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Adsorption of the Monohydrogen Nitrilotris(methylenephosphonato)hydroxylaminatonitrosyl Molybdate Complex on the Steel Surface and Its Thermochemical Behavior in the Isolated State and in Adsorbed Layers

F. F. Chausov[a, b, *], N. V. Lomova[a], N. Yu. Isupov[a], I. N. Shabanova[a], V. G. Petrov[c], and D. K. Zhirov[c]

[a] *Physical and Technical Institute, Ural Branch, Russian Academy of Sciences, Izhevsk, 426000 Russia*
[b] *Udmurt State University, Izhevsk, 426034 Russia*
[c] *Institute of Mechanics, Ural Branch, Russian Academy of Sciences, Izhevsk, 426067 Russia*
**e-mail: chaus@yandex.ru*

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Abstract—The adsorption and thermochemical behavior of the heteroleptic molybdenum(III) complex with nitrilotris(methylenephosphonic acid), hydroxylamine, and nitrogen(II) oxide are studied by X-ray photoelectron spectroscopy in situ. The adsorption of the complex on the steel surface is accompanied by the partial oxidation of molybdenum. Upon the thermal action, the free complex is reduced to Mo(II) and that in the adsorbed layer is reduced to metallic molybdenum. This makes it possible to use the complex described as a precursor for surface alloying of steel units.

Keywords: molybdenum, nitrilotris(methylenephosphonate), heteroleptic complex, adsorption, surface, redox reactions, X-ray photoelectron spectroscopy

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INTRODUCTION

Molybdenum is one of the most important alloying elements [1]. The density maximum of the bent-electronic 4*d* states is significantly remote from the nucleus than that of the kainosymmetric 3*d* states [2, 3], which provides a possibility of forming strong covalent bonds with atoms of the nearest environment and, as a consequence, the strength, endurance, and acid resistance of molybdenum-containing alloys can be enhanced [1, 4]. The search for economic methods of alloying steels and alloys is urgent due to a high cost of metallic Mo.

In coordination compounds Mo exhibits all possible oxidation states from 0 to +6 [5]. On the one hand, an analysis of the X-ray photoelectron (XPS) spectra of the coordination compounds of Mo showed a tight relationship between the effective charge (q_{eff}) on the Mo atom and the bond energy (E_b) of the components of the Mo3$d_{5/2}$–Mo3$d_{3/2}$ doublet [6, 7]. On the other hand, the formal oxidation state does not always correlate with the effective charge of the Mo atom [8]. The coordination compounds of Mo with the so-called non-innocent ligands, whose electron density distribution and effective charge can vary in a wide range with the retention of the molecular structure, play a special role [9, 10]. In the complexes with the non-innocent ligands, the formal oxidation state of the central atom loses the physical sense to a significant extent and the effective charge can experimentally be determined by indirect (voltammetry, optical spectroscopy, EPR) or direct methods. The direct methods mainly used for the determination of the effective charge of atoms are XPS and XANES/EXAFS.

The metal complexes of nitrilotris(methylenephosphonic acid) ($N(CH_2PO_3)_3H_6$, NTP) are significant as inhibitors of steel corrosion in aqueous media [11–14] and precursors of functional materials [15, 16]. The preparation of materials with beforehand specified properties from coordination compounds of NTP with metals requires the knowledge and taking into account the physicochemical regularities of their adsorption, thermochemical transformations, etc.

In this work we present the results of studying the adsorption on the steel surface and thermochemical (mainly redox) behavior of the earlier described heteroleptic molybdenum complex with NTP, hydroxylamine, and nitrogen(II) oxide, $Na_3[Mo(NO)(NH_2O)\{N(CH_2PO_3)_3H\}]$ (**I**) [17].

