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$CrVMoO_7$ and phase equilibria in the $V_9Mo_6O_{40}$–$CrVMoO_7$ system

Jadwiga Walczak, Elżbieta Filipek and Piotr Tabero

Department of Inorganic Chemistry, Technical University of Szczecin, Al. Piastów 42, 71-065 Szczecin (Poland)

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Abstract

The X-ray powder diffraction pattern of the $CrVMoO_7$ phase, which was found while studying phase equilibria in the $CrVO_4$–MoO_3 system, has been indexed. $CrVMoO_7$ appeared to crystallize in a triclinic system and the parameters of its unit cell have been calculated. The phase equilibria established in the $V_9Mo_6O_{40}$–$CrVMoO_7$ system have been studied by DTA and X-ray powder diffraction. These methods show that the system of interest is a real, simple, two-component eutectic system over the whole component concentration range up to 1000°C.

INTRODUCTION

The significance of heterogeneous catalysis for a large variety of manufacturing processes has given an impulse to development of comprehensive studies aimed at establishing, first of all, the relationship between activity and selectivity of a catalyst and its structure and properties. The catalysts most often employed in oxidation of organic compounds are the transition metal oxides, used alone or in many-component mixtures whose basic component is, in general, V_2O_5 and MoO_3 or WO_3. Other possible components are transition metal oxides such as Fe_2O_3 or Cr_2O_3.

By investigating the structure and properties of the phases, and also the phase equilibria established in the system of interest (this provides information about the range of thermodynamic stability of the phases), knowledge is obtained of the solid on whose surface an elementary act of catalysis occurs.

Our earlier studies on the three-component system, Cr_2O_3–V_2O_5–MoO_3, [1–4], where done under conditions selected so that the previously unknown $CrVMoO_7$ phase would be formed. The experimental results shown

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Correspondence to: J. Walczak, Department of Inorganic Chemistry, Technical University of Szczecin, Al. Piastów 42, 71-065 Szczecin, Poland.

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in this work furnish detailed information about $CrVMoO_7$ and the phase equilibria established in the $V_9Mo_6O_{40}$–$CrVMoO_7$ system up to 1000°C over the whole range of component concentrations. The phase equilibria established in this system in the solid state have already been presented [5].

$V_9Mo_6O_{40}$ is a compound occurring in the V_2O_5–MoO_3 system. It has been studied extensively, in the first place for its advantageous catalytic properties in the selective oxidation of hydrocarbons [6]. In the light of the present experimental results, $V_9Mo_6O_{40}$ crystallizes in a monoclinic system [7] and it melts congruently at 635°C [8], at 677°C [9] or, according to our findings, at 640 ± 10°C. The density of $V_9Mo_6O_{40}$ is 3.86 g cm^{-3} [9]. In this phase, 1/9 of the vanadium atoms are in the form of V^{4+} [8].

$CrVMoO_7$ melts incongruently at 820 ± 10°C, Cr_2O_3 being a solid product of meritectic reaction [1,2]. The structure of this phase has not yet been determined; only its X-ray characteristic at 2θ angles 12–65° and its density, 3.75 ± 0.05 g cm^{-3}, were determined [2].

In order to establish the crystallographic system for $CrVMoO_7$ and the parameters for the unit cell, indexing of the X-ray powder diffraction pattern was made by the programme POWDER developed by D.G. Taupen. Twenty-seven reflexions were selected to be indexed, 21 of them being successive reflexions scanned from the diffraction pattern in accordance with the ascending values, 2θ, whereas 6 reflexions were selected from among the others present in the diffraction pattern. The choice of these six reflexions was done by virtue of their intensities, i.e. the six most intense diffraction lines were selected from among the lines confined in the 2θ angle range 48–70°. Indexing of the $CrVMoO_7$ diffraction pattern in the triclinic system produced positive results (Table 1).

The parameters for the unit cell are $a = 5.53346$ Å, $b = 6.58901$ Å, $c = 7.86551$ Å, $\alpha = 96.1134°$, $\beta = 89.8311°$, $\gamma = 101.941°$, volume of the unit cell = 278.922 Å^3; type of unit cell, P, number of molecules in the unit cell, 2; calculated density $\rho_{rtg} = 3.71$ g cm^{-3}, $\Delta\rho = 0.04$ g cm^{-3}.

The small difference between the determined density and the calculated value and the high quality factors for each of the reflexions (all of them greater than 4) show that very probably $CrVMoO_7$ is a triclinic substance and its unit cell is characterized by the parameters calculated. To confirm the correctness of the calculations an indexing of the X-ray powder diffraction pattern of $CrVMoO_7$ was made by the programme designed by J.W. Visser. The result was identical with the indexing according to the Taupen programme.

