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STUDIES ON CHROMIUM(III) MOLYBDATE AND EQUILIBRIA IN THE $CrVO_4$–$Cr_2(MoO_4)_3$ SYSTEM

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ABSTRACT

The behaviour of $Cr_2(MoO_4)_3$ towards $CrVO_4$ up to 1000 °C over the entire range of component concentrations was investigated using differential thermal analysis and X-ray powder diffraction. The results are shown in the form of a phase diagram. Chromium(III) molybdate decomposes to Cr_2O_3 and MoO_3 before reaching its melting point. The decomposition of $Cr_2(MoO_4)_3$ takes place at 810 °C accompanied by the sublimation of MoO_3.

INTRODUCTION

Two- and three-component systems of transition oxides and the phases which exist in these systems are used as catalysts of many organic processes [1]. The systems whose basic components are V_2O_5 and MoO_3 with a third component of Fe_2O_3 or Cr_2O_3 have not been studied in great detail.

We have found from earlier studies of the Fe_2O_3–V_2O_5–MoO_3 system (from an investigation of the pseudodicomponent section $FeVO_4$–$Fe_2(MoO_4)_3$) that $Fe_2(MoO_4)_3$ reacts with $FeVO_4$ (one of the two components which exist in the binary Fe_2O_3–V_2O_5 system) to form a new compound, $Fe_4V_2Mo_3O_{20}$ [2,3]. Therefore we decided to investigate the behaviour of $Cr_2(MoO_4)_3$ (which is isostructural with $Fe_2(MoO_4)_3$ [4]) towards $CrVO_4$ and to find which of the phases of the $CrVO_4$–$Cr_2(MoO_4)_3$ system remain in permanent equilibrium up to 1000 °C over the entire range of component concentrations.

The structure and basic properties of the components of the system are known. Chromium(III) orthovanadate crystallizes in a rhombic system and belongs to the *Cmcm* space group [5]. $CrVO_4$ melts incongruently depositing solid Cr_2O_3; this has been reported to occur at 810 °C (Cirilli et al. [6]), 886 ± 4 °C (Amiel et al. [7]), 902 °C [8,9] and 917 °C [10]. We have found that the melting point of $CrVO_4$ is 860 ± 5 °C [11].

Like $Fe_2(MoO_4)_3$, chromium(III) molybdate occurs in two polymorphic modifications: a low-temperature form consisting of triclinic crystals and a

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high-temperature form consisting of orthorhombic crystals [4]. The temperature of the $Cr_2(MoO_4)_3$ polymorphic transition is 385 °C [12]. The structures of the two modifications of chromium molybdate are known [4]. Plasova and Kefeli [4] attribute the low-temperature modification of $Cr_2(MoO_4)_3$ to the $P2_1/a$ space group and the high-temperature form to the *Pnca* space group.

Information in the literature on the thermal properties of chromium(III) molybdate is inconsistent. Plasova and Kefeli [4] have found that $Cr_2(MoO_4)_3$ melts incongruently at 800–810 °C and Getman and Marchenko [13] have reported that chromium(III) molybdate in the solid state decomposes to Cr_2O_3 and MoO_3 before reaching its melting point. The decomposition of $Cr_2(MoO_4)_3$ starts at a temperature higher than 850 °C and is accompanied by sublimation of MoO_3.

EXPERIMENTAL

V_2O_5, MoO_3 (p.a.) and Cr_2O_3 (obtained by thermal decomposition of $(NH_4)_2Cr_2O_7$ at 100–150 °C followed by roasting at 1000 °C for 72 h in air) were used for the experiments. $Cr_2(MoO_4)_3$ and $CrVO_4$ also used in the experiments were obtained by roasting of the oxide mixtures. $Cr_2(MoO_4)_3$ was obtained from a mixture of Cr_2O_3 and MoO_3 containing 25 mol.% of Cr_2O_3 which was roasted under the following conditions: 400 → 500 °C (24 h), 550 °C (24 h), 600 °C (24 h), 650 °C (24 h) and 700 °C (48 h). $CrVO_4$ was obtained by roasting an equimolar mixture of Cr_2O_3 and V_2O_5 at 500 °C (24 h), 550 °C (24 h), 600 °C (24 h), 630 °C (24 h), 700 °C (24 h), 750 °C (24 h) and 800 °C (24 h).

