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PHASE RELATIONS IN THE V_2O_5–MoO_3–α-Sb_2O_4 SYSTEM IN THE SOLID STATE IN AIR ATMOSPHERE

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Abstract

The phase equilibria established in the V_2O_5–MoO_3–α-Sb_2O_4 system in the solid state in an air atmosphere were examined by using XRD and DTA methods. The obtained results allowed us to find that in this system a novel compound is formed involving three oxides. Its formula can be written as $Sb_3V_2Mo_3O_{21}$. The synthesis of this compound requires picking up the atmospheric oxygen. X-ray characteristics of this compound were determined and it was found that it melted incongruently at 740°C. The results obtained until now allow us to divide the investigated V_2O_5–MoO_3–α-Sb_2O_4 system into five partial subsystems.

Keywords: DTA, phase equilibrium, $Sb_3V_2Mo_3O_{21}$ compound, XRD

Introduction

The literature review showed that the corresponding two-component systems comprising the vanadium, molybdenum and antimony oxides have been a subject of studies for many years because of interesting properties – among others catalytic – both of the oxides and their mixtures as well as of the phases formed in the relevant systems [1–8].

Catalysts of this type show a good selectivity and activity in the process of obtaining maleic anhydride and formaldehyde [1, 3], in the reactions of ammoxidation of propane to acrylonitrile [2, 4, 5] and oxidation of isobutene to methacroleine [7, 8]. The kind of phases formed in the system of Sb–V–O, according to extensive literature data, depends not only on the kind of oxides used for the synthesis, but first of all, on the atmosphere the synthesis is performed in [9–13]. In recent years Lauda-Canovas *et al.* showed that heating an equimolar mixture of Sb_2O_3 and V_2O_5 at 800°C in the atmosphere of O_2/N_2 with varying the oxygen-nitrogen ratio yields a series of non-stoichiometric phases of rutile type structure, i.e. $Sb_{0.9}V_{0.9+x}\square_{0.2-x}O_4$ $0<x<0.2$ [13]. By heating the reactants in pure oxygen a compound of $Sb_{0.9}V_{0.9}\square_{0.2}O_4$ was obtained, whereas in pure nitrogen – $Sb_{0.9}V_{1.1}O_4$ [13]. Another series of phases of the $Sb_{0.9-y}V_{1.1+y}O_4$ formula, where $0<y<0.7$, was obtained by these authors in pure nitrogen from the oxide mixtures V_2O_5/Sb_2O_3 with varying their molar ratio from 1:1 to

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10:1. According to these authors heating an equimolar mixture of V_2O_5 and Sb_2O_3 at 800°C in an air atmosphere leads to obtaining a compound of $Sb_{1-x}V_{1-x}O_4$ formula, where $0<x<0.1$, which is in good accordance with many previous works [10–12].

Only few articles supply information on the compounds formed in the atmosphere of air in the α-Sb_2O_4–V_2O_5 [9, 11, 14]. Renaud [9] ascribed a formula of $Sb_2V_2O_9$ to the only compound in this system, whereas other authors consider this compound to be the same as is formed in air in the Sb_2O_3–V_2O_5 system, namely $Sb_{0.92}V_{0.92}O_4$ [13].

Our investigations on the phase equilibria established in this system in the atmosphere of air showed that heating an equimolar mixture of α-Sb_2O_4 and V_2O_5 at temperatures not higher than 650°C leads to obtaining another compound that was preliminarily attributed to a formula of $SbVO_5$ [14]. This compound differs from the already known compounds by the XRD and DTA characteristics as well as by the IR spectrum. $SbVO_5$ is stable up to 720°C and then it decomposes evolving oxygen and yielding $Sb_2V_2O_9$ or $Sb_{0.92}V_{0.92}O_4$ [14].

