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Abstract

Full Text

Chemistry

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Synthesis and Physicochemical Study of Oxygen Compounds in the System MoO_3–MoO_2

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As a result of a number of studies ([1–5]), the existence of seven individual phases has been established in the system MoO_3–MoO_2 (see Fig. 1): triclinic Mo_9O_{26} (ζ), monoclinic Mo_9O_{26} (β'), monoclinic Mo_8O_{23} (β), a tetragonal phase with molecular formula $MoO_{2.80}$ (ϑ), orthorhombic $Mo_{17}O_{47}$ (χ), monoclinic Mo_4O_{11} (η), and orthorhombic Mo_4O_{11} (γ).

Using differential-thermal and X-ray phase analyses, as well as microscopic examination in transmitted and reflected light, we have carried out a study of the composition, nature, and processes of formation of individual phases in the system MoO_3–MoO_2. In addition to the method of synthesizing preparations used by previous authors (thorough mixing of the initial MoO_3 with MoO_2 or Mo followed by annealing), in order to increase the activity of interaction we also used, as starting products, samples obtained by partial reduction of molybdenum trioxide MoO_3 with hydrogen (at temperatures from 450 to 600°) and samples obtained by dehydration in an inert atmosphere (at temperatures from 450 to 500°) of hydroxide compounds of molybdenum in lower oxidation states. The preparations synthesized in this way were subjected to annealing to an equilibrium state in evacuated quartz ampoules lined inside with platinum foil. The final products were analyzed for content by the gravimetric method; determination of the degree of reduction x in MoO_x was carried out by potentiometric and volumetric methods.

Fig. 1. System MoO_3–MoO_2. Solid vertical lines indicate compounds of definite composition according to Kihlborg' s data ([5]). Phases whose existence was confirmed in the present study:
a –MoO_3 (α),
b –Mo_9O_{26} (ζ),
c –Mo_9O_{26} (β'),
d –Mo_4O_{11} (η),
e –Mo_4O_{11} (γ),

Fig. 2. Intensity-$\sin^2\theta$ plots of the individual phases of the system

Figure 2: Fig. 2. Intensity-$\sin^2\theta$ plots of the individual phases of the system

f —$MoO_{2.80}$ (δ).
Horizontal dotted lines ab and cd are the boundaries of the transition η- to γ- and ζ- to β'-phase, respectively.

The thermographic study was carried out on an N. S. Kurnakov pyrometer with differential recording using a Pt—Pt Rh thermocouple in a nitrogen current, with heating and cooling rates of 1-2 and 8-9 deg/min. X-ray diffraction patterns were taken with CuK and CuK_α radiation by the powder method in a camera with cassette diameter 57.3 cm. Optical observations were performed with an MP-3 microscope in transmitted and reflected light, using an OPI opac-illuminator and an MIM-7 metallographic microscope.

On the composition—temperature diagram (Fig. 1) are plotted the compositions of several preparations investigated by us. As a result of the physicochemical study of samples annealed at temperatures from 500 to 850°, the existence of the following four intermediate phases with individual thermograms, X-ray diffraction patterns, and definite optical

properties: 1) a phase of composition $MoO_{2.89}$, formed at 650-740°, identical, apparently, to the ζ-oxide; 2) a phase of the same composition $MoO_{2.89}$ at 750°, analogous to the β'-oxide; 3) a phase of composition $MoO_{2.75}$ at 500-600°, identical to the η-oxide, and 4) a phase of the same composition $MoO_{2.75}$ at 610-700°, identical to the γ-oxide ([5]).

Fig. 2. Intensity-$\sin^2\theta$ plots of the individual phases of the system: 1 —MoO_3 (α); 2 —Mo_4O_{11} (γ); 3 —Mo_4O_{11} (η); 4 —Mo_9O_{26} (β'); 5 —Mo_9O_{26} (ζ); 6 —MoO_2 (δ).

