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In this study, X-ray amorphous double molybdates of rare earth elements and methylammonium  $\text{CH}_3\text{NH}_3\text{R}(\text{MoO}_4)_2 \cdot \text{H}_2\text{O}$  (where  $\text{R}=\text{Ce}-\text{Lu}$ ) were synthesized in aqueous solutions of rare earth elements salts and methylammonium chloride under the excess of methylammonium molybdate at the temperature of 20–25°C. It was established that these substances have a stoichiometric composition with the following formula  $\text{CH}_3\text{NH}_3\text{R}(\text{MoO}_4)_2 \cdot \text{H}_2\text{O}$ . The study demonstrated that the compounds  $\text{CH}_3\text{NH}_3\text{R}(\text{MoO}_4)_2 \cdot \text{H}_2\text{O}$  ( $\text{R}=\text{La}-\text{Y}$ ) belong to  $\alpha\text{-TiYb}(\text{MoO}_4)_2 \cdot \text{H}_2\text{O}$  structural type with distorted monoclinic structure of a layered rhombic  $\text{KY}(\text{MoO}_4)_2$ . According to the obtained data, the synthesized substances are X-ray amorphous with particle size less than 100 nm; therefore, they may be used in catalytic processes without additional grinding. We showed the possibility of deposition of double molybdates of rare earth elements and methylammonium on the carriers containing hydroxyl groups or oxygen-containing anions (such as hydroxides of aluminum, iron (III) or cobalt (II), silica gel and natural clays). It was stated that the prepared compounds may be used as components in catalysts of oxidative dehydrogenation of alkanes and alcohols. The products of thermal decomposition of  $\text{CH}_3\text{NH}_3\text{R}(\text{MoO}_4)_2 \cdot \text{H}_2\text{O}$  in a vacuum, protective or hydrogen atmosphere at the temperatures of up to 450°C can be used as catalysts for fuel cell anodes due to the lower degrees of molybdenum oxidation.

**Keywords:** double molybdates, rare earth elements, methylammonium, X-ray amorphous, precipitation, catalyst.

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**Introduction**

Double molybdates of rare earth elements (REE) and ammonium belong to the well-known and thoroughly studied compounds [1]. There are few publications describing similar methylammonium-containing compounds. Dimethylammonium polymolybdates that have photochromic properties are described elsewhere [2], while study [3] provides information on double molybdates of REE and methylammonium, which do not exhibit these properties and are not X-ray amorphous. This means that their particle size exceeds 100 nm.

Some recent publications reported on semiconducting [4,5] and catalytic [6] properties of methylammonium compounds. These properties are mainly exhibited by the compounds that have, along with methylammonium ion, a complex anion with

multi-electron atoms of  $\text{MeI}_3^-$  ( $\text{Me}=\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Sn}^{2+}$ ),  $\text{Mo}_3\text{O}_{10}^{2-}$ ,  $\text{Mo}_7\text{O}_{26}^{6-}$ , and the like. There are sufficient data on the activity of catalysts obtained from ammonium polymolybdates, metal molybdates and molybdenum oxides in the processes of organic synthesis [7,8]. However, information on the use of double molybdates of REE and ammonium or methylammonium as active components for the production of various purpose catalysts is not available in literature.

The purpose of this study was to synthesize X-ray amorphous double molybdates of REE and methylammonium, establish their composition, study their thermochemical properties and substantiate the possibility of the production of catalysts by using these substances.

High dispersion ability of activator particles is a key condition for high efficiency of catalysts based

on oxygenated molybdenum compounds. This factor ensures 5 to 10-fold increase in the catalytic activity [7,9,10]. The content of REE oxide in the catalyst contributes to its high selectivity [9]. Some recent studies have demonstrated that double molybdates of REE and methylammonium are promising catalysts when produced in an X-ray amorphous form.

#### **Experimental**

Double molybdates of REE and methylammonium were synthesized using solutions of nitrates, chlorides or acetates of REE with the concentrations of 0.2–0.3 mol/L and pH 4.0–5.0. Methylammonium molybdate solution was produced by the interaction of freshly prepared molybdenum acid and methylamine solution. The concentration of the resulting solution was 0.3 mol/L and pH 8.5. All starting compounds were of analytical grade.

