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Phase Relations in the Cupric Molybdates–Cuprous Molybdates System

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It has been found that the mechanism of oxidation of cuprous molybdates and reduction of cupric molybdates is different in different temperature ranges. Below 460°C $Cu_3Mo_2O_9$ is reduced by hydrogen directly to $Cu_6Mo_4O_{15}$, and $CuMoO_4$ disproportionates to a mixture of $Cu_6Mo_4O_{15}$ and $Cu_2Mo_3O_{10}$, metallic copper and MoO_2 being the common final products in both cases. Oxidation of $Cu_2Mo_3O_{10}$, $Cu_{4-x}Mo_3O_{12}$, and $Cu_6Mo_4O_{15}$ results in formation of $CuMoO_4$ in the mixture with MoO_3 or CuO, depending on the stoichiometry of the initial salt. The consecutive reaction $2CuMoO_4 + CuO \rightarrow Cu_3Mo_2O_9$ proceeds only at higher temperatures. Above 460°C liquid phases appear in the system. The final products of cupric molybdate reduction in this range are the same (MoO_2 and Cu) but "intermediary products" appear ($Cu_{4-x}Mo_3O_{12}$ for $Cu_3Mo_2O_9$ and mixtures of $Cu_2Mo_3O_{10}$ with $Cu_3Mo_2O_9$ and $Cu_6Mo_4O_{15}$ for $CuMoO_4$) resulting from crystallization equilibria frozen on cooling. Thermal decomposition (with simultaneous melting) of $Cu_3Mo_2O_9$ and $CuMoO_4$ begins under 10^{-1} Torr O_2 at about 690°C leading (if cooled) to the same products as that of mild reduction with hydrogen in the upper temperature range. The equilibrium in the univariant system solid $Cu_3Mo_2O_9$–liquid $Cu_6Mo_4O_{15}$–gaseous O_2 is described in the temperature range 700–855°C by the equation $\log P_{O_2} = -20.600/T + 20.4$. The more complex mechanism of thermal decomposition of $CuMoO_4$ is also described.

Introduction

As reported first by Thomas *et al.* (*1*) and then confirmed and developed by Nassau and Shiever (*2*) cupric molybdates $CuMoO_4$ and $Cu_3Mo_2O_9$ when heated in air above 800–850°C melt and decompose with evolution of oxygen. In the case of $CuMoO_4$ evaporation of MoO_3 was also observed (*2*). As one can conclude from Ref. (*1*) the temperatures of melting and decomposition are lowered under moderate vacuum down to about 700°C. It has been, however, a matter of controversy whether $Cu_2Mo_3O_x$ (*3*), $Cu_3Mo_2O_8$ (*1*), $Cu_{4-x}Mo_3O_{12}$ (*4*), or $Cu_6Mo_4O_{15}$ (*2*) are the solid products of decomposition. It has also not been cleared up whether decomposition proceeds in the presence of some liquid phase as mentioned in (*1*) or in certain cases takes place in solid state (according to (*2*) $Cu_6Mo_4O_{15}$ melts at 880°C).

The aim of the present work was to reexamine the mechanism of reduction of cupric molybdates and oxidation of the reduced phases formed. The present studies were preceded by the determination of the Cu_2O–CuO–MoO_3 phase diagram in the subsolidus range (*5*). As found $CuMoO_4$ and $Cu_3Mo_2O_9$ are stable in air up to 820 and 855°C, respectively, melting at these temperatures with simultaneous decomposition. Some further arguments for this conclusion will also be presented in this

