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Abstract

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SYNTHESIS AND PHYSICOCHEMICAL STUDY OF REDUCED MOLYBDENUM HYDROXIDE COMPOUNDS

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In the reduction of hexavalent molybdenum compounds in the presence of water, hydrated products of lower oxidation state are formed, known as molybdenum blues. The methods of preparation and the compositions of these compounds are very diverse ([1–5]). They have found wide application as catalysts; being partially dehydrated, they possess semiconducting properties ([2]). Glemser and Lutz ([4,5]) accept the existence of the following compounds: $Mo_8O_{15}(OH)_{16}$ ($MoO_{2.88} \cdot H_2O$); $Mo_4O_{10}(OH)_2$ ($MoO_{2.75} \cdot 0.25H_2O$); $Mo_2O_4(OH)_2$ ($MoO_{2.50} \cdot 0.5H_2O$); $Mo_5O_7(OH)_{10}$ ($MoO_{2.40} \cdot H_2O$); $Mo_5O_7(OH)_8$ ($MoO_{2.20} \cdot 0.8H_2O$).

We have carried out the synthesis under various conditions and a systematic study of hydroxide compounds of various oxidation states in the range from MoO_3 to MoO_2*. The starting products for the synthesis were: MoO_3, obtained by thermal decomposition of recrystallized chemically pure ammonium molybdate, and $MoO_3 \cdot 2H_2O$. The synthesis conditions and the results of the physicochemical study are given in Table 1.

The syntheses, washing, and all investigations were carried out in a stream of nitrogen.

Table 1

Preparation No.	Method of preparation	Molecular formula	X-ray diffraction pattern type
1	Reduction of MoO_3 with a mixture of Zn and conc. HCl until a yellow-green product formed; during washing and drying oxidation to a claret-red product occurred	$MoO_{2.20} \cdot 0.9H_2O$	I
2	Oxidation of preparation 1 in air for several hours. Violet color	$MoO_{2.39} \cdot 0.5H_2O$	II
3	Oxidation of preparation 1 under mother liquor in air for 3 months. Blue color	$MoO_{2.50} \cdot 0.5H_2O$	II
4	Oxidation of preparation 2 in air for one month	$MoO_{2.64} \cdot 0.3H_2O$	II
5	Reduction of an aqueous suspension of $MoO_3 \cdot 2H_2O$ with a hydrochloric-acid solution of $SnCl_2$ according to ([4])	$MoO_{2.55} \cdot 0.8H_2O$	II

Preparation No.	Method of preparation	Molecular formula	X-ray diffraction pattern type
6	Reduction of MoO_3 with conc. HCl and Zn until a claret-red product formed. After washing and drying– blue color	$MoO_{2.52} \cdot 0.5H_2O$	III
7	Oxidation of preparation 6 in air for 8 months	$MoO_{2.59} \cdot 0.4H_2O$	III
8	Reduction of MoO_3 with dilute HCl (1:5) and Zn	$MoO_{2.82} \cdot 0.2H_2O$	IV
9	Reduction of MoO_3 with dilute HCl (1:1) and Zn	$MoO_{2.83} \cdot 0.2H_2O$	IV
10	Heating a mixture of MoO_3, Mo, and H_2O in a ratio corresponding to the degree of reduction $MoO_{2.80}$ in a sealed ampoule at 110° for 18 days	$MoO_{2.79} \cdot 0.2H_2O$	IV

Fig. 1. Intensity–$\sin^2\theta$ plots for individual phases: I–$MoO_{2.20} \cdot 0.9H_2O$, preparation 1; II–$MoO_{2.50} \cdot 0.5H_2O$, preparation 3; III–$MoO_{2.50} \cdot 0.5H_2O$, preparation 6; IV–$MoO_{2.83} \cdot 0.2H_2O$, preparation 9; V–$MoO_{2.88} \cdot 0.7H_2O$, preparation 11; VI–$MoO_{2.89} \cdot 2H_2O$, preparation 12

Figure 1: Fig. 1. Intensity–$\sin^2\theta$ plots for individual phases: I–$MoO_{2.20} \cdot 0.9H_2O$, preparation 1; II–$MoO_{2.50} \cdot 0.5H_2O$, preparation 3; III–$MoO_{2.50} \cdot 0.5H_2O$, preparation 6; IV–$MoO_{2.83} \cdot 0.2H_2O$, preparation 9; V–$MoO_{2.88} \cdot 0.7H_2O$, preparation 11; VI–$MoO_{2.89} \cdot 2H_2O$, preparation 12

Preparation No.	Method of preparation	Molecular formula	X-ray diffraction pattern type
11	Heating a mixture of $MoO_3 \cdot 2H_2O$ and Mo in a ratio corresponding to the degree of reduction $MoO_{2.88}$ under the same conditions as preparation 10	$MoO_{2.88} \cdot 0.7H_2O$	V
12*	Mixing hydrochloric-acid solutions of Mo^{VI} and Mo^{V} in the ratio 2.6:1	$MoO_{2.89} \cdot 2H_2O$	VI

* K. N. Egorychev took part in obtaining the experimental results.