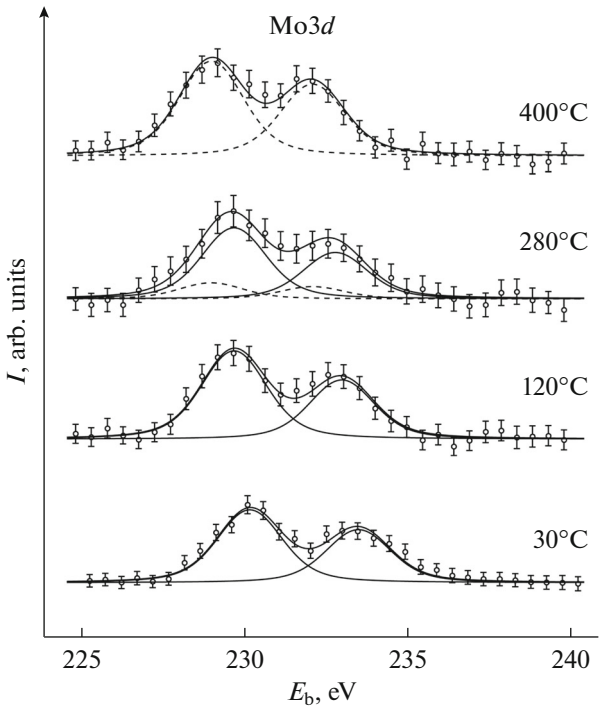

Fig. 1. XPS spectrum of complex **I** in the isolated state (on the Au support) upon the thermal action in situ at the temperatures from 30 to 400°C.

EXPERIMENTAL

Complex **I** was synthesized using a described procedure [17]. The obtained product was identified by IR spectroscopy and X-ray diffraction analysis.

To record the XPS spectra of complex **I** in the isolated state, the preparation was deposited on the Au (99.9%) support as a layer 1–3 μm thick.

Samples of steel 20 (State standard of Russia 1050-2013) were used for the preparation of adsorption layers. The samples were polished with an emery paper with the corundum grain no. 2000, etched with 15% hydrochloric acid for 1 min to remove the deformed metallic layer, and washed with distilled water. The samples were immersed into a 1% aqueous solution of complex **I** in acetate buffer solutions with pH 4.0, 5.0, 6.0, 6.8, and 7.6 [18]. Adsorption layers were obtained by immersing the steel samples into the solutions for 15 min.

The XPS spectra of the isolated preparation of complex **I** and adsorption layers of **I** were recorded on a RES-3 X-ray electron spectrometer (Physical and Technical Institute, Ural Branch, Russian Academy of Sciences) [19]. The AlK_α radiation ($h\nu$ = 1486.6 eV) was used for excitation. The residual pressure in the working chamber of the spectrometer was 10^{-4}–10^{-3} Pa. The spectra of the internal levels Na2*s*, P2*p*, Mo3*d*, C1*s*, N1*s*, O1*s*, and Fe2$p_{3/2}$ and the valence band spectrum were detected on heating the samples directly in the working chamber of the spectrometer from 30 to 400°C. The energy analyzer was calibrated by the C1*s* (E_b = 285.0 eV) and Na2*s* (E_b = 63.5 eV) spectra. The background and inelastic scattering were corrected according to Shirley [20]. The spectroscopic data were statistically processed on a computer using the Fityk 0.9.8 program [21]. The Poisson distribution law was accepted for the photoelectron flow. The 95% confidence intervals for the experimental values of the spectral intensity are shown in the spectral patterns by graphical intersections.

The contrast of the Mo3$d_{5/2}$ spectral line was used as a measure of the surface Mo concentration in the adsorbed layer and can be calculated by the equation

$$\gamma(\mathrm{Mo}3d_{5/2}) = I_{\max}(\mathrm{Mo}3d_{5/2})/I_b - 1,$$

where $I_{\max}(\mathrm{Mo}3d_{5/2})$ is the intensity at the maximum of a given spectral line, and I_b is the intensity of the background at the same point calculated according to Shirley [20]. To determine the atomic fraction of Mo in different oxidation states, the normalized values of contrast were used, which were calculated for each component of the spectrum by the equation

$$\gamma_i^*\left(\mathrm{Mo}3d_{5/2}\right) = \gamma_i\left(\mathrm{Mo}3d_{5/2}\right)\Big/\left[\sum_{i=1}^{N}\gamma_i\left(\mathrm{Mo}3d_{5/2}\right)\right],$$

where $\gamma_i(\mathrm{Mo}3d_{5/2})$ is the contrast of the *i*th component of the spectrum (i = 1, 2, ..., N).

