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Comparison between the synthesis in molybdenum and antimony oxides system by high-temperature treatment and high-energy ball milling

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Abstract The interactions between MoO_3 and Sb_2O_3 or α-Sb_2O_4 taking place in the solid state in air during high-temperature as well as mechanochemical treatments have been investigated. The high-energy ball milling of MoO_3 with Sb_2O_3 converts α-Sb_2O_3 to β-Sb_2O_3 and leads to formation of Sb_2MoO_6 and $Sb_4Mo_{10}O_{31}$ phases. They are the final products of thermal synthesis in an inert atmosphere but not in air. The solid solution of MoO_3 in β-Sb_2O_4 was obtained in high-temperature reaction of MoO_3 with Sb_2O_3 or α-Sb_2O_4 as well as by milling of mixture MoO_3/α-Sb_2O_4 for 14 h. The milling resulted in higher than 3 mol% solubility of MoO_3 in β-Sb_2O_4. The constructed phase diagram of MoO_3–α-Sb_2O_4 system is presented.

Keywords DTA curves · High-energy ball milling · Phase diagram · Thermal treatment · MoO_3–Sb_2O_3 (α-Sb_2O_4) system · XRD patterns

Introduction

The unusual properties of transition metal oxides with their extraordinary range of structures make them important materials for technological applications such as catalysis, gas sensors, piezoelectric, electronic, magnetic, optical elements.

However, there are several reports of the advantage of the properties of mixed oxides over those of pure oxides.

The mixed oxides, i.e. MoO_3 with Sb_2O_3 or with α-Sb_2O_4 as well as other compounds formed in the Sb–Mo–O system are effective as catalysts in the following reactions: oxidation of propene to acroleine [1, 2], oxidation of methanol to formaldehyde [3] in oxidative esterification of ethanol [4], dehydration of *N*-ethylformamide to propionitrile [5] and oxidation of isobutene to methacroleine [6–8].

The researchers [5, 6, 9, 10] give the synergic effect occurring between two oxides as an explanation of the higher performance of catalyst composed of MoO_3 and α-Sb_2O_4 in comparison with pure MoO_3 or α-Sb_2O_4. Another reason is proposed by the authors [10, 11]. They noted that during the catalytic oxidation of various hydrocarbons using the MoO_3 with Sb_2O_3 or MoO_3 with α-Sb_2O_4 mixtures, active phases such as Sb_2MoO_6, $Sb_2(MoO_4)_3$, $Sb_2Mo_{10}O_{31}$, $Sb_4Mo_{10}O_{31}$ or $Sb_4Mo_{20}O_{62}$ are formed.

There are some data (although incomplete and inconsistent) concerning the factors affecting the final products in the mentioned thermally treated systems [1–6]. In principle they are: initial reagents, synthesis method, the gaseous atmosphere (oxidizing/non-oxidizing) in which the processes are conducted.

In non-oxidizing atmosphere, i.e. in nitrogen or argon, MoO_3 interacts with Sb_2O_3 yielding two compounds: Sb_2MoO_6 and $Sb_2(MoO_4)_3$, whereas the H_2O/H_2 atmosphere favours formation of such compounds as: $Sb_{0.47}Mo_2O_5$, $Sb_2Mo_{10}O_{31}$ and $Sb_4Mo_{10}O_{31}$ [12–14].

The reaction of MoO_3 with α-Sb_2O_4 in air decreases the temperature of polymorphic transition α-$Sb_2O_4 \rightarrow \beta$-$Sb_2O_4$ with simultaneous formation of a low-concentration solid solution of MoO_3 in high-temperature modification of

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diantimony tetra oxide, i.e. β-Sb_2O_4 [11, 15]. It has been found that, the Mo^{+6} ions are incorporated between the β-Sb_2O_4 lattice nodes, and the charge compensation takes place via arising of vacancies at the Sb^{+3} sites. When the synthesis is carried out in sealed ampoules the solubility of MoO_3 in β-Sb_2O_4 is very low (1.5 mol%) [11]. One of the authors [16, 17] has already started the preliminary study on the thermal processes between molybdenum oxide and Sb_2O_3 or α-Sb_2O_4 oxides taking place in the solid state in air. Based on these results it is important to complete the investigations of relativities of the mentioned metal oxides.

