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STUDIES ON THE $Fe_2V_4O_{13}$–MoO_3 SYSTEM

JADWIGA WALCZAK and MARIA KURZAWA

Institute of Fundamental Chemistry, Technical University of Szczecin, 42 Al Piastów, 71-065 Szczecin (Poland)

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ABSTRACT

Using DTA and X-ray powder diffraction methods, the behaviour of MoO_3 in respect to $Fe_2V_4O_{13}$ at 1000 °C in a range of component concentrations has been studied The experimental results are presented in the form of a phase diagram

INTRODUCTION

Two and three component systems of transition metal oxides and phases existing in these systems have come into use as catalysts in many organic processes [1] Especially interesting and so far little known in this respect are systems in which V_2O_5 and MoO_3 are two substantial components, with a third component being an oxide of the third oxidation number, e g Fe_2O_3

We have found in our work on the Fe_2O_3–V_2O_5–MoO_3 system that MoO_3 forms, with $Fe_2V_4O_{13}$, one of the two compounds existing in the binary Fe_2O_3–V_2O_5 system [2,3], solid solutions with solubility limit of 18 mol% of MoO_3 at ambient temperature The solutions are formed by incorporation of Mo^{6+} ions into the $Fe_2V_4O_{13}$ lattice, in the place of V^{5+} ions [4]

Mossbauer spectroscopy results permitted us to theorize that compensation of an excessive positive charge takes place by reduction of an equivalent number of Fe^{3+} ions to Fe^{2+} ions [5] Thus, the solid solutions form phases of the formula $Fe^{3+}_{2-x}Fe^{2+}_{x}V_{4-x}Mo_xO_{13}$ ($X_{max} \simeq 0\ 60$) The behaviour of these phases has not hitherto been studied In screening tests of the $Fe_2V_4O_{13}$–MoO_3 system we have only established phase equilibria in the solid state [6] Investigations presented in this work have in view to work up a full diagram of phase equilibria of the system under consideration

The structure of $Fe_2V_4O_{13}$ has not so far been refined Also the properties of the phase have not yet been comprehensively recognized However, it is known that $Fe_2V_4O_{13}$ melts incongruently (Fotiev et al [2] (692 °C), Otsubo and Utsumi [7] (715 °C)) depositing $FeVO_4$, the other compound arising besides $Fe_2V_4O_{13}$ in the Fe_2O_3–V_2O_5 system [2,3,7] We have established through our study that the melting point of $Fe_2V_4O_{13}$ is 665 ± 5 °C [3] The

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X-ray powder diffractogram of the phase in the angle range of 2θ Co K_α 10–70 °C is also known Density of $Fe_2V_4O_{13}$ is 3 13 ± 0 05 g cm^{-3} [3]

The properties and structure of MoO_3 only will be discussed below, since the other components of the system of interest are well known [8,9] Molybdenum trioxide reacts with V_2O_5 to form solid substitution solutions of MoO_3 in this oxide [10,11] as well as a compound, $V_9Mo_6O_{40}$, which structurally belongs to a homologous series, M_nO_{3n-1}, with $n = 3$ [11–13] MoO_3 also reacts with Fe_2O_3 yielding $Fe_2(MoO_4)_3$ [14] In addition, we have found that MoO_3 reacts with $FeVO_4$ to form $FeVMoO_7$ [15] On the other hand, iron(III) orthovanadate reacts with $Fe_2(MoO_4)_3$, $Fe_4V_2Mo_3O_{20}$ being the product of the reaction [16] Both the compounds arise from the reaction between Fe_2O_3, V_2O_5 and MoO_3 [15–17]

