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Synthesis and some properties of a new compound in the Al–Sb–V–O system

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Bretsznajder Special Chapter

Abstract A new compound in the Al–Sb–V–O system of the composition $AlSbVO_6$ was successfully synthesized by a solid-state reaction and characterized by powder XRD diffraction. The structural and thermal properties of $AlSbVO_6$ were investigated. The infra-red spectrum of the new phase is presented.

Keywords $AlSbVO_6$ · Solid–solid synthesis · XRD · IR

Introduction

Mixed metal oxides of rutile or rutile-like structure have been the subjects of increasing interest because of their potential use as catalysts of many industrial processes, in particular in direct synthesis of acrylonitrile from propane [1–4]. This reaction is an attractive alternative to the currently used industrial process of production of acrylonitrile from propylene, because propane is much cheaper than the olefin [5, 6]. Acrylonitrile is an important industrial chemical intermediate used in the production of acrylic and modacrylic fibers, rubbers, other important chemicals, and resins. Several papers have been published on the catalysts used for propane ammoxidation, but the major part of the reported work has been concentrated on two types of catalysts, the antimonates of rutile structure [7, 8] and molybdates [9–11]. Vanadium-antimony mixed oxides have exhibited high selectivity and activity as catalysts of this process [12, 13]. Better performance was obtained when alumina was incorporated into V–Sb–O oxide owing to the occurrence of specific structural effects [14–16]. The active structure in the Al–Sb–V–O system is a bulk phase, which is directly formed in the catalyst synthesis. It is a trirutile-like phase $Al_{1-x}SbV_xO_4$ $(0 < x < 0.5)$, and the presence of excess of aluminum in the synthesis is critical for its formation [17, 18]. Thus, the aluminum is not only a catalysts support, but it is also a component of the active phase.

Our previous investigation and literature information have implied that there exist a series of new compounds of the general formula $M'MSbO_6$ (where $M' =$ Cr, Rh, Fe and $M =$ Ru, V, Ti, Te, Ge, Sn) of rutile-type structures [19–22]. Hence, the aim of this investigation was to check on the formation of $AlSbVO_6$ compound in the quaternary system Al–Sb–V–O. This compound can be a promising candidate for the development of a process of direct acrylonitrile synthesis from propane.

Another important objective of this study was an attempt to determine the structural and thermal properties of the compound obtained.

Experimental

In the experiments the following reactants were used: Al_2O_3, a.p. (POCh, Poland), V_2O_5, a.p. (POCh, Poland), and α-Sb_2O_4, obtained by oxidation of commercial Sb_2O_3 (Merck, Germany) in air, in the following stages: 500 °C (24 h) → 550 °C (72 h). The other compounds $AlVO_4$, $SbVO_5$, and $AlSbO_4$ were obtained separately. These compounds were obtained by the solid-state reaction between appropriate mixtures of the oxides Al_2O_3, V_2O_5, and α-Sb_2O_4, under conditions described in literature [23–25].

Mixtures of various reagents (Table 1) were weighed in suitable proportions, carefully homogenized by grinding

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and then shaped into tablets. The tablets were placed in porcelain crucibles and heated in air or argon atmosphere (at the flow rate of 10 dm^3/h) until a monophase sample was obtained. All the samples were heated at a temperature range from 550 to 750 °C. On each heating stage the samples were gradually cooled down to room temperature, weighed (their mass changes and their color were recorded), and homogenised by triturating. Finally, all the samples were examined by differential thermal analysis DTA/TG and by X-ray diffraction method to determine their composition.

The kind of phases contained in the samples was identified on the basis of X-ray phase analysis results (diffractometer HZG-4 (NRD) radiation Cu $K\alpha$/filter Ni) and the data found in PDF files [26] as well as in the works [23, 24, 27]. The powder diffraction pattern of $AlSbVO_6$ was recorded at an angular range of 8.5° to 80° 2θ the step size 0.02° (2θ), time per step = 5 s. The intensity of a diffracted beam was recorded using a scintillation counter. The temperature of data collection was equal to 25 °C. The powder diffraction pattern of $AlSbVO_6$ was indexed by means of POWDER program [28, 29].