The above described physical and chemical phenomena occurring between molybdenum and antimony oxides belong to the group of processes in the solid state, which are mostly slow and complex. They involve product formation at the interfaces of reactants. Furthermore, growth of solid product requires the diffusion of reactant phase atoms through the product.

High temperatures speed up the reaction, therefore in order this kind of reactions could proceed in a reasonable time they should be realized at high temperatures.

Moreover, in most cases solid phase reactions require charge transfer to be initiated. This can be carried out either thermally or via non-thermal route. In our project the attempt of rational synthesis of Mo and Sb oxides systems is undertaken. This requires an understanding of the principles of crystal chemistry in addition to phase equilibria, thermodynamics, and kinetics of reaction. We have shown the mechanochemical treatment employed for the synthesis of mixed oxides of molybdenum and antimony.

Experimental

For the study of reactivity of MoO_3 with antimony oxides during high-temperature and mechanochemical syntheses the following oxides were used: MoO_3, p.a., (POCh, Gliwice, Poland), Sb_2O_3, p.a. (Merck, Darmstadt, Germany). The α-Sb_2O_4 was obtained by heating in air of commercial Sb_2O_3 in the stages: 350 °C (1 h) → 400 °C (1 h) → 500 °C (1 h) → 600 °C (1 h) → 650 °C (24 h) [18]. Commercial Sb_2O_3 is a mixture of two polymorphic forms, i.e. α and β-Sb_2O_3.

Two series of mixtures were prepared for this study: eight mixtures of MoO_3 with Sb_2O_3 and fourteen MoO_3 with α-Sb_2O_4. They are shown in Tables 1 and 2, respectively. The oxide mixtures were homogenized by triturating in an agate mortar, then pelletized and heated in air. The results of the preliminary tests [16] indicated using following heating conditions in order to reach an equilibrium state: 300 °C → 400 °C (24 h) → 500 °C (24 h) → 600 °C (24 h) → 650 °C (24 h) → 700 °C (48 h) → 720 °C (2 × 24 h).

After each heating stage, the samples have cooled to room temperature, weighted, ground and analyzed using X-ray powder diffraction technique (XRD). The procedure has repeated until equilibrium state. Finally, the products were analyzed by XRD and differential thermal analysis (DTA) methods.

For high-energy ball milling processes selected samples containing: 3.00, 10.00, 25.00, 50.00 and 75.00 mol% MoO_3 in the mixtures with Sb_2O_3 or α-Sb_2O_4 were used. Some of milled samples were calcinated at 400 °C for 4 h.

Mechanochemical treatment took place in a laboratory planetary mill (Fritsch GmbH *Pulverisette 6*) with vials and balls (10 mm in diameter) made of hardened steel. The rotational speed was of 550 (rpm).

The milling processes were performed for 4 h, 8 h and 14 h in air atmosphere. The total mass of powders was 5 g and the ball-to-powder mass ratio (BPR) was 10:1. Small amounts of powder were taken out from the vial after selected milling times for the solid phase analysis [19–21].

For the phase identification of samples obtained by two methods of syntheses X-ray powder diffraction patterns (a Philips X'Pert diffractometer, CuKα in the 2θ range of 10–90°) and thermoanalytical curves (Derivatograph MOM system Paulik–Paulik–Erdey—MOM, Budapest, Hungary) and SDT 2960 TA Instruments were applied. The DTA measurements were made in air at 20–1000 °C. Samples of 500 mg were placed in quartz crucibles and heated at a rate of $10^\circ\ min^{-1}$.