A series of preparations was obtained with the more reduced products serving as the reductant. The water content in the preparations was determined by ignition in a stream of nitrogen at 450°, and the molybdenum content by precipitation as lead molybdate. Determination of the degree of reduction x in MoO_x was carried out by potentiometric and volumetric methods.

To establish the physicochemical nature of the phases, as in the study of anhydrous compounds ([6]), differential-thermal, thermogravimetric, and X-ray phase analyses were used in addition to chemical methods.

Fig. 1. Intensity–$\sin^2\theta$ plots for individual phases:

I –$MoO_{2.20} \cdot 0.9H_2O$, preparation 1;
II –$MoO_{2.50} \cdot 0.5H_2O$, preparation 3;
III –$MoO_{2.50} \cdot 0.5H_2O$, preparation 6;
IV –$MoO_{2.83} \cdot 0.2H_2O$, preparation 9;
V –$MoO_{2.88} \cdot 0.7H_2O$, preparation 11;
VI –$MoO_{2.89} \cdot 2H_2O$, preparation 12.

As a result, the existence of six types of reduced hydroxide compounds with individual thermograms, polytherms, and X-ray patterns was established. The most reduced product proved to be the burgundy-red preparation 1 (Table 1)–$MoO_{2.20} \cdot 0.9H_2O$–with an individual X-ray pattern 1 (Fig. 1). Thermogram 1 (Fig. 2) and polytherm 1 (Fig. 3) indicate the presence in the compound of water with different bond strengths. The portions of the endothermic effect at 136-190°, 236-306°, and 306-336° correspond: the first to the removal of adsorbed water, the second to the decomposition of the hydrate with $0.8H_2O$ (the stability region of which on polytherm 1 corresponds to the almost vertical segment v–g), and the third to the decomposition of the hydrate with $0.2H_2O$ (segment d–e of the polytherm). The exothermic effect at 364-390° corresponds to crystallization of the dehydrated product.

By partial oxidation of preparation 1, a series of products was obtained (preparations 2-4)–$MoO_{2.39–2.64} \cdot nH_2O$ ($n = 0.5$–$0.3H_2O$), the X-ray patterns of which (see X-ray pattern II, Fig. 1, of preparation 3–$MoO_{2.50} \cdot 0.5H_2O$) differ little from one another but are clearly distinct from X-ray pattern I of the preparation $MoO_{2.20} \cdot 0.9H_2O$. On the basis of comparison of the values of $\sin^2\theta$ and intensi-

From the intensities of the lines in the X-ray patterns it may be concluded that, in the course of oxidation of the preparation $MoO_{2.39} \cdot 0.5H_2O$ to the composition $MoO_{2.64} \cdot 0.3H_2O$, no noticeable change in the structure of the compounds occurs. Thermogram 2 (Fig. 2) and the powder pattern 2 (Fig. 3) of one of these oxidized products, preparation 3–$MoO_{2.50} \cdot 0.5H_2O$–show that the firmly bound water contained in it is removed at 284—323°, as a result of which decomposition of the compound and crystallization of the products formed occur (exothermic effect at 370°). Preparation 5 ($MoO_{2.55} \cdot 0.8H_2O$), obtained by another method (see Table 1), has an X-ray pattern close to the powder patterns of type II preparations (Fig. 1).

Reduction of MoO_3 with zinc and concentrated HCl to a certain intermediate stage gave blue preparation 6–$MoO_{2.52} \cdot 0.5H_2O$ with X-ray pattern III (Fig. 1), different from the X-ray patterns of preparations 1–5. Oxidation of it to the composition $MoO_{2.59} \cdot 0.4H_2O$ (preparation 7) did not lead to a noticeable change in the appearance of the X-ray pattern. With still more prolonged oxidation in air, from preparations with an X-ray pattern of type III, preparations of composition close to $MoO_{2.80} \cdot nH_2O$ with a new X-ray pattern IV (Fig. 1) can be obtained. Preparations of almost identical composition $MoO_{2.83–2.79} \cdot 0.2H_2O$ with the same X-ray pattern IV were synthesized by reduction of MoO_3 with hydrogen at the moment of its evolution (zinc + dilute HCl–preparations 8 and