The density of $AlSbVO_6$ was determined by degassing sample and hydrostatic weighing in pycnometric liquid (CCl_4) by the method described in article [30].

The DTA/TG investigations were performed using a Paulik–Paulik-Erdey derivatograph, a product of MOM (Budapest, Hungary). The measurements were conducted in air, in the temperature range 20–1,000 °C and at a constant heating rate of 10 °C/min. All investigations were performed in quartz crucibles. The mass of investigated samples always amounted to 500 mg. The accuracy of temperature reading determined on the basis of repetitions was established as ±5 °C. The DTA/TG measurements in the temperature range 20–1,300 °C were carried out, in inert atmosphere, with the use of an SDT 2960 (TA Instruments).

Initial mixtures and monophase samples were examined by IR spectroscopy. The IR spectra were recorded at wave numbers 1,200–250 cm^{-1}, using a spectrometer of SPECORD M80 (Carl Zeiss, Jena, Germany). A technique used in the measurements was pressing pastilles with KBr at a weight proportion of 1:300.

Results and discussion

The research presented in this study was started with attempts to obtain the compound $AlSbVO_6$ from stoichiometric mixtures of the oxides Al_2O_3, V_2O_5, and α-Sb_2O_4. Further investigation was aimed at preparation of $AlSbVO_6$ from reacting mixtures that contained $AlSbO_4/V_2O_5$, $Al_2O_3/SbVO_5$, $AlVO_4/\alpha\text{-}Sb_2O_4$, and $AlVO_4/AlSbO_4/SbVO_5$. The compositions of the initial mixtures and their heating conditions are presented in Table 1.

The XRD results for all samples after their final heating stage indicate that the initial compounds react with one another in the solid state according to the equations:

$$Al_2O_{3(s)} + V_2O_{5(s)} + \alpha\text{-}Sb_2O_{4(s)} = 2AlSbVO_{6(s)} \qquad (1)$$

$$2AlSbO_{4(s)} + V_2O_{5(s)} = 2AlSbVO_{6(s)} + \frac{1}{2}O_{2(g)} \qquad (2)$$

$$2AlVO_{4(s)} + \alpha\text{-}Sb_2O_{4(s)} = 2AlSbVO_{6(s)} \qquad (3)$$

$$Al_2O_{3(s)} + 2SbVO_{5(s)} = 2AlSbVO_{6(s)} + \frac{1}{2}O_{2(g)} \qquad (4)$$

$$AlVO_{4(s)} + AlSbO_{4(s)} + SbVO_{5(s)} = 2AlSbVO_{6(s)} + \frac{1}{2}O_{2(g)} \qquad (5)$$

The diffraction patterns of the samples obtained after the last heating stage in air were identical with the diffractograms of the samples obtained in argon atmosphere. $AlSbVO_6$ obtained according to the above reaction has a brownish color. The mass loss calculated on the basis of the reactions (2), (4), and (5) is compatible with the changes in the mass recorded after all the heating stages of samples and amounting to ~2.5 ± 0.2 wt%, which finally confirms that this synthesis does not involve atmospheric oxygen.

Figure 1 presents the XRD pattern of: (a) an equimolar mixture of Al_2O_3 and V_2O_5 with α-Sb_2O_4, (b) a mixture of 66.67 mol% $AlVO_4$ + 33.33 mol% α-Sb_2O_4, and (c) a mixture of 66.67 mol% $SbVO_5$ + 33.33 mol% Al_2O_3 as

Table 1 The composition of the initial mixtures and the conditions of synthesis all samples