Results and discussion

Reactivity of MoO_3 with Sb_2O_3 in air

Effects of high-temperature treatment

The phases found in MoO_3–Sb_2O_3 system after selected heating stages are shown in Table 1. As one can see β-Sb_2O_3, one of the component of initial mixtures (No. 1–8), oxidizes in air to α-Sb_2O_4 in the temperature range of 400–500 °C and α-Sb_2O_3 at higher temperatures (see: stage III). These processes are indicated by mass increase (α/β-Sb_2O_3 → α-Sb_2O_4). It is in accordance with the literature data [22]. Further heating (at 650 °C) of these samples did not cause changes in the system. From 700 °C solid solution of MoO_3 in β-Sb_2O_4 (β-$Sb_2O_{4(S.S.))}$ appears beside MoO_3 and α-Sb_2O_4. Finally, at 720 °C, β-$Sb_2O_{4(S.S.)}$ and MoO_3 are present in the system excluding the sample No. 8, which is monophase one.

The formation of solid solution at 700 °C was supported by the colour changes of samples during the syntheses. Thus, β-Sb_2O_4 is white and solid solution is orange.

Table 1 The contents of initial mixtures and phases found in MoO_3–Sb_2O_3 system after selected heating stages

No	Composition (mol%)		The phases found after stages		
	MoO_3	Sb_2O_3	I and II 400 °C (24 h) + 500 °C (24 h)	III 600 °C (24 h)	Last 720 °C (24 h)
1	2	3	4	5	6
1	90.00	10.00	MoO_3, α-Sb_2O_3, α-Sb_2O_4	MoO_3, α-Sb_2O_4	MoO_3, β-$Sb_2O_{4(S.S.)}$**
2	75.00	25.00	MoO_3, α-Sb_2O_3, α-Sb_2O_4	MoO_3, α-Sb_2O_4	MoO_3, β-$Sb_2O_{4(S.S.)}$
3	66.67	33.33	MoO_3, α-Sb_2O_3, α-Sb_2O_4	MoO_3, α-Sb_2O_4	MoO_3, β-$Sb_2O_{4(S.S.)}$
4	50.00	50.00	α-Sb_2O_4, MoO_3, α-Sb_2O_3	α-Sb_2O_4, MoO_3	β-$Sb_2O_{4(S.S.)}$, MoO_3
5	33.33	66.67	α-Sb_2O_4, MoO_3, α-Sb_2O_3	α-Sb_2O_4, MoO_3	β-$Sb_2O_{4(S.S.)}$, MoO_3
6	25.00	75.00	α-Sb_2O_4, MoO_3, α-Sb_2O_3	α-Sb_2O_4, MoO_3	β-$Sb_2O_{4(S.S.)}$, MoO_3
7	10.00	90.00	α-Sb_2O_4, MoO_3, α-Sb_2O_3	α-Sb_2O_4, MoO_3	β-$Sb_2O_{4(S.S.)}$, MoO_3
8	3.00	97.00	α-Sb_2O_4, α-Sb_2O_3, MoO_3*	α-Sb_2O_4, MoO_3^{*}	β-$Sb_2O_{4(S.S.)}$

* Very small; ** Solid solution of MoO_3 in β-Sb_2O_4

Table 2 The contents of initial mixtures and phases found at equilibrium in MoO_3–α-Sb_2O_4 system

No.	Composition (mol%)		The equilibrium phases
	MoO_3	α-Sb_2O_4	
1	90.00	10.00	MoO_3, β-$Sb_2O_{4(s.s.)}$
2	85.00	15.00	MoO_3, β-$Sb_2O_{4(s.s.)}$
3	75.00	25.00	MoO_3, β-$Sb_2O_{4(s.s.)}$
4	70.00	30.00	MoO_3, β-$Sb_2O_{4(s.s.)}$
5	66.67	33.33	β-$Sb_2O_{4(s.s.)}$, MoO_3
6	50.00	50.00	β-$Sb_2O_{4(s.s.)}$, MoO_3
7	35.00	65.00	β-$Sb_2O_{4(s.s.)}$, MoO_3
8	33.33	66.67	β-$Sb_2O_{4(s.s.)}$, MoO_3
9	25.00	75.00	β-$Sb_2O_{4(s.s.)}$, MoO_3
10	10.00	90.00	β-$Sb_2O_{4(s.s.)}$, MoO_3 traces*
11	7.50	92.50	β-$Sb_2O_{4(s.s.)}$, MoO_3 traces
12	5.00	95.00	β-$Sb_2O_{4(s.s.)}$, MoO_3 traces
13	3.00	97.00	β-$Sb_2O_{4(s.s.)}$
14	1.50	98.50	β-$Sb_2O_{4(s.s.)}$