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paper. There exist three potential reduced phases, namely, two cuprous molybdates, $Cu_2Mo_3O_{10}$ (mp 532°C, in argon) and $Cu_6Mo_4O_{15}$ (mp 466°C, in argon) (*5*), and one mixed-valence nonstoichiometric compound, $Cu_{4-x}Mo_3O_{12} = Cu_3^{2+}Cu_{1-x}^{0}Mo_3^{6+}O_{12}$ ($0.10 \leq x \leq 0.40$) (*5, 6*), which melts between 630 and 650°C depending on x and at 525–530°C undergoes polymorphic transformation. The above-mentioned six phases can be identified and distinguished even when mixed by X-ray phase analysis using the following data: $CuMoO_4$ (*7, 8*), $Cu_3Mo_2O_9$ (*9, 10*), low-temperature α-$Cu_{4-x}Mo_3O_{12}$ (*4*), $Cu_2Mo_3O_{10}$, $Cu_6Mo_4O_{15}$, and high-temperature β-$Cu_{4-x}Mo_3O_{12}$ (*5*).

As thus follows from our previous studies (*5*) cupric molybdates melt and decompose at temperatures much higher than the melting points of all phases that may appear as the reduction products. Thus the thermal decomposition should proceed in the presence of liquids, and its mechanism should involve the crystallization equilibria and may differ from the mechanism of reduction operating in the solid state range. To resolve this problem the studies on the reduction of cupric molybdates with hydrogen at low temperatures were included. The same arguments caused us to study the mechanism of oxidation of reduced phases as function of temperature.

Experimental

$CuMoO_4$, $Cu_3Mo_2O_9$, $Cu_2Mo_3O_{10}$, $Cu_6Mo_4O_{15}$, and $Cu_{4-x}Mo_3O_{12}$ were prepared by solid state reactions between respective weighted mixtures of MoO_3 and CuO or Cu_2O. The starting materials were commercial products of p.a. grade. Cu^{II}-containing salts were obtained by heating the initial mixtures in air at 600°C for 40 hr. The three other compounds were synthesized in sealed, evacuated quartz tubes at 520°C for 10 hr. The details of preparation were published in (*5*) and (*11*).

Phase analyses of the studied samples were performed at room temperature using a Rigaku–Denki Model D3F diffractometer and Co$K\alpha$ radiation. ASTM or literature data quoted in the introduction were used for identification of simple phases (MoO_3, MoO_2, CuO, Cu_2O, and Cu) and copper molybdates, respectively.

DTA, TG, and DTG analyses (20–900°C) were performed with Mettler Thermoanalyzer-2 at the heating rate of 3°C/min and the cooling rate of 15°C/min in a stream of air or purified argon (about 1 ppm oxygen). The samples of 100 mg were placed in platinum cups and Al_2O_3 was used as a reference compound. To change the decomposition degree of copper molybdates in some cases the samples before cooling were heated isothermally in the apparatus at 900°C for a certain period of time or cooling was started at temperatures somewhat lower than 900°C.

Thermal decomposition of cupric molybdates was followed quantitatively in the conventional vacuum apparatus provided with a quartz reactor, a furnace with quartz window for visual observations of the samples, and a butylphthalate manometer. The volume of the reactor (150 ml) and the sample weight (0.3–0.5 g) were adjusted after preliminary experiments in such a manner as to reach total conversion of the sample. In all experiments reported in the present paper involving reduction or oxidation of copper molybdates complete transformation of Cu^{II} to Cu^{I} or the converse (and equivalent oxygen loss or uptake) is assumed as 100% conversion. Before the experiment the sample was outgassed at 10^{-1} Torr and 500°C. As found in the preliminary experiments the evolution of oxygen at this pressure commences above 690°C. Starting from this point the temperature was successively increased by several degrees (up to 950°C), and after equilibrium was reached at each temperature (30–90 min) the pressure was read. Proceeding in the same manner on cooling the reversibility of the process was checked.

In the separate experiments the process of decomposition was stopped at certain known conversions by rapid evacuation and cooling and the phase composition of products was analyzed by the X-ray method.

