REACTIVITY OF FeVO₄ TOWARDS Mg₂V₂O₇ AND PHASE RELATIONS IN THE FeVO₄ - Mg₂V₂O₇ SYSTEM UP TO THE SOLIDUS LINE

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Reaction products of $FeVO_4$ with $Mg_2V_2O_7$ were investigated in the whole concentration range of the reacting substances. On the basis of the results obtained a diagram of phase equilibria was worked out for the system $FeVO_4 - Mg_2V_2O_7$ for the solid state. Methods applied in the investigations were XRD and DTA. The system $FeVO_4 - Mg_2V_2O_7$ is a real binary system in the concentration range up to 50.00 mol% $FeVO_4$ in initial mixtures. For higher initial $FeVO_4$ ratio, one obtains an intersection of the ternary system $MgO - V_2O_5 - Fe_2O_3$ crossing three subsidiary subsystems each being a three component solid phase equilibrium system.

INTRODUCTION

The system $FeVO_4 - Mg_2V_2O_7$ constitutes an interesting research object from the point of view of catalysis. Both vanadates, components of the system, catalyse oxidative dehydrogenation processes of a series of organic compounds [1-3]. It is also known that in the solid state $FeVO_4$ and $Mg_2V_2O_7$ react with each other at a molar ratio of 1:1 and a solid product of this reaction is $Mg_2FeV_3O_{11}$ - a compound which has become known only recently and is expected to become a promising catalyst [4,5].

The aim of the presented work was to investigate the reactivity of $FeVO_4$ towards $Mg_2V_2O_7$ over the whole concentration range of reacting substances as well as working out a phase diagram for the subsolidus area of the system $FeVO_4 - Mg_2V_2O_7$.

Physicochemical properties of the compounds of the system FeVO₄ – Mg₂V₂O₇ are known. Iron(III) orthovanadate(V) melts incongruently at 850°C with a separation of solid α -Fe₂O₃ [6]. Under normal pressure FeVO₄ does not exhibit polymorphism, but three highpressure modifications of this compound are known [7,8]. On the other hand, magnesium divanadate(V) exhibits trimorphism under normal pressure [9]. According to our investigations, the temperatures of the phase transformations of α -Mg₂V₂O₇ into β -Mg₂V₂O₇ and of β -Mg₂V₂O₇ into γ -Mg₂V₂O₇ amount to 760 ±5°C and 900 ±5°C, respectively. Mg₂V₂O₇ melts incongruently at 1135°C with a deposition of Mg₃V₂O₈ crystals [10].

EXPERIMENTAL

Reacting substances used in research were $FeVO_4$ and $Mg_2V_2O_7$ obtained as a result of heating the stoichiometric mixtures of V_2O_5 (p.a., from Riedel-de Haën, Germany) with Fe_2O_3 (p.a., from POCh, Poland) or V_2O_5 with $3MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$ (p.a., from POCh, Poland) in the following stages:

- synthesis of FeVO₄: 560°C (20 h) + 590°C (20 h)×2
- synthesis of Mg₂V₂O₇: 560°C (20 h) + 680°C (20 h)

In order to follow the solid-state reactions occurring between $FeVO_4$ and $Mg_2V_2O_7$, 12 mixtures of the reacting substances were prepared. Appropriate portions of vanadates, after homogenization and forming them into pellets, were heated in the atmosphere of air for several stages. On each heating stage all samples were slowly cooled in the furnace to ambient temperature, ground and next their contents were determined by using the XRD method. Some selected samples were investigated also by DTA method.

For verifying investigations 4 additional mixtures of compounds were prepared, comprising the compounds that according to presented research results ought to coexist at equilibium in the solid state. These mixtures after forming them into pellets were heated at

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580°C in two 20-hour stages. On each heating stage the samples were rapidly cooled to ambient temperature and their contents were investigated by XRD.

The measurements by XRD method were carried out using the X-ray diffractometer DRON-3 (Bourevestnik, Sankt Petersburg, Russia). The source of radiation was a cobalt tube with an iron filter (Co K α /Fe, $\lambda = 0.179021$ nm). Identification of phases was conducted on the base of XRD characteristics contained by the PDF cards [11] and the data reported in the works [5,12].

The DTA measurements were performed by means of the derivatograph Paulik-Paulik-Erdey (MOM, Budapest, Hungary). Samples of 500 mg by weight were placed in quartz crucibles. The measurements, conducted in the atmosphere of air at a heating rate of 10°C/min., covered the temperature range 20-1050°C.

RESULTS AND DISCUSSION

Table 1 presents the composition of initial mixtures, their heating conditions and XRD analysis results for the first eight samples obtained after the final heating stage.