The components of the other system under interest, i.e. V_2O_5–MoO_3, form two phases in the atmosphere of air. One of the phases is a substitution solid solution of MoO_3 in V_2O_5 with a general formula $(Mo_xV_{1-x})_2O_5$, where $0<x<0.3$ [15, 16]. The other phase is a compound which, according to Strupler [15] and Magneli and Blomberg [16] has a formula of V_2MoO_8, whereas the opinion of Bielański *at al.* it is a phase to be described by a formula of $V_9Mo_6O_{40}$ [17]. The literature information imply also that α-Sb_2O_4 and MoO_3 do not react with each other in the solid state in an air atmosphere to yield any chemical compounds [18, 19]. The presence of MoO_3 decreases only the α-Sb_2O_4 to β-Sb_2O_4 polymorph transition temperature from 935 to 850°C, leading to a low-concentrated solid solution of MoO_3 in β-Sb_2O_4 [18]. The compounds known in the Sb–Mo–O system, such as Sb_2MoO_6, $Sb_2(MoO_4)_3$, $Sb_2Mo_{10}O_{31}$, $Sb_4Mo_{10}O_{31}$, $Sb_4Mo_{20}O_{62}$, can be obtained only in an oxygen-free atmosphere by using Sb_2O_3 and MoO_3 or these oxides and Sb_2MoO_6 or these oxides and metallic Mo as reactants, respectively [20, 21]. The above mentioned compounds are unstable in the atmosphere of air and they decompose in the temperature range 350–550°C into Sb_2O_4 and MoO_3 [20, 21, 8].

The three-component oxide system of V_2O_5–MoO_3–α-Sb_2O_4, an object of research presented in this work, was investigated only preliminarily [22]. The results obtained so far suggest that a novel compound is formed by involving the three oxides – components of the system. The experimental results have not permitted to suggest any formula of the compound. Within this work a research was performed concerning the phase equilibria that established in the V_2O_5–MoO_3–α-Sb_2O_4 system in the solid state in the atmosphere of air. This research aimed at definite solving a problem whether and what compound was formed in the investigated system involving all three oxides. We intended to determine the composition of the formed compound, to describe the conditions of its preparation and to take its basic XRD and DTA characteristics.

Table 1 The contents of initial mixtures of oxides and X-ray analysis results for samples after the final heating cycle