The same apparatus was used to follow the oxidation of $Cu_2Mo_3O_{10}$, $Cu_6Mo_4O_{15}$, and $Cu_{4-x}Mo_3O_{12}$. In this case the samples were evacuated (10^{-1} Torr) at room temperature and 60 Torr of oxygen was introduced at the reaction temperature. The amount of oxygen contained initially in the reactor exceeded at least twice the quantity required for total oxidation of the sample.

Reduction of copper molybdates with hydrogen at a pressure of 27–33 Torr was studied with the static recirculation method described in detail in (*12*).

Results and Discussion

Reduction with hydrogen starts at a measurable rate at 360°C for $Cu_3Mo_2O_9$ and at 420°C for $CuMoO_4$. As seen from Table I at temperatures not exceeding 460°C the phase composition of the products follows simple logic regularities. $Cu_3Mo_2O_9$ reduces to $Cu_6Mo_4O_{15}$ with conservation of the Cu/Mo ratio. As none of the cuprous molybdates shows a Cu/Mo ratio equal to 1/1, $CuMoO_4$ disproportionates to a mixture of $Cu_2Mo_3O_{10}$ and $Cu_6Mo_4O_{15}$, which appear among products roughly in the same quantity. After considerable level of conversion to the above-mentioned products of mild reduction is reached, deep reduction products appear (Cu and MoO_2) which are apparently formed in the consecutive reaction.

If, however, the temperature of reduction exceeds 460°C the above-mentioned regularities are disturbed. $Cu_{4-x}Mo_3O_{12}$ appears as the main product of mild reduction of $Cu_3Mo_2O_9$. On the other hand the ratio $Cu_2Mo_3O_{10}/Cu_6Mo_4O_{15}$ in the reduction products of $CuMoO_4$ becomes dependent on conversion, the first salt prevailing at low reduction degrees and the second at higher ones.

It is noteworthy that the phase composition of thermally decomposed cupric molybdates (Table II) is governed by the

TABLE I

PHASE COMPOSITION OF COPPER MOLYBDATES REDUCED WITH HYDROGEN[a]

$Cu_3Mo_2O_9$			$CuMoO_4$		
Red. temp. (°C)	Conversion (%)	Phase composition	Red. temp. (°C)	Conversion (%)	Phase composition
400	15	3/2, 6/4	440	10	1/1, 6/4 ≈ 2/3
440	49	6/4, 3/2	460	30	1/1, 6/4 ≈ 2/3, traces of Cu and MoO_2
420	73	6/4, Cu, MoO_2	460	54	1/1, 6/4 ≈ 2/3, traces of Cu and MoO_2
400	109	MoO_2, Cu, 6/4	480	81	MoO_2, Cu, 6/4, 2/3
500	37	4 − x, traces of 3/2	500	28	2/3, 6/4, 1/1, traces of Cu and MoO_2
500	119	6/4, MoO_2, Cu	500	73	MoO_2, Cu, 6/4, traces of 1/1

[a] 1/1, $CuMoO_4$; 3/2, $Cu_3Mo_2O_9$; 2/3, $Cu_2Mo_3O_{10}$; 4 − x, $Cu_{4-x}Mo_3O_{12}$; 6/4, $Cu_6Mo_4O_{15}$. Compounds quoted in order of estimated concentration.

TABLE II

PHASE COMPOSITION OF THERMAL DECOMPOSITION PRODUCTS OF COPPER MOLYBDATES[a]

$Cu_3Mo_2O_9$			$CuMoO_4$		
Temp. (°C)	Conversion (%)	Phase composition	Temp. (°C)	Conversion (%)	Phase composition
780	27	3/2, 4 − x	740	3	1/1, 2/3
795	62	4 − x, 3/2, 6/4	770	40	1/1, 2/3, 3/2
890	90	6/4, 4 − x	890	89	6/4, 2/3, 1/2
990	100	6/4, traces of 4 − x	985	100	6/4
690	Reoxidized in 100% after previous red. in 100%	3/2	690	Reoxidized in 50% after previous red. in 97%	1/1, 3/2, 2/3, 6/4

