Investigation of the Surface of Mechanically Activated Manganese Oxides

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Abstract

The surface of oxides Mn_3O_4, Mn_2O_3 and MnO_2 subjected to mechanical activation with the help of high-intensity grinding was studied by means of X-ray photoelectron spectroscopy. It was discovered that the surface layers of all the three oxides were transformed during mechanical activation into Mn_2O_3 possessing increased chemical stability against environmental action. The results are due to the thermal effect and the catalytic action of extrinsic iron in the surface layer of Mn_mO_n particles.

Key words: mechanical activation, manganese oxides, surface, X-ray photoelectron spectroscopy

INTRODUCTION

During the recent years, intense search for the catalysts of deep oxidation is carried out for the purpose of maintaining the acceptable level of atmospheric pollution. One of the pretenders for the role of such a catalyst is the oxide Mn_2O_3 [1]. Tests showed that this oxide is able to work as a catalyst for a series of technologically and industrially important oxidation reactions [2−5]. Along with this, the oxide possesses high thermal stability (up to 1223 K) [6], and the composition of its surface is close to the volume composition [7]. The most important characteristic of the catalytic surface is the presence of electrophilic oxygen forms on it (O_2^{x-}, O^-) − the most reactive forms in deep oxidation processes [8, 9]. It is assumed that these forms exist on the surface of Mn_2O_3 [10].

For the directed action on the properties of oxide materials, promising methods are those involving their treatment with different fields. Previously we demonstrated for manganese compounds as example [11] that modification of the structure and properties of the surface of these materials can be achieved by means of mechanical activation. In particular, the surface of all mechanically activated compounds is characterized by improved diffusion characteristics. Mechanically activated $LaMnO_3$ powder possesses high stability to the action of atmospheric moisture. Along with this, more information of the systematic character is necessary to evaluate the consequences of such treatment.

The goal of the present work was to study the surface of mechanically activated Mn_mO_n oxides by means of X-ray photoelectron spectroscopy (XPES) in order to reveal the nature of effects accompanying mechanical treatment of oxides, and to determine the efficiency of mechanical treatment for the use of manganese oxides in catalysis.

EXPERIMENTAL

Sample preparation

Initial powders of Mn oxides were obtained from MnO_2 of kh. ch. reagent grade through annealing at a temperature of 823 (MnO_2), 1173 (Mn_2O_3) and 1523 K (Mn_3O_4) for 24 h. The X-ray phase analysis (D8 Advance diffractometer, Bruker, Germany) confirmed the single-phase content of the corresponding oxides. The crystallite size, measured with the help of the DelsaNanoC lase analyser (Beckman, Germany) was 1 μm as an average.

Mechanical activation of initial powders was carried out by means of dry grinding in AGO-2 planetary ball mill under the load of 60g. Steel balls were used as milling bodies. Each powder portion was ground in two stages; each lasting for 30 s. Additional protion of Mn_2O_3 material was subjected to grinding 20 times for 30 s each time. The average particle size of the resulting powders was 0.3–0.5 μm. To evaluate chemical stability under natural conditions, all the powders (initial and activated samples) were kept in the air at a temperature of (298±2) K and relative humidity 30–35 % for 2 months before experiments.

Investigation methods

Electron photoemission studies of Mn_nO_m oxides were carried out with the help of the Multiprob spectrometric unit (Omicron, Germany) using the exciting X-ray radiation MgK_α (in some cases AlK_α). The accuracy of bond energy determination in XPES experiments was 0.1 eV. To plot the profile of element concentra-tions over the depth of the material under investigation, we used surface etching with the beam of Ar^+ ions with the energy of 5 keV. The electron current strength was 5 μA; etching time was 70 min (a layer about 10 nm thick was removed from the oxide surface during this time).

Investigation of manganese oxides with the help of XPES first of all allows one to obtain the data on the chemical state of Mn ions; for this purpose, several approaches were tested. In [12], for many compounds and solid solutions of manganese, it was demonstrated that there is almost linear connection between the valence state of manganese and the exchange splitting of its 3s level, Δ(3s). In other works [13−16], in order to determine the valence state of manganese in simple oxides, the authors relied on the position of the Mn $2p_{3/2}$ level in the energy spectrum and on the shape of 2p lines depicting their complex multiplet and satellite structure. In the present work, in order to study the state of cations in mechanically activated manganese oxides, we made an attempt to unite several approaches. This is connected with the fact that the spectra may be distorted because of the high defect content of the treated material, so more thorough analysis of the spectra is necessary. We took into account the fact that the connection established by the authors of [12] between the valence state of Mn and the Δ(3s) parameter is independent of the nature of manganese compound (solid solution), unlike for the bonding energy of electron levels. In this connection, when determining the valence state of the cation in the oxides modified by high energy strain grinding, the value of the exchange splitting Δ(3s) was taken as the basis. Additional parameters (bond-