RESULTS AND DISCUSSION

The XPS spectra of complex **I** in the isolated state under the thermal action in situ are shown in Fig. 1. At room temperature the Mo3*d* spectral line is presented by two components of the spin-orbit doublet with a full width at half maximum (FWHM) of 2.0 eV, the intensity maxima at $E_b(\mathrm{Mo}3d_{5/2})$ = 230.2 eV and $E_b(\mathrm{Mo}3d_{3/2})$ = 233.4 eV, and the splitting value Δ = 3.2 eV. This situation corresponds to the effective charge on the Mo atom $q_{\mathrm{eff}}(\mathrm{Mo}) \approx (0.9–1.0)e$, where $e = 1.6 \times 10^{-19}$ C is the absolute value of the electron charge [7, 8, 17]. There are almost no spectral changes on heating the sample in the working chamber of the spectrometer. Only at 280°C the Mo3*d* spectral line with the low-intensity components and maxima at $E_b(\mathrm{Mo}3d_{5/2})$ = 229.3 and 232.5 eV corresponding to $q_{\mathrm{eff}}(\mathrm{Mo}) \approx (0.5–0.6)e$ appears. On further heating to 400°C, the component of the spectrum corresponding to $q_{\mathrm{eff}}(\mathrm{Mo}) \approx (0.9–1.0)e$ disappears completely and all molybdenum atoms gain an effective charge of (0.5–0.6)*e*.

The study of the samples of steel 20 with the adsorption layers of complex **I** deposited from the solutions with different pH showed a sharp dependence of the surface concentration of Mo (contrast of the characteristic line) on the pH of the medium (Fig. 2). At pH 4.0–6.0 the adsorption layer with a

noticeable molybdenum concentration is observed. At pH 6.8 and higher the content of molybdenum on the steel surface is close to the determination inaccuracy.

The XPS spectra of the steel surface with the adsorbed layers of complex **I** show that the Mo atoms on the steel surface exist in at least two nonequivalent positions. This is indicated by the observed (Fig. 3) at 30–60°C spectral components with FWHM = 2.0 eV and $E_b(Mo3d_{5/2})$ = 232.7 and 235.9 eV corresponding to the state with $q_{eff}(Mo) \approx (1.8–1.9)e$, which are absent from the spectrum of the starting crystalline complex **I**. Thus, the adsorption of complex **I** on the steel surface is accompanied by the chemical reaction. Possibly, the non-innocent ligand (molecular radical NO$^{\bullet}$) is eliminated from some molecules of the complex and serves as a donor of electrons to the Mo atom during the formation of complex **I** [17].

Iron exists in the surface layer (the analytical depth of the XPS method is 2–6 nm) predominantly in the oxidized state: the $Fe2p_{3/2}$ spectrum exhibits a broad maximum at 709–710 eV attributed to the unresolved components of Fe^{2+} and Fe^{3+} and a weak shoulder at 706.5 eV corresponding to metallic iron.

The thermal action on the sample in the working chamber of the spectrometer in a range of 120–180°C leads to a decrease in the relative content of the oxidized fraction of Mo atoms and the appearance in the spectrum of the component with FWHM = 2.0 eV and $E_b(Mo3d_{5/2})$ = 229.3 and 232.5 eV corresponding to the state of Mo with $q_{eff}(Mo) \approx (0.5–0.6)e$. The further heating to 280°C results in the almost complete disappearance of the oxidized components of molybdenum and the appearance of the spectral component with FWHM = 2.0 eV and $E_b(Mo3d_{5/2})$ = 227.5 and 230.7 eV corresponding to the metallic state of molybdenum with $q_{eff}(Mo) \approx 0$. At 400°C the metallic fraction of molybdenum is the main component of the adsorbed layer on the steel surface. Interestingly, as the temperature increases, the reduction of molybdenum is accompanied by the parallel reduction (but not oxidation!) of iron: at 180°C the spectral component with $E_b(Fe2p_{3/2})$ = 706.5 eV corresponding to metallic iron becomes equal in intensity to the component of iron oxides with $E_b(Fe2p_{3/2})$ = 710 eV. At 400°C the spectral component caused by the presence of iron oxides is completely absent, and only the spectrum of metallic iron with a maximum at 706.5 eV is observed.

It is most likely that the carbon–phosphorus moiety of the NTP molecule rather than metallic iron serves as a reducing agent in the thermochemical transformation of complex **I** both in the isolated state and on the steel surface. However, the thermochemical transformations of complex **I** in the adsorbed layer on the steel surface are significantly easier and deeper than those in the isolated state: Mo is reduced to $q_{eff}(Mo) \approx (0.5–0.6)e$ on the steel surface at 180°C, whereas the reduction of Mo in the isolated state occurs only at 280°C. At 400°C nearly all molybdenum on the steel surface transforms into the metallic state, which does not occur at all in the isolated state. It can be assumed that metallic iron (and probably other transition metals) present in the steel support serves as a catalyst of the redox process induced by the thermal action.