EXPERIMENTAL

Alpha-Fe_2O_3, V_2O_5 (commercial products of p a grade), and MoO_3 obtained by thermal decomposition of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ at 150–550 °C in air were used in the experiments. The oxides were weighed in appropriate proportions, ground, pastilled and heated in air under conditions established in screening tests [4,6] 400–500 °C, 24 h, 550 °C, 24 h, 550 °C, 72 h, 580 °C, 24 h The preparations obtained were cooled slowly to ambient temperature, ground, studied by the DTA method and, finally, their phase composition was determined The experimental results from the DTA method showed that the temperature of the initial melting of some of the preparations (72 5 and 75 0 mol% of MoO_3 in a starting mixture) is lower (570 °C) than the final temperature of their obtention (580 °C) Hence, it seemed advisable to verify the phase equilibria being established in the solid state at a temperature close to the solidus line temperature Therefore, all the preparations mildly cooled from 580 °C to ambient temperature were additionally heated at 550 °C for 72 h and then rapidly cooled to ambient temperature After grinding the preparations were studied by the DTA and X-ray powder diffraction methods

The experimental results permitted us to precisely state the coexistence ranges of individual phases in the subsolidus area After rapid cooling, the preparations obtained at 550 °C were additionally heated for 2 h at 605, 640, 670, 700, 740, 800 and 830 °C, respectively, and also rapidly cooled to ambient temperature On grinding, their phase composition was studied Based on experimental results the types of solid phases remaining at equilibrium with liquid at temperatures higher than the solidus line temperature were established

The phase composition of preparations was determined by X-ray powder diffraction (DRON-3, Co K_α) and on the data from the ASTM cards as well as from several sources [3,15–18]

DTA was performed using a derivatograph (F. Paulik–J. Paulik–L Erdey) in quartz crucibles in air at 20–1000 °C and with a heating rate of 10 °C min^{-1} The weight of the samples under study was 1000 mg Constructing a phase diagram, the solidus lines were assigned based on the DTA initial effect temperature, whereas the liquidus curves on the grounds of the apex effect temperature Accuracy of the temperature reading, ±5 °C, was determined via repetitions

RESULT AND DISCUSSION

Table 1 shows the composition of starting mixtures and X-ray powder diffraction results of preparations obtained after the second cycle of heating at 550 °C for 72 h and on rapid cooling The experimental results compiled in Table 1 show that MoO_3 does not remain at permanent equilibrium with $Fe_2V_4O_{13}$ because it does not occur in the phase composition of specimens at equilibrium Moreover, X-ray powder diffraction of preparations, which comprised 2 5–40 0 mol% of MoO_3 in a starting mixture, showed that they do not contain other molybdenum compounds Thus, the phase composition of the preparations proves that MoO_3 builds into $Fe_2V_4O_{13}$ lattice by dislodging V_2O_5 from it

$$Fe_2V_4O_{13(s)} + MoO_{3(s)} \rightarrow Fe_2V_4O_{13(s\,s)} + V_2O_{5(s)} \qquad (1)$$

Molybdenum trioxide forms a solid solution with the resultant V_2O_5 [11,12]

$$V_2O_{5(s)} + MoO_{3(s)} \rightarrow V_2O_{5(s\,s)} \qquad (2)$$

When preparations include more than 40 mol% of MoO_3 in their starting mixtures, besides the two solid solutions, viz $Fe_2V_4O_{13(s\,s)}$ and $V_2O_{5(s\,s)}$, a third stable phase, $FeVMoO_7$, appears in the system The appearance of

TABLE 1

The composition of starting mixtures and the X-ray powder diffraction results of the preparations at equilibrium

The composition of samples in terms of the system component (mol% MoO_3)	Phases found
2 5, 5 0, 7 5, 10 0, 12 5, 15 0, 20 0, 25 0, 30 0, 35 0, 40 0	$Fe_2V_4O_{13(s\,s)}$, $V_2O_{5(s\,s)}$
45 0, 50 0, 55 0, 60 0, 65 0, 67 5, 70 0	$Fe_2V_4O_{13(s\,s)}$, $V_2O_{5(s\,s)}$, $FeVMoO_7$
72 5, 75 0	$V_2O_{5(s\,s)}$, $FeVMoO_7$, $V_9Mo_6O_{40}$
77 5, 80 5, 82 5	$FeVMoO_7$, $V_9Mo_6O_{40}$, $Fe_2(MoO_4)_3$
85 0, 90 0, 95	$V_9Mo_6O_{40}$, $Fe_2(MoO_4)_3$, MoO_3