Differential thermal analysis (DTA) was performed using a derivatograph (F. Paulik–J. Paulik–L. Erdley (MOM, Budapest)) in quartz crucibles in air at 20–1000 °C at a heating rate of 10 °C min^{-1}. Specimens of 1000 mg were used. In the phase diagram construction the solidus lines were determined from the temperatures of the initial effects of DTA whereas the liquidus curves were based on the maximum temperatures of these effects. The accuracy of the temperature readings estimated by repetition was ± 5 °C.

The phase compositions of the specimens were determined by X-ray powder diffraction (NRD diffractometer, type A_2, with a goniometer HZG-4) using data from ASTM cards [14] and from refs. 11 and 15–17.

A study of the change in the diffraction spectra of the specimens was made in air in situ in a high-temperature chamber (UVD-2000) linked to a diffractometer (DRON-3). A basic series of 16 mixtures prepared from the oxides and three specimens prepared from the phases constituting the system of interest (i.e. $CrVO_4$ and $Cr_2(MoO_4)_3$) was used for the experiments. Appropriate amounts of the substrates were ground, pelleted and heated in air under the following conditions: 400 → 500 °C (24 h), 550 °C

(48 h), 600 °C (48 h), 650 °C (48 h) and 700 °C (48 h). The $CrVO_4$–$Cr_2(MoO_4)_3$ specimens were heated additionally at 700 °C (24 h), 750 °C (24 h), 750 °C (48 h) and 780 °C (72 h). Starting from 500 °C, the samples (after each roasting cycle) were cooled slowly to ambient temperature, ground and examined by DTA, their phase compositions were established and they were then pelleted again. After preparation was complete, they were heated at 780 °C for 48 h, cooled rapidly to ambient temperature, ground and finally examined by X-ray powder diffraction. In this way, the types of resultant phase and the range of their coexistence in the subsolidus area were established. The types of solid phase remaining in equilibrium with liquid at temperatures higher than the temperature of the solidus line were determined from investigation of the phase compositions of samples heated additionally at selected temperatures in the range 800–900 °C for 2–3 h followed by rapid cooling to ambient temperature.

RESULTS AND DISCUSSION

Since the information in the literature on the thermal properties of chromium(III) molybdate is inconsistent, we investigated the behaviour of $Cr_2(MoO_4)_3$ at temperatures up to 1000 °C. $Cr_2(MoO_4)_3$, obtained by roasting a mixture of Cr_2O_3 and MoO_3 (molar ratio, 1 : 3) under the given conditions, was heated in air at 1000 °C for 3 h and then cooled rapidly to ambient temperature. Under these conditions the sample does not melt, and X-ray powder diffraction reveals that it contains Cr_2O_3 exclusively. The experimental results indicate that, up to 1000 °C, $Cr_2(MoO_4)_3$ does not melt but is decomposed to solid Cr_2O_3 and MoO_3 with simultaneous sublimation of molybdenum trioxide.

Other investigations were carried out to determine the temperature at which the decomposition of $Cr_2(MoO_4)_3$ starts. These investigations were performed in a high-temperature chamber installed on a goniometer of a DRON-3 diffractometer. This allowed us to observe directly the changes in the diffraction spectrum of chromium(III) molybdate as a function of temperature. The sample of $Cr_2(MoO_4)_3$ was placed in the chamber which was maintained successively at temperatures of 700 °C (0.5 h), 750 °C (0.5 h), 800 °C (0.5 h), 810 °C (0.5 h and 1.5 h) and 830 °C (1 h). A diffraction spectrum was recorded at each of the temperatures. The X-ray powder diffraction results are shown in Table 1.

