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PHASE RELATIONS IN THE SYSTEM $SbVO_5$–$Sb_3V_2Mo_3O_{21}$ IN SOLID-STATE AND IN AIR

The solid solutions of MoO_3 in $SbVO_5$

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Abstract

It has been established by XRD, DTA and TG methods that phases of solid solution type of MoO_3 in $SbVO_5$ are formed in the system V_2O_5–MoO_3–α-Sb_2O_4. The Mo^{6+} ions are incorporated into the crystal lattice of $SbVO_5$ instead of both Sb^{5+} and V^{5+}, while the charge compensation occurs by a formation of cation defects (□) at Sb^{5+} and V^{5+}.

The phases $Sb_{1-6x}\square_xV_{1-6x}\square_xMo_{10x}O_5$ are stable in the solid-state up to 690±10°C and the limit of solubility of MoO_3 in $SbVO_5$ does not exceed 20.00 mol%.

Keywords: DTA, solid solution models, V_2O_5–MoO_3–α-Sb_2O_4 system, XRD

Introduction

Oxide catalysts with a composition that can be described by the system V–Mo–M–O, where *M*=Sb, Al, Ga, Bi and Te, show high activity and selectivity in processes of oxidation of light hydrocarbons [1]. In recent years intensive investigations are performed aimed at – first of all – obtaining new, active, highly selective catalysts for the reaction of obtaining acrylonitrile (ACN) by direct amoxidation of propane. Among various investigated catalysts of this reaction the most promising ones for technological applications appear to be those comprising V_2O_5, MoO_3 and α-Sb_2O_4 as well as compounds formed in respective systems built from these oxides [2–5].

Our earlier studies have shown that the components of the system V_2O_5–α-Sb_2O_4 react with each other in the solid-state in air with a formation of a previously unknown compound $SbVO_5$ that decomposes at ~720°C in the solid-state to $SbVO_{4.5}$ and oxygen [6]. It is also known that in the ternary system V_2O_5–MoO_3–α-Sb_2O_4 there exists a compound $Sb_3V_2Mo_3O_{21}$ [7]. This compound melts incongruently at 740°C and a solid product of its melting is $SbVO_{4.5}$ [7, 8]. The aim of this work was investigating the phase relations over the whole component concentration range in the system $SbVO_5$–$Sb_3V_2Mo_3O_{21}$ in air atmosphere as well as establishing whether MoO_3 forms solid solutions in $SbVO_5$.

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Experimental

The reacting substances used in research were Sb_2O_3 pure (Merck, Germany), V_2O_5 and MoO_3 pure (POCh, Gliwice, Poland), α-Sb_2O_4 – obtained by heating commercial Sb_2O_3 in air [6], $SbVO_5$ and $Sb_3V_2Mo_3O_{21}$ – both obtained by methods described in the works [6, 7]. For investigations of the phase relations in the system $SbVO_5$–$Sb_3V_2Mo_3O_{21}$, 10 samples were prepared from the oxides V_2O_5, MoO_3 and α-Sb_2O_4, and 4 samples from the compounds $SbVO_5$ and $Sb_3V_2Mo_3O_{21}$. The composition of the samples is presented in Table 1. The reacting substances mixed at appropriate proportions were homogenised by grinding, shaped into pellets and heated cyclically under conditions enabling for sure the equilibrium state to be established, i. e.: I cycle: 400°C (1 h)$\rightarrow$500°C (24 h)$\rightarrow$550°C (24 h); II cycle: 600°C (48 h); III cycle: 640°C (24 h); IV cycle: 650°C (24 h).

After each heating cycle the mass and colour changes of the samples were controlled, they were subjected to DTA analysis (a derivatograph of Paulik–Paulik–Erdey in air atmosphere in the temperature range 20–1000°C at a heating rate of 10°C min^{-1} and with the mass of samples equal to 500 mg) and their composition was established on the base of the XRD analysis results (Dron-3 diffractometer, CoK_α, radiation, iron filter) and the data contained in PDF cards [11] and in the works [6–8]. Attaining the equilibrium state was determined by following the procedure described among others in the works [9, 10, 12, 13].

Results and discussion

The XRD analysis results of both samples prepared from oxides and those prepared from ready phases, after their last heating samples, i. e. in equilibrium state, are presented in Table 1.