No.	Initial composition of samples	Conditions of synthesis stage/ temperature/time
1.	33.33 mol% Al_2O_3	I 550 °C (24 h)
	33.33 mol% V_2O_5	II 600 °C (24 h)
	33.34 mol% α-Sb_2O_4	III 650 °C (24 h)
		IV 700 °C (24 h)
		IV 750 °C (24 h)
2.	66.67 mol% $AlSbO_4$	I 600 °C (24 h)
	33.33 mol% V_2O_5	II 700 °C (24 h)
		III 750 °C (24 h)
3.	66.67 mol% $AlVO_4$	I 600 °C (24 h)
	33.33 mol% α-Sb_2O_4	II 700 °C (24 h)
		III 750 °C (24 h)
4.	66.67 mol% $SbVO_5$	I 600 °C (24 h)
	33.33 mol% Al_2O_3	II 700 °C (24 h)
		III 750 °C (24 h)
5.	33.34 mol% $SbVO_5$	I 600 °C (24 h)
	33.33 mol% $AlVO_4$	II 650 °C (24 h)
	33.33 mol% $AlSbO_4$	III 700 °C (24 h)

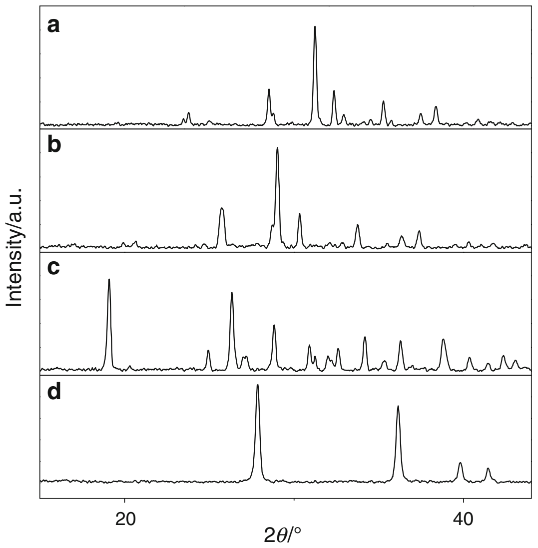

Fig. 1 The XRD spectra of (*a*) initial mixture of 33.33 mol% Al_2O_3 + 33.33 mol% V_2O_5 + 33.34 mol% α-Sb_2O_4; (*b*) initial mixture of 66.67 mol% $AlVO_4$ + 33.33 mol% α-Sb_2O_4; (*c*) initial mixture of 66.67 mol% $SbVO_5$ + 33.33 mol% Al_2O_3; (*d*) $AlSbVO_6$

well as the diffractogram pattern of compound $AlSbVO_6$ (d) obtained from these mixtures. The diffraction patterns of the finally obtained samples show only the set of diffraction lines characteristic of compounds of rutile-type structure [19–22, 27, 31, 32].

The results of indexing the powder diffraction pattern of $AlSbVO_6$ are shown in Table 2. The calculated lattice parameters are the following: $a = b = 0.44945$ nm, $c = 0.29498$ nm, $V = 0.0596$ nm^3, $Z = 2$. The X-ray calculated density amounts to $d_{rtg} = 4.96$ g/cm^3, while the experimentally measured density is equal to $d = 5.21$ g/cm^3.

The powder diffraction pattern, parameters of the elementary cell of $AlSbVO_6$, and the identical Miller indices (*hkl*) calculated for $AlSbVO_6$ are similar to their correspondents typical of the rutile phase, which implies this type of structure for the new phase $AlSbVO_6$. The structure proposed was confirmed by the similarity of the IR spectra which are presented in many articles [19, 20, 31, 32]. IR spectra of: an equimolar mixture Al_2O_3/V_2O_5/α-Sb_2O_4 (curve a), a mixture containing 66.67 mol% $AlVO_4$ and 33.33 mol% α-Sb_2O_4 (curve b), a mixture containing 66.67 mol% $SbVO_5$ + 33.33 mol% Al_2O_3 (curve c), and also the IR spectrum of the new compound $AlSbVO_6$ (curve d) are shown in Fig. 2.