Double molybdates of REE and methylammonium were synthesized using the following procedures. 200 mL flask was filled with 10 mL of 0.2–0.3 mol/L REE salt. Then, 4–5 g of methylammonium chloride was added. An excess of 0.3 mol/L methylammonium molybdate solution was added to the resulting solution to achieve 1:8 molar ratio of  $[R^{3+}]:[MoO_4^{2-}]$  in the reaction mixture. The resulting mixture was kept for 3–4 hours with intermittent stirring. Then, the mixture was allowed to stand for 2–3 hours and filtered through a thick paper filter. The precipitate on the filter was washed out first with 1% methylammonium chloride solution until there was no qualitative reaction to  $MoO_4^{2-}$  with lead acetate, and subsequently with distilled water, and then with acetone. The precipitates were air dried to a constant weight. Precipitation, filtration and drying procedures were carried out at the temperature of 22–25°C. According to the data of X-ray diffraction analysis, the resulting solids for R=Ce–Lu were X-ray amorphous, while similar substances with R=La and Y produced a diffraction pattern. The synthesis performed according to the procedure described in study [3], i.e. from hot solutions, resulted in the formation of  $CH_3NH_3R(MoO_4)_2 \cdot H_2O$  (R=Ce–Lu) compounds in the polycrystalline state.

Weight analysis of the obtained double molybdates of REE and methylammonium included the following sequence of steps. 0.3–0.4 g of the substance was dissolved in 120–150 mL of  $HNO_3$  solution (1:8), boiled until fully dissolved, adjusted to pH 2–3, and heated to 60–70°C with subsequent adding oxalic acid solution until complete REE precipitation in the oxalate form. After sedimentation, this oxalate precipitate was filtered through a paper

filter. The resulting precipitate underwent the following procedures: washing out, drying, ashing and burning at 800–850°C until  $R_2O_3$  was formed, according to which the REE content was calculated. After isolation of oxalate, the filtrate was analyzed to reveal the presence of molybdenum in the form of oxyquinolate, which was filtered through a glass filter (with drying at 100–120°C). The analyses demonstrated that the precipitate of REE oxalate seized only a negligible amount of molybdenum. The determination error was  $\pm 0.2\%$  and up to  $\pm 0.4\%$  for REE and molybdenum, respectively.

Following the determination of the composition, the obtained  $CH_3NH_3R(MoO_4)_2 \cdot H_2O$  double salts were studied using thermogravimetry, X-ray diffraction analysis (XRD), and IR spectroscopy.

The thermographic analysis of the resulting double molybdates of REE and methylammonium was carried out using a Paulik-Paulik-Erdey derivatograph system at a heating rate of 0.167 degrees per second (the weighed quantity of  $(0.2-0.5) \cdot 10^{-3}$  kg, corundum crucible, the accuracy of temperature measurements of  $\pm 10^\circ C$ , the Pt/Pt-Rh thermo-couple).

XRD analysis was performed by using a DRON-2 diffractometer at the copper radiation and computerized registration of the reflection angles with the accuracy of  $20 \pm 0.04^\circ$ . Infrared spectra were recorded by a UR-20 spectrograph (with prepared tablets of the test substances in KBr).

#### **Results and discussion**

The results of the analysis of double molybdates of REE and methylammonium are given in Table. These results demonstrate that the prepared substances have a stoichiometric composition and correspond to the general formula  $CH_3NH_3R(MoO_4)_2 \cdot H_2O$ . The XRD analysis of the resulting compounds showed that  $CH_3NH_3R(MoO_4)_2 \cdot H_2O$  (R=La–Y) belong to  $\alpha$ - $TiYb(MoO_4)_2 \cdot H_2O$  structural type, which has a distorted monoclinic structure of a layered rhombic  $KY(MoO_4)_2$  [11]. The X-ray diffraction patterns of  $CH_3NH_3R(MoO_4)_2 \cdot H_2O$  (where R=Ce–Lu) demonstrated no distinct lines of diffraction; there were blurred maxima only in the region of the reflection angles  $2\theta_1 \approx 4-9^\circ$  (the most intense reflection) and  $2\theta_2 \approx 21-33^\circ$  (the less intense one). These data suggest that the resulting substances were X-ray-amorphous and highly dispersed. Therefore, the use of these compounds in the catalytic processes does not require any mechanochemical activation. This may reduce the production cost of industrial catalysts containing  $CH_3NH_3R(MoO_4)_2 \cdot H_2O$

(R=Ce–Lu) or their thermal decomposition products.