TABLE 1

Average values of spectral parameters calculated from the data of different authors for manganese oxides

Oxides	E_b, eV			Δ(3s), eV	Ref.
	Mn $2p_{3/2}$	O 1s	Mn 3s		
MnO	640.7	529.4	нет св.	6.2	[12, 13, 17]
Mn_3O_4	641.4	529.4	83.6	5.7	[13−16]
Mn_2O_3	641.9	530.1	83.8	5.4	[10, 13, 15, 18]
MnO_2	642.3	529.6	84.5	4.6	[13, 15, 19, 20]

Note. If the value different from 285.0 eV was accepted for the C 1s line in the data presented, we made corresponding corrections.
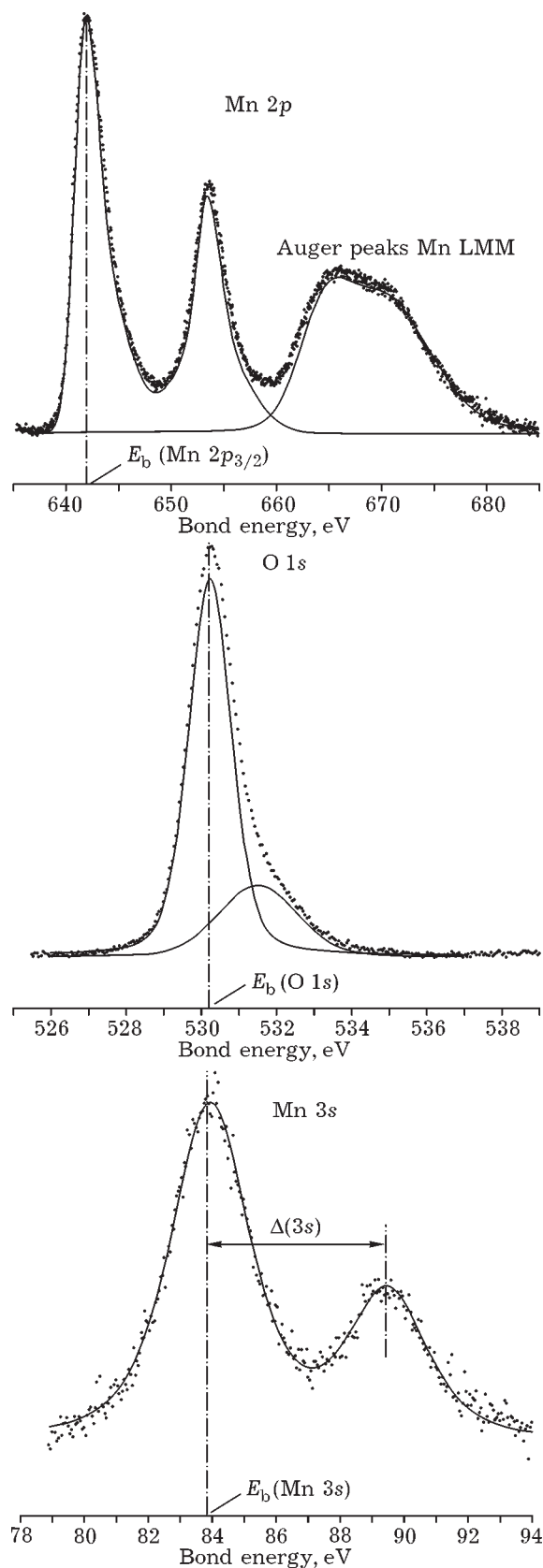
Fig. 1. XPES spectra recorded as the reference on the ceramic Mn_2O_3 oxide after subtracting the background (Shirly method) and X-ray satellites.

ing energy, width, asymmetry of the electron levels of Mn $2p$, O $1s$ and Mn $3s$) were used as indicators of the degree of deviation of the oxides under study from the stoichiometry.

Literature data on the spectral parameters corresponding to different valence states of manganese in its oxides are presented in Table 1. We used them to compare our experimental results. The experimental spectra of Mn $2p$, O $1s$ and Mn $3s$ recorded by us with freshly annealed ceramic Mn_2O_3 sample with the surface purified in the vacuum of the spectrometer with the help of mechanical scrubber are shown in Fig. 1. We chose this sample as a reference Mn_2O_3 sample. It follows from the analysis of the spectra of this sample that the results obtained by us do not contradict the data of the majority of authors.

