Adsorption and protolytic properties of nanocryptomelane and its activity in ozone decomposition reaction

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Introduction

Activity of polymorphic nanooxide forms of manganese(IV) in ozone decomposition reaction significantly depends on relative humidity of ozone–air mixture and residual content of hydrogen ions on the samples' surface. The influence of these two factors on the catalytic properties of manganese nanooxides is practically not discussed in the literature.

The hydration of hard surfaces of various functional materials is accompanied by protolysis of water molecules, the mechanism of which is determined by the nature of surface centers. Acid and basic centers of Lewis and Bronsted enhance the development of mechanisms of protolysis of water molecules:

protolysis at the main center of Lewis.

$$MO^- + HOH \leftrightarrow MOH + OH^-, \quad (1)$$

protolysis at the Lewis acid center

$$M^+ + HOH \leftrightarrow MOH + H^+, \quad (2)$$

protolysis at the Bronsted acid center

$$M\text{–}OH + HOH \leftrightarrow MOH_2^+ + OH^-. \quad (3)$$

Together with reactions (1)–(3) it is necessary to take into account the dissociation of surface groups:

$$MOH + H_2O \leftrightarrow MO^- + H_3O^+, \quad (4)$$

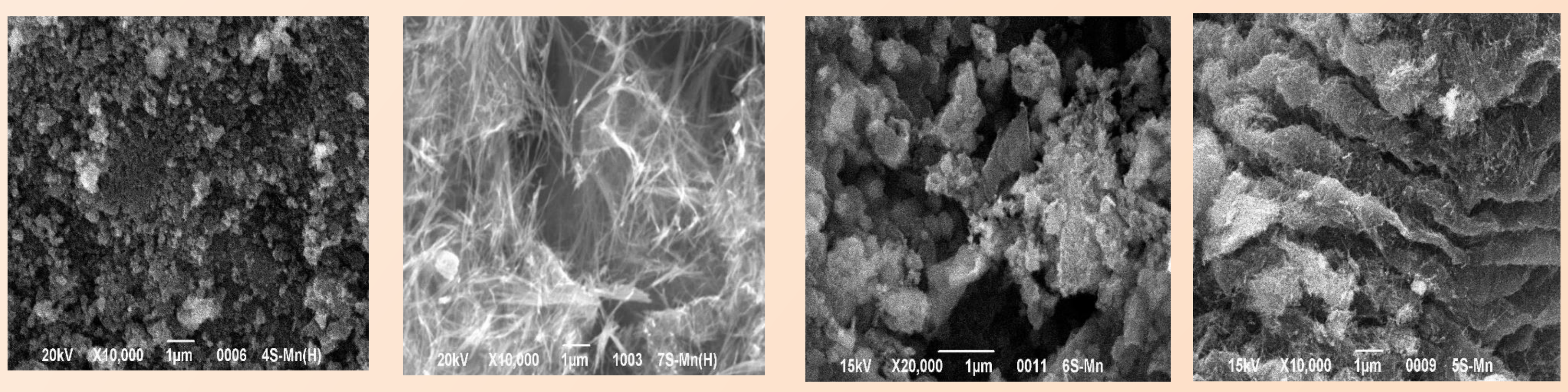
$$MOH_2^+ + H_2O \leftrightarrow MOH + H_3O^+, \quad (5)$$

Characterization

All the samples were characterized by XRD method, SEM, FT-IR spectroscopy.

Morphology

SEM images of surfaces of the synthesized OMS-2 samples indicate some morphological differences.



I II III IV

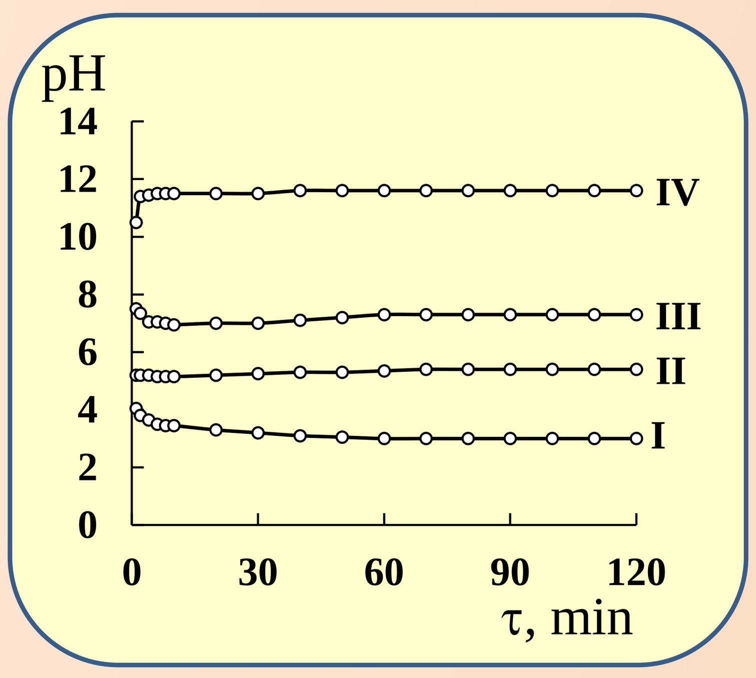
Protolytic properties

The protolytic properties of natural materials and transition metal oxides were investigated by pH metering by measuring the pH of an aqueous suspension. The value of the suspension effect (ΔpH_s) was calculated by the equation:

$$\Delta pH_s = pH_{st} - pH_0,$$

where pH_0, pH_{st} – the pH of the suspension, which was measured after 15 s and after reaching equilibrium, respectively.