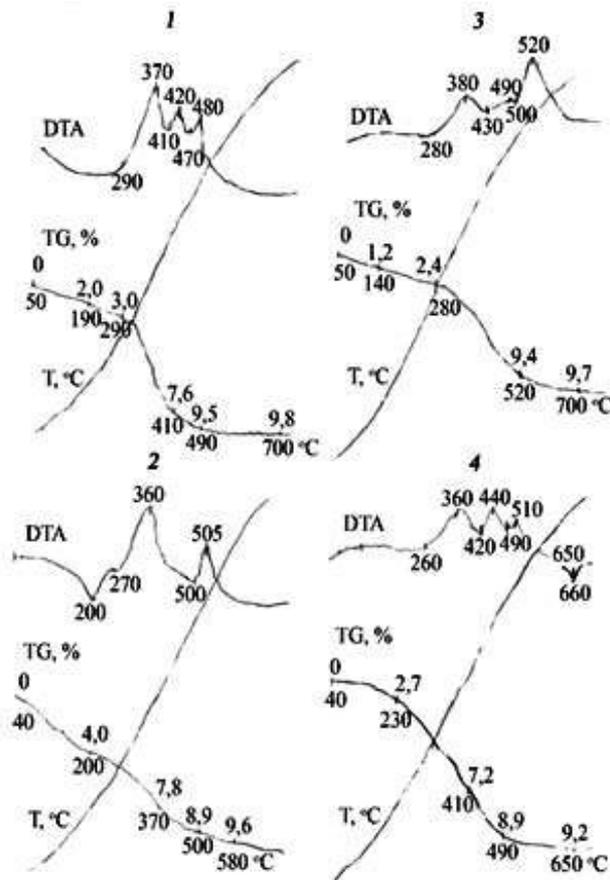
### Results of chemical analysis of double molybdates of REE and methylammonium

Formula	Calculated, %		Found, %	
	R	Mo	R	Mo
$\text{CH}_3\text{NH}_3\text{La}(\text{MoO}_4)_2 \cdot \text{H}_2\text{O}^*$	26.8	37.1	27.30	37.71
$\text{CH}_3\text{NH}_3\text{Pr}(\text{MoO}_4)_2 \cdot \text{H}_2\text{O}$	27.2	37.3	27.58	37.56
$\text{CH}_3\text{NH}_3\text{Nd}(\text{MoO}_4)_2 \cdot \text{H}_2\text{O}$	27.6	36.8	28.05	37.32
$\text{CH}_3\text{NH}_3\text{Sm}(\text{MoO}_4)_2 \cdot \text{H}_2\text{O}$	28.5	36.7	28.90	36.88
$\text{CH}_3\text{NH}_3\text{Eu}(\text{MoO}_4)_2 \cdot \text{H}_2\text{O}$	27.9	37.0	29.12	36.76
$\text{CH}_3\text{NH}_3\text{Gd}(\text{MoO}_4)_2 \cdot \text{H}_2\text{O}$	29.3	36.2	29.83	36.40
$\text{CH}_3\text{NH}_3\text{Tb}(\text{MoO}_4)_2 \cdot \text{H}_2\text{O}$	29.6	36.6	30.05	36.28
$\text{CH}_3\text{NH}_3\text{Dy}(\text{MoO}_4)_2 \cdot \text{H}_2\text{O}$	30.4	36.9	30.52	36.04
$\text{CH}_3\text{NH}_3\text{Y}(\text{MoO}_4)_2 \cdot \text{H}_2\text{O}^*$	19.1	42.0	19.38	41.82
$\text{CH}_3\text{NH}_3\text{Er}(\text{MoO}_4)_2 \cdot \text{H}_2\text{O}$	30.8	35.3	31.14	35.72
$\text{CH}_3\text{NH}_3\text{Tm}(\text{MoO}_4)_2 \cdot \text{H}_2\text{O}$	31.0	36.1	31.35	35.61
$\text{CH}_3\text{NH}_3\text{Lu}(\text{MoO}_4)_2 \cdot \text{H}_2\text{O}$	31.7	35.4	32.11	35.21

Note: \* – polycrystalline compounds.

The thermograms of  $\text{CH}_3\text{NH}_3\text{R}(\text{MoO}_4)_2 \cdot \text{H}_2\text{O}$  (where R=Pr, Eu, Dy, and Lu) are shown in Figure. The differential thermal analysis (DTA) curves in the 40–280°C region demonstrate a blurred endoeffect caused by water splitting. Starting from 260–290°C, this curve exhibits three exoeffects. The first two exoeffects are caused by the thermolysis of  $\text{CH}_3\text{NH}_3^+$  cation; its decomposition products partially restore  $\text{Mo}^{6+}$  to  $\text{Mo}^{5+}$  as evidenced by a dark blue color (the formation of molybdenum blue). Thereafter, the formed intermediate products undergo oxidation with a subsequent formation of polycrystalline REE tetramolybdates,  $\text{R}_2\text{O}_3 \cdot 4\text{MoO}_3$ . This process corresponds to the exoeffect starting at 470–500°C. Heating of  $\text{CH}_3\text{NH}_3\text{R}(\text{MoO}_4)_2 \cdot \text{H}_2\text{O}$  in a vacuum or inert atmosphere leads to the formation of dark blue products due to the reduction of molybdenum to lower oxidation states.

