Journal of Thermal Analysis, Vol. 29 (1984) 983–988

PHASE EQUILIBRIA IN THE $FeVO_4-Fe_2(MoO_4)_3$ SYSTEM

J. Walczak, J. Ziołkowski, M. Kurzawa and *L. Trzesniowska*

DEPARTMENT OF FUNDAMENTAL CHEMISTRY, THE TECHNICAL UNIVERSITY
OF SZCZECIN, AL. PIASTÓW 42, 71-065 SZCZECIN, POLAND

Phase equilibria have been investigated in the $FeVO_4-Fe_2(MoO_4)_3$ system for the whole concentration range of the components. In this system there is one compound which melts incongruently: $Fe_4V_2Mo_3O_{20}$. The results are presented in the form of a phase diagram.

The general aim of the present investigation is to seek for new phases which could exhibit catalytic properties of interest from both basic and applied points of view in reactions of partial oxidation of hydrocarbons. Within this framework, we have undertaken, among others, studies on the three-component $Fe_2O_3-V_2O_5-MoO_3$ system. The present communication reports some of the results obtained on the pseudo-binary $FeVO_4-Fe_2(MoO_4)_3$ section of this three-component system.

The properties of the components of the $FeVO_4-Fe_2(MoO_4)_3$ system are well known. $Fe_2(MoO_4)_3$ crystallizes in two polymorphic forms: a low-temperature monoclinic α form [1–4] and a high-temperature orthorhombic β form [5, 6].

The phase transition was observed at 518° during heating and at 480° during cooling [7]. Iron(III) molybdate has been reported to melt congruently at temperatures ranging from 940 to 975° [8–11].

$FeVO_4$ forms triclinic crystals [12, 13] and at normal pressure does not exhibit polymorphism. It melts incongruently with the deposition of α-Fe_2O_3 at 840–890°, depending on the source [14–17].

Experimental

V_2O_5 p. (Reachim), MoO_3 p. (POCh, Gliwice) and α-Fe_2O_3 obtained by precipitation of $Fe(OH)_3$, drying and thermal decomposition at 450° in air during a few tens of hours were used in our measurements. Oxides, in well weighed proportions, were ground in an agate mortar, pilled and heated in air at 600–700° for different periods of time. The obtained preparations were then slowly cooled down to room temperature and subsequently ground.

The phase compositions of the resulting samples were determined by Röntgen analysis (DRON-3–CoK$_\alpha$) and from the data in the ASTM cards [18] and the literature [4, 17].

Thermal analysis (DTA) was carried out in a Paulik–Paulik–Erdey Derivatograph (MOM, Budapest) in air atmosphere at a heating rate of 10 deg/min in the temperature range 20–1000°. Quartz crucibles were used and the sample weight was 1000 mg.

Preliminary investigations

It has been found earlier that $FeVO_4$ can be obtained by the successive heating of an equimolecular mixture of Fe_2O_3 and V_2O_5 at 600° for 24 h, at 650° for 24 h and at 700° for 72 h [19]. However, the synthesis of $Fe_2(MoO_4)_3$ requires heating of a mixture of Fe_2O_3 with a slight excess of MoO_3 to constant mass at 700°, and at 750° for 24 h. In our preliminary investigations we prepared two samples of $Fe_2O_3 + V_2O_5 + MoO_3$, with 94 mol % $FeVO_4$ + 6 mol % $Fe_2(MoO_4)_3$ (I), and 86 mol % $FeVO_4$ + 14 mol % $Fe_2(MoO_4)_3$ (II).

The samples were subjected to successive heating for 24 h at 600, 650, 700 and 750° (±10°), and after each heating step the samples were analyzed by Röntgen phase analysis and DTA. The aim of this experimental work was to determine heating conditions ensuring that the system reached the equilibrium state in the subsolidus range of the phase diagram. For both samples heated at 600° Röntgen phase analysis revealed the presence of $FeVO_4$, $Fe_2V_4O_{13}$, α-Fe_2O_3 and V_2O_5 (trace amounts), as well as a set of unidentified reflexions, ascribed to an as yet unknown phase Y.

In the preparations heated at 650° and 700°, $FeVO_4$ and the *Y* phase were found. Sample II heated at 750° additionally contained $Fe_2(MoO_4)_3$ and α-Fe_2O_3, whereas in sample I, apart from $FeVO_4$ and the Y phase, small amounts of α-Fe_2O_3 were also found.

The DTA curves for sample I heated at 650° and at 700° exhibited two endothermic effects. The first (745°) could be ascribed to the eutectic $FeVO_4$–Y phase, and the second, at the peak temperature of 820°, to the transition through the liquidus line.

