THE $FeVO_4$—MoO_3 SYSTEM

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A phase diagram of the $FeVO_4$—MoO_3 system has been constructed from the results of DTA and X-ray analysis. The components of the system form a compound $FeVMoO_7$. This compound melts incongruently at 680 ± 5 °C, with separation of the solid $Fe_4V_2Mo_3O_{20}$.

The literature on the subject shows that phases of oxysalt types or solid solutions in a matrix of oxysalts originating from some two- and three-component systems of transition metal oxides possess interesting catalytic properties for the selective oxidation of hydrocarbons. Such systems include, among others, Fe_2O_3—V_2O_5, Fe_2O_3—MoO_3, V_2O_5—MoO_3 and MO—V_2O_5—MoO_3 (M = Mn, Cu, Co, Zn) [1–10]. From our studies on the three-component system Fe_2O_3—V_2O_5-MoO_3, new phases with similar properties were expected to be found. In work on the $FeVO_4$—$Fe_2(MoO_4)_3$ system, one of the pseudobinary cross-sections of the three-component system Fe_2O_3—V_2O_5—MoO_3, it has been found that $Fe_4V_2Mo_3O_{20}$ arises [11, 12]. The results from preliminary investigation of the $FeVO_4$—MoO_3 system indicated the occurrence of yet another compound, not reported so far: $FeVMoO_7$ [13]. This induced us to examine the phase equilibria established in this system in the whole range of component concentrations.

The properties of the components of the system are known. Iron(III) orthovanadate, $FeVO_4$, forms triclinic crystals [14]; at atmospheric pressure it does not exhibit polymorphism. Only high-pressure forms of $FeVO_4$ are known [15]. Iron(III) orthovanadate melts incongruently, with separation of the solid α-Fe_2O_3 at $850 \pm 5°$ [16]. Molybdenum trioxide exhibits orthorhombic symmetry [17]. MoO_3 crystals melt congruently at $795°$ [18].

Experimental

Materials

MoO$_3$ was obtained by thermal decomposition of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ in air at 120–550° during several hours, and FeVO$_4$ by roasting of an equimolar mixture of α-Fe$_2$O$_3$ and V$_2$O$_5$ at 600° for 24 h, 650° for 24 h and 700° for 72 h.

The substrates, in weighed portions, were ground, pastilled and heated in air under conditions adopted in our earlier investigations, i.e. 400→500° for 24 h, 550° for 72 h and 600° ($\pm$10°) for 24 h [13]. One series of preparations obtained was cooled slowly to ambient temperature and ground afterwards, whereas the other was taken out from the furnace at the final temperature of their preparation, cooled rapidly and also ground. Some of the preparations which had been cooled slowly were heated additionally for 2 h at 650, 700, 750, 780, 800 and 850° ($\pm$10°), and then cooled rapidly to ambient temperature.

### Methods

The phase compositions of the preparations were determined by x-ray phase analysis (DRON–3, CoK$_\alpha$), from patterns given in ASTM cards [19] and from published data [11–13].

Thermal analysis (DTA) was performed with the use of a Paulik–Paulik–Erdey (MOM, Budapest) derivatograph, with the samples in quartz crucibles, in air, at 20–1000°, at a heating rate of 10 deg/min. The weight of the preparations examined was 1000 mg for each sample. The temperatures of solidus lines were fixed from the start temperatures and the liquidus curves from the peak temperatures of the DTA effects. The accuracy of temperature reading, determined from repetitions, was assessed to be $\pm$5°.

The preparation obtained from the equimolar mixture of FeVO$_4$ and MoO$_3$ was analysed chemically for its metal components, its density being determined too. The iron content was determined photometrically with a VSU–2G spectrometer ($\lambda = 522$ nm) [20], while vanadium was analysed by a manganometric method, and molybdenum with an AAS–1N atomic absorption spectrometer. The phase density was determined by the method described in [21].

Results and discussion

In our previous paper [13], we reported that the reaction

$$FeVO_{4(s)} + MoO_{3(s)} = FeVMoO_{7(s)}$$
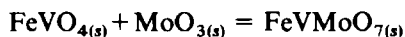
takes place in the system FeVO$_4$—MoO$_3$.

In order to confirm the formation of this phase, a mixture of FeVO$_4$ + MoO$_3$ in the molar ratio 1 : 1 and a mixture of Fe$_2$O$_3$ + V$_2$O$_5$ + MoO$_3$ in the ratio 1 : 1 : 2 were roasted under the given conditions. The metal contents of the preparations obtained were analyzed chemically, and their densities were determined. Independently of the methods of preparation of the products, the contents of their metallic components were Fe 18.55%, V 16.74% and Mo 29.60%, compared with the theoretically calculated values for the FeVMoO$_7$ phase of Fe 17.75%, V 16.19% and Mo 30.48%. The density of FeVMoO$_7$ was 3.74 ± 0.05 g/cm^3.