EXPERIMENTAL

Analytically pure V_2O_5 and MoO_3, also Cr_2O_3 obtained by thermal decomposition of ammonium dichromate, were used. The decomposition of $(NH_4)_2Cr_2O_7$ was carried out first at 100°C then at 150°C and afterwards

TABLE 1

The results of indexing of the $CrVMoO_7$ X-ray powder diffraction pattern

No.	d_{exp} (Å)	d_{calc} (Å)	hkl	No.	d_{exp} (Å)	d_{calc} (Å)	hkl
1	5.41202	5.41269	100	17	2.57517	2.57314	$20\bar{1}$
2	5.24031	5.24252	$01\bar{1}$			2.57502	$2\bar{1}1$
3	4.63699	4.63726	$1\bar{1}0$	18	2.51835	2.51922	$1\bar{2}2$
4	4.48971	4.49188	$10\bar{1}$	19	2.32775	2.32597	210
5	4.10329	4.10078	$1\bar{1}1$			2.32805	013
6	3.85180	3.88512	$1\bar{1}\bar{1}$			2.33053	103
7	3.76592	3.76726	110	20	2.30412	2.30378	$1\bar{2}\bar{2}$
8	3.51221	3.51078	$01\bar{2}$	21	2.22692	2.22620	$12\bar{2}$
9	3.29659	3.29577	111			2.22540	$11\bar{3}$
10	3.20067	3.20429	020	22	2.12078	2.11982	$03\bar{1}$
		3.19926	$10\bar{2}$	23	2.01596	2.01734	$1\bar{3}\bar{1}$
11	3.14051	3.14022	102	24	1.95359	1.95482	004
12	3.08443	3.08443	$02\bar{1}$	25	1.89698	1.89603	$20\bar{3}$
		3.08401	$1\bar{1}2$			1.89693	$1\bar{2}\bar{3}$
13	3.04935	3.04898	$1\bar{2}0$	26	1.85979	1.85949	130
14	2.90130	2.90239	$1\bar{1}\bar{2}$			1.85921	203
15	2.70619	2.70634	200			1.86001	$2\bar{3}1$
		2.70248	$2\bar{1}0$	27	1.79319	1.79482	$3\bar{1}1$
16	2.62151	2.62126	$02\bar{2}$			1.79467	032
						1.79243	$2\bar{3}\bar{1}$

the decomposition product was calcinated at 1000°C for 72 h. X-ray powder diffraction of the final product showed the presence of Cr_2O_3 only.

The samples for experiments were prepared from oxides weighed in selected proportions, ground, pressed into pastilles and heated in air under conditions which would establish the equilibrium state. The conditions required for equilibrium were established in preliminary investigations of samples containing initially 30.00, 60.00 and 90.00 mol.% of $CrVMoO_7$ in terms of the system components. On this basis, the samples were heated periodically under the conditions 400°C → 500°C (24 h) → 550°C (48 h) → 570°C (48 h) → 570°C (48 h).

After each heating cycle the samples were cooled gradually to ambient temperature, ground, formed again into pastilles and heated until equilibrium was reached. Achievement of equilibrium was verified by X-ray powder diffraction of preparations selected after two successive heating cycles. The identical diffraction patterns in respect of the position and intensity of diffraction lines showed that equilibrium had been achieved, so heating of all the preparations was terminated and X-ray powder diffraction and DTA measurements were taken.

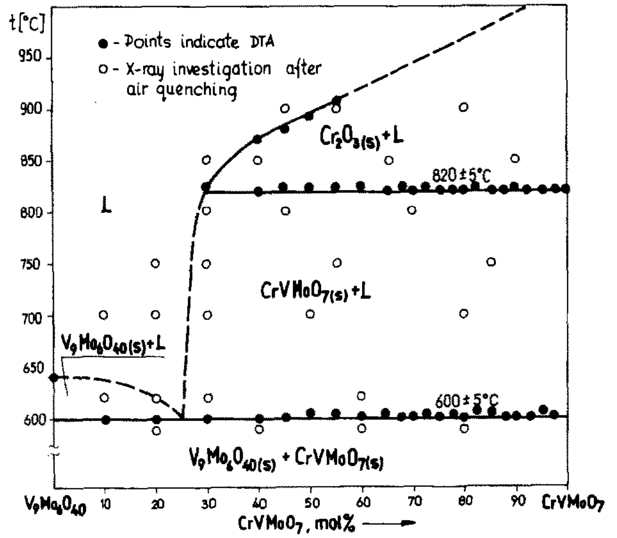

Fig. 1. Diagram of the phase equilibria of the $V_9Mo_6O_{40}$–$CrVMoO_7$ system.

The diffraction spectra of the preparations were taken with a HZG 4/A-2 type diffractometer, using a cobalt tube as radiation source. The phase composition of the preparations was determined by X-ray powder diffraction and by using the data included in the PDF cards and some data from the literature [2,9,10].