The data of Table 1 confirm that chromium(III) molybdate decomposes to Cr_2O_3 and MoO_3 before reaching its melting temperature. The decomposition of $Cr_2(MoO_4)_3$ starts at a very small rate at 800 °C; the rate increases with temperature, and at 810 °C it reaches a measurable value. In order to confirm this observation a specimen of $Cr_2(MoO_4)_3$ was heated in air at 810 °C for 7 days and was then cooled gently to ambient temperature,

TABLE 1

The decomposition of $Cr_2(MoO_4)_3$ observed in a high-temperature X-ray chamber

Conditions of measurement		X-ray powder diffraction results
Temperature (° C)	Time (h)	
700	0.5	$Cr_2(MoO_4)_3$
750	0.5	$Cr_2(MoO_4)_3$
800	0.5	$Cr_2(MoO_4)_3$, Cr_2O_3 (very little)
810	0.5	$Cr_2(MoO_4)_3$, Cr_2O_3 (little)
810	1.5	$Cr_2(MoO_4)_3$, Cr_2O_3
830	1.0	Cr_2O_3, $Cr_2(MoO_4)_3$

ground and analysed by X-ray powder diffraction. The presence of Cr_2O_3 was confirmed after this heating time. Thus at 810 °C, chromium(III) molybdate can be completely decomposed to Cr_2O_3 and MoO_3, although the rate of the process is very small. Molybdenum trioxide is evolved from the sample due to the high rate of sublimation under these conditions.

Table 2 shows the compositions of the initial mixtures and the X-ray powder diffraction results after each roasting cycle for samples prepared from the oxides and Table 3 shows analogous information for the samples prepared from $CrVO_4$ and $Cr_2(MoO_4)_3$. The X-ray powder diffraction results of the samples obtained from the oxides (Table 2) show that in this system there are no phases present containing a molar ratio of $CrVO_4$ and $Cr_2(MoO_4)_3$. X-ray powder diffraction of the samples obtained from the oxides with an initial composition corresponding to 2.5–20.0 mol% of $Cr_2(MoO_4)_3$ shows that they are a mixture of three phases: $CrVO_4$, Cr_2O_3 and $CrVMoO_7$. The sample containing 25 mol% of $Cr_2(MoO_4)_3$ is two phase and consists of Cr_2O_3 and $CrVMoO_7$. In the other samples three phases are present i.e. Cr_2O_3, $CrVMoO_7$ and $Cr_2(MoO_4)_3$.

When $CrVO_4$ and $Cr_2(MoO_4)_3$ were used as substrates, no change was observed in the phase compositions of the specimens up to 650 °C even though the same conditions were used as for the oxide preparations (Table 3). X-ray powder diffraction of the $CrVO_4$–$Cr_2(MoO_4)_3$ samples roasted at 700, 750 and 780 °C shows that the attainment of equilibrium requires either prolonged heating (when compared with samples obtained from the oxides) at temperatures lower than 700 °C or elevation of the heating temperature. It follows from the data of Table 3 that equilibrium in the $CrVO_4$–$Cr_2(MoO_4)_3$ samples is achieved only after the last heating cycle, i.e. after roasting for 72 h at 780 °C. The phase composition of the sample containing 10 mol.% of $Cr_2(MoO_4)_3$ and 90 mol% of $CrVO_4$ indicates that in the solid state a reaction takes place in the $CrVO_4$–$Cr_2(MoO_4)_3$ system

$$3CrVO_4(s) + Cr_2(MoO_4)_3(s) = 3CrVMoO_7(s) + Cr_2O_3(s) \tag{1}$$

TABLE 2

Composition of initial mixtures, preparation conditions and X-ray powder diffraction results for specimens prepared from the oxides (the basic series)

Preparation conditions		Phases present at initial compositions (mol% $Cr_2(MoO_4)_3$		
Temperature (°C)	Time (h)	2.5, 5.0, 7.5, 10.0, 15.0, 20.0	25.0	30.0, 33.33, 40.0, 50.0, 60.0, 66.67, 70.0, 80.0, 90.0
400 500	24	$CrVO_4$, Cr_2O_3, $CrVMoO_7$, V_2O_5 (little), MoO_3 (very little)	Cr_2O_3, $CrVMoO_7$, V_2O_5 (little), MoO_3 (little)	$Cr_2(MoO_4)_3$, $CrVMoO_7$, Cr_2O_3, V_2O_5 (trace), MoO_3 (little)
550	48	$CrVO_4$, Cr_2O_3, $CrVMoO_7$, V_2O_5 (trace), MoO_3 (trace)	Cr_2O_3, $CrVMoO_7$, V_2O_5 (trace), MoO_3 (trace)	$Cr_2(MoO_4)_3$, $CrVMoO_7$, Cr_2O_3, MoO_3 (trace)
600	48	$CrVO_4$, Cr_2O_3, $CrVMoO_7$	Cr_2O_3, $CrVMoO_7$	$Cr_2(MoO_4)_3$, $CrVMoO_7$, Cr_2O_3
650	48	$CrVO_4$, Cr_2O_3, $CrVMoO_7$	Cr_2O_3, $CrVMoO_7$	$Cr_2(MoO_4)_3$, $CrVMoO_7$, Cr_2O_3
780 [a]	48	$CrVO_4$, Cr_2O_3, $CrVMoO_7$	Cr_2O_3, $CrVMoO_7$	$Cr_2(MoO_4)_3$, $CrVMoO_7$, Cr_2O_3