X-ray phase analysis showed neither the presence of substrates nor any other phases known to contain iron, vanadium or molybdenum. Only an unknown series of reflections appeared in diffractograms of the preparations, to be attributed to FeVMoO$_7$. A list of interplanar distances of FeVMoO$_7$ and of relative intensities of the corresponding reflexions is given in Table 1.

Table 1 Interplanar distances for FeVMoO$_7$ and relative intensities of the corresponding relflexions

Lp.	d,Å	I, %	Lp.	d, Å	I, %
1	2	3	1	2	3
1	5.47	5	13	3.15	60
2	5.32	40	14	3.09	30
3	4.66	30	15	3.07	25
4	4.55	10	16	2.92	10
5	4.12	20	17	2.78	5
6	3.92	25	18	2.73	30
7	3.83	30	19	2.72	30
8	3.54	30	20	2.64	5
9	3.33	30	21	2.53	10
10	3.25	100	22	2.38	5
11	3.23	80	23	2.34	5
12	3.21	30	24	2.32	10

Two endothermic effects were recorded in the DTA curve of the FeVMoO$_7$ phase (Fig. 1). The first one, at 680 ± 5°, is characterized by incongruent melting of FeVMoO$_7$, and the second (t_{start} = 760 ± 5°) by melting of the solid substance separating during the incongruent melting of FeVMoO$_7$.

The results of x-ray phase analysis of the FeVMoO$_7$ phase, molten at 740 ± 10° and cooled rapidly to ambient temperature, showed that the substance of interest is Fe$_4$V$_2$Mo$_3$O$_{20}$. This phase was found to occur in the Fe$_2$O$_3$—V$_2$O$_5$—MoO$_3$ system through examination of phase equilibria established in the pseudobinary system FeVO$_4$—Fe$_2$(MoO$_4$)$_3$ [11, 12].
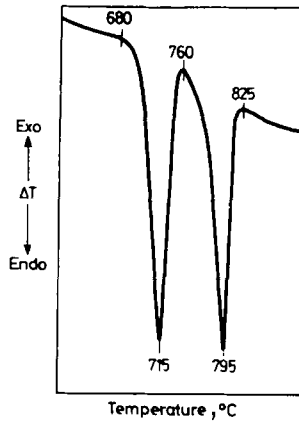
Fig. 1 The DTA curve of $FeVMoO_7$

Table 2 The composition of initial mixtures, the conditions of preparation and results from X-ray phase analysis of samples in equilibrium

Composition of samples in terms of compounds of the system, % mol MoO_3	Substrate	Condition of preparation		Phases found
		Temperature, °C	Time, h	
1	2	3	4	5
4; 6; 8; 10; 12.5; 15; 17.5; 20; 22.5; 25; 27.5; 30; 33.33;	$FeVO_4$, MoO_3	400→500 550 600	24 72 24	$FeVO_4$, $FeVMoO_7$
36.67; 40; 42; 44; 46; 48	$FeVO_4$ $FeVMoO_7$	550 600	72 24	$FeVO_4$, $FeVMoO_7$ $FeVO_4$, $FeVMoO_7$
	$FeVO_4$, MoO_3	400→500 550 540	24 72 24	$FeVMoO_7$, MoO_3 $FeVMoO_7$, MoO_3
52; 54; 56; 58; 60; 66.67	$FeVMoO_7$ MoO_3	540 590	48 24	$FeVMoO_7$, $Fe_2(MoO_4)$, $V_9Mo_6O_{40}$ $FeVMoO_7$, $Fe_2(MoO_4)$, $V_9Mo_6O_{40}$
	$FeVO_4$, MoO_3	400→500 550	24 72	$FeVMoO_7$, MoO_3
70; 75; 80; 85; 90; 95	$FeVMoO_7$ MoO_3	540 540	24 48	$FeVMoO_7$, MoO_3 $Fe_2(MoO_4)_3$, MoO_3 $V_9Mo_6O_{40}$
		590	24	$Fe_2(MoO_4)_3$, MoO_3, $V_9Mo_6O_{40}$

Assuming that the $FeVMoO_7$ phase and its reactions with the components of the Fe_2O_3—V_2O_5—MoO_3 system were not previously known, we carried out experiments to verify the phase diagram of the $FeVO_4$—MoO_3 system in the range 50–100 mol% MoO_3. The separately obtained phases $FeVMoO_7$ and $FeVO_4$, and $FeVMoO_7$ and MoO_3 were used to prepare the starting mixtures. The compositions of the mixtures and the conditions of production of equivalent preparations are listed in Table 2. After each roast cycle, the samples were cooled rapidly to ambient temperature and analyzed by x-ray diffraction. The phases found are also given in Table 2. The data in Table 2 show that $FeVMoO_7$ does not remain at constant equilibrium with MoO_3 [13]; in the range 52.00–66.67 mol% MoO_3, it reacts partially to $Fe_2(MoO_4)_3$ and $V_9Mo_6O_{40}$, whereas with $\geqslant 70$ mol% MoO_3 in the initial mixtures, $FeVMoO_7$ ceases to be a stable phase.

