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REACTIVITY OF MoO_3 TOWARDS $Cr_2V_4O_{13}$

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ABSTRACT

The reaction of MoO_3 with $Cr_2V_4O_{13}$ - the second phase, beside $CrVO_4$, existing in the Cr_2O_3-V_2O_5 system was studied by DTA and X-ray powder diffraction. It has been found that MoO_3 reacts with $Cr_2V_4O_{13}$ to form, in the first place, a solid solution. The Mo^{6+} ions are incorporated in the $Cr_2V_4O_{13}$ lattice, replacing V^{5+} ions, and this substitution gives rise to excessive positive charges whose compensation leads to the reduction of Cr^{3+} to Cr^{2+} or V^{5+} to V^{4+}.

INTRODUCTION

Very little information is found in the literature on the three-component system containing V_2O_5 and MoO_3 as the primary components and a third oxide, Cr_2O_3 - a transition oxide with the oxidation number three, as a secondary component. Besides, studies on the V_2O_5-Cr_2O_3 system has appeared to be incomplete since in this system, in addition to $CrVO_4$ (1-8), exists another compound - $Cr_2V_4O_{13}$ (9). Contrary to $CrVO_4$ - a compound rather well known, the structure and properties of $Cr_2V_4O_{13}$ are practically unknown. D.Olivier obtained $Cr_2V_4O_{13}$ only by co-precipitation and he found it to be stable up to 566°C(10).

Investigating the V_2O_5-Cr_2O_3 system we obtained $Cr_2V_4O_{13}$ by two methods, that is, by the reaction between Cr_2O_3 and V_2O_5 in the solid phase and by co-precipitation (11). Figure 1a shows the DTA curve of a product obtained in a case in which the initial composition corresponded to $Cr_2V_4O_{13}$, which, when heated to 635°C, appeared to be monophase,

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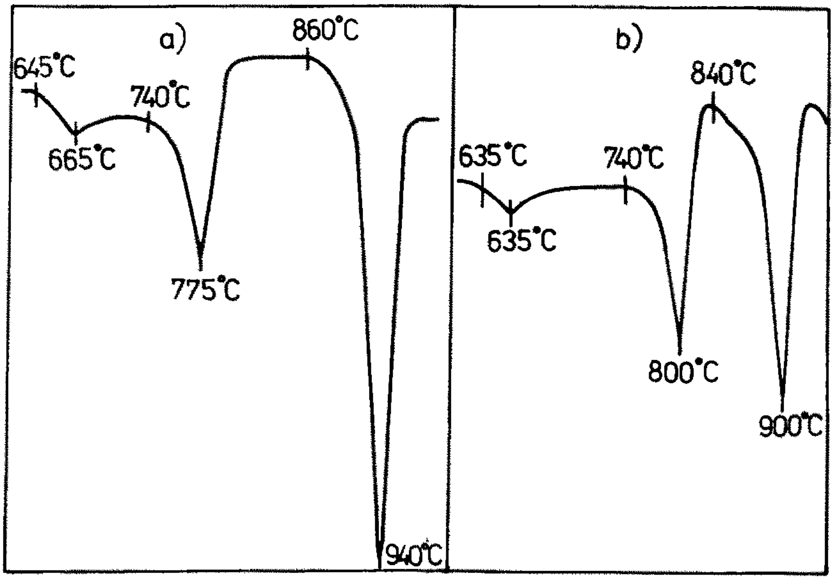

Fig. 1. The DTA curves of $Cr_2V_4O_{13}$ (a) and $Cr_2V_4O_{13(s.s)}$ containing 15.38% mol of MoO_3 (b).

as shown by X-ray powder diffraction. A small endothermic effect initiated at 645°C proves melting of an eutectic mixture of V_2O_5 and $CrVO_4$, that is, the decomposition of $Cr_2V_4O_{13}$.

From the study of three-component system of Cr_2O_3-V_2O_5-MoO_3 it seemed useful to study the behaviour of $Cr_2V_4O_{13}$ in the presence of MoO_3. The results from that study are presented in this work.

EXPERIMENTAL

V_2O_5 (commercial product of p.a. grade) and MoO_3 and Cr_2O_3 obtained by thermal decomposition of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and $(NH_4)_2Cr_2O_7$, respectively, were used. Differential Thermal Analysis (DTA) of all the praparations was made up to 1000°C by use of a derivatograph (MOM Budapest). The phase composition of the preparations was established by X-ray powder diffraction (Dron-3, CoK_α).

The studies were commenced by preparing from the oxides a mixture with composition equal to 90.00 % mol of $Cr_2V_4O_{13}$ and 10.00% mol of MoO_3. The mixture was ground and pastilled and was heated under conditions which resulted in the synthesis of $Cr_2V_4O_{13}$, i.e., 400-500°C (24 h) - 635°C (3 h × 4).

X-ray powder diffraction of the preparation obtained showed that it consisted of $Cr_2V_4O_{13}$ and V_2O_5 but it did not contain MoO_3. Consequently it was concluded that MoO_3 forms a solid solution with $Cr_2V_4O_{13}$, and that Mo^{6+} ions were incorporated into the $Cr_2V_4O_{13}$ lattice, in the place of the V^{5+} ions.