* Still identified by XRD method

From the practical point of view, it is important that the observed temperature of β-$Sb_2O_{4(S.S.)}$ formation in air is significantly lower that given in literature value for conversion of α-Sb_2O_4 → β-Sb_2O_4 from the range of 935 °C to 1130 °C [11, 17, 23, 24].

Effects of mechanochemical treatment

The mixture of MoO_3 with α/β-Sb_2O_3 after mechanical activation for 2 h in air is composed of MoO_3 and β-Sb_2O_3. The α-Sb_2O_3 phase disappears although is stable in air up to 575° [22]. Similar effect was observed by Berry & Ren during mechanical milling of Sb_2O_3 with other oxides [25]. Prolonging the milling process to 8 h gives only reducing of the particle size of both components in the mixture. However after 14 h of mechanical treatment two phases $Sb_4Mo_{10}O_{31}$ and Sb_2MoO_6 are formed beside of β-Sb_2O_3. It was unexpected result because until now these phases were obtained not in air but in non-oxidizing atmosphere using Sb_2O_3 and MoO_3 and metallic Mo as the reactants [12, 14]. These compounds are unstable in air decomposing into α-Sb_2O_4 and MoO_3 at 350–550 °C [8, 12, 14].

Monophase products being solid solution of MoO_3 in β-Sb_2O_4 have obtained after 4 h of annealing at 400 °C followed by 14 h of milling in the case of 3% mol MoO_3 as well as 10% mol in the initial mixtures of oxides. The colour of these two samples was a little bit different from the colour of monophase sample obtained by annealing.

Reactivity of MoO_3 towards α-Sb_2O_4 in air

Effects of high-temperature treatment

The mixtures of MoO_3 with α-Sb_2O_4 thermally treated up to 720 °C in the same way as MoO_3 with α/β-Sb_2O_3 attained the equilibrium in the solid state. Their compositions shows Table 2. The molybdenum(VI) oxide does not react with α-Sb_2O_4 up to 700 °C, however step-wise heating at 700 °C (24 h) and 720 °C (48 h) results in the formation of the solid solution of MoO_3 in β-Sb_2O_4 in equilibrium with MoO_3.

In the case of samples with small amount of MoO_3 (No. 13 and 14) the investigated system is monophase one, i.e. β-$Sb_2O_{4(S.S.)}$ with general formulae of $Sb_{2-2x}Mo_xO_4$, where $0 < x \leq 0.015$. Thus, according to these results the limit of solubility of MoO_3 in β-Sb_2O_4 does not exceed 3.00 mol%.

Based on the above results the phase diagram of the MoO_3–α-Sb_2O_4 over the whole component concentration range up to 1000 °C is shown in Fig. 1. The solidus line was determined by the onset temperatures of the first endothermic effects on the DTA curves of the samples at equilibrium (see: Fig. 2, curves a–d). The curves bordering