IR spectra of  $\text{CH}_3\text{NH}_3\text{R}(\text{MoO}_4)_2 \cdot \text{H}_2\text{O}$  double molybdates demonstrate stretching frequencies typical of tetrahedral anion  $\text{MoO}_4$ :  $\nu_1=925\text{--}930\text{ cm}^{-1}$  (moderate intensity);  $\nu_3=845\text{ cm}^{-1}$  (high intensity);  $742\text{ cm}^{-1}$  (high intensity);  $760\text{ cm}^{-1}$  (high intensity),  $778\text{ cm}^{-1}$  (high intensity);  $\nu_2=417\text{ cm}^{-1}$  (weak intensity) and  $440\text{ cm}^{-1}$  (weak intensity);  $\nu_4=406\text{ cm}^{-1}$  (moderate intensity),  $407\text{ cm}^{-1}$  (moderate intensity) and  $412\text{ cm}^{-1}$  (moderate intensity). IR spectra of  $\text{CH}_3\text{NH}_3\text{R}(\text{MoO}_4)_2 \cdot \text{H}_2\text{O}$  in the series of REE, when transiting from lanthanum to lutetium, show a



Curves of differential thermal analysis (DTA) of  $\text{CH}_3\text{NH}_3\text{R}(\text{MoO}_4)_2 \cdot \text{H}_2\text{O}$ , where R – Pr (1), Eu (2), Dy (3), and Lu (4)

decrease in the intensity of transmission lines along with their broadening. This indicates an increase in the deformations and inequality of Mo–O bonds in  $\text{MoO}_4^{2-}$  tetrahedral anion caused by REE ions.

The resulting  $\text{CH}_3\text{NH}_3\text{R}(\text{MoO}_4)_2 \cdot \text{H}_2\text{O}$  (R=Ce–Lu) are analogues of well-known  $\text{NH}_4\text{R}(\text{MoO}_4)_2 \cdot 2\text{H}_2\text{O}$  [1], however obtained in a nanosized form, which allows using in catalysts without further grinding. An important property of compounds containing methylammonium cation is the ability of  $\text{NH}_3$  hydrogen group to form both intramolecular and intermolecular hydrogen bonds with oxygen anion [12]. This allows precipitating double molybdates of REE and methylammonium on the carriers containing hydroxyl groups or oxygen-containing anions, such as hydroxides of aluminum, iron (III) or cobalt (II), silica gels, and natural clays. As a result of the formation of hydrogen bonds,  $\text{CH}_3\text{NH}_3\text{R}(\text{MoO}_4)_2 \cdot \text{H}_2\text{O}$  are grafted onto the surface of the mentioned carriers (up to 20 wt.% of activator content). As to the application of the resulting catalysts, they may be used in oxidative

dehydrogenation of alkanes [9] or alcohols [10]. Thermal decomposition products of  $\text{CH}_3\text{NH}_3\text{R}(\text{MoO}_4)_2 \cdot \text{H}_2\text{O}$  in a vacuum, protective atmosphere or hydrogen atmosphere at the temperatures of up to  $450^\circ\text{C}$  can be used as catalysts for fuel cell anodes due to lower degree of molybdenum oxidation.

### Conclusions

X-ray amorphous double molybdates of REE and methylammonium,  $\text{CH}_3\text{NH}_3\text{R}(\text{MoO}_4)_2 \cdot \text{H}_2\text{O}$  ( $\text{R}=\text{Ce}-\text{Lu}$ ) were produced by precipitation from aqueous solutions of REE salts in excess of methylammonium molybdate and under the presence of methylammonium chloride at the temperature of  $22-25^\circ\text{C}$ . These compounds were studied using XRD, thermogravimetry and IR spectroscopy. The possibility of the application of the synthesized compounds in catalysts of oxidative dehydrogenation of alkanes and alcohols was claimed.