Fig. 2

Figure 2: Fig. 2

Fig. 3 graph

Figure 3: Fig. 3 graph

9), and also by reducing MoO_3 with powdered molybdenum in the presence of water by heating in a sealed ampoule at 110° (preparation 10). Comparison of the values of $\sin^2\theta$ and the intensities of the lines in the powder patterns of preparations 8–10 and MoO_3 showed that, for small angles θ, the lines in the powder patterns of preparations 8–10 and MoO_3 coincide. With increasing angle θ, the displacement of the lines and the change in intensities increase. As a result, we came to the conclusion that, in the case of blue products of composition close to $MoO_{2.80} \cdot nH_2O$, distortion of the MoO_3 lattice takes place. As follows from consideration of thermogram 3 (Fig. 2), corresponding to preparation 9, removal of water from these compounds occurs at 284—322° in two stages (inflection at 312°).

Fig. 2. Thermograms of hydroxy compounds: 1 –$MoO_{2.20} \cdot 0.9H_2O$ –preparation 1; 2 –$MoO_{2.50} \cdot 0.5H_2O$ –preparation 3; 3 –$MoO_{2.83} \cdot 0.2H_2O$ –preparation 9; 4 –$MoO_{2.88} \cdot 0.7H_2O$–preparation 11; 5 –$MoO_{2.89} \cdot 2H_2O$ –preparation 12.

By prolonged heating of a mixture of $MoO_3 \cdot 2H_2O$ and Mo in a sealed ampoule at 110°, preparation 11–$MoO_{2.88} \cdot 0.7H_2O$ with an individu-

···by the individual Debye pattern V (Fig. 1). Thermogram 4 (Fig. 2) and polytherm 3 (Fig. 3) indicate the removal of water in two main stages: from 0.7 to 0.4 H_2O at 60-150° and complete dehydration at 150-290° (endothermic effects at 60-150° and 162-214°). Preparation 12, of the same degree of oxidation but more highly hydrated–$MoO_{2\cdot89} \cdot 2H_2O$–obtained by mixing hydrochloric-acid solutions of Mo^VI and Mo^V, gives an individual X-ray diffraction pattern VI (Fig. 1). As in the case of preparation 11, removal of water (thermogram 5, Fig. 2, and polytherm 4, Fig. 3) occurs in two stages. In both cases there is a break in the course of the thermogravimetric curves at about 190°, corresponding to the hydrate with $0.4H_2O$.

Fig. 3. Curves of the dependence of H_2O content (%) on temperature: 1 – $MoO_{2\cdot20} \cdot 0.9H_2O$ –preparation 1; 2 –$MoO_{2\cdot50} \cdot 0.5H_2O$ –preparation 3; 3 – $MoO_{2\cdot88} \cdot 0.7H_2O$ –preparation 11; 4 –$MoO_{2\cdot89} \cdot 2H_2O$ –preparation 12.

Thus, the physicochemical study we have carried out of molybdenum hydroxy compounds has shown the presence of individual compounds possessing characteristic X-ray diffraction patterns (I-VI, Fig. 1), thermograms, and polytherms; some of them (preparations 1, 3, 6, 11, 12), with respect to degree of reduction and, in a number of cases, degree of hydration (preparations 1, 3, 6), coincide with compounds cited in the literature (4, 5); however, the Debye patterns of

the compounds obtained by us do not coincide with the X-ray data reported by Glemser and Lutz (4). Comparison of the data obtained shows that part of the water in molybdenum blues is chemically bound, and moreover by bonds differing in strength. The presence of chemically bound water is a necessary condition for their existence, since removal of water from the preparations leads to decomposition. X-ray phase analysis of a number of preparations dehydrated at 450° showed the presence in them of a mixture of MoO_3 and MoO_2.

In thermograms 1 and 2 (Fig. 2), after the endothermic effect of removal of chemically bound water, an exothermic effect is recorded, corresponding to crystallization of the products of thermal decomposition—MoO_3 and MoO_2. In this case, with an increase in the degree of reduction and, consequently, with an increase in the amount of dioxide MoO_2 formed as a result of decomposition, the magnitude of the exothermic effect increases. With further increase in temperature, the oxides MoO_3 and MoO_2 formed react with one another, as described by us earlier (6), with formation of γ-Mo_4O_{11} and ζ-Mo_9O_{26} phases with thermal effects characteristic of their formation (Fig. 2, 1–5).

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Note: Figure translations are in progress. See original paper for figures.