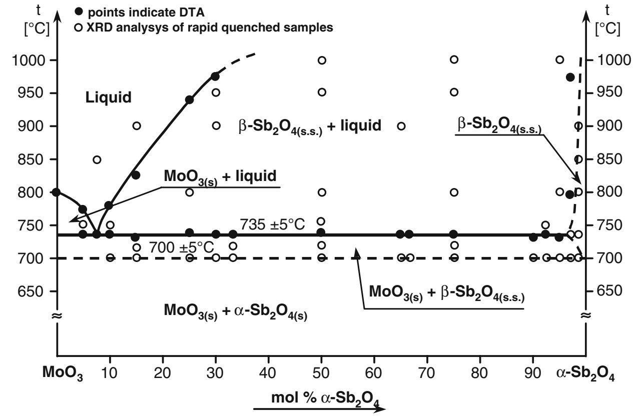

Fig. 1 Phase diagram of MoO_3–α-Sb_2O_4 system

the fields where solid phases remain in equilibrium have been drawn on the basis of temperatures of successive endothermic effects. The solid solution of MoO_3 in β-Sb_2O_4 forms the eutectic mixture composed of about 7.7 mol% β-$Sb_2O_{4(S.S.)}$ and 92.3 mol% MoO_3. This eutectic melts at 735 °C (Fig. 2, curve a). The liquidus lines of the area, where solid MoO_3 or β-$Sb_2O_{4(S.S.)}$ remains at equilibrium with liquid, were estimated on the DTA curves and phase analysis of „frozen" samples (i.e. rapidly quenched) [17, 18].

Effects of mechanochemical treatment

Comparing the results of mechanochemically activated with thermally treated MoO_3/α-Sb_2O_4 mixtures (in air)