Diffraction patterns of preparations containing in their initial oxide mixtures 10.00 or 15.00 mol% MoO_3 after the final heating cycle revealed the presence of a set of diffraction lines with positions consistent with the $SbVO_5$ characteristics [6]; the only difference was a change in their relative intensities. In these samples the presence of traces of α-Sb_2O_4 could not be excluded. Samples representing the remaining range of component concentration of the investigated system, i. e. comprising above 15.00 mol% MoO_3, contained $SbVO_5$ and $Sb_3V_2Mo_3O_{21}$, and some of them – also traces of α-Sb_2O_4. Moreover, in the samples comprising 50.00, 52.50 and 53.46 mol% MoO_3 the $SbVO_5$ phase was identified in small amounts. The synthesis of all preparations from oxides was accompanied by mass increases amounting to 0.3–1.2 mass%. The recorded DTA curves of all samples at equilibrium revealed two endothermic effects up to 1000°C, the first beginning at 690±10°C and the other ranging with its onset from 740 to 810°C. The first effect was associated with a mass loss of the samples (TG curve) that ranged with increasing the MoO_3 content in the initial mixtures from 3.0 to 2.5 mass%.

The obtained results of this part of research indicated that in the investigated system a solid solution of MoO_3 in $SbVO_5$ was formed and it finally remained at equilibrium with α-Sb_2O_4 or with α-Sb_2O_4 and $Sb_3V_2Mo_3O_{21}$. The first endothermic effect beginning at ~690°C is due to a decomposition of the solid solution of MoO_3 in $SbVO_5$, which is ev-

Table 1 Composition of initial mixtures of samples from system $SbVO_5$–$Sb_3V_2Mo_3O_{21}$ and results of XRD analysis for preparations in equilibrium state

No.	Composition of oxide mixtures/mol%			Contents of $Sb_3V_2Mo_3O_{21}$ calculated including components of system/mol%	Phase composition in equilibrium state
	MoO_3	V_2O_5	α-Sb_2O_4		
1	10.00	44.17	45.83	3.92	$SbVO_{5(s.s)}$+α-Sb_2O_4**
2	15.00	41.25	43.75	6.43	$SbVO_{5(s.s)}$+α-Sb_2O_4**
3	20.00	38.33	41.67	9.52	$SbVO_{5(s.s)}$+$Sb_3V_2Mo_3O_{21}$**
4	25.00	35.42	39.58	13.33	$SbVO_{5(s.s)}$+$Sb_3V_2Mo_3O_{21}$+α-Sb_2O_4**
5	30.00	32.50	37.50	18.18	$SbVO_{5(s.s)}$+$Sb_3V_2Mo_3O_{21}$+α-Sb_2O_4**
6	35.00	29.58	35.42	24.56	$SbVO_{5(s.s)}$+$Sb_3V_2Mo_3O_{21}$+α-Sb_2O_4**
7	40.00	26.67	33.00	33.33	$Sb_3V_2Mo_3O_{21}$+$SbVO_{5(s.s)}$
8	45.00	23.75	31.25	46.15*	$Sb_3V_2Mo_3O_{21}$+α-Sb_2O_4+$SbVO_{5(s.s)}$
9	50.00	20.83	29.17	66.67*	$Sb_3V_2Mo_3O_{21}$+α-Sb_2O_4+$SbVO_{5(s.s)}$**
10	52.50	19.38	28.12	82.35*	$Sb_3V_2Mo_3O_{21}$+α-Sb_2O_4+$SbVO_{5(s.s)}$**
11	53.46	–	–	90.00*	$Sb_3V_2Mo_3O_{21}$+α-Sb_2O_4+$SbVO_{5(s.s)}$**

* samples prepared additionally from the compounds $SbVO_5$ and $Sb_3V_2Mo_3O_{21}$
** traces

idenced by the composition of preparations heated at 720°C and the mass losses of samples recorded after this heating. The samples after heating at 720°C (24 h) did not contain $SbVO_{5(s.s.)}$ already, but were mixtures of $SbVO_{4.5}$ and $Sb_3V_2Mo_3O_{21}$, and samples above 20.00 mol% MoO_3 contained additionally β-Sb_2O_4.

Further investigations were aimed at determining the model of the formed solid solution of MoO_3 in $SbVO_5$. Taking into account the fact that ionic radii of Sb^{5+} (61 pm) and V^{5+} (54 pm) are close to each other, the possibility of replacing them in the crystal lattice of $SbVO_5$ by Mo^{6+} ions (59 pm) is probable to the same extent. Because of this the investigations dealt with the majority of theoretically possible models describing the formation of MoO_3 solution in $SbVO_5$. Thus, if the Mo^{6+} ions are incorporated into the crystal lattice of $SbVO_5$ instead of V^{5+} ions, the compensation of excessive positive charge is possible through:

- formation of cationic defects (□) in the V^{5+} sublattice; a solid solution corresponding to such model is described by the formula $SbV_{1-6x}\square_xMo_{5x}O_5$ (model I);
- reduction of V^{5+} ions to V^{4+}; then the solid solution formula can be written as $Sb^{5+}V^{5+}_{1-2x}V^{4+}_{x}Mo_xO_5$ (model II);
- reduction of V^{5+} to V^{3+}; the solution formula is as follows: $Sb^{5+}V^{5+}_{1-3x}V^{3+}Mo_{2x}O_5$ (model III);
- reduction of Sb^{5+} ions to Sb^{3+}; the solution formula has a form of $Sb^{5+}_{1-x}Sb^{3+}_{x}V^{5+}_{1-2x}Mo_{2x}O_5$ (model IV);
- formation of cationic defects in the Sb^{5+} sublattice; the solution formula gets a form of $Sb_{1-x}\square_xV_{1-5x}Mo_{5x}O_5$ (model V).

In the case of the models II, III and IV the composition of the samples in terms of oxides V_2O_5, MoO_3, α-Sb_2O_4 is identical and can be inferred from a common expression $SbV_{1-x}Mo_xO_{5+x/2}$.

Considering that the Mo^{6+} ions can be incorporated into the crystal lattice of $SbVO_5$ to the same extent instead of both V^{5+} and Sb^{5+}, one of possible models of the solution including a charge compensation through cationic defects at V^{5+} is described by the formula $Sb_{1-5x}V_{1-5x}\square_{2x}Mo_{10x}O_5$ (model VI).

Also the case has been taken into account, where the Mo^{6+} ions replace Sb^{5+} in the lattice of $SbVO_5$ with a simultaneous charge compensation through a formation of defects in the Sb^{5+} sites; such solution has a formula of $Sb_{1-6x}\square_xVMo_{5x}O_5$ (model VII).

Investigations aimed to determine whether in reality one of theoretically presented possible models are followed in the case of MoO_3 solution in $SbVO_5$ consisted of a synthesis of preparations from the oxides V_2O_5, MoO_3 and α-Sb_2O_4 with their composition corresponding to each presented model and containing 10.00 or 15.00 mol% MoO_3 in the oxides mixture. The oxide mixtures were used to form pellets that were heated cyclically under conditions identical with those for samples from the system $SbVO_5$–$Sb_3V_2Mo_3O_{21}$. The composition of the prepared samples and the XRD results after the final heating cycle are presented in Table 2.

The XRD analysis results have shown that all preparations with their composition consistent with the models I–VI contained after the final heating cycle only α-Sb_2O_4 in trace amounts beside the solid solution of MoO_3 in $SbVO_5$, whereas the preparations with their composition described by the model VII contained, beside $SbVO_{5(s.s.)}$, the

Table 2 Composition of initial mixtures of samples representing the theoretical models of MoO_3 solid solution in $SbVO_5$ and XRD analysis results for preparations after final heating cycle

No.	Composition of oxide mixtures/mol%			Model of solid solution	Phase composition
	MoO_3	V_2O_5	α-Sb_2O_4		
1	10.00	42.00	48.00	$SbV_{1-6x}\square_xMo_{5x}O_5$ (model I)	$SbVO_{5(s.s.)}$+ traces of α-Sb_2O_4
2	15.00	38.00	47.00		
3	10.00	42.50	47.50	$SbV_{1-x}Mo_xO_{5+x/2}$ (model II, III, IV)	
4	15.00	38.75	46.25		
5	10.00	43.00	47.00	$Sb_{1-x}\square_xV_{1-5x}Mo_{5x}O_5$ (model V)	
6	15.00	39.50	45.50		
7	10.00	44.50	45.50	$Sb_{1-5x}V_{1-5x}\square_{2x}Mo_{10x}O_5$ (model VI)	
8	15.00	41.75	43.25		
9	10.00	48.00	42.00	$Sb_{1-6x}\square_xVMo_{5x}O_5$ (model VII)	$SbVO_{5(s.s.)}$+$V_2O_{5(s.s.)}$
10	15.00	47.00	38.00		

solid solution of MoO_3 in V_2O_5. The obtained result suggested that the actual model of solid solution being formed could be realised in the system $SbVO_5$–MoO_3. In order to corroborate such suggestion, samples were prepared both from oxides and from $SbVO_5$ with MoO_3 containing, in terms of the oxides, 10.00, 15.00 or 20.00 mol% MoO_3. These samples were heated under conditions identical with those applied in the case of samples representing the system $SbVO_5$–$Sb_3V_2Mo_3O_{21}$. After the final heating cycle the samples comprising in their initial mixtures 10.00 or 15.00 mol% MoO_3 were monophase and contained only the solid solution of MoO_3 in $SbVO_5$, whereas the sample comprising in its initial mixtures 20.00 mol% MoO_3 beside $SbVO_{5(s.s.)}$ contained trace amounts of $Sb_3V_2Mo_3O_{21.}$

