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DETERMINATION OF MOLYBDENUM OXIDATION STATE IN THE MECHANOCHEMICALLY TREATED MoO$_3$

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The molybdenum oxidation degree in the MoO$_3$ samples after mechanochemical treatment in various media (air, water, ethanol) has been studied by titration, EPR and XANES methods. It has been shown that molybdenum reduction proceeds in all the media used and its degree is determined by powder loading (rotation speed and time treatment) and medium nature. The XANES spectra demonstrate that MoO$_3$ reduction leads to Mo^{5+} ions formation only. The maximal reduction degree is observed at treatment in ethanol. Existence of charged oxygen species located within Mo^{5+} environment was also shown.

Keywords: mechanochemical treatment, oxidation degree, MoO$_3$, EPR spectra

INTRODUCTION

It is well known that the reactivity of solids is strongly determined by their surface properties dependent on the methods and conditions of their preparation. These properties relate to the crystal particles size, porous structure, exposition of different crystallographic planes, nature and number of functional groups, valence state of basic elements which are generally the active sites in adsorption and catalysis [1–4]. Modification of the solids surface properties can be realized in their preparation processes or post-factum after synthesis by heat or other treatment. One of the latter methods is the mechanochemical treatment (MCT) [5–7]. In the number of publications the possibility was shown of this method in modification of the surface properties of molybdenum-containing compounds [8–11].

From the other hand, it is known that molybdenum oxide and related compositions are used as catalysts in the partial oxidation of hydrocarbons and their derivatives [1–3, 11–13]. However, the catalytic activity of MoO$_3$ in such reactions is low. It is connected with high thermodynamic stability of lattice oxygen [13]. But, it has been found [11, 14] that mechanochemical treatment of catalysts results in a considerable increase in conversion and specific rate of hydrocarbon oxidation. It could be explained by increasing specific surface area [1–4], exposition of different crystallographic planes

(structure sensitivity of MoO$_3$ in partial oxidation of propylene [15, 16]), and different nonstoichiometric phase of MoO$_3$, which provided after mechanochemical treatment. It was found [17, 18] that in the presence of reduced phase Magnelly χ-Mo$_8$O$_{23}$ in catalyst, it demonstrated high parameters in oxidation of benzene to phenol.

Another aspect concerns the influence of the oxidation state of Mo on the reactivity of oxides.

On one hand, several authors reported that, for various selective oxidation reactions or oxygen assisted reactions over molybdenum oxide catalysts, the oxidation state of the most active molybdenum species was Mo^{5+} [19–21]. On the other hand, it is known that the Mo^{5+} species are related to shear defects penetrating into the bulk of MoO$_3$ [22]. Consequently, molybdenum suboxides that present shear planes, and so are rich in Mo^{5+} species, could exhibit interesting reactivity in selective oxidation reactions.

However, a lack of information exists about influence of mechanochemical treatment of MoO$_3$ on the oxidation state of molybdenum. This paper describes our study on this problem.

EXPERIMENTAL

Molybdenum oxide MoO$_3$ («Specpure» grade) was mechanochemically treated for 0.5–16 h in air, ethanol, and water in a Pulvarizette-6 Fritsch planetary ball mill at 200–600 rpm. The working bodies used were 10 silicon nitride balls of 10 mm

in diameter. The MoO$_3$ powder was loaded in a silicon nitride bowl (250 mL) at BPR equal to 10:1. The initial reagent and MCT products were characterized by EPR, XANES, and titration methods. Electron paramagnetic resonance (EPR) spectra were collected at room temperature on a Bruker Elexsys E580 X-band spectrometer operating at 100 kHz field modulation. X-ray absorption measurements (Mo K-edge) were realized in HASYLAB (Hamburg, Germany) by DORIS accelerating ring.

An average oxidation state of molybdenum was determined by the double titration method with KMnO$_4$ [23]. This method permits to determine the reduction degree of molybdenum ions of Mo-containing compounds.

