

$V_9Mo_6O_{40}$ AND PHASE EQUILIBRIA IN THE SYSTEM $V_9Mo_6O_{40}-Fe_2O_3$

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ABSTRACT

The behaviour of Fe_2O_3 towards $V_9Mo_6O_{40}$ at temperatures of up to $1000^\circ C$ for the whole range of component concentrations was studied by the DTA method and X-ray phase powder diffraction. The experimental results are shown in a phase diagram. It has been found that components of the phase do not remain at constant equilibrium and that $V_9Mo_6O_{40}-Fe_2O_3$ is not a true two-component system, not even in the subsolidus area.

INTRODUCTION

The $V_2O_5-MoO_3$ system and its phase, $V_9Mo_6O_{40}$, have been comprehensively investigated with respect to their catalytic qualities utilizable for the oxidation of hydrocarbons. For example, catalysts used for the selective oxidation of benzene are a mixture of the solid solution of MoO_3 in V_2O_5 and $V_9Mo_6O_{40}$ [1]. Fe_2O_3 is another oxidizing agent to show catalytic properties [2]. In order to find new catalysts of commercial significance it seemed expedient to study the behaviour of $V_9Mo_6O_{40}$ and Fe_2O_3 , and to explore phases of this system which would remain at equilibrium up to $1000^\circ C$ for the whole range of component concentrations.

A review of the literature on the subject has shown that components of the $V_2O_5-MoO_3$ system undoubtedly form two phases, α and β [3-5].

The α phase, isostructural with V_2O_5 , is a substitution solid solution of MoO_3 in this oxide, with a general formula $(V_{1-x}Mo_x)_2O_5$, where $0 < x < 0.3$ [3,5,6]. The results of measurements of magnetic properties of the phase and results obtained by electron paramagnetic resonance have shown that introduction of Mo^{6+} ions into the V_2O_5 lattice in place of V^{5+} ions leads to the formation of V^{4+} ions [7,8]. But in general, the number of V^{4+} ions involved in the solid solution lattice is smaller than the number of Mo^{6+} ions incorporated [8]. Therefore, the α phase was in some publications defined by the formula $V_{2-x-y}^{5+}V_x^{4+}Mo_y^{6+}O_5$, where $x < y$ [9].

The β phase, another phase existing in the V_2O_5 - MoO_3 system, was studied by many authors. Magneli and Blomberg [10], Ęon et al. [11], Strupler and Morette [4], and Sperlich et al. [12] found it to be a chemical compound with the formula V_2MoO_8 . Eick and Kihlberg [13] obtained monocrystals of a compound crystallizing in the V_2O_5 - MoO_3 system with the formula V_2MoO_8 . They have suggested that structurally it belongs to a homologous series M_nO_{3n-1} , M_3O_8 being obtained at $n = 3$; V_2O_5 , obtainable when $n = 2$, may also be included in this series.

From a study of the structure of the β phase, Eick and Kihlberg proposed that a homogeneity range, $V_{2-x}Mo_{1+x}O_8$ at $x \geq 0$, is to be expected for the phase [13]. Munch and Pierron [1], and Bielański et al. [3] have ascribed the formula $V_9Mo_6O_{40}$ to the β phase and suggested that $1/9$ of the vanadium atoms occurs as V^{4+} . Jarman and coworkers [14,15] obtained $V_9Mo_6O_{40}$ and have proved that the lattice parameters of its unit cell are identical with data reported for the monocrystal formulated as V_2MoO_6 by Eick and Kihlberg [13]. Moreover, Jarman and Cheetham [15] have indicated that the β phase can be defined by the formula M_3O_8 in which the ratio of metals would vary from $(V_{0.5}Mo_{0.5})_3O_8$ at $500^\circ C$ to $(V_{0.6}Mo_{0.4})_3O_8$ at $600^\circ C$.

Some works imply that the β phase exists either as a solid solution of the type V_2MoO_{8-x} , where $0 < x < 0.5$ [13], or a substitution solid solution of MoO_3 in a hypothetical compound, V_2MoO_8 [16]. $V_9Mo_6O_{40}$ was reported to melt congruently according to Bielański et al. [3] at about $635^\circ C$, or according to Jarman et al. [14] at $677^\circ C$ or at $650^\circ C$ [1]. The density of $V_9Mo_6O_{40}$ is 3.86 g cm^{-3} [1].

Only in a few publications can one find information about the existence of the solid solution of V_2O_5 in MoO_3 . The formation of such a solution was observed in preparations containing up to 2mol% V_2O_5 by Khulbe et al. [17] and Zugin et al. [16].