As follows from Fig. 2, the IR spectrum of the new compound differs essentially from the IR spectra of the initial mixtures, both in the number of the absorption bands, in their positions and intensities. In the vibration spectrum of $AlSbVO_6$ two absorption bands can be distinguished. The first wide absorption band lying between 900 and 500 cm^{-1} displays absorption maxima at 720 and 570 cm^{-1}. This band reflects the stretching vibrations of Sb–O bonds in SbO_6 octahedron and those of Al–O bonds in AlO_6 octahedron [33–36]. The second absorption band lying over the wave-number range of 500–300 cm^{-1} with its absorption maxima at 420 and 380 cm^{-1}, has been ascribed to the bending vibrations of O–M–O (O–Al–O, O–Sb–O, O–V–O) and V–O bonds in the distorted MO_6 octahedra. It cannot be excluded that the absorption bands within this wave-number range correspond to the bending vibrations of Al–O–V or vibrations of a mixed character [33–39].

Table 2 Indexing results for powder diffraction pattern of $AlSbVO_6$

No.	Miller indices *hkl*	d_{exp}/nm	d_{calc}/nm	I/I_0/%
1	110	0.3188	0.3178	100
2	101	0.2467	0.2466	69
3	200	0.2250	0.2472	17
4	111	0.2165	0.2162	18
5	210	0.2012	0.2010	7
6	211	0.1665	0.1661	75
7	220	0.1591	0.1589	24
8	002	0.1475	0.1475	12
9	310	0.1421	0.1421	14
10	112	0.1332	0.1337	36

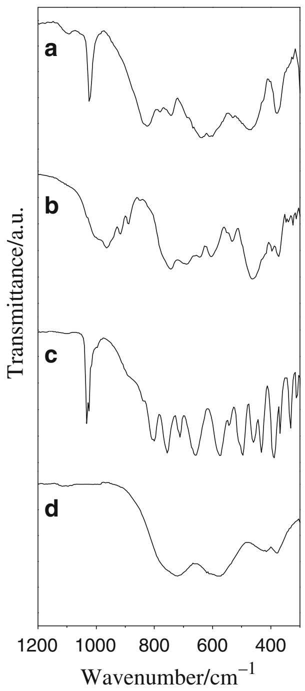

Fig. 2 IR spectra of (*a*) initial mixture of 33.33 mol% Al_2O_3 + 33.33 mol% V_2O_5 + 33.34 mol% α-Sb_2O_4; (*b*) initial mixture of 66.67 mol% $AlVO_4$ + 33.33 mol% α-Sb_2O_4; (*c*) initial mixture of 66.67 mol% $SbVO_5$ + 33.33 mol% Al_2O_3; (*d*) $AlSbVO_6$

At the next stage of the research, our investigation aimed at establishing the thermal properties of $AlSbVO_6$ compound. Two endothermic effects were recorded on the DTA curve of $AlSbVO_6$ up to 1,300 °C (Fig. 3). The first of them started at 820 ± 10 °C and reached its maximum at 1,125 °C. The other effect started at about 1,200 °C. With the view to establishing the nature of the effects recorded on DTA curve of $AlSbVO_6$, the samples containing only this compound were heated for 3 h at the following temperatures: 820, 1125, and 1200 °C, then rapidly cooled to ambient temperature and investigated by XRD method. The diffractogram of the sample additionally heated at 820 °C shows a set of diffraction lines, which according to the PDF cards (PDF cards no. 35-1485, 04-0564) belong to the sets of both $VSbO_4$ and $AlSbO_4$. Location of the diffraction lines and the corresponding interplanar distances characterizing $VSbO_4$ showed that this compound is a non-stoichiometric rutile-type phase $Sb^{5+}_{0.92}V^{3+}_{0.28}V^{4+}_{0.64}{}_{0.16}O_4$. XRD analysis of the sample melted at 1,125 °C demonstrated the presence of $AlSbO_4$ besides the phases α-Sb_2O_4 and V_2O_5 crystallizing from the liquid. The mass loss of sample recorded on the TG curve of $AlSbVO_6$ at 1,000 °C as shown in Fig. 3, testifies to the simultaneous sublimation or decomposition of α-Sb_2O_4. Phase composition of the sample heated additionally at 1,200 °C confirmed the literature data on thermal stability of $AlSbO_4$, which show that this compound melts incongruently at 1,200 °C with a deposition of solid Al_2O_3 [40]. The DTA curve of $AlSbO_4$ was presented in Fig. 4.