When the values of I and $\sin^2\theta$ (Fig. 2) for the indicated compounds were compared with the literature data ([3,5]), it was found that in a number of cases, despite good agreement of the $\sin^2\theta$ values, there is a discrepancy in the intensities I of certain lines.

Thermographic study of the process of interaction of the starting components and physicochemical investigation of the products obtained at various stages of heating show that, in contrast to the γ- and ζ-phases, the η- and β'-phases are formed only upon prolonged annealing of mixtures of MoO_3 and Mo or MoO_3 and MoO_2, taken in definite ratios; the formation of these phases is not manifested by thermal effects on the thermograms.

On heating curve 1 (Fig. 3) for MoO_3, an endothermic melting effect is recorded at 795°; on the cooling curve it corresponds to an exothermic effect at the same temperature. When MoO_2 was heated in a stream of nitrogen up to 1200°, no effects were observed on the thermogram.

Fig. 3

Figure 3: Fig. 3

The process of formation of the γ-phase during solid-state interaction of MoO_3 and MoO_2, taken in various ratios, is recorded on all thermograms (curves 2-5, Fig. 3) by endothermic effect 1 in the temperature range 620-650°. This effect is characteristic of all studied mixtures of molybdenum trioxide and dioxide, from compositions close to MoO_3, for example $MoO_{2.88}$ (thermogram 2), to compositions close to MoO_2 (for $MoO_{2.28}$ –thermogram 5).

Preparations obtained as a result of heating mixtures of average composition MoO_x ($x > 2.75$) to a temperature slightly exceeding the temperature of effect 1 were mixtures of the phases MoO_3 and γ, while those obtained as a result

heating mixtures of composition MoO_x ($x < 2.75$), after heating under the same conditions, corresponded to mixtures of γ and MoO_2.

The ξ-phase is formed in the interaction of MoO_3 and the γ-phase. The process of its formation is recorded on heating curves as endothermic effect II in the temperature region 770–780–790°.

This effect appears on thermograms 2 and 3 (Fig. 3) of mixtures of composition $MoO_{2.88}$ and $MoO_{2.78}$, i.e., those in which, after formation of the γ-phase from MoO_3 and MoO_2 (at 620–650°), an excess of molybdenum trioxide remains. The diminution of this effect is associated with a decrease in the amount of excess trioxide in the reaction products. On thermograms 4 and 5 (Fig. 3) of mixtures of compositions poorer in oxygen than $MoO_{2.75}$ ($x = 2.73$ and 2.28), this endothermic effect is absent, since after the reaction of MoO_3 and MoO_2 at a temperature of 620° an excess of molybdenum dioxide was present. The effect II under consideration (thermogram 2, Fig. 3) is composite, corresponding to the formation of the ξ-phase from MoO_3 and the γ-phase (at 772–782°) and to melting with partial decomposition of the ξ-phase (at 782–798°) (see below). Endothermic effect III in the temperature region 800–850°, recorded on the thermograms of mixtures of all compositions from $MoO_{2.88}$ to $MoO_{2.28}$, corresponds to the process of melting with partial decomposition of the γ-phase formed as a result of the preceding process.

Fig. 3. Thermograms of molybdenum trioxide MoO_3 (1) and mixtures of MoO_3 and MoO_2, taken in various ratios corresponding to the compositions: $MoO_{2.88}$ (2), $MoO_{2.78}$ (3), $MoO_{2.73}$ (4), and $MoO_{2.28}$ (5).

The synthesized oxides possess properties characteristic of each of them. Orthorhombic Mo_4O_{11} ($MoO_{2.75}$)-γ-oxide is formed as a dark-violet crystalline powder at 610°. Its opaque crystals in reflected light have the appearance of shapeless grains, among which elongated hexagons are encountered. Monoclinic Mo_4O_{11} ($MoO_{2.75}$)-η-oxide is formed at 500–600° as a violet crystalline powder. In reflected light, the opaque crystals are lead-colored plates having the form

Fig. 4. Thermograms of the individual phases of the MoO_3—MoO_2 system: 1 –Mo_4O_{11} (γ); 2 –Mo_4O_{11} (η); 3 –Mo_9O_{26} (β'); 4 –Mo_9O_{26} (ζ)

Figure 4: Fig. 4. Thermograms of the individual phases of the MoO_3—MoO_2 system: 1 –Mo_4O_{11} (γ); 2 –Mo_4O_{11} (η); 3 –Mo_9O_{26} (β'); 4 –Mo_9O_{26} (ζ)

of various geometric figures–triangles, trapezia, etc. Steps parallel to the faces are often observed on the surfaces of the plates.