RESULTS AND DISCUSSION

It has been found that the mechanical activation of MoO$_3$ produces significant changes in the colour of samples (Fig. 1). The appearance of samples blue color after treatment can testify the reducing of the initial molybdenum oxide [24]. The data obtained show an increase in intensity of blue color samples with an increase in treatment time or rotation speed (rpm).
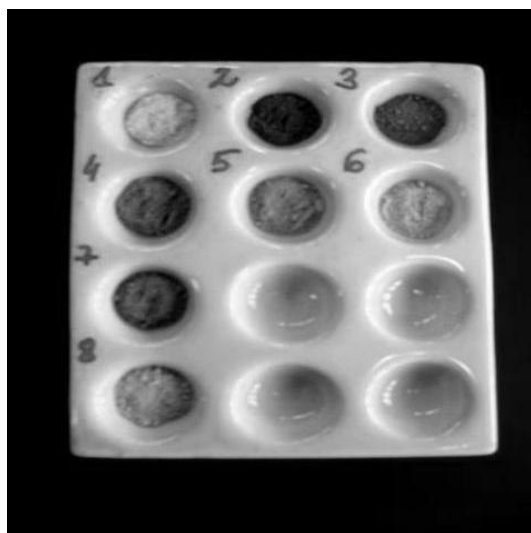

Fig. 1. Changes of MoO$_3$ samples colour after mechanochemical treatment in air. Rotation speed 600 rpm, time of treatment: 1 h – *2*, 2 h – *3*, 4 h – *4*, 8 h – *7*, 16 h – *8*. Time of treatment 4 h: at 400 rpm – *5* and at 200 rpm – *6*. The sample of initial MoO$_3$ – *1*

The data obtained by the double titration method with KMnO$_4$ confirm the visual observation based on the samples colour change. It has been found that increase in power loaded to molybdenum oxide at treatment (increase in

rotation speed or time treatment) is accompanied an increase in molybdenum ions reduction degree (Fig. 2). The presented results demonstrate that in case of treatment in air (curve *2*), the quantity of reduced ions increases lower than when ethanol was used as a treatment medium (curve *1*). The reduction of molybdenum under air treatment can be connected with oxygen removing from oxide as a result of MoO$_3$ lattice destruction analogous to that proposed in [13]. In the presence of ethanol, an additional reduction molybdenum as a result of alcohol interaction with molybdenum oxide can proceed. The rate of this reaction can increase as a result of defects formation due to mechanochemical treatment and local temperature increase in solid. However, this method gives the average oxidation state of molybdenum without distribution of ions content (Mo^{5+}, Mo^{4+}, Mo^{3+}).

EPR spectrum of the initial sample MoO$_3$ shows the presence of some amount of Mo^{5+} ions and is characterized by next parameters: $g_x = 1.976$, $g_y = 1.971$ and $g_z = 1.951$ (Fig. 3). According to [25], this anisotropic signal can be referred to axial distorted octahedral coordination of Mo^{5+} ions in orthorhombic modification of MoO$_3$. Low intensity of this signal shows that it can be assigned to local defects in MoO$_3$ lattice. Mechanochemical treatment of MoO$_3$ leads to essential changes in EPR spectra. The sample after treatment in air is characterized by a complex spectrum (Fig. 4, curve *1*): it is possible to determine three types of signals. The first signal with $g_x = 1.953$, $g_y = 1.947$, $g_z = 1.872$, according to [25], can be connected with the existence of Mo^{5+} ions in distorted pyramidal structure of orthorhombic MoO$_3$. It is necessary to note that formation of orthorhombic modification as a result of treatment was shown by XRD method in [26, 27]. The second signal with parameters $g_\perp = 1.930$ and $g_\parallel = 1.909$ can be referred [28] to Mo^{5+} centers in defect MoO$_6$ octahedra. The third intensive isotropic signal with $g = 2.003$, with value close to free electron signal ($g_e = 2.0023$) the most authors attribute [9, 29] to ion-radical O$_2^-$ localized in coordination sphere of Mo^{6+} ions. It is necessary to note that the spectrum magnitude increases in comparison with that of the initial sample.