[a] The samples were cooled rapidly to ambient temperature.

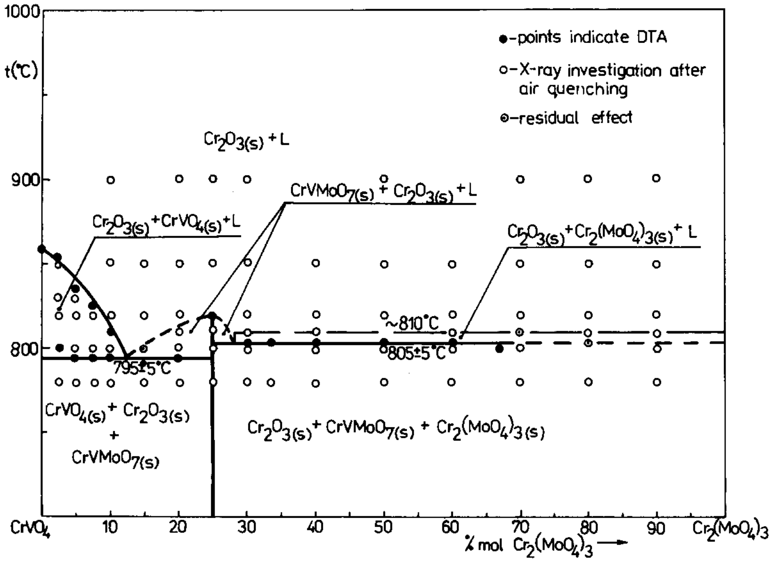

Fig. 1. The phase diagram of the $CrVO_4$–$Cr_2(MoO_4)_3$ system.

TABLE 3

Heating conditions and X-ray powder diffraction results for samples prepared from $CrVO_4$ and $Cr_2(MoO_4)_3$

Preparation conditions		Phases present at initial compositions		
Temperature (°C)	Time (h)	10mol%$Cr_2(MoO_4)_3$ -90mol%$CrVO_4$	25mol%$Cr_2(MoO_4)_3$ -75mol%$CrVO_4$	33.33mol%$Cr_2(MoO_4)_3$ -66.67mol%$CrVO_4$
400 500	24	$CrVO_4$, $Cr_2(MoO_4)_3$	$CrVO_4$, $Cr_2(MoO_4)_3$	$Cr_2(MoO_4)_3$, $CrVO_4$
550	48	$CrVO_4$, $Cr_2(MoO_4)_3$	$CrVO_4$, $Cr_2(MoO_4)_3$	$Cr_2(MoO_4)_3$, $CrVO_4$
600	48	$CrVO_4$, $Cr_2(MoO_4)_3$	$CrVO_4$, $Cr_2(MoO_4)_3$	$Cr_2(MoO_4)_3$, $CrVO_4$
650	48	$CrVO_4$, $Cr_2(MoO_4)_3$	$CrVO_4$, $Cr_2(MoO_4)_3$	$Cr_2(MoO_4)_3$, $CrVO_4$
700	48	$CrVO_4$, $Cr_2(MoO_4)_3$	$CrVO_4$, $Cr_2(MoO_4)_3$	$Cr_2(MoO_4)_3$, $CrVO_4$
700	24	$CrVO_4$, $Cr_2(MoO_4)_3$, Cr_2O_3 (trace), $CrVMoO_7$ (trace)	$CrVO_4$, $Cr_2(MoO_4)_3$, Cr_2O_3 (trace), $CrVMoO_7$ (trace)	$Cr_2(MoO_4)_3$, $CrVO_4$, Cr_2O_3 (trace), $CrVMoO_7$ (trace)
750	24	$CrVO_4$, $Cr_2(MoO_4)_3$, Cr_2O_3 (very little), $CrVMoO_7$ (little)	$CrVO_4$, $Cr_2(MoO_4)_3$, Cr_2O_3 (very little), $CrVMoO_7$ (very little)	$Cr_2(MoO_4)_3$, $CrVO_4$, Cr_2O_3 (very little), $CrVMoO_7$ (very little)
750	48	$CrVO_4$, $Cr_2(MoO_4)_3$, Cr_2O_3 (little), $CrVMoO_7$ (little)	$CrVO_4$, $Cr_2(MoO_4)_3$, Cr_2O_3 (little), $CrVMoO_7$ (little)	$Cr_2(MoO_4)_3$, $CrVO_4$, Cr_2O_3 (little), $CrVMoO_7$ (little)
780	72	$CrVO_4$, Cr_2O_3, $CrVMoO_7$	Cr_2O_3, $CrVMoO_7$	$Cr_2(MoO_4)_3$, Cr_2O_3, $CrVMoO_7$
780 [a]	48	$CrVO_4$, Cr_2O_3, $CrVMoO_7$	Cr_2O_3, $CrVMoO_7$	$Cr_2(MoO_4)_3$, Cr_2O_3, $CrVMoO_7$