X-ray patterns 2 and 3 (Fig. 2) of the γ- and η-oxides are individual. Their thermograms 1 and 2 (Fig. 4) are rather close. The endothermic effect recorded on thermogram 1 at 815–820–830° corresponds to melting of the γ-phase, occurring with partial decomposition into MoO_3 and MoO_2. The break at 818° in the region of the analogous effect on thermogram 2 for the η-phase probably corresponds to transformation of η- into the γ-phase with subsequent melting of the latter at 818–824°. Preparations obtained after heating the γ- and η-phases to 850° contained, in addition to MoO_3, MoO_2, and the γ-phase, considerable amounts of the ξ-phase, which apparently is a product of the interaction of MoO_3 with the γ-phase; with decreasing cooling rate, the amount of MoO_3 in them decreased, and that of the ξ-phase increased. The cooling curves

The $1'$ and $2'$ curves of the γ- and η-phases are very close. The exothermic effect recorded on them at 815—810° corresponds to crystallization of the γ-phase, and that at 770—760°, with an inflection at 765°, to crystallization of the ζ-phase and MoO_3.

Monoclinic Mo_9O_{26} ($MoO_{2.89}$)-β'-oxide is formed at 750° as opaque dark-blue conglomerates with a violet luster. The latter consist of parallel intergrowths of crystals with well-developed faces. Individual crystals in reflected light have the shape of parallelepipeds. Cleavage is along one plane; the cleavage fracture has a high reflecting power. The β'-phase has the typical X-ray pattern 4 (Fig. 2). The endothermic effect recorded on its thermogram 3 (Fig. 4) at 779—790—803° is a combined one; it corresponds to melting of the β'-phase, accompanied by partial decomposition into MoO_3 and the γ-phase, and to melting of the MoO_3 trioxide formed in this process. The second exothermic effect at 828—843—845°, corresponding to melting with decomposition of the γ-phase, is interrupted by an exothermic effect at 833—838—840°, which evidently corresponds to the interaction process of the phases formed during melting.

Fig. 4. Thermograms of the individual phases of the MoO_3—MoO_2 system: 1 –Mo_4O_{11} (γ); 2 –Mo_4O_{11} (η); 3 –Mo_9O_{26} (β'); 4 –Mo_9O_{26} (ζ)

Triclinic Mo_9O_{26} ($MoO_{2.89}$)-ζ-oxide is formed at 650—740° as a blue-black crystalline powder. The opaque crystals in reflected light have the appearance of elongated plates with high reflecting power. Their lateral faceting is not very clearly expressed. A very characteristic feature is the large number of steps on the surface of the plates, and these do not run in one direction. The ζ-phase has the typical X-ray pattern 5 (Fig. 2). On its thermogram 4 (Fig. 4), en-

dothermic effects are recorded in the temperature ranges 773—788—807° and 827—829—838—845°. The portion of the first effect at 773—781° corresponds to melting of the ζ-phase, proceeding with partial decomposition into MoO_3 and the γ-phase; the second portion of this effect at 781—792° corresponds to melting of MoO_3 formed as a result of thermal decomposition of the ζ-phase; the effects in the range 827—829—838—845° are analogous to the corresponding effects on thermogram 3 (Fig. 4). The exothermic effects recorded on the cooling curves 3′ and 4′ at 813—810° and 776—775—765° are, in their nature, analogous to the effects on the cooling curves 1′ and 2′.

The formation of other individual phases noted in the literature was not established in appreciable amounts under the conditions we used.

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