RESULTS AND DISCUSSION

The survey spectrum which can be treated as a representative one for all the oxide powders studied by us is shown in Fig. 2. These spectra are recorded in the high-sensitivity mode (at the high transmission energy of energy analyser), which allows us to follow the basic lines of all the elements represented in the surface layer of the material in the amount of more than 0.5 at. %. One can see that the peaks of the electron levels of manganese and oxygen are mainly represented in the spectrum; a clear signal at 711 eV is the evidence of the presence of a small amount of iron in the material (both in the initial sample and in the mechanically activated one). The C $1s$ line represents carbon-containing impurities of random character carried from the atmosphere. Using the maximum of this line (285.0 eV) we made a correction for the energy scale of the spectrometer taking into account the effect of sample charging during electron emission.

The spectra of the core electron levels O $1s$, C $1s$ and Mn $2p$ are shown in Figs. 3–5.

MnO₂ powder

The spectral parameters characterizing the state of manganese in MnO_2 powders are shown in Table 2. Comparing these results with the
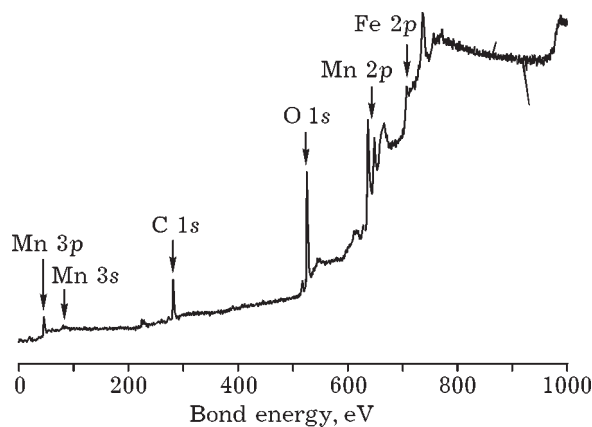
Fig. 2. Survey spectrum of mechanically activated Mn_2O_3.

data shown in Table 1 we may state that Mn^{4+} ions belonging to the major phase are prevailing on the surface of initial manganese dioxide. Judging from the structure of C 1s and O 1s spectra (see Fig. 3, *a*), admixture phases are also present on the surface in small amounts. As a result of etching with the ion beam, the Mn $2p_{3/2}$ peaks broaden and shift to lower bond energy values, which points to a decrease in the valence of Mn ions. A similar behaviour was observed by the authors of [21]. Comparative analysis of the data of Tables 2 and 1 allows us to conclude that the valence of manganese becomes mixed as a result of the treatment with the ion beam: Mn(III)−Mn(IV).

Mechanical activation causes changes of the chemical state of the oxide surface. Thus, for MnO_2 sample, the Δ(3s) parameter, which is sensitive to manganese valence, corresponds in the value to Mn(III) state (see Table 2). Bonding energies of Mn 2p and Mn 3s levels are observed to be higher with respect to the new state of Mn.

As a result of etching, the electron structure of mechanically activated MnO_2 powder

almost completely coincides with the structure of initial MnO_2 subjected to etching (see Table 2). This is the evidence that the surface layer of mechanically activated particles with the changed chemical state of manganese has been completely removed by etching, that is, its thickness did not exceed 10 nm.

Mn_2O_3 powder

The parameters of the spectra recorded from different Mn_2O_3 samples are shown in Table 3. One can see that the surface of the initial powder was partially degraded, likely due to the action of the environment during storage for 2 months. This is also indicated by the spectrum of oxygen (see Fig. 3, *b*): additional O 1s peaks situated at the high bonding energies are noticeably larger for this sample in comparison with initial MnO_2 (see Fig. 3, *a*) and the reference Mn_2O_3 (see Fig. 1). Taking into account the fact that the contribution from CO_3^{2-} group (~286.5 eV) is almost completely absent from the spectrum of carbon, one of the oxygen peaks (at E_b = 531.5 eV) corresponds with the high probability to OH^- groups [7, 22], and the other (at E_b ≥ 533 eV) to adsorbed water vapour [23−25]. All these facts provide evidence for the chemical instability of initial Mn_2O_3 to atmospheric moisture.