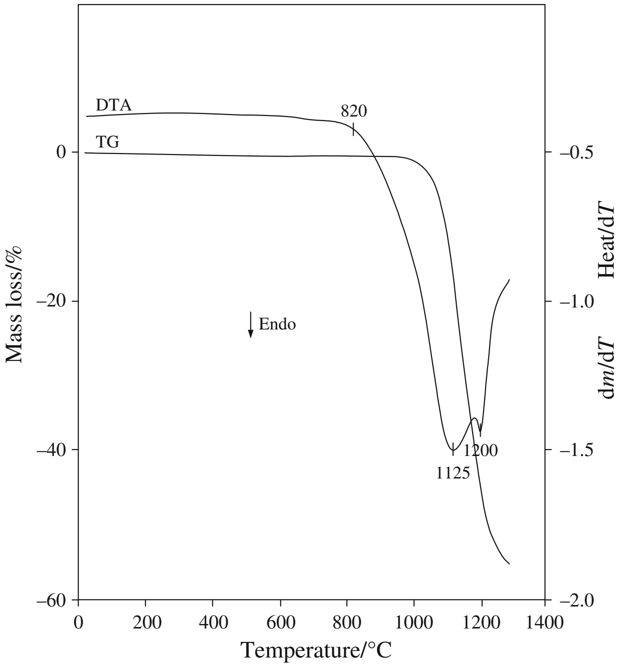

Fig. 3 The DTA/TG curves of $AlSbVO_6$

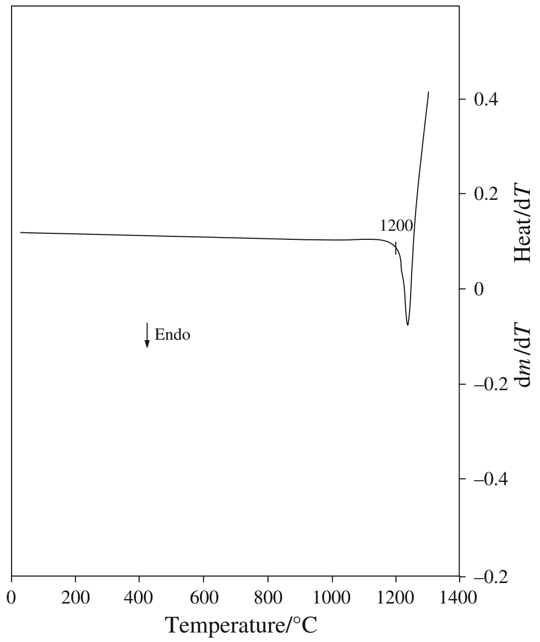

Fig. 4 The DTA curve of $AlSbO_4$

As follows from the above-discussed, $AlSbVO_6$ decomposes in the solid state, at 820 °C with release of the solid $VSbO_4$ and $AlSbO_4$. The first effect, recorded on the DTA curve of $AlSbVO_6$ is related to $VSbO_4$ decomposition. According to literature data, the compound $VSbO_4$ decomposes at 820 °C [41]. On the basis this part of the investigation, it was also found that the other effect recorded on the DTA curve of $AlSbVO_6$, is linked to the thermal properties of the solid product of its decomposition, $AlSbO_4$.

Conclusions

A new compound of the formula of $AlSbVO_6$ was prepared by the conventional solid-state reactions from stoichiometric mixtures of the oxides Al_2O_3, V_2O_5, and α-Sb_2O_4 as well as from the reacting mixtures containing $AlSbO_4/V_2O_5$, $Al_2O_3/SbVO_5$, $AlVO_4/\alpha$-Sb_2O_4 or $AlVO_4/AlSbO_4/SbVO_5$. The obtained compound crystallizes in the tetragonal system, in the rutile-type structure. The unit cell parameters are the following: $a = b = 0.44945$ nm, $c = 0.29498$ nm, $V = 0.0596$ nm^3, $Z = 2$. $AlSbVO_6$ in inert atmosphere is stable up to ~820 °C, after it undergoes decomposition to $VSbO_4$ and $AlSbO_4$.

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