No.	Contents of initial mixtures/mol%			Molar proportion of oxides	The phases found
	MoO_3	Sb_2O_4	V_2O_5		
1	10.00	45.00	45.00	2:9:9	$SbVO_5$, $V_2O_{5(s.s)}$, $Sb_3V_2Mo_3O_{21}$
2	20.00	40.00	40.00	1:2:2	$SbVO_5$, $V_2O_{5(s.s)}$, $Sb_3V_2Mo_3O_{21}$
3	30.00	35.00	35.00	6:7:7	$SbVO_5$, $V_2O_{5(s.s)}$, $Sb_3V_2Mo_3O_{21}$
4	40.00	30.00	30.00	4:3:3	$Sb_3V_2Mo_3O_{21}$, $SbVO_5$, $V_2O_{5(s.s)}$
5	41.18	29.41	29.41	7:5:5	$Sb_3V_2Mo_3O_{21}$, $SbVO_5$, $V_2O_{5(s.s)}$
6	42.86	28.57	28.57	3:2:2	$Sb_3V_2Mo_3O_{21}$, $SbVO_5$, $V_2O_{5(s.s)}$
7	44.44	27.78	27.78	8:5:5	$Sb_3V_2Mo_3O_{21}$, $SbVO_5$, $V_2O_{5(s.s)}$
8	45.46	27.27	27.27	5:3:3	$Sb_3V_2Mo_3O_{21}$, $SbVO_5$, $V_2O_{5(s.s)}$
9	47.38	26.31	26.31	9:5:5	$Sb_3V_2Mo_3O_{21}$, $SbVO_5$, $V_2O_{5(s.s)}$-traces
10	50.00	25.00	25.00	2:1:1	$Sb_3V_2Mo_3O_{21}$, $SbVO_5$-traces, $V_2O_{5(s.s)}$-traces
11	53.86	23.07	23.07	7:3:3	$Sb_3V_2Mo_3O_{21}$, $V_9Mo_6O_{40}$, $V_2O_{5(s.s)}$-traces
12	55.56	22.22	22.22	5:2:2	$Sb_3V_2Mo_3O_{21}$, $V_9Mo_6O_{40}$, MoO_3 -traces
13	57.14	21.43	21.43	8:3:3	$Sb_3V_2Mo_3O_{21}$, $V_9Mo_6O_{40}$, MoO_3
14	60.00	20.00	20.00	3:1:1	$Sb_3V_2Mo_3O_{21}$, $V_9Mo_6O_{40}$, MoO_3
15	63.64	18.18	18.18	7:2:2	$Sb_3V_2Mo_3O_{21}$, $V_9Mo_6O_{40}$, MoO_3
16	66.68	16.66	16.66	4:1:1	$Sb_3V_2Mo_3O_{21}$, $V_9Mo_6O_{40}$, MoO_3
17	70.00	15.00	15.00	14:3:3	$Sb_3V_2Mo_3O_{21}$, $V_9Mo_6O_{40}$, MoO_3
18	80.00	10.00	10.00	8:1:1	MoO_3, $Sb_3V_2Mo_3O_{21}$, $V_9Mo_6O_{40}$
19	90.00	5.00	5.00	18:1:1	MoO_3, $Sb_3V_2Mo_3O_{21}$, $V_9Mo_6O_{40}$
20	95.00	2.50	2.50	38:1:1	MoO_3, $Sb_3V_2Mo_3O_{21}$, $V_9Mo_6O_{40}$
21	53.66	24.39	21.95	22:10:9	$Sb_3V_2Mo_3O_{21}$, $V_9Mo_6O_{40}$, $V_2O_{5(s.s)}$-traces
22	53.33	26.67	20.00	8:4:3	$Sb_3V_2Mo_3O_{21}$, $V_2O_{5(s.s)}$-traces
23	54.55	27.27	18.18	6:3:2	$Sb_3V_2Mo_3O_{21}$
24	52.94	29.41	17.65	9:5:3	$Sb_3V_2Mo_3O_{21}$, Sb_2O_4-traces
25	56.25	25.00	18.75	9:4:3	$Sb_3V_2Mo_3O_{21}$, $V_9Mo_6O_{40}$, MoO_3-traces
26	25.00	50.00	25.00	1:2:1	$Sb_3V_2Mo_3O_{21}$, Sb_2O_4, $Sb_2V_2O_9$
27	27.00	27.00	46.00	1:1:1.7	$Sb_3V_2Mo_3O_{21}$, $SbVO_5$, $V_2O_{5(s.s)}$
28	50.00	10.00	40.00	5:1:4	$Sb_3V_2Mo_3O_{21}$, $V_9Mo_6O_{40}$, $V_2O_{5(s.s)}$
29	70.00	5.00	25.00	14:1:5	$V_9Mo_6O_{40}$, $Sb_3V_2Mo_3O_{21}$, MoO_3
30	75.00	20.00	5.00	15:4:1	MoO_3, $Sb_3V_2Mo_3O_{21}$, Sb_2O_4
31	60.00	30.00	10.00	6:3:1	$Sb_3V_2Mo_3O_{21}$, MoO_3, Sb_2O_4
32	50.00	33.33	16.67	3:2:1	$Sb_3V_2Mo_3O_{21}$, Sb_2O_4

Experimental

For the experiments there were used the following materials:

– V_2O_5, MoO_3 – commercial products of reagent grade (POCh Gliwice, Poland),
– Sb_2O_3 a commercial pure product (Merck, Darmstadt, Germany),
– α-Sb_2O_4, a reactant prepared by heating Sb_2O_3 in air [14].

32 mixtures from the oxides were prepared: V_2O_5, MoO_3 and α-Sb_2O_4, their contents covering the whole component concentration range of the system (Table 1). Homogenised mixtures of the oxides were shaped into pastilles and cyclicly heated in air under conditions enabling a preparation of thermally-treated samples being in an equilibrium state:

I cycle – 400°C (1 h) → 500°C (8 h) → 550°C (24 h);
II cycle – 575°C (24 h); III cycle – 600°C (24 h); IV cycle – 600°C (24 h).