Mechanically activated sample exhibits higher stability to the action of environmental factor in comparison with the initial powder: the surface of the sample activated for 1 min is close in parameters to the reference (see Table 3); in the case of activation for 10 min, it is identical to the reference. Analysis of the oxygen spectrum O 1s (see Fig. 4, *b*) shows that

TABLE 2

Spectral parameters of the studied MnO_2 powder samples

Samples	E_b, eV			Δ(3s), eV
	Mn $2p_{3/2}$	O 1s	Mn 3s	
Initial	642.2 (2.1)	529.6 (1.2)	84.4	4.5
The same after etching	641.8 (2.7)	529.8 (1.5)	83.8	5.2
Mechanically activated (60 s)	642.3 (2.4)	529.8 (1.3)	84.4	5.6
The same after etching	641.7 (2.6)	529.7 (1.5)	83.8	5.2

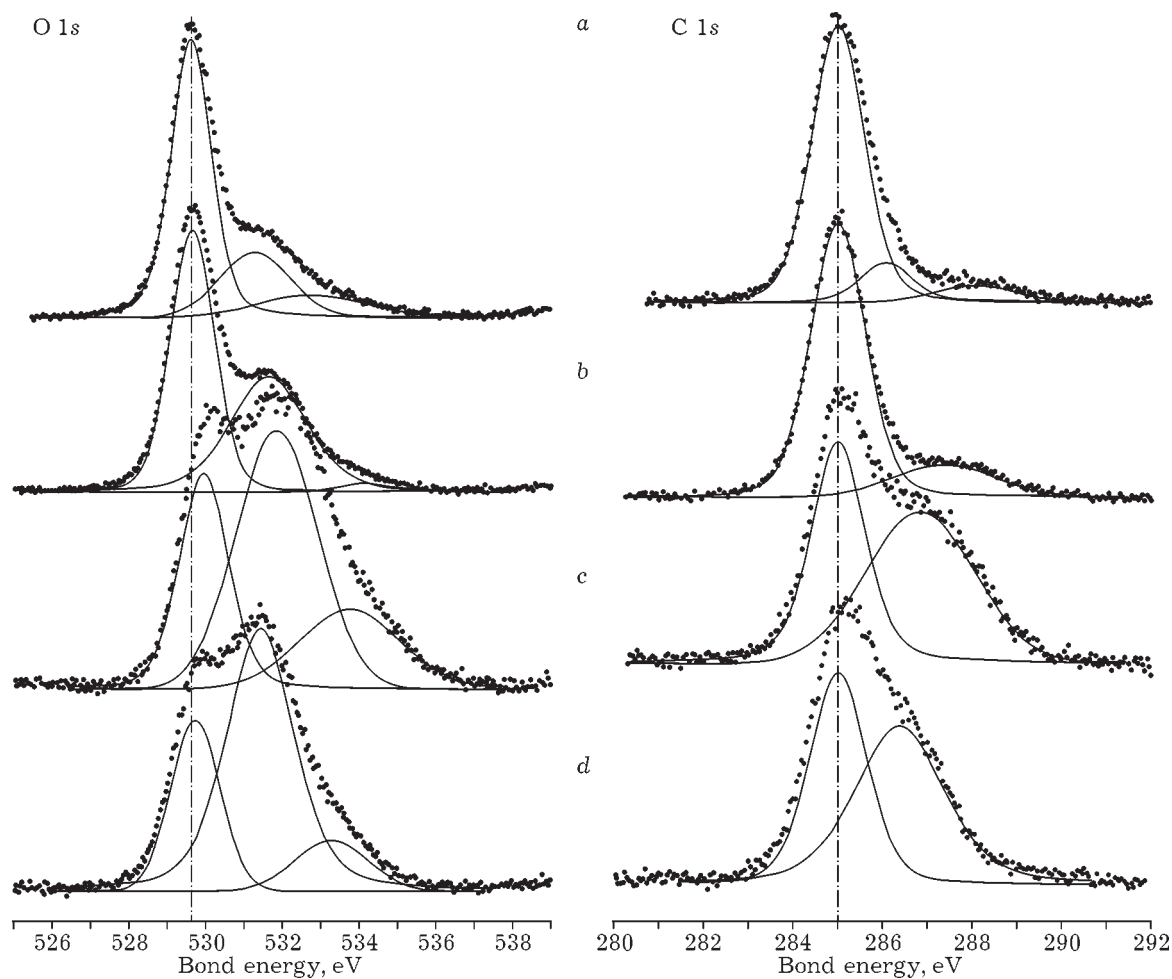*Note.* The width (FWHM) of the spectral line is given in parentheses.

Fig. 3. Spectra of O 1s and C 1s recorded for initial samples: MnO_2 (*a*), Mn_2O_3 (*b*), Mn_3O_4 (*c*) and Mn_3O_4 sample after etching (*d*).