The sample after mechanochemical treatment in ethanol demonstrates the presence of two types of signals in EPR spectra (Fig. 4, curve *2*). The first, analogous to that observed after treatment in air, is connected with octahedral distorted Mo^{5+} ions ($g_\perp = 1.930$,

$g_{\parallel}$ = 1.909). This fact well corresponds to XRD data [26, 27], which show that formation of orthorhombic MoO_3 under treatment in ethanol proceeds with lower rate than that in air. The second isotropic signal from ion-radical O_2^- has

less intensity in comparison to that from air treatment. It is necessary to note that intensity of this signal strongly depends on the treatment time (Fig. 5).
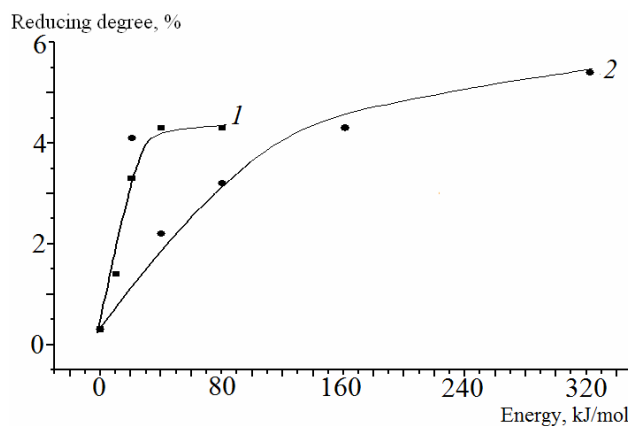

Fig. 2. Dependence of MoO_3 reducing degree on loaded energy under mechanochemical treatment in ethanol – *1* and air – *2*
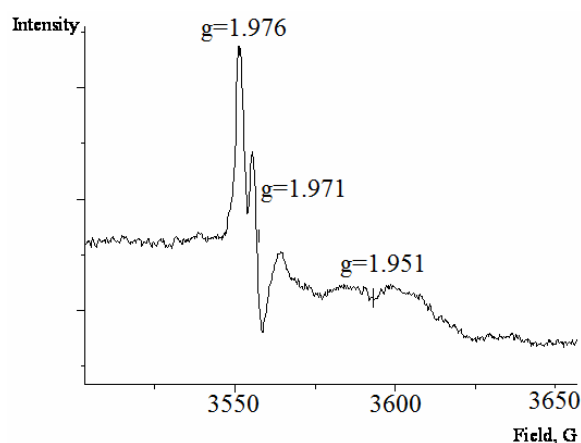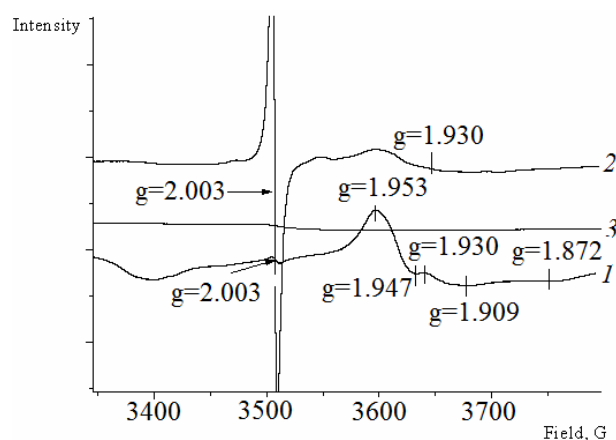

Fig. 3. EPR spectrum of initial MoO_3

Fig. 4. EPR spectra of MoO_3 samples after MCT for 4 hours in air – *1*, ethanol – *2*, and water – *3*
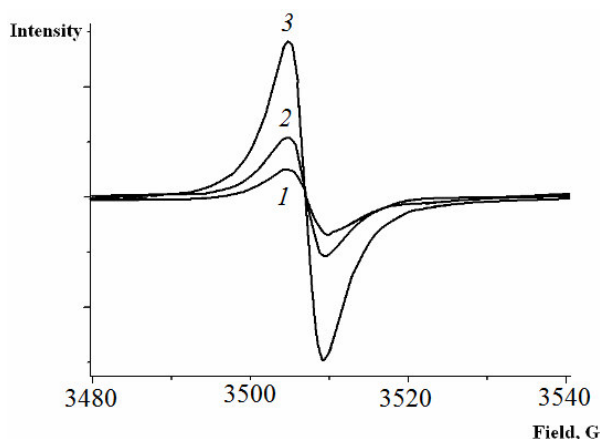
Fig. 5. The relative intensity of EPR signal with g – 2.003 in spectra of MoO$_3$ samples after MCT in ethanol for 1 h – *1*, 4 h – *2*, 8 h – *3*