We studied the protolytic (pH_s) and adsorption properties of these samples in relation to water vapor. Based on isotherms of water vapor adsorption by above cryptomelane samples at a constant adsorption value a = 2.0 mmol/g the thermodynamic activity of adsorbed water $a_{H_2O} = P/P_s$ and pH values were determined. These values depend significantly on the origin of cryptomelane (method of synthesis). So the pH_s values increases in a row **I < II < III < IV**, and corresponding a_{H2O} values are in the range of 0.76-0.92.



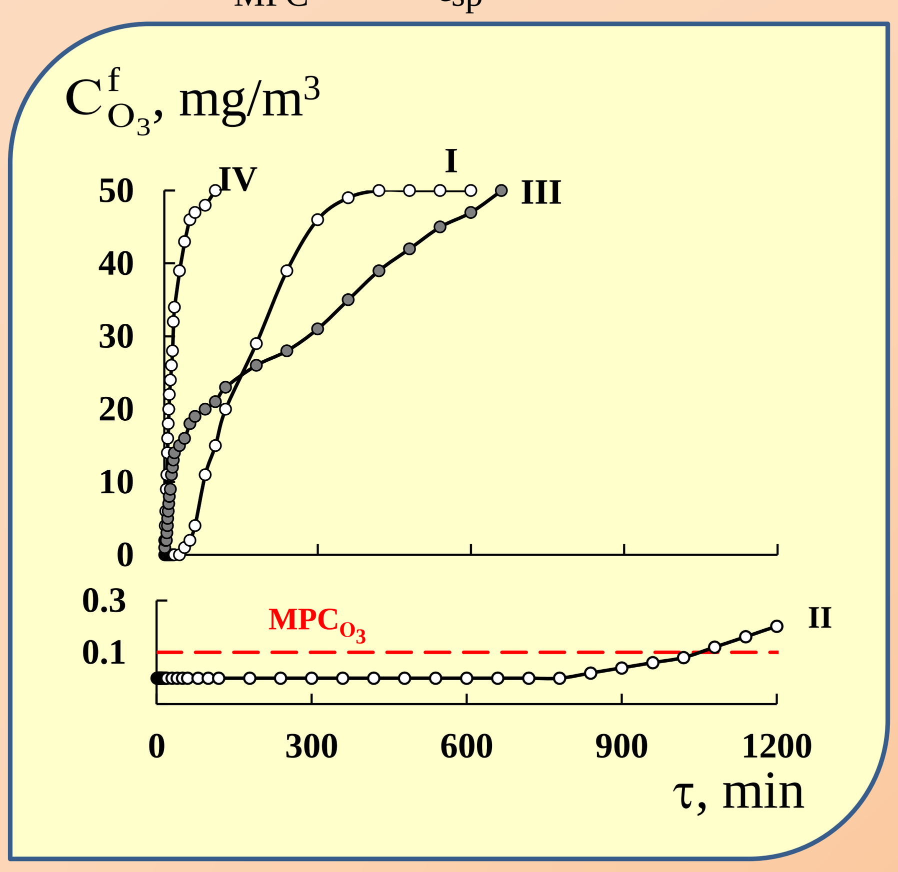
Sample	pH_0	pH_{st}	ΔpH_s	$a_{H_2O} = P/P_s$
I	4.05	3.05	-1.0	0.76
II	5.20	5.40	0.2	0.82
III	7.50	7.30	-0.2	0.92
IV	10.50	11.60	1.1	0.79

Cryptomelane (OMS-2) synthesis:

$$KMnO_4 + \left[\begin{array}{l} MnSO_4 + H_2O \\ 2KNO_3 + MnSO_4 \\ H_4C_4O_4 + H_2O \\ Mn(CH_3COO)_2 + H_2O \end{array}\right] \rightarrow \text{OMS-2} \quad \begin{array}{l} (I) \\ (II) \\ (III) \\ (IV) \end{array}$$

Catalytic properties

The activity of these samples in ozone decomposition reaction was characterized using two parameters: τ_{MPC} (time of protective action) and Q_{sp} (specific amount of ozone, which decomposed into half-life of ozone). The combined effect of the activity of water and hydrogen ions on the τ_{MPC} and Q_{sp} values was estimated using the values of the GTP = $\lg a_{H_2O}/a_{H_3O^+}$ (table). It was found that sample **II** with GTP = 5.40 is characterized by the maximum values of τ_{MPC} and Q_{sp}.



Time dependence of $C^f_{O_3}$ in the course of ozone decomposition by samples of manganese dioxide synthesized by different methods: reflux method (**I**), melting together (**II**), sol-gel method (**III**), solid-phase reaction (**IV**)

Characteristics of nanocryptomelan samples and their activity in ozone decomposition reaction

Sample	I	II	III	IV
GTP	2.87	5.40	7.10	11.50
$Q_{sp} \cdot 10^3$, moles of O_3/g	2.20	4.86	1.73	0.22
τ_{MPC}, min	30	1055	1	1