TABLE 3

Spectral parameters of studied Mn_2O_3 samples

Samples	E_b, eV			$\Delta(3s)$, eV
	Mn $2p_{3/2}$	O 1s	Mn 3s	
Ceramic (reference)	641.9 (2.6)	530.2 (1.4)	83.9	5.5
The same after etching	641.2 (2.8)	529.7 (1.4)	83.1	5.6
Initial powder	641.2 (2.3)	529.6 (1.4)	83.4	5.4
The same after etching	640.9 (2.8)	529.7 (1.4)	82.8	6.0
Mechanically activated (60 s)	641.9 (2.6)	530.0 (1.4)	83.6	5.5
The same after etching	641.1 (2.7)	529.7 (1.4)	82.9	5.9
Mechanically activated (10 min)	641.9 (2.5)	530.2 (1.4)	83.9	5.5
The same after etching	641.2 (2.7)	529.7 (1.4)	83.0	5.8

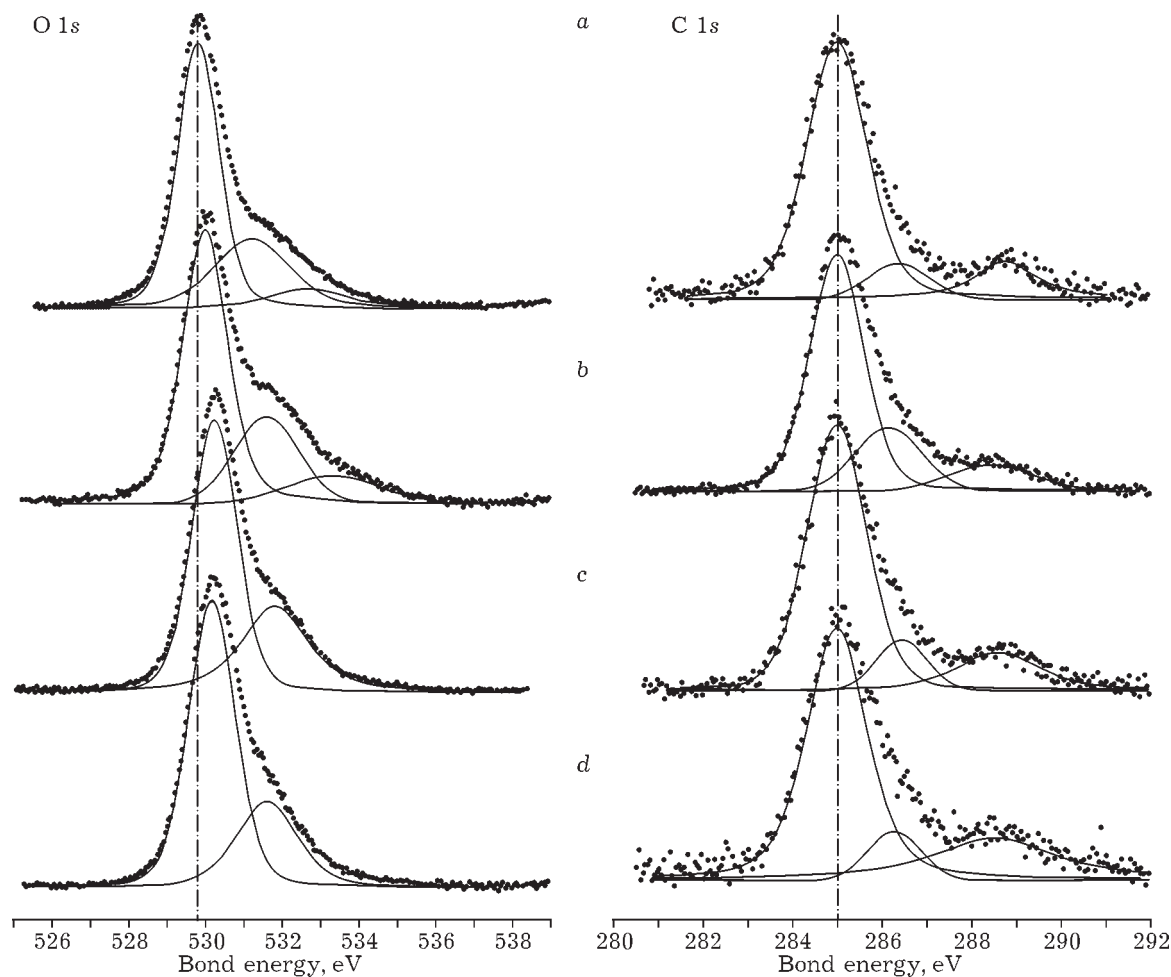*Note.* The width (FWHM) of the spectral line is given in parentheses.