$FeVMoO_7$ in addition to $Fe_2V_4O_{13(s\,s)}$ supports the statement that a reaction takes place in the system, in summary

$$Fe_2V_4O_{13(s)} + 2MoO_{3(s)} \rightarrow 2FeVMoO_{7(s)} + V_2O_{5(s\,s)} \tag{3}$$

The mechanism of this reaction requires special investigation but without doubt a decomposition of $Fe_2V_4O_{13(s\,s)}$ occurs when the MoO_3 content is greater than 40 mol%, which is proved to be the case by the formation of $FeVMoO_7$ X-ray powder diffraction shows that this decomposition is terminated at ~ 72.5 mol% of MoO_3 in the starting mixture X-ray powder diffraction results of specimens comprising ca 45 0–70 0 mol% of MoO_3 in their starting mixture show that the decomposition of $Fe_2V_4O_{13(s\,s)}$ is accompanied by formation of the solid solution of MoO_3 in V_2O_5 It is proved by the increase in the $V_2O_{5(s\,s)}$ content in preparations with increasing MoO_3 content in the starting mixtures

With further increase in the MoO_3 content in the substrates, an equilibrium phase, $V_9Mo_6O_{40}$, appears in the system In the range 72 5–75 mol% of MoO_3 in the starting mixtures a decomposition of the solid solution of MoO_3 in V_2O_5 takes place to deliver free MoO_3 and V_2O_5, which enables the formation of $V_9Mo_6O_{40}$

$$4\ 5V_2O_{5(s)} + 6MoO_{3(s)} \rightarrow V_9Mo_6O_{40(s)} + 0.25O_2 \tag{4}$$

In the range 77 5–82 5 mol% of MoO_3 in the starting mixtures, $FeVMoO_7$, $V_9Mo_6O_{40}$ and $Fe_2(MoO_4)_3$ remain at equilibrium Appearance of $Fe_2(MoO_4)_3$ in the system in this component concentration range, i e with excess of MoO_3 compared to $FeVMoO_7$ and $V_9Mo_6O_{40}$, shows that the hitherto stable $FeVMoO_7$ starts to react with MoO_3 according to the equation

$$18FeVMoO_{7(s)} + 21MoO_{3(s)} \rightarrow 9Fe_2(MoO_4)_{3(s)} + 2V_9Mo_6O_{40(s)} + 0\ 5O_2 \tag{5}$$

In the other component concentration range, MoO_3 remains at permanent equilibrium with $Fe_2(MoO_4)_3$ and $V_9Mo_6O_{40}$, respectively Figure 1 shows the phase diagram of the $Fe_2V_4O_{13}$–MoO_3 system constructed on the DTA curves and X-ray powder diffractograms of 26 preparations at equilibrium at 550 °C and on the basis of X-ray powder diffractograms of preparations heated, additionally, at temperatures higher than the solidus line temperature. The ranges of solid phases coexistent with liquid were determined using the DTA results of preparations at equilibrium, whereas the types of phase were established based on the X-ray powder diffraction results of samples which were additionally heated for 2 h at chosen temperatures, 605–830 °C, and cooled rapidly to ambient temperature

It follows from the diagram presented in the Fig 1 that the $Fe_2V_4O_{13}$–MoO_3 system in the whole range of component concentrations studied is not a real binary system, not even in the subsolidus area It is supported by the presence of fields in this area in which three solid phases remain at equilibrium Above the solidus line in appropriate fields of the