The presented results supply an evidence that iron(III) orthovanadate(V) and magnesium divanadate(V) react with each other with a formation of other phases the kind of which depends on the composition of initial mixtures.

Samples containing in their initial mixtures up to ~50.00 mol% FeVO₄ comprise in equilibrium state a mixture of Mg₂FeV₃O₁₁ and Mg₂V₂O₇. This is a proof showing that in this concentration range of the reacting substances FeVO₄ reacts till completion with Mg₂V₂O₇ according to the equation:

$$FeVO_{4(s)} + Mg_2V_2O_{7(s)} = Mg_2FeV_3O_{11(s)}$$
(1)

The reacting substance that remains in excess with respect to the occurring reaction is $Mg_2V_2O_7$. The quantitative course of reaction (1) is corroborated by a sample obtained by heating a mixture of 50.00 mol% FeVO₄ and 50.00 mol% $Mg_2V_2O_7$ (table 1).

Samples containing in their initial mixtures more than 50.00 up to 72.73 mol% FeVO₄, were heated at 600°C in six stages. Diffraction patterns of these samples after the individual heating stages indicated the presence of Mg₂FeV₃O₁₁, FeVO₄ and small amounts of Mg₃Fe₄V₆O₂₄. Figure 1a presents XRD pattern of sample comprising 72.73 mol% FeVO4 (in initial mixture) after heating at 600°C. With an elongation of the heating time a small increase of Mg₃Fe₄V₆O₂₄ content was observed together with a slight decrease in the contents of FeVO₄ and Mg₂FeV₃O₁₁. The obtained results indicated that $Mg_2V_2O_7$ had reacted till completion with FeVO₄, and Mg₂FeV₃O₁₁ formed as a result of the reaction (1) reacts with iron(III) orthovanadate(V) forming $Mg_3Fe_4V_6O_{24}$. On an assumption of a complete use-up of FeVO₄ in its reaction with $Mg_2FeV_3O_{11}$ or with $Mg_2V_2O_7$ the other product of the occurring reaction should be V₂O₅, which can be expressed by the equations:

$$3 Mg_2FeV_3O_{11(s)} + 5 FeVO_{4(s)} = 2 Mg_3Fe_4V_6O_{24(s)} + V_2O_{5(s)}$$
(2)

or:

Because a long-term heating of the samples at 600° C did not cause the complete use-up of FeVO₄ in the reaction, all samples from the considered range of components concentration were melted and next cooled very slowly to ambient temperature. After this stage of samples preparation a distinct change of their contents

Table 1. Composition of initial mixtures, their heating conditions and XRD analysis results of first eight samples obtained after final heating stage.

No.	Composition of initial mixtures (mol%)			Detected phases	
	FeVO ₄	FeVO4 $Mg_2V_2O_7$ Heating condi			
1	10.00	90.00			
2	20.00	80.00	680°C (20 h) + 720°C (20 h) +	$Mg_2FeV_3O_{11}$	
3	30.00	70.00	+ 820°C (20 h) + 920°C (20 h) ×2	$Mg_2V_2O_7$	
4	40.00	60.00			
5	50.00	50.00	680°C (20 h) + 750°C (20 h) +	Mg.FeV.O.	
	50.00		920°C (20 h) ×2		
6	60.00	40.00	600°C (20 h) ×6 +	$Mg_{2}FeV_{3}O_{11}, Mg_{3}Fe_{4}V_{6}O_{24}$	
7	66.67	33.33	800°C (3 h)	V_2O_5	
8	72 73	77 77	600°C (20 h) ×6 +	$Mg_3Fe_4V_6O_{24}$	
0	12.13	21.21	800°C (3 h)	V_2O_5	

occurred. In the samples comprising in their initial mixtures from ~50.00 to ~72.73 mol% of iron(III) orthovanadate(V) a complete use-up of FeVO4 in the reaction was determined. In accordance with the expectations three phases were identified in these samples, $Mg_2FeV_3O_{11}$, $Mg_3Fe_4V_6O_{24}$ and V_2O_5 . Thus as a result of a reaction between the previously formed Mg₂FeV₃O₁₁ and FeVO₄ the yielded products were Mg₃Fe₄V₆O₂₄ and V_2O_5 . The contents of a sample obtained after heating a mixture containing 72.73 mol% FeVO₄ and 27.27 mol% $Mg_2V_2O_7$ in the initial mixture proves that this reaction can be described by the equations (2) or (3). XRD pattern of this sample is presented in figure 1b. Mechanism of this reaction is not yet established. Most probably the intermediate product is Mg₂FeV₃O₁₁ that reacts with an excess of FeVO₄, but it cannot either be excluded that Mg₃Fe₄V₆O₂₄ is formed also directly as a result of a reaction between FeVO₄ and Mg₂V₂O₇.