[a] See Table I for explanation of symbols.

same rules as those which apply to products of reduction with hydrogen in the upper temperature range. This fact seems to be a common consequence of the appearance of some liquid phases in the system under study and crystallization equilibria on cooling. It may be useful to remember that $Cu_6Mo_4O_{15}$ melts at 466°C. As this salt is formed during the reduction of cupric molybdates with hydrogen, the liquid phase should appear at 466°C or, in the case of the existence of some eutectic, at even lower temperatures. What, however, can be said about melting and decomposition of cupric molybdates? Are they simultaneous or indepenent processes?

DTA of $CuMoO_4$ and $Cu_3Mo_2O_9$ show that they melt at 820 and 855°C in air and at 745 and 760°C in argon, respectively. In both media the initial deflections of the TG curves coincide with those of the DTA curves, indicating that melting and decomposition are simultaneous processes. For both salts the mass losses at the end of heating, i.e., at 900°C, correspond to 70–100% of conversion. On cooling in air the process is completely reversible for $Cu_3Mo_2O_9$ but only ~50% reversible for $CuMoO_4$.

DTA and TG curves recorded on cooling show considerable variety depending on the experimental conditions. Leaving the problem of the liquidus range of the system for the further detailed studies we would like to describe briefly some of the most characteristic properties. Decomposed $Cu_3Mo_2O_9$ cooled in air reoxidizes quickly ($\Delta m = 100\%$) above 750°C and no DTA peaks are observed at lower temperatures. Completely (100%) decomposed $Cu_3Mo_2O_9$, cooled in argon, shows a single, intense, narrow peak at 450°C which is ascribed to the freezing of $Cu_6Mo_4O_{15}$ (confirmed by X-ray analysis). Partly decomposed $Cu_3Mo_2O_9$, cooled in argon, shows two or three peaks; the last of these (intense) appears at 450°C, and the others, which are very weak, move along the temperature axis (500–650°C) depending on the degree of reduction. Decomposed $CuMoO_4$, cooled in argon ($\Delta m = 0$) or in air (reoxidation not higher than 50% and terminating at about 750°C), shows two to four exothermal peaks between 450 and 650°C of position and intensity dependent on the experimental conditions. A more detailed discussion of the observed thermal effects should be possible after performing the experiments under well-defined conditions (partial pressure of oxygen). It seems reasonable, however, to conclude that the thermal effects observed on cooling of partly reduced cupric molybdates reflect the stepwise crystallization of $Cu_{4-x}Mo_3O_{12}$ and $Cu_6Mo_4O_{15}$ (reduced and melted $Cu_3Mo_2O_9$) or $Cu_3Mo_2O_9$, $Cu_2Mo_3O_{10}$, and $Cu_6Mo_4O_{15}$ (reduced and melted $CuMoO_4$) with participation of the solid phases present in the system. The results obtained are thus qualitatively consistent with those presented in Table II.

The experiments performed with the manometric method (Fig. 1) together with visual observations show that at an initial pressure of 10^{-1} Torr the evolution of oxygen from $CuMoO_4$ and $Cu_3Mo_2O_9$ begins around 690°C, and at practically the same moment a liquid phase appears. With the increasing conversion the solid phase disappears gradually but it is still observed even at 90% of conversion. On cooling in the atmosphere of previously evolved oxygen, similar to the results of thermal analysis, the process is completely reversible for $Cu_3Mo_2O_9$ (oxygen was totally consumed and the liquid phase disappeared at about 690°C), but only in part for $CuMoO_4$ (after consumption of ~50% oxygen uptake is stopped at about 750°C, and the remaining liquid freezes at 450–500°C).