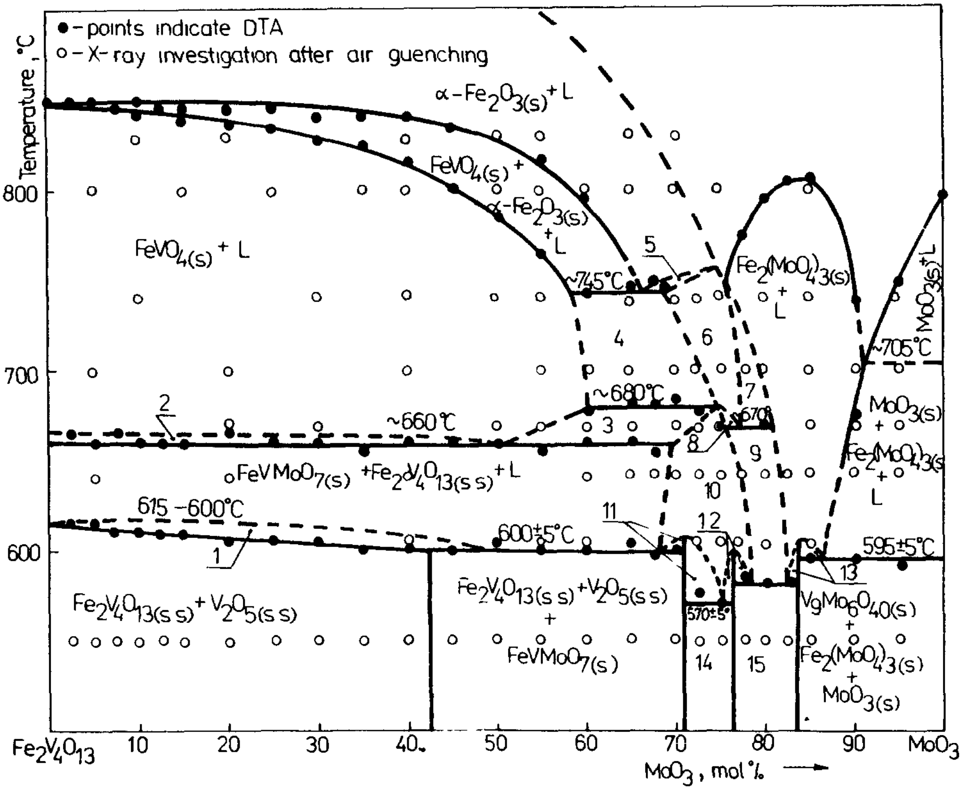

Fig 1 Phase diagram of the $Fe_2V_4O_{13}$–MoO_3 system 1, $Fe_2V_4O_{13(s\,s)}+V_2O_{5(s\,s)}$ + liquid, 2, $Fe_2V_4O_{13(s\,s)}+FeVO_{4(s)}$ + liquid, 3, $FeVO_{4(s)}+FeVMoO_{7(s)}$ + liquid, 4, $Fe_4V_2Mo_3O_{20(s)}+FeVO_{4(s)}$ + liquid, 5, $Fe_4V_2Mo_3O_{20(s)}+\alpha\text{-}Fe_2O_{3(s)}$ + liquid, 6, $Fe_4V_2Mo_3O_{20(s)}$ + liquid, 7, $Fe_2(MoO_4)_{3(s)}+Fe_4V_2Mo_3O_{20(s)}$ + liquid, 8, $Fe_4V_2Mo_3O_{20(s)}+FeVMoO_{7(s)}$ + liquid, 9, $Fe_2(MoO_4)_{3(s)}+FeVMoO_{7(s)}$ + liquid, 10, $FeVMoO_{7(s)}$ + liquid, 11, $FeVMoO_{7(s)}+V_2O_{5(s\,s)}$ + liquid, 12, $FeVMoO_{7(s)}+V_9Mo_6O_{40(s)}$ + liquid, 13, $Fe_2(MoO_4)_{3(s)}+V_9Mo_6O_{40(s)}$ + liquid, 14, $V_2O_{5(s\,s)}+FeVMoO_{7(s)}+V_9Mo_6O_{40(s)}$, 15, $FeVMoO_{7(s)}+V_9Mo_6O_{40(s)}+Fe_2(MoO_4)_{3(s)}$

phase diagram, there exist at equilibrium solid phases which are not present in the subsolidus area The phases, $FeVO_4$ and $Fe_4V_2Mo_3O_{20}$, occur above the solidus line due to incongruently melting $Fe_2V_4O_{13(s\,s)}$ and $FeVMoO_7$, respectively

$$Fe_2V_4O_{13(s\,s)} \rightarrow FeVO_{4(s)} + \text{liquid} \tag{6}$$

$$FeVMoO_{7(s)} \rightarrow Fe_4V_2Mo_3O_{20(s)} + \text{liquid} \tag{7}$$

The solid products of meritectic reactions also melt incongruently

$$FeVO_{4(s)} \rightarrow \alpha\text{-}Fe_2O_{3(s)} + \text{liquid} \tag{8}$$

$$Fe_4V_2Mo_3O_{20(s)} \rightarrow \alpha\text{-}Fe_2O_{3(s)} + Fe_2(MoO_4)_{3(s)} + \text{liquid} \tag{9}$$