Sample II heated at 650° and 750° exhibited only the first effect, indicating that the preparation composition was very close to that corresponding to the eutectic point. For the preparations heated at 600 and 750°, the DTA curves revealed a few additional thermal effects. The results discussed here indicate that the final preparation temperature should be somewhere between 600 and 700°.

The following conditions for the thermal treatment of the samples were applied in subsequent investigations: 600° for 24 h + 650° for 24 h + 700° for 72 h.

Results and conclusions

With the above procedure, 19 preparations with the $FeVO_4$ concentration increasing at 5 mol % intervals were prepared. These were subjected to DTA measurements and Röntgen phase analysis. Figure 1 presents the dependence of the intensity (for the most characteristic reflexions corresponding to $FeVO_4$, $Fe_2(MoO_4)_3$ and the Y phase) upon the general composition of the preparations. The figure clearly shows that the Y phase appears at an $FeVO_4$ concentration of about 66 mol %. At higher concentration it is accompanied by $FeVO_4$, and at lower ones by $Fe_2(MoO_4)_3$. This fact suggests that

$$Y = 2\ FeVO_4 \cdot Fe_2(MoO_4)_3 = Fe_4V_2Mo_3O_{20}$$

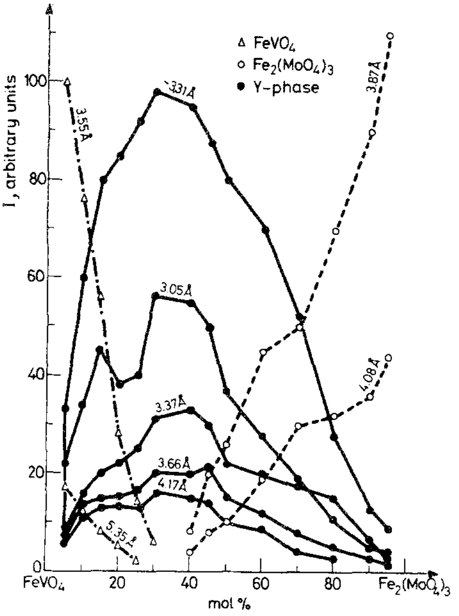

Fig. 1 Absolute intensities of the chosen diffraction lines for $FeVO_4$, $Fe_2(MoO_4)_3$ and the Y phase

Under the applied preparation conditions, $Fe_4V_2MoO_3O_{20}$ was obtained both from the mixture of $Fe_2O_3 + V_2O_5 + MoO_3$ and from the earlier produced $FeVO_4 +$ $+ Fe_2(MoO_4)_3$. Diffractograms of these samples contained exclusively the reflexions previously ascribed to the Y phase and now identified as $Fe_4V_2Mo_3O_{20}$. Table 1 lists interplanar distances for this compound, as well as the relative intensities of the corresponding reflexions. DTA of the $Fe_4V_2MoO_3O_{20}$ phase (Fig. 2) shows two endothermic effects; the first ($t_{\mathrm{init.}} = 760°$) can be ascribed to the incongruent melting of this phase, and the second ($t_{\mathrm{peak}} = 835°$) to the transition through the liquidus line.

Figure 3 presents a phase diagram of the $FeVO_4$–$Fe_2(MoO_4)_3$ system. The diagram has been constructed from the results of phase analysis and DTA curves obtained for 19 samples in the main series. The form of the diagram supports the hypothesis. Thus, in the $FeVO_4$–$Fe_2(MoO_4)_3$ system there is only one chemical

Table 1 Intraplanar distances for $Fe_4V_2Mo_3O_{20}$ and relative intensities of the corresponding reflexions

d, Å	I, %	d, Å	I, %
4.76	15	3.18	15
4.59	5	3.12	20
4.36	35	3.05	95
4.28	20	3.02	15
4.17	25	2.97	10
3.91	40	2.90	5
3.82	35	2.78	15
3.66	35	2.73	10
3.42	30	2.67	10
3.37	50	2.64	5
3.31	100	2.63	5
3.23	30	2.53	5

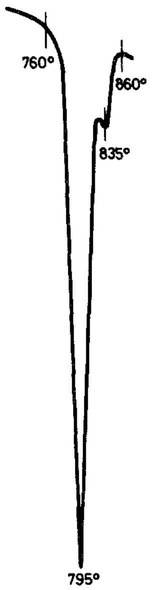

Fig. 2 DTA curve of $Fe_4V_2Mo_3O_{20}$

compound, $Fe_4V_2Mo_3O_{20}$, which melts incongruently at 760±5° with the deposition of α-Fe_2O_3 and $Fe_2(MoO_4)_3$. In the phase diagram range corresponding to $FeVO_4$–$Fe_4V_2Mo_3O_{20}$ there is an eutectic melting at 745±5°, at 88 mol % $FeVO_4$ and 12 mol % $Fe_2(MoO_4)_3$.