DTA was done with a derivatograph of the F. Paulik–J. Paulik–L. Erdey type in air, using quartz crucibles at 20–1000°C.

RESULTS AND DISCUSSION

Twenty-two samples were prepared in order to study equilibria being established in the $V_9Mo_6O_{40}$–$CrVMoO_7$ system over the whole range of component concentrations. Their compositions are shown in the phase diagram (Fig. 1). X-ray powder diffraction showed that the preparations at equilibrium were, over the whole range of the component concentrations, a mixture of the two phases, $V_9Mo_6O_{40}$ and $CrVMoO_7$.

Only one endothermic effect with an initial temperature of 600°C was recorded on the DTA curves of preparations at equilibrium, which contained 10.00 and 20.00 mol.% of $CrVMoO_7$. On the other hand, on the DTA curves of a preparation containing 30.00 mol.% of $CrVMoO_7$ two endothermic effects were recorded. One had an initial temperature of 600°C, the other one of 825°C. Three endothermic effects were recorded on the DTA curves of preparations containing 40.00, 45.00, 50.00 and 55.00 mol.% of $CrVMoO_7$. The first effect started at 600–605°C, the onset of the second effect occurred at 820–825°C while the initial temperature of the third effect was 870°C for a sample containing 40.00 mol.% of $CrVMoO_7$ and 905°C for a sample with 55.00 mol.% of $CrVMoO_7$. On the DTA curves of preparations which are representative of the odd component concentration range of the system under study, i.e. above 55.00 mol.% of $CrVMoO_7$, only the first and second effects were recorded. Their temperatures did not differ from the temperature of the effects recorded on the DTA curves of the other preparations.

The magnitude of the first effect recorded on the DTA curves of all the preparations varied with the change in the composition of samples, that is, at first it increased to approach the maximum for samples containing 20.00 and 30.00 mol.% of $CrVMoO_7$, then it decreased with increase in the $CrVMoO_7$ content in the samples.

In order to corroborate the initial temperature of melting in the system of interest, the samples at equilibrium with 10.00, 20.00, 30.00 and 60.00 mol.% of $CrVMoO_7$ were heated for 3 h at, say, 620°C, a temperature higher than the onset of the first effect recorded on the DTA curves of all these preparations. Afterwards, the samples were cooled rapidly to ambient temperature; they were found to have melted partially by that time. Hence, the experiments confirmed that the first effect was undoubtedly combined with melting of a eutectic mixture formed from $V_9Mo_6O_{40}$ and $CrVMoO_7$. As mentioned earlier, the magnitude of the effect approached maximum for samples containing 20.00 and 30.00 mol.% of $CrVMoO_7$, which means that the composition of the eutectic mixture was confined within that range of component concentrations. It was impossible with our experimental techniques to make precise measurements of the composition of the eutectic mixture.

The initial temperature of the second effect of 820°C recorded on the DTA curves of preparations at equilibrium and containing at least 30.00 mol.% of $CrVMoO_7$ indicated that this effect was related to the incongruent melting of $CrVMoO_7$. The third effect, on the other hand, occurring on the DTA curves of preparations which contained between 40.00 and 55.00 mol.% of $CrVMoO_7$ was attributed to melting of Cr_2O_3, the solid product of incongruent melting of $CrVMoO_7$.

The figure shows a diagram of phase equilibria of the $V_9Mo_6O_{40}$–$CrVMoO_7$ system, constructed on the basis of the DTA curves and X-ray powder diffraction patterns of the preparations at equilibrium. The solidus line was determined from the onset temperature of the first effect, whereas the line bordering the areas in which $CrVMoO_7$ or Cr_2O_3 exist at equilibrium with liquid, was fixed from the onset temperature of the second effect. The kinds of solid phases remaining at equilibrium with liquid were found by X-ray powder diffraction of samples selected from particular diagram areas, the samples being additionally heated for 3 h at 620, 700, 750, 800, 850 and 900°C, then cooled quickly to ambient temperature. The compositions of the samples studied are marked on the diagram.

The range of existence of the subsolidus area was corroborated by additional experiments, that is, samples being at equilibrium and containing 20.00, 40.00, 60.00 and 80.00 mol.% of $CrVMoO_7$ were reheated for 3 h at 590°C, then quickly cooled to ambient temperature. X-ray powder diffraction of those preparations showed that their composition did not differ from the phase composition of samples at equilibrium which were cooled gradually to ambient temperature.

The diagram shows that the $V_9Mo_6O_{40}$–$CrVMoO_7$ system is a real, simple, two-component eutectic system over the whole range of component concentrations up to 1000°C. The contents of the eutectic mixture are between 20.00 and 30.00 mol.% of $CrVMoO_7$, and its melting temperature is 600 ± 5°C.

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