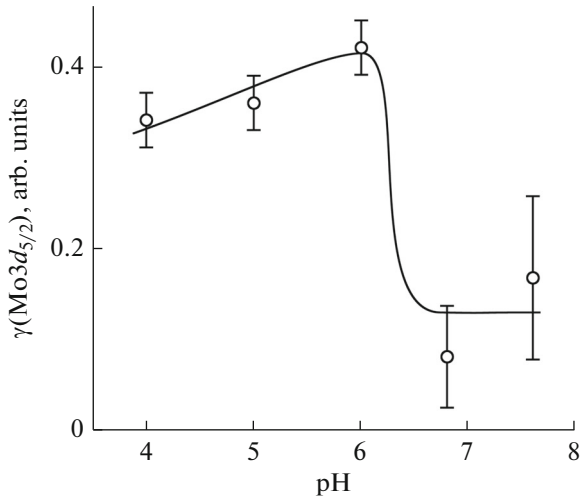

Fig. 2. Dependence of the contrast of the characteristic line $Mo3d^{5/2}$ (surface concentration of molybdenum) in the adsorbed layer of complex **I** on the steel surface on the pH of the solution.

The dependence of the normalized contrasts of the spectral lines corresponding to the fractions of molybdenum atoms in different oxidation states (Fig. 4) makes it possible to advance a hypothetical scheme of redox processes during adsorption and subsequent thermochemical transformations of complex **I** on the steel surface. The curve corresponding to the fraction of Mo atoms with $q_{eff}(Mo) \approx (0.9–1.0)e$, which are present in the adsorbed layer, is a little higher than 0.5 at room temperature and decreases monotonically on heating (Fig. 4, *1*). At temperatures below 100°C the fraction of oxidized Mo with $q_{eff}(Mo) \approx (1.8–1.9)e$ (Fig. 4, *2*) increases slightly, which corresponds to the reaction

$$Mo^{+(0.9–1.0)e} \xrightarrow{Fe_{surf};\quad t \le 100°C} Mo^{+(1.8–1.9)e}, \qquad (1)$$

where Fe_{surf} is the metallic iron-containing surface. The fraction with $q_{eff}(Mo) \approx (0.5–0.6)e$ increases in a range of 100–200°C (Fig. 4, *3*), indicating the parallel reduction of Mo from the states with $q_{eff}(Mo) \approx (0.9–1.0)$ and $(1.8–1.9)e$ to the state with $q_{eff}(Mo) \approx (0.5–0.6)e$

$$Mo^{+(0.9–1.0)e}, Mo^{+(1.8–1.9)e} \xrightarrow{Fe_{surf};\quad t \ge 100°C} Mo^{+(0.5–0.6)e}. \qquad (2)$$

The content of the fraction with $q_{eff}(Mo) \approx (0.5–0.6)e$ stops increasing above 200°C, and the surface

