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THE $CrVO_4$–MoO_3 SYSTEM

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ABSTRACT

The phase equilibria in the $CrVO_4$–MoO_3 system were studied up to 1000 °C over the entire range of concentration of components using differential thermal analysis and X-ray powder diffraction. The compound $CrVMoO_7$ exists in this system and melts incongruently at 820 ± 5 °C. This system appears to be a real two-component system up to the solidus line. All the results are shown in the form of a phase diagram.

INTRODUCTION

A comprehensive study of the mechanism of heterogeneous catalysis, occurring with a catalyst in the solid state, is possible only when the catalyst is determined precisely. Catalysts used in the organic industry are often multicomponent mixtures of transition oxides. Two-component systems of these oxides have been reported at some length, both in terms of the phase equilibria and the properties of the phases involved in these systems. However, information on three-component systems of transition oxides is much more fragmentary.

Studies on the three-component system Cr_2O_3–V_2O_5–MoO_3 [1] are scarce and have generally been carried out at low Cr_2O_3 concentrations, i.e. up to 10.00 mol%.

A preliminary investigation of the Cr_2O_3–V_2O_5–MoO_3 system has been carried out to determine whether compounds of the three oxides are formed in the system. Results from the preliminary investigation of the Cr_2O_3–V_2O_5–MoO_3 system [2] have indicated the formation of the compound $CrVMoO_7$ which has not been reported before. Therefore we decided to study the equilibria established in this system over the entire range of component concentrations.

The properties of the components of the $CrVO_4$–MoO_3 system are well known. Chromium(III) orthovanadate crystallizes in an orthorhombic system and under normal pressure does not show polymorphism [3]. We have

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found that it melts incongruently at 860 ± 5 °C depositing solid Cr_2O_3 [4]. Molybdenum trioxide has a typical orthorhombic symmetry [5]. Crystals of MoO_3 melt congruently at 795 °C [6]. The rather high vapour pressure of MoO_3 at the melting temperature can give rise to the oxide in a pure form by resublimation.

EXPERIMENTAL

V_2O_5 (a commercial product of p.a. grade), MoO_3 and Cr_2O_3 (obtained by the thermal decomposition of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ and $(NH_4)_2Cr_2O_7$ respectively) were used for the investigations. The decomposition of ammonium molybdate was carried out at 120–550 °C for 2 h. The decomposition of ammonium dichromate was firstly carried out at 100 °C and then at 150 °C. The decomposition product was then roasted at 1000 °C for 72 h. X-ray powder diffraction of the samples showed only the presence of the appropriate oxides MoO_3 or Cr_2O_3.

The oxides weighed in the appropriate amounts were homogenized by grinding to a powder, pelleted and roasted in air. Samples containing up to 50.00 mol% of MoO_3 (in the $CrVO_4$–MoO_3 system) were heated as follows: 400 → 500 °C (24 h), 550 °C (24 h), 600 °C (24 h), 650 °C (24 h) and 700 °C (24 h × 3). The preparations containing more than 50 mol% of MoO_3 were heated at 400 → 500 °C (24 h), 550 °C (24 h), 550 °C (48 h) and 570 °C (60 h). After each heat treatment the preparations were cooled gradually to ambient temperature, ground to a powder, examined by differential thermal analysis (DTA) and X-ray powder diffraction, and then pelleted and heated again until the preparations were at equilibrium. The condition of attainment of equilibrium in the preparations was established by preliminary studies of specimens containing 5.00, 20.00, 40.00, 60.00 and 90.00 mol% of MoO_3. To determine if equilibrium had been reached, selected samples were examined using X-ray powder diffraction after two successive heat treatments. When two identical analytical results proved that equilibrium had been reached, the heating of the samples was terminated and the investigation was commenced.

Differential thermal analysis was performed using a derivatograph (J. Paulik–J. Paulik–L. Erdey (MOM, Budapest)) at 20–1000 °C in quartz crucibles at a heating rate of 10 °C min^{-1}. Specimens of 1000 mg were used in each case. The phase composition of the samples was established using X-ray powder diffraction (A_2 type diffractometer with an HZ6H Co $K\alpha$ goniometer) and data from ASTM cards [7] and from ref. 8.

The density and concentration of metallic components in a sample obtained from an equimolar mixture of $CrVO_4$ and MoO_3 were also determined. The density of the $CrVMoO_7$ system was determined by the method given in ref. 9. The chromium and vanadium contents were determined using the Willard and Young method [10]. Molybdenum was determined by atomic absorption spectrometry using an AAS-3 device (Carl–Zeiss, Jena, G.D.R.) with a nitrogen monoxide–acetylene flame.