Some of the samples needed additional heating at 625 or 650°C for 24 h so that they could achieve a state of equilibrium.

After each heating cycle, the samples were carefully cooled to ambient temperature and weighed, in order to have the mass change determined. As soon as the phase composition of the thermally-induced and mechanically homogenised samples was established, the samples were re-shaped into pastilles and heated further. The procedure was repeated until identical results were achieved on two consecutive heating stages. Afterwards the final samples, i.e. those having their phase equilibria established, were examined by using the DTA method.

The phase composition of the samples was determined on the base of diffraction patterns taken from an X-ray diffractometer DRON-3 equipped with a cobalt anode (CoK_α radiation) and a Fe filter (Bourevestnik, Sankt Petersburg, Russia). Identification of individual phases was performed by comparing the patterns with X-ray characteristics of JCPDS files and following the data published [9, 10, 14].

Measurements carried out by means of the DTA method were conducted with the aid of a derivatograph (MOM, Hungary). The measurements were made in air at 20–1000°C. Samples weighing 500 mg each were calcined in quartz crucibles, at a heating rate of 10 deg min^{-1}.

Results and discussion

The research on the phase equilibria established in the three-component system of V_2O_5–MoO_3–α-Sb_2O_4 in the solid state in an air atmosphere was started with a preparation of 20 samples, their composition representing one of the sections of the investigated system, i.e. representing the $Sb_2V_2O_9$–MoO_3 system (Table 1 and Fig. 2).

Diffraction patterns of all samples on the first heating cycle showed not only the diffraction lines characteristic of the oxides: V_2O_5, MoO_3 and α-Sb_2O_4, but also a set of lines unattributable to any of the known compounds. The set of novel diffraction lines was compared with characteristics of compounds originating in suitable two-component systems i.e. V_2O_5–MoO_3, MoO_3–Sb_2O_4 and V_2O_5–Sb_2O_4 as well as with the characteristics of compounds existing in the Sb–V–O and Sb–Mo–O systems, which are formed in atmospheres different from the air [13, 20, 21].

Heating samples 1–10, viz. those comprising up to 50.00 mol% of MoO_3 in their initial mixtures, at 575°C resulted in a formation of two-type products: a solid solution of MoO_3 in V_2O_5 and a compound of $Sb_2V_2O_9$ [9]. In the light of the published data available, it is not unlikely that the $Sb_2V_2O_9$ compound occurring in the reaction mixtures is in fact a non-stoichiometric phase of a formula $Sb_{0.92}V_{0.92}O_4$ and of rutile-type structure [10, 13]. The further heating cycles, say, those at 600°C caused the $Sb_{0.92}V_{0.92}O_4$ compound to be oxidised (by the atmospheric oxygen) to $SbVO_5$ – a compound that finally was at equilibrium with the novel phase and with the solid solution of MoO_3 in V_2O_5. Analysing a diffraction pattern of the thermally-treated sample on the final heating stage, comprising 50.00 mol% of MoO_3 in an oxide mixture, has shown the sample to contain the novel phase apart from only trace quantities of the $V_2O_{5(s.s.)}$ phase and $SbVO_5$.

X-ray phase analysis of the diffraction pattern taken from the final thermally-induced sample 11, the initial mixture of which comprising the oxides: MoO_3, Sb_2O_4 and V_2O_5 at a molar ratio of 7:3:3, has shown that the sample is triphase and contains, apart from the novel compound, minor quantities of $V_2O_{5(s.s.)}$ and $V_9Mo_6O_{40}$. Samples 12–20, covering the remaining concentration range for components of the $Sb_2V_2O_9$–MoO_3 system, are also triphase and contain MoO_3, $V_9Mo_6O_{40}$ and the novel phase. However, in the sample 12 (55.56 mol% of MoO_3) only trace quantities of molybdenum(VI) oxide have been detected. The experimental results have permitted to predict that the oxides: V_2O_5, MoO_3 and α-Sb_2O_4 will interact in the solid state and in air to form a hitherto unknown compound. The participation of oxygen in the synthesis of this compound was indicated by the mass increases of all the samples representing the $Sb_2V_2O_9$–MoO_3 system. These mass increases were detected after each of three subsequent heating cycles in the furnace in the atmosphere of air and they amounted to 0.01–0.75 mass%.