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### ОСАДЖЕННЯ РЕНТГЕНОАМОРФНИХ ПОДВІЙНИХ МОЛІБДАТІВ РІДКІСНОЗЕМЕЛЬНИХ ЕЛЕМЕНТІВ І МЕТИЛАМОНІЮ ІЗ ВОДНИХ РОЗЧИНІВ

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В даній роботі із водних розчинів солей рідкісноземельних елементів, хлориду метиламонію в умовах надміру молібдату метиламонію при  $20-25^\circ\text{C}$  синтезовано рентгеноаморфні подвійні молібдати рідкісноземельних елементів і метиламонію  $\text{CH}_3\text{NH}_3\text{R}(\text{MoO}_4)_2 \cdot \text{H}_2\text{O}$ , де  $\text{R}=\text{Ce}-\text{Lu}$ . Встановлено, що одержані речовини мають стехіометричний склад і відповідають формулі  $\text{CH}_3\text{NH}_3\text{R}(\text{MoO}_4)_2 \cdot \text{H}_2\text{O}$ . Показано приналежність  $\text{CH}_3\text{NH}_3\text{R}(\text{MoO}_4)_2 \cdot \text{H}_2\text{O}$  ( $\text{R}=\text{La}-\text{Y}$ ) до структурного типу  $\alpha\text{-PuYb}(\text{MoO}_4)_2 \cdot \text{H}_2\text{O}$ , який має моноклінносптворюєну структуру шаруватого ромбічного  $\text{KY}(\text{MoO}_4)_2$ . Наведено дані, які свідчать про рентгеноаморфний і високодисперсний стан виділених речовин, що дозволяє використовувати їх для каталізаторів без додаткового подрібнення. Доведена можливість осадження подвійних молібдатів рідкісноземельних елементів та метиламонію на носії, що містять гідроксильні групи або оксигеновмісні аніони (гідроксиди алюмінію, заліза(III) або кобальту(II), силікагелі, природні глини). Показана можливість практичного використання одержаних сполук у складі каталізаторів окисного дегідрування алканів і спиртів, а також використання продуктів термічного розкладу  $\text{CH}_3\text{NH}_3\text{R}(\text{MoO}_4)_2 \cdot \text{H}_2\text{O}$  в вакуумі, в захисній атмосфері або атмосфері водню при температурах до  $450^\circ\text{C}$  як каталізаторів анодів паливних елементів за рахунок молібдену у нижчих ступенях окиснення.

**Ключові слова:** подвійні молібдати, рідкісноземельні елементи, метиламоній, рентгеноаморфні, осадження, каталізатор.

**PRECIPITATION OF X-RAY AMORPHOUS DOUBLE MOLYBDATES OF RARE EARTH ELEMENTS AND METHYLAMMONIUM FROM AQUEOUS SOLUTIONS**

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In this study, X-ray amorphous double molybdates of rare earth elements and methylammonium  $\text{CH}_3\text{NH}_3\text{R}(\text{MoO}_4)_2 \cdot \text{H}_2\text{O}$  (where R=Ce–Lu) were synthesized in aqueous solutions of rare earth elements salts and methylammonium chloride under the excess of methylammonium molybdate at the temperature of 20–25°C. It was established that these substances have a stoichiometric composition with the following formula  $\text{CH}_3\text{NH}_3\text{R}(\text{MoO}_4)_2 \cdot \text{H}_2\text{O}$ . The study demonstrated that the compounds  $\text{CH}_3\text{NH}_3\text{R}(\text{MoO}_4)_2 \cdot \text{H}_2\text{O}$  (R=La–Y) belong to  $\alpha$ -TlYb( $\text{MoO}_4$ )<sub>2</sub>·H<sub>2</sub>O structural type with distorted monoclinic structure of a layered rhombic KY( $\text{MoO}_4$ )<sub>2</sub>. According to the obtained data, the synthesized substances are X-ray amorphous with particle size less than 100 nm; therefore, they may be used in catalytic processes without additional grinding. We showed the possibility of deposition of double molybdates of rare earth elements and methylammonium on the carriers containing hydroxyl groups or oxygen-containing anions (such as hydroxides of aluminum, iron (III) or cobalt (II), silica gel and natural clays). It was stated that the prepared compounds may be used as components in catalysts of oxidative dehydrogenation of alkanes and alcohols. The products of thermal decomposition of  $\text{CH}_3\text{NH}_3\text{R}(\text{MoO}_4)_2 \cdot \text{H}_2\text{O}$  in a vacuum, protective or hydrogen atmosphere at the temperatures of up to 450°C can be used as catalysts for fuel cell anodes due to the lower degrees of molybdenum oxidation.

**Keywords:** double molybdates; rare earth elements; methylammonium; X-ray amorphous; precipitation; catalyst.

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