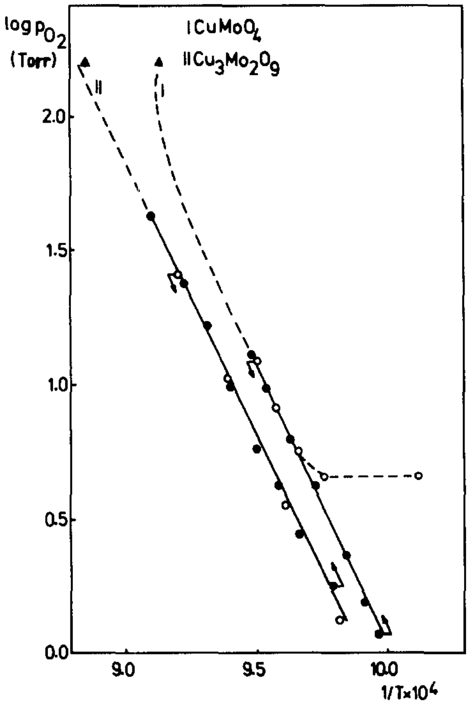

FIG. 1. Dependence of decomposition pressure of $Cu_3Mo_2O_9$ and $CuMoO_4$ on temperature. Solid circles and open circles indicate values determined with manometric method on heating and cooling, respectively. Triangles indicate values found with DTA in air.

The above-described results show that the temperatures of decomposition and melting of cupric molybdates strongly depend on the pressure of oxygen. A similar phenomenon has been observed in (*2*) at higher pressures ranging from 160 Torr to 2–3 atm. This dependence may not be ascribed to a physical factor (pressure dependence of mp) but rather results from the chemical equilibria.

As seen in Fig. 1 in the case of $Cu_3Mo_2O_9$ the dependence $\log P_{O_2} - 1/T$ is reversible, linear in the entire range studied (10^{-5}–160 Torr, 700–855°C), and may be represented as:

$$\log P_{O_2} = -\frac{20{,}600}{T} + 20.4$$

(P_{O_2} in Torrs, parameters determined with an accuracy of ±1.5%).

This fact combined with DTA results (cooling of completely decomposed $Cu_3Mo_2O_9$ in argon) suggests that we are dealing with a univariant system composed of three phases: solid cupric molybdate $Cu_3Mo_2O_9$, liquid cuprous molybdate $Cu_6Mo_4O_{15}$, and gaseous oxygen, comprising two independent components.

As already stated in the case of thermal decomposition of $CuMoO_4$ the phase equilibria are more complicated. The dependence $\log P_{O_2} - 1/T$ is nonlinear at higher temperatures and irreversible at lower temperatures. In the narrow range of linearity and reversibility (770–790°C) it may be formally represented as

$$\log P_{O_2} = -\frac{21{,}200}{T} + 21.3,$$

with parameters very close to those found for $Cu_3Mo_2O_9$.

As one can conclude from the results presented in Table II and discussed above, at the beginning of the process $CuMoO_4$ apparently decomposes to solid $Cu_3Mo_2O_9$ and liquid $Cu_2Mo_3O_{10}$, but some part of $Cu_3Mo_2O_9$ (dependent on temperature) dissolves in the liquid phase, changing its composition. Thus the system is no longer univariant.

During the manometric experiments it was observed also that if $CuMoO_4$ decomposes above about 900°C a white deposit is formed on the cold walls of the apparatus outside the furnace which is identified by X-ray analysis as MoO_3. This process takes place, however, only at very high temperatures. It is thus understandable why $Cu_6Mo_4O_{15}$ becomes the single final product of thermal decomposition at high temperatures not only for $Cu_3Mo_2O_9$ but also for $CuMoO_4$ (Table II).

There exists certain inconsistencies between the temperatures of the beginning of $CuMoO_4$ and $Cu_3Mo_2O_9$ decomposition observed in DTA (argon) and those of the manometric experiments (vacuum). This is apparently caused by the fact that it is extremely difficult to remove completely the traces of oxygen from the intergranular spaces of the sample in DTA conditions (stream of argon). Thus the results obtained under vacuum seem to be much more accurate.