In EPR spectra of MoO$_3$ samples after mechanochemical treatment in water, no signal from Mo^{5+} ions was fixed (Fig. 4, curve *3*). It can be explained by formation of sidwillite phase with oxidation state of molybdenum (+6) [26, 27] and by strong water adsorption on Mo^{5+} with electron transfer onto water oxygen also. A little intensity signal from O$_2^-$ stabilized at Mo^{6+} (see above) can be observed in this spectrum.

It is well known that X-ray absorption measurements (XANES) can give information about oxidation state of molybdenum in its compounds, their structure and Mo coordination. In this aim the value can be used of chemical shift peak form (presence of peaks near absorption edge – pre-edge). The theoretical analysis as well as the plot of the value of chemical shift (ΔE) on the effective charge (oxidation state) of transition metals (q) can be described as parabola equation ($\Delta E = aq + bq^2$) [30]. At the same time, if take in account that constant a is considerably much more than constant b, this dependence can be approximated by linear equation. This linear dependence was confirmed for some elements including Mo. If take in account that MoO$_3$ reduction to MoO$_2$ occurs without essential changes in molybdenum ion coordination, the observed shift of energy level must be connected with the change of molybdenum effective charge. This fact was demonstrated in [31] and a linear correlation between the value of energy and the oxidation state of molybdenum between (+6) and (+4) was shown.

The obtained experimental X-ray absorption spectra (Mo K-edge) of the samples after mechanochemical treatment are present in Fig. 6.

The spectra of MoO$_3$ and MoO$_2$ used as standards present in this Figure also. It is necessary to note, that for MoO$_3$ samples containing Mo^{6+}, the pre-edge peak is observed with lower value of energy than absorption edge of Mo (in Fig. 6 noted by a vertical line) which connected with electron transition $1s \rightarrow 4d$. This dipole-forbidden transition became possible owing to central position of Mo^{6+} ion in the distorted octahedron of MoO$_3$ [31, 32]. The reduction of molybdenum leads to appearance of electrons at $4d$- orbital and the intensity of pre-edge peak decreases, but in case of MoO$_2$ the presence of partially filled 4d-orbital results in disappearance of the pre-edge peak.
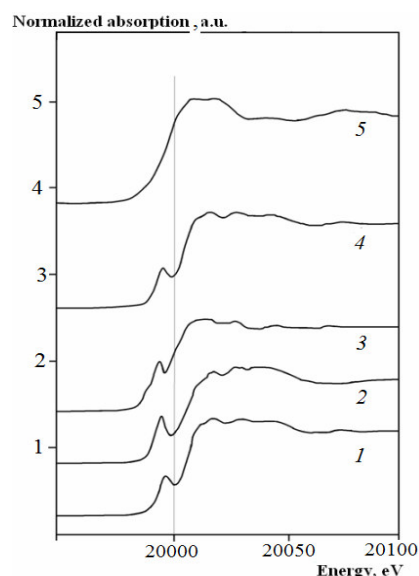

Fig. 6. Mo K-edge XANES spectra of MoO$_3$ samples after mechanochemical treatment in water – *1*, in air – *2*, in ethanol – *3*, and standards MoO$_3$ – *4*, MoO$_2$ – *5*