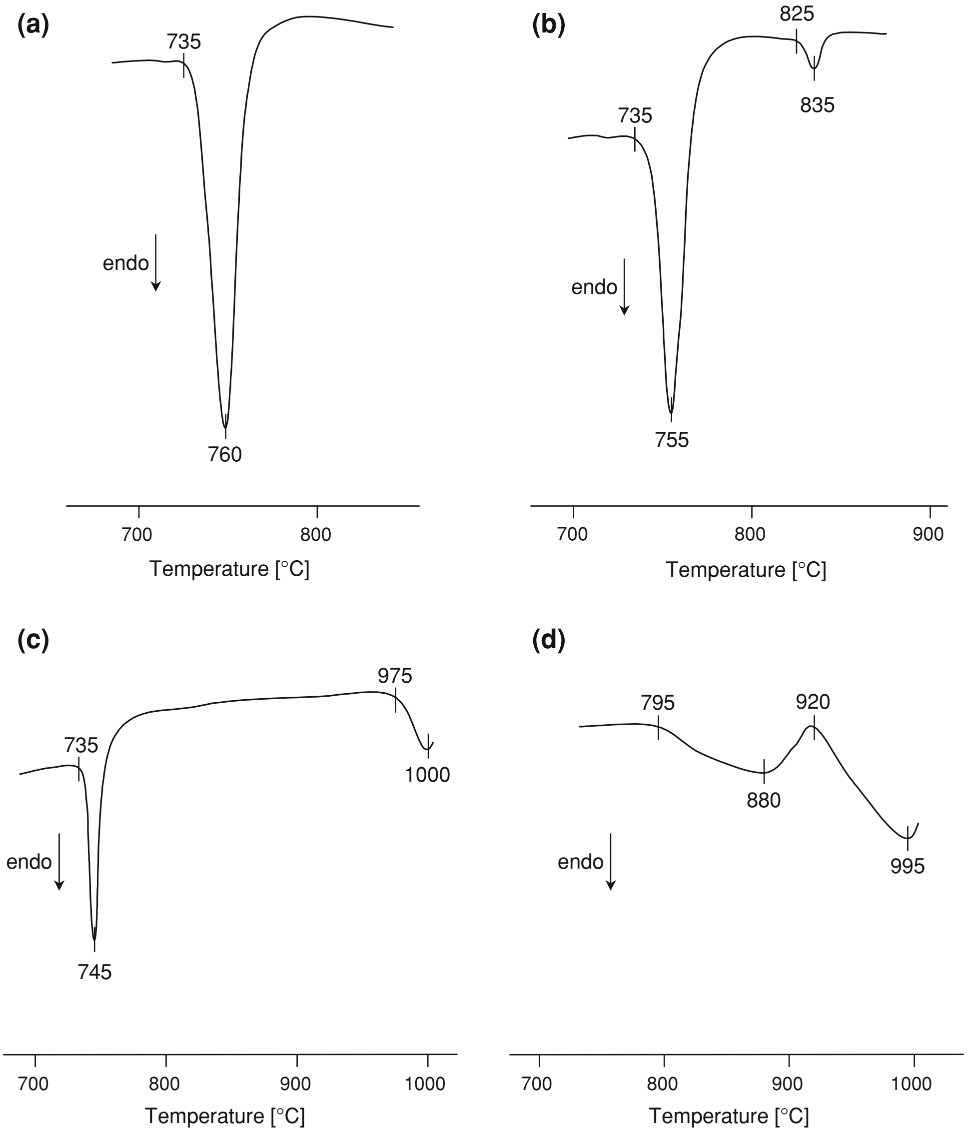

Fig. 2 The DTA curves of selected samples at equilibrium: **a** 7.7 mol% β-$Sb_2O_{4(s.s.)}$ + 92.3 mol% MoO_3(eutectic mixture), **b** 15.5 mol% β-$Sb_2O_{4(s.s.)}$ + 84.5 mol% MoO_3, **c** 30.9 mol% β-$Sb_2O_{4(s.s.)}$ + 69.1 mol% MoO_3, **d** β-$Sb_2O_{4(s.s.)}$($Sb_{1.94}Mo_{0.03}O_4$)

Table 3 The contents of initial mixtures and phases found in MoO_3–α-Sb_2O_4 system after mechanical treatment

No.	Composition (mol%)		The phases found after milling		
	MoO_3	α-Sb_2O_4	2 h	8 h	14 h
1	2	3	4	5	6
1	75.00	25.00	MoO_3, α-Sb_2O_4	MoO_3, α-Sb_2O_4, β-$Sb_2O_{4(S.S.)}$**	MoO_3, β-$Sb_2O_{4(S.S.)}$**
2	50.00	50.00	MoO_3, α-Sb_2O_4	MoO_3, α-Sb_2O_4, β-$Sb_2O_{4(S.S.)}$	MoO_3, β-$Sb_2O_{4(S.S.)}$
3	25.00	75.00	α-Sb_2O_4, MoO_3	β-$Sb_2O_{4(S.S.)}$, α-Sb_2O_4, MoO_3	β-$Sb_2O_{4(S.S.)}$, MoO_3
4	10.00	90.00	α-Sb_2O_4, MoO_3	β-$Sb_2O_{4(S.S.)}$, α-Sb_2O_4, MoO_3	β-$Sb_2O_{4(S.S.)}$
5	3.00	97.00	α-Sb_2O_4, MoO_3	β-$Sb_2O_{4(S.S.)}$, α-Sb_2O_4, MoO_3*	β-$Sb_2O_{4(S.S.)}$

* Very small; ** Solid solution of MoO_3 in β-Sb_2O_4

points out to many behaviour differences (Tables 2 and 3). As it was mentioned above, the solid solution of MoO_3 in β-Sb_2O_4 is formed at 700 °C; however high-energy ball milling provides to this synthesis during mechanical treatment from 8 h of milling. Phase composition of products after 14 h of milling is the same as in the samples being in equilibrium state of system which was formed during high-temperature synthesis between MoO_3 and α-Sb_2O_4. It also noted that milling of the oxide mixtures induces the higher solubility of MoO_3 in β-Sb_2O_4.

Conclusions

Based on the results of the study it was shown that using annealing as well mechanical activation the same type of product (solid solution of MoO_3 in β-Sb_2O_4) could be obtained. However, the products form under different conditions (in thermodynamic equilibrium state and far from equilibrium, respectively). The presented phase diagram of the MoO_3–α-Sb_2O_4 system within the whole concentration range of components up to 1000 °C was not been known till now.

Better solubility of MoO_3 in β-Sb_2O_4 as well as changes in dimensions of milled powders after mechanochemical treatment should make it more useful in practice of eco-friendly chemistry (e.g. in catalysis, gas sensors).

Our study continues.

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