The results of phase analysis of products of oxidation of $Cu_2Mo_3O_{10}$, $Cu_6Mo_4O_{15}$, and $Cu_{4-x}Mo_3O_{12}$ as function of conversion and temperature are presented in Table III. As seen effective oxidation of all three compounds proceeds already at 400–460°C and results in the formation of their common product $CuMoO_4$ in the mixture with MoO_3 or CuO, depending on the stoichiometry of the initial salt. The consecutive reaction between $CuMoO_4$ and CuO (as already mentioned in (*11*)) due to kinetic hindrances is possible only above 465°C. Neither on reduction of cupric oxides nor on oxidation

TABLE III

Phase Composition of Oxidation Products of Reduced Copper Molybdates[a]

Sample	Oxidation temp. (°C)	Conversion (%)	Phase composition
$Cu_6Mo_4O_{15}$	405	59	1/1, traces of 6/4 and CuO
	437[b]	64	1/1, CuO
	542[c]	77	1/1, 3/2
	470	59	3/2, traces of 1/1, 6/4 and $4-x$
	500[d]	32	$4-x$
	500[e]	81	3/2, traces of 1/1 and CuO
	533	83	3/2, traces of 1/1
$Cu_{3.85}Mo_3O_{12}$	423	82	1/1, CuO
	465	85	1/1, 3/2
	479	86	3/2, 1/1
	500	84	3/2, 1/1
	552	87	3/2, 1/1
$Cu_2Mo_3O_{10}$	439	93	1/1, traces of MoO_3 and 2/3
	548	61	MoO_3, 1/1, 2/3

[a] See Table I for explanation of symbols.

[b–e] *d* and *e* indicate further treatment of *b* and *c*, respectively.

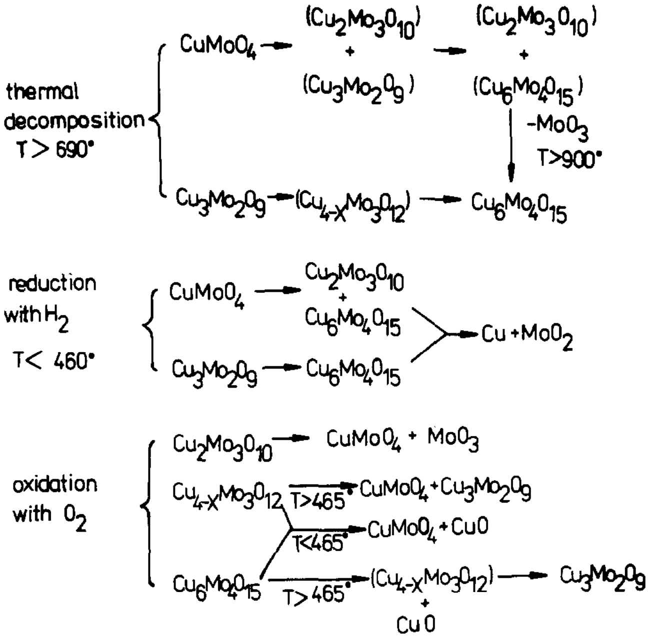

FIG. 2. Scheme of reduction–oxidation processes in the cupric molybdates–cuprous molybdates system. The phases placed in parentheses result from crystallization equilibria frozen on cooling.

of cuprous molybdates is $Cu_{4-x}Mo_3O_{12}$ formed below 460°C. If, however, $Cu_6Mo_4O_{15}$ is oxidized above this temperature $Cu_{4-x}Mo_3O_{12}$ appears due to the crystallization equilibria already discussed.

The main conclusion of the studies described in this paper is shown in Fig. 2 which demonstrates the scheme of the reduction–oxidation processes in the cupric molybdates–cuprous molybdates system.

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