Results of the investigations have also shown that the composition of the resulting compound is situated slightly beyond the $Sb_2V_2O_9$–MoO_3 intersection and it corresponds to the MoO_3 content within the range of 50.00–57.14 mol% MoO_3. In order to define a formula of the compound produced here, 5 extra samples 21–25 were prepared to be heated in cycles under conditions identical with those for the samples of the $Sb_2V_2O_9$–MoO_3 system. Table 1 shows the contents of initial mixtures and the compositions of thermally-induced samples. X-ray phase analysis of the samples resulting from the final heating cycle has allowed a statement that only sample 23, containing 54.55 mol% of MoO_3 in its initial mixture, is monophase. Its diffraction pattern shows the reflections characteristic of the novel compound only (Table 2). The other samples: 21, 22, 24, 25 contain the novel compound accompanied by trace quantities of other phases.

Table 2 Interplanar distances for $Sb_3V_2Mo_3O_{21}$ and relative intensities corresponding to their reflections

No.	d/Å	I/%	No.	d/Å	I/%	No.	d/Å	I/%
1	5.059	10	8	2.529	45	15	2.003	10
2	3.522	15	9	2.510	35	16	1.913	15
3	3.370	100	10	2.484	17	17	1.755	8
4	3.269	60	11	2.318	14	18	1.711	23
5	2.969	25	12	2.260	5	19	1.696	17
6	2.815	8	13	2.223	9	20	1.685	20
7	2.769	5	14	2.188	5	21	1.638	9

The phase composition of sample 23 on the final heating cycle points out that the initial MoO_3/α-Sb_2O_4/V_2O_5 mixture of a molar ratio 6:3:2 reacts in air to produce the novel compound according to the equation:

$$6MoO_{3(s.)}+3Sb_2O_{4(s.)}+2V_2O_{5(s.)}+O_{2(g)}=2Sb_3V_2Mo_3O_{21} \qquad (1)$$

The participation of the atmospheric oxygen during reaction 1 was evidenced by the mass increases of all the extra samples, making up 0.75–1.2 mass%. A theoretical mass gain of the sample with a composition corresponding to the novel compound should be 1.49 mass% when calculated according to Eq. (1). The result is in line with a suggestion that the obtained compound has a formula of $Sb_3V_2MoO_{21-x}$, where $x \leq 0.2$. Picking up the air oxygen during the synthesis of the $Sb_3V_2Mo_3O_{21}$ compound has been confirmed by the results of our other studies on reactivity of V_2O_5, MoO_3 and α-Sb_2O_4 in the atmosphere of argon, clearly indicating that the $Sb_3V_2Mo_3O_{21}$ compound cannot be formed in an oxygen-free atmosphere.

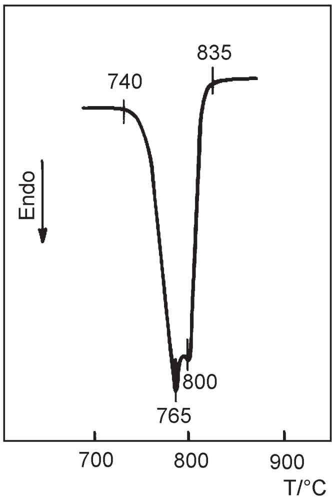

Fig. 1 The DTA curve of $Sb_3V_2Mo_3O_{21}$

A supplementary evidence for the existence of the new compounds was the presence of an endothermic effect, with its onset temperature equal to 740°C, on the DTA curve. The higher-temperature side of this effect showed a distinct bending on the line at ca 800°C, i.e. above the peak extremum temperature (Fig. 1). This bending indicated that melting the $Sb_3V_2Mo_3O_{21}$ compound is incongruent. This effect was accompanied with a mass loss record on the TG curve and amounted to 2.4 mass%.