Fig. 4. Spectra of O 1s and C 1s recorded fro mechanically activated samples: a – MnO$_2$, b – Mn$_2$O$_3$ (1 min), c – Mn$_2$O$_3$ (10 min), d – Mn$_3$O$_4$.

the fraction of admixture components on the surface of these powder samples decreases with an increase in the time of mechanical activation. So, we may speak of the special state of the surface layer of mechanically activated oxide, promoting an increase in its chemical stability.

Etching the surface of the reference sample by the ion beam caused the change of the valence state of Mn ions. Judging from the data presented in Table 3, the surface of the sample reduced to Mn$_3$O$_4$. However, some parameters differ from those characteristic of pure hausmannite, which can be explained by the high defect content of the lattice as a result of bombardment with Ar$^+$ ions [21].

As a result of etching the initial and mechanically activated oxides (for 1 and 10 min), their spectral parameters become close to each other. The electron structure of manganese cor-

responds to the oxidized state Mn(II) with a small contribution from the Mn(III) state (see Tables 3 and 1). In addition, it is necessary to stress that specific changes of the shape of Mn 2$p_{3/2}$ peak were detected for the initial and mechanically activated Mn$_2$O$_3$ samples after etching, in particular, the intensity at 646–647 eV increased substantially (see Fig. 5). In [13], with the help of high-resolution technique, the features of the multiplet structure of Mn 2$p_{3/2}$ lines recorded when studying different Mn oxides were revealed. For all these oxides except MnO, a compact multiplet structure with the splitting energy of multiplet approximately equal to 1 eV was established. This structure coincided in the shape of the envelope line with that calculated theoretically. For MnO, along with four main multiplets situated in the compact manner, separate low-intensity satellite

(645.5 eV) and multiplet (647.5 eV) peaks are observed, forming a low shoulder on the higher-energy side of the $2p_{3/2}$ line. A comparison of our results with the data reported in [13] confirms the assumption that the lower manganese oxide is formed as a result of etching the initial and mechanically activated Mn_2O_3 samples.

Deep reduction of initial Mn_2O_3 subjected to etching is explained by the fact that this powder has already been partially reduced during chemical degradation. Meanwhile, the same deep reduction of mechanically activated powders can be the evidence of the fact that the material degraded similarly to the initial Mn_2O_3 is hidden under the etched layer characterized by the special state. So, the protective effect for mechanically activated samples manifested itself as a particularly local one. The nature of this locality is not quite clear yet and requires further studies.