On the DTA curves of the samples containing only the solid solution of MoO_3 in $SbVO_5$, two endothermic effects were registered, the first beginning at ~690°C, the other at ~810°C. The first one is, according to the results of previous research, associated with a decomposition of the solid solution of MoO_3 in $SbVO_5$, while the other is due to melting one of products of the decomposition, i. e. $SbVO_{4.5}$. On this stage of investigations it cannot be excluded that in air atmosphere the decomposition product is a non-stoichiometric compound of $Sb_{0.92}V_{0.92}O_4$ possessing a rutile-type structure and an XRD characteristics almost identical with $SbVO_4$ [14, 15].

Selected theoretical models of the solid solution of MoO_3 in $SbVO_5$ and the system $SbVO_5$–$Sb_3V_2Mo_3O_{21}$ are marked on the component concentration triangle of the system V_2O_5–MoO_3–α-Sb_2O_4 (Fig. 1). Dividing the system V_2O_5–MoO_3–α-Sb_2O_4 into subsidiary subsystems was carried out on the base of the previous results and those presented in this work [7, 16].

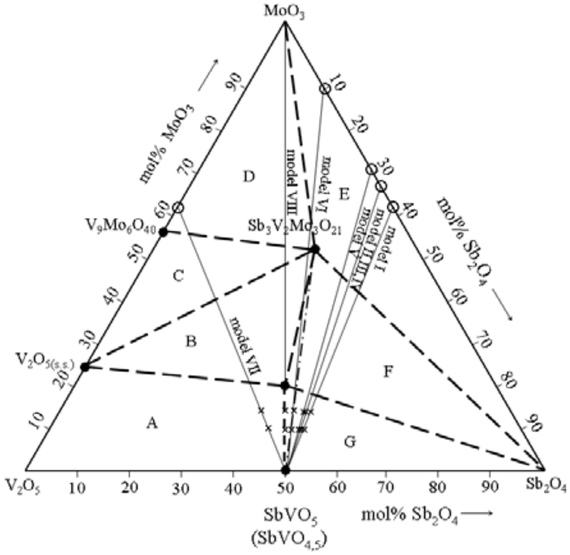

Fig. 1 The component concentration triangle of the V_2O_5–MoO_3–Sb_2O_4 system.
—— – position of theoretical models of the MoO_3 solid solution in $SbVO_5$;
–·–·– – $SbVO_5$–$Sb_3V_2Mo_3O_{21}$ intersection;
----- – division of the system studied into subsidiary system:
A– $V_2O_{5(s.s.)}$–$SbVO_{5(s.s.)}$; B – $V_2O_{5(s.s.)}$–$SbVO_{5(s.s.)}$–$Sb_3V_2Mo_3O_{21}$;
C – $V_2O_{5(s.s.)}$–$Sb_3V_2Mo_3O_{21}$–$V_9Mo_6O_{40}$; D – $V_9Mo_6O_{40}$–MoO_3–$Sb_3V_2Mo_3O_{21}$;
E – Sb_2O_4–$Sb_3V_2Mo_3O_{21}$–MoO_3; F – Sb_2O_4–$SbVO_{5(s.s.)}$–$Sb_3V_2Mo_3O_{21}$;
G – Sb_2O_4–$SbVO_{5(s.s.)}$

Conclusions

The obtained results of research allow a statement that in the ternary oxide system V_2O_5–MoO_3–α-Sb_2O_4 solid solution phases are formed, where MoO_3 is incorporated into the crystal lattice of $SbVO_5$. The limit of solubility of MoO_3 in $SbVO_5$ does not exceed 20.00 mol%. The DTA investigations indicate that phases of this type are stable up to 690±10°C.

On the base of the localisation of $SbVO_5$–MoO_3 intersection, in which the formation of solid solution has been established, it can be inferred that this is a substitutional solid solution, where the Mo^{6+} ions are incorporated into the crystal lattice of $SbVO_5$ instead of both Sb^{5+} and V^{5+}, and a compensation of excessive positive charge occurs through a formation cationic defects at Sb^{5+} and V^{5+} ($Sb_{1-6x}\square_xV_{1-6x}\square_xMo_{10x}O_5$ – model VIII). The presence of α-Sb_2O_4 only in trace amounts, beside $SbVO_{5(s.s.)}$, in the samples corresponding to the remaining models of solid solutions does not exclude the existence of homogeneity area of such-type phases. Investigations aimed at explaining the uncertainties and establishing the range of existence of the formed solid solution will be continued.

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