On the basis of presented results it was not possible to precisely state the existence of all fields in which the solid phases remain at equilibrium with liquid Thus the maximum temperatures of existence of fields 11, 12, 13 (Fig 1) were determined based on the results of our other investigations, that is, on the phase diagrams of the systems $FeVMoO_7$–V_2O_5 [19], $FeVMoO_7$–$V_9Mo_6O_{40}$ [20] and $Fe_2(MoO_4)_3$–$V_9Mo_6O_{40}$, respectively [21] The existence ranges of fields, $FeVMoO_{7(s)}$ + liquid as well as 6, 7, 9, were assigned exclusively on the X-ray powder diffraction results of preparations heated additionally at temperatures higher than the solidus line temperatures and cooled rapidly to ambient temperature On the other hand, the existence ranges of fields 1, 5, 8 and of the field in which $FeVO_{4(s)}$, $Fe_2V_4O_{13(s\,s)}$ and liquid coexist at equilibrium failed to be confirmed experimentally because of quite small parameter ranges, i e either temperature or component concentration, by which they are described Their existence is justified by the position of neighbouring fields whose presence on the phase diagram of the $Fe_2V_4O_{13}$–MoO_3 system is definite Therefore some curves bordering these fields have been drawn on the phase diagram with dotted lines

REFERENCES

1 T Wolkenstein, Physico-chimie de la surface des semiconducteurs, Mir Moscou, 1977, p 250
2 A A Fotiev, S M Cheshnitskii and L L Surat, Zh Neorg Khim, 28 (1983) 988
3 J Walczak, J Ziółkowski, M Kurzawa, J Osten-Sacken and M Łysio, Polish J Chem, 59 (1985) 255
4 J Walczak and M Kurzawa, J Therm Anal, 31 (1986) 531
5 J Walczak, J Frąckowiak, T Panek and M Kurzawa, J Mater Sci Lett, 5 (1986) 1224
6 J Walczak, M Kurzawa and L Trześniowska, Thermochim Acta, 92 (1985) 567
7 Y Otsubo and K Utsumi, J Chem Soc Jpn Pure Chem Section, 92 (1971) 737
8 N Z Wooster, Z Krist, 80 (1931) 504
9 O Kubaschewski, E L Ewans and C B Allock, Metallurgical Thermochemistry, Pergamon Press, London, 1967
10 E Burzo and L Stanescu, Mater Res Bull, 13 (1978) 237
11 A Bielański, K Dyrek, J Póżniczek and E Wenda, Bull Acad Polon Sci Ser Sci Chim, 19 (1971) 507
12 R H Jarman, P G Dickens and A J Jacobson, Mater Res Bull, 17 (1982) 325
13 R H Jarman and A K Cheetham, Mater Res Bull, 17 (1982) 1011
14 W Jager, A Rahmel and K Becker, Arch Eisenhuttenw, 30 (1959) 435
15 J Walczak, M Kurzawa and E Filipek, J Therm Anal, 31 (1986) 271
16 J Walczak, J Ziółkowski, M Kurzawa and L Trześniowska, J Therm Anal, 29 (1984) 983
17 J Walczak, J Ziółkowski, M Kurzawa and L Trześniowska, Polish J Chem, 59 (1985) 713
18 Joint Committee of Powder Diffraction, File 20-526, 20-1377, 24-541, 25-418, 31-642, 33-661, 34-527
19 J Walczak and M Kurzawa, Proc 31st Int Cong Pure Appl Chem, IUPAC '87, 13–18 July 1987, Sofia, Posters 1, p 5 172
20 J Walczak, M Kurzawa and P Tabero, Workbook, 4th Europ Symp Therm Anal Cal, 23–28 August 1987, Jena, p C56
21 J Walczak, M Kurzawa and K Wasąznik, Thermochim Acta, 92 (1985) 571