In the subsolidus range our results fit an unequivocal and consistent pattern. A full explanation of the nature of the phase transition above the solidus line needs deter-

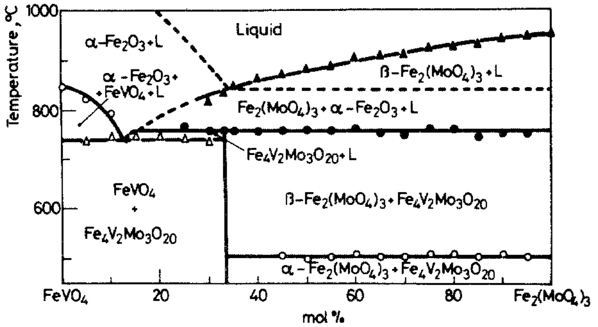

Fig. 3 Phase diagram for the $FeVO_4$–$Fe_2(MoO_4)_3$ system

mination of the complete diagram for the Fe_2O_3–V_2O_5–MoO_3 system, including that outside the $FeVO_4$–$Fe_2(MoO_4)_3$ section. Taking into account the nature of the products to which samples I and II decompose on heating to 750±10°, as well as the results of paper [19], in the high-temperature range of the diagram we have depicted (by broken lines) those ranges of the diagram the existence of which requires experimental evidence.

References

1 P. V. Klevcov, R. F. Klevcova, L. M. Kefeli and L. M. Plasova, Izv. AN SSSR, Neorg Mater., 1 (1965) 918.
2 L. M. Plasova, R. F. Klevcova, S. V. Borisov and L. M. Kefeli, Dokl. AN SSSR, 167 (1966) 84.
3 L. M. Plasova, S. V. Borisov and N. V. Belov, Kristalog., 12 (1967) 33.
4 G. Fagherozzi and N. Pernicone, J. Catal., 16 (1970) 321.
5 L. M. Plasova, R. F. Klevcova, S. V. Borisov and L. M. Kefeli, Kristalog., 12 (1967) 939.
6 L. M. Plasova and L. M. Kefeli, Neorg. Mater., 3 (1967) 906.
7 L. M. Plasova, Żur. Strukt. Chim., 17 (1976) 738.
8 J. D. Kozmanov, Żur. Fiz. Chim., 31 (1957) 1861.
9 J. D. Kozmanov and T. A. Ugolnikova, Żur. Neorg. Chim., 3 (1958) 1267.
10 W. Jäger, A. Ramel and K. Beker, Arch. Eisenhüttenwesen, 30 (1959) 435.
11 N. P. Burmistrova, R. M. Cecetkin and L. A. Segova, Żhur. Prikl. Chim., 5 (1969) 1166.
12 L. M. Levinson and B. M. Wanklyn, J. Solid State Chem., 3 (1971) 131.
13 B. Robertson and K. Kostiner, J. Solid State Chem., 4 (1972) 29.
14 V. Cirilli, A. Burdese and C. Brisi, Met. ital., 48 (1956) 309.
15 B. V. Slobodin, A. A. Fotiev and I. I. Miller, Żur. Neorg. Chim., 21 (1976) 327.
16 A. A. Fotiev, L. L. Surat, G. A. Korablev and A. I. Tretiakov, Żur. Neorg. Chim., 26 (1981) 242.
17 Y. Otsubo and K. Utsumi, J. Chem. Soc. Japan, Pure Chem. Sec., 92 (1971) 737.
18 Joint Committee of Powder Diffraction File 5–508; 9–387; 13–543; 20–526; 24–541; 25–418.
19 J. Walczak, M. Kurzawa and E. Filipek, The Third Polish Seminar to the memory of St. Bretsznajder, Płock, 14–16. IX. 1983.

Zusammenfassung — Phasengleichgewichte im System $FeVO_4$–$Fe_2(MoO_4)_3$ wurden über den ganzen Konzentrationsbereich der Komponenten hinweg untersucht. Eine Verbindung des Systems, $Fe_4V_2Mo_3O_{20}$, schmilzt inkongruent. Die Ergebnisse sind in Form eines Phasendiagramms angegeben.

Резюме — Исследовано фазовое равновесие системы $FeVO_4$–$Fe_2(MoO_4)_3$ во всей области концентраций компонентов. В изученной системе найдено соединение $Fe_4V_2Mo_3O_{20}$, плавящееся инконгруентно. Полученные результаты представлены в форме фазовой диаграммы.