Samples comprising more than 72.73 mol% FeVO₄ in their initial mixtures were also heated at 600°C for several stages, but under these conditions we did not



Figure 1. Fragments of XRD patterns of selected samples: a) comprising 72.73 mol% FeVO₄ in initial mixture after heating at 600°C; b) comprising 72.73 mol% FeVO₄ in initial mixture after heating at 800°C; c) comprising Mg₃Fe₄V₆O₂₄ and Fe₂V₄O₁₃ (sample 2 - table 2) after heating at 580°C. Mg₃Fe₄V₆O₂₄ - \blacklozenge ; FeVO₄ - \blacklozenge ; Mg₂FeV₃O₁₁ - $)(; V_2O_5 - O;$ Fe₂V₄O₁₃ - \Box .

succeed either in obtaining the equilibrium preparations. It is known from our other investigations that FeVO₄ remains at equilibrium with Mg₃Fe₄V₆O₂₄ [13]. It was expected therefore that the excess of FeVO₄ with respect to Mg₂V₂O₇, being completely used up in accordance with the reaction (3) for the formation of Mg₃Fe₄V₆O₂₄ and V₂O₅, reacts with V₂O₅ formed in the reaction (3) until its using up, with a formation of Fe₂V₄O₁₃:

$$V_2O_{5(s)} + 2FeVO_{4(s)} = Fe_2V_4O_{13(s)}$$
(4)

Thus in this concentration range the phases coexisting at equilibrium should be $Mg_3Fe_4V_6O_{24}$, V_2O_5 and $Fe_2V_4O_{13}$. The formation of $Fe_2V_4O_{13}$ could also be ascribed to the reactions:

$$10FeVO_{4(s)} + 3Mg_2V_2O_{7(s)} = 2Mg_3Fe_4V_6O_{24(s)} + Fe_2V_4O_{13(s)}$$
(5)

$$7FeVO_{4(s)} + 3Mg_2FeV_3O_{11(s)} = 2Mg_3Fe_4V_6O_{24(s)} + Fe_2V_4O_{13(s)}$$
(6)

that ought to occur quantitatively at a molar ratio of $FeVO_4/Mg_2V_2O_7$ equal to 10:3 or of $FeVO_4/Mg_2FeV_3O_{11}$ equal to 7:3. Such molar ratios correspond to the sample containing 76,92 mol% FeVO₄ in the initial mixture. Thus in the samples comprising more than 76.92 mol% FeVO₄ in their initial mixtures, i.e. samples richer in FeVO₄, the presence of this compound should be expected beside the presence of Mg₃Fe₄V₆O₂₄ and Fe₂V₄O₁₃ formed according to the reaction (5) or (6).

In no sample from this concentration range of the reacting substances taken either after heating at 600°C or after subsequent melting and next slow cooling, the compound Fe₂V₄O₁₃ was formed. The reasons of this fact can be ascribed to low detectability of the Fe₂V₄O₁₃ phase in its mixture with Mg₃Fe₄V₆O₂₄, which was corroborated by performed XRD tests of detectability as well as by incongruent melting of this phase at 665°C with a separation of $FeVO_4$ [6]. These experiments proved to be insufficient for describing the phase equilibria established in the investigated system in the concentration range above 72.73 mol% FeVO₄ in the initial mixtures. In order to check which phases coexist at equilibrium in this components concentration range, some additional verifying investigations were performed. Four mixtures of compounds were prepared that according to the presented reasoning should contain the compounds coexisting at equilibrium in this concentration range of the reacting substances. The composition of these mixtures is listed in table 2. They were heated in two 20-hour stages at 580°C (several dozen of °C lower than their melting temperatures). The contents of the prepared mixtures did not change after the heating. Figure 1c presents XRD pattern of mixture of $Mg_3Fe_4V_6O_{24}$ and $Fe_2V_4O_{13}$ (sample 2 - table 2) after heating at 580°C. This proves that the phases contained by the mixtures do not react with each other and the contents of their initial mixtures corresponded to the phases coexisting at equilibrium in the verified concentration range of the investigated system components.

In a subsequent stage of work a phase diagram was constructed for the system $FeVO_4 - Mg_2V_2O_7$ (figure 2) in the subsolidus area, based on DTA and XRD investigations results of equilibrium samples (up to 72.73 mol% $FeVO_4$ in the initial mixtures) as well as of additional verifying samples (above 72.73 mol% $FeVO_4$ in the initial mixtures). The solidus line temperatures were determined on the base of the onset temperatures of the first endothermic effects being not due to polymorphic transformations, recorded in DTA curves of corresponding samples. The polymorphic transformation lines for $Mg_2V_2O_7$ were also marked in the diagram, corresponding to thermal effects recorded in DTA curves of appropriate samples.