[a] The samples were cooled rapidly to ambient temperature.

Therefore $CrVMoO_7$ (a compound whose existence in the three-component system Cr_2O_3–V_2O_5–MoO_3 has recently been ascertained) is present in this system in addition to Cr_2O_3. It has been confirmed by X-ray powder diffraction of a specimen obtained by roasting the 25 mol%$Cr_2(MoO_4)_3$–75 mol%$CrVO_4$ sample at 780 °C that at a molar ratio of 3 : 1 ($CrVO_4$: $Cr_2(MoO_4)_3$) reaction (1) proceeds quantitatively. The third specimen obtained from a mixture of 33.33 mol% of $Cr_2(MoO_4)_3$ and 66.67 mol% of $CrVO_4$ is composed of three phases: $CrVMoO_7$, Cr_2O_3 and $Cr_2(MoO_4)_3$. This indicates that no compound analogous to $Fe_4V_2Mo_3O_{20}$ is present in the $CrVO_4$–$Cr_2(MoO_4)_3$ system.

Figure 1 shows the phase diagram of the $CrVO_4$–$Cr_2(MoO_4)_3$ system constructed using the DTA and X-ray powder diffraction curves of the basic series and the samples prepared from $CrVO_4$ and $Cr_2(MoO_4)_3$. The types of solid phase remaining at equilibrium with liquid were established by X-ray powder diffraction of samples selected from particular diagram areas and heated additionally for 2–3 h at 800, 810, 820, 830, 850 and 900 ° C followed by rapid cooling to ambient temperature. The compositions of the samples investigated in this way are marked in the figure.

It follows from the phase diagram that the $CrVO_4$–$Cr_2(MoO_4)_3$ system is not a real two-component system over the entire range of component concentrations. This is indicated by the existence of three solid phases at equilibrium in the subsolidus area. Therefore, in the range of component concentrations up to 25 mol% of $Cr_2(MoO_4)_3$, chromium(III) orthovanadate coexists with $CrVMoO_7$ and Cr_2O_3. At other component concentrations $CrVMoO_7$ and Cr_2O_3 remain in permanent equilibrium with chromium(III) molybdate.

CONCLUSIONS

(1) The following conclusions can be drawn from the results. Chromium(III) molybdate in the solid state is decomposed to Cr_2O_3 and MoO_3 before reaching its melting point.

(2) The $CrVO_4$–$Cr_2(MoO_4)_3$ system is not a real two-component system over the entire range of component concentrations because chromium(III) molybdate does not remain in permanent equilibrium with chromium orthovanadate and in the solid state at a molar ratio of 3 : 1 ($CrVO_4 : Cr_2(MoO_4)_3$) the components react to yield $CrVMoO_7$ and Cr_2O_3.

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