Mn_3O_4 powder

The characteristic parameters of XPES lines recorded for the studied Mn_3O_4 samples are shown in Table 4. It is necessary to stress that the initial Mn_3O_4 powder does not correspond in its spectral characteristics to any of manganese oxides and all XPES lines are broadened, which points to substantially non-monophase character of the material. In addition, the composition of the powder is characterized by the substantial portion of carbon and non-structural oxygen (see Fig. 3, c). Therefore, it can be concluded that its surface is composed of the stable products of the chemical interaction
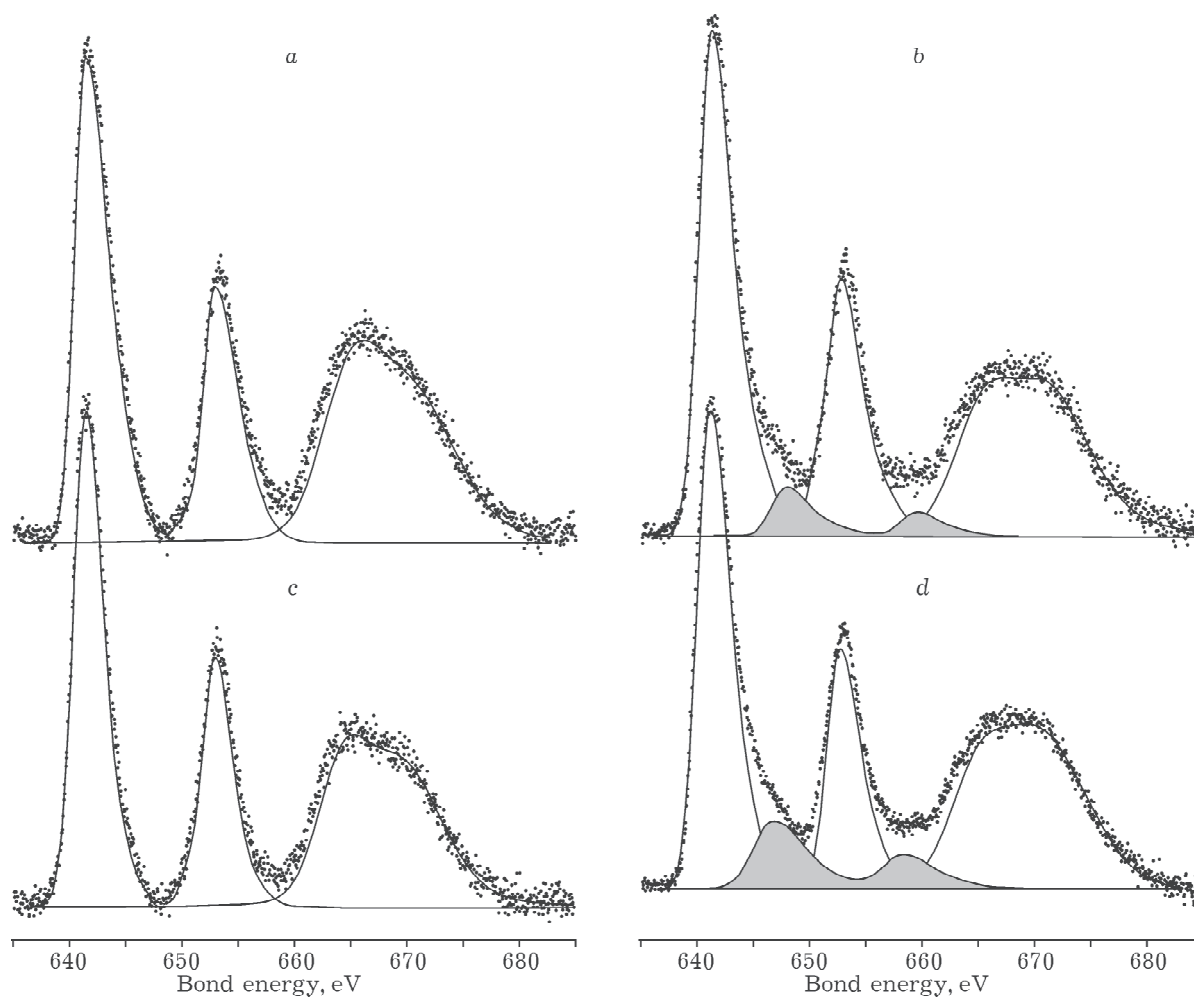

Fig. 5. Spectra of Mn $2p$ recorded for Mn_2O_3 samples: a − initial, b − initial after etching, c − mechanically activated, d − mechanically activated after etching.

TABLE 4

Spectral parameters of the studied Mn_3O_4 samples

Samples	E_b, eV			$\Delta(3s)$, eV
	$Mn\ 2p_{3/2}$	O 1s	Mn 3s	
Initial	642.5 (3.8)	529.9 (1.5)	84.3	5.5
The same after etching	641.8 (3.4)	529.7 (1.5)	83.6	5.9
Mechanically activated (60 s)	641.9 (3.0)	530.2 (1.5)	83.7	5.4
The same after etching	641.2 (2.9)	529.8 (1.5)	83.1	5.8

Note. The width (FWHM) of the spectral line is given in parentheses.

of initial oxide with atmospheric components: carbonate $MnCO_3$ and hydrate $MnO_2 \cdot xH_2O$.

As a result of etching the sample, the $\Delta(3s)$ parameter reaches the value corresponding to Mn_3O_4. Though the Mn $2p_{3/2}$ peak shifted to lower E_b values, the Mn_3O_4 sample still does not correspond to lower oxides. The high intensities of C 1s and O 1s signals (see Fig. 3, *d*) indicate that the non-monophase character of Mn_3O_4 powder surface is conserved and is likely the volume characteristic of this oxide material.

Directly the surface of mechanically activated sample is the Mn_2O_3 oxide that passes into Mn_3O_4 after etching (similarly to the above-considered powder of the nominal composition Mn_2O_3). The amount of admixture phases in this material is much smaller in comparison with initial Mn_3O_4 (see Fig. 4, *d*).

So, Mn_3O_4 powder turned out to be unstable in the air. The surface of the initial material is completely degraded, while the surface of mechanically activated sample is oxidized to Mn_2O_3.