Another compound of the system under consideration, Fe_2O_3 , reacts with V_2O_5 to yield two compounds, $FeVO_4$ and $Fe_2V_4O_{13}$ which melt incongruently at $850 \pm 5^\circ C$ and $665 \pm 5^\circ C$ respectively [18]. It also reacts with MoO_3 to give $Fe_2(MoO_4)_3$ melting congruently at $955^\circ C$ [19]. However, there are published accounts of the behaviour of Fe_2O_3 towards $V_9Mo_6O_{40}$.

By studying the pseudobinary sections of a tricomponent system, Fe_2O_3 - V_2O_5 - MoO_3 , we have found that MoO_3 forms a solid solution with $Fe_2V_4O_{13}$ [20] described by the formula $Fe_{2-x}^{3+}Fe_x^{2+}V_{4-x}Mo_xO_{13}$ for $x \leq 0.6$ [21]. We have also found that the oxides Fe_2O_3 , V_2O_5 and MoO_3 react with each other to yield two compounds $FeVMoO_7$ and $Fe_4V_2Mo_3O_{20}$ which melt incongruently at $680 \pm 5^\circ C$ and $760 \pm 5^\circ C$ respectively [22,23].

EXPERIMENTAL

V_2O_5 a.p. (Reachim), MoO_3 a.p. (POCh Gliwice) and α - Fe_2O_3 were used for experiments. α - Fe_2O_3 was obtained from $Fe(OH)_3$ by precipitating,

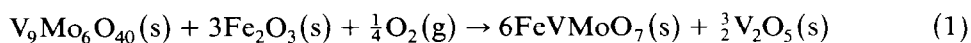
drying and thermally decomposing the substrate at 450 °C in air during several dozen hours. The oxides in weighed portions were ground, pastilled and heated in air under experimentally established conditions: 400–500 °C for 24 h, 550 °C for 72 h, and 570 °C for 24 h. Preparations whose original mixtures contained more than 70mol% Fe₂O₃ were additionally heated at 600 °C for 24 h, and specimens containing more than 85mol% Fe₂O₃ were heated at 700 °C for 24 h. The preparations were then slowly cooled to ambient temperature, triturated and finally studied by the DTA method for their phase composition. This was the technique by which types of the resultant phases and the ranges of their coexistence in the subsolidus area were found. The types of solid phases remaining at equilibrium with liquid in the high-temperature area of the phase diagram were established from results of the X-ray phase powder diffraction of preparations additionally heated for 2 h at 580–850 °C and then cooled rapidly to ambient temperature. The phase composition of the preparations was established by X-ray phase powder diffraction (diffractometer type HZG 4/A-2, GDR production), from the data of ASTM cards [24] and from refs. 18, 22 and 23.

The DTA studies were performed with the aid of a Paulik–Paulik–Erdey derivatograph in quartz crucibles, in air at 20–1000 °C with heating rate of 10 °C min⁻¹. The weight of the specimens under studying was 1000 mg. The phase diagram was constructed with the help of solidus lines determined on the basis of the DTA initial effect temperatures and with liquidus curves assigned by the apex effect temperatures. The accuracy of the temperature readings, assessed from the repeatability of measurements, was ±5 °C.

RESULTS AND DISCUSSION

The composition of the original mixtures, the preparation conditions and X-ray phase powder diffraction results are given in Table 1. The experimental results compiled in the Table suggest that Fe₂O₃ does not remain at constant equilibrium with V₉Mo₆O₄₀ because it is not found in the phase composition of specimens at equilibrium.

X-ray phase powder diffraction has shown that preparations containing 10–70mol% Fe₂O₃ in their original mixtures are a mixture of three phases, V₉Mo₆O₄₀, FeVMoO₇ and V₂O₅(solid solution). This indicates that Fe₂O₃ in amounts of up to 70mol% reacts with V₉Mo₆O₄₀ to completion yielding FeVMoO₇, and the excessive MoO₃ and V₂O₅ form a solid solution. It means that only in this range of component concentrations does the phase V₉Mo₆O₄₀ coexist with FeVMoO₇ and V₂O₅(solid solution). It also implies that in this range of component concentrations a reaction takes place



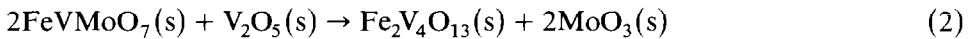
A solid solution of MoO₃ in Fe₂V₄O₁₃ occurs together with FeVMoO₇ and

TABLE 1

The composition of original mixtures and X-ray phase powder diffraction results of specimens at equilibrium