RESULTS AND DISCUSSION

Preliminary investigations of the $CrVO_4$–MoO_3 system have revealed that the compound $CrVMoO_7$ exists in this system [2]. This compound was obtained by two methods. From the reaction of the oxides

$$Cr_2O_3(s) + V_2O_5(s) + 2MoO_3(s) = 2CrVMoO_7(s) \tag{1}$$

or from the reaction of chromium(III) orthovanadate with molybdenum trioxide

$$CrVO_4(s) + MoO_3(s) = CrVMoO_7(s) \tag{2}$$

A mixture of Cr_2O_3, V_2O_5 and MoO_3 with a molar ratio of 1 : 1 : 2 and a mixture of $CrVO_4$ and MoO_3 with a molar ratio of 1 : 1 were heated under previously fixed conditions [2]. X-ray powder diffraction did not reveal the existence of the substrates or any other known phase that might occur in the Cr_2O_3–V_2O_5–MoO_3 system. Diffraction patterns of the samples showed a set of reflections which were attributed to the $CrVMoO_7$ system. In the set of diffraction lines, a line was found ($d = 2.516$) which was typical of $CrVO_4$; however the change in intensity observed during synthesis revealed that it also belonged to the set of reflections characteristic of $CrVMoO_7$. If the sample contained $CrVO_4$ as well as $CrVMoO_7$, its diffraction pattern should also have shown reflections characteristic of MoO_3. Table 1 shows the interplanar distances of $CrVMoO_7$ and the relative intensities corresponding to the reflections.

An endothermic effect with a starting temperature of 820 ° C was recorded on the DTA curve for the $CrVMoO_7$ phase (Fig. 1). In order to determine whether the phase melted congruently of incongruently the following experiment was carried out. The $CrVMoO_7$ phase was heated for 3 h at its melting temperature and was then rapidly cooled to ambient temperature. In the sample obtained $V_9Mo_6O_{40}$, Cr_2O_3 and $Cr_2(MoO_4)_3$ were found as shown by X-ray powder diffraction. Under the experimental conditions only Cr_2O_3 exists in the solid state. $Cr_2(MoO_4)_3$ is not thermodynamically stable under these conditions and undergoes decomposition [11]. $V_9Mo_6O_{40}$ melts congruently at 635 ° C [12] and is thus a liquid phase at 820 ° C. Thus the solid product of the incongruent melting of the $CrVMoO_7$ phase is chromium(III) oxide, and the course of the meritectic reaction is as follows

$$2CrVMoO_7(s) \rightarrow Cr_2O_3(s) + \text{liquid} \tag{3}$$

$CrVMoO_7$ obtained either by reaction (1) or reaction (2) was analysed to determine the concentrations of the metallic elements, and its density was

TABLE 1

The interplanar distances of $CrVMoO_7$ and the relative intensities corresponding to the reflections

d (Å)	I (%)	d (Å)	I (%)	d (Å)	I (%)
5.40	2	2.70	24	1.94	2
5.24	19	2.61	4	1.89	7
4.63	10	2.57	2	1.88	4
4.49	7	2.52	5	1.86	10
4.09	9	2.32	3	1.84	3
3.88	11	2.30	3	1.79	6
3.77	13	2.22	2	1.77	6
3.51	13	2.13	4	1.76	4
3.29	13	2.12	9	1.75	4
3.20	100	2.05	4	1.73	4
3.14	26	2.04	3	1.68	2
3.08	11	2.02	4	1.67	5
3.05	10	1.96	5		
2.90	5	1.95	14		

calculated. The analytical results show that the metallic element concentrations are as follows: Cr, 16.80%; V, 16.16%; Mo, 30.25%. The theoretical values for this phase are as follows: Cr, 16.73%; V, 16.39%; Mo, 30.86%. The density of $CrVMoO_7$ is 3.75 ± 0.05 g cm^{-3}.

In order to establish the types of phase which occur in the $CrVO_4$–MoO_3 system and the conditions under which they coexist in equilibrium up to 1000 °C over the entire range of component concentrations, 20 samples were prepared whose initial compositions are shown in Table 2.

The table also shows the phase compositions of the samples at equilibrium, i.e. after heating under previously fixed conditions. Figure 2 shows

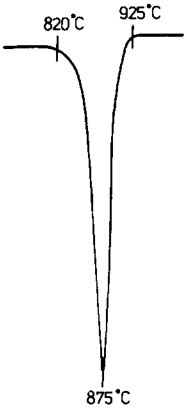

Fig. 1. The DTA curve of $CrVMoO_7$.