In order to define the product of melting, a sample of $Sb_3V_2Mo_3O_{21}$ was additionally heated for 3 h at 765°C (the extremum of the effect on the DTA curve). X-ray phase analysis of the sample melted has shown the presence of the $Sb_2V_2O_9$ phase, β-Sb_2O_4 and quite small amounts of the $Sb_2Mo_{10}O_{31}$ phase. According to the information published, $Sb_2Mo_{10}O_{31}$ does not occur as a solid at 765°C, since it melts at 575°C [21], which suggests that the compound had to crystallise from liquid. A high-temperature polymorphic modification of β-Sb_2O_4 has also been deemed to be a phase having had to crystallise from liquid, because the diffraction lines characterising the phase were slightly shifted towards smaller angles. Besides, their mutual intensity relations significantly differed from the intensity values given in other works. The obtained results allow us to consider the $Sb_2V_2O_9$ compound as the only solid product of melting the $Sb_3V_2Mo_3O_{21}$ phase. The solid $Sb_2V_2O_9$ phase is stable up to ca 830°C and then it decomposes into $SbVO_4$ and gaseous oxygen [9].

Another purpose of this work was to find out which component concentration ranges of the V_2O_5–MoO_3–α-Sb_2O_4 system can contain the novel compound, $Sb_3V_2Mo_3O_{21}$, coexisting in the solid state with other compounds. Table 1 shows initial contents of the mixtures (26–32) under investigation and X-ray analysis of the thermally-treated samples at equilibrium . The data of these preliminary investigations have given rise to a provisional dividing the system of interest into five subsidiary systems (Fig. 2):

I: $Sb_3V_2Mo_3O_{21}$–$V_9Mo_6O_{40}$–MoO_3;
II: $Sb_3V_2Mo_3O_{21}$–MoO_3–α-Sb_2O_4
III: $Sb_3V_2Mo_3O_{21}$–α-Sb_2O_4–$SbVO_5$;
IV: $Sb_3V_2Mo_3O_{21}$–$SbVO_5$–$V_2O_{5(s.s.)}$
V: $Sb_3V_2Mo_3O_{21}$–$V_2O_{5(s.s.)}$–$V_9Mo_6O_{40}$

DTA measurements of all the thermally-induced samples being in an equilibrium state, obtained in this work, imply that the $Sb_3V_2Mo_3O_{21}$ compound, when in the solid state and in air, coexists with $V_9Mo_6O_{40}$ and MoO_3 up to 610°C, whereas, it occurs beside MoO_3 and α-Sb_2O_4 up to ~705°C. The experiments and measurements have also shown that the melting temperature of a reaction mixture comprising the novel compound together with $SbVO_5$ and α-Sb_2O_4 is ~720°C, white mixtures of $Sb_3V_2Mo_3O_{21}$ with $SbVO_5$ and $V_2O_{5(s.s.)}$ melt at ~640°C. Furthermore, it has been found that $Sb_3V_2Mo_3O_{21}$ coexists, in the solid state, with a solid solution of MoO_3 in V_2O_5 and with $V_9Mo_6O_{40}$ up to ~605°C. The temperature that the above-mentioned phases co-exist in the solid state in the atmosphere of air up to was determined on the base of the onset temperatures of the first effects recorded on the DTA curves for the preparations in an equilibrium state.

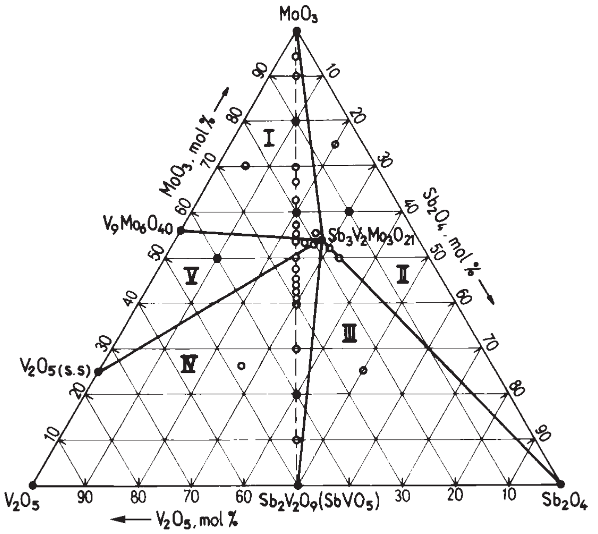

Fig. 2 The component concenration triangle of the V_2O_5–MoO_3–α-Sb_2O_4 system in air