Preparation conditions	Composition of samples in terms of the phase components (mol% Fe ₂ O ₃)	Phases found
400–500 °C for 24 h	10, 20, 25, 35, 40,	V ₉ Mo ₆ O ₄₀ , FeVMoO ₇ ,
550 °C for 72 h	45, 50, 55, 60, 65,	V ₂ O ₅ (solid solution)
570 °C for 24 h	67.5, 70	
	75, 76, 78	FeVMoO ₇ , V ₂ O ₅ (solid solution) Fe ₂ V ₄ O ₁₃ (solid solution)
400–500 °C for 24 h	80.5, 81.0,	FeVMoO ₇ , Fe ₂ V ₄ O ₁₃ (solid solution)
550 °C for 72 h		FeVO ₄
570 °C for 24 h		
600 °C for 24 h	84, 85	FeVMoO ₇ , FeVO ₄ , Fe ₄ V ₂ Mo ₃ O ₂₀
400–500 °C for 24 h	86.67	FeVO ₄ , Fe ₄ V ₂ Mo ₃ O ₂₀
550 °C for 72 h		
570 °C for 24 h	88, 90, 93, 96	FeVO ₄ , Fe ₄ V ₂ Mo ₃ O ₂₀ ,
600 °C for 24 h		α-Fe ₂ O ₃
700 °C for 24 h		

V₂O₅ (solid solution) as a stable phase in preparations which contain more than 70mol% Fe₂O₃ (an excess in respect to eqn. 1) in their initial mixtures [20,21]. At the same time, a decomposition of the solid solution of MoO₃ in V₂O₅ begins to yield free MoO₃ and V₂O₅, which involves the formation of Fe₂V₄O₁₃ according to the equation

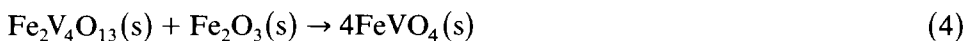


A synthesis of Fe₂V₄O₁₃ from the oxides may also take place



The resultant Fe₂V₄O₁₃ forms a solid solution with MoO₃.

Decomposition of V₂O₅(solid solution) nears completion when the Fe₂O₃ content of the original mixture does not exceed 80mol%. A further increase in the content of Fe₂O₃ in the substrates gives rise to an equilibrium phase, FeVO₄ [18]. It accounts for the reaction taking place at concentrations of Fe₂O₃ in the range 80–81mol%



The synthesis is accompanied by a decomposition of the solid solution of MoO₃ in Fe₂V₄O₁₃, MoO₃ being liberated.

FeVMoO₇, FeVO₄ and the phase Fe₄V₂Mo₃O₂₀ are at equilibrium in

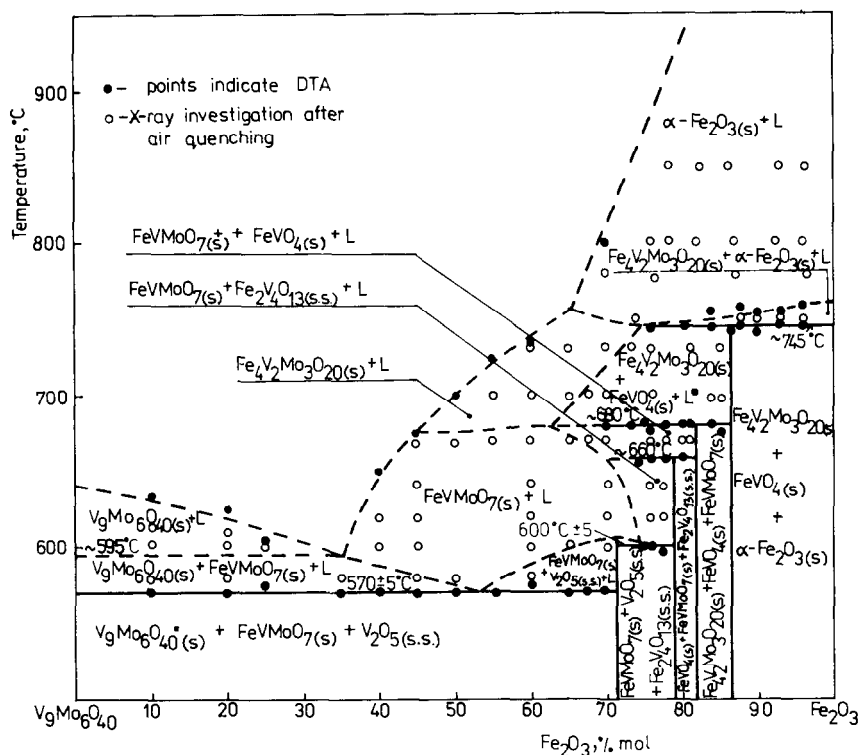
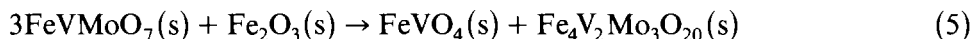