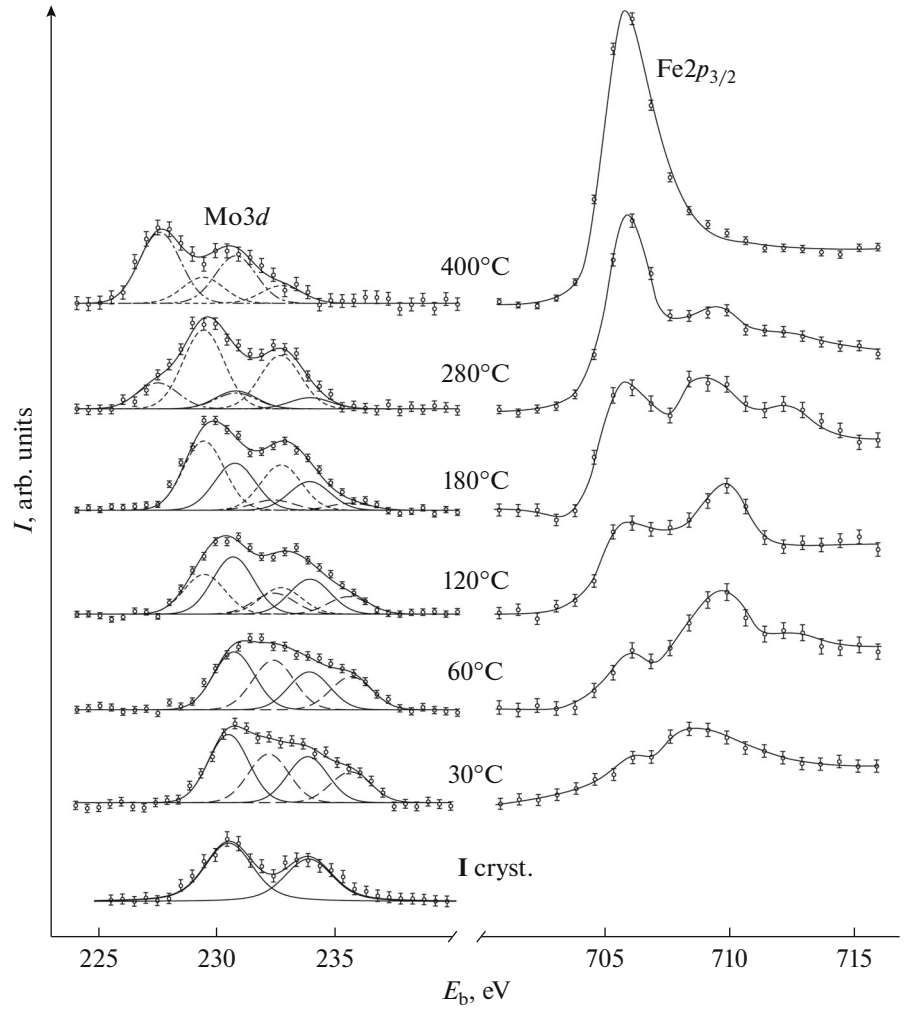

Fig. 3. XPS spectra of the steel surface with the adsorbed layer of complex **I** deposited at pH 6.0 under the temperature action in situ from 30 to 400°C. The XPS spectrum of the initial crystalline complex **I** at room temperature is presented for comparison.

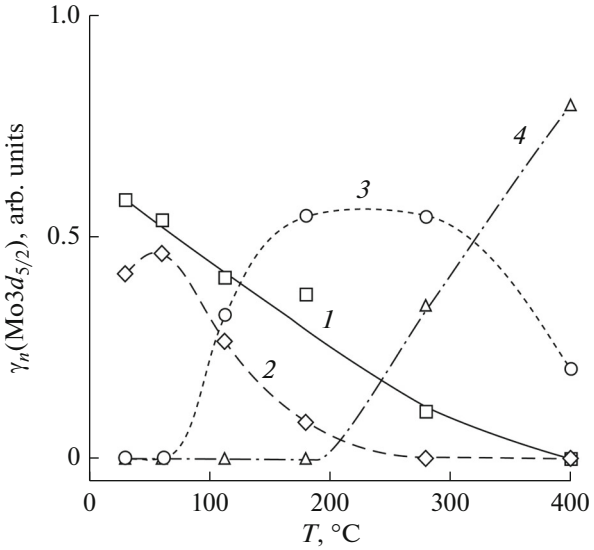

Fig. 4. Dependence of the normalized contrast of the Mo3$d^{5/2}$ spectra for the fractions of Mo atoms with q_{eff}(Mo) ≈ (0.9–1.0)e (*1*), q_{eff}(Mo) ≈ (1.8–1.9)e (*2*), q_{eff}(Mo) ≈ (0.5–0.6)e (*3*) and in the metallic state (*4*) in the adsorbed layer of complex **I** on the steel surface on temperature.

concentration of metallic molybdenum begins to increase (Fig. 4, *4*), indicating the occurrence of the following transformation along with reaction (2):

$$Mo^{+(0.5-0.6)e} \xrightarrow{Fe_{surf};\ \ t \geq 200°C} Mo^0. \qquad (3)$$

Reaction (2) stops above 300°C because of the consumption of the reagents, and process (3) leading to the formation of metallic molybdenum atoms on the surface of the layer becomes predominant.

The described above transformations of the layers of complex **I** adsorbed on the steel surface can serve for the preparation of thin uniform surface layers of metallic molybdenum for the subsequent thermodiffusion or stimulated by ion or electron bombardment surface alloying of steel units.

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