TABLE 2

The initial compositions, conditions of synthesis and results from X-ray powder diffraction of specimens at equilibrium

MoO_3 concentration in the initial mixtures (mol%)	Substrate	Condition of preparation		Phases detected
		Temperature (°C)	Time (h)	
5.00, 10.00,	Cr_2O_3,	400 → 500	24	$CrVO_4$,
15.00, 20.00, 25.00,	V_2O_5,	550	24	$CrVMoO_7$
30.00, 35.00, 40.00	MoO_3	600	24	
45.00		650	24	
		700	24×3	
50.00	Cr_2O_3,	400 → 500	24	$CrVMoO_7$
	V_2O_5,	550	24	
	MoO_3	600	24	
		650	24	
		700	24×2	
55.00, 60.00, 65.00,	Cr_2O_3,	400 → 500	24	$CrVMoO_7$,
66.67, 70.00, 75.00	V_2O_5,	550	24	MoO_3
80.00, 85.00, 90.00,	MoO_3	550	48	
95.00		570	60	

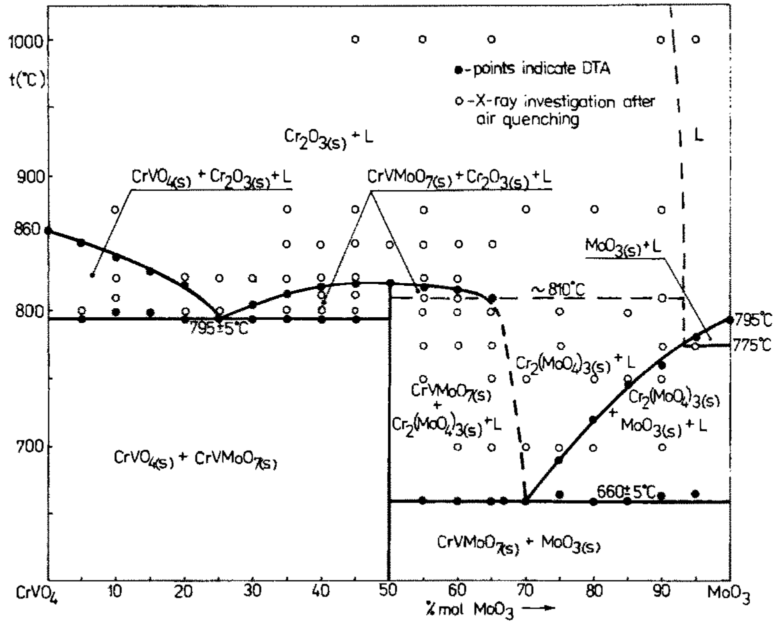

Fig. 2. The phase diagram of the $CrVO_4$–MoO_3 system.

the experimental results in the form of a phase diagram. The ranges of coexistence of the phases at equilibrium were established by DTA. The types of solid phase which exist in the subsolidus area were established using X-ray powder diffraction of samples at equilibrium. Results from experiments on the phase compositions of samples heated for 3 h at 700–1000 ± 5 °C followed by rapid cooling to ambient temperature were used. The compositions of samples subjected to such experiments are marked in the phase diagram (Fig. 2).

From the phase diagram it can be seen that $CrVO_4$ and $CrVMoO_7$ remain in equilibrium up to 795 ± 5 °C at a concentration of 50.00 mol.% of MoO_3. At other component concentrations the phases $CrVMoO_7$ and MoO_3 are in equilibrium up to 660 ± 5 °C. This means that the $CrVO_4$–MoO_3 system is a real two-component system up to the solidus line over the entire range of component concentrations. Above the solidus line, the system ceases to be a two-component system over the entire range of component concentrations due to the incongruent melting of the $CrVO_4$ and $CrVMoO_7$ phases. The occurrence of chromium molybdate (which is also in equilibrium with the liquid above the solidus line (as well as $CrVMoO_7$ and MoO_3)) in samples with MoO_3 concentrations exceeding 50.00 mol% is probably caused by the reaction of $CrVMoO_7$ with MoO_3 at 660 ± 5 °C and above with the formation of $Cr_2(MoO_4)_3$ and a liquid. Under these conditions, chromium molybdate is a solid phase.

CONCLUSIONS

The following conclusions can be drawn from the results.

(1) The compound $CrVMoO_7$ is formed in the $CrVO_4$–MoO_3 system. This compound has not been reported previously. It melts incongruently at 820 ± 5 °C depositing solid Cr_2O_3.

(2) $CrVMoO_7$ as a solid phase can be obtained from the reaction of $CrVO_4$ with MoO_3 or by reaction between Cr_2O_3, V_2O_5 and MoO_3. The X-ray characteristics of $CrVMoO_7$ were established at $2\theta = 10°–65°$ (Co $K\alpha$) and its density was determined.

(3) The experimental results shown in the form of a phase diagram are related to the phase equilibria established in the $CrVO_4$–MoO_3 system up to 1000 °C over the entire range of component concentrations.

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