Conclusions

The experimental results constitute a basis for reaching the following conclusions:

1. The experimental results have made it possible to detect a novel compound, attributed with a formula, $Sb_3V_2Mo_3O_{21}$, in the three-component V_2O_5–MoO_3–α-Sb_2O_4 system. Formation of the compound involves the oxides: V_2O_5, MoO_3 and α-Sb_2O_4, its synthesis running in the presence of atmospheric oxygen. X-ray characteristics of $Sb_3V_2Mo_3O_{21}$ have been determined. The compound melts with accompanying decomposition at 740°C, a solid product of this meritectic reaction being $Sb_2V_2O_9$.

2. The experimental results have created an opportunity to single out subsidiary partial systems by provisional dividing the three-component oxide system under investigation, as shown in Fig. 2.

References

1 A. Bielański and M. Najbar, Appl. Catal. A, 157 (1997) 223
2 G. Centi, S. Perathoner and F. Trifiro, Appl. Catal. A, 157 (1997) 143.
3 R. Castillo, K. Dewaele, P. Ruiz and B. Delmon, Appl. Catal. A, 153 (1997) L1- L8.
4 J. Nilsson, A. Canovas, S. Hansen and A. Andersson, Cat. Today, 33 (1997) 97.
5 J. Nilsson, T. Lindblad and A. Andersson, J. Catal., 148 (1994) 501.
6 L. T. Weng, P. Ruiz, B. M. Delmon and D. Duprez, J. Mol. Catal., 52 (1989) 349.
7 E. M. Gaigneaux, P. Ruiz and B. M. Delmon, Cat. Today, 32 (1996) 37.
8 E. M. Gaigneaux, M. Dieterle, P. Ruiz, G. Mestl and B. M. Delmon, J. Phys. Chem. B, 102 (1998) 10542.

9 R. Renaud, Rev. Chim. Miner., 8 (1971) 633.
10 R. Nilsson, T. Lindblad and A. Andersson, Catal. Lett., 29 (1994) 409.
11 F. J. Berry and M. E. Brett, Inorg. Chim. Acta, 81 (1984) 133.
12 S. Hansen, K. Stahl, R. Nilsson and A. Andersson, J. Solid State Chem.,102 (1993) 340.
13 A. Canovas, J. Nilsson, S. Hansen, K. Stahl and A. Andersson, J. Solid State Chem., 116 (1995) 369.
14 E. Filipek, J. Therm. Anal. Cal., 56 (1999) 159.
15 N. Strupler, Ann. Chim., 10 (1965) 345.
16 A. Magnelli and B. Blomberg, Acta. Chem. Scand., 5 (1951) 585.
17 A. Bielański, J. Camra and M. Najbar, J. Catal., 57 (1979) 326.
18 R. G. Teller, M. R. Antonio, J. F. Brazdil, M. Mehicic and R. K. Grasseli, Inorg. Chem., 24 (1985) 3370.
19 J. Walczak, E. Filipek and M. Bosacka, Proc. VIIth Eur. Conf. Solid State Chem., Switzerland, Zürich 1997, II. PB50.
20 M. Parmentier, A. Courtois and Ch. Gleitzer, Bull. Soc. Chim. France, 19 (1974) 75.
21 P. M. Parmentier, C. Gleitzer and R. J. D. Tilley, J. Solid State Chem., 31 (1980) 305.
22 E. Filipek, Proc. VIIth Eur. Symp. on Therm. Anal. Cal., Balatonfüred 1998, 1/P-26, 66.