Figure 3 presents fragments of DTA curves of selected samples at equilibrium. Curve a) and b) are connected with the same sample comprising at equilibrium Mg₂V₂O₇ and Mg₂FeV₃O₁₁. On curve a) (sample after heating at 720°C) were recorded three thermal effects. The first and the second are due to the polymorphic transitions α -Mg₂V₂O₇ $\rightarrow \beta$ -Mg₂V₂O₇ and β -Mg₂V₂O₇ \rightarrow γ -Mg₂V₂O₇, respectively. The third effect is related with melting of mixture $Mg_2V_2O_7$ and Mg₂FeV₃O₁₁. On curve b) (the same sample after heating at 920°C) effect with onset temperature 760°C was not recorded. First effects recorded on curves c), d) and e) are due to melting of mixtures of appropriate phases coexisting at equilibrium (tables 1 and 2). Further effects are related with phase relations establishing above solidus line.



Figure 2. Phase diagram of $FeVO_4 - Mg_2V_2O_7$ system up to solidus line.

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No.	Composition of verifying mixtures (mol%)	Composition of verifying mixtures on their recounting for system components (mol%)		
		FeVO ₄	$Mg_2V_2O_7$	
1	$Mg_{3}Fe_{4}V_{6}O_{24}, V_{2}O_{5}, Fe_{2}V_{4}O_{13}$	75.00	25.00	
2	$Mg_{3}Fe_{4}V_{6}O_{24}, Fe_{2}V_{4}O_{13}$	76.92	23.08	
3 —	$Mg_{2}Fe_{2}V_{2}O_{2}$, $Fe_{2}V_{2}O_{2}$, $FeVO_{2}$	80.00	20.00	
4	111 <u>5</u> 31 04 v 60 24, 1 02 v 40 13, 1 0 v 04	90.91	9.09	





Figure 3. Fragments of DTA curves of selected samples at equilibrium comprising in initial mixture: a) 30.00 mol% FeVO₄ after heating at 720° C; b) 30.00 mol% FeVO₄ after heating at 920° C; c) 60.00 mol% FeVO₄; d) 75.00 mol% FeVO₄; e) 80.00 mol% FeVO₄.

The presented diagram (figure 2) implies that in the system $FeVO_4 - Mg_2V_2O_7$ up to 50.00 mol% $FeVO_4$ there coexist at equilibrium two solid phases, so in this concentration range the system is in the subsolidus area a real binary system. In the remaining components concentration range the investigated system is an intersec-

tion of the ternary system $MgO - V_2O_5 - Fe_2O_3$ crossing three subsidiary subsystems in which there coexist three solid phases in each case:

 $\begin{array}{l} Mg_2FeV_3O_{11}-Mg_3Fe_4V_6O_{24}-V_2O_5\\ Mg_3Fe_4V_6O_{24}-V_2O_5-Fe_2V_4O_{13}\\ Mg_3Fe_4V_6O_{24}-Fe_2V_4O_{13}-FeVO_4 \end{array}$

CONCLUSIONS

1. FeVO₄ and $Mg_2V_2O_7$ are not inert towards each other. The kind of their reaction products depends on the composition of the initial mixture.

2. The system $FeVO_4 - Mg_2V_2O_7$ is in the solid state a real binary system in the components concentration range up to 50.00 mol% $FeVO_4$. Above 50.00 mol% $FeVO_4$ the investigated system is an intersection of the ternary system $MgO - V_2O_5 - Fe_2O_3$.

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REAKTIVITA FeVO₄ A Mg₂V₂O₇ A FÁZOVÉ POMĚRY V SYSTÉMU FeVO₄ – Mg₂V₂O₇ V OBLASTI SUBSOLIDUS

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Studovali jsme produkty reakce FeVO₄ a $Mg_2V_2O_7$ v celém koncentračním rozsahu. Na základě získaných výsledků jsme zkonstruovali fázový diagram systému FeVO₄ – $Mg_2V_2O_7$ v oblasti tuhých fází. Ke studiu byly použity metody rtg difrakce a termální analýzy DTA. Systém FeVO₄ – $Mg_2V_2O_7$ je pravý binární systém v koncentračním rozsahu do 50 mol% FeVO₄ ve výchozí směsi. Při vyšší počáteční koncentraci FeVO₄ jsme dostali řez ternárním systémem $MgO - V_2O_5 - Fe_2O_3$ protínající tři vedlejší podsystémy, z nichž každý je rovnovážným systémem tří tuhých fází.