Substitution of the Mo^{6+} ions for the V^{5+} ions in the $Cr_2V_4O_{13}$ lattice involved existence of excessive charges whose compensation was possible through:

- formation of cationic vacancies ($\emptyset$) in the Cr^{3+} sublattice with a concurrent removal of an equivalent number of the Cr^{3+} ions from the $Cr_2V_4O_{13}$ lattice. A solid solution corresponding with such a model is given by the formula:

$$Cr_{2-x}\emptyset_xV_{4-3x}Mo_{3x}O_{13} \qquad \text{(model I)}$$

- formation of cationic vacancies in the V^{5+} sublattice, the formula of the solid solution can be written:

$$Cr_2V_{4-6x}\emptyset_xMo_{5x}O_{13} \qquad \text{(model II)}$$

- reduction of the Cr^{3+} ions to Cr^{2+}:

$$Cr^{3+}_{2-x}Cr^{2+}_xV_{4-x}Mo_xO_{13} \qquad \text{(model III}_A\text{)}$$

- reduction of the V^{5+} ions to V^{4+}:

$$Cr_2V^{5+}_{4-2x}V^{4+}_xMo_xO_{13} \qquad \text{(model III}_B\text{)}$$

The composition of the initial composition for the models III_A and III_B results from the expression:

$$Cr_2V_{4-x}Mo_xO_{(13+\frac{x}{2})}.$$

Further investigations aimed at finding which of the theoretically possible models of the solid solution was formed.

These investigations depended on the synthesis of preparations corresponding with each of the presented models. And so, for each of the three models two mixtures were prepared from the oxides with an initial composition which leads to a final product containing 10.00 and 15.00 % mol of MoO_3, respectively. The ground and pastilled mixtures were roasted in air under the following conditions: 400°C - 500°C (24 h) - 600°C (24 h) - 620°C (9 h) - 635°C (9 h×3).

Table 1

X-ray powder diffraction of products suitable for determinations of the model of a solid solution

Model	The MoO_3 content (% mol) in the initial mixtures	Phases detected
1	2	3
I	10.00 15.00	$Cr_2V_4O_{13}$(s.s); V_2O_5
II	10.00 15.00	$Cr_2V_4O_{13}$(s.s); $CrVO_4$.- traces
III	10.00 15.00	$Cr_2V_4O_{13}$(s.s)

X-ray powder diffraction of the samples after the last roasting cycle (Tab. 1.) showed that the products consistent with models I and II were composed of two phases and, beside the solid solution, they contained V_2O_5 (model I) and $CrVO_4$ (model II) as well. On the other hand, preparations with compositions described with model III were monophase and contained only a solid solution of MoO_3 in $Cr_2V_4O_{13}$. In order to establish the existence range for the solid solution seven samples from oxides with compositions consistent with model III and with increasing MoO_3 content were prepared. All the samples were prepared and heated in the same way as were the preparations which veryfied the model of the solid solution. DTA and X-ray powder diffraction were made after each of the roasting cycles and the mass and colour changes of the products were measured.

RESULTS AND DISCUSSION

X-ray powder diffraction (Tab. 2.) showed no presence of MoO_3 in any of the products. Diffraction patterns showed no lines characteristic of Cr_2O_3 or V_2O_5. Products containing up to 15.38% mol of MoO_3 in their initial mixtures were monophase on the last roasting cycle and contained $Cr_2V_4O_{13(s.s.)}$ only. But it was found that the sample with 17.65% mol of MoO_3, in addition to $Cr_2V_4O_{13(s.s.)}$, contained $CrVMoO_7$ after the last roasting cycle. This phase was found in the Cr_2O_3-V_2O_5-MoO_3 system during our earlier studies (12). It melts incongruently at 840°C.

Three endothermic effects were recorded in the DTA curves of monophase products which contained in their initial composition up to 15.38%

Table 2.
X-ray powder diffraction of products containing the solid solution synthesis (model III)

Nr	The MoO_3 content (% mol) in the initial mixtures	Phases detected	Note
1	2	3	4
1	3.45	$Cr_2V_4O_{13(s.s)}$	The diffraction line shift increasing with a decrease in the contents of MoO_3 in a sample.
2	7.14	$Cr_2V_4O_{13(s.s)}$	
3	9.09	$Cr_2V_4O_{13(s.s)}$	
4	11.11	$Cr_2V_4O_{13(s.s)}$	
5	13.21	$Cr_2V_4O_{13(s.s)}$	
6	15.38	$Cr_2V_4O_{13(s.s)}$	
7	17.65	$Cr_2V_4O_{13(s.s)}$; $CrVMoO_7$	

mol of MoO_3. These effects are similar to those which are detected in the DTA curve of the pure $Cr_2V_4O_{13}$ (Fig. 1b).

The first effect is most likely a melting effect of the eutectic mixture of $CrVO_4$ and $V_2O_{5(s.s)}$ involved in the initiated decomposition of $Cr_2V_4O_{13(s.s)}$. However such an interpretation should be supported by additional investigations. The second effect recorded in the DTA curves of all the products corresponds to the incongruent melting of an undecomposed $Cr_2V_4O_{13(s.s)}$, and the third effect for the monophase products is a thermal effect caused by melting of $CrVO_4$ which is a permanent product of the $Cr_2V_4O_{13}$ melting. The initial temperature of the third effect in the DTA curve for the two-phase was decreased most likely due to the appearance of another phase, i.e., $CrVMoO_7$ in addition to $Cr_2V_4O_{13(s.s)}$.

CONCLUSIONS

The experimental results lead to the following conclusions: $Cr_2V_4O_{13}$ reacts with MoO_3 to form, first of all, a solid solution The solubility of MoO_3 at ambient temperature cannot be above 17.65 % mol of MoO_3. It is only on reaching maximum solubility by MoO_3 in $Cr_2V_4O_{13}$ when the components react to give the $CrVMoO_7$ phase. It has been found that the Mo^{6+} ions are incorporated into the $Cr_2V_4O_{13}$ lattice in the place of V^{5+} and a model for the solid solution has been established. The experimental results presented in this work do not allows a conclusion as to what kind of ions occurring in the matrix lattice undergoes reduction.

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