The data presented in Fig. 6 show that all the mechanochemically treated samples have the pre-edge peak and its intensity decrease (except the sample treated in water). We have no hard explanation of this fact today but a hypothesis can be connected with water adsorption and change Mo-ions coordination (see EPR data). The results obtained testify the partial reduction of Mo^{6+} in mechanochemical treatment and correspond to data presented above. On the other hand, those results evidence that reduction of MoO_3 proceeds with formation of Mo^{5+} only (without Mo^{4+} or Mo^{3+}). Determination of formal oxidation states of molybdenum was realized taking in to account the linear dependence between the Mo K-edge energy in the oxides shift relatively to its value for metallic Mo (ΔE) [32]. The data presented in [32] for MoO_3 and MoO_2 were used as standard values for Mo^{6+} and Mo^{4+}. The results of this comparison are presented in Fig. 7. So, the oxidation state of molybdenum in the initial MoO_3 was estimated as (+5.95). This fact well corresponds with results obtained by titration (Fig. 2) and EPR, which demonstrated the presence of Mo^{5+} signal (see Fig. 3). In the case of mechanochemically treated MoO_3 samples, the next values of the average oxidation state of molybdenum were obtained: treatment in air – (+5.80), treatment in water – (+5.72), and treatment in ethanol – (+5.45). It can be proposed that as a result of mechanochemical treatment, the amorphous phase of molybdenum suboxides ($Mo_{18}O_{52}$, Mo_9O_{26}, Mo_8O_{23}, Mo_4O_{11}) is formed and the presence of these compounds decrease the average oxidation state of molybdenum.
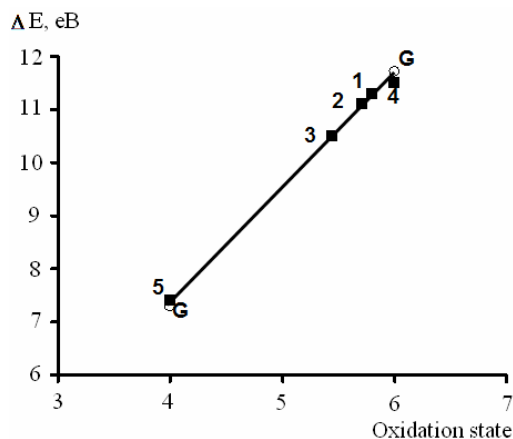

Fig. 7. A plot of Mo K-edge shift (ΔE) on oxidation state of molybdenum. The number of the sample corresponds to spectrum number in Fig. 6. Data for samples marked by the letter «G» – are taken from [31]

CONCLUSIONS

The reduction of MoO_3 at its mechanochemical treatment in air, water and ethanol with formation of Mo^{5+} only was shown by titration, EPR and XANES methods. The reduction degree is controlled by the power loading (rotation speed or time treatment) and treatment media nature. An increase in Mo reduction degree with the increase in treatment time was shown. The ethanol treatment can be accompanied by additional molybdenum reduction as a result of oxide reaction with alcohol, which leads to its maximal reduction in this medium. The formation of oxygen charged species localized at Mo^{5+} or Mo^{6+} (Mo distorted environment) was found.

Визначення ступеня окиснення молібдену механохімічно обробленого MoO₃

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Ступінь окиснення оксиду молібдену MoO₃ після механохімічної обробки в різних середовищах (повітря, вода, етанол) було досліджено титруванням, ЕПР та XANES спектроскопією. Було показано, що відновлення молібдену відбувається в усіх середовищах обробки, а ступінь відновлення залежить від енергетичного навантаження (швидкості обертання, тривалості) та середовища обробки. XANES спектри доводять, що відновлення MoO₃ веде до утворення лише йонів Mo^{5+}. Максимальний ступінь відновлення спостерігається при обробці в етанолі. Було показано присутність O_2^-, локалізованого в координаційній сфері йона Mo^{5+}.

Ключові слова: механохімічна обробка, ступінь окиснення, MoO₃, ЕПР спектри

Определение степени окисления молибдена механохимически обработанного MoO₃

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Степень окисления оксида молибдена MoO₃ после механохимической обработки в разных средах (воздух, вода, этанол) была исследована титрованием, ЭПР и XANES спектроскопией. Было показано, что восстановление молибдена происходит во всех средах обработки, а степень восстановления зависит от энергетической нагрузки (скорости вращения, длительности) и среды обработки. XANES спектры доказывают, что восстановление MoO₃ ведет к образованию только ионов Mo^{5+}. Максимальная степень восстановления наблюдается при обработке в этаноле. Было показано присутствие O_2^-, локализированного в координационной сфере иона Mo^{5+}.

Ключевые слова: *механохимическая обработка, степень окисления, MoO₃, ЭПР спектры*

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