Fig. 1. Phase diagram of the system $V_9Mo_6O_{40}-Fe_2O_3$.

original mixtures with 84–85mol% Fe_2O_3 . $Fe_4V_2Mo_3O_{20}$ involved in the system at this component concentration, i.e. when there is excess of Fe_2O_3 with respect to $FeVMoO_7$ and $FeVO_4$, shows that the hitherto stable $FeVMoO_7$ starts reacting with Fe_2O_3 in agreement with the equation



The phase composition of a preparation containing 86.67mol% Fe_2O_3 and 13.33mol% $V_9Mo_6O_{40}$ confirms that, at the molar ratio of $FeVMoO_7 : Fe_2O_3$ of 1 : 3 in the solid state, reaction 5 runs quantitatively, that is, $FeVMoO_7$ reacts with Fe_2O_3 to completion yielding $FeVO_4$ and $Fe_4V_2Mo_3O_{20}$. At the other component concentration range, Fe_2O_3 remains at constant equilibrium with $FeVO_4$ and $Fe_4V_2Mo_3O_{20}$.

Figure 1 shows a phase diagram of the $V_9Mo_6O_{40}-Fe_2O_3$ system constructed with DTA curves and X-ray phase powder diffraction results of 24 preparations at equilibrium. The coexistence ranges solid–liquid phase, were determined from DTA results of preparations at equilibrium and the phase types were assigned from results of X-ray phase powder diffraction of specimens of the given diagram areas, the samples being additionally heated for 2 h at 580, 600, 620, 640, 670, 700, 730, 750, 780, 800 and 850 °C, and

then cooled rapidly to ambient temperature. The compositions of samples investigated are shown in Fig. 1.

The results presented make it impossible to assign the precise coexistence range of all the areas in which the solid phase would remain in equilibrium with the liquid phase. Thus, the maximum temperature range for the existence of $\text{FeVMoO}_7(\text{s}) + \text{V}_2\text{O}_5(\text{solid solution}) + \text{L}$ area was determined from the results of our other studies, i.e. on the basis of a phase diagram of the $\text{FeVMoO}_7\text{-V}_2\text{O}_5(\text{solid solution})$ system [25]. However, determination of the coexistence range for the areas $\text{FeVMoO}_7(\text{s}) + \text{Fe}_2\text{V}_4\text{O}_{13}(\text{solid solution}) + \text{L}$, $\text{FeVMoO}_7(\text{s}) + \text{FeVO}_4(\text{s}) + \text{L}$, $\text{FeVO}_4(\text{s}) + \text{Fe}_4\text{V}_2\text{Mo}_3\text{O}_{20}(\text{s}) + \text{L}$ and $\text{Fe}_4\text{V}_2\text{Mo}_3\text{O}_{20}(\text{s}) + \text{Fe}_2\text{O}_3(\text{s}) + \text{L}$ was based on the DTA results as well as on results from X-ray phase powder diffraction of preparations additionally heated at temperatures higher than the solidus line temperatures and cooled rapidly to ambient temperature. Therefore, some of the curves which bound the areas on the phase diagram have been drawn with dotted lines.

The investigations made allow us to conclude the following.

(1) In the subsolidus area, the components of the system do not remain at constant equilibrium. $\text{V}_9\text{Mo}_6\text{O}_{40}$ is at constant equilibrium with FeVMoO_7 and $\text{V}_2\text{O}_5(\text{solid solution})$ in the component concentration range up to about 70mol% Fe_2O_3 . The Fe_2O_3 appears to be a phase stable at Fe_2O_3 contents exceeding 86.67mol% in the original mixtures. At the component concentration range 75–85mol% Fe_2O_3 , phases involved in a reaction between $\text{V}_9\text{Mo}_6\text{O}_{40}$ and Fe_2O_3 taking place in the solid state remain at equilibrium.

(2) The $\text{V}_9\text{Mo}_6\text{O}_{40}\text{-Fe}_2\text{O}_3$ system is not a true two-component system in the whole range of component concentrations, not even in the subsolidus area. It indicates the existence of areas in that region where three solid phases are at equilibrium.

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