Iron on the surface of oxide powders

In the survey spectrum shown in Fig. 2, there is a signal at 711 eV corresponding to iron in the form of Fe_2O_3. It was recorded both with the MgK_α radiation and with the AlK_α radiation (in the latter case, Auger peaks of manganese $L_2M_{23}M_{23}$ and $L_3M_{23}M_{23}$ that can be erroneously interpreted as a Fe 2p doublet do not fall within the region of 711 eV). In all the initial powders, iron content on the surface did not exceed 0.5 at. % (at the limit of the method sensitivity), while after etching iron was not detected at all. After mechanical activation (60 s), iron content increased to (2.5±0.3) at. % and remained practically unchanged as a re-

sult of etching the surface with the ion beam (even after double etching for 70 min each time, iron concentration remained at the level of 2.1 at. %). Mechanical activation was carried out using steel balls, so the increased iron content of powders subjected to this operation is quire reasonable. Iron atoms had enough time to diffuse into the particles of the material to a depth substantially larger than 20 nm.

According to the results of examination, initial oxides form the following sequence in which the stability in the air decreases: MnO_2 > Mn_2O_3 > Mn_3O_4, which corresponds to the existing ideas [26]. As a result of mechanical activation, the most stable oxide is Mn_2O_3: the electron structure of eth surface of all the three studied oxides [Mn(II), Mn(III), Mn(IV)] after this procedure corresponds or is close to the structure of Mn_2O_3.

The stability of Mn_2O_3 oxide is likely to be due to thermal effects accompanying mechanical activation. It is known [27] that rather high temperatures (up to 1000 K) develop on the surface of particles during grinding in ball mills. At the same time, the start of MnO_2 dissociation in the air according to the data of different authors lies within temperature range 503−923 K [28]. This explains the presence of the layer with stoichiometry Mn_2O_3 on the surface of manganese dioxide subjected to mechanical activation. The thickness of this layer does not exceed 10 nm.

From the viewpoint of existing notions, the oxidation of hausmannite grain surface to Mn_2O_3 under mechanical action seems improbable. It is well known [26] that the transformation

$4Mn_3O_4 + O_2 \rightarrow 6Mn_2O_3$

requires exposure to temperatures below 1123 K for tens or hundreds hours, while mechanical activation in our work was carried out for 60 s.

We confirmed in [29] that even in the presence of nucleation centres as α-Mn_2O_3 in the reaction zone the reaction of hausmannite to kurnakite is not realized. Along with this, it was established that due to a small amount of impurities entering the material from the mill materials (WC or Fe), the rate of Mn_3O_4 oxidation increases by several orders of magnitude. In the case of iron admixture, the oxidation proceeds through the formation of limited solid solution $Fe_xMn_{2-x}O_3$ at temperatures 473−973 K.

So, on the basis of the results obtained, we may state that the parameters of mechanical activation of manganese oxides, selected in our work, correspond to the region of Mn_2O_3 stability; manganese dioxide and hausmannite turn into manganese (III) oxide under these conditions (see Tables 2 and 4). The reaction is likely to be incomplete during the time of mechanical treatment (60 s), which is indicated by the noticeable deviation of bond energies for different levels from the reference values. For the reduction of degraded layer on the surface of initial Mn_2O_3 (see Table 3), one can see that the changed bond energies finally reach their reference values with an increase in the time of mechanical activation.

The interpretation of experimental results proposed by us does not take into account the direct effect of mechanochemical treatment on the phase composition of the surface layer of manganese oxides. This contradicts some works (for example, see [30, 31]) the authors of which demonstrate that mechanochemical dissociation of oxides occurs under the effect of mechanical treatment. It is accepted that the influence of thermal effects on these processes is minimal. However, we rely on the fact that the phase composition of mechanically activated surface for manganese oxide samples with different nominal compositions turned out to be of similar type. This most likely means the existence of identical thermodynamic conditions during mechanical treatment (temperature, p_{O_2}). No substantial distortions of thermodynamic equilibrium to the side of non-equilibrium (caused by the energy pumped into the system by mechanical energy) occurred under the conditions of our experiment, which is indicated by the data on the chemical stability of the formed Mn_2O_3 phase. More intense an long mechanical load is likely to be necessary to cause substantial non-equilibrium in the Mn−O system.

CONCLUSIONS

1. The stoichiometric composition of the surface layer differs from that of the volume of mechanically activated powders of manganese oxides; the surface zone reaches the depth of not more than 10 nm.

2. The accepted parameters of mechanical treatment correspond to the region of Mn_2O_3 stability because manganese dioxide and hausmannite are transformed into kurnakite under these conditions, while pure kurnakite remains unchanged. This phenomenon is explained by the thermal effect and the catalytic action of iron admixture in the surface layer of Mn_mO_n particles.

3. Due to mechanochemical treatment, the stability of Mn_2O_3 to degradation caused by the action of atmospheric components (H_2O, CO_2) increases.

4. Irradiation of the manganese oxide surface with Ar^+ ion beam causes a decrease in the valence state of Mn by unity.

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