OH) occurs in several stages. The first stage is situated in the temperature range of 60–350°C with a maximum at 140°C, where adsorbed water is removed from the particle surface and partial oxidation of manganese oxyhydroxide accompanied by MnO₂ formation takes place. The temperature region of 350–550°C is the second stage, where the final oxidation of MnO(OH) to manganese dioxide occurs. Subsequent heating above 600°C results in the decomposition of manganese dioxide to Mn₂O₃.

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