The phase diagram of the $FeVO_4$—MoO_3 system, constructed from the data of the DTA curves and X-ray phase analysis of all the preparations, is shown in Fig. 2. The types of the stable phases and the limits of their coexistence with liquid within the high-temperature area of the phase diagram were established by examination of the phase compositions of some samples, heated at 600–800 ± 10° and then cooled rapidly to ambient temperature. The compositions of samples subjected to such examinations are indicated in Fig. 2.
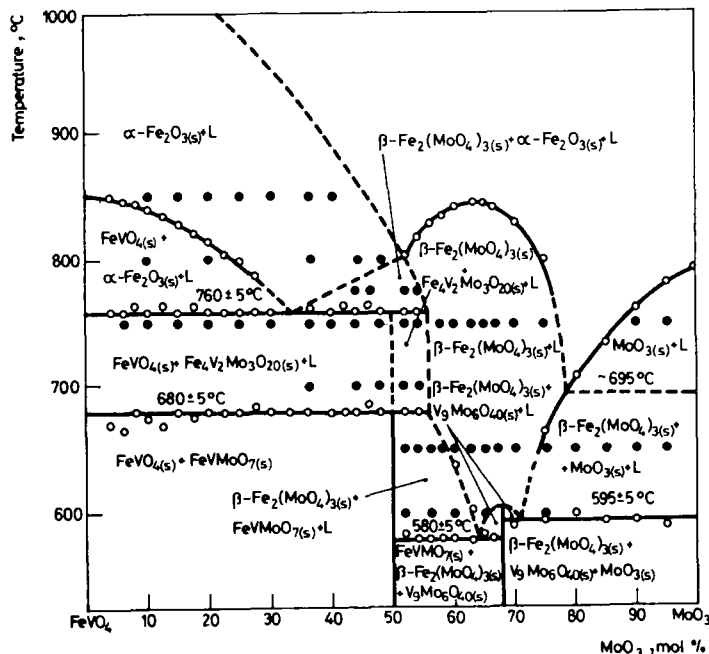

Fig. 2 The phase diagram of the $FeVO_4$ -MoO_3 system

Our investigations permit the following conclusions:

1. The components of the FeVO$_4$—MoO$_3$ system form a compound, not reported so far, whose composition corresponds to the formula FeVMoO$_7$. This compound melts incongruently at $680 \pm 5°$, with separation of the stable Fe$_4$V$_2$Mo$_3$O$_{20}$.

2. FeVMoO$_7$ can be obtained from the solid-phase reactions between FeVO$_4$ and MoO$_3$, as well as between Fe$_2$O$_3$, V$_2$O$_5$ and MoO$_3$. The X-ray powder diffraction data on FeVMoO$_7$ have been established at $2\theta = 10$ -60° (CoK$_\alpha$).

3. FeVO$_4$—MoO$_3$ is a real two-component system only in the range of component concentrations up to 50 mol% MoO$_3$, i.e. in the range of FeVO$_4$—FeVMoO$_7$, and only to the solidus line, while above 50 mol% MoO$_3$ and in the sub-solidus area, it is no longer a two-component system, for three solid phases are in equilibrium.

Above the solidus line, due to phases melting incongruently (FeVO$_4$, FeVMoO$_7$ and Fe$_4$V$_2$Mo$_3$O$_{20}$) the system FeVO$_4$—MoO$_3$ does not exist as a two-component system for any component concentrations.

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Zusammenfassung — Das Phasendiagramm des Systems FeVO$_4$—MoO$_3$ wurde basierend auf Ergebnissen der DTA und Röntgenanalyse aufgestellt. Die Komponenten des Systems bilden die Verbindung FeVMoO$_7$. Diese Verbindung schmilzt inkongruent bei 680±5° unter Abscheidung von festem Fe$_4$V$_2$Mo$_3$O$_{20}$.

Резюме — Фазовая диаграмма системы FeVO$_4$ - MoO$_3$ была установлена на основе измерений ДТА и фазового анализа. Компоненты системы образуют соединение FeVMoO$_7$, которое плавилось инконгрузнтно при 680±5 °C с выделением твердого вещества Fe$_4$V$_2$Mo$_3$O$_{20}$.